

SPIN DIFFUSION AND SPIN-LATTICE RELAXATION OF DEUTERIUM IN ROTATING SOLIDS**M. ALLA***Department of Physics, Institute of Cybernetics, Estonian Academy of Sciences, Tallinn 200001, USSR*

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Selective NMR T_1 measurements on deuterium in powders rotating at high speed at the magic angle indicate that dipolar spin diffusion which can be quenched by the orientational dependence of the quadrupole splitting, is partially restored by the sample rotation

1. Introduction

In a previous paper we demonstrated the first application of high speed magic angle sample spinning to deuterium NMR in solids [1]. The inhomogeneous broadening due to the quadrupole coupling was largely removed and isotropic chemical shift spectra were obtained. It therefore became important to understand the mechanism of deuterium spin-lattice relaxation in solids. It is well known that T_1 in this case can become some minutes and longer making the observation of deuterium resonances almost useless. However, we have found that certain spin-lattice relaxation rates were much faster than expected and that this was due to dipolar spin diffusion between crystallographically inequivalent deuterium nuclei.

Thus the question of spin diffusion in the deuterium system is a critical aspect of high resolution deuterium NMR in solids by magic angle spinning [1,2]. The related problem of cross relaxation between the Zeeman levels of a spin-1/2 system and the quadrupole levels of a spin > 1/2 system has been studied extensively [3]. In particular, Woessner and Gutowsky [4] have studied that problem in a very slowly rotating sample. In this paper, we describe the deuterium spin diffusion in a new regime of fast sample rotation in which the rotation period is much shorter than the relaxation times involved

We will show that one can exploit the existence of rapid molecular motions of the deuterons in solids to enhance T_1 in a rotating sample experiment. In the next two paragraphs we review the essential features of deuterium spin-lattice relaxation. In section 2 we discuss a simple model for relaxation in the rotating sample and an estimate of the deuterium T_1 values. These are compared with experiment in sections 3 and 4.

The spin-lattice relaxation of spin-1 deuterium in solids in high magnetic field at high temperature is normally dominated by its large quadrupole coupling [5]. When there is molecular motion, the time dependence introduced into the quadrupole coupling by the motion can be effective in producing spin-lattice relaxation. In the absence of such motion, T_1 can be orders of magnitude longer since other motions in the crystal, e.g. lattice vibrations, are much less effective in producing spectral density at the deuterium Larmor frequency. In a crystal containing both rapidly reorienting and rigid deuterium types, for example a typical organic molecular solid containing $-CD_3$ groups, the spin diffusion between deuterons attempts to bring both types into internal equilibrium at a common spin temperature. The complete system would then relax to the lattice temperature [6]. However, the dependence of the quadrupole coupling on orientation in the external magnetic field quenches the spin diffusion and causes the

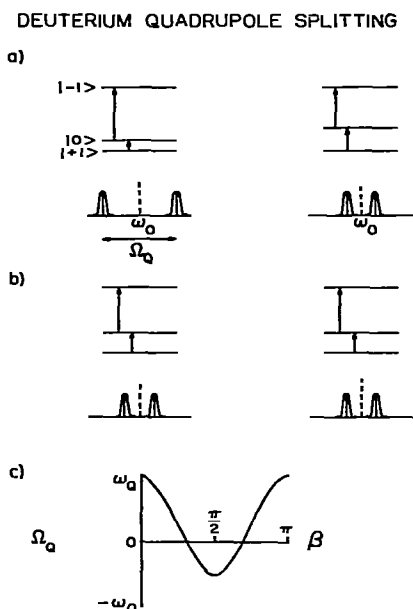


Fig. 1 Eigenstates and quadrupole splitting of spin-1 deuterium in an axially symmetric electric field gradient in high magnetic field. (a) Left and right hand sides indicate two unequal values of the quadrupole splitting, Ω_Q . Dipolar spin diffusion between deuterons with unequal Ω_Q is quenched. (b) When the quadrupole splittings of neighboring deuterons become equal, spin diffusion via $I_+^1 I_-^2 + I_-^1 I_+^2$ flip-flop transitions can occur. (c) The quadrupole splitting varies as the angle, β , between the unique quadrupole axis and the static magnetic field direction, as in eq. (1).

different deuterium types to relax at independent and widely different rates

This effect is described qualitatively for deuterium in high magnetic field in an axially symmetric electric field gradient in fig. 1. Neighboring deuterons in a crystal, illustrated by the left and right hand sides in figs. 1a and 1b, can have different orientations of the unique axis of their quadrupole interaction tensors with respect to the external magnetic field direction. They will then have largely different quadrupole splittings, Ω_Q , as indicated in fig. 1a, and a flip-flop transition due to the $I_+^1 I_-^2 + I_-^1 I_+^2$ term of their dipole-dipole coupling would not be allowed since it is not energy conserving. Thus the spin diffusion between these deuterons is quenched. For spin diffusion to occur, their quadrupole splittings must be equal to within a local field width. In other words, the quadrupole satellites of the two nuclei must

overlap as shown in fig. 1b. The dependence of the quadrupole splitting on orientation, illustrated in fig. 1c, is given by the expression

$$\Omega_Q = \frac{1}{2}(3 \cos^2 \beta - 1)\omega_Q, \quad (1)$$

where $\omega_Q = \frac{3}{4}e^2qQ/\hbar$ is the quadrupole coupling constant and β is the angle between the unique axis of the quadrupole tensor and the direction of B_0 . The quenching of spin diffusion in a powder sample occurs since there is an isotropic distribution of crystallite orientations. For neighboring deuterons in a crystallite, which have different directions of their unique quadrupole axis in the crystal fixed reference frame, to undergo spin diffusion the crystallite must fall at such an orientation in the lab frame that the two deuterons have the same quadrupole splitting, Ω_Q . Only a negligible fraction of the crystallites of the powder will meet that condition. Since the deuterium quadrupole coupling is much larger than its dipole-dipole couplings, the matching of quadrupole splittings occurs over a very small angular range.

2. Crossing point model and T_1 estimate

When the sample is rotated about the magic angle, the quadrupole splitting of the deuterons is modulated harmonically. This modulation is shown in fig. 2 for two deuterons which have different orientations, i.e. polar angles, of their unique quadrupole axis with respect to the axis of sample rotation. At some point

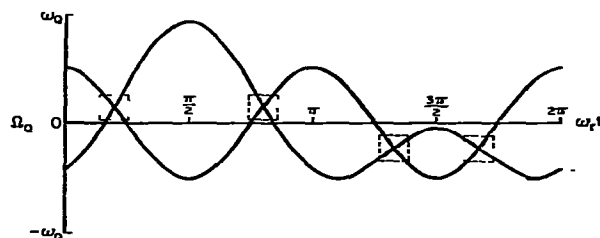


Fig. 2. Modulation of the quadrupole splitting, Ω_Q , of two deuterons in a rotating sample over one rotation cycle, $0 \leq \omega_r t \leq 2\pi$. The two spin-1 nuclei have different orientations of their unique quadrupole axis with respect to the axis of sample rotation. Dashed boxes enclose regions where spin diffusion between the two can occur since they have equal Ω_Q .

during the rotation cycle the quadrupole splittings of the two deuterons must become equal and during this crossing the spin diffusion can occur. The width of the crossing region depends on the magnitude of the dipolar coupling between the crossing deuterons and the steepness with which their quadrupole splittings cross. During the rotation cycle, the quadrupole splitting of each deuteron crosses with that of every other deuteron. Therefore, the sample rotation matches the quadrupole splittings of all pairs for some part of the cycle and partially restores spin diffusion in the deuterium system. This may also be viewed as a cross relaxation between crystallographically inequivalent deuterons.

To indicate the effect of the restored spin diffusion on T_1 we consider a crystal containing rotating methyl ($-\text{CD}_3$) and rigid aromatic ($-\phi\text{D}_4$) deuterons. In estimating the $-\phi\text{D}_4$ T_1 based on the crossing point mechanism, we assume (a) that the $-\text{CD}_3$ type relaxes to the lattice independently and at a much faster rate than the $-\phi\text{D}_4$ and (b) that the $-\phi\text{D}_4$ type relaxes to the lattice only by spin diffusion to $-\text{CD}_3$ types at crossing points over many rotor cycles. For the case of a single aromatic deuteron and a single methyl group we write the expression

$$(T_1^{\text{rigid}})^{-1} = f(T_1^{\text{sd}})^{-1}, \quad (2)$$

where rigid refers to the $-\phi\text{D}_4$ deuteron and $(T_1^{\text{sd}})^{-1}$ is the rate of spin diffusion between the two. The constant f is the fraction of the rotor period for which the spin diffusion is "turned on", i.e. the fraction of the rotor cycle for which there is crossing. As an order of magnitude estimate only, we take f as the frequency width for which the quadrupole splittings of the two deuterons are "equal" divided by the total range of the quadrupole splitting over the rotor cycle and we obtain $f \approx 100 \text{ Hz}/200 \text{ kHz} = 5 \times 10^{-4}$. We estimate the $(T_1^{\text{sd}})^{-1} \approx 200 \text{ Hz}$, and therefore $T_1^{\text{rigid}} \approx 10 \text{ s}$. In the limit of strong spin diffusion, $(T_1^{\text{sd}})^{-1}$ large, the T_1^{rigid} approaches that of the $-\text{CD}_3$ deuterons. This is the single spin temperature limit mentioned above. In the limit of weak spin diffusion, $(T_1^{\text{sd}})^{-1}$ small, the T_1^{rigid} will approach a value determined by some less efficient mechanism, e.g. fluctuating local dipolar fields.

3. Results

Spin-lattice relaxation times were measured selec-

Table 1
Deuterium solid state T_1 (in seconds)

Compound	$-\text{CD}_3$	$-\phi\text{D}_4$
terephthalic acid dimethylester- d_{10} ($\text{D}_3\text{CO}_2\text{C}\phi\text{D}_4\text{CO}_2\text{CD}_3$)	$0.86 \pm 7\%$	$28 \pm 7\%$
<i>p</i> -dimethoxybenzene- d_{10} ($\text{D}_3\text{CO}\phi\text{D}_4\text{OCD}_3$)	$0.26 \pm 4\%$	$5 \pm 20\%$
terephthalic acid dimethylester- d_4 ($\text{H}_3\text{CO}_2\text{C}\phi\text{D}_4\text{CO}_2\text{CH}_3$)	—	$640 \pm 13\%$

tively from the isotropic chemical shift spectra by a saturation-recovery sequence. Measurements were made at room temperature at $\omega_0(^2\text{D}) = 28 \text{ MHz}$ on deuterium enriched polycrystalline samples rotating about the magic angle at $\omega_r/2\pi \approx 1 \text{ kHz}$ and the results are shown in table 1. The T_1 values for $-\text{CD}_3$ deuterons are relatively short, less than one second. It is well known that the $-\text{CD}_3$ group reorients rapidly at room temperature about its C_3 axis. The aromatic deuterons, however, occupy rigid lattice positions. The values of T_1 for $-\phi\text{D}_4$ in terephthalic acid dimethylester- d_{10} and *p*-dimethoxybenzene- d_{10} are in agreement with the estimate given above.

To investigate the weak spin diffusion limit, we have measured the T_1^{rigid} of $-\phi\text{D}_4$ deuterons in partially deuterated terephthalic acid dimethylester, $\text{H}_3\text{CO}_2\text{C}\phi\text{D}_4\text{CO}_2\text{CH}_3$. Under the same conditions as the perdeuterated material, this value was found to be $6.4 \times 10^2 \text{ s}$ as shown in fig. 3. Thus by replacing the $-\text{CD}_3$ groups by $-\text{CH}_3$ groups, which eliminates the spin diffusion between aromatic and methyl groups (since the $^2\text{D}-^1\text{H}$ dipolar B term is non-secular) the T_1^{rigid} of the aromatic deuterons increased by a factor of 23.

In the real crystal the aromatic deuterons may be relaxed by more than one methyl group. Also, the total crossing time over many rotor cycles does not depend on ω_r . Thus the T_1 of the rigid deuterons should be independent of ω_r . Further work along these lines is in progress.

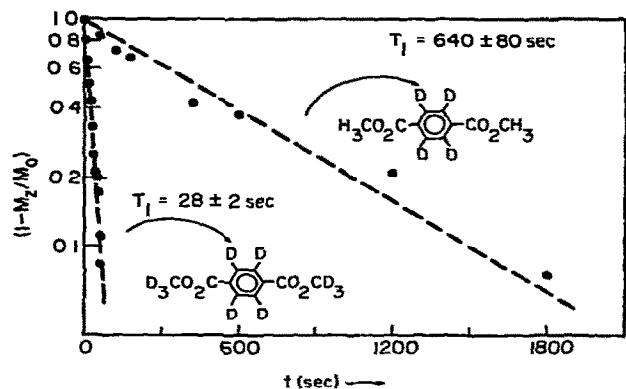


Fig. 3 Recovery of aromatic line ($-\phi D_4$) in deuterium solid state isotropic spectrum after saturation with sample rotation of about 1 kHz. The $-\phi D_4$ T_1 increases dramatically when the methyl group deuterons are replaced by protons. Spin diffusion occurs between $-\phi D_4$ and $-\text{CD}_3$ in the perdeuterated compound, but does not occur between $-\phi D_4$ and $-\text{CH}_3$ in the partially deuterated sample.

4. Conclusion

We conclude that spin diffusion occurs between the rigid and methyl deuterons and that this fact is critical to the application of high speed magic angle spinning to deuterium in solids. The sample rotation not only makes it possible to obtain isotropic high resolution type spectra, but also partially restores spin diffusion in the deuterium system. By exploiting the presence of methyl groups or other reorienting groups in solids which relax quickly, the sensitivity to all crystallographic positions can be enhanced. Of course, this feature also

applies to amorphous materials where magic angle spinning is particularly useful. The existence of crossing points also suggest the possibility of applying direct deuterium detection $^1\text{H}-^2\text{D}$ cross polarization [7] to obtain the isotropic spectra. Further quantitative details and description of the magic angle spinning experiments will be presented in a forthcoming paper.

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