

## Spin Diffusion and Orientation Dependence of Deuterium $T_1$ in Solids

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The study of spin diffusion in solids has been of recent interest. Spin diffusion occurs by flip-flop cross-relaxation due to the  $S_+^i S_-^j + S_-^i S_+^j$  term of the dipolar couplings among the spins ( $I$ ). When a large inhomogeneous interaction also exists for the  $S$  spin system, then the flip-flop transition may not conserve energy, i.e., the resonances of the coupled spins do not overlap and are separated by a frequency  $\Delta\Omega$ . In this case the rate depends on the possible mechanisms of cross-relaxation and spin diffusion. This situation is typical for spin systems with  $S = 1$  in solids, e.g.,  $^2\text{H}$ ,  $^{14}\text{N}$ , where the nuclear quadrupole interaction,  $H_Q$ , disperses the resonances. In a single crystal sample,  $\Delta\Omega$  can be adjusted very accurately using the orientation dependence of  $H_Q$ .

It was recently shown that when an  $S = ^{14}\text{N}$  spin system is coupled to an extraneous dipolar reservoir having a large heat capacity provided by a proton ( $I$ ) spin system, the cross-relaxation rate varies approximately as  $(\Delta\Omega)^{-2} = (|\Omega_{Q,i}| - |\Omega_{Q,j}|)^{-2}$ , where  $\Omega_{Q,i}$  and  $\Omega_{Q,j}$  are quadrupole coupling offset frequencies of the two  $S$  nuclei (2). For a three-level system ( $S = 1$ ) which is not coupled to an extraneous reservoir, a mechanism for cross-relaxation via double-quantum flip-flops has been proposed (3) and the transition rate depends on  $(\Delta\Omega)^{-2} = (\Omega_{Q,i} - \Omega_{Q,j})^{-2}$ . Thus double-quantum cross-relaxation should be sensitive to the relative signs of  $\Omega_{Q,i}$  and  $\Omega_{Q,j}$ . It has also been shown that single-quantum spin diffusion can be dramatically enhanced by sample rotation which modulates  $\Delta\Omega_Q$  and causes an effective overlap of resonances that are dispersed by the quadrupole coupling (4).

In this communication, we report measurements of the orientation dependence of  $T_1$  for deuterium in a single crystal of *para*-dimethylterephthalate- $d_{10}$  (99.5%- $d$ ),  $\text{CD}_3\text{CO}_2\phi\text{D}_4\text{CO}_2\text{CD}_3$ . In this crystal the methyl groups have  $T_1^{\text{me}} \simeq 1$  sec at room temperature due to rotation about their  $C_3$  axes. This is a useful model sample since the aromatic deuterons are in rigid lattice sites and are expected to be coupled to the lattice only by spin diffusion to the rapidly relaxing methyl sites. Thus the  $T_1^{\text{ar}}$  of the ring deuterons should have a marked orientation dependence.

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Spin-lattice relaxation times were measured by saturation recovery at a field of 8.5 T. The crystal was oriented in the field using a goniometer probe so that two conditions were fulfilled: (1) all methyl resonances overlap so that only one pair of methyl lines is observed, and (2) the first condition was maintained when the crystal was rotated about an axis perpendicular to the field. Thus the quadrupole splittings of aromatic deuterons could be varied while the methyl-group splitting remained nearly constant. A typical set of spectra is shown in Fig. 1. Pairs of satellites due to inequivalent aromatic sites, the lines of lesser intensity in Fig. 1, could be selectively observed and their  $T_1$ 's obtained as a function of position. The crystal orientation was chosen so that the sign of  $\Omega_Q^{\text{ar}}$  would change, i.e., would go through a zero crossing, as the methyl coupling,  $\Omega_Q^{\text{me}}$ , remained roughly constant (intense lines in Fig. 1). We note that to select such positions by the observation of spectra, the long  $T_1$ 's of aromatic deuterons had to be reduced. This was done by rotating the sample by  $2\pi$  rad over several seconds and returning to the desired position. The slow rotation enhances single-quantum spin diffusion to the methyl group and reduced  $T_1^{\text{ar}}$  by up to three orders of magnitude (4).

The orientation dependence of  $T_1$  is illustrated in Fig. 2. The total angular rotation of the crystal represented by the data was less than  $25^\circ$ . Thus we assume that the dipolar couplings among the various sites remain relatively constant. Under these conditions, we believe the data should represent the dependence of  $T_1^{\text{ar}}$  on  $\Delta\Omega = \Omega_Q^{\text{me}} - \Omega_Q^{\text{ar}}$ . The fact that the results obtained at low temperature are the same as that obtained at room temperature strongly indicates that  $T_1^{\text{ar}}$  is determined by cross-relaxation and not by some motion of the aromatic site. Also, the magnitude of  $T_1^{\text{ar}}$  shown here casts doubt on the conclusions of Ref. (5) with regard to cross-relaxation. Cross-relaxation times of a few seconds between deuterons occur only when  $\Delta\Omega$  is comparable to the linewidth.

In Fig. 2, the values of  $\Delta\Omega = 0, 70$  kHz represent overlap of the methyl and aromatic lines. At these values, single-quantum flip-flops occur and  $T_1^{\text{ar}} \simeq T_1^{\text{me}}$ . In the regions of the near overlap,  $-10 \text{ kHz} < \Delta\Omega < +10 \text{ kHz}$  and  $60 \text{ kHz} < \Delta\Omega < 70 \text{ kHz}$ , the  $T_1^{\text{ar}}$  clearly depends quadratically on the absolute frequency separation of the methyl and aromatic lines:  $T_1^{\text{ar}} \propto (|\Omega_Q^{\text{me}}| - |\Omega_Q^{\text{ar}}|)^2$ . The fact that the relative signs of the  $\Omega_Q$ 's are not involved suggests that double-quantum flip-flops are not involved (3). If  $T_1^{\text{ar}}$  were given by the inverse of the double-quantum cross-relaxation rate to the methyl group, the quadratic curve in Fig. 2 would rise much more slowly on the left, where  $\Delta\Omega \sim 0$ , than on the right, where  $\Delta\Omega \sim 70$  kHz. Except for the change of  $T_1^{\text{ar}}$  in the region  $35 \text{ kHz} < \Delta\Omega < 60 \text{ kHz}$ , which may be due to the changing dipolar coupling, the data showed no dependence on the relative signs of  $\Omega_Q^{\text{me}}$  and  $\Omega_Q^{\text{ar}}$ .

It should be noted that results similar to those in Fig. 2 were obtained for another general orientation of the crystal. In both experiments, more than one pair of satellites due to ring deuterons appeared in certain spectra (see Fig. 1). The observed dependence of  $T_1^{\text{ar}}$  was not sensitive to the number or position of aromatic resonances with respect to each other. This suggests that there was no "cross-coupling" due to interaction between the aromatic deuterons. This is understandable since at least four inequivalent pairs of satellites were observed and at some particular orientation, spins having small spectral separation may be spatially separated and therefore not be coupled (6).

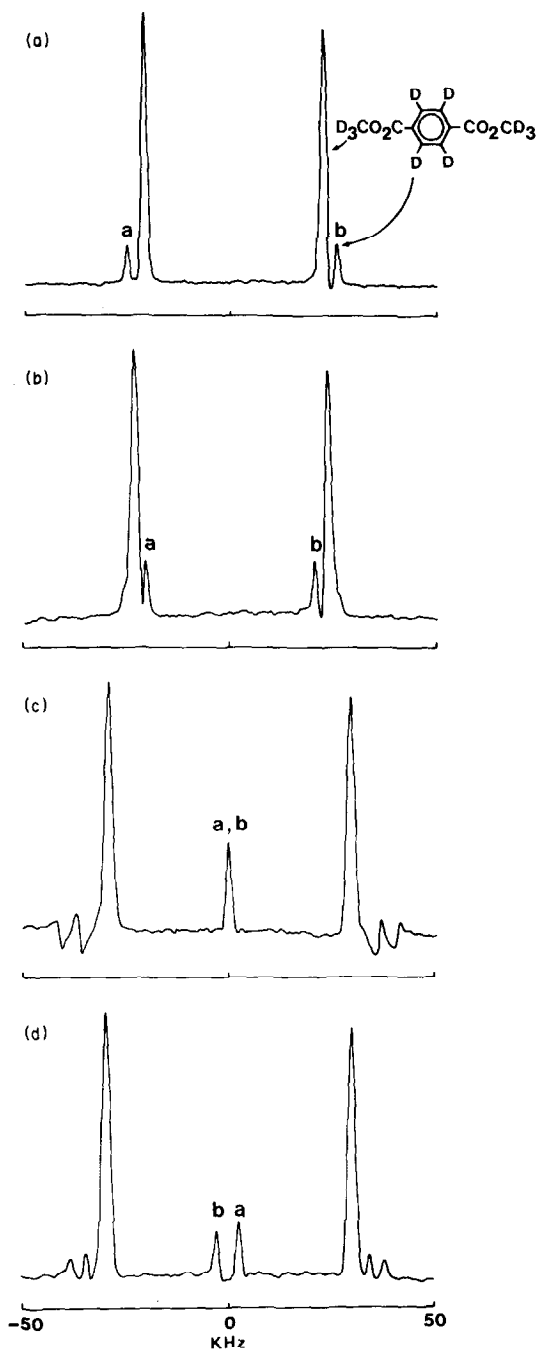


FIG. 1. Representative spectra of an oriented single crystal of per-deuterated *para*-dimethylterephthalate,  $\text{CD}_3\text{CO}_2\phi\text{D}_4\text{CO}_2\text{CD}_3$ . The methyl-group quadrupole splitting was held nearly constant as the aromatic-deuteron quadrupole splitting was varied and passed through zero.

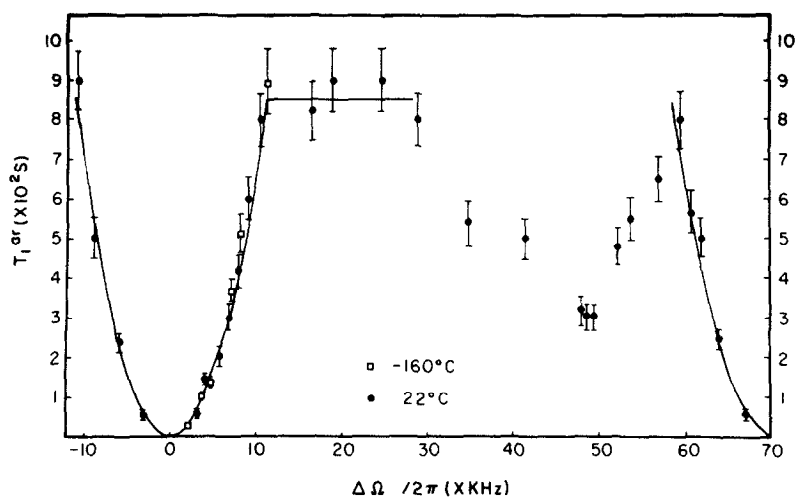


FIG. 2. Orientation dependence of  $T_1^{\text{ar}}$  for the aromatic-group deuterons in a single crystal of  $\text{CD}_3\text{CO}_2\phi\text{D}_4\text{CO}_2\text{CD}_3$ . The positions  $\Delta\Omega = 0, 70$  kHz represent overlap of the methyl and aromatic group resonances. The  $T_1^{\text{ar}}$  depends on  $[\Omega_Q^{\text{me}} - \Omega_Q^{\text{ar}}]^2$  in the regions of near overlap. The quadratic curves are the same on the left- and right-hand sides, indicating that spin diffusion does not depend on the relative signs of  $\Omega_Q^{\text{me}}$  and  $\Omega_Q^{\text{ar}}$ .

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