A New Nuclear-Quadrupole Double-Resonance Technique based on Solid Effect

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A new nuclear-quadrupole double-resonance technique is described. It has a higher sensitivity and a higher resolution than the conventional nuclear-quadrupole double-resonance technique based on solid effect. The new technique involves magnetic field cycling between a high and a low static magnetic field and simultaneous application of two *rf* magnetic fields when the sample is in the low static magnetic field. A strong *rf* magnetic field induces "forbidden" simultaneous transitions in a magnetic (usually ^{1}H) and in a quadrupole spin system and thus couples the two spin systems. A weak*rf* magnetic field induces transitions between the energy levels of the quadrupole nuclei and simulates a fast spin-lattice relaxation of the quadrupole nuclei when its frequency matches an NQR frequency. The sensitivity and resolution of the new technique are discussed and test measurements in tris-sarcosine calcium chloride are presented.

Key words: NQR, NMR, Double Resonance, Magnetic Field Cycling, Solid Effect

Introduction

An *rf* magnetic field of a frequency ν in solids containing nuclear spin species I and S with the resonance frequencies ν_I and ν_S, respectively, can induce transitions between the nuclear energy levels when $\nu = \nu_I$ or $\nu = \nu_S$, and also when $\nu = \nu_I \pm \nu_S$. The transitions at $\nu = \nu_I \pm \nu_S$ are allowed in solids due to the presence of the magnetic dipole-dipole interaction between the I and S nuclei [1]. They are called solid-effect transitions. The solid-effect transitions are actually simultaneous transitions between the energy levels of both spin systems. Absorption of a quantum of energy at the frequency $\nu = \nu_I + \nu_S$ causes an upward transition in the spin system I at the frequency ν_I and an upward transition in the spin system S at the frequency ν_S, etc.

The probability per unit time for a solid-effect transition, W_{SE}, is at the same amplitude B_1 of the *rf* magnetic field significantly lower than the probability per unit time for a direct transition at $\nu = \nu_I$ or at $\nu = \nu_S$. In case of a strong magnetic dipole-dipole interaction between the nuclei I and S, as for example when the atoms I and S are covalently bonded, the solid-effect rate $2W_{SE}$ is often of the order of $(\mathrm{ms})^{-1}$ when $B \approx 1\,\mathrm{mT}$ and the amplitude B_1 of the *rf* magnetic field is equal to a reasonable value of several mT. In such a case the solid-effect transitions may be used for an indirect detection of unknown resonance frequencies of the S nuclei via their effect on the NMR or NQR signal of the I nuclei.

A nuclear-quadrupole double-resonance (NQDR) technique based on the solid effect [2, 3, 4] is often used for an indirect detection of low nuclear quadrupole resonance (NQR) frequencies ν_{QS}. The technique involves magnetic field cycling.

A purely magnetic spin system I (usually protons) is first polarized in a high static magnetic field B_0. Then the external magnetic field is adiabatically reduced to a low value B, $B \approx 1$ mT. The sample is kept in the low magnetic field B for a time τ, shorter than the spin-lattice relaxation time $T_{1I}(B)$ of the spin system I in the low magnetic field B. Then the external magnetic field B_0 is adiabatically restored and the NMR signal $S_I(\tau)$ of the I system is measured. It is approximately equal to

$$S_I(\tau) = S_{I0} \exp(-\tau/T_{1I}(B)), \tag{1}$$

when $B \ll B_0$. Here S_{I0} is the NMR signal of the

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spin system I prior to the reduction of the external magnetic field. When during the time τ spent in the low magnetic field B an *rf* magnetic field of an amplitude B_1, $B_1 \sim$ 1 mT, is applied at the solid effect frequency $\nu = \nu_{QS} + \nu_I$, the simultaneous transitions in both spin systems establish in several milliseconds a quasi equilibrium, where $N_{1I}/N_{2I} = N_{2S}/N_{1S}$. Here N_{1S} and N_{2S} are the populations of the upper and lower quadrupole energy levels separated by $h\nu_{QS}$, whereas N_{1I} and N_{2I} are the populations of the upper and lower Zeeman energy levels of the I nuclei, respectively. During the process of establishing the quasi equilibrium, the magnetization of the I system usually decreases and therefore a lower NMR signal $S_I - \Delta S_I$ is observed at the end of the magnetic field cycle. The ratio $\Delta S_I/S_{I0}$ is of the order of N_S/N_I, where $N_S = N_{1S} + N_{2S}$ and $N_I = N_{1I} + N_{2I}$.

When the *rf* magnetic field is applied at another solid-effect frequency $\nu = \nu_{QS} - \nu_I$, a quasi equilibrium is established where $N_{1I}/N_{2I} = N_{1S}/N_{2S}$, and a drop ΔS_I of the NMR signal of the same order of magnitude as in the previous case is observed. A doublet around $\nu = \nu_{QS}$ is thus observed in the ν-dependence of S_I. The doublet is in general asymmetric and not very well resolved. The solid-effect rate $2W_{SE}$, namely, strongly decreases on increasing the low magnetic field B, whereas the spin-lattice relaxation time $T_{1I}(B)$ often strongly increases on increasing B. Therefore an optimal Larmor frequency γB is usually chosen as being equal to a few widths of the NMR line of the spin system I. When dealing with polycrystalline samples, the external magnetic field also broadens the NQR line. Thus in practice a reasonable value of B is approximately 1 mT or less.

The main disadvantage of this NQDR technique is its relatively low sensitivity as compared to the sensitivities of other NQDR techniques, and also its low resolution. The width of a line within the doublet is namely approximately equal to the width of the NMR line of the spin system I. The low resolution is not always a disadvantage since it allows us to determine the NQR frequencies in a short time. Some recent experiments [5, 6] show that the sensitivity of the NQDR technique based on the solid effect significantly increases when the spin-lattice relaxation rates of the quadrupole nuclei are high. In this case, namely, after establishing the quasi equilibrium, the coupled spin systems relax towards the thermal equilibrium with the crystal lattice faster than the I spin system alone. This led us to an idea of simulating the fast spin-lattice relaxation of the quadrupole nuclei by applying a second weak *rf* magnetic field of an amplitude B_2 and frequency ν_2, $\nu_2 \approx \nu_{QS}$, during the time when the first strong *rf* magnetic field at the frequency $\nu_1 = \nu_{QS} \pm \nu_I$ is switched on. In the ν_2-dependence of the NMR signal S_I at the end of the magnetic field cycle we namely expect a relatively sharp dip at $\nu_2 = \nu_{QS}$. The width of the dip depends on the homogeneous and inhomogeneous broadening of the NQR line as caused by the local electric and magnetic fields, as well as on the solid-effect rate $2W_{SE}$. In general we expect a width of a few kHz which is approximately an order of magnitude smaller than the width of the solid-effect doublet.

In the following we discuss the sensitivity of the NQDR technique based on the solid effect as well as the sensitivity of the new technique. Finally we present some experimental results obtained by the new technique in tris-sarcosine calcium chloride.

Sensitivity of the NQDR techniques

Immediately after the adiabatic reduction of the external magnetic field is completed ($t = 0$) the populations N_{1I} and N_{2I} of the upper and lower energy levels of the magnetic nuclei I,

$$N_{1I}(0) = \frac{1}{2}N_I(1 - x(0)),\ N_{2I}(0) = \frac{1}{2}N_I(1 + x(0)). \quad (2)$$

do not differ significantly from their initial values $N_{1I}^0 = \frac{1}{2}N_I(1 - \delta_0)$ and $N_{2I}^0 = \frac{1}{2}N_I(1 + \delta_0)$ prior to the the reduction of the external magnetic field ($x(0) \approx \delta_0$). Here $\delta_0 = \hbar\gamma B_0/2k_BT$.

Let us for the sake of simplicity assume that a quadrupole nucleus S exhibits only two nuclear quadrupole energy levels with the energy separation $h\nu_{QS}$. Immediately after the adiabatic reduction of the external magnetic field is completed, the populations N_{1S} and N_{2S} of the upper and lower quadrupole energy levels may be written as

$$N_{1S}(0) = \frac{1}{2}N_S(1-y(0)),\ N_{2S}(0) = \frac{1}{2}N_S(1+y(0)). \quad (3)$$

Here y_0 depends on the effectiveness of the level crossing [7] during the adiabatic decrease of the external magnetic field. If the level crossing is fully effective, i. e. if the ratios of the populations of the energy levels of the two spin systems equalize when the resonance frequencies match, then $x(0) = y(0)$. If this is not the case, then $y(0) < x(0)$.

The populations of the energy levels of the nuclei I and S are due to the spin-lattice relaxation governed by the rate equations

$$\frac{\mathrm{d}N_{1\mathrm{I}}}{\mathrm{d}t} = -W_\mathrm{I}(N_{1\mathrm{I}} - N_{2\mathrm{I}}), \quad \frac{\mathrm{d}N_{1\mathrm{S}}}{\mathrm{d}t} = -W_\mathrm{S}^\mathrm{d} N_{1\mathrm{S}} + W_\mathrm{S}^\mathrm{u} N_{2\mathrm{S}}. \tag{4}$$

Here W_S^u is the probability per unit time for an upward transition and W_S^d is the probability per unit time for a downward transition in the spin system S. In the high temperature approximation the two transition probabilities per unit time read

$$W_\mathrm{S}^\mathrm{u} = W_\mathrm{S}(1 - h\nu_\mathrm{QS}/2k_\mathrm{B}T), \quad W_\mathrm{S}^\mathrm{d} = W_\mathrm{S}(1 + h\nu_\mathrm{QS}/2k_\mathrm{B}T). \tag{5}$$

Here W_S is an average of W_S^u and W_S^d. In case of the I nuclei we assume that the energy separation of the Zeeman energy levels is low and we do not distinguish between the probability per unit time for an upward transition and the probability per unit time for a downward transition: $W_\mathrm{I}^\mathrm{u} = W_\mathrm{I}^\mathrm{d} = W_\mathrm{I}$.

Let us further assume that the number N_S of crystalographically equivalent quadrupole nuclei is lower than the number N_I of the purely magnetic nuclei, and that there are N_S strongly coupled I-S pairs. If the *rf* magnetic field is applied at the frequency $\nu = \nu_\mathrm{QS} + \nu_\mathrm{I}$, then only the pairs where both nuclei simultaneously occupy either the upper energy levels or the lower energy levels participate in the solid effect. The numbers of these pairs are $N_{1\mathrm{S}}(N_{1\mathrm{I}}/N_\mathrm{I})$ and $N_{2\mathrm{S}}(N_{2\mathrm{I}}/N_\mathrm{I})$, respectively. The rate equations governing the populations of the nuclear energy levels as a consequence of the solid effect transitions read

$$\frac{\mathrm{d}N_{1\mathrm{S}}}{\mathrm{d}t} = \frac{\mathrm{d}N_{1\mathrm{I}}}{\mathrm{d}t} = -W_\mathrm{SE}N_{1\mathrm{S}}\frac{N_{1\mathrm{I}}}{N_\mathrm{I}} + W_\mathrm{SE}N_{2\mathrm{S}}\frac{N_{2\mathrm{I}}}{N_\mathrm{I}}. \tag{6}$$

Here W_SE is the probability per unit time for a solid-effect transition. Combining (4) and (5), writing the populations $N_{1\mathrm{I}}$, $N_{2\mathrm{I}}$, $N_{1\mathrm{S}}$ and $N_{2\mathrm{S}}$ in the form $N_{1\mathrm{I}} = \frac{1}{2}N_\mathrm{I}(1-x)$, $N_{2\mathrm{I}} = \frac{1}{2}N_\mathrm{I}(1+x)$, $N_{1\mathrm{S}} = \frac{1}{2}N_\mathrm{S}(1-y)$ and $N_{2\mathrm{S}} = \frac{1}{2}N_\mathrm{S}(1+y)$ and assuming that $x, y \ll 1$ we obtain the following rate equations for x and y:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -2W_\mathrm{I}x - W_\mathrm{SE}\varepsilon(x+y), \quad \frac{\mathrm{d}y}{\mathrm{d}t} = -2W_\mathrm{S}(y - y_0) - W_\mathrm{SE}(x+y). \tag{7}$$

Here $\varepsilon = N_{1\mathrm{S}}/N_{1\mathrm{I}}$ and $y_0 = h\nu_\mathrm{QS}/2k_\mathrm{B}T$.

The steady-state solutions x^* and y^* of the Eqs. (7) are

$$y^* = y_0\frac{2W_\mathrm{S}W_\mathrm{I} + W_\mathrm{S}W_\mathrm{SE}\varepsilon}{2W_\mathrm{S}W_\mathrm{I} + W_\mathrm{S}W_\mathrm{SE}\varepsilon + W_\mathrm{I}W_\mathrm{SE}}, \quad x^* = -y^*\frac{W_\mathrm{SE}\varepsilon}{2W_\mathrm{I} + W_\mathrm{SE}\varepsilon}. \tag{8}$$

Here x^* is proportional to the NMR signal of the dynamically polarized I spin system. A dynamic polarization of hydrogen nuclei by the quadrupole ^{75}As nuclei using the solid effect has been recently observed in KH_2AsO_4 [8].

In a usual double resonance experiment $x(0)$ is much larger than y_0. We may therefore neglect the steady-state solutions x^* and y^* and assume that both x and y relax towards zero. The relaxation is two-exponential with the relaxation rates W_+ and W_-:

$$W_\pm = W_\mathrm{I} + W_\mathrm{S} + \frac{1}{2}(1+\varepsilon)W_\mathrm{SE} \pm \sqrt{A}, \quad A = [2(W_\mathrm{S} - W_\mathrm{I}) + (1-\varepsilon)W_\mathrm{SE}] + 4\varepsilon W_\mathrm{SE}^2. \tag{9}$$

Since we are interested in the sensitivity of the double resonance technique, we assume that $\varepsilon \ll 1$ and $W_\mathrm{SE} \ll W_\mathrm{I}$. In this case, the expressions (9) simplify:

$$W_+ \cong 2W_\mathrm{S} + W_\mathrm{WSE}, \quad W_- \cong 2W_\mathrm{I} + \varepsilon\frac{2W_\mathrm{S}W_\mathrm{SE}}{2W_\mathrm{S} + W_\mathrm{SE}}. \tag{10}$$

The population difference of the energy levels of the I nuclei is proportional to $x(t)$,

$$x(t) = x_+\exp(-W_+t) + x_-\exp(-W_-t), \tag{11}$$

where

$$x_- \cong x(0), \quad x_+ \cong \varepsilon\left(\frac{W_\mathrm{SE}}{2W_\mathrm{S} + W_\mathrm{SE}}\right)y(0) + \varepsilon\left(\frac{W_\mathrm{SE}}{2W_\mathrm{S} + W_\mathrm{SE}}\right)^2 x(0). \tag{12}$$

The magnetization M_I of the I spin system thus drops in a short time ($\approx W_+^{-1}$) for ΔM_I, $\Delta M_\mathrm{I}/M_\mathrm{I} = x_+/x(0)$, and then the rest of the magnetization relaxes towards zero with the spin-lattice relaxation rate W_-.

The maximum value of x_+ is obtained in case of a slow spin-lattice relaxation of the S nuclei ($W_S \ll W_{SE}$) when $x_+ \cong \varepsilon\,(x(0) + y(0))$.

When the spin lattice relaxation of the quadrupole nuclei is slow, $W_S \leq W_I \ll W_{SE}$, the maximum double resonance signal is obtained if $W_I\tau \ll 1$. In this case

$$\frac{\Delta S_I}{S_{I0}} = \frac{x_+}{x(0)} \cong \varepsilon \frac{x(0) + y(0)}{x(0)} \approx \varepsilon. \tag{13}$$

If, on the other hand, the quadrupole nuclei relax fast, i. e. when $\varepsilon W_S \geq W_I$, the maximum double resonance signal is obtained when the difference

$$\begin{aligned}\Delta x &= x(0)e^{-W_I\tau} - x_+e^{-W_+\tau} - x_-e^{-W_-\tau} \\ &\cong x(0)\left(e^{-W_I\tau} - e^{-W_-\tau}\right)\end{aligned} \tag{14}$$

is maximum. In this case Δx may be of the order of $x(0)$ ($\Delta S_I/S_{I0} \sim 1$), which is much more than $\Delta S_I/S_{I0} \sim \varepsilon$ (expression (13)) as obtained when the quadrupole nuclei relax slowly.

When the frequency ν of the *rf* magnetic field is equal to another solid effect frequency, $\nu = \nu_{QS} - \nu_I$, the relaxation rates W_+ and W_- are still given by (9) and (10), x_- is still approximately equal to $x(0)$, whereas x_+ is in case of slow spin-lattice relaxation of the quadrupole nuclei approximately equal to $\varepsilon(x(0) - y(0))$. The double resonance doublet is thus in case of a slow spin lattice relaxation of the quadrupole nuclei asymmetric: stronger at $\nu = \nu_{QS} + \nu_I$ and weaker at $\nu = \nu_{QS} - \nu_I$. In case of a fully effective level crossing ($x(0) = y(0)$) the line at $\nu = \nu_{QS} - \nu_I$ disappears.

The doublet obtained in case of a fast spin-lattice relaxation of the quadrupole nuclei is stronger and nearly symmetric.

In the new NQDR technique we apply two *rf* magnetic fields: a strong one, say, at the frequency $\nu_1 = \nu_{QS} - \nu_I$ and a weak one at a frequency ν_2, $\nu_2 \approx \nu_{QS}$. When the weak *rf* magnetic field is switched off, the largest part of the I-spin magnetization, which is proportional to x_-, relaxes towards zero with the spin-lattice relaxation rate W_-. When, on the other hand, the weak *rf* magnetic field is switched on at $\nu_2 = \nu_{QS}$, the transition probability per unit time between the quadrupole energy levels increases, and as a consequence the magnetization of the magnetic spin system relaxes towards zero value with a higher relaxation rate than W_-. If a large enough amplitude of the weak rf magnetic field is chosen so that the transition probability per unit time between the quadrupole energy levels exceeds W_{SE}, then the magnetization of the I spin system relaxes towards zero with a relaxation rate W_0, $W_0 = W_-(W_S \to \infty) = 2W_I + \varepsilon W_{SE}$.

The double resonance signal ΔS of the two-frequency irradiation technique is the difference between the NMR signals of the I system at the end of the magnetic field cycle as obtained under the single-frequency and under the two-frequency *rf* irradiation. It may be approximately expressed as

$$\Delta S \cong S_{I0}\left(e^{-W_-\tau} - e^{-W_0\tau}\right). \tag{15}$$

The sensitivity of the two-frequency irradiation technique critically depends on the spin-lattice relaxation rate $2W_S$ of the quadrupole nuclei, and on W_{SE}. The highest sensitivity is obtained when the quadrupole nuclei relax slowly, $W_S \ll W_{SE}$. In this case ΔS is of the order of S_{I0} when $W_{SE} \ll W_I$. When, on the other hand, the quadrupole nuclei relax very fast, $W_S \ll W_{SE}$, the relaxation rate W_- is already under the single-frequency *rf* irradiation equal to W_0 and the double resonance signal is zero. The solid effect doublet is in this case symmetric and strong but the resolution can not be improved. The new two-frequency irradiation technique is thus applicable when $W_{SE} \ll W_I$ and $W_S < W_{SE}$, whereas in the low-resolution NQDR based on the solid effect the best results are obtained when $W_{SE} \ll W_I$ and $W_S > W_{SE}$.

Experimental Results

As a test of the new NQDR technique we measured ^{35}Cl, ^{37}Cl and ^{14}N NQR frequencies in tris-sarcosine calcium chloride (TSCC) with the chemical formula $(CH_3NH_2{}^+COO^-)_3CaCl_2$. All measurements were performed at room temperature.

The parameters of the magnetic field cycle were $B_0 \cong 0.8$ T, $B = 0$, and $\tau = 0.3$ s. The cycles were repeated every 10 seconds. The ^1H-^{37}Cl solid-effect doublet as obtained by the single-frequency irradiation is shown in Figure 1a. The amplitude B_1 of the *rf* magnetic field was approximately 2 mT. The doublet in zero external magnetic field ($B = 0$) is the consequence of a finite dipole width $\delta\nu_D$ of the proton NMR line ($\delta\nu_D \sim 30$ kHz). The relative change $\Delta S_H/S_H$ of the proton NMR signal is at $\nu_Q \pm \delta\nu_D$ larger than $\varepsilon = N(^{37}Cl)/N(^1H) = 0.033$, what shows that the spin-lattice relaxation rate W_Q of the chlorine

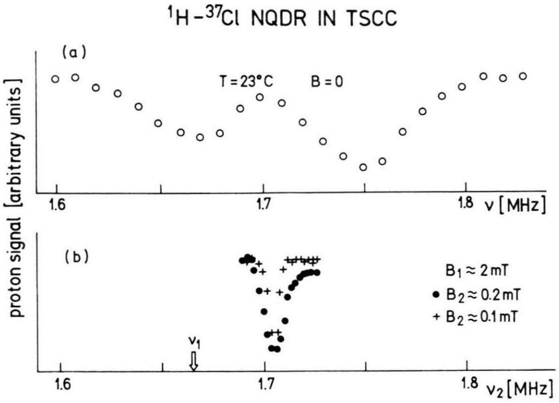

Fig. 1. ^1H-^{37}Cl NQDR spectra in TSCC as measured by the single-frequency irradiation technique (a) and by the new two-frequency irradiation technique (b).

nuclei multiplied by ε is higher than the proton spin-lattice relaxation rate W_H in zero magnetic field ($W_H \sim 4s^{-1}$). The doublet is slightly asymmetric and centered at approximately 1.7 MHz. A similar result was obtained in a previous experiment [9].

The effect of the two-frequency irradiation is shown in Figure 1b. The strong *rf* magnetic field with an amplitude B_1 of approximately 2 mT was applied at the frequency ν_1 = 1670 kHz and the magnetic-field cycles were repeated at different frequencies ν_2 of the weak *rf* magnetic field with the amplitude B_2. Two frequency scans are shown: one at $B_2 \approx 0.2$ mT and another at $B_2 \approx 0.1$ mT. The second scan gave a significantly narrower line than the first one. At still lower values of B_2 the intensity of the double resonance line decreases whereas the line width does not change significantly. Thus the ^{37}Cl NQR frequency $\nu_Q(^{37}Cl)$ is in TSCC at 23°C equal $\nu_Q(^{37}Cl)$ = (1705±3) kHz.

The NQR frequency of the more abundant ^{35}Cl nuclei was also measured by the new NQDR techniques. The parameters of a magnetic-field cycle as well as the amplitudes of the *rf* magnetic fields were the same as before. As a result we obtained $\nu_Q(^{35}Cl)$ = (2165±4) kHz. Thus the ratio of the nuclear quadrupole moments $Q(^{35}Cl)/Q(^{37}Cl)$ of the two chlorine isotopes is – if we neglect the influence of the isotope masses on the motional averaging of the electric-field-gradient tensor – equal to $Q(^{35}Cl)/Q(^{37}Cl)$ = 1.270±0.005.

A precise measurement of the ^{14}N (I = 1) NQR frequencies ν_+, ν_- and ν_0 in TSCC may also be performed. There are two positions of the sarcosine molecules in the crystal structure with the occupation ratio 2:1 [9]. We therefore expect two sets of three ^{14}N NQR lines.

The secular part of the proton-^{14}N dipole-dipole interaction is in zero external magnetic field equal to zero when the asymmetry parameter η of the electric-field-gradient tensor at the nitrogen site differs from zero [10]. The ^{14}N NQR lines are therefore narrow, but the highly sensitive nuclear-quadrupole double-resonance technique involving resonant coupling of nitrogens in the rotating frame and protons in the laboratory frame [11] can not be used. However a strong *rf* magnetic field with the frequency close to a ^{14}N NQR frequency still induces the solid-effect transitions [3, 4] and thus couples the two spin systems. In the single-frequency NQDR experiment a broad line between 400 kHz and 600 kHz and two narrower lines around 1 MHz were observed, indicating that there are indeed two crystallographically inequivalent nitrogen sites in the crystal structure and that the asymmetry parameter η is for both sites close to 1 [9]. The large value of η is in agreement with the electric-charge distribution within a C-NH_2^+-C group.

More precise measurements of the ^{14}N NQR frequencies in TSCC have been done by the new technique. The parameters of a magnetic field cycle were the same as before. The amplitude B_1 of the strong *rf* magnetic field was approximately 2 mT, whereas the amplitude B_2 of the weak *rf* magnetic field was approximately 0.1 mT. The results of the measurements of the ^{14}N NQR frequencies ν_+, ν_+ and ν_0 for the more abundant sarcosine molecules are shown in Figure 2. The observed NQR lines are of different widths and shapes, which is presumably the effect of the proton-nitrogen dipole-dipole interaction. The lowest ^{14}N NQR frequency ν_0 was observed at ν_0 = (430.1±0.4) kHz, the intermediate NQR frequency ν_- at ν_- = (471.3±1) kHz and the highest NQR frequency ν_+ between 901.1 kHz and 903.7 kHz. The quadrupole coupling constant eqQ/h is thus equal eqQ/h = (916±2) kHz, and the asymmetry parameter η is equal η = (0.939±0.003).

For the other nitrogen site we obtained by the same technique the following NQR frequencies: ν_0 = (484.6±0.5) kHz, ν_- = (540.7±0.5) kHz and ν_+ = (1025.0±1) kHz. The quadrupole coupling constant eqQ/h is equal to 1044±2) kHz and the asymmetry parameter η is 0.929±0.003.

The ^{14}N NQR frequencies as measured by the new technique are well resolved and determined with a much higher precision than by the single-frequency

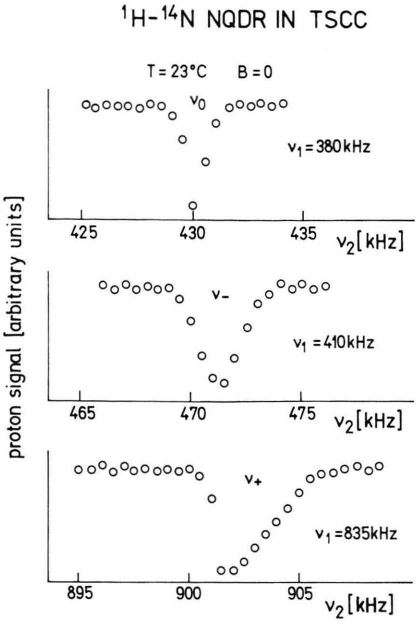

Fig. 2. ^{1}H-^{14}N NQDR spectra in TSCC as measured by the new two-frequency irradiation technique.

irradiation technique. The above measurements also manifest the power of the new technique in case of overlapping solid-effect spectra.

Conclusions

We present a new nuclear quadrupole double resonance technique based on the solid effect. The technique involves magnetic field cycling between a high and a low (~1 mT) static magnetic field. During the time spent in the low static magnetic field, a strong *rf* magnetic field of an amplitude B_1 applied at a solid-effect frequency $\nu_I \pm \nu_{QS}$ couples the magnetic spin system I and the quadrupole spin system S. A two-exponential relaxation of the I-spin magnetization M_I follows the application of the strong *rf* magnetic field. In a short time M_I drops to approximately $M_I N_S / N_I$, and then the rest of M_I relaxes towards zero with the relaxation rate W_-. The relaxation rate W_- is high when the spin-lattice relaxation rate W_S of the quadrupole spin system is high. If this is not the case, a high spin-lattice relaxation rate W_S can be simulated by a second *rf* magnetic field B_2 applied in resonance at $\nu_2 = \nu_{QS}$. Thus in the ν_2-dependence of the NMR signal of the I nuclei at the end of the magnetic-field cycle a sharp line is observed around $\nu_2 = \nu_{QS}$. The new technique gives the best results when the quadrupole nuclei relax slowly: $W_S \ll W_{SE}$. If this is not the case, then the new technique may be still applied until $W_S \cong W_{SE}$, but the sensitivity is strongly reduced.

The experiments performed in TSCC at room temperature show that the resolution of the new technique is indeed by more than one order of magnitude higher than the resolution of the single-frequency NQDR technique. Moreover, the new technique is particularly useful when the solid-effect spectra as obtained by the single-frequency NQDR technique overlap.

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