



Double resonance experiments in low magnetic field: Dynamic polarization of protons by ^{14}N and measurement of low NQR frequencies

J. Seliger^{a,b,*}, V. Žagar^a

^a Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

^b Faculty of Mathematics and Physics, Department of Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:

Received 10 February 2009

Revised 17 April 2009

Available online 9 May 2009

Keywords:

N-14

Quadrupole resonance

Dynamic polarization

Double resonance

ABSTRACT

The possibilities of dynamically polarizing proton spin system via the quadrupole ^{14}N spin system in low magnetic field are analyzed. The increase of the proton magnetization is calculated. The polarization rate of the proton spin system is related to the transition probabilities per unit time between the ^{14}N quadrupole energy levels and proton energy levels. The experiments performed in 1,3,5-triazine confirm the results of the theoretical analysis. A new double resonance technique is proposed for the measurement of nuclear quadrupole resonance frequencies ν_Q of the order of 100 kHz and lower. The technique is based on magnetic field cycling between a high and a low static magnetic field and observation of the proton NMR signal in the high magnetic field. In the low magnetic field the quadrupole nuclei and protons resonantly interact at the proton Larmor frequency $\nu_H = \nu_Q/2$. The quadrupole nuclei are simultaneously excited by a resonant *rf* magnetic field oriented along the direction of the low static magnetic field. The experimental procedure is described and the sensitivity of the new technique is estimated. Some examples of the measurement of low ^{14}N and ^2H nuclear quadrupole resonance frequencies are presented.

© 2009 Elsevier Inc. All rights reserved.

1. Introduction

Nuclear quadrupole double resonance (NQDR), as introduced by Slusher and Hahn [1], is a powerful technique which has been mainly used for the measurement of low nuclear quadrupole resonance (NQR) frequencies of nuclear isotopes (^6Li , ^7Li , ^{10}B , ^{14}N , ^{17}O , ^{39}K , etc.) which may also appear at a low natural abundance.

The NQDR technique is based on magnetic field cycling. A magnetic field cycle is schematically presented in Fig. 1. Here the sample first waits in a high magnetic field B_0 until the equilibrium proton magnetization is reached. This is called the polarization period. Then the sample is transferred into a second magnet, where the variable magnetic field B is lower than B_0 . In the original NQDR experiment [1] the low magnetic field B is set to zero. The sample remains in the second magnet for a time τ . During this time an *rf* magnetic field may be applied to the sample. The period the sample spends in the second magnet is called the mixing period. The sample is after the mixing period transferred back into the first magnet where the intensity S of the proton NMR signal is measured immediately after the sample stops in the magnet.

The high-field NMR techniques are recently approaching the resolution of either pure NQR techniques or NQDR techniques in the measurement of the nuclear quadrupole interaction of the half-integer spin nuclei in polycrystalline samples. In the high-field NMR spectrum of a half-integer nucleus there is the central $-1/2$ to $1/2$ transition. The frequency of this transition is only slightly shifted from the Larmor frequency and can easily be measured by NMR. The frequency distribution of the central transition in a polycrystalline sample reflects the nuclear quadrupole coupling constant and the asymmetry parameter η of the electric-field-gradient (EFG) tensor.

Nitrogen atoms are present in a series of organic compounds and the nuclear quadrupole interaction of its nucleus, ^{14}N , reflects the molecular structure, crystal structure, chemical bonds and molecular dynamics. A ^{14}N nucleus has a spin $I=1$ and there is no central transition in its high-field NMR spectrum. The satellite lines are in polycrystalline samples usually several MHz broad and therefore difficult to be detected by NMR. Pure NQR and NQDR techniques in this case still retain their power.

A ^{14}N nucleus has in zero magnetic field three, generally nondegenerated, nuclear quadrupole energy levels and consequently three NQR frequencies labeled as $\nu_+ \geq \nu_- \geq \nu_0 = \nu_+ - \nu_-$. The sensitivity of the original NQDR technique [1] is in case of ^{14}N strongly reduced due to the spin quenching effect [2] when the asymmetry parameter η of the EFG tensor is nonzero. Several ^1H – ^{14}N NQDR techniques [3–10] have been developed to overcome this problem.

* Corresponding author. Address: Faculty of Mathematics and Physics, Department of Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia. Fax: +386 1 2517281.

E-mail address: janez.seliger@fmf.uni-lj.si (J. Seliger).

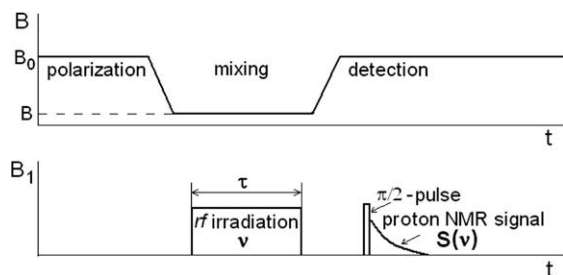


Fig. 1. Schematic presentation of a magnetic field cycle in a double resonance experiment.

The sensitivity and resolution of these techniques strongly depend on the experimental conditions, especially the proton spin-lattice relaxation rate, the ^{14}N spin-lattice relaxation rates, the proton- ^{14}N dipolar interaction and on the size of the NQR frequencies.

In the present paper we treat theoretically and experimentally three types of the ^1H - ^{14}N NQDR experiments:

- (i) Dynamic polarization of protons by ^{14}N using resonant ^1H - ^{14}N interaction in a low magnetic field B , where the proton Larmor frequency ν_{H} is equal to the lowest ^{14}N NQR frequency ν_0 .
- (ii) Dynamic polarization of protons by ^{14}N using the solid effect [10] and
- (iii) A new NQDR technique based on the interaction between the quadrupole nuclei and protons at $\nu_{\text{H}} = \nu_0/2$ and the rf irradiation the quadrupole nuclei with the rf magnetic field parallel to the static magnetic field. In this technique a two-quantum transitions in the proton spin system occurs simultaneously with a single-quantum transition in the quadrupole spin system conserving the total energy of the two spin systems. The rf irradiation at the NQR frequency ν_0 produces an energy flow to the coupled spin systems and consequently increases the proton relaxation rate towards the state with zero proton magnetization.

Spin-lattice relaxation of quadrupole nuclei in solids is often faster than the spin-lattice relaxation of protons. A molecular motion may in a nitrogen and hydrogen containing solid strongly modulate the nuclear quadrupole interaction of ^{14}N what results in a fast spin-lattice relaxation of the ^{14}N quadrupole spin system. The same molecular motion modulates also the proton dipolar interaction, but the intensity of this modulation is on the frequency scale weaker than the modulation of the ^{14}N quadrupole interaction. The spin-lattice relaxation rate of protons is in such a case lower than the spin-lattice relaxation rates of ^{14}N . Resonant coupling of protons and ^{14}N in a low magnetic field B where $\nu_{\text{H}} = \gamma_{\text{H}}B/2\pi = \nu_+$, ν_- or ν_0 may increase the spin-lattice relaxation rate of protons and allow the determination of the ^{14}N NQR frequencies and spin-lattice relaxation rates from the B -dependence of the proton spin-lattice relaxation rate.

Simultaneous coupling of protons and ^{14}N at $\nu_{\text{H}} = \nu_0$ and a continuous rf irradiation at a higher ^{14}N NQR frequency (ν_+ or ν_-) may dynamically produce a proton magnetization which is several times larger than the equilibrium proton magnetization at the same magnetic field at the temperature of the sample.

A dynamical increase of the proton magnetization above its equilibrium value can also be obtained using the solid effect [10]. This is the result of the “forbidden” transitions at the frequency $\nu_0 \pm \nu_{\text{H}}$, which occur simultaneously in both spin systems, and the spin-lattice relaxation of ^{14}N .

In the present paper we first discuss these two aspects of the dynamic polarization of protons by ^{14}N theoretically. In the experimental section we present a study of the dynamic polarization of protons by ^{14}N in 1,3,5-triazine (*s*-triazine).

The main problem which occurs in measuring low NQR frequencies of the order of 100 kHz or lower using a strong rf magnetic field is a direct absorption of the rf power by the proton spin system which destroys the proton NMR signal during the mixing period. The techniques which work in this frequency region are as follows.

The dependence of the proton spin-lattice relaxation time on the proton Larmor frequency ν_{H} , as measured by magnetic field cycling between a high magnetic field B_0 and a variable low magnetic field B , may exhibit dips at $\nu_{\text{H}} = \nu_0$ and $\nu_{\text{H}} = \nu_0/2$ [5–8]. This happens when the spin-lattice relaxation rate of the quadrupole nuclei exceeds the spin-lattice relaxation rate of protons. From the position of the dips in the ν_{H} -dependence of proton T_1 one can thus extract the NQR frequencies ν_0 . The resolution of this technique is dominated by the proton NMR linewidth and is usually low.

In the level-crossing technique [3,4] the low magnetic field B is set to zero. The two spin systems resonantly couple ($\nu_{\text{H}} = \nu_0$) on the way between the two magnets: first during the decrease of the external magnetic field ($B_0 \rightarrow B$) and secondly during the increase of the external magnetic field ($B \rightarrow B_0$). These couplings are called the level crossings. Three level crossings ($\nu_{\text{H}} = \nu_+$, ν_- , ν_0) occur for each ^{14}N nucleus on the way from the first to the second magnet and three level crossings ($\nu_{\text{H}} = \nu_0$, ν_-, ν_+) occur on the way back. The first set of level crossings strongly changes the population of the ^{14}N quadrupole energy levels and to some extent also the spin temperature of the proton spin system. During the second set of level crossings the proton spin system probes the population of the ^{14}N quadrupole energy levels. The application of a weak rf magnetic field of the frequency ν between the two sets of level crossings may change the final proton magnetization. When $\nu = \nu_0$ the rf magnetic field equalizes the population of the nuclear quadrupole energy levels separated by ν_0 . The final proton magnetization after the second set of level crossing is in this case smaller than in the case when $\nu \neq \nu_0$. A dip is therefore observed in the ν -dependence of the proton NMR signal S at the end of the magnetic field cycle when $\nu = \nu_0$. The level-crossing technique is limited to long quadrupole spin-lattice relaxation times. In addition the decrease and increase of the external magnetic field may not be too fast for the level-crossing process to be effective. The sensitivity of the level-crossing technique is moderate because only a single set of level crossings changes the proton magnetization after the rf irradiation, but its resolution may be high.

Zero field NMR and NQR with selective pulses and indirect detection [11–13] is based on magnetic field cycling between a high, intermediate and zero magnetic field and a selective pulse excitation of the quadrupole nuclei. These experiments yield well resolved, sharp line spectra in polycrystalline solids.

The application of a SQUID spectrometer [14–16] is another possibility for the determination of the low NQR frequencies at low temperatures.

Here we propose a new double resonance technique for the measurement of low NQR frequencies. The technique is based on the resonant coupling between the quadrupole and proton spin systems during the mixing period at $\nu_{\text{H}} = \nu_0/2$ and simultaneous irradiation of the quadrupole nuclei by a weak rf magnetic field B_1 with the frequency $\nu = \nu_0$. The resonant coupling at $\nu_{\text{H}} = \nu_0/2$ involves simultaneous two-quantum transitions in the proton spin system at the frequency ν_{H} and single-quantum transitions in the quadrupole spin system at the frequency ν_0 . These transitions, which conserve the total energy of the two spin systems, are allowed due to the strong proton-proton dipolar interaction in solids. They lead to a quasi equilibrium (neglecting the spin-lattice

relaxation) where the spin temperature associated with the quadrupole transition at the frequency ν_Q is one half of the proton spin temperature. The *rf* magnetic field B_1 is directed along the direction of the static magnetic field B . When the frequency of the *rf* magnetic field matches the NQR frequency ν_Q , the *rf* magnetic field saturates the NQR transition and the quasi equilibrium is obtained at the infinite spin temperature i.e. the proton magnetization is in the quasi equilibrium zero and the proton NMR signal S at the end of the magnetic field cycle is zero as well.

The new technique may be useful for the measurement of the NQR frequencies in case of a small quadrupole coupling constant (deuterium, ammonium ion...) or in search of the lowest ^{14}N NQR frequency ν in a polycrystalline sample.

2. Dynamic polarization of protons

A ^{14}N nucleus ($I = 1$) has in zero magnetic field three -generally nondegenerated-nuclear quadrupole energy levels, as shown in Fig. 2a. The nuclear quadrupole resonance (NQR) frequencies are given as

$$\begin{aligned} \nu_+ &= \frac{e^2qQ}{4h}(3 + \eta) \\ \nu_- &= \frac{e^2qQ}{4h}(3 - \eta) \\ \nu_0 &= \nu_+ - \nu_- = \frac{e^2qQ}{2h}\eta \end{aligned} \quad (1)$$

Here e^2qQ/h is the quadrupole coupling constant and η is the asymmetry parameter of the electric-field-gradient (EFG) tensor. The spin-lattice relaxation of ^{14}N is governed by three pairs of transition probabilities per unit time between the nuclear quadrupole energy levels: $W_+^{\uparrow}, W_+^{\downarrow}; W_-^{\uparrow}, W_-^{\downarrow}$ and $W_0^{\uparrow}, W_0^{\downarrow}$, as shown in Fig. 2b. The two transition probabilities per unit time within each pair are in the high-temperature approximation related as

$$\begin{aligned} W_i^{\uparrow} &= W_i(1 - hv_i/2k_B T) \\ & \quad i = +, -, 0 \\ W_i^{\downarrow} &= W_i(1 + hv_i/2k_B T) \end{aligned} \quad (2)$$

Here h is the Planck's constant, k_B is the Boltzmann's constant and T is the temperature of the sample.

In a weak magnetic field, in which the ^{14}N Larmor frequency is much lower than the lowest NQR frequency ν_0 , the Zeeman shifts of the ^{14}N NQR frequencies are negligible and the spin-lattice relaxation of ^{14}N may still be treated in the same way as in zero magnetic field.

The spin-lattice relaxation of protons can also be described by two transition probabilities per unit time, W_H^{\uparrow} and W_H^{\downarrow} :

$$\begin{aligned} W_H^{\uparrow} &= W_H(1 - hv_H/2k_B T) \\ W_H^{\downarrow} &= W_H(1 + hv_H/2k_B T) \end{aligned} \quad (3)$$

If the ^{14}N quadrupole spin system relaxes fast, the ^{14}N - ^{14}N resonant interaction at $\nu_H = \nu_i$ ($i = +, -, 0$) increases the spin-lattice relaxation rate of protons. In such a case the proton spin system approaches

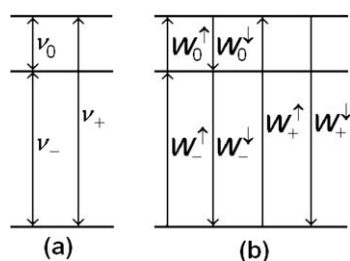


Fig. 2. ^{14}N NQR frequencies (a) and transition probabilities per unit time between the ^{14}N nuclear quadrupole energy levels (b).

the equilibrium magnetization faster than in absence of the resonant ^{14}N - ^{14}N interaction. This can be used for a fast determination of the ^{14}N NQR frequencies in a quite common situation where the proton spin-lattice relaxation time in the high magnetic field B_0 is long, say 10s of minutes, while the ^{14}N quadrupole spin-lattice relaxation time is short. If this is the case, we can repeat the field cycles quite fast, say every 5 s, and let the proton spin system to relax in the low magnetic field B for a time typically equal to a few seconds. The proton magnetization is in such a situation at the beginning of the mixing period lower than the equilibrium proton magnetization in the low magnetic field B . It therefore starts to relax towards the larger equilibrium value with the spin-lattice relaxation rate $(T_{1H})^{-1} = R_H = 2W_H$. In a special situation, where the proton spin system is in resonance with ^{14}N ($\nu_H = \nu_+, \nu_-,$ or ν_0), the spin-lattice relaxation rate of protons changes to the following value [8]

$$R_H(\nu_L = \nu_i) = (1 - \varepsilon)R_H + 2\varepsilon(W_i + W_jW_k/(W_j + W_k)). \quad (4)$$

Here R_H is the "pure" proton spin-lattice relaxation rate at the frequency $\nu_H = \nu_i$, ε is two thirds of the number of crystallographically equivalent nitrogen atoms N_Q divided by the number of hydrogen atoms N_H in the unit cell, while the indices j and k in the nitrogen contribution to the proton spin-lattice relaxation rate correspond to the two other ^{14}N NQR transitions that are not in resonance with protons. Expression (4) is derived for the case of $\varepsilon \ll 1$, but it can still be used as an approximate expression for a larger ε . If the nitrogen contribution to the proton spin-lattice relaxation rate exceeds the "pure" proton spin-lattice relaxation rate R_H , the proton spin system reaches its equilibrium magnetization much faster than in case of no resonance. The experiment is performed in such a way that we repeat the magnetic field cycles at different values of B so that the range of the ^{14}N NQR frequencies is scanned by the proton Larmor frequency ν_H , $\nu_H = \gamma_H B / 2\pi$ in steps of, say, 10–20 kHz. At the end of each magnetic field cycle we measure the proton NMR signal S . In the ν_H -dependence of the proton NMR signal S we expect peaks at $\nu_H = \nu_+, \nu_-$, and ν_0 . This is an opposite situation to a usual double resonance experiment [5–7], where we start at the beginning of the mixing period with a large proton magnetization, much larger than the equilibrium proton magnetization in the low magnetic field B , and let it relax towards its equilibrium value. In the ν_H -dependence of the proton NMR signal we observe in this case dips at $\nu_H = \nu_+, \nu_-$, and ν_0 . The width of a dip at a ^{14}N NQR frequency [6,7] is equal to the width of the peak obtained in the presently proposed experiment at the same ^{14}N NQR frequency. The intensity of the peak at $\nu_H = \nu_i$ ($i = +, -, 0$) is proportional to the NQR frequency ν_i . The intensity of the dip around the same NQR frequency is larger than the intensity of the peak by a factor $\nu_L \nu_i$. Here ν_L is the proton Larmor frequency in the high magnetic field B_0 , $\nu_L = \gamma_H B_0 / 2\pi$. The main advantage of the presently proposed experiment is its duration. The duration of the polarization period must be a few proton T_1 in the high magnetic field B_0 when the dips are measured. In the presently proposed experiment this time is not important and can be taken very short. What counts is only the duration of the mixing period, which is typically of the order of 1 s. The usefulness of the proposed experiment thus depends on the proton spin-lattice time in the high magnetic field B_0 . If it is several 100 s or longer, the presently proposed experiment may – even if the averaging is needed – give the equal-quality results in a shorter time than the cross relaxation spectroscopy [5–7].

The measurement of the ν_H -dependence of the proton NMR signal S at different durations of the mixing period can be used to estimate the proton spin-lattice relaxation rate R_H in the low magnetic field and the nitrogen contributions $2\varepsilon(W_i + W_jW_k/(W_j + W_k))$ to the proton spin-lattice relaxation rates in resonances. The transition probabilities W_+, W_- , and W_0 can further be related to the fluctua-

tions of the EFG tensor at the nitrogen positions and to the molecular dynamics.

When the proton spin system is resonantly coupled to the ^{14}N spin system at $\nu_{\text{H}} = \nu_0$, the proton spin system approaches its equilibrium magnetization with the relaxation rate given by Expression (4) with $i = 0$, $j = -$, and $k = +$. The equilibrium proton magnetization is proportional to $\nu_{\text{H}} = \nu_0$ and is therefore rather small. If in this case we apply during the mixing period an *rf* magnetic field at the frequency $\nu = \nu_+$ or $\nu = \nu_-$, the proton spin system may dynamically reach a much larger magnetization. Let's consider the situation when $\nu = \nu_-$. The situation is illustrated in Fig. 3. We assume that both spin systems are prior to the application of the *rf* magnetic field in thermal equilibrium with the lattice. The *rf* irradiation, which saturates the NQR transition at $\nu = \nu_-$ and the proton nitrogen cross relaxation, which makes the ratio of the populations of the nitrogen energy levels N_1/N_2 equal to the ratio of the populations of the proton energy levels n_1/n_2 , produce in a short time a quasi equilibrium population of the proton and nitrogen energy levels that can be expressed as

$$\begin{aligned} n_1 &= n(1 - z) \\ n_2 &= n(1 + z) \\ N_1 &= N(1 - 4z/3) \\ N_2 &= N(1 + 2z/3) \\ N_3 &= N(1 + 2z/3). \end{aligned} \quad (5)$$

Here $N = N_0/3$ is one third of the number of crystallographically equivalent nitrogen atoms in the unit cell and $n = N_{\text{H}}/2$ is one half of the number of protons in the unit cell. The time dependence of the parameter z , which is proportional to the proton magnetization, may be calculated from the equation

$$d(N_1 + n_1)/dt = -W_0^{\downarrow}N_1 - W_+^{\downarrow}N_1 + W_0^{\uparrow}N_2 + W_+^{\uparrow}N_3 - W_{\text{H}}^{\downarrow}n_1 + W_{\text{H}}^{\uparrow}n_2. \quad (6)$$

The equation for z in the high-temperature approximation reads

$$dz/dt = -W(z - z_0). \quad (7)$$

Here the relaxation rate W of the parameter z is expressed as

$$W = \frac{6}{3 + 4\varepsilon} [W_{\text{H}} + \varepsilon(W_0 + W_+)] \quad (8)$$

while its stationary value z_0 is

$$z_0 = \left(\frac{h\nu_0}{2k_{\text{B}}T} \right) \frac{W_{\text{H}} + \varepsilon(W_0 + (\nu_+/ \nu_0)W_+)}{W_{\text{H}} + \varepsilon(W_0 + W_+)}. \quad (9)$$

The equilibrium populations of the proton energy levels are in case of no *rf* irradiation equal $n_1 = n(1 - z^*)$ and $n_2 = n(1 + z^*)$, where

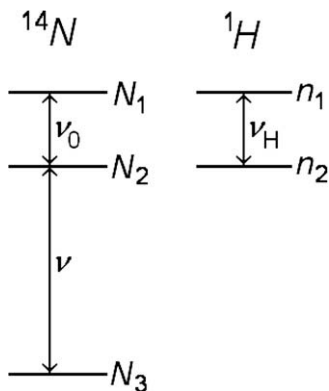


Fig. 3. Nuclear quadrupole energy levels of ^{14}N and Zeeman energy levels of ^1H in resonance at $\nu_{\text{H}} = \nu_0$, the population of the energy levels and the frequency ν of the *rf* irradiation in a dynamic polarization experiment at $\nu = \nu_-$.

$z^* = h\nu_0/2k_{\text{B}}T$. Under the influence of the *rf* irradiation the parameter z , which is proportional to the proton magnetization, reaches the value z_0 after several characteristic times τ^* , $\tau^* = W^{-1}$. The second fraction of Expression (9) represents the increase of the proton magnetization z_0/z^* under the influence of the dynamic polarization. The increase of the proton magnetization with respect to its equilibrium value, z_0/z^* , is in the extreme case, when $\varepsilon W_+ \gg W_{\text{H}}$, εW_0 , equal to ν_+/ ν_0 . The increase of the proton magnetization is in a realistic situation smaller.

When we apply the *rf* magnetic field at the frequency $\nu = \nu_+$ we can again describe the population of the proton and nitrogen energy levels by a single parameter z

$$\begin{aligned} n_1 &= n(1 - z) \\ n_2 &= n(1 + z) \\ N_1 &= N(1 - 2z/3) \\ N_2 &= N(1 + 4z/3) \\ N_3 &= N(1 - 2z/3). \end{aligned} \quad (10)$$

The rate equation in the form of Expression (7) is obtained also in this case with the relaxation rate W and the equilibrium value z_0 equal

$$\begin{aligned} W &= \frac{6}{3 + 4\varepsilon} [W_{\text{H}} + \varepsilon(W_0 + W_-)] \\ z_0 &= z^* \frac{W_{\text{H}} + \varepsilon(W_0 - (\nu_-/ \nu_0)W_-)}{W_{\text{H}} + \varepsilon(W_0 + W_-)}. \end{aligned} \quad (11)$$

In the extreme case, when $\varepsilon W \gg W_{\text{H}}$, εW_0 , we obtain $z_0 = z^*(\nu_-/ \nu_0)$. The proton magnetization by the factor ν_-/ ν_0 exceeds the equilibrium proton magnetization at $\nu_{\text{H}} = \nu_0$ and points antiparallel to the magnetic field direction.

Next possibility of dynamically polarizing the proton spin system via the quadrupole ^{14}N spin system is given by the application of solid effect. As shown in [10] the dynamic polarization of protons may occur if in a weak magnetic field B we irradiate the sample by a strong *rf* magnetic field with the frequency $\nu = \nu_i \pm \nu_{\text{H}}$, $i = +, -, 0$. When $\nu = \nu_i + \nu_{\text{H}}$, the magnetization of the dynamically polarized proton spin system points antiparallel to the direction of the magnetic field B . When $\nu = \nu_i - \nu_{\text{H}}$, the proton magnetization points parallel to the direction of the magnetic field B . The population of the proton energy levels may again be described by the parameter z as given in Expressions (5) and (10) and the equilibrium value of z in case of no *rf* irradiation may be again denoted as z^* , $z^* = h\nu_{\text{H}}/2k_{\text{B}}T$. The ratio of the magnetization of the dynamically polarized proton spin system and the equilibrium proton magnetization at the Larmor frequency ν_{H} , z_0/z^* , is under the *rf* irradiation at the frequencies $\nu = \nu_i \pm \nu_{\text{H}}$ equal [10]

$$z_0/z^* = \frac{W_{\text{H}}[2W_{\text{Q}}^2 + W_{\text{SE}}(W_j + W_k)] \mp \varepsilon W_{\text{SE}}W_{\text{Q}}^2\nu_i/\nu_{\text{H}}}{W_{\text{H}}[2W_{\text{Q}}^2 + W_{\text{SE}}(W_j + W_k)] + \varepsilon W_{\text{SE}}W_{\text{Q}}^2}. \quad (12)$$

Here W_{SE} is the transition probability per unit time for the solid effect transition, $W_{\text{Q}}^2 = W_+W_- + W_+W_0 + W_-W_0$, and the indices j and k stand for the two ^{14}N NQR transitions that are not hit by solid effect. The proton magnetization is in the extreme case, when $W_{\text{H}}[2W_{\text{Q}}^2 + W_{1,6}(W_- + W_0)] \ll \varepsilon W_{\text{SE}}W_{\text{Q}}^2$, dynamically increased by the factor ν_i/ν_{H} .

3. Measurement of low NQR frequencies

The quadrupole nuclei and protons strongly interact when $\nu_{\text{H}} = \nu_{\text{Q}}$. In this case the flip-flop transitions occur in the two spin systems leading towards an equilibrium where the ratio of the populations of the two proton energy levels is equal to the ratio of the population of the two quadrupole energy levels separated by ν_{Q} . It is also well known that the proton spin system in a solid sample absorbs energy also at the multiples of the Larmor frequency. This effect, which is the consequence of the proton–proton

dipolar interaction, is easily observed at low proton Larmor frequencies. Thus the two spin systems resonantly interact also when $\nu_H = \nu_Q/n$, $n = 2, 3, \dots$. In practice the resonance interaction at $\nu_H = \nu_Q/2$ is still rather strong [6–8], whereas at higher n the resonance interaction between the two spin systems is weaker.

An useful resonance interaction between the proton and the quadrupole spin systems can thus be established at a low magnetic field B equal to $B = 2\pi\nu_Q/\gamma_H$ ($\nu_H = \nu_Q$) or $B = \pi\nu_Q/\gamma_H$ ($\nu_H = \nu_Q/2$). Here γ_H is the gyromagnetic ratio of protons. If the proton and the quadrupole spin systems resonantly interact and the NQR transition is simultaneously saturated by an *rf* magnetic field, which does not produce transitions between the energy levels of the proton spin system, the proton relaxation rate increases. In the two-frequency irradiation technique, used for the measurement of the ^{14}N NQR frequencies [8], protons resonantly interact with nitrogen at the lowest ^{14}N NQR transition frequency ν , whereas the populations of the two nitrogen energy levels separated by ν are made equal by a simultaneous irradiation of the other ^{14}N NQR transitions at the frequencies ν_+ and ν_- .

Here we propose the application of an *rf* magnetic field parallel to the static magnetic field. When the proton Larmor frequency is large as compared to the dipolar width of the proton NMR line, this irradiation has no effect on the proton magnetization even if the frequency of the *rf* magnetic field is equal to the proton Larmor frequency. In the sub-100 kHz region this is no more the case. We base the new technique on the supposition that the *rf* irradiation of the quadrupole nuclei at $\nu = \nu_Q$ plus nitrogen–proton cross relaxation at $\nu_H = \nu_Q/2$ have a stronger effect on the proton relaxation than the direct absorption of the *rf* power by the proton spin system at $\nu = \nu_Q = 2\nu_H$. This supposition is tested in the experimental session.

The cycle of the proposed double resonance experiment are as follows:

1. Polarization of the proton spin system in a high magnetic field B_0 .
2. Sample transfer to a second magnet where the static magnetic field is B and the proton Larmor frequency is equal to $\nu_H = \gamma_H B/2\pi$.
3. Application of an *rf* magnetic field B_1 with the frequency $\nu = 2\nu_H$ during the stay of the sample in the low magnetic field. In order to ensure the parallel orientation of B and B_1 , both magnetic fields are produced by a single coil.
4. Transfer of the sample back into the first magnet and measurement of the intensity S of the proton NMR signal.
5. A change of the frequency of the *rf* magnetic field to $\nu\Delta\nu$ and of the low magnetic field B for such a value that the proton Larmor frequency ν_H in the low magnetic field changes to $\nu_H = \nu + \Delta\nu/2$.
6. The magnetic field cycles are repeated at different values of ν and ν_H ($\nu = 2\nu_H$) so that the range, where the NQR frequencies are expected, is scanned by the frequency ν . The step $\Delta\nu$ in the frequency scan is typically 0.1 Hz. When the frequency ν equals to a NQR frequency ν_Q , we expect a drop of the intensity of the proton NMR signal S at the end of the magnetic field cycle.

A possible variant of the technique uses the *rf* irradiation at the frequency $\nu = \nu_H$. The advantage is a stronger resonance interaction of the two spin systems at $\nu_H = \nu_Q$ than at $\nu_H = \nu_Q/2$. On the other hand the magnetic field broadening of a NQR line is larger and also the direct absorption of the *rf* power by the proton spin system is higher.

4. Experimental results and discussion

4.1. Dynamic polarization of protons

The experiments of proton polarization via ^{14}N are performed in 1,3,5-triazine ($\text{C}_3\text{H}_3\text{N}_3$). The ^{14}N NQR frequencies have been in this

compound previously measured by pure NQR [17,18]. In 1,3,5-triazine a phase transition occurs at 198 K. The three nitrogen positions in a molecule are crystallographically equivalent above the phase transition temperature. A molecule performs a slow reorientation around its threefold axis [17] what strongly influences the EFG tensor at the nitrogen position and causes a fast nitrogen spin–lattice relaxation. The threefold axis of a s-triazine molecule coincides with the principal axis Y of the EFG tensor [17]. The reorientation thus modulates the elements of the EFG tensor in the X–Z plane and produces transitions between the nuclear quadrupole energy levels separated by the NQR frequency ν . The transition probability per unit time W is thus expected to be larger than W_0 and W_+ as indeed observed by ^{14}N NQR [17]. The same molecular motion has a much weaker influence on the proton spin–lattice relaxation.

The dynamic polarization experiments were performed on a home made double resonance spectrometer using mechanical motion of the sample between two magnets. The high magnetic field B_0 is equal to 0.75 T, corresponding to the Larmor frequency $\nu_L = 32$ MHz. The time of the sample transfer between the two magnets is approximately 0.1 s. A commercial sample of 1,3,5-triazine was used.

The dependence of the proton NMR signal S at the end of the magnetic field cycle on the proton Larmor frequency ν_H in the low magnetic field B as observed in a field cycling experiment is presented in Fig. 4. The magnetic field cycles are repeated every 10 s and the duration of the mixing period is 1 s. The frequency range between 2 and 4 MHz is scanned in steps of $\Delta\nu_H = 100$ kHz. Each point in the figure represents an average of 16 measurements under the same experimental conditions. Two peaks are easily observed at around 2.7 and 3.5 MHz. They correspond to the proton–nitrogen resonance interaction at $\nu_H = \nu$ and $\nu_H = \nu$, respectively. The two peaks are relatively broad and their widths increase with increasing temperature in accordance with the increasing reorientation rate of the s-triazine molecules. At each temperature the scan lasted about 1 h. This may be compared to the proton spin–lattice relaxation time at $\nu_L = 32$ MHz, which is in the temperature range of the measurements approximately 10 min. Thus only a few magnetic field cycles can be repeated within an hour if a reasonable proton magnetization is expected at the end of the polarization period.

The NMR signal of the dynamically polarized proton spin system at $\nu_H \approx \nu = 775$ kHz is presented in Fig. 5. The experiments were performed at $T = 243$ K. The magnetic field cycles were repeated every 10 s, the duration of the mixing period was equal to 1 s and the amplitude of the *rf* magnetic field applied during the

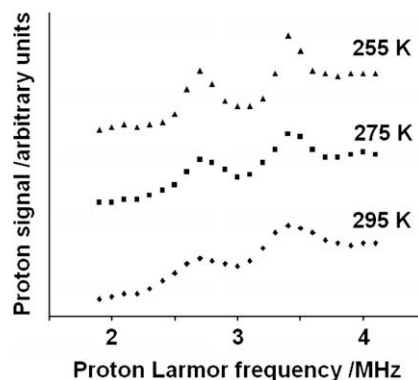


Fig. 4. Proton NMR signal as a function of the proton Larmor frequency in a magnetic field cycling experiment where the proton magnetization is negligible at the beginning of the mixing period and the proton– ^{14}N cross relaxation polarizes protons at $\nu_H = \nu$ and $\nu_H = \nu$. The duration of the mixing period is 1 s.

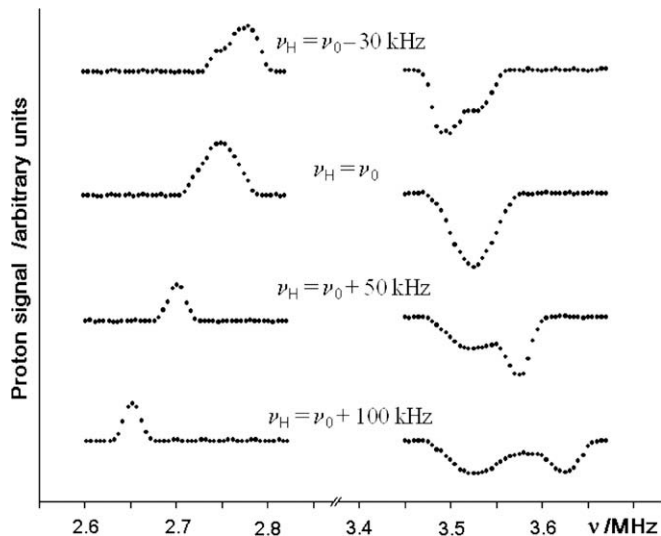


Fig. 5. Dynamic polarization of protons by ^{14}N in 1,3,5-triazine at $T = 243\text{ K}$ using direct resonance interaction ($\nu_{\text{H}} = \nu = 775\text{ kHz}$) and solid effect ($\nu_{\text{H}} \neq \nu$).

mixing period was approximately equal to 3 mT. Each measurement was averaged four times. When $\nu_{\text{H}} = \nu_0 = 775\text{ kHz}$ we observe a positive peak at $\nu = \nu_- = 2750\text{ kHz}$ and a negative peak at $\nu = \nu_+ = 3525\text{ kHz}$ in accordance with Expressions (9) and (11). The intensities of the positive and negative peaks are about 5 and 7% of the intensity of the equilibrium proton NMR signal at $\nu_{\text{L}} = 32\text{ MHz}$, respectively. If the sample is left in the low magnetic field at $\nu_{\text{H}} = \nu_0 = 775\text{ kHz}$ for a long time and then moved in the magnet where $\nu_{\text{L}} = 32\text{ MHz}$, we expect, before the proton spin-lattice relaxation considerably changes the proton magnetization, the proton NMR signal, with the intensity equal to $\nu_0/\nu_{\text{L}} = 2.4\%$ of the intensity of the equilibrium proton NMR signal at $\nu_{\text{L}} = 32\text{ MHz}$. The intensities of the experimentally observed peaks are larger than this value, so the proton spin system is indeed dynamically polarized in the low magnetic field where its magnetization exceeds the equilibrium proton magnetization at $\nu_{\text{H}} = \nu_0$. The maximum possible intensity of the positive peak is $\nu_+/\nu_{\text{L}} = 11\%$ of the intensity of the equilibrium proton NMR signal at $\nu_{\text{L}} = 32\text{ MHz}$. The maximum possible intensity of the negative peak is $\nu_-/\nu_{\text{L}} = 8.4\%$ of the intensity of the equilibrium proton NMR signal at $\nu_{\text{L}} = 32\text{ MHz}$. The intensities of the two experimentally observed peaks are lower than their maximum intensities. There are three main possible reasons for this difference.

- (i) A lower intensity of a peak is expected when the transition probability per unit time W_0 is not much lower than W_+ or W_- .
- (ii) If during the irradiation time τ the dynamic equilibrium is not yet established, the proton magnetization is lower than its maximum value.
- (iii) The ^1H - ^{14}N level crossings on going from the low into the high magnetic field alter the proton magnetization.

Fig. 5 also shows that if a different low magnetic field B is chosen, so that $\nu_{\text{H}} = \gamma_{\text{H}}B/2\pi \neq \nu_0$, the positive peak moves. It is observed at $\nu = \nu_+ - \nu_{\text{L}}$. The positive peak is in this case produced by the solid effect in agreement with Expression (12). A different situation is observed with the negative peak. It splits into two peaks. One negative peak remains at $\nu = \nu_+$, whereas the second peak occurs at $\nu = \nu_- + \nu_{\text{L}}$. The second negative peak is produced by the solid effect, while the first peak which occurs at $\nu = \nu_+$ independent on ν_{L} seems to be associated with the level crossings. If in

the time interval between the end of the rf irradiation and the set of level crossings on the way back into the first magnet the ^{14}N spin system does not reach thermal equilibrium with the crystal lattice, the effect of the saturation of the ^{14}N NQR transition at $\nu = \nu_+$ may be observed on the proton spin system. The saturation of the ^{14}N NQR transition at $\nu = \nu_-$ has in general a much weaker effect on the level crossing signals [3,10] and is not observed in the present experiment. The intensities of the solid-effect peaks are in the present case about 3% of the intensity of the equilibrium proton NMR signal at $\nu_{\text{L}} = 32\text{ MHz}$.

The polarization rate of the proton magnetization in s-triazine was studied at $T = 230\text{ K}$. Here the ^{14}N NQR frequencies are $\nu_+ = 3540\text{ kHz}$, $\nu_- = 2760\text{ kHz}$, and $\nu_0 = 780\text{ kHz}$. The low magnetic field B was adjusted to the resonance $\nu_{\text{H}} = \nu_0$ and the intensities of the positive and negative peaks were measured as functions of the irradiation time τ . The experimental results are presented in Fig. 6. The intensity of the positive peak at $\nu = \nu_- = 2760\text{ kHz}$ starts from zero and exponentially approaches its limiting value with the relaxation time $(W(\nu = \nu_-))^{-1} = 400 \pm 100\text{ ms}$. The intensity of the negative peak is nonzero already well below $\tau = 1\text{ ms}$. This is presumably the effect of level crossing. The rf magnetic field first saturates the NQR transition what after the second set of level crossings changes the proton magnetization. This change is observed for τ well below $\tau = 1\text{ ms}$ and is independent on τ . At larger values of τ the negative peak exponentially approaches its limiting value with the relaxation time $(W(\nu = \nu_+))^{-1} = 100 \pm 20\text{ ms}$. The large difference of the two relaxation times is not surprising. The pulsed NQR experiments in s-triazine [7] show the presence of two ^{14}N relaxation times: a short one associated with the NQR transition at the frequency $\nu = \nu_-$ and a long one associated with the NQR transition at the frequency $\nu = \nu_+$. At 230 K the short relaxation time is about $T_{1\text{s}} = 30\text{ ms}$ and the long relaxation time about $T_{1\text{l}} = 650\text{ ms}$. The short relaxation time steeply decreases on increasing temperature, while the long relaxation time only slightly varies with temperature. If we first concentrate on the short relaxation time $T_{1\text{s}}$, which is approximately equal to $T_{1\text{s}} \approx (2W_-)^{-1}$ [17,19], we obtain $W_- \approx 17\text{ s}^{-1}$. In the present experiment we have (Expression (11)) $W(\nu = \nu_+) = 10\text{ s}^{-1} \approx (6\varepsilon/(3+4\varepsilon))W_- \approx 0.7W_-$. From the last expression we obtain $W_- = 14\text{ s}^{-1}$, what is not far from the value obtained by pulsed NQR. A larger difference is observed in case of the long relaxation time. In the present case, when $W_- \gg W_+$, W_0 , the long relaxation time $T_{1\text{l}}$ may be expressed as $(T_{1\text{l}})^{-1} = (3/2)(W_+ + W_0)$ [17,19]. From this expression we obtain $W_+ + W_0 = 1.0\text{ s}^{-1}$. In the dynamic polarization experiment we have (Expression (8)), neglecting the “pure” proton spin-lattice relaxation, $W(\nu = \nu_-) = 2.5\text{ s}^{-1} \approx (6\varepsilon/(3+4\varepsilon))(W_0 + W_+)$. From this expression we obtain $W_0 + W_+$

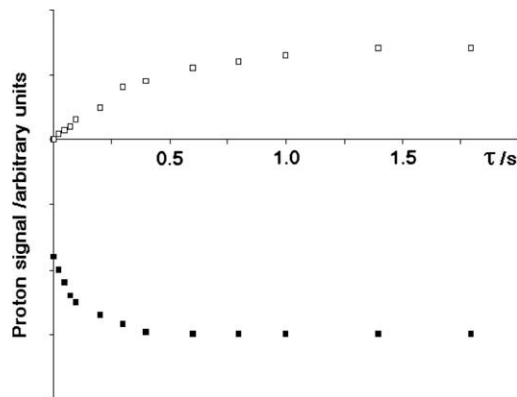


Fig. 6. The intensity of the positive peak at $\nu = \nu_- = 2760\text{ kHz}$ (open squares) and the intensity of the negative peak at $\nu = \nu_+ = 3540\text{ kHz}$ (full squares) as functions of the irradiation time τ in 1,3,5-triazine at $T = 230\text{ K}$.

$\approx 3.5 \text{ s}^{-1}$, what is more than obtained by pure NQR. The reason for this difference is not known. Proton spin-lattice relaxation may not account for the observed difference. A possible explanation may be the difference in the structure and purity of the commercial samples used.

4.2. Measurement of low NQR frequencies

The experiments were performed in a home made double resonance spectrometer previously described. The sample coil in the second magnet is perpendicular to the field lines of the magnetic field B_e in the second magnet (see Fig. 7).

The magnetic field B as produced by the DC current I in the sample coil (Fig. 7) was measured as follows. A water sample was shuttling between the magnets. The DC current I was set to zero and the frequency ν of the synthesizer was set to 40 kHz. The magnetic field B_e was varied between the magnetic field cycles by varying the electric current through the second magnet. In resonance, i.e. when $\gamma_H B_e / 2\pi = 40 \text{ kHz}$, we observed a drop of the proton NMR signal S at the end of the magnetic field cycle. Then B_e was fixed at this value and the DC current I through the rf coil was set to $I = 1 \text{ A}$. The magnetic field cycles were repeated at different values of the frequency ν . A drop of the proton signal S was observed when $\nu = 50.5 \text{ kHz}$, meaning that $\nu_H = \gamma_H B / 2\pi = \sqrt{(50.5 \text{ kHz})^2 - (40 \text{ kHz})^2} = 31 \text{ kHz}$. Proton Larmor frequency ν_H in the DC magnetic field B produced by the DC current I through the rf coil is thus $\nu_H = (31 \text{ kHz})[A]$. This relation was later used in adjusting the frequency ν_H to the irradiation frequency ν ($\nu_H = \nu/2$).

In the following experiments B_e was set to zero.

In order to determine the change ΔW of the proton relaxation rate which is due to the direct absorption of the rf power by the proton spin system at $\nu = 2\nu_H$ we performed measurements in $(\text{NH}_4)_2\text{SO}_4$ and KH_2PO_4 . Two values of the static magnetic field B were used with $\nu_H = 40 \text{ kHz}$ and $\nu_H = 60 \text{ kHz}$. The rf magnetic field had an amplitude of $B_1 = 0.011 \text{ mT}$. The magnetic field cycles were repeated with different duration τ of the period spent in the low magnetic field B . In $(\text{NH}_4)_2\text{SO}_4$ we obtained $\Delta W = 0.60 \text{ s}^{-1}$ at $\nu = 2\nu_H = 80 \text{ kHz}$ and $\Delta W = 0.40 \text{ s}^{-1}$ at $\nu = 2\nu_H = 120 \text{ kHz}$. In KH_2PO_4 we obtained $\Delta W = 0.55 \text{ s}^{-1}$ at $\nu = 2\nu_H = 80 \text{ kHz}$ and $\Delta W = 0.35 \text{ s}^{-1}$ at $\nu = 2\nu_H = 120 \text{ kHz}$. Thus at a typical value of τ between 0.3 s and 1 s the direct absorption of the rf power produces a minor decrease of the proton magnetization. Using the Fermi's golden rule we estimated the transition probability per unit time W between the quadrupole energy levels when subject to a rf magnetic field with the amplitude $B_1 = 0.01 \text{ mT}$. In case of a ^{14}N nucleus we obtained W of the order of 1000 s^{-1} , what is three orders of magnitude more than the direct proton absorption rate.

In an analysis of our previous measurements of the ^{14}N NQR frequencies by the two-frequency irradiation technique, which exhibit dips at $\nu_H = \nu_Q/n$, $n = 1, 2, 3, \dots$, we obtained W_{CR} at $\nu_H = \nu_Q/2$ of the order of 10 s^{-1} . The sensitivity of the new technique is thus

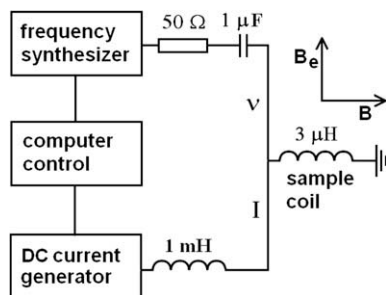


Fig. 7. Some details of the low-frequency part of the double resonance spectrometer.

mainly limited by the cross-relaxation rate W_{CR} between the proton and quadrupole spin systems at $\nu_Q = 2\nu_H$ and by the proton spin-lattice relaxation. If the proton spin-lattice relaxation in the low magnetic field allows τ to be equal to 1 s and if the signal to noise ratio of the detection of the proton NMR signal S is about 100, we expect the minimum number of the quadrupole nuclei which can be detected by the present technique to be equal to about 1% of the number of protons in the sample.

We measured also the frequency width $\Delta\nu$ of the absorption dip at $\nu = 2\nu_H$. In both samples we obtained $\Delta\nu \approx 25 \text{ kHz}$. This tells us, how sharp is the resonance condition $2\nu_H = \nu_Q$ which is dominated by the width of the proton absorption line. The resolution of the technique is much higher. It depends on the width of the ^{14}N NQR lines which is expected to be less than 1 kHz.

4.2.1. ^{14}N NQR in $(\text{NH}_4)_2\text{SO}_4$

As a test of the new technique we performed a measurement of the ^{14}N NQR frequencies in $(\text{NH}_4)_2\text{SO}_4$ at the room temperature. The proton polarization time in the high magnetic field was equal to 20 s and the time τ spent in the low magnetic field B was equal to $\tau = 0.3 \text{ s}$. The frequency scan was performed between $\nu = 40 \text{ kHz}$ and $\nu = 150 \text{ kHz}$. The amplitude B_1 of the rf magnetic field was $B_1 = 0.011 \text{ mT}$. The results are presented in Fig. 8. Six dips are observed in the double resonance spectrum corresponding to two non equivalent nitrogen positions in the crystal structure. For one nitrogen position N(1) we obtain $\nu_+(1) = (108.5 \pm 0.5) \text{ kHz}$, $\nu_-(1) = (65.5 \pm 0.5) \text{ kHz}$, and $\nu_0(1) = (43.0 \pm 0.5) \text{ kHz}$. For the other nitrogen position we obtain $\nu_+(2) = (141.5 \pm 0.5) \text{ kHz}$, $\nu_-(2) = (89.0 \pm 0.5) \text{ kHz}$, and $\nu_0(2) = (52.5 \pm 0.5) \text{ kHz}$. The obtained results are in good agreement with the results of zero field NMR and NQR [11].

4.2.2. ^{14}N NQR in NH_4NO_3

In order to check the resolution of the new technique we measured the low-frequency part of the ^{14}N NQR spectrum in NH_4NO_3 at room temperature. The ^{14}N NQR frequencies in NH_4NO_3 are known from a previous measurement [20]. The parameters of a magnetic field cycle and the amplitude of the rf magnetic field were the same as in the previous experiment. The results are presented in Fig. 9. Below 150 kHz we observe three ^{14}N NQR lines at the frequencies (72.1 ± 0.2) , (103.0 ± 0.2) , and $(131.6 \pm 0.2) \text{ kHz}$. The NQR frequency 72.1 kHz is the lowest ^{14}N NQR frequency (ν_0) from the nitrate ion. The NQR frequencies 103.0 and 131.6 kHz are the lowest (ν_0) and the intermediate (ν_-) ^{14}N NQR frequencies, respectively from the ammonium ion. The NQR lines,

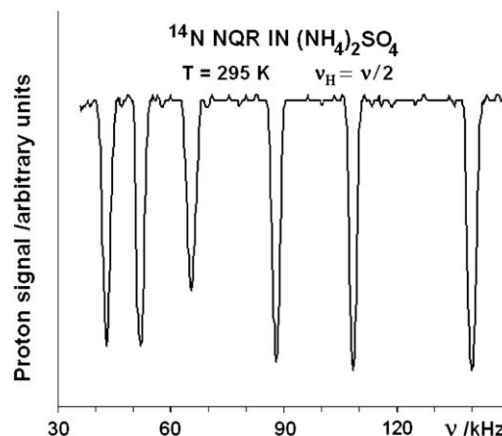


Fig. 8. ^{14}N NQR spectrum of $(\text{NH}_4)_2\text{SO}_4$ as measured by the new NQDR technique. The details of the experiment are given in text.

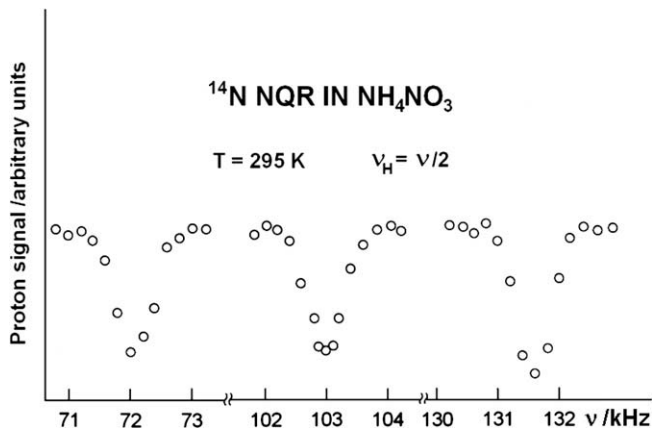


Fig. 9. The shapes of the ^{14}N - ^{14}N NQDR lines in the low-frequency part of the ^{14}N NQR spectrum in NH_4NO_3 .

as measured by the present technique, are much narrower than the same NQR lines previously measured by the two-frequency irradiation technique and by the solid-effect technique.

4.2.3. Deuterium NQR in $\text{K}(\text{H}_{1-x}\text{D}_x)_2\text{PO}_4$

In both previous cases we may neglect the magnetic field broadening of the NQR lines. A ^{14}N nucleus has namely a rather low magnetic moment and in addition the asymmetry parameter η of the EFG tensor at the position of the ammonium nitrogen is rather high in both compounds. In case of the NO_3 ion in NH_4NO_3 the NQR frequencies ν_+ and ν_- are much higher than ν_0 . In such a case the lowest NQR frequency can still be measured rather precisely by the above technique.

A completely different situation arises in case of $I = 1$ when the asymmetry parameter η is small and we want to apply the above technique to measure the upper NQR frequencies ν_+ and ν_- . Such a situation often occurs in deuterium NQR. Now the Larmor frequency ν_{LQ} of a quadrupole nucleus is no longer small as compared to the lowest NQR frequency ν and the magnetic shift of the two quadrupole energy levels separated by ν is not small. A significant magnetic broadening of the NQR lines at ν_+ and ν_- is expected.

In order to show the double resonance results in case of a large magnetic broadening of the NQR lines we performed measurement of deuterium NQR frequencies in polycrystalline $\text{K}(\text{H}_{0.65}\text{D}_{0.35})_2\text{PO}_4$. An extensive study of the deuterium quadrupole coupling in $\text{K}(\text{H}_{1-x}\text{D}_x)_2\text{PO}_4$ has already been published [21].

Measurements have been performed in the paraelectric phase at 230 K. The proton polarization time in the high magnetic field was 30 s. The time τ spent in the low magnetic field was 0.5 s. Protons and deuterons were in the low magnetic field coupled at $\nu_{\text{H}} = \nu_{\text{Q}}/2$. The amplitude B_1 of the rf magnetic field was equal to 0.011 mT.

The double resonance spectrum is shown in Fig. 10. A broad frequency distribution centered at 86 kHz is observed. The frequency distribution consists of two lines indicating that the asymmetry parameter η of the EFG tensor is nonzero. In order to determine the NQR parameters from the double resonance spectra we perform a fit of the double resonance spectra to a model where we first assume that the nonzero magnetic field B shifts infinitely sharp NQR lines ν_+ and ν_- . Instead of the NQR frequencies ν_+ and ν_- we observe in this case two resonance frequencies ν_1 and ν_2 :

$$\nu_{1,2} = \bar{\nu} \pm \sqrt{\left(\frac{\bar{\nu}}{3}\eta\right)^2 + \nu_{\text{LQ}}^2 \cos^2(\Theta)}. \quad (13)$$

Here $\bar{\nu} = (\nu_+ + \nu_-)/2$, $\nu_{\text{LQ}} = \gamma_{\text{D}}B/2\pi$ is the deuterium Larmor frequency and Θ is the angle between the direction of B and the prin-

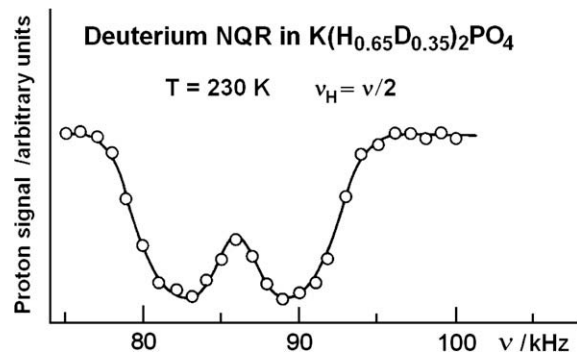


Fig. 10. ^1H - ^2H double resonance spectrum of $\text{K}(\text{H}_{0.65}\text{D}_{0.35})_2\text{PO}_4$ at 230 K. The full line represents the best fit to the model given in text.

cipal axis Z of the EFG tensor. Expression (13) is calculated in the first order perturbation theory assuming $\nu_{\text{LQ}} \ll \nu_+$, ν_- . When $B = 0$ we obtain $\nu_1 = \nu_+$ and $\nu_2 = \nu_-$, whereas in nonzero B $\nu_1 > \nu_+$ and $\nu_2 < \nu_-$. Since the frequencies ν_1 and ν_2 depend on the orientation of the external magnetic field B with respect to the principal axis Z of the EFG tensor we obtain in a polycrystalline sample two frequency distributions: $g_1(\nu)$ above ν_+ and $g_2(\nu)$ below ν_- :

$$g_1(\nu) = \frac{1}{2\nu_{\text{L}}} \frac{(\nu - \bar{\nu})}{\sqrt{(\nu - \bar{\nu})^2 - \left(\frac{\bar{\nu}}{3}\eta\right)^2}}, \quad \nu_+ = \bar{\nu} + \frac{\bar{\nu}}{3}\eta < \nu < \bar{\nu} + \sqrt{\left(\frac{\bar{\nu}}{3}\eta\right)^2 + \nu_{\text{L}}^2}$$

$$g_2(\nu) = \frac{1}{2\nu_{\text{L}}} \frac{(\bar{\nu} - \nu)}{\sqrt{(\bar{\nu} - \nu)^2 - \left(\frac{\bar{\nu}}{3}\eta\right)^2}}, \quad \nu_- = \bar{\nu} - \frac{\bar{\nu}}{3}\eta > \nu > \bar{\nu} - \sqrt{\left(\frac{\bar{\nu}}{3}\eta\right)^2 + \nu_{\text{L}}^2}. \quad (14)$$

The frequency distribution $g_1(\nu)$ has a square root singularity at $\nu = \nu_+$, whereas the frequency distribution $g_2(\nu)$ has a square root singularity at $\nu = \nu_-$.

The NQR lines ν and $\bar{\nu}$ are of course not infinitely sharp due to the dipole-dipole interaction and the distribution of the principal values of the EFG tensor. Also the line broadening caused by the rf magnetic field may not be neglected. We must therefore convolute the distributions $g_1(\nu)$ and $g_2(\nu)$ with the line shape function $L(\nu' - \nu)$ which we assume to be of the Gaussian form:

$$L(\nu' - \nu) = \frac{1}{\sigma\sqrt{\pi}} \exp\left(-\frac{(\nu' - \nu)^2}{\sigma^2}\right). \quad (15)$$

The best fits of the experimental data to the above model is in Fig. 10 shown as the full line. The best fit parameters are $\bar{\nu} = (86 \pm 0.5)$ kHz, $\eta = 0.04 \pm 0.01$ and $\sigma = (2.0 \pm 0.4)$ kHz. The deuterium quadrupole coupling constant is equal to $e^2qQ/h = (115 \pm 0.7)$ kHz. The deuterium NQR frequencies ν_+ and ν_- are (87.5 ± 1) and (85.0 ± 1) kHz, respectively. These results may be compared to the NMR results of Blinc et al. [22] who obtained in a single crystal of paraelectric KD_2PO_4 at 30 °C the following deuterium NQR parameters: $e^2qQ/h = 119.7$ kHz and $\eta = 0.048$. The presently observed asymmetry parameter η is close to the one observed by NMR. The deuterium quadrupole coupling constant, as observed by NMR, is larger than the deuterium quadrupole coupling measured by the present technique. However, as shown in [21], the deuterium quadrupole coupling constant in $\text{K}(\text{H}_{1-x}\text{D}_x)_2\text{PO}_4$ linearly increases with increasing deuterium concentration, which explains the difference.

The present results show that even in case of a large line broadening, which is due to nonzero external magnetic field and a small asymmetry parameter η the NQR frequencies ν_+ and ν_- can still be determined rather precisely from the double resonance spectrum obtained by the new technique.

5. Conclusions

Two types of NQDR experiments are treated in the present paper:

- (i) Experiments involving dynamic polarization of protons by ^{14}N in a low magnetic field and
- (ii) A new NQDR technique involving simultaneous two-quantum transitions in the proton spin system and single-quantum transitions in the quadrupole spin system conserving the total energy of the two spin systems plus resonant *rf* irradiation of the quadrupole transition which is coupled to the proton spin system.

It is shown theoretically that the resonant coupling of ^1H and ^{14}N at $\nu_{\text{H}} = \nu_0$ plus the *rf* irradiation at the ^{14}N NQR frequency $\nu = \nu_+$ or $\nu = \nu_-$ may dynamically lead to a proton magnetization that is larger than the equilibrium proton magnetization at $\nu_{\text{H}} = \nu_0$. The maximum ratio of the proton magnetization obtained by the dynamic polarization and the equilibrium proton magnetization in the same magnetic field is at $\nu = \nu_-$ equal to ν_+/ ν_0 , while it is at $\nu = \nu_+$ equal to ν_- / ν_0 . In the later case the proton magnetization points antiparallel to external magnetic field *B*.

A larger proton magnetization than the equilibrium one can also be obtained by the solid effect. Application of a strong *rf* magnetic field at the frequency $\nu = \nu_0 \pm \nu_{\text{H}}$ may in case of a fast nitrogen spin-lattice relaxation lead to a dynamical equilibrium where the proton magnetization exceeds the equilibrium proton magnetization at the Larmor frequency ν_{H} . The maximum ratio of the proton magnetization obtained by the dynamic polarization and the equilibrium proton magnetization at the Larmor frequency ν_{H} is in both cases equal to ν_0 / ν_{H} . When $\nu = \nu_0 - \nu_{\text{H}}$ the proton magnetization points parallel to the external magnetic field *B*, while when $\nu = \nu_0 + \nu_{\text{H}}$ the proton magnetization points antiparallel to the external magnetic field *B*.

An increase of the proton spin-lattice relaxation at $\nu_{\text{H}} = \nu_0$ may also be used for a fast determination of the ^{14}N NQR frequencies when the proton spin-lattice relaxation time in the high magnetic field is very long. The ν_{H} -dependence of the proton NMR signal *S* at the end of the magnetic field cycle exhibits a peak at $\nu_{\text{H}} = \nu_0$ in contrast to the usual cross relaxation spectroscopy [5–7] where the ν_{H} -dependence of the proton NMR signal *S* at the end of the magnetic field cycle exhibits a dip at the same proton Larmor frequency ν_{H} .

The experiments performed in 1,3,5-triazine confirm the results of the theoretical analysis.

In the second part of the paper we analyze a new double resonance technique, suitable for the measurement of low NQR frequencies of the order of 100 kHz and lower.

The technique is based on the resonant ^1H – ^{14}N (or ^1H – ^2H , etc.) interaction at $\nu_{\text{H}} = \nu_0/2$ and the application of a *rf* magnetic field at the frequency $\nu = \nu_0$ parallel to the external magnetic field *B*. In an actual experiment the frequency ν is changed between repetitive magnetic field cycles in steps of, say, 100 Hz. Also the low magnetic field is changed in steps between the repetitive magnetic field

cycles so that the condition $\nu_{\text{H}} = \nu/2$ is fulfilled. In resonance, when $\nu = \nu_0$ and $\nu_{\text{H}} = \nu/2 = \nu_0/2$, we expect a decrease of the proton NMR signal. The sensitivity of the new technique is estimated. The new technique is used for the measurement of low ^{14}N and ^2H NQR frequencies in $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , and $\text{K}(\text{H}_{0.65}\text{D}_{0.35})_2\text{PO}_4$. In the nitrogen containing compounds the NQR frequencies can be measured with an accuracy better than ± 0.5 kHz, while in $\text{K}(\text{H}_{0.65}\text{D}_{0.35})_2\text{PO}_4$ the asymmetry parameter η is low and the magnetic field broadening of the deuterium NQR lines is not small. The NQDR spectrum is analyzed in a simple model and the deuterium NQR frequencies are determined with an accuracy of ± 1 kHz.

References

- [1] R.E. Slusher, E.L. Hahn, Sensitive detection of nuclear quadrupole interactions in solids, *Phys. Rev.* 166 (1968) 332–347.
- [2] G.W. Leppelmeier, E.L. Hahn, Nuclear dipole field quenching of integer spins, *Phys. Rev.* 141 (1966) 724–731.
- [3] R. Blinc, M. Mali, R. Osredkar, A. Prelesnik, J. Seliger, I. Zupancic, L. Ehrenberg, ^{14}N NQR spectroscopy of some amino acids and nucleic bases via double resonance in the laboratory frame, *J. Chem. Phys.* 57 (1972) 5087–5093.
- [4] D.T. Edmonds, Nuclear-quadrupole double-resonance, *Phys. Rep.* 29 (1977) 234–290.
- [5] J. Seliger, R. Osredkar, M. Mali, R. Blinc, ^{14}N quadrupole resonance of some liquid crystalline compounds in the solid, *J. Chem. Phys.* 65 (1976) 2887–2891.
- [6] J. Seliger, R. Blinc, H. Arend, R. Kind, Proton– ^{14}N double resonance study of the structural phase transitions in the perovskite type layer compound $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$, *Z. Phys. B* 25 (1976) 189–195.
- [7] D. Stephenson, J.A.S. Smith, Nitrogen-14 quadrupole cross relaxation spectroscopy, *Proc. Roy. Soc. A* 416 (1988) 149–178.
- [8] J. Seliger, V. Žagar, R. Blinc, A new highly-sensitive ^1H – ^{14}N nuclear-quadrupole double-resonance technique, *J. Magn. Reson. A* 106 (1994) 214–222.
- [9] J. Seliger, V. Žagar, R. Blinc, ^1H – ^{14}N nuclear quadrupole double resonance with multiple frequency sweeps, *Z. Naturforsch.* 49a (1994) 31–34.
- [10] J. Seliger, V. Žagar, Measurement of the ^{14}N nuclear quadrupole resonance frequencies by the solid effect, *J. Magn. Reson.* 193 (2008) 54–62.
- [11] J.M. Millar, A.M. Thayer, A. Bielecki, D.B. Zax, A. Pines, Zero field NMR and NQR with selective pulses and indirect detection, *J. Chem. Phys.* 83 (1985) 934–938.
- [12] A. Bielecki, D.B. Zax, K.W. Zilm, A. Pines, Zero field NMR and NQR spectrometer, *Rev. Sci. Instrum.* 57 (1986) 393–403.
- [13] J.M. Millar, A.M. Thayer, H. Zimmerman, A. Pines, High resolution studies of deuterium by time domain zero field NQR, *J. Magn. Reson.* 69 (1986) 243–257.
- [14] J. Chang, C. Connor, E.L. Hahn, H. Huber, A. Pines, Direct detection of aluminum-27 resonance with a SQUID spectrometer, *J. Magn. Reson.* 82 (1989) 387–391.
- [15] C. Connor, J. Chang, A. Pines, Aluminum and boron nuclear quadrupole resonance with a direct current superconducting quantum interference device, *J. Chem. Phys.* 93 (1990) 7639–7646.
- [16] Dinh M. TonThat, J. Clarke, Direct current superconducting quantum interference device spectrometer for pulsed nuclear magnetic resonance and nuclear quadrupole resonance at frequencies up to 5 MHz, *Rev. Sci. Instrum.* 67 (1996) 2890–2893.
- [17] A. Zussman, M. Oron, ^{14}N NQR study of molecular reorientation and phase transition in s-triazine, *J. Chem. Phys.* 66 (1977) 743–753.
- [18] A.I.M. Rae, The structural phase change in s-triazine: reconciliation of X-ray diffraction and NQR measurements, *J. Chem. Phys.* 70 (1979) 639–642.
- [19] G. Petersen, P.J. Bray, ^{14}N nuclear quadrupole resonance and relaxation measurements of sodium nitrite, *J. Chem. Phys.* 64 (1976) 522–530.
- [20] J. Seliger, V. Žagar, R. Blinc, ^{14}N NQR study of the structural phase transitions in NH_4NO_3 , *Z. Phys. B Condens. Matter* 77 (1989) 439–443.
- [21] J. Seliger, V. Žagar, ^2H nuclear quadrupole resonance study of the Ubbelohde effect in $\text{K}(\text{H}_{1-x}\text{D}_x)_2\text{PO}_4$, *Phys. Rev. B* 59 (1999) 13505–13508.
- [22] R. Blinc, J. Stepišnik, M. Jamsšek-Vilfan, S. Žumer, Deuteron magnetic resonance and relaxation in ferroelectric KD_2PO_4 , KD_2AsO_4 , and CsD_2AsO_4 , *J. Chem. Phys.* 54 (1971) 187–197.