

Measurement of dipolar structure of ^{17}O nuclear quadrupole resonance lines by three-frequency irradiation

J. Seliger^{a,b,*}, V. Žagar^a

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

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

ARTICLE INFO

Article history:

Received 10 July 2009

Revised 20 November 2009

Available online 4 January 2010

Keywords:

O-17

Quadrupole resonance

Double resonance

Dipolar interaction

ABSTRACT

A modification of nuclear quadrupole double resonance with coupled multiplet is proposed which can be used for the measurement of the dipolar structure of the ^{17}O nuclear quadrupole resonance lines in case of a strong ^1H – ^{17}O dipolar interaction. The technique is based on magnetic field cycling between a high magnetic field and zero magnetic field and on the simultaneous application of three *rf* magnetic fields with the frequencies that are close to the three ^{17}O NQR frequencies $\nu_{5/2-1/2} > \nu_{5/2-3/2} \geq \nu_{3/2-1/2}$ during the time spent in zero static magnetic field. When the sum of the two lower irradiation frequencies $\nu_1 + \nu_2$ is not equal to the highest irradiation frequency ν , the three-frequency irradiation increases the proton relaxation rate in zero magnetic field and consequently decreases the proton NMR signal at the end of the magnetic field cycle. The new technique is theoretically analyzed and compared to the single-frequency and two-frequency irradiation techniques. It is shown that the sensitivity of the new technique exceeds the sensitivity of the two-frequency irradiation technique. As a test of the new technique we measured the shape of the highest-frequency ^{17}O NQR line in paraelectric KH_2PO_4 .

© 2009 Elsevier Inc. All rights reserved.

1. Introduction

^{17}O ($S = 5/2$) has in zero magnetic field three doubly degenerated nuclear quadrupole energy levels. Their energies E are calculated from the secular equation

$$x^3 - 7(3 + \eta^2)x - 20(1 - \eta^2) = 0, \quad (1)$$

where η is the asymmetry parameter of the electric field gradient (EFG) tensor at the position of the oxygen nucleus. An energy E is given as $E = (e^2qQ/20)x$, where x is a solution of the secular equation and e^2qQ is the quadrupole coupling constant e^2qQ/h multiplied by the Planck's constant h . The three nuclear quadrupole resonance (NQR) frequencies are usually named as $\nu_{5/2-1/2} > \nu_{5/2-3/2} \geq \nu_{3/2-1/2}$. They uniquely depend on the quadrupole coupling constant e^2qQ/h and the asymmetry parameter η , that are from the NQR frequencies determined in the following way. First the asymmetry parameter η is determined from the ratio $R = \nu_{3/2-1/2}/\nu_{5/2-3/2}$ which monotonously varies from $R = 0,5$ at $\eta = 0$ to $R = 1$ at $\eta = 1$. When η is known, the quadrupole coupling constant is calculated from any NQR frequency. The ^{17}O NQR frequencies are typically found in the range between 0.5 MHz and 7 MHz.

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

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

The energy levels of the quadrupole Hamiltonian are usually labeled as “5/2”, “3/2” and “1/2”. The corresponding eigenstates are generally expressed as [1]

$$|\psi_{\pm m}\rangle = c_{5/2}^m |\pm 5/2\rangle + c_{1/2}^m |\pm 1/2\rangle + c_{3/2}^m |\mp 3/2\rangle. \quad (2)$$

here $m = 5/2, 1/2$ and $3/2$. The coefficients c_k^m depend on the asymmetry parameter η . In the particular case of $\eta = 0$ only the coefficients $c_{5/2}^{5/2}, c_{3/2}^{3/2}$ and $c_{1/2}^{1/2}$ differ from zero. In this case the highest-frequency $5/2-1/2$ transition cannot be observed, because the difference Δm is for this transition equal $\Delta m = 2$. This transition is no more forbidden for $\eta \neq 0$, but the transition probability per unit time is at an equal amplitude of the *rf* magnetic field significantly lower than for the $5/2-3/2$ and $3/2-1/2$ transitions [2].

In an O–H bond the proton–oxygen dipolar interaction removes the degeneracy of the ^{17}O nuclear quadrupole energy levels. A proton ($I = 1/2$) has in zero magnetic field two degenerate energy levels. The two proton eigenstates we label as $|+\rangle$ and $|-\rangle$. The four states $|\psi_m, +\rangle, |\psi_m, -\rangle, |\psi_{-m}, +\rangle$ and $|\psi_{-m}, -\rangle$, written in the product space, have in absence of the proton–oxygen dipolar interaction the same energy. The dipolar interaction, which is strong in case of a short ^{17}O –H distance, removes the degeneracy of the four states. An energy level of a ^{17}O –H group is basically a nuclear quadrupole energy levels which obtains a dipolar structure. Each quadrupole energy level splits into a quartet of dipolar energy levels. A NQR transition consists thus in principle of sixteen dipolar lines. In practice the dipolar structure of a ^{17}O NQR line is not well

resolved due to the interaction of the ^1H – ^{17}O groups with the rest of protons. The dipolar structure of the ^{17}O NQR lines allows the determination of the proton–oxygen distance, the sign of the ^{17}O quadrupole coupling constant and the orientation of the O–H bond in the principal axis frame of the EFG tensor [3–5]. The O–H distance $R(\text{O–H})$, the angle θ between the O–H bond and the principal axis Z of the EFG tensor plus the angle ϕ between the projection of the O–H bond on the X – Y plane and the principal axis X of the EFG tensor can be determined from the widths of the three dipolar split NQR lines. The sign of the quadrupole coupling can be determined from the dipolar structure inside the lines.

The position of the ^{17}O NQR lines is usually first determined by the Slusher and Hahn's technique [6] using a strong phase-modulated rf magnetic field. The dipolar structure of the ^{17}O NQR lines is by this technique mainly not resolved.

A ^1H – ^{17}O nuclear quadrupole double resonance (NQDR) technique, named double resonance with coupled multiplets, has been developed for the determination of the ^{17}O NQR frequencies and dipolar structure of the ^{17}O NQR lines [3,4]. This technique can be also used to separate overlapping ^{17}O NQR lines.

Double resonance with coupled multiplets is based on magnetic field cycling. First the proton spin system is polarized in a high magnetic field B_0 . Then the external magnetic field is adiabatically reduced to zero. During this process the spin temperature of the proton spin system decreases and—on going into zero magnetic field—the proton Zeeman order transforms into the proton dipolar order and the spin temperature of the proton dipolar reservoir reduces to $T = T_L B_{\text{loc}}/B_0$. Here T_L is the sample temperature and B_{loc} ,

$$B_{\text{loc}}^2 = \frac{4}{h^2 \gamma_{\text{H}}^2 N_{\text{H}}} \text{Tr} H_{\text{DHH}}^2 / \text{Tr} 1, \quad (3)$$

is the local, dipolar, magnetic field which is typically of the order of a few tenths of mT. The proton spin temperature, which is after the demagnetization far below T_L , exponentially approaches T_L with the time constant $T_1(B=0)$ named the proton spin–lattice relaxation time in zero magnetic field.

When after a time τ , spent in zero magnetic field, the initial magnetic field B_0 is adiabatically restored, the proton magnetization M equals $M = M_0 \exp(-\tau/T_1(B=0))$. Here M_0 is the equilibrium proton magnetization in the high magnetic field B_0 . The proton NMR signal, which is measured immediately after the initial magnetic field B_0 is restored, is proportional to the proton magnetization M .

The relaxation of protons in zero magnetic field can be made faster by the simultaneous application of two rf magnetic fields with the frequencies ν_1 and ν_2 , both within a dipolar split ^{17}O NQR line [3,4]. The dipolar splitting of a ^{17}O quadrupole energy level is namely comparable to the width of the proton NMR line in zero magnetic field caused by the proton–proton magnetic dipolar interaction. The rare ^1H – ^{17}O groups therefore strongly interact with the rest of protons via the simultaneous flip–flop transitions in both systems. The two-frequency irradiation of the rare ^{17}O – ^1H groups produce an energy flow from the ^{17}O – ^1H groups to the cold proton dipolar system and a faster relaxation of the spin temperature of the proton dipolar system towards infinite temperature corresponding to zero proton NMR signal at the end of the magnetic field cycle.

Double resonance with coupled multiplets has been several times used for the detection of the ^{17}O NQR frequencies and for the determination of the O–H distances, especially in cases of O–H...O hydrogen bonds [3–5,7–23].

Here we propose a new technique for the determination of the dipolar structure of the ^{17}O NQR lines based on the simultaneous application of three rf magnetic fields with the frequencies $\nu_1 \approx \nu_{3/2,1/2}$, $\nu_2 \approx \nu_{5/2,3/2}$ and $\nu \approx \nu_{5/2,1/2}$. When $\nu_1 + \nu_2 \neq \nu$ the

three-frequency irradiation increases the relaxation rate of protons in zero magnetic field and causes a drop of the proton NMR signal at the end of the magnetic field cycle.

The relaxation rate of the proton dipolar reservoir in zero magnetic produced by the double resonance process is calculated for the single- two- and three-frequency irradiation technique. The sensitivity of the new three-frequency irradiation technique is analyzed and compared to the sensitivity of double resonance using two-frequency irradiation. As a test of the new technique we present the results of the measurement of the dipolar structure of the ^{17}O NQR lines in KH_2PO_4 .

2. Theory

In this session we consider the influence of the single-frequency, two-frequency and three-frequency off-resonance irradiation of the ^{17}O – ^1H spin system on the relaxation of the proton dipolar reservoir in zero magnetic field.

2.1. Single-frequency irradiation

Suppose we apply an rf magnetic field with the frequency $\nu = \nu_{3/2,1/2} + \delta$, as shown in Fig. 1. If the transition probability per unit time, produced by the rf magnetic field, is large as compared to the ^{17}O spin–lattice relaxation rate, a quasi equilibrium state establishes. The population N of the two dipolar energy levels, which are hit by the rf irradiation, becomes equal. The interaction with the proton dipolar reservoir establishes within each of the two dipolar split quadrupole energy levels Boltzmann distribution with the temperature T equal to the spin temperature of the proton spin system, which is assumed to be much lower than the temperature T_L of the sample. The population of the two quadrupole energy levels is in this situation equal

$$\begin{aligned} N_{3/2} &= \frac{1}{3} N_0 (1 + \beta h \delta / 2) \\ N_{1/2} &= \frac{1}{3} N_0 (1 - \beta h \delta / 2) \end{aligned} \quad (4)$$

here $\beta = 1/k_B T$ and N_0 is the number of crystallographically equivalent oxygen atoms having the ^{17}O nuclei in the sample. When $\delta > 0$ the population of the upper energy level exceeds the population of the lower energy level, while when $\delta < 0$ the population of the lower energy level exceeds the population of the upper energy level. This rearrangement within the two spin systems changes the proton spin temperature. The relative change of the proton spin temperature $\Delta T/T = -\Delta\beta\beta$ is of the order of N_0/N_{H} , where N_{H} is the number of protons in the sample. The ratio N_0/N_{H} is in a naturally abundant sample of the order of 10^{-4} . The relative change of the proton spin temperature is thus in such a case negligible.

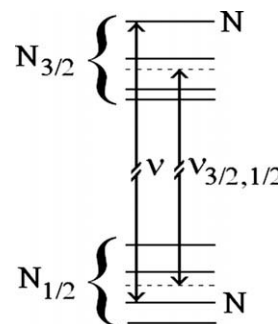


Fig. 1. Population of energy levels, the NQR frequency $\nu_{3/2,1/2}$ and the irradiation frequency $\nu = \nu_{3/2,1/2} + \delta$ in case on a single-frequency irradiation.

The situation changes if the ^{17}O quadrupole spin system relaxes fast so that the ^{17}O spin–lattice relaxation rate for several orders of magnitude exceeds the proton spin–lattice relaxation rate in zero magnetic field. In such a situation the population of the ^{17}O quadrupole energy levels, which is due to the off-resonance irradiation and interaction with the “cold” proton dipolar reservoir far from equilibrium, relaxes towards the equilibrium population. This relaxation influences also the relaxation of the proton dipolar reservoir. For the sake of simplicity we assume that the spin–lattice relaxation rate of the quadrupole $3/2$ – $1/2$ transition exceeds the spin–lattice relaxation of the $5/2$ – $1/2$ and $5/2$ – $3/2$ transitions and neglect the influence of the “ $5/2$ ” energy level. Further we assume that $T < T_L$. Under this assumption, which is justified if the proton Larmor frequency in the high magnetic field strongly exceeds the ^{17}O NQR frequencies, we may calculate as if the ^{17}O spin system relaxes towards complete disorder, where the population of each of the three quadrupole energy levels is equal $N_O/3$. If for example $\delta > 0$ and therefore $N_{3/2} > N_{1/2}$, the spin–lattice relaxation produces net transitions from the “ $3/2$ ” to the “ $1/2$ ” energy level with the average frequency $\nu_{3/2,1/2}$. The number of these transitions per unit time, dN/dt , is equal

$$\frac{dN}{dt} = W_{\text{SL}}(N_{3/2} - N_{1/2}) = \frac{1}{3} W_{\text{SL}} N_O h \delta \beta. \quad (5)$$

here W_{SL} is transition probability per unit time between the “ $3/2$ ” and “ $1/2$ ” energy levels produced by the interaction of the quadrupole ^{17}O spin system with the surrounding. The rf magnetic field, which together with the “cold” proton dipolar reservoir tends to establish the quasi equilibrium in the coupled spin systems, produces net transitions backwards from the “ $1/2$ ” to the “ $3/2$ ” energy level with the frequency $\nu = \nu_{3/2,1/2} + \delta$. The energy difference $h\delta$ is per each transition absorbed by the proton spin system. The time derivative of the energy of the proton spin system, dE/dt , equals

$$\frac{dE}{dt} = h\delta \frac{dN}{dt} = \frac{1}{3} W_{\text{SL}} N_O (h\delta)^2 \beta. \quad (6)$$

The energy E of the proton spin system is in zero magnetic field equal

$$E = -\beta \text{Tr} H_D^2 = -\frac{1}{4} N_H (h\nu_{\text{loc}})^2 \beta. \quad (7)$$

The proton frequency ν_{loc} , $\nu_{\text{loc}} = \gamma_H B_{\text{loc}}/2\pi$, is typically of the order of 10 kHz. From these equations we derive the equation for the inverse proton spin temperature β , which is proportional to the proton NMR signal at the end of the magnetic field cycle. We obtain

$$\frac{d\beta}{dt} = -\frac{4N_O}{3N_H} \left(\frac{\delta}{\nu_{\text{loc}}}\right)^2 W_{\text{SL}} \beta = -W_{\text{DR}} \beta. \quad (8)$$

In a real situation the proton spin–lattice relaxation with the relaxation rate W_H , $W_H = 1/T_{1H}(0)$, must be added as an independent process. We thus obtain

$$\frac{d\beta}{dt} = -(W_{\text{DR}} + W_H) \beta. \quad (9)$$

A significant change of the proton NMR signal at the end of the magnetic field cycle, produced by the double resonance process, may be observed when the double-resonance relaxation rate W_{DR} is comparable or larger than W_H . The double-resonance relaxation rate W_{DR} depends on the resonance offset δ . It is maximum at the edges of the dipolar split ^{17}O NQR line and zero in the middle.

Here we considered only the single-frequency irradiation of the $3/2$ – $1/2$ ^{17}O NQR transition, but we may arrive to similar conclusions if we irradiate the $5/2$ – $3/2$ or $5/2$ – $1/2$ transitions.

2.2. Two-frequency irradiation

Quite often the ^{17}O quadrupole spin system relaxes too slow for the single-frequency irradiation effects to be observed. In such a situation the two-frequency irradiation technique may be used.

Suppose we apply simultaneously two rf magnetic fields with the frequencies $\nu_1 = \nu_{3/2,1/2} + \delta_1$ and $\nu = \nu_{3/2,1/2} + \delta$, as shown in Fig. 2. Both rf magnetic fields hit the same NQR transition and there is no quasi equilibrium as obtained in case of a single-frequency irradiation. For the sake of simplicity we further assume that the transition probability per unit time between the energy levels hit by the first rf magnetic field with the frequency ν_1 is much larger than the transition probability per unit time W between the energy levels hit by the second rf magnetic field with the frequency ν . In this situation the first rf magnetic field is used to establish a quasi equilibrium in the spin systems, as in case of the single-frequency irradiation, while the second rf magnetic field is used to investigate the dipolar structure of the NQR line. The population difference ΔN of the two dipolar energy levels, hit by the second rf magnetic field is under the influence of the first rf magnetic field equal

$$\Delta N = \frac{1}{12} N_O h (\delta_1 - \delta) \beta. \quad (10)$$

The net number of transitions per unit time, dN/dt , produced by the second rf magnetic field, is equal $dN/dt = W \Delta N$. Each of these transitions is, as seen in Fig. 2, accompanied by two downward transitions between the dipolar energy levels of the ^{17}O – ^1H spin system and, due to the conservation of energy, by two upward transitions in the proton dipolar spin system. Energy gained by the proton spin system per unit time, dE/dt , is equal

$$\frac{dE}{dt} = h(\delta_1 - \delta) \frac{dN}{dt} = \frac{1}{12} N_O h^2 (\delta_1 - \delta)^2 W \beta. \quad (11)$$

Using expression (7) for the energy of the proton spin system we derive the expression for the time derivative of β due to the double resonance process as

$$\frac{d\beta}{dt} = -\frac{N_O}{3N_H} \left(\frac{\delta_1 - \delta}{\nu_{\text{loc}}}\right)^2 W \beta = -W_{\text{DR}} \beta. \quad (12)$$

The double-resonance relaxation rate W_{DR} quadratically depends on the frequency separation $\nu_1 - \nu = \delta_1 - \delta$. It is zero when $\nu_1 = \nu$ and reaches—at a constant value of W —maximum, when $\nu_1 - \nu = \pm(\Delta\nu_{3/2} + \Delta\nu_{1/2})$ i.e. when one of the rf magnetic fields hits the transition with the lowest possible frequency $(\nu_{3/2,1/2})_{\text{min}}$, while the second rf magnetic field hits the transition with the highest possible frequency $(\nu_{3/2,1/2})_{\text{max}}$.

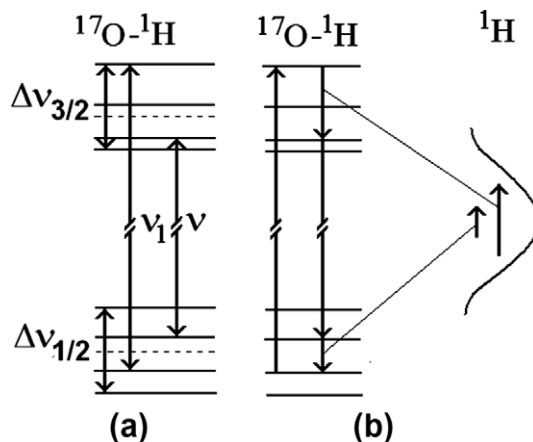


Fig. 2. Irradiation frequencies ν_1 and ν (a) and the net transitions in the coupled ^{17}O – ^1H and ^1H spin systems (b) in case of a two-frequency irradiation.

The same conclusions as obtained for the 3/2–1/2 transitions are valid also for the 5/2–3/2 and 5/2–1/2 transitions.

Two experiments are needed to investigate the dipolar structure of a ^{17}O NQR line. In the first experiment the frequency of the stronger rf magnetic field is fixed at the low-frequency edge of the NQR line and the high-frequency part of the NQR line is scanned by the frequency of the second rf magnetic field. In the second experiment the frequency of the stronger rf magnetic field is fixed at the high-frequency edge of the NQR line and the low-frequency part of the NQR line is scanned by the frequency of the second rf magnetic field.

2.3. Three-frequency irradiation

The modification of the two-frequency irradiation technique, as proposed in this paper, is the three-frequency irradiation technique, presented in Fig. 3. The two rf magnetic fields with the frequencies $\nu_1 = \nu_{3/2,1/2} + \delta_1$ and $\nu_2 = \nu_{5/2,3/2} + \delta_2$ establish a quasi equilibrium in the coupled spin system with the following population of the ^{17}O – ^1H energy levels

$$\begin{aligned} N_{5/2} &= \frac{N_0}{3} \left(1 + \frac{h}{3} (2\delta_2 + \delta_1) \beta \right) \\ N_{3/2} &= \frac{N_0}{3} \left(1 - \frac{h}{3} (\delta_2 - \delta_1) \beta \right) \\ N_{1/2} &= \frac{N_0}{3} \left(1 - \frac{h}{3} (\delta_2 + 2\delta_1) \beta \right) \end{aligned} \quad (13)$$

The population difference ΔN of the two dipolar energy levels hit by the third rf magnetic field with the frequency $\nu = \nu_{5/2,1/2} + \delta$ is equal

$$\Delta N = \frac{1}{12} N_0 h (\delta_1 + \delta_2 - \delta) \beta. \quad (14)$$

We again assume that the transition probability per unit time W between the energy levels hit by the third rf magnetic field, which is used to investigate the dipolar structure of the highest-frequency

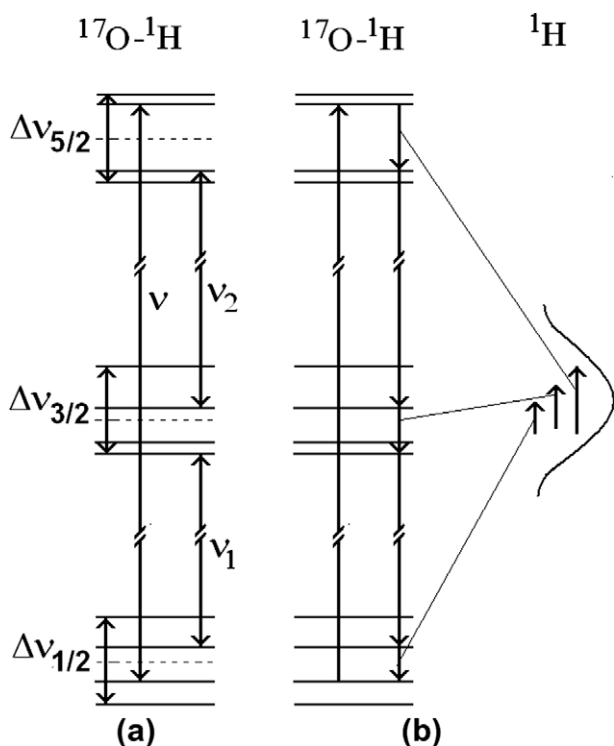


Fig. 3. Irradiation frequencies ν_1 , ν_2 and ν (a) and the net transitions in the coupled ^{17}O – ^1H and ^1H spin systems (b) in case of a three-frequency irradiation.

frequency ^{17}O NQR line, is lower than the transition probabilities per unit time between the energy levels hit by the first two rf magnetic fields. The net number of transitions per unit time, produced by the third rf magnetic field, is equal $\Delta N W$. Each of this transition is accompanied by three downward transitions between the dipolar energy levels of the ^{17}O – ^1H group and by three upward transitions with the same energies in the proton dipolar spin system. Energy gained by the proton spin system at each transition is in general equal $h|\delta_1 + \delta_2 - \delta|$. The double-resonance relaxation rate W_{DR} is expressed as

$$W_{\text{DR}} = \frac{N_0}{3N_{\text{H}}} \left(\frac{\delta_1 + \delta_2 - \delta}{\nu_{\text{loc}}} \right)^2 W = \frac{N_0}{3N_{\text{H}}} \left(\frac{\nu_1 + \nu_2 - \nu}{\nu_{\text{loc}}} \right)^2 W. \quad (15)$$

Two experiments are needed to determine the dipolar structure of the 5/2–1/2 NQR line. First the frequency ν_1 is set to the minimum transition frequency $(\nu_{3/2,1/2})_{\text{min}}$ between the dipolar split 3/2 and 1/2 energy levels and the frequency ν_2 is set to the minimum transition frequency $(\nu_{5/2,3/2})_{\text{min}}$ between the dipolar split 5/2 and 3/2 energy levels. The NQR line corresponding to the 5/2–1/2 transition is scanned by the frequency ν . The frequency dependent term $(\nu_1 + \nu_2 - \nu)^2$ in expression (15) ranges from $(\Delta\nu_{3/2})^2$ when $\nu = (\nu_{5/2,1/2})_{\text{min}}$ to $(\Delta\nu_{1/2} + \Delta\nu_{3/2} + \Delta\nu_{5/2})^2$ when $\nu = (\nu_{5/2,1/2})_{\text{max}}$. This should be compared to the investigation of the same NQR line by the two-frequency irradiation, when the frequency ν_1 is made equal to $(\nu_{5/2,1/2})_{\text{min}}$. The frequency dependent term $(\nu_1 - \nu)^2$ (expression (12)), which plays the same role in W_{DR} as the term $(\nu_1 + \nu_2 - \nu)^2$ in case of the three-frequency irradiation, ranges from zero when $\nu = (\nu_{5/2,1/2})_{\text{min}}$ to $(\Delta\nu_{1/2} + \Delta\nu_{5/2})^2$ when $\nu = (\nu_{5/2,1/2})_{\text{max}}$. The double-resonance relaxation rate W_{DR} is at the same value of W higher in case of the three-frequency irradiation than in case of the two-frequency irradiation. The ratio of the two double-resonance relaxation rates W_{DR} depends on the asymmetry parameter η and on the orientation of the O–H bond in the eigenframe of the EFG tensor [5]. It is approximately equal 2. This is of course true if the cross relaxation rate between the ^{17}O – ^1H groups and the rest of protons may be assumed high as compared to W . If this is not the case, the cross relaxation rate may limit the sensitivity of the two- and three-frequency irradiation techniques and the difference in W_{DR} may be smaller.

In the second experiment, where the low-frequency part of the 5/2–1/2 transition line is more pronounced, the frequency ν_1 is set to $\nu_1 = (\nu_{3/2,1/2})_{\text{max}}$ and the frequency ν_2 is set to $\nu_2 = (\nu_{5/2,3/2})_{\text{max}}$. The frequency dependent term $(\nu_1 + \nu_2 - \nu)^2$ in expression (12) is equal $(\Delta\nu_{3/2})^2$ when $\nu = (\nu_{5/2,1/2})_{\text{max}}$ and reaches the maximum value $(\Delta\nu_{1/2} + \Delta\nu_{3/2} + \Delta\nu_{5/2})^2$ when $\nu = (\nu_{5/2,1/2})_{\text{min}}$.

Similar experiments can be performed to investigate the 5/2–3/2 and 3/2–1/2 transition lines.

The high-frequency part of the 5/2–3/2 transition line can be investigated by setting $\nu_1 = (\nu_{3/2,1/2})_{\text{max}}$ and $\nu_2 = (\nu_{5/2,1/2})_{\text{min}}$, while the low-frequency part of the same transition line is investigated by setting $\nu_1 = (\nu_{3/2,1/2})_{\text{min}}$ and $\nu_2 = (\nu_{5/2,1/2})_{\text{max}}$.

The high-frequency part of the 3/2–1/2 transition line can be investigated by setting $\nu_1 = (\nu_{5/2,3/2})_{\text{max}}$ and $\nu_2 = (\nu_{5/2,1/2})_{\text{min}}$, while the low-frequency part of the same transition line is investigated by setting $\nu_1 = (\nu_{5/2,3/2})_{\text{min}}$ and $\nu_2 = (\nu_{5/2,1/2})_{\text{max}}$.

3. Experimental

We tested the new double resonance technique on the measurement of the dipolar structure of the ^{17}O NQR lines in paraelectric KH_2PO_4 . The NQR frequencies and the structure of the ^{17}O NQR lines have previously been measured at $T = 160$ K by the two-frequency irradiation technique [7].

We repeated the measurement at the same temperature by the three-frequency irradiation technique. The experimental details

are as follows. The proton spin system was polarized in $B_0 = 0.75$ T for 30 s. Then the sample was within 0.1 s pneumatically transferred into a second magnet where the external magnetic field was compensated to less than 0.1 mT. The sample was left in the second magnet for 0.5 s and then within 0.1 s transferred back into the first magnet. The proton NMR signal was measured immediately after the sample stopped in the first magnet.

The comparison of the sensitivity of the two-frequency irradiation technique and the three-frequency irradiation technique is presented in Fig. 4. The sample was in the two-frequency irradiation technique irradiated by repetitive pulses of rf magnetic fields with the frequencies 2485 kHz and ν . The duration of a pulse was 1 ms. The rf pulses were led to a 50 W broadband power amplifier connected to a resonance circuit which was tuned to the highest ^{17}O NQR frequency. In the three-frequency irradiation technique we used the same sequence of pulses. One sequence of pulses contained the rf signal with the variable frequency ν and with the same amplitude as in the two-frequency irradiation technique. The intermediate pulses contained two rf signals: one with the frequency $\nu_1 = (\nu_{3/2,1/2})_{\max} = 1030$ kHz and the second with the frequency $\nu_2 = (\nu_{5/2,3/2})_{\max} = 1480$ kHz. The rf signals are led to the same 50 W broadband power amplifier connected to a resonance circuit which was tuned to the highest ^{17}O NQR frequency. Each measurement was repeated four times and an average of the four proton NMR signals was stored. The maximum drop of the proton NMR signal was in case of the three-frequency irradiation technique approximately 30% while it was in case of the two-frequency irradiation technique approximately 20%. This measurement demonstrates that the three-frequency irradiation technique is indeed more sensitive than the two-frequency irradiation technique, what may be important in cases, when the double resonance signal is weak due to the short proton spin–lattice relaxation time in zero magnetic field.

The resolution of both techniques is comparable. It is determined by the proton–proton dipolar interaction and does not depend on the technique.

The shape of the ^{17}O NQR line corresponding to the $5/2-1/2$ transition as measured by the three-frequency irradiation technique is shown in Fig. 5. The dependence of the proton NMR signal S on the frequency ν as measured by two combinations of the frequencies ν_1 and ν_2 , amplifying the higher frequency and lower frequency part of the dipolar split NQR line, is presented in Fig. 5a. The amplitude of the third rf magnetic field is low enough so that the relative change of the proton NMR signal is less than 50%. In this case we are close to the linear regime where the drop of the proton NMR signal is proportional to $W_{\text{DR}}\tau$. The three widths of the NQR lines, $\Delta\nu_{5/2}$, $\Delta\nu_{3/2}$ and $\Delta\nu_{1/2}$, are in general not very much different [5]. In this case the average of the two drops of the proton NMR signal at a frequency ν only slightly depends on the frequency ν , as can be seen from expression (15). The average drop of the proton NMR signal therefore represents a good approximation of the

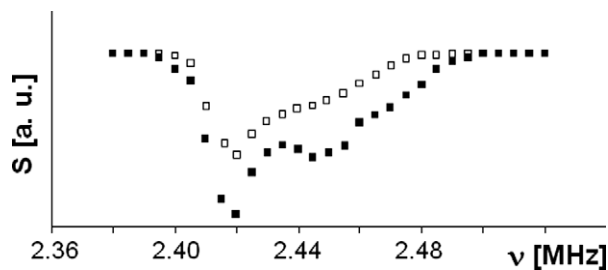


Fig. 4. Comparison of the sensitivity of the two-frequency (open squares) and three-frequency (full squares) irradiation techniques. The details are given in the text.

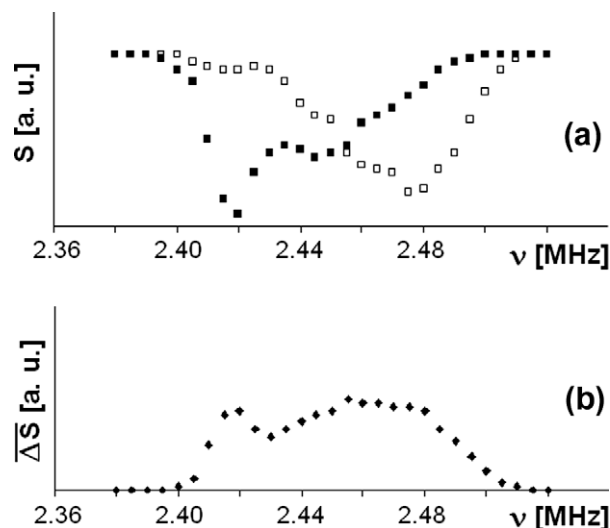


Fig. 5. (a) The shape of the ^{17}O $5/2-1/2$ NQR transition line in KH_2PO_4 as measured by the three-frequency irradiation technique with two different choices of ν_1 and ν_2 : $\nu_1 = 975$ kHz, $\nu_2 = 1430$ kHz (open squares) and $\nu_1 = 1030$ kHz, $\nu_2 = 1480$ kHz (full squares). (b) The average drop of the proton NMR signal representing the shape of the dipolar split NQR line.

NQR lineshape. It is for the $5/2-1/2$ ^{17}O NQR transition frequency presented in Fig. 5b. The dipolar structure of the NQR line is smeared out, because in case of a relatively long O–H distance (1.18 Å) the line splitting is of the order of 70 kHz and the separation between the dipolar lines is of the order of 10 kHz, what is comparable to the proton local frequency ν_{loc} representing the strength of the proton–proton dipolar interaction and the interaction between the $^{17}\text{O}-^1\text{H}$ groups and the rest of protons is mainly the proton–proton dipolar interaction.

4. Conclusions

A new nuclear quadrupole double resonance technique which may be used for the investigation of the dipolar structure of the ^{17}O NQR lines in case of strong $^{17}\text{O}-^1\text{H}$ interaction is proposed. The technique is based on magnetic field cycling between a high and zero magnetic field and the simultaneous application of three rf magnetic fields with the frequencies close to the three ^{17}O NQR frequencies $\nu_{3/2,1/2}$, $\nu_{5/2,3/2}$ and $\nu_{5/2,1/2}$, all within the dipolar split NQR lines in zero static magnetic field. When the sum of the two lower frequencies is not equal to the highest-frequency the three-frequency irradiation produces an energy flow to the proton spin system, which is initially cooled to a very low spin temperature by the adiabatic reduction of external magnetic field to zero. As a consequence of this energy flow, the proton NMR signal at the end of the magnetic field cycle drops to a lower value.

The new technique is analyzed and compared to the single-frequency and two-frequency irradiation technique. It is shown that the sensitivity of the new technique may exceed the sensitivity of the two-frequency irradiation technique, what is important when the proton spin–lattice relaxation time in zero magnetic field is short. A higher sensitivity also reduces the averaging time at each frequency ν .

As a test of the new technique we measured the shape of the dipolar split ^{17}O NQR line corresponding to the $5/2-1/2$ transition in KH_2PO_4 at $T = 160$ K. The sensitivity of the two-frequency and three-frequency irradiation technique are compared.

It is experimentally shown that the sensitivity of the three-frequency irradiation technique indeed exceeds the sensitivity of the two-frequency irradiation technique, while the two techniques have comparable resolution.

References

- [1] See for example: J. Seliger, Nuclear quadrupole resonance: theory, in: J.C. Lindon, G.E. Tranter, J.L. Holmes (Eds.), *Encyclopedia of Spectroscopy and Spectrometry*, Academic Press, San Diego, 2000, pp. 1672–1680.
- [2] J. Seliger, V. Žagar, Sensitivity of nuclear-quadrupole double-resonance detection of half-integer spin nuclei, *J. Magn. Reson.* 194 (2008) 175–181.
- [3] S.G.P. Brosnan, D.T. Edmonds, Fine structure detected in the nuclear quadrupole resonance spectrum of naturally abundant ^{17}O , *J. Magn. Reson.* 38 (1980) 47–63.
- [4] S.G.P. Brosnan, D.T. Edmonds, Double resonance with coupled multiplets, *J. Magn. Reson.* 45 (1981) 440–450.
- [5] J. Seliger, V. Žagar, R. Blinc, A. Novak, ^{17}O and ^{39}K quadrupole resonance study of the ferroelectric phase transition in $\text{KH}_3(\text{SeO}_3)_2$, *J. Chem. Phys.* 84 (1986) 5857–5861.
- [6] R.E. Slusher, E.L. Hahn, Sensitive detection of nuclear quadrupole interactions in solids, *Phys. Rev.* 166 (1968) 332–347.
- [7] S.G.P. Brosnan, D.T. Edmonds, An ^{17}O nuclear quadrupole resonance study of hydrogen atom motion in KH_2PO_4 , *Phys. Lett. A* 81 (1981) 243–245.
- [8] S.G.P. Brosnan, D.T. Edmonds, I.J.F. Poplett, An ^{17}O nuclear quadrupole resonance study of some carboxylic acids, *J. Magn. Reson.* 45 (1981) 451–460.
- [9] I.J.F. Poplett, M. Sabir, J.A.S. Smith, ^{17}O and ^2H quadrupole double resonance in some acid carboxylates, *J. Chem. Soc., Faraday Trans. 2* 77 (1981) 1651–1668.
- [10] I.J.F. Poplett, $^1\text{H}/^2\text{H}$ and $^1\text{H}/^{17}\text{O}$ nuclear quadrupole double resonance study of an oxonium ion in $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$, *J. Magn. Reson.* 44 (1981) 488–507.
- [11] C.R. Brett, D.T. Edmonds, ^{17}O and ^2H study of solid methanol near its melting temperature, *J. Magn. Reson.* 49 (1982) 304–311.
- [12] I.J.F. Poplett, $^1\text{H}/^2\text{H}$ and $^1\text{H}/^{17}\text{O}$ nuclear quadrupole double resonance study of several hydroxide compounds. I. The hydroxide ion, *J. Magn. Reson.* 50 (1982) 382–396.
- [13] I.J.F. Poplett, $^1\text{H}/^2\text{H}$ and $^1\text{H}/^{17}\text{O}$ nuclear quadrupole double resonance study of several hydroxide compounds. II. The water molecule, *J. Magn. Reson.* 50 (1982) 397–408.
- [14] M. Suhara, J.A.S. Smith, Interpretation of ^{17}O quadrupole resonance data in hydrogen-bonded systems involving carbonyl groups, *J. Magn. Reson.* 50 (1982) 237–248.
- [15] S.D. Goren, M. Shporer, Y. Margalit, ^{17}O nuclear quadrupole resonance measurements in the ferroelectric phase of potassium hydrogen phosphate: evidence of proton tunneling, *Phys. Rev. B* 27 (1983) 5419–5423.
- [16] J. Seliger, V. Žagar, R. Blinc, Oxygen-17 NQR study of the phase transition in squaric acid, *J. Magn. Reson.* 58 (1984) 359–369.
- [17] J. Seliger, V. Žagar, R. Blinc, A. Novak, S. Rodin, ^{17}O and ^{14}N quadrupole coupling and the mechanism of the ferroelectric transition in diglycine nitrate, *Ferroelectr. Lett.* 6 (1986) 93–102.
- [18] J. Seliger, V. Žagar, R. Blinc, ^1H – ^{17}O nuclear quadrupole double resonance study of hydrogen bonds in $(\text{CH}_3\text{COO})_2\text{KH}$ and $(\text{CH}_3\text{COO})_2\text{NaH}$, *Chem. Phys. Lett.* 164 (1989) 405–408.
- [19] J. Seliger, V. Žagar, R. Blinc, E. Hadjoudis, F. Milia, ^1H – ^{14}N and ^1H – ^{17}O nuclear quadrupole resonance in thermochromic N-5-chlorosalicylideneaniline, *Chem. Phys.* 142 (1990) 237–244.
- [20] J. Seliger, V. Žagar, R. Blinc, V.H. Schmidt, ^{85}Rb , ^{87}Rb , and ^{17}O nuclear-quadrupole-resonance study of $\text{Rb}(\text{H}_{1-x}\text{D}_x)_2\text{PO}_4$, *Phys. Rev. B* 42 (1990) 3881–3886.
- [21] D. Abramič, J. Seliger, V. Žagar, R. Blinc, Nuclear quadrupole double resonance in AHSO_4 ($\text{A} = \text{K}, \text{Rb}, \text{Cs}, \text{Tl}, \text{NH}_4$), *J. Phys.: Condens. Matter* 5 (1993) 3373–3380.
- [22] M. Torkar, V. Žagar, J. Seliger, ^1H – ^{17}O nuclear-quadrupole double-resonance study of hydrogen disorder in 2-nitrobenzoic acid, *J. Magn. Reson.* 144 (2000) 13–19.
- [23] J. Seliger, V. Žagar, ^1H – ^{17}O nuclear quadrupole double resonance in phenylphosphinic acid and phenylphosphonic acid. ^{17}O quadrupole coupling in $\text{P}=\text{O}$ and $\text{P}-\text{O}-\text{H}$ bonds, *Magn. Reson. Chem.* 46 (2008) 969–973.