NMR observations of molecular motions and Zeeman–quadrupole cross relaxation in 1,2-difluorotetrachloroethane

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We report measurements of $^19F$ NMR relaxation times $T_1$, $T_{1p}$, $T_{1D}$, and $T_s$ in the plastic crystal CFCL$_2$-CFCL$_2$. From the data near the melting point, we obtain the jump time for translational self-diffusion. At lower temperatures, we observe on the cold side of the $T_1$ and $T_{1p}$ minima an unusual field dependence which is substantially less than the normal field-squared dependence. We also observe a reduction in $T_1$ near 40 MHz due to cross relaxation between the Zeeman levels of the $^19F$ spins and quadrupole levels of the $^35Cl$ and $^37Cl$ spins. We measured the cross relaxation times $\tau_{rs}$ as a function of field and found good agreement with our theoretical calculation of $\tau_{rs}$.

I. INTRODUCTION

Solids composed of molecules of approximate spherical shape often form a plastic crystalline phase (as defined by Timmermans) prior to melting. In such a phase, the molecules sit in a regular lattice, usually cubic, but reorient rapidly in a manner characteristic of a liquid. Thus, a plastic crystal exhibits translational order but orientational disorder.

At some lower temperature $T_m$, the crystal undergoes an order–disorder transition below which the orientation of the molecules becomes ordered. It is possible normally to supercool the plastic crystal below $T^*$ by lowering the temperature rapidly. In a few cases where this has been done, a glass phase transition has been observed at a temperature $T_g < T^*$, below which a glassy crystalline phase (as defined by Adachi et al.) is formed. Such glassy crystals are in a metastable state in which the rate of molecular reorientation becomes so slow that a transition to the more thermodynamically stable ordered crystalline state is not observed over the time scale of a given experiment. Thus the molecules are "frozen" into a state of orientational disorder.

The compound CFCL$_2$-CFCL$_2$ forms a plastic crystalline phase below its melting point $T_m = 298$°K. The order–disorder phase transition occurs at $T_g = 170$°K. However, the plastic crystalline phase is so easily supercooled that the ordered crystalline phase is difficult to achieve. In the supercooled plastic crystalline phase, a glass phase transition occurs at $T_g = 90$°K below which molecular reorientations are frozen out. Another relaxation phenomenon was observed in heat capacity measurements at 130°K and has been ascribed to the freezing of conversion between the trans and gauche conformers of the molecule.

In this paper, we report NMR measurements in CFCL$_2$-CFCL$_2$ from its melting point $T_m$ down to 77°K. We interpret our results in terms of molecular motions (e.g., translational self-diffusion near $T_m$ and molecular reorientations at lower temperatures). In addition, we observe cross relaxation between the Zeeman energy levels of $^19F$ and the quadrupole levels of $^35Cl$ and $^37Cl$. We compare our data with a theoretical calculation of the cross relaxation time and find good agreement.

II. SECOND MOMENT CALCULATION

The structure of the CFCL$_2$-CFCL$_2$ molecules has been determined by electron diffraction from which the position coordinates of the atoms are obtained (see Table I). In the solid phase, these molecules lie in a body-cen-

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**TABLE I.** The position coordinates of the atoms in a CFCL$_2$-CFCL$_2$ molecule for the two isomers. The $z$ axis is chosen along the C–C bond with the origin at the midpoint.

<table>
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<tr>
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<th>$y$</th>
<th>$z$</th>
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TABLE II. Contributions to the second moment (in G$^2$) of the $^{19}$F NMR line shape.

<table>
<thead>
<tr>
<th>Isotropic Rotations</th>
<th>Intramolecular</th>
<th>Intermolecular</th>
<th>Chemical shift anisotropy</th>
<th>Total</th>
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<td>0.016</td>
<td>0.140</td>
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<tr>
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<td>0.84</td>
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<td>0.16</td>
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</tbody>
</table>

n. powder sample. Evaluation of Eqs. (1) and (2) gives the following expressions for a powder sample:

$$M_{2R}(\text{intra}) = 3[1+1\gamma_f^2 h^2 S(S+1)\sum_j \langle r^2_{jk} \rangle / 5]$$

and

$$M_{2S}(\text{intra}) = f_s S(S+1)\gamma_f^2 h^2 S(S+1)\sum_j \langle r^2_{jk} \rangle / 5$$

where the term $r_{jk}$ in Eq. (4) is the F–F distance and in Eq. (5) the F–Cl distance, summed over the four Cl nuclei in the molecule. These expressions are evaluated and given in Table II.

The calculation of the intermolecular contribution presents some problems. The orientations of the molecules are disordered, and thus we do not know the relative positions of nuclei. However, if we assume that the molecules are oriented randomly relative to each other (i.e., there are no preferred directions of orientation relative to each other), we can calculate the intermolecular contribution by averaging the second moment of each pair interaction over all possible orientations of the molecules. (Note that this is basically different from the previous case of rapid motion where we averaged the interaction rather than the second moment.) Thus, for a powder sample, we have

$$M_{2R}(\text{inter}) = 3[1+1\gamma_f^2 h^2 \sum_j \langle r^2_{jk} \rangle / 5]$$

and

$$M_{2S}(\text{inter}) = f_s S(S+1)\gamma_f^2 h^2 \sum_j \langle r^2_{jk} \rangle / 5$$

where the summation in Eq. (6) is over $I$ spins and in Eq. (7) is over $S$ spins. The term $\langle r^2_{jk} \rangle$ is the average of $r^2_{jk}$ over all orientations of the two molecules to which spins $j$ and $k$ are attached. $\langle r^2_{jk} \rangle$ can be calculated by an integration over the surfaces of two spheres, $S_j$ and $S_k$, generated by rotating the two molecules containing the $j$ and $k$ sites. Thus the radii $R_j$ and $R_k$ of the two spheres are the distances of the $j$ and $k$ sites from the centers of their respective molecules.

In the following paper, we carried out such an integration and from Eq. (42) of that paper, we obtain

$$\langle r^2_{jk} \rangle = \int_s dS_s \int_s dS_j \int_s dS_k (r^2_{jk})^\phi$$

and

$$\langle r^2_{jk} \rangle = \int_{r_{jk}} dR_{jk} R_{jk} dR_{jk}$$

Evaluating this integral, we have

$$\langle r^2_{jk} \rangle = \left( \frac{a^2_{jk}}{R_{jk}} \right)^\phi \left[ R_j^2 + R_k^2 - 2R_j R_k \cos \theta_{jk} \right]$$

Thus, using Eq. (9) we evaluate Eqs. (6) and (7) and give the results in Table II.

One more contribution to the rigid-lattice second moment needs to be considered: that of the chemical shift
FIG. 1. Block diagram of pulse spectrometer.

anisotropy. Assuming axial symmetry in the chemical shift $\sigma$, we write

$$M_{zz}(\sigma) = \frac{1}{2}(\sigma_n - \sigma_i)^2 H_0^2,$$

(10)

where $\sigma_n - \sigma_i$ has been measured\(^7\) in CFC\(_12\)-CFC\(_12\) to be $2.4 \times 10^{-4}$. The evaluation of Eq. (10) is given in Table II.

Adding together all the contributions, we obtain a total second moment $M_{zz} = 0.75$ and $1.44 \, \text{G}^2$ for the trans and gauche isomers, respectively, as shown in Table II. Since the crystal contains a mixture of trans and gauche isomers, the experimental second moment should lie somewhere in between.

The values calculated in Table II agree favorably with those calculated by Gutowsky and Takeda,\(^6\) Andrew and Tunstall,\(^7\) and Kishimoto.\(^4\) We differ only in the intermolecular contribution to the rigid-lattice value, which they only estimated. They then obtained different values for the trans and gauche isomers. Under our assumption of random orientation, we see clearly that the value should be independent of isomer, as shown in Table II.

III. EXPERIMENTAL PROCEDURES

The sample of CFC\(_12\)-CFC\(_12\) was obtained originally from PCR, Inc. It was then purified and transferred to a glass tube where it was sealed under vacuum. (The details of this sample preparation are given in an earlier paper.)\(^14\) Even though the sample was grown into a single crystal from the melt, it melted and recrystallized during the course of the NMR measurements. As a result, most of the data reported here was taken on a polycrystalline sample. However, because of the orientational disorder that exists in CFC\(_12\)-CFC\(_12\), anisotropy effects in a single crystal are probably negligible. This is supported by the fact that we observed no anisotropy (to within $10\%$) in $T_2$ at $116^\circ\text{K}$ or in $T_1$ at $100^\circ\text{K}$ in a freshly grown single crystal.

All of the NMR data was taken with a standard pulse spectrometer (see Fig. 1), using single-coil probes tuned to $50 \, \text{Q}$. Some of the $T_1$ data was taken using a transmission-line probe.\(^16-17\) This probe was constructed by winding 13 turns of copper ribbon (0.5 mm wide) on a 12-mm o.d. glass tube (see Fig. 2). This was covered with a layer of insulator (single layer of 0.5-mil Mylar obtained from a 400-V Mylar capacitor) and then with brass foil which was connected to ground. This arrangement gives the coil a distributed capacitance to ground and hence forms a transmission line.
which, as we will see, has a characteristic impedance $Z_0 = 50 \, \Omega$. By terminating the coil with a 50-\(\Omega\) resistor connected to ground, the input impedance $Z_{in}$ of the coil would be close to 50 \(\Omega\) over a wide range of frequency. We measured $Z_{in}$ with a vector impedance meter as a function of frequency and expressed the result in terms of the voltage-standing-wave ratio (VSWR) in dB, using

$$\text{VSWR} = 20 \log_{10} \left( \frac{|Z_{in} + Z_0| + |Z_{in} - Z_0|}{|Z_{in} + Z_0| - |Z_{in} - Z_0|} \right),$$

where $Z_0 = 50 \, \Omega$.

Since the VSWR in Fig. 3 is small, the input impedance of the probe is fairly close to 50 \(\Omega\) over the entire frequency range shown. Using this probe in the pulse spectrometer, we could easily make NMR measurements over a wide range of frequencies. In particular, we measured the $T_1$ of $^{19}$F in CFC$_2$ over the range 18–80 MHz. Using wide-band amplifiers, only the quarter-wavelength cables needed to be changed for different frequencies. We should note that none of the $T_{1p}$ or $T_{1D}$ data were taken using this transmission-line probe.

IV. RESULTS

We measured the spin–lattice relaxation time $T_{1p}$, the rotating-frame relaxation time $T_{1r}$, the dipolar relaxation time $T_{1D}$, and the spin–spin relaxation time $T_2$ of $^{19}$F in CFC$_2$ over a wide temperature range (see Fig. 4). Kishimoto previously measured $T_{1D}$ (at $\omega_{21}/2\pi = 60$ MHz) and $T_{1r}$ (at $H_{11}$ = 5.42 G) over approximately the same temperature range. For the most part, his measurements are consistent with our data but lack some of our detail. However, there are two major differences: (1) his $T_{1D}$ data for $T \leq 100\, ^\circ \text{K}$ has a much greater slope than ours, and (2) his $T_{1r}$ data (60 MHz) for $T \leq 130\, ^\circ \text{K}$ falls almost exactly on top of our $T_{1D}$ data for 80 MHz and is thus shifted upward from our expected positions for 60 MHz data. Concerning this last point of disagreement, we observed ourselves a sample-history dependence of $T_{1D}$ in this temperature region. On our first day of measurements, we obtained measurements of $T_{1r}$ at 24 MHz, shown in Fig. 5 as open squares. Three days later, we took more measurements and found that $T_{1r}$ was now significantly lower in value. These and all subsequent measurements (even months later) of $T_{1r}$ at 24 MHz are shown in Fig. 5 as filled squares and fall on a straight line. Kishimoto’s $T_{1D}$ (60 MHz) data is consistent with our $T_{1r}$ (24 MHz) data taken the first day.

In the following sections, we examine in detail some of the features of our NMR data and discuss its physical significance.

A. Second moments

We measured $T_2$ of the $^{19}$F NMR free induction decay (FID) at 24 MHz as a function of temperature (see Fig. 5).
At temperatures below about 90 °K, we find $T_2 = 50 \mu$sec. We observed the shape of the FID to be approximately Gaussian. (This is common for FID’s in solids.) If we assume a Gaussian line shape, then we find

$$M_2 = \frac{1}{\gamma^2 T_1}.$$  (12)

Using $T_2 = 50 \mu$sec, we obtain $M_2 = 1.26 \pm 0.08 \text{G}^2$. From Table II we see that this value is consistent with a rigid-lattice second moment arising from a mixture of the two isomers ($M_2 = 0.75$ and $1.44 \text{G}^2$ for the trans and gauche isomers, respectively). Note that Gutowsky and Takeda measured $M_2 = 1.4 \text{G}^2$, and Andrew and Tunstall measured $M_2 = 1.3 \text{G}^2$ for this temperature region. (They reported $1.1 \text{G}^2$, which had been corrected for chemical shift anisotropy.)

At about $T = 100^\circ\text{K}$, we see from Fig. 4 that $T_2$ increases (the line narrows) to a value $T_2 = 145 \mu$sec. Using Eq. (12), we find that $M_2 = 0.13 \pm 0.01 \text{G}^2$. From Table II we see that this value agrees closely with the second moment for isotropic rotation ($M_2 = 0.140 \text{G}^2$). Thus we conclude that the motion responsible for narrowing the line at $T = 100^\circ\text{K}$ is isotropic molecular reorientation. This is consistent with heat capacity measurements which indicate a “freezing out” of molecular reorientation at 90 °K. Note that Gutowsky and Takeda measured $M_2 = 0.18 \text{G}^2$ for this temperature region.

At $T = 200^\circ\text{K}$, we see from Fig. 4 another increase in $T_2$, this time due to translational self-diffusion which we will discuss in the next section.

### B. Translational self-diffusion

In plastic crystals, translational self-diffusion usually becomes a dominant spin–lattice relaxation mechanism near the melting point. Such is also the case in CFC$_12$–CFC$_12$ (see Fig. 4). This occurs in the temperature region of rapid molecular reorientation, where, as discussed in Sec. II, the intramolecular dipolar interactions are averaged to zero and the intermolecular interactions are averaged to values which one would obtain by placing all spins at the centers of their respective molecules. Thus, in this case, theories for relaxation in monoatomic crystals may be applied.

The dominant self–diffusion mechanism in plastic crystals is thought to be motion of vacancy defects. Accordingly, we will use relaxation theories for vacancy diffusion in a monoatomic bcc lattice of a polycrystalline sample. It is evident from Fig. 4 that all the data is on the low-temperature side of the $T_1$ minima. Thus, we need expressions for relaxation times only in the limit $\omega_0 T_2 \gg 1$, where $T_2$ is the average time between diffusion jumps of a molecule.

For high-field relaxation, we obtain from the random-walk theory of Wolf

$$T_1^{-1} = 2 \sqrt{2} \gamma^2 T_2^R (U + 1) \omega_0^2 a_0^2 (25.6),$$  (13)

$$T_2^{-1} = 2 \sqrt{2} \gamma^2 T_2^R (U + 1) T_2^D a_0^2 (39.0),$$  (14)

Furthermore,

$$T_{2}^{\text{eff}} = T_1^{\text{eff}}.$$  (15)

in the limit $\omega_1 T_2 \ll 1$, and

$$T_1^{\text{eff}} = 2 \times \frac{1}{\sqrt{2}} \gamma^2 T_2^R (U + 1) \omega_0^2 a_0^2 (18.9),$$  (16)

in the limit $\omega_1 T_2 \gg 1$. In the above expressions, $\omega_1 = \gamma H_1$, where $H_1$ is the magnitude of the rf field applied at frequency $\omega_0$. A factor 2 was included in Eqs. (13)–(16) to account for the two fluorine nuclei in each molecule of CFC$_12$–CFC$_12$. The F–Cl dipolar interactions are negligible here and are thus neglected. Note that our $\alpha_0$ as defined in this paper is twice the $\alpha_0$ in Ref. 23.

For low field relaxation, we obtain from the encounter model

$$T_1^{-1} = T_1^{\text{eff}} (0.822)$$  (17)

in the limit $T_2 \gg T_2^{\text{eff}}$.

Using Eqs. (13)–(17) we can calculate $T_2$ from the experimental values of $T_1$, $T_2$, and $T_{2}^{\text{eff}}$. (We also included the $T_{2}^{\text{eff}}$ data of Kishimoto.) As seen in Fig. 6, over six decades the result exhibits Arrhenius behavior,

$$\tau_2 = \tau_0 \exp(E_A /kT),$$  (18)

where $\tau_2 = 2 \times 10^{-15} \text{sec}$ and the activation energy $E_A = 43.0 \pm 0.3 \text{kJ/mole}$. From linewidth measurements, Kishimoto obtained $E_A = 44 \text{kJ/mole}$ for self-diffusion.

### C. Zeeman–quadrupole cross relaxation

At low temperatures, we observed in $T_1$ at 40 MHz anomalous behavior (see Fig. 4) which we attribute to cross relaxation between the Zeeman levels of the $^{19}$F spins and the quadrupole levels of the $^{35}$Cl and $^{37}$Cl spins.
spins. This cross relaxation causes a large reduction in the apparent $T_{1T}$. Similar effects have been observed in a number of experiments. To investigate this effect further, we measured $T_{1T}$ as a function of $\omega_0/2\pi$ at two different temperatures (see Fig. 7) and observed a broad minimum in $T_{1T}$ centered at about 40 MHz. Assuming that the quadrupolar $T_{1S}$ is much less than the cross relaxation time $\tau_{IS}$, we see that the apparent reduction in $T_{1T}$ is limited by $\tau_{IS}$. (Actually, the relaxation time is limited by the sum, $\tau_{IS} + T_{1S}$, where $T_{1S}$ is the spin-lattice relaxation time of the chlorines. Normally, for quadrupolar relaxation, $T_{1S}$ is very short and can be neglected compared to $\tau_{IS}$.) In particular,

$$T_{1T} = \tau_{IS} + T_{1S}^{\text{normal}},$$

(19)

where $T_{1S}^{\text{normal}}$ is the “normal” spin–lattice relaxation time shown as the dashed line in Fig. 7. By subtracting $T_{1S}^{\text{normal}}$ from $T_{1T}$, we obtain $\tau_{IS}$, which we plot in Fig. 8. Note that $\tau_{IS}$ is temperature independent as we would expect.

Generally, cross relaxation occurs at fields $H_s$ where the Zeeman splitting $\omega_0$ of the $I$ spins is equal to the quadrupolar splitting $\omega_{QS}$ of the $S$ spins. Of course, the presence of $H_s$ also splits the quadrupole resonance and, in the case of CFCI$_2$--CFCI$_2$ where the molecules are orientationally disordered, broadens the quadrupole resonance considerably, making it possible to satisfy the cross relaxation condition $\omega_0 = \omega_{QS}$ over a wide range of $\omega_0$. Hence we see a very broad minimum in $\tau_{IS}$ (Fig. 8).

We derived a theoretical expression for the cross relaxation time $\tau_{IS}$ (see the following paper). All parameters in the theory are well-known physical constants except for $\omega_{QS}$, the quadrupole splitting of $^{35}$Cl and $^{37}$Cl. Using this value (and hence $\omega_{QS}/2\pi = 31.5$ MHz for $^{37}$Cl), we calculated $\tau_{IS}$ (see the following paper) and plotted the result as a solid line in Fig. 8. Considering that there are no adjustable parameters in the theoretical calculation, the agreement with experimental data is excellent.

The cross relaxation effect disappears at $T > 125^\circ$K. In this temperature region, the rate of molecular reorientation is greater than 40 MHz and the Cl quadrupole splitting is thus motionally narrowed and “smeared” out (see pp. 67–68 in Ref. 36).

D. Molecular reorientation

At low temperatures (below 200 °K for $T_{1T}$ and below 150 °K for $T_{1s}$ and $T_{1p}$) we find some very unusual relaxation phenomena (see Fig. 4). Perhaps one of the most striking features present is the reduced field dependence on the cold side of the minima. If we plot, for example, $\ln T_{1s}$ vs $\ln H_s$ at $T = 83^\circ$K (see Fig. 9), we find it falls on a straight line with a slope $\alpha = 1$. This means that approximately $T_{1s} \propto H_s^{\alpha}$. Similarly, a plot of $\ln T_{1T}$ vs $\ln H_s$ at $T = 100^\circ$K (the lower dashed line in Fig. 7), we obtain $T_{1T} \propto H_s^{\alpha}$ with $\alpha \approx 1.2$. Furthermore, the field dependence between the $T_{1T}$ and $T_{1s}$ data also follows an approximate relation $T_{1s}/T_{1T} \propto (H_s/H_{J0})^\alpha$, only with $\alpha \approx 1.1$. The field dependence of $T_{1T}$ and $T_{1s}$ is thus self-consistent and indicates that both $T_{1T}$ and $T_{1s}$ are probably due to the same relaxation mechanism in this temperature region. This conclusion is further supported by the fact that the $T_{1T}$ and
$T_{1\sigma}$ data have similar slopes: 11.7 and 9.5 kJ/mole, respectively.

The values of $T_{1\nu}$ and $T_{1\sigma}$ at their minima also follow an unusual field dependence. Plotting in $T_{1\nu,\text{min}}$ vs $\ln H_{1\nu}$ (see Fig. 10), we see that $T_{1\nu,\text{min}} \propto H_{1\nu}^\beta$ with $\beta = 0.83 \pm 0.05$. Also, from the ratio of the $T_{1\nu}$ values at their minima at 80 and 24 MHz, we find $T_{1\nu,\text{min}} \propto H_{1\nu}^\beta$ with $\beta = 0.76 \pm 0.05$. Again, the similar field dependence of $T_{1\nu,\text{min}}$ and $T_{1\nu,\text{min}}$ is further evidence of a single relaxation mechanism for both $T_{1\sigma}$ and $T_{1\nu}$.

Another unusual aspect of the relaxation data is the large asymmetry in slopes on the two sides of the $T_{1\nu}$ minima. The slope on the hot side of the minima (33 kJ/mole) is more than three times the slope on the cold side. It appears that this asymmetry cannot simply be explained just in terms of an additional relaxation mechanism.

Now we note that the low-field $T_{1\sigma}$ minima occur near the onset of motional narrowing at $T = 100^\circ K$. This suggests that the same motion which is narrowing the line at $100^\circ K$ is also responsible for the $T_{1\sigma}$ relaxation. In Sec. IV A we showed that this motion is indeed molecular reorientation. Thus we conclude that the relaxation mechanism responsible for $T_{1\nu}$ and $T_{1\sigma}$ in the low temperature region is likewise molecular reorientation.

This conclusion is in some ways not surprising since one often finds in plastic crystals that molecular reorientation provides a strong relaxation mechanism at low temperatures. However, one usually also finds that the relaxation data is consistent with a Bloembergen, Purcell, and Pound-type theory38 (BPP), i.e.,

$$\frac{1}{T_{1\nu}} = \frac{3}{2} \gamma^2 \Delta M_{2\nu} \left[ \frac{\tau_r}{1 + \omega_0^2 \tau_r^2} + \frac{5}{2} \frac{\tau_r}{1 + \omega_0^2 \tau_r^2} \right],$$

and

$$\frac{1}{T_{1\sigma}} = \frac{3}{2} \gamma^2 \Delta M_{2\sigma} \left[ \frac{\tau_r}{1 + 4 \omega_m^2 \tau_r^2} + \frac{5}{2} \frac{\tau_r}{1 + 4 \omega_m^2 \tau_r^2} \right],$$

(20) (21)

where $\tau_r$ is the correlation time of the reorientation and $\Delta M_{2\nu}$ is the part of $M_{2\nu}$ which is modulated by the reorientation. These expressions have been successfully used in NMR studies of a number of plastic crystals.40-45

Our data follows some of the general aspects of the BPP-type theories given by Eqs. (20) and (21). $T_{1\nu}$ and $T_{1\sigma}$ are field independent on the hot side of the minima ($\omega_0 \tau_r \ll 1$ and $\omega_1 \tau_r \ll 1$) and are field dependent on the cold side of the minima ($\omega_0 \tau_r \gg 1$ and $\omega_1 \tau_r \gg 1$) with $T_{1\nu}$ and $T_{1\sigma}$ increasing with increasing field. However, in some ways, our data deviates substantially from this theory. Equations (20) and (21) predict that $T_{1\nu} \propto H_{1\nu}^\alpha$ and $T_{1\sigma} \propto H_{1\sigma}^\beta$ on the cold side of the minima and that $T_{1\nu,\text{min}} \propto H_{1\nu}$ and $T_{1\sigma,\text{min}} \propto H_{1\sigma}$ Furthermore, they predict that the slopes of each relaxation time are equal in magnitude on both sides of the minimum. As we have already pointed out in this section, our data departs sharply from these predictions of Eqs. (20) and (21).

We are not presently able to explain these phenomena theoretically. However we briefly discuss here a couple of possibilities. First of all, consider the possibility that these features arise from the nature of the motion involved in the molecular reorientation process. As an example, Walstedt et al.46 measured $T_{1\nu}$ of $^{23}$Na in Na$\beta$-alumina at 17.2 and 25.5 MHz. They observed an asymmetry in the slopes on the two sides of the $T_{1\nu}$ minima and also observed on the cold side of the minima a field dependence which is substantially less than the BPP-type field-squared dependence. They explained their data in terms of a distribution $G(E_a)$ of heights of the barriers to the motion. Assuming that, at each value of $E_a$, their relaxation follows a BPP-type behavior, they obtained

$$\frac{1}{T_{1\nu}} = \int dE_a \frac{G(E_a) \tau_r}{1 + \omega_0^2 \tau_r^2},$$

(22)

Using an appropriate distribution function $G(E_a)$, they were able to make a good fit of Eq. (22) to their data. We would find it much more difficult to fit such a theory to our data, since our unusual field dependence covers a range of over four orders of magnitude in field ($H_{1\nu} = 1.6$ G to $H_{1\sigma} = 20$ kG). (It should be noted that a reduced field dependence of $T_{1\nu}$ has also been observed by others47,48 in some polymers.)
Another approach to the explanation of our data may involve the nature of the interaction itself rather than the motion. For example, each fluorine nucleus in CFC12-CFC12 is in close proximity to two chlorine nuclei. As we commented in the previous section, the Cl quadrupolar relaxation time $T_{1S}$ is normally very short. The modulation of $S$ due to $T_{1S}$ processes can cause $I-S$ dipolar relaxation. Such an indirect relaxation process has been called "dipolar relaxation of the second kind" and has been observed in a number of cases. A field-squared dependence typically has been observed for this kind of relaxation. However, these observations have been made in systems undergoing motional narrowing. In our case of "slow" motion where $T_{1S} = \tau_{r}$ (see Ref. 5), it may be possible to obtain a different result which could produce some unusual features in $T_{1S}$ and $T_{1I}$, such as the ones that we have observed.

Even though we do not have a theory to explain our data, we can still learn something about the general behavior of the correlation time $\tau_{r}$ of the molecular reorientation. First of all, we know that $\tau_{r} \approx T_{1S}$ at the onset of motional narrowing. Thus we obtain $\tau_{r} = 50 \mu$sec at $T = 95^\circ$K. Second, we know that $\omega_{1/2} \tau_{r} \approx 1$ at the $T_{1S}$ minima and $\omega_{1/2} \tau_{r} = 1$ at the $T_{1I}$ minima. Hence we obtain approximate values of $\tau_{r}$ at those points. In addition, we measured $T_{1S}$ of the $^{35}$Cl NMR FID at 8 MHz near the melting point $T_{m}$ and obtained $T_{1S} \approx 20 \mu$sec. Such a short $T_{1S}$ is caused by lifetime broadening due to a strong quadrupolar relaxation in rapidly tumbling molecules. For this case of extreme narrowing, we have for $S = \frac{3}{2}$

$$T_{1S} = T_{1S}^{0} = 0.4 \omega_{1/2} \tau_{r},$$

from which we obtain $\tau_{r} = 2.0 \times 10^{-15}$ sec. We plot these values of $\tau_{r}$ obtained from $T_{1S}^{0}$, the $T_{1S}^{0}$, and $T_{1I}$ minima, and $T_{1S}$ in Fig. 11. Satija and Wang also obtained values of $\tau_{r}$ from depolarized Rayleigh scattering data over the range $T = 265$ to $297^\circ$K. Their results are shown as a dashed line in Fig. 11 and are seen to be in fair agreement with our $T_{1S}$ result.

We now have in Fig. 11 the general behavior of $\tau_{r}$ over a wide range of temperature. As we can see, the activation energy $E_{A}$ is not constant but seems to increase with decreasing temperature. Near the melting point, light scattering data gives $E_{A} \approx 7.3 \pm 0.5$ kcal/mole. At low temperatures, we can see from Fig. 11 that $E_{A} \approx 35$ kcal/mole. Note that we could not obtain $E_{A}$ directly from the slopes of the $T_{1I}$ and $T_{1S}$ data without knowing their $\tau$ dependences. For example, any relationship of the type $T_{1I} \tau_{r}$ would give us a straight line on a plot of $\ln T_{1I}$ vs $T^{-1}$ (as we observed) but with a slope $\nu E_{A}$. Without a theory to explain the data, we do not know the value of $\nu$ and thus cannot determine $E_{A}$ from the slope of the $T_{1I}$ data.

Note that there seems to be a sudden change in $E_{A}$ near $T = 125^\circ$K. This is very close to the temperature where the conversion between the trans and gauche conformers are frozen out ($T = 130^\circ$K). Thus these two phenomena may be related.

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