



## Sensitivity of nuclear-quadrupole double-resonance detection of half-integer spin nuclei

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### ABSTRACT

The sensitivity of the Slusher and Hahn's nuclear quadrupole double resonance technique is calculated in general for an arbitrary nuclear spin  $S$  of the quadrupole nuclei and for an arbitrary asymmetry parameter  $\eta$  of the electric field gradient tensor. The nuclear spin  $S = 5/2$  ( $^{17}\text{O}$ ,  $^{25}\text{Mg}$ , ...) is treated in details. The influence of the cross-relaxation rate between the quadrupole nuclei and the abundant spin system on the sensitivity of double resonance is discussed. The results of the theoretical analysis are applied in the analysis of the  $^1\text{H}$ - $^{17}\text{O}$  nuclear quadrupole double resonance spectra in *p*-toluenesulfonamide and 2-nitrobenzoic acid. The 170 nuclear quadrupole resonance frequencies from a sulfonamide group are determined for the first time. The proton-oxygen cross-relaxation rates and the proton local frequency in zero external magnetic field are experimentally determined from the nuclear quadrupole double resonance spectra.

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### 1. Introduction

Nuclear quadrupole double resonance (NQDR), as introduced by Slusher and Hahn [1], is a highly sensitive technique that is used for the measurement of low nuclear quadrupole resonance (NQR) frequencies of rare quadrupole nuclei. A high sensitivity is obtained when a quadrupole nucleus has a half integer nuclear spin. In case of an integer nuclear spin the sensitivity is strongly reduced due to the spin quenching effect [2]. The technique is based on the interaction of the quadrupole nuclei with the energy levels quantized in the interaction picture and the dipolar spin reservoir of an abundant system of nuclei, usually protons.

The technique presents an alternative to the high-field solid state NMR measurement of the nuclear quadrupole interactions in solids. Its advantage is the possibility to study the nuclear quadrupole interactions in polycrystalline samples with a high resolution. It has been mainly applied to  $^{17}\text{O}$  at natural abundance [3–24] and  $^{39}\text{K}$  [8,9,16,20,25,26], but may also be applied to  $^{25}\text{Mg}$ ,  $^{33}\text{S}$ , etc.

The NQDR technique and its sensitivity are in Ref. [1] well analyzed for the nuclear spin  $S = 3/2$ . In this paper we calculate the NQDR sensitivity for an arbitrary half integer nuclear spin  $S$  of

the quadrupolar nuclei and for an arbitrary asymmetry parameter  $\eta$  of the electric field gradient (EFG) tensor at the position of a quadrupole nucleus. The cross-relaxation between the two spin systems is treated phenomenologically. The nuclear spin  $S = 5/2$  is considered in details.

As experimental examples we analyze the  $^1\text{H}$ - $^{17}\text{O}$  NQDR spectra of *p*-toluenesulfonamide and 2-nitrobenzoic acid.

### 2. Theory

#### 2.1. Quadrupole nuclei in a strong resonant rf magnetic field: interaction picture

The nuclear quadrupole Hamiltonian reads as

$$H_Q = \frac{e^2qQ}{4S(2S-1)} \left( 3S_z^2 - S(S+1) + \frac{\eta}{2}(S_+^2 + S_-^2) \right). \quad (1)$$

Here  $e^2qQ$  is the quadrupole coupling constant multiplied by the Planck's constant  $h$  and  $\eta$  is the asymmetry parameter of the electric-field-gradient (EFG) tensor. The asymmetry parameter  $\eta$  ranges between 0 and 1.

The eigenstates of the nuclear quadrupole Hamiltonian are in case of  $\eta = 0$  the states  $|S, m\rangle$  with the well-defined projection  $m$  of the nuclear spin on the principal axis  $Z$  of the EFG tensor [27]. The energy  $E_m$ ,

$$E_m = \frac{e^2qQ}{4S(2S-1)} (3m^2 - S(S+1)), \quad (2)$$

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is in this case a quadratic function of  $m$ . The energies  $E_m$  and  $E_{-m}$  are equal what results in the double degeneracy of the nuclear quadrupole energy levels that can be labeled with the positive magnetic quantum number  $m$ . The double degeneracy of the nuclear quadrupole energy levels remains also when  $\eta$  differs from zero. It is the consequence of the time-inversion symmetry of the quadrupolar Hamiltonian. The energy level that is the continuation of the energy level “ $m$ ” at  $\eta = 0$  is still labeled as “ $m$ ”. The two eigenstates corresponding to the energy level  $m$  we label as  $|\psi_{+m}\rangle$  and  $|\psi_{-m}\rangle$ , where

$$|\psi_{+m}\rangle = \sum_{k=0}^{S-1/2} c_k^m |S, S-2k\rangle$$

$$|\psi_{-m}\rangle = \sum_{k=0}^{S-1/2} c_k^m |S, -S+2k\rangle. \tag{3}$$

The expansion coefficients  $c_k^m$  depend on  $\eta$ , and can be expressed analytically only for  $S = 3/2$ . For a higher nuclear spin they must be calculated numerically.

The nuclear quadrupole energy levels and the transition frequencies are for  $S = 3/2$  and  $S = 5/2$  shown in Fig. 1. In case of  $S = 3/2$  there are two doubly degenerated nuclear quadrupole energy levels labeled as “3/2” and “1/2” and a single NQR frequency  $\nu_{3/2-1/2}$ . In case of  $S = 5/2$  there are three doubly degenerated nuclear quadrupole energy levels labeled as “5/2”, “3/2”, and “1/2” and three NQR frequencies  $\nu_{5/2-1/2} > \nu_{5/2-3/2} \geq \nu_{3/2-1/2}$ .

Suppose we apply in zero static magnetic field an rf magnetic field with the amplitude  $\vec{B}_1$  and with the frequency  $\nu$  close to the NQR frequency  $\nu_{m-k}$ :  $\nu = \nu_{m-k} - \delta\nu$ . The Hamiltonian can be in this case expressed as

$$H = (\nu/\nu_{m-k})H_Q + (\delta\nu/\nu_{m-k})H_Q - \hbar\gamma_Q\vec{S}\vec{B}_1 \cos(2\pi\nu t). \tag{4}$$

Here we completely neglect the dipolar interaction between the quadrupolar nuclei. The dipolar interaction between the quadrupolar nuclei and protons is at the moment also neglected. We express the orientation of the rf magnetic field in the principal-axes system  $X, Y$ , and  $Z$  of the EFG tensor with the polar angle  $\theta$  and the azimuthal angle  $\varphi$ . Here  $\theta$  is the angle between the direction of the rf magnetic field and the principal axis  $Z$  and  $\varphi$  is the angle between the projection of the direction of the rf magnetic field on the  $X$ - $Y$  plane and the principal axis  $X$ . The scalar product  $\vec{S}\vec{B}_1$  may be expressed as:

$$\vec{S}\vec{B}_1 = B_1 \left[ n_z S_z + \frac{1}{2}(n_+ S_- + n_- S_+) \right]. \tag{5}$$

Here  $n_z = \cos\theta$  and  $n_{\pm} = \sin\theta \exp(\pm i\varphi)$ .

Further we perform the transformation into the interaction picture with the operator  $T = \exp\left(-\frac{i}{\hbar}\frac{\nu}{\nu_{m-k}}H_Q\right)$  and keep only the time-independent terms. In the subspace of the states  $|\psi_{+m}\rangle, |\psi_{-m}\rangle, |\psi_{+k}\rangle$ , and  $|\psi_{-k}\rangle$  we obtain in the interaction picture the following Hamiltonian  $H'$ :

$$H' = \hbar \begin{bmatrix} \delta\nu/2 & 0 & -a & -b^* \\ 0 & \delta\nu/2 & -b & a \\ -a & -b^* & -\delta\nu/2 & 0 \\ -b & a & 0 & -\delta\nu/2 \end{bmatrix} + c \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}. \tag{6}$$

Here  $a = \frac{\nu_+}{2} n_z \langle \psi_{+k} | S_z | \psi_{+m} \rangle$ ,  $b = \frac{\nu_+}{4} \langle \psi_{-k} | n_+ S_- + n_- S_+ | \psi_{+m} \rangle$ ,  $c = \frac{\delta\nu}{2\nu_{m-k}} (E_m + E_k)$ ,  $\nu_+ = \gamma_Q B_1 / 2\pi$ , whereas  $E_m$  and  $E_k$  are the energies of the energy levels  $m$  and  $k$ , respectively. We call this interaction picture the quadrupole rotating frame, not because it is a real rotating frame, but because of its similarity to the rotating frame as used in NMR.

The Hamiltonian  $H'$  has two doubly degenerated principal values  $E_+$  and  $E_-$ :

$$E_{\pm} = c \pm \hbar \sqrt{a^2 + bb^* + (\delta\nu/2)^2}. \tag{7}$$

The frequency splitting  $\Delta\nu$  of the two energy levels in the quadrupole rotating frame is equal to  $\Delta\nu = (E_+ - E_-)/\hbar$ . The splitting depends on the orientation of the rf magnetic field with respect to the principal axes of the EFG tensor and on the resonance offset  $\delta\nu$ . It is in resonance ( $\delta\nu = 0$ ) proportional to  $B_1$ .

The two eigenstates  $|\psi_1^+\rangle$  and  $|\psi_2^+\rangle$ , corresponding to the energy level with the energy  $E_+$ , may be in the basis  $|\psi_{+m}\rangle, |\psi_{-m}\rangle, |\psi_{+k}\rangle$ , and  $|\psi_{-k}\rangle$  expressed as

$$|\psi_1^+\rangle = \sqrt{\frac{\Delta\nu + \delta\nu}{2\Delta\nu}} \begin{pmatrix} 1 & 0 & -\frac{2a}{\Delta\nu + \delta\nu} & -\frac{2b}{\Delta\nu + \delta\nu} \end{pmatrix}$$

$$|\psi_2^+\rangle = \sqrt{\frac{\Delta\nu + \delta\nu}{2\Delta\nu}} \begin{pmatrix} 0 & 1 & -\frac{2b^*}{\Delta\nu + \delta\nu} & \frac{2a}{\Delta\nu + \delta\nu} \end{pmatrix}. \tag{8a}$$

In a similar way we express the two eigenstates,  $|\psi_1^-\rangle$  and  $|\psi_2^-\rangle$ , corresponding to the energy level with the energy  $E_-$  as:

$$|\psi_1^-\rangle = \sqrt{\frac{\Delta\nu + \delta\nu}{2\Delta\nu}} \begin{pmatrix} \frac{2a}{\Delta\nu + \delta\nu} & \frac{2b}{\Delta\nu + \delta\nu} & 1 & 0 \end{pmatrix}$$

$$|\psi_2^-\rangle = \sqrt{\frac{\Delta\nu + \delta\nu}{2\Delta\nu}} \begin{pmatrix} \frac{2b^*}{\Delta\nu + \delta\nu} & -\frac{2a}{\Delta\nu + \delta\nu} & 0 & 1 \end{pmatrix}. \tag{8b}$$

### 2.2. Double resonance

The NQDR process is schematically presented in Fig. 2. As the abundant spin system we consider protons.

The proton spin system is during the polarization phase polarized in a high magnetic field  $B_0$ . Then the external magnetic field is adiabatically reduced to zero. The spin temperature  $T_S$  of the proton spin system drops to the value  $T_S = (\nu_{loc}/\nu_L) T_L$ . Here  $T_L$  is the lattice temperature,  $\nu_L, \nu_L = \gamma_H B_0 / 2\pi$ , is the proton Larmor frequency in the high magnetic field  $B_0$  and the proton local frequency  $\nu_{loc}$  in zero external magnetic field is defined by the equation

$$\nu_{loc}^2 = \frac{4}{\hbar^2 N_H} \text{Tr} H_{DHH}^2 / \text{Tr} 1. \tag{9}$$

Here  $N_H$  is the number of protons in the sample and  $H_{DHH}$  is the proton-proton dipole interaction Hamiltonian. The frequency  $\nu_{loc}$  is

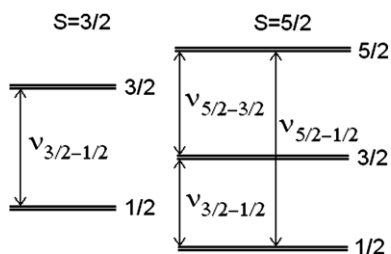


Fig. 1. Nuclear quadrupole energy levels and transition frequencies for  $S = 3/2$  and  $S = 5/2$ .

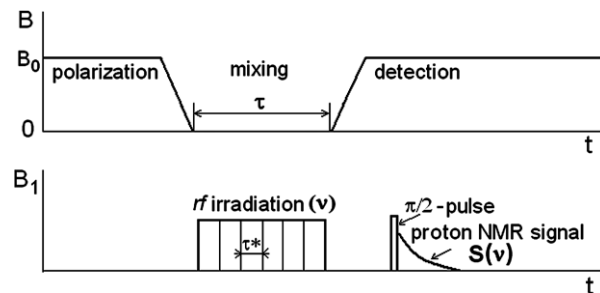


Fig. 2. Schematic presentation of a NQDR cycle.

typically of the order of 10 kHz and  $\nu_L$  is of the order of 100 MHz. The proton spin temperature thus drops for more than three orders of magnitude. The inverse proton spin temperature  $\beta$  is at the beginning of the mixing phase equal  $\beta = 1/k_B T_S$ . During the mixing phase  $\beta$  decreases towards  $\beta_L$ ,  $\beta_L = 1/k_B T_L$ , due to the spin–lattice relaxation as

$$\beta(t) = \beta_L + (\beta_0 - \beta_L) \exp(-t/T_{1H}(0)). \quad (10)$$

Here  $T_{1H}(0)$  is the proton spin–lattice relaxation time in zero external magnetic field. A faster decrease of  $\beta$  is observed, when the quadrupole nuclei are during the mixing phase irradiated by a phase-modulated resonant rf magnetic field (Fig. 2).

After the time  $\tau$  spent in zero magnetic field, the initial magnetic field  $B_0$  is adiabatically restored. The proton magnetization is at the beginning of the detection period proportional to  $\beta(\tau)$ , where  $\beta(\tau)$  is the inverse proton spin temperature at the end of the mixing period. The resonant rf irradiation of the quadrupole nuclei thus decreases  $\beta(\tau)$  as well as the proton signal  $S$  measured at the beginning of the detection period. The dependence of the proton NMR signal  $S(\nu)$  on the frequency  $\nu$  of the rf magnetic field exhibits dips at the NQR frequencies ( $\nu = \nu_{m-n}$ ). In the continuation we calculate the intensities of these dips.

At the beginning of the mixing phase, when the rf magnetic field is switched on, the flip-flop transitions occur between the energy levels of the quadrupole nuclei in the quadrupole rotating frame and between the proton dipolar energy levels. These transitions tend to equalize the spin temperature  $\beta$  of the proton spin system and the spin temperature of the quadrupole spin system in the quadrupole rotating frame:

$$N_+/N_- \rightarrow \exp(-\beta(E_+ - E_-)) \cong 1 - \beta(E_+ - E_-). \quad (11)$$

Here  $N_+$  and  $N_-$  are the populations of the energy levels with the energies  $E_+$  and  $E_-$ , respectively. The sum  $N'_Q = N_+ + N_-$  is in the high-temperature approximation, that is used in this analysis, equal  $N'_Q = 2N_Q/(S + 1/2)$  with  $N_Q$  being the number of equivalent quadrupole nuclei in the sample. In the further analysis we first assume that the two spin temperatures equalize during the time  $\tau^*$  between two repetitive 180° phase shifts of the rf magnetic field. In addition we assume that the number of the quadrupole nuclei  $N_Q$  is small as compared to the number of protons  $N_H$ . We are namely mainly interested in the detection of nuclei with low natural abundance and low NQR frequencies, as for example  $^{17}\text{O}$  and  $^{33}\text{S}$ .

The populations of the two energy levels in the quadrupole rotating frame are at the moment, before the 180° phase shift occurs, equal  $N_+ = (N'_Q/2)(1 - \beta h \Delta \nu / 2)$  and  $N_- = (N'_Q/2)(1 + \beta h \Delta \nu / 2)$ . Here  $\beta$  is the inverse spin temperature of the proton spin system at that moment. After the 180° phase shift of the rf magnetic field the Hamiltonian  $H'$  and its eigenstates change. The new eigenstates can be obtained from Expressions (8a and 8b) by the substitution  $a \rightarrow -a$  and  $b \rightarrow -b$ . The probabilities  $P_+$  and  $P_-$  of finding a quadrupole nucleus on the energy levels with the energies  $E_+$  and  $E_-$ , respectively, are before the 180° phase shift occurs ( $t = t_-$ ) equal:  $P_+(t_-) = (1 - \beta h \Delta \nu / 2) / 2$  and  $P_-(t_-) = (1 + \beta h \Delta \nu / 2) / 2$ . Immediately after the phase shift ( $t = t_+$ ) the probabilities change. They are equal:

$$\begin{aligned} P_+(t_+) &= KP_+(t_-) + (1 - K)P_-(t_-) = \frac{1}{2} \left( 1 + \frac{1}{2} (1 - 2K) \beta h \Delta \nu \right) \\ P_-(t_+) &= KP_-(t_-) + (1 - K)P_+(t_-) = \frac{1}{2} \left( 1 - \frac{1}{2} (1 - 2K) \beta h \Delta \nu \right) \end{aligned} \quad (12)$$

Here  $K = (\delta \nu / \Delta \nu)^2$ . In resonance ( $\delta \nu = 0$ ,  $K = 0$ ) we obtain the population inversion:  $P_+(t_+) = P_-(t_-)$  and  $P_-(t_+) = P_+(t_-)$ . In an off-resonant quadrupole rotating frame ( $\delta \nu \neq 0$ ) the probabilities change less.

After the 180° phase shift the simultaneous upwards transitions in the proton dipolar system and downwards transitions in the quadrupole rotating frame equalize the spin temperatures of the two spin systems. Assuming, that the proton spin temperature

negligibly changes between two repetitive 180° phase shifts, we may express the number  $\Delta N$  of these transitions as  $\Delta N = N'_Q [P_-(t_-) - P_-(t_+)] = N'_Q (1 - K) \beta h \Delta \nu / 2$ . The change of the energy of the proton spin system  $\Delta E$  is equal  $\Delta E = h \Delta \nu \Delta N = 2N'_Q \beta h^2 (a^2 + bb^*)$ .

The energy change  $\Delta E$  of the proton spin system is independent on the resonance offset  $\delta \nu$  as far as the spin temperatures of the two spin systems equalize during the time  $\tau^*$  between two repetitive 180° phase shifts. At a large  $\delta \nu$  the cross-relaxation time becomes longer than  $\tau^*$  and the two spin temperatures do not equalize between two repetitive 180° phase shifts. That results in a smaller energy change  $\Delta E$ .

Knowing  $\Delta E$  we may write the rate equation for the inverse proton spin temperature  $\beta$ . The energy  $E$  of the proton spin system in zero static magnetic field may be expressed as  $E = -\beta N_H h^2 \nu_{loc}^2 / 4$ . The rate equation for  $\beta$ ,  $d\beta/d\tau = -W\beta$ , is derived from the equation  $dE/dt = \Delta E/\tau^*$ . Here

$$\begin{aligned} W &= W(\theta, \varphi) = \frac{8N'_Q (a^2 + bb^*)}{N_H \nu_{loc}^2 \tau^*} \\ &= \frac{1}{2\tau^*} \frac{N'_Q}{N_H} \left( \frac{\nu_1}{\nu_{loc}} \right)^2 [4 \langle \psi_{+k} | n_{zS_z} | \psi_{+m} \rangle^2 \\ &\quad + \langle \psi_{-k} | n_{zS_-} + n_{zS_+} | \psi_{+m} \rangle^2] \end{aligned} \quad (13)$$

In a single crystal the double resonance relaxation rate  $W$  depends on the orientation of the rf magnetic field in the eigenframe of the EFG tensor. In a polycrystalline sample, which is usually used in a double resonance experiment, there is a distribution of the double resonance relaxation rates. In addition the proton spin–lattice relaxation in zero magnetic field must be considered as an independent process. The proton NMR signal  $S$  at the beginning of the detection period is in this case equal

$$\begin{aligned} S &= \frac{1}{4\pi} S_0 \exp(-\tau/T_{1H}(0)) \int_0^{2\pi} d\varphi \int_0^\pi \exp(-W(\theta, \varphi)\tau) \\ &\quad \times \sin \theta d\theta. \end{aligned} \quad (14)$$

If we limit ourselves to the case of a weak double resonance signal ( $W(\theta, \varphi)\tau < 1$ ), we may expand  $\exp(-W(\theta, \varphi)\tau)$  in Taylor series and keep only the two largest terms. We obtain

$$S \cong S_0 \exp(-\tau/T_{1H}(0)) (1 - \overline{W}\tau), \quad (15)$$

where,

$$\begin{aligned} \overline{W} &= \frac{1}{4\pi} \int_0^{2\pi} d\varphi \int_0^\pi W(\theta, \varphi) \sin \theta d\theta \\ &= \frac{1}{3\tau^*} \frac{N'_Q}{N_H} \left( \frac{\nu_1}{\nu_{loc}} \right)^2 R_{m-k}(\eta). \end{aligned} \quad (16)$$

The double resonance signal  $\Delta S(\tau)$ ,

$$\Delta S(\tau) \cong S_0 \exp(-\tau/T_{1H}(0)) - S_0 \exp(-\tau/T_{1H}(0)) (1 - \overline{W}\tau), \quad (17)$$

is equal to the difference between the proton NMR signal at the beginning of the detection phase with no rf magnetic field applied and the proton NMR signal at the beginning of the detection phase with the rf magnetic field applied. It is in the limit of low  $\overline{W}$ ,  $\overline{W}T_{1H}(0) \ll 1$ , maximum at  $\tau = T_{1H}(0)$ , when  $\Delta S(T_{1H}(0)) = S_0 \overline{W}T_{1H}(0)/e$ .

The term  $R_{m-k}(\eta)$ ,

$$R_{m-k}(\eta) = 2 \langle \psi_{+k} | S_z | \psi_{+m} \rangle^2 + \langle \psi_{-k} | S_+ | \psi_{+m} \rangle^2 + \langle \psi_{-k} | S_- | \psi_{+m} \rangle^2, \quad (18)$$

in general depends on the nuclear spin  $S$ , on the NQR transition ( $m - k$ ) and on the asymmetry parameter  $\eta$  of the EFG tensor. It can be easily calculated [26] for  $S = 3/2$ , where  $R_{3/2-1/2}(\eta) = 3$  independent on  $\eta$ . Numerically calculated values of  $R_{m-k}(\eta)$  are for  $S = 5/2$  presented in Table 1. The term  $R_{m-k}(\eta)$  is at the low values

**Table 1**  
The values of  $R_{m-k}(\eta)$  for  $S = 5/2$

Transition $\setminus \eta$	0.0	0.2	0.4	0.6	0.8	1.0
3/2–1/2	8	7.66	6.92	6.37	5.65	5.31
5/2–3/2	5	4.98	4.94	4.96	5.09	5.30
5/2–1/2	0	0.05	0.16	0.26	0.32	0.27

of  $\eta$  the largest for the lowest frequency 3/2–1/2 transition and nearly zero for the highest frequency 5/2–1/2 transition. Thus the double resonance signal at  $\nu = \nu_{3/2-1/2}$  is the strongest whereas the double resonance signal at the frequency  $\nu = \nu_{5/2-1/2}$  is often not observed. At a large value of  $\eta$  the intensities of the double resonance signals at  $\nu = \nu_{3/2-1/2}$  and  $\nu = \nu_{5/2-3/2}$  become nearly equal, but the intensity of the double resonance signal at  $\nu = \nu_{5/2-1/2}$  is still about 20 times lower.

### 2.3. The cross-relaxation limit

Until now we assumed that the spin temperature of the quadrupole spin system in the quadrupole rotating frame and the spin temperature of the proton spin system equalize during the time  $\tau^*$  between two repetitive phase shifts of the rf magnetic field. If this is not the case, the phase shift produces a smaller change of the spin temperature of the quadrupole spin system in the quadrupole rotating frame, resulting in a decrease of the double resonance signal. We define the cross-relaxation rate  $W_{CR}$  as the rate at which the spin temperature of the quadrupole spin system in the quadrupole rotating frame approaches the spin temperature of the proton spin system. It is of the order of  $W_{CR} \sim \mu_0 \nabla \gamma_H \gamma_Q / 4\pi r^3$ , where  $r$  is the shortest distance between a quadrupole nucleus and the surrounding protons. Here we do not calculate the cross-relaxation rate  $W_{CR}$ , but we model the cross-relaxation in the following way. We assume that there is a single cross-relaxation rate independent on the orientation of the rf magnetic field in the eigenframe of the EFG tensor. As before, we suppose that  $N'_Q \ll N_H$ . For the sake of simplicity we consider a resonant rf magnetic field ( $\delta\nu = 0$ ).

After a few phase shifts of the rf magnetic field at the beginning of the mixing period a quasi equilibrium is reached and the inverse spin temperature  $\beta^*$  of the quadrupole spin system undergoes the following time variation. Let's denote the inverse spin temperature of the quadrupole spin system at the moment before the phase shift occurs as  $\beta_0$  and the inverse spin temperature of the proton spin system as  $\beta$ . Immediately after the phase shift the inverse spin temperature of the quadrupole spin system changes to  $-\beta_0$ . In the time between the phase shifts  $\beta^*$  varies as

$$\beta^*(t) = \beta - (\beta + \beta_0) \exp(-W_{CR}t). \quad (19)$$

In the quasi equilibrium situation we have  $\beta^*(\tau^*) \cong \beta_0$ , what gives

$$\beta_0 = \beta(1 - \exp(-W_{CR}\tau^*)) / (1 + \exp(-W_{CR}\tau^*)). \quad (20)$$

The number  $\Delta N$  of simultaneous upward transition in the proton spin system and downward transitions in the quadrupole spin system between two repetitive phase shifts is equal  $\Delta N = N'_Q h \Delta\nu \beta_0 / 2$ . Inserting this expression into Expression (12) and performing the next steps we obtain  $\bar{W}$  as

$$\bar{W} = \frac{1}{3\tau^*} \frac{1 - \exp(-W_{CR}\tau^*)}{1 + \exp(-W_{CR}\tau^*)} \frac{N'_Q}{N_H} \left(\frac{\nu_1}{\nu_{loc}}\right)^2 R_{m-k}(\eta). \quad (21)$$

This expression reduces to Expression (16) when  $W_{CR}\tau^* \gg 1$ . On the other hand in the cross-relaxation limit, when  $W_{CR}\tau^* \ll 1$ , we obtain

$$\bar{W} = \frac{W_{CR}}{6} \frac{N'_Q}{N_H} \left(\frac{\nu_1}{\nu_{loc}}\right)^2 R_{m-k}(\eta). \quad (22)$$

The cross-relaxation rate  $W_{CR}$  may be assumed approximately constant when the frequency splitting  $\Delta\nu$  of the energy levels in the quadrupole rotating frame is smaller or comparable to  $\nu_{loc}$ . At a larger value of  $\Delta\nu$ , obtained in an off-resonant situation or at a large value of  $B_1$ ,  $W_{CR}$  strongly decreases.

## 3. Experimental results and discussion

We apply the above theoretical results to the analysis of the  $^1\text{H}$ – $^{17}\text{O}$  NQDR spectra of *p*-toluenesulfonamide and 2-nitrobenzoic acid. The structural formulas of the molecules are shown in Fig. 3.

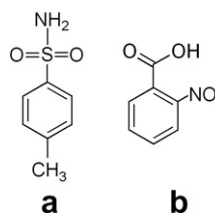
The details of the experiment are as follows. A home made NMR spectrometer operating at  $\nu_L = 32$  MHz is used to measure the proton NMR signal. The sample is moving between two magnets using pneumatic post. In the first magnet the proton spin system is polarized in  $B_0 \approx 0.75$  T during the polarization phase (Fig. 1). The proton NMR signal at the end of a magnetic field cycle is measured in the same magnet. In the second magnet the external magnetic field is compensated to  $B < 50$   $\mu\text{T}$ . The transfer time between the two magnets is 0.1 s. A 50 W broadband power transmitter connected to a tuned circuit consisting of a coil and a computer controlled capacity bank is used for the rf irradiation of the sample during the mixing phase. Signal averaging was used to improve the signal-to-noise ratio.

### 3.1. *p*-Toluenesulfonamide

The experiment was performed under the following experimental conditions. The temperature of the sample was  $T = -70$  °C. The polarization time in  $B_0 = 0.75$  T was 1 min. The sample was left in the second magnet for  $\tau = 1$  s. During this time we applied an rf magnetic field with the frequency  $\nu$ . The time  $\tau^*$  between two repetitive 180° phase shifts of the rf magnetic field was equal  $\tau^* = 0.3$  ms. The frequency range between 0.5 MHz and 4 MHz was scanned in steps of 20 kHz.

The NQDR spectrum of *p*-toluenesulfonamide in the frequency range between 0.5 MHz and 4 MHz is shown in Fig. 4. Three strong lines are observed around 3450 kHz, 2460 kHz, and 1000 kHz. Further investigations with the two-frequency irradiation technique in nonzero magnetic field [28] show that these lines correspond to  $^{14}\text{N}$ .  $^{14}\text{N}$  has a spin  $S = 1$  and thus three NQR frequencies  $\nu_+$ ,  $\nu_-$  and  $\nu_0 = \nu_+ - \nu_-$ . In the present case they are equal  $\nu_+ = 3414$  kHz,  $\nu_- = 2433$  kHz and  $\nu_0 = \nu_+ - \nu_- = 981$  kHz. The  $^{14}\text{N}$  quadrupole coupling constant is  $e^2qQ/h = 3898$  kHz and the asymmetry parameter is  $\eta = 0.503$ .  $^{14}\text{N}$  is not a good candidate for the Slusher and Hahn's NQDR technique because of spin quenching [2]. The  $^1\text{H}$ – $^{14}\text{N}$  NQDR lines as observed in the present NQDR spectrum (Fig. 4.) are also shifted towards higher frequencies for approximately 30 kHz. This is the result of the solid-effect contribution to the NQDR spectrum of  $^{14}\text{N}$  [29]. The  $^1\text{H}$ – $^{14}\text{N}$  NQDR lines do not change significantly when the time  $\tau^*$  between two repetitive phase shifts is changed. They are observed also when a non modulated rf magnetic field is applied.

The two weaker lines at 2010 and 2660 kHz are observed only when the phase-modulated rf magnetic field is applied. The fre-



**Fig. 3.** Structural formulas of *p*-toluenesulfonamide (a) and 2-nitrobenzoic acid (b).

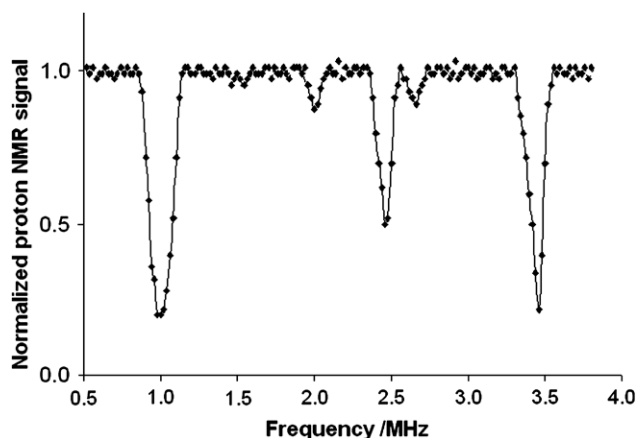


Fig. 4. NQDR spectrum of *p*-toluenesulfonamide.

quencies 2010 kHz and 2660 kHz seem to be compatible with the observed oxygen NQR frequencies in case of a S–O bond [5]. The  $^{17}\text{O}$  NQR frequencies are thus  $\nu_{3/2-1/2} = 2010$  kHz and  $\nu_{5/2-3/2} = 2660$  kHz. The 20 times weaker NQDR line at  $\nu_{5/2-1/2} = 4670$  kHz has not been observed. The two oxygen positions in a molecule are within the experimental resolution equivalent. The  $^{17}\text{O}$  quadrupole coupling constant and asymmetry parameter are  $e^2qQ/h = 9550$  kHz and  $\eta = 0.676$ .

In order to investigate the double resonance dynamics and the sensitivity of the NQDR technique, we measured the NQDR signals of  $^{17}\text{O}$  at two modulation times  $\tau^*$  of the rf magnetic field:  $\tau^* = 0.3$  ms and  $\tau^* = 3$  ms. The parameters of a magnetic field cycle and the amplitude of the rf magnetic field are kept unchanged. The results are presented in Fig. 5. Here  $S_0$  is the proton NMR signal observed with no rf irradiation and  $S$  is the proton NMR signal observed when the rf irradiation at the frequency  $\nu$  is applied. At  $\nu = 2010$  kHz the proton NMR signal drops only by approximately 30% when  $\tau^*$  is changed from  $\tau^* = 0.3$  ms to  $\tau^* = 3$  ms. The signal at  $\tau^* = 0.3$  ms is thus measured almost in the cross-relaxation limit. A similar situation occurs at  $\nu = 2660$  kHz. Using Eq. (21) we may calculate the cross-relaxation rate  $W_{\text{CR}}$  for the two NQDR lines. The results are as follows. For the NQDR line at  $\nu = 2660$  kHz we obtain  $W_{\text{CR}} = 800$  s $^{-1}$  whereas for the NQDR line at  $\nu = 2010$  kHz we obtain  $W_{\text{CR}} = 1100$  s $^{-1}$ .

The intensity of a NQDR line strongly depends on the amplitude  $B_1$  of the rf magnetic field. In order to check the consistency of the assignment of the NQDR lines we measured the amplitude  $B_1$  that was used at the NQDR measurement. The amplitude  $B_1$  of

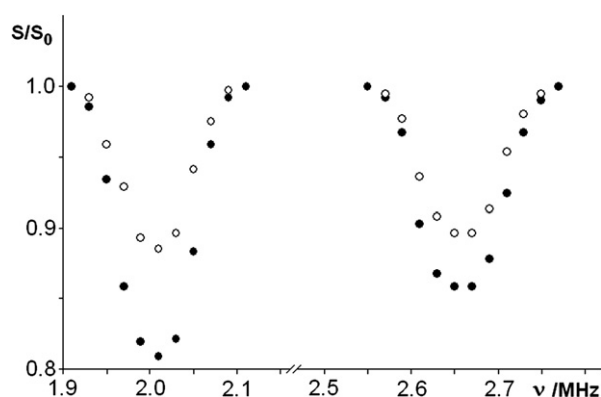


Fig. 5. The  $^1\text{H}$ – $^{17}\text{O}$  NQDR signals as measured at two values of the phase modulation time  $\tau^*$ :  $\tau^* = 3$  ms (open circles) and  $\tau^* = 0.3$  ms (full circles).

the rf magnetic field with the frequency  $\nu$  is measured in the following way. The magnetic field cycling is done between the high magnetic field  $B_0$  and a low magnetic field  $B$ , where the proton Larmor frequency is  $\nu_L = \gamma_{\text{H}}B/2\pi$ . During the stay in the low magnetic field we apply a short pulse of the rf magnetic field. The length of the pulse (2 ms in our case) is longer than the proton  $T_2$  and shorter than the proton  $T_1$ . After the pulse is switched on the proton magnetization projects first on the direction of the effective magnetic field in the rotating frame, that forms an angle  $\theta$ ,  $\theta = \arctg(\nu_{1\text{H}}/(\nu_L - \nu))$ , with the direction of the static magnetic field. Here  $\nu_{1\text{H}} = \gamma_{\text{H}}B_1/4\pi$ . After the switch-off of the rf magnetic field the proton magnetization projects back on the direction of the static magnetic field. The proton magnetization  $M$  after the pulse is related to the proton magnetization  $M_0$  at the moment before the pulse is applied as

$$M = M_0 \frac{(\nu_L - \nu)^2}{(\nu_L - \nu)^2 + \nu_{1\text{H}}^2}. \quad (23)$$

The proton magnetization as well as the proton NMR signal  $S$  at the end of the magnetic field cycle drop to zero when  $\nu_L = \nu$  and to one-half when  $\nu_L = \nu \pm \nu_{1\text{H}}$ . The  $\nu_L$ -dependence of the proton NMR signal  $S$  thus allows us to determine the frequency  $\nu_{1\text{H}}$ . The amplitude of the rf magnetic field is then calculated as  $B_1 = 4\pi\nu_{1\text{H}}/\gamma_{\text{H}}$ .

The measurement at the frequency  $\nu = 2010$  kHz is presented in Fig. 6. The width of the dip at the half depth is equal  $\Delta\nu_L = 180$  kHz, corresponding to  $\nu_{1\text{H}} = 90$  kHz and  $B_1 = 4.2$  mT. The oxygen frequency  $\nu_1 = \gamma_{\text{O}}B_1/2\pi$  is equal  $\nu_1 = 24$  kHz. In a similar manner we obtained at 2660 kHz  $B_1 = 4.5$  mT and  $\nu_1 = 26$  kHz.

Eq. (21) can further be used to calculate the proton local frequency  $\nu_{\text{loc}}$  from each of the three lines. From both NQDR lines we obtain the same value of  $\nu_{\text{loc}}$ ,  $\nu_{\text{loc}} = 12$  kHz. The two equal values of  $\nu_{\text{loc}}$  support the assignment of the NQDR lines we made. In order to make this point more clear we estimated (Eq. (10)) the intramolecular contribution to  $\nu_{\text{loc}}$ . A detailed crystal structure of the compound with known proton positions is necessary to obtain a precise value. In the calculation we used the following shortest H–H distances: 1.61 Å (–NH $_2$  group), 2.38 Å (ring) and 1.63 Å (rotating –CH $_3$  group). As the result we obtained  $\nu_{\text{loc}} = 14$  kHz. This result agrees well with the experimentally obtained value  $\nu_{\text{loc}} = 12$  kHz.

We also reduced the output power of the transmitter and measured the dependence of the NQDR signal  $S_0 - S$  on  $B_1$ . We used the shorter modulation time  $\tau^* = 0.3$  ms. At both NQR frequencies we obtained the quadratic dependence,  $S_0 - S \propto B_1^2$ , as expected after Eq. (21) when the NQDR signal is weak. The high-power limit,

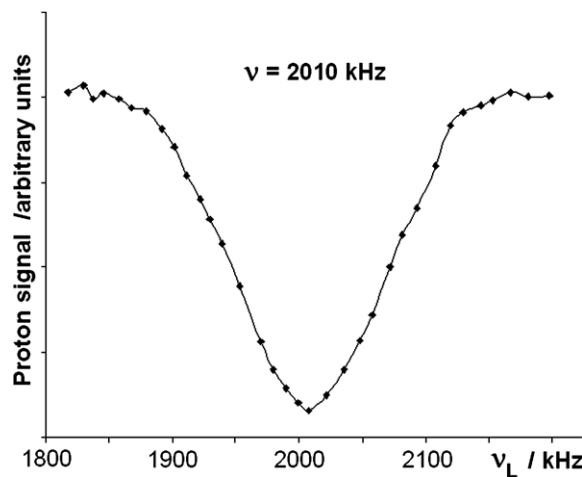


Fig. 6. Measurement of the amplitude  $B_1$  of the rf magnetic field. See details in text.

when the large value of  $\nu_1$  as compared to  $\nu_{loc}$  reduces the cross-relaxation rate, is at  $B_1 = 4.5$  mT not yet observed.

### 3.2. 2-Nitrobenzoic acid

In solid 2-nitrobenzoic acid the molecules form hydrogen bonded dimers. The proton–oxygen interaction for the oxygens participating in the O–H...O hydrogen bonds is stronger than the proton–oxygen interaction in *p*-toluenesulfonamide. A higher cross-relaxation rate is thus expected. The NQR frequencies of  $^{17}\text{O}$  participating in the O–H...O hydrogen bonds are known from a previous study [23]. In addition there is a nitro group in the molecule with the much weaker proton–oxygen interaction.

The experiment was performed at  $T = -70$  °C. The proton polarization time was 60 s and the duration of the mixing period was  $\tau = 1$  s. The amplitude of the rf magnetic field was in the whole frequency range approximately 4 mT. The frequency dependence of the proton NMR signal  $S$  as measured at two modulation times,  $\tau^* = 0.3$  ms and  $\tau^* = 3$  ms, divided by the proton NMR signal  $S_0$ , as measured with no rf irradiation, is presented in Fig. 7. The NQDR dips are observed around 1.2 MHz, 2.2 MHz, 2.5 MHz and 3.7 MHz. The  $^{17}\text{O}$  NQR frequencies and the corresponding oxygen positions are labeled on the frequency scale. Two NQR frequencies, 1160 kHz and 1240 kHz, correspond to the  $3/2-1/2$  NQR transition at the  $^{17}\text{O}-\text{H}$  and  $^{17}\text{O}\dots\text{H}$  positions, respectively. The NQR frequencies 2210 kHz and 2300 kHz correspond to the  $5/2-3/2$  NQR transition at the  $^{17}\text{O}-\text{H}$  and  $^{17}\text{O}\dots\text{H}$  positions, respectively. The NQR frequencies from the distinct oxygen positions are so close because of the concerted motion of protons in the two hydrogen bonds connecting two molecules in a centrosymmetric dimer [23]. The NQDR lines from the  $^{17}\text{O}-\text{H}\dots\text{O}$  oxygen position are broad due to the strong proton–oxygen dipolar interaction. The two somewhat weaker lines at 2510 kHz and 3730 kHz belong to the nitro group. The two oxygen positions in a nitro group are within the experimental resolution equivalent. At these positions the  $^{17}\text{O}$  quadrupole coupling constant is  $e^2qQ/h = 13,080$  kHz and the asymmetry parameter  $\eta$  is  $\eta = 0.543$ . These values agree with the previously determined values in compounds containing nitro groups [5,6,24].

The sensitivity of the NQDR technique is again limited by the cross-relaxation. For  $^{17}\text{O}$  from the nitro group the cross-relaxation rate is about  $1200$   $\text{s}^{-1}$ . For the  $^{17}\text{O}-\text{H}$  oxygen position the cross-relaxation rate is higher. The peak value at 1150 kHz is  $2300$   $\text{s}^{-1}$ ,

but this is lower than the real cross-relaxation rate. The lines are broad and structured and the off-resonance contribution to the NQDR line intensity with a lower cross-relaxation rate is important. The lines from the  $^{17}\text{O}\dots\text{H}$  oxygen positions overlap with the lines from the  $^{17}\text{O}-\text{H}$  oxygen positions. An independent determination of the cross-relaxation rate for the  $^{17}\text{O}\dots\text{H}$  oxygen position is thus not possible. The proton local frequency as calculated from the intensities of the two narrow  $^{17}\text{O}$  NQDR lines from the nitro groups are equal to  $\nu_{loc} = 17$  kHz.

## 4. Conclusions

The sensitivity of the Slusher and Hahn's NQDR technique is calculated in general for an arbitrary nuclear spin  $S$  of the quadrupole nuclei and for an arbitrary asymmetry parameter  $\eta$  of the EFG tensor. The case of  $S = 5/2$  ( $^{17}\text{O}$ ,  $^{25}\text{Mg}$ ,  $^{85}\text{Rb}\dots$ ) is treated in details. It is shown that the intensity of the NQDR line corresponding to  $\nu = \nu_{3/2-1/2}$  is generally stronger than the intensity of the NQDR line corresponding to  $\nu = \nu_{5/2-3/2}$ . The intensity of the highest frequency NQDR line at  $\nu = \nu_{5/2-1/2}$  is zero at  $\eta = 0$  and reaches about 5% of the intensities of the other two NQDR lines at  $\eta = 1$ .

The cross-relaxation between the quadrupole spin system in the quadrupole rotating frame and the dipolar proton spin system and its influence on the sensitivity of the NQDR technique is treated phenomenologically. The influence of the cross-relaxation rate on the intensities of the NQDR lines is calculated.

The results of the theoretical calculation are used in the analysis of the NQDR spectrum of *p*-toluenesulfonamide and 2-nitrobenzoic acid.

In *p*-toluenesulfonamide we observe besides the three strong  $^1\text{H}-^{14}\text{N}$  NQDR lines at 3414 kHz, 2433 kHz, and 981 kHz also two weaker NQDR lines at 2010 kHz and 2660 kHz. The weaker lines are assigned to  $^{17}\text{O}$ . The  $^{17}\text{O}$  quadrupole coupling constant is  $e^2qQ/h = 9550$  kHz and the asymmetry parameter  $\eta$  is  $\eta = 0.676$ . The intensities of the  $^1\text{H}-^{17}\text{O}$  NQDR lines are measured at two modulation rates of the rf magnetic field and the cross-relaxation rate  $W_{CR}$  is determined. It is equal  $1100$   $\text{s}^{-1}$  for the  $3/2-1/2$  transition and  $800$   $\text{s}^{-1}$  for the  $5/2-3/2$  transition. The amplitude of the rf magnetic field is measured and the proton local frequency in zero external magnetic field is determined from the intensities of the NQDR lines as being equal  $\nu_{loc} = 12$  kHz. The intramolecular contribution to  $\nu_{loc}$  is estimated and compared to the experimental value. The dependence of the NQDR signal intensities on the amplitude  $B_1$  of the rf magnetic field was measured. For  $B_1 \leq 4.5$  mT the high-power limit, when large  $\nu_1$ ,  $\nu_1 = \gamma_O B_1 / 2\pi$ , as compared to  $\nu_{loc}$  reduces the cross-relaxation rate, has not been observed.

In the NQDR spectrum of 2-nitrobenzoic acid we observed three oxygen positions: the two positions  $^{17}\text{O}-\text{H}$  and  $^{17}\text{O}\dots\text{H}$  in the O–H...O intermolecular hydrogen bonds and two equal oxygen positions in the nitro groups. The  $^{17}\text{O}$  NQR frequencies from the nitro groups,  $\nu_{3/2-1/2} = 2510$  kHz and  $\nu_{5/2-3/2} = 3730$  kHz, are determined by the present study. The  $^{17}\text{O}$  quadrupole coupling constant is  $e^2qQ/h = 13080$  kHz and the asymmetry parameter  $\eta$  is  $\eta = 0.543$ .

The proton–oxygen cross-relaxation rate for the  $^{17}\text{O}$  positions in the nitro groups has been determined as being equal  $W_{CR} = 1200$   $\text{s}^{-1}$ . For the oxygen positions in the hydrogen bonds the cross-relaxation rates cannot be precisely determined due to large dipolar linewidths and partial overlap of the NQDR lines. The proton local frequency in zero external magnetic field, as determined from the intensities of the NQDR lines, is equal  $\nu_{loc} = 17$  kHz.

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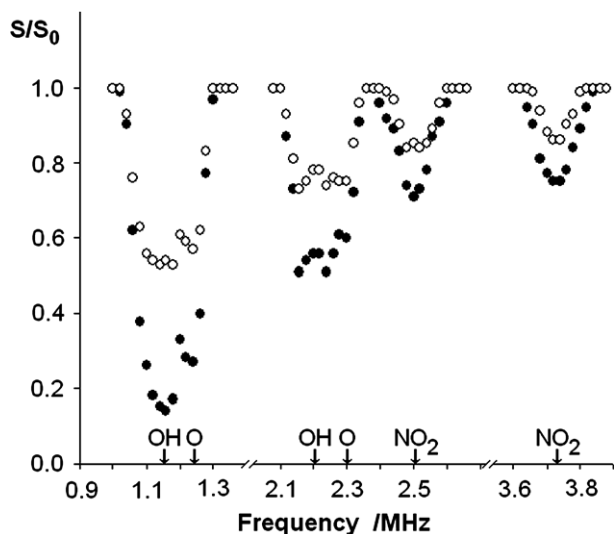


Fig. 7. NQDR spectrum of 2-nitrobenzoic acid as measured at  $\tau^* = 3$  ms (open circles) and  $\tau^* = 0.3$  ms (full circles).

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