

# ESR line shapes in the slow-motional region: Anisotropic liquids\*

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It is shown how the analysis of Freed *et al.* for ESR lineshapes in the slow tumbling region may be generalized to include anisotropic liquids. Particular emphasis is given to the case of nitroxide radicals in liquid crystal environments with cylindrically symmetric restoring potentials  $U(\beta)$ . It is found that when  $|U(\beta)| \lesssim kT$ , spectral appearances are qualitatively (but not quantitatively) similar to those for isotropic liquids. In particular, the spectra are sensitive to the model of reorientation. They are also predicted to be a very sensitive indicator of effects of anisotropic viscosity. The analysis given for the motional narrowing region yields analytic expressions for the needed spectral densities, where previously only numerical results had been obtained. The analytic expressions are valid when  $|U(\beta)| \lesssim kT$ . Analytic solutions to the rotational diffusion equation appropriate for  $|U(\beta)| \gg kT$  are given and it is outlined how they may be applied to magnetic resonance.

## I. INTRODUCTION

In the earlier papers in this series<sup>1-4</sup> we have developed a detailed theoretical analysis of ESR spectra in the slow tumbling region. This is the region where conventional relaxation theory does not apply. That is,  $|\mathcal{H}_1(t)| \tau_R \gtrsim 1$ , where  $\mathcal{H}_1(t)$  is the rotational-dependent perturbation in the spin Hamiltonian and  $\tau_R$  is the rotational correlation time. In II (Ref. 2) we have compared experimental results on the "nitroxide" peroxylamine disulfonate with the theoretical predictions and were able to obtain generally good agreement. More interesting, perhaps, was the demonstration that slow tumbling studies with nitroxides could effectively distinguish between models of molecular reorientation (e.g., jump diffusion vs simple Brownian motion).

There has, over the past several years, been considerable interest in the ESR of paramagnetic probes doped in liquid crystals,<sup>4,5</sup> since the probes may be effectively utilized to study the microscopic structure and properties of the liquid crystal in a number of cases.<sup>4,5</sup> A theory of ESR linewidths for liquid crystals was given in some detail by Glarum and Marshall,<sup>6</sup> who assumed a simple single exponential decay constant for the rotational motion, which is formally equivalent to a "strong collision" model.<sup>5a</sup> More recently, Nordio *et al.*<sup>7,8</sup> have developed a detailed analysis of ESR linewidths based on numerical solutions of the rotational diffusion equation with cylindrically symmetric restoring potentials. These theories have been conventional in the sense that the motional narrowing condition  $|\mathcal{H}_1(\Omega)| \tau_R \ll 1$  has been assumed to hold. However, in a number of laboratories,<sup>4,5,9</sup> slow tumbling ESR spectra have been obtained when viscous liquid crystals were utilized.

In view of the potentially interesting information one may hope to obtain about the molecular dynamics of a probe from such viscous liquid-crystal spectra, we thought it worthwhile to extend our theoretical analysis<sup>1-3</sup> of slow tumbling in isotropic liquids to include the anisotropic liquid case. This has permitted us to explore the kinds of results and information such stud-

ies might yield. The method we employ is a synthesis of our previous analysis<sup>1-4</sup> with those of Nordio *et al.*<sup>7,8</sup> This synthesis is conveniently obtained because both methods rely on eigenfunction expansions. We have, however, found that considerable simplifications of

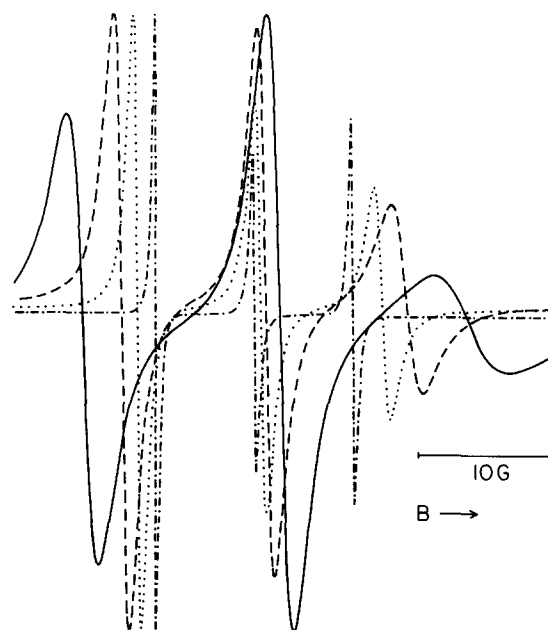


FIG. 1. First derivative line shapes for an axially symmetric nitroxide as function of  $\lambda_2$  ( $\lambda_4=0$ ) for Brownian diffusion. The different  $\lambda_2$  values are  $0$ ;  $---$   $-2.0$ ;  $\cdots$   $-3.5$ ;  $- \cdot -$   $-7.5$  with intensity factors of 11, 30, 96, and 956, respectively. All correspond to  $\tau_R=1.84 \times 10^{-9}$ ,  $g_{||}=2.0027$ ,  $g_{\perp}=2.0075$ ,  $A_{||}=33.4$  G,  $A_{\perp}=5.42$  G,  $(2/3^{1/2})T_2^{-1}/|\gamma_e|=0.1$  G, and are centered about  $B_0=3250$  G.

Nordio and Busolin's methods could conveniently be achieved, and we therefore discuss aspects of the motional narrowing theory from this point of view. Our slow tumbling results are developed for nitroxides in extension of our earlier work.<sup>1-3</sup> The availability of a

great variety of nitroxide spin labels of different shapes makes them potentially very useful for probing the structure and dynamics of liquid crystals.<sup>4,5,7-9</sup> Also, their spectra are simple enough to permit rigorous analysis even in the slow tumbling region.

The slow tumbling theoretical method is developed for anisotropic liquids in Sec. II and typical results are discussed in Sec. III. Our analysis of aspects of the motional narrowing region is given in Sec. IV including

perturbation results for the case when the restoring potential is comparable to or less than  $kT$ . A summary appears in Sec. V. The perturbation scheme for dealing with nonsecular terms, in particular nonsecular dynamic frequency shifts, for slow-motional spectra appears in Appendix A. Solutions to the diffusion equation in the presence of very strong axial restoring potentials appear in Appendix B with an outline of how they may be utilized for magnetic resonance spectra.

## II. THEORETICAL METHODS: ANISOTROPIC LIQUIDS

### A. Stochastic Liouville Equation

We start with the Stochastic Liouville equation of motion for the spin-density matrix<sup>1,4</sup>:

$$(\partial/\partial t)\rho(\Omega, t) = [-i\mathcal{H}(\Omega)^\times - \Gamma_\Omega]\rho(\Omega, t) \quad (2.1a)$$

with

$$\Gamma_\Omega P_0(\Omega) = 0, \quad (2.1b)$$

where  $\mathcal{H}(\Omega)^\times$  is the superoperator of the orientation-dependent spin Hamiltonian and  $\Gamma_\Omega$  is a Markoffian operator for the rotational reorientation of the molecule, with  $\Omega$  representing the orientational angles. Also  $P_0(\Omega)$  is the unique equilibrium probability distribution of  $\Gamma_\Omega$ . The unsaturated absorption of the  $\lambda_j$ th transition is obtained from  $\text{Im}\bar{Z}_{\lambda_j}$ , where<sup>1</sup>

$$\bar{Z}(\omega)_{\lambda_j} = \int d\Omega Z_{\lambda_j}(\Omega, \omega) P_0(\Omega) \quad (2.2)$$

and

$$\rho(\Omega, t)_{\lambda_j} = e^{i\omega t} Z(\Omega, \omega)_{\lambda_j}. \quad (2.3)$$

That is,  $Z(\Omega, \omega)_{\lambda_j}$  is the steady-state solution of  $\rho(\Omega, t)$  for the  $\lambda_j$ th transition and is time independent in the frame rotating with impressed frequency  $\omega$ . Also,  $\bar{Z}(\omega)_{\lambda_j}$  is the equilibrium average over all orientations  $\Omega$ . Substitution of Eq. (2.3) into Eq. (2.1a) leads, for the case of no saturation, to<sup>1</sup>

$$\{[\omega + \mathcal{H}_0^\times + \mathcal{H}_1(\Omega)^\times - i\Gamma_\Omega]Z(\Omega, \omega)\}_{\lambda_j} = \frac{1}{2}\omega_1[S_-^\times \rho_0]_{\lambda_j}, \quad (2.4)$$

where  $\mathcal{H}_0$  is the orientation-independent part of  $\mathcal{H}(\Omega)$ ,  $\mathcal{H}_1(\Omega)$  is the perturbing orientation-dependent part, while  $\omega_1 = \gamma_e B_1$  with  $B_1$  the strength of the applied microwave field. The averaging of Eq. (2.4) to obtain an expression for  $\bar{Z}(\omega)$  must follow the prescription of the first *post* multiplying Eq. (2.4) by  $P_0(\Omega)$  and then integrating over all  $\Omega$ .<sup>4</sup>

One generally expands  $Z(\Omega, \omega)_{\lambda_j}$  in a complete orthonormal set of eigenfunctions (when available) of  $\Gamma_\Omega$  to solve Eq. (2.4). However, when  $P_0(\Omega) \neq \text{const}$ , i.e., an anisotropic liquid, it is usually more convenient to define

$$\bar{Z}(\Omega, \omega) \equiv P_0^{-1/2}(\Omega) Z(\Omega, \omega) \quad (2.5)$$

and then expand the  $\bar{Z}(\Omega, \omega)$  in eigenfunctions of

$$\bar{\Gamma}_\Omega = P_0^{-1/2}(\Omega) \Gamma_\Omega P_0^{1/2}(\Omega), \quad (2.6a)$$

where [from Eq. (2.1b)]

$$\bar{\Gamma}_\Omega P_0^{1/2}(\Omega) = 0. \quad (2.6b)$$

Equation (2.6a) may be regarded as a "symmetrizing" transformation, since it transforms the non-Hermitian operator  $\Gamma_\Omega$  (i.e., its matrix representation in an appropriate basis is a Hermitian matrix) into the Hermitian operator  $\bar{\Gamma}_\Omega$  whose right- and left-hand eigenvectors are just complex conjugates.

One may then transform Eq. (2.1a) to be

$$(\partial/\partial t)\bar{\rho}(\Omega, t) = [-i\mathcal{H}(\Omega)^\times - \bar{\Gamma}_\Omega]\bar{\rho}(\Omega, t), \quad (2.7)$$

where

$$\bar{\rho}(\Omega, t) = P_0^{-1/2}(\Omega)\rho(\Omega, t) \quad (2.8)$$

and the equivalent of (2.4) becomes<sup>1</sup>

$$\{[\omega + \mathcal{H}_0^\times + \mathcal{H}_1(\Omega)^\times - i\bar{\Gamma}_\Omega]\bar{Z}(\Omega, \omega)\}_{\lambda_j} = (\omega_1/2) P_0^{-1/2}(\Omega) [S_-^\times \rho_0]_{\lambda_j}. \quad (2.9)$$

Then the matrix elements of  $\tilde{Z}(\Omega, \omega)_{\lambda_i}$  for the relevant transitions may be expanded in complete sets of orthonormal basis functions  $G_m(\Omega)$  as

$$\tilde{Z}(\Omega, \omega)_{\lambda_i} = \sum_m [C_m(\omega)]_{\lambda_i} G_m(\Omega) \tag{2.10}$$

and from Eq. (2.2) we have

$$\bar{Z}(\omega)_{\lambda_i} = \int d\Omega \tilde{Z}_{\lambda_i}(\Omega, \omega) P_0^{1/2}(\Omega). \tag{2.11}$$

Equation (2.11), utilizing Eq. (2.10), may be written as

$$\bar{Z}(\omega)_{\lambda_i} = \sum_m \langle G_m(\Omega) | P_0^{1/2}(\Omega) \rangle [C_m(\omega)]_{\lambda_i}, \tag{2.12}$$

where we have introduced a "matrix-element" formalism, e.g., for an orientation-dependent operator  $O(\Omega)$

$$\langle G_m(\Omega) | O(\Omega) | G_n(\Omega) \rangle \equiv \int G_m^*(\Omega) O(\Omega) G_n(\Omega) d\Omega; \tag{2.13}$$

while, from Eq. (2.9), we have<sup>1</sup>

$$[\omega - \omega_{\lambda_i}] [C_m(\omega)]_{\lambda_i} + \sum_{m'} \langle G_m(\Omega) | [\mathfrak{H}_1(\Omega) \times C_{m'}(\omega)]_{\lambda_i} - i \tilde{\Gamma}_\Omega [C_{m'}(\omega)]_{\lambda_i} | G_{m'}(\Omega) \rangle = q\omega_\lambda d_{\lambda_i} \langle G_m(\Omega) | P_0^{1/2}(\Omega) \rangle. \tag{2.14}$$

When the  $G_m(\Omega)$  are eigenfunctions of  $\tilde{\Gamma}_\Omega$  with eigenvalues  $E_m$ , then

$$P_0^{1/2}(\Omega) \equiv G_0(\Omega) \tag{2.15}$$

and Eqs. (2.12) and (2.14) become

$$\bar{Z}(\omega)_{\lambda_i} = [C_0(\omega)]_{\lambda_i} \tag{2.12'}$$

and

$$[(\omega - \omega_{\lambda_i}) - iE_m] [C_m(\omega)]_{\lambda_i} + \sum_{m'} \langle G_m(\Omega) | [\mathfrak{H}_1(\Omega) \times C_{m'}(\omega)]_{\lambda_i} | G_{m'}(\Omega) \rangle = d_{\lambda_i} q\omega_\lambda \delta_{m,0}. \tag{2.14'}$$

Equations (2.12') and (2.14') are formally equivalent to the expressions for isotropic liquids<sup>1</sup> and their method of solution is identical. Equations (2.14) or (2.14') may be written in matrix notation as

$$\mathfrak{A}\mathbf{C} = \mathbf{U}, \tag{2.14''}$$

where  $\mathbf{C}$  is a column vector of the coupled coefficients  $[C_m(\omega)]_{\lambda_i}$ ,  $\mathfrak{A}$  is the complex-symmetric matrix defined by the lhs of either Eq. (2.14) or (2.14'),  $\mathbf{U}$  is the column vector representing the rhs of either of these equations and Eq. (2.12) or (2.12') indicates which coefficients are needed for the absorption.

### B. Rotational Diffusion

For the case of rotational reorientation under a cylindrically symmetric restoring potential, one may write for Brownian motion<sup>7,8,10,11</sup>

$$\partial P(\Omega, t) / \partial t = -\Gamma P(\Omega, t) = R \nabla_\Omega^2 P(\Omega, t) - (R/kT) (\sin\beta)^{-1} (\partial/\partial\beta) [\sin\beta P(\Omega, t)], \tag{2.16}$$

where  $R$  is the rotational diffusion coefficient,  $\nabla_\Omega^2$  is the rotational diffusion operator in the Euler angles  $\alpha, \beta, \gamma$ , and  $\mathfrak{J}$  is the restoring torque. When  $\mathfrak{J} = 0$ , Eq. (2.16) is simply the equation for isotropic Brownian rotational diffusion. Note that the angle  $\beta$  is the angle between the molecular  $z$  axis and the director. The two "natural values" for perfect alignment for which the diffusion equation (2.16) is conveniently solved are  $\beta_{\text{eq}} = 0$  or  $\pi/2$ . They correspond, respectively, to prolate (rod) and oblate (disk) symmetric tops.<sup>7,8</sup> It is always possible to transform the magnetic parameters ( $\mathbf{A}$  and  $\mathbf{g}$ ) into the molecular coordinate frame<sup>5,7,8,11</sup> based on  $\beta_{\text{eq}} = 0$  or  $\pi/2$  (whichever is appropriate) when their principal axes do not include the molecular  $z$  axis. In the usual cases, the director axis will be taken to correspond to the laboratory  $z$  axis defined by the applied dc field, but when this is not so, one must apply a further transformation bringing the director axis into coincidence with that of the applied dc field.

That is, in general, we write  $\mathfrak{H}_1(\Omega)$  as (in the notation of Freed and Fraenkel<sup>12,13</sup>)

$$\mathfrak{H}_1(\Omega, \Psi) = \sum_{L, m, m', m'', \mu, i} \mathfrak{D}_{-mm', L}(\Omega) \mathfrak{D}_{m''m', L}(\Psi) F_{\mu, i}{}^{(L, m)} A_{\mu, i}{}^{(L, m')}, \tag{2.17}$$

where the  $F_{\mu, i}{}^{(L, m)}$  and  $A_{\mu, i}{}^{(L, m')}$  are irreducible tensor components of rank  $L$ , with  $F'$  in molecule-fixed coordinates, while  $A$  is a spin operator quantized in the lab axis system. The  $\mathfrak{D}_{m'', m'}{}^{(L)}(\Psi)$  terms then include the transformation which takes the lab  $z$  axis into the director axis and is specified by only two angles, while the  $\mathfrak{D}_{-m, m'}{}^{(L)}(\Omega)$  include the transformation from the axis system including the director, to an appropriate molecule-fixed axis (i.e., one for which  $\beta_{\text{eq}} = 0$  or  $\pi/2$ ). Equation (2.16) describes the motion of the  $\Omega$ , i.e., that of the mole-

cule relative to the director; while, if needed, a separate analysis may be given of the director motion relative to the applied dc field (cf. Appendix B).

The simplest restoring potential for a nematic liquid crystal would be of form

$$U \approx \gamma_2 \cos^2 \beta \quad (2.18)$$

although by general symmetry arguments

$$U = \sum_{n=1}^{\infty} \gamma_{2n} \cos^{2n} \beta = \sum_{n=1}^{\infty} \delta_{2n} P_{2n}(\beta), \quad (2.19)$$

where the  $P_{2n}(\beta)$  are Legendre functions. For the simple form, Eq. (2.18), one has

$$\mathfrak{J} = -\partial U / \partial \beta = 2\gamma_2 \sin \beta \cos \beta \quad (2.20)$$

and Eq. (2.16) becomes

$$\partial P(\Omega, t) / \partial t = R \nabla_{\Omega}^2 P(\Omega, t) + 2\lambda_2 R [\cos \beta \sin \beta [\partial P(\Omega, t) / \partial \beta] + (3 \cos^2 \beta - 1) P(\Omega, t)], \quad (2.21)$$

where  $\lambda_2 = -\gamma_2 / kT$ . The equilibrium distribution  $P_0(\Omega)$  is given by

$$P_0(\Omega) = (1/4\pi^2) P_0(\beta) = \exp(\lambda_2 \cos^2 \beta) / 4\pi^2 \int d\beta \sin \beta \exp(\lambda_2 \cos^2 \beta). \quad (2.22a)$$

The order parameter  $\langle P_2(\beta) \rangle$  is just

$$\langle P_2(\beta) \rangle = \int d\Omega P_0(\Omega) P_2(\beta). \quad (2.22b)$$

Note that for  $\beta_{\text{eq}} = 0$ , one requires  $\lambda_2 > 0$  from Eq. (2.22a), while for  $\beta_{\text{eq}} = \pi/2$  one has  $\lambda_2 < 0$ . The symmetrizing transformation, Eq. (2.6), leads to

$$-R^{-1} \tilde{\Gamma}_{\Omega} = \nabla_{\Omega}^2 + \lambda_2 f(\lambda_2, x), \quad (2.23a)$$

where

$$\begin{aligned} f(\lambda_2, x) &= [-1 + x^2(3 - \lambda_2) + \lambda_2 x^4] \\ &= \{ -(2/15)\lambda_2 \mathfrak{D}_{0,0}^0(\Omega) + [2 - (2/21)\lambda_2] \mathfrak{D}_{0,0}^2(\Omega) + (8/35)\lambda_2 \mathfrak{D}_{0,0}^4(\Omega) \} \end{aligned} \quad (2.23b)$$

and  $x = \cos \beta$ . The eigenfunctions of  $\tilde{\Gamma}_{\Omega}$  for  $\lambda_2 = 0$  are the normalized generalized spherical harmonics [or Wigner rotation matrices:  $N_L^{-1/2} \mathfrak{D}_{KM}^L(\Omega)$ , where  $N_L = 8\pi^2 / (2L+1)$ ]. One may use them as a convenient orthonormal basis set for anisotropic liquids,<sup>7,8</sup> where now the term in  $\lambda_2$  in Eq. (2.23a) will lead to off-diagonal "matrix elements" between the  $N_L^{-1/2} \mathfrak{D}_{KM}^L(\Omega)$  of different  $L$  values. That is, the eigenfunctions of  $\tilde{\Gamma}_{\Omega}$  now become linear combinations of the  $N_L^{-1/2} \mathfrak{D}_{KM}^L(\Omega)$ . When  $|\lambda_2| < 1$ , one may utilize simple perturbation theory, since  $\tilde{\Gamma}_{\Omega}$  is a symmetric operator, (cf. Sec. IV). When  $|\lambda_2| \gg 1$ , Eq. (2.23a) may be transformed to simple forms equivalent to a damped oscillator in angular coordinates, and this limiting case is discussed in Appendix B.

One may proceed to solve Eqs. (2.12) and (2.14') in the format of Eq. (2.14'') in either of two ways. One may first diagonalize  $\tilde{\Gamma}_{\Omega}$  in the O.N. basis set of  $N_L^{-1/2} \mathfrak{D}_{KM}^L(\Omega)$  to obtain the eigenfunctions (appropriate for cylindrically symmetric restoring potentials)

$$G_{KM}^n(\Omega) = \sum_L a_{KM}^{nL} \mathfrak{D}_{KM}^L(\Omega) / N_L^{1/2} \quad (2.24a)$$

with

$$a_{KM}^{nL} = \langle \mathfrak{D}_{KM}^L(\Omega) / N_L^{1/2} | G_{KM}^n(\Omega) \rangle \quad (2.24b)$$

and then apply Eqs. (2.12') and (2.14') in terms of these eigenfunctions. We have found it somewhat more convenient for computer simulation to simultaneously diagonalize the terms in  $\mathfrak{H}_1(\Omega) \times$  and  $\tilde{\Gamma}_{\Omega}$  in Eq. (2.14) utilizing as our basis set just  $G_m(\Omega) \rightarrow \mathfrak{D}_{KM}^L(\Omega) / N_L^{1/2}$ . Then the spectrum is just determined from Eq. (2.12).

We now note two useful variants of Eq. (2.23a): (1) For axially symmetric rotational diffusion we have,<sup>7,8,10,13</sup> in symmetrical form,

$$\tilde{\Gamma}_{\Omega} \mathfrak{D}_{KM}^L = \{ R_{\perp} L(L+1) + (R_{\parallel} - R_{\perp}) K^2 - R_{\perp} \lambda_2 f(\lambda_2, x) \} \mathfrak{D}_{KM}^L \quad (2.25)$$

while (2) for anisotropic viscosity referred to the laboratory frame or director axis<sup>10,14</sup>

$$\tilde{\Gamma}_{\Omega} \mathfrak{D}_{KM}^L(\Omega) = \{ \hat{R}_{\perp} L(L+1) + (\hat{R}_{\parallel} - \hat{R}_{\perp}) M^2 - \hat{R}_{\perp} \lambda_2 f(\lambda_2, x) \} \mathfrak{D}_{KM}^L(\Omega). \quad (2.26)$$

The combination of anisotropic rotational diffusion and anisotropic viscosity is extremely complex and does not appear to be solved. It follows from Eq. (2.25) that the term in Eq. (2.14) in  $\tilde{\Gamma}_{\Omega}$  becomes

$$\langle \mathfrak{D}_{KM}^L | \tilde{\Gamma}_{\Omega} | \mathfrak{D}_{K'M'}^{L'} \rangle = \{ [R_{\perp} L(L+1) + (R_{\parallel} - R_{\perp}) K^2] \delta_{L,L'} - R_{\perp} \lambda_2 \langle \mathfrak{D}_{KM}^L | f_2(\lambda_2, \cos \beta) | \mathfrak{D}_{K'M'}^{L'} \rangle \} \delta_{KK'} \delta_{MM'} \quad (2.27)$$

with a similar expression from Eq. (2.26). It thus follows that computer programs written for isotropic liquids are easily modified by (1) adding the contributions from  $\lambda_2 f(\lambda_2, x)$  in Eq. (2.27) to the matrix  $\mathbf{G}$  in Eq. (2.14''); and (2) utilizing the integrals  $\langle \mathfrak{D}_{0,0}^L/N_{L^{1/2}} | P_0^{1/2}(\Omega) \rangle$  in their appropriate places in Eqs. (2.12) and (2.14). Thus the (symmetrized)<sup>15</sup> form of the equations for isotropic liquids given in I and II are easily modified for anisotropic liquids by adding to each (symmetrized) equation on the lhs [cf. Eqs. (A1)–(A6) of II]

$$\begin{aligned}
 & -i\frac{2}{15}R\lambda_2^2 C_{K,M}^L(j) + i2R\lambda_2(1-\lambda_2/21)(2L+1)^{1/2} \\
 & \quad \times \sum_{L'} (2L'+1)^{1/2} (-1)^{K-M} \begin{pmatrix} L & 2 & L' \\ -M & 0 & M \end{pmatrix} \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} C_{K,M}^{L'}(j) \\
 & \quad + i\frac{8}{35}R\lambda_2^2(2L+1)^{1/2} \sum_{L'} (2L'+1)^{1/2} (-1)^{K-M} \begin{pmatrix} L & 4 & L' \\ -M & 0 & M \end{pmatrix} \begin{pmatrix} L & 4 & L' \\ -K & 0 & K \end{pmatrix} C_{K,M}^{L'}(j) \quad (2.28)
 \end{aligned}$$

and by changing the rhs side of each equation to be

$$\delta_{K,0} \delta_{M,0} [(2L+1)^{1/2}/I_0] \int_{-1}^1 \mathfrak{D}_{0,0}^L(0, \beta, 0) \exp(-U(x)/2kT) dx \quad (2.29)$$

with

$$I_0 = \int_{-1}^1 \exp\left(\frac{-U(x)}{2kT}\right) dx.$$

Then, for a nitroxide Eq. (2.12) becomes

$$\sum_j \bar{Z}(\omega)_j = I_0^{-1} \sum_{j=1}^3 \sum_{L \text{ even}} (2L+1)^{1/2} \left( \int_{-1}^1 \mathfrak{D}_{0,0}^L(0, \beta, 0) \exp\frac{1}{2}(x^2\lambda_2) dx \right) C_{0,0}^L(j), \quad (2.30)$$

with the absorption being given by  $\text{Im}\bar{Z}(\omega)_j$  (with  $\bar{Z} = \mathbf{U}^{\text{tr}} \cdot \mathbf{C}$ ).

The possibility that higher order terms in the expansion of  $U$  given by Eq. (2.19) has been considered by Luckhurst,<sup>5</sup> who found it useful to let

$$U \cong \gamma_2 \cos^2\beta + \gamma_4 \cos^4\beta. \quad (2.31)$$

The diffusion equation (2.21) then becomes

$$R^{-1}(\partial/\partial t)P(\Omega, t) = \nabla_{\Omega}^2 P(\Omega, t) + 2[\lambda_2(3 \cos^2\beta - 1) + 2\lambda_4 \cos^2\beta(5 \cos^2\beta - 3) + \cos\beta \sin\beta(\lambda_2 + 2\lambda_4 \cos^2\beta)](\partial/\partial\beta)P(\Omega, t), \quad (2.32)$$

where  $\lambda_4 = -\gamma_4/kT$ . Then  $\bar{\Gamma}_{\Omega} = P_0^{-1/2}(\Omega, U) \Gamma_{\Omega} P_0^{1/2}(\Omega, U)$  becomes

$$-R^{-1}\bar{\Gamma}_{\Omega} = \nabla_{\Omega}^2 + \sum_{m=0}^4 A_{2m} \mathfrak{D}_{0,0}^{2m}(\Omega), \quad (2.33)$$

where

$$A_0 = [-(2/15)\lambda_2^2 - (8/63)\lambda_4^2 - (8/35)\lambda_2\lambda_4], \quad (2.34a)$$

$$A_2 = [2\lambda_2(1-\lambda_2/21) + (12/7)\lambda_4 - (8/21)\lambda_2\lambda_4 - (200/693)\lambda_4^2], \quad (2.34b)$$

$$A_4 = [(96/1001)\lambda_4^2 + (128/385)\lambda_2\lambda_4 + (16/7)\lambda_4 + (8/35)\lambda_2^2], \quad (2.34c)$$

$$A_6 = (64/231)\lambda_2\lambda_4 + (832/3465)\lambda_4^2, \quad (2.34d)$$

$$A_8 = (512/6435)\lambda_4^2. \quad (2.34e)$$

Thus the additional terms to be added to the usual (symmetrized) nitroxide equations are just given by [cf. Eq. (2.28)]

$$iR \sum_{m=0}^4 A_{2m} (2L+1)^{1/2} \sum_{L'} (2L'+1)^{1/2} (-1)^{K-M} \begin{pmatrix} L & 2m & L' \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} L & 2m & L' \\ -M & 0 & M \end{pmatrix} C_{K,M}^{L'}(j) \quad (2.35)$$

while the rhs of each equation is still given by Eq. (2.29).

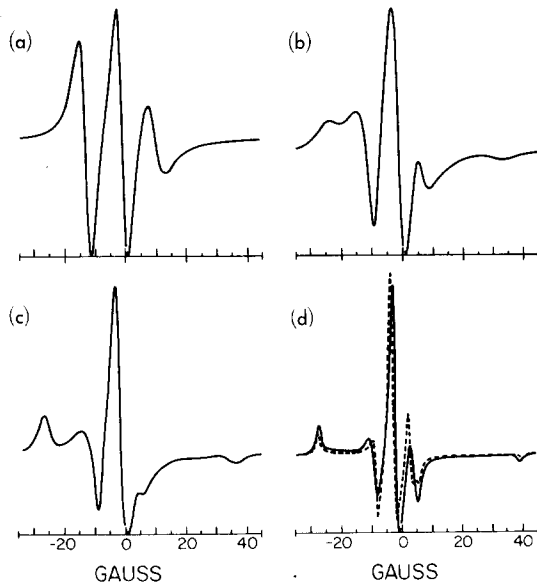


FIG. 2. First derivative line shapes for an axially symmetric nitroxide in the case of low ordering as function of  $\tau_R$  for Brownian diffusion: (a)  $\tau_R=3\times 10^{-9}$  intensity factor (a measure of the relative integrated intensity) is 5.08; (b)  $\tau_R=10^{-8}$ , intensity factor is 3.48; (c)  $\tau_R=3\times 10^{-8}$ , intensity factor is 4.38; (d) —,  $\tau_R=3\times 10^{-7}$ , intensity factor is 10.02; - - - rigid limit. All correspond to  $\lambda_2=-0.975$ ,  $\lambda_4=0$ ,  $g_{||}=2.0024$ ,  $g_{\perp}=2.0078$ ,  $A_{||}=33.75$  G,  $A_{\perp}=5.34$  G,  $(2/3^{1/2})T_2^{-1}/|\gamma_e|=1.0$  G, and centered about  $B_0=3235$  G. Note that all spectra are normalized to the same total height.

### C. Model Dependence

We have so far only considered the case of the Brownian motion limit. The opposite limit of strong collisions that randomize the orientations (subject to a Boltzmann distribution) with each collision may be conveniently obtained by first noting such a process is associated with the conditional probability distribution

$$P(\Omega_0 | \Omega, t) = P_0(\Omega) + [\delta(\Omega - \Omega_0) + P_0(\Omega)] \exp(-t/\tau), \quad (2.36)$$

where  $\tau^{-1}$  is the mean collision frequency. More generally one may write for a Markov process<sup>15</sup>:

$$P(\Omega_0 | \Omega, t) = \exp(-\Gamma_{\Omega} t) \delta(\Omega - \Omega_0), \quad (2.37)$$

where  $\Gamma_{\Omega}$  is the collision operator required in our stochastic-Liouville treatment. A comparison of Eqs. (2.36) and (2.37) with the second representation of  $\delta(\Omega - \Omega_0)$  of Eq. (4.5) yields

$$\Gamma_{\Omega} | u_n \rangle = [1 - \delta_{n,0}] \tau^{-1} | u_n \rangle \quad (2.38a)$$

or from Eq. (2.6)

$$\tilde{\Gamma}_{\Omega} | G_n \rangle = [1 - \delta_{n,0}] \tau^{-1} | G_n \rangle, \quad (2.38b)$$

where the  $| u_n \rangle$  and  $| G_n \rangle$  are the eigenfunctions of  $\Gamma_{\Omega}$  and  $\tilde{\Gamma}_{\Omega}$ , respectively, for the Brownian diffusion case.

Thus we may write

$$\tilde{\Gamma}_{\Omega} = [1 - |G_0\rangle\langle G_0|] \tau^{-1}. \quad (2.38c)$$

It is convenient to set  $\tau^{-1} \equiv R$ . Thus by analogy with model-dependent behavior for isotropic liquids we may more generally write

$$\tilde{\Gamma} | G_{KM}^n(\Omega) \rangle = B(n) E_n | G_{KM}^n(\Omega) \rangle, \quad (2.39)$$

where  $E_n$  is the Brownian diffusion eigenvalue [cf. Eq. (2.23a) after it has been diagonalized] and  $B(n)$  is the "model parameter," which, for strong collisions, is from Eq. (2.38b) just

$$B(n) = R/E_n \quad \text{for } n \neq 0 \quad (2.40)$$

while  $B(n)=1$  for Brownian diffusion. Intermediate jump cases may be obtained (by analogy with the correct isotropic liquid case) by weaker dependences of  $B(n)$  on  $E_n^{-1}$ , i.e., by interpolation between the two limits. Consideration of axially symmetric diffusion [cf. Eqs. (2.23a) and (2.25)] may also be included by analogy to II.<sup>16</sup>

Note that the above interpolation procedure requires first that Eq. (2.23a) or Eq. (2.32) are diagonalized to yield the  $E_n$ . The model parameter  $B(n)$  is then introduced and then the resulting diagonal matrix expressed by Eq. (2.39) is transformed to the  $\mathcal{D}_{KM}^L$  representation, in which the general computer program is written.

### III. RESULTS

Our slow tumbling programs<sup>2,3</sup> modified for anisotropic liquids as discussed in Sec. II have been studied for several cases. We note that running times on an IBM 360/65 computer are comparable to those for isotropic liquids<sup>3</sup> (typically only about 10%-25% longer). Some improvements in the programs have been made by (1) truncating the contributions of the pseudosecular terms for lower  $L$  values than needed for secular terms and (2) truncating the expansions in the "quantum number"  $K$  at a level where  $K < L$  when anisotropies in the magnetic parameters, e.g.,  $(g_x - g_y)$  [expressed in the molecular coordinate system in which the molecular  $z$  axis is the symmetry axis for the (anisotropic) rotational motion] are smaller than the axially symmetric portions of the parameters.

Typical results are shown in Figs. 1-5. Figure 1 shows the effect of varying the order parameter  $|\lambda_2|$  (for negative  $\lambda_2$ , i.e., an oblate top) in the incipient slow-tumbling region<sup>1-3</sup> for a nitroxide; in particular  $\tau_R = 1.84 \times 10^{-9}$  sec [where  $\tau_R \equiv (6R)^{-1}$ ]. One sees that the effect of increasing the orienting potential is (1) to decrease linewidths considerably, and (2) to introduce larger shifts in the positions of the line. (1) is due to the fact that the effective  $[\mathcal{H}_1(t) - \langle \mathcal{H}_1 \rangle]$  is being reduced as the motion is more hindered, while  $\langle \mathcal{H}_1 \rangle$ , the average part of the perturbation, which causes the shifts, departs more from its isotropic value of zero. In

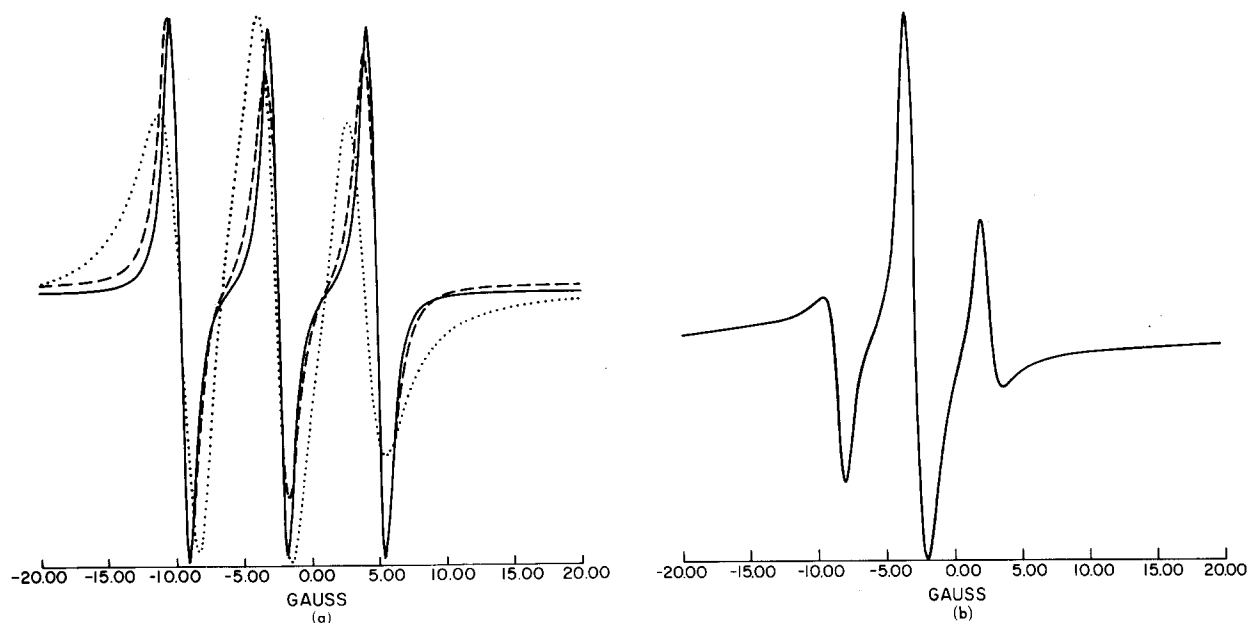


FIG. 3. First derivative line shapes for an axially symmetric nitroxide in a highly ordered case as a function of  $\tau_R$  for Brownian diffusion: (a) —  $\tau_R=3 \times 10^{-10}$ , intensity factor is 77.9; ---  $\tau_R=3 \times 10^{-8}$ , intensity factor is 52.9;  $\cdots$ ,  $\tau_R=3 \times 10^{-6}$ , intensity factor is 16.3; (b) rigid limit. All correspond to  $\lambda_3 = -7.5$ ,  $\lambda_4 = 0$ . All other parameters as in Fig. 2. Again all spectra are normalized to the same total height.

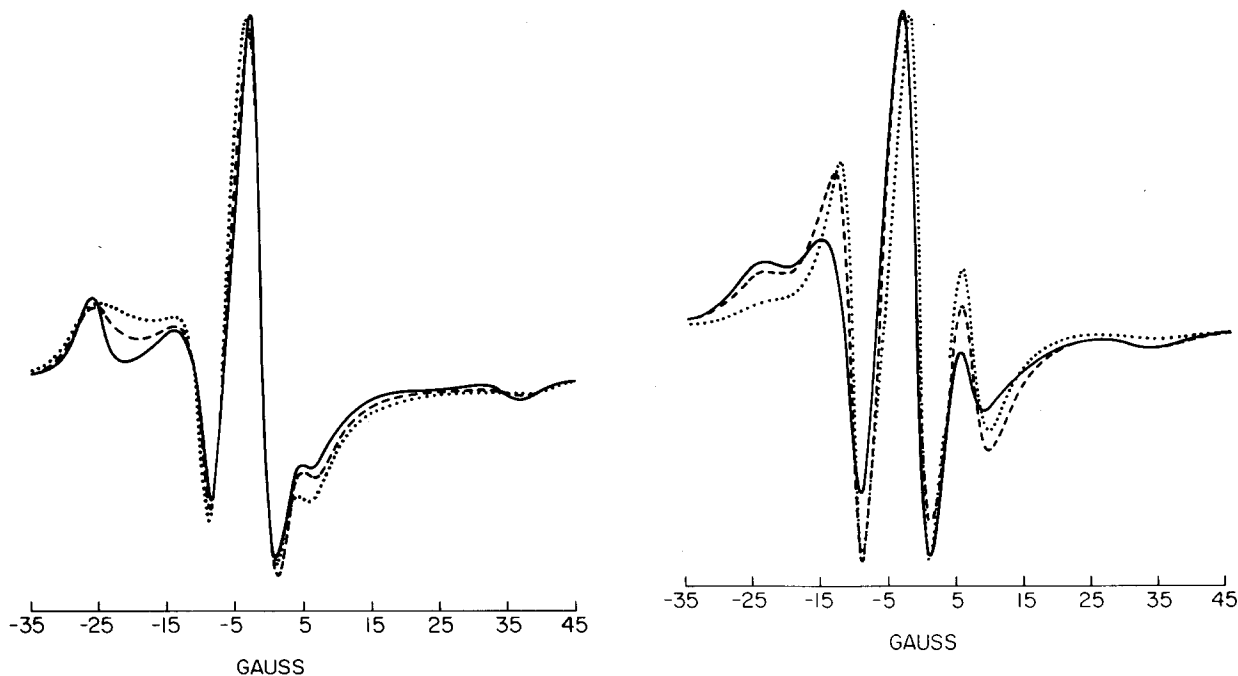


FIG. 4. A comparison of first derivative line shapes for different rotational models. — Brownian diffusion,  $\tau_R=3 \times 10^{-8}$ , intensity factor is 4.38; --- free diffusion,  $\tau_R=1.92 \times 10^{-8}$ , intensity factor is 3.61;  $\cdots$  jump diffusion,  $\tau_R=1.43 \times 10^{-8}$ , intensity factor is 3.01. All other parameters as in Fig. 2.

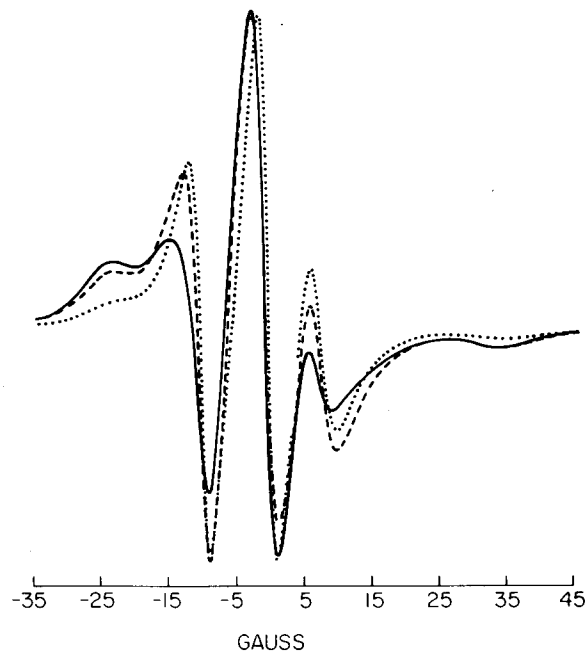


FIG. 5. First derivative line shapes for an axially symmetric nitroxide as a function of the anisotropic viscosity parameter  $N = \hat{R}_{||} / \hat{R}_{\perp}$  for Brownian diffusion. —  $N=1$ , intensity factor is 3.48; ---  $N=6$ , intensity factor is 3.30;  $\cdots$   $N=24$ , intensity factor is 5.33. All correspond to  $\tau_{\hat{R}_{\perp}} = 1 \times 10^{-8}$ . All other parameters as in Fig. 2.

general, the slow-tumbling spectra appear to look more like motional narrowing results as  $|\lambda_2|$  is increased with  $\tau_R$  held constant, although the frequency shifts are characteristic of anisotropic liquids. Also, we have not found much sensitivity of our results to having  $\lambda_4 \neq 0$ , if the combinations of  $\lambda_2$  and  $\lambda_4$  are chosen to keep  $\langle P_2(\cos\beta) \rangle$  constant. In Fig. 2,  $\lambda_2$  is held constant at a low degree of ordering,  $\lambda_2 \sim -1$ , a typical value for nitroxides,<sup>4,5,9b</sup> while  $\tau_R$  is varied over two orders of magnitude in the slow tumbling region:  $3 \times 10^{-9}$ – $3 \times 10^{-7}$  sec. These figures may be compared with Fig. 8B of I giving equivalent results for an isotropic liquid. Such a comparison shows that the trends are quite similar in the two cases, but there are very distinct quantitative differences in the details of the line shapes. Figure 3 also shows results for a range of  $\tau_R$  except here a large ordering,  $\lambda_2 = -7.5$ , was used. It is clear, from this figure, that the spectra are much less sensitive to changes in  $\tau_R$  when there is large ordering.

Typical model-dependent effects are shown in Fig. 4 for a region of  $\tau_R$  which is particularly sensitive to rotational model (cf. II). We have used the value of  $\lambda_2 \sim -1$ . One sees qualitatively the same type of effects in Fig. 4 for the partially ordered anisotropic liquid as compared to the results in II for isotropic liquids. Again, however, there are significant quantitative differences. We find about the same sensitivity of the line shape to choice of model for the low ordering parameters as for the isotropic case, but less sensitivity to model for higher ordering, i.e.,  $|\lambda_2| > 1$ . An important feature we wish to call attention to is the sensitivity of the absolute position of the center of the spectrum (i.e., the midpoint between the two outer extrema) as one goes from Brownian to moderate jump, to strong jump<sup>17</sup>; e.g., for  $\tau_R = 1 \times 10^{-8}$  sec, there are apparent  $\Delta g_{||}$  shifts of 0.9 G and 1.5 G, respectively, for moderate vs strong jump compared to the Brownian motion result. Similar results are found for isotropic liquids, although this feature had not been previously utilized.<sup>2,3</sup>

Some comments apply to the model-dependent computations. The model parameters  $B(n)$  utilized are given by unity and Eq. (2.40) for Brownian motion and strong collisions (or large jump), respectively, and these are the two limiting cases. We have chosen, as an intermediate case (by our interpolation procedure), the model parameter  $B(n) = (E_n/R)^{-1/2}$  for  $n \neq 0$ . For

$\lambda_2 = 0$ , this reduces to the intermediate jump case (or equivalently the "free diffusion" case) utilized in II. While our interpolation method is not rigorous for *anisotropic* liquids, the deviation of the Brownian rotational diffusion eigenvalues for  $|\lambda_2| \lesssim 1$  from their isotropic values when  $\lambda_2 = 0$  is found to be small (cf. Sec. IV). Therefore, in these cases, the interpretation of our intermediate jump models should be quite similar to that given for isotropic liquids.<sup>2</sup>

Another point to be made about Fig. 4 has to do with the parameter  $S$ , defined as the ratio of the separation of the outer hyperfine extrema to that for the rigid limit value.<sup>2,3</sup> It is important, in making model-dependent spectral comparisons, to adjust the apparent  $\tau_R$ 's for the different models to get  $S$  to be comparable<sup>2,3</sup> and this was done in Fig. 4. We have shown in Ref. 3 that for isotropic liquids  $S \approx S(\tau_R A_z)$  (where  $A_z$  is the  $z$  component of the hyperfine tensor with the molecular  $z$  axis taken as parallel to the nitrogen  $2p-\pi$  orbital) so that a measurement of  $S$  can be utilized to determine  $\tau_R$ . Similar comments apply to anisotropic liquids, but now  $S$  is a function of the restoring potential as well and this would considerably complicate such a procedure.

The effects of anisotropic viscosity on the slow-tumbling spectrum are illustrated in Fig. 5. This is the case where Eq. (2.26) applies. In this figure,  $\tau_{R\perp} \equiv (\delta R_{\perp})^{-1}$  is kept constant at  $1 \times 10^{-8}$  sec, while  $\lambda_2 \sim -1$ , and  $\tau_{R||} \equiv (\delta R_{||})^{-1}$  is varied. The effect of keeping  $\tau_{R\perp}$  constant is to keep the value of  $S$  virtually constant. However, one sees gross changes in the central region of the spectrum as  $\tau_{R||}$  is decreased from equality with  $\tau_{R\perp}$ . Such results encourage one in the expectation that the slow-tumbling spectra would be very sensitive to effects of anisotropy in the viscosity.<sup>18</sup> We note that such effects are much more dramatic than the dependence of slow-tumbling spectra on anisotropic diffusion of the radical [cf. Eq. (2.25)]. We also wish to call attention to the fact that if the spectrum is sensitive to the slow motion of the director itself,<sup>5</sup> then such a motion would introduce qualitative dependence on the "quantum number"  $M$  similar to that for effects of anisotropic viscosity. The inclusion of such motion into our programs can be attained by a straightforward, although complex, generalization of our stochastic-Liouville procedures.<sup>9b</sup>

#### IV. MOTIONAL NARROWING REGION

In the motional narrowing region, the linewidths are given by the relaxation matrix, which depends upon the spectral-density function<sup>12,13,15</sup>

$$J(\omega) = \text{Re} \int_0^{\infty} G(\tau) \exp(-i\omega\tau) d\tau, \quad (4.1a)$$

where

$$G(\tau) = \langle [\mathcal{I}C_1(t) - \langle \mathcal{I}C_1(t) \rangle] [\mathcal{I}C_1^*(t+\tau) - \langle \mathcal{I}C_1^*(t+\tau) \rangle] \rangle \quad (4.1b)$$



and  $\mathfrak{H}_1(t)$  may be written in the form of Eq. (2.17). We now assume that  $\mathfrak{D}_{m',m}{}^L(\Psi) = \delta_{m',m}$ , i.e., the director axis is parallel to the dc field (or else we write our expressions below in terms of  $A_{\mu,i}{}''(L,m') = \sum_{m'} \mathfrak{D}_{m',m}{}^L(\Psi) A_{\mu,i}{}^{(L,m')}$ ). Then the correlation function becomes<sup>13</sup>

$$G(\tau) = \sum_{L,L',m,m',\mu,\nu,i,i'} F_{\mu,i}{}^{(L,m)} F_{\nu,j}{}^{(L',m')} \times \sum_{q,q'} \mathfrak{C}(L, L'; m, m'; q, q'; \tau) [A_{\mu,i}{}^{(L,q)}] [A_{\nu,j}{}^{(L',q')}]^* \quad (4.2a)$$

with

$$\mathfrak{C}(L, L'; m, m'; q, q'; \tau) \equiv \langle [\mathfrak{D}_{-m,q}{}^{(L)}(t) - \langle \mathfrak{D}_{-m,q}{}^{(L)}(t) \rangle] \cdot [\mathfrak{D}_{-m',q'}{}^{(L')*}(t+\tau) - \langle \mathfrak{D}_{-m',q'}{}^{(L')*}(t+\tau) \rangle] \rangle. \quad (4.2b)$$

It is clear from Eqs. (4.1) and (4.2) that the real part of the Fourier-Laplace transform

$$K(L, L'; m, m'; q, q'; +i\omega) \equiv \int_0^\infty \exp(-i\omega t) \mathfrak{C}(L, L'; m, m'; q, q'; t) dt \quad (4.2c)$$

is needed for the linewidths. The ensemble averaging implied by the angular brackets may be written for any function (or operator)  $f_a(\Omega)$  as

$$\langle f_a(\Omega) \rangle = \int d\Omega P_0(\Omega) f_a(\Omega) \quad (4.3a)$$

and

$$\mathfrak{C}_{ab}(\tau) \equiv \langle f_a'(\Omega_t) f_b'^*(\Omega_{t+\tau}) \rangle = \int d\Omega \int d\Omega_0 f_a'(\Omega) P(\Omega; \Omega_0 t) f_b'^*(\Omega) P_0(\Omega_0), \quad (4.3b)$$

where, in general,  $P(\Omega; \Omega_0, t)$  is given by Eq. (2.37) and we use  $f_a'(\Omega) = f_a(\Omega) - \langle f_a(\Omega) \rangle$ . Now note that the eigenfunctions  $|G_n\rangle$  of  $\tilde{\Gamma}$

$$\tilde{\Gamma} |G_n\rangle = E_n |G_n\rangle \quad (4.4)$$

form a representation of  $\delta(\Omega - \Omega_0)$ , so

$$\delta(\Omega - \Omega_0) = \sum_n |G_n(\Omega)\rangle \langle G_n(\Omega_0)| = [P_0(\Omega_0)/P_0(\Omega)]^{1/2} \sum_n |u_n(\Omega)\rangle \langle u_n(\Omega_0)| = \sum_n |u_n(\Omega)\rangle \langle u_n(\Omega_0)|, \quad (4.5)$$

where

$$|u_n\rangle = |P_0(\Omega)^{1/2} G_n(\Omega)\rangle, \quad (4.6a)$$

$$\langle u_m| = \langle P_0(\Omega)^{-1/2} G_m(\Omega)| \quad (4.6b)$$

are, respectively, the right and left eigenvectors of  $\Gamma = P^{1/2} \tilde{\Gamma} P^{-1/2}$  such that

$$\langle u_m | \Gamma | u_n \rangle = E_n \delta_{m,n}. \quad (4.7)$$

The last equality in Eq. (4.5) results because  $\delta(\Omega - \Omega_0)$  is nonvanishing only if  $\Omega = \Omega_0$ . It then follows from Eqs. (2.37), (4.5), and (4.7) that

$$P(\Omega, \Omega_0, t) = \sum_n \exp(-E_n t) |u_n(\Omega)\rangle \langle u_n(\Omega_0)| = [P_0(\Omega)/P_0(\Omega_0)]^{1/2} \sum_n \exp(-E_n t) |G_n(\Omega)\rangle \langle G_n(\Omega_0)|. \quad (4.8)$$

Then one has from Eqs. (4.2c) and (4.3)

$$K_{ab}(s) = \sum_{n \neq 0} [\langle u_0(\Omega) | f_a(\Omega) | u_n(\Omega)\rangle \langle u_n(\Omega_0) | f_b'^*(\Omega_0) | u_0(\Omega_0)\rangle / (s + E_n)] \quad (4.9)$$

since

$$|u_0(\Omega)\rangle = |P_0(\Omega)^{1/2} G_0(\Omega)\rangle = P_0(\Omega) \quad (4.10a)$$

and

$$\langle u_0(\Omega)| = \langle P_0(\Omega)^{-1/2} G_0(\Omega)| = 1, \quad (4.10b)$$

where the unprimed  $f_a(\Omega)$  may be used in Eq. (4.9) provided the summation is restricted to  $n \neq 0$ . Alternatively, from Eq. (4.8),

$$K_{ab}(s) = \sum_{n \neq 0} [\langle G_0 | f_a | G_n \rangle \langle G_n | f_b'^* | G_0 \rangle / (s + E_n)]. \quad (4.9')$$

Equation (4.9') and its Laplace inverse transform  $\mathfrak{C}(t)$  give the useful result that needed spectral densities (where  $s \rightarrow i\omega$ ) or correlation functions for the case of anisotropic liquids are obtained in an *identical* fashion to that for isotropic liquids provided the eigenfunctions and eigenvalues of the symmetrized  $\tilde{\Gamma}$  are used instead of those for isotropic liquids [viz, the  $\mathfrak{D}_{KM}{}^L(\Omega)$ ]. One must, however, be careful for the fact that, in general,  $\langle f_a(\Omega) \rangle \neq 0$  (i.e., these are first order shifts) for anisotropic liquids and also that  $|G_0(\Omega)\rangle = P_0^{1/2}(\Omega)$ . The eigenfunctions  $|G_n\rangle$  and their eigenvalues may be obtained directly from the computer program that diagonalizes the matrix  $[-i\mathfrak{H}(\Omega) \times -\tilde{\Gamma}_a] = \alpha$  by first suppressing all terms in  $\mathfrak{H}(\Omega) \times$ . However, ordinary perturbation theory may be utilized, when the  $\lambda_i$  are small enough, since the matrices are symmetric.

### Perturbation Theory

We now consider Brownian diffusion of form Eqs. (2.25), (2.26) and/or (2.32) (i.e., cylindrically symmetric restoring potentials). Then in the limit when the  $|A_{2n}|$  of Eqs. (2.33), (2.34) are small (see below), we employ perturbation theory to yield the eigenfunctions of Eq. (2.33) [or (2.25) or (2.26)] in the form given by Eq. (2.24a). Then, if we let the  $a_{KM}^{nL}$  of Eqs. (2.24) become  $a_{KM}^{nL(j)}$  for ( $j$ )th order in perturbation theory, one has

$$a_{KM}^{nL(0)} = \delta_{n,L}, \quad (4.11a)$$

$$a_{KM}^{nL(1)} = (-1)^{K-M+1} (2n+1)^{1/2} \sum_{m=0}^4 A_{2m} (2L+1)^{1/2} \times \begin{pmatrix} n & 2m & L \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} n & 2m & L \\ -M & 0 & M \end{pmatrix} R_{\perp} [(E_{K,M}^{n(0)} - E_{K,M}^{L(0)})]^{-1}, \quad \text{for } L \neq n, \quad (4.11b)$$

where

$$E_{K,M}^{n(0)} = E_{KM}^{L'(0)} \delta_{n,L'} \quad (4.12)$$

is the zero-order eigenvalue from Eq. (2.25) or (2.26) when  $\lambda_2 = 0$  [more precisely replace  $R_{\perp}$  by  $\hat{R}_{\perp}$  in Eq. (4.12) and below when Eq. (2.26) is used]. The validity of the perturbation theory only depends on having

$$|a_{KM}^{nL(j)}| \ll 1. \quad (4.13)$$

The first- and second-order corrections to  $E_{K,M}^n$  are just

$$E_{K,M}^{n(1)} = (-1)^{K-M+1} (2n+1) \sum_{m=0}^4 A_{2m} \begin{pmatrix} n & 2m & n \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} n & 2m & n \\ -M & 0 & M \end{pmatrix} R_{\perp}, \quad (4.14a)$$

$$E_{K,M}^{n(2)} = (2n+1) \sum_{L \neq n} \left\{ \sum_{m=0}^4 A_{2m} (2L+1)^{1/2} \begin{pmatrix} n & 2m & L \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} n & 2m & L \\ -M & 0 & M \end{pmatrix} \right\}^2 R_{\perp}^2 / (E_{K,M}^{n(0)} - E_{K,M}^{L(0)}). \quad (4.14b)$$

One may then use Eqs. (2.24a), (4.10)–(4.14) to obtain explicit expressions for (4.9') [but written in terms of the more complete form of Eq. (4.2c) as needed for the linewidths]. One obtains, as a result of the cylindrical symmetry, that

$$K(L, L'; m, m'; q, q'; s) = K_{mq}^{(L,L')}(s) \delta_{m,m'} \delta_{q,q'} \quad (4.15)$$

and Eq. (4.15) is more general than just for the perturbation analysis. Since the terms of interest in  $\mathcal{H}_1(\Omega)$  are usually  $L=L'=2$ , we give the results for  $K_{mq}^{(2)}(s)$ . [Note that the summations in Eq. (4.2a) are accordingly simplified.] Also, we only give terms in  $\lambda_2$  (i.e.,  $\lambda_4=0$ ).<sup>19,20</sup>

$$K_{00}^{(2)} = \frac{1}{5} \{ 1 + [(4/21) + (4/7)R_{00}] \lambda_2 - (0.0775R_{00} + 0.0532) \lambda_2^2 / [s + 6R_{\perp}] \}, \quad (4.16a)$$

$$K_{01}^{(2)} = \frac{1}{5} \{ 1 + [(2/21) + (2/7)R_{01}] \lambda_2 - (0.1283R_{01} + 0.0106) \lambda_2^2 / [s + E_{0,1}^{2(0)}] \}, \quad (4.16b)$$

$$K_{02}^{(2)} = \frac{1}{5} \{ 1 - [(4/21) + (4/7)R_{02}] \lambda_2 + (0.0311R_{02} - 0.0166) \lambda_2^2 / [s + E_{0,2}^{2(0)}] \}, \quad (4.16c)$$

$$K_{11}^{(2)} = \frac{1}{5} \{ 1 + [(1/21) + (1/7)R_{11}] \lambda_2 - (0.0752R_{11} + 0.0093) \lambda_2^2 / [s + E_{1,1}^{2(0)}] \}, \quad (4.16d)$$

$$K_{12}^{(2)} = \frac{1}{5} \{ 1 - [(2/21) + (2/7)R_{12}] \lambda_2 - (0.0852R_{12} + 0.0214) \lambda_2^2 / [s + E_{1,2}^{2(0)}] \}, \quad (4.16e)$$

$$K_{22}^{(2)} = \frac{1}{5} \{ 1 + [(4/21) + (4/7)R_{22}] \lambda_2 - (0.0426R_{22} + 0.0020) \lambda_2^2 / [s + E_{2,2}^{2(0)}] \}. \quad (4.16f)$$

Also, as a further consequence of the cylindrical symmetry of the restoring potential one has

$$K_{K,M}^{(L)} = K_{-K,-M}^{(L)} = K_{-K,M}^{(L)} = K_{K,-M}^{(L)}. \quad (4.17)$$

We have in Eqs. (4.16) used the definition (but with  $s$  suppressed)

$$R_{KM}(s) \equiv R_{\perp} / [E_{KM}^{2(0)} + s]. \quad (4.18)$$

One notes from Eqs. (4.16) that it is sufficient to require  $|\lambda_2| \lesssim 1$  in order that the effect of the restoring potential on the spectral densities be considered as a perturbation.<sup>21</sup> This covers many actual experimental cases.<sup>4,5,6,9b</sup>

### V. SUMMARY

We have shown how our methods for describing slow-tumbling ESR spectra for isotropic liquids may be readily extended to include spectra for anisotropic liquids. We have developed these methods in detail

for dealing with spectra of nitroxide probes. One finds that as long as the restoring potentials are not much greater than  $kT$ , the analysis of the slow tumbling spectra for anisotropic liquids is qualitatively similar to, although quantitatively different from that for iso-

tropic liquids. More specifically, one should first study the motional narrowing spectra to extract out the ordering parameter  $\langle P_2(\cos\beta) \rangle$ , from the line shifts, and then use the Lorentzian widths to estimate  $\tau_R$ , the rotational correlation times. These results, extrapolated into the slow-motional region, aid in the interpretation of the latter (which are more sensitive to a choice of these parameters); and then a careful analysis of model dependences may be made for the latter. We find the slow-motional (anisotropic) spectra are usually as sensitive to the nature of the model of the reorientation (e.g., Brownian vs jump diffusion) as are those for isotropic liquids. However, in particular, the slow-motional spectra for anisotropic liquids are predicted to be very sensitive to effects of anisotropic viscosity.

The motional narrowing region for anisotropic liquids may be handled somewhat more conveniently than discussed by Nordio *et al.*<sup>7,8</sup> by first symmetrizing the hindered rotational diffusion operator. In particular, when the restoring potential is not greater than  $kT$ , a simple perturbation theory approach may then be utilized to obtain analytic expressions for the needed spectral densities, which Nordio *et al.*<sup>7,8</sup> obtained numerically. Analytic methods are outlined for handling the effects of residual damped oscillations when the restoring potential is much greater than  $kT$ . Such approaches could prove of some use in dealing with the motion of the director.

While there is a great abundance of nitroxide spin-label-type probes, the question exists whether our methods are applicable to other paramagnetic probes. In particular vanadyl acetylacetonate (Vacac), where

$I=7/2$ , is a very frequently used probe.<sup>4-9</sup> The coupling of the eight allowed transitions via the pseudosecular terms, which introduce effects of forbidden transitions,<sup>1</sup> requires methods that are formally equivalent to what we have utilized for nitroxides (where  $I=1$ ), if one wants to cover the whole range from fast through slow motion; but now many more coupled transitions are involved. Kaplan<sup>22</sup> has briefly outlined how the finite difference approach<sup>4</sup> may be applied to anisotropic liquids when only secular terms are kept and the allowed transitions are uncoupled. But, as noted, this is insufficient. One may hope to use perturbation methods on the pseudosecular terms, but (cf. Ref. 1 and Appendix A) if the anisotropic hyperfine terms are comparable to the (fast motional) nuclear-spin Larmor frequencies  $|\omega_n \pm a_n|$ , then this would not be a satisfactory approach. And this is the case for Vacac as well as for nitroxides. [One can, however, calculate approximate line shapes, valid for incipient slow tumbling, by repeatedly applying the central line in our nitroxide program to each of the Vacac lines, with proper inclusion of nonsecular terms, cf. Appendix A.<sup>9b,23</sup>] We note, however, that slow-tumbling spectra from aromatic ring protons (with large nuclear Larmor frequencies compared to dipolar terms) allow a decoupling of pseudosecular terms by perturbation methods, thus allowing a simplification of their analysis.

In conclusion, then, we note studies of ESR line shapes, especially in the slow-motional region, should prove valuable in elucidating molecular dynamics in liquid crystals.

## APPENDIX A: NONSECULAR TERMS

In previous slow-motional work, contributions from nonsecular terms have generally been neglected in discussions of the unsaturated lineshapes, although they have been included for saturation effects in I. In the high-field approximation, when  $|\mathcal{H}_1(\Omega)| \ll \omega_0$ , it is possible to use a perturbation-type scheme for the complex-symmetric matrices analogous to a Van Vleck transformation, and this has been utilized in I in our discussion of saturation effects. In the case of anisotropic liquids, where line shifts are an important index of the ordering parameter, the small dynamic frequency shifts from the nonsecular terms must be included. The application of (second-order) perturbation theory resulting from nonsecular terms in  $\mathcal{H}_1(\Omega)$  may be summarized by the addition to the equation for the coefficients of the  $i$ th transition [i.e.,  $C_{KM}^L(i)$ ] the terms

$$\sum_{j,L',L'',K',K'',M',M''} \langle LKM | \mathcal{H}_1^X(\Omega)_{ij} | L''K''M'' \rangle \langle L''K''M'' | \mathcal{H}_1^X(\Omega)_{ji} | L'K'M' \rangle V_{ij}(L, L', L'') C_{K'M'}^{L''}(i), \quad (A1)$$

where

$$| LKM \rangle \equiv N_L^{-1/2} \mathcal{D}_{KM}^L(\Omega). \quad (A2)$$

$\mathcal{H}_1^X(\Omega)_{ij}$  is the  $ij$ th "matrix element" of  $\mathcal{H}_1^X(\Omega)$  and

$$V_{ij}(L, L', L'') = \frac{1}{2} [(E_{i,L,K,M} - E_{j,L',K'',M''})^{-1} + (E_{i,L',K',M'} - E_{j,L'',K'',M''})^{-1}], \quad (A3)$$

where the dependence of  $V_{ij}$  on  $K, M$ , etc. is implied but not shown explicitly, with

$$E_{j,L,K,M} \equiv \omega(j) + iE_{L,K,M} \quad (A4)$$

[cf. Eqs. (2.23a), (2.24a), (2.25), (2.39), (4.4), and (4.14) for  $E_{L,K,M}$ ], where  $\omega(i)$  is the resonant frequency of the  $i$ th transition (including, in general, the diagonal contribution from the secular terms in  $\mathcal{H}_1(\Omega)$ , e.g.,  $\langle L, K, M | \mathcal{H}_1^X(\Omega)_{ii} | L, K, M \rangle$ ). Since for slow motion,

$$R, \lambda R \ll \omega_0 \quad (A5a)$$

[or more precisely  $L(L+1)R \ll \omega_0$  for  $L$  values of interest], and since in high fields

$$|\mathcal{H}_1(\Omega)| \ll \omega_0 \quad (\text{A5b})$$

one may approximate

$$V_{ij}(L, L', L'') \cong [\omega(i) - \omega(j)]^{-1} \cong \omega_0, \quad (\text{A6})$$

where the latter approximate equality follows because in high fields, if  $i$  is an observed ESR transition, then  $\mathcal{H}_1^\times(\Omega)^{\text{nonsec}}$  only couples to those  $j$ 's for which  $\omega(j) \approx 0$  (i.e., diagonal density-matrix elements), cf. I. Equation (A1) considers only the nonsecular shifts and width contributions to the regular transitions; thus we are ignoring the very weak "stealing" of intensity by the  $\omega(j) \approx 0$  transitions the relative magnitude of which is  $|\mathcal{H}_1(\Omega)|^2 / \omega_0^2 \ll 1$ .<sup>1</sup> [When  $\mathcal{H}_1^\times(\Omega)$  pseudosec are considered, then  $\omega(i) - \omega(j) \approx |a \pm \omega_n|$ , i.e., of the order of nuclear transition frequencies. It was shown in I, that if  $|D| \ll |a \pm \omega_n|$ , then perturbation theory may be applied to these pseudosecular terms, while if  $D \gtrsim |a \pm \omega_n|$ , then perturbation theory is not adequate. The latter is the case for  $^{14}\text{N}$ , while the former is true for ring protons. Note that if perturbation theory is applied for the pseudosecular terms for the case of ring protons, then since  $|a \pm \omega_n|$  may be of the order of  $R$  for slow tumbling, the full  $V_{ij}(L, L', L'')$  of Eq. (A3) is called for.]

When Eq. (A6) is utilized, then one may sum over the dummy indices  $L'', K'', M''$  in Eq. (A1) to achieve

$$\omega_0^{-1} \sum_j \sum_{L'K'M'} \langle LKM | \mathcal{H}_1^\times(\Omega)_{ij} \mathcal{H}_1^\times(\Omega)_{ji} | L'K'M' \rangle C_{K'M'}^{L'}(i). \quad (\text{A7})$$

Note that Eqs. (A1) or (A7) allow off-diagonal coupling between the  $C_{KM}^L(i)$  for the  $i$ th transition but different values of  $LKM$ . This is a result of the fact that we have in the van Vleck-type scheme, allowed for  $|\mathcal{H}_1(\Omega)| \gtrsim R$ , so that the different  $LKM$  levels may be near degenerate with respect to  $\mathcal{H}_1(\Omega)$ . Note also the neglect of the imaginary part of the  $E_{i,L,K,M}$  in the form Eq. (A6) means that nonsecular width contributions are ignored compared to nonsecular dynamic frequency shift terms since the former are [from Eq. (A5a)] much smaller. It is useful, in evaluating Eq. (A7), to utilize the relationship<sup>24</sup>

$$\mathcal{D}_{m_1', m_1}^{L_1}(\Omega) \mathcal{D}_{m_2', m_2}^{L_2}(\Omega) = \sum_{L, m, m'} (2L+1) \begin{pmatrix} L_1 & L_2 & L \\ m_1' & m_2' & m' \end{pmatrix} \begin{pmatrix} L_1 & L_2 & L \\ m_1 & m_2 & m \end{pmatrix} \mathcal{D}_{m', m}^{L*}(\Omega). \quad (\text{A8})$$

The nonsecular part of the Hamiltonian for the case of a single nuclear spin is given for example by Freed and Fraenkel.<sup>12</sup> We summarize the results for the nonsecular shifts for the three principal transitions utilizing the notation in the Appendix of II. The following is to be added to the lhs of the symmetrized form<sup>15</sup> of Eqs. (A1)–(A3) in II (where  $\lambda = 1, 2, \text{ or } 3$ , respectively):

$$\begin{aligned} & -\frac{1}{\omega_0} \left[ \frac{3}{2^0} (F_0^2 + 2F_2) + \frac{3}{1^0} (F_0 D' + 2F_2 D^{(2)'}) m + \frac{1}{1^5} (7I(I+1) - m^2) (D^2 + 2D^{(2)}) + 2b^2 (I(I+1) - m^2) \right] C_{K,0}^{L'}(\lambda) \\ & - \frac{(2L+1)^{1/2}}{\omega_0} \sum_{L'} (2L'+1)^{1/2} \left\{ \frac{3}{2^8} (F_0^2 - 2F_2^2) + \frac{3}{1^4} m (F_0 D' - 2F_2 D^{(2)'}) - \frac{2}{2^1} [5I(I+1) - 8m^2] (D^2 - 2D^{(2)}) \right. \\ & \left. + bD' [I(I+1) - m^2] \right\} \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} C_{K,0}^{L'}(\lambda) - \frac{(2L+1)^{1/2}}{\omega_0} \sum_{L'} (2L'+1)^{1/2} \\ & \times \left\{ -\frac{3}{3^5} (3F_0^2 + F_2^2) - \frac{6}{3^5} (3F_0 D' + F_2 D^{(2)'}) m + \frac{4}{3^5} [I(I+1) - 3m^2] (3D^2 + D^{(2)}) \right\} \\ & \times \begin{pmatrix} L & 4 & L' \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} L & 4 & L' \\ 0 & 0 & 0 \end{pmatrix} C_{K,0}^{L'}(\lambda) - \frac{(2L+1)^{1/2}}{\omega_0} \sum_{L'} (2L'+1)^{1/2} \\ & \times \left\{ -\frac{3}{1^4} F_0 F_2 - \frac{3}{1^4} (F_0 D^{(2)'}) + F_2 D' \right\} m + \frac{4}{2^1} [5I(I+1) - 8m^2] D D^{(2)} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} \\ & \times \left\{ \begin{pmatrix} L & 2 & L' \\ -K & 2 & K-2 \end{pmatrix} C_{K-2,0}^{L'}(\lambda) + \begin{pmatrix} L & 2 & L' \\ -K & -2 & K+2 \end{pmatrix} C_{K+2,0}^{L'}(\lambda) \right\}, \quad (\text{A9}) \end{aligned}$$

where  $m$  is the nuclear quantum number for the  $\lambda$ th transition. We have, in Eq. (A9), retained only those contributions that will add to already nonzero matrix elements of  $\mathcal{G}$  and have neglected those terms that would create new off-diagonal elements. This is readily justified by noting (1) the nonsecular correction terms are of order  $|\mathcal{H}_1(\Omega)|^2 / \omega_0$  or  $|\mathcal{H}_1(\Omega)| / \omega_0$  smaller than the secular and pseudosecular contributions, so (2) one may again use perturbation theory to essentially first order (cf. I).

We have found that the nonsecular corrections to the six forbidden transitions are not needed for nitroxides. In fact they are less than  $\omega_n$ , which has already been found to have a negligible effect for nitroxides at X band.

**APPENDIX B: ROTATIONAL DIFFUSION WITH A VERY STRONG AXIAL RESTORING POTENTIAL**

Consider the rotational diffusion equation, Eq. (2.16), which for  $\mathfrak{J}=0$  is analogous in form to the quantum mechanical equation of the spherical top.<sup>10</sup> Since the terms in  $\mathfrak{J}$  depend only on Euler angle  $\beta$ , for axially symmetric restoring potentials, it is still possible to separate variables by letting

$$G(\alpha\beta\gamma) = y(\beta) \exp(i(K\alpha + M\gamma)). \tag{B1}$$

Then the differential equation for  $y(\beta)$  is<sup>7,10,23</sup>

$$-R^{-1}\Gamma_\beta y = \frac{\partial^2 y}{\partial \beta^2} + \cot\beta \frac{\partial y}{\partial \beta} - \frac{M^2 + K^2 - 2MK \cos\beta}{\sin^2\beta} y + 2\lambda_2 \left( \cos\beta \sin\beta \frac{\partial y}{\partial \beta} + (3 \cos\beta - 1)y \right) = -R^{-1}E y \tag{B2}$$

or letting  $x = \cos\beta$  and symmetrizing  $\Gamma_\beta$  [cf. Eq. (2.6)], gives

$$-R^{-1}\tilde{\Gamma}_\beta y = (1-x^2) (\partial^2 y / \partial x^2) - 2x (\partial y / \partial x) - [(M^2 + K^2 - 2MKx) / (1-x^2)] y + \lambda_2 f(\lambda_2, x) y. \tag{B3}$$

We now assume that  $\lambda_2 \gg 1$ , i.e., the restoring potential is much greater than  $kT$ , so that the angle  $\beta$  does not deviate much from the perfect alignment value assumed to be zero (i.e., a prolate top). Then, to lowest order in  $\beta$  and  $\lambda_2^{-1}$ , one has

$$-R^{-1}\tilde{\Gamma}_\beta \cong (\partial^2 / \partial \beta^2) + \beta^{-1} (\partial / \partial \beta) - (\nu / \beta)^2 - \lambda_2^2 \beta^2 + 2\lambda_2 - MK, \tag{B4}$$

where  $\nu = |M - K|$ . The substitutions  $y(\beta) = v(\beta) / \beta^{1/2}$  and  $z = \lambda_2^{1/2} \beta$  yield the standard differential form

$$(\lambda_2 / \beta^{1/2}) \{ (d^2 v / dz^2) + v[(1 - 4\nu^2) / 4z^2] + 2 - z^2 \}, \tag{B5}$$

the solutions of which are expressible as generalized Laguerre polynomials.<sup>25</sup> One therefore finds that the eigenfunction solution to Eq. (B4) is given by

$$y_\nu^n(\beta) = N_\nu^n \exp(-\lambda_2 \beta^2 / 2) (\lambda_2^{1/2} \beta)^\nu L_\nu^n(\lambda_2 \beta^2), \tag{B6}$$

where  $L_\nu^n(z^2)$  are the generalized Laguerre polynomials (as defined in Ref. 25). The range of the variable  $\beta$  is now taken from 0 to  $\infty$  instead of from 0 to  $\pi$ , which is permissible since the condition  $\lambda_2 \gg 1$  renders  $y_\nu^n(\beta) \sim 0$  for  $\beta$  much different from zero. Over this range the  $y_\nu^n(\beta)$  are orthogonal polynomials and one can readily determine the normalization constants  $N_\nu^n$  from standard integrals<sup>25,26</sup>:

$$N_\nu^n = [2\lambda_2 n! / (\nu + n)!]^{1/2} \tag{B7a}$$

or

$$y_\nu^n(z^2) = [2\lambda_2 n! / (\nu + n)!]^{1/2} \exp[-z^2 / 2] z^{\nu/2} L_\nu^n(z^2) \tag{B7b}$$

and also

$$\tilde{\Gamma} y_\nu^n(\beta) = 2\lambda_2 R(2n + \nu) y_\nu^n(\beta) + MKR y_\nu^n(\beta) \tag{B8}$$

which for axially symmetric diffusion<sup>10,23</sup> [cf. Eq. (2.25)] one gets

$$-\tilde{\Gamma} y_{|K-M|^n}(\beta) = [2\lambda_2 R_\perp(2n + \nu) + MKR_\perp + K^2(R_{||} - R_\perp)] y_{|K-M|^n}(\beta). \tag{B9}$$

An equivalent result follows for anisotropic viscosity, cf. Eq. (2.26). The complete eigenfunction solution is then from Eq. (B1)

$$G_{K,M^n}(\alpha\beta\gamma) = \exp(iK\alpha) y_{|K-M|^n}(\beta) \exp(iM\gamma). \tag{B10}$$

We now must rewrite the rotation matrices [which appear in Eq. (2.17)]:

$$D_{m'm^l}(\alpha\beta\gamma) \equiv \exp(im'\alpha) d_{m',m^l}(\beta) \exp(im\gamma) \tag{B11}$$

so that the  $d_{m',m^l}(\beta)$  are in a more convenient form valid for small  $\beta$ . One may use the definition<sup>24</sup>

$$d_{m',m^l}(\beta) \equiv \langle lm' | \exp[(i\beta/\hbar) J_y] | lm \rangle, \tag{B12}$$

where  $J_y$  is the  $y$  component of the quantum mechanical angular-momentum operator with  $|lm\rangle$  an eigenfunction of  $J^2$  and  $J_z$ . Since  $\beta$  is small, it is sufficient to let

$$\exp[(i\beta/\hbar) J_y] \cong 1 + (i\beta/\hbar) J_y - (\beta^2/\hbar^2) J_y^2. \tag{B13}$$

Then

$$\begin{aligned} d_{m'm^l}(\beta) \cong & \delta_{m,m'} + (\beta/2) [\delta_{m',m+1} f_+(l, m) - \delta_{m',m-1} f_-(l, m)] \\ & + (\beta^2/4) [\{\delta_{m',m+2} f_+(l, m+1) - \delta_{m',m} f_-(l, m+1)\} f_+(l, m) \\ & - \{\delta_{m',m} f_+(l, m-1) - \delta_{m',m-2} f_-(l, m-1)\} f_-(l, m)], \end{aligned} \tag{B14a}$$

where

$$f_{\pm}(l, m) = [l(l+1) - m(m \pm 1)]^{1/2}. \tag{B14b}$$

Then the needed integrals involving the  $\mathfrak{D}_{m'm}^L(\Omega)$  that arise from the  $\mathfrak{H}_1(\Omega)$  [e.g., Eq. (2.17)] may be approximated to, lowest order in  $\beta$ , as

$$\begin{aligned} \langle n, K, M | \mathfrak{D}_{m'm}^L | n', K', M' \rangle \cong & \delta_{n,n'} \delta_{K,K'+m'} \delta_{M,M'+m} \delta_{\nu,\nu'} \\ & + (1/2\lambda_2) \delta_{K,K'+m'} \delta_{M,M'+m} [\delta_{\nu,\nu'+1} (\delta_{n,n'} (\nu+n)^{1/2} - (n+1)^{1/2} \delta_{n,n'-1}) \\ & + \delta_{\nu,\nu'-1} ((n+\nu+1)^{1/2} \delta_{n,n'} - n^{1/2} \delta_{n,n'+1})] [\delta_{m',m+1} f_+(L, m) - \delta_{m',m-1} f_-(L, m)], \end{aligned} \tag{B15}$$

where  $\nu = |K - M|$  and  $\nu' = |K' - M'|$ . (Note that

$$\int d\Omega \rightarrow \int_0^\pi \beta d\beta \int_0^{2\pi} d\alpha \int_0^{2\pi} d\gamma,$$

since  $\sin\beta \sim \beta$ .) The required ‘‘matrix elements’’ needed to obtain Eq. (B15) are obtained from the recursion relations (cf. Ref. 25):

$$\begin{aligned} x^{1/2} y_{\nu}^n(x) &= N_n{}^{\nu} \exp[-x/2] x^{\nu+1} L_n{}^{\nu}(x) = N_n{}^{\nu} \exp[-x/2] x^{\nu+1/2} [L_n{}^{\nu+1}(x) - L_{n-1}{}^{\nu+1}(x)] \\ &= (n+\nu+1)^{1/2} y_{\nu+1}^n(x) - n^{1/2} y_{\nu+1}^{n-1}(x) \end{aligned} \tag{B16a}$$

and

$$x^{1/2} y_{\nu}^n(x) = (n+\nu)^{1/2} y_{\nu-1}^n(x) - (n+1)^{1/2} y_{\nu-1}^{n+1}(x). \tag{B16b}$$

If  $|\lambda_2| \gg 1$ , but  $\lambda_2 < 0$  (i.e., an oblate top), then the appropriate expressions are somewhat different. One first defines,  $\delta = (\pi/2) - \beta$ , so that  $\delta$  represents the small deviation from  $\beta_{\text{eq}} = \pi/2$ . Then for small  $\delta$ ,  $x = \cos\beta \cong \delta$ . In this case one first transforms Eq. (B3) by letting  $y(x) = v(x)/(1-x^2)^{1/2}$ , and then keeping terms in lowest order in  $x$  and  $|\lambda_2|^{-1}$ , yielding

$$\{ (d^2v/dz^2) + [1 - z^2 - (M^2 + K^2)/|\lambda_2|] v \} |\lambda_2|, \tag{B17}$$

where  $z = |\lambda_2|^{1/2} x$ , the solutions of which may be expressed in terms of Hermite polynomials.<sup>25</sup> That is

$$y_{K,M}^{(n)}(\delta) = N_n \exp(-|\lambda_2| \delta^2/2) H_n(|\lambda_2|^{1/2} \delta), \tag{B18a}$$

where  $H_n(z)$  are the Hermite polynomials, with normalization coefficient

$$N_n = (|\lambda_2|^{1/2}/\sqrt{\pi} 2^n n!)^{1/2} \tag{B18b}$$

provided  $\delta$  is integrated from  $-\infty$  to  $+\infty$  (instead of  $-\pi/2$  to  $\pi/2$ ). Note, again, that this is, from Eq. (B18), a permissible approximation when  $|\lambda_2| \gg 1$ . One also has

$$\tilde{\Gamma} y_{K,M}^{(n)}(\delta) = R[2n|\lambda_2| + M^2 + K^2] y_{K,M}^{(n)} \tag{B19}$$

while for axially symmetric diffusion one has

$$\tilde{\Gamma} y_{K,M}^{(n)}(\delta) = [(2n|\lambda_2| + M^2) R_{\perp} + K^2 R_{\parallel}] y_{K,M}^{(n)} \tag{B20}$$

with an equivalent result for anisotropic viscosity [cf. Eq. (2.26)]. The complete solution is now

$$G_{K,M}^n(\alpha\beta\gamma) = \exp(iK\alpha) y_{K,M}^{(n)}(\delta) \exp(iM\gamma), \quad \delta = (\pi/2) - \beta. \tag{B21}$$

The rotation matrices may be handled in a manner analogous to the previous case by first letting

$$d_{m'm}^L(\beta) = \sum_{m''} d_{m''m'}^L(\pi/2) d_{m''m}^L(-\delta), \tag{B22}$$

where the  $d_{m''m'}^L(\pi/2)$  are found in tables,<sup>24</sup> and the  $d_{m''m}^L(-\delta)$  may be expanded as in Eqs. (B12)–(B14), (i.e., just replace  $\beta$  by  $-\delta$  in these equations). The integrals of type Eq. (B15) may then be obtained by application of the well-known matrix elements for the Hermite functions.

Equation (B8) for the highly ordered prolate top shows that the relaxation of a nonequilibrium orientation happens simply by the molecular  $z$  axis being rapidly [ $\tau \sim (\lambda_2 R)^{-1}$ ] restored to the lab  $z$  axis, and this process also randomizes  $\alpha$  and  $\gamma$  even for  $n=0$  corresponding to an equilibrium distribution in  $\beta$  (i.e., the rapid relaxation via the restoring torque also depends on  $\nu = |K - M|$ ) although if  $K = M \neq 0$  so  $\nu=0$ , the relaxation proceeds by normal diffusion. Equation (B19) for highly ordered oblate tops shows that a nonequilibrium orientation is relaxed by the molecular  $z$  axis being rapidly restored to an angle  $\beta_{\text{eq}} = \pi/2$ , while the  $\alpha$  and  $\gamma$  angles relax more slowly ( $\tau \sim R^{-1}$ ) by normal rotational diffusion when  $n=0$  (again corresponding to an equilibrium distribution in  $\beta$  but not in  $\alpha$  and  $\gamma$ ). Note that the macroscopic motion of the director itself would, on geometrical grounds, correspond to the prolate case of Eqs. (B7a)–(B10) (the angle  $\alpha$  would be unnecessary); however, proper account must then be taken of the frequency-dependent rotational diffusion coefficient  $R(\omega)$  for this phenomenon based on the long-range ordering of molecules.<sup>27</sup>

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<sup>1</sup>J. H. Freed, G. V. Bruno, and C. F. Polnaszek, *J. Phys. Chem.* **75**, 3385 (1971), hereafter referred to as I. Note that in the notation of I, we have  $\rho_0$  as the equilibrium value of  $\rho$  such that  $\Gamma_{\alpha\rho} = 0$ ; also  $d_{\lambda_j} = (1/2)\omega_j \langle S_- \rangle_{\lambda_j}$ , with  $\langle S_- \rangle_{\lambda_j}$  the matrix element of  $S_-$  for the  $\lambda_j$ th transition;  $\omega_{\lambda_j \xi}$  is the

Larmour frequency, from  $\mathcal{H}_0$ , of the  $\lambda_j$ th transition;

$q = \hbar/NkT$ , where  $N$  = number of spin eigenstates.

<sup>2</sup>S. A. Goldman, G. V. Bruno, C. F. Polnaszek, and J. H. Freed, *J. Chem. Phys.* **56**, 716 (1972), hereafter referred to as II.

<sup>3</sup>S. A. Goldman, G. V. Bruno, and J. H. Freed, *J. Phys. Chem.* **76**, 1858 (1972).

<sup>4</sup>For a recent review of both slow tumbling and ESR in liquid crystals as well as detailed listing of references, see J. H. Freed, *Ann. Rev. Phys. Chem.* **23**, 265 (1972).

<sup>5</sup>Detailed reviews of ESR in liquid crystals are given by G. R. Luckhurst in (a) *ESR Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (Plenum, New York, 1972), Chap. XV, and in (b) *Liquid Crystalline Systems*, edited by G. W. Gray and P. A. Winsor (Van Nostrand, New York, to be published), Chap. 7.

<sup>6</sup>S. H. Glarum and J. H. Marshall, *J. Chem. Phys.* **46**, 55 (1967).

<sup>7</sup>P. L. Nordio, G. P. Busolin, *J. Chem. Phys.* **55**, 5485 (1971).

<sup>8</sup>P. L. Nordio, G. Rigatti, and U. Segre, *J. Chem. Phys.* **56**, 2117 (1972).

<sup>9</sup>(a) G. C. Fryburg and E. Gelerinter, *J. Chem. Phys.* **52**, 3378 (1970). (b) C. F. Polnaszek and J. H. Freed (unpublished).

<sup>10</sup>L. D. Favro, *Fluctuation Phenomena in Solids*, edited by R. E. Burgess, (Academic, New York, 1965), p. 79.

<sup>11</sup>When the assumption of a cylindrically symmetric restoring potential is no longer valid [presumably due to the symmetry of the probe molecule, cf. L. C. Snyder, *J. Chem. Phys.* **43**, 4041 (1965)], then one must return to the more general expressions given for example by Favro,<sup>10</sup> i.e.,  $R^{-1}\Gamma = \pi^2 + \pi \cdot (\pi(U/KT))$ , where  $-\pi^2 \equiv \nabla_n^2$  and  $\pi$  is a general angular momentum operator. The complete solution would then proceed in a closely analogous manner to that given above for axially symmetric restoring potentials except that an azimuthal angle would be added.

<sup>12</sup>J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **39**, 326 (1963).

<sup>13</sup>J. H. Freed, *J. Chem. Phys.* **41**, 2077 (1964).

<sup>14</sup>A. N. Kuznetsov, *Zh. Strukt. Khim.* **11**, 535 (1970).

<sup>15</sup>J. H. Freed, *Electron Spin Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (Plenum, New York, 1972), Chap. VIII. The unsymmetrized Eqs. given in I and II become symmetrized when the O. N. functions  $D_{KM}^L/N_L^{1/2}$  are used instead of the

unnormalized  $\mathcal{D}_{KM}^L$ . The equations for isotropic liquids given in these references are easily rendered symmetric by making the replacement  $C_{K,0}^L(i) \rightarrow [(2L+1)/(2L+1)]^{1/2} C_{K,0}^L(i)$  [where  $L$  is for the diagonal element; cf. Eqs. A1-A6 of II], before forming the matrix  $\mathcal{G}$  of Eq. (2.15).

<sup>16</sup>Note that the strong collision model represented by Eqs. (2.38) (in the isotropic limit) is not quite the same as that

utilized in II. In II the "random distribution", where  $W(\epsilon) = 1/\pi$ , was used.  $W(\epsilon)$  is the normalized distribution function for diffusive steps by the angle  $\epsilon$ . For this case the model parameter for isotropic diffusion is  $B_L = [1 + L(L+1)]^{-1}$ . For the strong collision model of Eqs. (2.38), one requires  $W(\epsilon) = (1/\pi)[1 - \cos \epsilon] = (2/\pi)\sin^2(1/2)\epsilon$  (cf. II). This latter formula preferentially weights angular steps of the order of  $\pi/2$  over those  $\ll \pi/2$ . (In effect it implicitly includes the  $\sin \epsilon d\phi$  surface element of the unit sphere.) In this sense the strong collision model is less random than the "random distribution". We have found virtually no spectral model-dependent differences between these two cases for isotropic liquids, but some differences in the anisotropic liquid case when  $B(n) \approx [1 + E_n/R]^{-1}$  is utilized for the "random distribution".

<sup>17</sup>The "apparent"  $g$  shift is also very sensitive to the choice of molecular  $z$  axis, i.e., the axis that tends to align parallel (or perpendicular) to the director, and this is true even in the motional narrowing region where there is no dependence of the spectrum on jump model.

<sup>18</sup>M. Miesowicz, *Nature (Lond.)* **158**, 27 (1946), discusses anisotropic viscosity in the presence of a magnetic field.

<sup>19</sup>Note that  $\text{Re}K_{KM}^L(i\omega)$  is equivalent to the  $(2L+1)^{-1} \tau_{L,K}$

given by Freed<sup>13</sup> for  $\lambda_2 = 0$ . In Nordio's<sup>8</sup> notation it is (for  $L=2$ )  $J_{MK}(\omega)$ , while it is  $J_n(\omega)$  (but for a different rotational model)<sup>20</sup> in Glarum and Marshall's<sup>6</sup> notation.

<sup>20</sup>We note that Glarum and Marshall's model<sup>6</sup> is equivalent to letting  $E_n$  in Eq. (4.9a) be given by the strong collision value  $[1 - \delta_{n,0}]\tau^{-1}$  as given by Eqs. (2.38). Then Eq. (4.9a)

becomes  $K_{ab}(s) = (s + \tau^{-1}) \langle G_{ab} f_a' f_b'^* \rangle = (s + \tau^{-1}) \langle f_a' f_b'^* \rangle$ . This form [or more precisely  $K_{KM}^L(s)$ ] is easily calculated, as it only requires knowledge of  $P_0(\Omega)$ .

<sup>21</sup>In calculating Eqs. (4.15) it was only necessary to keep the  $n=2$  term in the summation of form Eq. (4.9a). The contributions from the  $n > 2$  terms in the summation were found never to exceed 0.25% of the contribution from the

$n=2$  terms when  $|\lambda_2| \leq 1$ . However, coefficients  $\alpha_{KM}^{OL(j)}$  and  $\alpha_{KM}^{2L(j)}$  for  $L=0, 2$ , and 4 and  $j=1$  and 2 were utilized in the expression for the  $G_{KM}^L(\Omega)$ . The complex forms of  $\alpha_{KM}^{nL(2)}$  are not given explicitly above.

<sup>22</sup>J. I. Kaplan, *ESR Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins, (Plenum, New York, 1972), Chap. XVI.

<sup>23</sup>Note that finite difference techniques coupled with an "adiabatic approximation" are an effective means of dealing with combined secular and pseudosecular terms provided the motion is slow enough that  $F/R \gg 1$ , where  $F$  is a measure of the magnitude of  $H_1(t)$ ; cf. Ref. 4.

<sup>24</sup>A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, N. J., 1957).

<sup>25</sup>M. Abramowitz and I. A. Stegun (eds.), *Handbook of Mathematical Functions* (Dover, New York, 1965), Chap. 22.

<sup>26</sup>P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), p. 784. However, the definition of  $L_n^\alpha(z^2)$  given by Ref. 14 has been utilized.

<sup>27</sup>P. Pincus, *Solid State Commun.* **6**, 839 (1969).