Chapter 4
Cross-Relaxation Enhanced NQR of Ammonium Nitrate in Low Magnetic Field

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Abstract Nuclear quadrupole resonance (NQR) with use of pulses of low magnetic field has been studied. The technique is based on the matching of proton frequency (ν_L) to one of the NQR frequencies (ν_0, ν_+ or ν_-) for the period of application of pulse magnetic field. Theoretical approach to analyse the NQR experiments in pulse magnetic fields is outlined. In this work the NQR on ammonium nitrate (AN) sample for specific case of $\nu_L = \nu_0$ have been studied. It has been shown that the technique provides essential shortening the effective spin-lattice relaxation time and can be applied for the detection of explosive materials.

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4.1 Introduction

During last 20 years essential efforts has been concentrated on Nuclear Quadrupole Resonance (NQR) as the method for explosive detection [1, 2]. The prototypes of NQR devices for luggage scanners and landmine detectors have been designed. However, there are still some issues preventing a wide practical application of this technology for explosive detection. These are: (1) a low signal-to-noise ratio (SNR) for some important explosives that makes the detection of these explosives very slow; (2) a strong influence on SNR of radiofrequency interference (RFI) due to external noise sources (such as AM radio); and (3) an effect of spurious signals due to various metal or piezoelectric materials. The explosive list, which can be easily detected by NQR, includes e.g. RDX ($C_3H_6N_6O_6$), HMX ($C_4H_8N_8O_8$), tetryl ($C_7H_5N_5O_8$), and their mixtures. However, explosives such as trinitrotoluene (TNT, $C_7H_5N_3O_6$), ammonium nitrate (AN), pentaerythritol tetranitrate PETN ($C_5H_8N_5O_{12}$) have much smaller signal-to-noise ratios because of lower NQR frequencies (<1 MHz) and longer spin-lattice relaxation times. The effect of radiofrequency interference can be reduced by shielding, advanced signal processing [3, 4] and various methods of active suppression of RFI noise [5, 6]. However, it is obvious that for the practical application of NQR for explosive detection, the development of novel physical methods increasing the detected signal intensity is highly desirable.

In this work we studied the detection of AN as one of the substances with very weak NQR signal. It is well known that multipulse sequences are commonly used in NQR to speed up the detection [7]. Further gain may be obtained by use of nitrogen-proton cross-polarization methods. There are two main modifications of these double resonance approaches. In the first one (direct method) the transfer of polarization from proton system results in the increase of intensity of NQR signal on nitrogen nuclei (see, e.g., [8]), while in the second one (indirect method) the nitrogen nuclei are detected through the proton NMR signal [9–11]. The gain in SNR depends on the strength of the static magnetic field. However, the indirect NMR method and cross-polarization NQR, which rely on use of rather high magnetic fields, are not feasible for implementation in commercial devices, such as the luggage scanners and mine detectors. There is an additional possibility to increase SNR by the cross-relaxation interactions between quadrupole and proton systems. As was already mentioned above, a very long spin-lattice relaxation time T_1 of some explosives (PETN, AN and TNT) is another obstacle in ^{14}N NQR detection that prevents a fast accumulation of quadrupole signal. For example, the longitudinal relaxation time for TNT lines is between 4.6 and 9 s, while such substance as hexamethylenetetramine, which is well-known as explosive precursor, relaxes for much shorter time of 23 ms. A long relaxation time T_1 makes the process of signal accumulation (averaging) in NQR slower due to a need to wait for a time of about $5T_1$ between successive pulse sequences before the nitrogen nuclei magnetization recovers. The cross-relaxation effects between ^{14}N and ^1H spin systems may be applied to reduce this time of recovering of the quadrupole magnetization [8, 12–14]. Two provisions are needed for application of these methods: (1) a substance contains both nitrogen and hydrogen nuclei, and (2) the "contact" (cross-relaxation interactions) between the proton and quadrupole spin-systems is created. For the second provision, so-called level crossings should be made as result of application of a static or quasistatic (i.e. slowly-changed) magnetic field. In the work [14] it has been shown that shortening up to 3.4 (4.4) times in the relaxation times of ν_+ (ν_-) NQR lines of AN sample is obtained as result of the cross-relaxation contact. The cited work reveals the potential prospects of this technique for practical use. However, the applied experimental protocols were based either on preparatory RF saturation of the transition under study or on the slowly sweeping the magnetic field from level crossing at the upper (detected) transition through other (lower frequency) double-resonance conditions of AN.

In our work we study in details those double-resonance protocols, which theoretically do not provide the largest gain, but are more feasible to apply in practice. In our scheme, we apply pulses of small magnetic field to match the proton resonance frequency ν_L to the lowest quadrupole resonance frequency ν_0. Then we detect the spin-echo NQR signal on the ν_- transition which is characterized by the smallest temperature shift of the resonance frequency. It has been revealed that this technique provides at least twofold shortening of the effective spin-lattice relaxation time and therefore can be applied in the detection of explosive materials.

4.2 Theory

The theoretical treatment of cross-relaxation effects in double NMR/NQR has been proposed in the Ref. [10]. In this approach one starts with consideration of two kinds of spins, which interact via dipole-dipole interactions: proton spins and ^{14}N quadrupole nuclei. The relaxation of quadrupole subsystem is defined by spin-lattice relaxation rates $W_{0,-,+}$. For the proton subsystem P in the contact with quadrupole subsystem Q, the quadrupole subsystem may also relax through the interaction with protons with the cross-relaxation time (T_{CR}). It is the time that required for the P and Q spin subsystems to come in equilibrium with a common spin temperature (if other relaxation channels are "switched off"). In the double resonance there is another important parameter – the time for polarization of proton subsystem. This time increases with value of the static magnetic field. Long polarization time of proton system will increase the total time of double resonance experiment [15]. Below we will discuss the case of $\nu_L = \nu_0$. Similar to work [10] the populations of three-level quadrupole system are considered. In Ref. [10] the effect of cross-relaxation on the proton spin-lattice relaxation and the proton polarization has been calculated, while in our case we consider the backward effect on the magnetization of quadrupole system. According to the results of the work [14] the rate of the proton-nitrogen cross-relaxation is much faster than the rates of both the proton relaxation and the nitrogen spin-lattice relaxation. It means that T_{CR} is very small and in the limiting case we can neglect it. We used the high temperature approximation with the same direct and reverse transition rates for both proton and

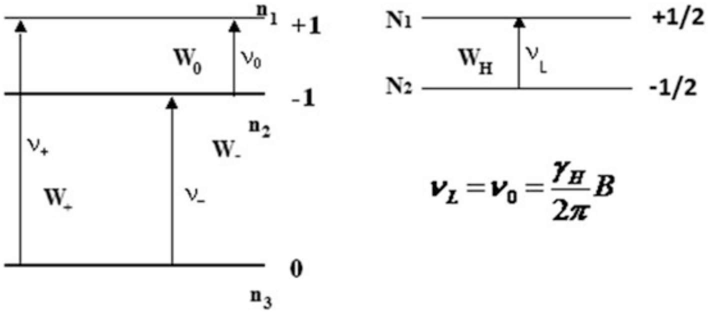

Fig. 4.1 The energy levels and populations of the quadrupole (at *left*) and proton (at *right*) systems

nitrogen systems. We suppose that the ratio of protons to nitrogen nuclei $\varepsilon = N_N/N_H$ is smaller than 1. The populations of energetic levels are defined by following rate equations [10]:

$$\begin{aligned} d(N_1 + n_1)/dt &= -W_H(N_1 - N_2) - W_0(n_1 - n_2) - W_+(n_1 - n_3) \\ d(N_2 + n_2)/dt &= W_H(N_1 - N_2) + W_0(n_1 - n_2) - W_-(n_2 - n_3) \\ dn_3/dt &= -W_+(n_3 - n_1) - W_-(n_3 - n_2), \end{aligned} \tag{4.1}$$

where n_1, n_2, n_3 are the populations of energy levels of the quadrupole system (Fig. 4.1); and N_1, N_2 are the populations of proton systems. $W_H = 1/(2T_1)$ is the proton spin-lattice relaxation rate at the magnetic field $\nu_L = \nu_0$ (without the cross-relaxation between the proton and quadrupole systems). W_0, W_+ and W_- are the nitrogen relaxation rates for the transitions ν_0, ν_+ and ν_-, respectively.

The energy of the ^{14}N levels with spin $I = 1$ may be presented as follows [11]:

$$E_1 = A\,(1+\eta)\,,\ E_2 = A\,(1-\eta)\,,\ \text{and}\ E_2 = -2A, \tag{4.2}$$

where $A = \frac{e^2Qq_{zz}}{4}$ and e^2Qq_{zz} is quadrupole coupling constant, η is asymmetry parameter of electric field gradient. Therefore, the transition frequencies of ^{14}N are:

$$\hbar 2\pi\nu_+ = A(3+\eta),\ \hbar 2\pi\nu_- = A(3-\eta),\ \text{and}\ \hbar 2\pi\nu_0 = 2A\eta \tag{4.3}$$

In the steady state the population differences may be presented as following

$$\begin{aligned} \Delta n_{21} &= n_2 - n_1 = n_2\left(1 - \exp\left(-\frac{\hbar\omega_0}{kT}\right)\right) \\ \Delta n_{32} &= n_3 - n_2 = n_3\left(1 - \exp\left(-\frac{\hbar\omega_-}{kT}\right)\right) \end{aligned} \tag{4.4}$$

Similar to work [10] we write the populations as follows:

$$\begin{aligned}\Delta n_{21} &= n_2\left(1-\exp\left(-z\right)\right) \approx n_3\left(1+z-1..\right) \approx nz \\ \Delta n_{31} &= n_3\left(1-\exp\left(-y\right)\right) \approx n_3\left(1+y-1..\right) \approx ny \end{aligned} \tag{4.5}$$

Then we used following relations:

$$\begin{aligned} n_1 &= \frac{N(N)}{3}\exp\left(-\frac{A\left(1+\eta\right)}{kT}\right) \approx \\ &\approx \frac{N(N)}{3}\left(1-\frac{A\left(1+\eta\right)}{kT}+\frac{2A}{kT}-\frac{2A}{kT}+\frac{2A\eta}{kT}-\frac{2A\eta}{kT}\right) = \\ &= \frac{N(N)}{3}\left(1-\frac{A\left(3-\eta\right)}{kT}+\frac{2A}{kT}-\frac{2A\eta}{kT}\right) \approx \frac{N(N)}{3}\left(1-y+x-z\right) \\ n_2 &= \frac{N(N)}{3}\exp\left(-\frac{A\left(1-\eta\right)}{kT}\right) = \frac{N(N)}{3}\left(1-\frac{A\left(1-\eta\right)}{kT}+\frac{2A}{kT}-\frac{2A}{kT}\right) = \\ &= \frac{N(N)}{3}\left(1-y+x\right) \\ n_3 &= \frac{N(N)}{3}\exp\left(\frac{2A}{kT}\right) \approx \frac{N(N)}{3}\left(1+\frac{2A}{kT}\right) = \frac{N(N)}{3}\left(1+x\right) \end{aligned} \tag{4.6}$$

For proton system we have

$$\begin{aligned} N_1 &= \frac{N(H)}{2}\exp\left(-\frac{1}{2}\frac{\hbar\omega_0}{kT}\right) \rightarrow \qquad N_1 = \frac{N(H)}{2}\left(1-z\right) \\ N_2 &= \frac{N(H)}{2}\exp\left(\frac{1}{2}\frac{\hbar\omega_0}{kT}\right) \rightarrow \qquad N_2 = \frac{N(H)}{2}\left(1+z\right) \end{aligned} \tag{4.7}$$

A similar approach was already used in the work [10]. We only partially changed the meaning of x, y, z in according our task.

Here x is proportional to deviation of the population of lowest level n_3, y is proportional to the magnetization on the transition with frequency ν_-, and z is proportional to the proton magnetization ν_0. The new parameters of x, y and z are introduced instead n_1, n_2, n_3, N_1, N_2.

We assume that in the quasi-steady approximation we can still use the same parameters of x, y and z to characterize the population differences of the spin levels.

Thus we arrive to the following equations:

$$-\left(\frac{1}{2}+\frac{\varepsilon}{3}\right)\frac{dz}{dt}-\frac{\varepsilon}{3}\frac{dy}{dt} = \left(W_H+\frac{\varepsilon}{3}W_0+\frac{2}{3}\varepsilon W_+\right)z+\frac{\varepsilon}{3}\left(2W_+ + W_-\right)y \tag{4.8}$$

$$\frac{1}{2}\frac{dz}{dt}-\frac{\varepsilon}{3}\frac{dy}{dt} = -\left(W_H+\frac{\varepsilon}{3}W_0-\frac{\varepsilon}{3}W_+\right)z+\frac{\varepsilon}{3}\left(W_+ + 2W_-\right)y \tag{4.9}$$

Finally, the following approximate solution for these equations is derived:

$$z(t) = c_1 exp(-k_1 t) + c_2 \exp(-k_2 t), \tag{4.10}$$

with the parameters k_1 and k_2 as follows:

$$k_1 = \frac{1}{2(\varepsilon + 3)} \left[2\varepsilon (W_+ + W_- + W_0) + 9 (W_+ + W_-)\right] \tag{4.11}$$

$$k_2 = \frac{1}{(\varepsilon + 3)} \left[\varepsilon (W_+ + W_- + W_0) + 6 W_H\right] \tag{4.12}$$

The solution has been obtained by symbolic calculations using the *Maple* 10 software packet. Comparing our solution and the solutions obtained in [10] we see that in our approximation k_1 coincide with value of W_1 in [10] for case $\varepsilon << 1$, while the value of k_2 does not match exactly, but it is still very close to the given in Ref. [10] (the numerical difference is only 10 %).

The relation between the quadrupole polarization $y(t)$ and the proton polarization $z(t)$ is obtained subtracting Eq. 4.8 from Eq. 4.9:

$$y = -\frac{\left(1 + \frac{\varepsilon}{3}\right)}{\frac{\varepsilon}{3}(d - c)} \frac{dz}{dt} - \frac{(a + b)}{\frac{\varepsilon}{3}(d - c)} z \tag{4.13}$$

with use of the following notations:

$$a = \left(W_H + \frac{2}{3}\varepsilon W_+ + \frac{1}{3}\varepsilon W_0\right), \ d = 2W_+ + W_-$$

$$b = \left(W_H - \frac{1}{3}\varepsilon W_+ + \frac{1}{3}\varepsilon W_0\right), \ c = W_+ + 2W_-. \tag{4.14}$$

Thus the solution for $y(t)$ similar to $z(t)$ is the two-exponential decay with relative weights of the terms, which depend on the relaxation parameters as well as on the initial state of the system in beginning of the magnetic field pulse. Our estimations reveals that the term with $\exp(-k_2 t)$ will govern the relaxation of the nitrogen spins if the proton relaxation rate W_H is faster than W_+, W_- or W_0. For the relaxation rates of AN we use the values given in the Ref. [14]: $W_0 = 0.024\ \mathrm{s}^{-1}$, $W_+ = 0.033\ \mathrm{s}^{-1}$, $W_- = 0.015\ \mathrm{s}^{-1}$, and $\varepsilon = 0.25$. An estimation of the proton “autorelaxation” time W_H of about $0.32\ \mathrm{s}^{-1}$ is given in Ref. [14]. The term with $\exp(-k_2 t)$ represents the slow NQR spin-lattice relaxation, while the term with $\exp(-k_2 t)$ describes the faster relaxation channel through the protons mediated by cross-relaxation between the nitrogen and proton spins. Therefore, it is expected that application of pulse magnetic field results in an essential shortening of the effective relaxation time.

4.3 Experimental Details

The sample consists of 120 g powder of 99.5 % pure ammonium nitrate NH_4NO_3 (AN). In general, five different crystalline phases of AN are known. However, at typical outdoor temperatures only three of them are relevant to the detection of AN. The form V (tetragonal phase) is stable below a temperature of −16.8 °C. The phase IV (β-rhombic) is stable from −16.8 to +32.3 °C and the phase III (α-rhombic) is stable from +32.3 to +84.2 °C. AN is a widely used component of explosives for industrial and military applications (ANFO, ammonite, amatol, ammonal, etc.). During experiments our sample of AN is at room temperature is in the IV phase.

The most suitable frequency for the detection of AN is $\nu_- = 424$ kHz (at room temperature). This transition has a smallest temperature coefficient, $\Delta\nu/\Delta T = +100$ Hz/K [16]. For the transition with a frequency of $\nu_+ = 496$ kHz (room temperature), the temperature coefficient is higher: −300 Hz/K. The spin lattice relaxation parameter T_1 is 13 and 16 s for the NQR frequencies of ν_+ and ν_-, respectively. The spin-spin relaxation parameter T_2 is 8 and 6 ms for ν_+ and ν_-, respectively. Our experiments have been performed at the frequency $\nu_- = 424$ kHz.

Tecmag Apollo NQR/NMR console (0.1–100 MHz) with two-channel transmitter and one-channel receiver modules, equipped by two *Tomco* power amplifiers with output power of up to 500 W have been used. For multifrequency NQR experiments the detector unit consists of the system of two orthogonal coils, each of which is connected to variable capacitor to form a serial/parallel resonance circuit tuned to its own resonance frequency. For single frequency measurements the probe consisting of solenoidal coil connected to a variable capacitor has been used. A low-noise single-channel preamplifier Miteq and auxiliary electronic circuits have been connected between the probe and *Tecmag* NMR/NQR Console. A special magnet system consisting of Helmholtz coil set and pulse current source has been designed. A set of Helmholtz coils provides a uniform magnetic field (2 % in the sphere with $D = 4$ cm) at the sample. The current source for creation of the pulse magnetic field was home-made. The control pulses were supplied by Apollo console. The output current of this modulator is in the range 100 mA to 30 A. *KEPCO-BOP*-20-50*MG* power supply has been used as a current source to the modulator. We tested magnet in a pulse mode up to 30 A which corresponds to the magnetic field of 11.88 mT for our Helmholtz coil system. The current stability was about of 2 % is for the pulse duration of 2 s. The NQR radiofrequency coil has been tested in two relative positions in our experiments: parallel to the pulse magnetic field and perpendicular to the pulse magnetic field. The magnetic field broadening of nitrogen resonance line at ν_0 is approximately $(\gamma_N/\gamma_H)^2\nu_0$ [10]. The ν_0 linewidth for AN in zero magnetic field is near 70 Hz, while in the magnetic field of 1.7 mT it is about of 370 Hz. It means that the peak value of the magnetic field pulse should be settled with accuracy of 0.5 %. Taking into account low current stability in our home made modulator and not very high uniformity, it is expected that use of the magnetic field which is oscillating or swept through the resonance could provide the better results. We also used a specially designed Q-switch to suppress ringing in the resonance circuit of NQR probe.

The spin-lock spin-echo (SLSE) sequence [7] was applied in our NQR experiments with AN sample. To measure the effect of the cross-relaxation in low magnetic field we change the time interval between sequences. Since the pulse magnetic field is switched off during the observation of NQR signal, the line broadening effect of the magnetic field on the effective relaxation time $T_{2\mathrm{eff}}$, which defines the decay of the signal during the SLSE sequence, is excluded.

4.4 Experiments and Discussion

For matching the energy levels of the proton and nitrogen spin systems we used two approaches. First one is an application of a single rectangular pulse of the magnetic field (Fig. 4.2a). Second one is use of series of m short pulses of magnetic field (Fig. 4.2b, c). In both cases the value of magnetic field B was settled to correspond to the double resonance conditions for ν_0 transition (Fig. 4.1). After switching off the pulse(s) of magnetic field, a multipulse spin-locked spin echo (SLSE) sequence (Fig. 4.2) was applied to detect an NQR signal at ν_- transition. The main goal of the application of static magnetic pulse B is a decrease of T_1 by cross-relaxation "contact" between the proton and nitrogen spins. On the other hand, the protons in the zero magnetic field have equal populations of the $+1/2$ and $-1/2$ energy levels before an application of magnetic field B. This state corresponds to saturation state of protons system. A pulse of the magnetic field transfers of the protons system to the double resonance condition. As a result of the matching of energy level

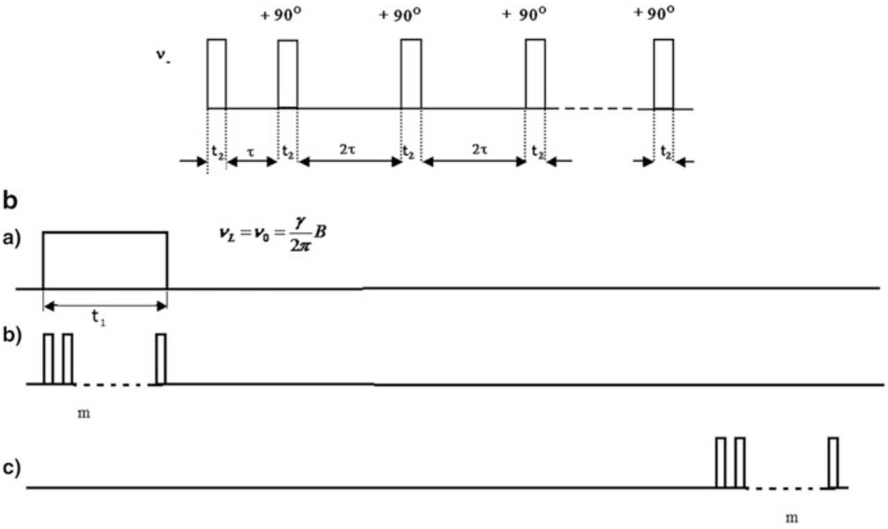

Fig. 4.2 The pulse sequence for cross level in AN with use pulse magnetic field

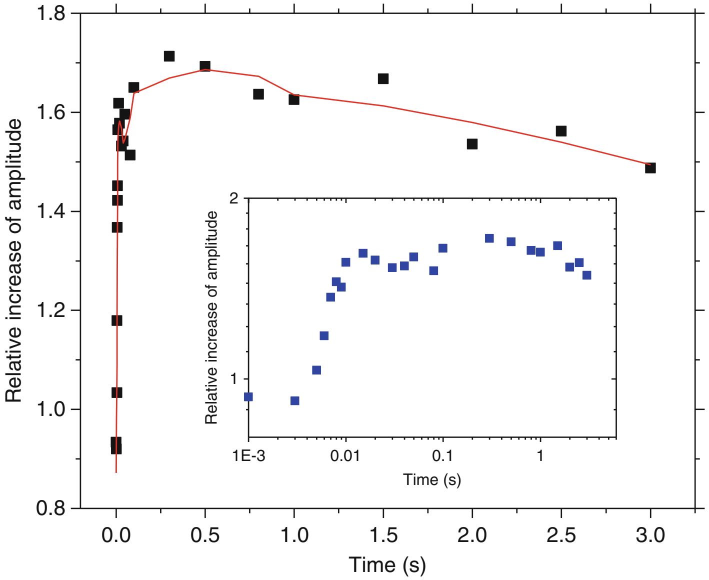

Fig. 4.3 The dependence of the signal increase on the duration of magnetic pulse t1 in comparison with usual signal. The time space between sequences is 10 s. The *solid line* is only guide for eyes. *Inset* is a same plot but given in the log –log scale

differences between the proton and nitrogen systems, the ν_0 transition of quadrupole spin system is saturated too. It is known that the saturation of the ν_0 transition increases the gain on the signal on the observable frequency ν_- [17].

Firstly we studied an effect of the duration of a pulse of the magnetic field on the signal intensity in the scheme shown in Fig. 4.2a. The time space between the successive SLSE sequences is 10 s, that is much shorter than the usually used delay times of $(3 \div 5)\cdot T_1$. The cross-relaxation time according to work [14] is an order of 10 ms. It is seen in Fig. 4.3 that the magnetic field pulse length less than 1 s is enough see an essential increase of the SLSE signal intensity. Figure 4.3 shows the ratio of the SLSE signal with magnetic field pulses to that without the magnetic field as a function of the magnetic pulse length t_1. It is seen that there is rapid increase in the signal intensity for $t_1 < 0.1$ s (the gain of 1.6 times is at $t_1 = 15$ ms), while with further increasing the pulse length at $t_1 < 0.5$ s we have a gradual decrease of the signal. It is obvious that the region of the fast increase of the signal intensity ($\sim$10 ms) agrees well with the cross-relaxation time estimated in the Ref. [14]. The signal amplitude increases due to shortening of the effective spin-lattice relaxation time T_1 for the detected transition ν_- as well as saturation of the transition ν_0 by polarization transfer from nitrogen spins to the non-polarized proton system. The first effect, related the cross-relaxation "contact", has been already discussed in Introduction, while the second contribution should be considered in more details. It

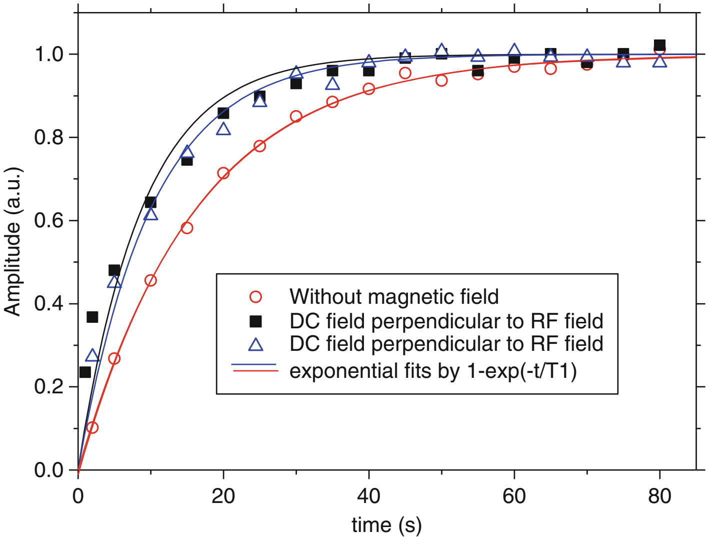

Fig. 4.4 The dependence of the NQR signal at ν− transition on the time interval between the SLSE sequences. The duration of magnetic pulse is 1 s. The *solid lines* are results of modelling. Both limiting orientations (perpendicular and parallel) of DC magnetic field with respect to RF field are given

is explained as a result of the polarization exchange between the proton system and the transition with frequency ν_0. The protons in the zero magnetic field have equal populations of the $+1/2$ and $-1/2$ energy levels. A pulse of the magnetic field means an adiabatic transfer of the system to the double resonance condition. As result of the matching of energy level differences between the proton and nitrogen systems, the ν_0 transition of quadrupole spin system is saturated. Very simple estimations (see, e.g., Fig. 4.5 in Ref. [13] or an appropriate formula in the Table 1 of Ref. [18]) shows that the later effect could contribute to an increase at most for 8.6 % (as a factor of $3-\eta/3$, $\eta = 0.24$ for AN). It is clear that the effect of the polarization transfer which equalizes the populations of nitrogen spin levels at ν_0 should vanish for longer pulse duration of the DC magnetic field because of polarizing the proton spins. Therefore the contribution of this effect vanishes at time of about $1/W_H$. Taking into account the estimation of the proton "autorelaxation" time $1/W_H = 3.1$ s given in Ref. [14], we see that the gradual decrease of the signal at time interval of $0.5 \div 3$ s in Fig. 4.3 agrees well with the spin-lattice relaxation time for protons. A slightly higher value (∼10−12 %) of this decrease could be attributed to a very small temperature shift of the sample temperature induced heating of Helmholtz coils for longer pulses (i.e. higher duty cycle) of the DC magnetic field.

Secondly we measured the NQR signals as function of the time interval between the multipulse series for two mutual orientations of RF and Helmholtz coils: parallel to each other (Fig. 4.4a) and perpendicular to each other (Fig. 4.4b). Depending on the time interval between the multipulse series we observed an increase of the signal amplitude up to 30–40 %. As it was already discussed above, the main contribution is due to shortening of the effective spin-lattice relaxation time T_1 for the detected transition ν_-. Modelling of the experimental results, obtained in the scheme shown in Fig. 4.2a, result in the following values of the effective spin-lattice relaxation time: (a) in the parallel configuration, T_1 is equal to 10.0 ± 0.5 s; (b) for the perpendicular one, T_1 is equal to 8.8 ± 0.8 s (see Fig. 4.4).

In very recent work of Prescott et al. [19] it has been shown that the effect of dipolar interactions between proton and quadrupole systems depends on the orientations of laboratory frame and principal axes of electric field gradient (EFG) on nitrogen nuclei with respect to displacement vectors connecting them to neighbouring protons. Furthermore, even in powder samples the cross-relaxation rates may be dependent on the mutual orientation of RF excitation and magnetic field axes.[1] Theoretical calculations of the cross-relaxation rates, which require the structural parameters and EFG axes to be accurately known, are beyond the scope of our paper. More detailed double-resonance experiments with single crystalline samples are desirable for experimental verification of the dependence of dipolar fields on orientations of the RF and static magnetic fields. In this work, we limit ourselves by making experiments with a powder sample for two possible extreme orientations of the RF field with respect to the static magnetic field: (1) the RF field is parallel to the static magnetic field and (2) the RF field is perpendicular to the static magnetic field.

Better results are obtained in the experimental scheme shown in Fig. 4.2b. We applied pulses with length of 20 ms and separation of 20 ms. Total number of the magnetic field pulses was 8. In this case we however applied the pulse magnetic field B with a peak value slightly larger than optimal one for the static cross–relaxation scheme in Fig. 4.2a. The results of the experiments are presented in Fig. 4.5 for both parallel and perpendicular geometries. The following values of T_1 have been obtained: (a) for the parallel geometry T_1 is equal to 8.6 ± 0.8 s; (b) for the perpendicular geometry T_1 is equal to 7.9 ± 0.6 s. We performed also the NQR experiment with use of the same spin-locked spin echo (SLSE) sequence to detect an NQR signal at ν_- transition ***without*** application of the pulse magnetic field. The SLSE NQR signal as function of the time interval between the multipulse series for the same two mutual orientations of RF and Helmholtz coils (parallel and perpendicular) has been obtained (they are shown by red lines in Fig. 4.4). Modelling of our experiment results provide the T_1 values with the average between two geometries equal to 16 ± 1 s, which is well corresponds to $T_1 = 16.9 \pm 1$ s cited in the work [16]. Thus, in the scheme shown in Fig. 4.2b at least twofold shortening the effective spin-lattice relaxation parameter for the ν_- transition has been obtained.

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[1] Combining of various types of double resonance experiments for all NQR transitions, allows, however, excluding the influence of a specific orientation of laboratory frame, thereby making possible to find experimentally the principal axes of EFG even in powder sample [19].

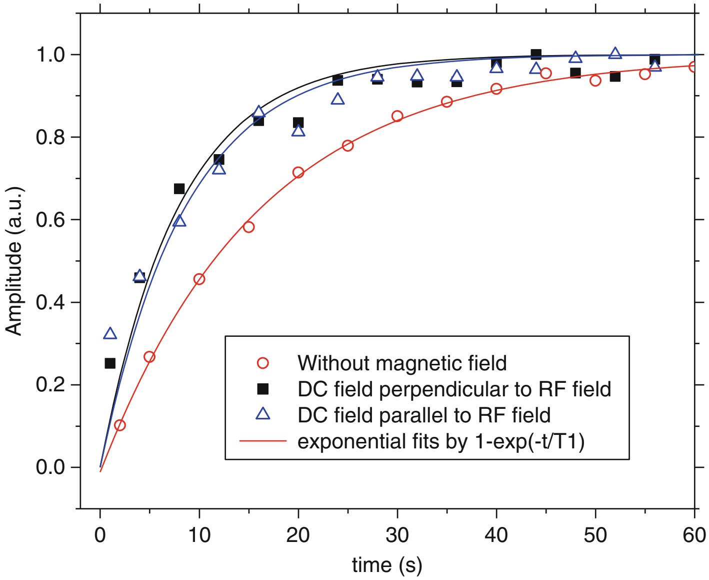

Fig. 4.5 The dependence of the signal in multipulse SLSE sequence with magnetic pulse sequence given in Fig. 4.2b on the interval between sequences. A comb consisting of eight pulses with individual duration of 20 ms and separated by 20 ms has been applied. The *solid lines* are results of modelling. Both limiting orientations (perpendicular and parallel) of DC magnetic field with respect to RF field are given

However, we established that the application magnetic field ***after*** the SLSE sequence is even more effective (Fig. 4.2c). Modelling experimental results for the parallel geometry gives the T_1 value of 3.9 ± 0.4 s (Fig. 4.6). Nearly the same result is obtained in the perpendicular geometry (not shown). Thus we established that the protocol, where the magnetic field in the form of the comb of pulses applied just after the NQR SLSE sequence, provides the most effective shortening of spin-lattice relaxation time. The more pronounced effect of the protocol in Fig. 4.2c is not clear yet, because in the limit of large number of repetitions both protocols are expected to give similar results (for the same number of repetitions).

As regards the results the difference between the results of the protocol in Fig. 4.2a–c we suppose that the application of the comb of magnetic pulses is more effective due to insufficient current stability in our home made modulator and not very high uniformity. Therefore, use of the magnetic field which is oscillating or swept through the resonance, could be more practical. In the case of the comb of the magnetic field pulses the proton-nitrogen spin systems move through the double resonance conditions many times. Owing to very fast cross-relaxation time (∼10 ms), the cross-relaxation works even in alternating (fast-switching) magnetic fields. We plan to study further an effect of switching frequency of the pulse magnetic fields, which in turn could provide information on the cross-relaxation rates of the proton-nitrogen spin systems.

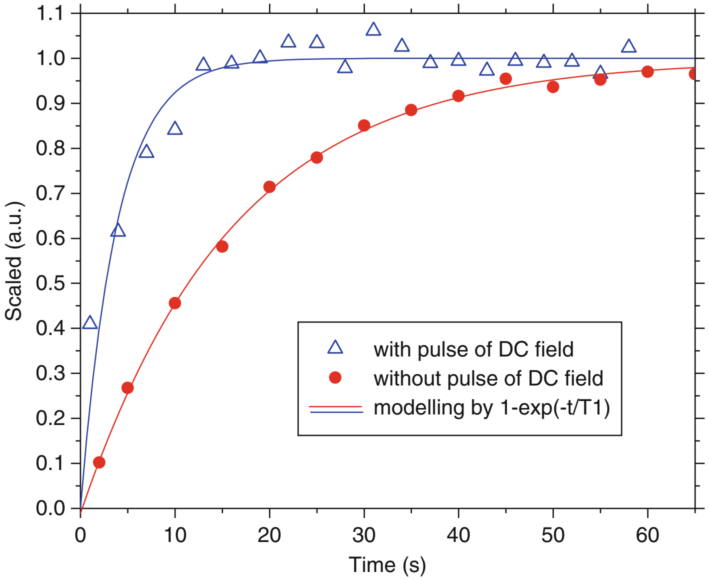

Fig. 4.6 The dependence of the NQR signal amplitude on the time interval between the successive sequences in the experimental scheme given in Fig. 4.2c. The DC magnetic field is applied ***after*** the SLSE NQR sequence as the comb consisting of m pulses. The DC magnetic field is aligned ***in parallel*** to the axis of RF coil. The *solid lines* are results of modelling. The value of $T_1 = 3.9 \pm 0.4$ s is obtained for the pulse of DC magnetic field applied

4.5 Conclusions

As was mentioned in the introduction, there are two possible double-resonance methods of the increasing the signal to noise ratio in the direct NQR detection: (1) pre-polarization of proton system with use of a high magnetic field with following level crossing to polarize the nitrogen spin system by cross-relaxation; (2) the cross-relaxation method in lower magnetic field to shorten the spin-lattice relaxation time of ^{14}N system. In the first case, the sample is needed to be pre-polarized with typical polarization time of about 30 s before decreasing the field down to zero with the following detection of NQR signal. Although the gain is quite large (an order of ten times), the long duration of the pre-polarizing magnetic field and need in the system providing a strong magnetic field prevent using this method in the luggage detection devices. In contrast, the second approach looks easier to realize in practice. In this work we studied an application of small magnetic fields (1.4–2.2 mT) of very short total duration (≤ 1 s). Although in our case the gain is not as high as in the pre-polarized double resonance, the method is more appropriate for practical use. The main advantage of the proposed approach is shortening of T_1. It is well known that the time delay between the multipulse series is needed to be $(3 \div 5) \cdot T_1$. The decrease of T_1 allows faster accumulation that make the detection time shorter. In our experiment we obtained the fourfold shortening of the effective T_1. Using rather low magnetic fields makes easier to implement this protocol in the luggage scanners for explosives with technical point of view as well as with respect of the safety regulations restricting the use of the magnetic field in such devices.

Thus, our cross-relaxation experiments revealed that it is possible to use a pulse or pulse series of the DC magnetic field of short duration both for increasing the amplitude of the NQR signal in the SLSE sequence and for shortening the spin-lattice relaxation time T_1. The later, in turn, results in increasing the signal intensity further due to increased rate of NQR signal averaging.

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