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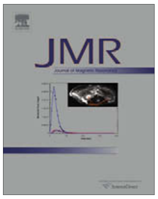

Measurement of dipolar structure of ^{17}O nuclear quadrupole resonance lines by three-frequency irradiation

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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 ^{1}H—^{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 $\nu_{5/2-1/2} > \nu_{5/2-3/2} \geqslant \nu_{3/2-1/2}$ 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.

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

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

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 $\nu_{5/2-1/2} > \nu_{5/2-3/2} \geqslant \nu_{3/2-1/2}$. 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.

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]

$$|\psi_{\pm m}\rangle = c^m_{5/2}|\pm 5/2\rangle + c^m_{1/2}|\pm 1/2\rangle + c^m_{3/2}|\mp 3/2\rangle. \tag{2}$$

here $m = 5/2$, 1/2 and 3/2. The coefficients c^m_k 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—^{1}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

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resolved due to the interaction of the ^{1}H—^{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(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 ^{1}H—^{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 $T = T_L B_{loc}/B_0$. Here T_L is the sample temperature and B_{loc},

$$B_{loc}^2 = \frac{4}{\hbar^2 \gamma_H^2 N_H} Tr H_{DHH}^2 / Tr 1, \tag{3}$$

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 ^{1}H—^{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—^{1}H groups produce an energy flow from the ^{17}O—^{1}H 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—^{1}H 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

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

here $\beta = 1/k_B T$ and N_O 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_O/N_H, where N_H is the number of protons in the sample. The ratio N_O/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.

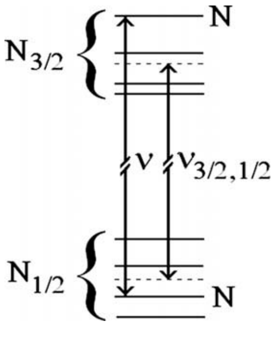

Fig. 1. Population of energy levels, the NQR frequency $\nu_{3/2,1/2}$ and the irradiation frequency $\nu = \nu_{3/2,1/2} + \delta$ in case on a single-frequency irradiation.