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PROTON-ENHANCED DEUTERIUM NMR IN ROTATING SOLIDS

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Proton-enhanced deuterium NMR spectra have been obtained in rotating solids with substantial gain in sensitivity. Cross polarization from proton to deuterium systems occurs via effective field mutual single-quantum flip–flops. Sample rotation modulates the deuterium quadrupole coupling which leads to complex dynamics and broad Hartmann–Hahn matching conditions

1. Introduction

The use of magic angle sample spinning to produce high-resolution deuterium NMR in solids has recently been demonstrated [1–4]. However, the relatively low sensitivity of deuterium requires a high degree of isotopic substitution in materials to be studied. Proton-enhanced nuclear induction spectroscopy is a powerful method for increasing the sensitivity of NMR in solids [5,6]. Its application to deuterium magic angle spinning should be of considerable use It has been applied successfully to enhance ^{13}C signals in magic angle spinning solids and those of various other spin-1/2 nuclei [7–10] The spinning modulates the dipole–dipole interactions which induce the transfer of polarization between the ^1H and ^{13}C Zeeman reservoirs in the rotating frame, but does not quench that process as long as the rotation frequency is somewhat smaller than the local dipole field [9].

Transfer of polarization between spin-1/2 (^1H) and spin-1 (^2H) systems has been investigated recently in non-rotating solids. Selective single- and double-quantum cross polarization have been demonstrated and their dynamics analyzed [11]. Also, deuterium quadrupole tensor polarization by thermal contact between proton dipole and deuterium quadrupole reservoirs has been reported [12, 13]. Sample rotation modulates the quadrupole coupling as well as the dipole couplings and this affects both the efficiency and dynamics of the transfer of polarization. In this letter we demonstrate proton-enhanced deuterium NMR in solids with magic angle spinning and analyze the conditions necessary for efficient transfer of polarization.

2. Proton-enhanced deuterium NMR in rotating solids

The hamiltonian for the deuterium spin system (S) in the rotating frame and on-resonance ($\Delta\omega \ll \omega_{1S}, \omega_Q$) in the rotating sample has the form

$$H_S = \omega_{1S} S_x + \tfrac{1}{3}\,\omega_Q(t)\,(3S_z^2 - S^2), \tag{1}$$

in frequency units, where ω_{1S} is the deuterium rf field amplitude and

$$\omega_Q(t) = \tfrac{3}{4}\,e^2qQ\,\{\tfrac{1}{2}\,[3\cos^2\beta(t) - 1]\} \tag{2}$$

is the time-dependent quadrupole coupling amplitude. For simplicity, we assume an axially symmetric quadrupole interaction where $\eta = 0$. H_S is diagonalized by a unitary transformation [14,15] and the result is given by

$$H_S^T = T^{-1}H_S T = \tfrac{1}{2}\,\omega_e(t)\,S_z - \tfrac{1}{6}\,\omega_Q(t)\,(3S_z^2 - S^2), \tag{3}$$

where

$$\omega_e(t) = [\omega_Q^2(t) + 4\omega_{1S}^2]^{1/2},$$

$$\tan\theta = \frac{2\omega_{1S}/\omega_e(t)}{\omega_Q(t)/\omega_e(t)},$$

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$$T = \begin{pmatrix} 2^{-1/2}\cos\frac{1}{2}\theta & -2^{-1/2} & -2^{-1/2}\sin\frac{1}{2}\theta \\ \sin\frac{1}{2}\theta & 0 & \cos\frac{1}{2}\theta \\ 2^{-1/2}\cos\frac{1}{2}\theta & 2^{-1/2} & -2^{-1/2}\sin\frac{1}{2}\theta \end{pmatrix}$$

are the effective field amplitude, tilt angle, and transformation matrix respectively. In this transformation, columns 2 and 3 in the matrix of eq. (37) in ref. [14] are permuted in order to preserve the numerical labeling of states and symmetry in the tilted frame of reference. Thus both the magnitude and orientation of the effective field are modulated by the magic angle spinning. If deuterium Zeeman polarization can be generated, it must be able to adiabatically follow that modulation in order to remain spin-locked. We have therefore solved the set of Bloch-like equations for an oscillating three-level system, which have previously been solved for a stationary three-level system [16,17], for the case that the frequency of sample rotation, $\omega_r < \omega_{1S}, \omega_Q$. The result is that the spin polarization can adiabatically follow the modulation if the condition is fulfilled that

$$\omega_{1S}^2 \gg \omega_r \omega_Q(t)_{\max}, \tag{4}$$

where $\omega_Q(t)_{\max}$ is the maximum value of $\omega_Q(t)$ during the spinner cycle. Explicitly, when $\omega_{1S}^2 > 10\,\omega_r\omega_Q(t)_{\max}$ the maximum deviation of the spin orientation from the quantization axis in the frame given by eq. (3) is less than 4°.

The hamiltonian for the combined deuterium (S) and proton (I) spin system in a double rotating frame defined by eq. (3) and an on-resonance rf irradiation at the proton Larmor frequency has the form

$$H^T = H_I^T + H_{II}^T + H_S^T + H_{IS}^T, \tag{5}$$

where H_S^T is given in eq. (3), H_{II}^T is the secular dipole–dipole coupling amongst the protons, and $H_I^T = \omega_{1I} I_x$. The transfer of polarization is induced by H_{IS}^T which is given by

$$H_{IS}^T = \sum_{ij} 2b_{ij}\left(-I_{x_i} S_{x_j}^{1-2}\cos\tfrac{1}{2} + I_{x_i} S_{x_j}^{2-3}\sin\tfrac{1}{2}\theta\right), \tag{6}$$

$$b_{ij} = -2\gamma_i\gamma_j r_{ij}^{-3} P_2(\cos\alpha_{ij}),$$

where θ is given in eq. (3) and the S_x^{p-q} are the fictitious spin-1/2 operators describing the spin-1 system [14,15]. By second-order perturbation, H_{IS}^T induces either effective field deuterium single-quantum flips 1–2 or 2–3 accompanied by a proton flip. The Hartmann–Hahn matching conditions for these energy conserving flip–flops are given by

$$\omega_{1I} = \tfrac{1}{2}[\omega_e(t) - \omega_Q(t)] \quad \text{for the 1–2 transition} \tag{7a}$$

and

$$\omega_{1I} = \tfrac{1}{2}[\omega_e(t) + \omega_Q(t)] \quad \text{for the 2–3 transition.} \tag{7b}$$

The result of the transfer of polarization can be calculated by application of the spin temperature theory. For a non-spinning sample one can set $\Delta\omega$, $\omega_{1S} \ll \omega_Q$ and thus $\theta \ll 1$ so that only the S_x^{1-2} term survives in H_{IS}^T. This makes selective double-quantum cross polarization possible [11]. In a rotating sample the modulation of $\omega_Q(t)$ causes both terms in H_{IS}^T to be non-zero at some point during the rotor cycle. This results in a complex transfer of polarization involving both 1–2 and 2–3 transitions. The deuterium polarization created after a cross-relaxation contact is represented by the operators S_z and $3S_z^2 - S^2$ in eq. (3) Transformation of these operators back into the original rotating frame of eq. (1) gives

$$TS_zT^\dagger = 2^{-1/2}\sin\theta(S_x) + \tfrac{1}{4}\cos\theta(S_+^2 + S_-^2)$$
$$+ \tfrac{1}{2}\cos\theta(3S_z^2 - S^2), \tag{8}$$

$$T(3S_z^2 - S^2)T^\dagger = -\tfrac{1}{2}(3S_z^2 - S^2) + \tfrac{3}{4}(S_+^2 + S_-^2). \tag{9}$$

Thus the proton-enhanced deuterium system will exhibit single-quantum, double-quantum and quadrupole tensor polarization as a function of the effective frame tilt angle, $\theta(t)$, which is determined by the relative strength of ω_{1S} to $\omega_Q(t)$

In a non-spinning polycrystalline sample only a few deuterium spins match the Hartmann–Hahn conditions of eqs. (7) and the polarization transfer is inefficient. However, rotation of the sample about the magic axis modulates the deuterium energy levels of eq. (3) and thus the corresponding transition frequencies as shown in fig. 1 (top). The 1–2 and 2–3 transitions oscillate with large amplitudes Setting the value of ω_{1I} within the range of that oscillation allows the deuterium spins to match the conditions of eqs. (7) at least once during the spinner cycle. Assuming an isotropic distribution for the orientation of the unique axis of the quadrupole interaction tensor in the sample, the fraction of deuterium spins that achieve the matching

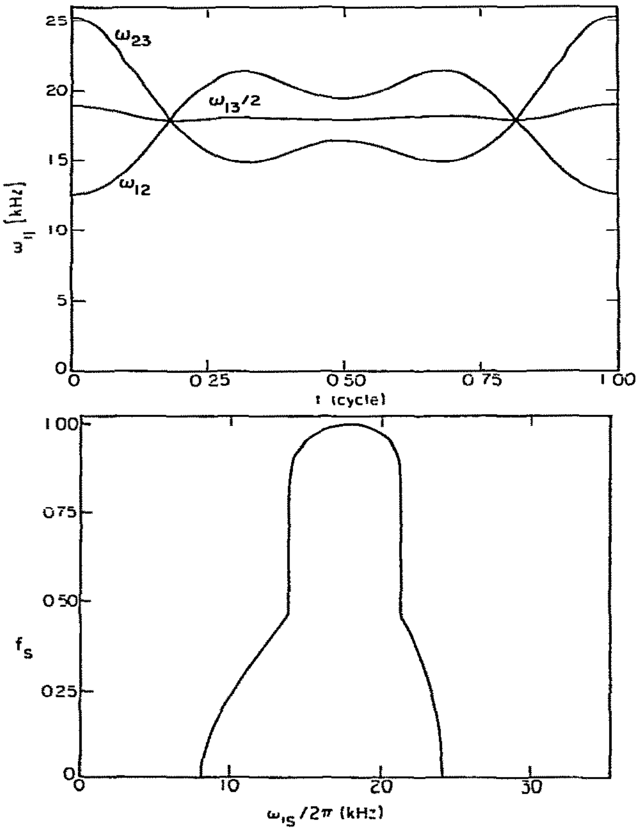

Fig. 1. Theoretical aspects of $^1H-^2H$ cross polarization in rotating solids. Top: Dependence of the transition frequencies, ω_{ij}, between the spin-1 deuterium energy levels on the sample rotation for one spinner cycle. The energy levels are those in the tilted rotating frame defined by eq. (3). Orientation of the unique axis of the axially symmetric ($\eta = 0$) quadrupole tensor is taken to be at 60° to the spinner axis. The coupling constant is taken $\frac{3}{4} e^2qQ = 14.2$ kHz and the deuterium rf amplitude is $\omega_{1S} = 18.0$ kHz. The effective field single-quantum transitions ω_{12} and ω_{23} are strongly modulated by the spinning. This leads to complex cross-polarization dynamics and a broad Hartmann–Hahn matching region where $\omega_{1I} = \frac{1}{2}[\omega_e(t) \pm \omega_Q(t)]$. The effective field double-quantum transition, plotted as $\frac{1}{2}\omega_{13}$, is much less modulated by the spinning. Bottom: Fraction of sample, f_S, which meets one of the single-quantum Hartmann–Hahn conditions of eqs. (7) at least once during a spinner cycle plotted as a function of ω_{1S}. An isotropic distribution is assumed for the orientation of the unique axis of the quadrupole tensor. The proton rf amplitude is taken $\omega_{1I} = 18.0$ kHz. In the center region where $\omega_{1S} \approx \omega_{1I}$, both conditions of eqs. (7) are met during the spinner cycle. In the outer regions, distinct tails occur since only one of those conditions can be met during the spinner cycle.

conditions is shown in fig. 1 (bottom) as a function of ω_{1S} for a constant ω_{1I}. In the region $\omega_{1S} \approx \omega_{1I}$ all spins achieve matching and efficient cross polarization is expected. The distinct tails in fig. 1 (bottom) represent regions where only one of the two conditions in eqs. (7) can be matched during the spinner cycle. Thus the polarization transfer induced by H_{IS}^T via effective field single-quantum flips is possible over a wide range of $\omega_{1S} - \omega_{1I}$, however, the matching is obtained only for a fraction of the spinner cycle, and this reduces the rate of transfer that is possible [2].

An alternative mechanism for polarization transfer is a transition in which the deuterium spin undergoes an effective field double-quantum flip accompanied by one or two proton flips [18,19]. This is the 1–3 transition in fig. 1 (top) which is forbidden by second-order perturbation and would require that $n\omega_{1I} = \omega_e(t)$, where $n = 1,2$. Since this transition oscillates over a much smaller range during the spinner cycle than the 1–2 and 2–3 transitions, it would lead to a much narrower matching region than that shown in fig. 1 (bottom).

3. Experimental

Proton-enhanced deuterium signals were obtained by spin-locking the proton magnetization followed by single-contact thermal mixing between the I and S reservoirs. The duration of the contact was a multiple of the spinner cycle. Both I and S rf irradiation were on-resonance. Following the mixing, the S irradiation was turned off and the I irradiation left on for proton decoupling while the S free induction decay was monitored directly. Experiments were performed at room temperature on a home-built spectrometer operating at $\omega_L/2\pi(^1H) = 182$ MHz and $\omega_L/2\pi(^2H) = 28$ MHz.

Results on proton-enhanced deuterium signals for a sample of polycrystalline 30% randomly deuterated hexamethylbenzene rotating at 1.47 kHz are shown in fig. 2. The experimental proton rf field amplitude was $\omega_{1I} = 20.8$ kHz. In fig. 2 (top) is shown the ratio of cross-polarized signal intensity, S^{CP}, to the intensity after a single 90° pulse, S^0, as a function of ω_{1S}. The duration of cross-relaxation contact was 25 cycles = 17 ms. The cross-polarization rates, $1/T_{IS}$, for this same data set are shown in fig. 2 (bottom). The cross-relaxation curves were fit to a single exponential to

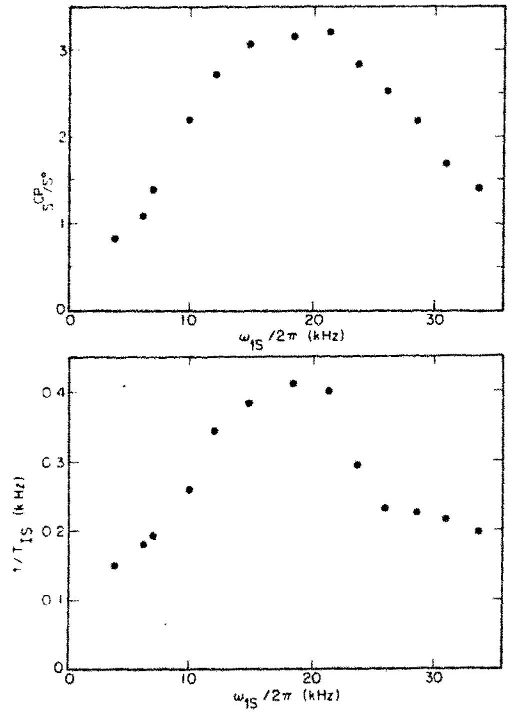

Fig. 2. Experimental results on $^1H-^2H$ cross polarization in polycrystalline 30% randomly deuterated hexamethylbenzene rotating about the magic angle at 1.47 kHz. Proton rf field amplitude was ω_{1I} = 20.8 kHz. Top: Ratio of cross-polarized deuterium signal to the signal after a 90° pulse, S^{CP}/S^0, as a function of deuterium rf field amplitude, ω_{1S}. The duration of cross-polarization contact was 25 cycles = 17 ms. Bottom: Cross-polarization rates, $1/T_{IS}$, for the same data set.

extract T_{IS}, however, the curves were not single exponential and the relative error in $1/T_{IS}$ is estimated to be ±20%.

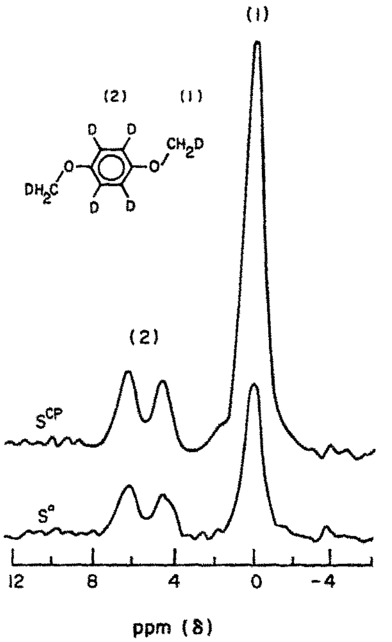

Fig. 3. High-resolution deuterium magic angle spinning NMR spectra of polycrystalline dimethoxybenzene, randomly deuterated to 60% in the aromatic position and selectively mono-deuterated to 98% in the methoxy position. Frequency of rotation was 1.07 kHz. Lower trace, S^0, was obtained from the FID after a single 90° pulse. Upper trace, S^{CP}, shows gain in sensitivity as a result of 9.3 ms single contact cross polarization from protons. Data are summarized in table 1.

The proton-enhanced high-resolution spectrum of polycrystalline dimethoxybenzene is shown in fig. 3. This sample was randomly deuterated to 60% in the aromatic position and selectively mono-deuterated to 98% in the methoxy position, $DH_2CO-\phi D_4-OCH_2D$. Here the linewidths are somewhat less than previously reported [3], which is attributed to a decrease in residual homonuclear $^2H-^2H$ dipole–dipole couplings when the level of isotopic substitution is decreased. The maximum enhancement factors, S^{CP}/S^0, for three polycrystalline samples are summarized in table 1. Good enhancement was obtained in each case. Rapid internal molecular reorientation produces the reduced average quadrupole couplings shown for three deuterium positions, while the rigid aromatic deuterons in dimethoxybenzene retain the full coupling. Theoretical values S^{CP}/S^0 for single-quantum spin-locked cross polarization were calculated from [6]

$$S^{CP}/S^0 = (\gamma^I/\gamma^S)(1+\epsilon)^{-1}$$

$$= 6.514\,(1 + 8N_S/3N_I)^{-1}, \qquad (10)$$

where $\epsilon = [S(S+1)/I(I+1)]\,N_S/N_I$. In comparing these values to experimental values, it should be noted that the experimental S^0 is somewhat smaller than expected since the pulse is not "strong" for the entire

Table 1
Deuterium signal proton-enhancement factors in magic angle spinning solids

Compound	S^{CP}/S^0		$\omega_Q/2\pi$ (kHz)
	theoretical [a]	experimental	
30% random-deutero hexamethylbenzene	3.0	3.2	14
4.9% random-deutero durene	5.7	4.4	34
dimethoxybenzene			
total	2.1	2.2	–
(1) [b]	–	2.7	33
(2) [c]	–	1.4	130

[a] See eq. (10).
[b] Signal from deuterium in the methoxy group.
[c] Signal from deuterium in the aromatic ring.

powder. When $\omega_{1S} < \frac{3}{4} e^2qQ$, the magnetizations of crystallites with different orientations are rotated by different angles. Thus a single pulse does not bring them all into the transverse plane [20] and it also generates some double-quantum coherence.

4. Conclusion

Proton-enhanced deuterium spectra in rotating solids have been obtained with good signal enhancement. Evidently most of the transferred polarization does remain locked along the effective field as its direction oscillates. The broad matching curve and cross-relaxation data of fig. 2 strongly support the conclusion that the transfer of polarization occurs by the two-spin single-quantum flip–flop process. In a rotating powder there is a continuum of oscillating Hartmann–Hahn conditions which leads to a very complex cross-polarization dynamics and a broad range of ω_{1S} over which the energy conserving heteronuclear flip–flops occur. In the limit that $\omega_{1S} \gg \omega_Q$ and $\omega_{1S} = \omega_{1I}$, pure single-quantum signal is generated by the transfer of polarization. However, when $\omega_{1S} \geqslant \omega_Q$ the single-quantum signal exceeds 95% of the total. Thus the observed polarization in fig. 2 (top) should fall off more quickly on the low-frequency side where $\omega_{1S} < \omega_{1H}$ than on the high-frequency side since in this region more of the transferred polarization appears as double-quantum coherence and quadrupolar polarization.

The experimental cross-polarization curve, fig. 2 (top), is broader than the theoretical matching curve, fig. 1 (bottom). Two reasons for this are: (1) the cross-relaxation spectral density function is considerably broadened by spinning sidebands as demonstrated by Stejskal et al. [9] and (2) the mismatch energy, $\omega_{1I} - \frac{1}{2}[\omega_e(t) \pm \omega_Q(t)]$, appears in the proton reservoir H_{II}^T and can be the limiting factor in cross relaxation in a non-rotating sample. However, it was recently demonstrated that sample rotation strongly couples this reservoir to the lattice [21].

In conclusion, we have demonstrated efficient single-quantum ^{1}H–^{2}H cross polarization in rotating solids. Substantial enhancement has been obtained for molecular positions with a wide range of quadrupole couplings. Cross polarization of deuterium nuclei in rigid molecular positions is desirable since in this case the deuterium spin–lattice relaxation time can become extremely long. It makes possible a much lower level of isotopic substitution which also contributes to increased resolution.

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