NMR Spectroscopy, User Guide

Varian NMR Systems
with VnmrJ Software

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VARIAN

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Chapter 1. Running Liquids NMR Experiments

Sections in this chapter:

- 1.1, “NMR Experiment Tasks,” this page
- 1.2, “Saving NMR Data (optional),” on page 26
- 1.3, “Stopping an Experiment,” on page 26

This introductory chapter describes the use of VnmrJ to run liquids NMR experiments with the VnmrJ experimental interface. The tasks involved in running a liquids NMR experiment generally follow the VnmrJ interface layout, moving from left to right over the interface from the Locator to the Start, Acquire, and Process tabs.

The VnmrJ experimental interface, see Figure 1, is described in Appendix 16, “VnmrJ Experimental Interface,” page 363.

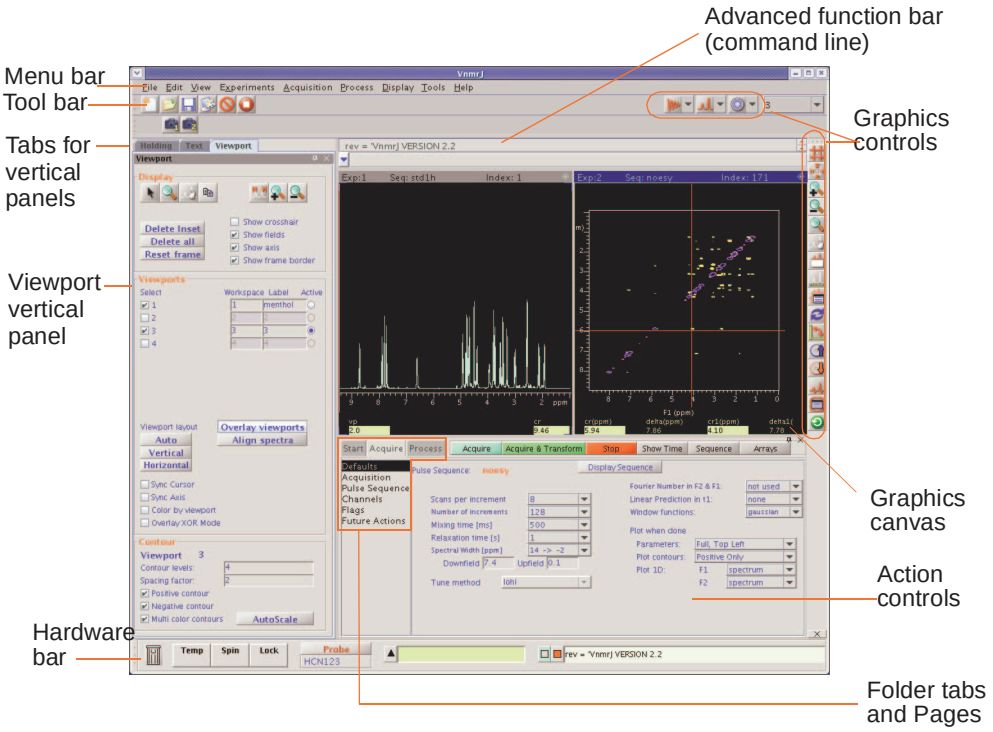


Figure 1. VnmrJ Experimental Interface

1.1 NMR Experiment Tasks

The following table lists the required tasks and where to obtain information.The VnmrJ panels and pages listed are typical but may vary depending upon the choice of experiments.

Task	*For more information*
Prepare for an experiment	Chapter 2, “Preparing for an Experiment,” page 27
Select an experiment	"Selecting an Experiment," page 39
Set up an experiment	Chapter 3, “Experiment Setup,” page 39
Acquire NMR data	Chapter 5, “Data Acquisition,” page 81
Process the data	Chapter 6, “Processing Data,” page 93
Display the data	Chapter 7, “Displaying FIDs and Spectra,” page 103
Print the data	Chapter 8, “Plotting and Printing,” page 131
Save the data	"Saving NMR Data (optional)," page 26

Prepare for an Experiment

Perform the following tasks before beginning an experiment:

- Start VnmrJ.
- Prepare the sample and position the sample tube in a turbine.
- Load the probe file, if changing the probe.
- Install the probe, tune, and calibrate if necessary.

See Chapter 2, “Preparing for an Experiment,” page 27.

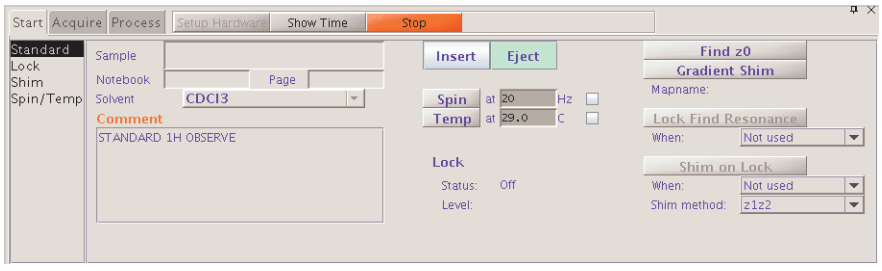
Select an Experiment

Select an experiment from the Experiments menu or drag-and-drop a protocol from the Locator. Refer to 3.1, “Selecting an Experiment,” on page 39 for more details.

Set Up an Experiment

The VnmrJ experimental setup and the functions available under the Start tab are described in Chapter 3, “Experiment Setup,” page 39.

Set up the experiment using the pages in the **Start** tab.



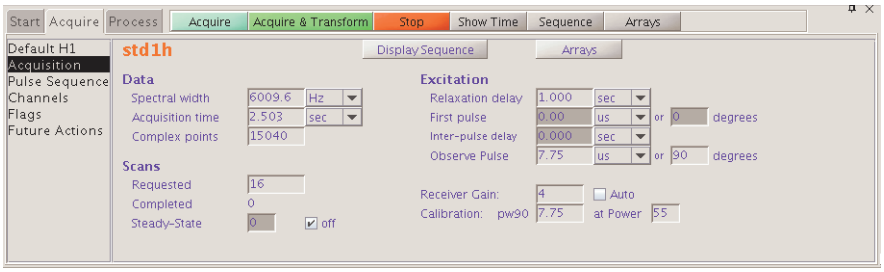
1. Select the **Standard** page.

   Fill in the information for the sample, select a solvent, and enter comments. Enter a name in the **Sample** field t to name the sample. Define the sample, if desired, by filling in the **Notebook** and **Page**.

2. Insert the sample.
3. Regulate spinning and temperature on the **Spin/Temp** page.
4. Find Z0 adjust the lock using the **Shim** and **Lock** pages.
5. Shim the system to adjust the field homogeneity using the controls provided on the **Shim** page.

Acquire a Spectrum

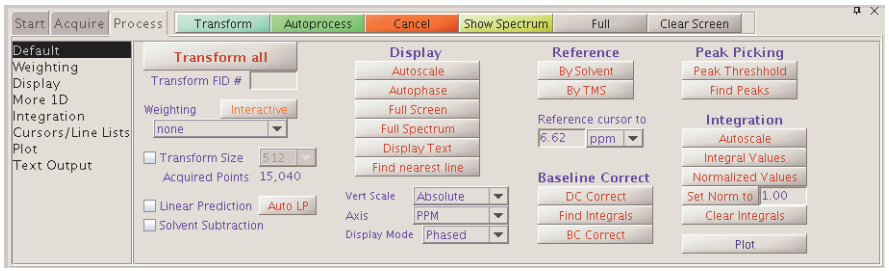
VnmrJ NMR data acquisition and the functions provided under the Acquire tab are described in Chapter 5, “Data Acquisition,” page 81. Set acquisition and acquire data using the pages in the **Acquire** tab.



1. Set up experimental parameters and post acquisition actions.
2. Click the **Acquire** button to acquire NMR data.

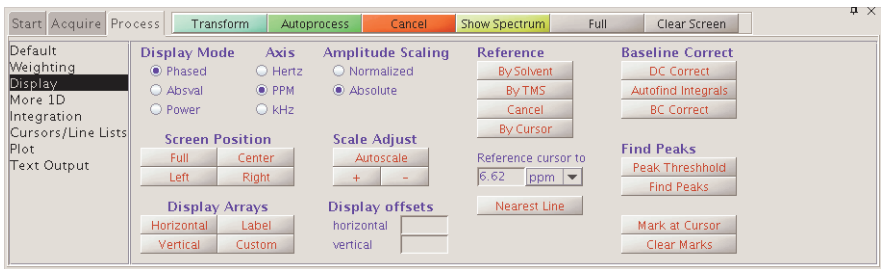
Process the Data

VnmrJ NMR data processing and the functions accessed by clicking on the **Process** tab are described in Chapter 6, “Processing Data,” page 93.



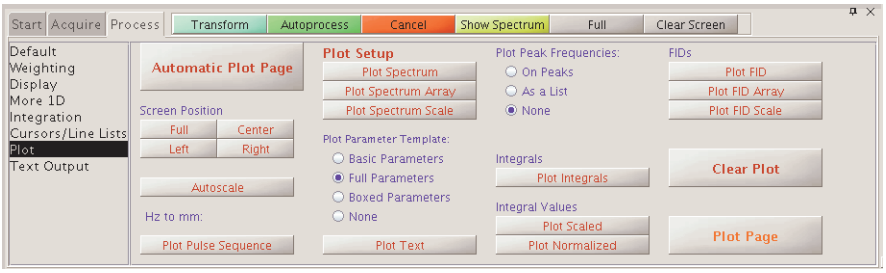
Display the Data

VnmrJ data display is described in Chapter 7, “Displaying FIDs and Spectra,” page 103. Click on the **Process** tab and select the **Display** page and the **graphic control** buttons to manipulate the display of the data.



Print or Plot the Data

VnmrJ data display is described in Chapter 8, “Plotting and Printing,” page 131. Use the **Plot** page to create a print or plot.



1.2 Saving NMR Data (optional)

Use either the Save Data Setup window or the Future Actions page to save the data if the data is acquired and the **Automatic FID save** feature in the **Future Actions** page under the **Acquire** tab is not selected.

Method	*Description*
Future Actions Page	Click on the **Acquire** tab, **Future Actions** tab, and **Save FID Now** button. Check the **Automatic FID Save** in the **Future Actions** panel before starting an experiment to automatically save upon completion of acquisition data acquisition.
Main VnmrJ Menu Options	Click on **File.** Select either **Save as…** or **Auto Save**. Selecting **Auto Save** saves the data as specified in **Save data setup…** Click on **Save data setup…** to customize where and under what name data is saved (see *VnmrJ Installation and Administration* manual).

1.3 Stopping an Experiment

There are four ways to stop an experiment:

- Click on the **Stop** button .
- Click on **Acquisition** in the main menu, then **Abort Acquisition**.
- Click on the **Stop** button in the **Acquire** panel.
- Enter **aa** on the command line.

Chapter 2. Preparing for an Experiment

Sections in this chapter:

- 2.1, “Starting VnmrJ,” on page 27
- 2.2, “Preparing the Sample,” this page
- 2.3, “Ejecting and Inserting the Sample,” on page 29
- 2.4, “Loading a Probe File,” on page 30
- 2.5, “Tuning Probes on Systems with ProTune,” on page 31
- 2.6, “Tuning Probes on Standard Systems,” on page 34

2.1 Starting VnmrJ

1. Log on to the workstation.
2. Double click on the **VnmrJ** icon.

2.2 Preparing the Sample

Sample preparation and positioning in the turbine affect the efficiency of auto shimming methods. Variations in bulk magnetic susceptibility at air-to-glass, glass-to-solvent, and solvent-to-air contact points can contribute a dominant portion of the variation of field homogeneity from sample to sample. The time spent shimming, or even the need to shim is largely dependent on the care in controlling the effects of these contact points.

- "Selecting a Solvent," page 27
- "Setting the Sample Height," page 27
- "Sample Position Using the Depth Gauge," page 28
- "Sample Tubes," page 29

Selecting a Solvent

Most samples are dissolved in a deuterated solvent that does not react or degrade the sample. The instrument can be run unlocked if the sample must be run using a solvent that is not deuterated.

Setting the Sample Height

Experimentation and calculation show that the liquid column length must be at least three times the length of the observe coil window to minimize end effects. A typical sample length is 5 cm regardless of the diameter of the NMR tube used. Solvent volumes of 0.6 ml

in a 5-mm tube and 3.1 ml in a 10-mm tube are adequate for removing the end effects. Refer to the manual provided with the probe in use for specific sample height and volume specifications.

Reduction of sample volume to attain higher concentration usually fails (special plugs for low volume samples are available and will help with line shape) because the increased signal is found around the base of the NMR resonance, not within the narrow portion of the signal. In fact, a well-shimmed 0.4 ml sample will be lower in sensitivity than the same solution diluted to 0.6 ml and also shimmed well. The questionable gain in sensitivity is further degraded by the longer time it will take to shim the system. Small variations of sample height that would be insignificant in a 0.6 to 0.8 ml sample can be dominant when the sample is only 0.4 ml in volume.

For best results and minimum shimming time, samples should be prepared to be the same height as much as possible. Above 0.7 ml there is little sensitivity to sample length as long as the bottom of the tube is positioned properly. Make every sample up to the same height and obtain shim values using samples of that height.

Typical samples with volumes for Wilmad 528 or 535 tubes with no restricting plugs listed in Table 1 are placed at the depths shown in the table. The depth is the distance in mm from the bottom of the turbine to the bottom of the sample tube.

Table 1. Sample Tube Depths

Volume	*Length*	*Depth (Range)*
700 µL	50 mm	68 mm (65–69 mm)
600 µL	42 mm	65 mm (63–67 mm)
500 µL	36 mm	62 mm (60–64 mm)
400 µL	28 mm	59 mm (58–62 mm)

Sample Position Using the Depth Gauge

Set the sample position to a repeatable position. Use the sample depth gauge provided, shown in Figure 2. Use location 0 on the sample tray if a sample changer is present.

1. Insert the turbine into the top of the sample depth gauge.

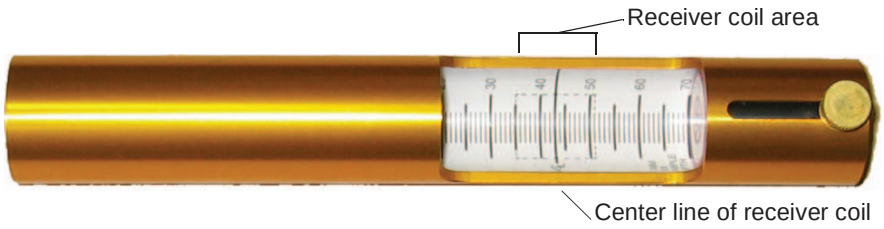


Figure 2. Sample Depth Gauge

2. Insert the NMR sample tube into the turbine. Gently push the sample tube down until it touches the moveable bottom of the sample depth gauge.
3. Loosen the knob on the sample depth gauge.
4. Raise the bottom of the gauge, along with the sample tube and turbine, until the sample volume is centered on the centering mark (CL, between 35 and 51 mm) in the back of the gauge.
5. Tighten the knob.
6. Remove the sample tube and turbine from the depth gauge.

7. Gently pull up on the sample tube in the turbine, replace the turbine/sample tube into the depth gauge, and gently push down on the sample tube until it touches the repositioned bottom of the depth gauge.

Sample Tubes

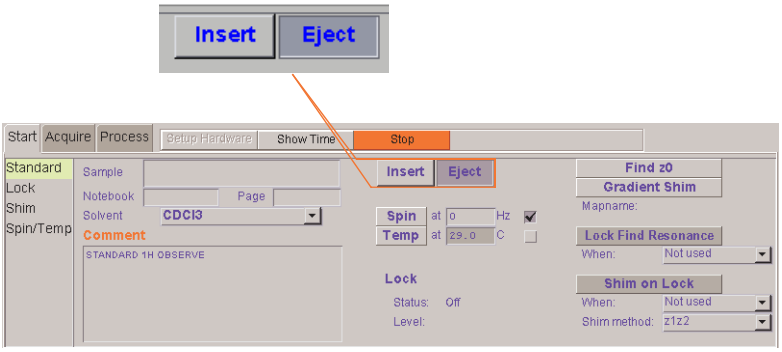
Buy the best quality NMR sample tubes and clean the outside of each tube with a solvent such as isopropyl alcohol, followed by a careful wiping with a wiper tissue before placing the tube in the probe.

Sample Changes and Probe Tuning

Probe tuning is required when there is a significant change in the polarity of the solvent. Changing from a non-polar organic solvent to a more polar organic solvent or aqueous solvent generally requires retuning the probe. Changes in the ionic strength of the solution (e.g., low salt to high salt) also require retuning of the probe.

2.3 Ejecting and Inserting the Sample

The spectrometer is equipped with hardware and software to provide computer control of sample ejection, insertion, spinning, locking, and shimming. This section covers computer-controlled sample ejection and insertion.



Ejecting a Sample

Always eject first (even if no sample is in the magnet) to start airflow to carry the sample. The eject air is turned on and, under computer control, the sample, if present, rises back to the top of the upper barrel. Remove the sample and replace it with another sample.

Using the Start Tab

The Insert and Eject buttons are on the Start tab.

1. Click the **Start** tab to open the setup tab.
2. Click the **Eject** button.

Inserting a Sample

The sample tube gradually lowers down the upper barrel under computer control. The bearing air is turned off momentarily allowing the turbine to seat properly into the bearing cylinder.

Using the Start Tab

1. Perform a sample ejection (even if no sample is in the magnet) to start airflow to carry the sample.
2. Insert the sample by placing it in the top of the upper barrel.
1. Click the **Start** tab to open the setup tab.
2. Click on the **Standard** page.
3. Click **Insert**.

2.4 Loading a Probe File

Probe files can be created at any time and are typically created during system or probe installation. Procedures for creating probe files and probe calibration files are provided in the *VnmrJ Installation and Administration* manual.

1. Click the **Probe** button on the Hardware bar (bottom left corner of the VnmrJ interface).

   The probe selection window appears.
2. Click the **Select Probe** dropdown menu and select the desired probe.
3. Click **Close** to dismiss the window.

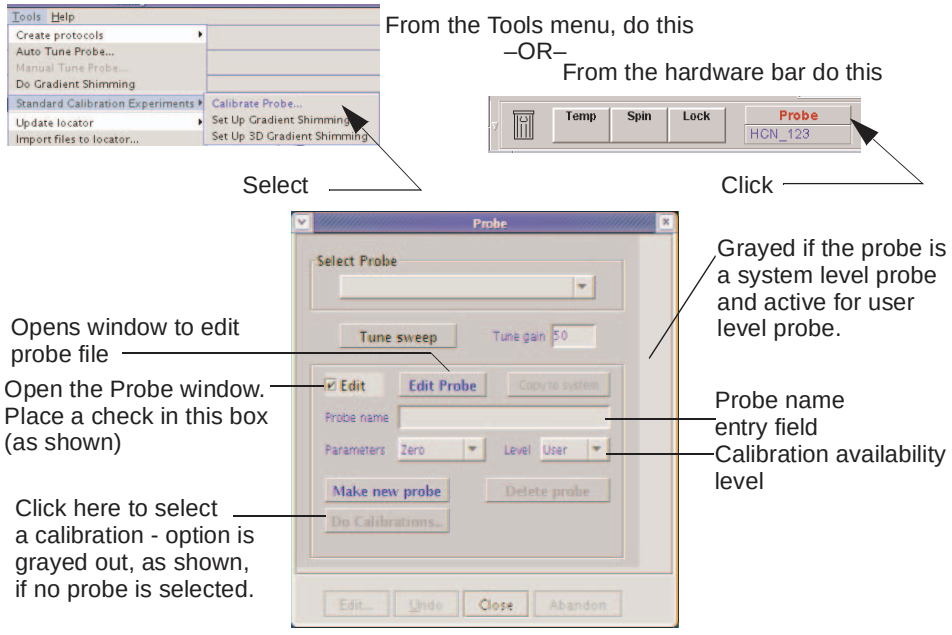


Figure 3. Calibrating a Probe

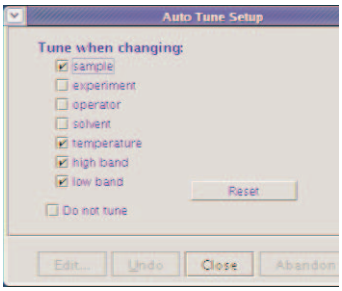
2.5 Tuning Probes on Systems with ProTune

This section applies to Varian NMR Systems spectrometers equipped with ProTune.

Configuring for Operation with Automated Sample Handlers

- Applies to systems equipped with ProTune.
- The system must be properly configured and ProTune-calibrated. Refer to the *VnmrJ Installation and System Administration* manual for configuring the software and calibrating ProTune.
- Data acquisition with an automated sample handler uses the Walkup interface.

1. Log in or switch operators to the walkup account administrator and start VnmrJ.
2. Click on the **Tools** button on the main menu bar.
3. Select **Probe Tuning**.
4. Select **Auto tune setup …** from the pop-out menu.
5. Specify when ProTune automatically tunes the probe.
   Placing a check in the box next to each change in condition results in automatically tuning the probe. Click the **Reset** button to return to the default conditions.
6. Check the box next to **Do not tune** if no tuning by walkup operators is allowed.

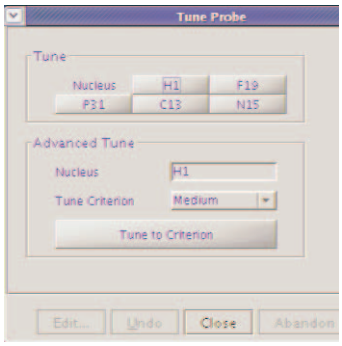


7. Selecting any option aside from **Do not tune** places a check box on the study panel, and selecting **Do not tune** removes the check box from the study panel.

   Gradient shimming will start after each auto tune event if both auto tune and gradient shimming are selected.
8. Click on **Close** to save the changes and exit the Setup Autotune window.

Running Protune

1. Click on the **Tools** button on the main menu bar.
   - **Walkup interface —** Select **Tune Probe…** from menu.
   - **Experimental interface —**Select **Auto Tune Probe…** from menu.
2. Click on a **nucleus button** next to Nucleus in the Tune region to set the tune frequency.
3. Select a criteria from the dropdown menu next to Tune Criterion in the Advanced Tune section:



Coarse – within 5 percent of optimum `pw`

Medium – within 2 percent of optimum `pw`

Fine – within 0.5 percent of optimum `pw`

The criteria function is available to the walkup operator depending on value set in the parameter `panellevel`.

4. Click on **Tune to Criterion** button.
5. Select the next nucleus and repeat step 2 through step 5 and continue with the next step when all desired tuning is completed.
6. Click on **Close** to exit the ProTune module.

Remote Tuning from the ProTune Window

The ProTune interface window (shown in Figure 4) can be used to tune the probe. Functions and features of ProTune are listed in Table 2.

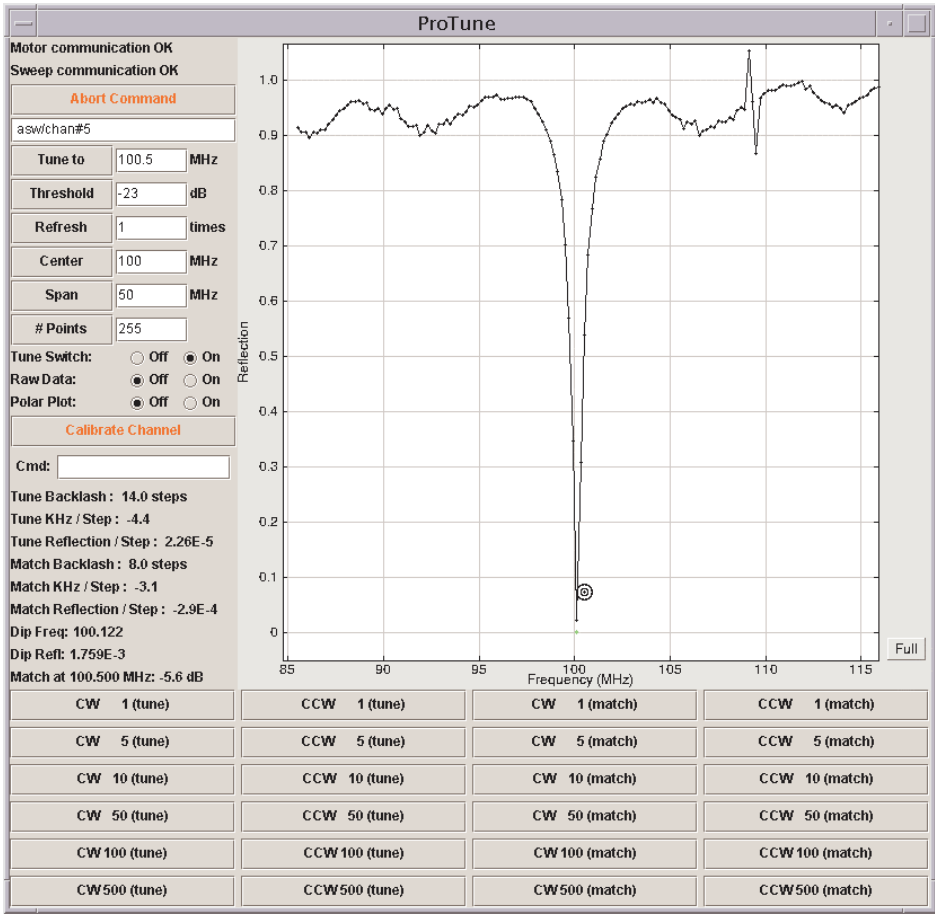


Figure 4. Protune Software Interface Example

1. Start ProTune by entering the following in the VnmrJ command line:

   `protune('calibrate')`

   The calibration files for the probe shown on the hardware bar of the VnmrJ interface, see Figure 5 are loaded.

Figure 5. Probe Name and VnmrJ Hardware Bar

2. Click on the **Refresh** button.
3. Make sure that the motor and sweep communication read **OK** before starting manual tuning after the ProTune window appears.

   Figure 4 shows the ProTune window with rf reflection at 499.5 MHz.
4. Enter the frequency (MHz) in the **Tune To box**.
5. Click the **Tune To** button.

   The software reads the appropriate channel file and starts tuning.
6. Do the following to stop the automatic tuning and tune manually:
   a. Click the **Abort Command** button (might require several clicks) to stop.
   b. Enter the corresponding chan # of the desired tune frequency.
   c. Click the appropriate **CCW (**counterclockwise) and **CW** (clockwise) buttons to adjust the tune and match.
   d. Enter a frequency in the **Center** box and click **Refresh** to update the reflection window to center the window.
   e. Enter a frequency width in the **Span** entry box and click **Refresh** to update the reflection window to set the window span.
7. Close the ProTune window — acquisition will stop automatically. Enter **`aa`** on the ProTune Window Description.

Table 2. ProTune Features and Functions

Feature	*Button, Label, or Message*	*Description*
Diagnostic and tuning	Motor Communication OK, Sweep Communication OK	Status of Ethernet communications between the module and the workstation.
	Abort Command	Stops current command
	Text Box	Probe name and channel number
	Tune Mode On/Off	Toggle TR Switch/Relay to tune
	Raw Data Mode On/Off	Toggle window to display raw data
	Tune Freq (MHz)	Tune frequency
	Match (dB)	Criteria for successful tuning
	Track Tune (s)	The number of times the plot should update with new data
	Center (MHz)	Sets center value of the sweep range
	Span (MHz)	Sets span value of the sweep range
	Number of Points	Number of the measurement points for all segments of the sweep table for each channel
	Initialize	Initialize tuning sensitivity. Run the tune and match motors and update backlash, frequency, and reflection values.
	Polar	Toggle between polar plot (imaginary and real reflection) and linear plot (reflection v. frequency). Polar plot does not work in raw data mode.
	Cmd:	Sends the command in the field directly to the motor modules

Settings	Tune/Match Backlash	Difference between the number of steps traveled from the tune frequency and the number of steps traveled back to the tune frequency. This value is the same for CW and CCW movements.
	Tune/Match KHz/Step	Number of KHz the dip moves in 1 step
	Tune/Match Reflection/ Step	Minimum dip movement in one step with no regard to frequency. Positive values are inside the circle of origin, and negative values are outside the circle of origin.
	Dip Frequency	Frequency the dip occurs
	Dip Refl	Reflection the dip occurs
	Match at Freq MHz	Value for the tuning criteria at the desired frequency
Controls and output	Tune	Tune motor control
	MATCH	Match motor control
	CC/CCW #	Clockwise or counter clockwise and number of steps to move
	Plot	Displays Reflection v. Frequency in a linear plot or imaginary and real Reflection on a polar plot. Right click to draw a box around an area of interest and expand the viewing area.
	Full	Displays the graph in full scale view; for polar plot, it shows the unit circle

2.6 Tuning Probes on Standard Systems

Typically, probes are tuned using the TUNE INTERFACE, shown in Figure 8.

- "Selecting Correct Quarter-Wavelength," page 34
- "Tuning Using Mtune," page 35
- "Tuning Using the TUNE INTERFACE Remote," page 36

Selecting Correct Quarter-Wavelength

When a large change is made in the frequency of the observe nucleus on broadband systems, such as switching from ^{13}C to ^{15}N, an additional change is made in the quarter-wavelength cable, a coiled cable located on the system as follows:

- Attached to the preamplifier housing for 500–900-MHz systems
- Attached to the inner face of the magnet console interface unit as part of the observe circuitry on other systems

The quarter-wavelength cable is *not* changed for each nucleus, but only for broad ranges of frequencies (for example, 40 to 80 MHz), usually covering a factor of two (an octave) in frequency. An incorrect cable does not typically affect signal-to-noise, but may have a profound effect on the 90° pulse length.

Tuning Using Mtune

The Mtune routine runs in the graphics canvas and uses VnmrJ panels. Start mtune as follows:

1. Click on **Tools** on the main menu
2. Select **Manual Tune Probe**... or call enter **`mtune`** on the command line.
3. Select the RF channel and center frequency of the nucleus to tune.

   For example, set H1 on channel 1.
4. Select **Start Probe Tune** on the mtune panel see Figure 6.

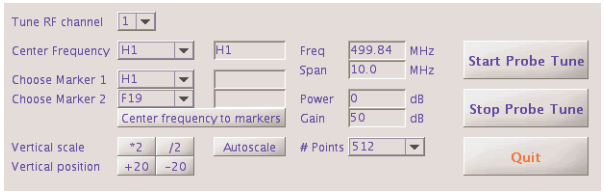


Figure 6. Manual Tuning Panel

5. Choose an appropriate tuning Power (may be channel dependent)–typical values are between 0 and 10 dB.
6. Set the tuning Gain to **50 dB** (a typical gain).
7. Set a frequency Span that shows the tuning dip in full size:
   - The frequency Span ^{1}H is approximately 10 MHz
   - The frequency Span for lower frequencies like ^{15}N of 1 MHz may be adequate.
8. Adjust any of the parameters as needed.

   All parameters (nucleus, frequency, span, power...) can be changed on-the-fly during tuning except the RF channel.
9. Set one or two markers.

   Up to two frequency markers are selectable. This is useful for tuning H1 and 19F at the same time, for example, with double-tuned coils like in the ATB or 4-nucleus probe families (Figure 7).

   a. Click on the **Center frequency to markers** button to set the tuning frequency in between the two tuning dips.

   b. Choose the **Span** with a sweep width covering both dips.

      A span of 50 MHz is typical to show 1H and 19F at 400 MHz as shown in Figure 7:.

   c. Maximize the graphics canvas horizontally to have the best screen resolution.
10. Click on the **Autoscale** button to fit the tuning dip vertically into the graphics canvas or scale.
11. Shift the display manually using the **Vertical scale/Vertical position**.
12. Keep the default number of acquired points of change the number of points by selecting a new value from the **# Points** drop-down menu.

    Increasing the number of points provides better resolution at large spectral widths. Higher resolutions will have smaller update rates.

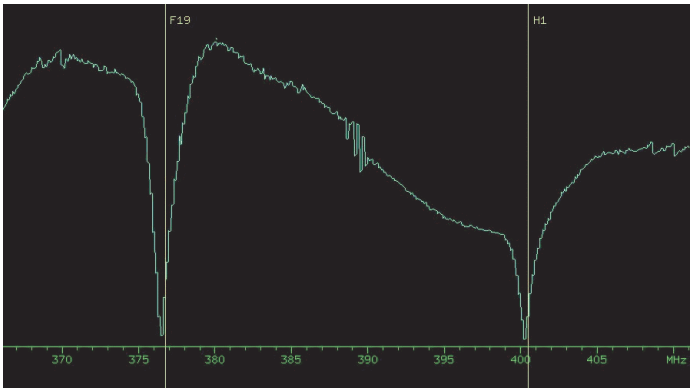


Figure 7. Frequency Span Display Showing both ^{19}F and ^{1}H Tune Dips

13. Tune the other channels as follows:
    a. Switch tuning off by selecting **Stop Probe Tune**.
    b. Select a different channel and nucleus.
    c. Switch tuning back on by selecting **Start Probe Tune**.
    d. Repeat step step 1 through step 13 for each channel.
14. Exit mtune after tuning is done:
    a. Click on **Stop Probe Tune**.
    b. Click on **Quit** to return to the previous NMR experiment.

Tuning Using the TUNE INTERFACE Remote

Using the Interface Remote

The Tune Interface remote is attached to the rf front end and can be extended to the magnet while tuning the probe.

- The TUNE INTERFACE display, a rectangular liquid-crystal display that shows a digital readout, is at the top of the panel.
- Two single-digit readouts labeled CHAN and ATTEN are below the display. The CHAN readout can be set to 0 for OFF or to the channel being tuned (1, 2, 3, etc.), and the ATTEN readout is the amount of attenuation. The attenuation is selected in units of 10 dB. The maximum attenuation is 79 dB, which is selected by a setting of 8. Above and below each readout are buttons for setting the value of the readout.

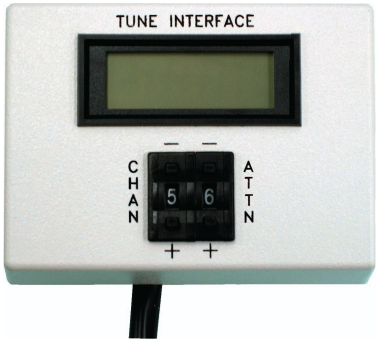


Figure 8. Tune Interface Remote

Tuning a Probe

Tuning a probe using the TUNE INTERFACE remote takes the following steps:

1. Set up the spectrometer to observe the nucleus of interest.

Often, the system is already set to the correct nucleus; if not, proceed as if to setup an experiment.

2. Set the nucleus for each channel.

   The TUNE INTERFACE remote will not work after powering on or after resetting the acquisition console until the tune frequencies are set.

   Enter `su`.

   When an `su` executes, the console frequency is set for each channel defined for the experiment. This frequency also becomes the one used during tune. The table below shows the relationships between the channel selected and the associated parameters:

Channel 1	`tn`	`sfrq`	`tof`
Channel 2	`dn`	`dfrq`	`dof`
Channel 3	`dn2`	`dfrq2`	`dof2`
Channel 4	`dn3`	`dfrq3`	`dof3`

   Refer to the *Command and Parameter Reference* for descriptions of these parameters.

3. Press the **CHAN** buttons until the readout is the number of the rf channel to tune. Start with channel 1.

   This turns on the tuning function for the channel. The TUNE INTERFACE display should show a number.

4. Press the **ATTEN** buttons until the readout is 6, 7, or 8.

5. Insert the appropriate sticks into the probe if necessary. Refer to the probe installation manual to choose which sticks are needed to tune to the desired nucleus.

6. Tune the probe. As the probe gets closer to being tuned, the number on the TUNE INTERFACE display will decrease.

7. Press the **ATTEN** button until the readout is 8, to increase the tuning level sensitivity. Continue tuning until the number displayed on the TUNE INTERFACE display is at a minimum.

8. Disconnect the tuning function by pressing the **CHAN** buttons until the readout is 0. (During normal operation, CHAN must be set to 0 or acquisition is *not* allowed.)

9. Repeat the steps above for each channel on the system.

For further information about probe installation and tuning, refer to the probe installation manual that shipped with your probe.

Chapter 3. Experiment Setup

Sections in this chapter:

- 3.1, “Selecting an Experiment,” on page 39
- 3.2, “Spinning the Sample,” on page 40
- 3.3, “Sample Temperature,” on page 43
- 3.4, “Spin and Temperature Error Handling,” on page 45
- 3.5, “Working with the Lock and Shim Pages,” on page 45
- 3.6, “Optimizing Lock,” on page 46
- 3.7, “Adjusting Field Homogeneity,” on page 50
- 3.8, “Selecting Shims to Optimize,” on page 52
- 3.9, “Shimming on the Lock Signal Manually,” on page 53
- 3.10, “Shimming PFG Systems,” on page 57
- 3.11, “Calibrating the Probe,” on page 58

These sections are in the same order as typically performed by most users.

3.1 Selecting an Experiment

VnmrJ provides several methods to choose and load an experiment. This section describes using the menu bar or the Locator. After an experiment is selected, VnmrJ reads and loads the standard parameters and then reads the probe file and loads the probe calibrations.

Main Menu Selections

Experiment

1. Click on **Experiments** in the menu bar.
2. Click on an experiment in the list to bring it into the active viewport, see "Experiments Menu," page 370.

   The list of experiments contains some submenus.

File

1. Click on **File**.
2. Select **Open**.
3. Navigate to the directory containing the experiment or data set.
4. **Click** on an experiment or data set from the Browser to a view port.

5. Click on **Open** to bring it into the active viewport.

Locator

1. Click on **Tools**.
2. Select **Locator…**
3. Click and drag an experiment from the locator to a view port or double-click on the experiment to bring it into the active viewport.

Browser

1. Click on **Tools**.
2. Select **Browser.**
3. Navigate to the directory containing the experiment or data set.
4. Click and drag an experiment or data set from the Browser to a view port.

Note: Loading a data set does not set parameter values from the current probe file so the settings may be incorrect for any new acquisition.

3.2 Spinning the Sample

Either the liquids Spinner panel or the MAS Spinner panel, depending on the spectrometer hardware, is displayed when the Spin/Temp page under the Start tab is selected.

- "Liquids Spinner," page 40
- "MAS Spinner," page 41

Liquids Spinner

Set **`spintype='liquids'`** to show the liquids spinner panel.

Adjust spin rate using the input window or the Acquisition window. Typical spin rates are 15 for 10-mm tubes and 20–26 for 5-mm tubes.

The last entered spin rate is used to regulate sample spinning when a new sample is inserted. The actual spin rate is indicated three ways:

- The Spin chart display button on the hardware bar displays a history of the sample spin rate.
- Acquisition Status window shows the actual rate as well as a spin regulation indication.
- The remote status unit, signals the spin rate using the spin light status:

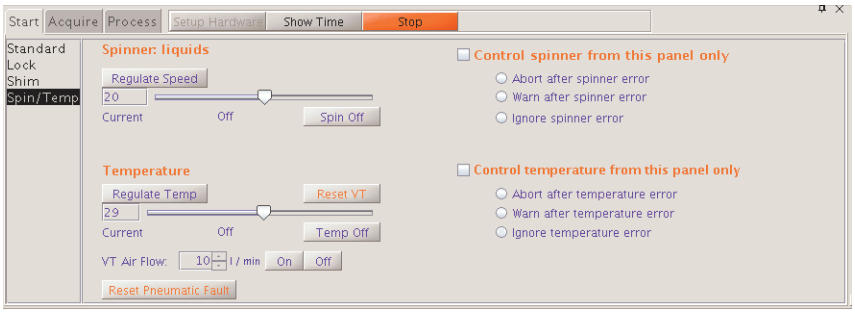
  off — the sample is not spinning.

  blinking — the sample is spinning but not at the last requested rate.

  on steady — the spin rate is being regulated at the last requested rate.

Using the Start Tab

The Spin/Temp page is under the Start tab.



1. Click the **Start** tab. Select the **Spin/Temp** page.

   The controls for changing spinning speed consist of an entry field, a slider bar, and a button for disabling or enabling spinning.

2. Adjust the spinning speed with either of these methods:
   - Enter a spin rate in the text entry field.
   - Drag the slide control. The value changes proportionally as the mouse moves.
   - Click in the slider bar to move the slider by one increment.

3. Optional:

   Specify error handing for spinner and temperature by placing a check in the box next to **Control spinner from this page only** and **Control temperature from this page only**, see "Spin and Temperature Error Handling," page 45.

The following safety measures have been implemented for the high speed spinner probes (e.g., MAS) to prevent rotor and stator damage:

- The air flow selected is ramped to the new value at a safe rate.
- Air flow is shut off if the spinner speed drops to zero, and the spin setting is nonzero to prevent spinner runaway if the tachometer fails.
- Air flow is shut off if for any reason the spinning speed cannot be reached to prevent continued attempts to spin a crashed rotor.

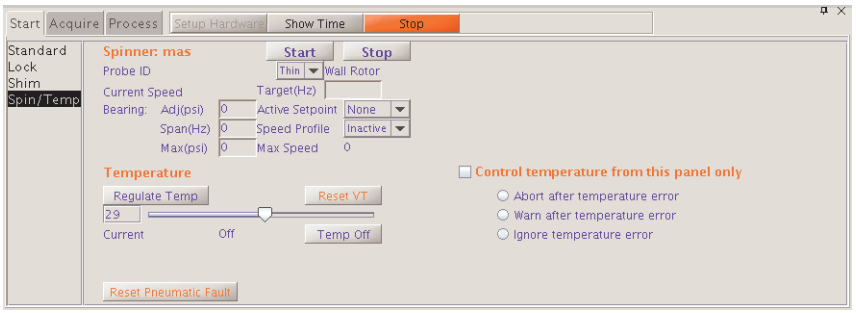
MAS Spinner

Set **`spintype='mas'`** to show the MAS Spinner control panel.

The MAS speed controller controls the flow of bearing gas according to a linear algorithm based on the speed of the spinning rotor. The bearing pressure profile starts from the final pressure at start up and increases linearly to the maximum bearing pressure in proportion to the speed of the rotor. The speed controller already has bearing profiles for all solids spinning modules stored in nonvolatile memory. Use the bearing control items to customize these settings. Changes made to the bearing profile remain in effect until the power is cycled or the probe is changd.

WARNING: **Thinwall rotors can shatter at high speeds, causing injury and damage. If a thinwall rotor is used, be sure that *Thin* is selected for *Rotor Wall*.**

The MAS Spinner panel (which controls the MAS Speed Controller) is accessed from the Spin/Temp page under the Start tab.



Setting `spintype='mas'` gives the MAS Spinner control panel described here. Setting `spintype='liquids'` gives the liquids spinner panel.

Start Button — Click the **Start** button to start the rotor spinning at the target set into the active setpoint.

Stop Button — Click the **Stop** button to initiate the speed controller stop cycle, which slows down the rotor in a controlled manner until it is stopped. The Stop button is intended to provide a normal stop and is not an emergency stop.

Target (Hz) — The Target Speed field is used to set the spinning speed stored in the active setpoint. Any changes made to the setpoints remain in effect until the power is cycled or the probe is changed. Setting the target will not start the rotor if it is not spinning, it just sets the value in the setpoint.
-- Only the currently active setpoint can be changed.
-- If neither setpoint is active, any change made to the value in the Target Speed field activates setpoint one and sets it to that value.
-- If the rotor is spinning and the active setpoint is changed, the rotor's spinning speed changes as soon as the return key is pressed.

Probe ID — The probe ID is detected automatically by the solids speed controller when the tachometer cable is plugged into the probe. Early solids probes (7.5 mm) had no designated ID type, so an unplugged cable or a cable plugged into an unknown probe may cause a 7.5 mm probe type to be displayed. Although the probe type is detected immediately by the speed controller when the probe is connected, the probe ID in the panel is updated about once per minute. It is also displayed in the hardware bar.

Current Speed — This item displays the current speed of the rotor. This value is also displayed in the hardware bar.

Wall Rotor — Displays rotor wall thickness. Setting the Rotor Wall to Thin causes the Max Speed to be reduced to protect the rotor from shattering. The value defaults to Thin after the probe is changed or the controller is reset. If the current rotor is a standard wall rotor, change the setting to Std to get the allowable rotor speed for the probe.

Bearing Adjust (psi) — The value in the Adjust field shifts the bearing profile up or down, up to ± 80 psi. The bearing adjustment profile can be a negative number, meaning that the operating profile is lower than the factory setting.

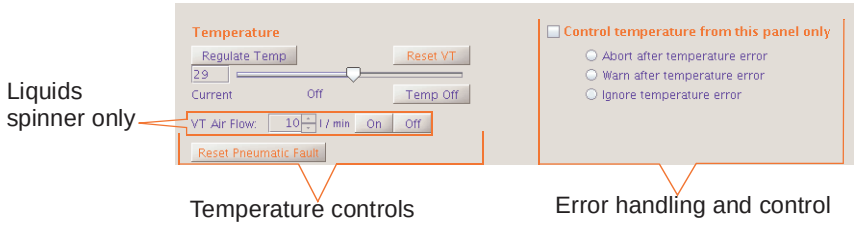
Bearing Span (Hz) — The value in the Span field determines when the controller stops following the bearing profile. When the speed of the rotor is within Span Hz, the speed controller freezes the bearing value and does not change it until the spinning speed error exceeds this value. The factory defined setting for Span is 100 Hz for all spinning modules. When adjusting the bearing profile, set Span to **0**, meaning that the bearing pressure is continuously controlled. Then, when finished entering values in the Adjust and Maximum fields, enter a new value in the Span field.

Bearing Max (psi)	The value in the Maximum field sets the maximum bearing pressure in psi. This value controls the upper cutoff point in the bearing profile. The maximum bearing pressure is limited to 80 psi.
Active Setpoint	Two setpoints are available. The one selected is used to control the speed and is the one set when the target is changed. Changing the setpoint while the rotor is spinning immediately changes the target to the value for that setpoint. Selecting **None** stops the control algorithm and leaves the bearing air and drive air unchanged, which is sometimes referred to as *coasting*.
Speed Profile	Select **Active** to activate the speed profile feature, which causes the speed controller to constantly compare the drive pressure required to spin the rotor against its preprogrammed estimate of the required pressure for the current speed. If the pressure required to spin the rotor falls outside this range, the speed controller assumes that the rotor is vibrating. If the speed controller cannot stabilize the rotor, it brings the rotor to a stop.
Strip Chart	Clicking the **Spin** button in the hardware bar will bring up a strip chart of the spinning speed with time.

3.3 Sample Temperature

Set the temperature for VT control in the **Standard** page and regulate the temperature by clicking on **Spin/Temp** page.

Refer to Chapter A, “Variable Temperature System,” page 415, for more information on using the Variable Temperature module. The following steps describe a typical operation sequence:



1. Open the **Spin/Temp** page under the Start folder.
2. Set the desired temperature by entering a value or using the slider, and click **Regulate Temp**.
3. Set up the acquisition for the experiment as usual, using the Acquire folder.
4. Click the **Temp** button on the hardware bar to display the temperature display chart.
5. Start temperature control with the **Setup Hardware** button on the Start folder, or with the **Acquire** button on the Acquire folder. These commands act as follows:
   - Setup Hardware

     The temperature control and acquisition hardware controls are set and the sample temperature changed to the desired temperature. The experiment is not started when the desired temperature is reached. Wait for the delay time, `vtwait`, (seconds), then push the **Acquire** button to begin data acquisition.
   - Acquire

     The same actions occur as in Setup Hardware, except that after reaching the desired temperature, the system waits the delay time, `vtwait`, then begins the pulse sequence and data acquisition. The delay time, `vtwait`, occurs every time the temperature is changed under program control.

Selection of the VT gas routing occurs after clicking Setup Hardware or Acquire. The VT controller begins to control the gas temperature in the probe at the requested temperature. The temperature readout will begin to change, and the VT indicator light will begin flashing. At this time, if the requested temperature is below ambient, add coolant liquid to the coolant bucket or reset any FTS device to a temperature 10° C or more below the desired operating temperature.

The VT indicator light stays on steadily after the temperature reaches the requested temperature (it may initially overshoot). A sample that could not be handled at ambient temperature can now be transferred into the probe. The VT readout is the temperature of the cooling/heating gas and may be different from the true sample temperature. The exact temperature of the sample is correctly determined by a calibration curve that must be constructed for each probe, and must include flow rate and equilibration time. Refer to the *VT Accessory Installation* manual for the NMR calibration method.

CAUTION: **Do not use aromatic, ketone (including acetone), and chlorinated solvents in the coolant bucket. Such coolant media attack the standard polystyrene bucket. Another type of container must be used (not supplied by Varian).**

CAUTION: **Operating the system with the coolant bucket filled with liquid nitrogen and with the temperature greater than the value of VT cutoff results in the condensation of liquid nitrogen inside the exchanger coil tube. If the exchanger coil is then warmed above –210°C or if nitrogen gas is passed through the coil (when temperature is less than VT cutoff), very cold liquid nitrogen is forced through the transfer line and into the probe. This will cause a sudden pressure surge in the transfer lines and probe as the liquid nitrogen boils, and it can blow the flexible connector apart. If the liquid nitrogen reaches the glass components of the probe and sample tube, the glass will probably break. Instrument damage can be avoided by following these precautions:**

Do not immerse the exchanger coil in liquid nitrogen when no nitrogen gas is flowing through the coil.

Do not stop the VT nitrogen gas flow while the exchanger is immersed in liquid nitrogen.

Arrayed VT experiments that have a temperature range from above VT cutoff to below VT cutoff should be set up starting at the lowest temperature and ending at the highest temperature. When the experiment passes the VT cutoff crossover, remove the liquid nitrogen coolant.

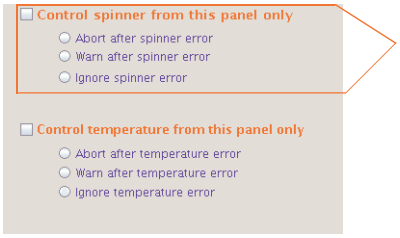
To avoid water in the exchanger when the low temperature experiment is complete, warm up the exchanger by removing it from the liquid nitrogen and maintain a flow of dry nitrogen until room temperature is reached.

WARNING: **Sealed samples containing volatile materials can rupture when heated, resulting in potential injury, exposure, and equipment damage. Before running sealed samples at elevated temperatures, heat the samples in an oven at a temperature higher than the highest temperature during the experiment. If the tube ruptures while in the probe, the glass components and insert coil will probably be destroyed.**

WARNING: **Sealed samples containing materials with boiling points at or below room temperature can rupture as the sample warms, causing potential injury, exposure, and equipment damage. Equilibrate the probe to a temperature below the sample boiling point before the sample is placed into the probe.**

3.4 Spin and Temperature Error Handling

Use the Spin/Temp page of the Start tab to select spin and temperature error handling. The provided choices specify the action to be taken based on spinner and temperature failure. Also use the Spin/Temp page to specify whether spinning and temperature can be controlled on panels other than the Start tab.



- *Ignore spinner/temperature error* – stops any system checking so that acquisition continues regardless of the spin speed or temperature.
- *Warn after spinner/temperature error* – makes the system check the spin speed and temperature. A warning message is added to the log file if the if the spin speed or temperature is set to a particular value and the spin speed or temperature goes out of regulation; however, acquisition is not stopped.
- *Abort after spinner/temperature error* – makes the system check the spin speed and temperature. Acquisition is halted if spin speed or temperature is set to a particular value and the spin speed or temperature goes out of regulation.

3.5 Working with the Lock and Shim Pages

- "Mouse Control of Buttons and Sliders," page 45
- "Lock Buttons and Controls," page 46
- "Shim Buttons and Controls," page 46

Mouse Control of Buttons and Sliders

To Change the Increment

1. Middle click the increment button until the increment value to change is displayed. The defaults are 1, 10, and 100.
2. Shift/middle-click the button, enter a new value, and press **Return**.

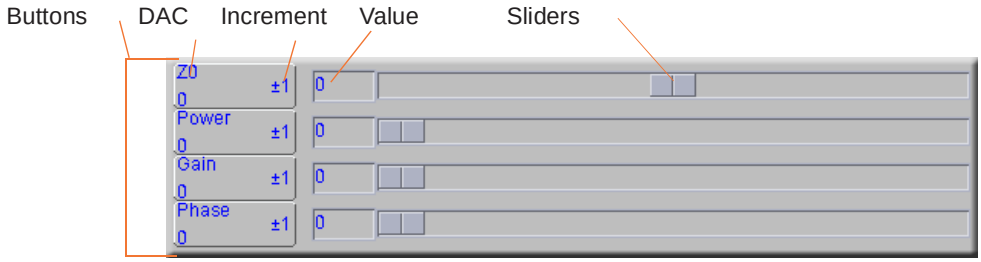
To Change the DAC Value

1. Shift/left -click on the DAC button.

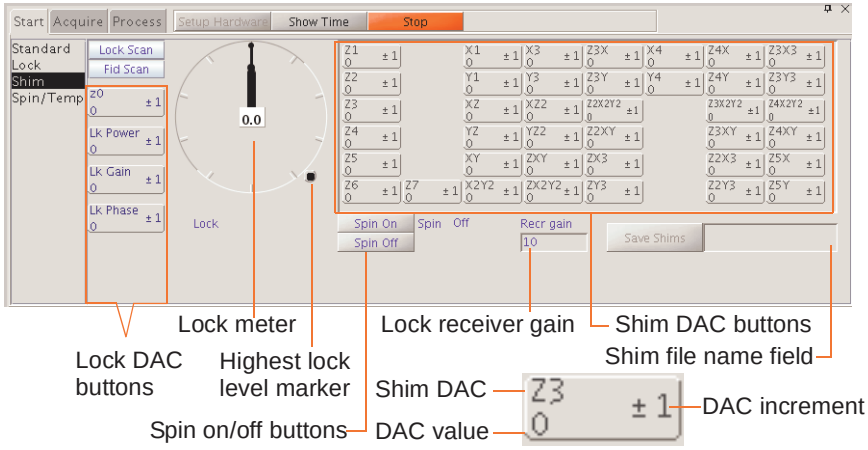
2. Enter a new value and press **Return**.

Lock Buttons and Controls

The Lock and Shim buttons (z0, Lock Power, Lock Gain, Lock Phase, and Z, X, and Y shims) provide on-the-fly adjustment. The slider values can be moved with the mouse or entered directly.



Shim Buttons and Controls



3.6 Optimizing Lock

Under computer control, the lock system maintains a constant field at the sample as the static field generated by the superconducting magnet drifts slowly with time or changes due to external interference. Locking makes the resonance field of the deuterium in the deuterated solvent coincide with the lock frequency.

The lock level can be viewed by clicking the **Lock** button on the hardware bar.

The entire lock optimization process can be skipped if optimum lock parameters are already known for a particular solvent and probe combination. Values for these parameters can be entered as part of a macro or using normal parameter entry (e.g., by entering `lockgain=30 lockpower=24`). These parameters do not take effect until an `su`, `go`, or equivalent command is given.

It is important to obtain an optimal lock signal if automatic shimming is to be used. Manual adjustment often is done to achieve the maximum lock amplitude. This can result in a partly saturating condition, and a true non-saturating power is usually 6 to 10 dB lower. The

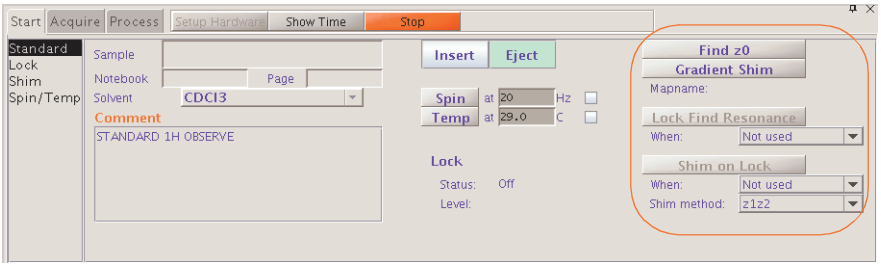
response of the lock level is governed by the T_1 of the deuterated lock solvent as well as the magnet-determined or chemical exchange-determined T_2^* of the solvent. This T_1 can vary widely, from about 6 seconds for acetone-d_6 to about 1.5 seconds for $CDCl_3$ and lower for more viscous solvents. To allow a reliable, repeatable selection of lock power, automatic optimization may be used.

- "Finding Z0 and Establishing Lock," page 47
- "Lock Power, Gain, and Phase," page 49
- "Lock Control Methods," page 49
- "Leaving Lock in the Current State," page 49
- "Running an Experiment Unlocked," page 49
- "Simple Autolock," page 49
- "Optimizing Autolock," page 50
- "Full Optimization," page 50

Finding Z0 and Establishing Lock

- "Manual or Simple Method," page 47
- "AutoLock," page 48

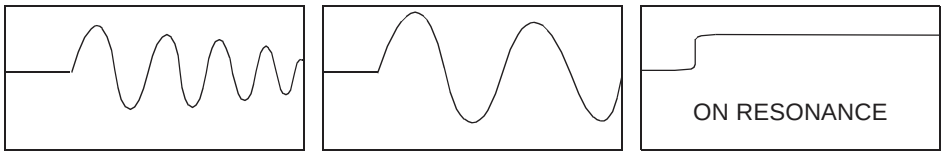
Find Z0 and establish the lock either manually or using Autolock through the **Standard** page of the **Start** tab.



Manual or Simple Method

Establish lock using simple or manual locking on the Lock page. The line that crosses the spectral window represents how close the deuterium resonance field is to the lock frequency. When the two are matched, the line should be flat (with perhaps some noise, depending on the lock gain and lock power). The poorer the match, the greater the number of sine waves in the line.

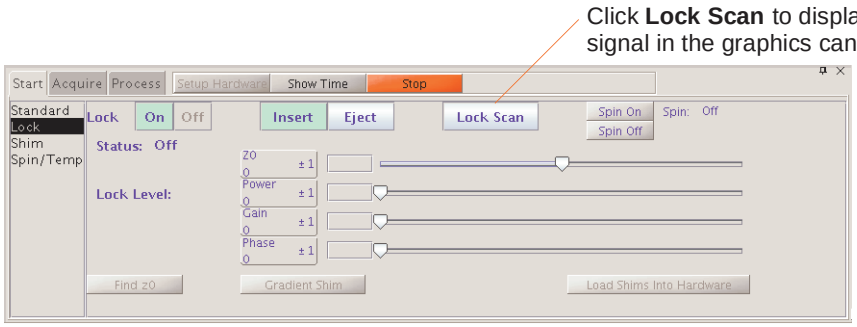
Changes from poor match to good match



1. Make sure a sample is inserted and seated properly. Spinning helps but is not required.
2. Click on the **Lock** page in the Start tab.
3. Click on either **Spin On** or **Spin Off**.

4. Click **Lock Scan** to open the lock display.
5. Find Z0 by clicking on and dragging the Z0 slider bar until lock signal is on resonance.
6. Adjust the lock power, gain, and phase by clicking on and dragging the slider bars, or click the button.

   The actual value needed for lockpower and lockgain depends upon the concentration of the deuterated solvent, the nature of the deuterated solvent—the number of deuterium atoms per molecule—and the relaxation time of the deuterium. At this point, do not be too concerned about optimizing power and gain; just look for a sine wave.
7. Click on the **±10** or **±100** button for Z0 until some discernible wave appears if no sine wave (perhaps just noise) is seen.
8. Reduce the lock power if the concentration of the lock solvent is high, (>50%).
9. Reduce the lock power if the signal oscillates (goes down and then back up) and it is difficult to establish lock. The deuterium nuclei become “saturated” if the lock power is too high. Acetone is more easily saturated than most solvents.
10. Adjust Z0 until the signal changes from a sine wave to an essentially flat line. The line may start to move up on the screen as the lock condition is approached if the solvent is concentrated.
11. Click the **Lock On** button.
12. Click **Lock Scan** again to close the lock display.



AutoLock with Probe File

This requires a probe file with the probe calibrations, refer to the *VnmrJ Installation and Administration* manual.

1. Click on the **Standard** page of the Start tab.
2. Click on either **Spin On** or **Spin Off**.
3. Click on **Find Z0**.

AutoLock

1. Click on the **Standard** page of the Start tab.
2. Click on either **Spin On** or **Spin Off**.
3. Selection an option for the menu next to the Autolock button.

4. Click on the **Autolock** button — the spectrometer will find Z0 and make all specified adjustments
5. Choose **Find Z0** or **AutoLock**.

Lock Power, Gain, and Phase

Lock power, gain, and phase are set by the lock parameters—`lockpower`, `lockgain`, and `lockphase`— when using autolock. The parameters set the following limits and step sizes:

- lock power is 0 to 68 dB (68 is full power), step size of 1 dB
- lock gain is 0 to 48 dB, step size of 1 dB
- lock phase is 0 to 360 degrees, step size of 1.4 degrees.

The Z0 field position parameter `z0` holds the current setting of the Z0 setting. The limits of `z0` are –2047 to 2047, in steps of 1, if the parameter `shimset` is set to 1, 2, or 10, and –32767 to +32767 if `shimset` is set to another value.

Lock Control Methods

Click on the **Start** tab and select the **Standard** page to access the following lock methods and controls:

- "Leaving Lock in the Current State," page 49.
- "Running an Experiment Unlocked," page 49.
- "Simple Autolock," page 49.
- "Optimizing Autolock," page 50.
- "Full Optimization," page 50

Each method is discussed in the following separate sections. Additional sections discuss error handling and lock loop time constant control.

Leaving Lock in the Current State

Set **Lock Find Resonance** to **Not Used**.

Lock is established upon insertion of the new sample if simple or optimized Autolock was previously selected.

The system only locks if the new sample has the same lock solvent, if simple lock was previously selected.

Running an Experiment Unlocked

Set **Lock Find Resonance** to **Unlocked**.

Lock is deactivated at the start of acquisition.

Simple Autolock

Set **Lock Find Resonance** to **Simple**.

The system searches for the lock signal and, if necessary, optimizes lock power and gain (but not phase), whenever an acquisition is initiated with `go`, `ga`, `au` or with any macro or

menu button using the `go`, `ga`, or `au` if **Lock Find Resonance** is set to **Simple** at the beginning of each experiment (each initiation of an acquisition).

Optimizing Autolock

Optimizing Autolock uses a sophisticated software algorithm to search the field over the full range of Z0 (as opposed to hardware simple Autolock), captures lock, and automatically adjusts lock power and gain (but not lock phase).

- Lock Find Resonance is set to **Every Sample**.

  The same process as **Simple** occurs but only if the sample has just been changed under computer control and acquisition is started (when manually ejecting or inserting a sample, the software cannot keep track of the action and **Every Sample** has no effect).

- `z0` is inactive and an autolock operation is started

  `autolock` searches for the lock signal by changing the lock frequency.

Spectrometer frequencies are computed from the lock frequency, so if the lock frequency changes as a result of an Autolock operation, frequencies for that acquisition are off by the amount of that change. Switching from chloroform to acetone requires a change in the lock frequency of about 5 ppm, which can cause problems in precision work. Changing lock frequency is only a problem when Autolock is selected with the `alock` parameter. It is *not* a problem for the lock experiment, since, by definition, the lock experiment is complete once the autolock operation is completed.

Full Optimization

Full optimization is the most complete optimization of lock parameters. A fuzzy logic autolock algorithm automates the parameter control process in order to find the exact resonance and the optimum parameters (phase, power, gain) automatically and quickly with high reliability. Fuzzy rules are used in the program to find the exact resonance frequency and for adjusting power and phase. The fuzzy rules are implemented at different stages of the autolock process. First, the software finds the resonance. If the exact resonance cannot be found, phase and power are adjusted and the software looks for the exact resonance again. The software then optimizes the lock power to avoid saturation, optimizes the lock phase, and optimizes the lock gain to about half-range.

RF frequencies, decoupler status, and temperature are also set during full optimization.

3.7 Adjusting Field Homogeneity

Refer also to Chapter 4, “Gradient Shimming,” on page 61, if the system is equipped with gradient shimming capabilities.

Shim coils produce small magnetic fields used to cancel out inhomogeneity in the static field. In shimming, the current in shim coils is adjusted to make the magnetic field as homogeneous as possible. Computer-controlled digital-to-analog converters (DACs) regulate the room-temperature shim coil currents. Adjust the shims every time a new sample is introduced into the magnet or probe is changed.

- "Loading Shim Values," page 51
- "Loading a Shim File," page 51
- "Saving a Shim File," page 51
- "Shim Gradients," page 51
- "Automated Shimming on the Lock," page 51

- "Which Shims to Use on a Routine Basis," page 52
- "Shimming Different Sample Geometries," page 53

See Appendix B, “Shimming Basics,” page 421, for more information about shimming.

Loading Shim Values

1. Click on the **Lock** page in the Start panel.
2. Click on the **Load Shims into Hardware** button

   This is the equivalent of the command line instructions: `load='y' su`. Shim values stored in the current experiment are loaded (this may not be suitable).

Loading a Shim File

Load a shim set from the Locator to the shim buttons area of the Shim page as follows:

1. Click the **Locator Statements** button (magnifying glass icon).
2. Select **Sort Shimsets**. Shim sets can also be sorted by probe or filename.
3. Select a shim set and drag-and-drop it onto the graphics canvas or shim buttons area of the Shim page.

Saving a Shim File

Save the shim values to a file as follows:

1. Enter a file name in the field next to the **Save Shims** button, and press **Return**.
2. Click the **Save Shims** button.

Shim Gradients

The shims are actually printed coils wrapped round a cylindrical form that encloses the NMR probe. A coil (or sum of coils) whose field is aligned along the axis of the magnet is called a Z axial shim gradient (Z1, Z2, Z3, etc.). Coils whose fields are aligned along the other two orthogonal axes are called X and Y radial shim gradients (X1, XY, X2Y2, Y1, YZ, etc.). The field offset coil Z0 (“zee-zero”) alters the total magnetic field.

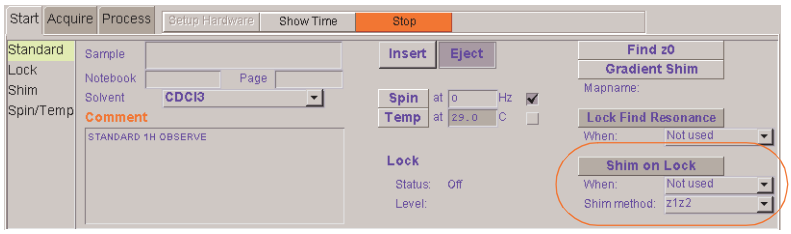
Each shim gradient is controlled by its own parameter; for example, the X1 shim gradient is controlled by a parameter named `x1`.

Depending on the value of the `shimset` parameter, shim values range from –2047 to +2047 or from –32767 to +32767, with a value of zero producing no current.

Automated Shimming on the Lock

Refer to section B.3, “Autoshim Information,” on page 428 for more information about Autoshim.

Like locking, shimming can be done by using the controls on the Shim page. Automated shimming is often preferred, however. It can be set up from the Standard page of the Start tab:



Shim on Lock options menu next to **When:**

- Not used — disables automatic shimming.
- Every sample — Shims before the start of data acquisition for each new sample.
- Every Experiment— Shims before the start of data acquisition for each new experiment.
- Every FID— Shims before the start of data acquisition for each FID.

Shim on Lock options menu next to **Shim method:**

- z1z2
- Low non-spins
- All z's
- Hi-res z's
- Fine z1z2
- Fine z1-z3

Autoshim is controlled by the selection made from the Shim method menu. This is a complete background Autoshim method that provides no interaction with the operator. The type of automatic shimming to be done during routine sample changes depends on the level of homogeneity required on any particular sample, the change in sample height, and the maximum time desired for shimming.

- **z1z2** shimming — average homogeneity needs with long samples of identical height.
- **all z's** — variable sample heights. More time is required. The method shims first Z1, Z2, and Z4, then Z1, Z2, and Z3, and finally Z1 and Z2.

3.8 Selecting Shims to Optimize

- "Which Shims to Use on a Routine Basis," page 52
- "Shimming Different Sample Geometries," page 53

Which Shims to Use on a Routine Basis

The following suggestions assist in routine shimming, especially on shim systems with a larger number of shim channels:

- Establish and maintain lineshape – Use Z to Z5, possibly Z6, X, Y, ZX, ZY, and possibly Z2X and Z2Y. The effects of Z7 and Z8 (and realistically Z6) are too small to see with the lineshape sample.

- Shim a new lineshape sample of different geometry – Use Z to Z5, possibly Z6, X, Y, ZX, ZY, and possibly Z2X and Z2Y.
- Shim a new sample of the same geometry – Use Z, Z2, and maybe Z3.
- Shim a new sample of different geometry – Use Z to Z4 and possibly Z5, X, Y, ZX, ZY.
- Shim for preset water suppression – Start with a shim set that produces a good lineshape for the same sample geometry. Next, tweak Z and Z2, and then vary Z5 and Z7 to minimize the width of the base of the water (Z and Z2 may need to be tweaked if Z5 changes by more than 100 to 200 coarse units). About 80 to 90 percent of the odd-order axial-gradient induced water width is probably dominated by Z5, with Z7 and perhaps some Z3 providing the rest.

  The even-order axial shims (Z2, Z4, Z6, and Z8) affect the asymmetry of the residual water line (using presaturation). All four of these even-order axial shims can affect the final water linewidth, with Z2 and Z4 being at about the 5 mM solute level and above, Z6 being at about the 1 mM solute level, and Z8 being at about the 0.3 mM solute level. The even-order axial shims perform as expected except when the sample is less than 40 mm in length, in which case the shims still control the water linewidth but much less responsively.

  Using Z4 to narrow an asymmetric residual water line of a sample shorter than about 40 mm can destroy the base of the standard lineshape faster than the residual water signal is narrowed. The residual water resonance width is affected by magnetic susceptibility interfaces as the sample gets shorter. Iterative use of Z5-Z7 with Z6-Z8-Z4-Z2 can narrow the residual water line for samples under 40 mm but the results obtained may be hard to reproduce on subsequent samples due to an increase in sensitivity to small changes in sample geometry.

Shimming Different Sample Geometries

Some suggestions when moving the sample:

- Moving the same sample up – Z, Z3, and Z5 need to become more positive.
- Shortening and centering (moving up) the sample – Z2 and Z4 need to become much more positive. The trends for Z and Z3 are mixed and more complex, but they tend to become a little more negative. It appears as if Z and Z3 are driven positive as the sample is pulled up, but they are driven negative faster as the sample shortens. When shimming a lineshape sample, plan on the following changes (starting from lineshape shims for a 700 µL sample at a depth 67-68 mm):

  700 µL to 600 µL: move Z2 +50 DAC units and move Z4 +250 units.
  700 µL to 500 µL: move Z2 +200 units and Z4 +600 units.

  The Z2 and Z4 changes track well with sample volume, but are relatively independent of tube depth. It is therefore easiest when changing sample geometries to make the appropriate Z2 and Z4 corrections, then adjust the more complex Z1-Z3-Z5 interactions as needed.

3.9 Shimming on the Lock Signal Manually

Monitor the intensity of the lock signal while adjusting the shim settings. Each shim setting controls the current through shim coils that control magnetic field gradients in different directions. The Z direction must be parallel to the vertical direction of the probe, and it is for this reason that the height of the sample in the NMR tube affects the Z shim settings rather dramatically.

- "Routine Shimming," this page
- "Setting Low-Order (Routine) Shims," page 55
- "Removing Spinning Sidebands (Non-Routine)," page 55
- "Setting the High-Order Axial Shims (Non-Routine)," page 56
- "Setting High-Order Radial Shims (Non-Routine)," page 56

Routine Shimming

1. Load the shim settings that have been most recently established for the probe in use as a starting point if the shim settings are way off the mark (e.g., if the temperature has changed).
2. Click **Setup Hardware**.
3. Make sure the probe has a sample, that it is spinning at the correct speed, and that the system is locked onto the deuterium resonance from the lock solvent.
4. Check that the lock signal is not saturated. The signal is saturated if changing the lock power by 6 units (6 dB) does not change the lock level by a factor of two. Set lock gain as necessary.
5. Open the **Shim** page.

   Try a change of +10 or - 10 in the setting for Z1. If the lock level goes up with one of these, continue in that direction until the level is maximized (it no longer increases, but instead begins to fall).
6. Change the setting for Z2C or Z2 by +10 or - 10 and continue in that direction until the level is maximized.
7. Adjust Z1 for maximized lock level; then adjust Z2 for the same. Continue this iterative process until the lock level goes no higher. If the lock level increases to 100, decrease lock gain and then continue to adjust Z1 and Z2. Lock power can be adjusted as needed.

The routine adjustment is sufficient in most cases. Critical experiments, in some cases, do require adjustment of higher order Z shims and the non-spin shims.

The following procedure is suggested for a second level of shimming:

1. After Z1 and Z2 have been adjusted for maximum lock signal, write down the lock level, adjust Z3 in one direction, by +10, and then repeat the optimization of Z1 and Z2 (iteratively) until the lock signal is at a maximum. Note this level of the lock signal. Continue changing Z3 in the same direction if the lock signal is higher than it was initially. Every change in Z3 must be followed by optimization of Z1 and Z2 until the lock level is at a maximum.
2. Repeat step 1 with Z4. That is, change Z4 in one direction, then optimize Z1 and Z2. If the lock level does not go up, change Z4 in the opposite direction and optimize Z1 and Z2. Continue until the highest possible lock level is obtained.
3. Repeat steps 1 and 2 iteratively until the highest possible lock level is obtained.
4. Turn the spinner off and go through the non-spin shims, one at a time, maximizing the lock level for each one. Then return and go through each again. Continue through all until the lock level is as high as possible. If lock is lost, increase the lock gain.

5. Turn the spinner on and optimize Z1 and Z2 as described above, return to the non-spins (turn the spinner off) and reoptimize these. Continue until the highest lock level is obtained.

Insert the lineshape sample ($CHCl_3$ in deuteroacetone for ^{1}H and dioxane in deuterobenzene for ^{13}C) for an ultimate check and examine the lineshape to make certain that the homogeneity is close to the original specs, especially for the lineshape at 0.55% and 0.11% of the total peak height. Also examine the height of the spinning sidebands. Refer to the *Probe Installation* manual that shipped with your probe.

Setting Low-Order (Routine) Shims

The following procedure describes how to set the low-order, or routine, shims. Resetting Z0 and lock phase is normal when making very large changes in the room temperature shims. With this procedure, concentrate on improving the symmetry of the main resonance as well as the half-height resonance and lineshape.

1. Adjust the lock level to about 80 if possible.

   Maximize lock level with Z1.

   Maximize lock level with Z1 and Z2. Do this by making a change in Z2 followed by maximizing with Z1 again. Continue to iterate in this manner until there are no further increases in the lock level.

2. Acquire the spectrum.

   Resonance lines are symmetric if the sample is properly shimmed.

3. Asymmetric or unusually broad at the base require added attention, refer to Table 42 on page 428 in Appendix B, “Shimming Basics,” page 421 for which shims to adjust. Adjust Z3, Z4, or the non-spins is not required for most routine samples.

4. Adjust Z3 by interactively shimming Z1 and Z3 in the manner described in step 3 for Z1 and Z2. Changes in Z3 may affect Z2 so after shimming Z3 maximize Z1 and Z2 again.

Removing Spinning Sidebands (Non-Routine)

Use this procedure to reduce or eliminate spinning sidebands that are not within specification them.

1. Write down the lock level, set SPIN to **OFF**, and write down the lock level.
2. Adjust lock to about 80 if possible.
3. Maximize lock level with X.
4. Maximize lock level with Y.
5. Maximize lock level with X and Y.

   Do this by making a change in Y followed by maximizing with X again. Continue to iterate in this manner until there are no further increases in the lock level.

6. Maximize lock level with X and ZX.

   Do this by making a change in ZX followed by maximizing with X again. Continue to iterate in this manner until there are no further increases in the lock level.

7. Maximize lock level with Y and ZY.

Do this by making a change in ZY followed by maximizing with Y again. Continue to iterate in this manner until there are no further increases in the lock level.

8. Repeat step 3 above.
9. Maximize lock level with XY and ZXY (ZXY not available on 13 or 14 channel shim systems).
10. Repeat step 3, through step 5.
11. Set SPIN to on and acquire a spectrum.

    If the sample is properly shimmed, the lines should be symmetric.
12. Refer to Table 42 on page 428 and the previous sections for which shims to adjust if the lines are not symmetric or are unusually broad at the base. For most routine samples, adjusting Z3, Z4 or the non-spins is not required.
13. Adjust Z3 by interactively shimming Z1 and Z3 in the manner described in step 3 in the previous procedure (“Setting Low-Order (Routine) Shims”) for Z1 and Z2.

    Changes in Z3 may affect Z2 so after shimming Z3 maximize Z1 and Z2 again.

Setting the High-Order Axial Shims (Non-Routine)

Refer to B.2, “Shim Interactions,” on page 422 for information about shim interactions.

1. Look at which side of the peak has asymmetry to determine how to adjust Z4, — low field to the left and high field to the right.
2. Use Figure 123 on page 424, which is in Appendix B, “Shimming Basics,” page 421, to determine which direction to move Z4. A large asymmetry implies that Z4 is far off. Change Z4 by a considerable amount to try to push the asymmetry to the other side of the peak. This provides two important pieces of information:
   - Confirms that Z4 is the problem if the asymmetry moves.
   - Indicates what the actual value of Z4 should be when Z4 is changed. Since the values that caused it to be on either side of the peak are know, the correct value must be between the two extremes.
3. Set Z4 to the value that produces neither a high-field nor low-field asymmetry.

   Z4 affects all the shims below it, so repeat the in the “Setting Low-Order (Routine) Shims” procedure.
4. Maximize the lock level with Z5.
5. Repeat step 3 and step 4 until no further increase is obtained.

Setting High-Order Radial Shims (Non-Routine)

Note that Z2X, Z2Y, ZX2–ZY2, Z3X, Z3Y, and Z5 are not available on 13-channel shim systems.

1. Set SPIN to **OFF** and write down the new lock level.
2. Set the lock level to about 80.
3. Maximize the lock level by shimming Z2X against ZX.
4. Maximize the lock level by shimming Z2Y against ZY.
5. Repeat the “Removing Spinning Sidebands (Non Routine)” procedure.

6. Maximize the lock level by shimming ZXY against XY.
7. Maximize the lock level by shimming ZX2–ZY2 against (X2-Y2).
8. Set SPIN to **ON** and adjust the lock level to 80.
9. Maximize the lock level by shimming Z1, Z2, Z4, and then Z1, Z2, Z3.
10. Repeat step 1.
11. Maximize the lock level by shimming X3 against Y3
12. Maximize the lock level by shimming Z3X against Z3Y if available.

    Refer to the installation data for your magnet for approximate Z3X and Z3Y values.
13. Look at the spectrum and decide where to concentrate your effort:
    - For a broad base, adjust Z4 and Z5.
    - For spinning sidebands, adjust the proper order radial shims.

The contribution of Z3 to the breadth of the base becomes evident (as does the contribution from the high-order radial shims) as Z4 and Z5 are optimized. Several cycles of shimming are required.

Local maxima are be encountered from time to time causing the problems. A local maxima is indicated if a high-order shim continues to increase and eventually reaches the maximum output of the shim supply, without having reached the optimal lock level.

Carefully reexamine the lower-order shims by making large excursions (systematically), beginning with the lowest-order shim and working up. This is a particularly difficult issue when dealing with the high-order radial shims such as X3, Y3, Z3X, and Z3Y, because their perturbation of the lock level is small relative to the change in the shim current.

The effects of X3, Y3, Z3X, and Z3Y on the spectrum are significant in experiments such as water suppression but can go unnoticed or may not be important in some routine 1D spectra where large solvent peaks are not encountered.

3.10 Shimming PFG Systems

These procedures apply to the Performa I, Performa II, and the Performa XYZ systems. Once in operation, leave the amplifier on while using the gradient system, to allow the amplifier to reach a long-term equilibrium.

- "Performa I and Performa II," page 57
- "Performa XYZ," page 57

Performa I and Performa II

1. Open the **System settings** window (Edit->System settings).
2. Click **Setup Hardware**.

Performa XYZ

1. Prepare the amplifier by moving the switch from STANDBY position to **ON**.
2. Open the **System settings** window (Edit->System settings) and set **Gradient amplifier X**, **Y**, and **Z** to **on**. Click **OK**.

3. Click the **Setup Hardware** button. This button is available when the Start tab is open.

   The yellow RUN light should turn on.

3.11 Calibrating the Probe

Probe calibrations are stored in the probe file. Use these procedures and the standard calibration samples to update and maintain the calibration file for the probe. Refer to the *VnmrJ Installation and Administration* manual for detailed instructions on automatic and manual probe calibration procedures.

Using Auto Calibration Procedures

1. Do one of the following to start the probe calibration, see Figure 9, and open the probe window:

   Use the main menu bar:

   a. Click on **Tools**.

   b. Select **Standard Calibration Experiments**.

   c. Select **Calibrate Probe…**

   Use the Hardware bar:

   Click on the **Probe** button.,

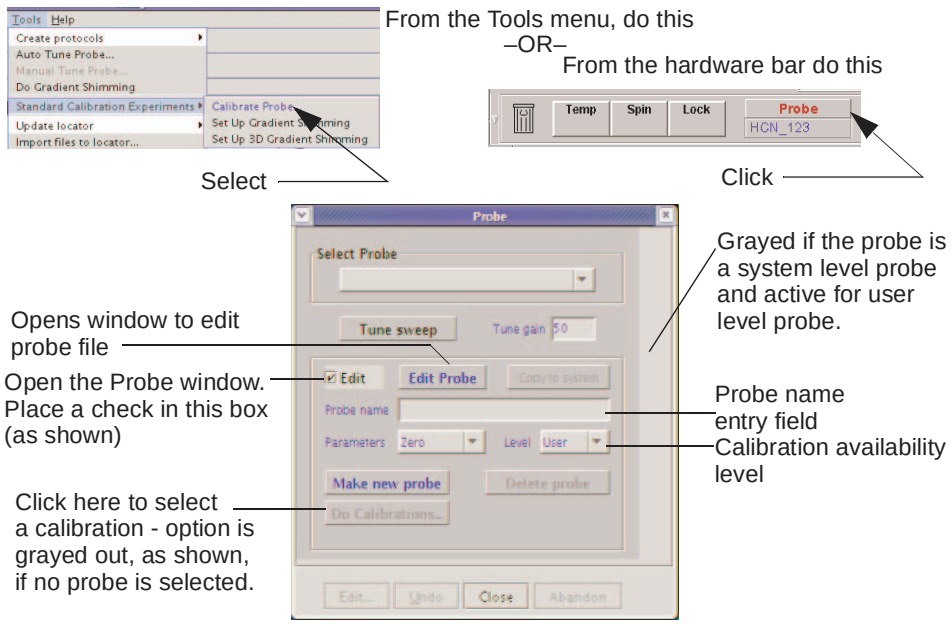


Figure 9. Calibrating a Probe

2. Check the box next to **Edit** in the Probe window

3. Click the **Do Calibration** button in the probe calibration popup window.

4. Select calibrations from the calibration popup window

5. Click a **radio** button in the Calibrate Probe window to select the calibration experiment, see Figure 10.
6. Enter the location of the calibration sample.
7. No entry field appears if a sample changer is not attached to system.
8. Insert the sample into the magnet manually using the **insert** and **eject** button located on the Lock page of the Start tab if a sample handler is not present or not used.

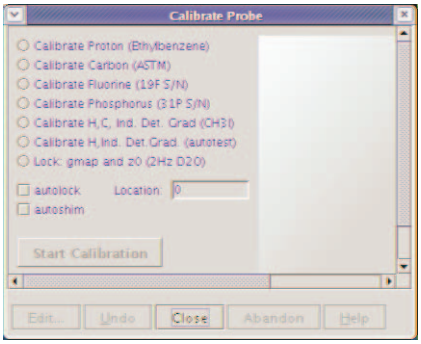


Figure 10. Probe

9. Select **AutoLOCK YES** or **NO**.
10. Click the **NO** button if the sample is already locked or to lock manually.
11. Select **AutoSHIM YES** or **NO**.
12. Click the **NO** button if the sample is already shimmed or to shim manually.
13. Click the **Start Calibration** button.
14. Follow the on line instructions and refer to the *VnmrJ Installation and Administration* manual for detailed instructions on automatic and manual probe calibration procedures.

Some probes, like the Autoswitchable and 4 nucleus probes, require additional calibrations not covered in this manual. For information on the calibration of these probes, see the installation, testing, and specifications manual for the probe.

Using Manual Calibration Procedures

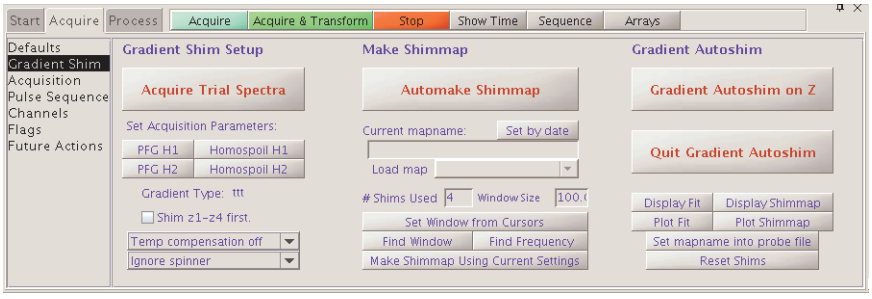
Refer to the manual calibration section of the *VnmrJ Installation and Administration* manual and the acceptance test procedures supplied with the probe.

Chapter 4. Gradient Shimming

Sections in this chapter:

- 4.1, “Introduction to Gradient Shimming,” on page 61
- 4.2, “Deuterium Gradient Shimming,” on page 62
- 4.3, “Homospoil Gradient Shimming,” on page 62
- 4.4, “Configuring Gradients and Hardware Control,” on page 63
- 4.5, “Mapping Shims and Gradient Shimming,” on page 64
- 4.6, “Shimmap Display, Loading, and Sharing,” on page 69
- 4.7, “Gradient Shimming for the General User,” on page 71
- 4.8, “Deuterium Gradient Shimming Procedure for Lineshape,” on page 72
- 4.9, “Calibrating gzwin,” on page 73
- 4.10, “Varying the Number of Shims,” on page 74
- 4.11, “Variable Temperature Gradient Compensation,” on page 75
- 4.12, “Spinning During Gradient Shimming,” on page 75
- 4.13, “Suggestions for Improving Results,” on page 76
- 4.14, “Gradient Shimming Pulse Sequence and Processing,” on page 77

4.1 Introduction to Gradient Shimming



Gradient autoshimming provides rapid, automatic adjustment of axial room-temperature shims. It is a very reliable way to set high-order shims, which eliminates many hours previously spent on shimming. Typical gradient autoshimming time is only a few minutes, and all steps are done with a few clicks of a mouse button.

Gradient autoshimming is implemented for use with the axial gradients (Z-gradients). A PFG amplifier and probe are recommended for optimal gradient shimming for their fast gradient recovery performance. However, if a PFG amplifier and probe are not available, gradient autoshimming can be performed using the homospoil gradient (Z1 room

temperature shim coil). Refer to the section ""Homospoil Gradient Type," page 62, for more details on how to set up the homospoil gradient.

Gradient autoshimming methods support shimming on a wide variety of samples with different volumes and solvents. For aqueous samples, water protons provide sufficient signal for shimming. For deuterated solvents, gradient shimming can be performed if there is sufficient deuterium signal. Deuterium gradient shimming is feasible on most samples where the lock solvent is a single, strong resonance, which includes the majority of solvents of interest for routine NMR use.

Proton gradient autoshimming with PFG is available on systems configured with a PFG accessory. Homospoil gradient shimming is available on all systems, with or without PFG. The Automated Deuterium Gradient Shimming module is required for deuterium gradient shimming with PFG or homospoil.

4.2 Deuterium Gradient Shimming

Deuterium gradient shimming is feasible for most deuterated solvents for which lock solvent has a single, strong deuterium resonance with sufficient signal.

Automated deuterium gradient shimming automatically holds the lock at its current value and switches the transmitter cable to pulse the lock coil when an experiment is run with `tn='lk'`.

The system administrator must make a shimmap on deuterium before deuterium gradient shimming can be used. Follow the procedure "Mapping Shims and Gradient Shimming," page 64, using the deuterium signal for all steps. The transmitter power (`tpwr`) should be kept low to avoid probe arcing, with a 90° pulse greater than about 200 µs.

4.3 Homospoil Gradient Shimming

- "Homospoil Gradient Type," page 62
- "Homospoil Gradient Shimming for ^{1}H or ^{2}H," page 63

Homospoil Gradient Type

VnmrJ allows homospoil (room temperature Z1 shim coil) as a general gradient type. It does not require the use of a pulsed-field-gradient module and thus is available on systems without PFG.

When homospoil is switched on in a pulse sequence, the shim current is set to maximum for a given period of time.

- To use homospoil as a quick homogeneity spoil in a pulse sequence, use `hsdelay`. This is the traditional homospoil method, and is usually done at the beginning of a relaxation recovery delay (e.g., `hsdelay(d1)`). The parameter `gradtype` is ignored. See the *User Programming* manual for details of how to use `hsdelay`.
- To use homospoil as a general gradient type in a pulse sequence, i.e., for gradient shimming during automation or gradient shimming in general:

1. Login as the system hardware administrator, typically this is the user vnmr1.
2. Select **Utilties** from the main menu.
3. Select **System settings**.

4. Click on the **System** tab.
5. Click on the **System config** button.
6. Click on the **Z Axis Gradient menu**.
7. Select **Homospoil** (this sets `gradtype='nnh'`).

   Using **`config`** and setting gradtype of `'nnh'` writes the setting of `gradtype` to the disk, and it is read as system global parameter.

   The parameter `pfgon` is ignored, since a separate gradient amplifier is not needed. Homospoil is then triggered by gradient statements such as `rgradient('z',gzlvl1)`. If the value of `gzlvl1` is non-zero, homospoil is switched on; if the value of `gzlvl1` is zero, homospoil is switched off. Only one sign and strength of gradient current is available during a pulse sequence and is set by hardware.

Homospoil gradients may be switched on only for a limited period of time, usually 20 ms. This time limit is determined by hardware in spectrometer systems (see Table 3 for system configurations). Check your pulse sequences to ensure this time limit is not exceeded.

Table 3. Homospoil Control

Shim Supply	*Homospoil Time Limit*
Varian 14	20 ms/200 ms
Varian 18 to 40	20 ms/200 ms

The behavior of homospoil gradients is quite different from that of a pulsed field gradient. The gradient strength is much weaker than the traditional PFG, and the recovery time is much longer because of eddy currents. The strength and recovery of the gradient depends on the shim coils and system hardware. Typically, these gradients are suitable only for profile-type experiments and unsuitable for gradient coherence-selection experiments such as GCOSY and GNOESY. For most gradient experiments, pulsed field gradients are preferred if available.

Homospoil gradients are suitable for ^{1}H and ^{2}H gradient shimming on some systems (see Table 3 for system configurations).

Homospoil Gradient Shimming for ^{1}H or ^{2}H

First configure the homospoil gradients to use homospoil gradient shimming. Follow the procedure in "Mapping Shims and Gradient Shimming," page 64. Use **Find z0** before gradient shimming to use homospoil deuterium gradient shimming with different solvents.

4.4 Configuring Gradients and Hardware Control

1. Confirm that PFG or homospoil gradients are installed on your system. See the previous sections in this chapter. A PFG probe is required.
2. Confirm that the gradients are active by checking that `gradtype` and `pfgon` are set appropriately for your system. Use `config` to change `gradtype` if necessary. Use System Settings to set `pfgon` if necessary.

4.5 Mapping Shims and Gradient Shimming

- "Recommended Samples for Gradient Shimming," page 64
- "Calibrating the 90° Pulse for ^{1}H and ^{2}H," page 64
- "Mapping the Shims," page 65
- "Starting Gradient Shimming," page 67
- "Quitting Gradient Shimming," page 67
- "Gradient Shim Commands and Parameters," page 67

The shims must be mapped before autoshimming is used. Mapping the shims is necessary when a new probe is installed, but can be repeated at any time.

Spinning the sample during gradient shimming can cause motion artifacts. In most applications using 5 mm or smaller NMR tubes, spinning is not recommended. Spinning larger 8 mm NMR can produce better results than not spinning the sample. Refer to "Spinning During Gradient Shimming," page 75, for instructions on spinning during gradient shimming.

Recommended Samples for Gradient Shimming

The following samples are recommended for gradient shimming.

1H shimming	10% to 90% H_2O in D_2O
2H shimming	doped 1%H_2O in 99%D_2O or autotest sample

Calibrating the 90° Pulse for ^{1}H and ^{2}H

1. Insert a sample and find lock.
2. Disable sample changer control (`loc='n'`).
3. Adjust lock power, lock gain, and lock phase. Make coarse shim adjustments on Z1, Z2, X1, and Y1.
4. Select the **Proton** protocol.
5. Click the **Acquire** tab.
6. Select the **Channels** page.
7. Do one of the following procedures.

   Lock (^{2}H) 90º pulse calibration:

   a. Set the Observe Nucleus to **lk.**
   b. Set 90 Degree Pwr to **42** (to avoid arcing).
   c. On the Acquisition page, set the Observe Pulse to **200**.
   d. Continue with step 8.

   Proton (^{1}H) 90º pulse calibration:

   a. Verify that the observe nucleus is set to **H1**.
   b. Continue with step 8.
8. Click the **Acquire** button or enter **`ga`** and wait for acquisition to finish.
9. Click the **Process** tab and select the **Cursors/Line List** page.

10. Click the **Transform** button.
11. Place the cursor near the peak and click the **Place on Nearest Line** button.
12. Click the **Move Transmitter** button.
13. Select the **Acquire** tab, then the **Acquisitions** page, and click the **Arrays** button.
14. Enter **pw** for the Param Name, Array size **20**
15. Set the following:

^{1}H shimming	*^{2}H shimming*
First value =4	First value =100
Increment =4	Increment =100

16. Select **Acquisition** -> **Acquire and WFT**, (or enter **`ga`**) and wait for acquisition to complete.
17. On the Acquisition page set **`pw90`** to the value of pulse width corresponding to first maximum.
18. Click **Arrays** and click **UnArray** in the Array window.
19. Set the observe pulse to the **pw90** value.
20. Enter `pw90` and `tpwr` in the probe file, if desired.

Note: The strong signal may cause an ADC overflow for ^{1}H operation. If so, set **gain = 0**.

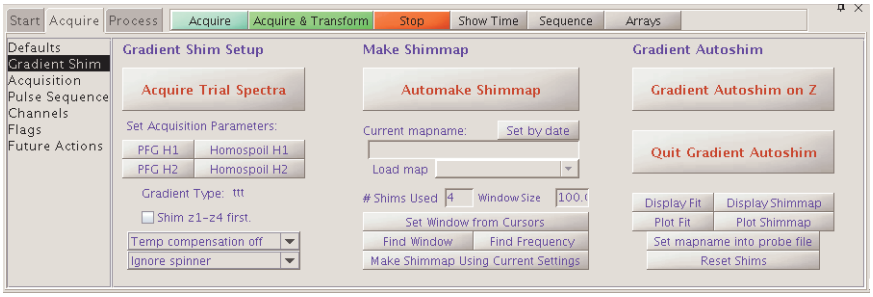
Mapping the Shims

1. Stop sample spinning.
2. Disable sample changer control (**`loc='n'`**).
3. Adjust lock power, lock gain, and lock phase. Make coarse shim adjustments on Z1, Z2, X1, and Y1.
4. Click on **Tools**.
5. Select **Standard Calibration Experiments**.
6. Select **Set up Gradient Shimming**.

   Standard parameters are retrieved from `gmapz.par` the first time Set Up Gradient Shimming is clicked, or if a shimmap was previously made, parameters are retrieved from the current shimmap.
7. Click the **Acquire** tab.
8. Select the **Gradient Shim** page.
9. Click one of the following buttons under Set Acquisition Parameters to retrieve the parameters from the probe file (if available) and set up gradient shimming acquisition parameters:

   PFG H1 **Homospoil H1**
   PFG H2 **Homospoil H2**

   Selecting Homospoil gradient shimming parameters requires enabling of homospoil gradients (4.3, “Homospoil Gradient Shimming,” on page 62).



10. Click the **Acquisition** page.
11. Set up the acquisition parameters. Typical parameters for different solvents for deuterium shimming are listed below.

Solvent	*Scans*	*Relaxation Delay, Sec.*
deuterochloroform	8-32	2
dmso-d6	4-16	2
D_2O	1-4	2
deuterobenzene	1-4	2
deuteroacetone	1-4	6-12

    Actual parameters might vary, depending on solvent concentration, probe, and system hardware.

12. Set `pw` as follows:
    - For PFG, set `pw` to the **90-degree pulse** or less.
    - For homospoil, set `pw` to the **90-degree pulse** and p1 to **180-degree pulse**.
13. Click the **Gradient Shim** page.
14. Click **Acquire Trial Spectra** on the Gradient Shim page to test the parameters.

    Two top-hat profile spectra should appear if the parameters are correctly set. If these spectra do not appear, check the following:
    - Gradients are active (`pfgon` is set correctly).
    - Acquisition parameters, `pw`, `tpwr`, `nt`, and `gain` are correct.
    - Adjust parameters to see good signal-to-noise with no ADC overflow.
15. Enter a map name for the shimmap in the **Current mapname** field (any string valid for a file name). Or click the **Set by date** button.
16. Click **Automake Shimmap** on the Gradient Shim page.

    The number of shims used to make the map is determined by the software.

    If the mapname already exists, a prompt appears for a new mapname and whether to overwrite the current mapname.
17. After acquisition is finished, click on **Set mapname into probe file** button on the Gradient Shim page.

Starting Gradient Shimming

Click **Gradient Autoshim on Z** on the Gradient Shim page to start shimming as a system administrator. This button starts gradient shimming using current parameters and displays the curve fit and shim adjustments for each iteration.

Quitting Gradient Shimming

Click the **Quit Gradient Autoshim** button to quit gradient shimming and exit the Gradient Shimming Set Up panel. This also retrieves the previous parameter set and data, including any data processing done on the previous data set.

Gradient Shim Commands and Parameters

The following commands and parameters are useful for performing special functions or can be set manually. Refer to the *VnmrJ Command and Parameter Reference* for full descriptions.

Commands	*Description*
`gmapshim<('files'|'quit')>`	Run gradient autoshimming, quit.
`gmapsys*`	Enter Gradient Shimming setup panels, make shimmap.
`gmapz<(mapname)>`	Get parameters/files for `gmapz` pulse sequence.
`*gmapsys<'shimmap'<,'auto'|'manual'|'overwrite'|mapname>`	

Parameters	*Description*
`d2`	Incremented delay for 1st indirectly detected dimension.
`d3`	Incremented delay for 2nd indirectly detected dimension; arrayed to two values
`gradtype*`	Gradients for x, y, and z axes
`gzlvl {DAC value}`	Pulsed field gradient strength
`gzsize {integer,1 to 8}`	Number of z-axis shims used by gradient shimming
`gzwin {0 to 100}`	Percentage of spectral window used by gradient shimming
`p1`	First pulse width—If > 0, it is used between the gradient pulses as a 180 refocusing pulse, and the gradients have the same sign.
`pfgon{'nny' if on}`	PFG amplifiers on/off control
`pw`	Pulse width; it can be <90° if p1=0.
`solvent`	Lock solvent
`vtcomplvl`	Variable temperature compensation for gradient shimming
`gmapspin`	Enable or disable spinning during gradient shimming
`gmap_z1z4`	Gradient shim initially on z1-z4
`* gradtype` {3-char string from `'c','d','n','w','l','p','q','s','t','u','h'}`	

How Making a Shimmap Works

An experiment with the shims arrayed is run to map the shims and processed to make the shimmap, see Figure 11.

Coarse shims are used if present. The parameters and data for the shimmap are stored in the file `userdir + '/gshimlib/shimmaps/' + mapname + '.fid'`. These parameters are retrieved the next time gradient shimming parameters are retrieved.

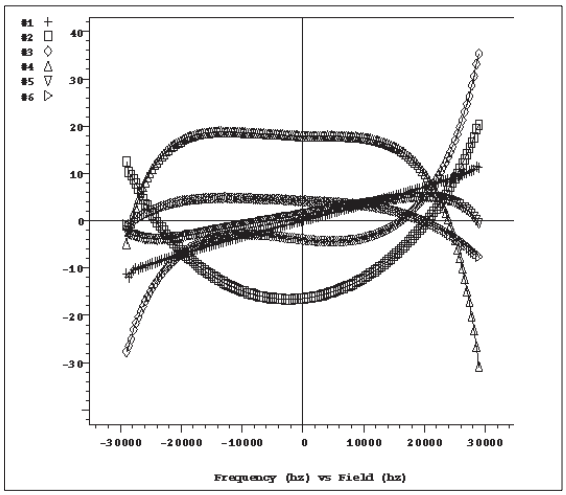


Figure 11. Shimmap Plot of Z1 Through Z6

How Automated Shimming Works

The shims must be mapped before gradient automated shimming is used, see "Mapping the Shims," page 65, for details.When gradient shimming is run from the Gradient Shim page, the curve fit plot is displayed for each iteration. The plot shows the raw data as #1 and the curve fit as #2 (see Figure 12).

Shim adjustments for each iteration are also displayed in the Text Output window (see Figure 13) and have converged when the rms error number is less than 1.0. Gradient shimming continues until convergence or until a maximum of 5 iterations are reached.

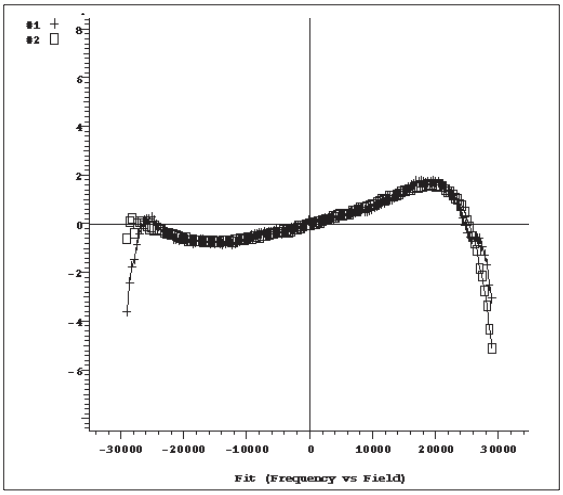


Figure 12. Curve Fit Plot

If a shim goes out of range, the shim is set to maximum and shimming continues with the remaining shims. If convergence is then reached, shimming is tried once more with all Z shims and continues unless a shim goes out of range again.

```
mapname 5mm_Triax_01
shimset 4  gzsize 6                          rms err 1.892

Shim     Offset      Old       New         Diff       Error
-------------------------------------------------------------
z1       800         -9405     -9269       -136       48
z2       800         -3118     -3104       -14        13
z3       3200        -4356     -4321       -35        37
z4       -3200       4049      4885        -836       104
z5       -3200       13443     14537       -1094      322
z6       3200        -15619    -12568      -3051      467
z7       3200        0         0           0          0
z8       3200        0         0           0          0
-------------------------------------------------------------
```

Figure 13. Display of Shim Adjustments for Each Iteration

4.6 Shimmap Display, Loading, and Sharing

- "Displaying the Shimmap," page 69
- "Loading a Shimmap," page 70
- "Sharing a Shimmap," page 70
- "Shimmap Files and Parameter Sets," page 70

Displaying the Shimmap

After the shims are mapped, display the shimmap by clicking the **Display Shimmap** button on the Gradient Shim page (under the Acquire tab).

The shimmap display is a multicolored plot of the shimmap, with Z1 as #1 and Z2 as #2, and so on (see Figure 14).

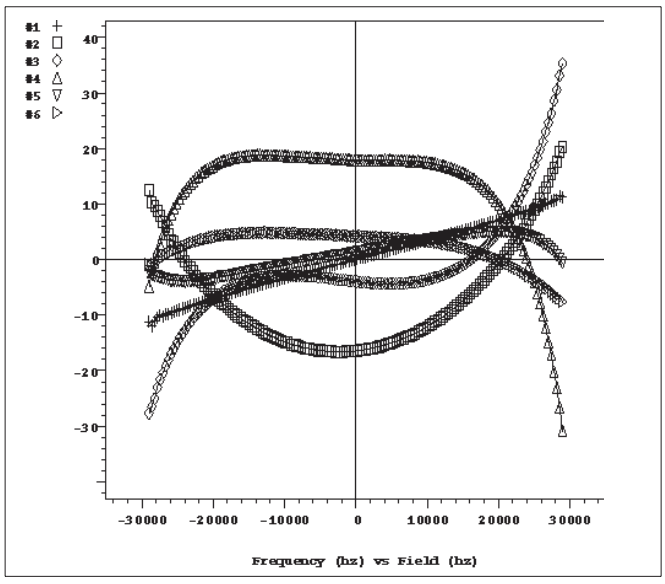


Figure 14. Shimmap Plot

The shimmap is specific to the probe used, and can also be dependent on sample volume for small volumes. The shimmap shows the actual field dependence of the shims, except for a dc offset added for display purposes. Good signal-to-noise in the shimmap is needed for the shimming to work well. Poor signal-to-noise might result in incorrectly set shims.

Loading a Shimmap

To change shimmaps as a system administrator, do the following:

1. Select the **Gradient Shim** page (under the Acquire tab).
2. Select a previously created shimmap from the choices in the Load Map menu. This loads parameters and loads the shimmap files `gshim.list` and `gshim.bas` from `gshimlib/shimmaps/mapname.fid` into `gshimlib/data`.

Sharing a Shimmap

The system administrator can copy a shimmap file from `vnmrsys/gshimlib/shimmaps` into the directory `/vnmr/gshimlib/shimmaps` so that the file is accessible to all users. To copy files, do the following steps:

1. Log in as **`vnmr1`**.
2. Open a terminal window.
3. Enter **`cd ~/vnmrsys/gshimlib/shimmaps`** and find the maps to copy.
4. Enter **`cd /vnmr`**
5. If `gshimlib` does not exist, enter **`mkdir gshimlib`**
6. Enter **`cd gshimlib`**
7. Enter **`cd shimmaps`**
8. For each map in `vnmrsys/gshimlib/shimmaps`, enter:

   `cp -r ~/vnmrsys/gshimlib/shimmaps/mapname.fid .`

   Remember the final dot at the end of the command and to substitute a name for *`mapname`*.
9. Do the following for each user account:
   a. Log in to the user's operating system account.
   b. Start VnmrJ.
   c. Click on **Tools**.
   d. Select **Standard Calibration Experiments**.
   e. Select **Set up Gradient Shimming**.
   f. Select a file from the Load Map menu on the Gradient Shim page.

Shimmap Files and Parameter Sets

The parameters and shimmap files saved under a mapname are retrieved when that mapname is retrieved. When reinserting a probe, reload the shimmap for that probe. If the correctness of shimmap is in doubt, make a new shimmap, which typically only takes a few minutes. The last parameters and files used are automatically retrieved the first time `gmapsys` is entered. If `gmapsys` is entered again, the parameters are not retrieved.

Gradient shimming uses the current parameters after the pulse sequence is loaded (`seqfil='gmapz'`).

4.7 Gradient Shimming for the General User

The general user can run gradient shimming from outside `gmapsys` from any experiment. Any one of the following methods is recommended for routine use:

- In the **Experimental** interface, click **Acquisition** -> **Do Gradient Shimming**. Parameters are retrieved from the current mapname, which is displayed at the start of shimming, and the spinner is automatically turned off. The curve fit and shim adjustments are not displayed. The previous parameter set and data are retrieved when shimming is finished. This button only functions after a shimmap is made.
- Under the Start tab, on the Standard or Lock pages, click the **Gradient Shim** button.
- Enter **`gmapshim.`** This performs the same action as clicking on **Gradient Autoshim on Z**.
- Within parameter sets, use **`wshim='g'`**.
- In the **Walkup** interface, select the **Gradient Shim** checkbox before submitting an experiment.

Use one of the following methods to stop gradient shimming before it is completed:

- Under the Acquire tab, select the **Gradient Shim** page and click the **Quit Gradient Autoshim** button. Quitting aborts the experiment and retrieves the previous parameter set and data.
- Abort the acquisition with **`aa`** and click on **Cancel Cmd**. Then enter **`gmapshim('quit')`** to retrieve previous data set and parameters.

Testing Solvents

Test gradient shimming for the solvents of interest by doing the following.

1. For each solvent of interest, do the following.
    a. Insert a sample with a solvent of interest.
    b. Select the solvent for the sample on the Study page.
    c. Set lock on resonance using one of the following methods.

       Click the **Find z0** button.

       Use the controls on the Lock page.
    d. Click on **Tools**.
    e. Select **Standard Calibration Experiments**.
    f. Select **Set up Gradient Shimming**.
    g. Click the **Acquire** tab.
    h. Select the **Gradient Shim** page.
    i. Set deuterium observe parameters as appropriate for the solvent. See , “Gradient Shim Commands and Parameters,” on page 67 for recommended parameters.
    j. Click the **Acquire Trial Spectra** button, and wait for acquisition to complete.

k. Click the **Gradient Autoshim on Z** button to test shimming if the signal-to-noise looks adequate in the spectra,.

l. Repeat steps (g)-(i) until the shimming works properly.

2. Once autoshimming works well for the solvents of interest, do the following:

a. Open a shell window.

b. Make a backup copy of the `gmapz` macro.

c. Edit the bottom portion of the gmapz macro to uncomment the solvents that will be used and make required corrections as needed. By default, the entire section is uncommented.

d. Save the edited gmapz macro.

e. Exit the shell window.

4.8 Deuterium Gradient Shimming Procedure for Lineshape

Use this procedure for optimizing both the spinning and non-spinning shims.

Setting up

1. Insert the appropriate lineshape sample (chloroform in acetone-d6) and find lock.
2. Turn off spinning and disable sample changer control.
3. Click on the **Start** tab.
4. Select the **Lock page**.
5. Adjust lock power, lock gain, and lock phase as necessary.
6. Do quick shimming on z1, z2, x1, y1 (use z1c, z2c, if present).

Making the ShimMap

1. Use 90° pulse for `tn='lk'`, see "Calibrating the 90° Pulse for ^{1}H and ^{2}H," page 64.
2. Click on **Tools**.
3. Select **Standard Calibration Experiments**.
4. Select **Set up Gradient Shimming**.

   Standard parameters are retrieved from `gmapz.par` the first time Set Up Gradient Shimming is clicked, or if a shimmap was previously made, parameters are retrieved from the current shimmap.
5. Click the **Acquire** tab.
6. Select the **Gradient Shim** page.
7. Click one of either the **PFG H2** or **Homospoil H2** buttons under **Set Acquisition Parameters** to retrieve the parameters from the probe file (if available) and setup gradient shimming acquisition parameters:

   Selecting Homospoil gradient shimming parameters requires that homospoil gradients are enabled (4.3, “Homospoil Gradient Shimming,” on page 62).

   - PFG — set **Observe Pulse** to one half the 90° pulse found in step 2 and set **Relaxation Delay** to `6`.

- **Homospoil H2**, — set **Observe Pulse** to the 90° pulse and **Relaxation Delay** to `6`.

8. Click **Acquire Trial Spectrum** and wait for acquisition to complete. A two profile spectra is displayed.
9. Click **Automake Shimmap** to map the shims.
10. Under **Current mapname**, click the **Set by date** button or, enter a file name.
11. Wait for acquisition to complete and the message to be displayed: `shimmap done`!

Starting Z Gradient Shimming

Shimming on all z's supported by the shim hardware.

1. Click on **Gradient Autoshim on Z**.
2. Wait for the acquisitions to complete, and the message to be displayed: `Gradient Autoshimming on Z done! N iterations`.
3. Click the **Start** tab and select the **Lock** page.
4. Click the **Lock Scan** button and adjust lock phase.

Optimizing Non-spinning Shims

1. Shim only on low-order nonspins (x1, y1, xz, yz, etc.).
2. Do not shim on z's (z1, z2, etc.).
3. Repeat "Starting Z Gradient Shimming," page 73.

Evaluating Homogeneity

1. Measure proton lineshape.
2. Turn on spinner if appropriate.
3. Click the **Lock Scan** button to make fine shim adjustment.
4. Shim on all shims as necessary.

4.9 Calibrating gzwin

- "Automatic Calibration of gzwin," page 74
- "Manual Calibration of gzwin," page 74

The parameter `gzwin` is the percentage of the spectral window used in calculating the field maps. `gzwin` should be adjusted only when making a new shimmap. If this parameter is not calibrated correctly, excess noise data at the edge of the shimmaps appears, which corresponds to the region in the profile spectrum where the signal goes to zero. It is normal to have a few noise data points at the edge of the shimmap, but if it is more than a few data points (greater than 25% of the window), `gzwin` may be incorrectly calibrated. This can occur if there is low signal-to-noise or if `gzwin` has not previously been calibrated for the current parameter set. If the gain is too high, "wings" will appear on the sides of the spectra and may result in incorrectly calibrated `gzwin`. This can also occur if there are multiple

chemical shifts for the nucleus chosen for gradient shimming in the presence of a weak gradient.

Automatic Calibration of gzwin

Click on the **Automake Shimmap** button or do the following:

1. Click the **Find gzwin** button on the Gradient Shim page. This calibrates `gzwin` and sets `tof` to center the window used for calculation.
2. Click **Make Shimmap Using Current Settings** button. This makes the shimmap with the current values of `gzwin`, `tof` and other parameters.

Optional: click through each step to verify correct calibration of `gzwin`. The box cursors at the end of step 1 should be at either edge of the profile.

Manual Calibration of gzwin

Manual calibration of `gzwin` can be used to avoid noise spikes in the spectrum, or other artifacts. To manually calibrate `gzwin`, do the following:

1. Click the **Acquire Trial Spectra** button on the Gradient Shim page. Wait until the experiment is done.
2. Display a spectrum using the graphics control buttons. Set the box cursors near the edges of the profile.
3. Click **Set Window from Cursors**.
4. Click on **Make Shimmap Using Current Settings**.

The parameter `gzwin` should be adjusted only when making a new shimmap. The calibrated value of `gzwin` is saved when the new shimmap is saved at the end of the mapping experiment. The same value of `gzwin` must be used in shimming as in making a shimmap, and should not be adjusted when shimming.

4.10 Varying the Number of Shims

The maximum number of shims available for gradient shimming is determined by the:

- shim hardware
- number of shims (up to the limit set by the hardware) used when the shimmap was created.

Changing the Number of Shims Used for Gradient Shimming

1. Map the shims, see "Mapping the Shims," page 65, or load an existing shimmap.
2. Enter a number in **# Shims Used** entry box on the Gradient Shim page. The number must be less than or equal to the number of shims used to make the shimmap.
3. Click on the **Gradient Autoshim on Z** button.

   All the shims specified in the # Shims Used entry box are used to optimize the field homogeneity.

Selecting Optimization of Z1 Through Z4 Shims First

Optimization of Z1 through Z4 shims before optimizing all the shims applies only to systems with room temperature shims Z5 and higher order. Gradient shimming takes longer and goes through more iterations, but this may avoid the problem on some systems where a high-order shim (e.g., Z5, Z6) goes out of range because it contains impurities from lower-order shims. Select this optimization as follows:

1. Load or make a shimmap of more than four shims.
2. Click on the **Shim z1-z4 first** check box.
3. Set the shims specified in the **# Shims Used** entry box to a value greater than **4**.

Shimming starts with Z1–Z4 optimization and then proceeds with all shims specified by # **Shims Used**. The check box may be set at any time before or after shimming from the Gradient Shim page. In order to use this parameter in user autoshimming, set it before making a shimmap, or in the corresponding parameter set in `gshimlib/shimmaps`.

4.11 Variable Temperature Gradient Compensation

Temperature gradients or convection currents may be compensated for with the addition of a 180º pulse in the pulse sequence prior to data acquisition. Sample viscosity, effective T2, and signal-to-noise affect the quality of the gradient shimming. Variable Temperature gradient compensation is compatible with spinning during gradient shimming. Enable variable temperature gradient shimming as follows:

1. Select one of the following from the Temperature Compensation menu on the Gradient Shim page.
   - **Temp compensation off** — no compensation.
   - **Temp compensation on** — systems with homospoil or PFG.
   - **Temp compensation plus** — systems with pulse field gradients, this option adds additional dephasing gradients.
2. Set **`p1`** to 180º pulse.
3. Map the shims; see "Mapping the Shims," page 65.
4. Start gradient shimming; see "Starting Gradient Shimming," page 67.

4.12 Spinning During Gradient Shimming

Spinning during gradient shimming is useful for sample sizes 8 mm and larger. Spinning the sample requires synchronization of the pulses and delays with the period of the rotor. Sample viscosity, effective T2, and signal-to-noise affect the quality of the gradient shimming. Spinning during gradient shimming is compatible with temperature gradient compensation.

Set up for spinning during gradient shimming as follows:

1. Select **Synch with spinner** from the menu options under Gradient Shim Setup on the Gradient Shim page.
2. Set the spinner speed either from the command line or from the panel as follows:
   a. Click on the **Start** tab.

b. Select the **Standard** page.

c. Enter the spinning speed in the box next to the **SPIN** button, press **enter**, and activate the spin setting by placing a check in the box next to the **Spin Speed** field.

d. Click on the **Acquire** tab.

e. Select the **Gradient Shim** page.

3. Select a nucleus and gradient option by clicking on one of the following Set Acquisition Parameter buttons:

PFG H1	**Homospoil H1**
PFG H2	**Homospoil H2**

4. Map the shims, see "Mapping the Shims," page 65.

   Verify that the spinner is on.

Note: The map must be made with the sample spinning at the speed set in step 2.

5. Start gradient shimming, see "Starting Gradient Shimming," page 67.

   Verify that the spinner is on.

Note: Gradient shimming *must be run with the sample spinning at the speed set in step 2.* The shims will not be set correctly if the sample is not spinning at the same speed that was used when the shimmap was created.

4.13 Suggestions for Improving Results

Calibrate the 90° pulse and adjust `tpwr`, `pw`, and `gain` to optimize signal-to-noise. Reduce gain if ADC overflow occurs, which may appear as wings on the profile. Optimal signal-to-noise is the most important criteria for gradient shimming.

Stimulated echoes may result for solvents with long T_1 and appear as excess noise, a beat pattern in the spectrum, or as secondary echoes in the FID (use `df` to observe this). Do one or more of the following:

- set `d1` to 3 to 5 times T_1
- use a smaller flip angle for `pw`

The phase encode delay `d3` is arrayed to two values, the first of which is zero. The second value can be increased for better signal-to-noise in the phase maps, up to about the point where the amplitude of the second profile is half that of the first (about 2/3 T_2 without radiation damping; radiation damping can be severe in water ^{1}H). However, longer `d3` values increase the phase excursion, and can make it difficult to shim large shim corrections (especially Z1). Typical ^{1}H values are 5 to 30 ms, and typical ^{2}H values are 30 to 200 ms. If the shims are far off when making a shimmap, the second value of d3 might be too small. If this problem occurs, decrease the second value of d3 temporarily to one-half to one-quarter its value.

When reinstalling a probe, make sure it is in the same vertical position in the magnet barrel as when the shimmap was made. If vertical position of the probe is uncertain, make a new shimmap, which typically takes only a few minutes.

Alternate between z-axis gradient shimming and shimming the low-order x- and y-axis shims by other methods (e.g., on lock level). The z-axis shims account for the majority of sample volume changes (changes in height), and the x- and y-shims are relatively

insensitive to change in height. Evaluate shimming for a particular application, since the ideal lineshape may vary with the application.

The high-order shims can sometimes be set off-scale during shimming. This may occur if the sample is short, or if the sample is improperly seated in the probe, or if the high-order shims are weak or other effects. In such cases, the off-scale shim is set to maximum, and shimming continues with lower-order shims. Superior results can be obtained in some cases by varying the number of shims used, see "Varying the Number of Shims," page 74. On a short sample it also can be useful to remap the shims.

Some shim systems may need additional time when running the shim-mapping experiment to allow the shims to settle. The added time is especially noticeable on some systems for Z4. To account for added time, lengthen the `d1` delay or add dummy scans in between each array element (e.g., `ss=-2`). Decreasing the amount a shim is offset also allows the shim to settle more quickly. Enter `gmapsys('vi')` to edit the values in the Offset column, and then enter **`gmapsys('shimmap','manual')`** on the command line to map the shims with user-defined offsets. A new mapname may also be set using `gmapsys('vi')`.

Coarse shims are used on systems on which they are available. To use fine shims on these systems, enter **`gmapsys('vi')`** to edit the entries in the shim column (e.g., change `z1c` to `z1`), and then enter **`gmapsys('shimmap','manual')`** to map the shims.

The water protons provide sufficient signal for shimming for samples in H_20. Deuterium gradient shimming is strongly recommended for samples other than water if there is sufficient deuterium signal. Proton gradient shimming can be made to work in samples other than water if there is sufficient proton signal and the signal is well-resolved (does not overlap with other strong resonances). Gradient shimming can also be done on a water sample of equal height of the sample of interest, and then the sample of interest can be inserted.

For further information, refer to the entries for `gmapshim`, `gmapsys`, and `gmapz` in the *Command and Parameter Reference*.

4.14 Gradient Shimming Pulse Sequence and Processing

The basis of gradient shimming is differential phase accumulation from field inhomogeneities during an arrayed delay. The phase is spatially encoded by a pulsed field gradient. Figure 15 shows the gradient shimming pulse sequence.

The gradient shimming pulse sequence in Figure 15 is shown with `p1=0`, in which case `pw` can be set to a small flip angle. If `p1>0`, the pulse field gradients are both set to the same sign, and `p1` should be set to 180° and `pw` to 90°, so that rf inhomogeneities are refocused. `p1=0` is usually sufficient for most cases.

Phase accumulation from all gradients present is as follows:

ϕ = z Gz(-at/2 + t) + dG(d3 + at/2 + 3*d2 + t)

where `t` is the time during acquisition `at`, `Gz` is the z-axis pulsed field gradient strength, and `dG` is the sum of the shim gradient fields, shown as being on during relevant times in the pulse sequence.

The effect of the shim gradients `dG` can be isolated by arraying `d3` and taking the difference in the phases:

$\Delta\phi$ = ϕ2 - ϕ1 = dG*(d3[2] - d3[1])

For example, at a particular point, $\Delta\phi$ can be 2π * 100 Hz * 10 ms, or 2π radians. Thus, a pair of profiles with different `d3` values can be used to calculate the B_0 field along z.

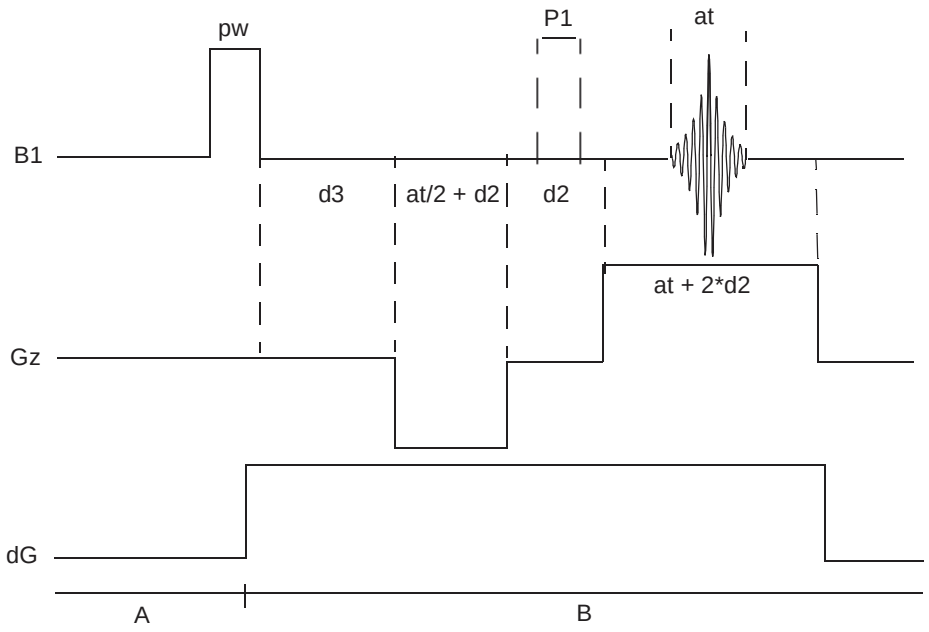


Figure 15. Gradient Shimming Pulse Sequence

The effect of any one shim gradient can be isolated by arraying the shim value, represented by dG, and taking the difference in the phase differences:

$$\Delta(\Delta\phi) = \Delta\phi 2 - \Delta\phi 1 = dG2*(d3[2]-d3[1]) - dG1*(d3[2]-d3[1])$$
$$= (dG2 - dG1)*(d3[2] - d3[1])$$

Therefore, two pairs of profiles can be used to map out the effect of a shim. By arraying all the shim values, a set of phase difference maps or shim field maps can be constructed for a given shim set. Shimming can then be performed by constructing a background field map for the starting shim values ($\Delta\phi$) and fitting the result to the shimfield maps. The calculations are quite fast, so the entire shimming process is usually limited by the data acquisition time, typically taking only a few minutes.

In practice, the phase is calculated from ϕ=arctan(x,y) from the real and imaginary values at each point in the spectrum, and $\Delta\phi$ is calculated from the difference in the phases of a pair of spectra with d3 arrayed. Figure 16 shows an example of mapping the z1 shim.

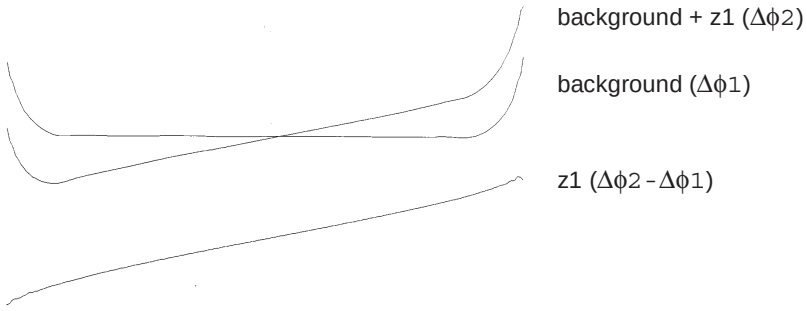


Figure 16. Mapping the z1 Shim

References

Van Zijl, P. C. M., et al. *J. Magn. Reson.* **1994**, *111* (Series A), 203–207.
Sukumar, S., et al. *J. Magn. Reson.* **1997**, *125* (Series A), 159–162.
Barjat, H., et al., *J. Magn. Reson.* **1997**, *125* (Series A), 197–201.
Evans C.L., et al., *J. Magn. Reson.* **2002**, *154* (Series A), 325–328.

Chapter 5. Data Acquisition

Sections in this chapter:

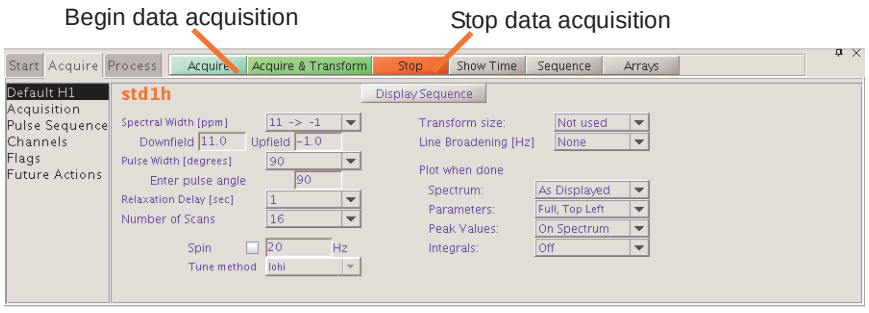
- 5.1, “Acquiring a Spectrum,” this page
- 5.2, “Acquisition Settings,” on page 82
- 5.3, “Pulse Sequences,” on page 84
- 5.4, “Parameter Arrays,” on page 88
- 5.5, “Stopping and Resuming Acquisition,” on page 89
- 5.6, “Automatic Processing,” on page 90
- 5.7, “Acquisition Status Window,” on page 90

The sample is in the magnet, spinning (or not as in the case of nD experiments), locked (typically but not always), and shimmed. Select an experiment and set the parameters to acquire data. There are two aspects to selecting parameters. The first is the frequency-related aspect—setting the position and size of the spectral window. The second is the pulse-sequence-related aspect.

5.1 Acquiring a Spectrum

VnmrJ reads the probe file and sets up the experiment either as a gradient experiment or non-gradient experiment based upon the type of probe in use.

Start an acquisition from the **Acquisition** menu, or use the pages under the **Acquire** tab.



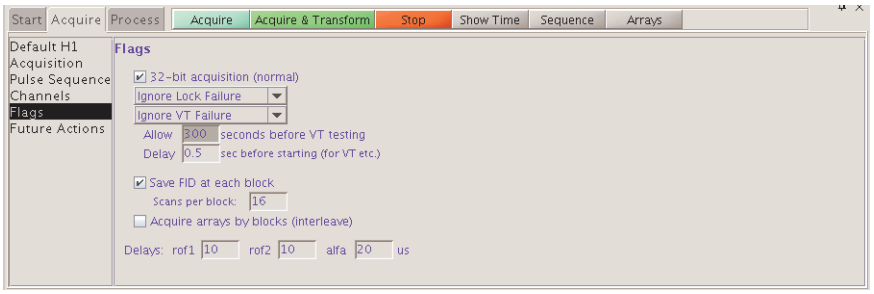
1. Accept the default settings or set acquisition parameters by clicking on the **Acquisition**, **Pulse Sequence**, or **Channels** page.
2. Set the parameters of the experiment and click the **Acquire** button.
3. Click the **Stop** button to stop the acquisition.

5.2 Acquisition Settings

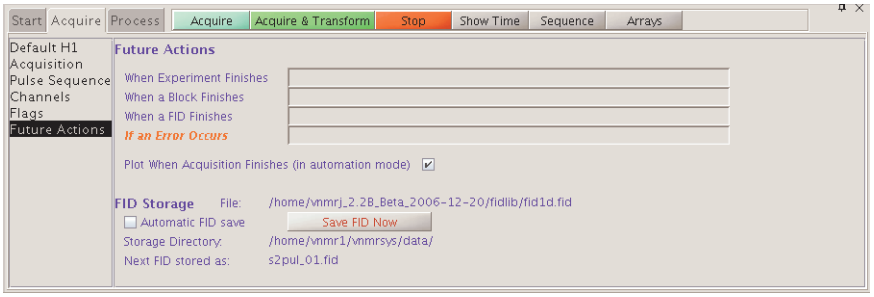
Acquisition and Post Acquisition Actions

Use the Flags page of the Acquire tab to determine the data acquisition precision, what actions to take during acquisition if the spinner or VT fails to remain in regulation, how often to save the FID during the acquisition (block size), and other acquisition-related actions .

Preacquisition delay	Usually set to 0.5 seconds to allow the hardware to set up at the beginning of the experiment. This parameter is also used for kinetics experiments.
Delays: `rof1`, `rof2`, `alpha`	**`rof1`** is normally fixed as 10 µs. After the final pulse in each pulse sequence, the receiver is gated off for **`rof2`** µs before the acquisition begins. **`alfa`** and **`rof2`** are important where the flatness of the baseline is of concern.

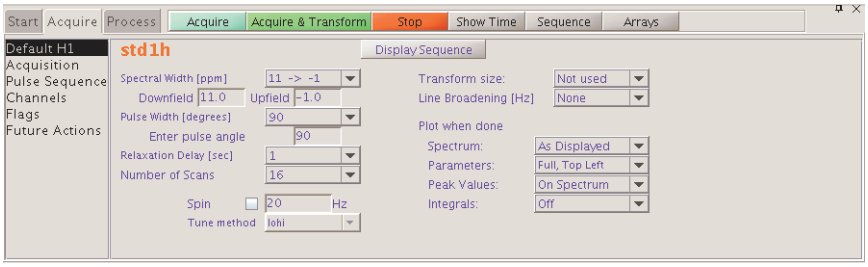


Specify actions that are to occur automatically after acquisition finishes on the Future Actions page. For example, Save FIDs or set automatic FID saving.



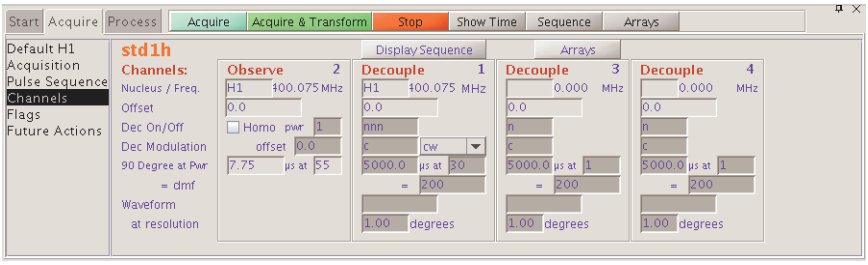
Nucleus-Specific Frequency Settings

Adjust nucleus-specific settings in the Default (*name of nucleus)* page, e.g., Default C13. The example window below shows the Default H1 page, which is used for setting the proton frequency. Other Default pages available are: Default C13, Default F19, and Default P31.



Transmitter and Decoupler Positioning

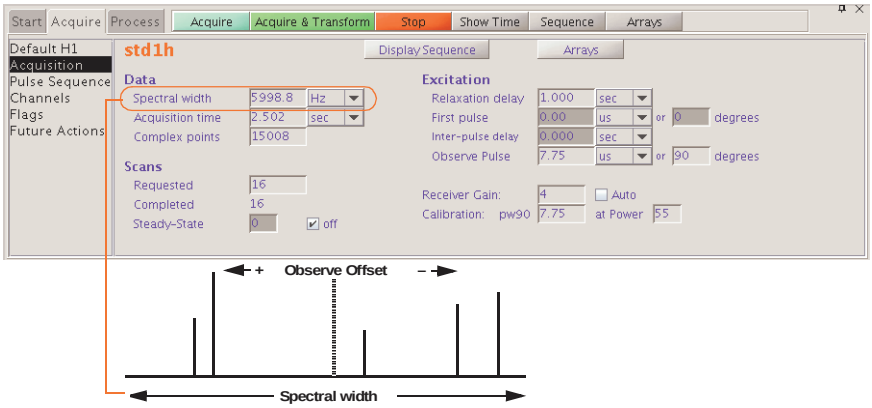
Set transmitter and decoupler values in the Channels page.



The **Observe Offset** field permits moving the observe transmitter offset. Specify the transmitter frequency directly, rather than using the cursor position, by entering a value in the **Offset** field. This provides a convenient method of moving the transmitter frequency outside the current spectral window. **Decouple 3** and **Decouple 4** input fields are available for the second and third decouplers on systems with 3 or 4 channels.

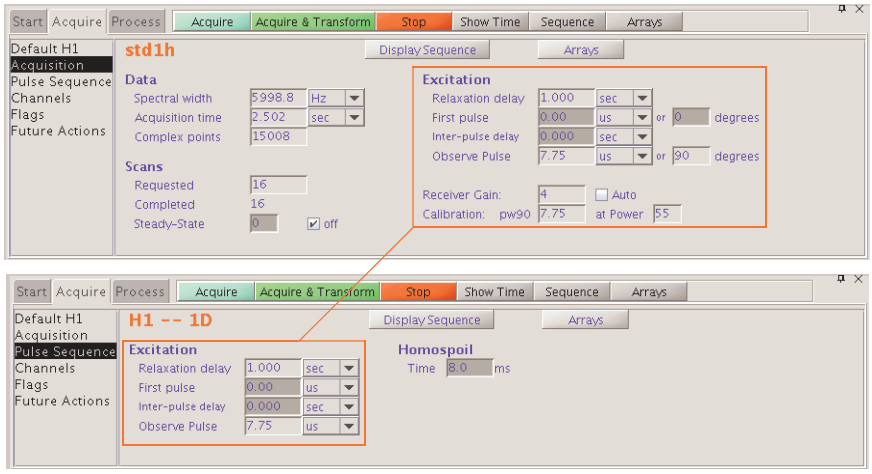
Spectral Window

Set the Spectral window size in the **Spectral width** field in the **Acquisition** page.



Pulse Sequence Settings (Standard Two-Pulse)

Use the Acquisition and Pulse Sequence pages to set the values for the pulse sequence.

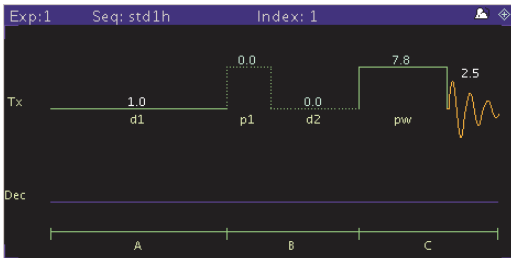


Complex points	Generally calculated automatically when spectral width or acquisition time is changed. VnmrJ calculates a new acquisition time spectral width value if a value is entered in the Complex points field.
Acquisition time	The length of time during which each FID is acquired. Acquisition time.
Steady-State	The number of complete executions of the pulse sequence not accompanied by data collection prior to the acquisition of the real data. In a multi-FID experiment, if Steady-State is a positive value, the steady-state pulses are applied at the start of the first FID only; if Steady-State is a negative value, the steady-state pulses are applied at the start of every FID.
Scans Requested	The number of repetitions or scans performed to make up the experiment—the number of transients acquired. Set Scans Requested to a very large number, (e.g., 1e9) to set up an indefinite acquisition. The **Scans Completed** field changes during the course of an experiment to reflect the number of completed transients.
Relaxation delay, **First pulse**, **Inter-pulse delay**	**First pulse** (p1) and **Inter-pulse delay** (d2) are zero for "normal" 1D NMR. The **Relaxation delay** (d1, used to allow recovery of magnetization back to equilibrium) may be zero as well, reducing the total pulse sequence to a pulse of the time entered in the **Observe Pulse** field (`pw`), followed by the **Acquisition time** (at).
Homospoil	Homospoil is a process by which the homogeneity is temporarily made very bad ("spoiled") to cause any transverse magnetizations present at that time to decay rapidly to zero.
Receiver Gain	Low gain in multiline, high-dynamic range samples can cause a number of problems, including intermodulation distortions, lower sensitivity, and extra lines in the spectrum. Too high a gain, on the other hand, can cause ADC overload and consequent baseline distortion. Autogain capability allows the observe channel to be set optimally for detecting and digitizing NMR signals from a wide variety of samples. `gain=60` represents the highest possible actual receiver gain and `gain=0` the lowest. `gain` increases in steps of 2 dB. `gain='n'` activates Autogain, in which the gain is automatically adjusted at the start of acquisition for an optimum value. After the acquisition is finished, disabling autogain then allows the value of `gain` to be read.
Calibration: pw90	Field displays the length of the 90° pulse, in µs. This value is determined when the probe is installed, calibrated and tested as described in the probe's installation manual and will usually need to be changed for a new sample.

5.3 Pulse Sequences

Display the Pulse Sequence

1. Click on the **Acquire** tab.
2. Select the **Pulse Sequence** page
3. Click on the **Display Sequence** button to display the pulse sequence in the graphics window.



Standard Two-Pulse Parameters

Most experiments will be acquired using a pulse sequence known as the standard two-pulse, or S2PUL. Figure 17 shows a two-pulse sequence and the associated labels from the Acquire pages.

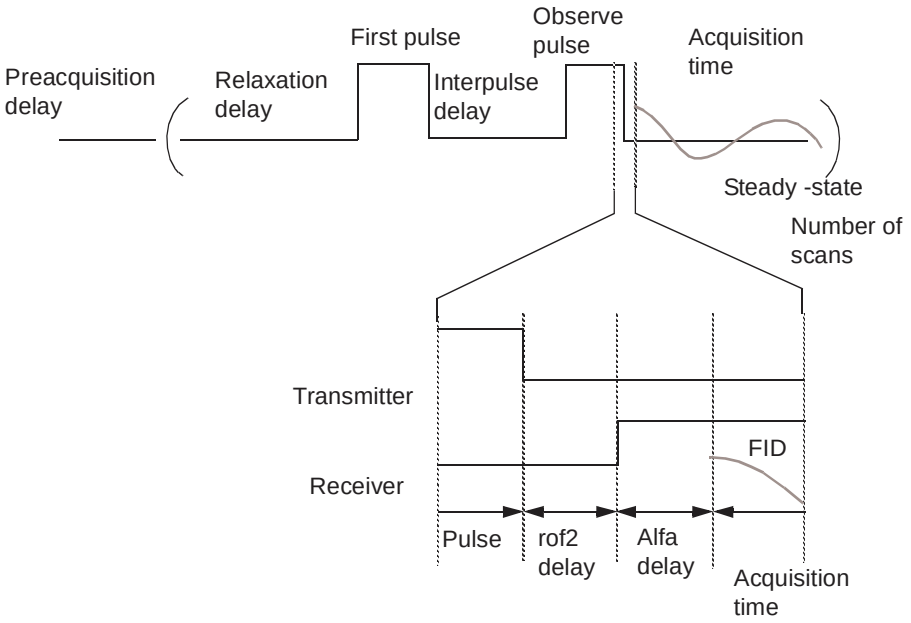


Figure 17. Acquisition Parameters for Standard Two-Pulse Sequence

A preacquisition delay (pad) is usually set to 0.5 seconds at the beginning of the experiment.

Following the preacquisition delay are:

1. Relaxation delay (d1)
2. First pulse (p1)
3. Inter-pulse delay (d2)
4. Observe pulse (pw)

Dead times `rof2` (with receiver off) and `alfa` (with receiver on) are put into the observe pulse. The complex data points are acquired during the acquisition time.

This process is repeated the number of times set for steady-state plus the requested Number of Scans field. Data is actually acquired only during the number of scans and not during the first steady-state transients.

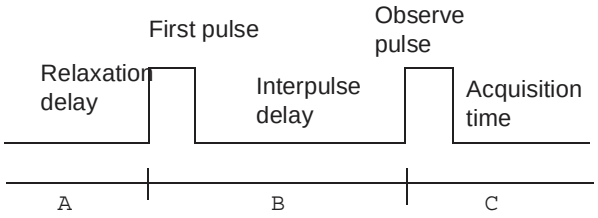
The receiver is off during the pulse sequence and on only during **Acquisition time**. The amplifier can be unblanked at any time but no longer than 10 ms. Blanking and unblanking are implicitly done around pulses.

After the final pulse in each pulse sequence, the receiver is gated off for **rof2** µs before the receiver is turned on and is followed by the Alfa delay ahead of the start of data acquisition.

The “Status” Concept

Every pulse sequence can be divided logically into “periods” of time. The standard two-pulse sequence, for example, can be divided as shown below. This sequence has three logical periods, referred to in the diagram as A, B, and C. These periods are used in controlling the decoupler “status” (as well as the “homospoil” status, discussed later in this chapter).

Logical Periods A, B, C in Standard Two-Pulse Sequence



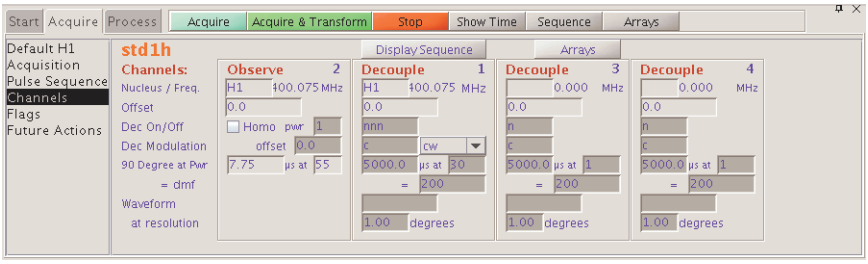
In the ON/OFF/Homo field in the Channels page, use the following letters:

n	no, or an off status
y	yes, or an on status

For example, to have the decoupler be ON during period A, ON during period B, and OFF during period C, describe the desired decoupler status as **yyn**. Setting the ON/OFF/Homo field to **yyn** will select this experiment, which in the heteronuclear case might produce a coupled spectrum with NOE, or in the homonuclear case might be used for solvent presaturation experiments. Setting nny would give us an experiment with the decoupler only ON during period C, the acquisition time, which in the heteronuclear case would be a decoupled spectrum without NOE.

Observe Transmitter and Decoupling Settings

Transmitter power levels are set through attenuators, which are in turn controlled through fields in the **Channels** page.



The observe transmitter power, which is under computer control, is set in the Observe power field. The power can be set to a value from –16 to 63 in 1 of 6 setups. 63 is the maximum power, not attenuation.

The Decouple ON/OFF/ field determines first decoupler output:

- **y**, **ynn**, **yyn**, etc., turns the first decoupler ON.
- **n** or **nnn** turns the first decoupler OFF.

The transmitter fine power level is controlled by the `tpwrf` parameter (if present). The attenuation is linear and spans 60 dB.

The Homo selection box sets the homonuclear decoupling control for the observe channel. Selecting Homo specifies that the receiver is gated, which is done by controlling the observe L.O. (local oscillator) line. The first rf, amplifier, and preamplifier are gated only if decoupling is on. If the decoupling is off, no gating of these signals takes place. When Homo is selected, Modulation should be set to c for continuous wave (CW) modulation.

CAUTION: **Decoupler power greater than 2 watts in a switchable probe will damage the probe. Always carefully calibrate high-power decoupling to avoid exceeding 2 watts of power. The maximum value for `dpwr` on a 200-, 300-, or 400-MHz system has been set to 49, corresponding to approximately 2 watts of power. Before using `dpwr=49` for continuous decoupling, ensure safe operation by measuring the output power. This safety maximum may be adjusted in the `config` program.**

The decoupler power is set in the Decouple power field, which is under computer control. This field be given values from –16 to 63. However, the output power should be measured to make sure a maximum of 2 watts is applied to switchable probes. This safety maximum, which limits the value that can be entered can be adjusted in the System Settings and System Configuration windows. The decoupler power for the second, third, and fourth decoupler channels, respectively. also have safety maximums.

Decoupler Modes

Several other efficient decoupling schemes are available from the Modulation pull-down menu, including GARP decoupling, MLEV-16 decoupling, and XY32 decoupling. Refer to the description of `dmm` in the *Command and Parameter Reference* for other modulation modes available.

Modulation normally has just a single “state” in the standard two-pulse sequence, since the decoupler modulation remains normally unchanged during the pulse sequence. Multiple states are possible; for example, `'ccw'` gives single-frequency decoupling during the first part of the pulse sequence and WALTZ-16 decoupling during acquisition.

Set `dmm` to `'p'` to select programmable decoupling. To specify the decoupling sequence during any period of waveform programmable decoupling, use the `dseq` parameter for the first decoupler, `dseq2` for the second decoupler, and `dseq3` for the third decoupler. The parameters `dres`, `dres2`, `dres3`, and `dres4` control the tip-angle resolution used within a programmable decoupling sequence on the first, second, third, and fourth decouplers, respectively. See the manual *User Programming* for further information.

The following values are typical for decoupling:

- Homonuclear decoupling:

`dm='y'`	Decoupler mode on
`homo='y'`	Homonuclear decoupling on
`dmm='c'`	Decoupler modulation mode is continuous wave
`dpwr=5–15`	Decoupler power level range

- Heteronuclear decoupling:

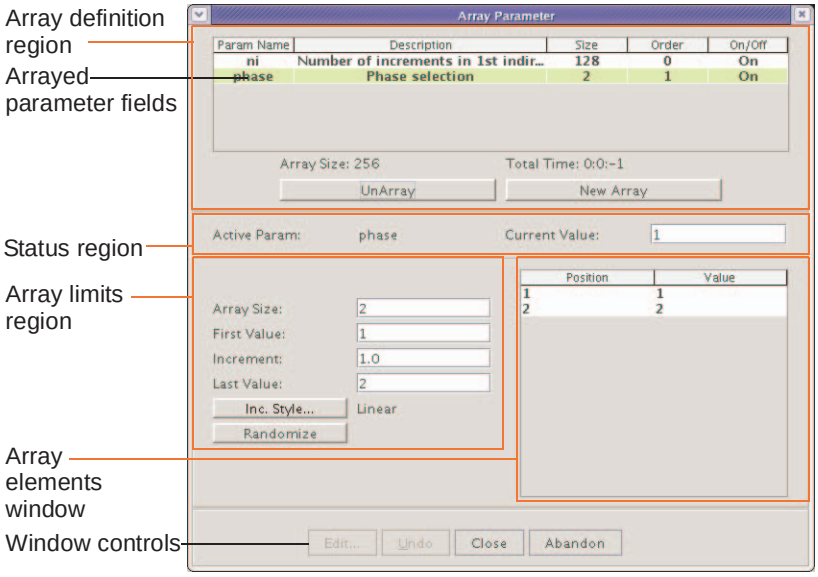
`dm='y'`	Decoupler mode on
`homo='n'`	Homonuclear decoupling off
`dmm='w'`	WALTZ-16 decoupling

`dpwr=40`	Decoupler power level
`dmf=10000`	Decoupler modulation frequency

5.4 Parameter Arrays

1. Click on **Acquisition** on the main menu.
2. Select **Parameter Array** to open the Array Parameter window to set arrayed parameters. Parameter arrays are explained in detail in "Multi-FID (Arrayed) Spectra," page 146.

   This window can be used both within or outside of a study.



Window Regions

Array definition

Arrayed parameter field columns:

Parm Name – enter name of arrayed parameter.

Description – displays text description of array.

Size – displays number of steps or increments in the array.

Order – displays precedence for running the array – double click in the field and enter the array order. Arrays with sequential numbers create a full matrix (array A x Array B) and each array can be a different size. Arrays with the same order number (and the same size) create a diagonal array.

On/Off – array is used / array not used.

Fields and buttons

Array Size field – shows size of selected array.

Total Time field – shows estimated time to compleat the array.

UnArray button – removes selected parameter from the list of arrayed parameters.

NewArray button – adds new row to list of arrayed parameters.

Status – shows active parameter during acquisition and current value.

Array limits

Array Size field – enter the size of the array and press return.

First Value – enter the starting value of the array and press return.

Increment – enter the array increment and press return.

Last Value – enter the ending value of the array and press return.

Inc. Style … button – click and select linear or exponential.

Randomize button – click to create a random array.

Array elements

Change the value of the array element by double clicking on the value of the array element associated with the array position, entering a new value, and pressing Enter.

Window buttons

Edit—Not active.

Undo—Click to undo click again to restore the change.

Close—Closes the window.

Abandon—Closes the window and makes no changes.

The top panel in the window is a table of currently arrayed parameters. The Parameter Name, Description, array Size, array Order and On/Off status are displayed. Add parameters with the **New Array** button and remove parameters with **Unarray**. Turn on or off an arrayed parameter by double-clicking **On/Off**. Edit the array order (except for implicit arrays `ni, ni2`, etc.) to enable nested or parallel arrays. Only parameters of the same array size can be parallel, i.e., have the same array order.

Highlight the array parameter table one row at a time with single clicks. The values of the highlighted array parameter (Active Param) are displayed in a table in the middle panel, along with editable entries for Array Size, First Value, Increment, and Last Value. Edit the parameter values. There are also buttons for increment style (Inc. Style), linear or exponential, and randomizing (Randomize) the order of array values. Specific values can also be entered manually for every element in the list of values. Letter values, (strings) can also be arrayed and modified.

The Current Value of the parameter is displayed above the array parameter values. Select this value from the arrayed values by double-clicking the position number in the list of values or change it manually. When the parameter is unarrayed or turned off, it is set to the current value.

Abandon restores the original state of the window (the state it was in when it opened) and closes the window. **Close** keeps the changes and closes the window.

5.5 Stopping and Resuming Acquisition

Click the **Stop** button  or the **Stop** button next to the Acquire button to stop an acquisition experiment that has been submitted for acquisition.

If the experiment is waiting for execution, no action is taken. If the experiment is active, it is stopped and data is retained.

An acquisition generally continues to completion. Several situations can stop the acquisition early. The system may detect an error, it may detect an overflow, or the operator may stop the system with an `aa` or an `sa` command.

Stop an acquisition (because sufficient signal-to-noise has been obtained or because the experiment has proved useless) by selecting **Acquisition->Abort Acquisition**. The acquisition is aborted immediately. All current FID data is discarded and the experiment is interpreted as an error. Any data collected from an earlier block size transfer or earlier FIDs are retained. All defined Future Actions processing occurs followed by any queued experiments.

5.6 Automatic Processing

Set up automatic processing on the Future Actions page.

Block-size provides a means to examine data while an experiment is in progress. By setting the parameter `bs` to a value (e.g., bs=64), the observe controller is instructed to send the accumulated data to the host computer at the end of every 64 transients. The host computer stores the data in an appropriate disk file (overwriting earlier data). An updated version of the experiment in progress is available for viewing by the user. Weighting and transforming the data processes the current FID as of the last block size transients and displays the resulting spectrum on the screen.

Use the Future Actions page (When Block Finishes field) to make the process automatic. Enter **`wft`** in the When Block Finishes field and Click **Acquire**. Data is transferred to the host computer after each `bs` number of transients is completed, the macro `wft` is run, and the data is transferred to the host computer and displayed in the active VnmrJ viewport. Any command or macro can be invoked to occur automatically using the When Block Finishes field.

“When block size”, `wbs`, processing can be started after acquisition is started. Enter a `wbs` command, (e.g., `wbs('wft')`) on the VnmrJ command line. The `wbs` processing may also be disabled by entering `wbs('stop')`. Setting `bs='n'` before starting the acquisition disables this block-size storage. *If bs='n', data are stored on disk only at the end of the experiment, and if the experiment is aborted prior to termination, data will be lost.*

There are other times when automatic processing is desirable:

- Automatically transform the FID upon completion of data acquisition.

  Set the `wnt` (for “when number of transients”) parameter, (e.g., `wnt='wft'`). This is automatically performed by the `ga` command.
- Automatically process data from an experiment that acquires data sets after all FIDs are collected. A 2D experiment is an example of such an experiment.

  Set the `wexp` (for “when experiment”) parameter, (e.g., `wexp='wft2da'`).
- Take correct action in the event of an acquisition error.

  Set the `werr` (when error) parameter, (e.g., `werr='react'`).

5.7 Acquisition Status Window

Click on the **black triangle** next to the status display to open the Acquisition Status window. The display contains fields for acquisition status information. Fields are displayed based upon the hardware configuration of the system or the parameters set on the system.

Table 4 lists the possible fields, with a description of each field.

Table 4. Fields in the Acquisition Status Window

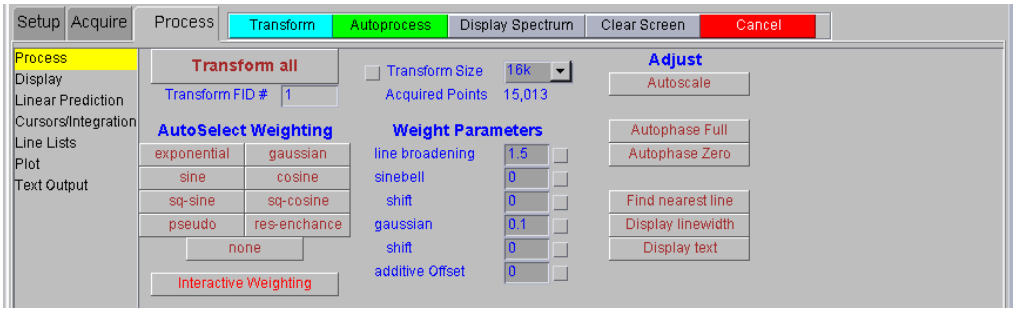
Field	*Description*
Status	Present status of acquisition. The values displayed should be self-explanatory (e. g., “Shimming”) with two exceptions: “Active” means that the acquisition computer started but the console is not active yet, and “Inactive” means that `acqstat` cannot communicate with the acquisition computer or that the acquisition computer is not executing.
Queued	Number of experiments queued by multiple `go` commands
Exp	Number of the active experiment (e. g., `exp1`, `exp2`, `exp3`)
FID	Number of the FID being acquired if in an arrayed experiment
CT	Number of completed transients
Decoupler	Decoupler state: On, Off, Gated
Sample	Sample number in magnet if in automation mode
Lock	Lock status: Off, Regulated, Not Regulated
Complete	Estimated time when experiment will complete
Vt	Variable temperature unit status: Off, Regulated, or Not Regulated (if VT is set as present and `vttype=2`)
Stored	Last time data was transferred to disk

Chapter 6. Processing Data

Sections in this chapter:

- 6.1, “Weighting Function,” this page
- 6.2, “Interactive Weighting,” on page 94
- 6.3, “Fourier Transformation,” on page 95
- 6.4, “Phasing,” on page 95
- 6.5, “Advanced Data Processing,” on page 97

After data are acquired, the next step in the process is applying a “weighting function” to the FID, which is an optional part of the process, and Fourier transformation, which is not. Both operations are done using the Process page on the Process panel.



6.1 Weighting Function

The weighting function used is governed by the following parameters:

- **exponential** – A positive value gives the desired line broadening in Hz, which is then used to calculate a decaying exponential function. A negative value gives a resolution enhancement function.
- **gaussian** – Time constant, in seconds, and defines a Gaussian function of the form `exp(-(t/gf)2)`.

  shift – shifts the center of the Gaussian function `exp(-((t-gfs)/gf)2)`.
- **sinebell** – A positive value, in seconds, applies a sinebell of the form `sin(t*p/(2*sb))`. A negative value applies a squared sinebell function of the form `sin2(t*p/(2*sb))`.

  shift – a sinebell shift constant, in seconds. It allows shifting the origin of the sinebell function according to the formula `sin((t-sbs)*p/(2*sb))`. Again, the square of this function is applied if `sb` is negative.

- **additive Offset** – An additive weighting constant that adds the constant `awc` to each value of the weighting function. It is applied *after* the sinebell and exponential function but *before* the Gaussian function.

All weighting functions are set and applied simultaneously to the data as part of the Transform process. To remove a particular weighting function from use, deselect its check box.

The effects of combining sinebell, exponential, and Gaussian weighting can be difficult to understand and should only be used after experimenting with the individual parameters. The use of either Gaussian apodization (which leads to Gaussian line shapes) or line broadening (greater than 0) (which leads to Lorentzian lineshapes) is especially critical for deconvolution.

Other line shapes cannot be handled by the deconvolution program, but may be appropriate for 1D resolution enhancement or in absolute-value 2D experiments. Weighting affects the integrals of different lines in different ways and should be used with great care if quantitative results are required.

The res-enhance button sets defaults of `a` equal to 0.1 and `b` equal to 0.3 into the formulas `lb=-0.318/(a*sw)`, and `gf=b*sw`, thereby calculating “reasonable” values for the resolution enhancement parameters `lb` and `gf`. The arguments `a` and `b` can also be selected by the user.

Several macros exist that set weighting parameters to give certain window functions. These include `gaussian`, `pi3ssbsq`, `pi4ssbsq`, `sqcosin`, and `sqsinebell`.

The parameter `wtfile` is available for handling user-written weighting functions; see the manual *VnmrJ User Programming* for details.

6.2 Interactive Weighting

Click the **Interactive Weighting** button on the Process panel to start interactive weighting,

Buttons next to the Interactive Weighting display provide access to the following functions:

Check box	*Icon*	*Function*
Line broadening		Selects line broadening or exponential weighting. A negative value gives resolution enhancement.
Sinebell		Selects the sinebell constant. A negative value gives squared sinebell. Change sign by clicking outside the box at the left.
Shifted Sinebell		Selects the sinebell shift constant (if sinebell is active).
Gaussian		Selects the Gaussian time constant.
Shifted Gaussian		Selects the Gaussian shift constant (if Gaussian is active).
Additive weighting		Selects the additive weighting constant.
Return		Returns to the previous menu.

Currently active weighting parameters can be changed by moving the mouse cursor to the appropriate field in the weighting function box and pressing the left mouse button. New values for weighting parameters can also be typed in. Note that all other parameters, unless set to “not used”, are also used to calculate the weighting function.

Use the center mouse button within the FID box to adjust FID intensity (parameter `vf`). Use the center mouse button within the spectrum box to adjust spectrum intensity (`vs`). Use the right mouse button to turn the display of the transformed spectrum off and on.

6.3 Fourier Transformation

The Transform button Fourier transforms one or more FIDs. Weighting is applied only if one or more options are used. Shift and phase rotation are applied according to the parameters set on the Linear Prediction page. Baseline Correct buttons are located on the Display page.

The Transform Size field is the number of points to be Fourier transformed (`fn`), and the number must be a power of two; typical numbers are 16384, 32768, or 65536 (listed as 16K, 32K, and 64K, where K is a multiplier of 1024). The most common entry for Transform Size is Default. This value specifies that however many data points (`np`) were acquired, the first power of two greater than or equal to `np` will be used as `fn`. If `fn` is greater than `np`, or if `fn` is `'n'` and `np` is not a power of two, the remaining points in the transform are filled in with values of zero (*zero-filling*). Thus there is no explicit zero-filling command; this process is an implicit one governed by `fn`. The number of complex data points is `fn`/2.

6.4 Phasing

Phasing spectra may be considered part of either data processing or data display. Performing a complex Fourier transformation produces two sets of data, referred to as the *cosine* and *sine* transforms, or the *real* and *imaginary* data sets, respectively. The absorption spectrum (peaks “in-phase”) and the dispersion spectrum (peaks “out-of-phase”) generally do not coincide with either the real or the imaginary channels, but must instead be produced from a linear combination of the two spectra.

Phasing can be adjusted using Phase button  for interactive phasing or using the Autophase functions on the Process page.

Phase Parameters

The process of phasing a spectrum requires the determination of an angle θ that can be used to "mix" these two data sets to produce one data set, according to the formula:

$$absorption\ spectrum_{\omega} = real * \cos\theta + imaginary * \sin\theta \qquad \text{[Eq. 1]}$$

The process is complicated by the fact that phase angle θ is a function of frequency:

$$\theta = \texttt{rp} + (\omega - \omega_0) * \texttt{lp} \qquad \text{[Eq. 2]}$$

where `lp` (left or first-order phase) and `rp` (right or zero-order phase) are constants that must be determined.

The following is clear about the terms in Equation 2:

- `rp` is *frequency independent*. Changes in `rp` affect all peaks in the spectrum equally.
- `lp` is *frequency dependent*. Changes in `lp` affect peaks with a differing amount as a function of frequency.

There are several ways in which `lp` and `rp` can be adjusted:

- Like any parameter, they can be recalled with a particular parameter set. Once entered, they can also be entered directly (e.g., `lp=-150`).
- Fully automatic phasing is also provided with the `aph` command, which optimizes both the frequency-dependent (`lp`) and the frequency-independent (`rp`) parameters, and is independent of the starting point. The `aph0` command only adjusts `rp`. The `aphx` macro optimizes parameters and arguments for the `aph` command. `aphx` first performs an `aph` then calculates a theoretical value for `lp`. If `lp` set by the `aph` is different from the calculated value by 10 percent, the calculated value is used and an `aph0` is performed.

The command `phase(phase_change)` changes the phase of all peaks in the spectrum by adding `phase_change` to the current value of `rp`, and can be used to remove any excess in `rp` more than 360°.

Autophase Algorithm

The automatic phasing algorithms `aph` and `aph0` have the following features:

- Weighting parameters do not affect the algorithms.
- Spectra with very low signal-to-noise can be phased.
- In vivo spectra can be phased and are very difficult for most autophasing algorithms.
- Spectra with inverted lines can be phased. Such spectra includes DEPT experiments or selectively inverted lines obtained with shaped pulses. This type of phasing is difficult for traditional autophasing algorithms, which cannot distinguish when a line is inverted and when a line is normal.

The autophasing algorithm uses many rules that are used in a manual phasing procedure. First, it finds the peak areas. Then, it estimates the correct phase for each peak. An initial guess of the first order phasing parameter `lp` is made based on the estimated phases of two "normal" peaks. The peaks are categorized into three classes: normal, inverted, and bad. The peaks in the normal and inverted group will be used to find the optimal values for the

phasing parameters `lp` and `rp`. A final check is made to determine whether autophasing was successful or unsuccessful.

Algorithms are complicated but fairly "intelligent." The key point of an algorithm is to use a set of fuzzy rules to estimate the correct phase for each peak. The use of these rules makes an algorithm less sensitive to the signal-to-noise ratio, weighting parameters, and the base line quality. Fuzzy logic also makes it possible to do the classifications on the peaks.

The command `aphb` autophases Bruker data. Refer to the *Command and Parameter Reference* for more information about this command.

Spectrum Display

The displayed spectrum is calculated in one of four *mutually exclusive* modes:

- The *phase-sensitive mode* is selected by the command `ph`. In this mode, the displayed spectrum is calculated using the phase parameters `lp` and `rp`.
- The *absolute-value mode* is selected by the command `av`. In this mode, the displayed spectrum is calculated according to the equation

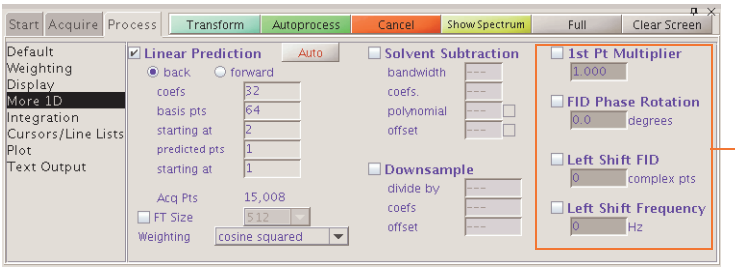
  $$absorption\ spectrum(\omega) = (real^2(\omega) + imaginary^2(\omega))^{1/2}$$

- The *power mode* is selected by the command `pwr`. In this mode, the displayed spectrum is the square of the displayed spectrum calculated in the absolute value mode.
- The *phase-angle mode* is selected by the command `pa`. In this mode, each point in the displayed spectrum is the arctangent of the phase angle of the real and imaginary point.

Once a spectrum is displayed using the interactive display command `ds`, the spectrum can be interactively phased by selecting the Phase button from the menu. Any integral and cursors displayed along with the spectrum are removed.

6.5 Advanced Data Processing

This section covers the functions available on the **More 1D** page: advanced data processing, including phase rotation, frequency shifting, linear prediction, and interleaving FIDs.



FID Manipulation

Check box	*Function*
1st Pt Multiplier	Allows correction of the first point of the FID if it is distorted. Refer to the `fpmult` parameter in the *VnmrJ Command and Parameter Reference*.

FID Phase Rotation	The parameter `phfid` is a zero-order FID phasing constant. If `phfid` is set to a value other than `'n'`, the FID is phase-rotated by `phfid` degrees before weighting or Fourier transformation is performed.
Left Shift FID	The parameter `lsfid` is a constant used in left-shifting the FID. If `lsfid` is set to a value other than `'n'`, the FID is left-shifted by `lsfid` complex points before weighting or Fourier transformation is performed. The value for `lsfid` must lie between `0` and `np/2`. The `tmove` macro provides a method of setting the parameter `lsfid`—position the right time cursor at the place that should be the start of the FID, then enter `tmove` to adjust the parameter `lsfid`.
Left Shift Frequency	Sets the frequency shift of spectral data, in Hz. Refer to `lsfrq` in the *VnmrJ Command and Parameter Reference*. Sets a frequency shift of spectral data, in Hz, with a negative value resulting in peaks being shifted upfield (to the right) and a positive value in peaks being shifted downfield (to the left). `lsfrq` operates in the time domain on complex FID data, and thus must be entered prior to Fourier transformation.

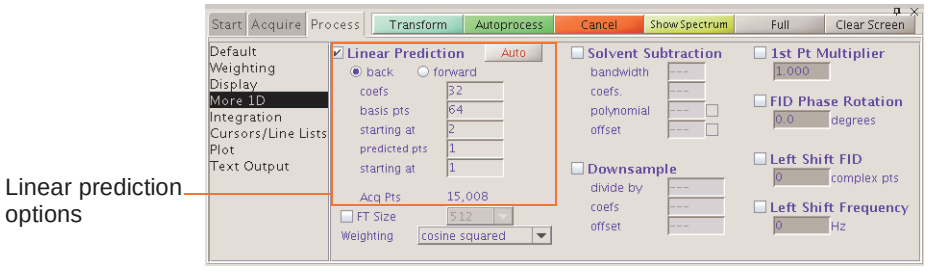
Data Processing Methods

All data processed in VnmrJ is processed using the method of Fourier transformation, but there are three variations that are governed by the `proc` parameter:

- Two orthogonal (real and imaginary, or *x* and *y*) data points form a single complex data point in the FID. Such data are processed using a normal complex Fourier transformation, using `proc='ft'`.
- Some spectrometers, notably those from Bruker Instruments, acquire pseudo-quadrature data by sampling two orthogonal data points *sequentially*, rather than simultaneously. Such data must be processed using a real Fourier transformation, with `proc='rft'`.
- For complex data only, it is possible to include as part of the Fourier transform process a “linear prediction,” described in the next section. `proc='lp'` is used to trigger this operation.

Linear Prediction

Use the Linear Prediction page to activate (default) or deactivate linear prediction and to adjust linear prediction parameters.



Linear Prediction in VnmrJ

Linear prediction is incorporated directly into the Fourier transform routine, so that normally one does not see the “improved” FID, but merely the spectrum which results from Fourier transforming the linear predicted FID. This is accomplished by selecting the

Linear Prediction check box in the Linear Prediction panel and clicking the **Transform** button.

Enter `ft('noft')` to suppress display of the linear predicted FID and perform all the steps of the Fourier transform routine except the actual Fourier transformation. Real points of the FID are displayed by setting `lp=0 rp=0`, or display the imaginary points by setting `lp=0 rp=90`.

Linear prediction involves solving a series of equations for appropriate coefficients based on the actual FID; it involves quite a number of parameters and can be somewhat tricky to optimize (if not optimized properly, or if the data are not amenable, the analysis may simply fail, just like any least-squares fit process may fail to converge).

Linear prediction can be run in a iterative fashion—first extending backward, then forward, and perhaps again backward for more complex problems. This is done by arranging the `LP` parameters.

Why Use Linear Prediction

Raw time-domain data acquired during a pulsed NMR experiment can have two flaws:

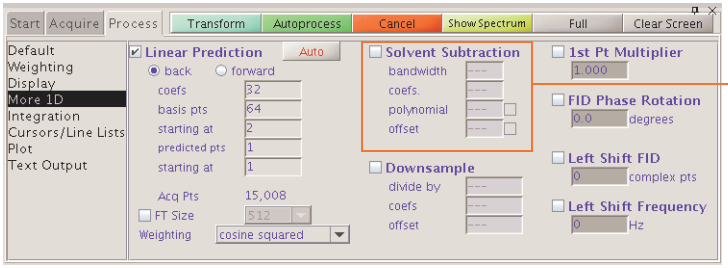
- Early points in the FID may be distorted due to a host of hardware characteristics, such as preamplifier saturation and probe ringing. Even on a perfect spectrometer, these distortions cannot always be avoided.
- The acquisition time of each FID may have been too short to allow for full decay of the signal, leading to distortion in the Fourier transformed spectrum.

Both types of distortions can be solved using *linear prediction*. This uses the “good” part of the FID to analyze for the frequencies that are present in the signal, and then uses that information to extend the FID either in a reverse direction (to “fix” the first few “bad” points) or in a forward direction (to eliminate truncation problems, even single “bad” points). Following this process, the “new, improved” FID is then Fourier transformed in the usual way.

Refer to H. Barkhuijsen, R. de Beer, W.M.M.J. Bovée, and D. van Ormondt, *J. Magn. Reson.*, **61**, 465-481 (1985) for more information on the algorithm implemented in the software, and on linear prediction in general.

Solvent Subtraction Filtering

Numerous solvent suppression pulse sequences exist that reduce the signal from a large solvent peak to a level where the desired resonances can be observed. Often, however, experimental solvent suppression does not entirely eliminate an unwanted solvent peak. Digital filtering of the data can further suppress or eliminate a solvent peak.

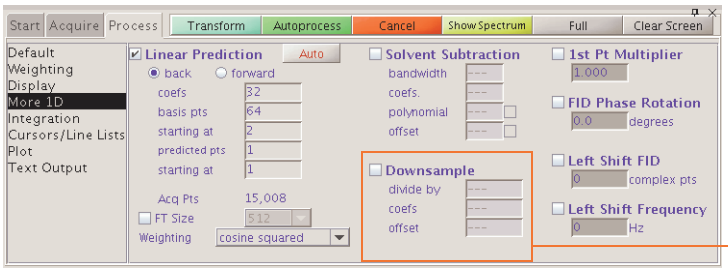


VnmrJ incorporates two algorithms for solvent subtraction by digital filtering:

- bandwidth — Sets the value of `ssfilter` to specify the full bandwidth of the low-pass filter applied to the original FID to yield a filtered FID. Its default value is 100 Hz.
- coefs. — Sets the value of `ssntaps` to specify the number of taps (coefficients) used for the digital filter. The default value is 121, but the value can range from `1` to `np/4`. The more taps in a filter, the flatter the passband response and the steeper the transition from passband to stopband, giving a more rectangular filter. The default is suitable for low-frequency suppression option. A value between 3 and 21 works better for the zero-frequency suppression option.
- polynomial — Sets the value of `ssorder` to determine the polynomial used to create a low-pass filter applied to the FID acquired with the solvent on resonance. The resulting FID is subtracted from the original FID to remove the on-resonance frequencies. Transforming the resulting FID produces a solvent-subtracted spectrum. Another name for this is zero-frequency suppression.

  The quality of zero-frequency suppression diminishes rapidly as the solvent peak moves off the exact center of the digital filter. Adjust `lsfrq` or `sslsfrq` to move the solvent peak to within ± 0.2 Hz of the center of the filter to obtain optimal solvent suppression.
- offset — Sets the value of `sslsfrq` to specify the location of the center of the solvent-suppressed region of the spectrum. Setting `sslsfrq` to a non-zero value shifts the solvent-suppressed region by `sslsfrq` Hz. Setting `sslsfrq` to `'n'` (the default value) solvent suppresses a region centered about the transmitter frequency. The parameters may be arrayed to achieve multiple frequency suppression.

Downsample



- divide by — Sets the value downsampling factor applied after digital filtering. The spectral width of the data set after digital filtering and downsampling is `sw` divided by `downsamp`, where `sw` is the acquired spectral width.
- coefs — Sets the value of `dscoef` to specify the number of coefficients used in the digital filter. This parameter is automatically adjusted by VnmrJ to give filter cutoffs that are the same value of downsamp by using `dscoef*downsamp/2` coefficients in the digital filter. VnmrJ always rounds dscoef*downsamp/2 to an odd number. The default is 61.
- offset — Sets the value of a bandpass filter, in Hz, that is not centered about the transmitter frequency. A positive value selects a region upfield from the transmitter frequency; a negative value selects a downfield region.

Interleave FIDs

The `ilfid` command converts a multiple FID element into a single FID by interleaving the FIDs. When invoked in an experiment of `nf` FIDs, each of `np` points, `ilfid` sorts the data into a single FID of `np*nf` points that can then be transformed. The interleaving takes

the first complex point of each of the `nf` FIDs and places them in sequential order in the new FID. It then takes the second complex point from each of the `nf` FIDs and appends them sequentially to the new FID. This operation is repeated for all complex points. Although `ilfid` adjusts `np` and `nf`, it does not alter other parameters such as `sw`. Refer to the *VnmrJ Command and Parameter Reference* for further information on `ilfid`, including an example.

CAUTION: **Because ilfid alters the data irrevocably, it is strongly recommended to save the FID before using ilfid.**

Chapter 7. Displaying FIDs and Spectra

Sections in this chapter:

- 7.1, “Displaying a FID or 1D Spectrum,” this page
- 7.2, “Display Tools,” on page 104
- 7.3, “Graphics Control Buttons,” on page 107
- 7.4, “Phasing,” on page 110
- 7.5, “Line Tools,” on page 111
- 7.6, “Spectral Referencing,” on page 112
- 7.7, “Display an Inset Spectrum Using Viewport Tab,” on page 113
- 7.8, “Stacked 1D Display,” on page 117
- 7.9, “Aligning and Stacking Spectra,” on page 119
- 7.10, “Integration,” on page 121
- 7.11, “Molecular Display and Editing (JChemPaint and Jmol),” on page 127

7.1 Displaying a FID or 1D Spectrum

Click the Display FID graphics control button to display a FID. Click the 1D Spectrum graphics control button to display a 1D spectrum.


1D Spectrum


FID Display

- "FID Display," page 103
- "1D Spectrum Display," page 103

FID Display

A FID is available for displaying upon completion of the acquisition of acquisition block (block size). Clicking the FID button  displays a FID and enables interactive manipulation of the FID display.

The FID display graphics buttons change to show that multiple FIDs can be viewed. Figure 18 shows a typical display with a FID and two vertical cursors (box mode).

The FID is also phase-rotated (zero-order only) by the number of degrees specified in the **FID Phase Rotation** field on the **Linear Prediction** page.

1D Spectrum Display

After data is transformed, a spectrum becomes available for display and plotting.

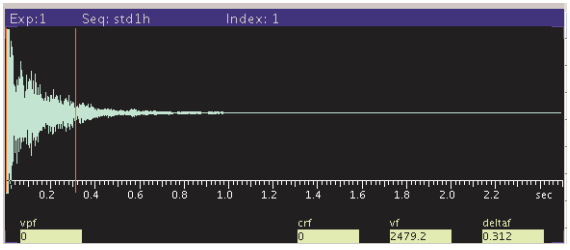


Figure 18. Interactive FID Display

The normal spectrum display enables interactive manipulation of a single 1D spectrum. A spectrum is displayed by clicking the 1D Spectrum graphics control button  or by transforming a data set.

A spectrum displays in the graphics window similar to Figure 19.

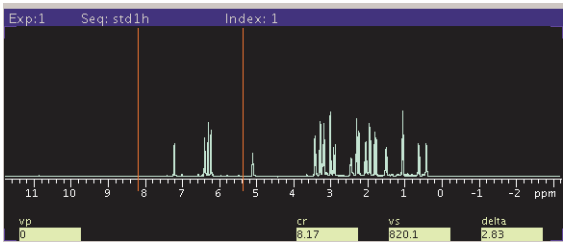


Figure 19. Interactive Spectrum Display

7.2 Display Tools

VnmrJ provides interactive tools for creating highly individualized displays of NMR data.

- "Interactive Display Tools," page 104
- "Display Parameters," page 105
- "Controlling Cursors and Vertical Scale," page 106
- "Display Limits," page 107

Interactive Display Tools

These tools are described below:

Mouse buttons	The mouse buttons correspond to the display parameters shown on the lower right part of the graphics window. The display parameter change as different graphics control functions are selected. Typically, the left button controls the left cursor position, the middle button controls vertical scaling, and the right button controls the right cursor or delta between the two cursors.
Graphics control buttons	The graphics control bar next to the graphics canvas provides graphics control buttons for cursors, zooming, scales, grab & move, threshold, phasing, and refresh. Different functions appear for FID or spectrum display.

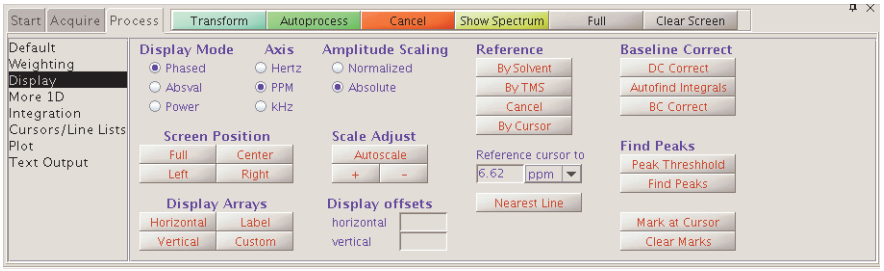
Display page	The Display page on the Process tab provides appropriate display parameters, including display mode, axis, and amplitude scaling.
Display menu	The Display menu provides tools for displaying multiple spectra, plotting, and creating insets.

A typical use of these tools might be to expand a region on a spectrum:

1. Display the spectrum -- click the **spectrum** icon on the graphics control bar.
2. Select the region to expand -- left click on the **spectrum** to place the cursor on the left boundary of the region of interest, and right click to designate the right boundary. Use the left mouse button to drag the left cursor and right button to drag the right cursor until the desired region is between the cursors.
3. Expand the region -- click the **magnifying glass** icon on the graphics control bar.

Display Parameters

FID and spectral display is governed by parameters on the Display page.



Display Mode

The Display Mode parameters set the display mode along the directly or indirectly detected dimension.

Phased	Each real point in the displayed spectrum is calculated from a linear combination of real and imaginary points comprising each respective complex data point.
Absval	(Absolute value mode) Each real point in the displayed spectrum is calculated as a square root of the sum of squares of the real and imaginary points comprising each respective complex data point.
Power	Each real point in the displayed spectrum is calculated as a sum of squares of real and imaginary points comprising each respective complex data point.

Axis

The Axis parameters set the labeling of plot scales, peak frequencies, etc. Typically, FID display is in seconds, and spectrum display is in PPM, Hz, or kHz.

Amplitude Scaling

The amplitude scaling, or vertical scale, parameters set the scale intensities for the display:

Normalized	The largest peak in the spectrum is automatically found, then the display is normalized to make the peak vertical scale on the plot in millimeters.
Absolute	The appearance on the display screen is used as a guide to adjust the vertical scale to produce the desired height. This mode enables comparing intensity from one experiment to another, a necessity for *all* arrayed experiments.

Full scale on the screen represents full scale on the plotter for vertical scaling. This relationship is used to adjust the vertical scale in Absolute display mode, since in that case vertical scale is not the height of the largest peak. In Normalized amplitude scaling mode, this is also used when the largest peak is desired to be off-scale.

An exception to the general rule of plotting is provided by the `wysiwyg` parameter. This parameter is set in the **Edit** -> **System settings** window, on the **Display**/**Plot** tab: *Set display from plotter aspect ratio* `(wysiwyg)` .

Checked	Scales the image to the current plotter setting (wysiwyg).
Unchecked	Scales the image to the full window, which is easier to view. This option scales the window but does not change the ratio of the image.

Screen Position

The screen position parameters set the horizontal position of the display on the screen and the plotter. Clicking one of the buttons updates the display:

Full	Display or plot on the entire screen or page.
Center	Display or plot in the center of the screen or page.
Left	Display or plot in the left half of the screen or page.
Right	Display or plot in the right portion of the screen or page.

Controlling Cursors and Vertical Scale

Click the mouse buttons in the graphics display window to position cursors and adjust the FID or spectral vertical scale and position.

Left cursor	Click the left mouse button to position the cursor and update the value displayed for the `crf` or `cr` parameter (`crf` for a FID or `cr` for a spectrum).
Right cursor (box)	Click the right mouse button to display and position a second cursor to the right of the original cursor. The value of the parameter `deltaf` for a FID or `delta` for a spectra changes with the position of the right cursor and is the difference in seconds or Hz between the two cursors.
Two cursors	If both cursors are displayed, the left mouse button moves both cursors simultaneously, leaving the distance between them (`deltaf` or `delta`) unchanged.
Vertical scale	Click the middle mouse button to adjust the vertical scale of the FID (`vf` parameter) or spectrum (`vs` parameter).
Vertical position	Adjust the vertical position of the FID by clicking and holding the middle mouse button near the left edge of the graphics display and sliding the FID or spectrum up or down. The value of `vpf` or `vp` (or `vpfi` if the imaginary channel) is will change.

Display Limits

The Screen Position buttons (Full, Enter, Left, Right) on the Display page place the display and plot in the desired portion of the page.

The `wysiwyg` parameter is useful for scaling the image to a full window instead of the same size as the plot. This parameter is set in the Edit -> System settings window, on the Display/Plot tab: *Set display from plotter aspect ratio* (`wysiwyg`)

Checked	Scales the image to the current plotter setting (wysiwyg).
Unchecked	Scales the image to the full window, which is easier to view. This option scales the window but does not change the ratio of the image.

7.3 Graphics Control Buttons

The graphics control bar for the active viewport is to the right of the graphics canvas. Use the buttons in the bar to control the interactive display in the graphics canvas.

- "Common Graphics Display Toolbar Controls," page 107
- "1D Display Spectrum Toolbar Controls," page 108
- "Display FID Toolbar Controls," page 108
- "nD Display Toolbar Controls," page 108

Common Graphics Display Toolbar Controls

The following tools are common to 1D, nD, and fid display toolbars.

Icon	*Description*
	Zoom in.
	Zoom out.
	Select zoom region.
	Redraw display.
	Return to previous tool menu.

1D Display Spectrum Toolbar Controls

Icon	Description
	One cursor in use, click to toggle to two cursors.
	Two cursors in use, click to toggle to one cursor.
	Click to expand to full spectral display.
	Pan or move spectral region.
	Display integral.
	Display scale.
	Toggle threshold on or off.
	Phase spectrum.

Display FID Toolbar Controls

Icon	Description
	One cursor in use, click to toggle to two cursor.
	Two cursors in use, click to toggle to one cursor.
	Click to expand to full FID display.
	Pan and stretch.
	Click to show real and imaginary.
	Click to show real and zero imaginary.
	Click to show real only.
	Toggle scale on and off.
	Phase FID.

nD Display Toolbar Controls

- "Main nD Display Bar Tools," page 109
- "nD Graphic Tools," page 109

Main nD Display Bar Tools

Icon	Description
	Display color map and show common nD graphics tools.
	Display contour map and show common nD graphics tools.
	Display stacked spectra and show common nD graphics tools.
	Display image map and show common nD graphics tools.

nD Graphic Tools

Icon	Description
	One cursor in use, click to toggle to two cursors.
	Two cursors in use, click to toggle to one cursor.
	Click to expand to full display.
	Pan and stretch.
	Show trace.
	Show projections. Click on  to show horizontal maximum projection across the top of the 2D display. Click on  to show horizontal sum projection across the top of the 2D display. Click on  to show vertical maximum projection down the left side of the 2D display. Click on  to show vertical sum projection down the left side of the 2D display.
	Rotate axes.
	Increase vertical scale 20%.
	Decrease vertical scale 20%.
	Phase spectrum. Click on  to select the first spectrum.

Icon	*Description*
	Click on  to select the second spectrum.
	Enter peak pick menu.

7.4 Phasing

The Phase button starts the interactive phasing mode. Any integral and cursors that are displayed along with the spectrum are removed. The width of the update region is set by the *Spectrum updating during phasing (0-100)* field in Edit->System settings->Display/ Plot tab, which sets the percentage of the screen display to be updated:

- "FID Phasing," page 110
- "Spectrum Phasing," page 110

FID Phasing

The Phase button activates the interactive phasing mode:

1. Position the mouse arrow on a FID region of interest, about halfway vertically up the screen, and click the left mouse button.

   A horizontal cursor intersects at the mouse arrow, and two vertical cursors are placed on either side of the mouse arrow. A small region of FID is displayed in a different color if a color display is present; only this spectral region is interactively updated.

2. Move the mouse above or below the horizontal cursor, but within the two vertical cursors. Click the left or right button to adjust the FID phase parameter `phfid`.

   Click the mouse above the horizontal cursor to increase `phfid`. Click below the horizontal cursor to decrease `phfid`. Place the mouse arrow right on the horizontal cursor and click the left button to restore the initial phase.

3. To exit the interactive phasing mode, make another selection from the menu. Select the **Cursor** or **Box** button if no other choice is desirable.

Spectrum Phasing

1. Position the mouse arrow on a spectral region of interest toward the right side of the spectrum, about halfway vertically up the screen, and click the left mouse button.

   A horizontal cursor will intersect at the mouse arrow. Two vertical cursors will be placed on either side of the mouse arrow. A region of the spectrum will be displayed in a different color if a color display is present, and only this spectral region will be interactively updated (for the case of less than 100% updating).

2. Move the mouse above or below the horizontal cursor, but within the two vertical cursors. Click the left or right button to adjust the zero-order or frequency-independent phase parameter `rp`.
   - Click above the horizontal cursor to increase `rp` (cause a clockwise rotation of the peaks).
   - Click below the horizontal cursor to decrease `rp` (and cause a counter-clockwise rotation).

- Place the arrow on the horizontal cursor and click the left button to restore the initial phase.

The left and right button of the mouse differ only in their sensitivity. Full scale (top to bottom of the screen) corresponds to approximately 180° for the left button, and 20° for the right button. The left button is a “coarser” adjustment and the right button a “finer” adjustment.

3. Move the mouse arrow to another region of the spectrum, near the left edge of the display, outside the vertical cursors, and click the left mouse button again.

   The frequency-independent phase-correction made so far is first applied to the entire spectrum. A new horizontal cursor is displayed at the mouse arrow, and two new vertical cursors are displayed on either side of the mouse arrows. The mouse now controls the first-order or frequency-dependent phase parameter `lp`.

4. Click the left or right button above or below the horizontal cursor to increase or decrease `lp` so that the phase at the center of the previous region bracketed by the vertical cursors is held constant.

   This process eliminates or substantially reduces the necessity to iteratively adjust the two parameters `rp` and `lp`. As with the zero-order correction, the left button acts as a “coarse” adjust, and the right button as a “fine.”

   Define a new update region by clicking the mouse outside the two vertical cursors.

   Subsequent first-order phase changes causes the zero-order phase to be adjusted so that the phase angle at the center of the previous region bracketed by the vertical cursors remains constant. Click the **Phase** button again if to return to the zero-order phase correction,

   Adjust the vertical scale and apply the latest phase correction by clicking the middle mouse button at the top of a peak that is on scale. This leaves the vertical scale unaffected but recalculates the phase of the entire spectrum. Clicking the center button above or below the peak raises or lowers the vertical scale.

5. Exit the interactive phasing mode by clicking another graphics control button.

7.5 Line Tools

- "Find Nearest Line and Line Resolution," page 111
- "Display Line List," page 112

Find Nearest Line and Line Resolution

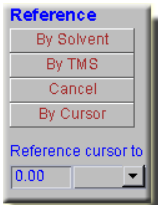
1. Place a cursor near the line of interest.
2. Select the **Process** page and click the **Find nearest line** button. The cursor moves to the nearest line and displays its height and frequency (in Hz and ppm) in the message window.
3. Click **Display linewidth** to display the resolution of a line, as well as the limiting digital resolution of the spectrum.The resolution is determined by a width at half-height algorithm and not by least-squares.

Display Line List

1. Click the **Threshold** graphics control button and use the middle mouse button to vertically position the yellow threshold line.
2. Select the **Line List** page and click the **Display Line List** button. This process displays line frequencies and intensities that are above a threshold.

7.6 Spectral Referencing

Frequency referencing is set on the **Display** page



By Solvent	Reference the spectrum for selected solvent.
By TMS	Reference the spectrum to a TMS line. In the case of other signals (e.g., from silicon grease) immediately to the left of the TMS line (even if they are higher than the reference line), `tmsref` tries avoiding those signals by taking the line furthest to the right in that area, as long as it is at least 10% of the main Si-CH_3 signal. Large signals within 0.6 ppm for ^{1}H (or 6 ppm for ^{13}C) to the right of TMS might lead to misreferencing.
Cancel	Clears the reference line by removing any spectral referencing present, and turns off referencing.
By Cursor	References the spectrum based on the current cursor position. To reference the spectrum based on a line position in the spectrum, first use the **Find nearest line** button on the Process page, then click **By Cursor**.

Parameters used in spectral referencing.:

Reference line (frl)	The distance, in Hz, of the reference line from the right edge of the spectral window. This line is the spectral position used to set the referencing. It can be the signal of a frequency standard (such as TMS), or any line (such as a solvent signal) with a known chemical shift (in ppm), or a position in the spectrum where such a line is expected to appear.
Reference position (rfp)	The difference between the reference line and the reference frequency (zero position of the scale), in Hz. Referencing a spectrum using the signal of a frequency standard, such as TMS, use reference position is 0. The distance of the reference frequency from the right edge of the spectrum is *reference line - reference position*.
Spectrometer frequency	The absolute frequency, in MHz, of the center of the spectrum (the transmitter position). Use the `spcfrq` command in order to see the accurate value of the spectrometer frequency (`sfrq` parameter).
Reference frequency	The frequency, in MHz, of the frequency standard, i.e., the zero position of the frequency scale, *and* the divider (unit) for the calculation of ppm scales (`reffreq`).

The By Solvent and By TMS buttons assume that the system is locked (and that the lock solvent is defined in `/vnmr/solvents`). Ensure that the field offset has been adjusted so that the lock frequency is on resonance with a sample of similar susceptibility if the

experiment is to run unlocked and these buttons are used to set the field offset. Adjust the field offset is adjusted using the following procedure:

1. Insert a sample with deuterated solvent.
2. Adjust `z0` (or `lkof`) in `acqi` so that the lock frequency is on resonance.
3. Switch off the lock.
4. Insert the nondeuterated sample.

The accuracy of the solvent and TMS referencing buttons is mostly limited by the accuracy of the chemical shift of the lock resonance line, which may depend on the concentration and the chemical properties (acidity/basicity) of the components in the sample. But they should normally be accurate enough to find an actual reference line close to its predicted position.

Estimate the position of the reference frequency in spectra from unlocked samples, provided the spectrometer is first locked on a sample with similar susceptibility, then the lock is disengaged and the field offset adjusted such that the lock signal is on-resonance. Now, acquire a spectra without lock and calculate their (estimated) referencing using `setref`, provided the `solvent` parameter is set to the solvent that was last locked on.

7.7 Display an Inset Spectrum Using Viewport Tab

- "Viewport Tab," page 113
- "Display Region Tools and Controls," page 114

Viewport Tab

Click on the **Viewport** tab to display the viewport controls. If not visible, use the **View** menu.

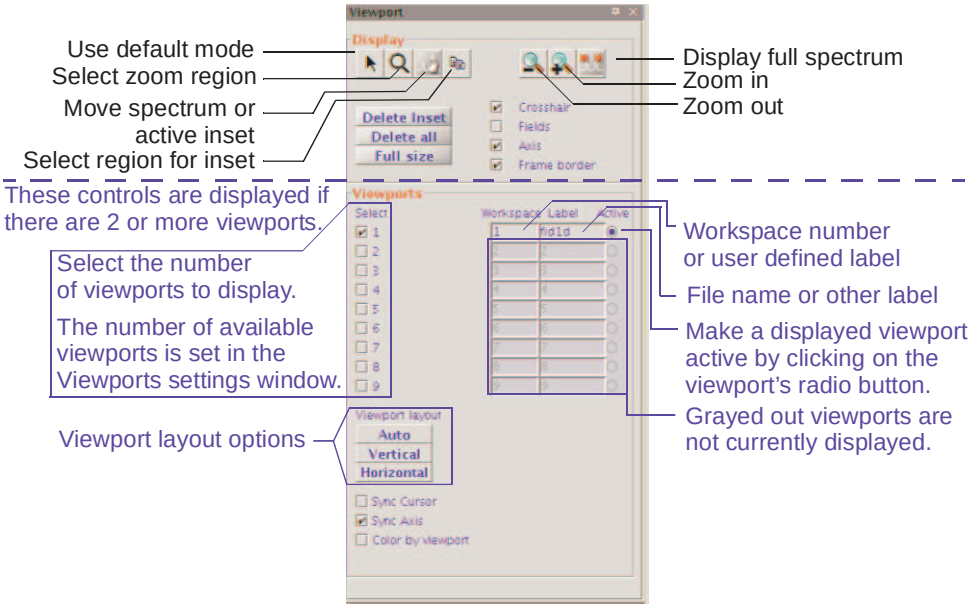


Figure 20. Viewport Tab and Controls

Display Region Tools and Controls

The display region, see Figure 21, of the viewport tab has the following tools, button, and check boxes:

- "Viewport Tools," page 114
- "Inset Frame Buttons," page 114
- "Display Check Boxes," page 115

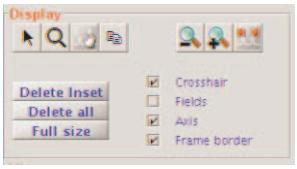


Figure 21. Display Tools and Controls

Viewport Tools

Icon	*Function*
	Default mode — left mouse click moves the left cursor and right mouse click moves right mouse cursor.
	Zoom mode — left mouse drag across a region zooms in the region. Left mouse double click on a peak or any point — center the point and zoom in. Right mouse double click on a peak or any point — center the point and zoom out. Exit zoom mode — click any button on the panel, graphics toolbar, or redraw button.
	Pan mode — left mouse drag moves the spectrum. Left mouse double click — centers the point. Right mouse drag up — expands the spectrum. Right mouse drag down — contracts the spectrum. Exit pan mode— click any button on the panel, graphics toolbar, or redraw button.
	Inset mode — left mouse drag a box over a spectrum region creates an inset frame of the region. A viewport can have multiple inset frames. Exit inset mode — release mouse button.
	Zoom out to the full spectrum if there is no cache (see zoom in function).
	Zoom in one step per mouse click. Current box (left cursor and right cursor) is used to zoom in if there is no cache for zoom in or the right cursor is clicked. The spectrum is zoomed in automatically with the center unchanged if the box spans the entire displayed spectrum region. Zoom percentage of automatic zoom in is set to 50% by default. Zoom actions are cached to allow zoom out or zoom step by step using zoom in or zoom out button.
	Expand to full spectrum.

Inset Frame Buttons

The buttons delete one or all inset frames and restore the default frame to full size.

Button	*Function*
Delete Inset	Delete the selected inset.
Delete all	Delete all inset frames.
Full size	Restore the default frame to its full size.

Display Check Boxes

The check boxes control optional display features.

Check box	*Function*
Cross hair	Display cross hair and chemical shift(s) of the cursor position when mouse is moved over the spectrum. A useful function when the fields are not shown, not in cursor mode (default mode), or when chemical shift of a peak without moving the left cursor is required while in the cursor mode.
Fields	Display cr, delta, vp etc... fields at the bottom of the viewport.
Axis	Show scale of the axis.
Show frame border	Check the box to display a box around the frame. Un-check the box to display the four corners of the selected frame as *hot spots* for resizing. No border or corner will be displayed if a frame is not selected. An empty frame is not visible until it is selected.

Working with Viewports and Inset Frames

All VnmrJ graphics are displayed in frame(s). The viewport has a default frame that occupies the entire viewport graphics area. An inset frame initially shares the same workspace and data as the original frame and is manipulated in the same way as the default frame.

- "Creating an Inset Frame," page 116
- "Zooming in on a Region Within an Inset Frame.," page 116
- "Resizing an Inset Frame," page 117
- "Moving an Inset Frame," page 117

Creating an Inset Frame

An inset frame has the full capability of the default frame. The only difference is that the default always exists, while an inset frame can be created and removed. Create an inset frame within the default viewport frame as follows:

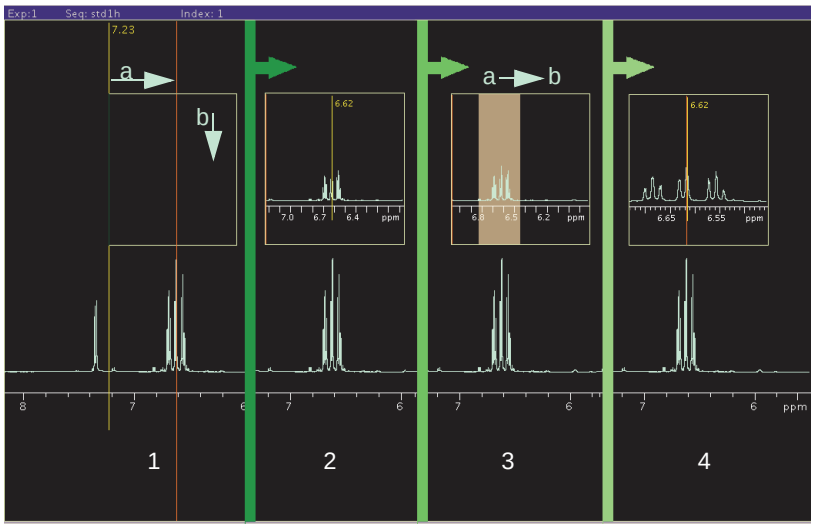


Figure 22. Creating an Inset Frame

1. Select the inset mode tool .
2. Place the cursor at the low field (left) side of the region to be expanded as shown in Figure 22 frame 1a.
3. Hold the left mouse button down and drag the inset window to the high field (right) side of the region.
4. Drag the cursor down to set the height of the inset frame as shown in Figure 22 frame 1b.
5. Release the mouse button to create the inset frame, see Figure 22 frame 2.

Zooming in on a Region Within an Inset Frame.

1. Select the default mode tool .
2. Click inside the frame to make the frame active.

   A frame has a yellow border when it is active and white border when it is inactive (these are the default colors of inactive and active frames).
3. Select the zoom mode tool .
4. Place the cursor at the low field (left) side of the region to be expanded as shown in Figure 22 frame 3a.
5. Hold the left mouse button down and drag the inset window to the high field (right) side of the region, Figure 22 frame 3b.

   The region selected is indicated by a transparent gray rectangle.
6. Release the mouse button and the selected region expands to fill the inset box, Figure 22 frame 4.

Resizing an Inset Frame

1. Select the default mode tool  .
2. Click inside the frame to make the frame active. An active frame has a yellow border.
3. Move the mouse cursor to a corner of the inset frame. The cursor changes from a single-headed arrow to a double-headed arrow.
4. Hold down the left mouse button and grab the corner of the frame.
5. Drag the corner to resize the frame.
6. Release the mouse button when the frame is at the desired size.

Moving an Inset Frame

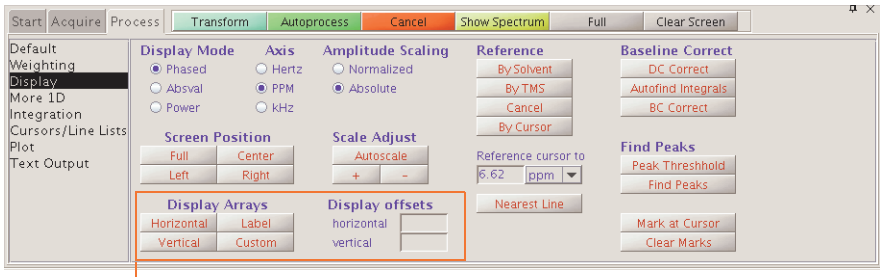
1. Select the default mode tool  .
2. Click inside the frame to make the frame active. An active frame has a yellow border.
3. Move the mouse cursor to an edge of the inset frame. The cursor changes from a single-headed arrow to a four-headed arrow.
4. Hold down the left mouse button and grab the edge of the frame.
5. Drag the frame to the new position.
6. Release the mouse button when the frame is at the desired position.

7.8 Stacked 1D Display

Stacked Display Using the Main Menu Display

1. Click on **Display** on the main menu.
2. Select a display mode from the dropdown menu:
   - Display Multiple Spectra Horizontally
   - Display Multiple Spectra w/ Labels
   - Display Multiple Spectra Vertically
   - Increase vertical Separation by 20%
   - Decrease vertical Separation by 20%
   - Create an Inset of the current Display
     — Save Current Display Parameters
     — Plot Current Display before Making Inset
     — Make Inset
     — Plot Inset and Return Original Display

Stacked Display Using the Display Page



Buttons used to control the display of arrayed data

1. Click on the **Process** tab.
2. Select the **Display** page.
3. Click on a Display Arrays button:
   - **Horizontal** — Display arrayed spectra horizontally and divide available display width into equal portions.
   - **Vertical** —Display arrayed spectra stacked vertically with each spectrum displayed using the full width of the screen.
   - **Label** — add a label to the spectra.
   - **Custom** — Use a custom Label.
4. Enter values for the Display offsets
   - **horizontal** — enter a value in mm for the separation between spectra.
   - **vertical** — enter a value in mm for the separation between spectra.

Stacked Spectra Display Using the Graphics Tools

Icon	*Function*
	Display the first arrayed spectrum and display 1D graphics toolbar with the following icons at the top (or left side if the bar is horizontal).
	Display next spectrum.
	Display previous spectrum.
	Display arrayed spectra stacked vertically with each spectrum displayed using the full width of the screen.
	Display arrayed spectra horizontally and divide available display width into equal portions.
	Hide or show axis under the spectra.
	Label the spectra.
	Return to previous graphics display tool.

Stacked FID Display Using the Graphics Tools

Icon	*Function*
	Display the first arrayed FID and display 1D FID graphics tool bar with the following icons at the top (or left side if the bar is horizontal).
	Display next FID.
	Display previous FID.
	Display arrayed FIDs stacked vertically with each spectrum displayed using the full width of the screen.
	Display arrayed FIDs horizontally and divide available display width into equal portions.
	Label the FIDs.
	Return to previous graphics display tool.

7.9 Aligning and Stacking Spectra

Requirements for Aligning and Stacking Spectra

Spectra can be a mixture of 1D and 2D data sets, all 2D data sets, or all 1 D data sets provided these requirements are met:

- All selected viewports need to use a common scale.

  Data in the viewports may have different nuclei, different spectrum width, or different spectral regions. The common scale is determined based on data in all selected viewports and determines whether alignment or stacking is possible. Overlaid and stacked spectra are drawn based on the common scales.
- Alignment is enabled if more than one axis in more than one viewport have the same axis (H1, C13 etc.).
- Stacking is enabled when data in all viewports have the same axis/axes.

Setting up Stacked Aligned Spectra

1. Select the **Viewport** tab from the vertical tabs panel.
2. Load each data set into a different viewport and process the data. Data must meet the "Requirements for Aligning and Stacking Spectra," page 119.
3. Select viewports containing spectra to overlay by placing a check in the check box under **select**.
4. Click on the **Overlay viewports** button to overlay all selected viewports.

The Stack Spectrum button, Figure 23, is displayed below Overlay Viewports button if all spectra have the same dimension (all 1D or all 2D) and all axis/axes (nuclei) match. Stacked spectra are aligned and each spectrum is shifted along x and y. The shift between spectra is

specified by **x** and **y** offset in the entry fields below Stack Spectrum button. Spectral axes are also synchronized to enable zoom and pan of the spectrum without losing the alignment.

Figure 23. 1D Stacked Spectra

The Align spectra button, Figure 24, is available if it is a mix of 1D and 2D spectra when multiple spectra are overlaid. All 2D spectra must have matching axes. All 1D data must match one of the 2D axes. 1D spectra are aligned and displayed at the margins of the 2D

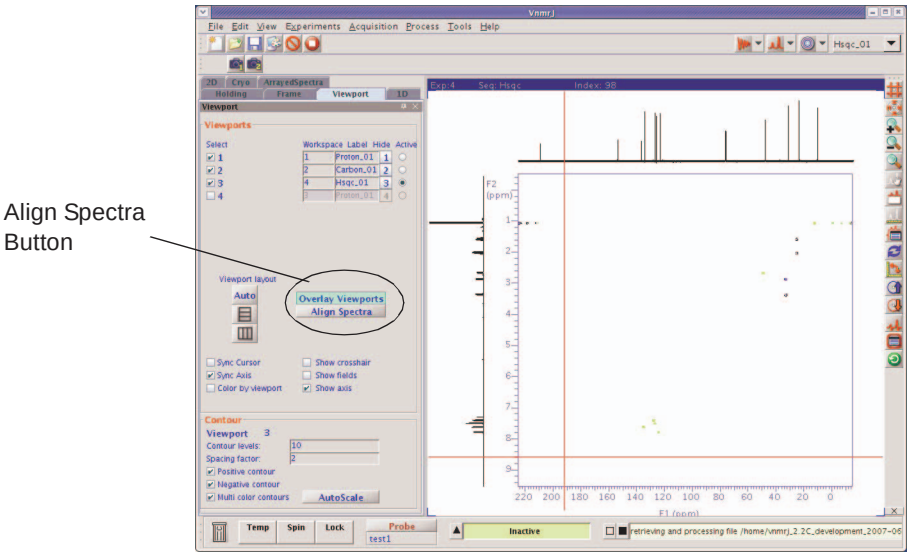


Figure 24. 2D Spectra with Overlaid 1D's

spectrum. 1D spectrum will be rotated if necessary to align with the 2D spectrum. Zoom and pan are synchronized when the spectra are aligned.

The stacked spectrum button for 2Ds, Figure 24, is displayed below Overlay Viewport if all 2D spectra axes and nuclei match. Spectral axes are synchronized to enable zoom and pan of the spectra without losing alignment.

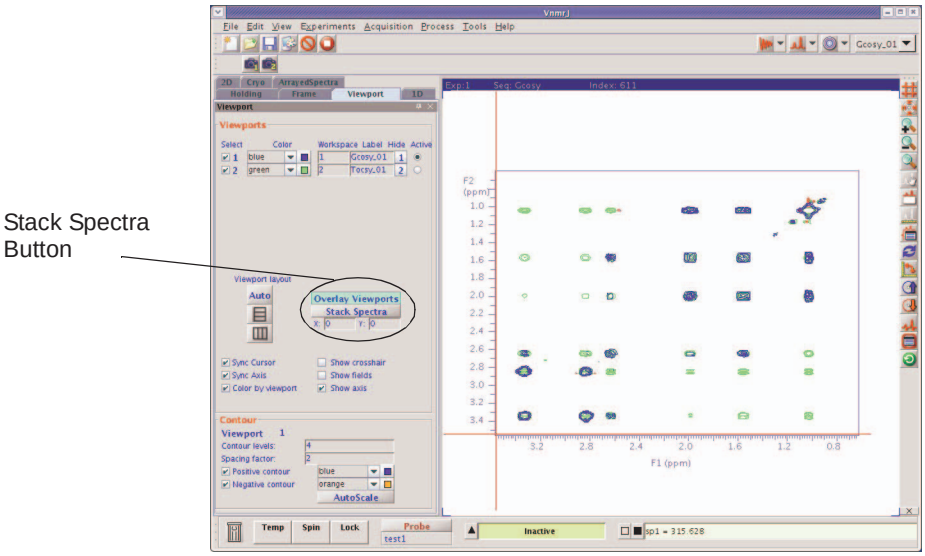
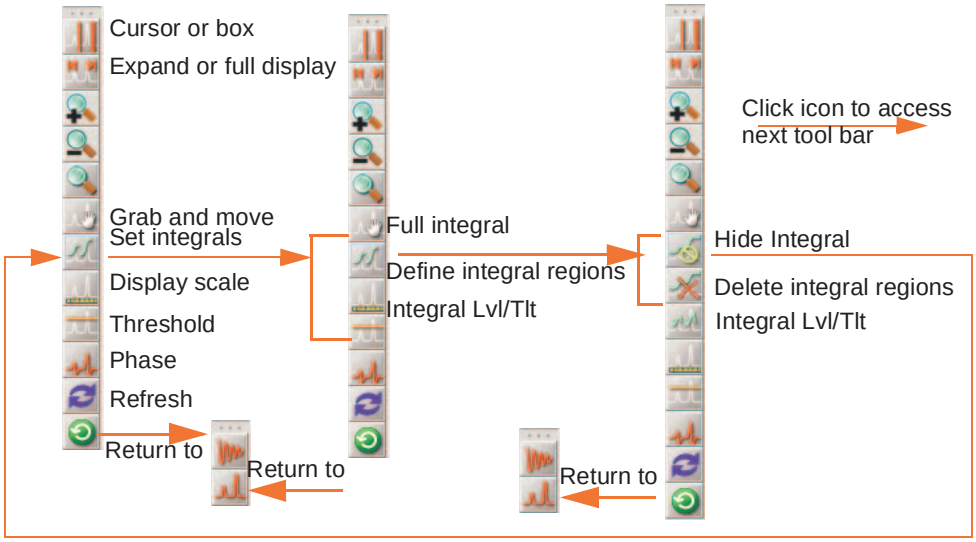
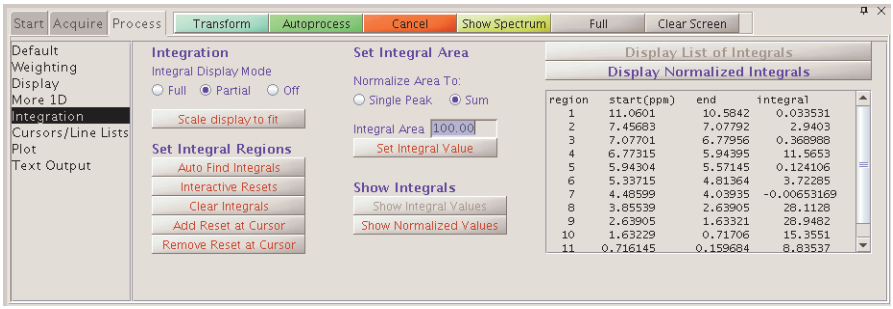


Figure 25. Stacked Overlaid 2D Spectra

7.10 Integration

This section describes methods and tools for displaying and plotting integrals.





Interactive Zero- and First-Order Baseline Correction Mode

The Integral Lvl/Tlt button activates interactive zero and first order baseline correction mode. The zero order correction is represented by the `lvl` parameter; the first order correction is represented by the `tlt` parameter. If no integral is displayed when the Integral Lvl/Tlt button is activated, the integral is automatically displayed.

1. Left click on an integral region of interest, about halfway vertically up the screen.

   A horizontal cursor intersects at the mouse arrow. Two vertical cursors are placed on either side of the mouse arrow.

2. Right or left click above or below the horizontal cursor, but within the two vertical cursors, to adjust the zero-order baseline correction parameter `lvl`.

   - Clicking the above the horizontal cursor increases `lvl`.
   - Clicking below the horizontal cursor decreases `lvl`.
   - Clicking on the horizontal cursor restores the initial baseline correction value.

3. Left click on another region of the spectrum, outside the vertical cursors.

   A new horizontal cursor displays at the mouse arrow, two new vertical cursors display on either side of the mouse arrow, and a single vertical cursor displays in the middle of the region where `lvl` was being updated. The mouse now controls the first-order baseline correction parameter `tlt`.

4. Right or left click above or below the horizontal cursor to increase or decrease `tlt`, and change `lvl` so that the total drift correction at the single vertical cursor in the middle of the previous region is held constant.

   This process eliminates or substantially reduces the necessity to iteratively adjust the two parameters `lvl` and `tlt`. As with the zero-order correction, placing the mouse arrow right on the horizontal cursor and clicking the mouse button will restore the initial baseline correction values.

   Each time the mouse is clicked outside the two vertical cursors, new vertical and horizontal cursors display.

   The left and right mouse buttons both adjust the baseline correction parameters and differ only in their sensitivity. The left button causes changes a factor of eight times larger than the right button making the left button a “coarse” adjust and the right button a “fine” adjust. The overall sensitivity of these adjustments can also be controlled by the parameter `lvltlt`. This parameter is a multiplier, with a default value of 1.0, for the size of the changes. To make larger changes, make `lvltlt` larger than 1.0. To have finer control, set `lvltlt` to be between 0.0 and 1.0.

The middle mouse button adjusts the integral scale (parameter `is`) or the integral offset (parameter `io`), exactly as whenever an integral is displayed.

5. Exit the interactive baseline correction mode by clicking on another graphics control button.

Displaying Integrals Step-by-Step

The following methods provide an opportunity to compare procedures. Before starting each procedure, be sure to obtain a typical spectrum by entering:

1. Load a data file into the active viewport using the file browser or the Locator.
2. Transform the data if necessary.
3. Click on the **Process** tab.
4. Select the **Integration** page.
5. Click on an Integration Display Mode radio button: **Full, Partial**, or **Off**.

   Full shows integrals over the entire spectrum, including the noise.

   Partial shows even integrals regions and hides all the odd integral regions.

   Off turns off the integral display.
6. Click on **Auto Find Integral**s to automatically set the integral resets and display the data as set by the Integration Display Mode radio button.
7. Click on **Scale display to fit** button to automatically scale the display.
8. Set the integral area:
   a. Enter a value in the Integral Area field.
   b. Click on one of the following radio buttons under the **Normalize Area to: page** region.

      Single Peak — select the region or peak under the cursor as the reference and set the single peak integral to the value in the Integral Area field when the **Set Integral Value** button is clicked.

      Sum — sets the entire integral to the value in the Integral Area field. Do not click on the Set Integral Value button; this button sets the single peak reference.
9. Display the integral results as follows:
   - **Single Peak** — both the Show Integral Values and Show Normalized Value buttons are active.

     Integral Values

     Click on the **Show Integral Values** to display the values of the integral regions on the screen below the spectrum.

     Click on **Display Lists of Integrals** to list the display regions and the value of the integral over each region.

     Normalized Integral Values

     Click on the **Show Normalized Values** to display the values of the integral regions normalized to the reference region on the screen below the spectrum.

     Click on Display **Normalized Integrals** to list the display regions and the value of the integral over each region normalized to the reference region.

Manual Method

1. Load a data file into the active viewport using the file browser or the Locator.
2. Transform the data if necessary.
3. Click on the **Process** tab.
4. Select the **Integration** page.
5. Click on **Clear Integrals**.

   Any currently defined integral reset points are cleared.
6. Set up the integral resets from left to right (down field to up field).
   a. Click on the **Interactive Resets** button.
   b. Place the cursor to the left of the first integral region.
   c. Click the left mouse button.
   d. Move the cursor to the right of the first integral region.
   e. Click on the left mouse button.
   f. Repeat step b through step e until all the required integral regions are defined.
7. Click on **Scale display to fit** button to automatically scale the display.
8. Set the integral area:
   a. Enter a value in the Integral Area field.
   b. Click on one of the following radio buttons under the **Normalize Area to: page** region.

      Single Peak — select the region or peak under the cursor as the reference and set the single peak integral to the value in the Integral Area field when the **Set Integral Value** button is clicked.

      Sum — sets the entire integral to the value in the Integral Area field.

      Do not click on the Set Integral Value button; this button sets the single peak reference.
9. Display the integral results as follows:
   - Single Peak — both the Show Integral Values and Show Normalized Value buttons are active.

     Integral Values

     Click on the **Show Integral Values** to display the values of the integral regions on the screen below the spectrum.

     Click on **Display Lists of Integrals** to list the display regions and the value of the integral over each region.

     Normalized Integral Values

     Click on the **Show Normalized Values** to display the values of the integral regions normalized to the reference region on the screen below the spectrum.

     Click on Display **Normalized Integrals** to list the display regions and the value of the integral over each region normalized to the reference region.

Command Line Equivalents for VnmrJ Interface Driven Integration

Use the parameter page editor to view the commands on the current parameter page.

1. Click on **Edit** on the main menu.
2. Select **Parameter Pages**.
3. Place the mouse cursor on a button or entry field.
4. Double click (left mouse button).
5. Read the associated command next to the field *Vnmr Command*:

Baseline Correction

Almost all of the operations performed on spectra assume a “good” baseline. Line lists, integrations, resolution measurements, 2D volume integrations, etc., all measure intensities from “zero” and do not perform any baseline adjustments. Perform a baseline correction operation before performing further data reduction if the baseline in your spectrum is not “good.” Two types of baseline correction are provided, linear and non-linear, and are available using the buttons on the Display page.

Baseline Correction Commands

The `dc` command turns on a linear baseline correction, using the beginning and end of the displayed spectrum to define a straight line to be used for baseline correction. `dc` calculates a zero-order baseline correction parameter `lvl` and a first-order baseline correction parameter `tlt`. The `cdc` command turns off this correction. The results of the `dc` or `cdc` command is stored in the `dcg` parameter, which can be queried (`dcg?`) to determine whether drift correction is active. If active, `dcg=''`; if inactive, `dcg='cdc'`.

The `bc` command performs a 1D or 2D baseline correction. The 1D baseline correction uses spline or second to twentieth order polynomial fitting of predefined baseline regions. `bc` defines every other integral, that is, those integrals that disappear in partial integral mode (`intmod='partial'`) as baseline and attempts to correct these points to zero. A variety of parameters can be used to control the effect of the `bc` command.

For more information about the `bc` command, refer to the entry for `bc` in the *Command and Parameter Reference*.

Integral Reset Points Commands

The `z` command (or the equivalent button or icon) resets the integral to zero at the point marked by the displayed cursor. `z(reset1,reset2,...)` allows the input of the reset points as part of a command, instead of using the position of the cursor. Reset points do not have to be entered in order. The resets are stored as frequencies and will not change if the parameter `fn` is changed. The command `cz` (or the equivalent button) removes all such integral resets. `cz(reset1,reset2,...)` clears specific integral resets.

The `liamp` parameter stores the integral amplitudes at the integral resets points, and the `lifrq` parameter stores the frequencies of integral reset points, for a list of integrals. To display the values of `liamp`, enter `display('liamp')` with a **Text Output** page selected. Frequencies are stored in Hz and are not adjusted by the reference parameters `rfl` and `rfp`.

Integral Regions Commands

The `region` command divides a spectrum into regions containing peaks. A variety of parameters can be used to control the effect of the `region` command; see the *Command and Parameter Reference* for details.

Integral Display and Plotting Commands

Display and plotting of the integral trace is independent of the values of the integrals. The height of the trace is controlled by the parameter `is` and can be interactively adjusted with the `ds` command. Also, the macro `isadj(height)` (or the equivalent button) adjusts the integral height so that largest integral fits the paper or is `height` mm tall if an argument is provided, for example, `isadj(100)`.

The command `dli` (or the equivalent button) displays a list of integral values at the integral reset points. The frequency units of the reset points are defined by the parameter `axis`. The reset points are stored as Hz and are not referenced to `rfl` and `rfp`. The amplitudes are stored as actual values; they are not scaled. The integral values are scaled by the parameters `ins` and `insref` and the Fourier number. Typically, `ins` is set to the number of nuclei in a given region. For example, if a region represented a single methyl group, the following procedure would scale the integral values of that region:

1. Set **`ins=3`**.
2. Set **`insref`** to the Fourier-number-scaled-values of that integral.
3. Enter **`dli`**. The integral value of that region is displayed as 3 and all other integral values are accordingly scaled.

Integral value scaling can be interactively set with the `ds` command. The `setint` macro can also be used to adjust integral value scaling. `setint` sets the value of an integral and is used in conjunction with the command `dli` to scale integral values. Normalized integral values can also be selected. In this case, `ins` represents the total number of nuclei. The individual integral values will be scaled so that their sum is equal to `ins`. The normalized mode may be selected by setting `insref` to “not used.” The integral is scaled by `ins` and `insref`.

Two commands are closely related to `dli`:

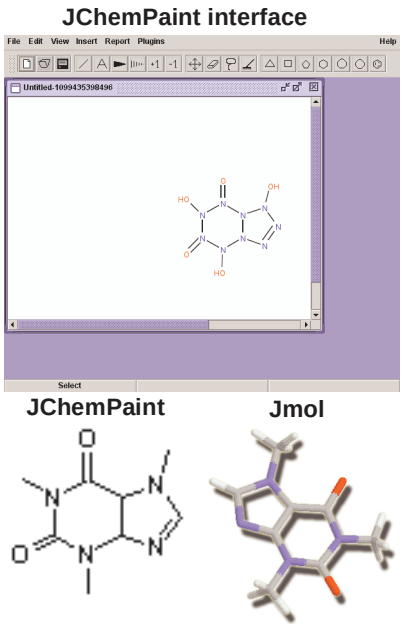
- `nli` is equivalent to `dli` except that no screen display is produced.
- `dlni` normalizes the values from `dli` using the integral normalization scale parameter `ins` and then displays the list.

The `dpir` command displays numerical integral values below the appropriate spectral regions, using the integral blanking mode in which only every other integral is plotted. The command `dpirn` shows the normalized integral values in an analogous fashion.

The `pir` command plots digital integral values below the spectrum, using the integral blanking mode in which only every other integral is plotted. The command `pirn` plots the normalized integral values in an analogous fashion.

7.11 Molecular Display and Editing (JChemPaint and Jmol)

- "Running JChemPaint," page 127
- "File Formats," page 127
- "Molecular Structures," page 128
- "Jmol Interface in VnmrJ," page 128
- "Full-Featured Jmol," page 129
- "Licenses for JChemPaint and Jmol," page 130



Tools for editing, viewing, and printing molecular structures are installed as options with VnmrJ. These tools are derived from *JChemPaint* and *Jmol*.

JChemPaint and Jmol are open source software packages available from `http://sourceforge.net/`

JChemPaint is a graphical editor for 2D molecular structures. Jmol is a visualization and analysis tool for 3D structures.

Running JChemPaint

1. Click on **Tools**.
2. Select **Molecular Structures**.
3. Select **JChemPaint menu**.

Refer to `http://jchempaint.sourceforge.net` for documentation.

File Formats

JChemPaint can edit, save, and export the file formats listed here.

1. Save files as MDL MOL (*.mol) in one of the `mollib` directories: `/vnmr/mollib` or `~username/vnmrsys/mollib`.
2. Import an existing mol file into VnmrJ by copying it into the `mollib` directory.
3. Click on **Tools** on the main menu.
4. Select **Open**, browse to the file, and drag it to the VnmrJ graphics screen.

Format	*Action*
MDL MOL	edit, save
SMILES	edit, save
IUPAC Chemical Identifier	edit
MDL SDF Molfile	edit
MDL RXN Molfile	edit
Chemical Markup Language	edit, save
Scalable Vector Graphics	save
CDK source code fragment	save
BMP	save
JPEG	save
PNG	save
TIFF	save
Gaussian Input	export

Molecular Structures

Molecular structures are displayed and manipulated in the VnmrJ graphics window. View as many graphics as wanted. The graphics are displayed in the current experiment, and they are saved per experiment.

Use the following steps to display a molecular structure in the VnmrJ graphics window:

1. Click on **Tools** on the main menu.
2. Select **Browser**, browse to the `mollib` directory:

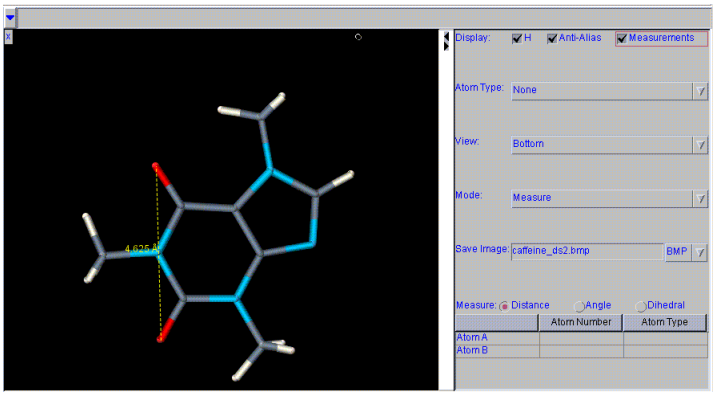
   `/vnmr/mollib` or `~username/vnmrsys/mollib`
3. Select the appropriate files and drag them to the VnmrJ graphics window:
   - Molecule file -- select a file from the `mollib` directory that ends in the `mol` extension.
   - Graphic file -- open the `icons` directory and select a TIFF, GIF, JPEG, or PNG file.

After a molecular structure is displayed, use the mouse to move, resize, delete, or view the corresponding 3D version with Jmol.

To:	*Do:*
Select	Double-click the molecule
Move	Select the molecule and drag with the left mouse button.
Resize	Select the molecule and drag with the middle mouse button.
Delete	Select the molecule and drag to the trash can.
View a molecule with Jmol	Select the molecule and click the right mouse button. This only works with MOL files. Refer to "Jmol Interface in VnmrJ," this page.

Jmol Interface in VnmrJ

VnmrJ provides some Jmol tools to view a molecule.



Menu	*Description*
Display:	H– Displays hydrogen atoms. Anti-Alias – Turns on anti-aliasing and smooths the graphics display. Measurements – Display measurements.

Menu	*Description*
Atom Type:	Display the atoms with atomic symbols, atom types, atom numbers, or nothing.
View:	View the molecule from front, tom, bottom, right, or left.
Mode:	Rotate – rotates the image. Zoom – zooms in/out. Translate – moves the image. Select – selects the atoms. Measure– measures distance, angle, or dihedral. Refer to"Measuring a Molecule," page 129.
Save Image:	Saves the molecule image as BMP, JPEG, PPM, PNG, or PDF. The image is saved in the directory `~username/vnmrsys/mollib/icons` with the name entered in the field. Refer to "Saving a Molecule Image," page 129.

Measuring a Molecule

1. Select the measure mode: distance, angle, dihedral.
2. Click on the appropriate atoms to create the measurement:
   - distance – click two atoms.
   - angle – click three atoms
   - dihedral – click four atoms
3. Display the measurement by selecting the **Measurement** display option.

Saving a Molecule Image

1. Select the file format for the image: BMP, JPG, PPM, PNG, or PDF.
2. Enter a name for the image and add a file extension that corresponds to the file format chosen in step 1.
3. Press Enter.

   The file is saved in the directory `~username/vnmrsys/mollib/icons/`.

Jmol Display Options

- Change the foreground color of the molecule window: enter the following command on the VnmrJ command line:

  `vnmrjcmd('mol','foreground','color')`

  where *`color`* is a color name or a hex value. The foreground color by default is set to the most visible color according to the background color.
- Change the font of the labels on 3D molecule graphics: use the Edit->Display Options window and change the font of Plain Text.
- Click on the ⓧ to exit Jmol.

Full-Featured Jmol

Select **Tools**->**Jmol** to view a molecule with the full-featured Jmol software package,

Refer to `http://jmol.sourceforge.net/` for Jmol documentation.

Licenses for JChemPaint and Jmol

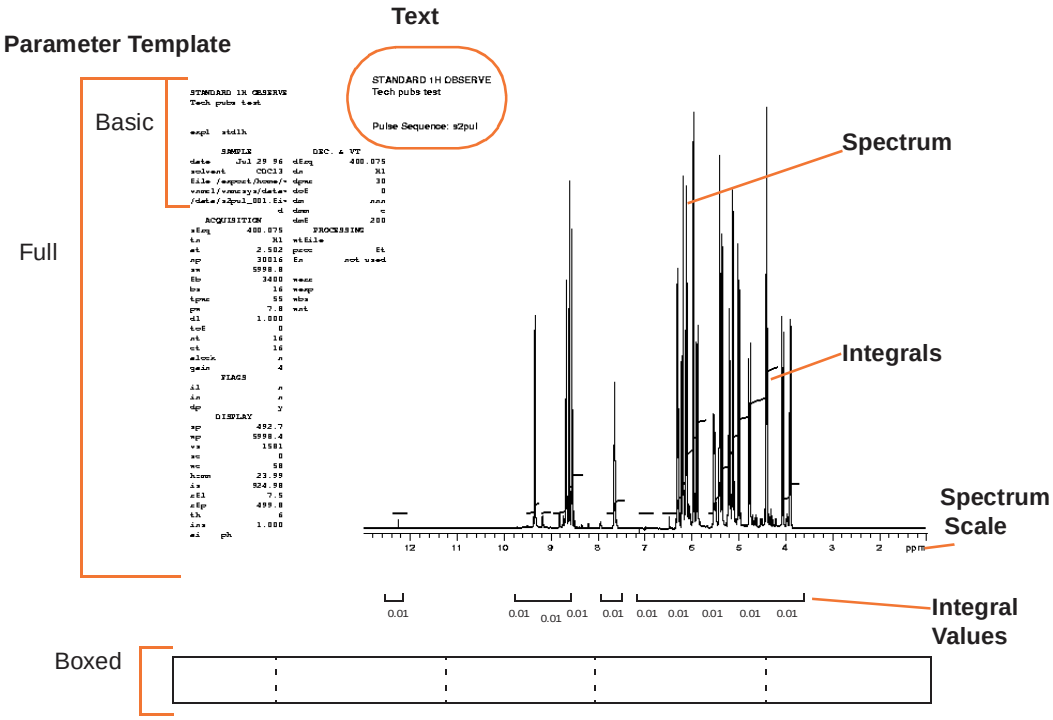
The licenses for JChemPaint and Jmol are included on the VnmrJ CD in the `licenses` directory.

Chapter 8. Plotting and Printing

Sections in this chapter:

- 8.1, “Plotting,” on page 131
- 8.2, “Plot Designer,” on page 133
- 8.3, “Color Printing and Plotting,” on page 141

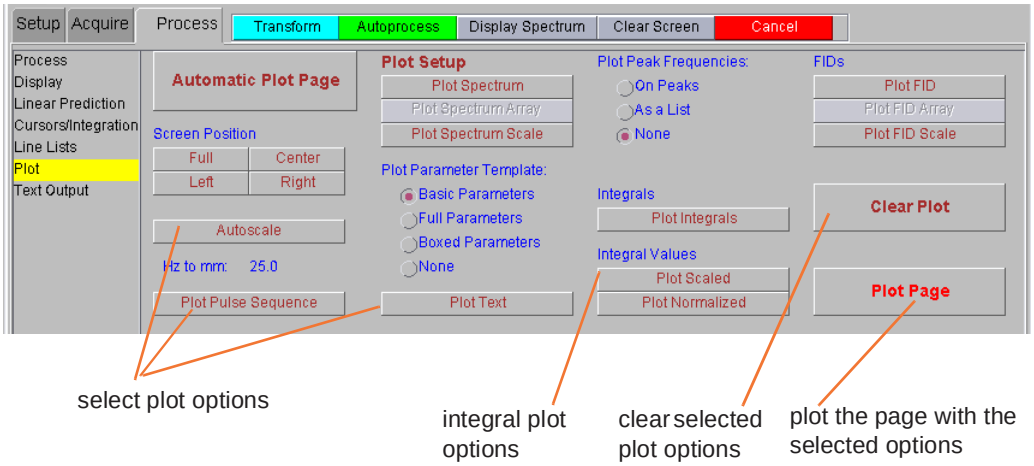
Plotting and printing of data are highly individualized activities. Each user has specific ideas about proper formats, necessary expansions, etc.



8.1 Plotting

Plotting is based around the concept of a plot file. Items selected on the Plot page are added to a temporary plot file, and the Plot Page button submits the plot file to the plotter. The Clear Plot button removes the plot file

Set up and submit a plot using the selections on the Plot page under the Process tab after the spectrum or FID is displayed.



To Plot:	*Select:*	*Click:*
Spectrum and scale		Automatic Plot Page
Pulse sequence		Plot Pulse Sequence
FID		Plot FID, Plot Page
FID and scale		Plot FID, Plot FID Scale, Plot Page
Spectrum		Plot Spectrum, Plot Page, Clear Plot
Spectrum and scale		Plot Spectrum, Plot Spectrum Scale, Plot Page
Spectrum, scale, and text		Plot Text, Plot Spectrum, Plot Spectrum Scale, Plot Page
Spectrum, scale, and parameters	Parameter Template option	Plot Spectrum, Plot Spectrum Scale, Plot Page
Spectrum, scale, and peak frequencies	Peak Frequencies option	Plot Spectrum, Plot Spectrum Scale, Plot Page
Spectrum, scale, and integrals		Plot Spectrum, Plot Spectrum Scale, Plot Integrals, Plot Page
Spectrum, scale, and integrals, integral values		Plot Spectrum, Plot Spectrum Scale, Plot Integrals, Plot Page
Parameters only	Parameter Template option	Plot Page
Text only		Plot Text, Plot Page
Peak frequencies only	Peak Frequencies option	Plot Page
Integrals only		Plot Integrals, Plot Page
Scaled integral values only		Plot Scaled, Plot Page
Normalized integral values only		Plot Normalized, Plot Page

8.2 Plot Designer

- "System Requirements," page 133
- "Using Plot Designer," page 133
- "Creating a Customized Template," page 134
- "Plot Designer Tools," page 138
- "Customizing Plot Designer," page 139

Plot designer provides the following tools:

- Interactive plot composition fine-tuning of the layout on the screen prior to plotting.
- Label spectra with text in various fonts and draw lines, boxes, and arrows.
- Save customer plot layouts and templates for reuse.
- Export plots for further annotation and incorporation into reports and publications.

System Requirements

Plot Designer is a Java-based application. The Java Runtime Environment (JRE) provides an environment in which Java applications run. Any required updates are available from the update area of the Sun Microsystems Web site at http://www.sun.com.

Using Plot Designer

Select a viewport and process the data set for plotting.

1. Start the Plot Designer program as follows:
   a. Click on **File**
   b. Select **Create a Plot Design**.
      The Plot Designer window opens, seeFigure 26.

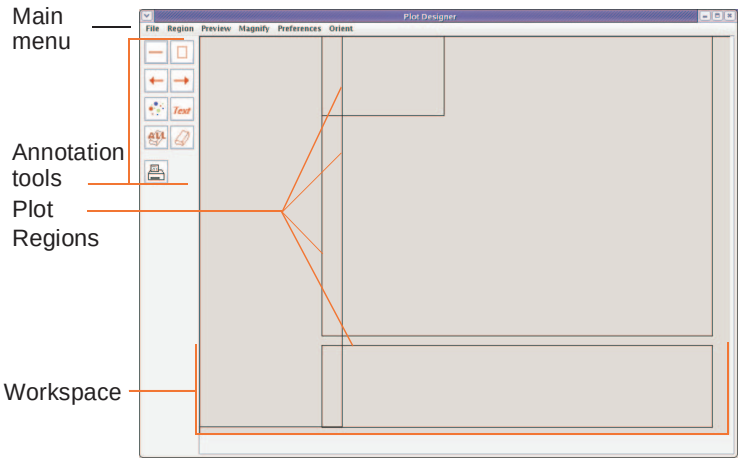


Figure 26. Plot Designer with Current Default Template

2. Load a template
   a. Click on **File**.
   b. Click on **Templates**.
   c. Click on a **Plot template**.

Select from the following standard templates or any custom user-created template (see "Creating a Customized Template," page 134):

deptB	dicom.default	chemParray	chemP1d
basic2D	oneD	whitewash	ChemP2d

d. Place a check in **Use this template as default** to keep this as the template that loads each time Plot Designer is started. The name of the default template is shown on the message line above the Plot Templates window control buttons.

e. Click on **Open**.

3. Select **Preview** from the Plot Designer Menu.

4. Select **All**.

   The data from the active viewport is imported into the various regions of the template based upon the commands associated with each region.

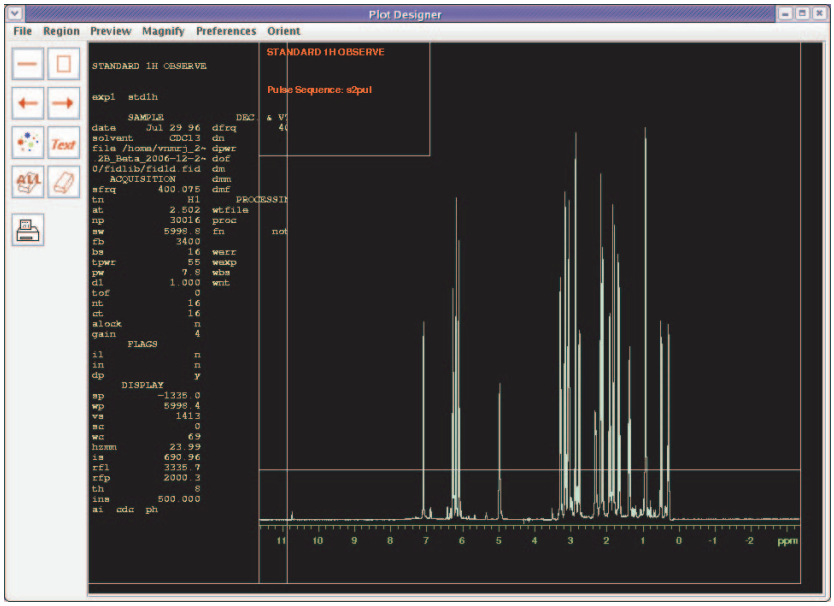


Figure 27. Default oneD Template with Imported Data

Creating a Customized Template

Create a template from scratch or base a customized template on one of the supplied templates.

- "Preparing to Customize a Template," page 135
- "Editing Plotting Commands in a New or Existing Plot Region," page 135
- "Resizing and Moving Plot Regions and Objects," page 136
- "Adding and Editing Text and Graphics Elements," page 136
  - "Changing Line Width," page 136
  - "Changing Fonts," page 137
  - "Changing Colors," page 137
  - "Adding Text," page 137
- "Saving a Custom Template," page 138

Preparing to Customize a Template

1. Start Plot Designer.
   a. Click on **File**
   b. Select **Create a Plot Design**.
2. Load a template or use the default template.
3. Do any or all of the following:
   - Click on a region to delete – see "Deleting a Region," page 135.
   - Delete all the regions – see "Clearing all Regions from the Workspace Permanently," page 135.
   - Add a new region – see "Adding a Region," page 135.
   - Edit an existing region – double on a region, click on **Region** on main menu, select **Edit**, and enter the plotting command for the content of the selected region, see "Editing Plotting Commands in a New or Existing Plot Region," page 135.
   - Add text and graphics elements – see "Adding and Editing Text and Graphics Elements," page 136.

Adding and Removing Regions

Deleting a Region

1. Double click on a region.
2. Click **Region-Delete**.

Restoring a Single Deleted Region

Click **Region-Undelete**.

Clearing all Regions from the Workspace Permanently

Click **Delete All** – no undelete. Regions removed with Delete All cannot be restored with Undelete.

Adding a Region

1. Click on **Region** on main menu
2. Select **New** (mouse cursor changes to a cross hair).
3. Draw the new region on the screen.

Editing Plotting Commands in a New or Existing Plot Region

1. Double click on a region to make it active. Active regions have red borders with control handles.
2. Enter new plotting commands or edit existing plotting commands in the region editor window. Any plotting currently support plotting command is allowed

   The Region Editor window control buttons as listed in Table 5:.

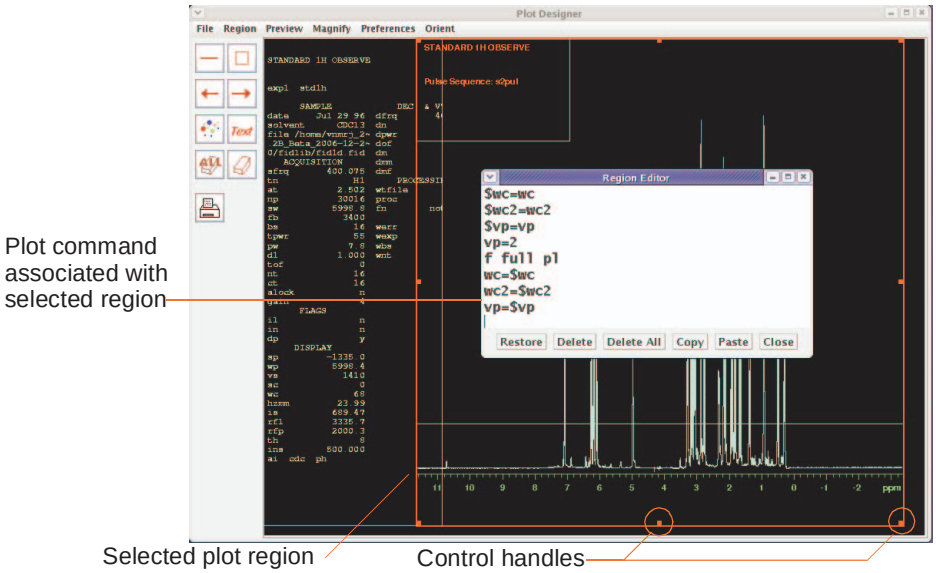


Figure 28. Editing a Plot Region Commands

Table 5. Region Editor Buttons

Button	*Function*
Restore	Applies the original template to a region. Restore template to its original design if it was opened and changes were made to it, using this button.
Delete	Removes text. This option is not similar to **Copy**. Deleted text is not stored in a buffer; do not use **Delete** to cut and paste text.
Delete all	Clears all text from the input area.
Copy	Duplicates text.
Paste	Inserts copied text in the input area.
Close	Exit the Region Editor

Resizing and Moving Plot Regions and Objects

Move an object or region by double clicking on it and dragging the mouse across the workspace. The arrow keys can be used to move objects.

Resize a region by double clicking on it, grabbing a control handle (see Figure 28) on the border, and dragging it to the new size.

Adding and Editing Text and Graphics Elements

Change the size and color of objects in a region with the Item Preferences window, shown in Figure 29.

Click on **Region-Preferences** to open this window or click on the **Item Preferences** tool  , described on page 138.

Changing Line Width

Change the width of a line by doing the following procedure:

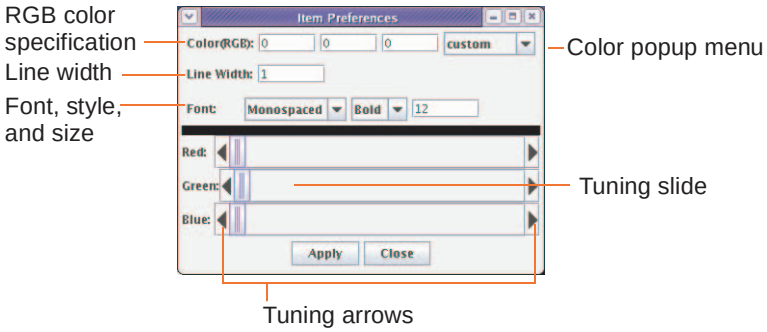


Figure 29. Item Preferences Window

1. Highlight the line or region by double clicking on it.
2. Enter a new width in the Line Width field.
3. Click **Apply** to change the line.
4. Click anywhere in the workspace to deselect the line.

Changing Fonts

Plot Designer has three font families: Sans Serif, `Monospaced`, and Serif. Fonts can be Plain, **Bold**, or *Italic*. Change the family, style, and size of a font as follows:

1. Highlight the text or region.
2. Click on the Item Preferences tool  to open the Item Preferences window.
3. Choose a family, style, and enter a size in the Font field.
4. Click **Apply** to change the text.

Changing Colors

Change the color of a line by doing the following:

1. Highlight the line or region.
2. Click on the color button  to open a pop-up menu showing a range of colors.
3. Move the tuning slider either left or right to change a color, or change a color by clicking on the left or right arrows in the Red, Green, and Blue fields; the values in the Color(RGB) field automatically change as the slider moves.
4. Click **Apply** when the required colors are selected.
5. Place the cursor anywhere in the workspace and click once to apply the color change.

Adding Text

Do the following to add text into your design:

1. Click on the text input tool  to open the text input window.
2. Type text in the field at the top of the window.

   Customize the text by clicking on the desired options and entering a font size in the indicated field.
3. Click on **Put** and drag the cursor into the workspace, then click once to paste in the text.

Use the following procedure to copy and paste text that is already on the workspace and change the font styles:

1. Highlight the text.
2. Click on the text input tool 

to open the Text Input window shown in Figure 30.
3. Select a Font family and Font style, and enter a Font size.
4. Click **Put** to paste the text in the workspace.

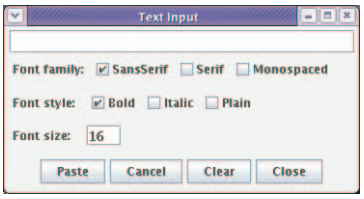


Figure 30. Text Input Window

Changing Font Color

Repeat the procedure given in "Changing Colors," page 137 to change font colors.

Saving a Custom Template

Save the custom a template as follows:

1. Click **File**.
2. Select **Templates** to open the Plot Templates window.
3. Enter a name in the Template field.
4. Optional – click the box next to **Use this template as default** to make the file the default template. The default template automatically loads when Plot Designer is started.
5. Click **Save** to store the template in `$vnmruser/templates/plot` directory.

   A warning is displayed if the saved template overwrites a current template. Click **Cancel** to not replace the file.
6. Quit the Plot Templates window by clicking on **Close**.

Plot Designer Tools

Plot designer tools listed in Table 6. Press and hold down the left mouse button and drag the cursor in the workspace to use a drawing tool.

Table 6. Plot Designer Tools

Icon	*Function*	*Description*
	**Line Drawing**	Draws a line.
	**Box**	Draws a box.
	**Arrows**	Draws an arrowhead and places it at the origin of the line. Draws an arrowhead and places it at the point of the line.
	**Item Preferences**	Sets the color and size of lines and fonts. Select an object to edit by double clicking on it. See "Adding and Editing Text and Graphics Elements," page 136 for a description of its properties.

Table 6. Plot Designer Tools

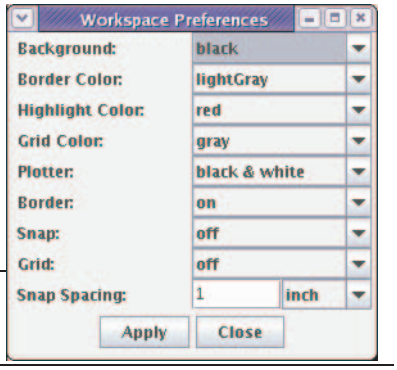
Icon	*Function*	*Description*
	**Text Input**	Adds text into the design and controls the size and appearance of the text; see "Adding Text," page 137.
	**Erasers**	The **ALL** eraser removes all objects. The eraser tool removes selected objects. See also "Adding and Removing Regions," page 135.
	**Print**	Prints a file.

Customizing Plot Designer

- "Changing an Aspect or Property of Plot Designer," page 139
- "Changing the Shape of the Plot Designer Window," page 140
- "Changing the Size of the Plot Designer Window," page 140

Changing an Aspect or Property of Plot Designer

1. Click on **Preferences** in the main menu.
2. Select **Set Up** to open the Workspace Preferences panel.
3. Click on the corresponding button to open a pull-down menu.
4. Select a color preference.
5. Click **Apply** to execute the changes.
6. Click **Close** to exit the window.
7.



Workspace Preference Controls

Control	*Function*
Background	Changes the background color of the window.
Border Color	Changes the color of the border surrounding the workspace.
Highlight Color	Color of an object after double-clicking on an object to indicate that it is selected.
Grid Color	Changes the color of the grid.
Plotter	Select a black and white or color plotter.
Border	Shows (**on**) and hides (**off**) region borders.
Grid	Shows (**on**) and hides (**off**) grid in the workspace.
Snap	The center of the border of an object snaps to the grid when an object is created or moved if snap is turned ON. Turn Snap **OFF** to disable this feature.
Snap Spacing	Controls the amount of space on the grid to which an object snaps. Spacing is in inches, centimeters, or points.

Changing the Shape of the Plot Designer Window

Plot Designer can be viewed in two orientations, Landscape or Portrait (which is the default orientation). Change the shape of the Plot Designer window in the Orient menu.

Changing the Size of the Plot Designer Window

Increase or decrease the size of the Plot Designer window by clicking on the sizes listed in the Magnify menu.

Saving and Printing a Plot

- "Saving a Plot File," page 140
- "Printing a Plot," page 141

Saving a Plot File

Do the following procedure to save a plot:

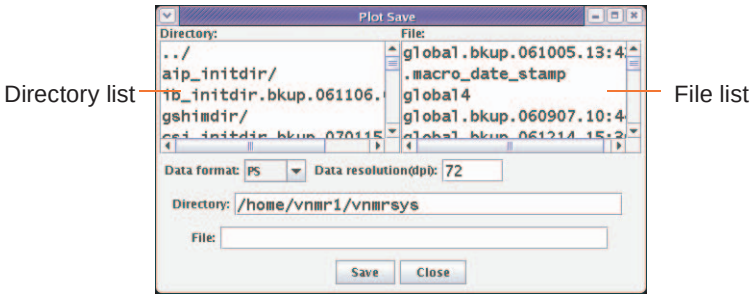


Figure 31. Plot Save Window

1. Click on **File** in the Main Menu, then **Save Data** to open the Plot Save window shown in Figure 31.
2. Scroll down the list of directories and choose a directory or enter a path for the file in the Directory field.
3. Select a **Data format** for your file and enter a **Data resolution**. Table 7 lists the formats that are available.

Table 7. Output Formats Supported by Plot Designer

Format	*Description*
AVS	AVS X image file
BMP	Microsoft Windows bitmap image file
EPS	Adobe Encapsulated PostScript file
FAX	Group 3 FAX
FITS	Flexible Image Transport System
GIF	Compuserve Graphics Interchange Format (version 89a)
GIF87	Compuserve Graphics Interchange Format (version 87a)
JPEG	Compressed format from Joint Photographic Experts Group
MIFF	Magick image file format
PCD	Photo CD
PCX	ZSoft IBM PC Paintbrush file

Table 7. Output Formats Supported by Plot Designer

Format	*Description*
PDF	Portable Document Format
PICT	Apple Macintosh QuickDraw/PICT file
PGM	Portable gray map
PNG	Portable Network Graphics
PS	Adobe PostScript file
PS2	Adobe Level II PostScript file
SGI	Irix RGB image file
SUN	Sun Rasterfile
TGA	Truevision Targa image file
TIFF	Tagged Image File Format
VIFF	Khoros Visualization image file
XBM	X11 bitmap file
XPM	X11 pixmap file
XWD	X Window System window dump image file

4. Label your file by entering a name in the File field.
5. Click **Close** to exit the window.

Printing a Plot

Click on the print tool. 

Exiting Plot Designer

Click on **File-Quit**.

Any design in the window when Plot Designer is closed is automatically opened in the workspace the next time the program is started.

8.3 Color Printing and Plotting

- "Setting Colors," page 141
- "Loading a Color File," page 143
- "Changing or Renaming a Color File," page 143
- "Removing a Color File," page 143
- "Closing the Color Selection Window," page 143

Printer and Plotter color output is defined using the Styles and Themes window. This same window provides access to the display colors and the VnmrJ interface colors.

Setting Colors

View the current settings or define new color settings as follows:

1. Click on **Edit**.
2. Select **Display options…**

The Style and Themes window opens, see Figure 32.

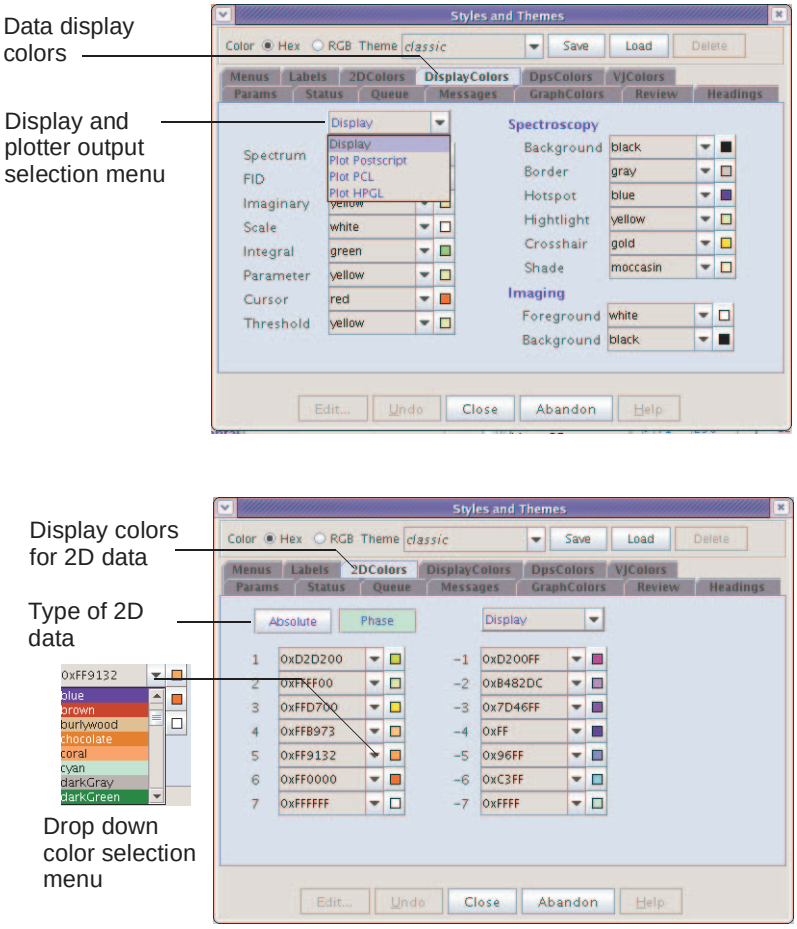


Figure 32. Styles and Themes for Display and 2D Colors

3. Select the **Display** tab to set the colors for the spectra, axis, parameters, etc.
4. Click on the **display and output** selection drop down menu.
5. Select the output device: **Display**, **Plot Postscript**, **Plot PCL**, or **Plot HPGL**.
6. Select a color or keep the current color for each display or function shown.
7. Enter a name in the field next to the Save button to save the selection to a user defined file **or** continue with the next step to overwrite the current file.
8. Click on **Save** to save the color selections to the specified file.
9. Click on **2D colors**.
10. Click on **Phase** to set the colors for this 2D display mode.
11. Select the output device: **Display**, **Plot Postscript**, **Plot PCL**, or **Plot HPGL**.
12. Select a color or keep the current color for each contour level.
13. Click on **Absolute** to set the color for this 2D display mode.
14. Select a color or keep the current color for each contour level.

15. Enter a name in the field next to the Save button to save the selection to a user defined file **or** continue with the next step to overwrite the current file.
16. Click on **Save** to save the color selections to the specified file.

Loading a Color File

To retrieve a color file:

1. Click on the T**heme** dropdown menu.
2. Select a theme file.
3. Click on **Load**.

Changing or Renaming a Color File

To change the colors in a file:

1. Click on the T**heme** dropdown menu.
2. Select a theme file.
3. Click on **Load**.
4. Follow procedure in "Setting Colors," page 141
5. Click **Save** to save the file.

To change the name of a color file:

1. Click on the T**heme** dropdown menu.
2. Select a theme file.
3. Click on **Load**.
4. Enter a new name in the field next to the Save button.
5. Click **Save** to save the file.
6. Optional: delete the file with the old name - "Removing a Color File," page 143.

Removing a Color File

To remove a color file from the list:

1. Click on the T**heme** dropdown menu.
2. Select a theme file.
3. Click on **Load**.
4. Click on the **Delete** button. The deleted file is removed from the bottom list box.
5. Click **OK**, when prompted, to delete the file, or **Cancel** to keep the file.

Closing the Color Selection Window

Click on **Close** to exit the window.

Chapter 9. Advanced 1D NMR

Sections in this chapter:

- 9.1, “Working with Experiments,” this page
- 9.2, “Multi-FID (Arrayed) Spectra,” on page 146
- 9.3, “T_1 and T_2 Analysis,” on page 150
- 9.4, “Kinetics,” on page 151
- 9.5, “Filter Diagonalization Method (FDM),” on page 152

This chapter describes working with 1D NMR liquids experiments.

9.1 Working with Experiments

In the Locator, NMR experiments are contained in Workspaces (also called experiments).

- View the experiments in the Locator by clicking the **Locator Statements** icon () and selecting **Sort Workspaces**.
- Open (connect to or join) an experiment by dragging it to the graphics window.
- Create a new experiment by clicking **File -> New Workspace**.
- Delete an experiment by dragging the experiment from the Locator to the trash can icon.

Enter `explib`. to view the experiments on a system in the Process tab Text Output page. The monitor displays the Experiment library of the currently available experiment files (`exp1`, `exp2`, ..., `exp9999`).

An issue arises concerning how to individually work with each experiment when multiple experiments are created. Only one experiment is allowed at a time to be currently active (i.e., in the foreground for manipulation) to resolve this issue, although background processing can occur in other experiments at the same time.

The `mp`, `mf`, and `md` commands move (copy) files between Experiments:

1. Click on **Edit**.
2. Select one of the following options:
   - Move Parameters…
   - Move FID…
   - Move Text…
   - Move Display parameters…
3. Fill in the information requested in the popup window.

9.2 Multi-FID (Arrayed) Spectra

Many NMR experiments require obtaining a series of FIDs, related to each other through the variation of one or more parameters. For example, suppose it is necessary to run a series of spectra at four different temperatures: 30°C, 50°C, 70°C, and 90°C. Instead of acquiring four separate sets of data, it is possible to create an array in which the `temp` parameter is given four successively different values. These four subexperiments are now all treated as a single experiment. Entering `go` begins successive acquisition of all four experiments. One command is used to transform all the spectra, one command to display all the spectra on the screen simultaneously, one command to plot all the spectra, and one command to save all the spectra.

- "Arrayed Parameters," this page
- "Multiple Arrays," page 146
- "Setting Array Order and Precedence," page 147
- "Interactively Arraying Parameters," page 147
- "Resetting an Array," page 147
- "Array Limitations," page 148
- "Acquiring Data," page 148
- "Processing," page 148
- "Display and Plotting," page 148
- "Pulse Width Calibration Step-by-Step," page 149

Arrayed Parameters

Use the Array Parameter window, see "Parameter Arrays," page 88, to create an array for a numeric parameter or create an array by entering the parameter and arrayed values separated by commas (e.g., `temp=30,50,70,90` or `pw=5,10,15,20,25`) on the command line. Alphanumeric parameters can also be arrayed.

Example (command line):

Use `dm='n','y'` to perform two experiments in with the decoupler off in experiment and on in the other experiment.

Not all parameters can be arrayed. Non-arrayable acquisition parameters include processing parameters, display parameters, and any parameter that changes the number of data points to be acquired, such as `np`, `sw`, `dp`, and `at`.

Open the Array Parameter window or type `da<(par1<,par2><,par3...>)>` to display the values of the arrayed parameter. `da` displays all values of arrayed parameters if entered without an argument. If one or more parameters are listed as an argument, `da` displays only the specified parameters.

Multiple Arrays

Two or more parameters can be arrayed in an experiment. For example, an experiment to perform a series of decoupling experiments using an array of decoupler power levels and an array of decoupler frequencies might be set up with `dpwr=17,20,23` and `dof=295.1,345.6,507.2,1245.5`. In this example, *twelve* experiments are performed (i.e., three different values of decoupler power `dpwr` are used), and for each of those values, four different values of the decoupler offset `dof` are used.

Setting Array Order and Precedence

Whenever an array of one or more parameters is set up, the parameter `array` becomes important. This parameter tells the system the name of the parameter or parameters that are arrayed and the order and precedence in which the arraying is to take place. The Array Parameters window, see "Parameter Arrays," page 88, may be used for setting all of the parameters associated with setting up the array.

The string parameter `array` can have one of several forms:

- `array=''` means no parameter is arrayed (this value is two single quotation marks with no space between, not a double quotation mark).
- `array='x'` means parameter `x` is arrayed.
- `array='y,x'` means parameters `x` and `y` are arrayed, with `x` taking precedence. The order of the experiments is x_1y_1, x_2y_1, ...x_ny_1, x_1y_2, x_2y_2, ...x_my_2 ...x_my_n, with a total of `m×n` experiments being performed.
- `array='x,y'` means parameters `x` and `y` are arrayed, with `y` taking precedence. The order of the experiments is x_1y_1, x_1y_2,...x_1y_n, x_2y_1, x_2y_2,...x_2y_n,...x_my_n, with a total of `m×n` experiments being performed.
- `array='(x,y)'` means parameters `x` and `y` are jointly ("diagonally") arrayed. The number of elements of the parameters `x` and `y` must be identical, and the order of experiments is x_1y_1, x_2y_2, ...x_ny_n, with `n` experiments being performed.

Entering one or more arrayed parameters automatically sets up `array`. It is necessary to enter `array` directly only if the order or precedence needs to be changed.

Interactively Arraying Parameters

Separate from the `array` *parameter* is the `array` *macro*. Entering the `array` macro without an argument starts it in the interactive mode and it prompts for the following information in this order:

- The name of the parameter to be arrayed.
- The number of values of the parameter.
- The starting value.
- The magnitude of the difference between elements in the array.

An arrayed parameter is set up using the information provided. The restrictions are that only numeric parameters can be arrayed and all values of the array must satisfy the limits of the parameter.

Entering `array` with a parameter name as an argument, (e.g., `array('pw')`) still starts an interactive mode, but the program only asks for the remaining three items of information.

`array` bypasses the interactive mode completely it is started with all four arguments (in this order—parameter name, number of steps, starting value, and step size). For example, entering `array('tof',5,1000,-50)` sets the `tof` parameter to have 5 elements with the values in the order 1000, 950, 900, 850, 800.

Resetting an Array

Once an array is created, it is possible to change the value of a single element of the array by typing, for example, `pw[2]=11.3`, where the `2` enclosed in brackets indicates which element of the array to modify (array elements are counted starting at 1).

Set a single value for the parameter (e.g., `pw=10`) to reset an arrayed parameter to a single value. The `array` parameter is automatically modified to reflect this change.

Array Limitations

Regular multiple arrays can include up to 20 parameters, each of which can be a simple parameter or a diagonal array (a set of parameters), which can include up to 10 parameters. The total number of elements of all arrays is essentially unlimited (2^{32}–1).

Acquiring Data

Once any parameter is arrayed, acquisition generates not just one, but an entire array of spectra. These spectra can then be examined either individually or as a group, as described below.

Autogain cannot be used in an arrayed experiment. Either use `gain='y'`, which sets the gain (gain cannot be arrayed) to the previously determined value, or set `gain` equal to a fixed value.

Processing

The command `ft` or `wft` is used to transform all of the spectra. Both commands take the same arguments and options:

- `'acq'` does not transform elements that have already been transformed.
- `'nods'` prevents an automatic spectral display (same as `ds` command).
- `'zero'` zeroes the imaginary channel of the FID before Fourier transform.

Phasing can be done on any spectrum. Only one set of phase correction parameters exists, so all spectra have the same phase at any one time (although the phase can of course be changed when examining different spectra).

Display and Plotting

The Vertical Panel “Arrayed Spectrum” can be used for displaying arrayed data. The command `ds(index)` or the  and  icons, interactively displays the requested spectrum from the array. The index can have one, two, or three numbers, depending on the dimensionality of the spectral array. Spectra are always scaled according to the number of completed transients `ct`; if `nt` is arrayed (`nt=1,2,4,8`), each spectrum is scaled by its *own* `ct`.

Other spectra display commands are `dss`, `dssn`, `dssa`, `dssan`, `dssh`, `dsshn` and `dssl`. These are not interactive like the `ds` command. They display stacked spectra in which each spectrum is offset with respect to the previous spectrum. The order of stacking can be left to right, right to left, top to bottom, or bottom to top, depending on whether the horizontal offset (`ho`) and vertical offset (`vo`) parameters are positive or negative. Some of these commands set `ho` and `vo` automatically.

The spectra display commands function as follows:

- `dss` displays stacked spectra using the current values of `ho` and `vo` to set the order of stacking.
- `dssn` displays stacked spectra the same as `dss`, but the graphics window is not erased before starting the display. This allows composite displays of many spectra to be created.

- `dssa` displays stacked spectra automatically (i.e., `vo` and `ho` are automatically adjusted to fill the screen in a lower left to upper right presentation).
- `dssan` displays stacked spectra automatically the same as `dssa`, but the graphics window is not erased before starting the display.
- `dssh` displays stacked spectra horizontally (i.e., `vo` is set to zero, and `ho` is adjusted to fill the screen from left to right).
- `dsshn` displays spectra horizontally the same as `dssh`, but the graphics window is not erased before starting the display.
- `dssl` displays a label for each element in a set of stacked spectra. The label is an integer value starting with 1 and extending up to the number of spectra in the display.

The command `pl` plots stacked spectra with the same format as displayed by `dss`.

The argument syntax `<(start,finish<,step>)><,options>)>` is used by the `dss` command, variants of `dss`, and by the `pl` command. The arguments are the following:

- `start` is the index of the first spectra when displaying multiple spectra. It is also the index number of a particular trace to be viewed when displaying arrayed 1D spectra or 2D spectra.
- `finish` is the index of the last spectra when displaying multiple spectra. Because the parameter `arraydim` is automatically set to the total number of spectra, it can be used to set `finish` to include all spectra.
- `step` is the increment for the spectral index when displaying multiple spectra. The default step is 1.
- `options` can be any of the following:

  `'all'` is a keyword to display all of the spectra.

  `'int'` is a keyword to only display the integral, independently of the value of the parameter `intmod`.

  `'top'` or `'side'` are keywords that cause the spectrum to be displayed either above or at the left edge, respectively, of a contour plot. This assumes that the parameters `sc`, `wc`, `sc2`, and `wc2` are those used to position the contour plot. This option does not apply to `dssa`, `dssan`, `dssh`, or `dsshn`.

  `'dodc'` is a keyword for all spectra to be drift corrected independently.

  `'red'`, `'green'`, `'blue'`, `'cyan'`, `'magenta'`, `'yellow'`, `'black'`, and `'white'` are keywords that select a color. This option does not apply to `dssa`, `dssan`, `dssh`, `dsshn`, or `pl`.

  `'pen1'`, `'pen2'`, `'pen3'`, etc. specify a pen number on a plotter. This option does not apply to `dss` or any of its variants.

Pulse Width Calibration Step-by-Step

Note, for illustration, how the following steps perform a pulse width calibration using arrays:

1. Set up parameters and obtain a normal spectrum of any sample. For best results, one or more intense signals should appear near the center of the spectrum.
2. Enter 5 for the value of **pw** or use some other small value.
3. Enter 1 for the value of **nt**.
4. Obtain a spectrum and phase it properly. Set **`d1`** to $5*T_1$.

5. Make an array of **pw** from 5 to 30 in steps of 5 or use some other set of suitable values for the `pw` array.
6. Select **Absolute Intensity** and acquire.
7. Transform and display the stacked data after the experiment finishes acquisition.
8. Find the experiment where the signal goes through its 180° or 360° null. Enter **`da`** to remind yourself of the values of the `pw` array.
9. Enter **`pw`** equal to one-half of `pw180` or one-quarter of `pw360` to reset the array.

9.3 T_1 and T_2 Analysis

One relatively common form of arrayed experiment is the inversion-recovery T_1 experiment. In this experiment, the nuclei are allowed to relax to equilibrium (`d1`), then inverted with a 180° pulse (`p1`), given a variable time to return to equilibrium (`d2`), and finally given a monitoring 90° pulse (`pw`) to measure their peak height as a function of `d2`. Under most circumstances, the behavior of the peak heights as a function of `d2` will be exponential, and this exponential time is the T_1.

- "Setting Up The Experiment," this page
- "Processing the Data," page 150
- "Analyzing the Data," page 151
- "T_1 Data Workup: Step-by-Step," page 151

Setting Up The Experiment

The standard two-pulse sequence is set up to perform the T_1 experiment. The experiment can be set up by:

- Entering appropriate values for `p1`, `pw`, `d1`, and an array of values for `d2` or by enter
- Using the `dot1` macro. `dot1` sets up all parameters to perform a T_1 experiment, including `d1`, `pw`, `p1`, `nt`, and an array of `d2` values, based on information entered. The three arguments that can be input are the minimum expected T_1, the maximum expected T_1, and the total time in hours the experiment should take. If no arguments are provided, `dot1` prompts the user for the information.
- Using the menu as follows:
    a. Click on **Experiment**.
    b. Select **Relaxation Measurements**.
    c. Select **T1**.
    d. Fill in the information on the **Standard** panel of the **Start** tab.
    e. Adjust any parameters on the panels of the **Acquire** tab.

The parameter `pw90` must contain a correctly calibrated 90-degree pulse width because `dot1` uses this information.

Processing the Data

Once the data is acquired and processed, do the follows:

1. Display the last spectrum for a T_2 experiment to display the first spectrum).

2. Phase this spectrum properly.
3. Select a threshold and adjust the threshold line position.
4. Enter **dpf**, **dll**, or click on the appropriate button to display a line list and locate lines for the system.
5. Enter **fp** to measure the peak height of each peak in an array of spectra. If optional line indexes are supplied to `fp` as arguments (e.g., `fp(1,3)`), only the peak heights of the corresponding lines are measured.

   The `npoint` parameter (if defined and set "on") determines the range of data points over which the `fp` command searches for a maximum for each peak.

Analyzing the Data

T_1 and T_2 analysis is performed by the `t1` and `t2` macros, respectively. `t1` and `t2` measure relaxation times for all lines in the line listing and display an extended listing of observed and predicted peak intensities. `t1s` and `t2s` perform the same calculation as `t1` and `t2` but produce a shorter output, showing only a summary of the measured relaxation times.

The command `expl` displays exponential/polynomial curves resulting from T_1, T_2, or kinetic analysis. Optional input of line numbers as arguments allows display of only selected lines. Similarly, the command `pexpl` plots the same curves.

The macro `autoscale` returns the command `expl` to autoscaling in which scale limits (set by `scalelimits`) are determined that will display all the data in the `expl` input file. The macro `scalelimits` causes the command `expl` to use typed-in scale limits. If no arguments are given, `scalelimits` asks for the desired limits. The limits are retained as long as an `expl` display is retained.

Enter `dels(index1<, index2>...)` to delete spectra from the `t1` or `t2` analysis (or from `t1s` or `t2s`). This command deletes the spectra selected by the indexes from the output file `fp.out` of the `fp` command used by the `t1` or `t2` analysis. Spectra can be restored by rerunning `fp`.

T_1 Data Workup: Step-by-Step

The following procedures accomplish a manual T_1 analysis:

1. Enter **`rt('/vnmr/fidlib/t1data.fid')`**.
2. Enter **`wft dssh full ds(arraydim) aph`**.
3. Use the left mouse button to set the threshold.
4. Enter **`dll fp t1 center expl`**.

9.4 Kinetics

The arraying capability of the VnmrJ software provides for the acquisition of data for the study of kinetics.

- "Setting Up the Experiment," this page
- "Processing the Data," this page
- "Kinetics Step-by-Step," this page

Setting Up the Experiment

Usually, the best procedure is to array the preacquisition delay parameter `pad`. For example, if `pad=0,3600,3600,3600,3600`, the system acquires the first spectrum immediately (`pad[1]=0`), waits 3600 seconds (`pad[2]=3600`), acquires the second spectrum, waits another 3600 seconds, etc. Because 3600 seconds is 1 hour, this inserts a wait of one hour between acquisitions. After all the spectra have been obtained, they are processed much like T_1 or T_2 data.

Processing the Data

If the signal decreases exponentially with time, the output is matched to the equation `I=A1*EXP(-T/TAU)+A3`. The analysis is done by the macro `kind`, or by macro `kinds` if a short output table is desired.

If the signal increases exponentially with time, the output is matched to the equation `I=-A1*EXP(-T/TAU)+A3-A1` with analysis done by the macro `kini`, or by the macro `kinis` for a short output table.

Kinetics Step-by-Step

The following steps are typical in processing a kinetics experiment using the command line:

1. Enter **`wft dssh full ds aph`**.
2. Click on **Threshold** icon in the graphics control menu. Use the left mouse button to set the threshold.
3. Enter **`dll fp`**.
4. Enter **`kind`**, **`kini`**, **`kinds`**, or **`kinis`**, as appropriate.
5. If desired, adjust `sc`, `wc`, `sc2`, and `wc2` by entering **`center`** or **`full`**.
6. Enter **`expl`**.

9.5 Filter Diagonalization Method (FDM)

Filter Diagonalization Method is an optional package that must be purchased and requires a password.

This section contains the following:

- "Using FDM," page 153
- "Reprocessing a Spectrum," page 154
- "Changing Parameters," page 154
- "FDM Global Parameters," page 154
- "Changing Local FDM Variables," page 154
- "Seeing Parameter Values," page 155
- "FDM References," page 156

Filter Diagonalization Method (FDM) is a non-Fourier data processing method that extracts spectral parameters (peak positions, line widths, amplitudes, and phases) of Lorentzian lines directly from the time-domain signal by fitting FID data to a sum of damped complex

sinusoids. The spectral parameters (saved in `curexp/datdir/fdm1.parm`) are also called “line list” and are used to construct an “ersatz” spectrum of the NMR data.

FDM is slower than Fast Fourier Transform, but it offers better resolution in the case of truncated signals and the option of processing only a selected spectrum region. FDM has the potential to work well with corrupted data, and the potential to produce a line list with each line representing a true NMR peak.

FDM reads input parameters from a file created by the `fdm1` macro, using default (optimal) values. Change any of the parameters from the command line as needed. Table 8 lists `fdm1` parameters. If the spectrum is not referenced with `rl`, the reference `rfl` is also read from `curpar` in the local parameter set. The section "Changing Local FDM Variables," page 154 describes how to override the default setting.

Only the number of data points to be used and the spectrum window to be processed need to be set in most cases. The default setting uses half of the FID data or 3000 data points, whichever is smaller.

Using FDM

The following steps describe how to do normal activities such as phasing, zooming in, zooming out, and processing a spectrum window with the `fdm1` macro.

1. Display the FID data and use the right mouse button to select the data points to be used by FDM.
2. Process the data with `ft` (it uses all FID points), then display and reference the spectrum.
3. Place the cursor on a region of interest, zoom in on it, then type `fdm1` or **Process**....**1D FDM**...from the main menu. Selecting and not zooming in on a region causes the whole spectrum in display to be processed.

Table 8. fdm1 Parameters

Parameter	*Description*
`cheat`	No cheat if `cheat=1`, lines are narrower if `cheat<1`.
`cheatmore`	No cheatmore if `cheatmore=0`.
`error`	Error threshold for throwing away poles.
`fdm`	1 for `fdm`, –1 for `dft`.
`Gamm*`	Smoothing width (line broadening).
`Gcut`	Maximum width for a pole.
`idat`	–4 for ASCII complex FID file, –5 for FID file.
`kcoef`	`kcoef>0`; use “complicated” `dk(k)`. –1 always preferred.
`Nb*`	Number of basis function in a single window.
`Nbc*`	Number of coarse basis vectors.
`Nsig*`	Number of points to use, 3000 is ok.
`Nskip*`	Number of points to skip.
`rho`	`rho=1` is optimal.
`ssw`	A test parameter.
`t0`	Delay of the first point.
`theta`	Overall phase of FID (`rp` in radians).
`wmin`	Minimum spectrum frequency in hertz.
`wmax`	Maximum spectrum frequency in hertz.

* Global; see "FDM Global Parameters," page 154 for more information.

A new menu appears with Start and Abort buttons. The calculation might take a few seconds to a few minutes depending on the number of data points used and the size of spectrum window to be processed. To abort the process, click on **Abort**. The process is finished when the message *"FDM Execution Stopped Successfully"* is displayed. If the process is finished, display the spectrum.

Reprocessing a Spectrum

The Start button is displayed in the Process...1D FDM... drop-down menu. Use this button to reprocess a spectrum.

Changing Parameters

Relevant `fdm1` global parameters are displayed on the 1D FDM... popup window with current values. These parameters can be changed. The value of a global parameter is saved to `curpar`, and it remains the same until changed from the parameter panel or a new assignment using the command line is made. The parameters can also be changed from the `fdm1` command line as described in the section "Changing Local FDM Variables," page 154.

FDM Global Parameters

The following FDM parameters are global.

- `Nsig` is the number of FID points to use. Initialize it with the right mouse button position (`crf + deltaf`) `*sw`. If `Nsig=0`, half of the FID data points or 3000, whichever is smaller, is used. `Nsig` can be changed from the command line `Nsig=nnnn`, the right mouse button (when the FID is displayed), or the command line `fdm1('Nsig',nnnn)`. In general, the more peaks, the more data points it takes to fit the spectrum. Check the reliability of the FDM method by changing `Nsig` a few times, and reprocess the data to see if the result is the same.
- `Nskip` is the number of data points to skip at the beginning of a FID. By default, zero points are skipped. In some cases, baseline can be improved by skipping the first one or two points.
- `Nb` is the number of basis functions (poles) used to fit each of the windows in an FDM calculation. The default is 10. FDM breaks down the specified window into smaller windows. In general, bigger `Nb` gives better results, especially better baseline. Sensible values for `Nb` are between 10 and 50.
- `Nbc` is the number of additional poles (coarse basis functions) to be used. The default is zero, but setting `Nbc` to an integer larger than zero (typically 4-10) might improve the baseline.
- `Gamm` is the smoothing width (line broadening). The default is `0.2*sw/Nsig`, which is about a tenth of the FT resolution. Typical values are 0.1 to 1.0.

Using bigger `Nsig`, `Nb`, `Nbc`, or a spectral window significantly slows down the calculation.

Changing Local FDM Variables

FMD parameters that are not commonly used are set as `fdm1` local variables. These parameters are listed with global parameters in Table 8. Local variables can be changed only from the command line. Parameter values are lost after the completion of the macro.

To use a value again, it must be reentered; otherwise, `fdm1` sets the value to the default. To change more than one local variable, enter the variables from the same command line.

Any of the FDM parameters in the `fdm1` command and both global and local variables can be changed. Values entered from the `fdm1` command override the default, the change from the **1D FDM** panel, and the value selected with the cursor. Enter command line arguments by giving the parameter name in single quotation marks and a value separated by a comma, for example:

```
fdm1('cheat',0.8)
fdm1('Nsig',3000)
fdm1('Nsig',3050)
fdm1('Nb',20)
fdm1('Nbc',10,'Nb',20)
fdm1('Nsig',3000,'Nb',20,'Gamm',0.5)
fdm1('wmin',-1600,'wmax',1600)
fdm1('wmin',-1600,'wmax',0)
```

`cheat` is a factor multiplied to the line width. There is no cheat when `cheat=1`; lines are narrower when `cheat<1`.

`wmin` is the minimum spectrum frequency in Hz. The default is `sp+rfl-sw/2`. `wmin` is the upper field.

`wmax` is the maximum spectrum frequency in Hz. The default is `wmin+wp`. `wmax` is the lower field.

The center of the full spectrum is zero.

Seeing Parameter Values

Parameters are set to their default values. Normally, it is not necessary to change these parameters. Values of local `fdm1` parameters can not be queried with `echo`. To see the values of all parameters used, look in the `fdm1.inparm` file created by the `fdm1` macro in the `datdir` directory of the current experiment. Figure 33 shows the format of the `fdm1.inparm` file; the number of spaces and tabs is arbitrary.

```
fid_filename            idat
t0              theta
fdm
par
fn_Sp1D     spectype    axis
wmin            wmax
Nsig
Nskip
rho             Nb
error
Npower          Gamm            Gcut
cheat           cheatmore
Nbc     kcoef
ssw    sw
fidmt    specfmt
i_fid
```

Figure 33. `fdm1.inparm` File

FDM References

J. Chen and V. A. Mandelshtam, *J. Chem. Phys.* (2000) **112:** 4429-4437.

V. A. Mandelshtam, *J. Magn. Reson.* (2000) **144:** 343-356.

A. A. De Angelis, H. Hu, V. A. Mandelshtam and A.J. Shaka, *J. Magn. Reson.* (2000) **144:** 357-366.

Chapter 10. DOSY Experiments

Sections in this chapter:

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- 10.2, “DOSY Experiments,” on page 160
- 10.3, “General Considerations,” on page 161
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- 10.5, “2D-DOSY Spectroscopy,” on page 163
- 10.6, “DOSY Sequences for Biological Samples in H_2O,” on page 169
- 10.7, “Convection Compensated DOSY Experiments,” on page 172
- 10.8, “Comparison of DOSY and Convection Compensated DOSY,” on page 180
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- 10.12, “Phase Sensitive 3D-DOSY,” on page 192
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- 10.17, “References,” on page 210

The DOSY (**D**iffusion **O**rdered **S**pectroscop**Y**) application is an optional package that must be purchased and requires a password.

The DOSY application separates the NMR signals of mixture components based on different diffusion coefficients. Generally speaking, DOSY increases the dimensionality of an NMR experiment by one. The initial diffusion weighted NMR spectra are one-dimensional; adding diffusion weighting to a 2D NMR experiment such as COSY or HMQC gives 3D DOSY spectra.

The DOSY analysis involves two steps.

1. Set up and acquire a DOSY spectrum.
2. Determine the diffusion coefficients for each line (or cross-peak) in the spectrum. Take line (or cross-peak) positions and diffusion coefficients and show the results in a DOSY plot. All of these steps are executed by the `dosy` macro. Each step is described in more detail in the following sections. Table 9 lists the tools available for DOSY.

10.1 Early Diffusion Experiments

The pulse sequences diagrammed in Figure 34 illustrate the two early pulsed-gradient experiments. These early experiments are fully described in the literature by Stejskal and Tanner (Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* 1965, *42*, 288-292, and Tanner, J. E. *J. Chem. Phys.* 1970, *52*, 2523–2526).

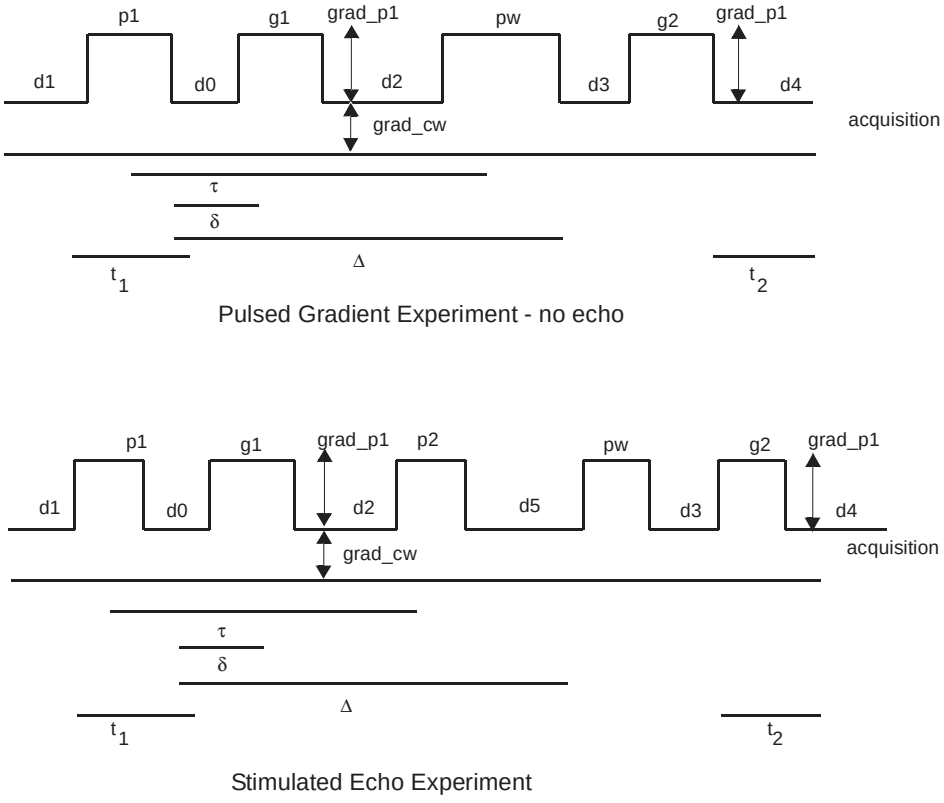

Figure 34. A Pulse Field Gradient Experiment Pulse Sequences

The diffusion coefficient is calculated using Equation 1:

$$A_i = A_0 \exp -\gamma^2 D\left\{\frac{2}{3}t^3 \times \texttt{grad\_cw}^2 + \delta^2\left(\Delta - \frac{1}{3}\delta\right)\texttt{grad\_p1}i^2\right.$$

$$\left. - \delta\left[(t1^2 + t2^2) + \delta(t1 + t2) + \frac{2}{3}\delta^2 - 2\tau^2\right]\texttt{grad\_p1}i \times \texttt{grad\_cw}\right\}$$

where A_i is the observed integral value of an NMR resonance for the i^{th} element of the gradient array. A_0 is the integral value of an NMR resonance just after the first 90° pulse in the pulse sequence. Δ is the self-diffusion coefficient. In the case of the two-pulse echo sequence, the variables τ, δ, Δ, *t1*, and *t2* (refer to Figure 34) are calculated from the pulse sequence variables as follows:

In the case of the stimulated-echo sequence, the equation for Δ is as follows:

D = `g1 + d2 + p2 + d5 + pw + d3`

$$\tau = \frac{(p1)}{2} + d0 + g1 + d2 + \frac{pw}{2}$$

$$\delta = g1$$

$$\Delta = g1 + d2 + pw + d3$$

$$t1 = \frac{p1}{2} + d0$$

$$t2 = d4$$

Equation 1 can be recast as the following, which becomes Equation 2:

$$1n(A_i) = 1n(A_0) + D \times C0 + D \times C1 \times grad\_p1i + D \times C2 \times grad\_p1i \times grad\_p1i$$

where:

$$C0 = \frac{2}{3}\gamma^2\tau^3 grad\_cw^2$$

$$C1 = \gamma^2\delta\left[(t1^2 + t2^2) + \delta(t1 + t2) + \frac{2}{3}\delta^2 - 2\tau^2\right] \times grad\_cw$$

$$C2 = -\gamma^2\delta\left(\Delta - \frac{1}{3}\delta\right)$$

The fitting program `analyze` accepts two arguments that instruct it to perform a polynomial fit. The selection of which polynomial to fit depends on whether `grad_cw` is zero. If it is zero, the second and third terms of Equation 2 vanish and a first-order polynomial $y = c0 + c1 \times x$ is used where:

$y = 1n(A_i)$
$c0 = 1n(A_0) + D \times C0$
$c1 = D \times C2$
$x =$ `grad_p1`i

Otherwise, a second-order polynomial $y = c0 + c1 \times x + c2 \times x \times x$ is used, where:

$y = 1n(A_i)$
$c0 = 1n(A0) + D \times C0$
$c1 = D \times C0$
$c2 = D \times C2$
$x =$ `grad_p1`i

Another argument of `analyze` is the complete name of a text file (`analyze.inp`) that contains the *x*–*y* data pairs. The output of this calculation is written into a text file in the current experiment directory. The name of this text file reflects the integral region on which the analysis was performed. This name has the form `regionx_results`, where the `x` is the integral region number. Using the experimental delays, `grad_cw` and `gamma`, the `pge_results` macro calculates the diffusion constant and the time-zero integral amplitude from the fitting parameters `c0`, `c1`, and `c2`. The results of these calculations are appended to the text file that contains the least-squares analysis results.

The diffusion coefficients of both components of a two component mixture can be calculated assuming the following condition is met. It is possible to find one integral region where the NMR resonance is due to only one component of the mixture. The diffusion coefficient is calculated using that integral region with the processing already described. For integral regions, where the NMR intensity results from both components of a two component mixture, Equation 1 transforms to the following, which becomes Equation 3:

$A_i = a0 \times exp[D \times (C0 + C1 \times \texttt{grad\_p1}i + C2 \times \texttt{grad\_p1}i \times \texttt{grad\_p1}i)]$
$+ a2 \times exp[a1 \times D \times (C0 + C1 \times \texttt{grad\_p1}i + C2 \times \texttt{grad\_p1}i \times \texttt{grad\_p1}i)]$

The diffusion coefficient *D* is available from the separate reference integral region. The constants *C*0, *C*1, and *C*2 are defined in Equation 2. The fitting parameters are *a*0, *a*1, and *a*2. In order to perform the non-linear least squares analysis of Equation 3, the `pge_results` macro is supplied with two arguments (e.g., `pge_results(1,3)`). The first argument is the region on which to perform the analysis (just as for the single-component analysis case), and the second argument is the integral region used to get the value of *D*. The fitting parameter a0 corresponds to the time-zero integral amplitude of the reference component; *a2* corresponds to the time-zero amplitude of the other component; *a1* corresponds to the ratio of the two diffusion coefficients.

10.2 DOSY Experiments

2D DOSY Experiments

- "Dbppste (DOSY Bipolar Pulse Pair Stimulated Echo) Experiment," page 166
- "DgcsteSL (DOSY Gradient Compensated Stimulated Echo with Spin Lock)," page 167
- "Oneshot," page 168

2D DOSY Experiments for Biological Samples

- "DgcsteSL_dpfgse (DOSY Gradient Compensated Stimulated Echo with Spin Lock)," page 169
- "Dbppste_wg - (DOSY Bipolar Pulse Pair Stimulated Echo)," page 170
- "Dbppsteinept (DOSY Bipolar Pulse Pair Stimulated Echo INEPT)," page 171

Convection Compensated DOSY Experiments

- "Dgcstecosy (DOSY Gradient Compensated Stimulated Echo AV COSY)," page 188
- "Dgcstehmqc (DOSY Gradient-Compensated Stimulated Echo HMQC AV mode)," page 189

Absolute Value 3D DOSY Experiments

- "Dgcstecosy (DOSY Gradient Compensated Stimulated Echo AV COSY)," page 188
- "Dgcstehmqc (DOSY Gradient-Compensated Stimulated Echo HMQC AV mode)," page 189

Phase Sensitive 3D DOSY Experiments

- "Dgcstehmqc_ps (DOSY Gradient-Compensated Stimulated Echo HMQC)," page 193
- "Dbppste_ghsqcse (Bipolar Pulse Pair Stimulated Echo Gradient HSQC, Sensitivity-Enhanced)," page 194

Inclusive DOSY Experiments

- "Dcosyidosy - (COSY-IDOSY)," page 197
- "Dhom2djidosy - (Homonuclear 2D J-resolved IDOSY)," page 198
- "Dghmqcidosy - (Gradient HMQC-IDOSY)," page 199

10.3 General Considerations

The DOSY experiments are probably the most demanding gradient sequences in NMR. Experimental conditions for a given gradient setting are typically optimized in conventional coherence-pathway-selected experiments. Very often the whole scale of available gradient power is used in DOSY while maintaining high-resolution NMR conditions. Convection, i.e., moving liquid columns along the sample axis (primarily due to temperature gradients), does not seriously hurt coherence-pathway-selected-experiments (apart from the obvious intensity losses), but it can make the DOSY analysis completely useless.

DOSY pulse sequences use the gradient-stimulated echo element (or one of its modifications), shown in Figure 35.

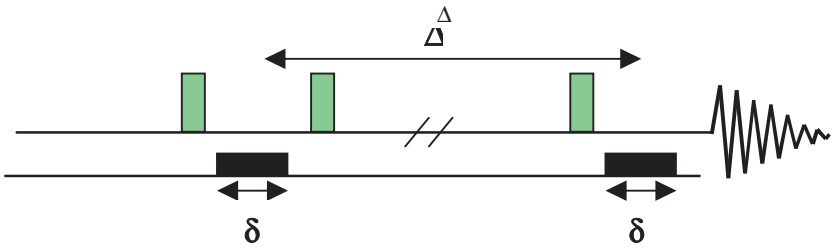

Figure 35. Gradient Stimulated Echo Element

In the DOSY experiments the strength of the diffusion encoding gradient is arrayed, and the diffusion coefficients are calculated according to the Stejskal-Tanner formula:

$$S(G_{zi}) = S(0)\exp(-D_i\gamma^2\delta^2(G_{zi})^2(\Delta - \delta/3))$$

where $S(G_{zi})$ and $S(0)$ are the signal intensities obtained with the respective gradients strengths of G_{zi} and 0. D is the diffusion coefficient. γ is the gyromagnetic constant, δ is the gradient pulse duration and Δ is the diffusion delay.

The formula itself provides valuable hints on how to set DOSY-related parameters in different pulse sequences.

- $(\gamma*\delta*G_{zi})^2$ is the gradient pulse area.
  Nuclei with higher γ are more sensitive to diffusion than the low-γ nuclei. If possible, observe ^1H, ^{19}F, or at least do the diffusion encoding step on the high-γ nucleus.
- Shaping a gradient dramatically reduces its phase encoding efficiency. Although VnmrJ software allows gradients to be shaped, it is not really recommended with DOSY.
- δ is the gradient pulse duration.
  During δ (and the subsequent gradient stabilization delay, `gstab`) the magnetization is transverse and subject to T_2 relaxation and homonuclear J-evolution. Do not use

long δ values in the presence of large homonuclear couplings or short T_2 relaxation times ($\delta << T_2$ or 1/J).

- Δ is the diffusion delay. Convection can always be an unwanted competitor to diffusion, and T1 relaxation attenuates the signal intensities. Do not use unnecessarily long diffusion delays (Δ < T1).

Some of the recommendations might seem contradictory and in real cases an acceptable compromise between them must be found.

The separation efficiency in the diffusion domain is determined by the accuracy of the measured diffusion coefficients. DOSY does not necessarily intend to get absolute diffusion coefficients (in mixtures, it is difficult to discuss “absolute” numbers anyway); the relative differences in the D values might be adequate for separation. Changing the solvent of a DOSY mixture might change the diffusion coefficients and the separation power of the method. The solvent might play a similar role in DOSY as the different columns in HPLC.

Diffusion coefficients errors can either be statistical or systematic. The most obvious source of statistical errors is inappropriate signal-to-noise ratio; therefore in DOSY experiments, relatively high S/N values must be reached even with the strongest phase encoding gradients. Systematic errors are primarily caused by instrumental imperfections (such as gradient nonlinearity over the active sample volume, phase distortions, changes in experimental lineshape as a function of gradient amplitude). Systematic errors can be minimized by careful pulse sequence design (see *Magn. Reson. Chem.* (1998), **36:** 706) and by adding a suitable internal reference to the sample (a component producing a strong, well isolated singlet peak in the spectrum) suitable for reference deconvolution (FIDDLE) when processing DOSY.

When setting up DOSY experiments, consider the following recommendations:

- Be sure that the `probe` parameter is set to the probe to use and `Probegcal` has the right value (the setup macros extract the gradient strength, `gcal`, from the probe file and store it in the local parameter DAC_to_G). Pulse power levels and pw90 values are also read from the probe calibration file.
- Set z0 precisely on resonance and carefully adjust the lock phase. Incorrect adjustment might cause progressive phase errors with increasing gradient power.
- Do not spin the sample.
- Use an adequate number of data points for proper spectral digitization.
- When running long experiments, use interleaved acquisition `(il='y')`.
- Avoid using extreme (low and high) temperatures to minimize temperature gradients (and convection). For solutions with very low viscosity, it might be preferable to completely switch off the VT controller.
- Add substance suitable for reference deconvolution, it one is available, to the mixture before running DOSY (TMS is a typical choice in proton spectra).

10.4 Gradient Strength Calibration

The measurement of accurate diffusion coefficients is only possible if the gradient strengths used in the DOSY experiments are properly calibrated. Calibration of gradient strengths using a gradient profile is sufficient for most gradient experiments but not for diffusion experiments. Calibrate in a DOSY sequence as follows:

1. Select a sample with known diffusion coefficient.

A doped water sample is a good choice for this calibration at 25º C temperature. The diffusion coefficients of HDO are:10.34*10^{-10} m^2/sec at 5º C, 19.02*10^{-10} m^2/sec at 35º C, and 30.27*10^{-10} m^2/sec at 40º C.

2. Equilibrate the sample temperature at 5ºC, 25º, or 40º C before starting the gradient calibration. Diffusion coefficients are strongly temperature dependent.
3. Run a proton detected 2D-DOSY sequence with a diffusion delay of 50-70 msec and 12-15 gzlvl1 values.

   The signal attenuation between the weakest and strongest gradients ideally is a factor of 6-7.
4. Process the data using proper window functions and baseline correction
5. Calculate the D value of the sample.
6. Enter **`dosy_grad_calib`** and the correct diffusion coefficient for the temperature of the sample during the experiment. (i.e. 19.02 at 25º C) on the command line.

   The current DAC_to_G value is recalculated and, if requested, the `gcal` value of the probe file is also updated. The proper gradient strengths are automatically used the next time a DOSY is set up.

10.5 2D-DOSY Spectroscopy

The base 2D DOSY sequences are: `Dbppste`, `DgcsteSL`, `Oneshot`, `Dbppsteinept`.

- "Setting Up 2D-DOSY Experiments," page 163
- "Dbppste (DOSY Bipolar Pulse Pair Stimulated Echo) Experiment," page 166
- "DgcsteSL (DOSY Gradient Compensated Stimulated Echo with Spin Lock)," page 167
- "Oneshot," page 168
- "Dbppsteinept (DOSY Bipolar Pulse Pair Stimulated Echo INEPT)," page 171

Setting Up 2D-DOSY Experiments

1. Start setting up any of the four experiments by recording a normal s2pul spectrum on the nucleus to be observed.
2. Calibrate (or check) pulse widths if necessary.
3. Before calling the `setup` macro, which always has the same name as the pulse sequence itself, reduce the spectral window to the region of interest.
4. Each sequence has a parameter called `delflag`. By setting `delflag='y'`, the actual DOSY sequence is activated. Setting `delflag='n'` enables returning to the basic s2pul (`Dbppste`, `DgcsteSL`, `Doneshot`) or INEPT (`Dbppsteinept`) sequence without changing the experiment or the parameter set.
5. Set the phase encoding gradient.

   The phase encoding gradient duration is defined by the `gt1` parameter (the total defocusing time) in all of the sequences. Its strength is defined by the `gzlvl1` parameter and the diffusion delay by the `del` parameter. The actual DOSY setup determines the proper relationship among these three parameters. The best setting primarily depends on the sample itself (e.g., solvent, viscosity, molecular size and shape, the isotope to be detected) and on the experimental conditions

(e.g., temperature). Using the DOSY sample to optimize the experimental parameters is recommended. For small or medium sized molecules, useful settings are: `gt1=0.002` and `del=0.05` sec and an array the gradient strength using either of the following methods:

- Enter one of the following arrays on the command line:

  `gzlvl1=500,5000,15000,20000,25000,30000` for Performa II
  `gzlvl1=50,500,1000,1500,2000` for Performa I gradient systems.

- Use the Setup Coarse Gradient array button in the on the Pulse Sequence page of the Acquisition panel.

6. Select the maximum gradient power used in the DOSY experiment.

   Select the `gzlvl1` value, which attenuates the signal intensities to 5% to 15% of the intensities obtained with the weakest gradient pulse. Increase `del` or `gt1` if the intensity drop is not sufficient at the end of the array. Decrease `del` or `gt1` if no signal is detected towards the end of the array, and repeat the procedure again.

7. Optimize the `alfa` and `rof2` (and on VNMRS systems the `ddrtc`) delays to reach ideal baseline performance.

8. Determine suitable values for `gt1`, `del`, and the maximum gradient power, then call the `setup_dosy` macro.

   `setup_dosy` asks for the number of gradient levels for the weakest and strongest gradient power to be used in the experiment and sets up a range of `gzlvl1` values with their squares evenly spaced. The minimum gradient strength may be set to 0.3-0.5 G/cm.The number of different pulse areas to use depends on the range of diffusion coefficients to be covered and the balance between systematic and random errors but typically is in the range of 10 to 30. As in any quantitative experiment, there is a balance to be struck when choosing a repetition rate between signal-to-noise and accuracy. But in DOSY experiments, a delay of 1-2 T_1 suffices, provided that care is taken to establish a steady state before acquiring data. Set `ss = -8` or `–16` to have steady-state pulses at every new array element and run the acquisition interleaved (`il='y'`).

Each sequence is equipped with tabs and pages that provide direct access to parameters and setup-related commands. Figure 36 shows the Acquisition Tab and Default page of the `Doneshot` sequence. Table 9 shows the available tools for DOSY.

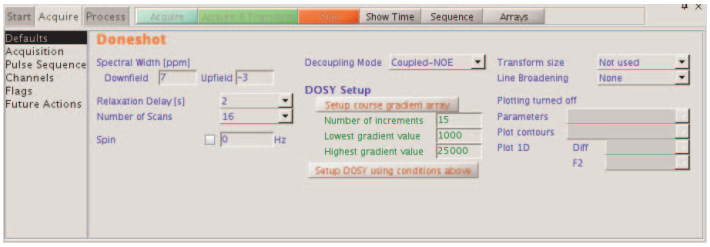

Figure 36. Doneshot Acquisition Tab and Default Page

Table 9. Tools for the DOSY Experiments

Command or Macro	*Description*
`Dbppste`	Sets up parameters for the Dbppste.c pulse sequence
`Dbppste_cc`	Sets up parameters for the Dbppste_cc.c pulse sequence
`Dbppste_ghsqcse`	Sets up parameters for the Dbppste_ghsqcse.c pulse sequence

Table 9. Tools for the DOSY Experiments

Command or Macro	*Description*
`Dbppsteinept`	Sets up parameters for the Dbppsteinept.c pulse sequence
`Dbppste_wg`	Sets up parameters for the Dbppste_wg.c pulse sequence
`Dcosyidosy`	Sets up parameters for the Dcosyidosy.c pulse sequence
`Dgcstecosy`	Sets up parameters for the Dgcstecosy.c pulse sequence
`Dgcstehmqc`	Sets up parameters for the Dgcstehmqc.c pulse sequence
`Dgcstehmqc_ps`	Sets up parameters for the Dgcstehmqc_ps.c pulse sequence
`DgcsteSL`	Sets up parameters for the DgcsteSL.c pulse sequence
`DgcsteSL_cc`	Sets up parameters for the DgcsteSL_cc.c pulse sequence
`DgcsteSL_dpfgse`	Sets up parameters for the DgcsteSL_dpfgse.c pulse sequence
`Dghmqcidosy`	Sets up parameters for the Dghmqcidosy.c pulse sequence
`DgsteSL_cc`	Sets up parameters for the DgsteSL_cc.c pulse sequence
`Dhom2djidosy`	Sets up parameters for the Dhom2djidosy.c pulse sequence
`Doneshot`	Sets up parameters for the Doneshot.c pulse sequence
`Dpfgdste`	Sets up parameters for the Dpfgdste.c pulse sequence
`makedosyparams`	Creates DOSY-related parameters (only called by DOSY sequences)
`setup_dosyVJ`	Sets up gradient levels for DOSY experiments in VNMRJ
`cleardosy`	Deletes any temporarily saved data in the current (sub) experiment
`dosy`	Starts the 2D-DOSY or 3D AV-DOSY analysis
`undosy`	Restores the original 1D NMR data from the subexperiment
`redosy`	Restores the previous 2D DOSY display from the subexperiment
`dosy2d`	Executes protocol actions of apptype dosy2d
`dosy3d`	Executes protocol actions of apptype dosy3d
`dosy3Dps`	Starts phase sensitive 3D Dosy analysis
`dosy_grad_calib`	Calibrates gradient strengths based on HDO diffusion
`sdp`	Shows diffusion projection
`fbc`	Applies baseline correction for each spectrum in the array
`makeslice`	Synthesizes 2D projection of a 3D DOSY spectrum in diffusion limits
`showoriginal`	Restores the 1st 2D spectrum in a 3D DOSY experiment
`showdosyfit`	Displays the fit of the DOSY analyses for a given line
`showdosyresidual`	Displays the difference between experimental data and the fit for a given line
`unpack_DOSY3Dps`	Breaks up arrayed phase sensitive 3D DOSY fits into individual 2Ds
`update_wrefshape`	Creates solvent suppression selective shape for DgcsteSL_dpfgse sequence
`ddif`	Synthesizes and displays DOSY plot
`setgcal`	Sets the gradient calibration constant
`fiddle`	Performs reference deconvolution

The dosy macro attempts to identify the relevant information from the parameters and the pulse sequence name. If it fails, it starts a dialog asking for three pieces of information required to do the experiment: the width of the pulse(s) used for dephasing before diffusion, the diffusion delay between the dephasing and rephasing, and, for bipolar sequences, the time between the positive and negative gradient pulses.

The sequences starting with D calculate the time portion of the exponent governing diffusional attenuation, storing this as dosytimecubed, and the Larmor frequency of the diffusing spins, storing this as dosyfrq.

Dbppste (DOSY Bipolar Pulse Pair Stimulated Echo) Experiment

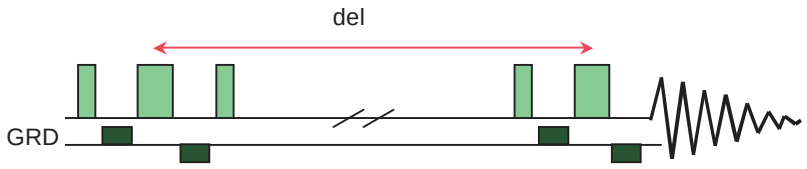

Figure 37. Dbppste Experiment

Table 10. Dbppste Parameters

Parameters	*Description*
delflag	'y' runs the Dbppste sequence. 'n' runs the normal s2pul sequence. del is the actual diffusion delay
gt1	total diffusion-encoding pulse width gzlvl1(diffusion-encoding pulse strength)
gstab	gradient stabilization delay (~0.0002-0.0003 sec)
satmode	'y' turns on presaturation during d1 and/or during the diffusion delay satfrq (presaturation frequency)
satdly	saturation delay (part of d1)
satpwr	saturation power
alt_grd	flag to invert gradient sign on alternating scans (default = 'n')
lkgate_flg	flag to gate the lock sampling off during the diffusion sequence sspul- flag for a GRD-90-GRD homospoil block.
gzlvlhs	gradient level for sspul
hsgt	gradient duration for sspul
fn2D	Fourier number to build up the 2D display in F2

Experiments using a nano probe require synchronization of the diffusion gradients (gzlvl1) with sample spinning i.e.: gt1=1.0/srate*(trunc((gt1*srate)+0.5)) where srate is the sample spinning speed.

Reference: Wu, D.; Chen, A.; Johnson, C.S., Jr., *J. Magn. Reson.* 1995, **115**, Series (A), 260-264.

DgcsteSL (DOSY Gradient Compensated Stimulated Echo with Spin Lock)

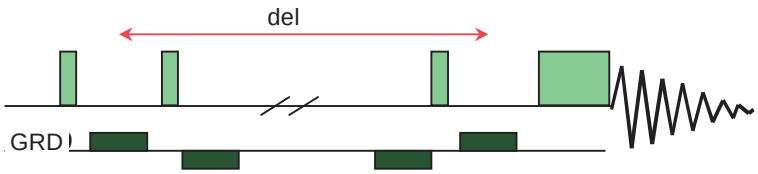

Figure 38. DgcsteSL Experiment

The optional purging pulse can effectively eliminate the dispersion signal components. Be careful not to create convection in the sample by the trim pulse. With a low `prgpwr` power level and slightly larger `prgtime` (e.g. 20 ms), the spin lock can also be used as a T_2 filter to eliminate undesired broad signals.

Table 11. DgcsteSL Parameters

Parameters	*Description*
`calibflag`	Correct systematic errors in DOSY experiments.
`DAC_to_G`	Store gradient calibration value in DOSY sequences.
`del`	Actual diffusion delay.
`delflag`	`'y'` runs the DgcsteSL sequence.
	`'n'` runs the normal s2pul sequence.
`fn2D`	Fourier number to build up the 2D display in F2.
`gstab`	Gradient stabilization delay (~200-300 µs).
`gt1`	Total diffusion-encoding pulse width.
`gz_alt`	Flag to invert the gradient sign on alternating scans (default is `n`).
`gzlvl1`	Diffusion-encoding pulse strength.
`prg_flg*`	`'y'` selects purging trim pulse (default).
	`'n'` omits purging pulse.
`prgpwr*`	Power level for the purge pulse (~0.002 s).
`lkgt_flg`	Flag to gate off the lock receiver during gradient pulses (default = 'n')
`prgtime*`	Purging pulse length (in second).
`tweek`	Tuning factor to limit eddy currents. It can be set between 0 and 1, usually set to 0.0.

Reference: Pelta, M.D.; Barjat, H.; Morris, G.A.; Davis, A.L., Hammond, S,.*J. Magn. Reson. Chem*. **36**, 1998, 706.

Oneshot

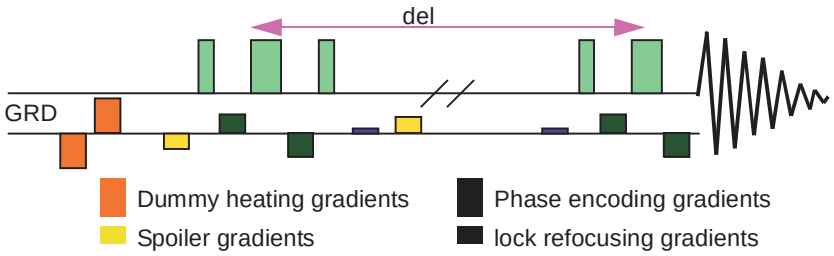

Figure 39. Oneshot DOSY Experiment

Table 12. Oneshot Parameters

Parameter	*Description*
DAC_to_G	Store gradient calibration value in DOSY sequences.
del	Actual diffusion delay.
delflag	'y' runs the Doneshot sequence. 'n' runs the normal s2pul sequence.
fn2D	Fourier number to build up the 2D display in F2.
gstab	Gradient stabilization delay (~200-300 µs).
gt1	Total diffusion-encoding pulse width.
gt3	Spoiling gradient duration (sec). Destroys transverse magnetization during the diffusion delay.
gzlvl1	Diffusion-encoding pulse strength.
gzlvl3	Spoiling gradient strength.
gzlvl_max	Maximum gradient strength accepted. (32767 with Performa II or III, 2047 with Performa I)
kappa	Unbalancing factor between bipolar pulses as a proportion of gradient strength (recommended:~0.2).
phasecycleflag	Flag to turn on or off the phase cycle.
startflip	Flip angle of the first pulse to eliminate radiation damping for very concentrated.
samples alt_grd	Flag to invert gradient sign on alternating scans (default = 'n')
lkgate_flg	Flag to gate the lock sampling off during gradient pulses
phasecycleflag	Flag to turn on and off the phase cycle
sspul	Flag for a GRD-90-GRD homospoil block
gzlvlhs	Gradient level for sspul
hsgt	Gradient duration for sspul
satmode	Flag for optional solvent presaturation 'ynn' - does presat during satdly 'yyn' - does presat during satdly and the diffusion delay
satdly	Presaturation delay before the sequence (part of d1)
satpwr	Saturation power level
satfrq	Saturation frequency
fn2D	Fourier number to up the 2D display in F2
DAC_to_G	Parameter to store the gradient calibration value (set by setup_dosy)

Reference: Pelta, M.D., Morris, G.A., Stchedroff, M.J., Hammond S.J., “A One-Shot Sequence for High-Resolution Diffusion-Ordered Spectroscopy.” *Magnetic Resonance in Chemistry* **40**, 2002, 147-152.

The parameters for the heating gradients (`gt4`, `gzlvl4`) are calculated in the sequence. They cannot be set directly. `tau` is defined as time between the mid-points of the bipolar diffusion encoding gradient pulses.

The diffusion gradients (`gt1`) must be synchronized with sample spinning when using a nano probe: `gt1=1.0/srate*(trunc((gt1*srate)+0.5))` where `srate` is the sample spinning speed.

The lock refocusing gradient is determined by `kappa` and `gzlvl1`. The dummy heating gradients are automatically adjusted by the sequence. Use the maximum gradient power available in the experiment by setting: `gzlvl_max > gzlvl1*(1+kappa)`.

The total gradient power transmitted to the sample remains independent on the phase encoding gradient power. Although the sequence design makes phase cycling unnecessary, and, unlike other DOSY sequences, the `Doneshot` sequence can be run with a single transient per array element, it is recommended to turn on the cyclops cycle: `phasecycleflag='y'`

10.6 DOSY Sequences for Biological Samples in H_2O

Presaturation is typically insufficient to reduce the water amplitude in biological samples dissolved in H2O/D2O to a level where signal intensities of the dispersive component from the solvent signal do not adversely affect the residual signal of the sample. Presaturation must be combined with efficient solvent suppression scheme like Watergate 3-9-10 or excitation sculpting. A digital solvent suppression filter applied during processing produces the best results, especially in sample concentrations below millimolar.

DgcsteSL_dpfgse (DOSY Gradient Compensated Stimulated Echo with Spin Lock)

This sequence incorporates DPFGSE solvent suppression.

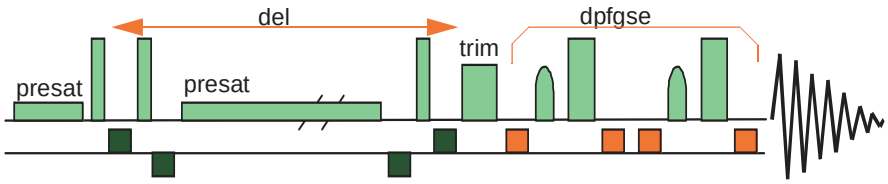

Figure 40. DOSY Gradient Compensated Stimulated Echo with Spin Lock

Table 13. DgcsteSL_dpfgse Parameters

Parameter	*Description*
`delflag`	'y' runs the DgcsteSL sequence
	'n' runs the normal s2pul sequence del — the actual diffusion delay
`gt1`	total diffusion-encoding pulse width
`gzlvl1`	diffusion-encoding pulse strength
`gstab`	gradient stabilization delay (~0.0002-0.0003 sec)

Table 13. DgcsteSL_dpfgse Parameters

Parameter	*Description*
`tweek`	tuning factor for limiting eddy currents (can be set from 0 to 1, usually set to 0.0)
`prg_flg`	'y' selects purging pulse (default) 'n' omits purging pulse
`prgtime`	purging pulse length (~0.002 sec)
`prgpwr`	purging pulse power
`lkgate_flg`	lock gating flag, if set to 'y', the lock is gated off during gradient pulses (default = 'n')
`fn2D`	Fourier number to build up the 2D display in F2
`satmode`	'y' turns on presaturation
`wrefshape`	shape file of the 180º selective refocusing pulse on the solvent (may be convoluted for multiple solvents)
`wrefpw`	pulse width for wrefshape (as given by Pbox)
`wrefpwr`	power level for wrefshape (as given by Pbox)
`wrefpwrf`	fine power for wrefshape by default it is 2048 needs optimization for multiple solvent suppression only with fixed wrefpw
`gt2`	gradient duration for the solvent suppression echo
`gzlvl2`	gradient power for the solvent suppression echo
`alt_grd`	alternate gradient sign(s) in dpfgse on even transients (default = 'n')
`sspul`	flag for a GRD-90-GRD homospoil block
`gzlvlhs`	gradient level for sspul
`hsgt`	gradient duration for sspul

The diffusion gradients (`gt1`) must be synchronized with sample spinning when using a nano probe: `gt1=1.0/srate*(trunc((gt1*srate)+0.5))` where `srate` is the sample spinning speed.

Use the `update_wrefshape` macro to create or updated the water refocusing shape.

Dbppste_wg - (DOSY Bipolar Pulse Pair Stimulated Echo)

This sequence incorporates Watergate 3-9-19 solvent suppression.

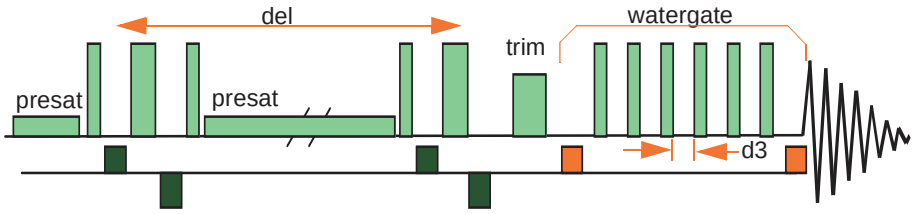

Figure 41. DOSY Bipolar Pulse Pair Stimulated Echo

Table 14. Dbppste_wg Parameters

Parameter	*Description*
`delflag`	'y' runs the Dbppste sequence 'n' runs the normal s2pul sequence
`del`	the actual diffusion delay

Table 14. Dbppste_wg Parameters

Parameter	*Description*
gt1	total diffusion-encoding pulse width
gzlvl1	diffusion-encoding pulse strength
alt_grd	flag to invert gradient sign on alternating scans (default='n')
lkgate_flg	flag to gate the lock sampling off during the diffusion sequence
d3	watergate delay (the excitation maximum is defined by 1.0/(2.0*d3)
ex_max	excitation maximum from XMTR (=1/(2*d3)
gt2	watergate diffusion-encoding pulse width
gzlvl2	watergate encoding pulse strength
gstab	gradient stabilization delay (~0.0002-0.0003 sec)
satmode	'y' turns on presaturation during d1 and/or del
prg_flg	'y' selects purging trim pulse 'n' omits purging pulse
prgtime	purging pulse length (~0.002 sec)
prgpwr	purging pulse power
sspul	flag for a GRD-90-GRD homospoil block
gzlvlhs	gradient level for sspul
hsgt	gradient duration for sspul
fn2D	Fourier number to build up the 2D display in F2

The diffusion gradients (gt1) must be synchronized with sample spinning when using a nano probe: gt1=1.0/srate*(trunc((gt1*srate)+0.5)) where srate is the sample spinning speed.

Dbppsteinept (DOSY Bipolar Pulse Pair Stimulated Echo INEPT)

This sequence uses the higher resolving power of the wide ^{13}C chemical shift range with phase encoding and decoding on the ^{1}H magnetisation.

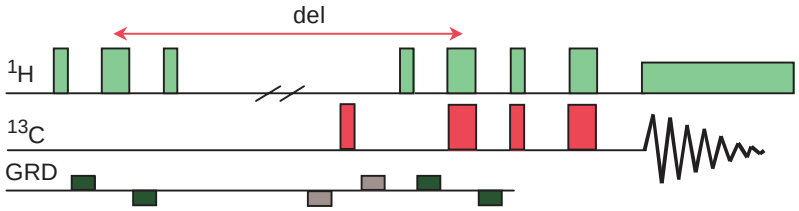

Figure 42. DOSY Bipolar Pulse Pair Stimulated Echo INEPT

Table 15. Dbppsteinept Parameters

Parameter	*Description*
delflag	'y' runs dosyinept 'n' runs normal inept without dosy del- the actual diffusion delay
gt1	total length of the phase encoding gradient
gzlvl1	strength of the phase encoding gradient
pp	90º hard 1H pulse

Table 15. Dbppsteinept Parameters

Parameter	*Description*
`pplvl`	decoupler power level for pp pulses
`sspul`	flag for a GRD-90-GRD homospoil block
`gzlvlhs`	gradient level for sspul
`hsgt`	gradient duration for sspul
`sspulX`	flag for a GRD-90-GRD homospoil block during del to destroy original X magnetization (using hsgt and gzlvlhs)
`j1xh`	one-bond X-H coupling
`mult`	multiplicity; 1 selects CH's (doublets); 1.5 gives CH2's down, CH's and Ch3's up; 0.5 enhances all protonated carbons
`alt_grd`	flag to invert gradient sign on alternating scans (default = 'n')
`lkgate_flg`	flag to gate the lock sampling off during gradient pulses
`fn2D`	Fourier number to build up the 2D display in F2

The diffusion gradients (`gt1`) must be synchronized with sample spinning when using a nano probe: `gt1=1.0/srate*(trunc((gt1*srate)+0.5))` where `srate` is the sample spinning speed.

Reference: D.Wu, A.Chen and C.S.Johnson, Jr., *J. Magn. Reson*. Series A, **123**, 222-225 (1996)

10.7 Convection Compensated DOSY Experiments

- "Convection Compensation," page 172
- "Dbppste_CC (DOSY Bipolar Pulse Pair Stimulated Echo with Convection Compensation)," page 175
- "DgsteSL_CC (DOSY Gradient Stimulated Echo with Spin Lock and Convection Compensation)," page 176
- "DgcsteSL_CC (DOSY Gradient Compensated Stimulated Echo with Spin Lock and Convection Compensation) Experiment," page 178
- "Dpfgdste (Pulsed Field Gradient Double-Stimulated Echo)," page 179

Convection Compensation

Convection within the sample is a serious problem affecting diffusion experiments, in particular at elevated temperatures. Convection currents are caused by small temperature gradients in the sample and result in additional signal decay that can be mistaken for faster diffusion. The convection conditions are described by the Rayleigh-Bénard equation:

$$R_a = ((g\beta R^4)/(\upsilon\nu\chi))((\partial T)/(\partial z))$$

R_a = 67 for insulating walls

R_a = 162 for conducting walls

where g is the gravitational acceleration, ν is the viscosity, χ the thermal diffusivity, β the expansion coefficient of the liquid, R is the internal diameter of the NMR tube and $\partial T)/(\partial z)$ is the temperature gradient along the sample axis. When the critical Rayleigh number (Ra) is exceeded, convection will occur. Convection typically causes the following anomalies in diffusion experiments:

- Anomalously large diffusion coefficients (D)

- D values that are not independent of gradient duration (δ) and the diffusion delay (del)
- Stejskal-Tanner plots that show periodicity
- Non-Arrhenius temperature dependence of D

A simple calculation based on the Rayleigh-Bénard equation indicates that, for a solvent like chloroform, a temperature gradient of as little as 0.05 K/cm is sufficient to cause convection flow. In general, larger temperature gradients are needed for more viscous solvents.

A uniform sample flow velocity ν introduces a phase modulation of the signal in a typical DOSY experiment:

$$S(G_{zi})=S(0)exp(-D_i\gamma^2\delta^2(G_{zi})^2\Delta)*exp(\imath\gamma\delta G_{zi}\nu\Delta)$$

Representing convection by a crude model of equal and opposite flows each of uniform velocity leads to cancellation if the imaginary part above and the result is a cosine modulation:

$$S(G_{zi})=S(0)exp(-D_i\gamma^2\delta^2(G_{zi})^2\Delta)*cos(\imath\gamma\delta G_{zi}\nu\Delta)$$

Observing such an oscillatory behavior of the signal decay (see also Figure 51) is a clear indication of convention. Assuming convection is constant in time and strictly laminar, the effect of convection on diffusion spectra can be efficiently eliminated. Figure 43 displays the necessary modifications (orange box) on a gradient-stimulated echo pulse sequence: halfway through the diffusion delay the magnetization is moved back to the transverse plane by a 90° pulse and gets refocused by the first (green) gradient pulse. The second green gradient, identical in sign, duration and length to the previous one, phase labels the spins in the opposite direction. The magnetization is then converted back to axial for the second half of the diffusion delay. The ordered nature of convection assures that the phase evolution due to convection is opposite during the two halves of the diffusion delay and therefore compensate each other, while diffusion–being a random process –does not get affected. In order to detect only desired coherences, homospoil gradient pulses (shown in red) are used in both halves of the diffusion delay.

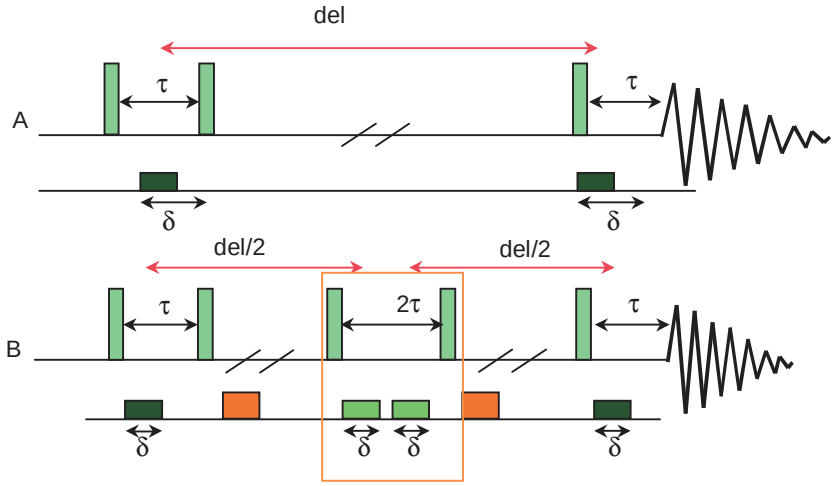

Figure 43. Modification of a `DgsetSL` Adding Convection Compensation

Pulse Sequences

- `DgsteSL_cc` (Gradient STimulated Echo with Spin-Lock and Convection Compensation) has only the absolute minimum number of gradients (six) necessary for the pulse sequence to work.
- `DgcsteSL_cc` (Gradient Compensated Stimulated Echo with Spin-Lock and Convection Compensation) is a direct derivative of the `DgcsteSL` sequence and contains an identical number of positive and negative gradients to provide "internal" Eddy-current compensation as well. Note that of the 12 gradient pulses used in the pulse sequence only two (the black ones) are used to measure diffusion.
- `Dbppste_cc` (Bipolar Pulse Pair Stimulated Echo with Convection Compensation) is a direct derivative of the `Dbppste` sequence. Apart from the *heating gradients*, the pulse sequence has all the features of the Oneshot sequence discussed earlier.
- `Dpfgdste` (Pulse Field Gradient Double STimulated Echo) is a variant of the `DgcsteSL_cc` sequence with no spin-lock and with a different phase cycle.

Reduced Sensitivity of Convection Compensated DOSY Experiments

DOSY pulse sequence convection compensation contains an extra stimulated echo step that attenuates the signal 50% with respect to its equivalent without convection compensation. The non-compensated pulse sequences provide twice the signal-to-noise and should be used if the experimental conditions exclude the possibility of convection compensation.

Determining the Need for Convection Compensation

The NMR pulse sequence is the most sensitive test to measure diffusion. Complete convection compensation can only be achieved if the compensation block (box in Figure 43b) is applied exactly halfway through the diffusion delay. Shifting the block towards the beginning or the end of the diffusion delay (i.e., time symmetry is broken) causes signal attenuation and/or phase distortion in the presence of convection, while without convection, the signal amplitudes and phases remains unaffected. Each of the following pulse sequences has an auxiliary delay parameter, `del2`, that allows the operator to move the convection compensation block systematically along the diffusion delay and by doing so to record a so-called velocity profile. This can be used either for qualitative (Figure 44) or quantitative characterization of convection in diffusion experiments. See N.M. Loening and J. Keeler, *J. Magn. Reson.*, **139**, 1999, 334-341, for details.

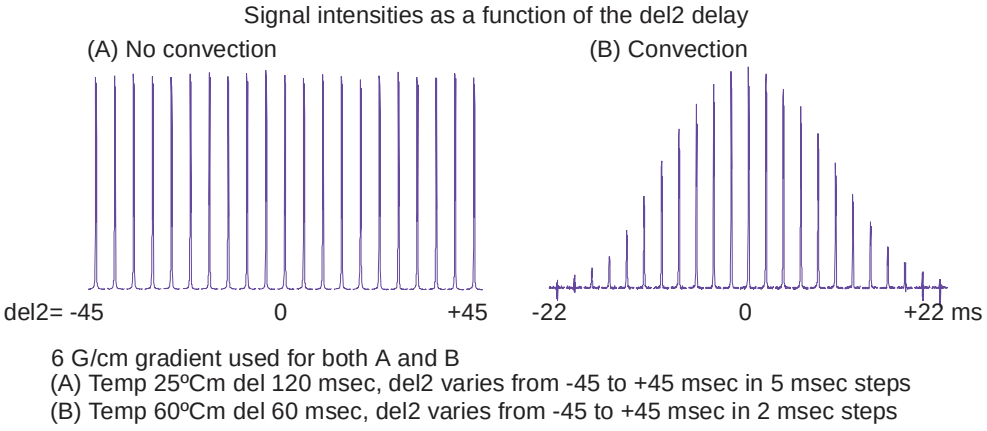

Figure 44. Velocity Map of a Sample Dissolved in D_20 Using Dbppse_CC

Dbppste_CC (DOSY Bipolar Pulse Pair Stimulated Echo with Convection Compensation)

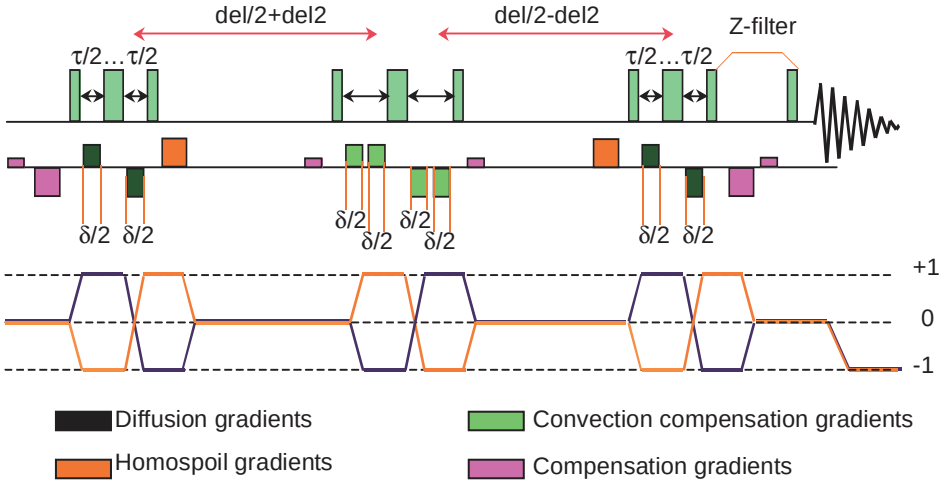

Figure 45. DOSY Bipolar Pulse Pair Stimulated Echo with Convection Compensation

Table 16. Dbppste_CC Parameters

Parameter	*Description*
`delflag`	'y' - runs the Dbppste_cc sequence
	'n' - runs the normal s2pul sequence
`del`	the actual diffusion delay
`del2`	delay parameter that can shift the convection compensation sequence elements off the center of the pulse sequence allowing running a velocity profile (can also be negative but in absolute value cannot exceed del/2 minus the gradient and gradient-stabilization delays; default value for diffusion measurements is zero)
`gt1`	total diffusion-encoding pulse width
`gzlvl1`	diffusion-encoding pulse strength
`gstab`	gradient stabilization delay (~0.0002-0.0003 s)
`triax_flg`	flag for using triax gradient amplifiers and probes
	'y' - homospoil gradients are applied along X- and Y- axis (all the diffusion gradients are Z-gradients)
	'n' - all gradients in the sequence are Z-gradients
`gzlvl_max`	maximum accepted gradient strength (32767 with Performa II, 2047 with Performa I)
`kappa`	unbalancing factor between bipolar pulses as a proportion of gradient strength (~0.2)
`gt2`	1st homospoil gradient duration
`gzlvl2`	1st homospoil gradient power level (will be X-gradient if triax_flg is set and triax amplifier and probe is available)
`gt3`	2nd homospoil gradient duration

Table 16. Dbppste_CC Parameters

Parameter	*Description*
`gzlvl3`	2nd homospoil gradient power level (will be Y-gradient if triax_flg is set and triax amplifier and probe is available
`satmode`	flag for optional solvent presaturation
	'ynn' - does presat during satdly
	'yyn' - does presat during satdly and the diffusion delay
`satdly`	presaturation delay before the sequence (part of d1)
`satpwr`	saturation power level
`satfrq`	saturation frequency
`sspul`	flag for a GRD-90-GRD homospoil element
`gzlvl0`	gradient level for sspul
`gt0`	gradient duration for sspul
`sspul`	flag for a GRD-90-GRD homospoil block
`gzlvlhs`	gradient level for sspul
`hsgt`	gradient duration for sspul
`fn2D`	Fourier number to build up the 2D display in F2

Reference: A. Jerchow and N. Müller, *J. Magn. Reson.* **125**, 372-375 (1997).

The diffusion gradients (`gt1`) must be synchronized with sample spinning when using a nano probe: `gt1=1.0/srate*(trunc((gt1*srate)+0.5))` where `srate` is the sample spinning speed.

DgsteSL_CC (DOSY Gradient Stimulated Echo with Spin Lock and Convection Compensation)

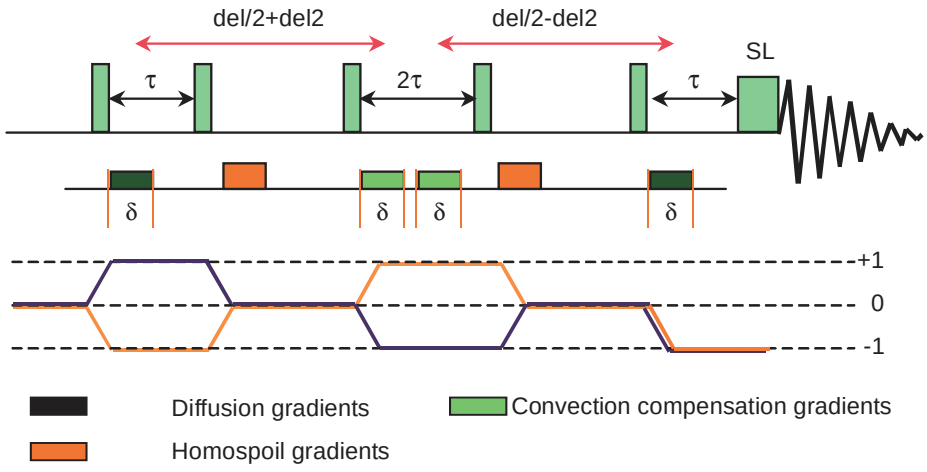

Figure 46. Gradient-Stimulated Echo with Spin Lock and Convection Compensation

Table 17. DgsteSL_CC Parameters

Parameter	*Description*
`delflag`	'y' - runs the DgsteSL_cc sequence
	'n' - runs the normal s2pul sequence
`del`	the actual diffusion delay
`del2`	delay parameter that can shift the convection compensation sequence elements off the centre of the pulse sequence allowing running a velocity profile. Can also be negative but in absolute value cannot exceed del/2 minus the gradient and gradient-stabilization delays (default value for diffusion measurements is zero)
`gt1`	total diffusion-encoding pulse width
`gzlvl1`	diffusion-encoding pulse strength
`gstab`	gradient stabilization delay (~0.0002-0.0003 s)
`triax_flg`	flag for using triax gradient amplifiers and probes
	'y' - homospoil gradients are applied along X- and Y- axis (all diffusion gradients are Z-gradients)
	'n' - all gradients in the sequence are Z-gradients
`gt2`	1st homospoil gradient duration
`gzlvl2`	1st homospoil gradient power level (is an X-gradient if triax_flg is set and triax amplifier and probe is available)
`gt3`	2nd homospoil gradient duration
`gzlvl3`	2nd homospoil gradient power level (is a Y-gradient if triax_flg is set and triax amplifier and probe is available)
`prg_flg`	'y' - selects purging pulse (default)
	'n' - omits purging pulse
`prgtime`	purging pulse length (~0.002 s)
`prgpwr`	purging pulse power
`satmode`	flag for optional solvent presaturation
	'ynn' — does presat during satdly
	'yyn' — does presat during satdly and the diffusion delay
`satdly`	presaturation delay before the sequence (part of d1)
`satpwr`	saturation power level
`satfrq`	saturation frequency
`sspul`	flag for a GRD-90-GRD homospoil block
`gzlvlhs`	gradient level for sspul
`hsgt`	gradient duration for sspul
`fn2D`	Fourier number to build up the 2D display in F2

Reference: A. Jerchow and N. Müller, *J. Magn. Reson*. **125**, 372-375 (1997).

The diffusion gradients (`gt1`) must be synchronized with sample spinning when using a nano probe: `gt1=1.0/srate*(trunc((gt1*srate)+0.5))` where `srate` is the sample spinning speed.

DgcsteSL_CC (DOSY Gradient Compensated Stimulated Echo with Spin Lock and Convection Compensation) Experiment

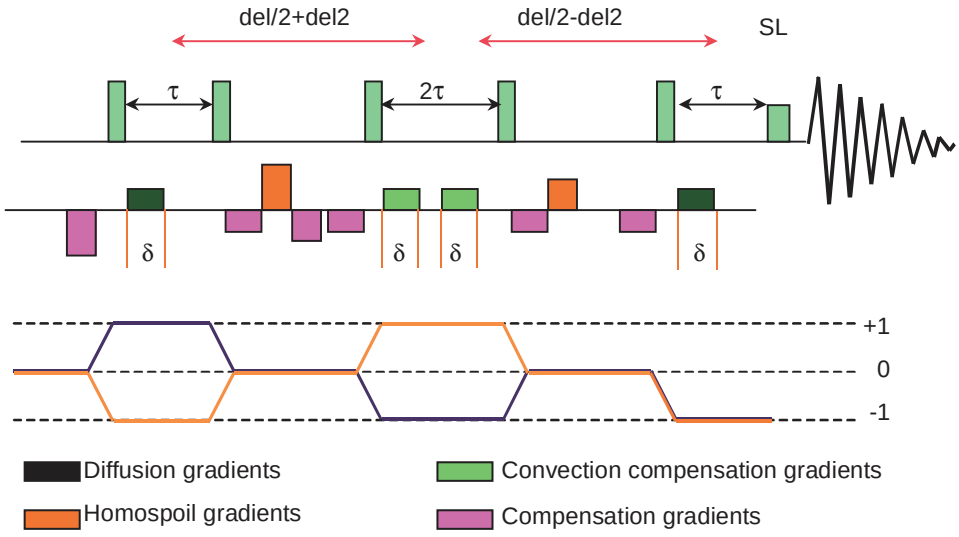

Figure 47. Gradient-Compensated Stimulated Echo with Spin Lock and Convection Compensation

Table 18. DgcsteSL_CC Parameters

Parameter	*Description*
`delflag`	'y' runs the DgcsteSL_cc sequence
	'n' runs the normal s2pul sequence
`del`	the actual diffusion delay
`del2`	delay parameter that can shift the convection compensation sequence elements off the center of the pulse sequence allowing running a velocity profile; can also be negative but in absolute value cannot exceed del/2 minus the gradient and gradient-stabilization delays (default value for diffusion measurements is zero)
`gt1`	total diffusion-encoding pulse width
`gzlvl1`	diffusion-encoding pulse strength
`gstab`	gradient stabilization delay (~0.0002-0.0003 s)
`alt_grd`	flag to invert gradient sign on alternating scans (default = 'n')
`lkgate_flg`	flag to gate the lock sampling off during
`triax_flg`	flag for using triax gradient amplifiers and probes
	'y' - homospoil gradients are applied along X- and Y-axis (all the diffusion gradients are Z-gradients)
	'n' - (all gradients in the sequence are Z-gradients)
`gt2`	1st homospoil gradient duration
`gzlvl2`	1st homospoil gradient power level (will be X-gradient if triax_flg is set and triax amplifier and probe is available
`gt3`	2nd homospoil gradient duration
`gzlvl3`	2nd homospoil gradient power level (will be Y-gradient if triax_flg is set and triax amplifier and probe is available)

Table 18. DgcsteSL_CC Parameters

Parameter	*Description*
`prg_flg`	'y' selects purging pulse (default)
	'n' omits purging pulse
`prgtime`	purging pulse length (~0.002 s)
`prgpwr`	purging pulse power
`satmode`	flag for optional solvent presaturation
	'ynn' - does presat during satdly
	'yyn' - does presat during satdly and the diffusion delay
`satdly`	presaturation delay before the sequence (part of d1)
`satpwr`	saturation power level
`satfrq`	saturation frequency
`sspul`	flag for a GRD-90-GRD homospoil block
`gzlvlhs`	gradient level for sspul
`hsgt`	gradient duration for sspul
`fn2D`	Fourier number to build up the 2D display in F2

Reference: personal communication (G.A. Morris, University of Manchester).

The diffusion gradients (`gt1`) must be synchronized with sample spinning when using a nano probe: `gt1=1.0/srate*(trunc((gt1*srate)+0.5))` where `srate` is the sample spinning speed.

Dpfgdste (Pulsed Field Gradient Double-Stimulated Echo)

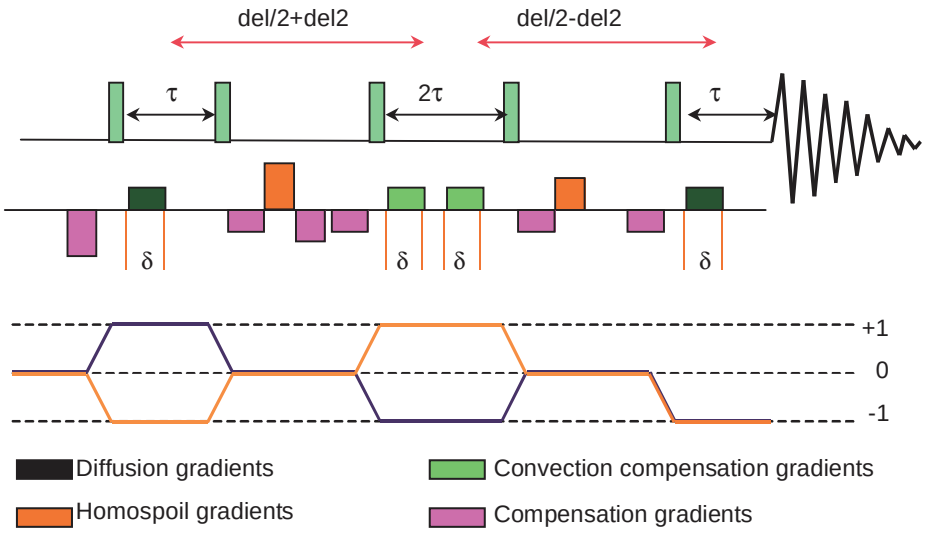

Figure 48. Pulsed Field Gradient Double Stimulated Echo

Table 19. Dpfgdste Parameters

Parameter	*Description*
`delflag`	'y' runs the Dpfgdste sequence 'n' runs the normal s2pul sequence del the actual diffusion delay
`del2`	delay parameter that can shift the convection compensation sequence elements off the center of the pulse sequence allowing running a velocity profile; can also be negative, but in absolute value cannot exceed `del` minus the gradient and gradient-stabilization delays (default value for diffusion measurements is zero)
`gt1`	total diffusion-encoding pulse width
`gzlvl1`	diffusion-encoding pulse strength
`gzlvl3`	gradient power for the 2nd homospoil gradient
`gt3`	gradient duration for the homospoil gradient
`gzlvl3`	gradient power for the 1st homospoil gradient
`gstab`	gradient stabilization delay (~0.0002-0.0003 sec)
`satmode`	'y' turns on presaturation during d1 and/or during the diffusion delay
`satfrq`	presaturation frequency
`satdly`	saturation delay (part of d1)
`satpwr`	saturation power
`alt_grd`	flag to invert gradient sign on alternating scans (default = 'n')
`lkgate_flg`	flag to gate the lock sampling off during gradient pulses
`sspul`	flag for a GRD-90-GRD homospoil block
`gzlvlhs`	gradient level for sspul
`hsgt`	gradient duration for sspul
`fn2D`	Fourier number to build up the 2D display in F2

The diffusion gradients (`gt1`) must be synchronized with sample spinning when using a nano probe: `gt1=1.0/srate*(trunc((gt1*srate)+0.5))` where `srate` is the sample spinning speed.

Reference: Nilsson M, Gil AM, Delgadillo I, Morris GA. *Anal Chem* 2004;**76**:5418-5422

10.8 Comparison of DOSY and Convection Compensated DOSY

Diffusion experiments discussed in this section were run on a mixture of nicotinic acid amide and amikacin (see Figure 49 for the structural formulas) in D_2O at 30 and 60 °C in a 5 mm sample tube on a 500 MHz spectrometer using *Dbppst* (no compensation) and *Dbppst_cc* (compensated) sequences. Data for both experiments were run. The sample components differ significantly in size (or molecular weight), have no signal overlap between the aromatic and the sugar protons in the 500 MHz spectrum of the mixture, and numerous proton lines (DOSY analysis handles multiple components individually), making the sample particularly suitable to provide information about the accuracy of the diffusion data.

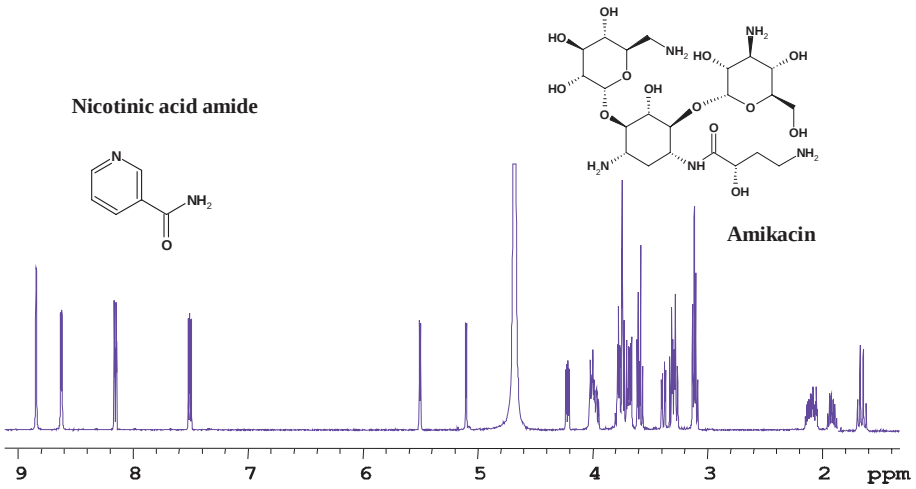

Figure 49. 500 MHz Proton Spectrum of a Mixture Nicotinic Acid Amide and Amikacin in D_2O

The experiments at 30 °C were run using the same diffusion delays (`del = 120 ms`), gradient duration (`gt1 = 2 ms`), and the same 20 values of gradient strengths (varied between 1 and 30 G/cm) for both the *Dbppst* (no compensation) and *Dbppst_cc* (compensated) sequences.

Visual inspection of the signal intensities (Figure 50a) does not reveal obvious anomalies, i.e., the individual lines show exponentially attenuated intensities with increasing gradient power (note that the HDO signal is truncated in the first 9 spectra). The DOSY analysis (Figure 50b) shows a clear separation of the two components and the solvent line along the diffusion axis. Practically all proton signals of the same molecule exhibit the same diffusion coefficient, indicating high relative accuracy of the calculated *D* values. From this point of view there is no difference between the results of the two different measurements. Consequently, if the only aim is the separation of the NMR spectra of the mixture components, then the *Dbppste* sequence may be preferred as it has twice the sensitivity compared to its convection compensated counterpart, *Dbppste_cc*.

Comparison of the extracted *D* values reveals that the coefficients without convection compensation tend to be consistently bigger. The slower the diffusion of a certain component the bigger the deviation is (21% on amikacin but only 9% on the water). This demonstrates that convection here is contributing to the calculated *D* values and providing a false indication that the mobility of the molecules is higher than in reality.

Moving away from ambient temperatures increases the risk of convection. This is demonstrated by repeating the previous pair of experiments at 60 °C. In Figure 51a. the attenuation of the signal intensities are far from being exponential (in reality they show an oscillatory behavior), and, apart from the amplitude distortions, serious phase deviations may also occur (see the inset of third spectrum in Figure 51a). The exponential fit of the signal amplitudes in the experiment without convection compensation is extremely inaccurate, the resolution of the 2D DOSY plot (Figure 51b) is dramatically reduced, and the experimental results are hardly usable. By comparison, the convection-compensated pulse sequence provides excellent diffusion separation and reliable diffusion data.

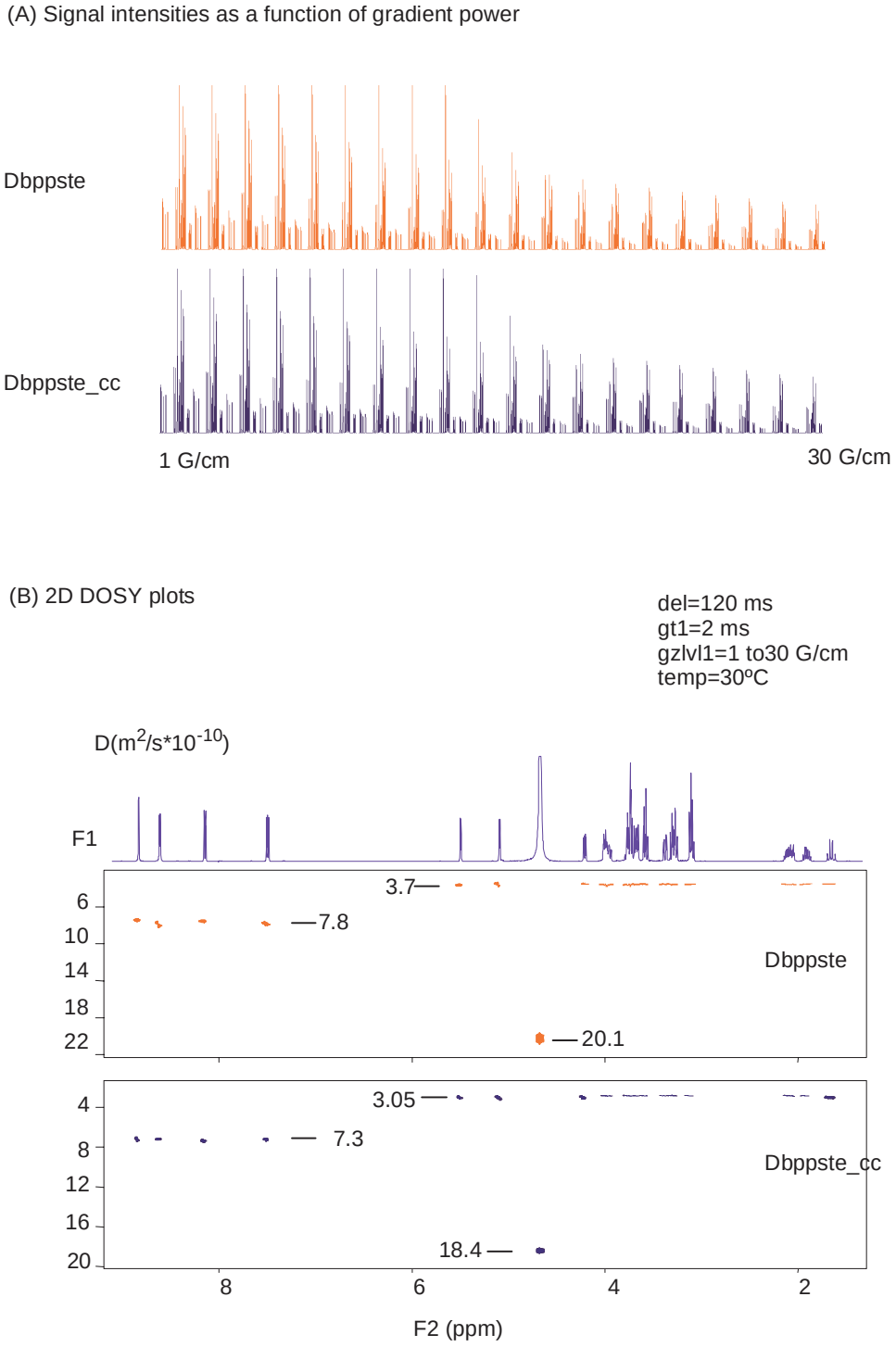

Figure 50. Signal Intensities and 2D DOSY Plots of the Nicotinic Acid Amid-Amikacin Mixture at 30ºC.

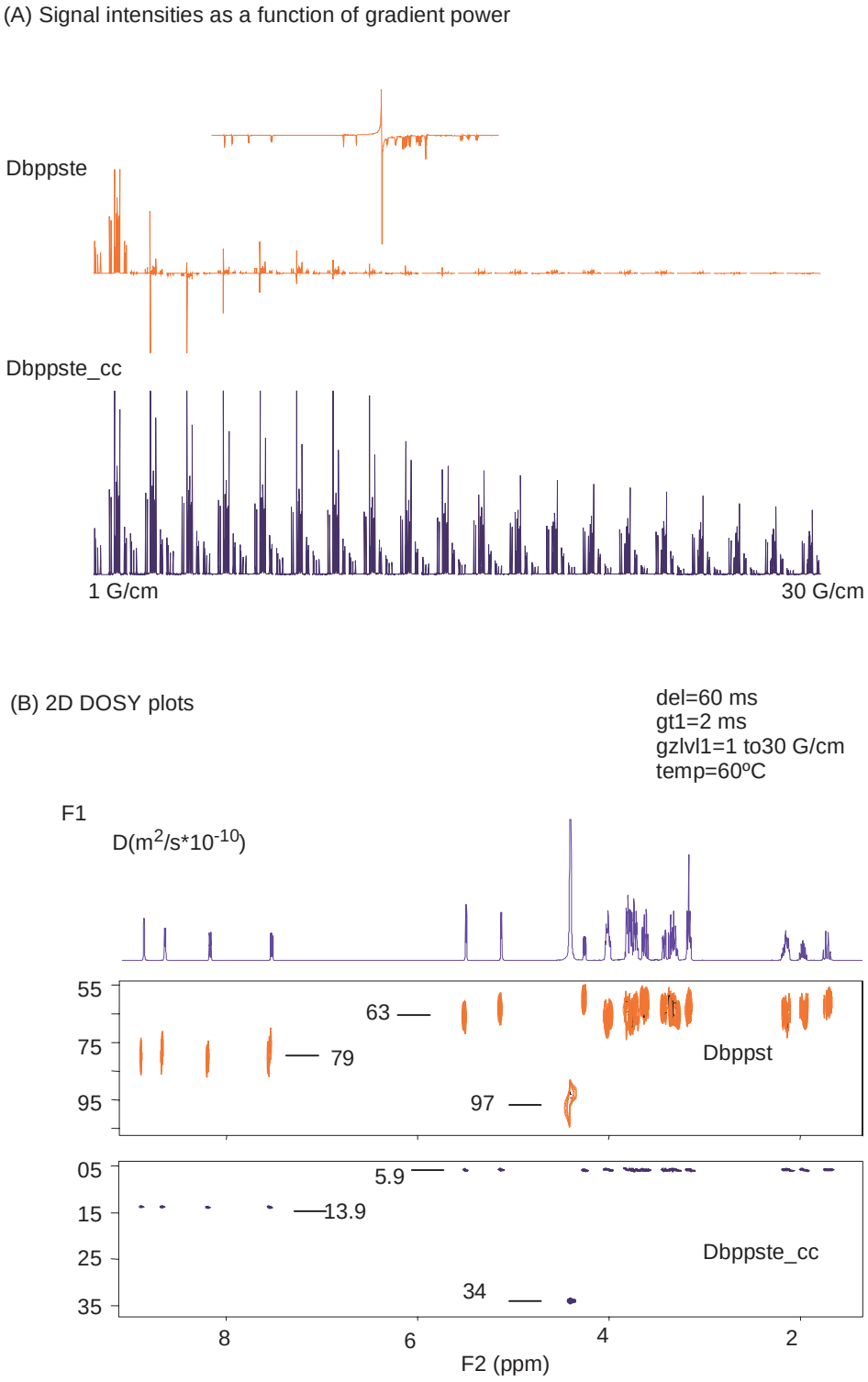

Figure 51. Signal Intensities and 2D DOSY Plots of the Nicotinic Acid Amid-Amikacin Mixture at 60ºC.

10.9 Processing 2D-DOSY Experiments

- "Processing Steps," page 184
- "Correcting Systematic Gradient Errors," page 184
- "Extracting Spectra," page 184
- "Displaying Integral Projection," page 185
- "DOSY Processing Buttons.," page 185

Do not process the data with the `dosy` macro until the acquisition is complete.

Processing Steps

The buttons for processing DOSY data are described in "DOSY Processing Buttons.," page 185. Process the acquired DOSY data to give a 2D DOSY spectrum as follows:

1. Click on the **Calculate Full DOSY Spectrum** button to extract the diffusion data from the spectra and synthesis of a 2D DOSY spectrum with the macro `dosy`.

   Refer to "Calculate Full DOSY Spectrum," page 186 for a description and limitations of data processing. The two-dimensional DOSY display (and plot) is constructed by taking the band shape of a given signal from the first (lowest gradient area) spectrum. The shape is then convoluted in a second dimension with a Gaussian line centred at the calculated diffusion coefficient. The linewidth is determined by the estimated error of the diffusion coefficient as obtained from the fitting process.

2. The following steps, although not required, are recommended:

   a. Click on either the **Fiddle (TMS)** and **Fiddle (no TMS)** button if there is a suitable reference line that slowly diffuses.

   b. Click on the **Basline Correct All Spectra** button to apply baseline correction using the macro `fbc`.

Correcting Systematic Gradient Errors

1. Set the display/threshold parameters to select a few strong, well-resolved signals known to arise from single species, i.e., the signals are not composites of overlapping signals from species with different diffusion coefficients.:

2. Click **Recall Original NMR Data**.

3. Check the **Calibration Flag** checkbox.

   The analysis uses the shapes of the decay curves in the first analysis to correct for systematic errors. Set `calibflag` back to 'n' to stop using the internal gradient calibration.

4. Click **Calculate full DOSY Spectrum (with dialog)** (or type `undosy calibflag='y' dosy`).

   If the initial DOSY run was used with a dialog (prune argument), the same increments must be deleted in the second run, using **Calculate full DOSY with dialog** (`undosy calibflag='y' dosy('prune')`) and specifying the same increment number(s).

Extracting Spectra

Extract spectra of the mixture components separated along the diffusion axis as follows:

1. Select the region of interest using the two cursors in the interactive 2D display (`dconi`) mode.
2. Click on **Proj** (projection).
3. Click on **Hproj**(sum) (horizontal projection).
4. Plot using the Plot menu.

Displaying Integral Projection

Displays the integral projection of a DOSY data set onto the diffusion axis as follows:

1. Copy the data to a second experiment.
2. Join the experiment with the copy of the original data.
3. Enter **`sdp`** on the command line

   The macro `sdp` (show diffusion projection) displays the integral projection of a DOSY data set onto the diffusion axis. The macro uses the file `userdir+'/Dosy/diffusion_spectrum'` as input for the `sdp` command. The macro modifies parameters such as `sw`, `at`, etc.

DOSY Processing Buttons.

- "Fiddle (TMS) and Fiddle (no TMS)," page 185
- "Basline Correct All Spectra," page 186
- "Calculate Full DOSY Spectrum," page 186
- "Calculate full DOSY with dialog," page 186
- "Calculate partial DOSY spectrum," page 186
- "Calculate partial DOSY with Dialog," page 187

Processing tools for 2D DOSY data are on the DOSY Process page, see Figure 52.

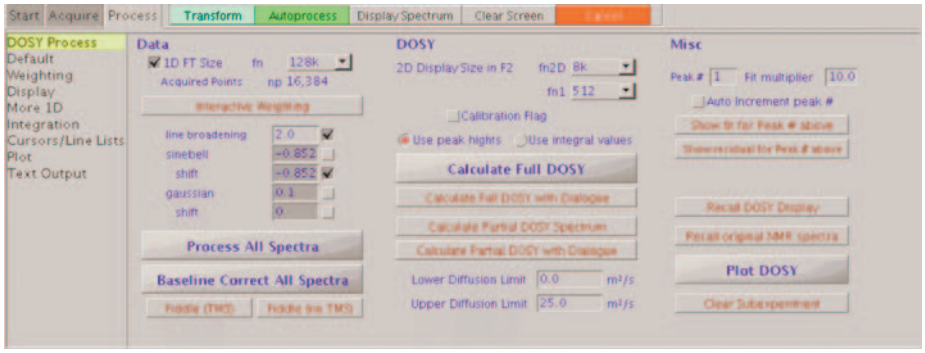

Figure 52. DOSY Processing Tab and Pages

Fiddle (TMS) and Fiddle (no TMS)

The `fiddle` program enables reference deconvolution to correct the line shapes, frequencies, phases, etc. of the signals caused by instrumental imperfections and systematic errors caused by the disturbance of the magnetic field and field/frequency lock caused by gradient pulses. Use `fiddle` with the `writefid` option to store the corrected data, recall the corrected data, and set all the weighting parameters to `n` before Fourier transforming and proceeding to the next step.

Basline Correct All Spectra

Applies `bc` type baseline correction (`fbc` macro) to all spectra in an array. Use the partial integral mode to set integral regions to include all significant signals. Leave blank as large an area of baseline as possible; this minimizes systematic errors in diffusion coefficient fits caused by baseline errors.

Calculate Full DOSY Spectrum

Applies the commands `dll` and `fp` macros to determine the heights of all signals above the threshold defined by the parameter `th`. The decay curve for each signal is fit to a Gaussian using the program `dosyfit`.

The `dll` program is limited to handling 512 lines, so very crowded spectra must be processed in sections by appropriately choosing `sp` and `wp`. `dosy` then runs the command `ddif` to synthesize the 2D DOSY spectrum.

A summary of all diffusion coefficients, estimated standard errors, and other results are stored in the `$HOME/vnmrsys/Dosy` directory:

- diffusion_display.inp (a second copy is stored in the current experiment)
- general_dosy_stats
- calibrated_gradients
- fit_errors
- diffusion_spectrum

The peak representation and the accuracy of the peak heights might increase with higher digital resolution, i.e., zero-filling the FIDs (`fn>np`) can occasionally improve the quality of the DOSY data. In extreme cases, even `fn=512k` is allowed by the software. Building up a 2D data set (and a 2D display) with this data size would not make sense; therefore a new parameter, `fn2D` (with a maximum limit of 64k), is introduced in the 2D-DOSY sequences, replacing `fn` when setting up the 2D display.

The 2D DOSY display is set up in the same experiment where the data processing takes place. The synthesized spectrum contains `fn1/2` traces in the diffusion domain (`f1`), and `fn2D` real data points in the spectral domain (`f2`); `fn1` is limited to the range 128-1024. Normally `fn2D` of 16k suffices. If `fn2D*fn1` is too large, spectral synthesis and display slows down and/or out of disk space exhausted.

The variable `ni` is set to `fn1/2` (this setting is required by `dconi`) after displaying a 2D spectrum. `ni` must be back to zero if more data is to be acquired or the sequence is to be displayed (`dps`). The Calculate Full DOSY Spectrum button defaults to uses all the experimental spectra and covers the whole diffusion range seen in the experimental peaks. Three auditioning processing buttons are provided.

Calculate full DOSY with dialog

Start a dialog to allow one or more spectra to be omitted from the analysis – calls `dosy('prune')`

Calculate partial DOSY spectrum

`d1` and `d2` are numbers causing the diffusion range of the synthesized spectrum to be limited to $d1*10^{-10}$ m^2/sec and $d2*10^{-10}$ m^2/sec — calls `dosy(d1,d2)`

Calculate partial DOSY with Dialog

Combine the previously described arguments; `dosy('prune',d1,d2)`. The message *Systematic Gz deviations* indicates that the random errors in the data are sufficiently small that it may be worthwhile to correct for the small systematic errors in the field gradients produced by the spectrometer hardware. This is done by using the decay curves of selected signals to provide an internal calibration of the relative gradient strengths.

10.10 Absolute value 3D-DOSY

DOSY-COSY (Dgcstecosy) and DOSY-HMQC (Dgcstehmqc) add diffusion encoding to the COSY or HMQC experiments to create 3D DOSY sequences. An arrayed set of 2D experiments is run using different values of gradient strength (gzlvl1). The data processed and the 1st 2D spectrum are used to define 2D integral regions manually, followed by the dosy analysis. The dosy analysis fits the integral volumes in successive increments to Gaussians and synthesizes 2D integral projections of the 3D data set.

Setting up absolute value 3D-DOSY experiments

1. Set up the pulse width, transmitter offset, spectral window, etc., required parameters for a COSY or HMQC experiment. Determine suitable lower and upper bounds for the gradient strength gzlvl1.

   Using the 1st increment from a 2D run is adequate.

   - A COSY experiment with higher quantum filter (`qlvl>1`) contains no signal in the first increment.

   a. Set `d2` to a value between 0.05 and 0.1 during the gradient optimization process.

   b. Set d2 back to 0 before starting the 3D-DOSY experiment.

2. Click on the **Setup coarse gradient array** button to set up an array of trial `gzlvl1` values or enter **`setup_dosy`** on the command line.

3. Set the number of increments from the lowest and to the strongest diffusion strength

4. Click on the "**Setup DOSY using conditions above**" button in the Pulse Sequence panel (Figure 53)

   The total experiment time is determined by the number of gzlvl1 values, ni, and nt.

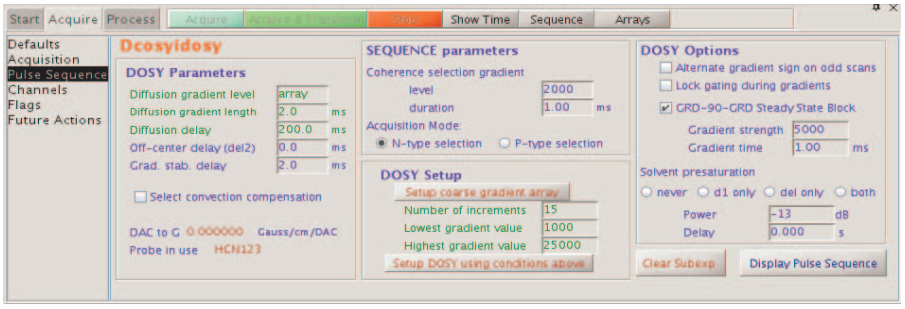

Figure 53. Absolute Value 3D-DOSY Pulse Sequence Panel

Dgcstecosy (DOSY Gradient Compensated Stimulated Echo AV COSY)

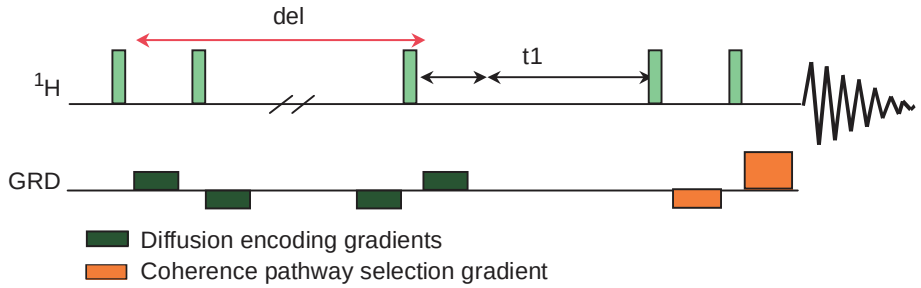

Figure 54. DOSY Gradient Compensated Stimulated Echo AV COSY

Table 20. Dgcstecosy Parameters

Parameter	*Description*
`delflag`	'y' runs the Dbppste sequence 'n' runs the normal s2pul sequence
`del`	the actual diffusion delay
`gt1`	total diffusion encoding pulse width
`gzlvl1`	diffusion encoding pulse strength
`gstab`	gradient stabilization time (~0.0002-0.0003 sec)
`tweek`	tuning factor to limit eddy currents, (can be set from 0 to 1, usually set to 0.0)
`gzlvl2`	gradient power for pathway selection
`gt2`	gradient duration for pathway selection
`sspul`	flag for a GRD-90-GRD homospoil block
`gzlvlhs`	gradient level for sspul
`satmode`	'yn' turns on presaturation during satdly; 'yy' turns on presaturation during satdly and del; the presaturation happens at the transmitter position (set tof right if presat option is used)
`satdly`	presaturation delay (part of d1)
`satpwr`	presaturation power
`hsgt`	gradient duration for sspul
`alt_grd`	flag to invert gradient sign on alternating scans (default = 'n')
`lkgate_flg`	flag to gate the lock sampling off during the diffusion sequence
`qlvl`	quantum filter level (1=single quantum, 2=double quantum)
`DAC_to_G`	parameter to store the gradient calibration value (set by setup_dosy)

The diffusion gradients (`gt1`) must be synchronized with sample spinning when using a nano probe: `gt1=1.0/srate*(trunc((gt1*srate)+0.5))` where `srate` is the sample spinning speed.

Process N-type data with `wft2d(1,0,0,1)`, optional: add the ('`t2dc`') argument to `wft2d`.

Reference: Wu, D.; Chen, A.; Johnson, C.S.,Jr., *J. Magn. Res*. 1996, **121**, (Series A), 88-91.

Dgcstehmqc (DOSY Gradient-Compensated Stimulated Echo HMQC AV mode)

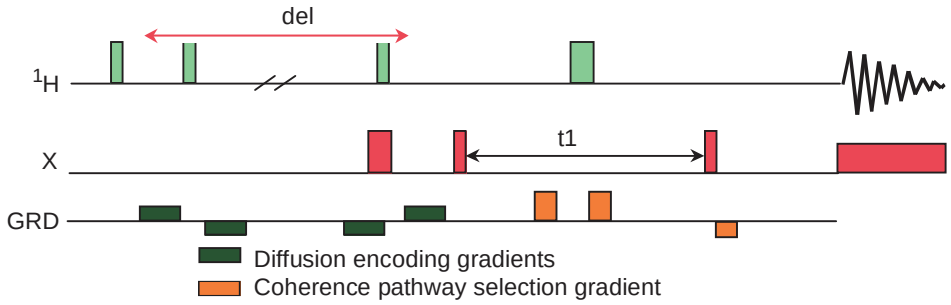

Figure 55. DOSY Gradient-Compensated Stimulated Echo HMQC AV Mode

Table 21. Dgcstehmqc Parameters

Parameter	*Description*
`delflag`	'y' runs the Dgcstehmqc sequence 'n' runs the normal s2pul sequence
`del`	the actual diffusion delay
`gt1`	total diffusion encoding pulse width
`gzlvl1`	diffusion encoding pulse strength
`gt2`	coherence pathway selection gradient length in HMQC
`gzlvl2`	gradient power for gt2
`gt3`	refocusing gradient length in HMQC
`gzlvl3`	gradient power for gt4
`gstab`	gradient stabilization time (~0.2-0.3 ms)
`sspul`	flag for a GRD-90-GRD homospoil block
`gzlvlhs`	gradient level for sspul
`hsgt`	gradient duration for sspul
`alt_grd`	flag to invert gradient sign on alternating scans (default = 'n')
`lkgate_flg`	flag to gate the lock sampling off during gradient pulses
`pwx`	90 deg. X-pulse
`pwxlvl`	power level for pwx
`j1xh`	one-bond H-X coupling constant
`jnxh`	multiple-bond H-X coupling constant (for mbond =’y')
`mbond`	flag to select multiple-bond correlations (HMBC)
`c180`	flag to make the 180 deg. X-pulse a composite pulse
`satmode`	presaturation flag 'yn' activates presat during satdly; 'yy' activates presat during satdly and del
`satfrq`	saturation frequency
`satdly`	saturation delay
`satpwr`	saturation power
`phase`	1 – selects N-type transitions 2 – selects P-type transitions

The diffusion gradients (`gt1`) must be synchronized with sample spinning when using a nano probe: `gt1=1.0/srate*(trunc((gt1*srate)+0.5))` and the gradients `gt2=gt3=gt4=1.0/srate*(trunc((gt2*srate)+0.5))` where srate is the sample spinning speed.

Process:

N-type data (phase=1) with `wft2d('t2dc')`
Process P-type data (phase=2) with `wft2d('t2dc','ptype')`

Reference: H. Barjat, G. A. Morris and A. Swanson: *JMR*, **131**, 131-138 (1998)

Calibrate the coherence pathway selection gradients for the probe and gradient amplifier before using the sequence for the first time. Low levels of decoupler power will cause sample heating and generate convection currents. Select an efficient decoupling method for the DOSY-HMQC experiment. Adiabatic decoupling schemes for the X channel such as WURST and STUD have worked well.

10.11 Processing Absolute Value 3D-DOSY data

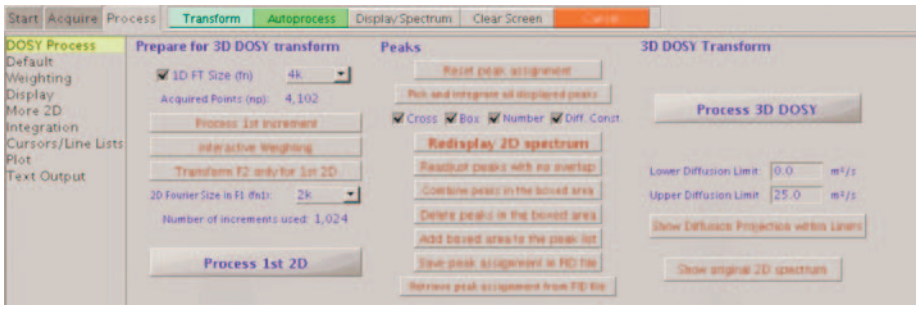

Figure 56. Absolute Value 3D-DOSY Process Panel

1. Save the DOSY FID and retrieve it before continuing.
2. Define the individual signal regions in the 2D spectrum manually:
   a. Fourier transform the first increment of the 3D data set (i.e., that with the lowest gzlvl1 value), using proper weighting functions in both dimensions:

      `wft2d(1)` for COSY

      `wft2d(1)` for phase=1 and `wft2d('ptype',1)` for phase=2 for HMQC

   b. Set vs2d and th properly.

      Click on the **Process** tab.

   c. Select the **DOSY Process** panel, see Figure 56.

      Define the signal regions in the first spectrum using the standard `ll2d` command and its options (`reset`, `volume`, `clear`, `combine`, etc.)

      Include all the components of a given multiplet (cross-peak) in a single signal region and exclude contamination by other signals. This grouping maximizes the signal-to-noise ratio available for data fitting and makes it possible to exclude spectral artefacts (t1-noise, decoupling sidebands, spurious peaks, etc.) from the DOSY analyses.

   d. Click on the **Save peak assignment in FID file** button.

This will save the peak selections. The DOSY FID must be saved and retrieved for processing in step 1. The parameter file will contain the full filename of the stored FID if it was stored and retrieved.

3. Click on the **Process 3D DOSY** button or enter **`dosy`** on the command line.

   The macro determines the volume of each region and value of gzlvl1 and fits the volumes as functions of gzlvl1. Process data is displayed with each signal region labelled with its diffusion coefficient (10-10 m2/sec) and standard error in brackets.

4. Display the coefficients using the label facility of the `ll2d` command.

   A label of `6.05(0.05)` indicates a diffusion coefficient of: $6.05*10^{-10}$ m_2/sec (+/- $0.05*10^{-10}$ m^2/sec).

   The 2D spectrum on which the display is based is the first 2D increment of the 3D experiment. The diffusion results are saved in the file `userdir+/Dosy/diffusion_display_3D.inp`. Data is presented in 3 columns: the peak number (as obtained by `ll2dmode='nynn'`), the diffusion coefficient, and the standard error.

5. Use the `ll2dmode` parameter (for details see the *Command and Parameter Reference* Manual and Figure 49) to control the display of diffusion coefficients and reduce crowding of the display, which makes the analyses easier.

6. Copy the data to an available experiment other than exp5 and use `sdp` (macro overwrites the data in the current experiment) to obtain the integral projection of the 3D data set onto the diffusion axis.

   This diffusion spectrum can be used to choose suitable diffusion regions for which to examine 2D projections of the 3D DOSY data.

7. Join the experiment containing the 3D data.

8. Use the 3D DOSY Transform tools on the DOSY Process page, see Figure 56:

   a. Enter a value in the Lower Diffusion Limit: field.

   b. Enter a value in the Upper Diffusion Limit: field.

   c. Click on the **Show Diffusion Projection within Limits** button to display the resulting projections.

   d. Click on **Show original 2D spectrum** to return to the original 2D spectrum; start over with new upper and lower diffusion limits if needed.

9. Optional command line procedure:

   a. Enter **`makeslice(d1,d2)`** on the command line.

      The diffusion limits are `d1` and `d2` (in units of 10-10 m2/s) between which the 2D projection of the 3D DOSY spectrum is required. The `makeslice` command uses the diffusion information in the file: `userdir+'/Dosy/diffusion_display_3D.inp'`.

   b. Enter **`showoriginal`** on the command line to return to the original spectrum. This reverts to the original 2D spectrum for the first value of gzlvl1.

   c. Repeat step a and step b as needed with different diffusion values (or slice thickness).

10.12 Phase Sensitive 3D-DOSY

The Dgcstehmqc_ps and the Dbppste_ghsqcse pulse sequences are optimized for ^{15}N-labeled peptide and protein samples. The cancellation of ^{14}N or ^{12}C - bound protons in natural abundance is not optimal.

Setting Up Phase Sensitive 3D-DOSY Experiments

1. Set the conventional parameters: pulse width, transmitter offset, spectral window etc., correctly.
2. Optimize the `alfa`, `rof2` (and on VNMRS systems the `ddrtc`) delays for ideal baseline performance.
3. Determine suitable lower and upper bounds for the gradient strength `gzlvl1`.

   There is no need to run 2D NMR experiments for this purpose. Use the 1st increment from a 2D run.
4. Press the **Setup coarse gradient array** button (or use the `setup_dosy` macro) to set up an array of trial `gzlvl1` values.
5. Set the number of increments covering the lowest to the strongest diffusion strength.
6. Click on the **Setup DOSY using conditions above** button in the Pulse Sequence panel; see Figure 57.

   The total experiment time depends upon the number of gzlvl1 values, ni, and nt.
7. Set **phase=1,2**.

   Phase sensitive 3D DOSY sequences require the simultaneous arraying of gzlvl1 and phase. Data acquisition in the VNMR software is fully compatible with a double array.
8. Set up phase sensitive 3D DOSY experiments in either of the following ways to facilitate easy data processing:
   - Set up, run, and save each phase sensitive of the 2D FIDs, one for each gzlvl1 value. All parameters must be the same, apart from gzlvl1.
   - Set up the double phase, gzlvl1 array with `array=gzlvl1,phase`. This setup is simpler but requires an extra step with data processing (see "Processing Phase-Sensitive 3D-DOSY Data," page 195).

The VNMRJ Pulse Sequence panel of the phase-sensitive 3D-hmqcidosy pulse sequence is shown in Figure 57.

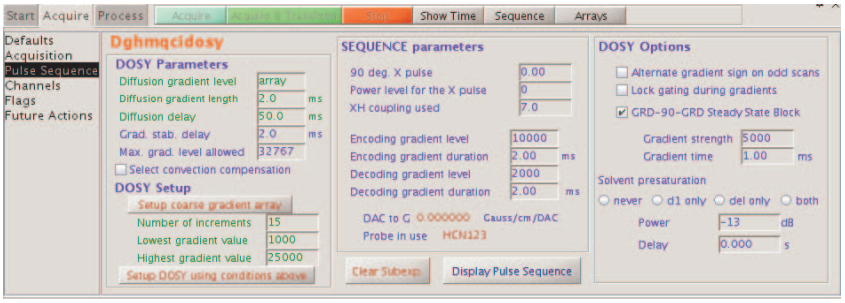

Figure 57. Pulse Sequence Panel for the 3D-hmqcidosy pulse sequence

Dgcstehmqc_ps (DOSY Gradient-Compensated Stimulated Echo HMQC)

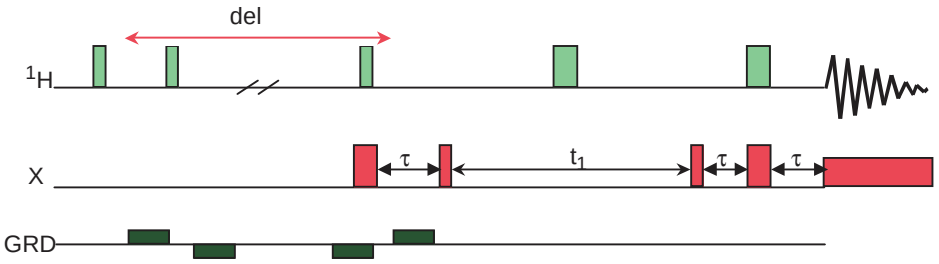

Figure 58. DOSY Gradient-Compensated Stimulated Echo HMQC, Phase Sensitive

Table 22. Dgcstehmqc_ps Parameters

Parameter	*Description*
`del`	the actual diffusion delay
`gt1`	total diffusion encoding pulse width
`gzlvl1`	diffusion encoding pulse strength
`gstab`	gradient stabilization delay
`pwx`	90 deg. X-pulse
`pwxlvl`	power level for pwx
`j1xh`	one-bond H-X coupling constant
`c180`	flag to make the 180 deg. X-pulse a composite pulse
`satmode`	flag for optional solvent presaturation 'ynn' - does presat during satdly 'yyn' - does presat during satdly and the diffusion delay
`satdly`	presaturation delay before the sequence (part of d1)
`satpwr`	saturation power level
`satfrq`	saturation frequency
`alt_grd`	alternate gradient sign(s) for odd scans
`lkgate_flg`	flag to gate the lock sampling off during the diffusion sequence
`sspul`	flag for a GRD-90-GRD homospoil block
`gzlvlhs`	gradient level for sspul
`hsgt`	gradient duration for sspul
`phase`	1,2 for States-Haberkorn acquisition

The diffusion gradients (`gt1`) must be synchronized with sample spinning when using a nano probe: `gt1=1.0/srate*(trunc((gt1*srate)+0.5))` where `srate` is the sample spinning speed.

Run the phase sensitive 2D HSQC spectra in separate experiments and process the data with the dosy3Dps macro.

Dbppste_ghsqcse (Bipolar Pulse Pair Stimulated Echo Gradient HSQC, Sensitivity-Enhanced)

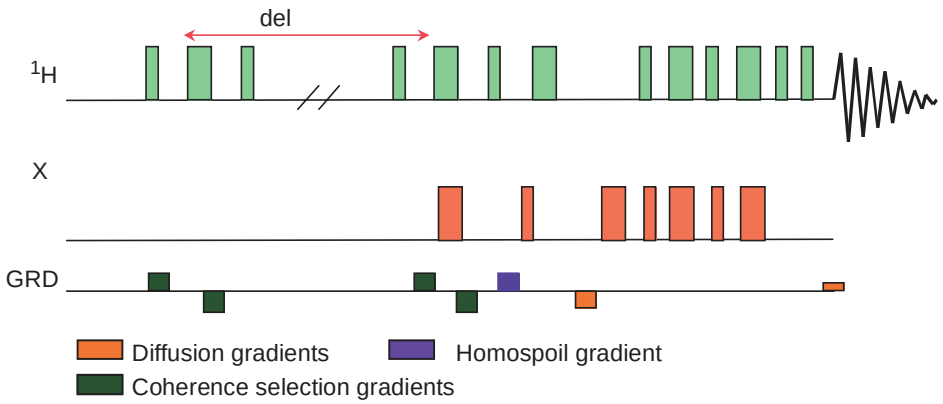

Figure 59. Bipolar Pulse Pair Stimulated Echo Gradient HSQC, Sensitivity-Enhanced

Table 23. Dbppste_ghsqcse Parameters

Parameter	*Description*
d1	relaxation delay
pw	90 degrees 1H pulse
tpwr	1H pulse power
pwx	90degrees X pulse
pwxlvl	X pulse power level
j1xh	1JXH in Hz (140 for 1H-13C)
xhn	2, 1 or 3 flag for signal selection in reverse INEPT sensitivity enhancement factors for different X-multiplicities against normal gHSQC:

Flag	CH enhancement	CH enhancement	CH3 enhancement
1	2.0	1.0	1.0
2	1.71	1.41	1.21
3	1.5	1.37	1.25

sspul	flag for a GRD-90-GRD homospoil block
gzlvlhs	gradient level for sspul
hsgt	gradient duration for sspul
gzlvl2	1st gradient amplitude
gt2	1st gradient time in seconds
gzlvl3	2nd gradient amplitude
gt3	2nd gradient time in seconds
gstab	delay for stability (~ 0.0003 seconds)
edit	'y' makes multiplicity selection (CH & CH3 same sign CH2s opposite sign)
f1180	flag to set initial delay for t1 for phase (-90,180)
satmode	'y' or 'n' turns presat on or off

Table 23. Dbppste_ghsqcse Parameters

Parameter	*Description*
`satfrq`	transmitter frequency for presat
`satpwr`	transmitter power for presat
`satdly`	duration of presaturation in seconds
`del`	diffusion delay
`gzlvl1`	gradient level for diffusion
`gt1`	gradient duration for gzlvl1
`alt_grd`	flag to invert diffusion gradient sign on alternating scans (default = 'n')
`lkgate_flg`	flag to gate the lock sampling off during the diffusion sequence

The diffusion gradients (`gt1`) must be synchronized with sample spinning when using a nano probe: `gt1=1.0/srate*(trunc((gt1*srate)+0.5))` where `srate` is the sample spinning speed.

Run the phase sensitive 2D HSQC spectra in separate experiments and process the data with the dosy3Dps macro.

Reference: S. Rajagopalan, C. Chow, V. Vinodhkumar, C. G. Fry and S. Cavagnero; *J. Biomol. NMR*. **29**.505-516, 2004.

10.13 Processing Phase-Sensitive 3D-DOSY Data

Figure 60 shows the VNMRJ DOSY Process panel of the phase sensitive 3D-DOSY sequences.

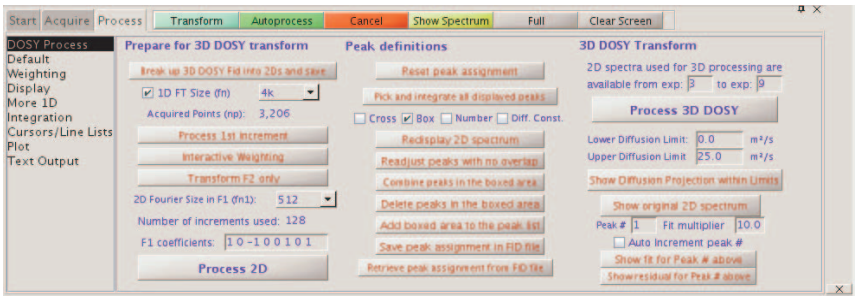

Figure 60. DOSY Process panel of the phase sensitive 3D-DOSY

Pre-Processing

Simultaneously Arrayed Data

Phase-sensitive data acquired with a simultaneous array of the parameters phase and gzlvl1 require unpacking of the single complex FID before DOSY processing as follows:

1. Load the FID into any available experiment (other than exp5).
2. Click on the **Process** tab.
3. Select the **DOSY-Process** panel.

4. Press the **Break up 3D DOSY Fid into individual 2Ds and save** button (see Figure 60) or enter **`unpack_DOSY3Dps`** on the command line.

   The 2D FIDs are automatically saved in the `~/Unpacked_DOSY3D_FIDs` directory under the sequence name and a serial number in the order of the diffusion gradient levels.

5. Continue with "Processing Data from a 3D DOSY Experiment," page 196.

Phase-Sensitive Data Acquired by Gradient Level

1. Save each phase-sensitive 2D data acquired for each diffusion gradient level separately.
2. Continue with "Processing Data from a 3D DOSY Experiment," page 196.

Processing Data from a 3D DOSY Experiment

1. Load separate 2D FIDs into subsequent experiments (for example, in experiments 10-15 if 6 different `gzlvl1` values were used).
2. Join each experiment and process the data individually (`wft2da`).

   Use the same processing conditions: window functions, data size etc., for each data set.
3. Join the experiment with the weakest gradient value.
4. Define the cross peaks and do volume integration using the integration, deleting, selecting, or combining cross peaks tools from the DOSY Process panel.
5. Set the `startexp` to the experiment numbers with the weakest diffusion power.
6. Set the `lastexp` parameters to the experiment numbers with the strongest diffusion power.
7. Click on the **Process** tab.
8. Select the **DOSY-Process** panel.
9. Click on the **Process 3D DOSY** button or enter **`dosy3Dps`** on the command line.

   The original 2D with the weakest gradient is displayed with the individual diffusion coefficients and their standard deviation at the end of the processing in `startexp`.

10.14 IDOSY (Inclusive DOSY)

There are three strategies for creating a DOSY pulse sequence:

- placing the diffusion encoding first (DOSY-X)
- placing the diffusion encoding last (X-DOSY)
- incorporating the diffusion encoding internally (X-IDOSY).

Most published pulse sequences before 2006 have been X-DOSY or DOSY-X types.The IDOSY approach can be simpler, quicker and more sensitive where the parent pulse sequence either includes or can accommodate a diffusion delay Δ of a few tens of ms. Absolute value COSY-IDOSY and 2DJ-IDOSY sequences incorporate the diffusion encoding in the Hahn echo (or anti-echo) and spin echo, respectively. The coherence transfer pathways are identical to those in the parent experiment in both cases. Long-range

HMQC allows the incorporation of two separate diffusion weighting segments to form an HMQC-IDOSY sequence.

As the magnetization is transverse during the diffusion delays, there is an inherent possibility for convection compensation with no sensitivity loss at all. I-DOSY sequences provide this option by setting the `convcomp` ='y'.

Dcosyidosy - (COSY-IDOSY)

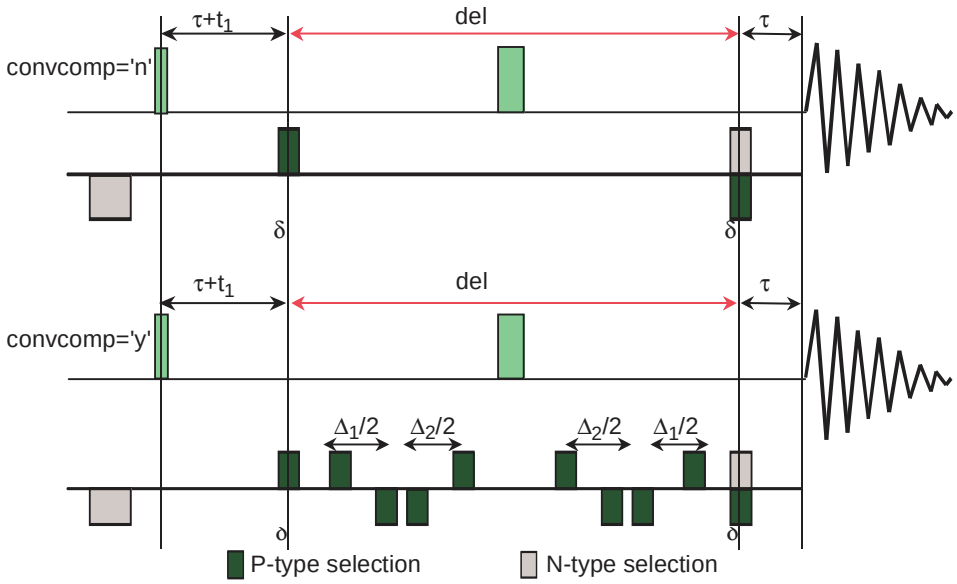

Figure 61. Dcosyidos (COSY-IDOSY) Pulse Sequence

Table 24. Dcosyidosy Parameters

Parameter	*Description*
`del`	the actual diffusion delay.
`gt1`	total diffusion-encoding pulse width.
`gzlvl1`	diffusion gradient amplitude
`gt1`	gradient duration in seconds (0.001)
`gzlvl2`	coherence selection gradient amplitude
`gt2`	gradient duration in seconds (0.001)
`gstab`	optional delay for stability
`alt_grd`	flag to invert gradient sign on alternating scans (default = 'n')
`lkgate_flg`	flag to gate the lock sampling off during the diffusion sequence
`del2`	delay parameter that can shift the convection compensation sequence elements off the center of the pulse sequence allowing running a velocity profile– can also be negative but in absolute value cannot exceed del/2 minus the gradient and gradient-stabilization delays (default value for diffusion measurements is zero)
`satmode`	'yn' turns on presaturation during satdly 'yy' turns on presaturation during satdly and del the presaturation happens at the transmitter position (set tof right if presat option is used)

Table 24. Dcosyidosy Parameters

Parameter	*Description*
satdly	presaturation delay (part of d1)
satpwr	presaturation power
sspul	flag for a GRD-90-GRD homospoil block
gzlvlhs	gradient level for sspul
hsgt	gradient duration for sspul
phase	1 (selects echo N-type coherence selection; default) 2 (selects anti-echo P-type coherence selection)
convcomp	'y': selects convection compensated cosyidosy 'n': normal cosyidosy

The diffusion gradients (gt1) must be synchronized with sample spinning when using a nano probe: gt1=1.0/srate*(trunc((gt1*srate)+0.5)) where srate is the sample spinning speed.

Processing (the ('t2dc' argument for wft2d is a useful option):

N-type data with wft2d(1,0,0,1)

P-type data with wft2d(1,0,0,-1)

Reference: Nilsson M, Gil AM, Delgadillo I, Morris GA. *Chem. Comm*. 2005, 1737-1739.

Dhom2djidosy - (Homonuclear 2D J-resolved IDOSY)

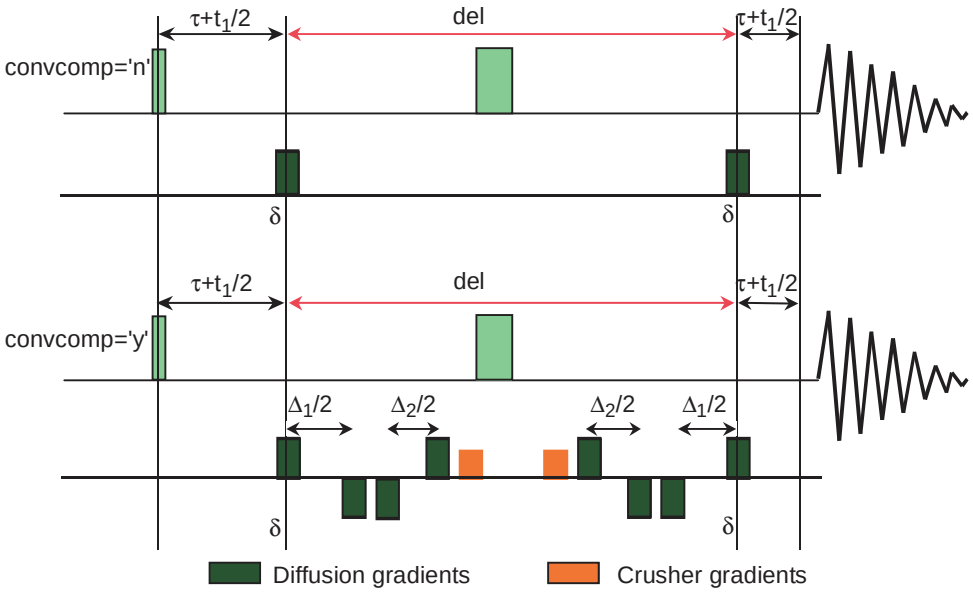

Figure 62. Dhom2djidosy - (Homonuclear 2D J-resolved IDOSY)

Table 25. Dhom2djidosy Parameters

Parameter	*Description*
del	the actual diffusion delay
del2	delay parameter that can shift the convection compensation sequence elements off the center of the pulse sequence allowing running a velocity profile – can also be negative, but in absolute value cannot exceed del minus the gradient and gradient-stabilization delays (default value for diffusion measurements is zero)
gt1	total diffusion-encoding pulse width
gzlvl1	diffusion encoding gradient power
gzlvl2	gradient amplitude of the crusher gradients flanking the p1 pulse
gt2	gradient duration for gzlvl2
gstab	optional delay for stability
pw	90 degree xmtr pulse
p1	180 degree xmtr pulse
satmode	'yn' turns on presaturation during satdly 'yy' turns on presaturation during satdly and del the presaturation happens at the transmitter position (set tof right if presat option is used).
satdly	presaturation delay (part of d1)
satpwr	presaturation power
alt_grd	flag to invert gradient sign on alternating scans (default = 'n').
lkgate_flg	flag to gate the lock sampling off during gradient pulses
sspul	flag for a GRD-90-GRD homospoil block
gzlvlhs	gradient level for sspul
hsgt	gradient duration for
sspul nt	multiple of 1 (minimum) multiple of 16 (maximum and recommended)
convcomp	'y': selects convection compensated cosyidosy 'n': normal cosyidosy

The diffusion gradients (gt1) must be synchronized with sample spinning when using a nano probe: gt1=1.0/srate*(trunc((gt1*srate)+0.5)) where srate is the sample spinning speed.

Reference: Nilsson M, Gil AM, Delgadillo I, Morris GA. *Anal Chem.*, 2004;**76**:5418-5422

Dghmqcidosy - (Gradient HMQC-IDOSY)

This DOSY sequence is applicable for long-range couplings and is phase-sensitive. This pulse sequence requires that 1/(2*j1xh) > del, i.e. the transfer delay is longer than the diffusion delay.

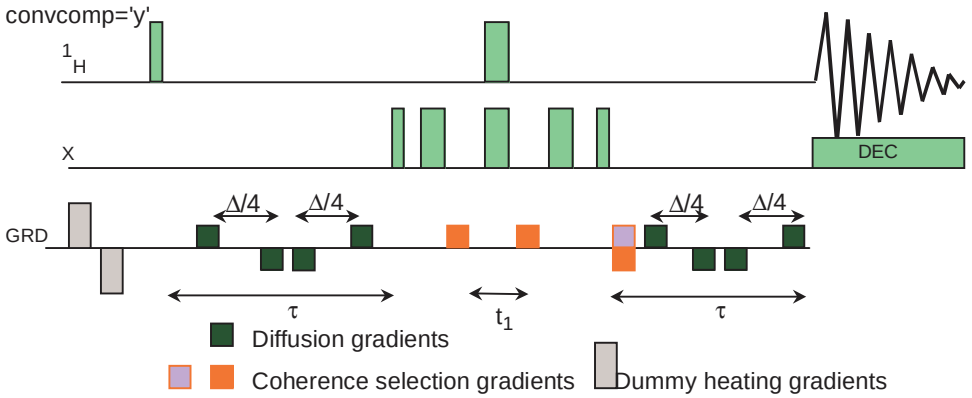

Figure 63. Dghmqcidosy - (Gradient HMQC-IDOSY)

Table 26. Dghmqcidosy Parameters

Parameter	*Description*
`del`	the actual diffusion delay.
`gt1`	total diffusion-encoding pulse width.
`gzlvl1`	gradient amplitude (-32768 to +32768)
`gzlvl2`	dephasing gradient amplitude for HMQC
`gt2`	gradient duration in seconds (0.002)
`gzlvl3`	rephasing gradient amplitude for HMQC
`gt3`	gradient duration in seconds (0.002)
`gzlvl_max`	maximum gradient power 2048 for Performa I 32768 for Performa II, IV, and Triax.
`gstab`	optional delay for stability
`pwx`	90 deg. X-pulse
`pwxlvl`	power level for pwx
`alt_grd`	flag to invert gradient sign on alternating scans (default = 'n')
`lkgate_flg`	flag to gate the lock signal during diffusion gradient pulses
`j1xh`	heteronuclear coupling for the `Xfer` delay
`satmode`	'yn' turns on presaturation during `satdly` 'yy' turns on presaturation during `satdly` and `del` the presaturation happens at the transmitter position (set `tof` right if presat option is used)
`satdly`	presaturation delay (part of d1)
`satpwr`	presaturation power
`sspul`	flag for a GRD-90-GRD homospoil block
`gzlvlhs`	gradient level for `sspul`
`hsgt`	gradient duration for `sspul`
`lkgate_flg`	flag to gate the lock signal during diffusion gradient pulses
`phase`	1,2 for phase-sensitive data
`convcomp`	'y': selects convection-compensated hmqcidosy 'n': normal hmqcidosy

The diffusion gradients (`gt1`) must be synchronized with sample spinning when using a nano probe: `gt1=1.0/srate*(trunc((gt1*srate)+0.5))` where `srate` is the sample spinning speed.

Reference: M.J. Stchedroff, A.M. Kenwright, G.A. Morris, M. Nilsson and R.K. Harris *Phys. Chem. Chem Phys.* **6**, 3221-3227 (2004).

10.15 Processing I-DOSY data

Process I-DOSY data using either of the following:

- "Processing Absolute Value 3D-DOSY data," page 190
- "Processing Phase-Sensitive 3D-DOSY Data," page 195

10.16 Sample FIDs to Practice DOSY Processing

Sample 2D and 3D FIDs are in `/vnmr/fidlib/Dosy` to practice DOSY processing.

- "Dbppste.fid," page 201
- "DgcsteSL.fid," page 202
- "DgcsteSL_dpfgse.fid," page 203
- "Dbppsteinept.fid," page 203
- "Dgcstecosy.fid," page 205
- "Dgcstehmqc.fid," page 207
- "Si29-1H_Dghmqcidosy.fid," page 208

Dbppste.fid

The sample is a mixture of three dipeptides (Phe-Val, Phe-Glu, and Phe-Gly) and 3 (trimethylsilyl)-1-propane-sulfonic acid dissolved in D_2O.

VnmrJ Processing via the DOSY Process Panel

1. Load the data file into the experiment.
2. Select line broadening and the gaussian window function.
3. Click on **Process All Spectra**.
4. Click on **Baseline Correct All Spectra**.
5. Deselect line broadening (keep only the gaussian window function).
6. Place the cursors on either side of the TMS line (including the satellites).
7. Click on **Fiddle(TMS)**.
8. Click on **Baseline Correct All Spectra**.
9. Select the threshold.
10. Click on **Calculate Full DOSY**.
11. Two zoom into the region of the dipeptides; set the lower and upper diffusion limits to 3.0 and 7.0 respectively.

12. Click on **Recall Original NMR data**.
13. Click on **Calculate Partial DOSY spectrum**.

Command Line Processing

1. Enter **`cd('/vnmr/fidlib/Dosy')`**.
2. Enter **`rt('Dbppste.fid')`**.
3. Select **`lb`** and **`gf`** then type **`wft`** and adjust the phase of the 1st spectrum.
4. Set the cursor to the TSP singlet.
5. Enter **`nl rl(0)`**.
6. Set the cursors 80 Hz either side of the TSP singlet.
7. Set **`lb='n'`** and **`gf=0.75`**
8. Enter **`fiddle('satellites','TMS')`**.

   Deconvolution of the data normalizes the lineshapes so that the peak heights in successive spectra accurately reflect the signal integrals.
9. Enter **`fbc`** to perform baseline correction.
10. Enter **`vs=500 th=3`** to set the threshold below the peaks of interest.
11. Enter **`dosy`**.
12. Enter **`undosy dosy(4,7)`** to zoom into the diffusion region of interest.

DgcsteSL.fid

The sample is a mixture of adenosine mono-, di-, tri-phosphate (AMP, ADP, ATP) and K_2HPO_4 in D_2O (pH=7). The data were acquired in a 3mm probe with direct ^{31}P observe.

VnmrJ Processing via the DOSY Process Panel

1. Select an experiment.
2. Load the **DgcsteSL.fid** into the current experiment.
3. Click on the **Process tab**.
4. Select the **DOSY Process panel**.
5. Click on the **Process All Spectra** button.
6. Click on the **Baseline Correct All Spectra** button.
7. Set the threshold.
8. Click on the **Calculate Full DOSY Spectrum** button.

Calculate a partial dosy spectrum if better resolution is required:

1. Click on the **Show original 2D spectrum** button and recall original NMR spectra.
2. Enter the upper diffusion limit in the field next to Upper Diffusion Limit:.
3. Enter the lower diffusion limit in the field next to Lower Diffusion Limit:.
4. Click on the **Show Diffusion Projection within Limits** button to display the resulting projections.

- Plotting: join another experiment; click on **Plot DOSY** to plot. Return to the previous experiment.

5. Click on **Show original 2D spectrum** to return to the original 2D spectrum; start over with new upper and lower diffusion limits if needed.

Command Line

1. Recall the FID: **`cd('/vnmr/fidlib/Dosy')`**.
2. Enter **`rt('DgcsteSL.fid')`**.
3. Enter **`lb=2 wft`**.
4. Enter **`fbc`** to do baseline correction.
5. Set the threshold.
6. Enter **`dosy`**.

Calculate a partial dosy spectrum if better resolution is required:

1. Enter **`undosy`** to recall original NMR spectra.
2. Select upper and lower diffusion limits.
3. Enter **`dosy(6.1,7.1)`** to calculate partial DOSY spectrum.
4. Join another experiment.
5. Enter **`sdp`**.

   Displays (and plots) the diffusion spectrum.

DgcsteSL_dpfgse.fid

This sample is a 0.2 mmolar 28 member polypeptide in a H_2O/D_2O 9:1 mixture with some low molecular weight impurities. This experiment is designed for studying the aggregation of the peptide, not to separate a mixture into components.

Process the data using the procedures for "DgcsteSL.fid," page 202. The experiment is an example of what water suppression quality can (needs to) be achieved when working with dilute samples in H_2O.

Dbppsteinept.fid

The sample is a mixture of sucrose, methyl-alfa-D-glucopyranosid, 1,3,5,-O- methylidene-mio-inosytol (dioxane added as internal reference) in D2O. The experiment was run using an AutoSwitchable gradient probe.

VnmrJ Processing via the DOSY Process Panel

1. Select an experiment.
2. Load the **Dbppsteinept.fid** into the current experiment.
3. Click on the **Process tab**.
4. Select the **DOSY Process panel**.
5. Uncheck box next to **all** of the weighting functions below the Interactive Weighting button.

6. Click on the **Process All Spectra** button.
7. Click on the **Baseline Correct All Spectra** button.
8. Enter **0.4** in the field next to line broadening and check box next to the field to activate **line broadening**.
9. Enter 0.7 in the field next to gaussian and check box next to the field to activate **gaussian**.
10. Expand the spectrum.
11. Place the cursors on either side, +/-15 Hz, of the most intense line (dioxane)
12. Click on **Fiddle(TMS)**.
13. Click on **Calculate Full DOSY**.
14. Click on **Recall original NMR spectra**.
15. Enter **2.0** for the lower diffusion limit in the field next to Lower Diffusion Limit:.
16. Enter **5.0** for the upper diffusion limit in the field next to Upper Diffusion Limit:.

Calculate a partial dosy spectrum if better resolution is required:

1. Click on **Calculate Partial DOSY spectrum**.

   Optional: Click on **Recall original NMR spectra** to return to the original 2D spectrum; start over with new upper and lower diffusion limits if needed.
2. Join an available experiment.
3. Click on **Recall DOSY Display** to display the results.

   Click on **Plot DOSY** to plot the results.

Command Line

1. Recall the FID: **`cd('/vnmr/fidlib/Dosy')`**.
2. Enter **`rt('Dbppsteinept.fid')`**.
3. Enter **`lb='n' gf='n'`**.
4. Enter **`wft`**.
5. Enter **`fbc`** to do baseline correction.
6. Enter **`lb=-0.4 gf=0.7`**.
7. Expand the spectrum.
8. Place the cursors on either side, +/-15 Hz, of the most intense line (dioxane)
9. Enter **`Fiddle`**.
10. Enter **`dosy`**.

Calculate a partial dosy spectrum if better resolution is required:

1. Enter **`undosy`** to recall original NMR spectra.
2. Enter **`dosy(2.0,5.0)`** to calculate partial DOSY spectrum.
3. Join another experiment.
4. Enter **`sdp`**.

   Displays (and plots) the diffusion spectrum.

Dgcstecosy.fid

The sample is a mixture of sucrose, methyl-alfa-D-glucopyranosid and 1,3,5,-O-methylidene- mio-inosytol in D_2O. The experiment was run using an AutoSwitchable gradient probe. By accident this cosy spectrum was run with an unusual parameter setting (`sw<>sw1`) and does not affect the DOSY processing.

VnmrJ Processing via the DOSY Process Panel

1. Select an experiment.
2. Load the **`Dgcstecosy.fid`** into the current experiment.
3. Click on the **Process** tab.
4. Select the **DOSY Process** panel.
5. Click on the **Process 2D** button.
6. Click on the **Retrieve peak assignment from FID file** button.
   The signal regions for this file were saved with the FID file.
7. Place a check in the box to the left of **Box**.
8. Remove any checks in the boxes to the left of **Cross**, **Number**, and **Diff.Cornst**.
9. Click on the **Redisplay 2D Spectrum** button.
10. Click on the **Process 3D DOSY Spectrum** button.
    The cosy spectrum is displayed with the cross peaks labelled with the diffusion coefficient and error bar.
    The crosspeaks of interest are:
    4.1-4.8 - 1,3,5,-O-methylidene-mio-inosytol
    3.6-3.9 - methyl-alpha-D-glucopyranosid
    2.8-3.1 - sucrose
    the 3 lines between 3.2 and 3.6 D (10-10 m2/sec) are overlapping diagonal peaks.
11. Rejoin the DOSY experiment.
12. Remove any checks in the boxes to the left of **Cross**, **Box**, **Number**, and **Diff.Cornst**.
13. Click on the **Redisplay 2D Spectrum** button.
14. Display the following projections:
    - **Inosytol**
      a. Enter **4.1** in the field next to Lower Diffusion Limit:.
      b. Enter **4.8** in the field next to Upper Diffusion Limit:.
      c. Click on the **Show Diffusion Projections within limits** button.
    - **Glucopyranosid**
      a. Click on the **Show original 2D spectrum** button.
      b. Enter **3.6** in the field next to Lower Diffusion Limit:.
      c. Enter **3.9** in the field next to Upper Diffusion Limit:.
      d. Click on the **Show Diffusion Projections within limits** button.
    - **Sucrose**

a. Click on the **Show original 2D spectrum** button.

b. Enter **2.8** in the field next to Lower Diffusion Limit**:**.

c. Enter **3.1** in the field next to Upper Diffusion Limit:.

d. Click on the **Show Diffusion Projections within limits** button.

Command LIne

1. Enter **`cd('/vnmr/fidlib/Dosy')`**.
2. Enter **`rt('Dgcstecosy.fid')`**.
3. Enter **`wft2d('t2dc',1)`**.
4. Enter **`ll2d('readtext',file+'/ll2d_text')`** to recall the `ll2d` file.
5. Enter **`ll2dmode='nnyn'`**.
6. Check the preset signal regions and verify that each cross peak of interest is boxed.
7. Enter **`dconi`**.
8. Enter **`dosy`**.

   The cosy spectrum is displayed with the cross peaks labelled with the diffusion coefficient and error bar.
9. Join another experiment.
10. Enter **`sdp`**.

    The crosspeaks of interest are:

    4.1-4.8 - 1,3,5,-O-methylidene-mio-inosytol

    3.6-3.9 - methyl-alpha-D-glucopyranosid

    2.8-3.1 - sucrose

    The 3 lines between 3.2 and 3.6 D (10-10 m2/sec) are overlapping diagonal peaks.
11. Rejoin the DOSY experiment.
12. Enter **`ll2dmode='nnnn'`** – resets the peak labels.
13. Enter **`dconi`** – displays the spectrum.
14. Display the following projections:

    - **Inosytol**

      Enter **`makeslice(4.1,4.8)`**; this sets the lower limit to 4.1 and upper limit to 4.8.
    - **Glucopyranosid**

    a. Enter **`showoriginal`** – recalls the original 2D

    b. Enter **`makeslice (3.6,3.9)`**; this sets the lower limit to 3.6 and upper limit to 3.9.

    - **Sucrose**

    a. Enter **`showoriginal`** – recalls the original 2D.

    b. Enter **`makeslice (2.8,3.1)`**; this sets the lower limit to 2.8 and upper limit to 3.1.

Dgcstehmqc.fid

The sample is a mixture of quinine, geraniol, camphene (and TMS) in deutero-methanol. (see: *J. Magn. Reson*. 1998, **131**, 131-138.)

VnmrJ Processing via the DOSY Process Panel

1. Select an experiment.
2. Load the `Dgcstehmqc.fid` into the current experiment.
3. Click on the **Process tab**.
4. Select the **DOSY Process panel**.
5. Click on the **Process 2D** button.

   The signal regions for this file have already been saved.
6. Place a check in the box to the left of **Box**.
7. Remove any checks in the boxes to the left of **Cross**, **Number**, and **Diff.Cornst**.
8. Click on the **Redisplay 2D Spectrum** button.
9. Click on the **Process 3D DOSY** button.

   The cosy spectrum is displayed with the cross peaks labelled with the diffusion coefficient and error bar.

   The crosspeaks of interest are:

   7.0-8.5 - quinine

   10.0-11.6 - geraniol

   14.0-15.4 - camphene

   The other lines around 18 D (10-10 m2/sec) are methanol and TMS.
10. Rejoin the DOSY experiment.
11. Remove any checks in the boxes to the left of **Cross**, **Box**, **Number**, and **Diff.Cornst**.
12. Click on the **Redisplay Spectrum** button.
13. Display the following projections:
    - **Quinine**

    a. Enter **7.0** in the field next to Lower Diffusion Limit.

    b. Enter **8.5** in the field next to Upper Diffusion Limit.

    c. Click on the **Show Diffusion Projections within limits** button.

    - **Geraniol**

    a. Click on the **Show original 2D spectrum** button.

    b. Enter **10.0** in the field next to Lower Diffusion Limit.

    c. Enter **11.6** in the field next to Upper Diffusion Limit.

    d. Click on the **Show Diffusion Projections within limits** button.

    - **Camphene**

    a. Click on the **Show original 2D spectrum** button.

    b. Enter **14.0** in the field next to Lower Diffusion Limit.

c. Enter **15.1** in the field next to Upper Diffusion Limit.

d. Click on the **Show Diffusion Projections within limits** button.

Command LIne

1. Enter **`cd('/vnmr/fidlib/Dosy')`**.
2. Enter **`rt('Dgcstehmqc.fid')`**.
3. Enter **`wft2d('ptype',1)`**.
4. Enter **`ll2d('readtext',file+'/ll2d_text')`** to recall the `ll2d` file.
5. Enter **`ll2dmode='nnyn'`**.
6. Check the preset signal regions and verify that each cross peak of interest is boxed.
7. Enter **`dconi`**.
8. Enter **`dosy`**.

   The cosy spectrum is displayed with the cross peaks labelled with the diffusion coefficient and error bar.
9. Join another experiment.
10. Enter **`sdp`**.

    The cross peaks of interest are:

    7.0-8.5 - quinine

    10.0-11.6 - geraniol

    14.0-15.4 - camphene

    The other lines around 18 D (10-10 m2/sec) are methanol and TMS.
11. Rejoin the DOSY experiment.
12. Enter **`ll2dmode='nnnn'`** – Resets the peak labels.
13. Enter **`dconi`** – Displays the spectrum.
14. Display the following projections:

    - **Quinine**

      Enter **`makeslice(7.0,8.5)`**; this sets the lower limit to 7.0 and upper limit to 8.5.
    - **Geraniol**

    a. Enter **`showoriginal`**– recalls the original 2D.

    b. Enter **`makeslice (10.0,11.6)`**; this sets the lower limit to 10.0 and upper limit to 11.6.

    - **Camphene**

    a. Enter **`showoriginal`** – recalls the original 2D

    b. Enter **`makeslice (14.0,15.4)`**; this sets the lower limit to 2.8 and upper limit to 3.1.

Si29-1H_Dghmqcidosy.fid

The sample is a mixture of cyclic dimethyl-siloxanes -((CH_3)$_2$-SiO)n- (n=3….~20) (see *Phys. Chem. and Chem. Phys*., 2004, **6**, 3221-3227.) This example demonstrates processing of phase-sensitive 3D DOSY data.

VnmrJ Processing via the DOSY Process Panel

1. Select an experiment.
2. Load the **29Si-1HDhmqcidosy.fid** into the current experiment.
3. Click on the **Process tab**.
4. Break up the acquired data into individual phase sensitive 2D FID files for each gradient level as follows:
    a. Click on the **Break up 3D DOSY id into 2D and save** button.
    b. Load each 2D data set into a succeeding experiments – data must be loaded into sequential experiments.

       Starting with the original data in exp 6 load, each 2D data is loaded in order into exp 7, exp 8, exp 9, etc.
5. Join the first experiment with a 2D data set.
6. Click on the **Process 2D** button
7. Join the next experiment with a 2D data set.
8. Repeat step 6 and step 7 until all the data sets are processed.
9. Join the experiment with the weakest gradient value.
10. Place a check in the box to the left of **Box**.
11. Remove any checks in the boxes to the left of **Cross**, **Number**, and **Diff.Cornst**.
12. Click on the **Redisplay Spectrum** button.
13. Enter the experiment numbers in the field next to **available from exp**: and next to **to exp:**.
14. Click on the **Process 3D DOSY** button.
15. Rejoin the DOSY experiment.
16. Remove any checks in the boxes to the left of **Cross**, **Box**, **Number**, and **Diff.Cornst**.
17. Click on the **Redisplay Spectrum** button.
18. Display the projections for a region as follows:
    a. Enter **lower diffusion limit value** in the field next to Lower Diffusion Limit:.
    b. Enter **upper diffusion limit value** in the field next to Upper Diffusion Limit**:**.
    c. Click on the **Show Diffusion Projections within limits** button.
    d. Repeat the process for each region of interest.

Command LIne

1. Enter `cd('/vnmr/fidlib/Dosy')`.
2. Enter `rt('29Si-1HDhmqcidosy.fid')`.
3. Break up the acquired data into individual phase sensitive 2D FID files for each gradient level as follows:
    a. Enter **Unpack_DOSY3Dps**.

b. Load each 2D data set into a succeeding experiments – data must be loaded into sequential experiments.

   Starting with the original data in exp 6, load each 2D data in order into exp 7, exp 8, exp 9, etc.

4. Join the first experiment with a 2D data set.
5. Enter **`wft2da`**.
6. Join the next experiment with a 2D data set.
7. Repeat step 5 and step 8 until all the data sets are processed.
8. Join the experiment with the weakest gradient value.
9. Define the volume integrals:
   a. Enter **`ll2d('volume')`**.
   b. Enter **`ll2dmode='nnyn'`**
10. Enter **`deconi`**.
11. Enter **`Dosy3Dps(startext,lastexp)`**.
12. Display the a projection:

    Enter **`makeslice(lower limit value,upper limit value)`**.

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Chapter 11. Multidimensional NMR

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- 11.3, “Weighting,” on page 218
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2D NMR is similar to an arrayed 1D experiment in some respects. A series of FIDs are acquired in 2D experiments as a function of time (one of the time variables in the pulse sequence) and transformed into a series of spectra. 2D experiments do not explicitly specify the times for each experiment. Times are specified by two parameters, `sw1` and `ni`, that describe the “2D” spectral width (to be discussed shortly) and the number of increments that determine the number of different experiments. The implicit time variable is updated from experiment to experiment as determined by `sw1`.

Real-Time 2D

Real-time 2D performs 2D actions while the experiment is still in progress. A full 2D transform on the data can be performed once eight or more increments are completed.

Experiments such as heteronuclear chemical shift correlation and homonuclear 2D-J experiments require only a few increments to resolve the resonances of interest. Other experiments require more increments. The experiment can be stopped at any time if there is sufficient data to solve the problem.

Interferograms

Interferograms are produced by transposing a matrix created from a series of spectra in the acquisition dimension. The peaks’ heights in a 1D arrayed experiment, like an inversion-recovery T_1 experiment, behave exponentially as a function of time.The oscillation of the

peaks' heights in a 2D experiments contains the information of interest that is extracted from the *interferograms.*

Each slice of the interferogram contains a series of points that represent the peak height at a particular frequency in the original spectrum as a function of time. Many slices of the interferogram contain only noise because at that point the original spectrum contained only noise. Interferogram slices that correspond to the peaks in the original spectrum contain useful information.

Evolution time or t_1 is the time that is varied in a 2D experiment and is the first of two evolution time periods in the 2D experiment. Evolution time is controlled by the parameter `d2`. This time is normally calculated by setting the number of increments to the value of the parameter `ni` and the increment value to `1/sw1`. The value of `ni` determines if a 2D experiment will be run. `d2` is usually set to zero but can be set to any value.

A `d2` array does not appear in the display `da` (i.e., `d2` is "implicitly" arrayed). Only the first value of `d2` appears as the parameter value in the display `dg`. A minimum of eight increments is required for a 2D transform. Typical range is 32 to 512.

Detection time or t_2 is the time during which the signal is detected and is the second of the two time periods. After transform of the signals detected during the time t_2, the "normal" spectrum appears along the f_2 axis. The second transform reveals information about the frequencies of oscillations during the t_1 time period along the f_1 axis.

Parameters that refer to the f_1 axis in a 2D experiment are identified by the number 1 (e.g., `sw1`, `lb1`, `fn1`), whereas the normal 1D parameters control f_2.

The process of transformation, transposition to interferograms, and second transformation may seem complicated, however, it can all be reduced to literally a single command, or even a single menu choice, that starts an acquisition of a 2D experiment and performs all the necessary processing when the experiment is done.

Phase-Sensitive 2D NMR

Phase-sensitive 2D NMR acquisition and processing offers better sensitivity, resolution, and ability to display and plot *phased data*, as opposed to absolute-value data. There are four kinds of experiments in which a user might want to examine phase-sensitive data:

- A 2D experiment in which the data are not expected to appear in absorption mode in both directions, but in which it is nonetheless desirable to observe the data in a phase-sensitive presentation.
- A 2D experiment in which the data, processed in a suitable way, *are* expected to appear in absorption mode in both directions , i.e., Heteronuclear 2D-J.
- An experiment in which two different experiments are performed for each value of t_1, typically using different phase cycles or gradients, producing a full complex data set for the second transformation. This method is called , in the case of phase cycling, (popularized by States, Haberkorn, and Ruben, *J. Magn. Reson.* 1982, ***48***, 286), the *hypercomplex method.*
- An experiment in which the phase of the excitation pulse is updated as a function of t_1 (TPPI or Time Proportional Phase Incrementation (see Marion and Wuthrich, *Biochem. Biophys. Res. Commun.* 1983, ***113***, 967), which produces real data along the t_1 axis.

Complex transforms are usually performed along t_1, which is the ideal situation for the hypercomplex method. TPPI data can be processed along t_1 with either a complex FT or a real FT, depending upon the method of data collection.

The hypercomplex method (generally the method of choice) requires *two* data tables instead of one as does the TPPI method but does not require twice as much storage for the same reason that a real 1D transform, sampled at twice the sample rate of a complex transform covering the same spectral width, requires exactly as much data as a complex 1D transform. TPPI requires sampling at twice the frequency along t_1 to create one data table twice the data size per data table as the hypercomplex method to produce the same real resolution. The experiments are equivalent in terms of data storage requirements and execution time.

11.1 2D Experiment Set Up

1. Use the Locator to list the available 2D experiments:
   a. Click the **Locator Statements** button (magnifying glass icon), and select **Sort Protocols** for experiments.
   b. Set the columns to name, **apptype**, and **seqfil**.
   c. Modify the Locator Statement to show hetero2d (heteronuclear 2D) or homo2d (homonuclear 2D).
2. Drag-and-drop or double click the desired experiment.

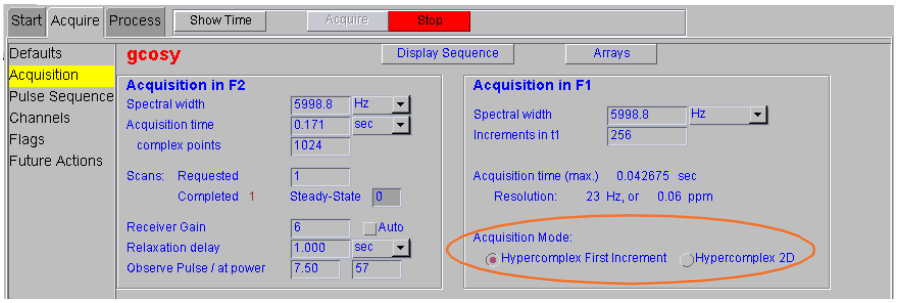
11.2 Data Acquisition: Arrayed 2D

2D experiments have one implicitly “arrayed” parameter, `d2` and can have explicitly arrayed parameters like 1D experiments. Explicitly arrayed parameters have nothing to do with phase-sensitive 2D but are used in experiments such as a series of 2D-NOE experiments using different mixing times. This feature opens up a variety of experiments, including addition/subtraction of two or more 2D experiments.

- "Hypercomplex Method," this page
- "TPPI Method," page 218

Hypercomplex Method

The hypercomplex method of phase-sensitive 2D NMR requires two data tables. A pulse sequence must generate a sequence of pulses or pulse phases suitable for generating the two component experiments of the hypercomplex method.



Any parameter may be used for this purpose. VnmrJ uses the parameter `phase` for many pulse sequences, which takes on values of 0, 1, or 2:

- A value of `phase=0` produces a phase cycle suitable for a non-phase-sensitive 2D experiment.

- Running an array of experiments with `phase=1,2` produces two experiments suitable for the hypercomplex method.

TPPI Method

The TPPI method of phase-sensitive 2D NMR requires one data table. The data is processed along t_1 with a complex Fourier transform by setting `proc1` (which sets the type of data processing to be performed on the t_1 interferogram) to `'ft'`. This manner of implementing TPPI leads to a doubling of the f_1 frequency axis.

When an arrayed 2D experiment is run in this manner, there is in reality a double array: `d2` (the evolution time) and `phase`. The order of these arrays is such that the `phase` array is cycled the most rapidly; observe the order of these experiments, for example:

Method	*Evolution Time*	*Phase*
States-Haberkorn	`d2=0`	`phase=1`
	`d2=0`	`phase=2`
	`d2=1/sw1`	`phase=1`
	`d2=1/sw1`	`phase=2`
TPPI (non-arrayed)	`d2=0`	`phase=3`
	`d2=1/sw1`	`phase=3`
	`d2=2/sw1`	`phase=3`
	`d2=3/sw1`	`phase=3`

Not all pulse sequences have the TPPI method incorporated. The acquisition status window displays a count of the current FID and the number of completed transients (`ct`) in that FID. The current FID number is the *total* count of completed FIDs to this point, including all arrays. Since the `phase` parameter is cycling the most rapidly, and since, typically, `phase` is an array of two values, the current FID number is typically *twice* the number of the current increment. For example, when the counter reads FID 54, this means that 27 FIDs of the first type of experiment have been completed, 26 of the second type, and the system is working on the 27th experiment of the second type.

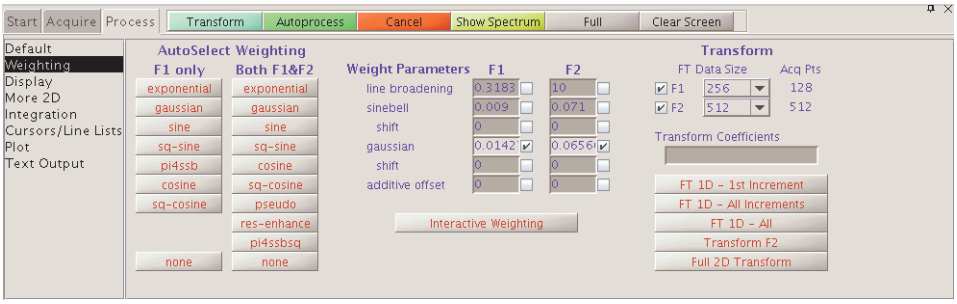
11.3 Weighting

This section describes weighting functions for processing 2D experiments.

- "2D Weighting Parameters," this page
- "Interactive Weighting," page 219

2D Weighting Parameters

The 2D weighting parameters used for processing the t_1 domain (the interferogram) or first indirectly detected dimension (`ni`) are set on the Process page in the Process panel, and are analogous to weighting parameters for 1D experiments.



Non-phase-sensitive (absolute-value and power) 2D experiments: "pseudo-echo," sinebell, or sinebell-squared weighting is typically used to attenuate long dispersion tails. This weighting is often responsible for a significant loss in sensitivity in such 2D experiments.

Weighting	*AutoSelect Weighting Button*
pseudo-echo	pseudo
sinebell	sine
sinebell-squared	sq-sine

Phase-sensitive 2D experiments:

The key in using weighting functions is to ensure that the weighted FID or interferogram decays to zero by the end to avoid "truncation wiggles." The Gaussian function is ideally suited for this; typical values might be `gf=0.6*at`, `gf1=0.6*ni/sw1` (`=0.6*at1`), which are entered in the Weight Parameters fields. Resolution enhancement (using negative line broadening) may be helpful in cases of spectral overlap, but can also be dangerous, since the "dips" that it can induce around the sides of peaks show up as peaks of opposite sign in the 2D plot, complicating analysis.

Interactive Weighting

The Interactive Weighting button on the Process page (or the `wti` command) allows interactive setting of weighting parameters for both t_2 FIDs and t_1 interferograms (both the

`ni` and `ni2` dimension). The currently active element or trace is used in adjusting the weighting parameters.

The following graphics toolbar buttons control these parameters used with interactive weighting:

Check box	*Icon*	*Function*
Line broadening		Selects line broadening or exponential weighting. A negative value gives resolution enhancement.
Sinebell		Selects the sinebell constant. A negative value gives squared sinebell.
Shifted Sinebell		Selects the sinebell shift constant (if sinebell is active).
Gaussian		Selects the Gaussian time constant.
Shifted Gaussian		Selects the Gaussian shift constant (if Gaussian is active).
Additive weighting		Selects the additive weighting constant.
return		Returns to the previous menu.

The values displayed in the graphics display window correspond to the values displayed in the Weight Parameters fields on the Process page. Clicking a graphics control button toggles the weighting function on and off.

Enter values in the fields next to the Weight Parameters and check the box to activate the parameter. Press **Return** to enter the value.

The left mouse button also changes the selected parameters. The right mouse button turns off the spectrum for a faster response to changes in the weighting function.

11.4 Baseline and Drift Correction

Baseline and drift correction are done using the Linear Prediction and the Display pages under the Process panel.

- "Calculating the Preacquisition Delay," this page
- "Setting the Receiver Gating Time," page 221
- "First-Point Multiplier," page 221
- "Baseline Correction," page 222
- "Spectral Drift Correction," page 222

Setting the Receiver Gating Time

Set the relevant receiver gating time (typically `rof2`) to a value appropriate for probe and/or to observe nucleus used. For example, the appropriate approximate gating time for a cold probe is 20 µsec to prevent ringing, and the appropriate gating time for a room temperature probe is 4 µsec.

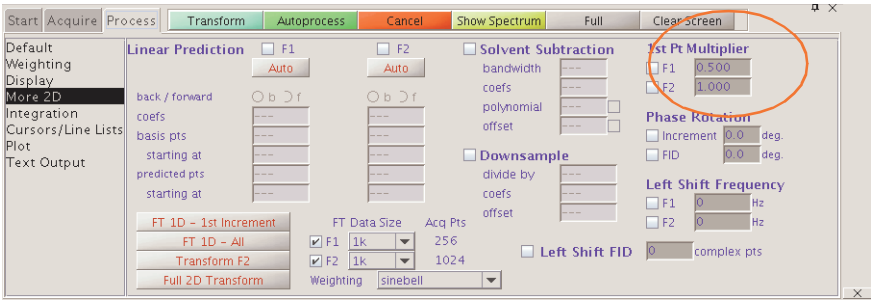
Calculating the Preacquisition Delay

Unless first-order phase in the directly-detected dimension is approximately zero, the non-zero lp value will affect both the spectral drift correction (`dc`) offset and the curvature of the spectrum during 2D data processing. Delay values are shown on the Flags page under the Acquire panel. The first-order phase correction should be close to zero. To accomplish this do the following:

1. Obtain a trial spectrum and phase it to pure absorption. This spectrum provides the current pre-acquisition delay and first-order phase values. Using these values, the `setlp0` macro can calculate proper values for pre-acquisition delays so that `lp` is rendered approximately 0.
2. Enter `setlp0` to calculate a new value for the pre-acquisition delay (`alfa`) so that `lp` is rendered approximately 0.

First-Point Multiplier

The fields under 1st Pt Multiplier (on the Linear Prediction page) multiply the first point of each FID by the F2 value (the default `fpmult` value is 1.0, except that if the processing



involves backward extension of the time-domain data with linear prediction, the default value is then 0.5) and the first point of each interferogram by the F1 value (default `fpmult1` value is 0.5) for the indirectly-detected dimension. 1st Pt Multiplier compensates for first point distortion (see Otting, Widmer, Wagner and Wüthrich, *J. Magn. Reson.* 1986, ***66***, 187).

The effect of using the F2 value in 1st Pt Multiplier is to perform a linear baseline correction on all f_2 data, reducing negative-going ridges along f_2 in phase-sensitive 2D data. This correction is not needed in experiments such as COSY where the FID *starts* at zero and grows or in absolute-value mode presentation if pseudo-echo or sinebell processing is used, because the processing function goes to zero at t_2=0, forcing all FIDs to start at zero amplitude.

Determine the best value of 1st Pt Multiplier empirically. It can be determined manually before, during, or after the 2D experiment by using FT 1D -1st Increment button on the Process page.

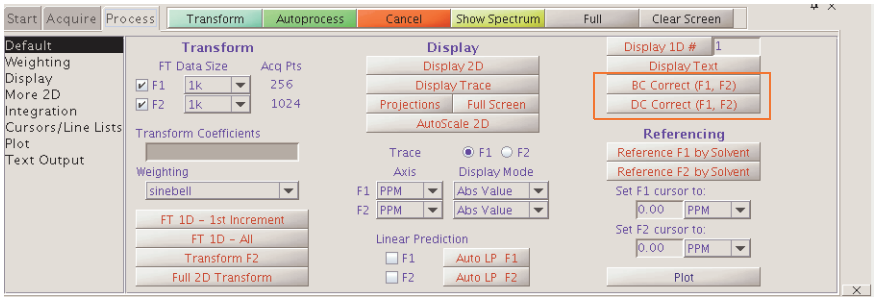
1. Enter **`dc`** or use the **DC Correction** button with a properly phased first increment spectrum on the screen.
2. Position the mouse at the right edge of spectrum baseline (to keep track of the ideal baseline position).
3. Enter **`cdc`** and observe the new position of the baseline. It typically drops.
   - Baseline goes negative: set the F2 1st Pt Multiplier to greater than 1.0 (try 1.5) and click **FT 1D -1st Increment** on the Process page.
   - Baseline rises but does not return to the position indicated by the mouse arrow: increase the value of F2 1st Pt Multiplier and click **FT 1D -1st Increment** again. If in doing so the baseline rises above the ideal level, reduce value and try again.

   Only a few tries are required before the proper value of F2 1st Pt Multiplier is found.

Normally, no correction for 1st Pt Multiplier is necessary. Automatic setting of `fpmult` is available through the macro `cfpmult`. Unchecking the boxes next to F1 and F2 disables the first-point multiplier feature. This is the usual value for sinebell or pseudo-echo processing.

Spectral Drift Correction

Use the DC F1 and DC F2 buttons on the Display page only after the 2D transform. Use **DC F1** for corrections along f_1 and **DC F2** for corrections along f_2. The drift correction calculation is done separately for each trace in the 2D data set.



Baseline Correction

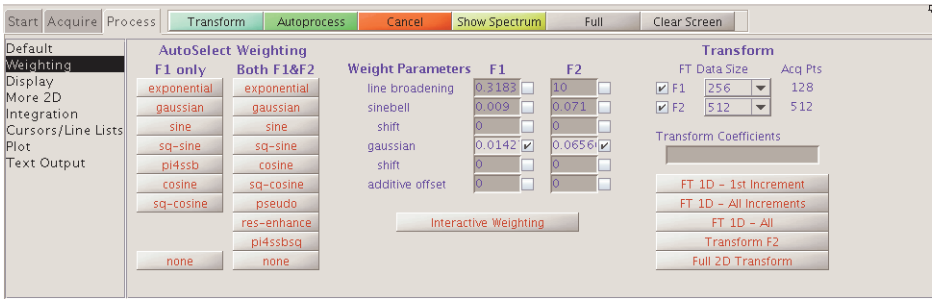
An alternative to the use of 1st Pt Multiplier for baseline correction is using the BC F1 and BC F2 buttons on the Display page. Baseline correction in 2D processing uses the spline or second to twentieth order polynomial fitting of predefined baseline regions. These regions are set up prior to the use of `bc` by setting integral resets so that integrals appear only over regions of the spectrum with signals present. These can be set after clicking **FT 1D - 1st Increment**. The quality of the baseline correction can be assessed by `bc(1)`.

In setting baseline regions near the ends of the spectrum, the `bc` operation does the equivalent of 1st Pt Multiplier because this represents a simple spectral drift correction.

11.5 Processing Phase-Sensitive 2D and 3D Data

- "Processing Programs," page 224
- "Common Coefficients for wft2d Processing," page 225
- "2D Solvent Subtraction Filtering," page 226
- "Left Shift FID, Left Shift Frequency, Phase Rotation," page 226
- "2D Processing of 3D Data," page 226

The complete 2D transformation can be performed after 2D data has been acquired using one of the Transform buttons on the Process page.



A series of complex FIDs, obtained as a function of t_1, are transformed to become a series of spectra. Each spectrum consists of a real and imaginary part. Each spectrum is then phase- rotated, according to the phase correction determined from an individual spectrum. There is now a series of spectra, each consisting of an absorptive and a dispersive part, formed as linear combinations of the original real and imaginary parts. Complex interferograms then form out of corresponding points along the frequency axis from each of the spectra and transform to produce the final 2D spectrum.

The real and imaginary part of the interferograms can be formed from any linear combination of the real and imaginary parts of one or more spectral sets after the first Fourier transformation. Refer to these coefficients below according to the following scheme: `RR1` is the coefficient used to multiply the real part (first `R`) of spectra in set `1` (the `1`) before it is added to the real part (second `R`) of the interferogram. `IR2` thus represents the contribution from the imaginary part of spectra in set 2 to the real part of the interferogram, and so on.

Another set of complex interferograms are formed from these two sets of f_2 spectra for some experiments. This set of interferograms is 90° out-of-phase in f_2 to the previous set and can be constructed without any *additional* coefficients.

Different experiments require different coefficients. Some, such as heteronuclear 2D-J experiments, consist of only one FID and spectral set, and hence there will be a total of four coefficients. Others, including hypercomplex 2D experiments, consist of two original data sets and hence a total of eight coefficients. Other experiments are possible with three or even more data sets, requiring in each case four times as many coefficients as the number of data sets (see the macro `wft2dac`).

4*n* coefficients must be supplied if there are *n* data sets to be transformed, as in typical phase-sensitive experiments. The first 2*n* coefficients are the contributions to the real part of the interferogram, alternating between real and imaginary parts of the successive data

sets. The next 2*n* coefficients are the contributions to the imaginary part of the interferogram, in the same order.

Thus, using the definition that the first letter refers to the source data set, the second letter refers to the interferogram, and the number identifies the source data set, we have the cases shown in the table on the right.

Data Sets	*Coefficient Order*
1	RR1, IR1, RI1, II1.
2	RR1, IR1, RR2, IR2, RI1, II1, RI2, II2.
3	RR1, IR1, RR2, IR2, RR3, IR3, RI1, II1, RI2, II2, RI3, II3.
. . .	...

The coefficients are generally 1, 0, or –1, but other coefficients are acceptable. Any *real* coefficient can be used, and as many coefficients can be non-zero as is desired. Up to 32 coefficients can be supplied, which at four per data set allows the addition, subtraction, etc., of eight 2D data sets (that is, eight different phase cycles). See the macro `wft2dac` for more information.

Processing Programs

A number of processing programs are available:

- `ft1d(coefficients)` performs only the first Fourier transformation along the f_2 dimension (without weighting) and matrix transposition, allowing the display of interferograms with the `wti`, `dcon`, and `dconi` commands.
- `wft1d(coefficients)` functions the same as `ft1d` except weighting is included.
- `ft2d<(<option,>coefficients)>` performs a complete transformation in 2D, without weighting, after 2D data has been acquired. If the first Fourier transformation has already been done using `ft1d`, `wft1d`, `ft1da`, or `wft1da`, then `ft2d` performs only the second (t_1) transform. `'ptype'` or `'ntype'` can be used as the first argument to select P-type or N-type peak selection. The `coefficients` argument are discussed below.
- `wft2d<(<option,>coefficients)>` performs the same as `ft2d` except weighting is included. To perform a normal 2D transform on the `n`-th element in an arrayed 2D experiment, type `wft2d(n)`.
- `ft2da<('bc',polynomial_order)>` runs complete phase-sensitive Fourier transform after the 2D FID data has been acquired. `'bc'` is a keyword to perform a baseline correction on the f_2 spectra prior to the Fourier transform along f_1. `polynomial_order` is the order of the polynomial used in the baseline correction.
- `wft2da<('bc',polynomial_order)>` functions the same as `ft2da` except weighting is included.
- `ft1da` functions the same as `ft2da` except a Fourier transform along f_1 is omitted.
- `wft1da` functions the same as `ft1da` except weighting is included.

Save much time, for some 2D data sets, by selectively transforming the t_1 interferograms. `ft2d('f2sel')` allows only preselected f_2 regions to be transformed along t_1; the t_1 interferograms in the non-selected f_2 regions are zeroed but *not* transformed. The same mechanism used to select baseline regions for baseline correction (`bc`) is used to select the f_2 regions that are to be transformed along t_1. Partition the integral of the spectrum into several regions. The even numbered f_2 regions, e.g., 2, 4, etc., will be transformed along t_1; the odd numbered ones will not be transformed along t_1.

Unreliable peak heights can be caused by Fourier transformation of truncated time-domain data, instead of Fourier numbers `fn` and `fn1` being too low, as might be intuitively expected. To obtain properly defined signals, take one of the following steps:

- Collect data until the signal has decayed to zero in the time domain
- Transform the data with zero-filling (`fn>=2*np`, `fn1>=4*ni`)

Taking one of these steps is particularly important in 2D spectra with antiphase or dispersive signals, where underdigitization can lead to signal cancellation.

Common Coefficients for wft2d Processing

To enter process coefficients, use the Transform Coefficients field on the Process page. Typically, the coefficients are already set in the 2D parameter sets (4 coefficients for absolute value mode and 8 coefficients for phase sensitive).

A magnitude-mode transform, in which the real part of the interferogram is formed from the real part of the spectra and the imaginary part of the interferogram is formed from the imaginary part, would require **`1,0,0,1`**. Changing the sign of the imaginary part of the interferogram serves to change the effective direction of the f_1 frequency axis, as is required for data in which N-type peaks are detected. This can be done with **`1,0,0,-1`**.

In some experiments, including heteronuclear 2D-J, the basic data are purely amplitude modulated, with a starting amplitude of +1. After the first transformation and phasing operation are complete, the dispersion part of each spectrum serves only to produce a phase-twist in the final spectrum without contributing any information. Setting the imaginary part of the second transform to zero produces a pure absorption display in both domains: **`1,0,0,0`**.

In the hypercomplex method for pure absorption 2D data, we have two complete sets of spectra and must therefore provide eight coefficients to specify the composition of the interferograms. A typical execution of the method described by States, Haberkorn, and Ruben, assuming that the first spectrum of the first data block has been phased for absorption, requires **`1,0,0,0,0,0,1,0`** to produce pure absorption spectra.

Other manipulations of two data blocks are formatted similarly. A magnitude-mode 2D experiment that is the sum of the two different experiments can be constructed by **`1,0,1,0,0,1,0,1`**. For a COSY experiment, this would produce the P-type experiment. Subtracting data block two from block one, which for a COSY experiment gives the N-type COSY, would be accomplished by **`1,0,-1,0,0,1,0,-1.`** Thus two different absolute-value 2D experiments, (P-type and N-type) and a phase-sensitive 2D experiment, can be produced from the *same* data set, without acquiring the data again.

Different combinations of data sets with appropriate phase cycling might allow selection of various quantum orders in a *single* experiment. Note that since the coefficients may be different from one, it is possible essentially to phase shift each experiment *separately* (phase shift the receiver) *after* the experiment is done. For TPPI data with `phase=3`, only one data set is collected, and the imaginary part of the second transform is set to zero: **`1,0,0,0`**.

The parameter `f1coef` and `f2coef` is used to store the above coefficients as text strings and is displayed under the label *Transform Coefficients*.

2D Solvent Subtraction Filtering

2D solvent subtraction is set up on the Linear Prediction page under the Process panel. In a 2D transform, solvent subtraction is invoked on t_2 FIDs. The parameters `ssfilter` and `ssorder` select the processing option as follows:

- The zfs (zero-frequency suppression) option is selected if both bandwidth (`ssfilter`) and polynomial (`ssorder`) are set to a value.
- The lfs (low-frequency suppression) option is selected if bandwidth is set to a value and polynomial is not checked.
- The zfs and lfs options are both turned off if bandwidth is blank.

Left Shift FID, Left Shift Frequency, Phase Rotation

Use the Linear Prediction panel to adjust the Left Shift FID, Left Shift Frequency, and the Phase Rotation.

Check **Left Shift FID** to left-shift the interferogram by the entered number of complex (or hypercomplex) points before weighting and Fourier transformation are performed. The value must be between 0 and number of increments minus 1.

Enter a negative value for Left Shift Frequency to shift the peaks upfield (to the right) or a positive value to shift the peaks downfield (to the left). The Left Shift Frequency values operate only on complex `np` FID data (t_2 dimension in a 2D experiment).

To phase-rotate the interferogram, check the appropriate box and enter a value in degrees (zero-order phase rotation). This causes zero-order phase rotation before weighting and Fourier transformation are performed.

2D Processing of 3D Data

Acquisition and full processing of 3D data requires the parameters `ni2` and `sw2` (`d3` is the delay increment in the `ni2` dimension). 2D processing of “slices” of the 3D data matrix is accomplished using the following commands:

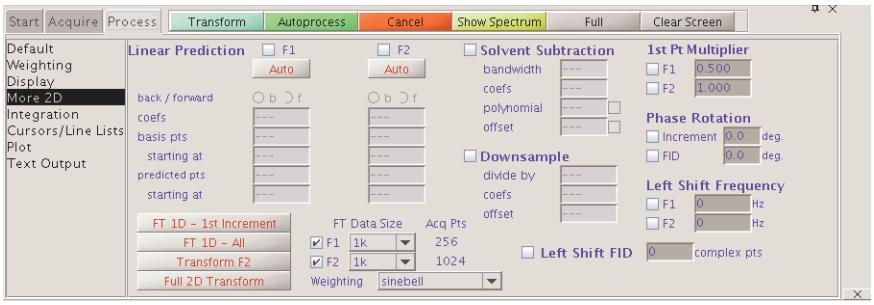
`ft2d('ni2')`	transforms non-arrayed 2D data that have been collected with `ni2` and `sw2` (instead of `ni` and `sw1`). The `addpar('3d')` macro creates the necessary processing parameters for the `ft2d('ni2')` operation (`par3d` functions the same as `addpar('3rf')`).
`ft2d('ni',#)`	selectively transforms selected `np`–`ni` 2D plane within a non-arrayed 3D data set; # is an integer that can range from `1` to `ni2`.
`ft2d('ni2',#)`	selectively transforms selected `np`–`ni2` 2D plane within a non-arrayed 3D data set; # is an integer that can range from `1` to `ni`.
`wft2d`	acts the same as ft2d, but applies weighting before transformation.

The format of the arguments to `ft2d` changes if an arrayed 3D data set is selectively processed. For example, `ft2d('ni',#1,#2)` performs a 2D transform along `np` and `ni` of the #2-th `ni2` increment and the #1-th element within the explicit array. This yields a 2D `np`–`ni` frequency plane. #1 ranges from `1` to `ni2`; #2 ranges from `1` to `[arraydim/(ni*ni2)]`.

Arrayed 3D data sets can also be subjected to 2D processing to yield 2D absorptive spectra. If the States-Haberkorn method is used along both f_1 (`ni2` dimension) and f_2 (`ni` dimension), there will generally be four spectra per (`ni`,`ni2`) 3D element. In this case, the command `ft2d('ni2',#1,<16 coefficients>)` performs a 2D transform along `np` and `ni2` of the #1-th `ni` increment using the ensuing 16 coefficients to construct the

2D t_1-interferogram from appropriate combinations of the four spectra per (`ni`,`ni2`) 3D element. Use the `proc2` parameter to specify the type of data processing to be performed on the `ni2` interferogram (3D): `'ft'` for complex FT, `'rft'` for real FT, or `'lp'` for linear prediction processing on complex data. The macro `dg2` displays 3D processing parameters in the test output page.

11.6 2D and 3D Linear Prediction



Linear prediction parameters are adjusted on the Linear Prediction page. F1 controls the transformation process along t_1, and F2 controls the transformation process along t_2. Using the same method of transformation is not necessary along two (or three axes). For example, employ a backwards linear prediction in t_2 of a 2D experiment and a forward linear prediction along t_1, or perhaps a simple Fourier transformation along t_2 and a backwards linear prediction along t_1.

11.7 Hadamard Spectroscopy

- "Acquiring the Data.," page 228
- "Processing the Data," page 228
- "Implementing the Method," page 228
- "Using 2D Hadamard Spectroscopy," page 228
- "Commands, Macros, and Parameters," page 231
- "Reference," page 233

Hadamard spectroscopy is a technique for acquiring multidimensional data sets using a small number of transients and reconstructing the nD spectrum using a Hadamard transform based on selective excitation of a predetermined set of frequencies using Hadamard encoding.

Acquiring the Data.

A list of selectively excited frequencies is created from a 1D spectrum or other means. A series of shaped pulses is created from the frequency list using a Hadamard matrix to selectively excite or invert the signals of interest. The matrix size is greater than the number of frequencies in the list. A typical Hadamard matrix is shown in Figure 64.

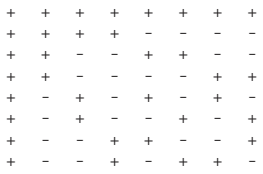


Figure 64. 8x8 Hadamard Matrix

The first shaped pulse selectively excites all the frequencies in the 8 x 8 matrix above. A second shaped pulse selectively excites the first four frequencies and inverts the second four frequencies. Frequencies 1, 2, 5 and 6 are selectively excited and frequencies 3, 4, 7 and 8 inverted by the third shaped pulse.The process is repeated until each row of the Hadamard matrix has been acquired.

Processing the Data

Hadamard processing in the indirect dimension is done by summing, adding, or subtracting the acquired data increments in combinations according to the Hadamard matrix elements. Each sum gives a trace corresponding to a frequency in the list and is placed at the appropriate frequency in the indirect dimension. Areas between the frequencies in the list are zero-filled. The data sets acquired in the direct dimension are Fourier transformed to produce a 2D spectrum.

The trace for the first frequency in the list is usually found in the second row of the Hadamard matrix. The second row in an 8 x 8 Hadamard matrix is created by adding the first four acquired elements and subtracting the second four acquired elements. The process is repeated until all traces for the selected frequencies are complete. A Hadamard matrix is created that is greater in size than the number of frequencies and contains more Hadamard sums than are needed.

2D and higher dimensional experiments using the Hadamard method are run and processed in a significantly shorter time than the same experiment acquired using hypercomplex or TPPI methods. Current software supports only 2D Hadamard spectroscopy.

Implementing the Method

A list of frequencies used for 2D Hadamard spectroscopy is contained in the parameter `htfrq1`. The Hadamard matrix size is set to a value that is both greater than the number of frequencies contained in the parameter `htfrq1` and a power of two multiplied by 1, 12, 20, or 28. All shaped pulses are created in the pulse sequence using Pbox.

Hadamard data is processed using `ft2d` (or one of its variations) with `proc1='ht'`. The zero-filling size in the indirect dimension is set by fn1, which may be used to adjust the separation of the frequencies of interest.

Using 2D Hadamard Spectroscopy

- "Setting Up a Homonuclear 2D Hadamard Sequence," page 229
- "Setting up a Heteronuclear 2D Hadamard Sequence," page 229
- "Editing or Creating Hadamard Frequencies," page 229
- "Edit HT Freq Window Buttons," page 230

Setting Up a Homonuclear 2D Hadamard Sequence

1. Acquire a 1 D spectrum (^{1}H or other nucleus).
2. Process and phase the spectrum.
3. Enter **`editht`** on the command line to open the Edit HT Freq dialog window.
4. Enter a line width in the Min line width entry box.
5. Press the **Create Line List** button and edit the line list.
6. Click on **Save HT Frequencies** button to save the frequency list.
7. Load the Hadamard experiment `TocsyHT`.

   Use either the Experiments menu or enter the macro on the command line.
8. Edit the Hadamard frequencies using the Edit HT Freq dialog window.
9. Start acquisition.
10. Process using the **Full 2D Transform** button on the Default Process page or enter **`wft2da`** on the command line.

Setting up a Heteronuclear 2D Hadamard Sequence

1. Acquire a 1 D spectrum (^{13}C or other nucleus).
2. Process and phase the spectrum.
3. Enter **`editht`** on the command line to open the Edit HT Freq dialog window.
4. Enter a line width in the Min line width entry box.
5. Press the **Create Line List** button and edit the line list.
6. Click on **Save HT Frequencies** button to save the frequency list.
7. Acquire a 1D ^{1}H spectrum and adjust the spectral width and decoupling as desired.
8. Load the Hadamard experiment `HsqcHT`.

   Use either the Experiments menu or enter the macro on the command line.
9. Edit the Hadamard frequencies using the Edit HT Freq dialog window.
10. Start acquisition.
11. Process using the **Full 2D Transform** button on the Default Process page or enter **`wft2da`** on the command line.

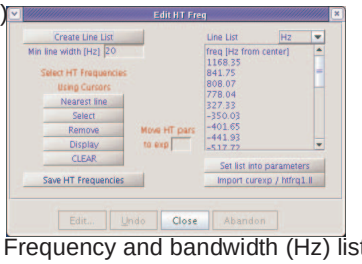
Editing or Creating Hadamard Frequencies

1. Enter **`editht`** on the VnmrJ command line to open the Edit HT Freq window.
2. Edit the Hadamard frequencies from a 1D spectrum using the editable text entry window under Line List.

   Two line listings are available, see Figure 65.
3. Click on the drop down menu next to Line List and select one of following:
   - Select **Hz** to display the line list and frequencies in Hz from the center of the spectrum. The bandwidth is also displayed if it is arrayed.
   - Select the **ppm** from the drop down menu to display the frequencies in ppm.
4. Click **Display** to show the Hadamard frequencies.

5. Create or edit a Hadamard frequency list using the Edit HT Freq window buttons.

(A)

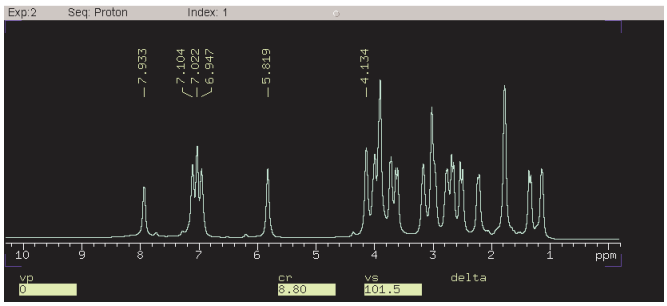


Frequency and bandwidth (Hz) listing

(B)

PPM line listing

(C)

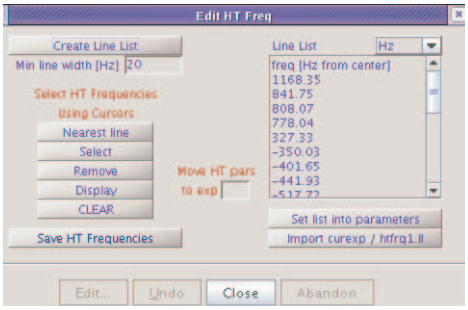


Proton Spectrum with Line List in PPM

Figure 65. Spectrum and Edit HT Freq Window

Edit HT Freq Window Buttons

Button	*Function*
Create Line List	Processes the spectrum using the line broadening specified in field next to Min line width [Hz] to smooth out multiplet structures. Peak thresholds are adjusted automatically and a line list is created. The line list is set into the parameter `htfrq1`. Only frequencies separated by the minimum line width are used.
Nearest line	Places the cursor on the nearest line.
Select	Adds the current cursor position to the line list. The cursor must be more than the minimum line width from an existing frequency in the line list.
Remove	Removes the line nearest the cursor position from the line list.
Display	Displays the frequency list. If a 1D spectrum is displayed, show the frequencies using dpf in units set by the axis parameter.
CLEAR	Clears all frequencies from the frequency list.
Save HT Frequencies	



Saves the current frequency list as a Hadamard line list for the current nucleus (`tn`). It saves the frequency list, band width, current nucleus, spectral width, and frequency offset in a persistence file. The frequencies and other parameters are loaded from the persistence file when loading a Hadamard experiment.

Line List — Displayed in the editable text entry window under Line List. The first column contains the Hadamard frequency list (parameter `htfrq1`). The second column of numbers, if present, contains the bandwidth, in Hz, for each frequency.

Hz/ppm menu — Select Hz or ppm to display the line list in Hz or ppm. The line list is displayed in Hz from the center of the spectrum if Hz is selected.

Set list into parameters

Sets the changes from the Line List text entry window into the parameters `htfrq1` and `htbw1`.

Import list from curexp

Copies a line list file from `curexp` into the current line list, and sets the line list into the parameters. The file name: `/export/home/vnmr1/vnmrsys/exp2/htll.htfrq1` has the same format as the Line List in the text entry window.

Commands, Macros, and Parameters

Refer to the *VnmrJ Command and Parameter Reference* for more information about the following commands, macros, and parameters.

Commands, Macros and Parameters

Command/Macro	*Description*
`dll`	Display listed line frequencies and intensities (C)
`editht`	Edit a Hadamard frequency list (M)
`ft1d`	Fourier transform along f_2 dimension (C)
`ft1da`	Fourier transform phase-sensitive data (M)
`ft2d`	Fourier transform 2D data (C)
`ft2da`	Fourier transform phase-sensitive data (M)
`getht`	Retrieve or save a Hadamard frequency list file (M)
`nll`	Fine line frequencies and intensities (C)
`selexHT`	Set up the selexHT experiment (M)
`sethtfrq1`	Set a Hadamard frequency list from a line list ((M)
`ToscyHT`	Set up the TocsyHT experiment (M)
`HsqcHT`	Set up the HsqcHT experiment (M)
`wft1d`	Weight and Fourier transform f_2 for 2D data (C)
`wft1da`	Weight and Fourier transform phase-sensitive data (M)
`wft1dac`	Combine arrayed 2D FID matrices (M)
`wft2d`	Weight and Fourier transform 2D data (C)
`wft2da`	Weight and Fourier transform phase-sensitive data (M)

Required parameters

Commands, Macros and Parameters	
Parameter	*Description*
`htfrq1`	Hadamard frequency list in ni (P)
`ni`	Number of increments in 1st indirectly detected dimension (P)
`htofs1`	Hadamard offset in ni (P)
`proc1`	Type of processing on ni interferogram (P)
`fn1`	Fourier number in 1st indirectly detected dimension (P)
Optional parameters	
Parameter	*Description*
`htbw1`	Hadamard pulse excitation bandwidth in ni (P)
`pxrep`	Flag to set the level of Pbox reports (P)
`pxbss`	Bloch-Siegert shift correction during Pbox pulse generation (P)
`htbitrev`	Hadamard bit reversal flag (P)
`htss1`	Stepsize for Hadamard waveforms in ni (P)
`htcal1`	RF calibration flag for Hadamard waveforms in ni (P)
`htpwr1`	Power level for RF calibration of Hadamard waveforms in ni (P)
`nimax`	Maximum limit of ni (P)

11.8 Phasing the 2D Spectrum

The phase constants `lp1` and `rp1` control the phase correction along f_1 in phase-sensitive data. These should be near zero in most 2D experiments, but because of finite pulse widths and delays present in the pulse sequence, they may be far from zero. If the pulse sequence properly compensates for these pulse widths and delays, it is possible to have zero `lp1` and `rp1`. Most of the setup macro set `lp1` and `rp1` to zero so that the first display will indicate the need (if any) for phase correction in f_1. The same techniques as used in 1D phasing are employed here, with a minor difference.

1. Enter **`f full`** to display the full data matrix in a full chart display.
2. To phase the 2D spectrum, use the horizontal cursor present in the interactive display to identify a peak toward the right-hand edge of the spectrum. Note the trace number indicated at the top of the display (“memorize” this by setting **`r1`** equal to its value.)
3. Select one or more other traces at f_1 values more toward the center and left parts of the spectrum. These will be the most sensitive to work with if there is a diagonal in the spectrum with large peaks. Use **`r2`**, **`r3`**, etc. to “memorize” these trace values. A minimum of two is needed, one at the far right and one at the far left.
4. Enter **`ds(r1)`**. Phase this spectrum like a 1D spectrum using the Phase button in the displayed menu. Click the mouse on the peak displayed near the right edge of the spectrum. Phase up this spectrum (thus setting `rp1`). Do not click in the left part of the spectrum at this time.
5. Enter **`ds(r2)`**. The second trace appears. Click the mouse near the right edge of the spectrum (to fix `rp1` at the previously determined value) and do not rephase. Move the mouse to the peak at the left, click and phase it (thus setting `lp1`).
6. Enter **`ds(r1)`** to recheck `rp1`. Repeat the process again if necessary.

Use the diagonal peaks for phasing in homonuclear correlation spectra (such as NOESY, TOCSY, and ROESY). Phase an f_1 trace exactly like a 1D spectrum if there are strong cross-peaks. Phase HMQC spectra by progressively working from right to left, with several peaks selected along the way to make sure that `lp1` does not go through an extra revolution that would induce some baseline roll.

Corrections in f_2 phasing may be obvious in the 2D data when they are not in the first increment 1D spectrum. If `pmode='full'` before the 2D transform, f_2 phasing may be corrected without retransforming by setting `trace='f2'` and using the same approach as described for f_1 phasing. Transformation of the data again is necessary if `pmode=''` or `pmode='partial'`. No f_1 phasing is possible after transformation if `pmode=''`; f_1 rephasing after the transform is possible (but not f_2 rephasing) if `pmode='partial'`. Do baseline corrections such as `dc2d` or `bc` only after data are properly phased in f_1 and f_2.

Reference

E. Kupce and R. Freeman, “Two-dimensional Hadamard spectroscopy”, *J. Magn. Reson.* (2003), **162**:300-310.

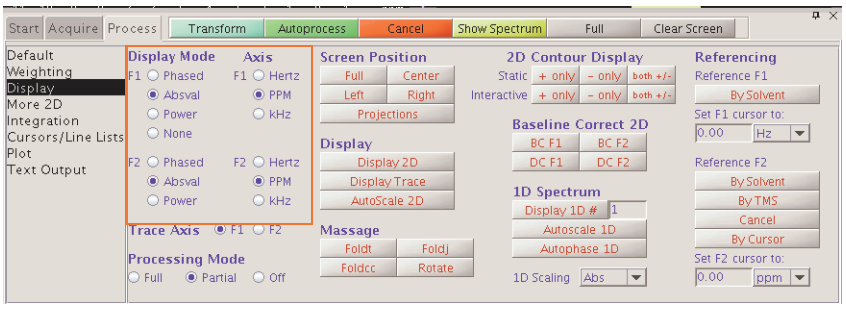
11.9 Display and Plotting

This section discusses noninteractive 2D display and plotting.

- "Display Modes," page 233
- "Display and Plot Limits," page 234
- "Display Scaling," page 234
- "Grid Lines," page 234
- "Whitewashed Spectra," page 234
- "Label Display," page 234
- "2D Referencing," page 235
- "Rotating Homonuclear 2D-J Spectra," page 235
- "Setting Negative Intensities to Zero," page 235

Display Modes

Select display modes in the Display page.



Display and Plot Limits

The `center`, `left`, `right`, and `full` set the spectrum to display (and subsequent plot) in the relevant portion of the screen (and page).

Display Scaling

The `peak2d` command searches the area defined by `sp`, `wp`, `sp1`, and `wp1` in a 2D data set for a maximum intensity. It returns the maximum intensity value found, the trace number of the maximum, and the data point number of the maximum on that trace.

The AutoScale 2D button on the Display page uses `peak2d` to set up the vertical scaling and threshold for a 2D contour plot and color map display.

Grid Lines

A grid of horizontal and vertical lines over a 2D display can be drawn by the `grid` macro. By default, grid lines are drawn in blue at approximately 1 cm intervals, rounded so that the intervals fall at a multiple of 1, 2, or 5 of Hz or ppm. To change the defaults, enter `grid` with a different spacing (in cm) or a different color (`'red'`, `'green'`, etc.); for example, `grid(2,'white')` gives white grid lines at 2 cm intervals.

The `grid` command also can define a grid, using the following syntax:

`grid<(startf2,incrf2,startf1,incrf1,color)>`

The arguments define the frequency and increments between grid lines in the f_2 and f_1 directions and the color of the grid lines.

The `plgrid` macro uses the same arguments as `grid`, but plots the `grid` instead.

Whitewashed Spectra

The `dsww<(start,finish,step)>` command displays one or more spectra with whitewashing (traces in front "block" the view of traces behind them). Use the argument `'all'` to display all spectra. `plww<(start,finish,step)>` plots the same spectra.

Use the Stacked Plot graphics button in the Plot page to display a stacked display of 2D spectra in the whitewash mode.

Label Display

The `dssl` macro displays a label for each element in a set of stacked spectra. The label is an integer value starting with 1 and ranging to the number of spectra in the display.

Labels can appear at incorrect positions if `wysiwyg='n'`. The positions were empirically determined for a large screen display and are not guaranteed to be correct for all displays.

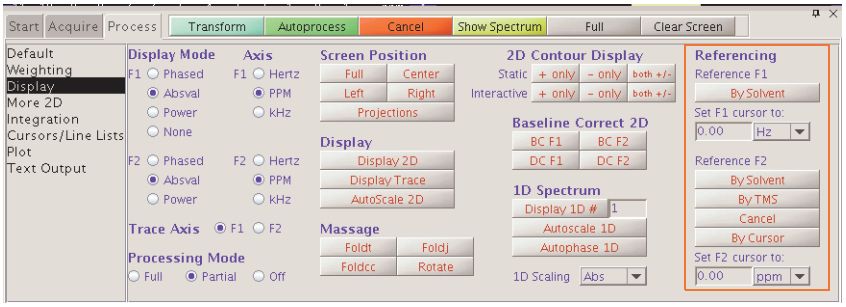
The following `options` control the `dssl` display (more than one option can be entered as long as the options do not conflict with each other):

- `'center'`, `'left'`, `'right'`, `'top'`, `'bottom'`, `'above'`, and `'below'` are keywords setting the position of the displayed index relative to each spectrum.
- `'value'` is a keyword that produces a display of the values of each array element, instead of an integer index.
- `'list=xxx'` produces a display of the values contained in the arrayed parameter `xxx`.

- `'format=yyy'` uses the format `yyy` to control the display of each label. See the `write` command for information about formats.

2D Referencing

Use the Referencing buttons on the Display page to set up 2D referencing.



By default, each reference line is set at the cursor position after taking into account any frequency scaling.

Enter a frequency (in Hz or PPM) to set the reference lines to other than the cursor position. For example, reference a 2D experiment in which the indirect axis is determined by the decoupler channel (i.e., HMQC or HETCOR experiment) by entering `10 ppm`, which is equivalent to 10*decouple frequency.

Click the **Cancel** button to clear referencing along f_2 and f_1.

Use the `centersw` macro for the directly detected dimension, and the `centersw1` macro for the first indirect dimension to center the cursors in the spectrum.

Use the macro `setsw1(nucleus,downfieldppm,upfieldppm)` to set the spectral width for a given spectral window,.

Rotating Homonuclear 2D-J Spectra

The `rotate<(angle)>` command rotates homonuclear 2D-J data 45° (rotation in frequency-space) to line up multiplets. Use the `angle` argument to specify other angles.

Setting Negative Intensities to Zero

The command `zeroneg` is used for the projection of proton 2D-J spectra at 45° to strip a high resolution proton spectrum down to a list of chemical shifts. `zeroneg` sets all negative intensities to zero.

11.10 Interactive 2D Color Map Display

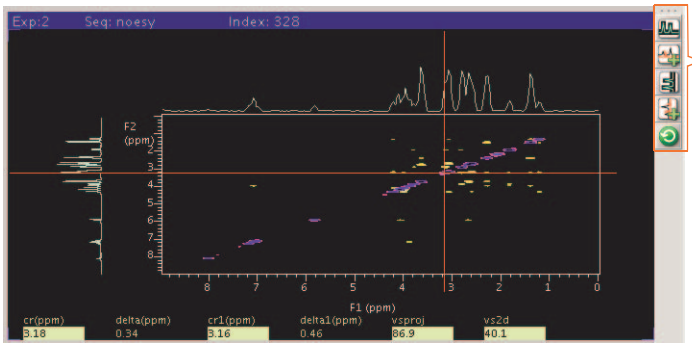
Use the graphics control buttons and the mouse to control the display in the graphics window.

- "2D Display," this page
- "Interactive nD Display Control Buttons," page 236
- "Cursors," page 237
- "Traces," page 238

- "Projections," page 238
- "Expanding the Display," page 238
- "Setting the Vertical Scale," page 239
- "Adjusting the Threshold," page 239
- "Treating 2D Traces as 1D Spectra," page 239

2D Display

Below is an example of a 2D display with the projection graphics control buttons selected.



The color/grayscale adjustment appears on the right side of the window. The interactive display parameters are displayed across the bottom of the graphics window:

`cr`	Shows the current cursor position.
`cr1`	shows the current cursor position along the first indirectly detected dimension.
`delta`	Shows the cursor difference.
`delta1`	Shows the cursor difference along the first indirectly detected dimension.
`vs2d`	Shows the vertical scale of the display.
`vsproj`	Shows the vertical scale of the trace or projection.

Interactive nD Display Control Buttons

- "Main nD Display Bar Tools," page 236
- "nD Graphic Tools," page 237

Main nD Display Bar Tools

Icon	*Description*
	Display color map and show common nD graphics tools.
	Display contour map and show common nD graphics tools.
	Display stacked spectra and show common nD graphics tools.
	Display image map and show common nD graphics tools.

nD Graphic Tools

Icon	*Description*
	One cursor in use, click to toggle to two cursors.
	Two cursors in use, click to toggle to one cursor.
	Click to expand to full display.
	Pan and stretch.
	Show trace.
	Show projections.
	Click on  to show horizontal maximum projection across the top of the 2D display.
	Click on  to show horizontal sum projection across the top of the 2D display.
	Click on  to show vertical maximum projection down the left side of the 2D display.
	Click on  to show vertical sum projection down the left side of the 2D display.
	Rotate axes.
	Increase vertical scale 20%.
	Decrease vertical scale 20%.
	Phase spectrum.
	Click on  to select the first spectrum.
	Click on  to select the second spectrum.
	Enter peak pick menu.

Cursors

Use the left and right mouse buttons to move cursors, and the center button to adjust the vertical scale of traces, projections, and contour maps, as well as to adjust the threshold in the color bar. The cursors can be used to select regions for expansions of the display. The cursors can also be used to select positions to “mark” using the `ll2d('mark')` command, which displays and records spectral frequencies, maxima, intensities, and volumes.

The left mouse button adjusts the position of the 2D cursor. The corresponding frequencies are displayed at the bottom of the graphics window. Both the horizontal and vertical cursors move if the left mouse button is pressed within the 2D display box.

Above and below the box, only the vertical cursor can be moved; at the left and the right of the box, only the horizontal cursor can be moved. In addition, holding the mouse button down and then moving the mouse moves the cursor with the mouse.

The function of the center mouse button depends on the location of the cursor:

- Cursor is within the 2D display box: in gray scale images, pressing the center button sets the point to medium gray. Otherwise, for color map and contour displays, if there is no intensity at that point, the center button changes vertical scale to show intensity at that point. If there is intensity at the point, the center button changes the scale to show no intensity, then changes the parameter `vs` and redraws.
- Cursor is near an active trace and active horizontal or vertical projection: pressing the center button changes the vertical scale of trace or projection, so that spectrum goes through the current mouse position.
- Cursor is near the color/grayscale bar and in the color mode: pressing the center button sets the threshold to remove low intensity peaks. If in the grayscale mode, pressing the center button sets the grayscale intensity (the right button adjusts contrast).

A second cursor pair is displayed with the right mouse button. The second pair can be moved in exactly the same way as the first pair, and is used to select a box within the 2D display. The right mouse button also switches the display into the box mode, the same as clicking on the Box button in the menu.

Traces

1. Click the **Trace** button. A trace displays for the position of the horizontal cursor.
2. Move the horizontal cursor to change the displayed trace.
3. Adjust the vertical scale of the trace by clicking the middle mouse button on the trace, not in the 2D spectrum.

Exit the trace mode by displaying a box with the right mouse button, or by selecting another display mode.

Projections

1. Click the **Projection** button to open the Projection graphic control buttons.
2. Select type of direction (horizontal or vertical) and mode (maximum or summary).
3. Adjust the vertical scale of the projections with the middle mouse button.

Expanding the Display

1. Use the Box cursors to select the region in the spectrum to expand.
2. Click on the **Expand** button to obtain an expanded display.

Setting the Vertical Scale

If a peak is expected at a certain position in the spectrum but is not visible, click once at that position with the middle mouse button. This selects a new vertical scale, so that the intensity at that point is by a factor of 2 above the threshold, and the display is redrawn.

Adjusting the Threshold

If noise is visible at a certain position in a spectrum, but should be suppressed below the threshold, click once at that position with the middle mouse button. A vertical scale is calculated so that this intensity falls by a factor of 2 below the threshold, and again the spectrum is redrawn.

Treating 2D Traces as 1D Spectra

Enter the command `ds` after a trace has been selected in the interactive 2D display program to allow the trace to be displayed as if it were a simple 1D spectrum. All standard 1D data manipulations, including line listing, integration, etc., are then accessible for that trace. The command `ds(tracenumber)` also can be used to display an f_1 or f_2 trace, depending on the value of `trace`.

11.11 Interactive 2D Peak Picking

The `ll2d` program is used to automatically or interactively pick peaks in 2D spectra or 2D planes of 3D spectra. The peaks can be displayed on top of the spectrum in the `dconi` display or can be plotted using the `pll2d` command.

The results of all peak picking operations are stored in a binary file in the `ll2d` subdirectory of the current experiment directory:

- The results are stored in the file `peaks.bin` for 2D spectra.
- The results are stored in `peaks_f#f#_#.bin` for 2D planes of 3D spectra, where `f#f#` denotes the orientation of the plane being picked (e.g., `f1f3` or `f2f3`), and the last # denotes the number of the plane.

Binary peak files can be converted to text files for printing or for export to other programs.

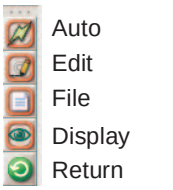
For each peak in a peak file, the following information is stored:

- Peak number
- Interpolated peak frequency in both dimensions
- Interpolated peak amplitude
- Full width at half-height (FWHH) in both dimensions
- Bounds of the peak in both dimension
- Volume of the peak
- 15-character peak label
- 80-character comment

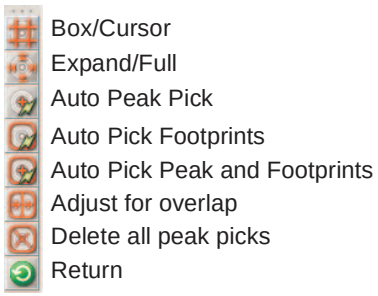
Interactive 2D Peak Picking Buttons

Most of the above options are accessible through a series of graphics control buttons. From the 2D Display, the Peak Picking button brings up the 2D Peak Picking buttons.

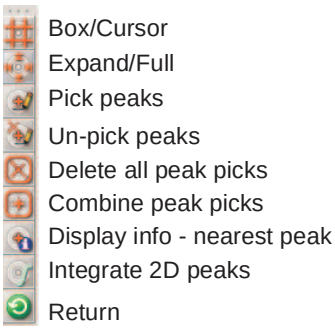
Peak Picking Main Menu



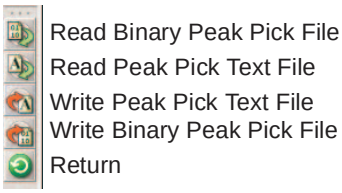
Automatic Peak Picking



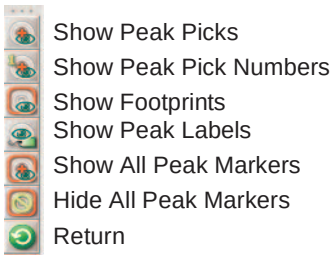
Edit Peaks



Peak Files



Display Peaks



These buttons provide access to the following menus (depending on the mode, the labels on some buttons change).

2D Peak Picking Main Menu

This menu selects another 2D Peak Picking menu. The buttons function as follows:

Auto	Displays the buttons for automatically picking peaks.
Edit	Displays the buttons for interactively editing peaks.
File	Displays the buttons for manipulating peak files.
Display	Displays the buttons for controlling the display of peaks.
Return	Returns to the 2D Color Map Display buttons.

2D Peak Picking Automatic Menu

This menu provides automatic peak picking. The buttons functions as follows:

Box/ Cursor	Selects cursor mode.
Expand/ Full	Selects expanded or full display.
Peak	Automatically finds peaks in the 2D spectrum. If one cursor is visible, all peaks above the current threshold in the currently displayed region of the spectrum are found and marked. A peak is defined as a data point that is higher than the eight points around it. Once such a point is found, the actual peak location is determined by interpolation in both dimensions.

Volume	Automatically finds the bounds of a peak and the integral of all points within these bounds. The bounds are found by descending down the sides of a peak until the point is reached where the amplitude of a data point is less than `th2d` times the current threshold. Thus, using a smaller value for `th2d` will cause `ll2d` to find and integrate a larger area for the bounds of the peaks. The peak volume is calculated by summation of all data points within these bounds. If the bounds of a peak already exist, the volume is recalculated.
Both	Picks peaks and calculates volumes. The Both button does both the peak and volume operations at once.
Adjust	Adjusts peak bounds so that none overlap. The Adjust button adjusts all peak bounds in the displayed region of the spectrum so that none overlap and recalculates peak volumes with the new peak bounds.
Reset	Deletes all peaks that have been found in the current spectrum.
Return	Displays the 2D Peak Picking buttons.

2D Peak Picking Edit Menu

This menu provides interactive peak editing. The buttons functions as follows:

Box/ Cursor	Selects cursor mode.
Expand/ Full	Selects expanded or full display.
Mark	In `dconi` cursor mode, this button inserts a peak at the current cursor location. In `dconi` box mode, the cursors are taken as peak bounds, and the area inside the cursors is integrated. These peak bounds are then assigned to all peaks within the cursors that do not already have their bounds defined. If a peak without bounds does not exist inside the area defined by the cursors, the highest point within that area is found, marked as a peak, and assigned the bounds defined by the cursors.
Unmark	In `dconi` cursor mode, this button deletes the peak nearest the cursor. In `dconi` box mode, this button deletes peak bounds from peaks whose bounds are entirely within the area defined by the cursors.
Clear	In `dconi` cursor mode, this button deletes all peaks in the area of the spectrum displayed in `dconi`. In `dconi` box mode, the Clear button deletes all peaks that are within the area defined by the cursors.
Combine	This button works only in `dconi` box mode. It combines all peaks within the area defined by the cursors into a single peak. This combination peak is located at the average frequencies of all of the original peaks and has bounds that encompass all of the original bounds of the peaks. The volume of the combination peak is calculated by summation of all data points within its bounds. Use the Backup File button in the 2D Peak Picking File Menu (see below) prior to using the Combine button to save the original peaks if this data must be kept. Crating the combination peak are permanently deletes the contents of the current file.
Label	Prompts for a 15-character label to be assigned to the peak nearest the cursor (`dconi` cursor mode) or to all peaks within the area defined by the cursors (`dconi` box mode). Based on the value of the parameter `ll2dmode`, this label can be displayed next to the peak in `dconi`.

Comment	Prompts for an 80-character string to be assigned to the peak nearest the cursor (cursor mode) or to all peaks within the area defined by the cursors (box mode).
Info	Prints the peak file information about the peak nearest the cursor to the text window.
Set Int	Sets the value of the peak volume.
Return	Displays the 2D Peak Picking Main Menu (see above).

2D Peak Picking File Menu

Read	Prompts for the filename of a binary peak file and reads that file into VnmrJ. When a file is read in, the current peak file (`peaks.bin` for 2D spectra) is overwritten by a copy of the peak file that was read in.
Read Text	Prompts for the file name of a text peak file and reads that file into VnmrJ. When a file is read in, the current peak file (`peaks.bin` for 2D spectra) is overwritten by a new binary copy of the peak file that was read in.
Write Text	Prompts for a filename to write a text version of the current `ll2d` peak file.
Backup File	Prompts for a file name to copy the current binary peak file. Do this occasionally when doing a significant amount of interactive peak editing so that intermediate versions of the peak file can be recovered in the event of an error (such as inadvertently selecting the Clear or Reset button or making a mistake using the Combine button).
Return	Displays the 2D Peak Picking Main Menu (see above).

2D Peak Picking Display Menu

Show Peak/ Hide Peak	Show Peak: the “+” is hidden and this button shows a “+” at the location of each peak. Hide Peak: the “+” is shown and this button hides the “+” at the location of each peak.
Show Num/ Hide Num	Show Num: the peak numbers are now hidden, and this button shows a peak number next to each peak. Hide Num: the peak numbers are now shown, and this button hides the peak numbers.
Show Box/ Hide Box	Show Box: the box is now hidden, and this button shows a box with the area integrated to get the volume of the peak. Hide Box: the box is now shown, and this button hides this box.
Show Label/ Hide Label	Show Label: the peak labels are now hidden, and this button shows a peak label next to each peak. Hide Label: the peak labels are now shown, and this button hides peak labels.
Show All/ Hide All	Show All: displays a “+”, the peak number, the peak bounds, and the peak label for each peak. Hide All: hides all peak information.
Return	Displays the 2D Peak Picking button.

11.12 3D NMR

VnmrJ includes full support for 3D NMR, including acquisition, processing, and display.

Many of the 3D-related macros and parameters—for example, `centersw2`, `cr2`, `crl2`, `delta2`, `dmg2`, `lp2`, `lsfid2`, `phfid2`, `rfl2`, `rfp2`, `rp2`, `sp2`, `wp2`—are normally used in the same manner as their 1D and 2D counterparts and are not described further in this section.

In a non-arrayed 3D experiment, there are two implicitly arrayed parameters: `d2` and `d3`. `d2` is associated with `ni` and `sw1`, `d3` with `ni2` and `sw2`. The order of these two arrayed parameters is such that `d2` is cycled the most rapidly.

In an arrayed 3D experiment, such as a single 3D with "superhypercomplex" data acquisition (States-Haberkorn method applied along both t_1 and t_2), there are, in reality, at least three arrayed elements. By convention, such an arrayed 3D experiment is implemented using four arrayed elements: `d3` (t_2 evolution time), `phase2`, `d2` (t_1 evolution time), and `phase`.

Assuming that `array='phase,phase2'` (see below), the order of arrays is such that the `phase2` array is cycled the most rapidly, followed by the `phase`, `d2`, and `d3` arrays.

3D Acquisition

3D data acquisition is accomplished with pulse sequences using the parameter `d3`, which is updated according to the parameters `ni2` and `sw2`. This is analogous to incrementing `d2` according to `ni` and `sw1` for 2D NMR (of course, `d2`, `ni`, and `sw1` are active in 3D as well). In addition, the parameter `phase2` is used to control the "mode" of acquisition (hypercomplex, TPPI, or absolute value) in the third frequency domain, just like `phase` in the second domain. All of these 3D parameters are created with the macro `addpar('3d')` along with other 3D parameters, including `fiddc3d` for 3D time-domain dc correction, `ptspec3d` for region-selective 3D processing, and `path3d` for the path to the currently displayed 2D planes extracted from a 3D data set. (The macro `par3d` is functionally equivalent to `addpar('3d')`.)

By convention, 3D sequences are described with the first evolution time being known as t_1, the second evolution time as t_2, and the time during which data are acquired as t_3. After transformation, these same dimensions are called the f_1, f_2, and f_3 dimensions.

3D Processing

Data processing includes the `ft3d` command for full 3D processing, governed by the usual parameters to control transform sizes, weighting, phasing, etc., with a "2" at the end of the parameter name signifying the third dimension. Unlike other commands, `ft3d` occurs in the background by default; that is, it is run as a separate task, leaving VnmrJ free to continue with other tasks (including 1D and 2D processing of the same data set). To increase the speed of 3D transforms further, the `wftt3` macro allows the software to process one dimension (the acquisition or t_3 dimension) as the data are being acquired. Also, the `ft3d` software can be configured to run on several computers simultaneously, for even greater speeds. The `killft3d` macro terminates any `ft3d` program that has been started in an experiment.

3D Display

Display the data as two-dimensional planes of the 3D data set in any of the three orthogonal directions. Skew planes are not supported, nor are “full 3-dimensional” displays. One command, `getplane`, extracts the 2D planes from the 3D data set in one or more of the three orientations. After the planes are “extracted” in this manner, they are displayed with the `dplane` macro. The parameter `index2` keeps track of which plane is on display. The macro `nextpl` displays the next plane from the plane currently on view. Another macro, `prevpl`, shows the previous plane from the current plane.

The `dsplanes(start_plane,stop_plane)` macro produces a graphical 2D color or contour map for a subset of 3D planes specified by the arguments. The `dconi` program is used to display the planes. The `plplanes` macro is available to plot a series of 3D planes.

The new concept of time-domain frequency shifting can be employed to good use in 3D NMR, where spectra in the indirectly detected directions are often “folded” by accident or by choice. The parameters `lsfrq`, `lsfrq1`, and `lsfrq2` cause the frequency of the spectrum to be shifted as part of the Fourier transformation process.

3D Pulse Sequences

Simply write a sequence that includes a `d2` and `d3` delay (these delays may also be `d2/2` or `d3/2`) when are writing sequences. Use the parameters `phase` and `phase2` to select between the two orthogonal components of the hypercomplex experiment in the relevant domain if your sequence is to operate in the hypercomplex (or the hyper-hypercomplex) mode. Ensure that your experiment is processed correctly. Use the default processing coefficients and write your pulse sequence so that the `phase=2` (and `phase2=2`) experiments leave the receiver unchanged (compared to `phase=1`) and either increment the phase of the pulse (or pulse sandwich) just prior to the relevant evolution or decrement the phase of the pulse following evolution by 90 degrees (or for multiple-quantum experiments, b y 90/*n*).

Experiment Set Up

Set up is necessary in 3D experiments to position transmitters and decouplers, adjust pulse widths, etc. Just as the set up of 2D experiments can often be assisted by performing “first increment” experiments (i.e., a 1D experiment that represents the first increment of the 2D), so 3D experiments can be assisted not only by 1D setup experiments, but also by “first plane” 2D experiments. To perform a 2D experiment in the `sw1` dimension, set `ni2=1` and `phase2=1`, with `ni` greater than 1 and `phase=1,2` (or `phase=3` for TPPI experiments). This combination of parameters will perform a “normal” 2D experiment, incrementing `d2`, and the data can be processed with the `wft2da` command (or its variants).

The “third dimension” 2D experiment is performed by setting `ni=1` and `phase=1`, with `ni2` greater than 1 and `phase2=1,2` (or `phase2=3`, as desired). These parameters will produce a 2D experiment in which `d3` is incremented, resulting in a spectral width `sw2`. The `wft2d` command must be given the special argument `ni2` to process this data correctly, for example, `wft2d('ni2',1,0,0,0,0,0,-1,0)`. Use `wft2da('ni2',1)` to transform the first `F2 X F3` plane of a 3D data set.

When processing a “first plane” 2D experiment the axes are always labeled f_1 and f_2 because this is considered to a 2D experiment and the axis labeling corresponds to conventions used in 2D NMR.

After setting up the 3D experiment, reset ni, ni2, phase, and phase2 to their desired values. Check the value of the parameter array and make sure that array='phase,phase2' and not 'phase2,phase', which will acquire data in the incorrect order. To ensure the correct order, always enter phase before phase2, or simply enter array='phase,phase2'.

Data Processing

Processing of 3D NMR requires coefficients to select various components of the data to be combined to form the final data set. There are up to 40 coefficients; see the *Command and Parameter Reference*.The coefficients are normally transparent to the user, just as the 2D coefficients are. The set3dproc command can create a 3D coefficient file for processing 3D FID data under certain conditions.

The ft3d command determines from the values of phase and phase2 what the expected coefficients are, based on whether a hypercomplex ("States-Haberkorn") or TPPI experiment has been performed in a particular dimension. This assumes that the pulse sequence has been written to perform "standard" phase cycling as described above. If the data are reflected along a particular dimension, it is possible (or probable) that different coefficients are required for data processing. In this case, the ft3d('nocoef') form is used to allows coefficients to be specified (which are found in a text file named coef in the 3D experiment directory, unlike in ft2d, where they are given as arguments to the command). By default, ft3d calls the make3dcoef macro to create a coefficient file using the f1coef and f2coef string parameter values.

The format for the 3D coefficient file is an extension of that used for 2D coefficients. The coefficient file contains four rows of eight coefficients used to construct the t_2 hypercomplex interferograms and a final row of eight coefficients used to construct the t_1 interferogram. The actual values of the coefficients depend on the order in which the States-Haberkorn components of the 3D FID data set were collected. This order depends in turn on the values of the parameters phase, phase2, and array.

If TPPI phase cycling is used to collect data along one or both of the indirectly detected dimensions, instead of four data sets per (ni,ni2) increment, there are only two or one data sets, respectively, per (ni,ni2) increment. If there are only two data sets per (ni,ni2) increment, the coef file contains four rows of four coefficients that are used to construct the t_2 hypercomplex interferograms, and a final row of eight coefficients that are used to construct the t_1 interferogram. If there is one data set per (ni,ni2) increment, the coef file contains four rows of two coefficients that are used to construct the t_2 hypercomplex interferograms and a final row of eight coefficients that are used to construct the t_1 interferograms.

Phasing a 3D data set is best accomplished using 2D transforms. In general, the recommended method in writing 3D pulse sequences is to attempt to minimize frequency-dependent phase shifts in f_1 and f_2. Even so, there are generally small phase shifts that must be dealt with. The following steps are suggested:

1. Set **pmode='full'** to allow full phasing in both dimensions after a 2D transform.
2. Adjust rp and lp on a 1D spectrum (the first increment of the 3D), just as for 2D (e.g., by typing wft(1)).
3. Enter **wft2d('ni',1,1,0,0,0,0,0,0,0,0,0,0,0,-1,0,0,0)** to adjust f_1 phasing (there are 11 consecutive zeros in the middle of this argument).

4. Fix the f_1f_3 2D spectrum (with incorrectly labeled axes). Set **`trace='f1'`** to adjust the f_1 phase, then set **`trace='f2'`** to trim the f_3 phasing. Now adjust `rp1` and `lp1` (as well as `rp` and `lp`).
5. Enter **`wft2d('ni2',1,1,0,0,0,0,0,0,0,0,0,-1,0,0,0,0,0)`** to adjust f_2 phasing (note that this argument has nine consecutive zeros in the middle and five zeros at the end).
6. Adjust f_2f_3 2D spectrum phase. Set **`trace='f1'`** to adjust the f_2 phasing (**`rp2`** and **`lp2`**), then set **`trace='f2'`** to trim the f_3 phasing if necessary.

Some pulse sequences are written to result in a 180° phase shift across the spectrum. Remember that in VnmrJ, the "origin" for phasing is defined as the right edge of the spectrum; however, in "real" terms, the actual origin of phasing (i.e., the zero-frequency point) is at the center of the spectrum. If a certain `lp1` or `lp2` value is expected, such as –180°, simultaneously use a value of `rp1` or `rp2` equal to `-lp1/2` or `-lp2/2` (e.g., 90°).

Adjust the weighting functions for the 3D transform by using the `wti` command and examine interferograms. Do so along either the t_1 or t_2 axes. Use the same commands given above to adjust the phasing (the commands with the long series of zeros), but use `wft1d` instead of `wft2d`.

For the final transformation, the `specdc3d` parameter controls the dimensions in which a spectral drift correction is performed on the data. A three-letter value of `'ynn'` gives drift correction along f_3 (the first letter) but not along f_1 (the second letter) or f_2 (the third letter); this value is probably a good starting point for your efforts.

The `pmode` parameter is ignored by the 3D transformation; no phasing is possible after the 3D transform.

The 3D transformation process needs to be followed by the process of extracting the 2D planes from the full 3D data set. This can be done separately, with the `getplane` command, but most often is combined with the `ft3d` command. In general, and especially for heteronuclear experiments, the f_1f_3 and f_2f_3 planes are the most interesting. The f_1f_2 plane is not only generally less useful, but also is considerably slower to extract from the data. The recommended command to use for 3D transformation, therefore, is `ft3d('f1f3','f2f3')`, which performs the 3D transform and extracts the two interesting planes in one step.

Solvent suppression works on t_3 FIDs of 3D spectra just like in the 1D and 2D cases.

Following the transform, set `plane='f1f3'` or `'f2f3'` and then use the `dproj` macro to display the projection of the data on that plane, or `dplane(n)` to display the nth plane. The `resetf3` macro will reset parameters after a partial 3D Fourier transform.

11.13 4D NMR Acquisition

The `addpar('4d')` macro creates the parameters `ni3`, `sw3`, `d4`, and `phase3` that can be used to acquire a 4D data set (the macro `par4d` functions the same as `addpar('4d')`).

The parameter `ni3` is the number of t_2 increments; `sw3` is the spectral width along the third indirectly detected dimension; `d4` is the incremented delay, and `phase3` is the phase selection for 4D acquisition. Processing and display in 4D are currently not available in VnmrJ.

Chapter 12. Indirect Detection Experiments

Sections in this chapter:

- 12.1, “Probes and Filters,” this page
- 12.2, “The Basic HMQC Experiment for ^{13}C,” on page 250
- 12.3, “Experiment Manual Setup,” on page 253
- 12.4, “Cancellation Efficiency,” on page 258
- 12.5, “Pros and Cons of Decoupling,” on page 259
- 12.6, “^{15}N Indirect Detection,” on page 259
- 12.7, “Pulse Sequences,” on page 259

This chapter describes one indirect detection experiment known as *heteronuclear multiple-quantum coherence* (HMQC). Indirect detection experiments show correlations between heteronuclei while detecting high-sensitivity protons. HMQC differs from the older heteronuclear correlation techniques that detect the low-sensitivity heteronucleus (for example, ^{13}C or ^{15}N).

12.1 Probes and Filters

Indirect Detection Probes

The most commonly used probes for indirect detection experiments are the Varian, Inc. “indirect detection” NMR probes, such as the Triple Resonance, Penta, Tunable Triple, Indirect Detection, gHX Nano, Cold Probes, and others. Indirect detection probes have a ^{1}H coil and an X-nucleus coil with the ^{1}H coil positioned closer to the sample for the highest possible sensitivity of the observed nucleus. When connecting cables to the probe, ignore words like “observe” and “decouple” and think of ^{1}H (for observe) and X (for decouple) for connections.

Normal “broadband” probes similarly have a ^{1}H coil and an X-nucleus coil and can be used for indirect detection. But broadband probes have significantly lower proton sensitivity (about half that of indirect detection probes) and so are not optimum for indirect detection experiments. Nevertheless, broadband probes usually provide some sensitivity improvement over direct detection heteronuclear correlation experiments. Four-nucleus and “Switchable” probes also have a ^{1}H coil and an X-nucleus coil, with the X coil closer to the sample, and can satisfy the needs for indirect detection experiments.

For more information on Varian, Inc. NMR probes, go to the NMR probe product pages at `www.varianinc.com`. Refer the manual that shipped with the probe for installation and tuning instructions.

Filters

Bandpass filters might be needed on the transmitter, receiver, decoupler, and lock channels. Filters are part of the probe kit shipped with each indirect detection probe that Varian sells.

Install a ^{2}H bandpass filter in the lock channel line. Expect the lock phase to change when the filter is added. This filter can be left in the system at all times; it will, however, cause a small (about 3 dB) loss in lock sensitivity.

The following table lists part numbers for the bandpass filters supplied with indirect detection probes.

Filter	*300-MHz*	*400-MHz*	*500-MHz*	*600-MHz*	*750-MHz*
^{15}N	BE30.4-7.6-9BB	BE40-14-9BB	BE53-15-8BB	BE61-10-8BB	BE77-15-4BB
^{2}H	BE46-4-6BB	BE61-10-8BB	BE77-3.8-8BB	BE95-12-8BB	BE115-11-6BB
^{13}C	BE75-15-8BB	BE109-22-8BB	BE135-35-8BB	BE151-40-8BB	BE188-20-7BB
^{31}P	BE135-35-8BB	BE151-40-8BB	BE175-60-8BB	BE240-100-8BB	BE301-46-8BB

There is a “catch” with this configuration—the filters used for indirect detection tend to degrade specifications approximately 10% in terms of longer pulse widths and lower signal/noise. The user thus faces a classic trade-off of performance (manually insert filters only when needed but achieve better specs) versus convenience (leave filters in place continuously and achieve worse specs). The convenience factor, of course, is nonexistent if the instrument does anything other than ^{13}C and ^{1}H, because the ^{13}C bandpass filter can not be left in place on the X line while doing ^{31}P, ^{15}N, or anything else. All standard specifications are given with the indirect detection filters *not* in place.

12.2 The Basic HMQC Experiment for ^{13}C

The essence of the HMQC experiment is the cancellation or elimination of the signals from proton magnetization attached to ^{12}C, leaving only signals from proton magnetization attached to ^{13}C, contributing to a ^{13}C–^{1}H chemical shift correlation spectrum. The three basic independent mechanisms to generate this discrimination are:

- "Spin-Echo Difference Experiment," page 250
- "BIRD Nulling," page 252
- "Transmitter Presaturation for High-Dynamic Range Signals," page 253

Spin-Echo Difference Experiment

The heart of the HMQC sequence can be reduced to a heteronuclear spin-echo difference experiment that looks like Figure 66.

In Figure 67, *a*, *b*, and *c* represent the proton magnetization attached to carbons, where *a* are the proton magnetization attached to up-^{13}C, *b* are proton magnetization attached to ^{12}C, and *c* are proton magnetization attached to down-^{13}C. Assume that we are at the resonance frequency of the proton magnetization attached to the ^{12}Cs. In the rotating frame, the following steps (shown in Figure 67) occur:

1. The first proton 90° pulse places all proton magnetization along the *y* axis.
2. After a time $\Delta = 1/(2J)$, the *b* proton magnetization are still along the *y* axis, but the *a* proton magnetization are along the *–x* axis and the *c* proton magnetization are along the *+x* axis.

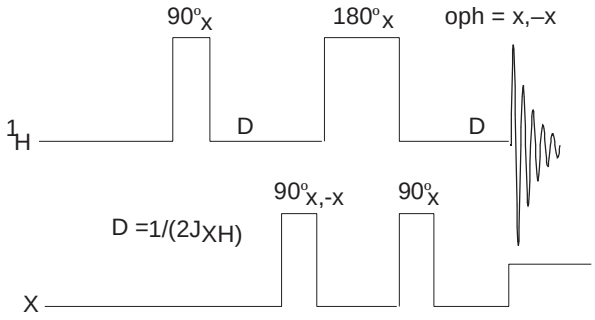


Figure 66. Heteronuclear Spin-Echo Difference Experiment

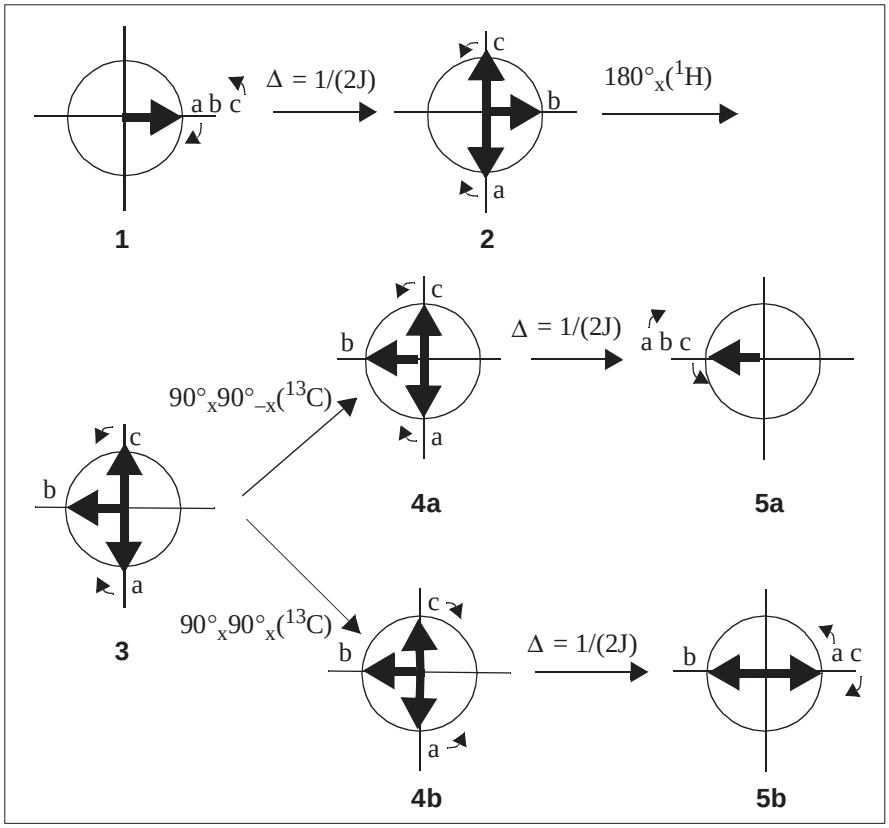


Figure 67. HMQC Pulse Sequence, Showing Movement of Attached Protons

3. Next, the $180°_X$ proton pulse places the *b* proton magnetization along the *–y* axis but does not affect the *a* and *c* proton magnetization.
4. The next pulse has the following effect:
   a. The $90°_X90°_{-X}$ carbon pulse is effectively a null pulse. All rotational directions are maintained.
   b. The $90°_X90°_X$ ($= 180°_X$) carbon pulse reverses the ^{13}C, which makes the *a* proton magnetization attach to the down-^{13}C and the *c* proton magnetization attach to the up-^{13}C, essentially reversing their rotational direction.

5. After another period Δ = 1/(2J), the following occurs:
   a. The *a*, *b*, and *c* proton magnetization are refocused along the –*y* axis.
   b. The *b* proton magnetization are still along the –*y* axis, and the *a* and *c* proton magnetization are refocused along the +*y* axis.

Subtracting the signal resulting from step 5b and 5a, by changing the receiver phase `oph`, results in cancellation of the *b* proton magnetization, while the signal for the *a* and *c* proton magnetization doubles.

To create a 2D experiment with information about heteronuclear chemical shifts, we introduce an evolution time t_1 that occurs between the two X-nucleus 90° pulses, as shown in Figure 68.

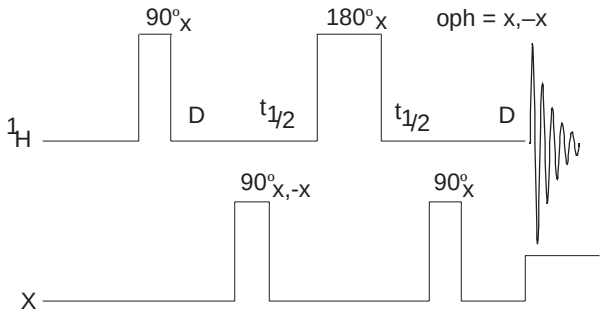


Figure 68. Evolution Time Added Between X-Nucleus Pulses

In this 2D experiment, which is now a full HMQC experiment, proton magnetization attached to ^{12}C show no different behavior and are still cancelled after two scans. For the ^{13}C nuclei, however, whether they experience a 180° pulse, a 0° pulse, or something in between, depends on the time between the two 90° pulses and their rate of precession during that time (i.e., their chemical shift). Therefore, this experiment produces a modulation of the intensity of the ^{13}C-bound proton magnetization, and the Fourier transform of that modulation yields the chemical shift of the ^{13}C bound to that proton.

Thus we detect ^{13}C chemical shifts with the intensity of proton magnetization, and, simultaneously, we obtain a correlation of the ^{13}C and ^{1}H chemical shifts. Appropriate variations of the experiment produce long-range coupling information.

BIRD Nulling

The second (optional) type of cancellation that can occur during an HMQC sequence is the so-called BIRD (Bilinear Rotation Decoupling) pulse nulling effect (Summers, Marzilli, and Bax, *JACS*, 1986, **108,** 4285). A particular sequence of the BIRD pulse, three pulses on the ^{1}H channel and one on the X channel, inverts the z-magnetization of proton magnetization bound to ^{12}C and leaves the z-magnetization of proton magnetization bound to ^{13}C unaffected. The full sequence is illustrated in Figure 69, where $\Delta=1/2J_{XH}$.

After the BIRD pulse, a variable waiting period (τ in Figure 69) is inserted, allowing the ^{12}C-bound proton magnetization to relax back to equilibrium. If τ is adjusted so that the ^{12}C-bound proton magnetization are approximately at a null, then when the remainder of the pulse sequence (the normal HMQC sequence) is executed, cancellation of the ^{12}C-bound proton magnetization is enhanced (since those proton magnetization had very little magnetization at the start of the HMQC sequence). Obviously, not all proton magnetization will have the same relaxation time, so the choice of τ must be a compromise; generally,

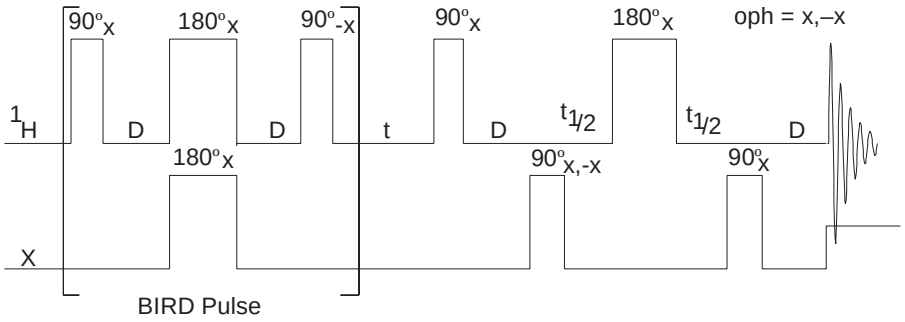


Figure 69. HMQC with BIRD Pulse Nulling Effects

unless only one proton is involved, the additional suppression from the BIRD nulling will be a factor of two to five.

For systems that exhibit a negative NOE, such as macromolecules, cross-relaxation between the inverted proton magnetization on ^{12}C and the noninverted proton magnetization on ^{13}C will decrease the intensity of the desired proton signal. The extent of this decrease can vary between 0% and 100%. For this reason, omission of the BIRD part of the sequence is advised for macromolecules.

BIRD pulse nulling is also not possible when long-range indirect detection experiments (Heteronuclear Multiple-Bond Coherence, or HMBC) are performed. In this case, proton magnetization that have long-range couplings to ^{13}C are directly bonded to ^{12}C (99% of them, anyway) so that BIRD pulse nulling would lose all intensity in the proton magnetization of interest.

Transmitter Presaturation for High-Dynamic Range Signals

When high-dynamic range situations, such as observing signals in H_2O, are involved, HMQC phase cycling and/or BIRD pulse nulling may be insufficient to produce cancellation of the large proton signals. For this reason a third mechanism, presaturation, may be necessary. Since one channel of the instrument is set to an X-nucleus like ^{13}C or ^{15}N, this presaturation must be accomplished with the other channel; that is, the same channel that will be applying observe pulses to the proton magnetization. During one or two different periods of the sequence (during the initial delay and during the τ delay), a change in power level and possibly frequency will be appropriate in order to perform the presaturation.

12.3 Experiment Manual Setup

HMQC and other indirect detection experiments are set up using StudyQ or by selecting Experiment.....^{1}H Detected Proton-Carbon 2D Correlation Experiments...`Hmgc`. This process retrieves ^{1}H and ^{13}C calibrations from the active probefile and results in a parameter set in which the only significant choices are how long to run the experiment (`nt`) and how much resolution is need in f1 (`ni`). However, a step-by-step process is described in this section to detail the choices that can be made and the impact of the choices.

A good “normal” sample to use for your first natural abundance sample is the 1% 3-heptanone in $CDCl_3$ sample (Part No. 00-968120-93). Throughout the following

instructions, refer to Table 27 to understand which parameters control the features in your configuration.

1. Insert the sample and, after shimming, leave the spinner off. Regulate the temperature if the experiment is run at a controlled temperature.
2. Set up to obtain a normal carbon spectrum and narrow the spectral width to the appropriate region. The ^{13}C spectrum will be too weak to observe in a reasonable amount of time in some cases. Two approaches can be taken to set the parameters controlling the ^{13}C frequency and spectral width if this is the case.
   - Use the same parameters as used in similar experiments in the past on similar samples.
   - Set up a standard Carbon experiment and an appropriate solvent.

     The spectrum obtained should be properly referenced. Apply the appropriate knowledge of the expected chemical shift range, even if the peaks in the spectrum can not be seen, to place two cursors where the edges of that range will be, and narrow the spectral width.
3. Obtain a proton spectrum and narrow the spectral width. Check the calibration of the pulse width by entering **pw=4*pw ga**. Look only at the signals near the center of the spectrum and see if they produce a null signal. If they are negative, enter **pw=pw+0.8 ga**; if they are positive, enter **pw=pw-0.8 ga**; repeat until a good null is found, then enter **pw=pw/4**.
4. Switch to the HMQC experiment and set the relevant parameters based on the results of steps 2 and 3.
5. Enter **phase=1 ni=1 dm='nnn' null=0 ai wexp='wft dssh'**. Set **j** to an appropriate value (normally 140 for C–H), and set **nt** to 4 or more transients, depending on the concentration of the sample (signal to noise needs to be sufficient to see the ^{13}C satellites). Now set **pwx** to an array of 0 and 90° and enter **au** to acquire two spectra. Proceed only if the two spectra are sufficiently different to be confident that the second spectrum is showing satellite peaks only and not just residual uncanceled intensity of the protons attached to ^{12}C.

   Skip ahead to step 8 if convinced of a correct connection but not the quality of the spectra achieved at this step, and optimize the `null` parameter, then return here to check and optimize `pwx`. In either case, go over the checklist in the section "Cancellation Efficiency," page 258, making sure everything possible has been done to optimize cancellation.

   The spectrum in Figure 70 shows the result of this experiment on a sample of 1% 3-heptanone at 300 MHz, using `nt=64 null=2.0` and `d1=2`.
6. Now run an array of **pwx** around your expected 90° value, picking the one that gives the largest satellite signals.
7. Set **pwx** to its 90° value and enter an array of **dm='nnn','nny'** if decoupling is used during acquisition. These two experiments should show coupled and decoupled spectra, respectively.
8. Now, if appropriate, optimize the parameter `null`. Set **nt=1 ss=4** and enter an array of **null** values with at least one very short value (e.g., 0.001) and one very long value (e.g., 2.0). This experiment depends on the relaxation times of the spins involved. Set **at** and **d1** to the same values being used in the 2D experiment. Run the array and select the value of **null** for which either most of the peaks, or the biggest peaks, or the peaks of most interest (choose the criterion), are approximately zero; remember, no one value of `null` is correct for all peaks. Figure 71 shows this

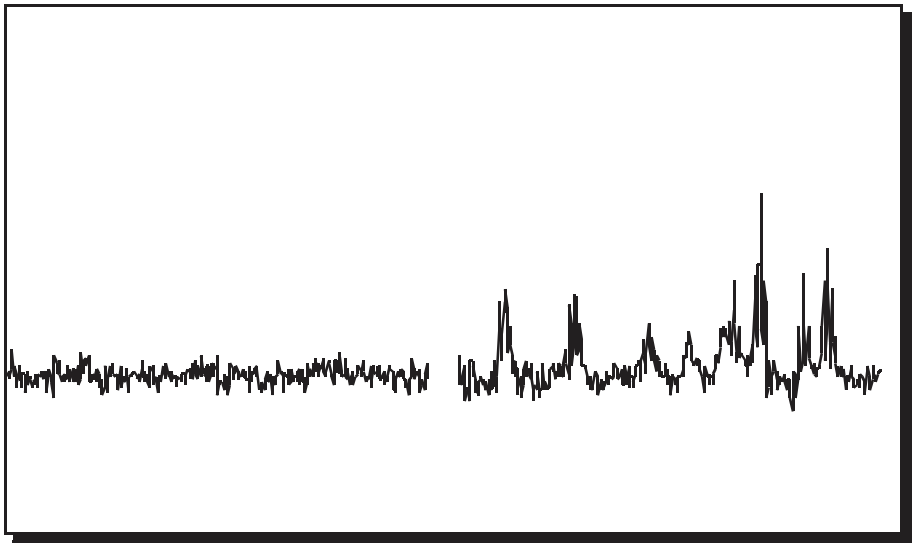


Figure 70. Verifying Cancellation with `pwx=0,90`

experiment run on a sample of 28 mg of gramicidin, with `null` arrayed over the range of values: 0.001, 0.05,0.1,0.2,0.3,0.4,0.5, and 2.0; examination of the spectra shows clearly how different values of `null` might be chosen.

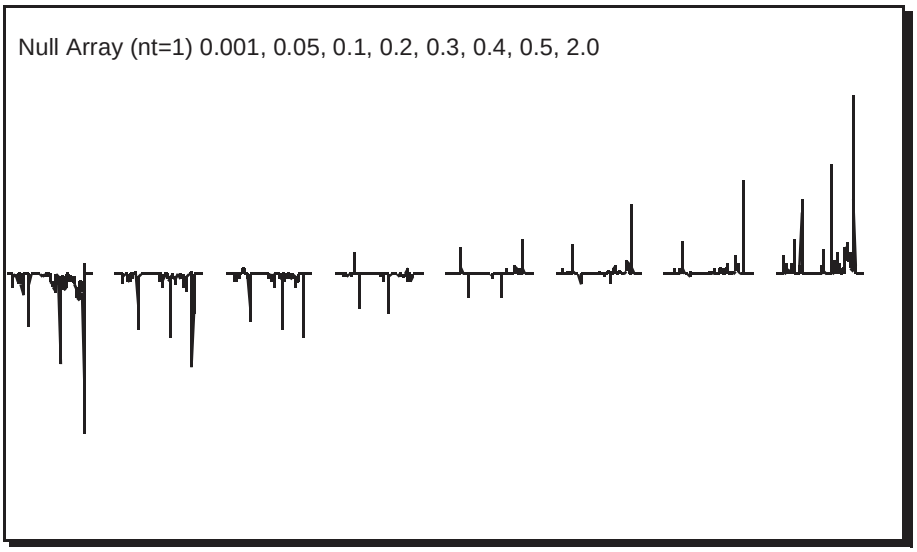


Figure 71. Optimizing the BIRD Nulling Time

9. Set up presaturation, if desired, in the following manner. It is necessary to observe the ^{12}C-bound protons, so set **`nt=1 dm='nnn'`**, and set **`null=0`** to omit the nulling period (for now at least).
    a. Enter **`ga`** and a proton spectrum will be observed.
    b. Move the FID to a different experiment, join the different experiment, and re-transform the data (e.g., **`mf(1,2) jexp2 wft`**).

c. Set the cursor on a peak that is to be removed by presaturation, and enter **`nl movetof`**. Note the value of `tof` selected and then copy this value back to your original experiment into the parameter `satfrq` (e.g., `jexp1 satfrq=x`).

d. Now set **`satflg='yn'`** and **`satdly`** equal to a time significant compared with T_1 of the peaks (e.g., `satdly=1`).

e. Array **`satpwr`** to find the minimum value for which the peak will be removed (e.g., `satpwr=10,7,4,1 au`).

Set **`satflg='yy'`**, reset **`null`**, and set `satpwr` to the value determined to use presaturation.

Set **`satflg='nn'`** to not use presaturation.

10. Set up the 2D experiment.

Set `ni` between 128 and 256, **`phase=1,2`**, and `nt` to an appropriate number (comparable to value used in step 5).

11. Phasing in f_2 is accomplished by performing a 1D transform on the first increment with `wft(1)` and phasing the spectrum, paying attention only to the ^{13}C satellite peaks. In f_1, the combination of the usually large spectral width and the pulse in the center of the evolution time produces large negative values for `lp1`.

Reasonably good starting points for the f_1 phase can be calculated according to the following formulas:

$$lp1 = -sw1 \times 360^{\circ} \times ((4 \times pwx)/\pi)$$
$$rp = -lp1/2$$

Expect to see artifacts in these spectra. The residual uncanceled signals from protons attached to ^{12}C show up as stripes parallel to the f_1 axis at the frequency of each ^{1}H peak. This artifacts will be larger for peaks with long T_1, such as solvent peaks (e.g., residual protons on a deuterated solvent) or methyl groups. In Figure 72 they are seen at 2.4 ppm, 1.0 ppm, and 0.9 ppm.

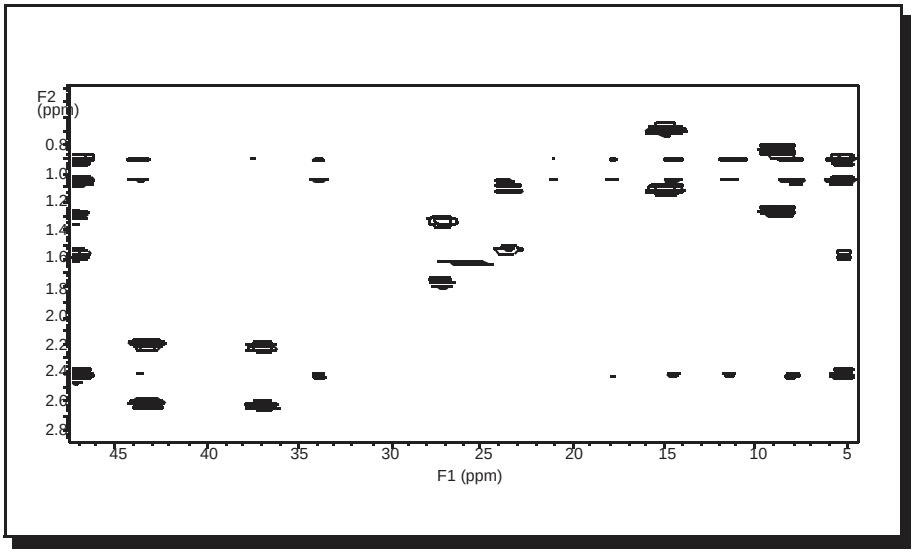


Figure 72. Coupled HMQC Spectrum of 3-Heptanone

Axial peak artifacts, which are common, will show up either at f_1=0 (the center of the spectrum in f_1) or, as in Figure 72, at the edges of the spectrum in f_1 (if FAD is used), again

at f_2 frequencies corresponding to each ^1H peak and possibly through the entire spectrum. Another common artifact seen in Figure 72 is the “0,0” artifact in the exact center of the spectrum. Some peaks in the ^1H spectrum, of course, will not appear in the HMQC spectrum, because they represent protons that are not bound to ^{13}C (e.g., protons from water or NH groups). This is not the case with 3-heptanone, however.

Multiple structures are typical with HMQC spectra. During the detection period a (i.e., with ^1H-^1H couplings) proton spectrum of only those protons attached to ^{13}C is acquired. The proton attached to the carbon at 37.2 ppm is a quartet (it’s adjacent to a CH_3 group) and the proton attached to the carbon at 43.4 ppm is a triplet (it’s adjacent to a CH_2 group), see Figure 73. In the ^1H spectrum itself, these two groups of protons are heavily overlapped

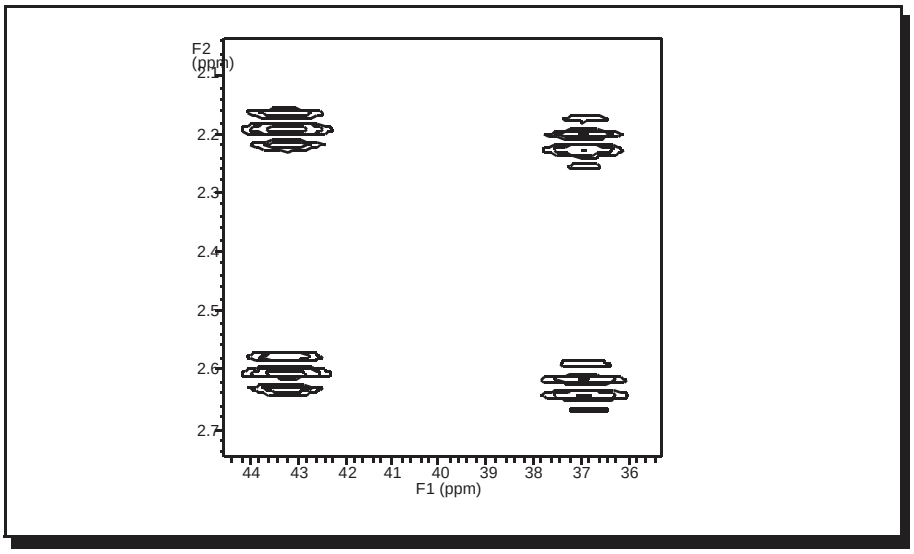


Figure 73. Expansion of Coupled 3-Heptanone HMQC Showing Multiplets

(see Figure 74).

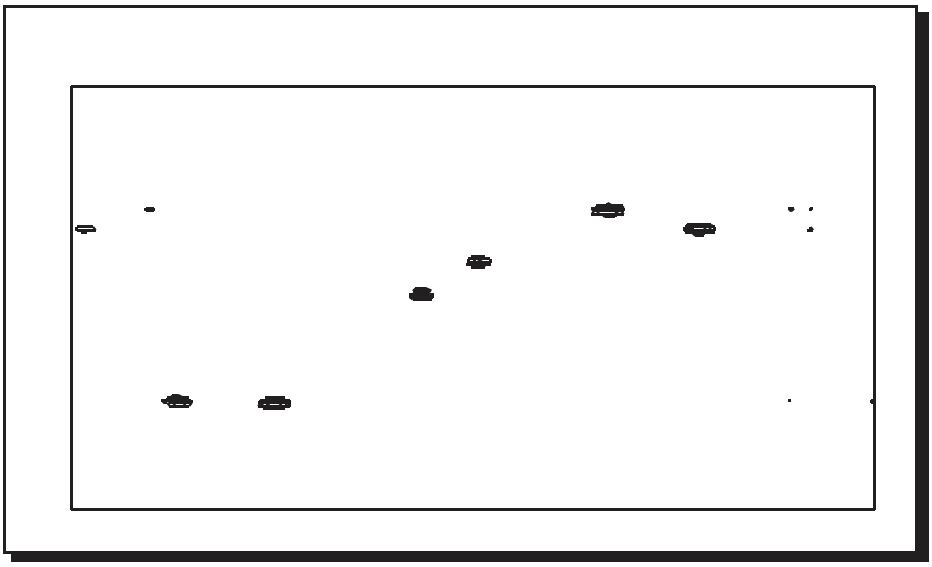


Figure 74. Decoupled HMQC Spectrum of 3-Heptanone

12.4 Cancellation Efficiency

Cancellation efficiency is critical because indirect detection experiments involve cancellation of non-^{13}C-bound protons that are two orders of magnitude more intense (assuming unlabeled compounds). Cancellation efficiency, in turn, depends on the fundamental stability of the system rf and the reproducibility of anything else that can affect the signal. Stability is fixed by the instrumentation A number of operating conditions that influence the quality of any cancellation experiment (NOE difference experiments are another good example) are under the control of the operator. Some of these conditions are discussed here, roughly in order of importance:

- Run experiments non-spinning. This is a must.
- Use the highest lock power at which the lock is stable (be sure to shim with a non-saturating level, however) and keep the lock gain as low as possible, sufficient only to be sure that lock is not lost during the experiment.
- Use a ^{2}H band-pass filter in the lock line. Interference between X-nucleus decoupling or even X-nucleus pulses can affect the lock and cause field instabilities, limiting the ability to perform cancellation experiments (if such a filter is not available, run a short-term experiment in the unlocked mode as a test).
- Use VT regulation, even at room temperature. Large changes in temperature of the environment can affect the VT gas stream. The frequency of peaks in the spectrum and of the lock resonance (which affects all peaks) is temperature-sensitive to some degree. Shimming may also change if the probe temperature varies, which can affect the lineshape.
- Be sure the system is in thermal equilibrium. Applying large amounts of power to the system, if experiments with X-nucleus decoupling are run, the temperature of the probe, the sample, or both, is almost certain to change even with VT regulation. The best way to ensure thermal equilibrium is to set up a “dummy” experiment with *identical* conditions (in terms of duty cycle) to the actual experiment, but which runs for perhaps several minutes (easily accomplished by setting *ni* to a small number). Now, queue the real experiment to follow the dummy one, and the sample and probe are properly equilibrated.
- Be sure the system is in an NMR steady-state by using steady-state pulses.
- Use a large value of `nt`. Cancellation improves with larger `nt`, so the relevant cancellation is that which occurs at `nt` comparable to what will be used in an indirect detection experiment (16 to 1024). Do not expect perfect results with `nt=2`.
- Minimize floor vibration. Install an antivibration system if this cannot be fixed by spectrometer placement.
- Use a moderate flow of body air through the probe to eliminate “rattling” from turbulent flow.
- Use lengthened pulses (attenuated rf) if there is a rise time or phase glitch problem.

Before beginning an HMQC experiment, assess the quality of the reproducibility by performing some simple difference experiments. The standard S2PUL pulse sequence is a good one to use for this purpose. The first pulse of S2PUL, controlled by `p1`, is held at a constant phase, while the receiver varies in phase. Thus, after four scans with `p1` set to the 90° value, `pw=0`, no signal should be seen. This can be compared to four scans with `pw` set to the 90° value, `p1=0`, which produces a full signal. Taking the ratio of these two spectra gives a concrete measurement of cancellation efficiency, while repeating the null spectrum a number of times gives a measure of the reproducibility of the cancellation. Use this test to assess the value of the various steps and modifications described above, or of other

differences (for example, the relative cancellation efficiency of experiments with and without X-nucleus decoupling).

12.5 Pros and Cons of Decoupling

Decoupling of X during acquisition seems advantageous—the spectrum is less crowded, with only half as many peaks, and each peak has twice the sensitivity—but problems soon arise.

The disadvantage of X-nucleus decoupling stems from the need to use large (up to 8 kHz) decoupling fields. This high power can cause significant heating, particularly in lossy samples. As a consequence of sample heating, experiments with X-nucleus decoupling are generally limited to relatively short acquisition times, which in turn may produce less resolution in f_2 as well as less sensitivity for molecules with long T_2. Furthermore, the heating that does occur frequently produces worse cancellation efficiency. And, finally, to prevent the buildup of heat in the sample, the duty cycle of the experiment may need to be limited to 10 to 20%, again possibly reducing sensitivity. Therefore, experiments performed without X-nucleus decoupling are perfectly reasonable, and may well be preferable.

It is important to avoid sample heating if X-nucleus decoupling is desired. This form of sample heating can be non-uniform within the sample and can cause microconvection, producing poor cancellation. Keep the acquisition time short and the overall duty cycle less than 20%.

When WALTZ decoupling is used, the maximum power level for decoupling is the level that provides an rf field strength (in Hz) comparable to half the range of expected X shifts. The normal spread of protonated carbons is 150 ppm, which is 15 kHz on a 400-MHz system, and, consequently, a ^{13}C 90° pulse of 25 µs (corresponding to an rf field strength of 8 kHz) is adequate. The somewhat long proton pulses on broadband and switchable probes does not seem to present a problem because indirect detection experiments demand no more proton pulse power than DEPT or HETCOR.

12.6 ^{15}N Indirect Detection

Calibrations and operations for ^{15}N proceed largely along the lines outlined above for ^{13}C. In the standard sample, 2% ^{15}N-benzamide (Part No. 00-968120-97), the ^{15}N satellite lines are partially obscured by other resonances in the conventional 1D spectrum, and so the ^{15}N pulse width calibration must be done using multi-transient HMQC experiments as described in "The Basic HMQC Experiment for ^{13}C," page 250. Be sure to use a J appropriate for NH couplings (90 Hz) in this case.

A step that can often be done in ^{15}N work of peptides is to make sure that the γB_2 is sufficient to decouple the relatively narrow range of ^{15}N chemical shifts expected in such samples but no more. This minimizes heating effects and improves cancellation. Typical acquisition times (`at`) are 0.075 to 0.1 seconds.

12.7 Pulse Sequences

Indirect detection experiments can use the HMQC or HSQC pulse sequences.

- "HMQC Pulse Sequence," this page

- "HSQC Pulse Sequence," page 263

HMQC Pulse Sequence

The `hmqc<(isotope)>` macro sets up parameters for a HMQC (heteronuclear multiple-quantum coherence) pulse sequence. The optional `isotope` argument is the isotope number of the heteronucleus of interest, for example, `hmqc(1)` for ^{1}H (the default is ^{13}C). Figure 76 is a diagram of this sequence. The first `2*pwx` pulse on the X heteronucleus is a composite 180 consisting of 90(`v9`) – 180(`v1`) – 90(`v9`).

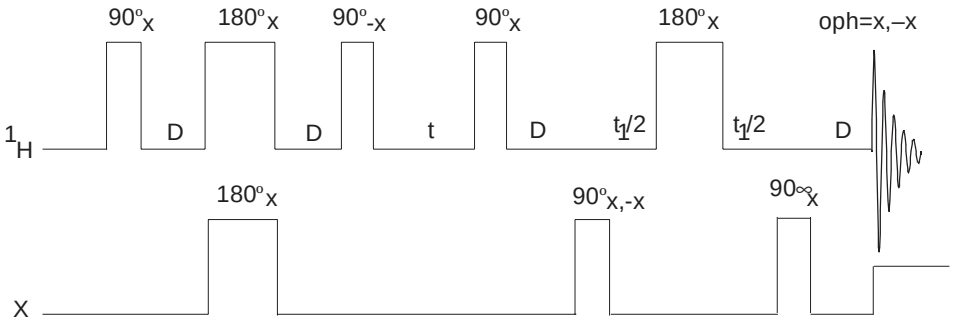


Figure 75. Basic HMQC Pulse Sequence

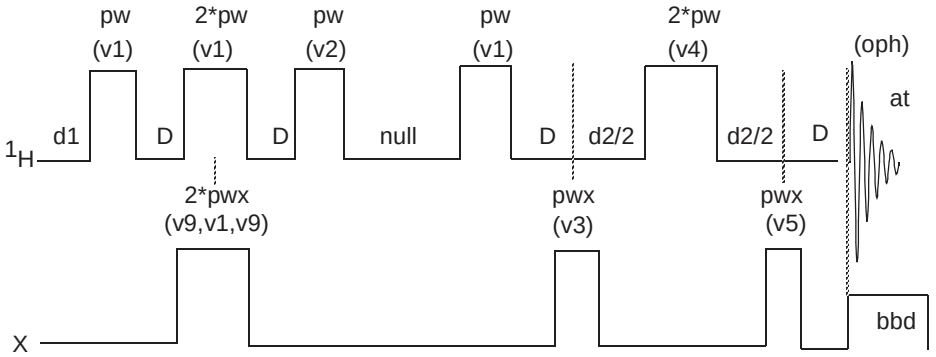


Figure 76. HMQC Pulse Sequence with `null`<>0 and `mbond='n'`

Phase-Sensitive Aspects of the Sequence

The parameter `phase`, as in other phase-sensitive 2D experiments, controls the f_1 phase detection. Use `phase=1` for 1D setup experiments or a 2D experiment without quadrature detection in f_1. Use `phase=1,2` for a normal 2D experiment using the States-Haberkorn-Ruben (hypercomplex) method. Use `phase=3` to acquire data with TPPI and make sure `sw1` is twice the expected range.

The FAD, for "F1 Axial Displacement," technique (Marion, D.; Ikura, M.; Tschudin, R.; Bax, A. *J. Magn. Reson.* 1989, ***85***, 393) involves a change of phase cycling that shifts the axial artifacts in a hypercomplex experiment to the edge of the spectrum, giving the hypercomplex version the benefit of TPPI with none of the disadvantages. It is also referred to as "States-TPPI." The `hmqc` macros include FAD. Once implemented, use of the

technique is totally transparent—just perform a standard hypercomplex experiment with `phase=1,2`.

Parameters

Table 27. Parameters for HMQC Pulse Sequences

Parameter	*HMQC*
^{1}H 90° pulse	`pw`
^{1}H 180° pulse	derived from `pw`
^{1}H amplifier power (if appropriate)	`tpwr`
^{1}H frequency	`tn, tof`
^{1}H spectral width	`sw`
X 90° pulse	`pwx`
X 90° pulse for WALTZ decoupling	`1/(4¥dmf)`
X 180° pulse	derived from `pwx`
X amplifier power for pulses (if appropriate)	`pwxlvl`
X amp power for decoupling (if appropriate)	`dpwr`
X frequency	`dn, dof`
X spectral width	`sw1`
Δ delay	`1/(2j) [if j=0, D=0]`
τ delay for BIRD nulling (if `null=0`, entire BIRD sequence is skipped)	`null`
Coupled experiment	`dm='nnn'`
X decoupling during acquisition.	`dm='nny'`
Setup experiments	`phase=1`
Hypercomplex experiment	`phase=1,2`
TPPI	`phase=3`
Minimum `nt` possible	`2`
Presaturation and/or multiple-bond correlation	see text
Axis parameter for proper ppm on both axes	`pd`

`pw` is a 90° pulse on the observed nucleus (protons) at power equal to `tpwr`.

`pwx` is a 90° pulse on the heteronucleus at power equal to `pwxlvl`.

`dpwr` is the decoupler power level for broadband X-decoupling.

`dmf` sets the modulation frequency ($4*\gamma B_1$) at decoupler power (`dpwr`).

`dmm` is decoupler modulation mode. `dmm='ccg'` is recommended.

`dm='nny'` activates heteronuclear broadband decoupling (recommended) during acquisition. Note that `dm` can be set to either `'nnn'` or `'nny'`, and that the duty cycle for the decoupler should be less than 20%.

`j` is the average scalar coupling constant between the protons and the heteronucleus (usually one-bond constants). `j` is 140 for ^{13}C or 90 for ^{15}N. The time Δ, shown in Figure 76, is calculated as `1/2j`.

`null` is a WEFT-like delay used to improve the suppression of the protons connected to ^{12}C (and not to ^{13}C) that have been inverted by the preceding BIRD pulse. Try a `null`

value of 0.3 for ^{13}C, 1.0 for ^{15}N, and 0 for macromolecules. To optimize, set `ss=-8` and array `null` with `nt=1` and `phase=1`. This selects the value of `null` that best minimizes the sample's signals (typically 0.2 to 0.7 seconds). If `null` is set to 0, the BIRD element is omitted from the pulse sequence.

`at` is the acquisition time (t_2 period).

`ni` is the number of t_1 increments (set up with default values for either ^{13}C or ^{15}N).

`ss` is the number of complete executions of the pulse sequence not accompanied by data collection prior to the acquisition of the real data: if `ss` is positive, `ss` steady-state pulses are applied on the first increment only; if `ss` is negative, –`ss` transients are applied at the start of each increment.

`nt` is a multiple of 4 (minimum) or multiple of 8 (recommended).

`phase=1,2` (2D hypercomplex data with hypercomplex-TPPI method) or `phase=3` 2D TPPI data). `phase=1,2` is suggested. For `phase=3`, remember that `hmqc` sets `sw1` to *twice* the desired value for heteronuclear experiments.

`satflg='yn'` gives presaturation during `satdly`, and `satflg='yy'` gives presaturation during `satdly` and `null`.

`satfrq=x` is the presaturation frequency (using the transmitter), `satdly` is the length of saturation time during the relaxation period (immediately after `d1`), `satpwr` is the power level for presaturation using the transmitter.

`hs='yn'` gives a homospoil pulse at beginning of `d1` (length=`hst`). `hs='yy'` gives a homospoil pulse at beginning of both `d1` and `null`.

`taumb` is a fixed delay associated with the multiple-bond HMQC experiment (`taumb=0.055` is recommended).

`mbond='n'` is a normal HMQC experiment. `mbond='y'` is a multiple-bond HMQC experiment (HMBC).

(1) Set `null=0` to run HMBC (mbond='y'), otherwise, only protons that are both long-range and short-range (one-bond) coupled to a given heteronucleus (^{13}C, for example) will not be suppressed, (2) set `dm='nnn'`, (3) set `taumb`, and (4) run the single-bond (HMQC) and multiple-bond (HMBC) experiments with `phase=1,2` or `phase=3`.

Phase Cycling

The phase cycling is the following:

`v1`, `v2`, `v3`, `v4`, `v5`, `v9` are phases for pulses. `oph` is the phase for receiver.

```
v1  =  x  x  y  y
v2  = -x -x -y -y
v3  =  x -x  y -y
v4  =  x  x  y  y  y  y -x -x
v5  =  x  x  y  y  x  x  y  y
v9  =  y  y -x -x
oph =  x -x  y -y
```

These phases are for `phase=1`. For `phase=2`, add 90° to `v3`. For `phase=3`, add 90*(`ix` - 1)° to `v3`, where `ix` is the increment counter.

Technique

The usual setup is to place a ^{1}H bandpass filter between the observe port on the probe and the $^{1}H/^{19}F$ preamplifier, and to place a 250-MHz lowpass LC filter and either a ^{13}C bandpass or a ^{15}N bandpass filter in the decoupler line just before the probe connection.

The experiment should be performed non-spinning and with VT regulation.

HSQC Pulse Sequence

The `hsqc` macro sets up parameters for the HSQC pulse sequence.

Parameters

`sspul='y'` selects for *trim(x)-trim(y)* sequence at the start of the pulse sequence; `sspul='n'` selects a normal experiment.

`satmode='yn'` gives presaturation during relaxation period (`satdly`) with the transmitter; `satmode='nn'` gives no presaturation during relaxation period (`satdly`); `satmode='ny'` gives presaturation during only the null period.

`satfrq` sets the presaturation frequency.

`satdly` sets the saturation time during the relaxation period.

`satpwr` sets the saturation power for all periods of presaturation with xmtr.

`hs='yn'` sets a homospoil pulse (`hst`) during the d1 relaxation delay.

`null` is the delay associated with the BIRD nulling.

`tpwr` is the power level for ^{1}H transmitter pulses.

`pw` is a 90° transmitter pulse length for protons (the observed nucleus).

`pwxlvl` is the power level for X decoupler pulses.

`pwx` is a 90° decoupler pulse length for X.

`jxh` is a one-bond heteronuclear coupling constant to X (in Hz).

`phase=1,2` for hypercomplex experiment with F1 quadrature (complex F1-FT).

Chapter 13. Solids Experiments

Sections in this chapter:

- 13.1, “Solids Pulse Sequences and VnmrJ,” on page 265
- 13.2, “Running a Solids Experiment,” on page 266
- 13.3, “Setting up for Solids Experiments,” on page 268
- 13.4, “Calibration of ^{13}C-^{1}H CPMAS Probes,” on page 285
- 13.5, “Basic 1D Experiments,” on page 299
- 13.6, “HX2D Experiments,” on page 302
- 13.7, “HXY Experiments,” on page 303
- 13.8, “Quadrupole Experiments,” on page 305
- 13.9, “Multipulse Experiments,” on page 305

13.1 Solids Pulse Sequences and VnmrJ

The section describes pulse sequences and protocols used for solid-state NMR experiments in VnmrJ versions 2.2C and later. These sequences include basic experiments for cross-polarization, single-pulse experiments, and experiments such as MQMAS, REDOR, HETCOR, and WISE. This section includes proton multi-pulse acquisition CRAMPS sequences such as BR24 and windowed PMLG.

All of the Solids sequences described here use a new set of consistent parameter definitions. These experiments can be set up from either set-up macros or protocols on the command line, set up from the Experiments pull-down menu of either the Experimental or Walkup interface (Study Q turned off), or by drag-and-drop from protocols in the Experiment Selector (Walkup interface only).

Solids parameter sets are not consistent with parameter sets for other non-solids sequences, including very basic sequences such as `s2pul.c`, older solids sequences such as `xpolar1.c`, and those sequences of the older SolidsLib for UNITYINOVA. The sequence `onepul.c` replaces `s2pul.c` for solids (or `xpolarv1.c` with `xpol = 'n'`) and the sequence `tancpx.c` replaces `xpolarv1.c` with `xpol = 'y'`. All the functions of `xpolarv1.c` (TOSS, relaxation measurements, and dipolar dephasing) are distributed among individual sequences. Sequences with multiple functions are avoided.

Solids pulse sequences use a new logical method of naming parameters based upon parameter groups. Each parameter group refers to a single NMR function (for example cross polarization or TPPM decoupling) and each parameter group has it's own interface on the Pulse Sequence page of the Acquire tab for the sequence. A pulse-sequence module (a set of C-functions in the pulse-programming language that execute the NMR function in a pulse sequence) is also associated with each parameter group.

The VnmrJ solids sequences do not use legacy parameter names such as `pw`, `tpwrm`, or the older ad hoc names for solids such as `dipolr`, `level1`, or `evolve`. VnmrJ solids sequences do not use the `status()` command for decoupling and the associated parameters, `dm`, `dmm`, `dres`, `dmf` and `dseq`. Equivalent choices for solids decoupling methods (`CW`, `TPPM`, `SPINAL64` and `off`) are made through the decoupler parameter group and module. More information about parameter groups and pulse-sequence modules can be found in the *User Programming* manual.

Descriptions of the sequences are included in this chapter. The same information can be obtained through the **Sequence Manual** button on the **Text** page of **Process** tab or the `man(seqfil)` command on the command line.

13.2 Running a Solids Experiment

The following is a generalized procedure for running a solids experiment. Steps in the procedure are referenced to sections in this an other manuals where more detailed information or procedures are provided. Use these procedures only if the spectrometer is set up for solids experiments and all probes have been installed, tested, and calibrated.

Set the user profile to **AllSolids** before starting this procedure if the Experiment Panel does not contain solids related protocols, see "Loading a Protocol," page 269.

1. Do one of the following procedures:
   - Systems operating in either the liquids or solids mode and the last used probe is either unknown or a liquids probe:
     a. Load any liquids probe file.
     b. Click on the **Start** tab.
     c. Select the **Spin/Temp** page
     d. Click on the **VT Air Off** button
     e. Type **`su`** on the command line.
     f. Continue with step 2.
   - System that operate only as solids systems or the last probe used was a solids probe.

     Continue with step 2.
2. Load the sample into the rotor and install the probe in the magnet.

   Refer to the probe installation and operation manuals and related rotor packing manuals.
3. Load the **Settancpx** protocol to initialize the workspace for solids experiments.

   See "Initializing a Workspace for Solids Experiments," page 268.
4. Load the correct probe file.

   See "Setting Up a Probe File for a Solids Probe," page 271.
5. Do one of the following:
   - Recall a data set acquired with the protocol to be used (if such a data set exists) into the workspace initialized for solids.

     The data set contains the last used calibrations and shim sets. The referenced adamantane spectrum that was saved during the probe calibration procedure is a good initial set up, see "Shimming with Adamantane," page 292.

- Load the protocol for the experiment to be run and set the parameters as needed.

6. Optional: Calibrate the system if the values in the recalled data set or the probe file are not known to be correct or to update the file. Follow the procedure in "Calibration of ^{13}C-^{1}H CPMAS Probes," page 285 using a probe designed for cross polarization experiments.
7. Set the sample temperature regulation, see "Setting the Temperature," page 274.
8. Set the MAS Spin rate, see "Setting the MAS Spin Rate," page 272.
9. Set up for either:
   - One pulse experiments, see "Setting up Single-Pulse Experiments," page 276.
   - Cross polarization experiments, see "Setting up Cross Polarization," page 276.
10. Set up the decoupler parameters, see "Setting up Decoupling," page 277.
11. Set up the acquisition parameters, see "Acquisition Parameters," page 278.
12. Tune the probe using one of the procedures in "Tuning Solids Probe," page 281.
13. Acquire the data.
14. Reference spectrum, see "Referencing for Solids," page 282
15. Save the data.
16. Do one of the following:
    - **Experimental** interface and **Walkup** interface with the **Study Queue inactive**.

      Select the next experiment from the **Experiments** menu to load the protocol into the current workspace for data acquisition, see "Experimental Interface," page 270.
    - **Walkup — Study Queue inactive**

      Click on a **Protocol** in the **Experiment Panel** to load the protocol into the current workspace, see "Walkup Interface - Study Queue Disabled," page 270.
17. Lower the probe from the magnet to change sample or to change to another probe as follows:
    a. Bring the sample to room temperature by adjusting the temperature setting on the **MAS Spin/Temp** panel, refer to "Setting the Temperature," page 274.
    b. Press the **Temp Off** button to turn the temperature regulation off when the probe reaches room temperature.
    c. Stop spinning rotor. Press the **Stop** button on the **MAS Spin/Temp** panel.
    d. Lower the probe from the magnet.
    e. Change samples and begin again at step 2.

13.3 Setting up for Solids Experiments

- "Initializing a Workspace for Solids Experiments," page 268
- "Loading a Protocol," page 269
- "Setting Up a Probe File for a Solids Probe," page 271
- "Setting the MAS Spin Rate," page 272
- "Setting the Temperature," page 274
- "Setting up Single-Pulse Experiments," page 276
- "Setting up Cross Polarization," page 276
- "Setting up Decoupling," page 277
- "Acquisition Parameters and Other Pages," page 278
- "Receiver Parameters for Solids," page 279
- "Tuning Solids Probe," page 281
- "Shimming and Referencing for Solids," page 282
- "Using probeConnect with Solids," page 283
- "Using preAmpConfig with Solids," page 284
- "Using hipwrampenable for Solids," page 284
- "Using Amplifier Blanking and Unblanking for Solids," page 285

Solids experiments are initiated with a protocol corresponding to the sequence. Type the name of the protocol on the command line (first character is upper case) to invoke a protocol.

Initializing a Workspace for Solids Experiments

A workspace must be initialized with standard solids parameters before any solids experiments are run.

1. Load the probe file corresponding to the probe in use, see "Loading a Probe File," page 30.

   Create a probe file if one does not exist for the probe, see "Setting Up a Probe File for a Solids Probe," page 271 and *VnmrJ Installation and Administration* manual for instructions on creating a probe file.

2. Load the protocol **Settancpx** from either the Experiment Panel, see Figure 77A, or from the Experiments drop down menu, see Figure 78, to initialize a workspace for the solids experiments.

   The protocol **Settancpx** retains the values of `tn`, `dn`, `dn2`, etc. and uses the `rtp` command to load the parameter set, `Settancpx.par`, from `/vnmr/parlib` and replace all remaining parameters.

   Settancpx loads basic calibrations for requested nuclei from the probe file if a probe file is defined. Alternatively, load an existing dataset derived from a experiment initiated with **Settancpx** using the **Open** window in the **File** pull-down menu. Unpredictable system behavior results if a Solids protocol is run in a workspace with parameters that have not been initiated for solids with **Settancpx**.

   The **solids1d** apptype, see Figure 77A, has a single protocol **Settancpx** that is used to initialize a workspace. All remaining solids protocols are apptype **solidsseq1d**, see Figure 77B. Protocols of apptype **solidsseq1d** preserve calibrations in the workspace and can be run in any order.

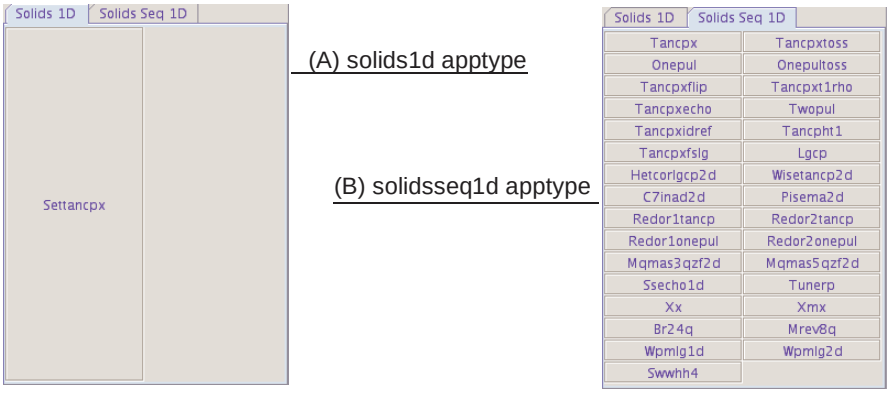


Figure 77. Solids Protocols Tabs

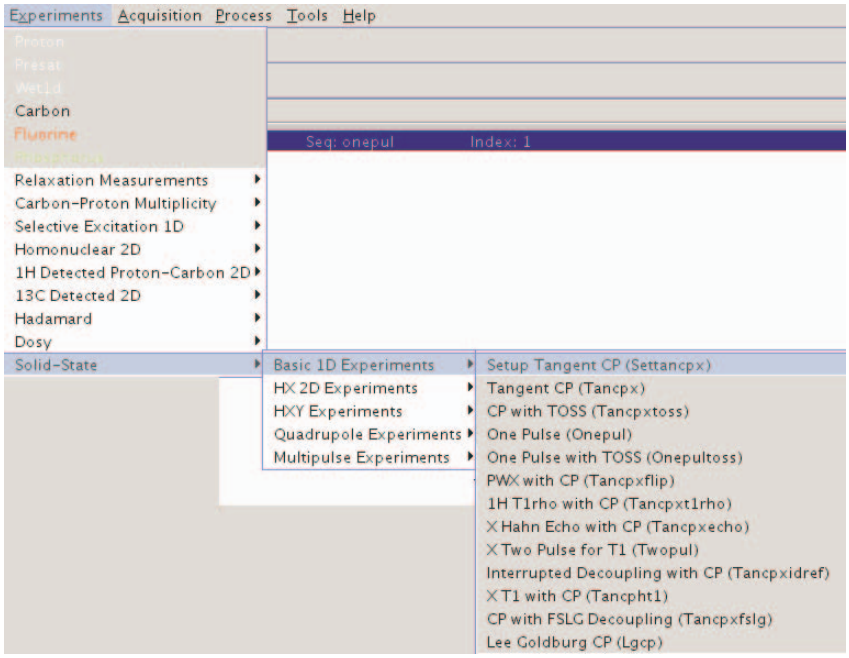


Figure 78. Solids Experiments and Menus

3. Calibrate the probe beginning with the **Settancpx** protocol.

   Refer to "Calibration of ^{13}C-^{1}H CPMAS Probes," page 285 for a CP-MAS probe calibration procedure.

4. Save a standard dataset with calibrations and begin all experiments with that dataset.

Loading a Protocol

The user interface (Experimental or Walkup) determines the choices for loading a protocol. Follow the procedure related to the interface in use.

- "Experimental Interface," page 270
- "Walkup Interface - Study Queue Disabled," page 270

Experimental Interface

1. Click on **Experiments** on the main menu.
2. Select **Solid State**.
3. Select an **experiment group**, see Figure 78.
4. Click on the **specific protocol** to load, see "Experiments Menu," page 370.

Walkup Interface - Study Queue Disabled

1. Disable the Study Queue:
   a. **Switch operators** to the Walkup administrator (account owner).
   b. Click on **Acquisition** on the main menu.
   c. Remove the **check mark** from the box next to Use Study Queue.
2. Switch operators or remain as the Walkup administrator.
3. Select a solids protocol using either of the following:
   - **Experiments drop down menu**

   a. Click on **Experiments** on the main menu.
   b. Select **Solid State**.
   c. Select an **experiment group**, see Figure 78.
   d. Click on the **specific protocol** to load, see "Experiments Menu," page 370.

   - **Protocols vertical panel**

     The VnmrJ system administrator must assign the walkup operator the user profile **`AllSolids`** to use the vertical panel protocols tab. Only solids protocols are displayed. The **`AllLiquids`** profile is required to display the liquids protocols. Refer to the *VnmrJ Installation and Administration* manual for instructions on assigning profiles and creating custom profiles.

   a. Select a the **Protocols** tab from the vertical panel tabs.
   b. Click on a **Protocol Type** type on the **Experiment Panel**, see Figure 77.

      The tabs of the **Experiment Panel** have the apptypes **solids1d** with one protocol (**Settancpx**) and **solidsseq1d** with a list of experiments.
   c. Select a **Protocol** (click and drag to the active viewport).

      The experimental protocol is loaded in the current active viewport as a foreground process.

Setting Up a Probe File for a Solids Probe

The **Channels** page of the **Acquire** tab shows the values of the nucleus and basic calibrations for each pulse-sequence channel `obs`, `dec`, `dec2`, etc., up through a potential of 5 channels. The basic parameter calibrations and functions are listed in Table 28.

Table 28. Basic Solids Calibration Parameters

Channel type (synthesizer)	*Offset: (synthesizer offset)*	*Channel Identifier*	*Power: (course power)*	*Amplitude: (fine power)*	*Pulsewidth:*
`obs`	`tof`	X	`tpwr`	`aX90`	`pwX90`
`dec`	`dof`	H	`dpwr`	`aH90`	`pwH90`
`dec2`	`dof2`	Y	`dpwr2`	`aY90`	`pwY90`
`dec3`	`dof3`	Z	`dpwr3`	`aZ90`	`pwZ90`
`dec4`	`dof4`	W	`dpwr4`	`aW90`	`pwW90`

Basic calibrations for each channel and number of the hardware channel associated with the the channel are contained on the Channels page, see Figure 79.

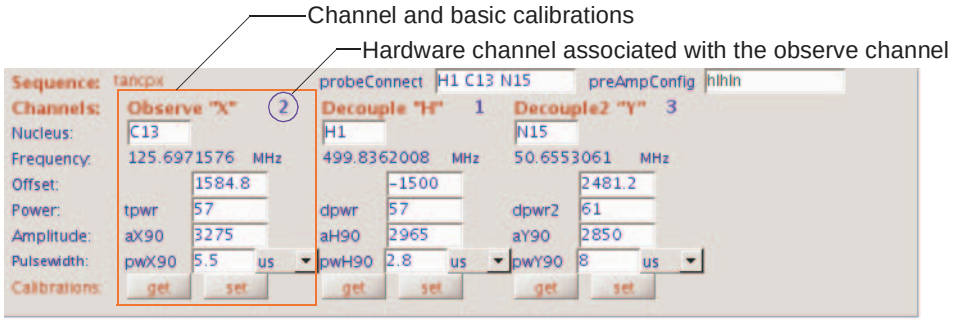


Figure 79. Channels Page and Basic Calibrations

The first column contains the standard name for each channel, see Table 28. The second column contains the standard name of the synthesizer offset. All parameters use channel identifiers (column three), upper-case X, H, Y, Z and W, that correspond to `obs`, `dec`, `dec2`, `dec3`, and `dec4`. Column four, the coarse power, is the second parameter. Fine power, associated with the linear modulator, is the third parameter. The fourth parameter (column five) is the standard pulse-width calibration based on the power settings.

Click on the **Set** button for each channel to save changes to the probe file for the set of basic calibrations for each nucleus to the probe file. The current value of the nucleus is attached to the values in the probe file. If needed, a new nucleus will be added to the probe file. An acknowledgement that the data is saved appears in the Message Window.

Click on the **Get** button for each channel to retrieve calibrations from the probe file. An error message appears in the Message Window if calibrations are not present. The current nucleus for the channel is used to choose the calibrations.

Use the Set and Get functions when the observe and decouple channel nuclei are interchanged.

The **Settancpx** protocol loads basic calibrations from the probe file if the probe file is defined and the nuclei are present in the file. The basic calibrations are the only values stored in the probe file by solids protocols.

Setting the MAS Spin Rate

The MAS spin rate is controlled through the **MAS Spin/Temp** page of the **Start** tab, see Figure 80. VnmrJ sends commands to the MAS automated speed controller by way of the console master controller.

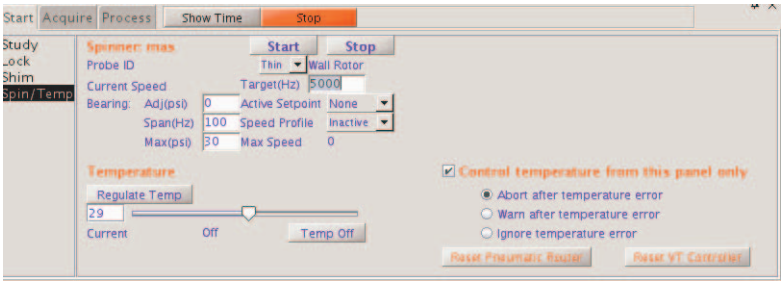


Figure 80. Solids Spin/Temp page with: spintype ='mas'

Varian T3 probes provide the name of the module (e.g.” 3.2 MM PENCIL”) to the MAS automated speed controller so that the appropriate values are set for start-up and regulation. The module name is also sent to VnmrJ and it is displayed on the **MAS Spin/Temp** page as Probe ID. VnmrJ uses the module name with underscores between words to automatically set the probe parameter.

Loading the Probe File

Do one of the following:

- Select and load the probe file corresponding to the probe in use as follows:
  a. Click on **Probe** on the hardware toolbar to open the Probe pop-up window.
  b. Select a **probe** from probes shown in the drop down menu.
  c. Click **Close** to load the probe and exit the Probe pop-up window.
- Create the probe file for the probe in use if one does not exist.
  a. Click on **Probe** on the hardware toolbar to open the **Probe** pop-up window.
  b. Check the **Edit** box.
  c. Enter a **name** for the probe.
  d. Click the **Make new probe** button.
  e. Click on the **Edit Probe button** to open the **Probe Edit** pop-up.
  f. Click on the **Probe** tab.
  g. Enter the following information into the probe file:

Probe File Field	*Value*	*parameter set*
Probespintype	mas	`spintype`
Probespinmax	Maximum rotor speed in Hz	`spinmax`

Press return after typing each entry into the specified field.

The probe name and these entries are required to display the **MAS Spin/Temp** page:

  h. Click **OK** to save and close the pop-up.

i. Select any **probe** from probes shown in the drop down menu.

j. Select the **name** of the solids probe from the dropdown menu.

The probe name must be explicitly selected after the probe file has been created.

k. Click **Close** to load the probe file and exit the pop-up window.

Starting the Rotor

1. Set the MAS automated speed controller to **AUTO** mode.
2. Verify that the correct module name is shown on the **Spin/Temp** page.

   Load (or reload) the correct probe file for the installed probe if the module name is not correct.
3. Select **Thin** or **Std** to select the correct **Max Speed**.
4. Set the **Target(Hz)** for spinning.
5. Press **Start** on the **Spin/Temp** page.
6. **Wait** for the speed to regulate.

   The LOCKED light on the controller is on when spinning is in regulation. The current speed is displayed on the **Spin/Temp** page and on the controller.

Changing the Rotor Speed

1. Enter a new **Target(Hz)** value.
2. Press **return**.
3. **Wait** for the speed to regulate.

Stopping the Rotor

Press **Stop** to stop the rotor.

Setting the Bearing Pressure

The bearing pressure is set automatically based on the value of **Bearing: Max(psi)** as roughly a linear function of the **Target(Hz)** spin rate.

Make a fine adjustment for the bearing as follows:

1. Set Bearing: **Span = 0**
2. Set the **Bearing: Adjust(psi)** to the change in pressure, positive or negative.
3. Reset **Span = 100** to lock the new bearing pressure in place.

   The new bearing pressure can be read from the display on the automated MAS speed controller.

Starting the Rotor Manually

Start a rotor manually and then put it in regulation as follows:

1. Set the **Target(Hz)** on the **Spin/Temp** page.
2. Set the knobs for the drive and bearing pressure valves on the controller counter clockwise.

3. Press the **Auto/Manual** button on the controller to put it in manual mode.
4. Obtain stable spinning near the desired speed using the knobs.
5. Press the **Auto/Manual** button again to put the rotor in regulation.
6. Reset the pressure valves **counterclockwise**.
7. Stop the rotor as follows:

   Press **Stop** button on the **Spin/Temp** page.

   It is not possible to return to manual mode while the rotor is spinning.

The **Start Spin** and **Stop Spin** buttons on the MAS automated speed controller have the same function as the **Start** and **Stop** buttons on the **MAS Spin/Temp** page.

Setting the Temperature

- "Starting Temperature Regulation," page 274
- "Stopping Temperature Regulation," page 275
- "Recovering from a VT Fault," page 276

The temperature of the rotor is controlled through the VT stack that, for wide bore magnets, sits in the upper barrel of the magnet and must be installed before starting solids VT operations. The VT stack inserts into the liquids upper barrel and mates to the top of the probe for wide-bore magnets. The VT stack sits inside the liquids upper barrel in narrow-bore magnets. A heater and thermocouple are present at the exit of the VT stack to provide temperature-controlled gas to the module. Both bearing and drive gas for MAS spinning are maintained at ambient temperature and are separate from the gas used for VT operation. Low temperature cold gas is supplied to the VT stack using a gas cooler such a cold trap in a liquid nitrogen Dewar or FTS unit.

Starting Temperature Regulation

A Solids/Liquids NMR System pneumatics router has separate gas regulation systems for solids and liquids and a common regulator valve for the VT-gas pressure. Solids gas flow is controlled with a manual valve below the flow meter. A typical flow rate is 40 lpm.

Start temperature regulation as follows:

1. Load the solids **probe file** if it is not already loaded.

   The solids meter is selected by loading a solids probe file and entering **`su`**.
2. Click on the **Start** tab.
3. Select the **Spin/Temp** page.

   Liquids gas flow is set from the liquids **Spin/Temp** page, see Figure 80. A set of LED's are lit on the selected pneumatic router meter.
4. Set the value of the parameter `vtc` above the highest expected temperature that requires cooling gas.

   A typical value for `vtc` is 5 ºC to 10 ºC below the ambient room temperature or the temperature of the VT supply gas.

   The choice of gas cooling or the bypass is determined by the parameter `vtc`, the variable temperature cutoff. A set temperature below `vtc` chooses gas cooling and a set temperature above `vtc` chooses the bypass. Choose a value of `vtc` in the dataset that corresponds to the desired operation.

The standard protocol **Settancpx** automatically resets `vtc = -100` and effectively makes gas cooling is impossible. Save a copy the parameter set, `Settancpx.par`, with the new value of `vtc` in `~/vnmrsys/parlib`. This new parameter set is loaded each time protocol **Settancpx** is loaded by the current user. The change does not affect any of the other users. Make the change available to all users by logging in as the system administrator, vnmr1, and saving `Settancpx.par` with the new value of `vtc` in `/vnmr/parlib`. The system administrator can edit the file `/vnmr/parlib/Settancpx/procpar`
and change the entry for `vtc:`
`vtc 1 1 250 -100 0.1 2 1 2 1 64 1` **`-100`**
using `vi` or any `ASCII` text editor supplied with the operating system to reflect the new cut off temperature by changing the value of entry `-100` at the end of the `vtc` line to a new value such as 15. The new entry reads:
`vtc 1 1 250 -100 0.1 2 1 2 1 64 1` **`15`**
The entries for `vtc` of primary interest are:
`vtc 1 1 [`**`upper temperature limit`**`] [`**`lower temperature limit`**`] [`**`precision`**`] 2 1 2 1 64 1 [`**`bypass cutoff`**`]`

5. Enter **`su`** on the command line.

   Press **Pneumatics Reset** button once or twice if the set up (**`su`**) does not proceed.

   Liquids flow may persists after selection of solids. Do the following if this happens:

   a. Load a liquids probe file.

   b. Press the **VT Air Off** button on the **Spin/Temp** panel.

   c. Reload the solids probe file.

6. Move the **Temperature** slider control left or right on the **Spin/Temp** page until the required temperature (ºC) is displayed in the field to the left of the slider or enter the temperature regulation **value**, in ºC, in the field to the left of the slider on the **Spin/Temp** page and press return.

7. Press the **Regulate Temp** button.

   Press the **Reset Pneumatics Router** and/or **Reset VT Controller** buttons before proceeding if the temperature regulation does not set up.

8. Place a check in the box for **Control Temperature from This Panel Only**.

9. Check on an error reporting radio button.

   The radio button choices below **Control Temperature from This Panel Only** are:

   - Abort after temperature error
   - Warn after temperature error
   - Ignore temperature error

   The parameter `temp` is a passive indicator of the temperature set in the panel when the **Control Temperature from This Panel Only** check box is checked. The current value of the parameter `temp` is used to set the temperature at `su` or at the start of acquisition if the **Control Temperature from This Panel Only** is checked.

Stopping Temperature Regulation

1. Press the **Temp Off** button.
2. Reselect a liquids probe and press the VT Air **Off** button on the **Spin/Temp** panel.
3. Turn **Off** the solids gas-flow valve when selecting liquids.

Recovering from a VT Fault

The solids VT stack is equipped with a high temperature bypass that bypasses the installed gas cooler supplying ambient temperature gas to the stack. Narrow bore VT stacks have a gas-flow sensor, a probe-stack integrity sensor, and a bore-temperature sensor that may fault under a variety of error conditions. The temperature controller is disabled and the gas flow is switched to bypass if a fault condition detected. A small amount purge gas is vented through the gas cooler to keep it from freezing up.

1. Correct the problem causing the fault condition.
2. Press the **Reset Pneumatics Router** and/or **Reset VT Controller** buttons.
3. Reset the temperature to resume operation.

Setting up Single-Pulse Experiments

Single-pulse excitation is run using the **Onepul** protocol. The protocol uses the calibrated 90-degree pulse `pwX90` from the Channels page of the Acquire tab and provides acquisition with a standard Decoupling parameter group, see "Setting up Decoupling," page 277. Decoupling parameters are located on the Pulse Sequence page.

Setting up Cross Polarization

Cross polarization is run using the **Tancpx** protocol. The protocol uses the **cpHX** parameter group for constant, linear, or tangent-ramped cross polarization. The **cpHX** parameter group is located on the Pulse Sequence page of the Acquire tab and it used in any pulse sequence where cross polarization is needed, see Figure 81.

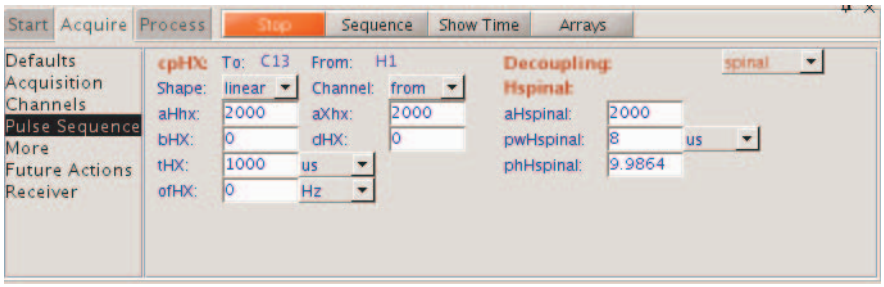


Figure 81. Tancpx Pulse Sequence page of the Acquire tab

Calibrate the probe, see "Calibration of ^{13}C-^{1}H CPMAS Probes," page 285.

Tancpx provides excitation with the basic calibrated 90-degree pulse `pwH90` from the Channels page and acquisition with standard Decoupling parameter group located on the Pulse Sequence page, see "Setting up Decoupling," page 277.

The **cpHX** parameter group and upper-case channel identifiers specify the channels involved in cross polarization. The first character is the channel from which the starting polarization is derived and the second is the channel that is polarized. The **cpHX** parameter group used with **Tancpx** indicates cross polarization from the `dec` channel to the `obs` channel.

The Pulse Sequence page of the Acquire tab for **Tancpx**, see Figure 81, contains two parameter groups: **cpHX** for cross polarization and **Decoupling** for proton decoupling.

These parameter groups are used in all sequences that contain cross polarization and proton decoupling functions.

Menu or Parameter	*Description*
Shape menu	Values are: **const**, **linear**, or **tan**. Pulse shape used on one of the two channels for the **cpHX** parameter group.
Channel menu	Values are: **from** — channel used to apply the shape to the decoupler channel. **to** — channel used to apply the shape to the observe channel.
`aHhx` parameter	The median amplitude of the decoupler channel and **aXhx** is the median amplitude of the observe channel.
`dHX` parameter	The +/- amplitude excursion of a linear or tangent ramp about the median value and has no effect on constant CP.
`bHX` parameter	Curvature factor for tangent ramps only. `bHX` > 10000.0 applies a linear ramp. `bHX` < 1.0 applies a tangent ramp that is nearly constant with extreme excursions at the beginning and end. Values in between provide tangents of various curvatures.
`tHX` parameter	Contact time.
`ofHX` parameter	Frequency offset applied to the shaped channel as designated by the **Channel** menu choice.

The CP parameter group generates it's offset with a phase ramp and the offset adds or subtracts from the value of the synthesizer offset (`tof` or `dof`) for the channel.

Setting up Decoupling

Decoupling during acquisition is carried out in nearly all pulse sequences with the **Decoupling** parameter group on the Pulse Sequence page of the Acquire tab, see Figure 81. Select from the choices: **TPPM**, **SPINAL64**, **CW decoupling** or **decoupler off**.

Parameter or Group	*Description*	
Decoupling parameter	Menu choices TPPM or SPINAL determines which of the **Htppm** or **Hspinal** parameter groups is displayed.	
TPPM	`aHtppm`	Decoupling amplitude
	`pwHtppm`	Width in microseconds of each of the two pulses (usually just less than a 180-degree pulse)
	`phHtppm`	The +/- phase of each of the two pulses. The sign of the phase is that of the first pulse.
SPINAL	`aHspinal`	Decoupling amplitude
	`pwHspinal`	Width in microseconds of each of the two pulses. (usually just less than a 180-degree pulse).
	`phHspinal`	The +/- phase of each of the two pulses of the base cycle. The sign of the phase is that of the first pulse.
	SPINAL	Applies +/- pulse pairs with a phase of +/-1.0, +/-1.5 and +/-2.0 times `phHspinal` in a 64-member supercycle.
CW decoupling	**On** with either the TPPM or the SPINAL parameter groups when `phHtppm` or `phHspinal` is 0.0. **Off** either the TPPM or the SPINAL parameter groups when `aHtppm` or `aHspinal` is 0.0.	

Parameter or Group	*Description*
	The decoupling module explicitly associates a `decoff()` command with an amplitude of 0.0 to gate the decoupler fully off. The typical application with an amplitude of 0.0 sets the linear modulator to full attenuation.

Acquisition Parameters and Other Pages

Acquisition Parameters

The Acquisition page of the Acquire tab provides a customized display of the standard 1D Acquisition parameters and the Receiver gain, see Figure 82.

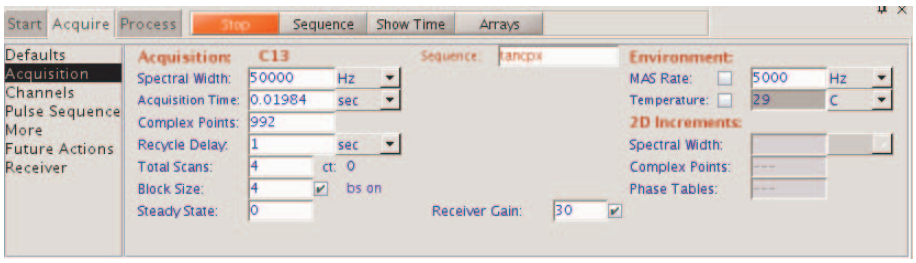


Figure 82. Acquisition Parameters - Solids

Field	*Parameter*	*Description and Settings*
Spectra Width	`sw`	Spectral width, menu select units: Hz, kHz, MHz, or ppm
Acquisition Time	`at`	Data acquisition time, menu selections: sec, ms, or us.
Complex Points	`np`	Total number of points collected during the acquisition time.
Recycle Delay	`d1`	First delay in the sequence, menu selections: sec, ms, or us.
Total Scans	`nt`	Total number of transients collected.
Block Size	`bs`	Enter number of scans for block size and place a check in the check box to enable. Remove the check from the box to set `bs='n'`, not used, and the block to Total Scans, `nt`.
Steady State	`ss`	Number of dummy scans run before starting data acquisition
Receiver Gain	`gain`	Gain of the receiver. Set the value from 0 to 30 in the field. Place a check in the box to turn off the autogain function. Do not use autogain with solids
MAS Rate	`srate`	Rotor spin rate, menu select units: Hz, kHz, MHz, or ppm. `srate`, identifies the spin rate for automatic calculation of synchronized delays in some sequences. The `srate` parameter is not the same as the set point for the MAS Automated Speed Controller on the Spin/Temp page and must be set manually to a value equal to the spin rate. A check box next to `srate` sets the parameter `hsrotor`. Checking this sets the value of `srate` automatically from the measured spin rate at run time and cannot be used to track the spinning rate while the sequence is running.
Temperature	`temp`	Temperature regulation point, select C (centigrade) or K (Kelvin)

Field	*Parameter*	*Description and Settings*
Other		2D parameters that are specific to a sequence. Fields are grayed out if the field is not defined. Use `par2d` if the undefined parameters are required.

Default Pages

The Defaults page of the Acquire tab is empty. The More page is used in some sequences to provide space for additional parameter groups that do not fit on the Pulse Sequence page. Content of these pages is specific to the pulse sequence.

Other Pages and Tabs

The Acquisition, Channels, and Receiver pages that are set up when the **Settancpx** protocol is loaded have content that is specific to solids sequences. Future Actions page, Start tab, and Process tab are common to all liquids and solids protocols.

Receiver Parameters for Solids

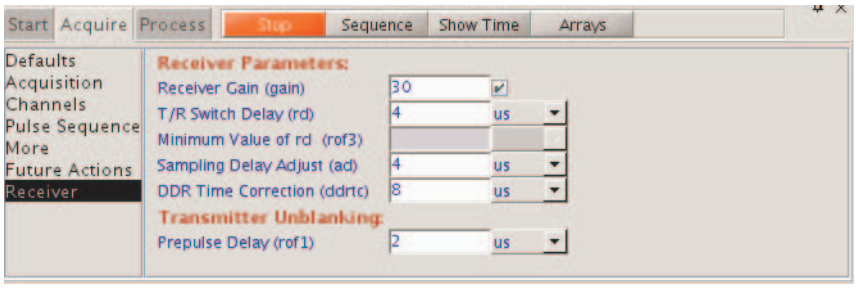


Figure 83. Receiver Page of the Acquire tab, Solids

The Receiver page of the Acquire tab contains parameters that affect the receiver gain, the dead time and phase correction, see Figure 83. The dead time is the time after the pulse or cross polarization before acquisition of the first data point.

All solids pulse sequences make use of explicit code for acquisition and avoid using `rof2` and `alfa`. The parameter `ddrtc` controls the digital receiver time correction and is explicitly defined in solids data sets. Solids protocols do not automatically set `ddrtc`. The user must set it manually as described below.

Field name	*Parameter*	*Values / Description*
Receiver Gain (gain)	`gain`	Values between 0 and 60, default is 30. Gain can be as low as 0 for very strong signals as for proton experiments. A gain greater than 30 is usually of no benefit.
T/R Switch Delay (rd)	`rd`	Values range from 2.0 and 4.0 µs for ^{1}H or ^{13}C to many hundreds of microseconds for low-gamma nuclei with acoustic ringing. The application of `rd` in solids sequences is analogous to that of the `rof2` in other sequences. Set `rd` to avoid probe ring-down in the first few points of the FID. The delay follows the last pulse or the cross polarization and precedes opening the T/R switch.
Minimum Value of rd (rof3)	`rd` `rof3`,if defined	Controls the time between the opening of the T/R switch and the receiver turn-on. The value of `rof3` can be set greater or less than 2.0 µs. The default time is 2.0 µs if `rof3` is not defined.

Field name	*Parameter*	*Values / Description*
		Multi-pulse sequences explicitly set the value of `rof3` so that it can be set less than 2.0 µs. The value associated with `rof3` for multi-pulse sequences such as BR24 is part of the parameter group of the multi-pulse waveform and is labeled with the prefix `r3`. Always set `rof3 = r3` when running multiple-pulse sequences.
Sampling Delay Adjust (ad)	`ad`	Values between 4.0 to 10 µs. The application of `ad` in solids sequences is analogous to that of `alfa` in other sequences. Typically the T/R switch (if used) is opened at the beginning of the delay and the receiver is turned on 2.0 µs later. In this case `ad` cannot be less than 2.0 µs. The first point is acquired at the end of the delay.
DDR Time Correction (ddrtc)	`ddrtc`	Controls automatic back-prediction of the FID in the digital receiver. The first-order phase correction `lp` will be approximately 0.0 if `ddrtc = rd + ad`. Fine tune `ddrtc` to obtain `lp = 0.0`. The parameter `ddrtc` corrects the phase for all spectral widths of 1.25 MHz and less. A correct setting of `ddrtc` is very effective for automatic phasing, but it does not necessarily produce a flat baseline. One can expect a flat baseline if the value of `ddrtc < 1/(2.0*sw)` (a usual situation for CPMAS but not for larger spectral widths) and if the true first point of the FID is not distorted.

First point distortion of the baseline resulting from time correction has characteristic hooks at the outer edges. The spectrum appears to sit in a trough or on a pedestal. Ringing in the back-prediction calculation by bad first points in the FID is the typical cause. The ringing may extend well beyond the first points so this problem cannot be corrected with linear prediction.

Fix the first point distortion by increasing `rd` until the first point is good. Estimate the first point distortion and set `rd` by observing the FID with `sw = 5.0e6`. Choose the new value of `rd` and then obtain the data with the original spectral width.

Mitigate the effect of a first-point distortion by decreasing the slope of the digital-filter cut-off using the parameter `ddrcr` as follows:.

1. Create the parameter `ddrcr` (if it does not already exist) by entering the following on the command line:

   ```
   create('ddrcr')
   ```

2. Set `ddrcr` a value in the range of 5 to 10.

   The default value (if the parameter does not exist) is 75 and produces steep filters. A lower number decreases the slope of the filters and mitigates the ringing created by bad first points.

   Linear prediction can readily correct the baseline with a value of:
   `ddrtc >1/(2.0*sw)`
   and a good first point.

The prepulse delay, `rof1`, used in liquids sequences to unblank the transmitter and to preset the phase of pulses, is displayed but it is not generally used in solids sequences. Solids sequences explicitly preset the phase of pulses at the beginning of the previous delay and the transmitters are continuously unblanked making the pre-pulse delay unnecessary. A pre-pulse delay for multi-pulse sequences, such as BR24, is part of the parameter group of the multi-pulse waveform and is prefixed `r1`.

Tuning Solids Probe

- "Low Power or In-Line Tuning Using Tune Sweep," page 281
- "High-power tuning," page 282

Solids experiments require frequent probe tuning, usually for each new rotor. Varian NMR Systems provide in-line 30-db directional couplers to tap off the reflected power of each channel. A set of reversible 50-db directional couplers are available as an option for solids systems. Probe tuning is carried out with the standard **Tune Sweep** function of the Probe pop-up window or with the Tunerp protocol associated with the group of solids Sequences.

Low Power or In-Line Tuning Using Tune Sweep

Tune the probe using the in-line tune (or low power) method as follows:

1. Install the 30-db couplers correctly with the arrow pointing **towards** the **Front End**. Be sure that the arrows on the reversible 50-db couplers point towards the **Front End**, not the **Probe**.
2. Click on the **Probe** button.
3. Click on the **Tune Sweep** button in the probe pop-up window.

   The Probe tune page replaces the pages in all of the tabs, see Figure 84.

   The Tune RF channel menu displays the hardware channel to be tuned. The default nuclei selections are: **1H** for channel 1, **13C** for channel 2, and channels 3 and 4 undefined. The nuclei and frequencies that appear on the Probe tune page are unrelated to those in the Workspace.
4. Select the **Channel** to be tuned.

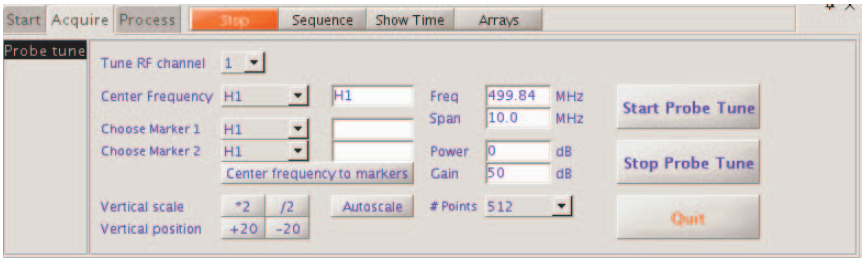


Figure 84. Tune Panel - Solids

5. Select **Center Frequency** by entering the nucleus from the menu or enter the frequency in the field next to **Freq**.
6. Choose a value (between 1MHz and 10 MHz) in the field next to **Span**.
7. Click **Start Probe Tune** button.
8. Press **Autoscale** to obtain a useful display.
9. Increase the power from 0 to 10 db if the signal-to-noise of the pattern is low.

   The tune pulse sequence does not accept powers above 10 db to protect the probe.
10. Decrease the gain if the pattern clips.
11. Adjust the **Vertical** scale and the **Vertical** position of the pattern with the buttons or with the center mouse button.
12. Adjust the **Span** to the region of the tuning dip and adjust the vertical scale as needed.

The large sinusoidal changes of the tuning baseline are expected for tuning in-line with a directional coupler. These sinusoidal changes are the result of standing waves on the input cables between the preamplifier and the probe caused by the effectively infinite impedance of the probe outside the region of the tuning dip.

Some systems have channels with High-Power Low-band preamplifiers. These preamplifiers use passive diodes that cut off the input tune signal if it falls to too low a value and in some frequency ranges the pattern has no amplitude. Increase the gain to 10 on the channel if this occurs. The gain may still be to low to observe a tune dip. Bypass preamplifier by connecting the cable on the XMTR port of the preamp to the cable attached to the PROBE port if increasing the gain is not enough. The amplitude of the pattern is affected by the presence of filters in-line with the input cables.

13. Tune the probe (see the probe manual for tuning).

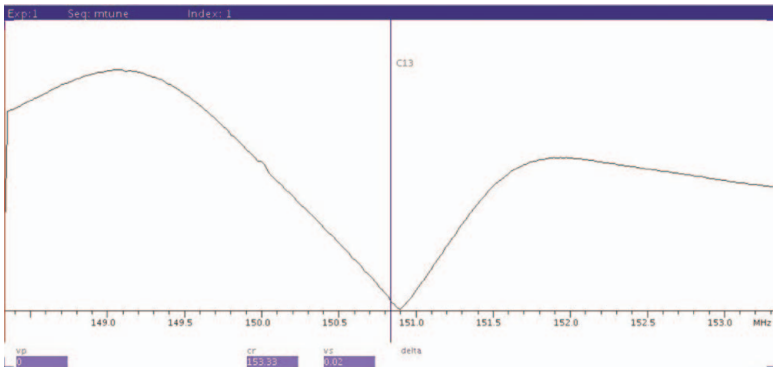


Figure 85. Tuning Pattern, Solids

The tuning pattern, see Figure 85, is a dip of the reflected power near zero when the probe is tuned. The width of the dip approximates the bandwidth of the probe.

14. Press **Stop Probe Tuning** to halt tuning.
15. Press **Quit** to return to the data in the Workspace.

High-power tuning

See "High Power Pulse Tuning (Tunerp)," page 307 for tuning with pulses using the Protocol **Tunerp** and the reversible 50-db directional couplers.

Shimming and Referencing for Solids

Shimming

The field homogeneity for a MAS probe is usually optimized with a sample of adamatane. Follow the procedure in "Shimming with Adamantane," page 292.

Referencing for Solids

Referencing for Solids is complicated by the fact that a solids probe has no lock channel and there is no lock solvent and as a result the lock frequency is not necessarily on resonance. VnmrJ automatic referencing uses the `setref` command, the file `/vnmr/nuctables/nuctabref`, and is dependant upon the lock being on resonance.

Set the lock frequency on resonance as follows:

1. Recall a referenced ^{13}C spectrum of adamantane.

2. Click on the **Start** tab.
3. Select the **Lock** page.
4. Click on the Lock **OFF** radio button
5. Enter **0.0** in the field next to the **Z0** button if the value in the field it is no 0.0.
6. Insert a rotor containing adamatane and install the probe.
7. Shim using the adamantane signal.
8. Acquire a spectrum.
9. Type **`setref`**.
10. Adjust the lock frequency **`lockfreq`**.
11. Repeat the collection of data and type **`setref`** again until the frequency of the low field line of adamantane is 38.3 ppm, see Figure 86.

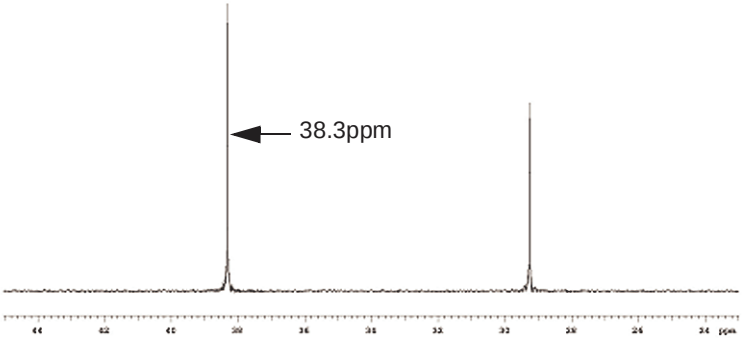


Figure 86. Adamantane Reference Spectrum

12. The `lockfreq` is set to the fourth and fifth places after the decimal.
13. Set the correct value for `lockfreq` into the configuration parameters in the vnmr1 user. The value of `lockfreq` is lost when logging out of the user if it is not saved.

The correct value of the lock frequency depends upon the choice of the lock solvent. Choose a constant value of solvent (for example CHCL3) to be used for solids data. Referencing remains correct until the magnet has drifted outside the solids lineshape, usually after a couple of days.

The reference display of VnmrJ does not correct itself if the spectral width `sw` or the offset `tof` is reset. Re-establish the reference based on the lock with `setref`.

Using probeConnect with Solids

The hardware channel (transmitter associated with each pulse-sequence channel) is displayed to the right of the channel name in the **Channels** page of the **Acquire** tab, see Figure 79.

A two channel Varian NMR System is always configured with channel 1 as the high-band channel and channel 2 as the low-band channel. The system always sets the correct band based on the nucleus.

Varian NMR System with more than two channels and a pulse sequence that uses more than two channels must use the parameter `probeConnect`. The `probeConnect` parameter does not need definition if only channels 1 and 2 are used. Channels 3 and 4 can be

configured as either high-band or low-band. Entry boxes for **probeConnect** and **preAmpConfig** are on the top line of the **Channels** page (Figure 79). The value of **probeConnect** is initially undefined, as indicated by dashes in the box.

Creating the probeConnect Parameter

1. Verify the existence of the `probeConnect` parameter as follows:
   a. Enter **`probeConnect`** on the command line.
   b. Continue with the step 2 if the message in the message box is:
      `Variable “probeConnect” doesn’t exist`
   c. Skip to step 3 if there is no message reporting that the variable does not exist.
2. Entering the following on the command line:
   `create('probeConnect','string','global')`
3. Enter the nucleus associated with each channel in order, channel 1, channel 2, etc. and separate each entry with a space.
   The entries in the **probeConnect** field identify the nuclei that are associated with each hardware channel. Change the entries in the **probeConnect** field to correspond to a new probe-tuning configuration.

Using probeConnect During the Decoupler Calibration Process

1. Set the decoupler nuclei one by one in the **Nucleus:** field of the **Observe ''X''** section of the **Channels** page of the **Acquire** tab and determine the basic calibrations using the **Onepul** experiment.
2. Click the **Set** button to enter the calibration into the probe file.
3. Return each nucleus to its proper decoupler channel when the calibrations are complete.
4. Click the **Get** button to reload the decoupler calibrations.

Using preAmpConfig with Solids

The value of `preAmpConfig` indicates which type of preamplifier, high-band or low-band, is associated with each hardware channel. The default is `preAmpConfig = 'hlnnn'` where `'h'` means high-band, `'l'` means low-band and `'n'` means no preamplifier. The characters of `preAmpConfig` are the hardware channels. The third to fifth characters of `preAmpConfig` should be changed to their correct values if preamplifiers are present on channels 3 to 5.

Using hipwrampenable for Solids

A Varian NMR System with high-power (kilowatt) amplifiers contains relay boards to select high power for solids or low power for Liquids. The default selection for the relay board is low power by default unless the parameter `hipwrampenable` is created. High power is defined as the specified amplifier output (usually a kilowatt, but a bit less for high-band amps at 600 MHz and above). Low power is defined as 50 Watts for high-band and 300 Watts for low band. High power NMR Systems use the high-band driver to provide the 50 Watts and they attenuate input of the low-band kilowatt amp to provide the 300 Watts.

1. Verify the existence of the `hipwrampenable` parameter as follows:

a. Enter **hipwrampenable** on the command line.

b. Continue with the step 2 if the message in the message box is:

```
Variable "hipwrampenable" doesn't exist
```

c. Skip step 2 if there is no message reporting that the variable does not exist.

2. Entering the following on the command line:

```
create('hipwrampenable','string','global')
```

The parameter `hipwrampenable` is a global parameter and applies to all data sets in a user and can only be accessed from the command line.

`'y'` enables high power or the rf channel.

`'n'` enables low power and disables high power for the rf channel.

A character is required for each hardware channel up to the total number of channels `numrfch`. The value of `numrfch` is 3 for system with three rf channels and high power on channel 1 and low power on the remaining channels is specified as:

```
hipwrampenable='ynn'
```

Using Amplifier Blanking and Unblanking for Solids

All solids sequences are written to maintain amplifiers on all channels as unblanked throughout the pulse sequence, except during acquisition. This convention is different from the convention used by the Varian NMR System for liquids sequences (and older Solids sequences). Continuous unblanking maintains each amplifier temperature on or hot to provide greater amplifier stability.

Solids sequences execute the unblank command on the `obs` channel before the recycle delay `d1` and the sequence ends with an unblank after the acquisition. The same pattern of blanking and unblanking is repeated for the decouplers. Liquids sequences (and older solids sequences) execute the unblank on the `obs` channel before the first pulse or turn it on and off before and after the pulses. The decouplers have no blank and unblank commands and they use the decoupler amplifiers in continuous mode.

Solids sequences provide the option to blank decouplers during acquisition. The decoupler amplifiers must be set to pulsed mode by setting the decoupler channel `ampmode` to `'p'` instead of `'d'`. All solids data sets contain the `ampmode` parameter for this purpose. Blanking `dec2` or `dec3` during acquisition when using a 3-channel HXY probe delivers better performance.

Very high stability also requires that amplifiers remain on between experiments. A special solids mode can be set when the software is booted with `setacq` that ensures unblanking between experiments. Consult the *VnmrJ Installation and Administration* manual to set solids mode. The solids mode has no effect on the state of the amplifiers when the sequence is running.

13.4 Calibration of ^{13}C-^{1}H CPMAS Probes

- "Sample Preparation," page 286
- "Setting Up the Workspace for Calibration," page 286
- "Tuning the Probe," page 286
- "Calibrating the ^{1}H pw90," page 287
- "Calibrating the ^{13}C pw90," page 289

- "Magic-Angle Adjust with KBr.," page 291
- "Shimming with Adamantane," page 292
- "Matching the Hartmann-Hahn Condition," page 295
- "HMB Signal-to-Noise," page 296

Use the following calibration procedure for ^{13}C-^{1}H CPMAS probes and VnmrJ2.2C released sequences. Use the signal to noise test to verify the calibrations and as a routine system performance check.

These procedures use the `Onepul` and `Tancpx` protocols and related sequences.

Sample Preparation

Pack 2 rotors as follows:

- 50% (by weight or volume) adamantane and potassium bromide (Adamatane/KBr).
- Full rotor of hexamethylbenzene (HMB).

Setting Up the Workspace for Calibration

Do one of the following:

- A calibration data set does not exist:
  a. Select the protocol **Settancpx** from the **Solids 1d** directory of the **Experiment Panel**.
  b. Set **`tn = 'C13'`** and **`dn = 'H1'`**.
  The **Settancpx** protocol loads any existing calibrations from the probe file. Do not use the calibrations that are shown unless they are know to be correct.
- A calibration data set does not exits:
  Load a previous ^{13}C-^{1}H spectrum or parameter set for the particular solids probe configuration to be used, if one is available.

Tuning the Probe

1. Verify that all cables are correctly connected to the probe.
2. Place the adamantane/KBr rotor in the module.
3. Raise the probe into the magnet.
4. Spin the sample at **5.0 kHz**.
5. Press the **Probe** button on the lower bar.
6. Click on **Tune Sweep** in Probe pop-up window.
   Tune Sweep starts the `mtune` program and loads the Tune Panels.
7. Set **Channel 1** to **H1** using the dropdown menu.
8. Click **Start Probe Tune**.
9. Follow the procedures in "Tuning Solids Probe," page 281
10. Set **Channel 2** to **C13** using the dropdown menu.
11. Click **Start Probe Tune**.

12. Follow the procedures in "Tuning Solids Probe," page 281
13. Repeat the tuning of channels 1 and 2 iteratively until the optimal tuning is obtained.
14. Press **Quit Probe Tune** to return the workspace.

Calibrating the ^{1}H pw90

1. Load the **Onepul** protocol from the **Solidsseq 1D** tab of the **Experiment Selector** or select it from the **Experiment** menu on the main menu bar.
2. Click on the **Acquire** tab.
3. Select the **Acquisition** page.
4. Set the following

Field	*Value*
Spectral Width	1.0e5 Hz
Acquisition Time	0.003 s
Recycle Time	5.0 s
Gain	0.0
Scans	1

5. Click on the **Channels** page.
6. Enter **H1** in the **Nucleus:** field for the **Observe "X"** channel.
7. Enter **C13** in the **Nucleus:** field for the **Decouple "H"** channel.
8. Remove any entries in the **Nucleus:** fields for the **Decouple2 "Y"** and **Decouple3 "Z" channels** if these fields are present.
9. Set the starting calibrations if necessary.

CAUTION: **Excessive power can damage to the probe and amplifiers. Verify the type and placement of installed attenuators on the system before setting `tpwr>54`. Some system managers choose to use attenuators on the input of the transmitter to allow a tpwr setting higher than 54 with a high power amplifier.**

- Low-power system (100 Watts ^{1}H)

Field	*Value*
tpwr	63
aX90	2000
pwX90	4.0 µs.

- High-power system (nominally 1000 Watts ^{1}H)

Field	*Value*
tpwr	54
aX90	2000
pwX90	4.0 µs.

10. Click on the **Acquire** tab.
11. Select the **Pulse Sequence** page.
12. Select the **TPPM** decoupling option.
13. Set **aHtppm = 0.0** to turn off the decoupler.
14. Set **phHtppm = 0.0** to set CW decoupling for future tests.
15. Click on the **Acquire** button to start the experiment
16. Put a cursor on the center peak and type **movetof** on the command line to move the transmitter on resonance.
17. Array **pwX90** from **1.0 to 25.0** µs in steps of **1.0** µs.
18. Click on the **Acquire** button to obtain the array.

    The data will look similar to Figure 87.

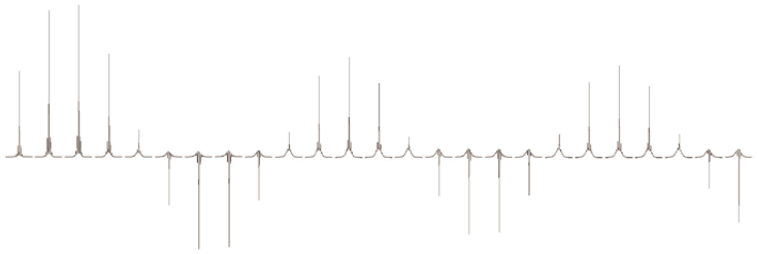


Figure 87. CPMAS pwX90 ^{1}H Calibration Array

19. Estimate the 90-degree pulse as one-half the 360-degree minus the 180-degree pulse. Ignore the broad line. It is probe ^{1}H background.
20. Adjust the value of **aX90** to obtain a 90-degree ^{1}H pulse **pwX90** equal to the ^{1}H target pulse width or pulse specification.
21. Reduce **tpwr** and increase **aX90** as required to place **aX90** in the range of **3500** to **4095**. Lowering **tpwr** by 6 db increase **aX90** by 2 fold.
22. Save the data and record the values.

    The value of aX90 serves as the maximum value for **aHtppm** or **aHspinal**.
23. Readjust the value of **aX90** to obtain a ^{1}H 90-degree ^{1}H pulse `pwX90` equal to the ^{13}C pulse specification, see Figure 88.
24. Save the data and record the values.

    Use this ^{1}H amplitude for cross polarization as **aHhx** in the **cpHX** parameter group.

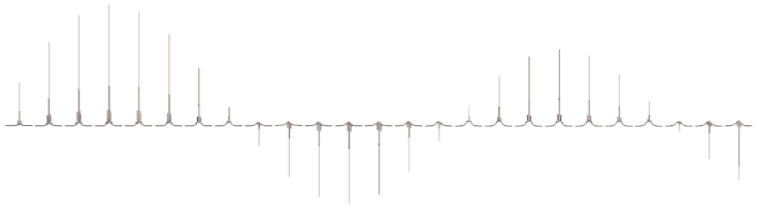


Figure 88. CPMAS pwX90 for 4.0 µs ^{1}H 90-degree pulse

CAUTION: **Damage to the probe can result if this field strength is exceeded. This field strength is the maximum that should be used in cross polarization. Calibrate a cross-polarization amplitude lower than the specification as required by the experiment or general operating practice. A ^{1}H pulse width of 4.0 to 5.0 μs works for most experiments and the lower power reduce wear and tear on the probe.**

25. Enter these second ^{1}H basic calibrations on the Channels page of the Acquire tab.
26. Press the **Set** button for **obs** and **dec** on the Channels page to save the ^{1}H calibration and the existing ^{13}C numbers in the probe file.

Calibrating the ^{13}C pw90

Continue in the same workspace using the Onepul protocol and maintain the Adamantane/ KBr sample at 5.0 kHz.

1. Click on the on the **Acquire** tab.
2. Select the **Acquisition** page.
3. Set the following:

Field	*value*
Spectral Width	5.0e4 Hz
Acquisition Time	0.02 s
Recycle Time	5.0 s
Gain	30
Scans	1

4. Click on the **Channels** page.
5. Enter **C13** in the **Nucleus:** field for the **Observe "X"** channel.
6. Enter **H1** in the **Nucleus:** field for the **Decouple "H"** channel.
7. Press the **Get** button for **Observe:** and **Decouple:** to retrieve the most recent ^{1}H and ^{13}C calibrations from the probe file under the correct nucleus settings.
8. Set the starting calibrations for ^{13}C if necessary.

CAUTION: **Excessive power can damage to the probe. Verify the type and placement of installed attenuators on the system before setting `tpwr>54`. Some system managers choose to use attenuators on the input of the transmitter to allow a tpwr setting higher than 54 with a high power amplifier.**

- Low-power system (300 Watts ^{13}C)

Field	*Value*
tpwr	63
aX90	2000
pwX90	4.0 μs.

- High-power system (nominally 1000 Watts ^{1}H)

Field	*Value*
tpwr	54
aX90	2000
safety limit -ON	54

9. Click on the **Acquire** tab.
10. Select the **Pulse Sequence** page.
11. Select the **TPPM** decoupling option.
12. Set **aHtppm = aH90** value and use the **aH90** from the Channels page.
13. Set **phHtppm = 0.0** for CW decoupling.
14. Enter **`lb = 50`** to set the line broadening to 50 Hz.
15. Click on the **Acquire** button.
16. Place the transmitter between the two peaks of Adamantane.
17. Put one cursor on each peak.
18. Enter **`split movetof`** on the command line.
19. Reduce the Spectral Width to 5 to 10 kHz (600 MHz and above).
20. Array **`pwX90`** from **`1.0`** to **25.0** µs in steps of **1.0** µs.
21. Click on **Acquire** button to acquire the arrayed data.
22. The result is similar to Figure 89.

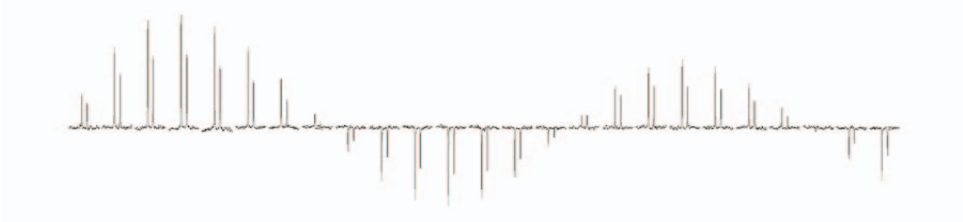


Figure 89. CPMAS pwX90 for 4.0 µs ^{13}C 90-degree pulse

23. Adjust the value of **aX90** to obtain a 90-degree ^{13}C pulse pwX90 equal to the ^{1}H values. The values may either be the ^{13}C specification or a lower value as determined for the second ^{1}H calibration.
24. Reduce **`tpwr`** and increase **aX90** as required to place **aX90** in the range of **3500** to **4095**. Lowering **`tpwr`** by 6 db increase **aX90** by 2 fold.
25. Save the data and record the values.

    The value of **aX90** is used for cross polarization as **aXhx** in the **cpHX** group.
26. Enter the ^{13}C basic calibrations on the Channels page.
27. Press the **Set** button for **Observe:** and **Decouple:** on the Channels page to save the ^{13}C and ^{1}H calibrations in the probe file.

Magic-Angle Adjust with KBr.

Continue in the same workspace using the Onepul protocol and the Adamantane/KBr sample at 5.0 kHz.

1. Click on the **Acquire** tab.
2. Select the **Acquisition** page
3. Set the following:

Field	*Value*
Spectral Width	1e5 Hz
Acquisition Time	0.02 s
Recycle Delay	0.2 s
Gain	30
Scans	16

4. Select on the **Channels** page.
5. Enter **Br79** in **Nucleus:** field for the **Observe "X"** channel and be sure the following transmitter number is **2**.
6. Do not readjust probe tuning for ^{79}Br.
7. Click on the **Pulse Sequence** page.
8. Select the **TPPM** decoupling option.
9. Set **aHtppm = 0** to turn off decoupling.
10. Click on the **Acquire** button.
11. Place the cursor on the tall center band.
12. Enter **`movetof`** command.
13. Click on the **Acquire** button.

    The result is similar to Figure 90.

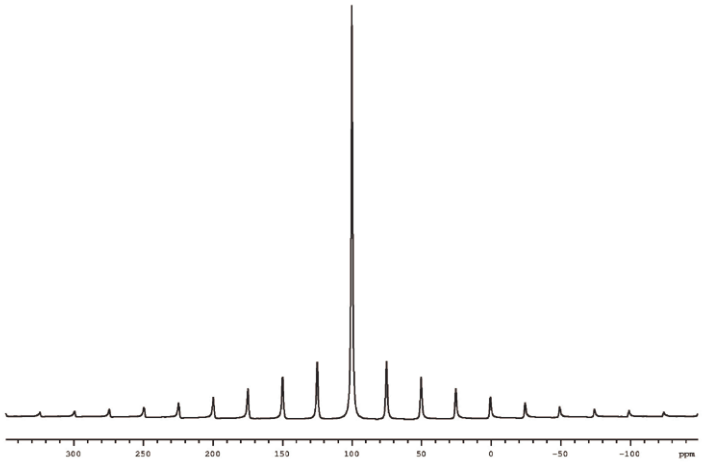


Figure 90. Spectrum of KBr to Optimize the Magic Angle

14. Enter the **Interactive** mode with the **Fidscan** button on the **Shims** page of the **Start** tab.
15. Adjust the magic-angle adjust-knob or screwdriver-adjust on the bottom of the probe to maximize the number of spikes (rotational echoes).

    The result is similar to Figure 91A when the rotor angle is adjusted match the magic angle. The rotational echoes have the same T2 as the central line and the magic angle is optimal.

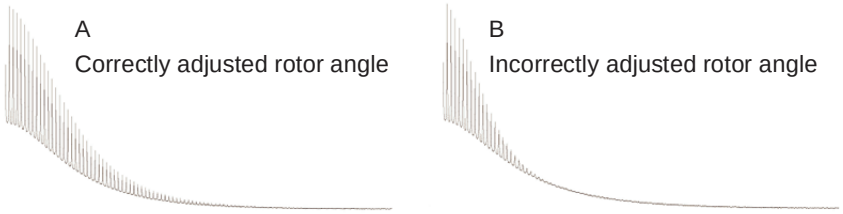


Figure 91. KBr FID for Magic Angle Adjustment

    Improperly set rotor angle produces echoes that decay more quickly and the result is similar to Figure 91B.
16. Save the data.
17. Continue with "Shimming with Adamantane," page 292.

Shimming with Adamantane

Continue in the same workspace using the Onepul protocol and the Adamantane/KBr sample at 5.0 kHz.

1. Click on the **Acquire** tab.
2. Select the **Acquisition** page.
3. Set the following parameters:

Field	*Value*
Spectral Width	5e3 Hz
Acquisition Time	0.1 s
Recycle Delay	5 s
Gain	30
Scans	1

4. Select the Channels page.
5. Enter **C13** in the **Nucleus:** field for the **Observe "X"** channel.

    The transmitter will remain set to **2**. The ^{13}C calibrations were not changed and should remain from the previous step. Press the **Get** button for both the **Observe "X"** and **Decouple "H"** channels to retrieve the calibrations or if there is any doubt that the calibrations shown are not correct.
6. Click on the **Pulse Sequence** page.
7. Select **TPPM** decoupling.

8. Set **aHtppm = aH90/3.0**, use the value of **aH90** determined in step 23 on page 288.

CAUTION: **Adamantane shimming will ultimately use an Acquisition Time = 0.4 s. Probe damage will result if the amplitude of decoupling with acquisition time exceeds aH90/2.0. Do not exceed the probe specification for the maximum time the decoupler can be on at an amplitude greater than aH90/2.0. That number is usually 50 ms.**

9. Set **phHtppm = 0** for CW decoupling.
10. Enter **0.0** in the field next to **line broadening** under **Weighting Parameters** and remove checks from the boxes next to any of the other weighting parameters. This sets lb = 0.0 and places a check in the box next to line broadening field.
11. Click on the **Acquire** button to acquire the data.

    A spectrum similar to Figure 92B is a typical example of data acquired when the field homogeneity is poor (poorly shimmed field). A well-shimmed field produces a

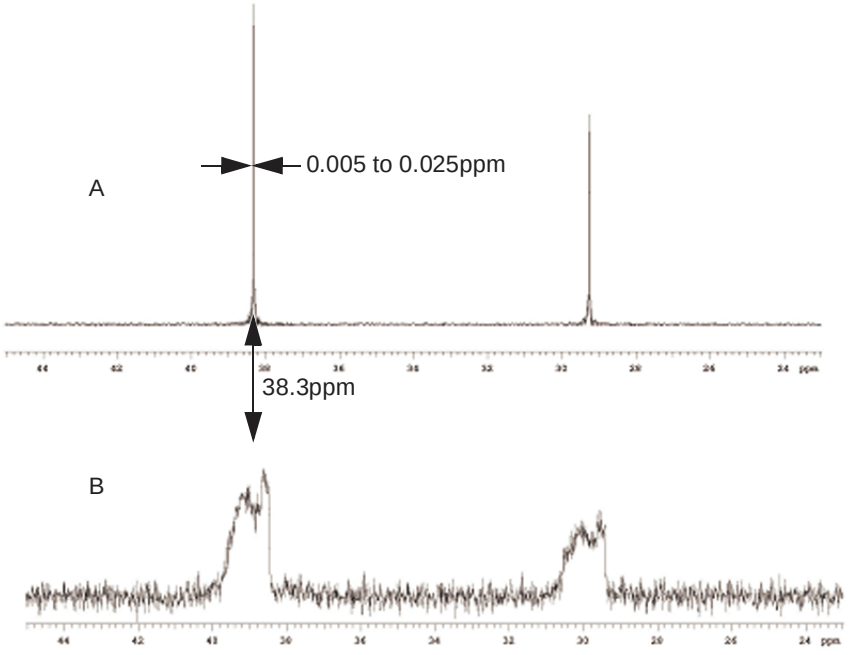


Figure 92. Adamantane Spectra

spectrum of Adamantane, see Figure 92A, with a line width between 0.005 and 0.025 ppm (2 to 10 Hz at 400 MHz). The left hand line is referenced at 38.3 ppm.

12. Place the transmitter between the two lines of Adamantane.
    a. Select 2 cursors and place them on the two lines of Adamantane.
    b. Enter **`split movetof`** on the command line.
    c. Click on the **Acquisition** page.

13. Set the spectra width as follows:

System Frequency	*Spectral Width*
500 MHz and lower	5 kHz
600 MHz and above	10 kHz

14. Click on the **Acquire** button to acquire the data.
15. Click on the **Channels** page.
16. Set an **array** of the decoupler offset **dof** from **-10000 Hz to 10000 Hz** in steps of **1000 Hz**.
17. Click on the **Acquire** button to acquire the data.

    Figure 93 shows the decoupler offset dependence of a shimmed Adamantane sample. The decoupler must be on resonance.

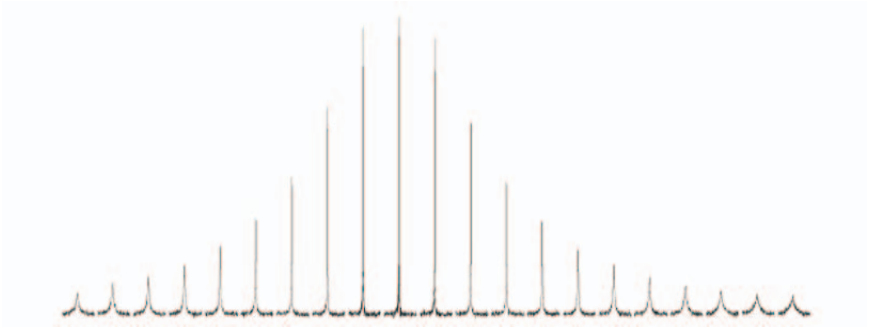


Figure 93. Optimizing Decoupler Offset for Adamantane

18. Enter the value of **dof** corresponding to the spectrum with the greatest peak height.
19. Click on the **Acquisition** page.
20. Set the following:

Field	*Value*
Recycle Delay	5.0 s
Scans	4.

21. Click on the **Acquire** button.
22. Use **Fid Scan** on the **Shims** page of the **Start** tab to obtain repeating display of the Adamantane spectrum.
23. Optimize the shims to obtain a minimum line width.

    Typical shims are X1, Y1, Z1 and Z2.

    Remove the hump at the base of the line with XY and X2Y2.
24. Record a well-shimmed Adamatane spectrum similar to Figure 92A and save the shims with `svs` on the command line.
25. Continue with "Matching the Hartmann-Hahn Condition," page 295.

Matching the Hartmann-Hahn Condition

Setting up Tancpx

1. Change samples.
   a. Replace the Adamantane/KBR sample with the HMB sample.
   b. Adjust probe tuning.
   c. Set spin to 3300 Hz or the value in the probe specification sheet.
2. Load the **Tancpx** protocol using either of the following:
   - Use the Experiment Panel
   a. Click on the **Solids Seq 1D** tab of the **Experiment Panel**
   b. Click on **Tancpx**
   - Use the main menu.
   a. Click on **Experiments**.
   b. Select **Solid-State**.
   c. Select **Basic 1D Experiments**.
   d. Click on **Tancpx**.
3. Click on the **Acquire** tab.
4. Click on the **Acquisition** page.
5. Set the following:

Field	*Value*
Spectral Width	5.0e4
Acquisition Time	0.02 s
Recycle Delay	5.0 s
Gain	30
Scans	4

6. Click on the **Channels** page.
7. Enter **C13** in the **Nucleus:** field for the **Observe ''X''** channel.
8. Enter **H1** in the **Nucleus:** field for the **Decouple ''H''** channel.
9. Press the **Get** button for both the **Observe ''X''** and **Decouple ''H''** channels to retrieve the ^{13}C and basic ^{1}H basic calibrations from the previous steps.
10. Click on the **Pulse Sequence** page.
11. Select **tppm** form the **Decoupling:** drop-down menu.
12. Select **const** from the **Shape** menu in the **cpHX:** parameter group.
13. Set the following parameters in the fields in the **cpHX:** parameter group

Field (Parameter)	*Set or Enter the Following Value in the Field*
aHhx	calibrated ^{1}H amplitude (`aH90` from the Channels page)
aXhx	calibrated ^{13}C amplitude (`ax90` from the Channels page)
tHX	7000 µs.

Field (Parameter)	*Set or Enter the Following Value in the Field*
aHtppm	calibrated ^{1}H amplitude (`aH90` from the Channels page)
phHtppm	0.0 for CW decoupling.

14. Click on the **Acquire** button.
15. Set the transmitter offset **`tof`** to place the tall methyl line in the center of the spectrum.
16. Place a cursor on the line and type **`movetof`** on the command line.

Adjusting the ^{13}C Match Condition.

1. Array **aXhx** about +/- 1000 units.
2. Click on the **Acquire** button.
3. Enter the value of `aXhx` producing the maximum signal in the field next to **`aXhx`**: on the Pulse Sequence page.

   An example of a 12 step aXhx array is shown in Figure 94.

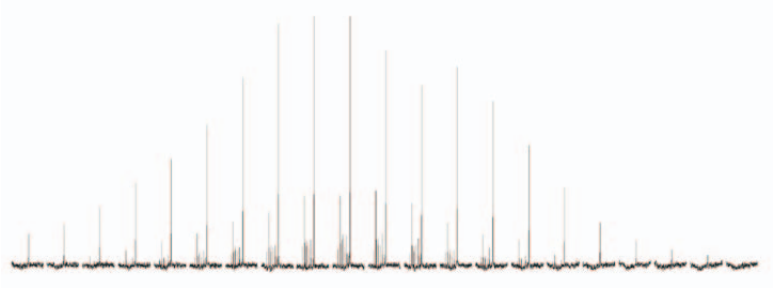


Figure 94. Array of `aXhx` for ^{13}C Hartmann Hahn Match

*Making the Fine Adjustment to **pwH90**.*

1. Select the Channels page.
2. Array **pwH90** from **1.0** to **25.0** µs in steps of **1.0** µs.
3. Click on the **Acquire** button.
4. Enter the value of `pw90` producing the maximum signal in the field next to **pwH90:** on the Channels page.
5. Continue with "HMB Signal-to-Noise," page 296.

HMB Signal-to-Noise

1. Set an array of the number of Scans, **`nt = 10`**, repeated values of 4.
2. Click on the **Acquire** button.

   10 spectra are acquired with the optimum values from "Matching the Hartmann-Hahn Condition," page 295.
3. Save the data.

4. Set two cursors with **`delta = 100p`** for each spectrum and place the right cursor at the right edge of the spectrum.
5. Type **`dsnmax`** on the command line to measure the signal-to-noise ration.
6. Record the value.
7. Average 10 values.

   Typical array is shown in Figure 95.

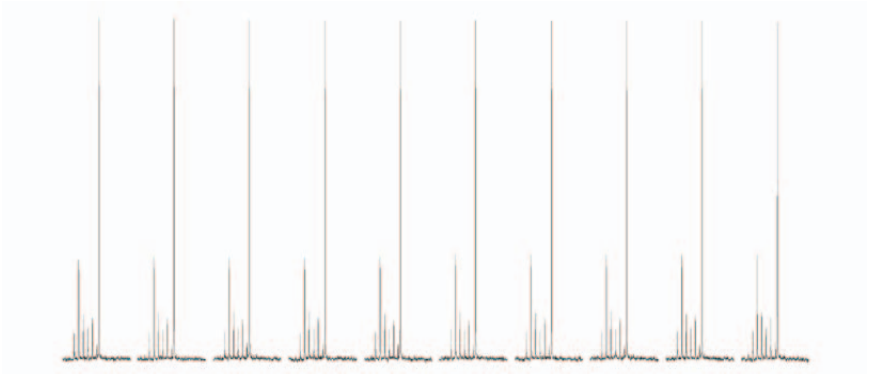


Figure 95. HMB Signal to Noise, 10 repetitions

8. Continue with "Create a Starting Data Set," page 297.

Create a Starting Data Set

1. Load the data from "HMB Signal-to-Noise," page 296.
2. Place the cursor at 100 ppm.
3. Enter **`movetof`**.

   This set the transmitter offset at 100 ppm.
4. Click on the **Acquire** button.
5. Reference the methyl line of the spectrum at 17.3 ppm.
   a. Set the cursor on the methyl line.
   b. Enter **`rl(17.3p)`** on the command line.
6. Click on the **Acquire** button.
7. Set **Shape = 'linear'** and **dHX about 200** in the **cpHX** parameter group.
8. Optional: set ramped cross polarization.
9. Set the receiver parameters correctly and **ddrtc = ad + rd**.
10. Click on the **Acquire** button.
11. Save the dataset.

A standard HMB spectrum centered at 100 ppm, see Figure 96, obtained with ramped cross polarization. This spectrum is a starting point for all ^{13}C CPMAS experiments.

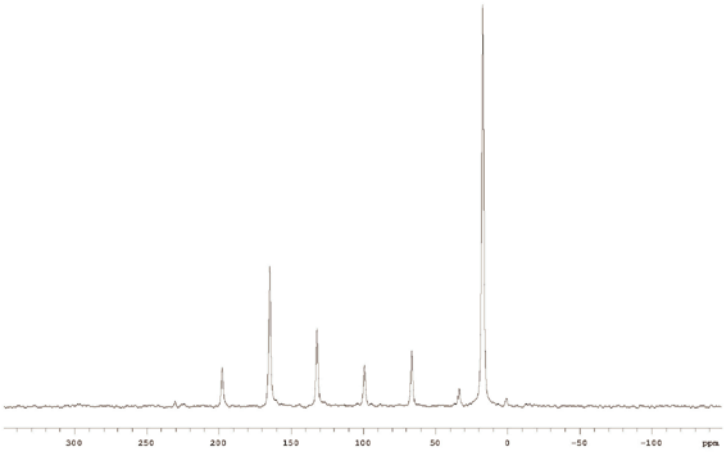


Figure 96. A standard HMB spectrum centered at 100 ppm

13.5 Basic 1D Experiments

- "Constant, Linear, or Tangent Cross Polarization (CP) (Tancpx)," page 299
- "One Pulse (Onepul)," page 299
- "Lee-Golburg CP (Lgcp)," page 299
- "One-Pulse with TOSS (Onepultoss)," page 300
- "pwX90 Measurement with CP (Tancpxflip)," page 300
- "CP with FSLG Decoupling (Tancpxfslg)," page 300
- "X T_1 with CP (Tancpht1)," page 300
- "Interrupted Decoupling with CP (Tancpxidref)," page 301
- "^{1}H T_{1rho} with CP (Tancpxt1rho)," page 301
- "CP with TOSS (Tancpxtoss)," page 301
- "X Two Pulse for T_1 (Twopul)," page 301
- "X Hahn Echo with CP (Tancpxecho)," page 302

Constant, Linear, or Tangent Cross Polarization (CP) (Tancpx)

Protocol	*Sequence*	*Apptype*
`Tancpx`	`tancpx.c`	`solidsseq1d`

Description

Constant, linear or tangent-ramped cross polarization (CP) between H and X with a choice of SPINAL64 or TPPM decoupling. Used for calibration of the Hartmann-Hahn Match and calibration of the 90º pulse width `pwH90` with X detection.

One Pulse (Onepul)

Description

Protocol	*Sequence*	*Apptype*
`Onepul`	`onepul.c`	`solidsseq1d`

Single-pulse preparation with a choice of SPINAL64 or TPPM decoupling. Used for calibration of the 90 pulse width `pwX90`.

Lee-Golburg CP (Lgcp)

Description

Protocol	*Sequence*	*Apptype*
`Lgcp`	`lgcp.c`	`solidsseq1d`

X Lee-Goldburg cross polarization (CP) between H and X with a choice of SPINAL or TPPM decoupling. Used for selective CP with suppression of homonuclear dipolar interactions and for setup of Lee-Goldburg HETCOR.

One-Pulse with TOSS (Onepultoss)

Protocol	*Sequence*	*Apptype*
`Onepultoss.c`	`Onepultoss.c`	`solidsseq1d`

Description

Four pulse TOSS side-band suppression is applied to X after single-pulse excitation, with a choice of SPINAL64 or TPPM decoupling. Used to obtain sideband-free spectra.

pwX90 Measurement with CP (Tancpxflip)

Description

Protocol	*Sequence*	*Apptype*
`Tancpxflip`	`tancpxflip.c`	`solidsseq1d`

Constant, linear or tangent-ramped cross polarization (CP) between H and X with an X flip-back pulse and a choice of SPINAL64 or TPPM decoupling. Used for calibration of pwX90 with CP and X detection.

CP with FSLG Decoupling (Tancpxfslg)

Description

Protocol	*Sequence*	*Apptype*
`Tancpxfslg`	`tancpxflslg.c`	`solidsseq1d`

Constant, linear or tangent-ramped cross polarization (CP) between H and X followed by FSLG decoupling during acquisition. Used to evaluate FSLG decoupling for use in HETCOR. Tancpxfslg automatically sets up FSLG based upon calibrated values of `aH90` and `pwH90`, using the macro `reset_fslg`.

X T_1 with CP (Tancpht1)

Description

Protocol	*Sequence*	*Apptype*
`Tancpht1`	`tancpht1.c`	`solidsseq1d`

An H T_1 measurement using inversion recovery followed by X detection with constant, linear or tangent-ramped cross polarization (CP) between H and X with a choice of SPINAL64 or TPPM decoupling. Used for proton T_1 measurements with CP.

Interrupted Decoupling with CP (Tancpxidref)

Description

Protocol	*Sequence*	*Apptype*
`Tancpxidref`	`tancpxidref.c`	`solidsseq1d`

Interrupted decoupling for suppression of the signals of protonated X nuclei. Follows constant, linear or tangent -ramped cross polarization (CP) between H and X with a choice of SPINAL64 or TPPM decoupling. Provides a refocusing pulse, synchronized with two rotor periods to avoid a large first order phase correction. Used to edit protonated X nuclei from a CPMAS spectrum.

^{1}H T_{1rho} with CP (Tancpxt1rho)

Description

Protocol	*Sequence*	*Apptype*
`Tancpxt1rho`	`tancpx1rho.c`	`solidsseq1d`

Measurement of the X $T_{1\rho}$ with a spinlock following constant, linear or tangent-ramped cross polarization (CP) between H and X, with a choice of SPINAL64 or TPPM decoupling. Used for measurement of the X $T_{1\rho}$ with CP preparation and X detection.

CP with TOSS (Tancpxtoss)

Protocol	*Sequence*	*Apptype*
`Tancpxtoss`	`tancpxtoss.c`	`solidsseq1d`

Description

Constant, linear or tangent-ramped cross polarization (CP) between H and X with a choice of SPINAL64 or TPPM decoupling. Four pulse TOSS side-band suppression is applied to X between the CP and acquisition. Used to obtain sideband free spectra.

X Two Pulse for T_1 (Twopul)

Description

Protocol	*Sequence*	*Apptype*
`Twopul`	`twopul.c`	`solidsseq1d`

A two-pulse X experiment with a delay d2 and with a choice of SPINAL64 or TPPM decoupling. Used for inversion recovery T_1 measurements.

X Hahn Echo with CP (Tancpxecho)

Description

Protocol	*Sequence*	*Apptype*
`Tancpxecho`	`tancpxecho.c`	`solidsseq1d`

Constant, linear or tangent-ramped cross polarization (CP) between H and X followed by a Hahn echo with a choice of SPINAL64 or TPPM decoupling. Used for simple measurements of T_2 and to avoid ring down for static samples. The first delay must be synchronized with the rotor if this sequence is used with MAS.

13.6 HX2D Experiments

- "2Q-1Q with CP and C7 Mixing (C7inad2d)," page 302
- "Hetcorlgcp2d," page 302
- "PISEMA2d," page 303
- "WISE (Wisentancp2d)," page 303

2Q-1Q with CP and C7 Mixing (C7inad2d)

Apptype: solidsseq1d

Protocol	*Sequence*	*Apptype*
`C7inad2d`	`c7inad2d.c`	`solidsseq1d`

Description

1Q-2Q correlation using C7 mixing, with TPPM or SPINAL decoupling. A sequence to correlate X nucleus pairs with double quantum filtering. F1 is the evolution of double-quantum coherence and F2 is single quantum chemical shift. The spectral appearance is similar to the INADEQUATE experiment. Polarization (along "Z") is created with a constant, linear or tangent ramped CP followed by a flip-back pulse on X. C7 is used to recouple double quantum coherence and a second pulse returns polarization to X. TPPM or SPINAL decoupling is applied during acquisition and CW decoupling with an amplitude `aHmix` is applied during C7.

Hetcorlgcp2d

Protocol	*Sequence*	*Apptype*
`Hetcorlgcp2d`	`hetcorlgcp2d.c`	`solidsseq1d`

Description

H to X HETCOR using FSLG during F1 followed by a Lee-Goldburg CP, with SPINAL64 or TPPM decoupling. Frequency switched Lee Goldburg decoupling is used during F1 to suppress the proton homonuclear dipolar interaction. HETCOR is used to resolve the proton chemical shift spectrum and to assign X-H pairs.

PISEMA2d

Description

Protocol	Sequence	Apptype
Pisema2d	pisma2d.c	solidsseq1d

A sequence to correlate X chemical shift with the X-H dipolar interaction in the rotating frame. PISIMA is used to characterize ^{15}N-^{1}H dipolar interactions for static, oriented membrane protein samples.

`reset_pisema` - This macro uses the calibrated values of `pwH90` and `aH90` to calculate the initial parameters for the fslgH waveform and sets up 2D parameters. `reset_pisema2d` is run from the protocol.

WISE (Wisentancp2d)

Description

Protocol	Sequence	Apptype
Wisetancp2d	wisetancp2d.c	solidsseq1d

2D correlation between the X chemical shift and the H wideline spectrum using constant, linear or tangent-ramped cross polarization (CP) between H and X with a choice of SPINAL64 or TPPM decoupling. Used for separation of the proton wideline spectra of X-H pairs with `tHmix = 0`. Used for spin diffusion measurements with `tHmix` > 0.0.

13.7 HXY Experiments

- "One Pulse REDOR with XY8 on X and Y (Redor1onepul)," page 303
- "CP REDOR with XY8 on X and Y (Redor1tancp)," page 304
- "One Pulse REDOR with XY8 Y and X inversion (Redor2onepul)," page 304
- "CP REDOR with XY8 on Y and X Inversion (Redor2tancp)," page 304

One Pulse REDOR with XY8 on X and Y (Redor1onepul)

Protocol	Sequence	Apptype
Redor1onepul	redor1onepul.c	solidsseq1d

Description

Rotational Echo Double Resonance (REDOR) with one-pulse preparation, XY8 decoupling with pulses alternating on X and Y, with a choice of SPINAL64 or TPPM decoupling during both acquisition and REDOR evolution. Used to measure XY bond distances for organic materials where one-pulse preparation is preferred.

CP REDOR with XY8 on X and Y (Redor1tancp)

Description

Protocol	*Sequence*	*Apptype*
`Redor1tancp`	`redor1tancp.c`	`solidsseq1d`

Rotational Echo Double Resonance (REDOR) with constant, linear or tangent-ramped preparation, XY8 decoupling with pulses alternating on X and Y, with a choice of SPINAL64 or TPPM decoupling during both acquisition and REDOR evolution. Used to measure XY bond distances for organic materials.

One Pulse REDOR with XY8 Y and X inversion (Redor2onepul)

Description

Protocol	*Sequence*	*Apptype*
`Redor2onepul`	`redor2onepul.c`	`solidsseq1d`

Rotational Echo Double Resonance (REDOR) with one-pulse preparation, XY8 decoupling with pulses on Y, and a refocusing pulse on X, with a choice of SPINAL64 or TPPM decoupling during both acquisition and REDOR evolution. Used to measure XY bond distances for inorganic and organic materials where one-pulse preparation is preferred.

`redor2onepul` is the favored REDOR sequence if homonuclear coupling or quadrupole coupling is present for the X nuclei. Rotationally synchronized pi pulses interfere with the refocusing of these interactions into rotational echoes and dephase the magnetization. `redor2onepul` has only one refocusing pulse on X.

CP REDOR with XY8 on Y and X Inversion (Redor2tancp)

Description

Protocol	*Sequence*	*Apptype*
`Redor2tancp`	`redor2tancp.c`	`solidsseq1d`

Rotational Echo Double Resonance (REDOR) with constant, linear or tangent-ramped preparation, XY8 decoupling with pulses on Y, and a refocusing pulse on X, with a choice of SPINAL64 or TPPM decoupling during both acquisition and REDOR evolution. Used to measure X-Y bond distances for inorganic and organic materials.

`redor2tancp` is the favored REDOR sequence if homonuclear coupling or quadrupole coupling is present for the X nuclei. Rotationally synchronized pi pulses interfere with the refocusing of these interactions into rotational echoes and dephase the magnetization. `redor2tancp` has only one refocusing pulse on X.

13.8 Quadrupole Experiments

- "3Q-1Q MQMAS with Z-filter (Mqmas3qzf2d)," page 305
- "5Q-1Q MQMAS with Z-filter (Mqmas5qzf2d)," page 305
- "Quadrupole Echo (Ssecho1d)," page 305

3Q-1Q MQMAS with Z-filter (Mqmas3qzf2d)

Description

Protocol	*Sequence*	*Apptype*
`Mqmas3qzf2d`	`mqmas3qzf2d.c`	`solidsseq1d`

3-quantum multiple-quantum MAS with a third Z-filter pulse and a choice of SPINAL64 or TPPM decoupling. Used to obtain a 2D MQMAS spectrum for all spins 3/2 to 9/2.

5Q-1Q MQMAS with Z-filter (Mqmas5qzf2d)

Protocol	*Sequence*	*Apptype*
`Mqmas5qzf2d`	`mqmas5qzf2d.c`	`solidsseq1d`

Description

5-quantum multiple-quantum MAS with a third Z-filter pulse and a choice of SPINAL64 or TPPM decoupling. Used to obtain a 2D MQMAS spectrum for all spins 5/2 to 9/2.

Quadrupole Echo (Ssecho1d)

Protocol	*Sequence*	*Apptype*
`Ssecho1d`	`ssecho1d.c`	`solidsseq1d`

Description

A two-pulse solid or quadrupole echo with a choice of SPINAL64 or TPPM decoupling. Used primarily for wideline deuterium NMR.

13.9 Multipulse Experiments

- "BR24 with Quadrature Detection (Br24q)," page 306
- "MREV8 with Quadrature Detection (Mrev8q)," page 306
- "Semiwindowless WaHuHa (Swwhh4)," page 306
- "High Power Pulse Tuning (Tunerp)," page 307
- "Windowed PMLG-N (Wpmlg1d)," page 307
- "2D F1 and Windowed PMLG-N (Wpmlg2d)," page 307
- "XX Tuneup (Xx)," page 308
- "XmX Tuneup (Xmx)," page 308

BR24 with Quadrature Detection (Br24q)

Description

Protocol	*Sequence*	*Apptype*
Br24q	br24q.c	solidsseq1d

X acquisition with interleaved BR24. Quadrature phase cycle.

Quadrature BR24 multiple-pulse acquisition for high resolution proton NMR. This sequence uses a variable-length preparation pulse and fine-phase array to preparation are the magnetization in quadrature perpendicular to the multiple-pulse axis of precession (1,1,1). The four variable length pulses are calculated assuming that pwXprep has a 90-degree flip angle. BR24 has a cycle time of 36 tau with 24 pulses per cycle.

Set phXprep = -45 degrees. Br24q is used with slow spinning (< 2500 Hz).

MREV8 with Quadrature Detection (Mrev8q)

Protocol	*Sequence*	*Apptype*
Mrev8q	mrev8q.c	solidsseq1d

Description

Quadrature MREV8 multiple-pulse sequence is used for acquisition for high resolution proton NMR. The sequence uses a variable-length preparation pulse and fine phase array to prepare the magnetization in quadrature perpendicular to the multiple-pulse axis of precession (sqrt(1/2),0,sqrt(1/2)).

The four variable-length pulses are calculated assuming that pwXprep has a 90-degree flip angle. MREV8 has a cycle time of 12 tau with 8 pulses per cycle. Set **phXprep = 0** degrees. Mrev8q is used with slow spinning (< 2500 Hz).

Semiwindowless WaHuHa (Swwhh4)

Protocol	*Sequence*	*Apptype*
Swwhh4	swwhh4.c	solidsseq1d

Description

Semi-windowless WaHuHa (SWWHH4) multiple-pulse acquisition for high resolution proton NMR. This sequence uses 90-degree preparation pulses on X and -X offset by -45 degrees to prepare the magnetization perpendicular to the multiple-pulse axis (1,1,1). SWWHH4 has a cycle time of 6 tau with 4 pulses per cycle. Set phXprep = -45 degrees. SWWHH4 is used with medium speed spinning (8.0 to 14.0 kHz).

Reference

I. Schnell, A. Lupulescu, S. Hafner, D.E. Demco, H.S. Spiess, J. Magn. Reson. 133, 66-69 (1998).

High Power Pulse Tuning (Tunerp)

Protocol	*Sequence*	*Apptype*
`Tunerp`	`tunerp.c`	`solidsseq1d`

Description

A pulse sequence for pulse tuning through the directional couplers in the VNMRJ display. Tunerp is used for high-power pulsed tuning and for characterization of phase transient. It provides a phase detected output of the pulse that can be displayed in phased or absolute value mode. Launch Tunerp with the **Fidscan** button on the Shims page in Setup tab.

Measure the ratio of forward to reflected power when using Tunerp. The standard directional couplers are wired to measure reflected power only. The arrow on the side of the coupler should point back toward the Front End to measure reflected power. To measure forward power reverse the coupler so that the arrow points toward the probe.

A second optional bidirectional coupler is available on some systems. With this coupler reverse the direction of the arrow by turning the knob on the top.

Windowed PMLG-N (Wpmlg1d)

Protocol	*Sequence*	*Apptype*
`Wpmlg1d`	`wpmlg1d.c`	`solidsseq1d`

Description

Quadrature, windowless PMLG-N (wPMLG) is used for multiple-pulse acquisition. The sequence uses a composite preparation pulse involving a quadrature phase-shifted 90 and a 54.7-degree pulse along Y to prepare the magnetization perpendicular to the multiple-pulse axis of precession (sqrt(2/3), 0 sqrt(1/3)). The recycle time for wPMLG is:
`tauXwpmlg = 2.0*(4.0*pwX90)*sqrt(2/3) + B`
where `pwX90` is the 90-degree pulse and B is the window time.

The pulse time is fixed. Changing `tauXwpmlg` changes the window time B. `Wpmlg1d` is used with moderate spinning speeds of 8 to 14 kHz.

2D F1 and Windowed PMLG-N (Wpmlg2d)

Protocol	*Sequence*	*Apptype*
`Wpmlg2d`	`wpmlg2d.c`	`solidsseq1d`

Description

2D homonuclear correlation with PMLG in F1, a spin diffusion mixing period and quadrature windowed PMLG (wPMLG) for multiple-pulse acquisition in F2. This sequence uses the composite preparation pulse to put the magnetization along -Y perpendicular to the PMLG axis of precession. After F1 PMLG, a tilt pulse returns precession to the XY plane and puts the Y axis along Z for cosine peaks and the X axis for sine peaks. A delay of `tXmix` allows mixing by spin diffusion. A quadrature wPMLG

sequence similar to wpmlg1d.c then samples the Z axis magnetization in F2. PMLG and wPMLG are used with moderate-speed spinning (8 to 14 kHz).

XX Tuneup (Xx)

Description

Protocol	*Sequence*	*Apptype*
Xx	xx.c	solidsseq1d

X pulses with interleaved acquisition. Used for multipulse calibration of pwX90. Usually performed with a liquid sample or a sample of RTV silicon rubber with slow spinning. Xx can also be used to examine sampling windows and set the blank/unblank delays r1Xxx and r2Xxx.

Xx subtracts probe ring-down with a two-scan (0,2) phase cycle of the preparation pulse and the receiver. The xmxX has 0 phase for all scans. The oscillating pattern will not be symmetric about zero due to a constant signal from probe ringing and background For very short values of tau and when probe proton background is present. Use 2 scans to see the signal without ringing.

XmX Tuneup (Xmx)

Description

Protocol	*Sequence*	*Apptype*
Xmx	xmx.c	solidsseq1d

X pulses with interleaved acquisition and alternating phase. Used for multi-pulse calibration to minimize phase transient. Usually performed with a liquid sample or a sample of RTV silicon rubber with slow spinning. Xmx can also be used to examine sampling windows and set the blank/unblank delays r1Xxmx and r2Xxmx.

Xmx subtracts probe ring-down with a two-scan (0,2) phase cycle of the preparation pulse and the receiver. The xmxX sequence has 0 phase for all scans.The oscillating pattern is not symmetric about zero for very short values of tau and when probe proton background is present due to a constant signal from probe ringing and background. Use 2 scans to see the signal without ringing.

Chapter 14. Data Analysis

Sections in this chapter:

- 14.1 “Spin Simulation,” this page
- 14.2 “Deconvolution,” page 317
- 14.3 “Reference Deconvolution Procedures,” page 322
- 14.4 “Addition and Subtraction of Data,” page 326
- 14.5 “Regression Analysis,” page 332
- 14.6 “Cosy Correlation Analysis,” page 340
- 14.7 “Chemical Shift Analysis,” page 340

14.1 Spin Simulation

- “Introduction to Spin Simulation,” page 309
- “Spin Simulation Window Tabs and Controls,” page 310
- “Spin Simulation Step-by-Step,” page 311
- “Spin Simulation Related Commands, Parameters, and Files,” page 313

Introduction to Spin Simulation

The software includes an iterative spin simulation program based on the FORTRAN program LAME, also known as LAOCOON with magnetic equivalence added. LAME calculates the theoretical spectrum for spin-1/2 nuclei, given the chemical shifts and the coupling constants.

Up to eight closely coupled, non-equivalent spins (ABCDEFGH) can be handled. Equivalent spins can be treated by magnetic equivalence factoring to extend the simulation to systems such as A3B2CD3. The X-approximation can be used to handle different types of nuclei. Nuclei are treated as different types if there is at least one spare letter in the alphabet between their groups (e.g., ABD and ABX are both systems using the X-approximation.) Frequencies, intensities, energy levels and transitions can be listed, and simulated spectra can be displayed and plotted.

Parameters can be adjusted by iteration to approach a given experimental spectrum. One or several parameters can be kept constant for iterative runs and one or several parameters can be set equal to each other and held equal during the course of the iteration.

A worked through example is provided in “Spin Simulation Step-by-Step,” page 311. The menus and dialog windows simplify the procedure. A number of specialized commands and parameters are also available. Table 29 lists these commands and parameters

References for the spin simulation algorithms:

- Bothner-by, A.A. and Castellano, S., *J. Chem. Phys.*, **41**, 3863 (1964).
- Emsley, Feeney, and Sutcliffe, eds. 1966. *Progress in Nuclear Magnetic Resonance Spectroscopy*, Vol.1, Chap. 3. Oxford: Pergamon Press.
- Stanley, R.M.; Marquardt, D.W.; and Ferguson, R.C., *J. Chem. Phys.*, **41**, 2087 (1964).

Spin Simulation Window Tabs and Controls

- "Spin Selection Tab, Buttons and Fields," page 310
- "Spin Assignment Tab," page 311

Spin Selection Tab, Buttons and Fields

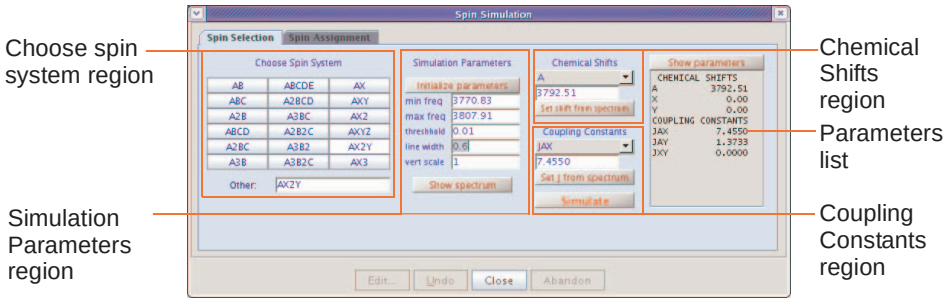


Figure 97. Spin Simulation – Spin Selection Tab

The Spin Selection Tab has the following buttons and fields, refer to Figure 97 as needed:

Region and Button or field	*Description or Function*
Choose Spin System region	
Choose Spin System radio buttons.	Click on a button to select the spin system.
Other:	Enter the spin system in this field if the required spin system is not associated with a button.
Simulation Parameters section.	
Initialize parameters button	Initializes the spin simulation parameter using the default values displayed.
Parameter fields.	Enter a new value for any of these parameters. Click the **Initialize parameters** button to initialize the parameter fields from the current spectrum.
Show spectrum button	Display the Fourier-transform spectrum.
Chemical Shifts section.	
Chemical shift menu	Select a chemical shift from the menu (A, B etc.)
Chemical shift entry field	Enter a chemical shift value in the entry field.
Set shift from spectrum button	Set the chemical shift using the current position of the cursor in the spectrum.
Coupling Constants section.	
Coupling constant menu	Select a coupling constant (JAX, JAY etc.) from the menu.
Coupling constant entry field	Enter a coupling constant value in the entry field.
Set J from spectrum button	Use the current positions of the left and right cursors in the spectrum to set the coupling constant.

Region and Button or field	*Description or Function*
Simulate button	Simulate and display the spectrum using the selected spin system, chemical shifts, and coupling constants.
Show parameters button	Display the chemical shifts and coupling constants in a single list in the field below.

Spin Assignment Tab

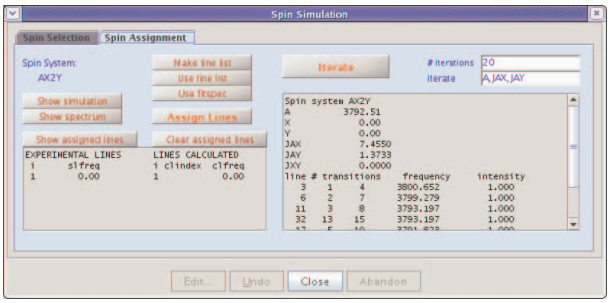


Figure 98. Spin Simulation – Spin Assignment Tab

The Spin Assignment Tab has the following buttons and fields, refer to Figure 98 as needed:

Button or Field	*Description*
Spin System:	Displays the spin system selection.
Show simulation button	Display simulated spectrum.
Show spectrum button	Fourier transform and display the spectrum.
Make line list button	Create a line list from the current spectrum and threshold and copy the list into the spin simulation line assignment file.
Use line list button	Copy the current line list into the spin simulation line assignment file.
Use fitspec button	Copy the `fitspec` line list into the spin simulation line assignment file.
Show assigned lines button	Display the spin simulation line assignment file `spini.la`.
Clear assigned lines button	Clear the line assignments.
Iterate button	Iteratively fit the simulated transition lines to the experimental lines.
# Iterations field	Displays the maximum number of iterations used for fitting the data.
Iterate field	Shows the `iterate` parameter containing the chemical shifts and coupling constants used in the iterative fit.

Spin Simulation Step-by-Step

A step by step procedure is provided using a worked out example that includes comments at each step.

Setting Up the Spectrum for Spin Simulation

1. Click on **File** on the main menu.

2. Select Open.

   The text window displays a list of directories (entries with a backslash as the last character in the name) and files (if any). The menu (near the top of the screen) displays the pathname of the current directory.

3. Select the top directory (/) from the **Look In** menu of the **File Open** dialog.

4. Select **`/vnmr`** from the file display.

   The text window displays the list of subdirectories.

5. Select **`fidlib`** from the list.

6. Double click on the file **`Proton_01fid`**.

   The file is retrieved to the current experiment and viewport.

7. Click on the **Process** tab.

8. Click on the **Transform** button.

   The graphics window displays a spectrum and the menu from the interactive spectrum display program (`ds`) appears.

9. Click the left mouse button near 7.7 ppm and the right mouse button near 7.5 ppm.

10. Click on  .

    The spectrum expands to show the six-line pattern that will be simulated as an AX2Y system.

11. Click the **Show Spectrum** button.

    The spectrum is now set up.

Simulating the Spectrum

1. Click on **Process** on the **Main Menu**.

2. Select **Analyze**.

3. Select **Spin Simulation…**

   The Spin Simulation dialog box appears.

4. Click on **Spin Selection Tab**.

5. Click on **AX2Y** button.

   This picks the spin system.

6. Click on **Initialize Parameters**.

   The parameters are initialized from the spectrum and displayed.

7. Enter **0.6** in the **linewidth** entry field.

8. Click on the one cursor icon on the graphics toolbar.

9. Move the cursor to the center of the six-line pattern.

10. Click the **left** mouse button.

11. Select **A** from the **Chemical Shifts** menu.

12. Click on the **Set shift from spectrum** button.

    This sets the chemical shift of spin A to the position of the cursor.

13. Move the cursor to the center of the left-most line.

14. Click the **left** mouse button.
15. Move the cursor to the center of the second left-most line.
16. Click the **right** mouse button.
17. Select **JAY** from the **Coupling Constants** menu to set the JAY coupling.
18. Click the **Set J from spectrum** button.s

    This sets the JAY coupling constant to match the difference frequency.
19. Click the right button on the center of the third line from the left.
20. Select **JAX** from the **Coupling Constants** menu to set the JAX coupling.
21. Click the **Set J from spectrum** button.
22. Click on **Show Parameters**.

    This confirms your entry of the spin system parameters.
23. Click on **Simulate**.

    A simulated spectrum is displayed.

Running an Iterative Spin-simulation

1. Click on the **Spin Assignment** tab.
2. Verify that the values in the entry box are: `A, JAX, and JAY`.

    This verifies that the `iterate` parameter is set correctly.
3. Enter the number of iterations in the **# iterations** field, enter 20 as a starting point.
4. Click on **Show/Hide** threshold button  to show the threshold.

    Use the left mouse button to move the threshold line below the tops of the peaks.
5. Click the **Make Line List** button.
6. Click on the **Assign Lines** button.

    The `assign` macro is executed and assigns the lines from the line listing to the lines from the previous simulation.
7. Click on the **Iterate** button.

    This performs an iterative optimization, displays the resulting spectrum, and outputs the results of the iteration to the iterate window.
8. Click on **Spin Selection** tab.
9. Click on the **Show parameters** button.

    The listing contains the values of the `A`, `JAX`, and `JAY` parameters that give the best iterated fit to the experimental spectrum.

Spin Simulation Related Commands, Parameters, and Files

- "Commands and Parameters," page 314
- "Spin Simulation Global Parameters," page 315
- "Iterative Mode Related Commands," page 315
- "Spin Simulation Files," page 316

Commands and Parameters

Related commands and parameter are listed in Table 29.

Table 29. Spin Simulation Related Commands and Parameters

Command	*Description*
`assign*`	Assign transitions to experimental lines
`cla`	Clear all line assignments
`dga`	Display group of spin simulation parameters
`dla<('long')>`	Display spin simulation parameters arrays
`dlalong`	Long display of spin simulation parameter arrays
`dll*`	Display listed line frequencies and intensities
`dsp<(file)>`	Calculates the simulated spectrum (using the current value of parameter `slw` for the linewidth) and displays the spectrum using the current table of transitions and intensities. `dsp` can only be used after the `spins` program has been run. `dsp` with a filename as an argument uses the spectral information taken from that file. The result is displayed and can be modified and plotted like any other 1D spectrum.
`initialize_iterate`	Set iterate string to contain relevant parameters
`spinll<('mark')>`	Set up a slfreq array

`spins <(options)>`	Performs a spin simulation using the current spin system parameters when the Simulate button is clicked. The following variations are available:
	`spins('calculate','energy')`
	Puts an energy level table in the output file.
	`spins('calculate','transitions')`
	Puts a second table of transitions ordered by transition number in the output file.
	`spins('iterate')`
	Runs in an iterative mode to match experimental and calculated lines.
	`spins('iterate','iteration')`
	Lists parameters after each iteration in the output file.

`spsm(spin_system)`	Enter spin system
`undospins`	Restore spin system as before last iterative run
`* dll<('pos'<,noise_mult>)><:lines>` `assign<('mark')>, assign(transistion_number,line_number)`	

Parameters

`cla` {array of real values}	Calculated transition number
`clamp` {array of real values}	Calculated transition amplitude
`clfreq` {real values}	Calculated transition frequency
`clindex` {array of real values}	Index of experimental frequency of a transition
`iterate` {string of parameters}	Parameters to be iterated
`niter` {1 to 9999}	Number of iterations
`slfreq` {real values}	Measured line frequencies
`slw` {0.01 to 1e6}	Spin simulation linewidth
`smaxf` {–1e10 to 1e10}	Maximum frequency of any simulated transition
`sminf` {–1e10 to 1e10}	Minimum frequency of any simulated transition
`sth` {0 to 1.00}	Minimum intensity threshold
`svs` {0 to 1e10}	Spin simulation vertical scale

Spin Simulation Global Parameters

Commonly used spin simulation global parameters and descriptions:

Parameter	*Description*
`cla` and `clfreq`	Make up a table consisting of line numbers assigned by the spin simulation program and the corresponding frequency of a measured line when the intensity of the line is above a threshold value set by the parameter `th`.
`clamp`	Sores the transition amplitude of calculated transitions when they are above a threshold set by parameter `sth`.
`clindex`	Index of experimental frequency of a transition.
`slfreq`	List of measured line frequencies.
`sminf` and `smaxf`	Minimum and maximum frequency limits for calculation of the final simulated spectrum. These should be set before the calculation is performed. If the Initialize Parameter button is used, `sminf` is initialized to `sp`, and `smaxf` is initialized to `sp+wp`.
`sth`	Minimum intensity threshold above which transitions are listed and included in the simulated spectrum. A typical value is 0.05.
`svs`	Maximum intensity of calculated transitions.
`slw`	Spin simulation line width
`dga`	Displays the file of simulation parameters in the Text Output window of the Process Panel.

Iterative Mode Related Commands

The following commands are used to set up files for the “iterative” mode of spin simulation in which the calculated spectrum approximates an experimental spectrum.

Command	*Button*	*Description*
`spins('iterate')`	**Iterate**	Performs the simulation in the iterative mode
`initialize_iterate`	**Initialize parameters**	Selects a default value for the parameter `iterate` that causes iteration of all parameters. The string parameter, `iterate`, contains a list of parameters (separated by commas) to be iterated during iterative spin simulations. Typical value is `'A,B,JAB'`. Initializes the parameter `iterate` to a string containing parameters appropriate to the current spin system and `niter` to 20.
`cla`	**Clear assigned lines**	Clears the file of line assignments used for spin simulation.
`dla`	**Show assigned lines**	Displays the file containing the line assignments.
`dlalong`		Writes the line assignments to the file `spini.la` of the current experiment. This command is useful in more complex problems where the text window is too small for the `dla` display. `dlalong` displays the file in the text window.

Command	*Button*	*Description*
`spinll`	**Use Line List**	Copies the frequency list from the last `nll` or `dll` line listing (contained in the parameter `llfrq`) into the simulation line frequency parameter `slfreq`. `spinll`, clears previous line assignments, and runs `dla`.
`spinll('mark')`		Places the line positions in the file `mark1d.out` into the parameter `slfreq`. This is useful for to manual line assignment.
`assign`	**Assign Lines**	The nearest calculated transitions are assigned to the lines from a `dll` or `nll` listing after `spinll` places them in `slfreq`. If a frequency in `slfreq` exists with a line number, the next entry of the same frequency is assigned a unique line. Optional: Assign positive lines only. Run `dll('pos')` from the command line first. Only lines transitions greater than `sth` (typically $\geq$0.05 to prevent assignment of extremely small lines) are assigned.
`assign('mark')`		The same as `assign` except the file `mark1d.out` is used instead of the `dll` listing. Use the cursor and the mark button to place the lines to be assigned in the `mark1d.out` file. This file is cleared by `mark('reset')`. Use `nl` to move the cursor to the center of a selected line.
`assign(t#,l#)`		Assigns a single calculated transition number (`t#`) to a line from a `dll` listing (the index is `l#`). Use `assign(t#,0)` to remove the calculated transition assignment.
`undospins`		Restores a spin system as it was before the last iterative run. Chemical shifts, coupling constants, and transition assignments are returned to those existing immediately before an iterative spin simulation.

Refer to the descriptions in the *VNMR Command and Parameter Reference.*

Spin Simulation Files

The `spins.list` file is an output table made by the spin simulation program. This file can be displayed by clicking on the list button. The following files can exist in the current experiment. Only the file `spini.la` is normally of interest when spin simulation is run:

File	*Description*
`spini.indata`	Line assignment input (deleted by `spins` after iterations are completed) for the `spins` program.
`spini.inpar`	List of parameters whose values are to be determined by `spins('iterate')`.
`spins.inpar`	List of initial settings of a number of spin simulation parameters.
`spini.la`	Current transition assignments for an iterative spin simulation (produced by the `dlalong` command).

File	*Description*
`spins.list`	Name of the output file and it is located in the current experiment. This file always includes the calculated transitions ordered by frequency.
`spins.outdata`	File of frequencies, amplitudes, and transition numbers from a spin simulation. It is used in calculating the displayed spectrum.
`spini.outpar`	Values of the chemical shifts and coupling constants after an iterative spin simulation.
`spini.savela`	Transition line assignments for iterative spin simulation in a format readable by the macro `undospins`.
`spins.stat`	Constants related to iteration (deleted by the `spins` program).

14.2 Deconvolution

- "Introduction to Deconvolution," page 317
- "Deconvolution Window and Controls," page 317
- "Deconvolution Step-by-Step," page 318
- "Deconvolution Related Commands, Parameter, Macros, and Files," page 320

Introduction to Deconvolution

The software supports the deconvolution of observed spectra into individual Lorentzian and/or Gaussian lines. Up to 2048 data points from an expansion of an experimental spectrum can be deconvoluted at one time, and up to 25 lines can be fit to this section of the observed spectrum. Each line's shape can be defined to be Lorentzian, Gaussian, or a combination of both.

The following parameters are available for each line:

- Frequency (in Hz) of line
- Intensity of line
- Linewidth (in Hz) at half-height of line
- Gaussian fraction of line: 0.0 (completely Lorentzian) to 1.0 (completely Gaussian)

All parameters can be fit at the same time, or selected parameters can be removed from the fit. In addition, a linear baseline correction is always added to the fit to avoid large errors produced by base line offsets.

Deconvolution Window and Controls

Figure 99. Deconvolution Window and Controls

The Deconvolution window, see Figure 99, provides access to deconvolution functions via the following buttons:

Button	*Function*
Auto Make Line List	Create a line list from the current spectrum and threshold using the `nll` command
Use Line List	Use the current line list as a starting point for deconvolution
Set Mark	Add the current cursor position to the mark file.
Reset Mark	Clear all lines from the mark file.
Use Mark	Use the current mark list as a starting point for deconvolution.
Fit it	Perform deconvolution on the selected line list using the `fitspec` command and display the results.
Show Results	Display the deconvolution fit results in the Text Output page.
Show Fit Spectrum	Display the spectrum calculated by deconvolution.
Show Spectrum	Fourier-transform the current FID file and display the spectrum.
Add/Subtract	Enter the add / subtract mode using the FT spectrum and fit spectrum.
Plot Fit Spectrum	Plot the deconvolution fit spectrum, FT spectrum, and component analysis using the `plfit` macro

Deconvolution Step-by-Step

1. Click on **File** on the main menu.
2. Select Open.

   The text window displays a list of directories (entries with a backslash as the last character in the name) and files (if any). The menu (near the top of the screen) displays the pathname of the current directory.
3. Select the top directory (/) from the **Look In** menu of the **File Open** dialog.
4. Select **`/vnmr`** from the file display.

   The text window displays the list of subdirectories.
5. Select **`fidlib`** from the list.
6. Double click on the file **`Proton_01.fid`**.

   The file is retrieved to the current experiment and viewport.
7. Click on the **Process Tab**.
8. Select the **Default** page.
9. Select **32k** from the **Transform Size** menu.

   Use a larger Fourier transform size than normal for proper digitalization of the line shape when the spectrum is to be deconvoluted. A typical transform size for deconvolution is `2*np`.
10. Click on the **Transform** button.
11. Expand the six-line pattern near 7.6 ppm until it fills the center third of the display, with baseline on both sides.
12. Click on the **Vert Scale** menu on the Default page of the Process folder and select **Absolute** intensity mode.

    The absolute intensity mode is required for deconvolutions, simulations, etc.

13. Click on **Process** on the Main menu bar.
14. Select **Analyze**.
15. Select **Deconvolution**.

    The Deconvolution window opens, seeFigure 99.
16. Click on the **Show Spectrum** button.
17. Set a threshold that lists exactly six lines.
18. Click on the **Auto Make Line List** button.
19. Click on the **Use Line List** button.

    A line list and a file containing starting point for the deconvolution is created. The linewidth of the tallest line on the screen is measured automatically and used as the starting linewidth for the calculation.
20. Click on the **Fit it** button.

    The analysis is performed. This particular example is an 18 parameter fit (6 frequencies, 6 intensities, and 6 linewidths). The calculated spectrum is displayed in the graphics window when the analysis is done. Numerical results appear in the Text Output panel of the Process folder. The numerical output should be similar to this:

```
Number of data points:            660
Final chi square:                 32611.957
Total number of iterations:       29
Successful iterations:            29
Digital resolution                0.152 Hz/point

ITERATION HAS CONVERGED

Parameters
line        frequency   intensity   integral   linewidth   gaussian fraction
1           3800.740    57.543      45.723     0.506       0.000*
2           3799.480    57.509      44.546     0.493       0.000*
3           3793.290    89.616      116.212    0.826       0.000*
4           3792.020    86.232      102.826    0.759       0.000*
5           3785.870    82.859      63.909     0.491       0.000*
6           3784.610    79.897      59.166     0.471       0.000*
```

21. Click on the **Plot fit Spectrum** button.

    The original spectrum, the calculated spectrum, and each of the component lines is plotted automatically, along with the numerical results of the calculation. At the end of this operation, the original spectrum replaces the calculated one.
22. Click on the **Show Fit Spectrum** button to return to viewing the calculated spectrum.
23. Click on the **Add/Subtract** button to view the original spectrum simultaneously with the calculated one.
24. Click on  icon on the graphics tool bar to view the difference between the measured and calculated spectra.

Using Mark

Producing a suitable line list for starting a deconvolution is not always possible. Use the **Set Mark** button following a previous spectral display (`ds` program) to provide a starting point. Information from marks made with a single cursor is written to the file `mark1d.out` and contains only a frequency and intensity. The starting linewidth is taken

from the parameter slw. Information from marks made with two cursors, placed symmetrically about the center of each line at the half-height point, is written to the file mark1d.out and contains two frequencies, an intensity and an integral. The starting frequency is taken as the average of the two cursor positions; the starting linewidth is taken as their difference.

Deconvolution Related Commands, Parameter, Macros, and Files

- "Commands and Parameters," page 320
- "Deconvolution Commands, Parameters, and Buttons," page 321
- "Deconvolution Display and Plotting Commands and Macros," page 321
- "Deconvolution Files," page 322

Commands and Parameters

Table 30 lists the associated commands and parameters with a short description.

Table 30. Deconvolution Commands and Parameters

Commands	*Description*
dsp<(file)>	Display calculated spectrum
fitspec<(<'usell'><,><'setfreq'>)>	Perform spectrum deconvolution (VNMR)
fitspec	Perform spectrum deconvolution (UNIX)
mark*	Determine intensity of spectrum at a point
plfit	Plot deconvolution analysis
setgauss(fraction), setgauss(fraction*)	Set a Gaussian fraction for line shape
showfit	Display numerical results of deconvolution
usemark	Use mark as deconvolution starting point

```
* mark<(f1_position)><:intensity>,
  mark<(left_edge,region_width)><:intensity,integral>
  mark<(f1_position,f2_position)><:intensity>
  mark<(f1_start,f1_end,f2_start,f2_end)><:intensity,integral,c1,
c2>
  mark<('trace',<options>)><:intensity,integral,c1,c2>,
  mark('reset')
```

Parameter	*Description*
slw {0.01 to 1e6}	Starting default linewidth for deconvolution calculations.

Deconvolution Commands, Parameters, and Buttons

Command or Parameter	*Button*	*Description*
`fitspec`	**Fit it**	Performs spectrum deconvolution by fitting experimental data to Lorentzian and/or Gaussian line shapes. `fitspec` uses data in a file `fitspec.inpar` as a starting point for the calculation. `fitspec` writes a text representation of the spectral data to the file `fitspec.indata`. The results of the fit are contained in a file after the calculation is finished. `fitspec.outpar` format is identical to `fitspec.inpar`. All lines are set to have a linewidth of `slw`, and a fixed Gaussian fraction of 0. (Refer to the *VNMR Command and Parameter Reference* for information about keyword options available with `fitspec`.)
`setgauss`		Modifies the output of the last deconvolution (`fitspec.outpar`) and makes it the input for a subsequent analysis (`fitspec.inpar`), after first modifying the Gaussian fraction:
`setgauss(fraction)`		Use the format `setgauss(fraction)` where `fraction` is the Gaussian fraction of the line shape, a number naturally limited from 0 to 1, for example, `setgauss(0.4)` to allow this fraction to vary.
`setgauss(fraction*)`		Use the format `setgauss(fraction*)`. Suffix the `fraction` value (defined the same as above) with an asterisk and enclose the value in single quotes, for example, `setgauss('1.0*')` to fix the fraction.

Deconvolution Display and Plotting Commands and Macros

Macro	*Button*	*Description*
`showfit`	**Show Results**	Displays deconvolution results and converts the data to a format suitable for printing.
`dsp('fitspec.outpar')`	**Show Fit Spectrum**	Displays the theoretical spectrum described by the parameters produced by a deconvolution calculation.
`plfit`	**Plot Fit Spectrum**	Produces a complete output plot of a deconvolution analysis, plotting the observed spectrum, the full calculated spectrum, each individual component, as well as the numerical results of the analysis.

Deconvolution Files

The deconvolution program writes these text files into the user's current experiment directory:

File name	*Description*
`fitspec.inpar`	Contains the starting parameters (frequency, intensity, linewidth, and Gaussian fraction) for a subsequent fitting operation. Optionally, this file contains the Gaussian fraction of the line shape. Any number followed by an asterisk (*) is held fixed during the calculation; all other parameters are varied to obtain the best fit. Edit this file before deconvolution to set different fixed Gaussian fractions for each line.
`fitspec.indata`	Contains the point-by-point intensity of the spectrum in the region of interest displayed when the fitting is begun (the part of the spectrum between `sp` and `sp+wp`).
`fitspec.outpar`	Contains the final parameters (frequency, intensity, linewidth, and Gaussian fraction) after a fit has been done.
`mark1d.out`	Contains the result of a `mark` operation during a spectral display. By using the **Use Mark** button, this file may be used as an alternative to the last line list in setting up initial guesses for a fitting operation.

14.3 Reference Deconvolution Procedures

- "Fiddle Program Options," page 322
- "Reference Deconvolution of 1D Spectra," page 323
- "Reference Deconvolution of 2D Spectra," page 325
- "References," page 325

All reference deconvolution is done from the command line. The following is a description of the `fiddle` program and the procedures for reference deconvolution of 1D and 2D data sets. Table 31 list commands for 1D and 2D variations of the `fiddle` program.

Table 31. Fiddle Command and Variants

Commands	*Description*
`fiddle*`	Perform reference deconvolution
`fiddled*`	Perform reference deconvolution subtracting alternate FIDs
`fiddleu*`	Perform reference deconvolution subtracting successive FIDs from first
`fiddle2d*`	Perform 2D reference deconvolution
`fiddle2D*`	Perform 2D reference deconvolution
`fiddle2dd*`	Perform 2D reference deconvolution subtracting alternate FIDs
`fiddle2Dd*`	Perform 2D reference deconvolution subtracting alternate FIDs

`* (option<,file><,option<,file>><,start><,finish><,increment>)`

Fiddle Program Options

The `fiddle` program and its variants, see Table 31, performs reference deconvolution, using a reference signal with known characteristics to correct instrumental errors in experimental 1D or 2D spectra. The main command to start the program or any of its variants can take multiple string and numeric arguments:

Syntax:
`fiddle(option<,file><,option<,file>><,start><,finish><,increment>)`

Arguments:

`option` can be the following keywords:

`'alternate'`	Alternate reference phase + / – (phase sensitive gradient 2D data).
`'autophase'`	Automatically adjust phase.
`'displaycf'`	Stop at the display of the correction function.
`'fittedbaseline'`	Use cubic spline baseline correction defined by integral regions.
`'invert'`	Invert the corrected difference spectrum/spectra.
`'noaph'`	Do not automatically adjust zero order phase of the reference region.
`'nodc'`	Do not use dc correction of the reference region.
`'nohilbert'`	Do not use Hilbert transform algorithm; use the extrapolated dispersion mode reference signal unless `'noextrap'` is also used as an option.
`'normalise'`	Keep the corrected spectrum integrals equal to the first spectrum.
`'readcf'`	Read the correction function from `file`; the argument `file` must immediately follow `'readcf'`.
`'satellites'`	Use the satellites defined in `file` in the ideal reference region; `file` should be in `/vnmr/satellites`.
`'stop1'`	Stop at the display of the experimental reference FID.
`'stop2'`	Stop at the display of the correction function.
`'stop3'`	Stop at the display of the corrected FID.
`'stop4'`	Stop at the display of the first corrected FID.
`'verbose'`	Show information about processing in the main window.
`'writecf'`	Write the correction function to `file`; the argument `file` must immediately follow `'writecf'`.
`'writefid'`	Write out the corrected FID to `file`; if `file` does not begin with `/` it is assumed to be in the current working directory.

`file` — name of the file used with the `'satellites'` and `'writefid'` options.

`start` and `finish` — indices of the first and last array elements to be processed.

`increment` — specifies the steps in which the index is to increment. The default is to process all the transformed spectra in an array.

Reference Deconvolution of 1D Spectra

Only spectra that contain a well-resolved reference signal dominated by a single component (i.e. not a simple multiplet) are suitable for reference deconvolution.

1. Fourier transform the raw FID with **`ft`**, preferably having zero filled (i.e. set `fn` >= 2*`np`). (If there are sinc wiggles, use `wft` with `gf` = `at`*0.6.)
2. Set the reference line to the chosen signal using the **`rl`** command, and then use two cursors on either side of the line to define a region of spectrum that includes all of the reference signal plus a little clear baseline but no other signals. This reference region will be used to define the instrumental line shape.

3. Decide what line shape to convert the instrumental line shape to, and set the weighting parameters accordingly. Create a 1-Hz wide Lorentzian by setting **lb** to 1 and all other weighting parameters to 'n'.

   Remember the signal-to-noise ratio penalty for resolution enhancement: if the experimental line is 2 Hz wide lb=0, an infinitely sharp line with infinitely poor signal-to-noise is produced. For most purposes, a sensible strategy is to set lb to *minus* the expected *natural* linewidth, and choose gf to give reasonable S/N; this strategy should convert the instrumental line shape to Gaussian. Where the signals of interest are broader than those of the reference, resolution enhancement can easily be obtained by making lb more negative.

4. Enter the **fiddle** command to carry out the reference deconvolution and display the corrected spectrum. The integral should remain unchanged, so any resolution enhancement will result in an increase in the amplitude of both signal and noise.

5. To save the corrected data, use the option 'writefid' when doing the reference deconvolution. For example, to store the file correctedfid.fid in the current working directory, enter fiddle('writefid','correctedfid').

   The options 'writecf'<,file> and 'readcf'<,file> respectively write and read the correction function. Performing reference deconvolution on one FID using fiddle with the 'writecf' option and then use fiddle with 'readcf' to process another FID applies the first correction function to the second FID. Reference deconvolution can be useful for heteronuclear lineshape correction (provided that the spectral widths for the two nuclei are in the ratio of the respective magnetogyric ratios) or for correcting spectra in which a reference signal has been suppressed (e.g., an INADEQUATE spectrum can be corrected for lineshape errors by using a correction function derived from the normal carbon spectrum).

Correct a series of spectra in an arrayed or 2D experiment:

Use numeric arguments:
fiddle(1) corrects spectrum 1, fiddle(2,3) spectra 2 and 3, etc.

Common Satellites Associated Reference Signals:

^{13}C satellites
^{29}Si satellites
quartet satellites (normally unresolved) from three-bond coupling to ^{13}C.

^{13}C satellites are typically small enough to be ignored in samples that are not ^{13}C enriched. Referencing requiring high accuracy in which there are strong (e.g. ^{29}Si) satellites is accomplished by including the satellites in the specified form of the ideal reference signal by using the 'satellites' option.

The /vnmr/satellites directory contains the file TMS with details of the TMS satellite signals. The command fiddle('satellites','TMS') allows for the satellite signals when deconvoluting using TMS as a reference.

The format for satellite files is that each line in the file consists of three real numbers in the following order:

- Separation of the satellite line from the parent signal, in Hz (0.5 JXH in the absence of homonuclear coupling).
- Intensity relative to the parent signal (natural abundance divided by the number of satellite lines [usually 2]).
- Isotope shift to high field, in ppm.

For example, the line

```
3.3     0.023     0.001
```

corresponds to a pair of satellite signals from a spin-1/2 isotope with an abundance of 4.6%, a coupling to the observed nucleus of 6.6 Hz, and an isotope shift to high field of 0.001 ppm.

Multiple lines in the satellite file account for multiple satellite signals on the parent peak.

Corrected-difference Spectroscopy:

Use the command `fiddled` to produce the corrected difference between successive spectra, which divides `arraydim` in half. The difference spectrum is written into the second element of the pair. Because the main aim of reference deconvolution here is to optimize the purity of the difference spectrum, the target line shape would normally be chosen to give the best possible S/N; this method corresponds to choosing a target line shape approximately twice the width of the raw experimental signals of interest. The command `fiddleu` produces corrected differences between successive FIDs and the first FID.

Reference Deconvolution of 2D Spectra

The commands `fiddle2d`, `fiddle2D`, `fiddle2dd`, and `fiddle2Dd` function in just the same way as the parent `fiddle` program. Because the principal objective in 2D reference deconvolution is usually the reduction of t1-noise, ideal line shape parameters are normally chosen for optimum S/N ratio rather than resolution enhancement.

1. Choose **`fn`** (preferably with `fn>=2*np`) and **`fn1`**.
2. Enter **`ft`** to transform the raw data (as mentioned earlier, if there is significant signal left at the end of `at`, it might be necessary to use `wft` with `gf` set).
3. Display the first increment with **`ds(1)`**, adjust the phase of the reference signal, and use **`rl`** to select the reference signal.

   In earlier versions of `fiddle`, it was necessary to create a parameter, `phinc`, to anticipate the changes in the reference signal phase with increasing evolution time. The current algorithm automatically adjusts the phase (unless the `'noaph'` option is selected). Deconvolution will set the reference signal phase as a function of `t1` to place the reference signal at frequency `rfp1` in `f1`. Therefore, remember to set `rfl1` and `rfp1` before using `fiddle2D` or the `f1` frequencies might unexpectedly change.
4. Define the reference region with the two cursors, and then enter the command **`fiddle2D('writefid',<file>)`** (or `fiddle2Dd` if a 2D difference spectrum is required, as with corrected HMBC). The `'writefid'` option is essential, because `fiddle2D` alone does not store the corrected time-domain data. If phase-sensitive gradient-enhanced 2D data is to be processed, alternate FIDs will have opposite phase modulations (i.e., the experimental array will alternate N-type and P-type pathways); in such a case, use the `'alternate'` option.

The corrected 2D FID data can be read into an experiment and processed as normal after deconvolution is complete. The value of `arraydim` no longer matches the arrays set if `fiddle2Dd` has been used and it might be necessary to set the arguments to `wft2d` explicitly rather than using `wft2da`.

References

Further information on reference deconvolution can be found in the following literature:

Taquin, J. *Rev. Physique App*. **1979**, *14***,** 669.

Morris, G. A. *J. Magn. Reson.* **1988**, *80***,** 547.

Morris, G. A.; Cowburn, D. *MRC* **1989**, *27***,** 1085.

Morris, G.A., Barjat, H., Horne T.J., *Prog. NMR Spectrosc*.**1997**, *31*, 197.

Gibbs, A; Morris, G. A. *J. Magn. Reson.* **1991**, *91***,** 77.

Gibbs, A.; Morris, G. A.; Swanson, A.; Cowburn, D. *J. Magn. Reson.* **1983,** *101*, 351–356.

Rutledge, D. N. Ed. *Signal Treatment and Signal Analysis in NMR*, Chapter 16. Elsevier Science, 1996.

14.4 Addition and Subtraction of Data

- "Introduction to Adding and Subtracting Data," page 326
- "Add/Subtract Tools," page 326
- "Interactive Add/Subtract," page 327
- "Non interactive Add/Subtract," page 329
- "Add / Subtract Related Commands and Parameters," page 331

Introduction to Adding and Subtracting Data

Individual 1D spectra, FIDS, individual 1D traces from nD data sets, or spin simulated spectra can be added and subtracted. The process uses one experiment to display the results and experiment 5 as the add/subtract buffer file. Any data in experiment 5 (`exp5`) is overwritten.

Add/Subtract Tools

- "Menu for Add and Subtract," page 326
- "Interactive Add/Subtract Toolbar," page 326

Menu for Add and Subtract

Access the Add / Subtract experiments from the Main Menu as follows:

1. Click on **Process** on the Main Menu.
2. Select **Add and Subtract 1D Data**.

   The following sub-menu items are presented:

   Clear Buffer and Add Current Spectrum

   Clears buffer (experiment 5) or creates experiment 5 and places current spectrum in experiment 5

   Add Second Spectrum into Buffer

   Adds current spectrum (algebraically) to data in experiment 5

Interactive Add/Subtract Toolbar

The Interactive Add/Subtract toolbar has the following buttons (the labels on some buttons change depending on the current mode):

Each button, name (tool tip), and function is listed in Table 32.

Table 32. Add/Subtract Toolbar Buttons

Button	*Name*	*Description*
	Box	Box is shown when the display is in the cursor mode. Click to change to the box mode with two cursors.
	Cursor	Cursor is shown when the display is in the box mode. Click to change to the cursor mode.
	Select	Selects the current, addsub, or result mode. Text in the field next to `active` matches the color of the spectrum. Arrow colors: Green — current mode (spectrum) is selected Yellow — addsub mode (spectrum) is selected Blue — result mode (spectrum) is selected.
	Expand	The third button is labeled Expand or Full, depending on the selected mode; box or cursor. When Expand appears the box mode is active, and clicking on this button expands the area between the cursors.
	Full	When Full appears, the cursor mode is active, and clicking on this button displays the full area.
	sp wp	Adjusts the start and width of the active spectrum.
	sub	The fifth button is labeled sub, min, or add. When sub appears, clicking on the button makes the result spectrum to be the difference between the current and the add/sub spectra.
	min	When min appears, clicking on the button makes the result spectrum to be a minimum intensity of either the current or the add/sub spectra.
	add	When add appears, clicking the button makes the result spectrum to be a sum of the current and the add/sub spectra.
	save	Saves the result spectrum in the add/sub spectrum in experiment 5 and returns to the last menu.
	return	Returns to the last menu without saving the result.

Interactive Add/Subtract

- “Adding and Subtracting Spectra,” page 327
- “Manipulating the Spectra,” page 328

Interactive add/subtract is a multi-step process using the menu system to call the `addi` command and uses `exp5` as an add/subtract buffer file.Two spectra can be Interactively added or subtracted using the menu and add and subtract tools on the add/subtract tool bar, see Table 32. Both horizontal displacement and vertical scale of the two spectra to be added or subtracted are under interactive control. Spectra that can be phased can be phased independently. The result can be manipulated using any of the standard software (e.g., the command `pl`), including further interactive add/subtract with another data set.

Adding and Subtracting Spectra

1. Select any available experiment or create a new experiment. Do not use or create experiment 5.
2. Click on **File** on the main menu.
3. Select **Open**.

The text window displays a list of directories (entries with a backslash as the last character in the name) and files (if any). The menu (near the top of the screen) displays the pathname of the current directory.

4. Select the top directory (/) from the **Look In** menu of the **File Open** dialog.
5. Select **`/vnmr`** from the file display.

   The text window displays the list of subdirectories.
6. Select **`fidlib`** from the list.
7. Select an arrayed 1D data set such as **dept.fid**.
8. Click on the **Transform** button on the action bar.
9. Click on **Process** on the Main Menu.
10. Select **Add and Subtract 1D Data**.
11. Select **Clear Buffer and Add Current Spectrum** from the sub-menu.

    Clears buffer (experiment 5) or creates experiment 5 and places current spectrum (spectrum 1) in experiment 5.
12. Select the spectrum to add or subtract from the first spectrum by doing either of the following:
    - Click on either the  or  until the desired spectrum is displayed.
    - Enter **`ds(#)`** where # is the number of the spectrum in the array.
13. Select **Add and Subtract 1D Data**.
14. Select **Add Second Spectrum into Buffer** from the sub-menu.

    The default operation is to add the spectra. The current spectrum (spectrum 2) is added algebraically to data in experiment 5 (spectrum 1) and displays the three spectra as shown in Figure 100.

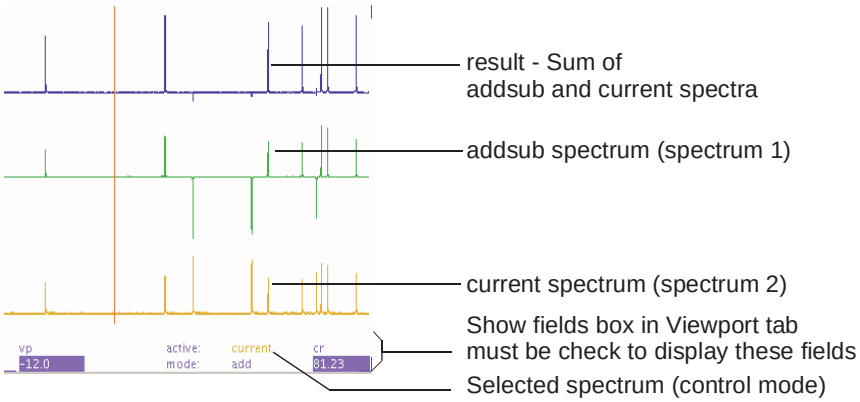


Figure 100. Add Spectra and Display Result

15. Optional: Click on  icon on the add/subtract toolbar to subtract the current spectrum (spectrum 2) from the first spectrum.

Manipulating the Spectra

1. Use the  button to step sequentially through the current, addsub, and result, spectra (control modes).

The mode is displayed next to `active`: at the bottom of the viewport. Show fields box in the Viewport tab must be checked to show the fields.

2. Manipulate the spectra using the mouse:

   Left mouse button positions the cursor or pair of cursors.

   The left mouse button adjusts the start of the display if  is selected.

   Center mouse button changes the vertical scale of the spectrum so that it goes through the current mouse position.

   The horizontal position of the spectrum is adjusted if the mouse is positioned at the left edge of the spectrum.

   Right mouse button positions the second cursor relative to the first cursor.

   The right mouse button adjusts the width of the display if  is selected.

3. Adjust any of the parameters related to the selected spectrum (except `wp`, it always controls all the spectra). The spectrum can be phased, scaled, or shifted relative to the other spectrum.

4. Click on **Process** on the Main menu bar.

5. Select **Analyze**.

6. Select **Deconvolution**.

   The Deconvolution window opens, seeFigure 99.

7. Click on the **Add / Subtract** button to display the resulting spectra and return to the interactive add and subtract mode.

8. Optional: Save the addsub spectrum after all the manipulation of the data has been completed if further operations, plotting, adding another spectrum, etc. are required.

   a. Click on  to save the addsum spectrum into experiment 5.

      Spectrum 1, which was in the add/subtract buffer of experiment 5 is overwritten by the sum or difference spectrum. The interactive Add / Subtract routine exits.

   b. Save the result in experiment 5 to a file or move it to another available experiment.

Non interactive Add/Subtract

- “Adding and Subtracting FIDs,” page 329
- “Adding and Subtracting Spectra,” page 330

The non interactive add / subtract procedure is run from the command line. The buffer (`exp5`) is first cleared using `clradd`. Different FIDs or spectra are then added to or subtracted from the accumulating total by the commands `add`, `sub`, `spadd`, and `spsub`.

Adding and Subtracting FIDs

The `add` and `sub` commands add and subtract the last displayed or selected FID to and from the contents of the add/subtract experiment, respectively. An optional argument allows the FID to first be multiplied by a multiplier (the default is 1.0). The parameters `lsfid` and `phfid` can be used to shift or phase rotate the selected FID before it is combined with the data in the add/subtract experiment.

A multi-FID add/subtract experiment with FIDs 1 and 2 is created with the `add` or `sub` command using the keyword `'new'` as follows:

1. Create the add/subtract experiment with a single FID by entering the following commands from some experiment:

   `clradd select(1) add`

2. Make the add/subtract experiment contain an array of two FIDs corresponding to the original FIDs 1 and 2 by entering:

   `select(2) add('new')`

   Entering the following makes the add/subtract experiment contain a single FID that is the sum of the original FIDs 1 and 2 instead of an array:

   `select(2) add`

The `arraydim` parameter may need to be updated after constructing a multi-FID add/subtract experiment.

1. Type **`jexp5`** to join `exp5`.
2. Use `setvalue('arraydim',numFIDs,'processed')` to place `numFIDs` of FIDs into `exp5`.

   The number of FIDs in the experiment is `numFIDs`.

   Example:

   `setvalue('arraydim',12,'processed')` places 12 FIDs into exp5.

Individual FIDs in a multi-FID add/subtract experiment can be added to and subtracted from one another. The `add` and `sub` commands without the keyword `'trace'` adds or subtracts from the first FID in the add/subtract experiment. Adding the keyword `'trace'` followed by the required index number selects specific FID to be the target of the add/subtract.

Example:

`select(4) add('trace',6)` takes the fourth FID from the current experiment and adds it to the sixth FID in the add/subtract experiment.

The FID must already exist in the add/subtract experiment by using an appropriate number of `add('new')` or `sub('new')` commands when using the keyword `'trace'`.

Adding and Subtracting Spectra

Noninteractive spectral addition and subtraction uses the `spadd` and `spsub` commands. The last displayed or selected spectrum is added to (`spadd`) or subtracted from (`spsub`) the current contents of the add/subtract experiment.

Each spectrum can be optionally multiplied and shifted using the `multiplier` and `shift` arguments, respectively. For example, entering `spadd(0.75,10)` multiplies the spectrum by 0.75 and shifts the spectrum by 10 to the left. A positive value of `shift` shifts the spectrum being added or subtracted to higher frequency, or to the left. A negative value of `shift` shifts the spectrum being added or subtracted to lower frequency, or to the right. To shift a spectrum without multiplying it, use a multiplier of 1.0.

A multi-element add/subtract experiment with spectra 1 and 2 can is created with the `spadd` or `spsub` command using the keyword 'new' as follows:

1. Create the add/subtract experiment with a single spectrum by entering the following commands from some experiment:

   `clradd select(1) spadd`

2. Make the add/subtract experiment contain an array of two spectra corresponding to the original spectra 1 and 2 by entering:

   `select(2) spadd('new')`

   Entering the following makes the add/subtract experiment contain a single spectrum that is the sum of the original spectra 1 and 2 instead of an array:

   `select(2) spadd`

Individual spectra in a multi-element add/subtract experiment can subsequently be added to and subtracted from. The `spadd` and `spsub` command without the keyword 'trace' adds to or subtracts from the first spectrum in the add/subtract experiment. Adding the keyword `'trace'` followed by the index number of the spectrum selects that spectrum to be the target of the add/subtract. Entering `select(4) spadd('trace',6)` takes the fourth spectrum from the current experiment and adds it to the sixth spectrum in the add/subtract experiment.

The indexed spectrum must already exist in the add/subtract experiment by using an appropriate number of `spadd('new')` or `spsub('new')` commands with the `'trace'` argument. Join experiment 5 (`jexp5`) and use the normal spectral display (e.g., `ds`) and plotting commands to examine the results.

Add / Subtract Related Commands and Parameters

The add/subtract experiment related commands are listed in Table 33 and parameters are listed in Table 34.

Table 33. Add/Subtract Related Commands

Commands	*Description*
`add*`	Add current FID to add/subtract experiment
`addi`	Start interactive add/subtract mode
`clradd`	Clear add/subtract experiment
`jexp1, ..., jexp9999`	Join existing experiment
`select*`	Select a spectrum or 2D plane without displaying it
`setvalue*`	Set value of a parameter in a tree
`spadd*`	Add current spectrum to add/subtract experiment
`spmin`	Take minimum of two spectra in add/subtract experiment
`spsub*`	Subtract current spectrum from add/subtract experiment
`sub*`	Subtract current FID from add/subtract experiment

```
*
add<(multiplier<,'new'>)>, add('new'), add('trace',index)
select<('next'|'prev'|selection)><:index>,
select<(<'f1f3'|'f2f3'|'f1f2'><,'proj'>
      <,'next'|'prev'|plane>)><:i>
setvalue(parameter,value<,index><,tree>)
spadd<(multiplier<,shift>)>, spadd('new'), spadd('trace',index)
spsub<(multiplier<,shift>)>, spsub('new'),spsub('trace',index)
sub<(multiplier<,'new'>)>, sub('new'), sub('trace',index)
```

Table 34. Add/Subtract Related Parameters

Parameters	*Description*
`arraydim {number}`	Dimension of experiment

Table 34. Add/Subtract Related Parameters

`lsfid {'n',-fn/2 to ni or fn/2}`	Number of complex points to left-shift `np` FID
`phfid {'n',-360 to 360, in degrees}`	Zero-order phasing constant for `np` FID

14.5 Regression Analysis

The process of establishing correlations between two or more variables is called *regression analysis* or *correlation analysis*. The established regression or correlation can then be used to predict one variable in terms of the others. Often, paired data indicate that a regression may have a certain functional form, but we do not want to make assumptions about any underlying probability distributions of the data.

This type of problem is often handled by the least squares curve-fitting method. Specific examples of this are used for the analysis of T_1 and T_2 NMR data and for the analysis of kinetics data. Tools for fitting arbitrary data to selected functional forms are also available.

The regression process takes a set of data pairs from the file `regression.inp` and attempts to fit a curve to the set. The implemented curves are first, second, and third order polynomials and an exponential in the form:

```
y = a1 * exp(-x/tau) + a3
```

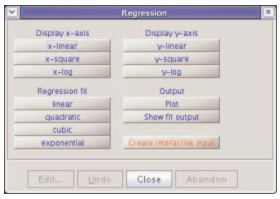
There are further possibilities as the original data may be displayed against a choice of linear, squared, or logarithmic scales.

Regression Window and Controls

Access the regression window as follows:

1. Click on **Process** on the Main Menu.
2. Select **Analyze**.
3. Select **Regression**.

The regression window is displayed. The function of the buttons are as follows:



Button and Button Group	*Function*
Display x-axis buttons	
x-linear	Display output with a linear x-axis
x-square	Display output with a quadratic x-axis
x-log	Display output with a logarithmic x-axis
Display y-axis buttons	
y-linear	Display output with a linear y-axis
y-square	Display output with a quadratic y-axis
y-log	Display output with a logarithmic y-axis
Regression fit buttons	
linear	Perform a linear regression analysis.
quadratic	Perform a quadratic regression analysis
cubic	Perform a cubic regression analysis
exponential	Perform an exponential regression analysis

Button and Button Group	*Function*
Output buttons	
Plot	Plot the regression analysis
Show fit output	Display regression output
Create interactive input	The program displays a series of prompts requesting input

Regression, Step-by-Step Using the Regression Window

1. Click on **Create interactive input** button.

   The program displays a series of prompts requesting the axis label titles and the data pairs.

   a. Enter an X and Y pair separated by a space.

   b. Enter the next X and Y pair.

   c. Finish the data set by pressing the Enter key

   d. Respond to the prompt and press **y** to enter another data set or **n** to end the data entry.

   The file `regression.inp` is created in the correct format when all the data is input and the data points and axis are displayed on the screen.

2. Click on any one of the buttons **Display x-axis** or **Display y-axis** group.

   Each buttons scales the display and shows either the x or y axis as labeled on the button.

3. Click on one of the buttons in the **Regression fit** to select a fitting routing. These buttons include displaying the results using `expl`.

Fitting Routine	*analyze option*	*Button in Regression fit group*
linear	`'poly1'`	linear
quadratic	`'poly2'`	quadratic
cubic	`'poly3'`	cubic
exponential curve	`'exp'`	exponential

Figure 101 shows quadratic fittings for the data set in Table 35.

Table 35. Sample Data Table

`Data set 1`	
X value	*Y value*
`0.0`	`5.0`
`1.0`	`9.0`
`2.0`	`12.0`
`3.0`	`20.0`
`4.0`	`33.0`
`5.0`	`42.0`
`Data set 2`	

Table 35. Sample Data Table

X value	*Y value*
0.0	20.0
1.0	22.0
2.0	27.0
3.0	29.0
4.0	37.0
5.0	45.0

Data is written to the `regression.inp` and `analyze.out` files. Contents of these files are explained in "Contents of "regression.inp" File," page 338 and "Contents of "analyze.out" File," page 335.

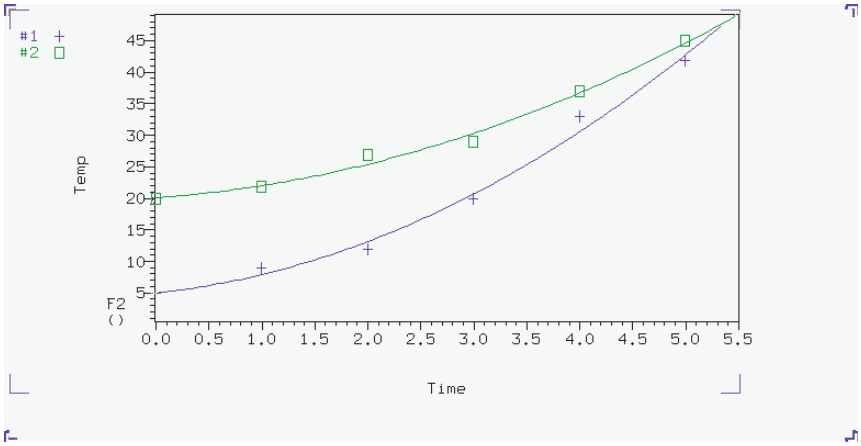


Figure 101. Display of Regression Fittings

4. Click on the **Plot** button to plot the analysis .

   The scale automatically to show all points (if possible).

5. Click on the **Show fit output** button to show the results of the analysis in the Text Output window.

Regression, Step-by-Step Using the Command Line.

1. Write and save the text file `regression.inp` that contains the data pairs to analyze. The next section describes the format of this file. Create it by one of the following methods:

   - Enter **`rinput`** on the command line.

     The program displays a series of prompts requesting the axis label titles and the data pairs. The file `regression.inp` is created in the correct format when all the data is input. The data can be corrected using a text editor after the program writes the file.

   - Use a text editor such as `vi` or `textedit`.
   - Create a MAGICAL II macro for this purpose.

2. Enter the command **`expl('regression')`** for single data sets or **`expl('regression', line#, line#,...)`** for multiple data sets.

The `expl` command uses the values in the `regression.inp` file to display a graph of the data points. It also creates the files `analyze.inp` (needed by `analyze` to run the analysis) and `expl.out` (display information for `expl`).

Optional: Use the `poly0` macro to calculate and display (as horizontal lines) the mean of the data in the file `regression.inp`.

3. Enter **`analyze('expfit','regression',option,'list')`** the command line.

   The fitting routine choices for `option` are `'poly1'`, `'poly2'`, `'poly3'`, or `'exp'`.

Fitting Routine	*analyze option*
linear	`'poly1'`
quadratic	`'poly2'`
cubic	`'poly3'`
exponential curve	`'exp'`

   The program `expfit` is called by this usage of the `analyze` command.

   `expfit` creates the files `analyze.out` (used by `expl` to display the results) and `analyze.list` (a table of results).

4. Enter **`expl`** to see the results as a graph.

   Figure 101 shows quadratic fittings for the data given in the example of the `regression.inp` file in the next section.

5. Enter **`pexpl page`** to plot one data set or enter **`pexpl(index#,index#,...)`** to plot multiple data sets.

   Both `expl` and `pexpl` set the scale automatically to show all points (if possible).

6. Optional.

   Enter the **`scalelimits`** macro to set limits for the scales using one of the following:

   - Enter **`scalelimits`** with no argument to start an interactive process that prompts for the four scale limits.
   - Enter **`scalelimits(x_start,x_finish, y_start,y_finish)`** with limits for the x-axis and y-axis as arguments.

     The limits are retained as long as an `expl` display is retained. Enter **`autoscale`** to return to automatic scaling by `expl`.

7. Enter **`cat(curexp+'/analyze.list')`** to show the results of the analysis in the Text Output panel.

Contents of “analyze.out” File

The data input file is `analyze.out`, except for regression when the input file is `regression.inp`. The file `expl.out` saves certain display and plot parameters.

Values can be 2048 points maximum from a data set, 2048 points maximum from all sets displayed/plotted, 8 data sets maximum displayed, and 128 data sets maximum are read.

The following is an example of `analyze.out`. Numbers identify lines in the example and are not part of the actual file:

```
Line
number
1       exp 7 regression
2       D1 C0 C1 C2
3           1  5   linear linear
4        Exponential Data Analysis
         time
         amp
5          NEXT  5
6       1  -248.962  22.8025  226.157
7               2        4
                3        9
                4       16
                5       25
                6       36
```

Curve types supported are listed in Table 36.

Table 36. Curve Type

Type	*Function*	*Functional Form*
0	T_1/T_2	$(a0 - a2)*exp(-t/a1) + a2$
1	Increasing kinetics	$a0*exp(-t/a1) + a2$
2	Decreasing kinetics	$-a0*exp(-t/a1) + a2 + a0$
3	Diffusion	$a0*exp(-D1*uu) + a2*exp(-a1*D1*uu)$ where $uu=C0+C1*t+C2*t^2$
4	None	No theoretical curve (use `'link'`)
5	Linear	$a0 + a1*t$
6	Quadratic	$a0 + a1*t + a2*t^2$
7	Exponential	$a0 * exp(-t/a1) + a2$
8	Contact time	$(a3 -(a3 - a0)*exp(-t/a1)) *exp(-t/a2) + a0$
9	Cubic	$a0 + a1*t + a2*t^2 + a3*t^3$

The following is a description of the numbered parts of this file:

Line number	*Description*
1	The keyword `exp` is followed by a number for a curve type from Table 36. The keyword `regression`, if present, indicates regression output
2	Floating point constants *D1*, *C0*, *C1*, and *C2*, if present, are used only with the diffusion function (curve type 3).
3	An integer for the number of data sets (curves), followed by an integer for the number of data point pairs in the set. For regression, the words are scale types for the *x* and *y* axes: `linear`, `square`, and `log`.

4	Title line. Use `No Title` when a title is not desired. Two additional text lines for the *x* and *y* axis titles are present in output from regression.
5	The keyword `NEXT` identifies the start of a data set, and the integers that follow give the number of data point pairs in the data set.
6	The first integer specifies the number (usually 1) of the data point symbol used for the data set. The next three integers are the coefficients *a0*, *a1*, and *a2* (see Table 36) and must all be present, even for functions that do not use all three (e.g., first-order polynomial). If a particular number is not appropriate, put any number there. *a3* must be also be present for cubic and contact time functions (curve types 7 and 8).
7	Data point pairs in the set.

Next is an example of `regression.inp` file for generalized curve fitting:

Line number	
1	`time`
2	`amp`
3	`0 0`
4	`NEXT`
5	`2.000000 4.000000`
	`3.000000 9.000000`
	`4.000000 16.000000`
	`5.000000 25.000000`
	`6.000000 36.000000`

Description of this example:

Line number	*Description*
1	Line with text for *x*-axis label displayed by `expl('regression')`.
2	Line with text for *y*-axis label (line must not be too long, usually less than 20 characters). The first non-blank character must not be a digit.
3	Line containing an integer for the number of data sets followed by another integer for the number of pairs per data set. Both values are `0` if the number of pairs is variable.
4	A line beginning with the keyword `NEXT` is inserted at the start of each data set when the number of pairs per peak is variable.
5	The data pairs, listed one pair to a line.

The final example uses the `'file'` argument to the `expl` command:

Line number	
1	`exp 4`
2	`1 5`
3	`time`
4	`1 0 0 0`
5	`2 4`
	`3 9`
	`4 16`

```
    5    25
    6    36
```

Description of this example:

Line number	*Description*
1	Keyword `exp` followed by curve type number.
2	Number of data sets, followed by number of data point pairs.
3	Title.
4	Data point symbol number, followed by three coefficients.
5	Data point pairs in the set.

Contents of “regression.inp” File

The data input text file `regression.inp` contains a listing of axis labels and data pairs.The data file can contain up to 128 data sets. Data sets are selected by `expl` indexes (up to 6, depending upon length of data sets) with a default to the beginning data sets. The analysis is limited to 1024 data points, with the first part of larger data sets selected.

The following is an example of a `regression.inp` file that shows the format used. Numbers identify lines in the example and are not part of the actual file:

Line number

```
1       time
2       temp
3         0   0
4        NEXT
5         0.000000    5.000000
          1.000000    9.000000
          2.000000    12.000000
          3.000000    20.000000
          4.000000    33.000000
          5.000000    42.000000
4       NEXT
5         0.000000    20.000000
          1.000000    22.000000
          2.000000    27.000000
          3.000000    29.000000
          4.000000    37.000000
          5.000000    45.000000
```

Description of this file:

Line number	*Description*
1	X-axis label for display by `expl('regression')`. The label is optional. If used, the first non-blank character in the label must not be a digit.
2	Y-axis label for display by `expl('regression')`. The label is optional. If used, it must be less than about 20 characters and the first non-blank character in the label must not be a digit.
3	If the number of pairs per data set is fixed, this line contains an integer for the number of data sets, followed by another integer for the number of data pairs per data set. If the number of pairs per data set is variable (as in this example), both integers are set equal to 0.
4	If the number of pairs per data set is variable, a line with the word `NEXT` is inserted at the start of each data set.
5	Data pairs, one to a line, are listed for each data set, in this order: first pair of first set second pair of first set third pair of first set . . . first pair of second set second pair of second set

Regression Commands

Table 37 lists the commands associated with regression analysis

Table 37. Regression Commands

Commands	*Button*	*Description*
`analyze*`	Any of the buttons in the **Regression fit** group.	Generalized curve fitting in regression mode
`autoscale`	Any of the buttons in the **Output** group.	Resume autoscaling after limits set by scalelimits
`expfit*`	Any of the buttons in the **Regression fit** group.	Make least-squares fit to exp. or poly. curve (Linux)
`expl<(<options,>line1,...>)>`	Any of the buttons in the **Display x-axis** or **Display y-axis** group	Display exponential or polynomial curves
`pexpl<(<options,>line1,...>)>`	**Plot**	Plot exponential or polynomial curves
`poly0`		Display mean of data in regression.inp file
`rinput`	**Create iterative input**	Input data for regression analysis
`scalelimits*`	Any of the buttons in the **Output** group.	Set limits for scales in regression

```
* analyze('expfit',xarray<,option,option,...>)
  expfit options <analyze >analyze.list
  scalelimits(x_start,x_end,y_start,y_end)
```

14.6 Cosy Correlation Analysis

Cosy Data Chemical Shift Analysis Window and Controls.

Button	*Function*
Create 2D Line List	Write a 2D line listing to the file ll2d.out and displays the results in the Text Output panel.
Find Correlations	Analyze the current 2D line listing and display the results on the screen.
Redisplay	Display an interactive 2D contour map.
Plot Correlations	Analyze the current 2D line listing and plot the results.
Plot Contours	Plot the 2D contours
Plot Page	Send plot to the printer

Analysis of COSY Data Step-by-Step

1. Process and display a COSY data set.
2. Click on **Process** from the Main Menu.
3. Select **Analyze**.
4. Select **Cosy Correlations…**

   Opens Cosy Correlations window if current viewport contains an appropriate data set.
5. Click on the **Create 2D Line List** button to create a line list for the COSY data set.
6. Click on the **Find Correlations** button display the correlations of the COSY data set on the screen.
7. Optional:

   Click on the **Redisplay** button to redisplay an normal interactive 2D contour map and make any changes or adjustments to the data as needed. Start over again at step 4.
8. Click on the **Plot Correlations** button to create plot of the line list for the COSY data set.
9. Click on the **Plot Contours** button to create a contour plot of the COSY data set.
10. Click on the **Plot Page** button to send the plot to the printer.

14.7 Chemical Shift Analysis

Chemical shifts are analyzed using the commands in Table 38. These commands write a list of chemical shifts to the file `pcss.outpar`.

Table 38. Chemical Shift Analysis Commands

Commands	*Description*
`do_pcss`	Calculate proton chemical shifts spectrum
`pcss`	Calculate and show proton chemical shifts spectrum

Chapter 15. Pulse Analysis

Sections in this chapter:

- 15.1, “Pandora’s Box,” on page 341
- 15.2, “Pulse Shape Analysis,” on page 354

15.1 Pandora’s Box

Pandora’s Box (Pbox) software creates shape pattern files for experiments involving shaped rf pulses, composite pulses, decoupling and mixing patterns, adiabatic rf sweep waveforms, and pulsed field gradient shapes. The goal of Pbox is to simplify generation and use of different waveforms in NMR experiments so that the user does not need to be an expert in selective excitation. Pbox makes the use of complex waveforms as simple as using ordinary rectangular pulses. Not only does Pbox provide all the necessary parameters (pulse width, power, `dmf`, `dres`, etc.) when the shape files are created, but this information can be extracted at any time from Pbox shape files by macros or directly within pulse sequences. More than 160 different shapes are available from the Pbox library.

- "Create a New Waveform," page 341
- "Calibrating the RF Field," page 343
- "Creating Waveforms by Macros," page 344
- "Creating Waveforms in an Operating System Terminal Window," page 345
- "Pbox File System," page 345
- "Pbox Parameters," page 349
- "Wave String Variables," page 351
- "Pbox Macro Reference," page 352
- "Pbox Commands Using a Terminal," page 353

Create a New Waveform

1. Open the Pbox window to access the tools for creating waveforms.
   a. Click **Edit** on the menu bar.
   b. Select **New Pulse Shapes…**
      The Pbox window opens.
2. Click the **Make Waveform** tab.
3. Click the **New Waveform** button and the tools for creating a wave form are displayed in the Pbox window, see Figure 102.
4. Select the desired shape from the **Shape type** menu.

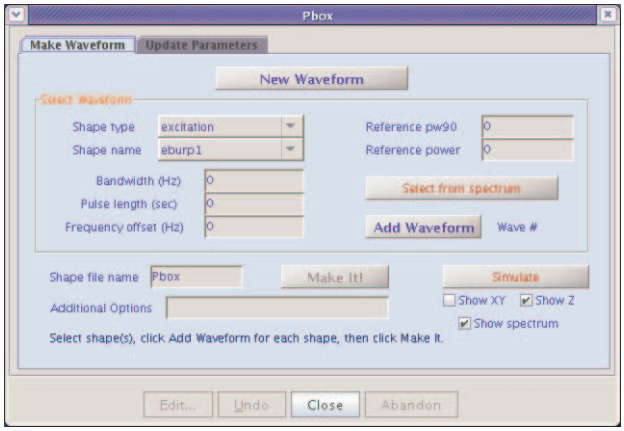


Figure 102. Pbox Make Waveform

5. Select the desired shape name from the Shape name menu. The Shape name choices depend on the selected Shape type.
6. Set the **Reference pw90** and **Reference power**.
7. Set the waveform selection region as follows:
   a. Display a spectrum.
   b. Select a selective excitation band using two cursors.
   c. Click the **Select from spectrum** button. This sets the **Bandwidth**, **Pulse length**, and **Frequency offset** from the cursors.
   d. Optional: explicitly enter Bandwidth, Pulse length, and Frequency offset.
8. Click **Add Waveform**. The Wave # field updates and the Make It! button becomes active.
9. Add additional waveform shapes into a waveform by repeating step 5 through step 8. The Wave # field updates for each selective shape added to the waveform.
10. Enter a name for the shape in the Shape file name file. The field contains a default file name of Pbox.
11. Enter any **Additional Options** (refer to Table 39 for Pbox commands and parameters).
12. Click **Make It!** to generate and save the shape file.
13. Request simulations, see Figure 103, as follows:

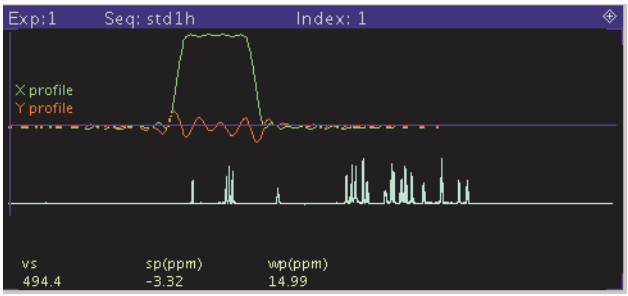


Figure 103. Shaped Pulse Simulations Reference Spectrum

a. Select a **Show XY** or **Show Z** radio button.

b. Select **Show spectrum** to show the spectrum.

c. Click **Simulate**. The simulation displays in the graphics window.

Update Parameter Values

Update the parameter values used by the waveform into experimental parameters as follows:

1. Click the **Update Parameters** tab, see Figure 104.

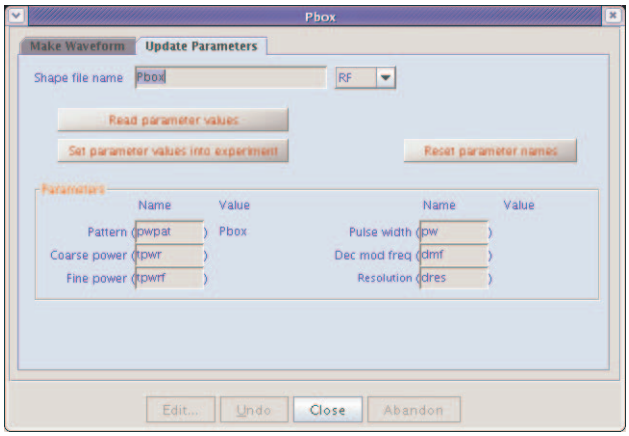


Figure 104. Pbox Update Parameters

2. Enter a shape file name in the entry box.
3. Click **Read parameter values** to read parameter values from the Pbox shape file.
4. Enter names for the parameters or use the suggested defaults to use for the waveform.
5. Click **Reset parameter names** to reset the parameter names to the default values, if desired.
6. Click **Set parameter values into experiment** to set the parameter values into the experimental parameters. Parameters that do not exist are not set in the experiment. Parameter limits are not checked (especially for pulse width) — check them.

Calibrating the RF Field

Provide the rf field calibration data `ref_pwr` and `ref_pw90` in the input to obtain the pulse calibration numbers in the Pbox output before waveform creation. Make sure the rf field has been calibrated for the length of the 90° pulse at a given power level.

The rf field can be calculated at any power using spectrometers with linear amplifiers such as those on Varian NMR spectrometer systems. Maximum accuracy for the calibration is obtained when the calibration is made as close as possible to the field used in the experiment. Provide approximate calibration data and use `cal` as an output file name for Pbox to permit an estimate of the rf field. No waveform is created and only the calibration results appear in the output.

Creating Waveforms by Macros

Pbox macros provide useful tools for customizing NMR experiments. The simplest way to create a shape is using the pxshape macro. For example, a single band excitation pulse using the E-BURP-1 shape, covering 400 Hz, and shifted off-resonance by –880 Hz from the carrier frequency (middle of the spectrum) can be created and stored in the `alpha.RF` file as follows:

```
pxshape('eburp1 400.0 -880','alpha.RF')
```

The following steps are necessary to create multiply-selective pulses. Use the cursors if the spectrum of interest is on the screen. The parameters `ref_pwr90` and `refpwr` must be present and set correctly in the current parameter set.

1. Enter **`opx('hadamard.RF')`** to open the `Pbox.inp` file and write the file header.
2. Select an excitation band using cursors.
3. Enter **`selex('rsnob')`**.
4. Select the second excitation band using cursors.
5. Enter **`selex('rsnob')`**.
6. Repeat steps 2 to 5 as many times as needed.
7. Enter **`cpx`** to close the `Pbox.inp` file.
8. Enter **`dshape`** to display the last created shape.

The following slightly different set of macros are used if an experimental spectrum is not available. The parameters `ref_pwr90` and `refpwr` must be present and set correctly in the current parameter set.

1. Enter **`opx('myshape')`** to open Pbox and provide a file name.
2. Enter **`setwave('sech 400.0 -880.0')`** to select first band at –880 Hz.
3. Enter **`setwave('sech 400.0 1240.0')`** to select second band at 1240 Hz.
4. Enter **`cpx(ref_pw90, ref_pwr)`** to close Pbox.
5. Enter **`dshape`** to display the shape file.

The `pbox_pw` and `pbox_pwr` macros are used to load the parameters of the last created shape file into the current experiment:

```
pbox_pw:selpw
pbox_pwr:selpwr
```

Alternatively, the calibration data is directly retrieved from the shape file provided as an argument to the `pbox_dmf` and `pbox_dres` macros:

```
pbox_dmf('ccdec.DEC'):dmf
pbox_dres('ccdec.DEC'):dres
```

where `ccdec.DEC` is the name of the decoupling shape file.

The excitation profile of shaped pulses is conveniently verified using the Pbox Bloch simulator. The parameters `ref_pwr90` and `refpwr` must be present and set correctly in the current parameter set.

1. Enter **`opx`** to open Pbox.
2. Enter **`setwave('iburp2 400.0 -880')`** to select first band at –880 Hz.
3. Enter **`setwave('iburp2 400.0 1240.0')`** to select second band at 1240 Hz.

4. Enter **pbox_rst** to reset par-s and write comments.
5. Enter **pboxpar('name','test.DEC')** to define the output file name.
6. Enter **pboxpar('bsim','y')** to activate the Bloch simulator.
7. Enter **cpx** to close Pbox.
8. Enter **dshape** to display the shape file.
9. Enter **dprofile('z')** to display inversion (Mz) profile.

Pbox reads the corresponding wave file in `wavelib` directory to determine the waveform being created is a 90° excitation pulse, 180° inversion pulse, and the type of wave form required (.RF, .DEC, or .GRD). Pbox can be forced to change the waveform type by providing the required extension to the output shape file name. Modify wave files by copying it into the local user `wavelib` and editing the text file as required. See "Pbox Macro Reference," page 352, for a more complete description of macros.

Creating Waveforms in an Operating System Terminal Window

Creating waveforms using an operating system terminal window can be more convenient in some cases:

```
> Pbox
```

The name of the output shape file is passed as an argument:

```
> Pbox filename
```

The input data are typically stored in the `Pbox.inp` file in your `vnmrsys/shapelib` directory and are modified using standard text editors. Alternatively, most of the necessary data can be provided as arguments to the `Pbox` command. For example,

```
> Pbox myfile -w "eburp1 480 -1200" -p 40 -l 104
```

generates an E-BURP-1 excitation pulse covering 480-Hz-wide band and shifted –1200 Hz off-resonance using for calibration 104 µs pw90 at 40 dB power level and stored in `myfile.RF`. Note that the name of the output shape file is always passed as the first argument.

Several other options are accepted by `Pbox`; for example, `-b` activates the Bloch simulator, `-c` calibrates the waveform without creating a shape file, and `-o` print out the available options. See "Pbox Commands Using a Terminal," page 353, for further information.

Pbox File System

All the information about the waveform to be created (e.g., calibration data, output file name, excitation band definition) is stored in the `Pbox.inp` text (ASCII) file in the user directory `vnmrsys/shapelib`. This file is generated whenever Pbox menus or macros are used or create it by using one of the standard text editors.

Any shape file can consist of one or several shapes that are combined into a single waveform. Each excitation band is defined by a wave definition string (a string of wave variables enclosed between delimiters {and}). The number of wave definition strings in a single `Pbox.inp` file is unlimited. In order to simplify the input file format, the wave variables are entered without names in a strongly predefined order:

```
sh bw(/pw) ofs st ph fla trev d1 d2 d0 wrap
```

The following list describes each of the variables.

sh	Shape name as stored in wavelib
bw(/pw)	Bandwidth in Hz, or pulsewidth in sec, or both
ofs	Offset from transmitter offset or carrier in Hz
st	Spin status (0 for Mz or 1 for Mxy)
ph	Phase or phase cycle
fla	Flip angle
trev	Time reversal flag
d1	Prepulse delay
d2	Postpulse delay
d0	Delay before the pulse
wrap	Wraparound parameter

The order of parameters has been chosen such that the importance of parameters is decreasing, and rarely used parameters can be omitted or defaulted by assigning a value of n (not used). The following examples are valid wave definition strings.

{qsneeze}	q-SNEEZE pulse applied on resonance; the pulse length will be internally defaulted to 5 ms
{G3 800}	G3 pulse covering bandwidth of 800 Hz and applied on-resonance
{sech 400/0.05 -1200}	50 ms long hyperbolic secant pulse covering 400Hz and shifted off-resonance by –1200 Hz
{WURST2 2k/5m 12k n t5}	5 ms long WURST-2 decoupling pulse covering 2 kHz and shifted off-resonance by 12 kHz uses t5 phase cycle
{eburp1 450 0.0 n 180} {eburp1 450 820 1 0.0}	Two E-BURP-1 pulses mixed in a single waveform, both covering 450 Hz wide band. The first pulse is applied on-resonance with a phase of 180 deg. The second pulse is shifted to 820 Hz of-resonance, has zero phase and is a de-excitation pulse (status 1). By default such a pulse is time reversed.

A set of Pbox parameters can be used to define the waveform to be generated. The syntax of the Pbox.inp file is straightforward, parameter=value, for instance, name=myshape.RF, or simply name=myshape. The following list describes Pbox parameters and their default values (see "Pbox Parameters," page 349, for more details):

name=Pbox	Shape file name, the extension is optional
type=r	Shape type, r - RF, d - DEC, g - GRD
dres=9.0	Default value is stored in wavefile.
steps=200	Minimum number of steps (< 64k). The default value is stored in a wave file.
maxincr=30	Max phase incr, deg (<<180).
attn=i	Attenuation, i (internal), e (external) or d (nearest dB step)
sfrq=0	Spectrometer frequency, MHz.
refofs=0	Reference offset, Hz (/ppm)
sucyc=d	Super Cycle, d (default), n (no), name as in wavelib/supercycles. The default value is stored in wavefile.
reps=2	Amount of reports (0-4)
stepsize=n	Size of a single step (ms)

wrap=0	Wraparound parameter (0-1).
header=y	Shape header, y (yes) n (no) i (imaging)
bsim=n	Bloch simulation, y (yes), n (no), a (add), s (subtract), 200 (time in sec)
T1=n	Relaxation time T1 (sec)
T2=n	Relaxation time T2 (sec)
dcyc=1	Duty cycle (0 - 1)
sw=0	Spectral width (Hz)
ptype=selective	pulse type (for imaging only)

The number and order of input parameters is optional and not important.

Redefine the internally defaulted Pbox parameters by entering the default values in the . Pbox_globals file.

Parameters describing software and hardware limitations are also pre-defined internally and can be redefined by the user in the . Pbox_globals file that is stored in user's home directory. The following list describes global parameters and their default values.

shdir=$HOME/vnmrsys/shapelib/	default shape directory
wvdir=/vnmr/wavelib	default wave directory
maxst=65500	maximum number of steps in waveform
defnp=100	default number of steps
minpw=0.2	minimum step length, in µs
minpwg=2.0	minimum gradient step length, in µs
drmin=1.0	minimum dres
maxamp=1024.0	maximum amplitude
maxgr=32767.0	maximum gradient amplitude
amres=1.0	amplitude resolution
phres=0.1	phase resolution, in degrees
tmres=0.05	time resolution, in µs
dres=9.0	default dres
maxpwr=63	maximum power level, in dB
minpwr=-16	minimum power level, in dB
maxitr=5	maximum number of iterations
maxdev=2.0	maximum deviation, in percent
cmpr=y	waveform compression
minstps=64	minimum steps in Bloch simulation
pw=0.005	default .RF and .DEC pulse length, in sec
pwg=0.001	default .GRD pulse length, in sec

The parameters of individual shapes—Gaussian, E-BURP-1, or hyperbolic secant pulse, etc.—are stored in the wavelib directory, which has several subdirectories, such as excitation, inversion, refocusing. Every individual shape is defined by a set of parameters that can be grouped in several categories.

Wave definition parameters are the following:

amf	amplitude modulation function
fmf	frequency modulation function
su	default supercycle
fla	default flip angle on resonance

pwbw	pulsewidth to bandwidth product
pwb1	pulsewidth to B1max product
pwsw	pulsewidth to sweepwidth product
adb	adiabaticity on resonance
ofs	offset of excitation bandwidth
dres	default tipangle resolution, in degrees
dash	dash variable
wf	window function
st	default status
dutyc	duty cycle
c1	constant
c2	constant
c3	constant
steps	default number of steps

Wave truncation parameters are the following:

min	minimum truncation threshold (0 to 1)
max	maximum truncation threshold (0 to 1)
left	truncation from left (0 to 1)
right	truncation from right (0 to 1)
cmplx	flag, retain real (1), imag (–1) or complex(0) part of wave
wrap	wraparound factor (0 to 1)
trev	time reversal flag (yes = 1, no = 0)
srev	frequency sweep reversal flag (0 to 1)
stretch	stretching factor (>= 0)
dcflag	dc correction, y/n

Additional parameters are usually data matrices, such as Fourier coefficients or square wave parameters, e.g., length, phase, amplitude, etc. These matrices are listed without parameter names. The size of the data matrix given is defined by:

cols	number of columns
rows	number of rows

Pbox incorporates the following amplitude modulation (AM) functions:

sq	square (constant amplitude)
sqa	square wave amplitude modulation (used for “composite” pulses)
gs	Gaussian
lz	Lorentzian
sch	sech (hyperbolic secant)
hta	tanh (hyperbolic tangent)
tra	triangular amplitude (ramp)
sc	sinc function
csp	cosine power
wr	wurst (wideband uniform rate smooth truncation)
sed	seduce-1, mixture of sech and sin
qp	quadrupolar
ata	amplitude mod for CA atan frequency sweep pulse

exa	exponential amplitude
tna	tangential amplitude
fs	Fourier Series
ft	inverse Fourier Transform

Pbox incorporates the following frequency modulation (FM) functions:

ls	linear sweep (chirp)
tns	tangential sweep (tan)
ht	hyperbolic tangent sweep (tanh)
lzs	constant adiabaticity Lorentzian sweep
ca	constant adiabaticity (CA) sweep (frequency modulated frame)
cas	constant adiabaticity sweep (phase modulated frame)
cs	cosine / sine pulse frequency sweep
cs2	CA cosine square frequency sweep
ccs	CA cosine frequency sweep
sqw	squarewave phase modulation
fsw	frequency switch (step function)
fslg	frequency switched as per Lee-Goldburg

Pbox Parameters

The following list describes Pbox parameters.

name	Name and extension of the output shape file. If the extension is not given, the shape type is set according to the type parameter. The default name is internally set as Pbox. This can be changed in the .Pbox_globals file.
type	Shape type. Allowed values are r (.RF type), d (.DEC) or g (.GRD). If the shape type is not defined and the shape file is given without an extension, the shape file type is determined from the wave file according to the following criteria: • type is set to r if pwbw > 0.0. • type is set to d if dres > 0.0. • type is set to g otherwise.
dres	Corresponds to dres parameter in VMNR. Active only with .DEC files.
steps	Defines the required number of steps in the waveform. The default number of steps is stored with each individual shape in the corresponding wave file. This number can be overridden by Pbox if it is smaller than the internally calculated minimum number of steps, which is necessary to maintain the functionality of the waveform. This number is defined according to the following criteria: • By the minimum number of steps necessary for adequate representation of the waveform (as in wave file). • If the waveform is shifted off-resonance, by the Nyquist condition (see maxincr).
maxincr	Maximum phase increment. Default is 30°. This number is active only if the waveform is shifted off-resonance or the shape itself is frequency modulated (e.g., adiabatic sweeps). In order to satisfy the Nyquist condition, maxincr should not exceed 180°, otherwise the waveform gets folded back. In fact, the degradation of performance and interference with sidebands can be observed even with a maxincr of greater than 90°, but a maxincr of less than 90° is recommended.

attn	Fine attenuation mode, which uses the following allowed values: i (Internal), default.Fine attenuation is implemented by internally rescaling the waveform within the amplitude range set by maxamp (0 to 1023). e (External) Fine attenuation is implemented by externally rescaling the waveform using linear modulators. The internal amplitude is set to maxamp (1023.0), and the required fine attenuator setting is produced in the output. d Attenuate to the nearest dB step by changing the pulse width, which will affect the excitation bandwidth typically within 5%, which is tolerable in most applications. The internal amplitude is set to maxamp (1023.0) 4.5i Internally attenuate to a given (4.5 kHz) B1 field strength by adjusting the pulse length. 4.5e Externally attenuate to a given (4.5 kHz) B1 field strength by adjusting the pulse length. 45I Internally attenuate, keeping course power level at a given (45 dB) power level. 45E Externally attenuate (with fine power), keeping course power level at a given (45 dB) power level. 45d Attenuate to a given (45 dB) power level by changing the pulse width. The internal amplitude is set to maxamp (1023.0).
sfrq	Spectrometer frequency in MHz.
refofs	Reference offset, usually 0.0. Can be specified if the excitation bands are shifted by or referenced to some frequency. Units: Hz, kHz, or ppm (if sfrq is defined).
sucyc	Super cycle. Allowed values are n (no), d (default) or any name of a super cycle stored in the wavelib/supercycles directory. By default, it is internally set to d. Super cycles can be nested by separating the names with a comma, for example, t5,m4 represents 5 step TPG super cycle nested in four step MLEV-4 super cycle.
reps	Defines level of reporting. Allowed values are 0-4: 0=silent, 1=single line, 2=minimum, 3=medium, 4=maximum. The default is 2.
stepsize	The length of a single step in a waveform. The default units are µs. Note that stepsize disables the maxincr parameter.
bscor	Initiates correction for Bloch-Siegert effect in multiple band excitation, inversion or refocusing pulses. Allowed values are y (yes) or n (no, default). Active only if the number of bands is two or more. Reduces the rf interference effects (see M. Steffen, L.M.K. Vanderseypen and I.L.Chuang, Abstracts of the 41st ENC, p. 268, Asilomar 2000).
wrap	Wraparound parameter. It allows wrapping around the waveform. The allowed values are between 0 and 1.0.
header	Shape file header. Allowed values are y (yes, default), n (no shape file header) and i (imaging). Information required for imaging systems is stored in the shape file header.
bsim	Bloch simulator. Performs Bloch simulation for the given waveform at the moment of waveform generation. Allowed values are y (yes), n (no, default), a (add to the previous simulation), s (subtract from the previous simulation) and any positive integer limiting the simulation time in seconds. The default maximum length of simulation is internally set to 60 seconds and can be redefined in the .Pbox_globals file. Note, that Bloch simulator can also be externally activated, e.g., from menus or using the dprofile macro.
T1	Longitudinal relaxation time, T1 in seconds. Can be required by some waveforms (e.g. SLURP pulses). Optional for the Bloch simulation.
T2	Transversal relaxation time T2, in seconds. Can be required by some waveforms (e.g., SLURP pulses). Optional for the Bloch simulation.

dcyc	Duty cycle. Usually required for homonuclear decoupling applications. Only values between 0.0 and 1.0 are active. Outside these boundaries dcyc is reset to 1.0 (default).
sw	Spectral width. If given, the step size of waveform is set equal to the dwell time (1/sw). Recommended for H-H homo-decoupling applications. It also helps to make sure that excitation sidebands are kept outside the spectral window. Also required for Bloch simulation.
ref_pw90	Reference 90° pulse width (in µs) at ref_pwr. Required for calibration of waveforms. If set to 0.0, the maximum B1 field intensity (in kHz) is reported instead of the power setting.
ref_pwr	Reference power level (in dB steps). See ref_pw90.
ptype	Pulse type. Only necessary with imaging header. By default, set to selective.

Wave String Variables

A reminder is given in Pbox.inp files generated by menus and macros because these parameters appear without names. The wave string variables are listed as they appear in the reminder.

sh	Shape name as in wavelib.
bw/pw	Bandwidth and/or pulsewidth. For most waveforms, only one of the two parameters is required. Pbox distinguishes between bw (in Hz), which is always greater than 1.0, and pw (in sec), which is always less than 1.0. Choose which of the two parameters to provide for input, because they are mutually related via the pw*bw product, which is stored with each individual shape in wavelib. Some waveforms (e.g., adiabatic sweep pulses) can require both bw and pw. In such cases, both variables can be provided in a single string using the "/" separator. For example, {WURST2 200.0/0.05} denotes a 50-ms long WURST-2 pulse covering 200 -Hz-wide band. Alternatively, units can be used for clarity, e.g., {WURST2 0.2k/50m}. If the sfrq parameter is defined, bandwidth can also be specified in ppm, e.g., {WURST 20p/5m}.
ofs	Offset from the center of the excitation band in Hz with respect to the carrier frequency (middle of the spectrum). Note that if the sfrq spectrometer frequency, (in MHz) is defined, ofs can also be specified in ppm. In order to specify ofs in terms of absolute frequency, the reference offset refofs (i.e., chemical shift value of carrier frequency) must be defined. For instance, {WURST2 20p/5m 170p} sfrq=225.0 refofs=55p.
st	Spin status. Defines whether the waveform is used for excitation (st=0), refocusing (st=0.5) or de-excitation (st=1), which, in turn, defines whether the wave starts with phase defined by ph (st=1), the ph occurs in the middle of the pulse (st=0.5), or the pulse ends with phase ph (status 0). In addition, the waveforms are time reversed if status is 1, as required for proper de-excitation. Undesired time reversal can be undone using the trev parameter. Furthermore, if several waves of different width are generated, they are bound to the beginning (st=1), middle (st=0.5), or end (st=0) of the waveform. The spin status of the first wave is also used by Bloch simulator as the starting magnetization.
ph	Phase in degrees or phase cycle (super cycle). Usually phase is externally set in the pulse program, and this parameter is not required. Apply any phase cycle (super cycle) from wavelib/supercycles. The difference between this phase cycle and the sucyc parameter is that phase cycling is carried out before waveform mixing and is therefore independent of other Super cycles, whereas sucyc is applied to the final (mixed) waveform. In this way, several waves of different width can be independently phase cycled and use different super cycles.
fla	Flip angle, in degrees. Usually, fla is defined in the wave file and there are very few applications where intermediate flip angles are required.

trev	Time reversal flag (see st). Allowed values are y (yes) and n (no, default).
d1	Prepulse delay, in seconds. Normally not required. If defined, it disables the internal wave shifting according to the spin status.
d2	Postpulse delay, in seconds. Normally not required. If defined, it disables the internal wave shifting according to the spin status.
d0	Pre-d1 delay, in seconds. Essentially repeats d1. It is used only for convenience, e.g., if internal duty cycle is defined in shape parameters in wavelib. If set to 'a', the wave is appended to the previous wave.
wrap	Wraparound parameter. Can take values between 0 and 1.0.

Pbox Macro Reference

Most selective pulse generation can be satisfied using the Pbox window. A set of macros is also available. The following table lists the macros in the order of decreasing importance. For additional information on Pbox macros, refer to the manual *Command and Parameter Reference*.

pboxvnmrj	Opens the Pbox dialog window.
opx	Opens Pbox, writes the Pbox.inp file header, and resets parameters r1-r7 and n1-n3.
selex	Defines the excitation band from the position of cursors in the graphics window and reports them to the user. It also sets r1 to excitation bandwidth and r2 to offset. selex uses the pbox_bw and putwave macros.
cpx	Calls the Pbox command, which generates the specified waveform as defined by the Pbox.inp file. cpx also checks if parameters ref_pwr and ref_pw90 exist in the current experiment and puts their values into the Pbox.inp file. If the parameters do not exist, cpx creates them and asks the user for parameter magnitudes.
setwave	Sets up a single excitation band in the Pbox.inp file. An unlimited number of waves can be combined by reapplying setwave.
putwave	Sets up a single excitation band in the Pbox.inp file. An unlimited number of waves can be combined by reapplying putwave.
pxshape	Generates a single-band waveform based on wave definition provided as a single string of wave parameters.
pboxpar	Adds a parameter definition to the Pbox.inp file.
pboxget	Extracts calibration data from the file shapefile.ext generated by Pbox or, if the file name is not provided, from the pbox.cal file containing parameters of the last created Pbox shape file. Note that the parameter is not changed by this macro if it was set to 'n' (not used)!
pbox_pw	Extracts pulse length from the file shapefile.RF generated by Pbox or, if the file name is not provided, from pbox.cal file containing parameters of the last created Pbox shape file.
pbox_pwr	Extracts the power lever from the file shapefile.ext generated by Pbox or, if the file name is not provided, from the pbox.cal file containing parameters of the last created Pbox shape file. Note that the parameter will not be changed by this macro if previously set to 'n' (not used).
pbox_pwrf	Extracts the fine power lever from the file shapefile.ext generated by Pbox or, if the file name is not provided, from the pbox.cal file containing parameters of the last created Pbox shape file. Note that the parameter will not be changed by this macro if it was previously set to 'n' (not used).

pbox_dmf	Extracts the dmf value from the file shapefile.DEC created by Pbox or, if the file name is not provided, from the pbox.cal file containing parameters of the last created Pbox shape file.
pbox_dres	Extracts the dres value from the file m shapefile.DEC created by Pbox or, if the file name is not provided, from the pbox.cal file containing parameters of the last created Pbox shape file.
pbox_name	Extracts name of the last shape file generated by Pbox and stored in the pbox.cal file. Note, that the file name extension is not stored explicitly and is not provided by this macro.
dshape	Displays real (X) and imaginary (Y) components of a shaped pulse. Any type of waveform (.RF, .DEC or .GRD) can be displayed.
pshape	Generates a single-band waveform based on wave definition provided as a single string of wave parameters.
dshapef	Displays the real (X) and imaginary (Y) components of last generated shaped pulse, stored in pbox.fid file.
dshapei	Interactively displays the real (X) and imaginary (Y) components of last generated shaped pulse, stored in pbox.fid file
dprofile	Displays the X, Y, and Z excitation (inversion) profile for a pulse shape generated by the Pbox software.
pprofile	Plots the X, Y, and Z excitation (inversion) profile for a pulse shape that has been generated with the Pbox software. If a shape name is not provided, the last simulation data stored in shapelib/Pbox.sim are plotted.
pph	Prints out the shape file header (i.e., all lines starting with #).
pbox_bw	Defines the excitation band from the position of cursors in the graphics window and reports them to the user. It also sets r1 to excitation bandwidth and r2 to offset. This macro is used mainly in Pbox menus and macros.
pbox_bws	Defines the excitation band from the position of cursors in the graphics window and reports them to the user. It also sets r1 to excitation bandwidth and r2 to offset. Note, the left cursor should be placed on the left side of the excitation band and the right cursor on resonance of the solvent signal. This macro is mainly used in Pbox menus and macros.
pbox_rst	Resets r1=0, r2=0, r3=0, r4=0, n2='n', n3='', and adds some standard comment lines to the Pbox.inp file. This macro is used in menus and other Pbox macros.
pbox_files	This macro is used only in conjunction with Pbox file menus.

Pbox Commands Using a Terminal

The Pbox program is always executed when a shaped pulse is created. Any of the Pbox parameters can be used as an argument followed by the parameter value. The arguments

and shortcuts listed in Table 39 are available. Note that the output filename is optional and is always the first argument.

Table 39. Pbox Commands and Parameters

Command	*Parameter*	*Action*
`Pbox*`	`-b time`	Activates Bloch simulator, `opt=a` (add), `s` (subtract), or time in sec.
	`-c`	Calibrate only, do not create a shape file.
	`-f file`	Sets name of the output file.
	`-h wave`	Prints wave file header.
	`-i wave`	Prints wave file parameters.
	`-l ref_pw90`	Length (in µs) of reference pw90 pulse.
	`-o`	Lists options.
	`-p ref_pwr`	Reference power level (dB).
	`-r file`	Reshapes Pbox pulse.
	`-s stepsize`	Defines the length (in µs) of a single step in the waveform.
	`-t wave`	Prints shape title from wave file.
	`-u userdir`	Sets user home directory.
	`-w wavestr`	Sets wave definition string.
	`-v`	Runs in verbose mode. Also print Pbox version.
	`-x`	Prints all Pbox parameters.
	`-value`	Sets reps to value.
`Pxsim`		Used in Pbox menus and macros for simulation of excitation profiles of shaped pulses.
`Pxfid`		Used by `dshape` and `dshapei` to format shape file into a FID-format text file.
`Pxspy`		Converts alien shapes (.RF, .DEC and .GRD) into Pbox compatible file format. Essentially converts a time-domain shape file into (frequency-domain) Fourier coefficients, which can be used to create a wave file in the `wavelib` directory.

Examples:

```
Pbox -i eburp2
Pbox newshape -wc "eburp1 450 -1280.0" -1
Pbox sel.RF -w "eburp1 420 -800" "eburp1 420 1200"
Pbox -w "eburp1 200 -1200" -attn e -pl 45 54.2 -b
Pbox tst.RF -w "esnob 20p 170p" -sfrq 150.02 -refofs 55p -refpwr 45  \
-ref_pw90 54.2
```

15.2 Pulse Shape Analysis

- "Starting and Using Pulsetool," page 355
- "Using Pulsetool," page 356
- "Simulation," page 358
- "Creating a Pulse," page 360

The `pulsetool` program is designed to display and examine shaped rf pulses. The standard pulse template file format is the same as for shaped pulses in `/vnmr/shapelib`. Data points are listed as `phase amplitude time-count`, where `phase` is in degrees, `amplitude` is a value between 0 and 1023, and `time-count` is an integer which describes the relative time duration of the step.

Starting and Using Pulsetool

- "Starting Pulsetool from VnmrJ.," page 355
- "Starting Pulsetool from an Operating System Terminal Window.," page 355

Starting Pulsetool from VnmrJ.

1. Click **Edit** on the menu bar.
2. Select **View Pulse Shapes…**

   The Pulsetool starts, see Figure 105.

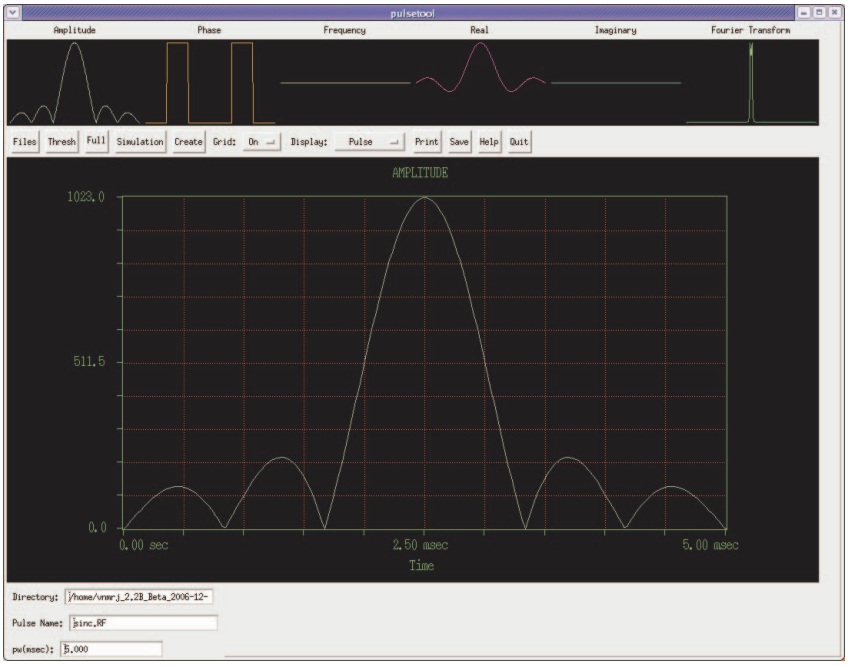


Figure 105. Pulsetool Spin Simulation Window

Starting Pulsetool from an Operating System Terminal Window.

1. Log in a VnmrJ login account owner.
2. Open a terminal window.
3. Start Pulsetool, see Figure 105, using one of these procedures:
   - Enter **`pulsetool&`** at the prompt to start the Pulsetool and use the file navigation tools within Pulsetool to load files.

- Enter **`pulsetool<-shape filepath>&`** at the prompt to start the Pulsetool, and load the specified shape file (`-shape`) from the specified location (`filepath`).

Using Pulsetool

- "Attribute Selection," page 356
- "Control Panel Buttons," page 357
- "Cursors," page 358

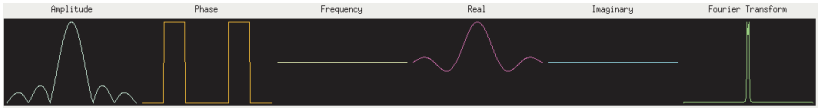
Table 40 summarizes the command and parameters associated with pulse shape analysis.

Table 40. Pulse Shape Analysis Commands and Parameters

Command	
`pulsetool <-shape filepath>`	RF pulse shape analysis
Parameters	
`phi`	Amount of rotation about the Z-axis
`theta`	Declination relative to XY-plane

The `amplitude` and `phase` are displayed in the small windows at the top of the display, along with the effective frequency of the pulse, the quadrature components of the pulse, and its Fourier transform. Click on any graphic displayed in the small windows at the top of the display to display it in the large graphics window in the center of the screen.

Attribute Selection



The six small graphics windows at the top of the tool initially display the different attributes of the current pulse:

- Amplitude
- Phase
- Effective off-resonance frequency
- Real and imaginary quadrature components
- Fourier transform

Display any of these six windows in the large graphics window by clicking in the appropriate small window with either the left or middle mouse buttons:

- The left mouse button causes the large window to be cleared before drawing and sets the clear mode to ON.
- The middle mouse button turns off the clear mode and displays the selected attribute, overlaying any current display in the large graphics window.

Repeated selection of the small Fourier transform window will result in the large window cycling through the magnitude of the Fourier transform, the real component, and the imaginary component.

Control Panel Buttons

The control panel below the small windows contains the following control buttons:

Button	*Function*
Files	Starts a file browser listing the contents of the current directory. A trailing slash "/" following a member of the list indicates a subdirectory, and an asterisk "*" an executable file. Selected from this listing by clicking on it with the left mouse button: **File browser** buttons and function: **Done** — closes file browser **Load** — selected file is read, and displayed in the graphics windows. An error message is displayed if the file does not correspond to the proper format for pulse template files. Comment lines beginning with the pound character "#" are ignored. Descriptive information about the pulse is displayed in the bottom panel—the name of the file, the number of steps in the pulse, the Fourier size required to do the FFT of the pulse, and a "power factor" calculated for the pulse. The power factor is based on the mean square amplitude of the pulse. **Chdir** — changes to and then lists the selected directory. **Parent** — changes to and then lists the parent of the current directory.
Thresh	Activates the horizontal cursor. Refer to "Cursors," page 358
Full	
Simulation	Opens the Bloch Simulation window. Refer to "Simulation," page 358
Create	Opens a dropdown menu of pulse types appears after a right mouse click on the button. Hold down the mouse button and select one of the pulses in the menu. Release the mouse button to load the selected pulse type. Refer to "Creating a Pulse," page 360
Grid:	ON/OFF menu — Turns main window grid on or off.
Display:	Pulse/ Simulation menu — Displays the shaped pulse or, if the simulation has been run, a Block simulation of the response of the spins to the pulse
Print	Click to print the main graphics window on a PostScript printer.
Save	Saves the data currently displayed in the main graphics window to a file. 1. Click on **Save**. A filename entry field and a Done button are displayed 2. Enter a filename. 3. Click on **Save** to write the file. Repeat this needed while in the save mode — display a different attribute in the main window, enter a new file name, and select Save. 4. Click **Done** to exit the save mode.
Help	
Quit	Close Pulsetool

Cursors

Interactive left, right, and horizontal cursors are available, and display a readout of position at the bottom of the large window when active. Click, using the left mouse button, anywhere on the large window to activate the left. Activate the right cursor by clicking the right mouse button anywhere to the left of the current single cursor. The right mouse button controls the position of the right cursor independently and the left mouse button moves the cursors in tandem.

The control panel button marked Full when one cursor is active changes to Expand when both cursors are active. The display can be expanded to show the region between the two cursors. (Note that the clear mode will always be set to ON after an Expand or Full operation.)

Turn off a cursor by holding down the control key and clicking the mouse button associated with the cursor. The right cursor is turned off by clicking the right mouse button in the large window while simultaneously pressing the Control key.

The horizontal cursor is activated with the Thresh button located in the control panel. When this cursor is active, it is controlled interactively with the middle mouse button. The interactive scale and reference functions normally controlled with the middle mouse are not available when the horizontal cursor is present. Select the Scale button in the control panel to turn off the horizontal cursor and reactivate the scale and reference functions (vertical scale and reference can be adjusted even with the horizontal cursor active by direct entry in the appropriate fields in the bottom panel).

Simulation

- "Overview," page 358
- "Parameters," page 359
- "Performing a Simulation," page 360

Overview

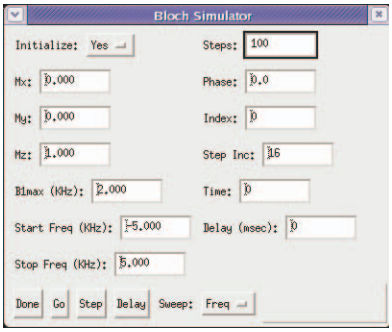
The simulation routine simulates the effects of an rf pulse by use of the classical model of nuclear spin evolution described by the Bloch equations. T_1 and T_2 relaxation effects are ignored, in which case the evolution of a magnetization vector in the presence of an applied rf magnetic field can be evaluated by multiplication with a 3 by 3 rotation matrix. The simulation consists of repeated multiplication by such a matrix, whose elements are determined at each step by the values of amplitude and phase found in the pulse template file, and by user input values of initial magnetization, B_1 field strength, pulse length, and resonance offset. The simulation is performed over one of three possible independent variables— resonance offset, B_1 field strength, or time, and is determined by the Sweep cycle in the small button panel.

Parameters

1. Click on the **Simulation** button in the control panel to activate the Bloch Simulation window.

   The Block Simulation window contains fields for entry of all required parameters (the pulse length is taken from the value in the bottom panel of the main window).

2. Change or enter a value for any parameter by selecting it with the left mouse button entering a value from the keyboard.



3. Enter values for the parameters Mx, My, and Mz for the starting values of the magnetization components. Their vector sum must be less than or equal to 1.Click on the Initialize button and select **YES** or **NO**.This feature works for Frequency and B_1 sweep only, not Time.

   Initialize cycle determines if the magnetization is re-initialized to the values of Mx, My, and Mz, or if the simulation uses the values at each point that were the result of the previous simulation. The effect of a series of pulses can be evaluated by loading the first pulse and performing the simulation with Initialize set to YES, loading subsequent pulse, setting Initialize to NO, and selecting Go after each pulse is loaded.

4. Click on the **Sweep:** button and select **Freq**, **B_1**, or **Time** for the sweep.

   - **Freq**

   a. Enter a value in the B1max for B_1 at the maximum pulse amplitude.

   b. Enter a value in the Start Freq (KHz) field for the starting frequency.

   c. Enter a value in the Stop Freq (KHz) field for the ending frequency.

   - **B1**

   a. Enter a value in the Frequency (KHz) field for the how far the magnetization is off resonance.

   b. Enter a value in the B1 Start (KHz) field for the starting B_1 field.

   c. Enter a value in the B1 Stop (KHz) field for the ending B_1 field.

   - **Time**

     The results are displayed in the form of a projected three-dimensional coordinate system, showing the path of the magnetization over the course of the pulse.

   a. Enter a value in the B1max for B_1 at the maximum pulse amplitude.

   a. Enter a value in the Frequency (KHz) field to see how far the magnetization is off resonance.

5. Accept the default values or enter values or for each of the following:

   a. **Steps** (not available if sweep is set to Time) — the number of steps used in the simulation.

   b. **Phase** — Enter the phase of the pulse

c. **Index** — Counter that displays the current index. No entry is required for this parameter. Setting a value of **0** and clicking the **Steps** button updates the parameters.

d. **Step Inc.**— Enter the number of intermediate steps to be calculated each time the Step button is clicked.

e. **Time** — Enter a nonzero integer value in this field to see the 3D display drawn in real-time.

f. **Delay** — Pre-pulse delay, in seconds. Normally not required. If defined, it disables the internal wave shifting according to the spin status.

Performing a Simulation

1. Click on the **Go** button.

   This does simulation calculations and then displays the results in the first five small graphics windows, replacing (but not destroying) the pulse information that was displayed there. The Fourier transform information remains unaffected, so that comparisons can be made between this and the exact simulation results.

   All of the display functions described elsewhere are active as well, with the simulation data. Additionally, the original pulse data is still present in the background and can be swapped into view with the Display cycle found in the main control panel.

2. Click on the **Step** button to view the course of the magnetization at intermediate stages through the pulse based on the value in the Steps Inc. field, starting at the current value of Index. The intermediate result is then displayed in the normal fashion.

During a Go simulation, a small panel containing a Cancel button will pop into view. Use this to stop the simulation if necessary (there may be some delay between selecting the button and the end of the process (wait, do not click on Cancel more than once).

Clicking on the **Go** button with **Sweep: Set to Time** displays the results in the form of a projected three-dimensional coordinate system, showing the path of the magnetization over the course of the pulse. This display is obtained by selecting the **3D** button after first selecting the **Go** button. The left mouse button controls the viewing angle from within the canvas region delineated by the blue corner markers when the 3D display is active. This viewing angle is described by the two parameters `phi` (the amount of rotation about the Z-axis) and `theta` (the declination relative to the XY-plane). A “family” of trajectories can be displayed by first selecting any of the small canvases with the middle mouse button, then selecting the 3D button. Changing either the B_1 field strength or the resonance offset followed by the Go button will result in display of the result without clearing the display. Select any of the small canvases with the left mouse button to reactivate the automatic clearing feature.

Creating a Pulse

The pulse creation routine currently offers the following pulse types:

Square	Hermite 90	Tan swept inversion
Sinc	Hermite 180	Sin/cos 90
Gaussian	Hyperbolic secant inversion	

A file containing the pulse template for any of these pulses can be created from scratch with this utility. Alternatively, pulses can be created for examination only, using the display capabilities of `pulsetool`. Each pulse is generated with user-definable parameters appropriate for the pulse in question.

1. Click on the **Create** button and hold the right mouse button down.
2. Select a pulse type from the menu and release the mouse button.

   Move the mouse arrow out of the menu area and release the button if none of the choices are acceptable.

   A small window appears with a brief description of the characteristics of the pulse and a set of changeable attributes values when a pulse type is selected. The number of steps in the pulse is limited to powers of 2 and can be set by clicking the left mouse button or by holding the right mouse button down and selecting the desired value from the resulting menu. All other attributes, which vary depending on the pulse type, can be altered from their default values by first selecting the appropriate field with the left mouse button, deleting with the Delete key, and typing in the desired value (pressing Return is not required).
3. Select one of the following buttons at the bottom of the window:

   - **Preview** — use the attributes as they appear on the screen to create a pulse that is loaded internally into `pulsetool`. All `pulsetool` features can then be used to examine and evaluate the new pulse. Any previous pulse information is deleted.
   - **Execute** — use the attributes as they appear on the screen to create a pulse and write it to a text file. The name of the file is taken from the file name field in the Create window and written into the current directory, listed in the Directory field in the bottom panel. If a file of the same name already exists, a prompt requests confirmation to overwrite the file. An error message appears if the program is unable to write to the named file. This is generally symptomatic of not having write permission in the current directory.

   No new pulse types can be added to the list. User-created shaped pulse may be examined using the Files button.

Chapter 16. VnmrJ Experimental Interface

The chapter describes the VnmrJ experimental interface.

- 16.1, “VnmrJ Experimental NMR Interface,” on page 364
- 16.2, “Main Menu Bar,” on page 365
- 16.3, “System Tool Bar,” on page 379
- 16.4, “User Tool Bar,” on page 380
- 16.5, “Advanced Function and Hardware Bars,” on page 381
- 16.6, “Action Controls, Folder Tabs, and Pages,” on page 384
- 16.7, “Graphics Canvas,” on page 384
- 16.8, “Graphics Control Buttons,” on page 385
- 16.9, “Vertical Panels,” on page 389
- 16.10, “Applications Directories,” on page 404
- 16.11, “Setting Colors in VnmrJ,” on page 405

16.1 VnmrJ Experimental NMR Interface

Classic (top) and default (bottom) color schemes for the experimental interface can show, Figure 106, multiple viewports. This viewport layout in the classic color scheme shows four viewports arranged by clicking on the **side-by-side** button under Viewport layout. The layout in the default color scheme was created by clicking on the **Auto** button under viewport layout.

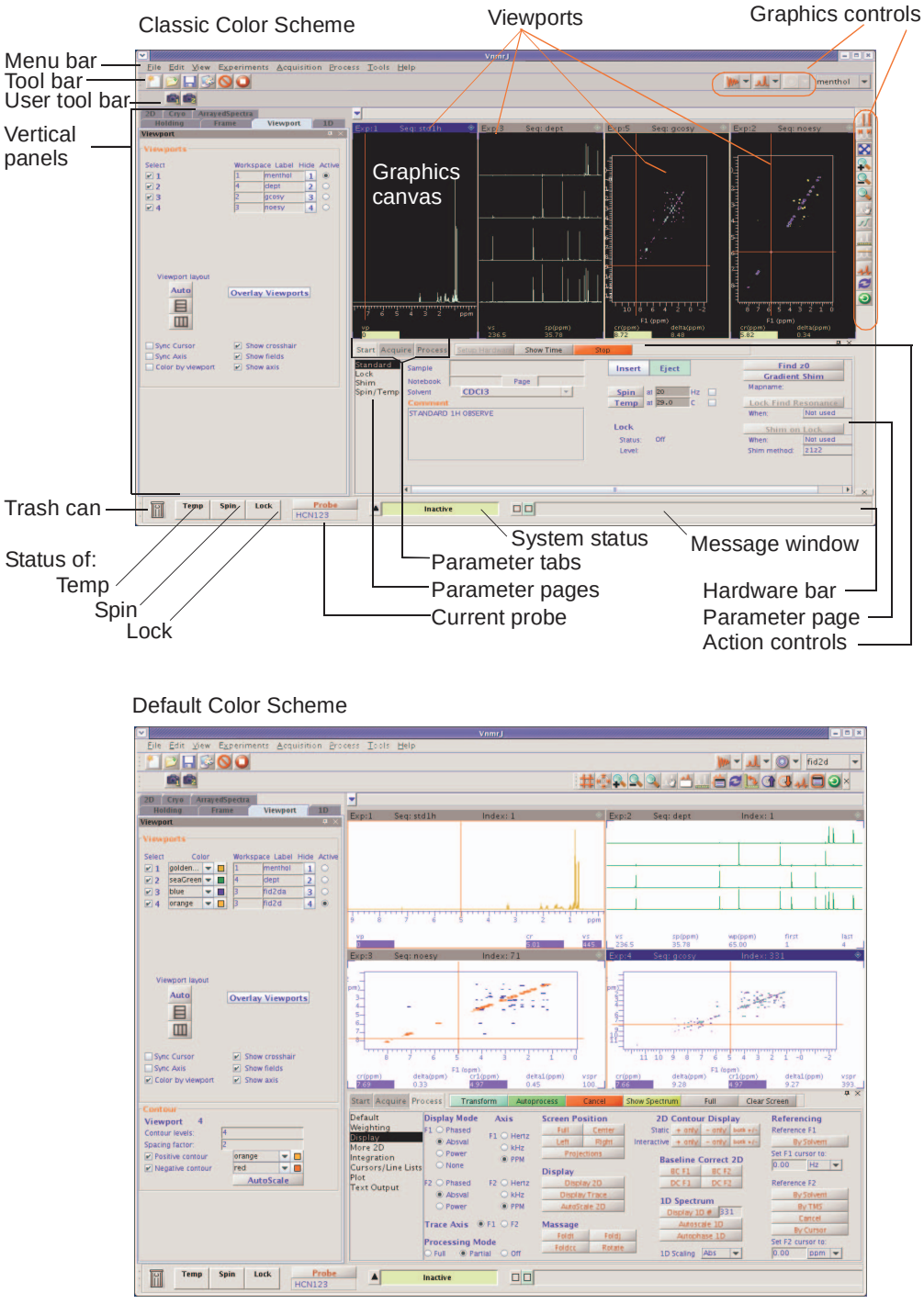


Figure 106. VnmrJ Interface

16.2 Main Menu Bar

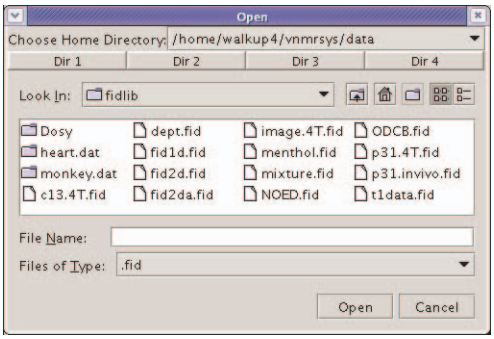
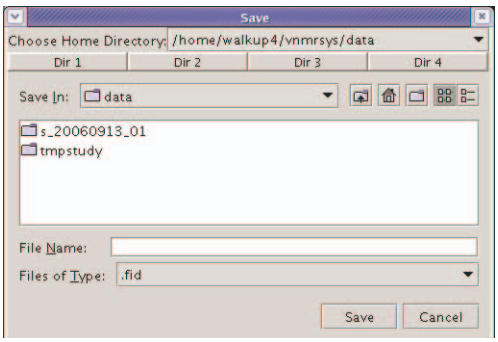
The menu bar sits along the top of the interface. Its function is twofold: first, the menu bar provides access to operations needed to acquire, process, display, and plot a spectrum; second, the menu bar provides access to little-used features, settings, and preferences.

The menu bar contains the following menus:

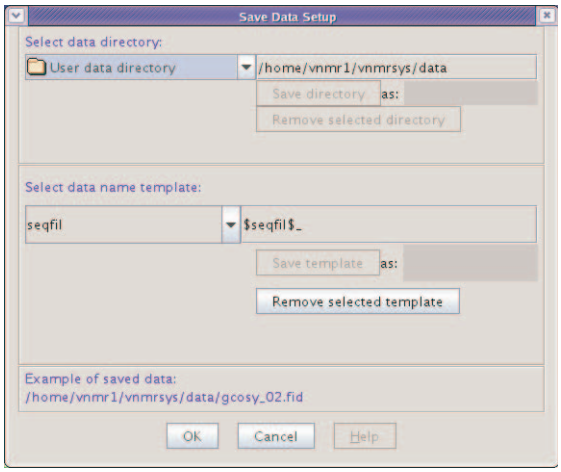
- "File Menu Selections," page 365
- "Edit Menu," page 367
- "View," page 369
- "Experiments Menu," page 370
- "Acquisition Menu," page 373
- "Process Menu," page 374
- "Tools Menu," page 376
- "Help Menu," page 379

File Menu Selections

The File menu selections are:

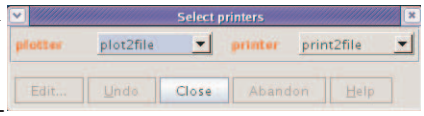
Menu Items	*Descriptions*
New Workspace	Make and join a the next available workspace.
Open	Opens the file navigation window to the locate the required file. Click the **file** and click on the **Open** button. 
Save as …	Opens the file navigation window to the locate the required directory. Enter a file name in the Save As field and click **OK** to save. 
Auto Save	Save files using the auto save parameters set up; refer to *VnmrJ Installation and Administration* manual.

Menu Items	*Descriptions*
Save data setup …	Opens the Save Data Setup window for customizing where data is saved and file naming; refer to *VnmrJ Installation and Administration* manual.



Printers... Opens a window for selecting printers and plotters.

Printers and plotters defined through VnmrJ Admin are displayed; see the *VnmrJ Installation and Administration* manual for information about connecting printers and plotters.



Print Screen … Prints part or all of the VnmrJ screen to current the printer to either a file or printer using the options selected.

Printer Region of window

Printer radio button – send output to printer

File radio button – save output to the file named in the File field

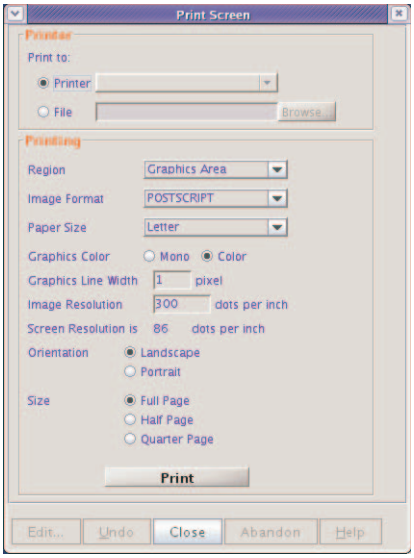
Printing Region of window

Select Region dropdown menu choices:

Graphics Area
VnmrJ Screen

Format dropdown menu choices:

JPEG, GIF, TIFF, or BITMAP



Page Size – click on a radio button for: Full, Half, or Quarter page

Graphics Color – click on a radio button to select Mono or Color

Graphics Line Width – enter a line width in pixels

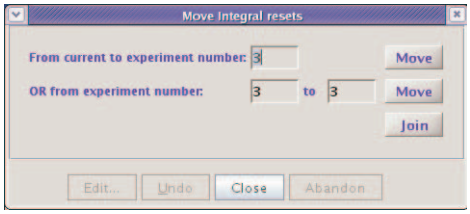
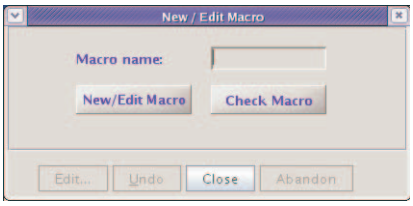
Image Resolution – enter an image resolution in dots per inch

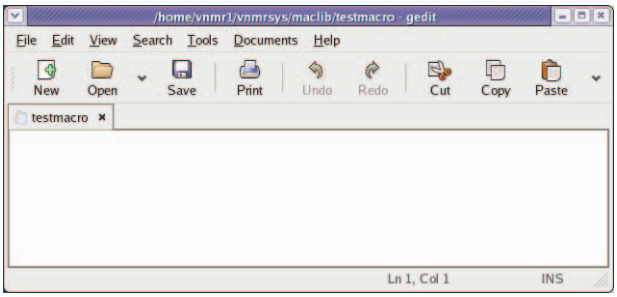
Screen Resolution is –displays current screen resolution in dots per inch

Menu Items	*Descriptions*
	Orientation – Click a radio button for Landscape or Portrait **Size** – Click a radio button for Full Page, Half Page, or Quarter Page **Print** button – sends screen to default printer **Close** button – close the Print Screen window
Auto Plot	Plots current data using protocol plotting and printing defaults.
Create a Plot Design…	Opens Plot Designer, see "Plot Designer," page 133.
Exit VnmrJ	Exits VnmrJ.

Edit Menu

The Edit menu selections are:

Edit Menu Items	*Descriptions*
Move Parameters… **Move FID…** **Move Text…** **Move Display parameters…** **Move Integral resets…**	All the **Move …** selections open a popup window similar to the Move Integral resets window shown.  Do either of the following or click **Close**: • Enter a target experiment number in the field next to **From current to experiment number:** to move the selection from the current experiment. Click the **Move** button. • Enter the number of the source experiment in the field next to **OR from experiment number:** and the number of the target experiment in the **to** field. Click the **Move** button. Click the **Join** button to join the target experiment. Click **Close.**
New Pulse Shapes (Pbox) …	Opens Pbox window, see "Pandora's Box," page 341.
View Pulse Shapes…	Opens Pulse Tool window, "Pulse Shape Analysis," page 354.
New/Edit Macro…	Opens a dialog window to create a new macro, edit an existing macro, or test a specific macro.  1. Enter the name of a new or existing macro in the field next to Macro name. 2. Click on the **New/Edit Macro** button to open the gedit tool. Instruction for using the gedit tool are accessed by clicking on **Help** button on the tool's menu bar.

Edit Menu Items	*Descriptions*
	. 
	3. Edit or write the new macro; refer to the section in the *VnmrJ User Programming* manual for instructions on writing macros using the Magical II language. 4. Save the new or edited macro or abandon the new or changed material. 5. Click on the **Check Macro** button to test the macro. 6. Click on the **Close** button to exit the New/Edit Macro dialog window.
Tool Bar	Opens the tool bar editing tool. Refer to the *VnmrJ Installation and Administration* manual for more details.
Display options...	Opens a window for setting symbolic colors and fonts in the interface.
Edit config profile…	Opens the Edit User Config Profile window. Refer to the *VnmrJ Installation and Administration* manual options and permission related to this window.
Parameter Pages…	Opens the parameter panel editing tool.
Viewports	Opens the Viewport Settings panel to set the number of viewports, the geometry of the graphics area, and the workspaces attached to each viewport. See "Viewports," page 389, for instructions on how to use and work with viewports. To set the geometry of viewports, click the geometry after selecting the number of viewports, e.g., for 3 viewports click 1x3, which displays 1 row and 3 columns. 3x1 displays 3 rows and 1 column. Fill in the workspace number for each viewport to set the workspace attached to each viewport. Select **Switch Layout for Viewports** to switch the layout of VnmrJ to the last viewed layout of a specific viewport. By default, this is selected; deselect it to turn it off, and the layout will stay the same for the viewports. Click **Set 3 Default Viewports** and click **Close** to set the viewports to the default settings.
Applications…	Opens the Applications Directories editing window, see "Applications Directories," page 404.

Edit Menu Items	*Descriptions*
System Settings...	Opens the System Settings window, used to set system parameters. **System** tab – provides system-level settings. **Display/Plot** tab – provides display and plot settings. **Display configuration check box** – displays system configuration in the text output panel (config).
Window tab	
System tab:	**Application mode** – Walkup, Standard, or Imaging pulse; any interface based on installed optional software packages. **Gradient amplifier** – On/Off selection for each gradient axis that is installed. **Hardware Z1 Shimming** – drop down menu: none, delay, and presat **Probe protection** check box – enabled if checked **VT cutoff (0 – 50)** entry field – enter value above which the VT air flow will not use the heat exchanger. **Process data after acquisition** check box –enabled if checked. **Autosave data after acquisition** check box – enabled if checked.
Display/Plot tab	**Process data on drag-and drop** – check to enable **Set display from plotter aspect ratio (wysisyg)** – check to enable **Spectrum updating during phasing (0-100)** – set the percentage of the display that is updated during interactive phasing. 100 is recommended **Max # of pens** – number of plotter pens to use **Show Tooltips** – check to enable **Day Limit of files in Locator (neg=forever)** – enter an integer value **Turn Locator Off** – check to enable

View

The View menu selections are:

View Menu Items	*Descriptions*
Command Line	Displays the command line if it is hidden– default is account owner only.
Holding Panel	Opens the vertical Holding Panel.
Parameter Panel	Opens the horizontal parameter panels if they are hidden.
Frame	See "Frame Panel," page 394.
Viewport	See "Viewports," page 389.
1D	See "1D," page 402.
2D	See "2D," page 403.
Cryo	Controls for cryogenic system and probe. Refer to the related manuals for instructions.

View Menu Items	*Descriptions*
Arrayed Spectra	See "Arrayed Spectra and FIDs," page 399.
Toolbars	Opens a popout menu. Place check next to a tool bar to show the tool or remove the check to hide the tool bar.
System Toolbar	 Refer to “System Tool Bar” on page 40 for a description of the system tool bar functions.
User Tool bar	
Graphics Toolbar	 Tool bar for spectra Tool bar for FIDs
Hardware Toolbar	

Experiments Menu

Not all experiments are available on all spectrometer systems. System configuration and options selected at installation determine the available experiments.

Experiments Menu Items	*Sub menu choices*	
Proton **Presat** **Wet1D** **Carbon** **Fluorine** **Phosphorus**		
Relaxation Measurements	T1 Measure	T2 Measure
Carbon-Proton Multiplicity	Apt	Dept/DeptQ
Selective Excitation 1D	Noesy1d Tocsy1d	Roesy1d
Homonuclear 2D	Cosy Dqcosy	Gcosy Gdqcosy
	Noesy	Roesy
	Tocsy	Homo2dj
1H Detected Proton-Carbon 2D	Hsqc Hmqc	Ghsqc Ghmqc
	Hmbc	Ghmbc
	Hsqctoxy	Ghsqctoxy
	Hmqctoxy	Ghmqctoxy
	Hsqcad	Ghsqcad
	Ghmbcad	Cigar2j3j
	AdequateAD	
13C Detected 2D	Hetcor	Ghetcor
Hadamard Experiments	Setup Hadamard	
	TocsyHT	HsqcHT
Dosy		
	2D DOSY	

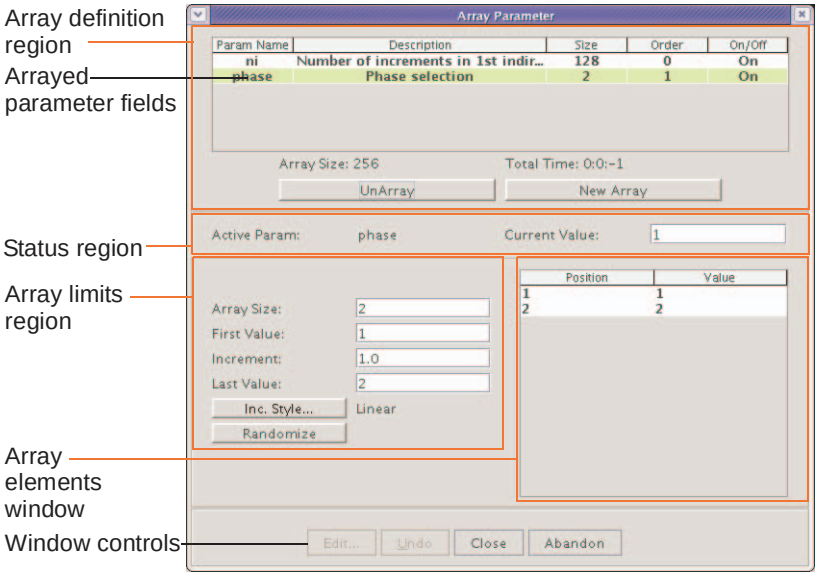
Experiments Menu Items	*Sub menu choices*
	Bipolar Pulse Pair Stimulate Echo
	Bipolar Pulse Pair STE with Watergate 3-9-19 Solvent Suppression
	Gradient Compensated Stimulated Echo
	Gradient Compensated STE with DPFGSE Solvent Suppression
	ONESHOT-DOSY
	DOSY-INEPT
	2D DOSY with Convection Compensation
	Bipolar Pulse Pair Stimulated Echo
	Gradient Stimulate Echo
	Gradient Compensated Stimulate Echo
	PFG Double Stimulated Echo
	Absolute Value 3D DOSY Sequences
	Gradient Compensated Stimulate Echo COSY
	COSY-IDOSY
	Gradient Compensated Stimulate Echo gHMQC
	HOM2J-IDOSY
	Phase Sensitive 3D DOSY Sequences
	Sensitivity Enhanced gHSQC-DOSY
	Gradient Stimulated Echo HMQC
	gHMQC-IDOSY
Solid-State Experiments	
	Basic 1D Experiments
	Setup Tangent CP (Settancps)
	Tangen CP (Tancpx)
	CP with TOSS (Tancpxtoss)
	One Pulse (Onepul)
	One Pulse with TOSS (Onepultoss)
	PWX with CP (Tancpxflip)
	1H T1rho with CP (Tancpxt1rho)
	X Hahn Echo with CP (Tancpxecho)
	X Two Pulse for T1 (Twopul)
	Interupted Decoupling with CP (Tancpxidef)
	X T1 with CP (Tancpht1)
	CP with FSLG Decooupling (Tnacpxfslg)
	Lee Golburg CP (Lgcp)
	HX2D Experiments
	FSLG with Lee-Goldburg CP (Hetcorlgcp)
	WISE (Wisentancped)
	2Q-1Q with CP and C7 Mixing (C7inad2d)

Experiments Menu Items	*Sub menu choices*
	PISMA using FSLG
	HXY Experiments
	CP REDOR with XY8 on X and Y (Redor1tancp)
	CP REDOR with XY8 Y and X inversion (Redor2tancp)
	One Pulse REDOR with XY8 on X and Y (Redor1onepul)
	One Pulse REDOR with XY8 Y and X inversion (Redor2onepul)
	Quadrupole Experiments
	Quadrupole Echo (Ssecho1d)
	3Q-1Q MQMAS with Z-filter (Mqmas3qzf2d)
	5Q-1Q MQMAS with Z-filter (Mqmas5qzf2d)
	Multipulse Experiments
	High Power Pulse Tuning (Tunexp)
	XX Tuneup (Xx)
	XmX Tuneup (Xmx)
	BR24 with Quad Detection (BR24q)
	MREV8 with Quad Detection (Mrev8q)
	Semiwindowless WaHuHa (Swwhh4)
	Windowless PMLG-N (Wpmlg1d)
	2D F1 and Windowed PMLG-N (Wpmlg2d)

Acquisition Menu

The Acquisition menu selections are:.

Menu Items	*Descriptions*
Parameter arrays…	Open Array Parameter window.



Array Parameter Window Regions

Array definition

Arrayed parameter field columns:

Parm Name – enter name of arrayed parameter.

Description – displays text description of array.

Size – displays number of steps or increments in the array.

Order – displays precedence for running the array – double click in the field and enter the array order. Arrays with sequential numbers create a full matrix (array A x Array B) and each array can be a different size. Arrays with the same order number (and the same size) create a diagonal array.

On/Off – Array is used / array not used.

Fields and buttons

Array Size field – shows size of selected array.

Total Time field – shows estimated time to complete the array.

UnArray button – remove selected parameter from the list of arrayed parameters.

NewArray button – add new row to list of arrayed parameters.

Status – show active parameter during acquisition and parameter's current value.

Array limits

Array Size field – enter the size of the array and press return.

Menu Items	*Descriptions*
	First Value – enter the starting value of the array and press return.
	Increment – enter the array increment and press return.
	Last Value – enter the ending value of the array and press return.
	Inc. Style … button – click and select linear or exponential.
	Randomize button – click to create a random array.
Array elements	
	Change the value of the array element by double clicking on the value of the array element associated with the array position, entering a new value, and pressing **Enter**.
Window buttons	
	Edit—Not active.
	Undo—Click to undo click again to restore the change.
	Close—Closes the window.
	Abandon—Closes the window and makes no changes.
Acquire Data	Acquire data only. No post acquisition processing (`go`).
Acquire and WFT	Acquire and process data post acquisition using current weighting functions and values (`go`).
Acquire and Process	Acquire and process data post acquisition using the current settings, including active `wbs`, `wnt`, `wcxp` and `werr` functions (`an`).
Abort Acquisition	Abort data acquisition for the current sample. Sample handlers systems remove the sample, insert the next queued sample in the magnet, and start data acquisition.

Process Menu

The Process menu selections are:

Menu Items	*Descriptions*
Process and Display 1D	Process and display the 1D data.
Full Process	Process and display the 1D data using the processing and display parameters and setting set in the Process tab panels.
Drift Correct Spectrum	Apply drift correction along both axes of a 2D data set
Automatically Set Integrals	
Baseline Correct	Apply baseline correction
Set Spectral Width between Cursors	Mark new spectral width on the graphics screen using the left and right cursors, then select this option to set the new spectral width.
Set Transmitter at Cursor	Mark new transmitter location on the graphics screen using the cursor, then select this option to set the transmitter.

Menu Items	*Descriptions*
Add and Subtract 1D Data	Results are shown displayed in experiment 5

Sub-menu items

Clear Buffer and Add Current Spectrum

Clears buffer (experiment 5) or creates experiment 5 and places current spectrum in experiment 5

Add Second Spectrum into Buffer

Adds current spectrum (algebraically) to data in experiment 5

Full Process 2D	Processes and displays the 2D data using the processing and display parameters and setting set in the Process tab panels
Process 2D (Individual Steps)	Step-by-step processing of 2D data

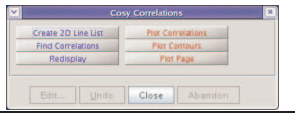
Popout-Menu Choices

Phase and Set Weighting F2
Do first FT (t2 Domain)
Adjust Weighting in F1 (must do first FT)
Baseline Correct F2
Full 2D-FT (t1, t2 domains)
Baseline Correct F1

Analyze

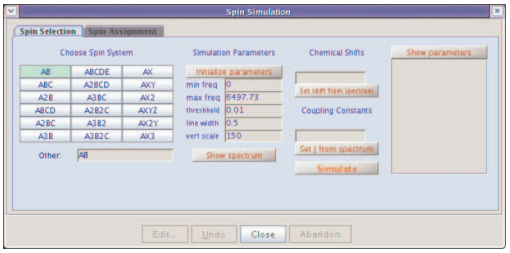
Popout-Menu Choices and Dialog Windows

Cosy Correlations…
opens Cosy Correlations window if current viewport contains an appropriate data set.

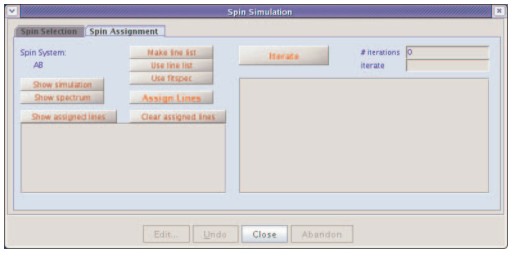


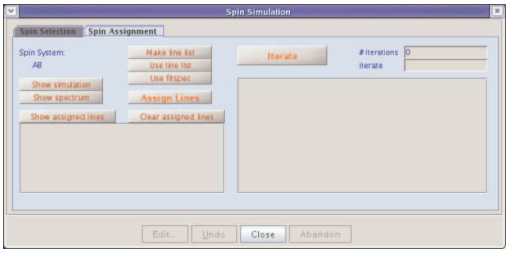
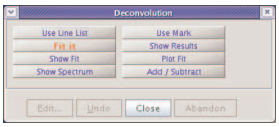
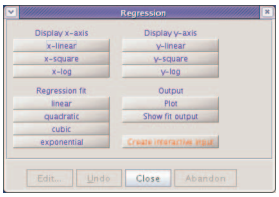
Spin Simulation… opens Spin Simulation window.

Spin Selection Tab



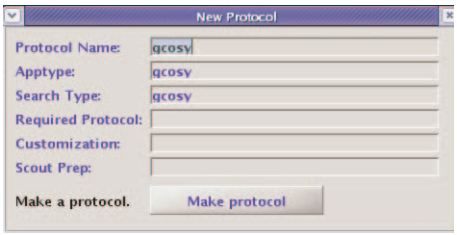
Spin Assignment tab



Menu Items	*Descriptions*
Stars… opens the Stars window: This window is only available if the optional Stars software module was installed.	 
Deconvolution… opens the Deconvolution window:	
Regression… opens the regression window:	

Tools Menu

The tools menu selections available are:

Menu Items	*Descriptions*
Create Protocols	A submenu with the following items:
Sub-menu items	
Make a New Protocol	Opens a window for saving the current parameter set as a part of a new protocol. 

1. Enter the name of an existing protocol or a name for a new protocol in the field next to **Protocol Name:**
2. Keep or change the application type of an existing protocol or enter new application type for the new protocol in the field next to **Apptype:**

Menu Items	*Descriptions*

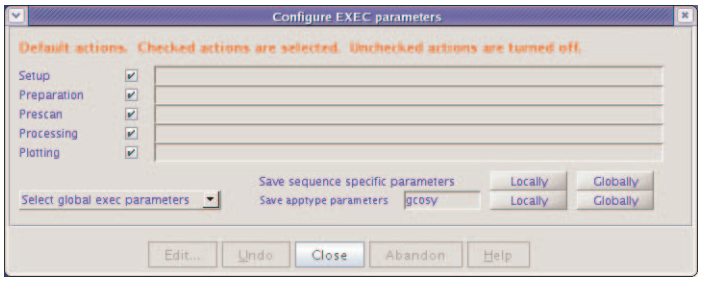
3. Keep or change the search type (used by the Locator) of an existing protocol or enter new search type for the new protocol in the field next to **Search Type:**
4. Keep or define a new required protocol for existing protocols or, if required, enter a required protocol for a new protocol in the field next to **Required Protocol:**
5. Keep or define any new customization for existing protocols or, if required, enter required customization for a new protocol in the field next to **Customization:**
6. Keep or define any new scout preps for existing protocols or, if required, enter required scout preps for a new protocol in the field next to **Scout Preps:**
7. Press the **Make protocol** button.

   The new protocol is written to the user's local directory tree. The local protocol is used when the protocol is loaded if the protocol has the same name as a system level protocol. Only the system administrator (typically vnmr1) has permission to edit or create new global protocols.

Configure EXEC parameters

Opens the Configure EXEC Parameters window to access parameters controlling **Setup**, **Preparation**, **Prescan**, **Processing**, and **Plotting** functions. Functions are defined in the field next to the function name.

Place a check in the check box next to the function to make the function active.



The button to save Globally is only available to the system administrator, typically vnmr1, and to users with system level access.

Select global exec parameters

Dropdown menu of application types. The Setup, Preparation, Prescan, Processing, and Plotting fields are filled in or remain empty as appropriate. The default action is active if a check mark appears in the box next to the action. The fields are editable.

Menu Items	*Descriptions*
	Save sequence specific parameters The sequence specific parameters are saved when the button labeled ***Locally*** is clicked. If the account administrator has permission, a button labeled *Globally* appears next to the Locally button, to save the parameters globally.
	Save apptype parameters field Specify an application type. The save process occurs when button labeled ***Locally*** is clicked. If account administrator has permission, a button labeled *Globally* appears next to the Locally button, to save the parameters globally.
Auto Tune Probe…	Option is displayed if ProTune hardware and software are installed. Opens Tune Probe window for autotuning, see "Tuning Probes on Systems with ProTune," page 31
Manual Tune Probe…	Option is displayed if ProTune hardware and software are not installed. Loads manual tuning parameters and panels for manual probe tune, see "Tuning Probes on Standard Systems," page 34.
Do Gradient Shimming	Starts the gradient shimming using the gradient shimmap associated with the current probe and the gradient shimming parameters set when Set Up Gradient Shimming was last run.
Standard Calibration Experiments	Provides the interfaces for probe calibration and gradient shimming setup:
Sub-menu items	
Probe Calibration	Opens a window for running a series of experiments to calibrate the probe. Refer to "Calibrating the Probe," page 58, and the *VnmrJ Installation and Administration* manual.
Set Up Gradient Shimming	Loads the pulse sequence and panels for making a shim-map for gradient shimming.
Set Up 3D Gradient Shimming	Selection appears only if this option is installed. Loads the pulse sequence and panels for making a 30-shim map for gradient shimming.
Applications directory Enabled/Disabled Sub-menu selections (refer to "Applications Directories," page 404):	
Start AutoTest	Starts AutoTest; see *AutoTest* manual for a description of the AutoTest.
AutoTest Settings	Opens the AutoTest test settings window; see the *AutoTest* manual for a description of settings and options.
Update locator	Opens a submenu that provides choices for updating the different parts of the Locator.
Import files to locator	Opens a window for importing files to the locator.
Save custom locator statement	Opens a window for saving the current locator view.
Delete custom locator statement	Opens a window for deleting custom locator statements.

Menu Items	*Descriptions*
Molecular Structures	Refer to "Molecular Display and Editing (JChemPaint and Jmol)," page 127.
Sub-menu items	
Display all	Displays all molecular structures.
Plot all	Plots all molecular structures.
JChempaint…	Opens the open source application JChempaint in a separate window. Refer to the online manual provided with JChempaint.
Jmol…	Opens the open source application Jmol in a separate window. Refer to the online manual provided with Jmol.
Browser…	Opens a file browser window "Locator and File Browser," page 407.
Locator…	Opens Locator, see "Locator and File Browser," page 407.

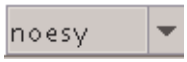
Help Menu

Starts VnmrJ online help. This is an HTML based online help system that opens in a Web browser. The help files must be loaded from the VnmrJ Manuals CD. Or, the CD must be left in the CD-ROM drive.

16.3 System Tool Bar

The system tool bar directly below the menu bar provides quick access to common functions. The following tools are the defaults available in this tool bar:

Button	*Function*
	Creates a new work space.
	Opens the file browser to locate a directory, select a file, and load the file. Click on the file to load, and click on the **Open** button to load the file into the current workspace (experiment).
	Save As… Opens a file browser to locate a directory, name a file, and save a data set. Enter a file name in the **File Name:** field, select the file type from the dropdown menu, and click on the **Save** button.
	Opens the display options Styles and Themes window.
	Cancels command.
	Stops acquisition.

Button	*Function*
	Shows the FID display toolbar, see "Graphics Control Buttons," page 107.
	Shows the spectrum display toolbar, see "Graphics Control Buttons," page 107.
	Shows the contour controls (grayed out if the data set is 1D); see "Graphics Control Buttons," page 107.
	Dropdown menu of viewports and experiments in the viewport. The experiment in the active viewport is displayed on the button.

16.4 User Tool Bar

Button	***Description***
	Saves layout view 1.
	Saves layout view 2.

The tool bar and buttons can be edited. Click on **Edit** and **Select Tool** to start the editor; refer to *VnmrJ Installation and Administration* manual for more information. Save the current screen layout (graphics, a parameter panel, locator sizes) as follows:

1. Place cursor over one of the layout view buttons.
2. Hold the left mouse button down.
3. Wait for *layout saved* to appear in the message box on the hardware bar (approximately five seconds). The same message appears on the command line if the command line is visible.
4. Release the mouse button.

Click on a **Saved Layout** button to return to the saved layout.

Hiding and Showing the Tool Bars

Hide or show a tool bar from the main menu:

1. Click on **View** from the main menu.
2. Select **Toolbars**.
3. Check on a **toolbar name** to toggle the tool bar ON (place a check mark to the left of the toolbar name) or OFF (remove the check mark to the left of the toolbar name).

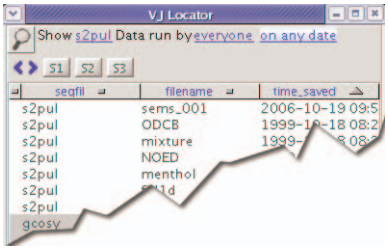
A tool bar with an **X** at the bottom can be hidden or closed by clicking on the **X**.

Locator

The Locator provides access to data sets, experiments, shim sets, and commands (see Locator in "Locator and File Browser," page 407). Open the VJ Locator popup window as follows:

1. Click on **Tools** on the main menu.
2. Click on **Locator…**
3. Click the magnifying glass with the left mouse button to open a menu of searches.

   Search results are displayed in the list. Those items in the white part of the list satisfy the search sentence. Those in the gray part do not. Three attributes are displayed for each item that is found by the search.



   The attributes correspond to the three columns in the list. Clicking on the attribute name at the top of the list with the left mouse button opens a menu of attribute choices.

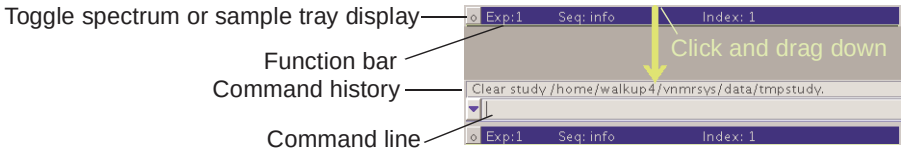
4. Click on an item in the Locator list to select that item.

   Drag the selected item to the graphic area or the parameter panel area to load the data into the current experiment. For example, dragging a data set to the graphic canvas retrieves that data set into the current workspace (experiment) and displays the spectrum. Dragging a workspace to the graphic canvas causes that workspace (experiment) to be *joined* with the graphic area. Double-clicking on an item performs the same action as dragging the item to the graphics canvas.

16.5 Advanced Function and Hardware Bars

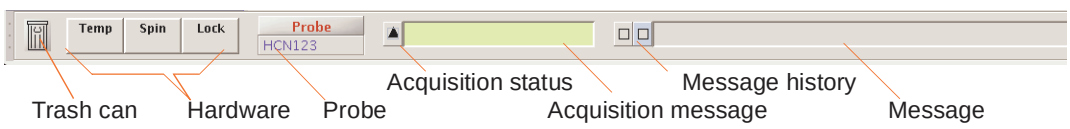
- "Advanced Function Bar," page 381
- "Hardware Bar," page 381

Advanced Function Bar



Drag down the advanced function bar to open a command, macro, and parameter entry field and a text output field. The default settings make the click and dragdown feature display the command line available; see *VnmrJ Installation and Administration* manual for changing this default. Open or close the field by clicking once on the button, which restores it to its most recent view. Error and information messages are displayed in the scrolling text window above the command line in addition to the hardware bar. Click on the arrow with the left mouse button to view the command history. Select a command from the command history by highlighting it and pressing **Return** to execute it.

Hardware Bar



The hardware bar contains the following:

- "Trash Can," page 382
- "Hardware Monitors," page 382
- "Probe Selection," page 382
- "Acquisition Status Details," page 383
- "Acquisition Status Display," page 383
- "History of Acquisition Messages," page 383
- "History of All Messages," page 383
- "Message Display," page 383

Click on the bar  to the left of the trash can with the left mouse button to hide or show the hardware bar. The current state of the acquisition system and system messages are displayed on the right side of the hardware bar.

Trash Can

Drag an item to the trash can from the Locator or other area to remove the item and add it to the trash can. The locator must be open.

Double click on the trash to view items in the trash can area, and restore objects from the trash can by selecting them and then clicking the **Restore items** button. Double click on the trash can to exit this mode.

Note: Emptying the trash can delete data from the disk.

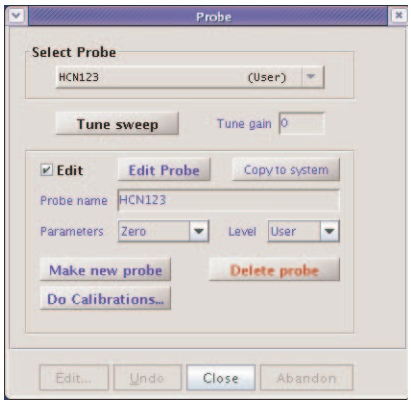
Hardware Monitors

Click **Temp**, **Spin**, or **Lock**, to open a window with a line graph showing the history of the relative hardware function. Click the icon again to close the window.

Button	*Description*
Temp	Shows a history of the sample temperature
Spin	Shows a history of the sample spin rate
Lock	Shows of a history of the sample lock level

Probe Selection

Click on this button to open the Probe window. Use it to perform the following actions:



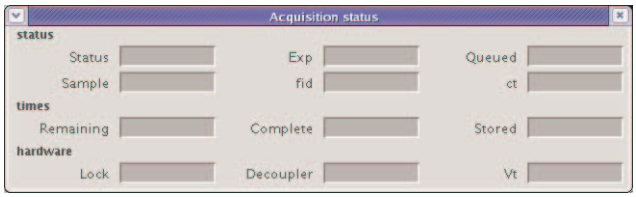
- Select a probe from the list of available probes: click on the **Select Probe** menu.
- Open the probe tuning (Q tune) window: click on **Tune sweep**. Do not use this for normal probe tuning.
- Edit a probe entry: click on **Edit Probe**.
- Edit probe attributes for a particular nucleus: click on the nucleus menu.
- Select initial parameter attributes for adding a probe: click the **Parameters** menu.
- Add a new probe:

enter a new probe name and then click **Add Probe**.

- Remove a probe name from the list of available probes: enter the probe name and then click **Delete probe**.
- Open a window for running a series of probe calibration experiments: click **Edit Probe**, **Select Calibration**, and **Start Calibration**. Refer to the *Installation and Administration* manual for detailed calibration procedures.

Acquisition Status Details

Click on the  icon to open a window showing acquisition status details. Click on the icon again to close the window.



Acquisition Status Display

The acquisition status bar 

is always visible in the hardware bar. During an acquisition, the bar shows the remaining experiment time as a thermometer display. Click the right mouse button inside the bar to change the displayed text.

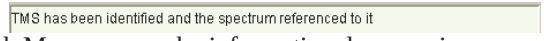
History of Acquisition Messages

Click on the left  icon to see a history of all acquisition messages. Click on the icon again to close the window. Click the right mouse button within the scrolling message window to change the text view options. Right mouse click on the icon to change the properties of the displayed items as well as to clear the buffer.

History of All Messages

Click on the right  icon to see a history of all spectrometer messages. Click on the icon again to close the window. Click the right mouse button within the scrolling message window to change the text view options. Right mouse click on the icon to change the properties of the displayed items as well as to clear the buffer.

Message Display

The message display 

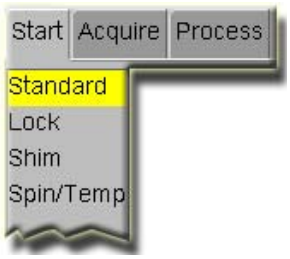
shows the last message that occurred. Messages can be informational, a warning, or an error message.

16.6 Action Controls, Folder Tabs, and Pages

Action Controls

Action buttons to the right of the parameter panel selection tabs (Setup, Acquire, Process), change, depending on the currently displayed panel as shown. Click on an action button to execute the indicated process using the parameters set on the parameter pages.

Folder Tabs, and Pages



Select folders by clicking on the tabs on the Action Controls bar.

Use the **Start** panel to perform basic functions for setting up a new sample and preparing to run experiments.

Use the **Acquire** panel to set acquisition parameters.

Use the **Process** panel to adjust processing parameters and process data.

Each tab contains a list of relevant pages.

Editing Parameter Pages

To edit a page, select the **Edit** menu, then select **Parameter Pages**. This template editor is also useful for viewing commands and parameters that are used in the panels (see the Parameter Panel Editing section in the *VnmrJ User Programming* manual for details).

16.7 Graphics Canvas

This portion of VnmrJ, shown in Figure 107, is used to display and interact with graphic and text information.

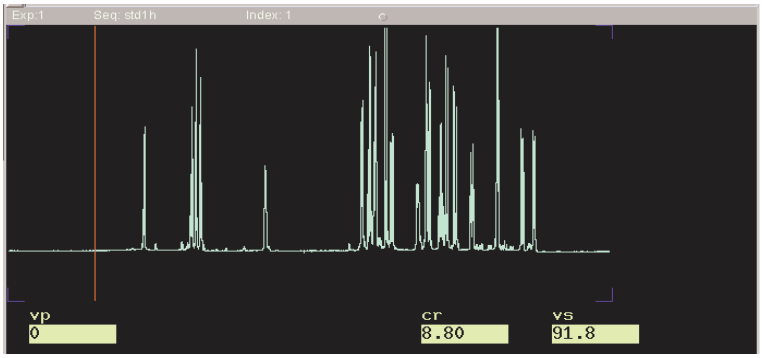


Figure 107. Graphics Canvas

Resize the graphics canvas by clicking on the canvas boundary line with the left mouse (the cursor changes form) and dragging the line (e.g., between graphics and parameter templates or between graphics and Locator).

16.8 Graphics Control Buttons

The graphics control bar for the active viewport is normally placed to the right of the graphics canvas. The control bar can be dragged to the top of graphics canvas or to the left side. It can also be positioned in a Toolbar. Use the buttons in the bar to control the interactive display in the graphics canvas.

- "Select Spectra or FID Display Tools," page 385
- "Common Graphics Display Toolbar Controls," page 385
- "1D Display Spectrum Toolbar Controls," page 386
- "Display FID Toolbar Controls," page 386
- "nD Display Toolbar Controls," page 386
- "Stacked Spectra Display Using the Graphics Tools," page 388
- "Integration and Graphics Controls," page 388

Select Spectra or FID Display Tools

Icon	*Description*
	Display Spectra
	Display FID

Common Graphics Display Toolbar Controls

The following tools are common to 1D, nD, and FID display toolbars.

Icon	*Description*
	Reset to full display.
	Zoom in.
	Zoom out.
	Select zoom region.
	Redraw display.
	Return to previous tool menu.

1D Display Spectrum Toolbar Controls

Icon	Description
	One cursor in use, click to toggle to two cursors.
	Two cursors in use, click to toggle to one cursor.
	Click to expand to full spectral display.
	Pan or move spectral region.
	Display integral. See "Integration and Graphics Controls," page 388
	Display scale.
	Toggle threshold on or off.
	Phase spectrum.

Display FID Toolbar Controls

Icon	Description
	One cursor in use, click to toggle to two cursor.
	Two cursors in use, click to toggle to one cursor.
	Click to expand to full fid display.
	Pan and stretch.
	Click to show real and imaginary.
	Click to show real and zero imaginary.
	Click to show real only.
	Toggle scale on and off.
	Phase fid.

nD Display Toolbar Controls

- "Main nD Display Bar Tools," page 387
- "nD Graphic Tools," page 387

Main nD Display Bar Tools

Icon	*Description*
	Display color map and show common nD graphics tools.
	Display contour map and show common nD graphics tools.
	Display stacked spectra and show common nD graphics tools.
	Display image map and show common nD graphics tools.

nD Graphic Tools

Icon	*Description*
	One cursor in use, click to toggle to two cursors.
	Two cursors in use, click to toggle to one cursor.
	Click to expand to full display.
	Pan and stretch.
	Show trace.
	Show projections.
	Click on  to show horizontal maximum projection across the top of the 2D display.
	Click on  to show horizontal sum projection across the top of the 2D display.
	Click on  to show vertical maximum projection down the left side of the 2D display.
	Click on  to show vertical sum projection down the left side of the 2D display.
	Rotate axes.
	Increase vertical scale 20%.
	Decrease vertical scale 20%.
	Phase spectrum.
	Click on  to select the first spectrum.

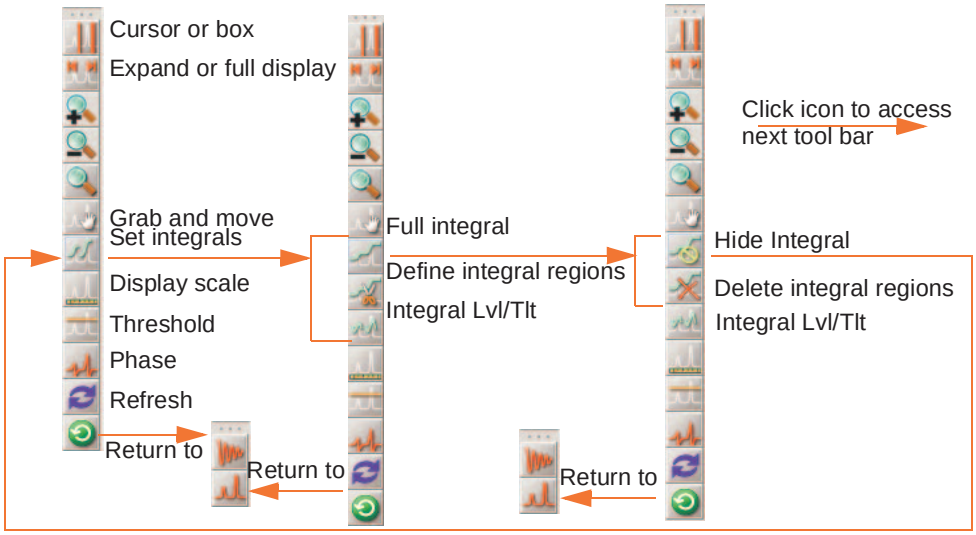
Icon	Description
	Click on  to select the second spectrum.
	Enter Peak Pick menu.

Stacked Spectra Display Using the Graphics Tools

Icon	Function
	Display the first arrayed spectrum and display 1D graphics toolbar with the following icons at the top (or left side if the bar is horizontal).
	Display next spectrum.
	Display previous spectrum.
	Display arrayed spectra stacked vertically with each spectrum displayed using the full width of the screen.
	Display arrayed spectra horizontally and divide available display width into equal portions.
	Hide or show axis under the spectra.
	Label the spectra.
	Return to previous graphics display tool.

Integration and Graphics Controls

This section describes methods and tools for displaying and plotting integrals.



16.9 Vertical Panels

- "Viewports," page 389
- "Frame Panel," page 394
- "Holding," page 399
- "Arrayed Spectra and FIDs," page 399
- "1D," page 402
- "2D," page 403

Viewports

- "Setting the Number of Available Viewports," page 389
- "Setting Colors Used with Viewports," page 390
- "Viewport Tab," page 390
- "Using Viewports Region Controls," page 390
- "Synchronizing Cursors and Axes," page 393
- "Setting Crosshair, Fields, and Axis Display Options," page 393
- "Assigning Colors to Spectra by Viewport," page 393
- "Contour," page 394

Setting the Number of Available Viewports

A maximum of 9 viewports can be created and displayed. The number of viewports and the viewport numbers are not linked to the number of workspaces and the workspace number (or experiment number). Enter **`explib`** on the command line to display a list of the current experiments in the Text Output panel. The experiment number corresponds to the workspace number.

1. Click on **Edit** on the main menu.
2. Select **Viewports…** to open the Viewports settings window, see Figure 108.

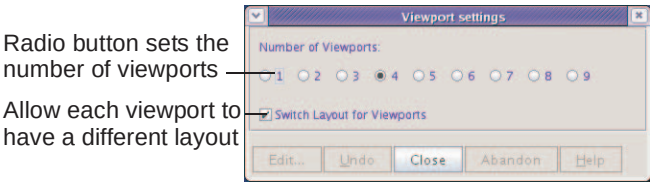


Figure 108. Viewport settings window

3. Click on a **radio button** under **viewports** next to the number of viewports to create and add the viewports to the vertical tool bar Viewport tab.
4. Check the box next to **Switch Layout for Viewport** to allow each viewport to have a different layout (see the Parameter Panel Editing section in the *VnmrJ User Programming* manual for details).

Setting Colors Used with Viewports

Access the Styles and Themes window as follows:.

1. Click on **Edit** on the main menu.
2. Select **Display options …**
3. Click on the **Display Colors** tab to show the current color scheme, see Figure 109
4. The default colors for the viewports are listed in Table 41.

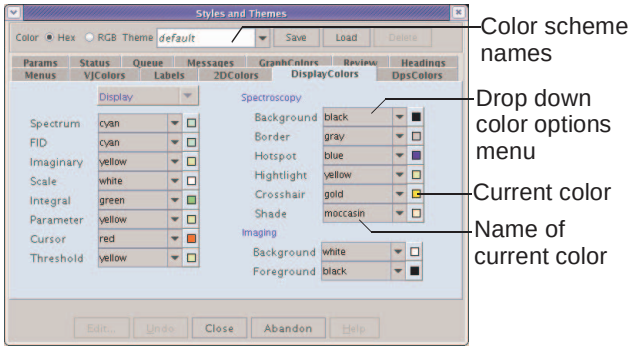


Figure 109. Setting Display Colors

Table 41. Default Viewport Control Colors

Control	*Default Color Name*
cross hair	yellow
frame border, not selected	gray
hot spot: frame corners	blue
shade for selected area	moccasin

Viewport Tab

Click on the **Viewport** tab to display the viewport controls.

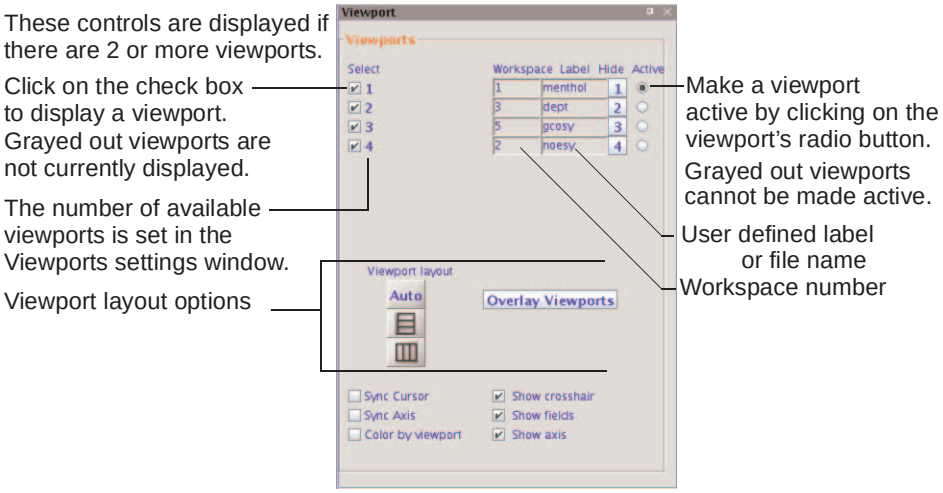


Figure 110. Viewport Tab and Controls

Using Viewports Region Controls

The viewport controls are present if there are two or more viewports (see "Viewports," page 389).

- "Showing and Hiding Viewports," page 391
- "Making a Viewport Active," page 391

- "Adding a Label to the Viewport," page 391
- "Changing the Workspace Displayed in a Viewport," page 391
- "Overlay Viewports," page 392

Showing and Hiding Viewports

The selected viewports are arranged on the graphics canvas based the layout selection, see "Setting the Number of Available Viewports," page 389.

1. Place a check in the check box next to each viewport to show on the graphics canvas.
2. Remove the check from a check box next to a view port to hide the viewport.
3. Temporarily hide a viewport by placing the cursor over the box next to the viewport label and holding down the left mouse button. Release to mouse button to show the viewport. The viewports do not change their layout on the graphics screen. This tool is used when overlay viewports is selected.

Making a Viewport Active

1. Click on the radio button associated with a viewport to make the viewport active. The title bar of the active viewport is colored. The inactive viewports have gray title bars.
2. Use the horizontal and vertical panel tools to work on the data in active viewport or begin data acquisition using the active panel. Experiments started from the current active panel are run in the order of submission. Systems running an automated sample changer use only experiment 1 (which is in viewport 1) to submit samples to the automation queue. All other viewports are used for data processing and analysis.

Adding a Label to the Viewport

The default label for a viewport is the currently loaded experiment's file name.

1. Click inside a viewport's label box (viewport does not have to be active).
2. Select the contents of the box and overwrite the text with new text.
3. Click outside the text box. The new label associated with this viewport.

Changing the Workspace Displayed in a Viewport

1. Make the a viewport active by:
   - Clicking on the radio button under the active viewport title to the right of the viewports.
   - Add a new viewport, see "Setting the Number of Available Viewports," page 389 and make the new viewport active.
2. Do one of the following:
   - Enter the number of the workspace to be displayed in the active viewport.

     The selected workspace is displayed in the current viewport if it is not associated with a viewport (active, inactive, or not available). A new workspace (or experiment) is created and displayed in the viewport if the workspace (or experiment) does not already exist. Use the explib macro to display a list of the current experiments in the Text Output panel.
   - Use the Main menu:

     a. Click on **File**

b. Select **New Workspace**.

A new workspace (experiment) is created using the next available workspace number and the new workspace is displayed in the current viewport.

- Use the command line to create a new experiment (if needed) and jump to the specified experiment as follows:

a. Enter **`cexp#`**, # is the number of the new experiment or workspace

b. Enter **`jexp#`**, # is the number of the experiment or work space to jump to and display in the current viewport.

Overlay Viewports

See "Aligning and Stacking Spectra," page 119, for details on overlaying viewports.

Synchronizing Cursors and Axes

Check Box	*Function*
Sync cursor	Check this box to link and synchronize the cursors and cross hairs in multiple viewports.
Sync Axis	Check this box to link and synchronize axes in multiple viewports.

Setting Crosshair, Fields, and Axis Display Options

Check Box	*Function*
Show crosshair	Check this box to show crosshairs and display current position.
Show fields	Check this box to show information fields at the bottom of the active viewport canvas: 
Show axis	Check this box to show the axis or remove the check to hide the axis.

Assigning Colors to Spectra by Viewport

Check Box	*Function*
Color by viewport	Check this box to display the spectral data using colors assigned by the viewport, see Figure 111. **Default color assignment**: spectra are displayed using a different color for each viewport if the box is checked. The spectra are displayed using the defaults assigned in the Display options window if this box is not checked **Change a color assignment:** Click on the dropdown **color menu** for a viewport and select a color for the spectral display in the viewport.

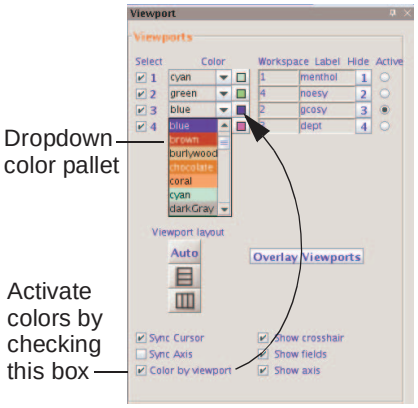


Figure 111. Setting Spectra Colors by Viewport

Display Check Boxes

The check boxes control optional display features.

Check box	*Function*
Cross hair	Display cross hair and chemical shift(s) of the cursor position when mouse is moved over the spectrum. Useful when the fields are not shown, or not in cursor mode (default mode), or when chemical shift of a peak without moving the left cursor is required while in the cursor mode.
Fields	Display cr, delta, vp etc... fields at the bottom of the viewport.

Check box	*Function*
Axis	Show scale of the axis.
Show frame border	Check the box to display a box around the frame. Uncheck the box to display the four corners of the selected frame as *hot spots* for resizing. No border or corner will be displayed if a frame is not selected. An empty frame is not visible until it is selected.

Contour

The contour sub-panel, see Figure 112, appears exclusively for the active viewport with 2D data loaded and displayed in contour mode (`dpcon`).

Color by viewport not selected Color by viewport selected

Figure 112. Contour Controls

The Contour panel has the following controls

Control	*Function*
Contour levels	Enter a number of contours between 4 and 32 in the field.
Spacing factor	Enter a number in the field to specify the spacing between contours. A number between 1.1 and 2 is recommended.
Positive contour	Check this box to show positive contours using the default color red.
Negative contour	Check this box to show negative contours using the default color blue.
Color dropdown	Each contour has a color dropdown menu. Select a color from the menu to use a color other than the default color.
Multi color contours	Options is not displayed if the Color by Viewport box is checked. Check this option to use the colors defined in Display Option.
AutoScale	Automatically scale the spectrum.

Frame Panel

- "Text Insert," page 394
- "Creating, Deleting, and Using Text Templates," page 397
- "Creating a Spectrum Inset Frame," page 397

Text Insert

- , “Text Frame Tools,” on page 395
- "Creating a Text Frame with Text," page 395
- "Moving a Text Frame," page 396
- "Resizing a Text Frame," page 396
- "Editing Text Inside a Text Frame," page 396
- "Deleting One Text Frame," page 396

- "Deleting All Text Frames," page 396
- "Hiding and Showing Text Frames," page 396
- "Creating, Deleting, and Using Text Templates," page 397

Text Frame Tools

Text is placed into a text frame within the default frame of the active viewport using the text insert tools, see Figure 113. Select, move and resize in the same way as an inset or default spectrum frame.The content of each text frame is defined by a file.

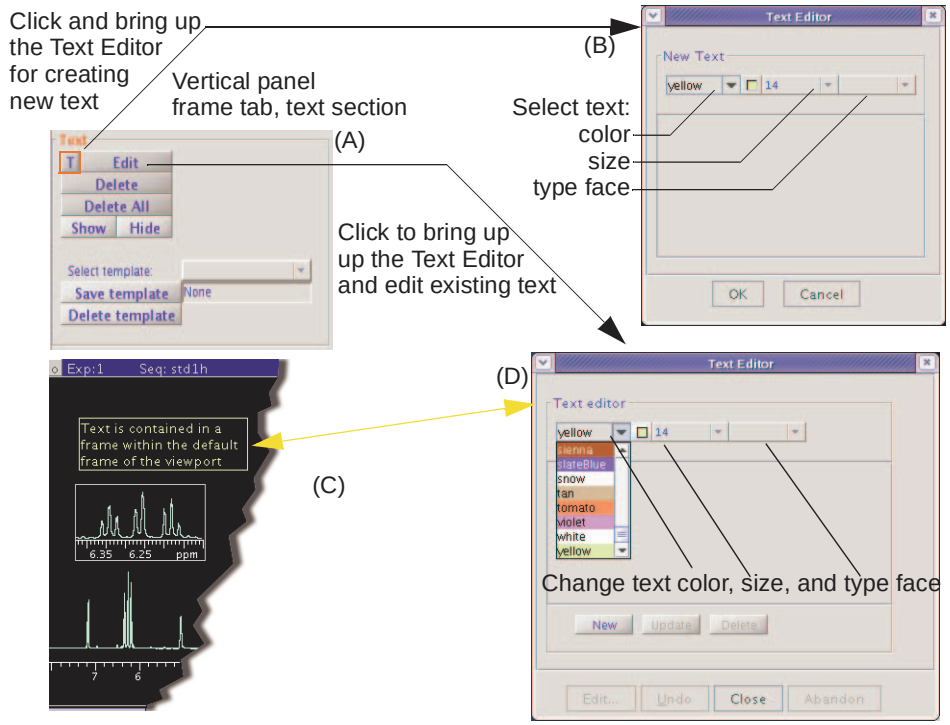


Figure 113. Text Panel Controls and Text Editor

Creating a Text Frame with Text

1. Do the following if the Text tab is not displayed to the left of the graphics canvas:
   a. Click on **View** on the main menu bar.
   b. Select **Text**.
2. Click on the **Text** tab, see Figure 113(A).
3. Click on the **T** button, see Figure 113(A).
4. The Text Edit window, see Figure 113(B), appears.
5. Use the default text colors, text size, and type face or select different text colors, text size, and type face using the dropdown menus.
6. Enter the text in the text box.

   The frames do not have a word-wrap feature.

   Press the **Enter** key to create a new line of text within the same text frame.
7. Click the **OK** button to place the text and text frame on the graphics canvas and close the window.

Click the **Cancel** button to close the window without placing any text on the graphics canvas.

Editing Text Inside a Text Frame

1. **Double click** inside the frame to make the frame active; see Figure 113(C).
   An active frame has a yellow border.
2. Click on the **Text** tab; see Figure 113(A).
3. Click on the **Edit** button on the Text tab.
   The Edit Text window is displayed; see Figure 113(D).
4. Click a text frame to edit or change the type color, size, and or type face style.
5. Click **Update** to apply and display the changes to the text in the active text frame.

Moving a Text Frame

1. **Double click** inside the frame to make the frame active, see Figure 113(C).
   An active frame has a yellow border.
2. Move the mouse cursor to an edge of the inset frame.
   The cursor changes from a single-headed arrow to a four-headed arrow.
3. Hold down the left mouse button and grab the edge of the frame.
4. Drag the frame to the new position.
5. Release the mouse button when the frame is at the desired position.

Resizing a Text Frame

1. **Double click** inside the frame to make the frame active; see Figure 113(C).
   An active frame has a yellow border.
2. Move the mouse cursor to a corner of the inset frame.
   The cursor changes from a single-headed arrow to a double-headed arrow.
3. Hold down the left mouse button and grab the corner of the frame.
4. Drag the corner to resize the frame.
5. Release the mouse button when the frame is the desired size.

Deleting One Text Frame

1. **Double click** inside the text frame to make the frame active.
   An active frame has a yellow border.
2. Click on the **Delete** button.

Deleting All Text Frames

- Click on the **Delete All** button.

Hiding and Showing Text Frames

- Hide – click on the **Hide** button.
- Show – click on the **Show** button.

Creating, Deleting, and Using Text Templates

- "Creating a Text Template," page 397
- "Using a Text Template," page 397
- "Deleting Text Template," page 397

The supplied default template, `sampleInfo`, displays the content of the text file in the current `exp` directory, created from the comment text field in Study panel under the Start tab.

Creating a Text Template

1. Create one or more text frames on the graphics canvas.
2. Enter a name in the field next to the Save template button.
3. Click the **Save template** button.

   A template may contain one or more text frames. The current text display layout is saved as new template using the name entered in the field next to the Save template button. The template will be overwritten if the name already exists in template menu.

Using a Text Template

1. Click on the dropdown menu next to Select Template:
2. Select a named template.
3. Click on the a text frame to edit the content.

   The Edit Text window is displayed, see Figure 113(D).
4. Edit the text or change the type color, size, and or type face style.
5. Click **Update** to apply and display the changes to the text in the active text frame.

Deleting Text Template

1. Click on the dropdown menu next to Select Template:
2. Select a named template.
3. Click on the **Delete from menu** button.

Creating a Spectrum Inset Frame

- "Inset Frame Buttons and Tools," page 398
- "Creating the Inset Frame," page 398
- "Zooming in on a Region Within an Inset Frame.," page 398
- "Resizing an Inset Frame," page 399
- "Moving an Inset Frame," page 399

Inset Frame Buttons and Tools

The buttons delete one or all inset frames and restore the default frame to full size.

Buttons and tools	*Function*
Delete Inset	Delete the selected inset.
Delete all	Delete all inset frames.
Full size	Restore default frame size.
 .	Select the inset mode tool
 .	Default mode tool

Creating the Inset Frame

An inset frame has the full capability of the default frame. The only difference is the default always exists and an inset frame can be created or removed.

Create an inset frame within the default viewport frame as follows:

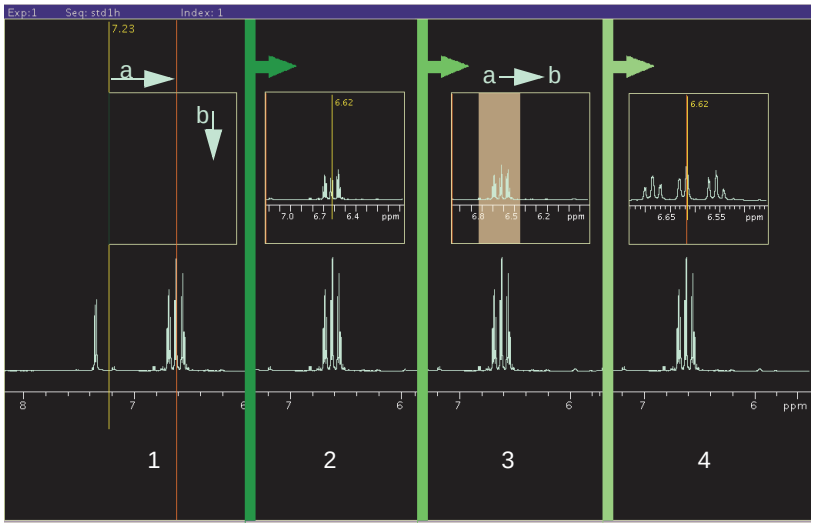


Figure 114. Creating an Inset Frame

1. Select the Frame vertical panel.
2. Select the inset mode tool  .
3. Place the cursor at the low field (left) side of the region to be expanded as shown in Figure 114 frame 1a.
4. Hold the left mouse button down and drag the inset window to the high field (right) side of the region.
5. Drag the cursor down to set the height of the inset frame, see Figure 114 frame 1b.
6. Release the mouse button to create the inset frame, see Figure 114 frame 2.

Zooming in on a Region Within an Inset Frame.

1. Select the default mode tool  .
2. Click inside the frame to make the frame active.

   A frame has a yellow border when it is active and white border when it is inactive (these are the default colors of inactive and active frames).

3. Select the zoom mode tool  .
4. Place the cursor at the low field (left) side of the region to be expanded as shown in Figure 114 frame 3a.
5. Hold the left mouse button down and drag the inset window to the high field (right) side of the region, Figure 114 frame 3b.

   The region selected is indicated by a transparent gray rectangle.
6. Release the mouse button, and the selected region expands to fill the inset box, Figure 114 frame 4.

Resizing an Inset Frame

1. Select the default mode tool  .
2. Click inside the frame to make the frame active. An active frame has a yellow border.
3. Move the mouse cursor to a corner of the inset frame. The cursor changes from a single-headed arrow to a double-headed arrow.
4. Hold down the left mouse button and grab the corner of the frame.
5. Drag the corner to resize the frame.
6. Release the mouse button when the frame is at the desired size.

Moving an Inset Frame

1. Select the default mode tool  .
2. Click inside the frame to make the frame active. An active frame has a yellow border.
3. Move the mouse cursor to an edge of the inset frame. The cursor changes from a single-headed arrow to a four-headed arrow.
4. Hold down the left mouse button and grab the edge of the frame.
5. Drag the frame to the new position.
6. Release the mouse button when the frame is at the desired position.

Holding

Use the holding panel to store commonly accessed items from the Locator. To add an item from the Locator to the holding pen, select (click on) the item and drag it into the holding pen. The item remains in the holding pen even if the Locator view changes.

Selecting an item or dragging it from the holding pen performs the same actions as selecting an item or dragging it from the Locator.

Remove an item from the holding pen by selecting it and dragging it to the trash can.

Arrayed Spectra and FIDs

This procedure applies equally to the display and plotting of both spectra and FID arrays.

1. Select the type of presentation by selecting from the following choices of display modes for the arrayed spectra or FID:
   - **horizontally** shows the spectra side-by-side.
   - **vertically** aligns the spectra one above another.

- **auto** depends on the previously chosen display mode:

  Spectra are aligned vertically, and the vertical offset is chosen so that all spectra together will cover the entire vertical space if the previous mode showed the spectra full screen (vertical mode or showing only a single 1D).

  A vertical offset is added to show the spectra along a diagonal if the previous mode was horizontal.

- **whitewash** aligns the spectra one above another like the vertical mode, but does not show spectra behind each other, avoiding overprinting. Horizontal and vertical offsets can be adjusted.

- **custom** takes over the display properties of either horizontal, vertical, or auto modes but allows the choice of horizontal and vertical offsets.

2. Specify the elements of the arrayed data that are displayed by entering the following information in the Choice of Values region:

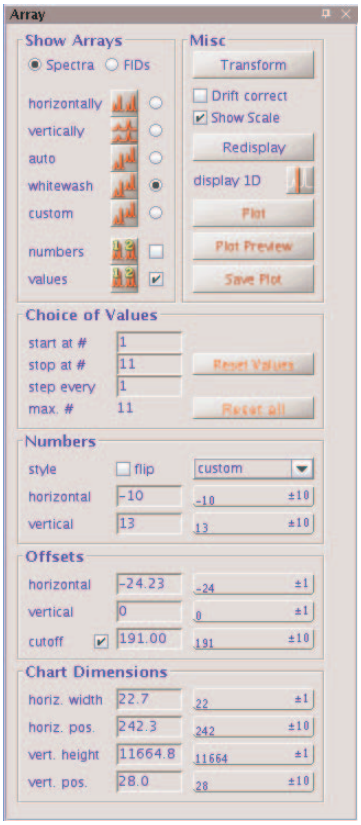
   a. Enter a starting value (the first element of the array to display) in the field next to **start at #**.

   b. Enter a stop value (the last element of the array to display) in the field next to **stop at #**.

   c. Enter a step value (the element between the beginning and end of the array to display) in the field next to **step every**.

   d. Enter a maximum number of elements to display in the field next to **max #**.

   e. Use the **Reset Values** and **Reset all** buttons to return to the default settings.



3. Optional: turn on numbering of the array elements displayed by placing a check in the check box next to **number** or **values** in the Show Arrays region. Suppress all numbering by leaving the check boxes next to number and values in the Show Arrays region un-checked.

   a. Specify the orientation of the numbers, either upright or place a check in the check box next to flip to display the numbers rotated 90 degrees counter clockwise.

   b. Specify the position of the numbers from the options on the drop-down menu next to the flip check box.

   c. Specify a horizontal and vertical positioning of the number with respect to the spectrum by selecting **custom** for the drop-down menu and entering the positions of the numbers in the fields next to **horizontal** and **vertical**.

4. Specify the vertical and horizontal offsets for the display of the array in the vertical, whitewash, or custom array mode (offsets entries are enabled only for these modes) as follows:

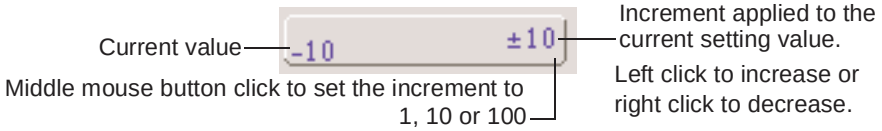
   a. Enter a value for horizontal offset in the field next to **horizontal**.

      The horizontal width (see below) must be smaller than the screen width to apply any horizontal offset.

   b. Enter a value for vertical offset in the field next to **vertical**.

   c. Adjust the positions as needed using the buttons next to each field.

      Right mouse click on the button to increase the value, or left mouse click on the button to decrease the value of the increment shown on the left side of the button.



   d. Switch on or off a cutoff to avoid overlapping large lines that may reach into the spectra above.

5. Set the chart dimensions as follows:

   a. Enter a value for horizontal width in the field next to **horiz. width**.

   b. Enter a value for horizontal position in the field next to **horiz. pos**.

   c. Enter a value for vertical height in the field next to **vert. height**.

   d. Enter a value for vertical position in the field next to **vert. pos**.

   e. Adjust the positions as needed using the buttons next to each field.

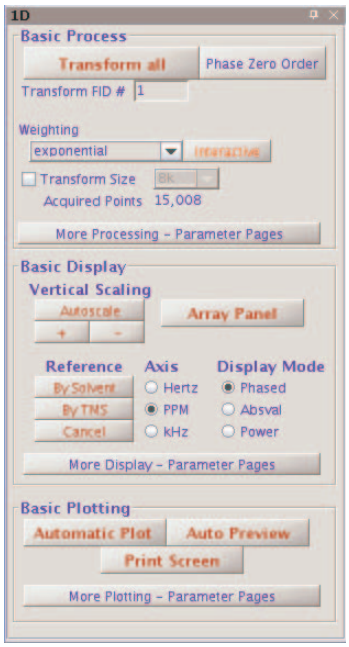
6. Use the functions in the Misc region to do the following as needed:

   - Click on the **Transform** button to Fourier transform the current FID data.
   - Check the **Drift box** to apply drift correction (corresponds to "dc" command) to all subspectra of the array.
   - Check the **Show scale** box to switch on or off a scale below the first spectrum or FID of the array.
   - Click on the **Redisplay** button to refresh the screen.
   - Click on the display 1D icon  to show a single spectrum/FID and use the toolbox to manipulate and zoom.
   - Click on the **Plot** button to send the current array display to the current plotter
   - Click on the **Plot Preview** button to plot the array to a PDF file and open Acrobat reader with the PDF of the current array.
   - Click on the **Save Plot** button to save a plot file in the format as chosen on the Plot parameter panel.
   - Settings on the Plot parameter panel for parameter printing are used. Plotting from the ArrayedSpectra vertical panel controls does not plot integrals, integral values, and peak frequencies.

1D

Panel provides a reduced set of the full 1D process, display, and plot parameters available on the parameter pages of the process tab.

Control	*Description or Function*	*1D Vertical Panel*
Basic Process Controls		
Transform All Button	Transforms the data displayed in the active viewport using the parameters specified on the parameter pages and the values of the processing parameters in the Basic Process region.	
Transform FID #	Enter a value corresponding a FID in an arrayed data set.	
Transform Size	Check the box and select a transform size from the drop down menu. The number of acquired points is shown below the drop down menu.	
More Processing – Parameter pages	Opens Default page of the Process tab.	
Basic Display		
Vertical Scaling buttons: Autoscale, (+), and (-).	Autoscale optimizes the display to utilize the available display area.	
	The (+), and (-) buttons increase or decrease the vertical scale by a factor of 2.	



Reference buttons

By Solvent	Use the standard chemical shift of the solvent as reference.
By TMS	Uses TMS at 0.0 PPM as the chemical shift reference.
Cancel	Cancels either of the above two choices.

Axis radio buttons

Hertz	Sets axis scale in Hz.
PPM	Sets axis scale in PPM.
kHz	Sets axis scale in kHz.

Display Mode radio buttons

Phased	Displays a phased spectrum.
Absval	Displays an absolute value spectrum.
Power	Displays a power spectrum.

More Display – Parameter Pages button — Opens Display page of the Process tab.

Opens Display page of the Process tab.

Basic Plotting buttons

Automatic Plot Uses current plotting parameters and plots to the current plotter.

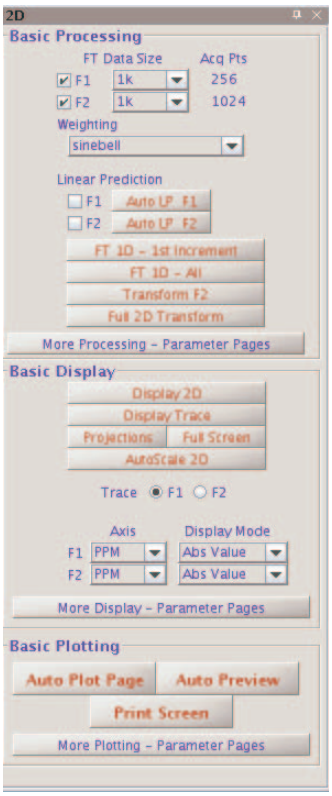
Auto Preview Same as Automatic plot but creates a PDF and starts a PDF reader.

Print Screen Prints the current screen to the current output device.

More Plotting – Parameter Pages button — Opens Plot page of the Process tab.

2D

Panel provides a reduced set of the full 2D process, display, and plot parameters available on the parameter pages of the process tab.

Control	*Description or Function*	*2D Vertical Panel*
Basic Process Controls		
F1 check box	Check box to make F1 FT Data Size dropdown menu active. Select the size of the F1 data set. F1 Acquired points are shown to the right of the menu.	
F2 check box	Check box to make F2 FT Data Size dropdown menu active. Select the size of the F2 data set. F2 Acquired points are shown to the right of the menu.	
Weighting	Select a weighting function from the dropdown menu.	
Linear Prediction	Click on either or both the Auto LP F1 and Auto LP F2 buttons to enable or disable linear prediction during data in process. Placing or removing a check mark from a box is the same as clicking on a button.	
Processing Buttons	Data is processed as stated on the button using the processing parameters in the Basic Processing frame and on the parameter pages.	

FT 1D - 1st Increment

FT 1D - All

Transform F2

Full 2D Transform

More Processing – Parameter Pages button

Opens the Default page of the Processing tab.

Basic Display

Display 2D	Displays a contour plot of the 2D data.
Display Trace	Displays a trace based on the Trace F1 F2 radio button selection.
Projections	
Full Screen	Display data using the full size of the active viewport.
AutoScale 2D	Sets tallest peak to the maximum color level, calculates the noise threshold, and optimizes the vertical scale.
Axis	F1 and F1 dropdown menus for selection of scale in PPM, Hz, or KHz.
Display move	F1 and F1 dropdown menus for selection Phased, Abs Value, or Power.

More Display – Parameter Pages button

Opens the Display page of the Processing tab.

Basic Plotting buttons

Automatic Plot Uses current plotting parameters and plots to the current plotter.

Auto Preview Same as Automatic plot but creates a PDF and starts a PDF reade.r

Print Screen Prints the current screen to the current output device.

More Plotting – Parameter Pages button

Opens Plot page of the Process tab.

16.10 Applications Directories

- "Applications Directories," page 404
- "Using the Applications Directories Interface," page 404

Applications Directories

VnmrJ application directories (`appdir`) are: `templates`, `maclib`, `manual`, `menulib`, `parlib`, `probes`, `seqlib`, `shims`, `tablib`, `shapelib`, `gshimlib`, and `mollib`. These are directories that VnmrJ uses during its normal operation. The `exists` command can search for other files and directories in the applications directories and provides users with flexibility to customize their applications. VnmrJ does not look for `expN` directories, `global`, `psg`, `psglib`, or other files or directories.

The `appdir` is an ordered list of paths to search for a specific item. Applications directories may be updated at any time. Operator specific applications directories are set when a new operator logs into the walkup interface.

Using the Applications Directories Interface

Applications directories interface is available to the user if the VnmrJ administrator has set permission to allow the user to edit the applications path. Users of the experimental interface have access permission by default. The system administrator, typically vnmr1, who has permission to set the system write permissions can set applications directories for all users. Individual users have permission to set and edit only their private applications directories.

1. Click on **Edit** on the main menu.
2. Select **Applications…**

   The Applications Directories interface opens, see Figure 115. The current applications directories are listed in the Application Directory fields. The label (default or user) for each directory is shown in the fields under Application Label.
3. Do one of the following for each application directory:
   - Click on the drop-down menu next to each applications directory and select one of the following:

     Enabled

     Disabled

     Remove(d)
   - Do nothing and keep the current setting.
4. Optional:

a. Add a custom applications directory by entering the full path in the Applications Directory path.

b. Enter an label in the field next to the new applications directory.

c. Click on the dropdown menu next to the applications directory and select one of the following:

Enabled

Disabled

Remove(d)

5. Click on one of the following radio buttons.
   - **Save as global** application directories (displayed only if the user has write permission to the system directory –typically this is the system administrator, vnmr1).
   - **Save as private** application directories.
   - Reset to **system default** application directories.
6. Click on **OK** to save or **Cancel** to exit without making any changes.

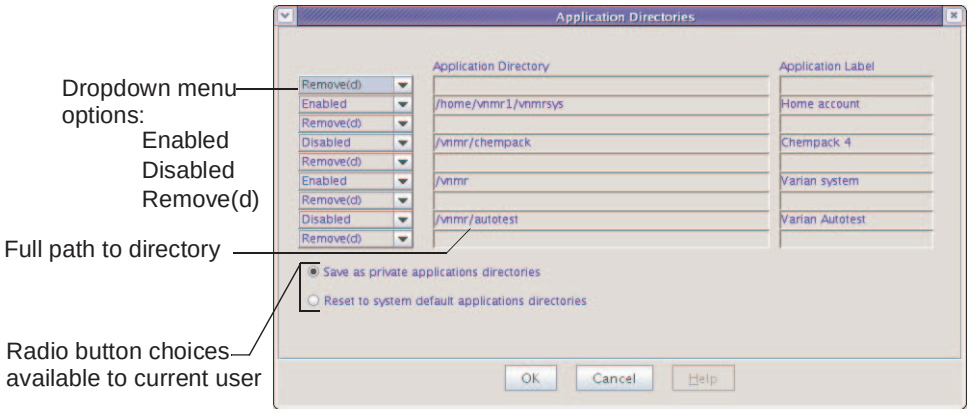


Figure 115. Applications Directories Interface for Users

16.11 Setting Colors in VnmrJ

- "Using Standard Styles and Themes," page 405
- "Creating, Editing, and Applying Styles and Themes," page 406
- "Deleting Styles and Themes," page 406

Using Standard Styles and Themes

Access the Styles and Themes window as follows:

1. Click on **Edit** on the main menu.
2. Click on the **Display Colors** tab to show the colors of the current color scheme; see Figure 116.

   Styles and themes supplied with VnmrJ are displayed in italics: *classic*, *default*, and *beach_house*.

3. Select a theme.
4. Click on **Load** to apply the theme.
5. Click on **Close** to exit the window or **Abandon** to exit and make no changes in the current display.

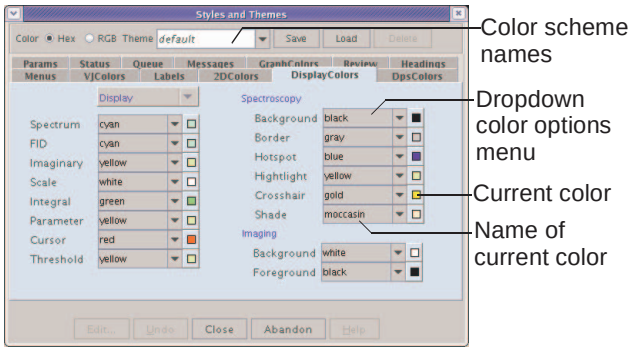


Figure 116. Setting Display Colors

Creating, Editing, and Applying Styles and Themes

1. Click on **Edit** on the main menu.
2. Click on the **Display Colors** tab to show the colors of the current color scheme, see Figure 116.
3. Do one of the following:
   - Enter a name in the color scheme field and click **Save**.
   - Select a theme to edit from the list of themes.

   Names of user defined styles and themes are listed in a bold regular type face.
4. Click on a radio button next to Color to show color definitions in either **Hex** or **RGB**.
5. Click on a tab and edit colors and type faces as required using the drop-down menus.
6. Click on **Save** to save the changes to the file named in the theme field.
7. Click on **Load** to load the new color scheme.
8. Click on **Close** to exit the window.

Deleting Styles and Themes

1. Click on **Edit** on the main menu.
2. Click on the **Display Colors** tab to show the colors of the current color scheme, see Figure 116.
3. Select a theme to delete from the list of themes.
4. Click on **Delete** to remove the theme.
5. Click on **Close** to exit the window.

Chapter 17. Locator and File Browser

Sections in this chapter:

- 17.1, “VJ Locator,” on page 407
- 17.3, “File Browser,” on page 413

17.1 VJ Locator

- "Locator Statements and Menu," page 408
- , “Using the Locator,” on page 410
- 17.2, “Locator Statements,” on page 411

The VJ Locator, Figure 117, is a database browser that provides access to data sets, experiments, shim sets, commands, etc.

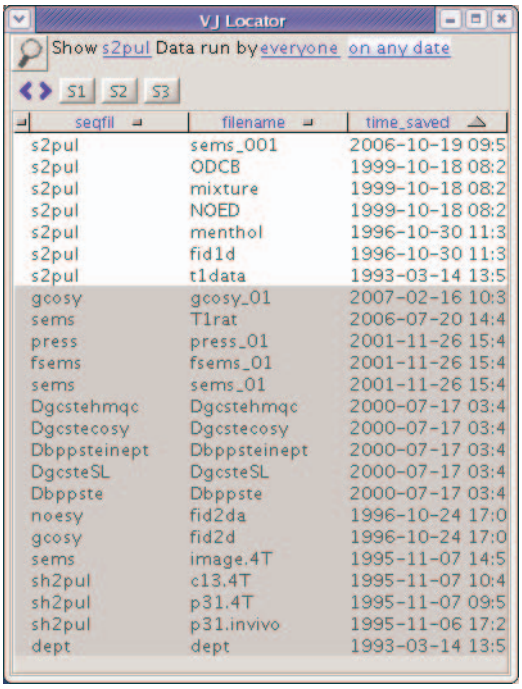


Figure 117. VJ Locator

The Locator provides fast access to information on all or part of the disk environment. The scope of the Locator’s actions is determined by the administrator.

The Locator works similar to a directory or file manager, uses minimal filtering of the information, and has lists of information. Three lists are shown in the Locator; they show when terms have a boolean relationship:

- Objects that meet all criteria
- Some of the boolean terms met
- Remaining objects

Which of these lists is shown is determined by the construction of the underlying Locator statement.

Within each list, the Locator displays three attributes for each object. The displayed attributes need not necessarily be those in the Locator statement. Any one of the attributes can be designated as the sort attribute, in which case the objects in each list are sorted by the value each has for this attribute.

Locator Statements and Menu

- "Locator Menu and Controls," page 408
- "Navigation in the Locator," page 409
- "Attributes, Attribute Lists, and Wildcards," page 409

Locator Menu and Controls

The magnifying glass and the current Locator statement is at the top of the VJ Locator window, as shown in Figure 118.

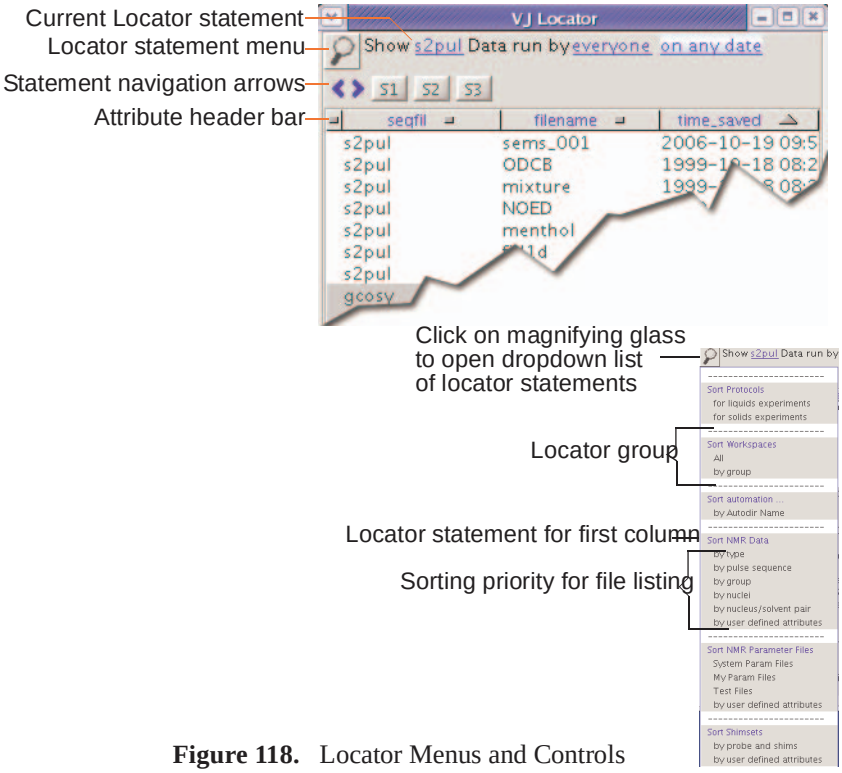


Figure 118. Locator Menus and Controls

Click on the magnifying glass to open a menu of currently available Locator statements. This menu includes both statements provided by Varian, Inc. and those customized and saved by the user.

Statements are Locator sentences in which a number of words or phrases are colored and underlined in a manner reminiscent of links in a web page. Each link hides a menu of choices, of which the currently displayed phrase is one. The choices available vary with the types of data currently known to the Locator.

Navigation in the Locator

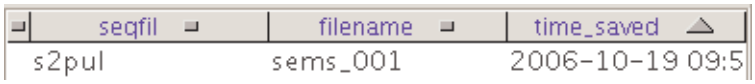
A pair of arrows (statement navigation arrows) below the Locator statement enables searching forward and back through past Locator operations, applying each to the current Locator environment. Thus a set of Locator statements can be rapidly applied in a changing environment.

Attributes, Attribute Lists, and Wildcards

- "Attributes," page 409
- "Attribute Lists," page 409
- "Wildcards," page 410
- "Configuration Files," page 410

Attributes

The Attribute Header bar is below the icons. This bar enables selection of the attributes displayed and arrangement of the objects in each list in a number of ways.



The boundaries between the attribute labels are adjustable. Place the mouse cursor on the boundary to adjust. When the adjust cursor appears, click and drag the boundary to its new position, and release.

Objects in the Locator are available for a number of actions. Currently, a single click selects an object. The selected object can then be dragged to another part of VnmrJ, in which case the action taken will depend on the type of object and where the object is dropped. Alternatively, a double click on an object will cause the most likely action to occur. These actions are discussed below.

The value of an attribute might be longer than the width of the column in the Locator. When the mouse cursor rests on an attribute value, a tool tip appears for a period of time. The tool tip contains the full value of the attribute.

Attribute Lists

The list of attributes in the dropdown lists are controlled by configuration files. There are three file names, for three different types of items in the locator. These are:

- shuffler_param_list for 'vnmr data' and 'vnmr parameter' files
- study_param_list for 'study' items
- data protocol_param_list for 'protocol' items

Each of these can exist for each of the appmode types and for individual users. That is, appmode types of 'imaging', 'standard' (experimental liquids and solids) and 'walkup'. The attributes visible in the dropdown menu for each appmode type will be controlled by files

in the appropriate directories. If a user does not have an individual file, the file in the appropriate appmode directories will be used. If there is no file in the imaging or walkup directories listed above, then the file in `/vnmr/shuffler` will be used. If users have their own individual files, the attributes listed must also be in the appmode directory file. That is, a user's files can limit attributes shown, but cannot add to the list of attributes shown beyond the attributes in the system files.

Wildcards

Wildcards can be used in attribute values, but not for the attribute name itself. For example, `'file*'` to specify the autoboot `'filename'` is not allowed. Selecting an attribute of `'filename'`, then editing the selection value to be `'p31*'` to show all files whose names start with `'p31'`.`'?31*'` shows all file starting with any single character followed by `'31'`, followed by `0` or more characters. The leading `'?'` would allow upper or lower case `'P'` as well as any other character. This does not apply to dates.

The following wildcards can be used:

- `'*'` or `'%'` can be used to match any number of characters
- `'?'` or `'_'` can be used to match any single character

Configuration Files

Configuration files for the locator are contained in the following directories for the different appmode types:

Interface	*Directory*
Standard (experimental)	`/vnmr/shuffler`
Imaging	`/vnmr/imaging/shuffler`
Walkup	`/vnmr/walkup/shuffler`
Individual users	`$vnmruser/shuffler`

Using the Locator

Use the mouse to select or drag-and-drop items in the Locator interface.

- "Searches," page 410
- "Dragging and Dropping Items from the Locator," page 411
- "Editing File Names from the Locator," page 411
- "Configuration Files," page 410

Searches

Clicking the magnifying glass with the left mouse button brings up a menu of searches. Selecting one changes the *search sentence* displayed at the top of the Locator. The results of the search are displayed in the list. Those items in the white part of the list satisfy the search sentence. Those in the gray part do not. For each item that is found by the search, three attributes are displayed. These correspond to the three columns in the list. Clicking on the attribute name at the top of the list with the left mouse button brings up a menu of attribute choices.

Dragging and Dropping Items from the Locator

Clicking on an item in the Locator list selects that item. That item can then be dragged to the graphic area or the parameter panel area to cause the appropriate action. For example, dragging a data set to the graphic area retrieves that data set into the current workspace (experiment) and (optionally) displays the spectrum. Dragging a workspace to the graphic area selects that workspace (experiment). Dragging on an object causes the most likely action to occur.

An item can be dragged from the Locator and dropped into the holding pen. The item is then available for further selection no matter what Locator statements are active. One such example might be to use the Locator to inspect the available shim sets. Select the current best set and put this into the holding pen. This set of shims is then immediately available.

Dragging and dropping an item has an action appropriate to the context. In many cases the same effect can be obtained by double-clicking on an object. Some examples are:

- Drag a protocol experiment into the graphics canvas to load the experiment.
- Drag a FID from NMR data to retrieve the FID. The process macro can also be invoked so that the FID is transformed.
- Double click a workspace to join that workspace. Dragging and dropping a workspace into the graphics area also joins the workspace (`jexp`).
- Double click a parameter set to load that set in the current workspace, or drag and drop a parameter set.
- Double click a shim set to load the shims. Dragging and dropping a shim set to the current shim buttons also loads the shims into acquisition.
- Drag either data or shims and drop them in the trash can (in the lower left portion of the hardware bar) to move the item to the trash can. Retrieve an object from the trash can by double-clicking on the trash can, selecting it, and then clicking the **Restore items** button.

Editing File Names from the Locator

A new file added to the locator from within VnmrJ appears in its appropriate spot in the Locator, and it appears in green at the top of the locator window. If one of the columns in the Locator is *filename*, click on the green file name to change it.

Change the file name, press Return or click on another line to remove the old name from the Locator and add the new one. The Locator redisplays to show the new name.

17.2 Locator Statements

Varian supplies a number of Locator statements with VnmrJ. Add to or edit these statements in the following ways:

- Save the current Locator statement by clicking on **Tools** in the main menu, then **Save Custom Locator Statement**. Enter a name for the statement in the Custom Locator Statement popup window.
- Click on **Tools**, then **Delete Custom Locator Statement** to delete a Locator statement. A Custom Locator Statement Removal window appears. Select the statement from the list in the window, then click on **Delete** to remove it or **Cancel** to exit the window without removing the statement.

- Sort **Protocols Entries** shows the known protocol experiments. Double click on the protocol to execute the associated macro.

Locator statements are defined in a file named:
`locator_statements_default.xml`.
This file can reside in the system `appmode` directories (see "Configuration Files," page 410), but not in users' individual directories.

Editable Fields

Click the right mouse button on the blue and underlined items in the locator statements to show a menu of choices, and edit by clicking on them with the left mouse button. Left-clicking puts an editing cursor on the item. Place the cursor at the point to be edited and click the left mouse button. Edit the field, then press Return to cause a new locator search using this edited value.

Sorting Locator Statements

Sort Locator items as follows:

- "Sort Workspaces," page 412
- "Sort NMR Data," page 412
- "Sort NMR Parameter Files," page 413
- "Sort Shimsets," page 413
- "Sort Command Macros," page 413

Sort Workspaces

Sort all workspace in numeric order. Double click on a workspace to join the workspace.

Sort NMR Data

Entries show the known NMR data sets, but differ in the actual format of the statement as well as the initial set of attributes shown. The most comprehensive statement is the last one, **by user defined attributes and date** (this is also the one least likely to be used, but it is discussed here to explore the scope of the data statements).

The generic statement is shown in Figure 119.

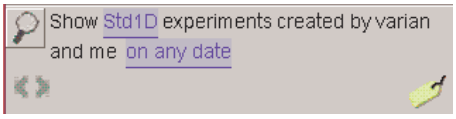


Figure 119. Generic Locator Statement

There are two separate underlined choices in this statement: `Std1D` and `on any date`.

Click on either of the underlined phrases to produce a dropdown menu of the choices in this position. The menus are environment sensitive so they will not display choices that do not exist.

The logic of this statement is of the form:

Show attributes A and B of type C with additional limitations.

First, the additional limitations phrases enables selection of the owner of the data. Currently this selection is determined by the administrator at the time a directory is made available to the Locator. In in the future, it will become a more rich criterion.

Second, the additional limitations enables reordering by date. There are various dates associated with data, for example, the time started or the time saved. Specify these date fields in any of several ways, for example, since a certain date, by changing **on any date** to **since**.

Alter the date by using the left or right arrows to decrease or increase the date by one day with each click.

All other statements supplied are simpler than the generic one. Promote statements used frequently to the top of the menu by saving them again as your local variants.

Sort NMR Parameter Files

The statements in this category show the list of NMR parameter sets. One major category of parameter set is **My Param Files**. Select the statements **Test Files** and **by user defined attributes** to do other selective searches. The Locator statement changes after selecting a category, e.g., Test Files.

Sort Shimsets

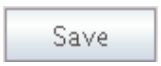
The statements in this category enables access to the saved shim sets. Note that the shim sets can be saved with a descriptive shim name provided by when using the Save Shims button in the Shim panel.

Sort Command Macros

The generic statement in this category enables finding a VnmrJ command or macro based on its attributes. The Locator enables reordering commands and macros by a number of attributes. Find the command to use and double click to execute it.

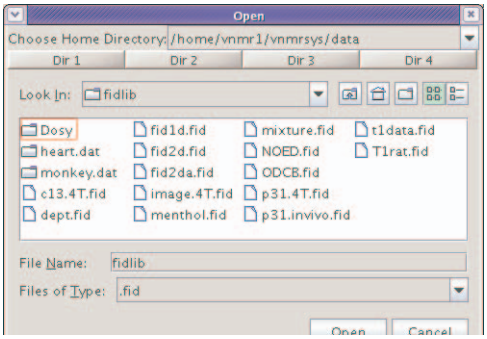
17.3 File Browser

File Browser Buttons and Drop Down Menus

Button	*Description*
	Go up one level in the directory tree.
	Go to user's home directory.
	Make a new folder in the current directory.
	Show list of files and directories at the current directory level.
	Show details of files and directories at the current directory level.
	Open selected file. Load into current experiment if it is a VnmrJ data file, sequence, or parameter set.
	Save file with the name shown in the **File Name:** field using the extension shown in the **Files of Type:** field.
	Cancel selection and close the file browser.

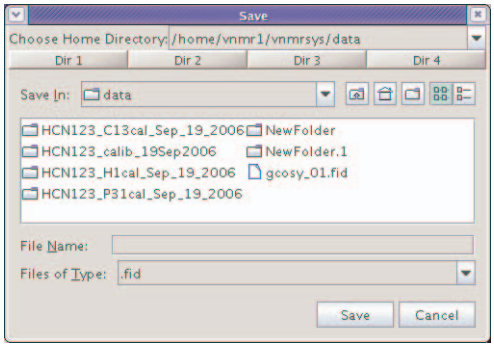
Open a File

1. Click on **File**.
2. Select **Open** to open the file navigation window to locate the required file.
3. Click the **file** and click on the **Open** button .



Save a File

1. Click on File.
2. Select **Save as…** to open the file navigation window to locate the required directory.
3. Enter a **file name** in the Save as field and click **OK** to save.



Appendix A. Variable Temperature System

Sections in this chapter:

- A.1 “VT Setup,” this page
- A.2 “VT Startup,” this page
- A.3 “Temperature Array,” page 416
- A.4 “Operating Considerations,” page 416
- A.5 “VT Error Handling,” page 418
- A.6 “VT Controller Safety Circuits,” page 419

This chapter describes startup and operation of the optional variable temperature (VT) unit. A VT unit is available for Varian, Inc. NMR spectrometers to vary the sample temperature. A thermocouple senses the temperature, which the VT controller continuously displays on the front panel. The controller compares the user-requested value with the current probe temperature and changes the heater current accordingly. The VT controller then reports the temperature of the gas flow and status to the spectrometer through a serial port at the rear of the console.

A.1 VT Setup

Use the System Settings window to configure the spectrometer for the VT accessory and to enter a variable temperature cutoff value. The variable temperature cutoff (Edit->System settings: VT cutoff) determines the temperature below which the gas is cooled.

1. Open the **System Configuration** window (Edit->System settings->System config) if the VT controller is off and it cannot be turned on.
2. Check that the VT Controller label is set to **Present**.
3. Open the **System settings** window (Edit->System settings) and enter an appropriate value for **VT cutoff** and click OK.

   Set the VT cutoff to a temperature near the ambient VT gas temperature (normally VT cutoff is correct and need not be changed). Based upon the value of VT cutoff compared to the entered temperature, the system routes the VT gas flow for either heating or cooling.

A.2 VT Startup

The VT hardware must be installed and calibrated as described in the *VT Accessory Installation* manual. Starting up the VT unit takes the following steps:

1. Turn it on with the unit power switch if the VT unit is off.

2. Reset the VT controller if the system power has been off or the VT unit has been disconnected from the probe by pressing the **POWER** switch to turn the unit OFF, then press **POWER** again to turn it ON. The VT controller also can be reset with the **Reset VT** button on the Spin/Temp page in the Start folder.

CAUTION: **Use either dry nitrogen gas or air for VT and probe operation. A mixture of nitrogen gas and air can cause spikes in the baseline adjacent to the large peaks in the spectra. The use of air as the VT gas is not recommended for temperatures above 100°C. Such use will destructively oxidize the heater element and the thermocouple.**

3. Use dry nitrogen gas if the requested temperature is over 100°C or below the dew point or 0° C, whichever is higher. Otherwise, air may be used as the VT gas. If the requested temperature is below –40°C, dry nitrogen gas is recommended for cooling the bearing, spinner, and decoupler. This prevents moisture condensation in the probe and spinner housing.

   The source of heating or cooling gas is not automatically selected. To use nitrogen, attach a nitrogen gas source to the VT system. The same is true when using air. The VT system only selects the routing of the gas flow.

4. Use the flow control meter on the magnet leg to adjust the flow to about 10 LPM (as shown on the flow gauge).

5. A sample that can be handled at ambient temperature can now be placed in the probe, NMR lock obtained, and field homogeneity adjusted. Samples that cannot be handled at ambient temperature should wait until the system reaches the requested temperature.

A.3 Temperature Array

Set, if the temperature is an array, a pre acquisition delay that allows sufficient time for the sample to equilibrate after a temperature change. The system will then wait the specified delay between each temperature before starting data acquisition. Delays of several minutes are optimum because the sample will take longer to equilibrate than it takes the VT controller to stabilize the heating/cooling gas at the set point.

1. Open the **Acquire** folder, select the **Acquire** page, and click the **Arrays** button. The Array Parameter window opens.
2. Click **New Array** and enter **temp** in the Param Name column.
3. Specify Array Size, First Value, Increment, and Last Value.
4. Click **Close**.
5. Set the preacquisition delay in the Flags page under the Acquire folder.:

   ```
   Delay __ sec before starting (for VT etc.)
   ```

A.4 Operating Considerations

The following recommendations should help achieve better VT performance.

- The spectrometer system was designed and tested with a VT gas flow rate of about 10 – 15 LPM. Sizable deviation from this rate can result in significant inaccuracy in temperature calibration and reduce the attainable temperature limits.

- Initial cooldown of the exchanger and transfer tubing after the coolant is added increases the initial time required to reach regulation (about 5 to 10 minutes for –40°C with liquid nitrogen). Because this may be longer than the `vtwait` parameter, a `su` command is the best way to start up.
- Below –40° use dry nitrogen gas for the spinner and bearing air supply to avoid moisture and frost buildup on the spinner housing and turbine. Should this happen, the sample spinning can become erratic or stop altogether.
- Every sample has some vertical temperature gradient. Minimize the gradient by *not* filling the sample tube more than about 25 to 32 mm (1 to 1.25 in.), by inserting a vortex plug or glass wool plug in the tube just above the sample solution, and by entering the liquid column to the probe coil center lines. The plug reduces refluxing of the solvent in the upper portion of the tube. Any mass movement, such as refluxing or convection, can seriously degrade resolution and lock stability.
- Above 100°C, use dry nitrogen gas to reduce heater and thermocouple oxidation.
- High-power decoupling adds heat to the sample. The increase in temperature depends on the dielectric of the solution and the power level. Under these conditions, the temperature accuracy under VT control is significantly affected. If necessary, reduce decoupler power and use a more efficient decoupling mode.
- Overnight or long-term unattended VT operation at low temperatures is hampered by the fact that the usual coolant, liquid nitrogen, provides only about 1 to 2 hours of operation on a single fill of the coolant bucket. Some other coolant that lasts longer can be used if the operating temperature does not require the low temperature of liquid nitrogen. A common alternative is a mixture of dry ice and acetone. Another option is a fluid such as isopropyl alcohol or ethylene glycol cooled indirectly by a refrigerating device. Do not use aromatic, ketone, and chlorinated solvents (including acetone) in the coolant bucket. Such coolant media attack the standard polystyrene bucket.
- The ability of the VT unit to achieve temperature stability is directly affected by the stability of the room temperature. The VT unit compensates for about 80% of external changes (leaving 20% uncompensated for). Thus if the temperature of the room changes by 1°, the sample temperature will change by about 0.2°, which will not be reflected in a change in the numerically displayed temperature. For best results, the room temperature should be made as stable as possible. Any cycling of the temperature due to air conditioning or heating should be limited to the shortest possible cycle time and the minimum possible temperature variation.
- High stability and independence from room temperature can be achieved if the VT controller is equipped with an optional cold junction (CJ) compensator. With the high-stability feature, the VT controller is no longer compensated for room temperature changes, but instead receives its reference from the cold junction device. The influences of the VT gas supply become more apparent as the CJ compensator reduces the room temperature influences on the system. The flow and temperature of the VT gas supply must be as stable as possible for optimum performance of the CJ compensator.
- A possible setup to help stabilize the VT gas supply is to run the VT gas through a heat-exchanger coil in a water bath at a regulated temperature. For best results, use an ice bath to cool down the VT gas to between 5°C and 10°C, and keep the flow as stable as possible for experiments below 40°C. Generally, the VT gas supply temperature should be a minimum of 10°C below the set temperature for best performance of the VT controller and heater in the probe.
- A temperature calibration curve must be made for each probe used for exact determination of sample temperature. All data, such as gas flow, must be noted.

Samples of ethylene glycol are used for high-temperature calibration, and samples of methanol are used for low-temperature calibration.

a. Obtain a spectrum after bringing the sample to the desired temperature and allowing sufficient time for equilibration, .

b. Display two cursors and align them on the two resonances in the spectrum.

c. Enter `tempcal('e')` if the sample is ethylene glycol; if the sample is methanol, enter `tempcal('m')`.

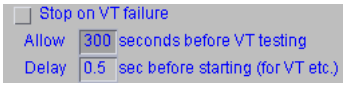
d. The temperature is calculated and displayed based on the difference in frequency between the cursors.

A.5 VT Error Handling

Select how VT errors are handled in the Spin/Temp page under the Start folder.

Interlock selections
(Start folder, Spin/Temp page)

Wait setting
(Acquire folder, Flags page)



Abort after temperature error	The VT regulation light is monitored during the course of the experiment, and if it starts to flash (regulation lost), the current data acquisition is stopped. The acquisition does not resume automatically if regulation is regained. With Abort selected, a maximum limit is imposed on the time that the system waits for regulation to be established. This limit is determined by the wait before testing setting and is independent of the delay setting. If regulation is not established after the wait time (normally set to 180 seconds), the system displays the message `VT FAILURE` and does not proceed with the experiment. If the regulation problem is later corrected, the experiment can be resumed.
Warn after temperature error	The VT regulation light is monitored during the course of the experiment, and if it starts to flash (regulation lost), a warning is generated but acquisition is not stopped.
Ignore temperature error	The temperature interlock feature is turned off.

The temperature interlock selections (Abort, Warn, or Ignore) and VT wait time (Acquire folder, Flag page) check VT operation and stop the experiment if temperature regulation is lost.

The lost regulation causes error processing to occur for both the Abort and Warn selections, thus providing a user-selectable mechanism to respond to VT failure.

The interlock operation does not apply when VT regulation is temporarily lost as a result of a programmed temperature change in an experiment where temperature is an array. The VT gas flow has no sensor or interlock. The heater is protected, if gas flow stops, by an internal temperature limit sensor that turns off the heater current before the element overheats. Any experiment in progress is stopped if Abort is selected because a loss of gas flow will result in a loss of regulation,. Only the sample is left unprotected if VT gas stops.

CAUTION: **Do not run unattended a sealed sample of highly volatile materials that must be kept cold to avoid excessive pressure buildup. The undetected loss of VT gas or exchanger coolant could result in the rupture of the sample tube and damage to the probe components.**

A.6 VT Controller Safety Circuits

The VT controller includes safety circuits to avoid damage to the heating element and probe. The following error conditions produce an error code:

- Open circuit in the thermocouple circuit.
- Open circuit, short circuit, or over-temperature at safety sensor.
- Short circuit or software/microprocessor failure at the output transistor.

Over-temperature at the safety sensor initially turns off the heater. If this method fails to correct the condition within 5 seconds, either the gas flow has been interrupted or an output transistor failure has occurred, whereupon a protective relay operates, isolating the heater from the control electronics. Failure of any of the sensors also results in this relay operating.

Once the protective relay has operated, the output will remain off. A power-down and power-up cycle of the VT controller is required to release the relay.

The over-temperature circuit can be inadvertently tripped if the VT is started at a below ambient temperature and the temperature is increased greater than 70°C. If the circuit is tripped, reset it by turning the VT off and on, then change to the desired temperature in 50°C steps.

Excessive heat requirements that cause the current to remain near the maximum can also trip the second circuit. Therefore, when using liquid nitrogen for cooling and when operating from 0°C through +25°C, reduce the gas flow rate to between 8 and 9 LPM. Reset will also occur if the VT cable is removed from the probe while the VT is on.

Refer to the *VT Accessory Installation* manual for system failure analysis.

Appendix B. Shimming Basics

Sections in this appendix:

- B.1 “What are Shims?,” this page
- B.2 “Shim Interactions,” page 422
- B.3 “Autoshim Information,” page 428
- B.4 “Homogeneity Commands and Parameter,” page 434

B.1 What are Shims?

Shims are a set of coils inside the magnet that induce changes in the shape of the magnetic field. Each shim produces a specific change in the magnetic field that can be easily shown. The approximate shapes of the axial gradients (spinning shims) are shown in Figure 120 to provide a visual reference for the interactions of the shims,.

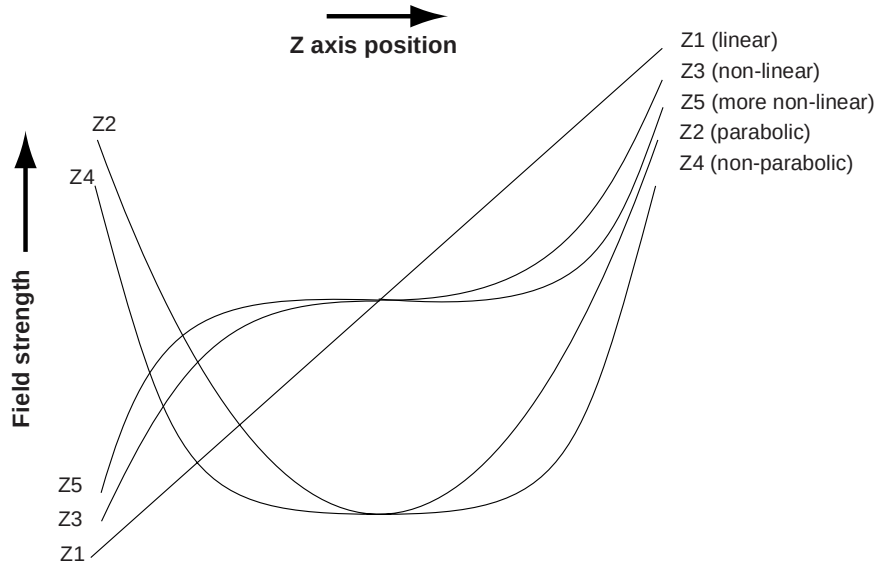


Figure 120. Approximate Shape of Axial Gradients

Understanding the effect of various shims on symmetry of the resonance is important in simplifying the shimming process. The following two points must be considered:

- The effect of a given shim on the spectral lineshape.
- How the shims interact with each other.

Understanding how the shims interact is critical to simplifying the task of shimming. Pure shim gradients produce a very specific and predictable effect on the magnetic field and, to a lesser extent, on the resonance lineshape.

B.2 Shim Interactions

The following sections show theoretically predicted changes in lineshape caused by changes in shim DAC values. Shim sets with pure shims, such as the Varian Ultra•nmr shims, follow the theoretically predicted response very closely. Other shim systems, with more interactions between shims, produce somewhat different results.

- "Theoretically Perfect Lineshape and Effect of Z1 Shim," page 422
- "Effects of Even-Order Shims Z2 and Z4," page 423
- "Effects of Odd-Order Shims Z3 and Z5," page 425
- "Effects of Improperly Adjusted Shims," page 426
- "Effects of Non-Spin Shims," page 427
- "Summary of Shim Interactions," page 428

Theoretically Perfect Lineshape and Effect of Z1 Shim

Figure 121 shows a theoretically perfect lineshape (at left) produced in a perfectly homogeneous field (at right). The magnetic field shape appears as a flat line, indicating that the magnetic field does not change across the length of the sample.

Figure 122 shows how changing the linear shim Z1 affects the lineshape and the magnetic field.

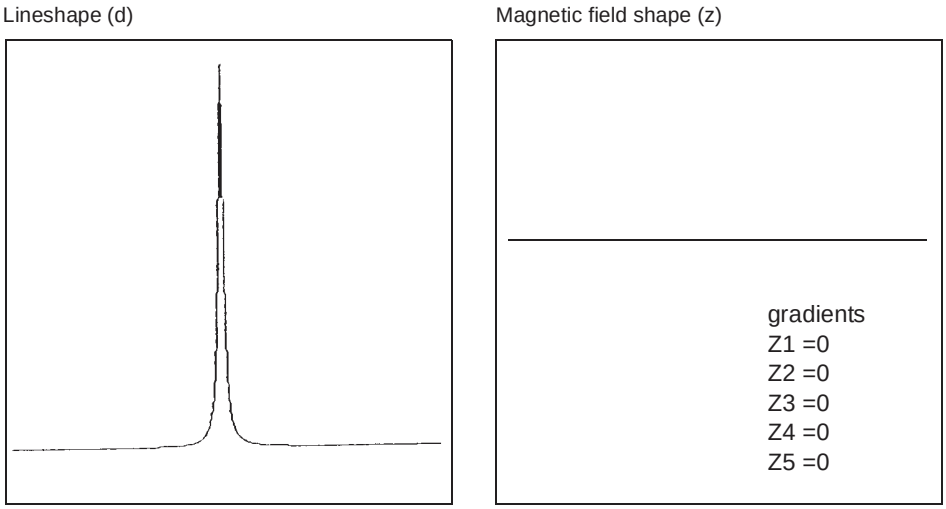


Figure 121. Theoretically Perfect Lineshape

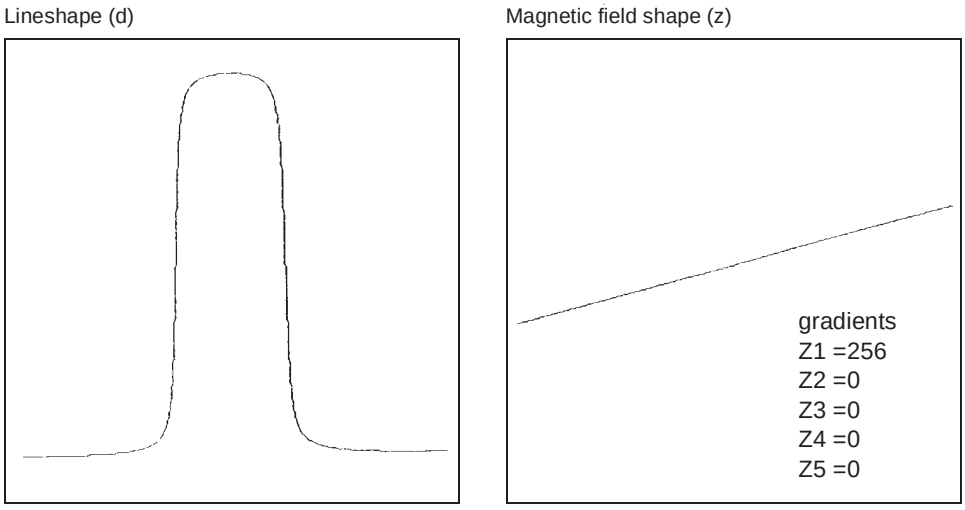


Figure 122. Effects of Linear Shim Z1

Effects of Even-Order Shims Z2 and Z4

Figure 123 shows the effect of the even-order shims, Z2 and Z4, on the lineshape. Notice that a positive misadjustment of both shims produces an upfield tail on the peak. If Z2 and Z4 are misadjusted in the negative direction, the asymmetry occurs on the downfield side of the peak. The difference between Z2 and Z4 is in the height of the asymmetry. The Z2 shim causes asymmetry higher on the peak than Z4.

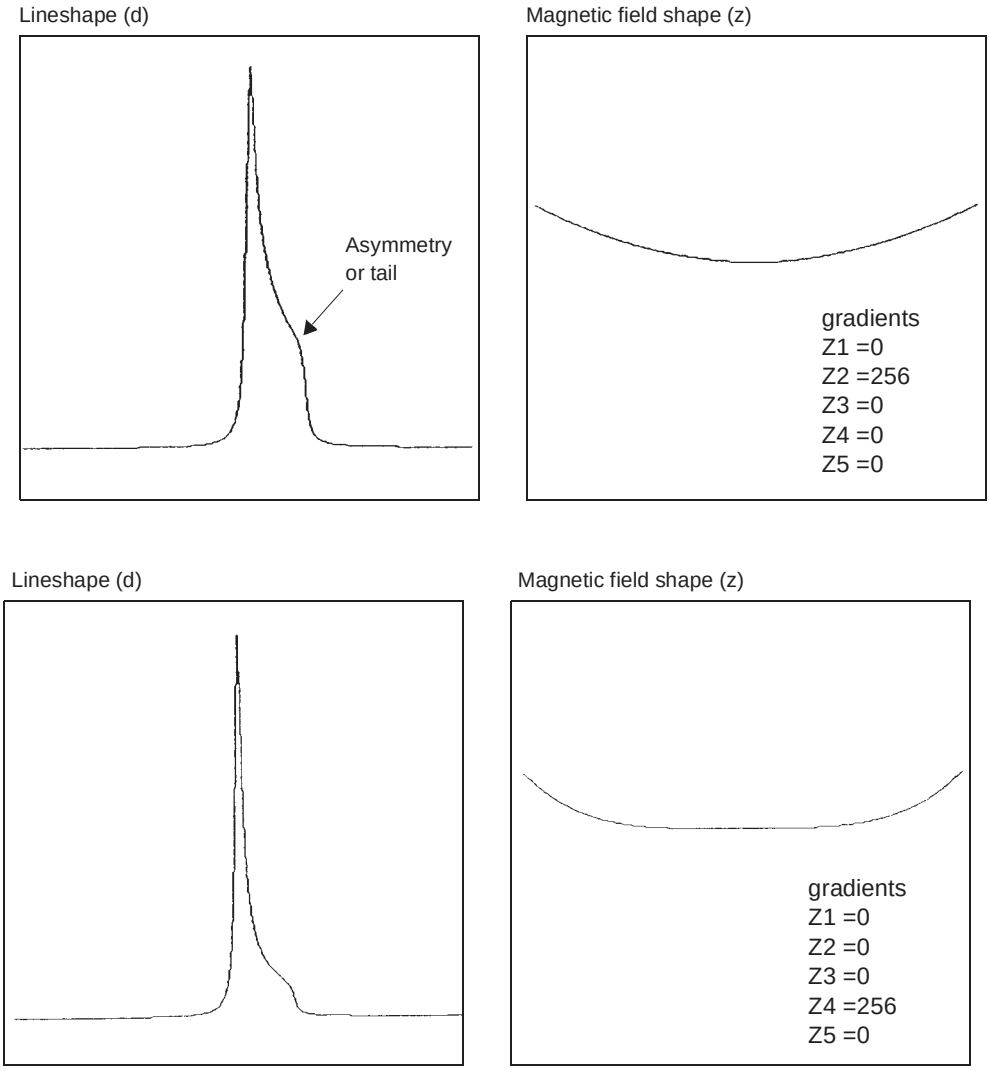


Figure 123. Effects of Even Order (Parabolic) Shims Z2 and Z4

Effects of Odd-Order Shims Z3 and Z5

Figure 124 shows the effects of the odd-order shims Z3 and Z5 on the lineshape. The odd-order shims cause broadening of the peak and therefore affect resolution.The Z5 shim is unavailable on systems with 13-channel shim sets (`shimset=1`).

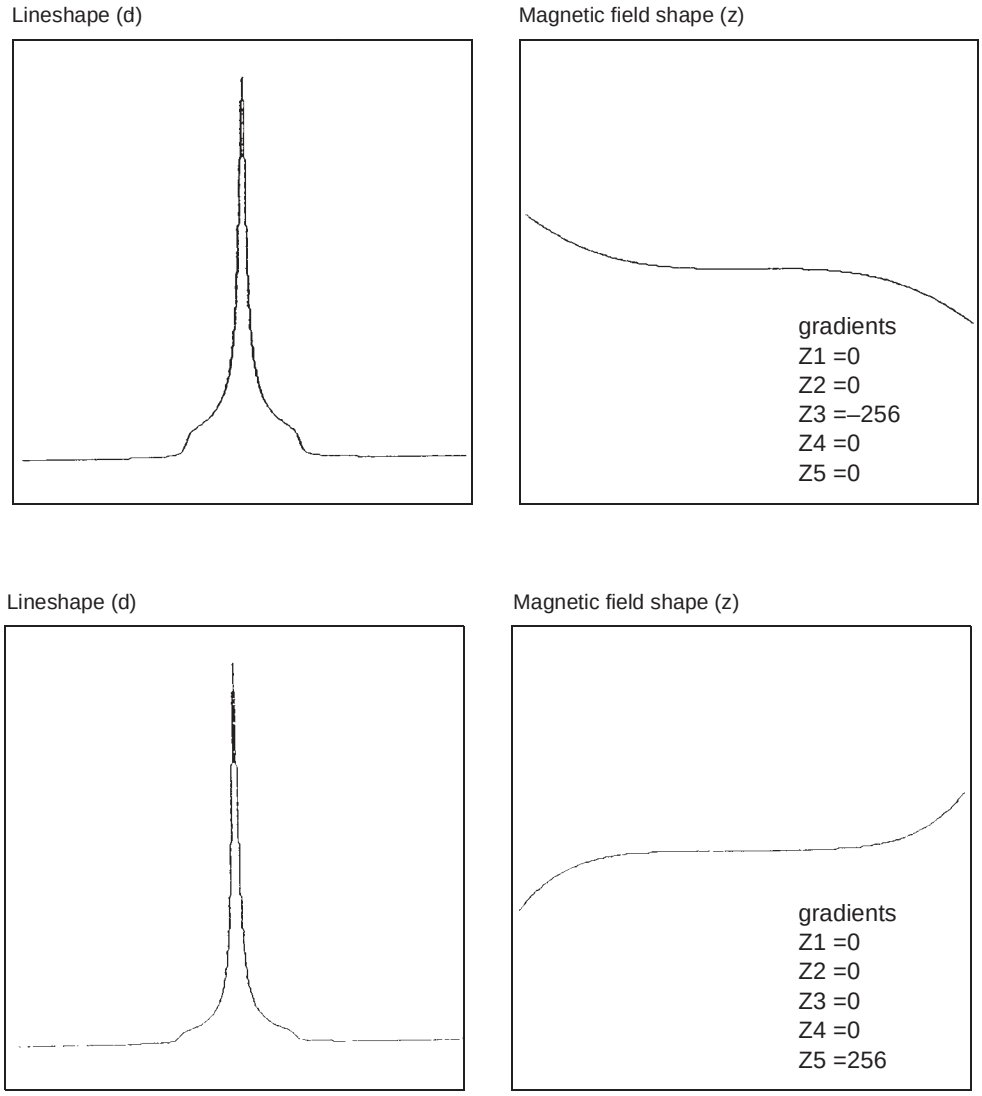


Figure 124. Effect of Odd Order (Non-Linear) Shims Z3 and Z5

Effects of Improperly Adjusted Shims

Figure 125 shows two examples of the effects when more than one shim is improperly adjusted. This is the typical case with real samples. The complex lineshapes make simple visual analysis difficult. A procedure for correcting the shims that can be used as a guide when adjusting shims is provided later in this section.

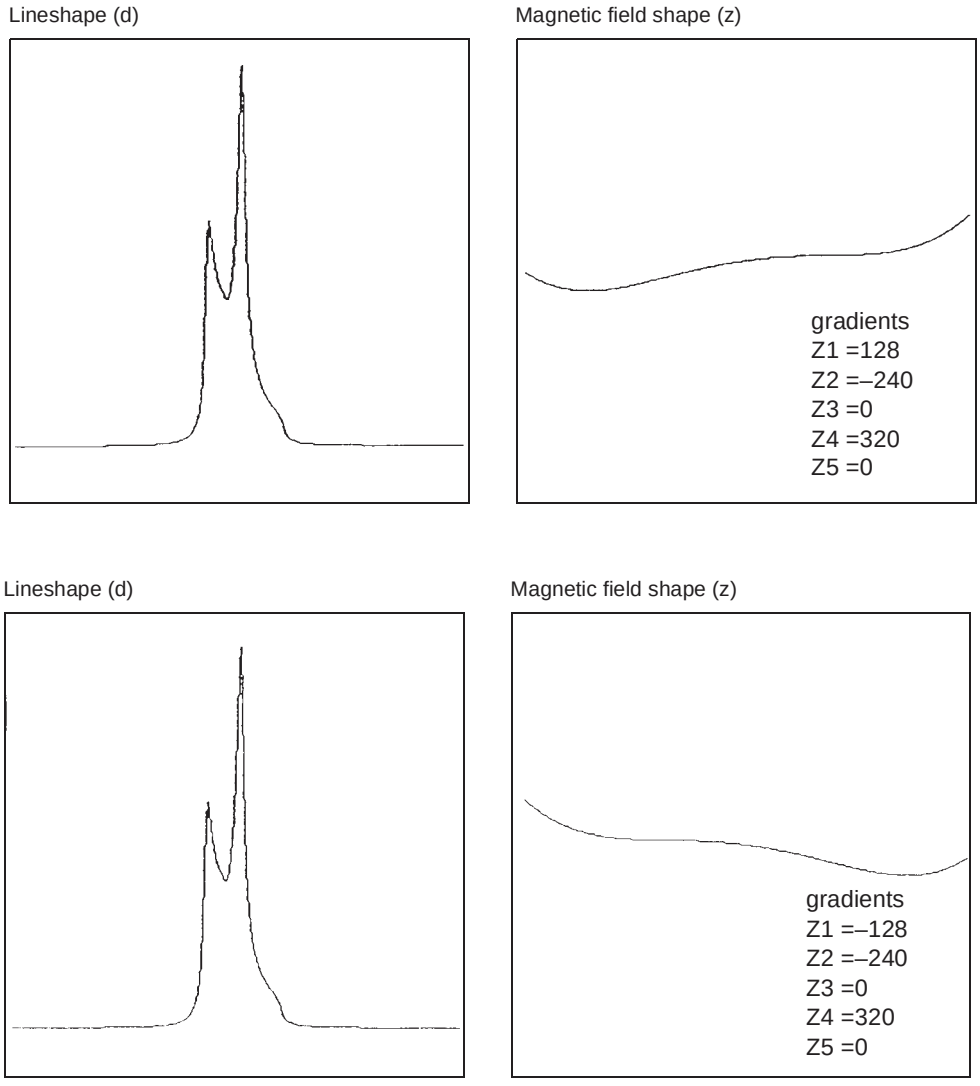


Figure 125. Effects of Misadjusted Shims

Effects of Non-Spin Shims

Figure 126 shows the effect of the non-spin shims on the spectrum (note that Z3X and Z3Y are not available on 13- or 14-channel shim systems). If set wrong, the first-order non-spin shims (X, Y, ZX, and ZY) can cause first-order spinning sidebands. XY and X2–Y2 can cause second-order spinning sidebands. High-order non-spin shims can cause a broad peak base.

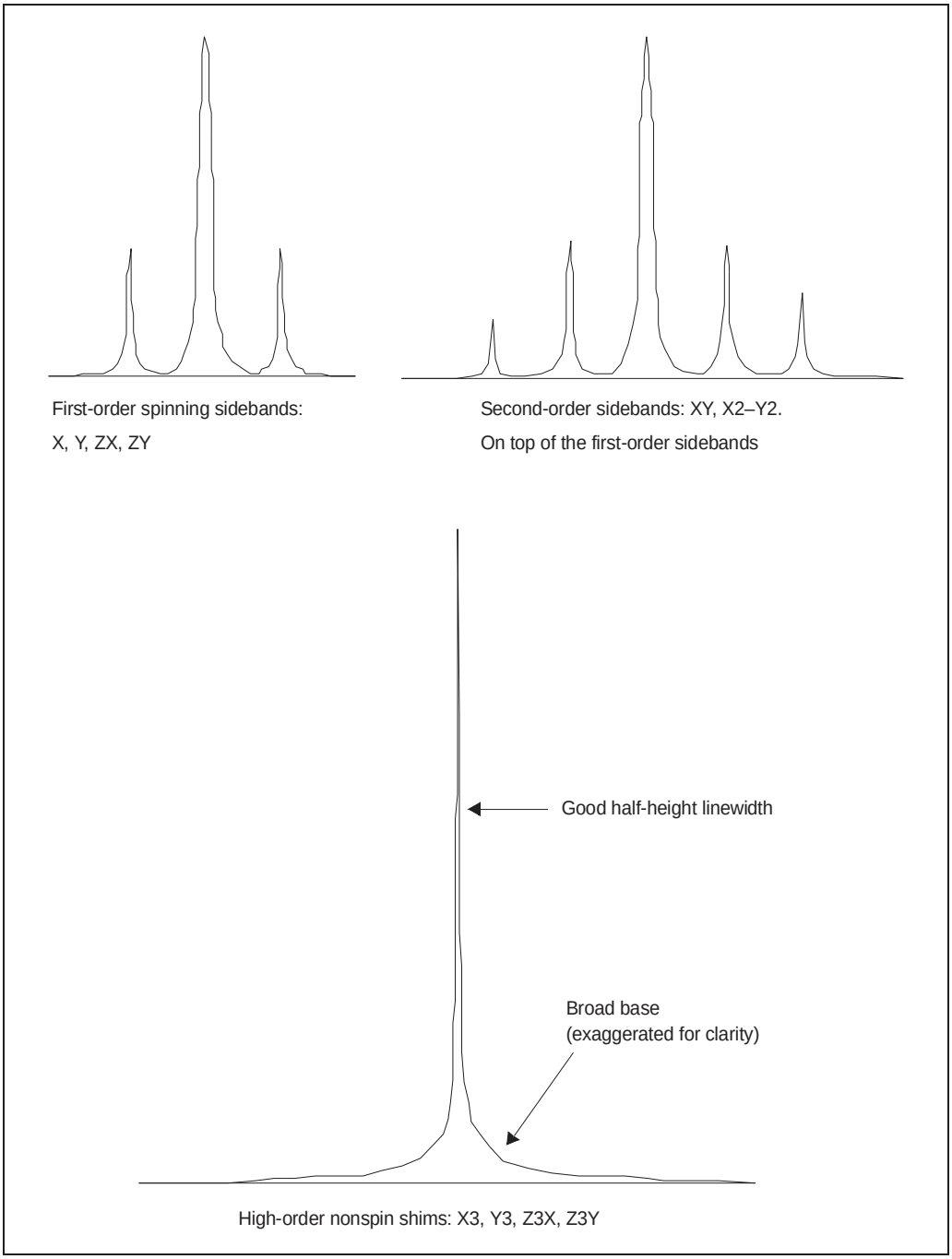


Figure 126. Effects of Nonspin Shims

Summary of Shim Interactions

Table 42 lists some lineshape effects associated with shims. Note that 13-channel shim systems (`shimset=1`) do not have Z5, Z3X, ZXY, etc., and that 14-channel shim systems (`shimset=10`) have Z5 but do not have Z3X, ZXY, etc.

Table 42. Lineshape Effects and Their Associated Shims

Lineshape Effect	*Shims*
Split peak	Z4 and Z1
Asymmetry greater than half-way up	Z2
Asymmetric foot	Z4
Symmetric feet and or low broad base	Z5
Symmetrically broad base	Z3
Spinning sidebands	Low-order radials X1, Y1
Symmetric broad base	High-order radials X3, Y3, etc.

Typical interactions for axial shims:

- Z1 and all other axial shims, to some extent
- Z2 and Z1
- Z3 and Z1
- Z4 and Z2 (with large delta Z4s: Z4 and Z3)
- Z5 and both Z3 and Z1 (Z5 not available on 13-channel shim systems)

B.3 Autoshim Information

- "Background Autoshim," page 429
- "Hardware Autoshim," page 428
- "Shimming Criteria for Background Autoshim," page 430
- "Shim Methods for Autoshim," page 430
- "User-Defined Shim Methods for Autoshim," page 432

Gradient autoshimming is the preferred method for shimming. There are other (slower) methods that use the lock signal. These methods are Hardware and Background Autoshim.

Hardware Autoshim

Hardware autoshim methods vary according to which system is involved. They are used primarily to maintain a well-shimmed homogeneity over long runs.

The `hdwshim` parameter enables the commands `go`, `ga`, or `au` to turn on and off "hardware" autoshimming, which is done using a software emulation of hardware autoshim. Shimming is active only while a pulse sequence is executing:

- `hdwshim='y'`: shimming is active only during the first delay of the pulse sequence.
- `hdwshim='p'`: shimming is active only during the first presaturation pulse, defined as a change in power level followed by a pulse (e.g., `presat.c`).

Shimming during subsequent delays or presaturation pulses can be activated by using the `hdwshiminit()` statement before the delay or presaturation pulse. Shimming uses the `z1` shim by default.

If the parameter `hdwshimlist` is created, shimming uses the specified list of shims to shim on. Only the following shims are allowed:

`z1, z1c, z2, z2c, x1, y1`

Shimming is done in the order of `z1`, `z1c`, `z2`, `z2c`, `x1`, `y1`, regardless of the order in which the shims are used in `hdwshimlist`, and is performed on each shim in intervals of 20 seconds. The fine shims (`z1`, `z2`, `x1`, and `y1`) are recommended for routine use.

Using the Input Window

- Enter **`hdwshim='y' su`**
  Hardware shimming starts at the next acquisition during the first delay and stops when acquisition is complete.
- Enter **`hdwshim='p' su`**.
  Hardware shimming starts at the next acquisition during the first presaturation pulse, and stops when acquisition is complete.
- Enter **`hdwshim='n'`** `su` to turn off hardware shimming.

Background Autoshim

Background Autoshim is controlled by the parameter `method` and the command `shim`. This is a complete background Autoshim method that provides no interaction with the operator. The type of automatic shimming to be done during routine sample changes depends on the level of homogeneity required on any particular sample, the change in sample height, and the maximum time desired for shimming.

- Average homogeneity needs with samples which are either long or all of identical height: simple `z1z2` shimming is usually sufficient.
- Sample height might vary: the method `allzs` has been found to be the most reliable, at the expense of greater time spent in shimming. This method shims first Z1, Z2, and Z4, then Z1, Z2, and Z3, and finally Z1 and Z2.

The standard parameter sets `stdpar/h1` and `stdpar/c13` have `method` set to `z1z2`. Recall those parameter sets if more shimming is routinely necessary in your applications, change `method` to `allzs` (or another method of your own devising) and save the parameter set, overwriting the original parameter set.

Using the Input Window

Enter **`method=`*`file`*` shim`**, where *`file`* is the name of a file in the directory `shimmethods` (e.g., `method='z1z2' shim`).

Two `shimmethods` directories can exist. A user can have a private copy of `shimmethods` in a personal `shimmethods` directory. A system-wide set of shim methods is also located in the `/vnmr/shimmethods` directory. The user's private library is searched first for a given method. If the method is not found in the user's directory, then the directory `/vnmr/shimmethods` is searched.

Shimming methods can be used in succession or strung together. For example, entering `method='lz12m' shim shim` would cause the method in the file `lz12m` (Z1, Z2 shimming) to be used, as indicated by its code, twice in succession, and entering

`method='lz12m' shim method='nsm' shim shim shim` would cause the first method to be used once and the second method three times.

Shimming Criteria for Background Autoshim

Two aspects of Autoshim must in some way be specified by the user. One is the resolution of the starting point—good or bad? If good, only small changes need to be made to the shim settings to find the optimum; if bad, larger changes are necessary. The second is how good must the final resolution be? Clearly, the better the desired resolution, the smaller the steps that Autoshim must take as it approaches the maximum in order to find the absolute maximum to within a specified degree.

As shown in Table 43, for each there are five criterion values: B (bad), L (loose), M (medium), T (tight), and E (excellent). (The lower-case letters are used when entering criterion values into a shim method, discussed below.)

Table 43. Permissible Shimming Criterion Values

Criterion	*Meaning*	*Recommended Usage*
B or b	Bad	No decent starting shim values available
L or l	Loose	Extreme change in sample height
M or m	Medium	Typical sample change
T or t	Tight	Resolution desired above average
E or e	Excellent	Resolution desired less than 0.2 Hz

A full criterion consists of two letters, for example, L > M indicates a loose starting criterion (the shims are expected to be far from their desired values) and a medium ending criterion (end with “normal” shim quality). Tight and excellent are only used for extremely high resolution where the beginning resolution is very nearly that desired.

Specify the starting and ending points as L >M if poor resolution is suspected and improvement is needed without spending the time necessary to get excellent resolution. In the interactive Autoshim mode, these criteria are specified on a pulldown menu after clicking the auto button in the SHIM display.

The time of automatic shimming is a function of these criteria. Therefore, try to make an informed choice in light of the resolution needed and, in particular, for FID shimming, the choice of acquisition time `at` specified in the parameter table. An acquisition time of 2 seconds gives a limiting *digital* resolution of 0.5 Hz, a resolution that would be inconsistent with shimming to a tight criterion. In the interactive shimming mode using `acqi`, only the most important criteria are accessible to the user: L > M, M > M, M > T, and T > T (B and E are inaccessible).

The starting criterion should never affect the final result, only the time in which that result is produced. If the starting criterion is specified as T, for example, and the optimum shim is far off, this shim will eventually be found. The search will, however, take longer than if a starting criterion of L had been specified.

Shim Methods for Autoshim

Table 44 lists standard two-character codes for shim gradient combinations.

Table 44. Codes for Standard Shim Gradient Combinations

Standard Code	*Gradients*	*Hexadecimal Code*
z1	Z1C	0000008
z2	Z2C	0000020
z3	Z3	0000040
z4	Z4	0000080
z5	Z5	0000100
zq	Z1C, Z2C	0000028
zt	Z1C, Z2, Z3	0000068
zb	Z1C, Z2C, Z4	00000A8
za	Z1C, Z2C, Z3, Z4, Z5	00001E8
ze	Z2C, Z4	00000A0
zo	Z1C, Z3, Z5	0000148
zc	Z1C, Z2C, Z5	0000128
zm	User-selected gradients	User-entered
tx	X, Z1	0010004
ty	Y, Z1	0020004
t1	X, Y, Z1	0030004
t2	X, Y, XY, YZ, X2Y2, Z1	03B0004
tz	X, Y, XZ, YZ, Z1	0270004
tt	X, Y, XZ, XY, X2Y2, YZ, Z1	03F0004
t3	X, Y, XZ2, YZ2, Z1	5030004
t4	X, XZ, X3, XZ2, Z1	4450004
t5	Y, YZ, Y3, YZ2, Z1	1A20004
t6	XY, X2Y2, ZX2Y2, ZXY, Z1	A180004
t7	X, Y, XZ, XY, X2Y2, YZ, X3, Y3, YZ2, ZX2Y2, XZ2, ZXY, Z1	FFF0004
ta	X, Y, XZ, XY, X2Y2, YZ, YZ2, XZ2, Z1	53F0004
tm	User-selected gradients	User-entered

A shim method consists of a text string contained in a file within the VNMR system's or a user's `shimmethods` directory. That text string will be interpreted as a series of instructions describing the shimming method. Commands in elements include:

- Turn on and off the spinner.
- Set maximum shim time per element.
- Set the delay between lock level samplings.
- Specify the gradients to be shimmed and the criterion used for shimming.

A complete method consists of one or more elements, separated by commas and terminated with a semicolon (e.g., `f,ry,t600,szq:cmm;`). The element setting for specific gradient or gradients to be shimmed has the syntax `sxx:cyz`, where `s` identifies the shim part of the form, `xx` is a two-character code for a specific shim gradient or gradient combination, `c` identifies the criterion part of the form, `y` is the starting criterion, and `z` is the desired ending criterion.

Refer to the description of the `shimset` parameter in the *VnmrJ Command and Parameter Reference* for a list of shims in each type of shim set.

The following examples show the meaning of a few standard shim methods:

- `szq:cmm;` means set shims Z1C and Z2C with a medium to medium criterion.
- `sza:clm;` means shim all Z gradients with a loose to medium criterion.
- `szt:clm,szb:clm,szq:cmm;` means shim Z1C, Z2, and Z3 with a loose to medium criterion, then shim Z1C, Z2C, and Z4 with a loose to medium criterion, and lastly shim Z1C and Z2C with a medium to medium criterion.

User-Defined Shim Methods for Autoshim

The shim methods supplied with the system are based on a series of “standard” coil groupings. Automatic shimming operation using other groups of shims than are provided is supported by creating user-defined shim methods. For example, shimming Z1, Z3, and Z4 while holding Z2 fixed.

Certain combinations of shim coils can be selected by constructing a 7-digit hexadecimal (base 16) number based on the shim coil diagram below to allow this operation.

8 4 2 1	8 4 2 1	8 4 2 1	8 4 2 1	8 4 2 1	8 4 2 1	8 4 2 1
ZXY	Y3	XY	—	—	Z4	Z1C
XZ2	X3	XZ	—	—	Z3	Z1
ZX2Y2	YZ	Y1	—	—	Z2C	Z0
YZ2	X2Y2	X1	—	Z5	Z2	—

To construct a method for this example, first notice in the diagram that Z1 is represented by a 4 in the first digit (on the far right) and that Z4 and Z3 are represented by a 8 and 4, respectively, in the second digit, which gives a total of 12 (or C in hexadecimal notation). The rest of the digits are 0 because no other shimming is desired. Thus, the seven-digit hexadecimal number representing Z1, Z3, and Z4 is `00000C4`. This number is then prefixed by *zm* or *tm* (the two are equivalent) making `szm00000C4` the method desired.

Some examples of user-selected methods:

- `stm0A30004:clm;` means shim Z1, X1, Y1, YZ, Y3 with loose to medium criterion.

The hexadecimal code for each standard coil grouping is listed in the third column of Table 44.

The following codes enable control of other aspects of automatic shimming:

- `l` sets shimming on the lock instead of the FID (default).
- `f` sets shimming on the FID instead of the lock.
- `f:0,90` sets shimming on the FID with limits for the FID evaluation range. Full range is 0 to 100 percent of the duration of the FID. Sensitivity to higher-order spinning gradients is increased with a start of 0 and a finish limit of about 5 or 10, which weights the evaluation to the front of the FID.
- `ry` (rotation yes) turns the spinner on.
- `rn` (rotation no) turns the spinner off.
- `dx` sets a delay *x* hundredths of seconds between lock samplings. Variations in lock solvent T_1 and T_2^* relaxation times affect the ability of automatic shimming to attain good resolution in reasonable times. If too short, automatic shimming will not perform

properly. If too long, the shimming will become unacceptable in duration. `dx` allows setting an appropriate delay and can be used one or more times within a text string. If no entry is made using `dx`, the system automatically measures the lock response and sets a delay accordingly.

- `tx` sets the maximum shimming time to *x* seconds. Once `tx` is set, it governs all future shim elements within a method string, just as `dx` governs the lock sampling interval for all shim elements until changed. If `tx` is not set, the shimming will proceed based on internal program criteria.
- `q` recalls an algorithm's internal parameters so that shimming starts quickly. `q` is a background autoshim that keeps the magnetic field at an optimum during experiments of long duration. Shimming is performed at the time `wshim` instructs. Only the portion of the shim methods following the letter `q` is executed after the experiment's first increment. Any shim method may follow `q`; however, the `sz1` (Z1 only) and `szq` (Z1, Z2) are the most effective. Multiple shim methods may follow `q`, but time effectiveness is reduced.

Methods may be entered into the `shimmethods` file using a text editor such as `vi`. The macros `newshm` and `stdshm` provide an interactive method of defining shim methods. Note that unlike normal text files, which have unrestricted size, the maximum text file size for a shim method is 128 characters.

The following examples show complete user-defined shim methods:

- `szq:cmm,rn,stz:cmm,ry,szq:cmm;` means shim Z1C, Z2C with medium to medium criterion, turn off spinner, shim X, Y, XZ, YZ, Z1 with medium to medium criterion, turn on spinner, and then shim Z1C, Z2C again with medium to medium criterion throughout.
- `d50,szq:cmm,d150,sza:cmm;` means to sample every 0.5 seconds while shimming Z1C, Z2C, and then to sample every 1.5 seconds while shimming all Z gradients. Use medium to medium criterion throughout.
- `t60,szq:cmm,t240,sza:cmm;` means shim Z1C, Z2C for 60 seconds maximum, then shim all Z gradients for a maximum of 4 minutes. Use medium to medium criterion throughout.
- `f,ry,t600,szq:cmm;` means turn on spinner and FID shim Z1C, Z2C with medium to medium criterion for 10 minutes maximum (not available on *GEMINI 2000*).
- `t60,sza:cmm,q,t30,sz1:cmm;` (with `wshim='f20'`) means initially shim on all Z gradients for 60 seconds, then shim Z1. After every 20 FIDs, shim Z1 for 30 seconds.
- `sza:cmm,q,t30,szq:cmm;` (with `wshim='f10'`) means initially shim on all Z gradients (with no time out) and then perform a Z1, Z2 shim for 60 seconds every 10 FIDs.

B.4 Homogeneity Commands and Parameter

Command	*Description*
`dgs`	Display shim & automation parameter group
`diffshims(shimfile1,shimfile2)`	Compare two sets of shims (VNMR)
`diffshims shimfile1 shimfile2`	Compare two sets of shims (Linux)
`dshim<(file)>,dshim('method'|'help')`	Display a shim “method” string
`gmapshim<('files'|'mapname'|'quit')>`	Start gradient autoshimming
`gmapsys`	Setup gradient shimming
`newshm`	Interactively create shim method
`readallshims`	Read all shims from hardware
`readhw(par1,par2,…)<:var1,var2,…>`	Read acquisition hardware values
`rts(file)<:status>`	Retrieve shim coil settings
`setallshims`	set all shims into hardware
`sethw*`	Set acquisition hardware values (shim-related)
`shim`	Submit an Autoshim experiment
`stdshm`	Interactively create a shim method
`svs(file)<:status>`	Save shim coil settings

`* sethw(<'wait'|'nowait',>par1,val1<,par2,val2,...)`

Parameters

`gmap_findtof {'n','y'}`	Find tof before start of gradient shimming
`gmap_z1z4 {'n','y'}`	Gradient shim z1-z4, then higher-order shims
`hdwshim {'n','y','p'}`	Hardware shimming (if available)
`hdwshimlist {'z1','z1z2x1y1'...}`	List of shims for hardware shimming
`load {'n','y'}`	Load status of displayed shims
`method {file in shimmethods}`	Autoshim method
`shimset {1,2,3,...14}`	Type of shim set
`shimspath {absolute path}`	Path to user’s shims directory
`wshim {'n','e','s','g','f','f#'}`	Conditions when to shim
`x1, y1, z1,...`	Shim gradients X1, Y1, Z1, ...
`z0 {-2048 to 2047, –32768 to 32767}`	Z0 field position

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