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## Electron Spin Resonance Studies of Anisotropic Ordering, Spin Relaxation, and Slow Tumbling in Liquid Crystalline Solvents. 2<sup>1a</sup>

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A study is reported of the ESR line shapes in the slow-tumbling region for a cholestane (CSL) spin probe in nematic phase V solution. The line shapes are analyzed in terms of the Polnaszek, Bruno, Freed theory for spectra from slowly tumbling probes in ordered fluids. Rather good agreement with experiment is obtained from the slower motional spectra ( $\tau_R > 5 \times 10^{-9}$  s where  $\tau_R$  is the rotational correlation time) utilizing a single term ordering potential. For these slow-motional spectra, effects of proton inhomogeneous broadening are relatively small. It is shown in this study on CSL that for  $\tau_R > 10^{-9}$  s a motional-narrowing theory will lead to erroneous predictions for  $\tau_R$  and ordering that become more serious as  $\tau_R$  increases. The previous application of motional-narrowing theory by other workers to this probe is discussed in this light. The effects of various other factors upon the spectral simulations are discussed. In particular, it is shown that the spectra for this highly ordered probe should not be very sensitive to various aspects of model dependence of the reorientational motion as discussed in part I nor to effects from director fluctuations. Also the slower tumbling spectra are rather insensitive to anisotropy in  $\tau_R$  (but the anisotropy may be determined from the faster motional spectra). Nevertheless, contributions from these effects could modify somewhat the values of  $\tau_R$  and ordering that are obtained. The slow tumbling spectra are also insensitive to the angle of tilt of the nitroxide magnetic-tensor principal axis system in the  $x$ - $y$  plane with respect to the molecular orientational axes. Our results show that the tilt angle of the magnetic  $z$  axis should not be very different from  $0^\circ$ .

### I. Introduction

In part I we presented a detailed study of anisotropic ordering, line shapes, and relaxation for the weakly ordered perdeuterated 2,2,6,6-tetramethyl-4-piperidone *N*-oxide (PD-Tempone) nitroxide radical.<sup>2</sup> This radical offered the advantages that one could achieve a high degree of spectral resolution for accurate spin-relaxation studies, because inhomogeneous broadening due to unresolved intramolecular proton or deuteron interactions is minimized. A major objective of that work was to apply the Polnaszek, Bruno, Freed (PBF) theory<sup>3</sup> (appropriately generalized<sup>2</sup>) for slow tumbling in ordered fluids to a system exhibiting good resolution and definition. That study indicated the existence of anomalies in the line shape, particularly in the

incipient slow-tumbling region, which was later borne out by studies as a function of pressure,<sup>4</sup> and were tentatively ascribed to slowly relaxing components of torque acting on the probe molecule.

The importance of slow-tumbling analyses increases when one employs larger and more highly ordered probes. One such probe that is commonly used is 3-spiro-[2'-*N*-oxyl-3',3'-dimethylloxazolidine] (5 $\alpha$ -cholestane) or CSL. It is highly ordered to a degree more typical of the liquid crystal molecules than is Tempone. While only preliminary accounts of the analysis of its ESR spectrum, when dissolved in liquid-crystalline systems, in terms of slow tumbling theory has previously been given,<sup>5-7</sup> we note that many workers have unhesitatingly applied motional-

TABLE I: Magnetic Parameters for CSL in Phase V<sup>a</sup>

$A_z = 33.44$	$g_z = 2.0021$
$A_x = 5.27$	$g_x = 2.0089$
$A_y = 5.27$	$g_y = 2.0058$
$a_N = 14.66 \pm 0.01$	$g_0 = 2.0056 \pm 0.0001$

<sup>a</sup> See text.

narrowing theory, in various degrees of sophistication, to the spectra obtained in nematic and smectic phases. We wish, in this work, to give a more detailed account of our efforts to simulate observed spectra from nematic solutions of the cholestane spin label in terms of the PBF theory. One important question we deal with is the extent to which motional-narrowing theories are adequate vs. the need for complete simulations. The other questions relate to our ability to interpret these spectra in terms of molecular ordering and motional dynamics. The fact that the cholestane ESR spectrum is significantly broadened by proton inhomogeneous structure reduces the resolution, hence the sensitivity of the spectrum to subtle effects of ordering and motional dynamics. Thus, we have not felt that an analysis as thorough and detailed as the one we have given for PD-Tempone is entirely appropriate. In particular, we focus much of our attention on the lower-temperature, slower-tumbling spectra ( $5 \times 10^{-9} \text{ s} < \tau_R \leq 10^{-7} \text{ s}$ ), in part because this is a region wherein the inhomogeneous proton broadening is of less significance in the spectral simulations. It is in that region that we are able to achieve good fits to the experimental data by means of the PBF theory, and it is quite clear that motional narrowing theory is inadequate even though it has been extensively employed by other workers.

## II. Experimental Section

The spin probe (3-spiro-[2'-N-oxyl-3',3'-dimethyl-oxazolidine]) 5 $\alpha$ -cholestane was obtained from Synvar Associates and the liquid-crystalline solvent phase V from EM Laboratories.

Most of the ESR measurements were performed on a Varian E-12 spectrometer. The temperature in the active region of the cavity was controlled by a Varian E-257 variable temperature control unit. The other aspects of the experimental methods are as described earlier.<sup>2,4,6,8,9</sup>

## III. Analysis and Discussion

(A) *Magnetic Parameters.* The rigid, but isotropic, spectrum of CSL was recorded at  $-152^\circ\text{C}$  in order to obtain magnetic parameters. However, because of proton inhomogeneous broadening it was impossible to resolve the central part of the spectrum. Therefore only  $a_z$  and  $g_z$  could unambiguously be determined for CSL in phase V. The magnetic parameters have been reported<sup>10</sup> for CSL in single crystals of cholesteryl chloride. The value of  $a_z$  (31.9 G) is different from the value obtained (33.44 G) for CSL in phase V, but the  $g_z$  values obtained for the two systems are the same. So we used the  $g$  values observed for CSL in cholesteryl chloride.<sup>10a</sup> We also measured the isotropic values of  $a_N$  and  $g$ . The value of  $a_{\perp}$  was obtained by assuming  $a_{\perp} = a_x = a_y$ , so the equation  $a_{\perp} = 1/2(3a_N - a_z)$  applies, where  $a_N$  is the measured value of isotropic splitting constant. The magnetic parameters for CSL in phase V used in the present work are given in Table I. Various results for  $a_N$  and  $a_z$  are presented in Table II for CSL in different solvents. The  $a_N$  and  $a_z$  values observed for CSL in phase V are similar to those observed in non-hydrogen bonding solvents, as one would expect.

(B) *Slow Tumbling Simulations.* The spectra of CSL in the nematic phase V were recorded from  $-26$  to  $+65^\circ\text{C}$ . We have simulated the ESR spectra of CSL in phase V

TABLE II:  $a_N$  and  $a_z$  Values for CSL in Different Solvents

Solvent	$a_N$	$a_z$	Ref
Phase V	14.66	33.44	Present work
CF <sub>3</sub> CH <sub>2</sub> OH	15.75	35.4	<i>a</i>
EtOH	15.0		<i>a</i>
Pentane/heptane	14.2	32.3	<i>a</i>
Perdeuterated benzene	14.4	33.5	<i>a</i>
Me <sub>2</sub> SO	14.8		<i>a</i>
Egg lecithin	15.1	34.2	<i>b</i>
Brain lipid	14.67	33.3	7a
Brain lipid + cholesterol (30%)	15.56	35.0	<i>a</i>
Lecithin + cholesterol (50%)	15.01	32.7	17
Cholesteryl chloride	14.7	31.9	10

<sup>a</sup> C. F. Polnaszek, unpublished. <sup>b</sup> J. Israelachvili et al., *Biochim. Biophys. Acta*, **382**, 125 (1975).

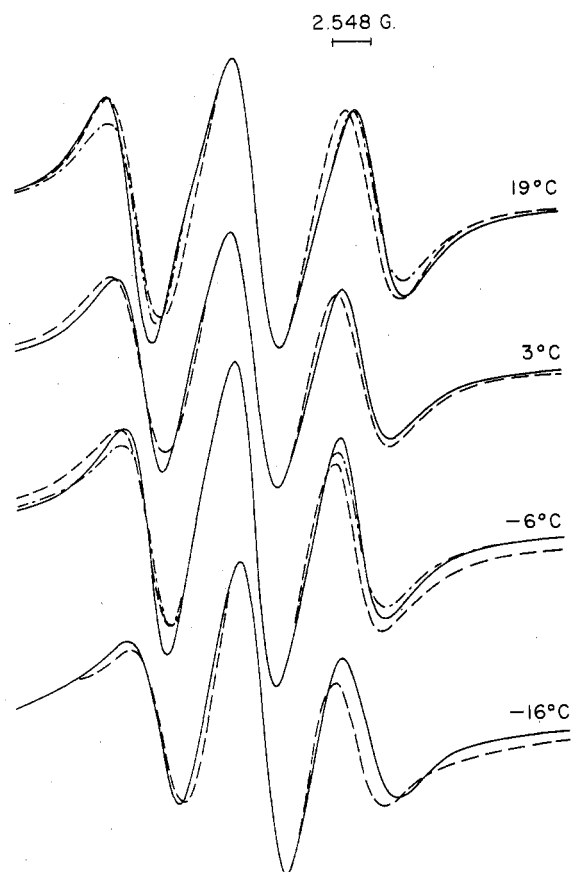


Figure 1. Comparison of experimental and simulated spectra at several temperatures for CSL in phase V: (---) experimental results; (—) theoretical result based upon isotropic Brownian diffusion with the  $\tau_R$ ,  $\lambda$ , and  $A'$  values given in Table III; (---) theoretical result based upon anisotropic Brownian diffusion model. The values used for the simulations with the anisotropic diffusion model at  $19^\circ\text{C}$  are  $\tau_{R\perp} = 1.7 \times 10^{-8} \text{ s}$ ,  $N_y = 5$ ,  $\lambda = 4.3$ , and  $A' = 0.9 \text{ G}$ , and at  $-6^\circ\text{C}$ ,  $\tau_{R\perp} = 7.8 \times 10^{-8} \text{ s}$ ,  $N_y = 5$ ,  $\lambda = 6.0$ , and  $A' = 1.3 \text{ G}$ .

by using the PBF approach.<sup>2-4</sup> Typical spectra simulated at temperatures  $-16$ ,  $-6$ ,  $+3$ , and  $+19^\circ\text{C}$  along with the experimental spectra at these temperatures are shown in Figure 1. The appropriate values of  $\tau_R$ , the isotropic rotational correlation time, and ordering potential parameter  $\lambda$  were obtained by trial-and-error for each slow-motional spectrum in order to achieve the best agreement.<sup>11a</sup> We used a simple one term potential  $U(\beta)$  given by  $U(\beta)/kT = -\lambda \cos^2 \beta$ , where  $\beta$  is the angle between the molecular symmetry axis and the director aligned along the dc-magnetic field (cf. section C for further discussion). It is seen from Figure 1 that the agreements are quite good,

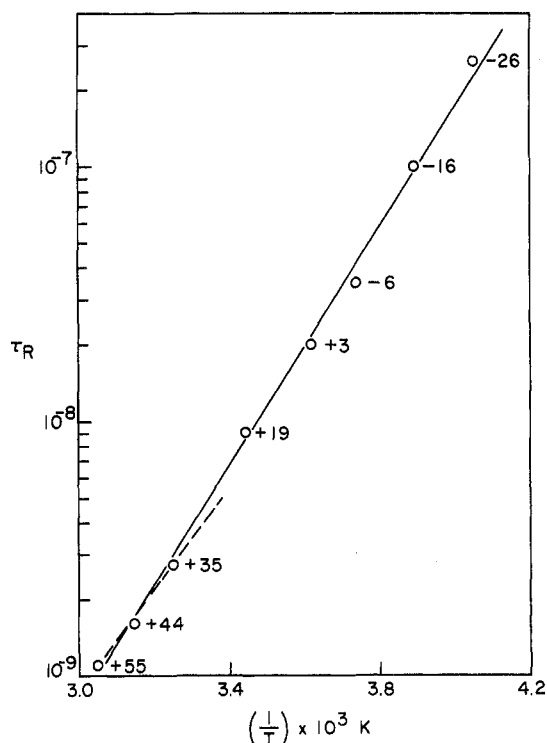


Figure 2. Graph of  $\tau_R$  vs.  $(1/T) \times 10^3$  K for CSL in phase V. The values of  $\tau_R$  at the different temperatures are given in Table III.

TABLE III: Correlation Times,  $\lambda$ , and  $A'$  Values for CSL in Nematic Phase V at Different Temperatures

Temp, °C	$10^9 \tau_R$ s	$\lambda$	$\langle D_{00}^2 \rangle$	$A'$ , G <sup>a</sup>
65	0.9	2.65	0.40	1.75
55	1.1	3.3	0.48	1.75
44	1.6	4.0	0.56	1.7
35	2.7	4.1	0.57	1.5
19	9	4.5	0.61	1.45
3	20	5.3	0.67	1.5
-6	35	6.0	0.71	1.8
-16	100	6.9	0.76	2.2
-26	260	7.6	0.78	2.5

<sup>a</sup> These are based on assuming an overall Lorentzian broadening. When the spectra were simulated by a Gaussian convolution to better represent the effects of inhomogeneous broadening, then the residual line width  $A'$  attributable to a Lorentzian component is significantly reduced for the higher temperature spectra (e.g., for 55 °C,  $A' = 0.3$  G with Gaussian width 2.15 G), but only slightly reduced for the lower temperature spectra (e.g., for -16 °C,  $A' = 1.5$  G with the Gaussian width 2.0 G).

although not perfect. Also, the values of  $\tau_R$  so obtained yield a good Arrhenius-type plot vs.  $1/T$  with an activation energy of 10.9 kcal/mol from the lower temperature spectra (cf. Figure 2). This is only a little greater than the value 9.6 kcal/mol obtained for PD-Tempone in phase V.<sup>2</sup> Hence the  $\tau_R$  values used here are probably close to the correct values (see also section C). The  $\tau_R$  values obtained in this manner (in which an isotropic rotational diffusion model was used for CSL in phase V) and the corresponding  $\lambda$ ,  $\langle D_{00}^2 \rangle$  (the usual order parameter  $S$ ), and  $A'$  (the residual line width which is the difference between experimental and theoretical values<sup>2,4</sup>) at the different temperatures are given in Table III. A plot of  $\lambda$  and the corresponding  $\langle D_{00}^2 \rangle$  values vs. temperature is shown in Figure 3. The temperature dependence of  $\lambda$  and  $\langle D_{00}^2 \rangle$  is similar to that observed for PD-Tempone in different liquid crystal solvents<sup>2,6</sup> although the values for  $\lambda$  and  $\langle D_{00}^2 \rangle$  are, as expected, greater in the present case. A plot

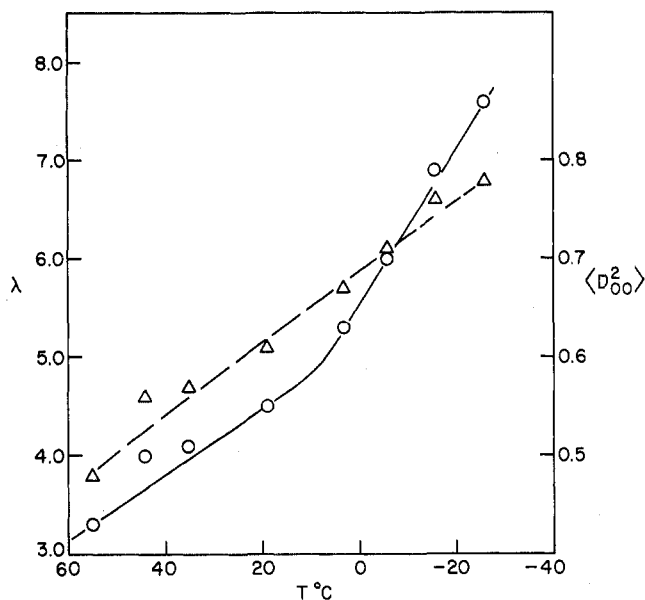


Figure 3. Graph of  $\lambda$  (O) and  $\langle D_{00}^2 \rangle$  ( $\Delta$ ) vs. temperature: (—)  $\lambda$  vs.  $T$ ; (---)  $\langle D_{00}^2 \rangle$  vs.  $T$ . The  $\lambda$  and  $\langle D_{00}^2 \rangle$  values at different temperatures are given in Table III.

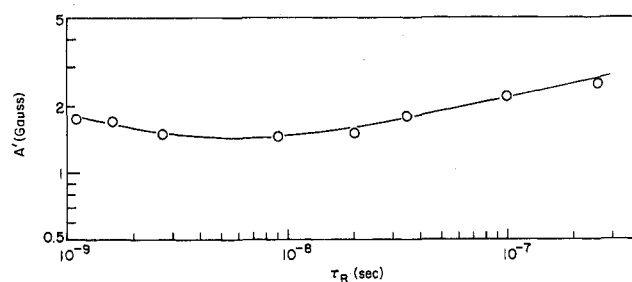
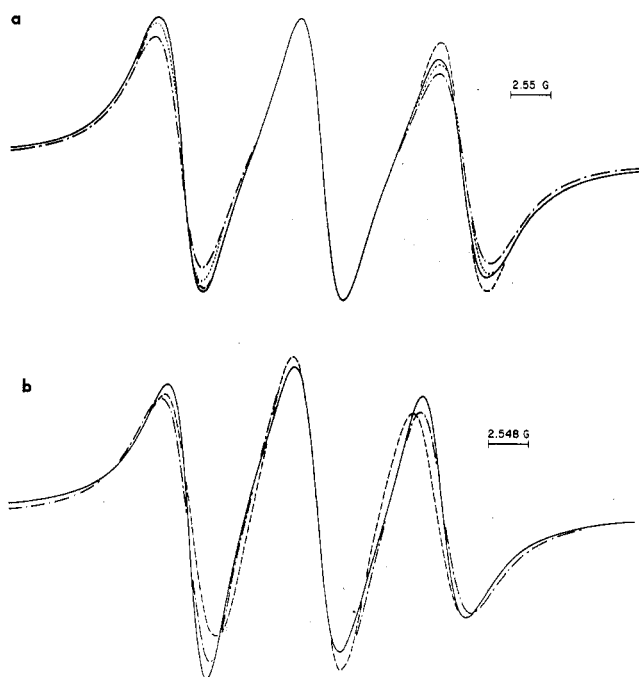


Figure 4. Graph of the residual line width  $A'$  in G vs.  $\tau_R$ . The values of  $A'$  and  $\tau_R$  are given in Table III.

of  $A'$  vs. temperature is shown in Figure 4. The values of  $\tau_R$  and  $\lambda$  required to simulate the spectra at the highest temperature does not appear to fit the extrapolated curves from the lower temperature results (cf. Figures 2 and 3). The probable reasons are (1) the onset of model-dependent effects in the slow motional region at lower temperatures which are not apparent in the higher temperature spectra;<sup>8,9</sup> (2) the appearance of anomalies observed for PD-Tempone in isotropic<sup>9</sup> and in anisotropic solvents<sup>2,4</sup> for  $\tau_R$  of the order of  $10^{-9}$  s; (3) hydrodynamic and critical effects on the magnitude and direction of the director; and (4) the pronounced effects of inhomogeneous broadening upon the higher temperature spectral line shapes. We discuss these factors below.

For small nitroxides such as PD-Tempone, it has been shown earlier that in the slow motional region a moderate jump diffusion model gives a better fit with the experimental spectrum than the Brownian model. The  $\tau_R$  values needed<sup>9</sup> to fit a slow motional spectrum with the moderate jump model are somewhat smaller than the  $\tau_R$  values obtained by using a Brownian model. This is in agreement with the observation that a linear extrapolation of  $\tau_R$  values at high temperatures (55, 44, and 35 °C) will give lower values at the lower temperatures (19, 3, -6, and 16 °C) than the  $\tau_R$  values obtained by using Brownian model at the corresponding temperatures. Thus, if the moderate jump diffusion model were used, the values of activation energy would be reduced somewhat, and then would be in better agreement with the value obtained for PD-Tempone in phase V. (We note that the use of these different models has very little effect on the overall best-fit line shapes for



**Figure 5.** (a) Comparison of the simulated spectra at  $\tau_R = 1.8 \times 10^{-9}$ ,  $\lambda = 4.5$  with different values of  $\epsilon'$ : (—)  $\epsilon'_{ps} = 20$ ,  $\epsilon'_s = 1.0$ ,  $A' = 2.5$  G; (---)  $\epsilon'_{ps} = 5$ ,  $\epsilon'_s = 1$ ,  $A' = 2.4$  G; (· · ·)  $\epsilon'_{ps} = \epsilon'_s = 1.0$ ,  $A' = 2.15$  G; and (— · —)  $\epsilon'_{ps} = \epsilon'_s = 5.0$ ,  $A' = 2.4$  G. (b) Comparison of the simulated spectra with and without including the contributions due to director fluctuations. (· · · ·) Experimental spectrum at 19 °C; (—) simulated spectrum with  $\tau_R = 7.5 \times 10^{-9}$ ,  $\lambda = 4.3$ ,  $A'$  for  $M = 0$  line = 1.0 G and  $A'$  for  $M = \pm 1$  lines = 0.75 G; (---) simulated spectrum with  $\tau_R = 7 \times 10^{-9}$ ,  $\lambda = 4.3$ ,  $A'$  for all the three lines = 1.0 G.

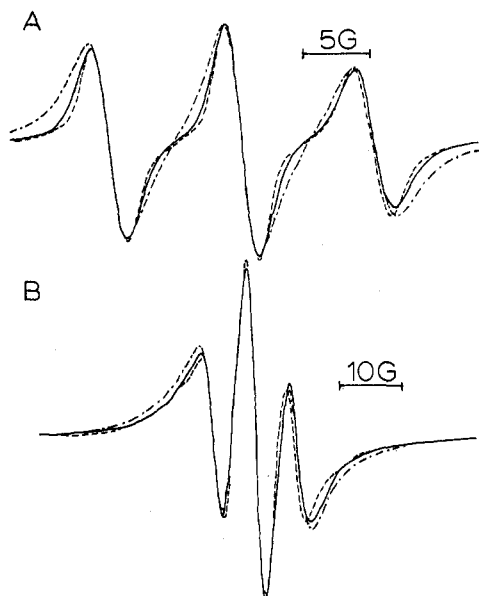
these highly ordered and broad line shapes.) In particular, a least-squares fit of all the  $\tau_R$  values vs.  $(1/T)$  gives an activation energy of 10.5 kcal/mol. However, except for the possibility of some model dependence, the lower temperature results are the more reliable ones, as we have noted.

Incipient slow tumbling spectra (i.e.,  $\tau_R \sim 10^{-9}$  s) of PD-Tempone in different solvents have been successfully explained only after taking into account the effects of fluctuating torques and slowly relaxing local structure, with the most prominent effects showing up in liquid-crystalline<sup>2,4,9</sup> solvents. Some spectra of CSL in phase V were simulated including the fluctuating torques in terms of  $\epsilon'$  (i.e., the spectral densities,  $j(\omega) = \tau_R/[1 + \epsilon'\omega^2\tau_R^2]$ ) as was done for PD-Tempone.<sup>2,4,9</sup> A major difficulty in any attempt to fit these spectra with values of  $\epsilon' \neq 1$  is the absence of accurate motional-narrowing results for  $\tau_R$  and  $\lambda$  which could then be extrapolated into the slow-tumbling region as initial guides to the fitting. Another is the problem that the spectra are not well resolved, so the effect on the simulated spectra of varying  $\epsilon'$  is small. This can be seen from Figure 5a, which shows simulated spectra for CSL in phase V, at  $\tau_R = 1.8 \times 10^{-9}$ ,  $\lambda = 4.5$ , and with  $\epsilon'$  values of 20, 5, and 1. These spectra are not as sensitive to the value of  $\epsilon'$  as the spectra of PD-Tempone.<sup>2,4,9</sup> Hence even if the anomalies observed for PD-Tempone<sup>2,4,9</sup> are present in CSL in phase V, the nature of the spectra observed does not really allow an identification of such anomalies. Some attempts at varying  $\epsilon'$  (which required changes in  $\tau_R$  and  $\lambda$  in order to obtain reasonable fits) were made, but they tended to emphasize the uncertainty of such fits. [Note that in ref 9, it was pointed out that apparent jump-model effects on slow tumbling spectra may on more fundamental grounds also be ascribed to a fluctuating torque model which gives rise to a predicted

$\epsilon'$  effect in the incipient slow-motional region.]

We now note that at temperatures close to the nematic-isotropic transition temperature, there may be effects of the critical orientational fluctuations that have been observed<sup>11b</sup> for PD-Tempone in MBBA. The critical fluctuations may extend over a larger temperature range than was observed for PD-Tempone in MBBA,<sup>11b</sup> because of the greater ordering of the CSL probe. Furthermore, we have not included any effects from possible director fluctuations in the nematic region. At present, it is difficult to assess to what extent these will contribute static (or inhomogeneous) broadening effects vs. dynamic (or homogeneous) broadening. This is because the range of correlation times for the independent hydrodynamic modes extends from very slow to rather fast,<sup>2</sup> so it is not clear at which point motional averaging with respect to such fluctuations is important. If we were to blithely assume the applicability of the motional-narrowing formula given in ref 2 (and  $y$ -axis ordering, cf. section C), then we would estimate a contribution to  $A'$  of 0.24 G and to  $C$  (i.e., width contributions only to the  $M_I = \pm 1$  ESR transitions) of -0.12 G (noting that the equations in ref 2 require an additional factor of 2 which was omitted), and the contributions should be rather temperature insensitive. We show a simulation in Figure 5b in which this effect is exaggerated (to allow for slow motional and static contributions) by using an  $A'$  for the  $M_I = \pm 1$  transitions which is  $1/4$  G smaller than that for the  $M_I = 0$  transition. This leads to greater disagreement with experiment. However, the spectral effect is seen to be roughly opposite to that from the  $\epsilon'$  correction in Figure 5a. Thus the possibility of nearly canceling contributions cannot really be ruled out for these fairly small effects. [One can, of course, attempt to fit an experimental spectrum by simultaneously adjusting  $\tau_R$ ,  $\lambda$ , the  $\epsilon'$  corrections, hydrodynamic corrections, as well as the rotational anisotropy and tilt of the molecular magnetic axes discussed in section C while using different rotational diffusion models, but there is no justification for this in view of the very limited spectral resolution, so we content ourselves with considering these effects individually.]

Another complicating factor for the spectra at the higher temperatures is the effect of inhomogeneous broadening. In the isotropic phase V these splittings were partially resolved. Marriott et al.<sup>12</sup> have resolved these splittings in nonviscous solvents and assigned them by partial deuteration of CSL. They showed that there are three different proton splittings greater than 0.6 G. In the nematic phase V, the proton splittings were not resolved, even though the experimental line width at the highest temperature was less than in the isotropic phase. A proper analysis of their inhomogeneous broadening would involve a consideration of the effects of the only partially averaged anisotropic proton hyperfine components.<sup>2</sup> Since no such information was conveniently obtainable, and since the ensuing analysis of the line shapes (including slow-motional effects) is still complex, we have not attempted the corrections for inhomogeneous broadening as were done in our previous studies.<sup>2,4,9</sup> A convolution of the spectrum with a Gaussian envelope<sup>6,13</sup> is a reasonable way to include the effects of many (unknown) proton splittings in the nematic phase, but introduces one further adjustable parameter. We have in most of our analyses included inhomogeneous broadening effects into the residual broadening contribution  $A'$  added to each transition. Since the inhomogeneous broadening effects are relatively minor for the broad lines obtained for  $\tau_R > 5 \times 10^{-9}$  s, there is no problem in getting good agreement in line shapes



**Figure 6.** Effect of Gaussian convolution on calculated line shapes at (A) 55 °C and (B) -16 °C. All values as in Figure 1 and Table III: (---) experimental result; (—) Gaussian convolution; (- · - ·) Lorentzian shape.

between simulation and experiment (cf. for Figure 1). However, as  $\tau_R$  becomes shorter, the discrepancies between simulated and experimental line shapes become greater, and we have found that a Gaussian convolution does improve the overall agreement of the line shapes without significantly changing the relevant relaxation parameters except for  $A'$  (cf. Table III). This is illustrated in Figure 6.

(C) *Ordering and (Anisotropic) Rotational Diffusion.*

Since the overall shape of CSL may be approximated as a cylinder of length 24 Å and diameter of 6 Å,<sup>12</sup> it is expected to align so that the cylinder axis is parallel to the director of the liquid crystal. In the coordinate system used in our earlier studies<sup>2,4,9</sup> the magnetic  $y$  axis of the nitroxide group is nearly parallel to the cylinder axis. Thus the ordering tensor can reasonably be assumed to be axially symmetric along the magnetic  $y$  axis (or slightly tilted). Our previously quoted spectral simulations and the values of  $\lambda$  given are based upon this assignment.

CSL is also expected to exhibit axially symmetric rotational diffusion about its long axis. A theoretical anisotropy ratio  $N_y$  can be estimated using the dimensions of the molecule<sup>12</sup> and the appropriate expression.<sup>9,14</sup> For CSL we predict  $N_y = 4.7$ . Also our estimated value of  $N_y$  is 5 for CSL in the isotropic phase of phase V at 85 °C and  $\tau_R = 2.5 \times 10^{-10}$ . We have simulated the ESR spectra with a value of  $N_y = 5$  at +19 °C and at -6 °C. The correlation time  $\tau_{R\perp}$  for rotation about an axis perpendicular to the symmetry axis that is required for the best fit at +19 °C with  $N_y = 5$  is  $1.7 \times 10^{-8}$ , so the value of the correlation time,  $\tau_{R\parallel}$ , for rotation about the symmetry axis is  $3.3 \times 10^{-9}$ . (Note that  $N \equiv \tau_{R\perp}/\tau_{R\parallel}$ ). The mean correlation time  $\bar{\tau}_R$ , which is defined as  $(\tau_{R\perp}\tau_{R\parallel})^{1/2}$ , is  $7.5 \times 10^{-9}$  compared to  $7.0 \times 10^{-9}$ , the value obtained for an isotropic diffusion model. At -6 °C the value of  $\bar{\tau}_R$  is the same as  $\tau_R$  in the isotropic diffusion model. The value of  $\lambda$  that has to be used for simulation of the best fit with  $N_y = 5$  is nearly the same as the value used in isotropic diffusion at both 19 and -6 °C. There is very little difference for such long  $\tau_R$ 's between the theoretical spectra for an isotropic diffusion model and anisotropic diffusion for  $N_y \approx 5$  as has previously been shown (cf. Figures 13 and 14 of ref 8). However, one can obtain the  $B$  and  $C$  line width coeffi-

cients in the usual manner.<sup>2,4,8,9</sup> For the spectra at 55, 44, and 35 °C, the ratio  $C/B$  is nearly independent of the procedure for obtaining  $B$  and  $C$ ; i.e., we have used (1) the uncorrected values, (2) the values corrected for inhomogeneous broadening using the isotropic proton splittings,<sup>22</sup> or (3) the values obtained by convolution with a Gaussian.<sup>13</sup> For these spectra in the incipient slow tumbling region we obtain  $N_y \approx 3-4$ , assuming no tilt in the nitroxide,  $x$ - $y$  plane. [Note that the "apparent" value of  $N_y$  increases close to the transition point on both sides of the phase transition.<sup>23</sup>]

Thus, even if there is some anisotropy in the rotation of CSL in phase V, its effect on the  $\tau_R$  and  $\lambda$  values seems to be small. Also, the effects of anisotropic diffusion on the spectral line shapes decreases as  $\tau_R$  gets larger. This is in part due to the decreasing sensitivity of ESR spectra to motional effects as correlation times become larger than  $10^{-7}$  s. [Also as the  $N_y$  value gets larger, the relative change in the simulated spectrum becomes smaller.]

We now wish to estimate the values of  $\tau_R$  expected from the geometry of CSL and a modified Stokes-Einstein theory to see whether our results in Table III are reasonable for CSL. More precisely, we let  $\tau_R = 4\pi r_e^3 \eta / 3kT$ , which defines  $r_e$ , the effective rotational radius. We then follow the procedure in I used for PD-Tempone to estimate  $r_e \approx 3.6$  Å for CSL from our experimental values of  $\tau_R$  over the range of temperature from +15 to -6 °C (compared to 1.13 Å for PD-Tempone). The estimated geometric hydrodynamic radius  $r_0$  (cf. part I and ref 9) is for CSL, about 6.2 Å, so that  $\kappa \equiv (r_e/r_0)^3 \approx 0.2$ . We have found, in our previous work on PD-Tempone in a variety of solvents that the Wirtz theory<sup>15</sup> [which gives  $\kappa = [6(r_e/r_0) + (1 + r_e/r_0)^{-3}]^{-1}$ , with  $r_s$  the equivalent of  $r_0$  but for the solvent] predicts very well the value of  $\kappa$  obtained from experiment as above. Since CSL and the phase V molecules are of similar size and shape, let us take  $r_s/r_0 \sim 1$ , which yields  $\kappa \sim 1/6$  or very good agreement considering our rough approximations. It appears, therefore, that our experimental  $\tau_R$  values are of the correct order.

We now consider the possibility that the magnetic axis of the nitroxide radical in DSL is tilted from the symmetry axis of alignment of the molecule by rotation in the  $x$ - $y$  plane of the nitroxide magnetic tensor principal axes.<sup>12,16,18</sup> Luckhurst et al.<sup>16</sup> estimate the tilt (or rotation) angle to be 20°, whereas Hemminga and Berendsen<sup>17b</sup> estimate the angle to be smaller than 15°. We attempted to fit the slow motional spectrum of CSL in phase V at 3 °C by simulations with a tilt angle of 20°. The main effects of the tilt upon the simulated ESR spectrum for CSL in phase V are found to be an increase in the apparent  $g$  value of the calculated spectrum and an increase in the ratio  $a_{10}/a_{0-1}$  (cf. section IV) of the two hyperfine splittings when compared to spectra simulated with no tilt. Best agreement is obtained with a tilt of about 15°. However the simulated spectra were otherwise identical and the calculated  $C/B$  ratio was unaffected. Note that increased values of  $a_{10}/a_{0-1}$  may also result from fluctuating torques and presumably also slowly relaxing local structure,<sup>2</sup> thus we do not believe our result to be conclusive. The effect of tilt was not investigated in the higher temperature nematic spectra, but in the isotropic phase, the effect of a 20° tilt is merely to increase the estimated value of  $N_y$  from 5 to 8.

We have also investigated the effect of rotating the nitroxide magnetic  $z$  axis from its presumed orientation perpendicular to the long molecular axis. This has much more dramatic effect on the spectrum, by increasing the apparent splittings and widths, roughly equivalent to a

TABLE IV: Correlation Times from Slow Motional Simulations and from Subsequent Motional Narrowing Analysis and  $\lambda$  Values from Slow Motional Simulations and from Observed Splittings

Temp, °C	$\tau_R$ , ns, from slow motional theory	$\tau_R$ , ns, from motional narrowing analysis <sup>b</sup>	$\lambda$ from slow motional theory	$\lambda$ from obsd splittings
	0.3 <sup>a</sup>	0.296	0.29	
	0.52 <sup>a</sup>	0.50	1.09	
	0.72 <sup>a</sup>	0.69	1.52	
65	0.9		2.65	2.75
55	1.1	1.4	3.3	3.5
44	1.6	1.56	4.0	4.3
35	2.7	1.08	4.1	4.8
19	9	1	4.5	6.4
3	20	1.2	5.3	7.8
-6	35	1.3	6.0	9.9
-16	100	2.04	6.9	14.0
-26	260		7.6	20.0

<sup>a</sup> These fast  $\tau_R$  values are just to show the agreement between the slow motional and fast motional analyses. They do not correspond to any experimental temperatures for CSL in nematic phase V. <sup>b</sup> The calculated  $\tau_R$  values are from  $B$  coefficients. The  $N_y$  values, calculated from motional narrowing analysis, for some temperatures are given in the caption of Figure 7.

reduction in  $\lambda$ . However, increasing  $\lambda$  does not significantly improve the simulations (since the probe is already so highly ordered that  $\lambda$  can only have a marginal effect on the splittings). Thus we can conclude that this rotation angle is close to zero.

#### IV. Validity of Motional Narrowing Approach and Relation to Other Work

Several studies of the relaxation behavior of CSL in ordered systems have recently been published.<sup>7,16-22</sup> These studies have typically used simple motional narrowing theory for the line width analysis. We have found that the ESR spectrum of phase V at the elevated temperature of 55 °C<sup>23</sup> has asymmetric lines. Also the low-field splitting constant  $a_{1,0}$  (the separation between the low field and the central line) is greater than the high field splitting constant  $a_{0,-1}$  (the separation between the high field line and the central line). These features are usually indicative of the onset of the slow motional region in ESR.<sup>5</sup> Since the value of  $\tau_R$  at +55 °C ( $1.1 \times 10^{-9}$  s) is still quite fast, the observed asymmetries might be largely due to the overlap of the three broadened lines. Such overlap effects (including modified relaxation behavior) are automatically included in the slow motional analysis developed by PBF.<sup>3</sup> In the previous studies on CSL (with the exception of ref 7a, b) no such analysis was attempted. Also, those "simple" motional narrowing studies neglected the frequency dependence of secular and pseudo-secular terms. This is not justified for  $\tau_R > 10^{-9}$  s.

In an effort to determine the range of validity of a motional-narrowing analysis for CSL in ordered fluids, we have performed the following test. We have taken typical simulated slow tumbling spectra using the PBF theory in which  $\tau_R$  ranged from  $3 \times 10^{-10}$  to  $10^{-7}$  s and we measured the line widths of the three lines. Then the fast motional theory (as given by PBF) and the already determined values of  $\lambda$  were utilized to obtain  $\tau_R$ . These values are given in Table IV. One clearly sees that the correlation times obtained from the motional-narrowing theory do not agree with those obtained from the complete slow-motional theory for values of  $\tau_R \gtrsim 2 \times 10^{-9}$  s.<sup>24</sup> To further emphasize the inadequacy of motional-narrowing theory for these

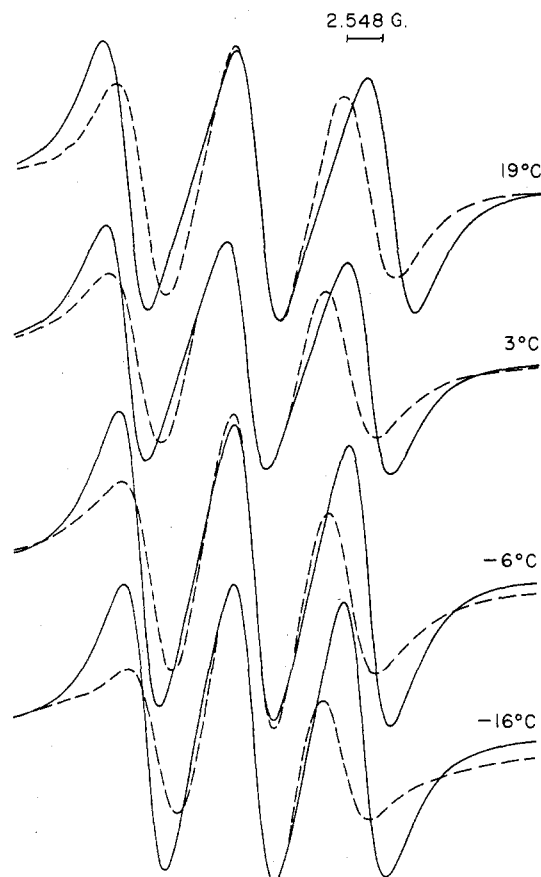


Figure 7. Comparison of experimental and simulated spectra at 19, 3, -6, and at -16 °C for CSL in phase V: (---) experimental result; (—) theoretical result based on anisotropic Brownian diffusion with the values, at +19 °C,  $\tau_R = 1 \times 10^{-9}$ ,  $N = 1.5$ ,  $\lambda = 4.3$ , and  $A' = 2.7$  G; at +3 °C,  $\tau_R = 1.2 \times 10^{-9}$ ,  $N = 1.5$ ,  $\lambda = 5.3$ , and  $A' = 2.7$ ; at -6 °C,  $\tau_R = 1.3 \times 10^{-9}$ ,  $N = 17$ ,  $\lambda = 6.0$ , and  $A' = 2.4$ ; and at -16 °C,  $\tau_R = 2.04 \times 10^{-9}$ ,  $N = 44$ ,  $\lambda = 6.8$ , and  $A' = 2.0$  G.

spectra, we have used the PBF theory to simulate the spectra for 19, 3, -6, and -16 °C, but with the  $\tau_R$  and  $N_y$  values obtained from the motional narrowing analysis. They are compared with the experimental spectra in Figure 7. It is obvious from this figure that the spectra simulated in this way are not at all in agreement with the experimental spectra.

In the usual analysis, appropriate for motional-narrowing spectra, the ordering parameters, hence  $\lambda$ , are obtained from the spectral line position shifts. We have also checked this approach for the CSL spectra by comparing the values of  $\lambda$  obtained in this simple manner with the values found from the complete simulations employing the PBF theory. They are also given in Table IV, and one can see that the two  $\lambda$  values do not agree except for  $T \gtrsim 65$  °C. Hence it is not justified to use the values of the order parameter calculated from the splittings for CSL in phase V. From the analysis of the  $\tau_R$  and  $\lambda$  values given above, it appears that the simple motional narrowing theory should not be used for the analysis of CSL in phase V over most of the accessible temperature range.

Luckhurst et al.<sup>16b</sup> have studied CSL in a smectic A liquid crystal. They calculated  $\langle P_4 \rangle$  (the average of the fourth rank Legendre polynomial) using the strong jump model. In the strong jump diffusion model, the spectral densities may be shown to depend<sup>16,25</sup> explicitly on  $\langle P_4 \rangle$  in the motional narrowing region. However, one must be careful that the molecular dynamics, which can be complex,<sup>24,11b</sup> is treated correctly. No temperature dependence of the system has been reported. This study also neglects



the effect of the inhomogeneous broadening on the  $B$  and  $C$  coefficients. The calculated values of  $\tau_{R\perp}$  are  $1.4 \times 10^{-8}$  from  $B$  and  $3.0 \times 10^{-8}$  from  $C$ . These  $\tau_R$  values are, as we have seen, too large for motional narrowing theory to be valid.

Luckhurst and Poupko<sup>19</sup> have studied the CSL in phase IV. They have again used the motional narrowing theory to estimate the ordering term  $\langle P_4 \rangle$ . The observed line shape asymmetry was attributed by these authors to a spread in director orientations due to thermal fluctuations. Also the calculated value of anisotropy in rotation depended on temperature ranging from  $N = 16.7$  to  $7.6$  as the temperature decreased. These features are most likely indications of slow motional effects. Their calculated values of  $\tau_{R\perp}$  are  $1.6 \times 10^{-9}$  at  $70^\circ\text{C}$ ,  $2 \times 10^{-9}$  at  $49^\circ\text{C}$ , and  $7 \times 10^{-9}$  at  $23^\circ\text{C}$ . Hence, at the lower temperatures one is not justified in using motional narrowing theory. This study also neglects the effect of ordering on the unresolved proton splitting.

Luckhurst and Yeates<sup>22</sup> have recently reported ESR studies of CSL in phase V along with other mesogens. They studied the angular dependence of the line width coefficients, by aligning the nematic phase using a strong electric field, to get the value of  $\langle P_4 \rangle$ . The  $\lambda$  value calculated from the value of  $\langle P_2 \rangle \equiv \langle D_{00}^2 \rangle$  given at  $34^\circ\text{C}$  is  $4.7$  which very nearly agrees with our value of  $4.8$  at  $35^\circ\text{C}$  given in Table V based on the motional-narrowing analysis. However, the spectrum at  $35^\circ\text{C}$  can be correctly simulated by a complete analysis only with a value of  $4.1$ . Hence, it is not justified to use the  $\langle P_2 \rangle$  value calculated from the splittings. This study also neglected the effect of ordering on the proton splitting constant (hence on the inhomogeneous broadening) and its dependence on the angle between the director and the magnetic axis. Here also, the calculated rotational anisotropy,  $N$ , appeared to vary with temperature. The reported  $\tau_{R\perp}$  values are at  $34^\circ\text{C}$ ,  $4.4 \times 10^{-9}$  from  $B$ ,  $6.8 \times 10^{-9}$  from  $C$  and at  $21^\circ\text{C}$ ,  $6.3 \times 10^{-9}$  from  $B$ , and  $1.26 \times 10^{-8}$  from  $C$ . These  $\tau_{R\perp}$  values are again too long for the motional narrowing theory to be applicable (cf. Table IV), and for meaningful values of  $N$  to be obtained.

Hemminga<sup>17a</sup> has included the angular dependence of the proton splitting constant in his corrections for inhomogeneous broadening. He obtained a value of  $N = \tau_{R\perp}/\tau_{R\parallel} = 40$  with  $\tau_{R\perp} = 4.6 \times 10^{-8}$  for CSL in lecithin:cholesterol model membrane system using a motional narrowing analysis. Again this motion is too slow for motional narrowing theory to be valid. Also at these long  $\tau_R$  values, the simulated spectra using slow motional analysis are rather insensitive to changes in the value of  $N$  especially when  $N$  is large. Hence it is not possible to obtain accurate values of  $N$ .

Pusnik et al.<sup>20</sup> and Pusnik and Schara<sup>21</sup> have also studied CSL in the nematic and in smectic A and B phases of a mesogen. They also used motional narrowing theory to estimate the value of  $\langle P_4 \rangle$ , but they estimate  $\tau_{\perp} \geq 10^{-8}$  s which is clearly too slow for motional narrowing theory to be valid. Also, they have not included the effects of unresolved proton splittings.

Schindler and Seelig<sup>18b</sup> studied CSL in a liquid-crystalline bilayer at  $24^\circ\text{C}$ . They report  $N_y = 5.5$  and  $\tau_{R\perp} = 1.2 \times 10^{-9}$ . The motional narrowing approximation should be valid for this system.

## V. Conclusions

It has been possible to simulate slow tumbling spectra using the PBF theory that are in good agreement with experimental spectra obtained with CSL in phase V solvent. Rather good and consistent results are obtained

particularly for the reduced temperatures, where  $\tau_R > 5 \times 10^{-9}$  s, since the effects of inhomogeneous broadening due to proton superhyperfine structure as well as fluctuations in director magnitude and/or direction should be relatively less important. Our best fits were obtained with a single parameter ordering potential, no tilt of the magnetic  $z$  axis, and a somewhat anisotropic  $\tau_R$  with an activation energy of  $10.9$  kcal/mol, almost in agreement with the activation energy obtained from the accurate study of PD-Tempone probe in the same solvent. These spectral fits were fairly insensitive to various model-dependent features such as anisotropy in rotation (except for the higher temperatures upon which our assignment of  $N_y \approx 3-4$  is based), deviations from Brownian motion, and tilt of the magnetic axes in the  $x-y$  plane relative to the molecular ordering axes. However, it appears that if such features are existent, then they are probably not very prominent in most of our cases. It was shown that for CSL in phase V a motional narrowing analysis is inadequate for obtaining accurate values of ordering parameter  $\lambda$  and  $\tau_R$  over most of the nematic range, so the complete PBF theory is needed. Recent results using CSL probes in other studies on ordered fluids have typically not faced up to this necessity.

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## References and Notes

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values of  $\tau_R \lesssim 10^{-9}$  s for all temperatures and the mean value of  $N$ , was 0.4 for Brownian diffusion. For strong jump diffusion, we could not get any meaningful solutions for  $\tau_{R\perp}$  or  $N$ .  
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## An Electron Spin-Lattice Relaxation Mechanism Involving Tunneling Modes for Trapped Radicals in Glassy Matrices. Theoretical Development and Application to Trapped Electrons in $\gamma$ -Irradiated Ethanol Glasses

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A new electron spin-lattice relaxation mechanism for molecular radicals in glassy matrices is developed theoretically and tested experimentally. The mechanism depends on modulation of the electron nuclear dipolar interaction between a trapped radical and nearby magnetic nuclei by the motion of tunneling nuclei or groups of nuclei in the disordered glass. In glassy systems it appears that modulation by tunneling modes is much more effective than modulation by lattice phonons for electron spin-lattice relaxation in low and intermediate temperature ranges, typically to  $\sim 100$  K. The quantitative mechanism predicts: (a) that the spin-lattice relaxation rate  $T_1^{-1}$  is linearly proportional to temperature, (b) that  $T_1^{-1}$  is dependent on glass preparation to the extent that this affects the number and distribution of tunneling groups, (c) that  $T_1^{-1}$  is sensitive to the isotopic composition of the glass, (d) that  $T_1^{-1}$  for a given radical is larger by several orders of magnitude in a glassy environment than in a crystalline one, and (e) that  $T_1^{-1} \propto \omega^{-2}$  where  $\omega$  is the EPR frequency. Predictions (a) to (d) have been tested and supported by  $T_1$  measurements vs. temperature on trapped electrons in  $C_2H_5OH$ ,  $C_2D_5OH$ , and  $C_2H_5OD$  glasses. The measurements were made with a pulsed EPR spectrometer by the saturation recovery technique.

### I. Introduction

The electron spin-lattice relaxation of transition metal ions and rare earth metal ions in ionic crystals has been extensively studied in the past 45 years since Waller's original paper on spin-lattice relaxation in 1932.<sup>1</sup> As a result, nearly all the spin-lattice relaxation mechanisms that have been investigated both experimentally and theoretically are constrained by the conditions found in these systems. That is, strong crystalline fields and spin-orbit coupling are assumed for the ion in the crystal and the dynamics of the lattice is described in terms of the Debye model with only few modifications for the effects of phonon lifetime and crystal defects.<sup>2</sup>

The study of the spin-lattice relaxation of molecular radicals in molecular crystals and glasses is still in its infancy. The first report of the temperature dependence of the spin-lattice relaxation of an organic radical was made in 1957.<sup>3</sup> The spin-lattice relaxation time ( $T_1$ ) was measured at four temperatures between 1.2 and 300 K and no attempt was made to explain either the magnitude of  $T_1$ , which was many orders of magnitude longer than that of transition metal ions, or the spin-lattice relaxation mechanisms involved. Nine years later, three surveys of different classes of radicals (organic, organosulfur, and peroxy) were reported.<sup>4-6</sup> Over the limited range of temperature in these studies,  $T_1$  was proportional to  $T^{-n}$  where  $n$  varied from 1 to 3. More importantly, for determining the relaxation mechanism, the spin-lattice relaxation rates in each study were found to be highly correlated with the square of the  $g$  factor deviation from

the free electron value of 2.0023 and hence with spin-orbit coupling. This suggested that the Kronig-VanVleck spin-lattice relaxation mechanism was important. Other studies have supported this.<sup>7,8</sup> The internal motions and hindered rotations of a molecular radical have also been suggested as an important relaxation mechanism.<sup>9-12</sup>

At this same time, careful studies of the spin-lattice relaxation mechanisms of F centers (trapped electrons) in alkali halide crystals have shown that the electron nuclear dipolar (END) and isotropic hyperfine interactions between the unpaired electron and its surrounding magnetic nuclei can make important contributions to the electron relaxation.<sup>13,14</sup>

An extensive study of the spin-lattice relaxation of a number of hydro-, deuterio-, and fluorocarbon radicals produced by ionizing radiation in single crystals of the parent compound has been made by Dalton, Kwiram, and Cowen.<sup>15,16</sup> They report that the Kronig-VanVleck relaxation mechanism is responsible for the spin-lattice relaxation of all but the fluorinated radicals. The spin-lattice relaxation of the fluorinated radicals is dominated by modulation of the END interaction. In addition, they report observing an Orbach-like process in some of the samples in which the intermediate state is suggested to be an excited vibrational state of the radical instead of an excited electronic state as in the usual Orbach process.

Although these studies have demonstrated several important relaxation mechanisms for molecular radicals in single crystals, they by no means include all the dominant mechanisms in molecular glasses. DPPH in polystyrene has been the subject of two spin-lattice relaxation studies.<sup>17,18</sup> Between 1 and 300 K, the relaxation rate is proportional to the temperature. This is a surprising

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