SELECTIVE DOUBLE-QUANTUM NMR IN SOLIDS

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A simple method for selective double-quantum NMR in solids is described The spin system is first prepared in a state having only dipolar, or quadrupolar, order. Selective excitation and detection of double-quantum coherence is then achieved by the $90^\circ_{x,y}-t-45^\circ_y$ pulse sequence.

1. Introduction

In the last few years there has been a growing interest in multiple-quantum NMR spectroscopy, see e.g. refs [1–7] and references therein, where the Zeeman quantum-number selection rule becomes $\Delta M = n$, with arbitrary n, instead of the usual $\Delta M = 1$ of ordinary NMR spectroscopy. With non-selective excitations, however, spectral resolution is usually rather poor especially in solids and intensities of the lines decreased rapidly with increasing n. Moreover, the intensities, even within a given order, depend strongly on preparation; therefore some sort of averaging is necessary to get appreciable intensities of all the lines [3,8]

Recently Warren et al. [9] have developed a method for wideband selective excitation of n-quantum coherence. Their method consists of a combination of multiple pulse averaging [10] and phase shifts [8].

In the present paper we propose a simple method for wideband selective excitation and detection of double-quantum coherence in dipolar or quadrupolar solids. We note that the present study applies to multilevel spin systems and is quite different from the double-quantum NMR of a spin 1 system [2,11].

2. Theory

Consider a system of dipole-coupled spins in solids, subject to a high magnetic field. The relevant hamiltonian, in the frame with (x, y, z) axes rotating around the z axis with angular frequency ω, is given by

$$H = \Delta I_z + H_D^{(0)}, \qquad \Delta = \omega_0 - \omega, \tag{1}$$

where $\omega_0 I_z$ is the Zeeman system, ω_0 being the Larmor precession frequency, and $H_D^{(0)}$ is the truncated dipolar interaction, which commutes with I_z. Terms leading to relaxation are neglected in eq (1). The density matrix of the spin system in equilibrium, in the high-temperature approximation, is given by

$$\rho = 1 - \beta I_z. \tag{2}$$

Now we bring the spin system into a state having only dipolar order. One way to do this is by applying a phase shifted pulse pair [12] $90^\circ_x-\tau_1-45^\circ_y$, either on-resonance ($\Delta = 0$) or off-resonance, see fig. 1. In the latter case, to avoid Zeeman order τ_1 must be chosen such that $\sin \Delta\tau_1 = 0$ [13]. After waiting for a time τ_W which must be longer than the decay time T_2 of the off-diagonal elements, i.e. multiple-quantum coherences [7,14], the density matrix becomes

$$\rho = 1 - \beta H_D^{(0)}, \tag{3}$$

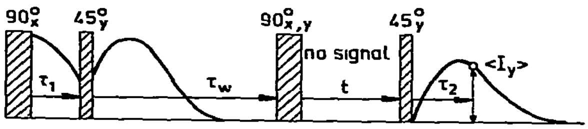

Fig. 1. Selective excitation and detection of double-quantum coherence First dipolar order is prepared using the $90^\circ_x-\tau_1-45^\circ_y$ pulse sequence and waiting for a time τ_W longer than the decay of the off-diagonal elements of the density matrix. Selective excitation and detection is then achieved with a $90^\circ_{x,y}-t-45^\circ_y$ pulse sequence. The double-quantum coherence is measured by observing $\langle I_y \rangle$ as a function of t, for a certain value of τ_2.

where β will be time-dependent because of spin–lattice relaxation, but we shall pay no attention on this aspect.

Selective excitation of double-quantum coherence is achieved by applying a 90°_x, or 90°_y, pulse. This follows easily from the known transformation property of $H_D^{(0)}$, see e.g. ref. [7]. We get for $90^\circ_{x,y}$ pulse:

$$\rho = \exp(\tfrac{1}{2}\pi i I_{x,y})\,(1-\beta H_D^{(0)})\exp(-\tfrac{1}{2}\pi i I_{x,y}) ,$$

so

$$\rho_{x,y} = 1 + \tfrac{1}{2}\beta H_D^{(0)} \pm (6^{1/2}/4)\beta(H_D^{(2)} + H_D^{(-2)}) , \qquad (4)$$

where the + sign refers to the 90°_x and the − sign to the 90°_y pulses and $H_D^{(2)} + H_D^{(-2)}$ are double-quantum dipolar operators ($\Delta M = \pm 2$), containing $I_{ix}I_{jx} - I_{iy}I_{jy}$, i and j denote the ith and jth spins. The opposite signs in eq. (4) for 90°_x and 90°_y pulses respectively, can easily be understood since the latter pulse can be obtained from the first one by a rotation of 90° about the z axis (90° phase shift), changing x into y in $H_D^{(\pm 2)}$. It is also a well-known property of double-quantum coherence which changes in phase by twice the phase shift.

After excitation of the double-quantum coherence we let the system evolve for a time t:

$$\rho_{x,y}(t) = 1 + \tfrac{1}{2}\beta H_D^{(0)} \pm \rho_2(t) ,$$

$$\rho_2(t) = (6^{1/2}/4)\beta \exp[i(\Delta I_z + H_D^{(0)})t]$$
$$\times (H_D^{(+2)} + H_D^{(-2)}) \exp[-i(\Delta I_z + H_D^{(0)})t] , \qquad (5)$$

where the double-quantum coherence is entirely contained in $\rho_2(t)$. The above evolution takes place without an observable signal in the transverse plane, since $\rho_{x,y}(t)$ does not contain single-quantum coherences. (N.B The absence of an observable signal during the evolution period t can be taken as a criterion for correct adjustment of pulse widths and phase settings.) From eqs. (4) and (5) it follows that the combination $\rho_x - \rho_y$ further selects the double-quantum coherence from the rest.

Detection of the double-quantum coherence in eq. (5) is achieved by a 45°_y pulse. This transforms part of $\rho_2(t)$, and also of $H_D^{(0)}$, into single-quantum coherence [1–8]. The evolution of the double-quantum coherence can thus be detected by observing $\langle I_y \rangle$ as a function of t, for a certain value of τ_2 after the last pulse, i.e. for the double-quantum coherence:

$$\langle I_y \rangle = \mathrm{Tr}\, I_y \exp[i(\Delta I_z + H_D^{(0)})\tau_2] \exp(\tfrac{1}{4}\pi i I_y)$$
$$\times \rho_2(t) \exp(-\tfrac{1}{4}\pi i I_y) \exp[-i(\Delta I_z + H_D^{(0)})\tau_2] . \qquad (6)$$

The whole sequence is depicted in fig. 1. We note that the detection pulse need not be a 45° pulse, other angles will do, except a 90° pulse when $\Delta = 0$. As is well-known [1–7] $\langle I_y \rangle$ will be modulated with a frequency 2Δ, since $\rho_2(t)$ contains $\exp(\pm 2i\Delta t)$, and it will change sign upon applying a 90°_y instead of a 90°_x excitation pulse as explained above. In addition to the signal as given by eq. (6) there will be a common baseline for the two excitation pulses. This baseline corresponds to the dipolar signal, cf. eq. (5) and ref. [14]; it is independent of phase shift and Δ.

We end this section with three remarks: (i) The above results apply also when $H_D^{(0)}$ is a quadrupole interaction, because the latter interaction transforms in the same way under rotations as the dipolar interaction. (ii) Actually only the last two pulses in fig. 1 belong to the selective excitation and detection of the double-quantum coherence, because dipolar order can be created in other ways, viz. by ADRF [15], by off-resonance saturation [13,16] and in some cases by sample heating [17,18]. (iii) In the usual excitation scheme, e.g. with $90^\circ_x-\tau-90^\circ_{-x}$, intensities of multiple-quantum lines are sensitive functions of combinations of τ with off-set Δ and with the strengths of spin–spin interactions. In our method excitation of the double-quantum is achieved by a single pulse; there is no τ involved. Consequently, the intensities of the double-quantum lines are independent of preparation, cf. eqs. (4) and (5). This distinct feature is of great practical importance, since the double-quantum spectra to be obtained by this method will be characteristic of the sample considered.

3. Experimental results

To illustrate the method we have done measurements at room temperature on the protons of adamantane ($C_{10}H_{16}$), partly deuterated 1-alanine ($ND_3^+CHCH_3COO^-$) and gypsum ($CaSO_4 \cdot 2H_2O$). The samples were powders and have been chosen for no particular reason except that their relaxation times were rather short ($\lesssim 1$ s) which is convenient to do the experiments. The measurements have been done on a Bruker CXP pulse spectrometer at 60 MHz. The 90° pulse width, $\tau_{90°} = 2.85$ μs, corresponded to an rf amplitude $\gamma H_1/2\pi \approx 88$ kHz.

Fig. 2 shows $\langle I_y \rangle$ as a function of t for $\Delta = 0$. The dots are for the 90°_x excitation pulse and the open circles are for the 90°_y excitation pulse. The common baselines have been subtracted Fig. 2a: adamantane, $\tau_1 = 46$ μs, $\tau_W = 500$ μs, $\tau_2 = 46$ μs, linewidth ≈14 kHz. Fig. 2b: 1-alanine, $\tau_1 = 16$ μs, $\tau_W = 200$ μs, $\tau_2 = 18$ μs, linewidth ≈30 kHz. Fig. 2c gypsum, $\tau_1 = 12$ μs, $\tau_W = 200$ μs, $\tau_2 = 18$ μs, linewidth ≈30 kHz. For adamantane the signal at $t \approx 100$ μs has been chosen as the baseline of $\langle I_y \rangle$. For 1-alanine and gypsum the baseline is the signal at $t \approx 70$ μs. In all the three cases the change of sign of $\langle I_y \rangle$, i.e. a 180° phase shift, for 90°_y compared to 90°_x excitation pulse is evident. It was also observed that with correct adjustments of pulse widths and phases there was indeed no signal after the excitation (third) pulse.

Fig. 3 shows $\langle I_y \rangle$ as a function of t for the three samples for $\Delta/2\pi = 40$ kHz. Since the pulse widths are finite the condition for zero Zeeman order becomes $\sin \Delta(\tau_1 + \delta) = 0$. We found experimentally that this

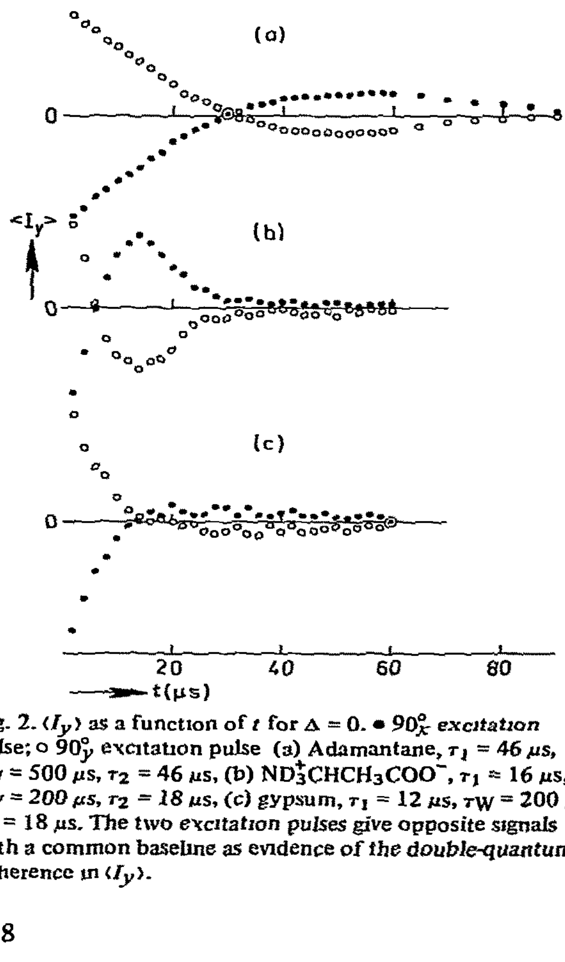

Fig. 2. $\langle I_y \rangle$ as a function of t for $\Delta = 0$. • 90°_x excitation pulse; ○ 90°_y excitation pulse (a) Adamantane, $\tau_1 = 46$ μs, $\tau_W = 500$ μs, $\tau_2 = 46$ μs, (b) $ND_3^+CHCH_3COO^-$, $\tau_1 = 16$ μs, $\tau_W = 200$ μs, $\tau_2 = 18$ μs, (c) gypsum, $\tau_1 = 12$ μs, $\tau_W = 200$ μs, $\tau_2 = 18$ μs. The two excitation pulses give opposite signals with a common baseline as evidence of the double-quantum coherence in $\langle I_y \rangle$.

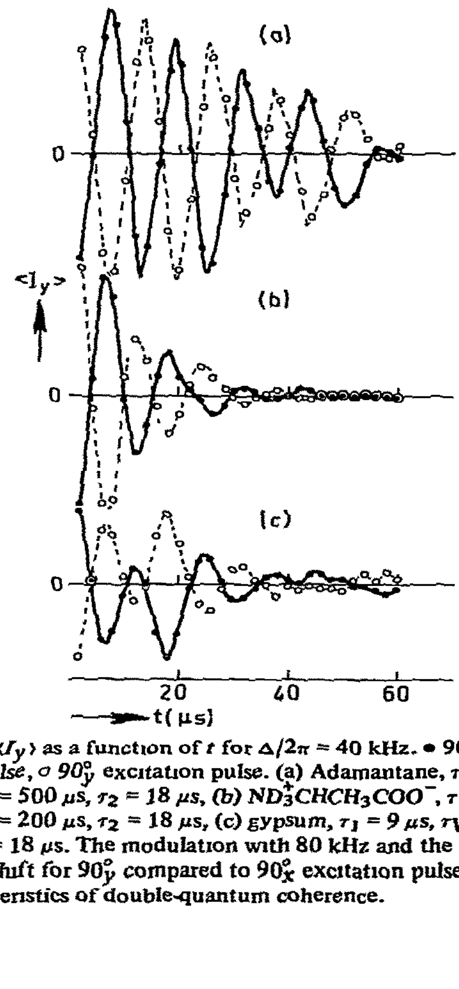

Fig. 3. $\langle I_y \rangle$ as a function of t for $\Delta/2\pi = 40$ kHz. • 90°_x excitation pulse, ○ 90°_y excitation pulse. (a) Adamantane, $\tau_1 = 46.5$ μs, $\tau_W = 500$ μs, $\tau_2 = 18$ μs, (b) $ND_3^+CHCH_3COO^-$, $\tau_1 = 21.5$ μs, $\tau_W = 200$ μs, $\tau_2 = 18$ μs, (c) gypsum, $\tau_1 = 9$ μs, $\tau_W = 200$ μs, $\tau_2 = 18$ μs. The modulation with 80 kHz and the 180° phase shift for 90°_y compared to 90°_x excitation pulse are both characteristics of double-quantum coherence.

was the case for $\tau_1 = 9, 21.5, 34$ and 46.5 μs, so $\delta = 3.5$ μs. Fig. 3a: adamantane, $\tau_1 = 46.5$ μs, $\tau_W = 500$ μs and $\tau_2 = 18$ μs. Fig. 3b: 1-alanine, $\tau_1 = 21.5$ μs, $\tau_W = 200$ μs and $\tau_2 = 18$ μs. Fig. 3c: gypsum, $\tau_1 = 9$ μs, $\tau_W = 200$ μs and $\tau_2 = 18$ μs. In fig. 3 the expected modulations with a frequency of 80 kHz as well as the 180° phase shifts are clearly seen. The baselines have been chosen as in fig. 2 and subtracted from the signals. In contrast to the case of $\Delta = 0$, in the present case the signal after the third pulse was not exactly zero. This is due to the fact that γH_1 was not much larger than Δ and consequently the pulses were not correct 90° and 45° pulses anymore.

The functional dependence of $\langle I_y \rangle$ on phase shift and Δ shows that $\langle I_y \rangle$ contains only double-quantum coherence, so the prediction of the theory is experimentally confirmed. We note that the responses to 90°_x and 90°_y excitation pulses have been observed separately only to verify experimentally the proper dependence of $\langle I_y \rangle$ on phase shift, whereas the signal from $H_D^{(0)}$ is independent of phase shift. It should be obvious that the double-quantum coherence could be observed directly, with zero baseline, simply by subtracting the responses to the two excitation pulses from each other.

4. Conclusion

We have proposed a rather simple method for selective excitation and detection of double-quantum coherence in spin systems with dipolar, or quadrupolar, interaction. The method consists of first creating dipolar order. Selective excitation and detection has then been achieved by the $90^\circ_{x,y}$–t–45°_y pulse sequence. The method is particularly suitable for solids, where free induction decay time T_2 is much shorter than spin–lattice relaxation time, T_{1D} in this case, so that one can choose $\tau_W \ll T_{1D}$, fig. 1. However, with the following modification it can be applied to spin systems dissolved in liquid crystals where $T_2 \approx T_{1D}$. After creation of dipolar order one can apply a strong pulsed field gradient [19,20] to dephase possible off-diagonal elements in a time $T_2^* \ll T_{1D}$, so that again one can choose $\tau_W \ll T_{1D}$. This technique is also a proper alternative to the method proposed earlier [14] for dipolar relaxation measurements in liquid crystals.

In addition to the simplicity of the method the created double-quantum coherence is independent of details of preparation, in contrast to usual excitation schemes of multiple-quantum coherences [1–7]. This distinct feature of the method is of immense practical importance. It allows obtaining double-quantum spectra which are characteristic of the spin systems considered, like in ordinary single-quantum spectroscopy, independent of parameters used during preparation, whereas usual multiple-quantum spectroscopy was deficient in this respect.

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