

Spin relaxation for biradical spin probes in anisotropic environments

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The large zero-field splitting of certain biradicals makes them important candidates for spin probes of anisotropic systems such as liquid crystals and membranes. The electron resonance spectrum of a biradical dissolved in a liquid crystal may be influenced by the zero-field splitting in two quite distinct ways. Firstly the line positions are affected because the spin probe is partially oriented by the liquid crystal solvent. In addition the zero-field splitting coupled with the molecular reorientation constitutes a powerful spin relaxation process and so may determine the widths of the spectral lines. Here we develop a theory of such line broadening, within the limit of fast motion, and show how it results in an angular dependence of the linewidths. The application of the theory is illustrated by studying the line broadening for a nitroxide biradical dissolved in a nematic mesophase. An analysis of the angular dependence of the linewidths suggests that the diffusion model provides a better account of molecular reorientation in a liquid crystal than the strong-collision approach. Finally we draw attention to the potential value of the theory for understanding the linewidth variations in the deuteron magnetic resonance spectra of liquid crystals.

1. INTRODUCTION

Electron resonance spectroscopy can often be used to investigate a diamagnetic system simply by adding a radical, or spin probe, whose interaction with its environment is reflected in the electron resonance spectrum. The nature of the system should, of course, play a dominant role in the choice of spin probe. For example, if the system to be studied is a liquid crystal, such as a membrane, then two properties of the spin probe are of prime importance. The molecules must deviate significantly from spherical symmetry so that they may be highly oriented by their anisotropic environment. Secondly there must be considerable anisotropy in the magnetic interactions in order for the extent of the partial alignment to be readily discernible in the electron resonance spectrum [1]. These anisotropic interactions may also influence the widths of the lines as well as their positions because the anisotropy coupled to the molecular reorientation invariably constitutes a powerful spin relaxation process [2]. Consequently the spectrum of the spin probe may often exhibit a characteristic linewidth variation and, because of the anisotropic nature of the environment, this variation will depend on the sample orientation with respect to the magnetic field. An understanding of such linewidth effects is important not only as an aid to a correct spectral analysis but also because the linewidths contain valuable information relating to both the dynamic and static behaviour of the system [2-4].

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Nitroxide monoradicals are the most common spin probes and the theory needed to understand the linewidths of such doublet state species dissolved in anisotropic environments is well advanced [2–5]. Indeed it has been employed to considerable advantage in the study of membranes [5, 6] as well as nematic [7] and smectic liquid crystals [4]. The synthesis of stable nitroxide biradicals has meant that they are also candidates for use as spin probes of anisotropic systems. They possess one clear advantage over their monoradical counterparts, for in addition to the anisotropic hyperfine and Zeeman interactions there is also the totally anisotropic zero-field splitting. This interaction can be of particular importance because, unlike the other two, its magnitude can be varied dramatically by modifying the structure of the biradical [8]. Several preliminary studies [8, 9] have already demonstrated the potential of nitroxide biradicals as spin probes although there is no theory available with which to interpret and exploit the linewidth variations observed in such experiments. We therefore develop, in this paper, a theory of spin relaxation for a triplet state spin probe dissolved in an anisotropic system. The predictions of the theory are then tested by comparison with the angular dependence of the linewidths observed for a nitroxide biradical dissolved in a nematic mesophase.

Finally we would emphasize that the problem which we have solved is identical in form to quadrupole relaxation of a nucleus of spin 1 in a magnetic field. Our theory could therefore be of considerable value in the recent important studies of membranes and other liquid crystals employing deuteron magnetic resonance [10].

2. THEORY

The majority of stable biradicals are formed by linking two nitroxide groups together; consequently the dominant magnetic interactions are the zero-field splitting together with the Zeeman and nitrogen hyperfine couplings. However, in developing the theory, we shall find it convenient to ignore all hyperfine interactions and such an assumption will be permissible provided the zero-field splitting exceeds the hyperfine interaction. In situations where the hyperfine terms are important it would be a straightforward matter to extend the present theory although the book-keeping could become somewhat involved [11]. We begin by obtaining the static spin hamiltonian for a biradical in an anisotropic environment and then proceed to the spin relaxation problem.

2.1. Statics

The spin hamiltonian for a given orientation of a biradical may be written, in irreducible spherical tensor notation [12], as

$$\mathcal{H} = \mathcal{H}^0 + \sum_p (-1)^p D^{(2,p)} T^{(2,-p)}, \quad (1)$$

where \mathcal{H}^0 contains the orientation independent Zeeman and exchange interactions. In the second term, $D^{(2,p)}$ is the p th component of the zero-field splitting tensor and $T^{(2,-p)}$ is the appropriate combination of total electron spin operators. We list the components of the spatial and spin operators, which we use, in table 1 because various definitions are encountered in the literature.

This spin hamiltonian is written in a molecular coordinate system and so the spin operators fluctuate in time as the molecule reorients; it is this motion which combines with the zero-field splitting to yield the spin relaxation process. The time dependence may be removed from the spin operators by transforming to a

| p | $D^{(2,p)}$ | $T^{(2,p)}$ |
|---------|---------------------------------------|--|
| 0 | $(3/2)^{1/2} D_{zz}$ | $(2/3)^{1/2} \{S_z^2 - (1/4)(S_+S_- + S_-S_+)\}$ |
| ± 1 | $\mp (D_{xz} \pm iD_{yz})$ | $\mp (1/2)(S_{\pm}S_z + S_zS_{\pm})$ |
| ± 2 | $(1/2)(D_{xx} - D_{yy} \pm 2iD_{xy})$ | $(1/2)S_{\pm}^2$ |

Table 1. The irreducible spherical tensor components.

space fixed coordinate system which we choose to contain the symmetry axis of the ordering potential responsible for the partial alignment of the spin probe. This gives

$$\mathcal{H}(t) = \mathcal{H}^0 + \sum_{p,q} (-1)^p D^{(2,p)} \mathcal{D}_{q,-p}^{(2)}(t) T^{(2,p)}, \quad (2)$$

where $\mathcal{D}_{q,-p}^{(2)}(t)$ is a second rank Wigner rotation matrix which contains the complete time dependence of the spin hamiltonian. The molecular motion is assumed to be sufficiently fast that the static spin hamiltonian may be obtained by taking a time or ensemble average of equation (2). In other words, the relevant rotational correlation times are smaller than the inverse of the zero-field splitting. We therefore require the average $\overline{\mathcal{D}_{q,-p}^{(2)}}$ and for an environment with $D_{\infty h}$ symmetry, such as a nematic or smectic A liquid crystal, this quantity vanishes unless q is zero. The static spin hamiltonian is then

$$\overline{\mathcal{H}} = \mathcal{H}^0 + \overline{\hat{D}^{(2,0)}} T^{(2,0)}, \quad (3)$$

where the partially averaged zero-field splitting is defined by

$$\overline{\hat{D}^{(2,0)}} = \sum_p (-1)^p D^{(2,p)} \overline{\mathcal{D}_{0,-p}^{(2)}}, \quad (4)$$

and $\overline{\mathcal{D}_{0,-p}^{(2)}}$ is a measure of the alignment of the spin probe by its environment. This spin hamiltonian corresponds to a triplet state with a cylindrically symmetric zero-field splitting tensor and the magnetic behaviour of such a system is completely understood [13]. When the magnetic field is parallel to the symmetry axis of \mathbf{D} the three triplet spin functions $|1\rangle$, $|0\rangle$ and $|-1\rangle$ are eigenfunctions of $\overline{\mathcal{H}}$. For all other orientations of the sample these spin states are mixed by the zero-field splitting, however provided \mathbf{D} is small in comparison with the Zeeman splitting then the triplet functions are good approximations to the eigenfunctions. Within this high-field approximation the two allowed transitions are

$$\text{and } \left. \begin{aligned} |0\rangle \leftrightarrow |1\rangle &\equiv |+\rangle \\ |-1\rangle \leftrightarrow |0\rangle &\equiv |-\rangle \end{aligned} \right\} \quad (5)$$

The electron resonance spectrum therefore contains two lines with resonant fields

$$B_{\pm} = \frac{\hbar\omega_0}{g\beta} \mp \frac{3\overline{D}_{\parallel}}{2g\beta} P_2(\cos\gamma), \quad (6)$$

where \overline{D}_{\parallel} is the cartesian component of the partially averaged zero-field splitting tensor parallel to its symmetry axis and so to the director; the angle between the magnetic field and the director is γ . The spacing between the two spectral lines changes dramatically with this angle and we shall now see that the linewidths should also exhibit a pronounced angular dependence.

2.2. Dynamics

It is necessary to calculate the linewidths using the Binsch formalism [14] because for certain orientations of the sample the separation between the two spectral components is comparable to the linewidth. Under such conditions Redfield's relaxation theory alone is unable to predict the line shape in contrast to the situation when the transitions are either degenerate or well resolved [15]. Since the motion is assumed to be fast the line shape in a slow-passage, low-power electron resonance experiment is given by [14]

$$\mathcal{L}(\omega) \propto \text{Re} \{ \mathbf{S}_+ \cdot \mathbf{M}_0^{-1} \cdot \boldsymbol{\sigma} \}. \quad (7)$$

The vector \mathbf{S}_+ is composed of the matrix elements $\langle \kappa | S_+ | \kappa' \rangle$, where $|\kappa\rangle$ denotes an eigenfunction of \mathcal{H} ; $\boldsymbol{\sigma}$ is defined as

$$\sigma_{\kappa\kappa'} = \langle \kappa | S_+ | \kappa' \rangle (\rho_{\kappa\kappa} - \rho_{\kappa'\kappa'}), \quad (8)$$

and ρ is the density matrix describing the spin system. The matrix \mathbf{M}_0 is related to Redfield's relaxation matrix \mathbf{R} [15] and the transition frequencies by

$$M_{0; \kappa\kappa', \lambda\lambda'} = i(\omega_{\kappa\kappa'} - \omega) \delta_{\kappa\lambda} \delta_{\kappa'\lambda'} + R_{\kappa\kappa', \lambda\lambda'}. \quad (9)$$

For the triplet-state problem the vectors \mathbf{S}_+ and $\boldsymbol{\sigma}$ are both proportional to (1,1). The resonant frequencies may be replaced by resonant fields because, according to equation (6) there is a 1 : 1 correspondence between magnetic field and frequency. The relaxation matrix is calculated, in the usual way, from the dynamic spin hamiltonian $\mathcal{H}'(t)$ which is obtained by subtracting the static spin hamiltonian from its instantaneous value $\mathcal{H}(t)$. Thus

$$\mathcal{H}'(t) = \sum_{p,q} (-1)^p D^{(2,p)} \{ \mathcal{D}_{q,-p}^{(2)}(t) - \overline{\mathcal{D}_{0,-p}^{(2)} \delta_{0q}} \} T^{(2,q)}, \quad (10)$$

where $T^{(2,q)}$ depends on the orientation of the director with respect to the magnetic field. This angular dependence is removed by transforming the spin operator to a laboratory frame containing the field

$$\mathcal{H}'(t) = \sum_{p,q,r} (-1)^p D^{(2,p)} \{ \mathcal{D}_{q,-p}^{(2)}(t) - \overline{\mathcal{D}_{0,-p}^{(2)} \delta_{0q}} \} \mathcal{D}_{r,q}^{(2)} T^{(2,r)}, \quad (11)$$

which we write formally as

$$\mathcal{H}'(t) = \sum_r (-1)^r F^{(2,r)} T^{(2,-r)}, \quad (12)$$

where $F^{(2,r)}$ contains both the time and angular dependence of the dynamic perturbation. The relaxation matrix is then found to be

$$\mathbf{R} \equiv \begin{matrix} \langle + | & \langle - | \\ \left[\begin{array}{cc} A & B \\ B & A \end{array} \right] & \end{matrix}, \quad (13)$$

where the basis functions correspond to the two allowed transitions; the matrix elements are

$$A = -\left(\frac{3}{2}J_0 + \frac{3}{2}J_1 + J_2\right) \quad (14)$$

and

$$B = -J_1. \quad (15)$$

These spectral densities are related to the fourier transform of the correlation function for the spatial operator $F^{(2,r)}$ by

$$J_r = \frac{1}{2} \int_{-\infty}^{\infty} \overline{F^{(2,r)}(0) F^{(2,r)*}(t)} \exp(-ir\omega_0 t) dt. \quad (16)$$

The matrix \mathbf{M}_0 is then

$$\mathbf{M}_0 \equiv \begin{bmatrix} i(\omega_0 + \delta - \omega) + A & B \\ B & i(\omega_0 - \delta - \omega) + A \end{bmatrix}, \quad (17)$$

within the same basis. The angular dependence of the spectrum is contained entirely within \mathbf{M}_0 for, as we have seen, the relaxation matrix elements depend on the sample orientation and in addition

$$\delta = \frac{3}{2} \bar{D}_{\parallel} P_2(\cos \gamma). \quad (18)$$

The general expression for the absorption spectrum is found to be

$$\mathcal{L}(\omega) \propto -\text{Re} \left\{ \frac{A - B + i(\omega_0 - \omega)}{[A + i(\omega_0 - \omega)]^2 + \delta^2 - B^2} \right\}. \quad (19)$$

This adopts a particularly simple form for three limiting situations. One occurs when $\cos \gamma$ equals $1/\sqrt{3}$, for then the two transitions are degenerate, and setting δ equal to zero in equation (19) shows that this single line has a lorentzian shape with a width

$$T_2^{-1} = -(A + B). \quad (20)$$

At the other extreme the two lines are well resolved and so the line separation δ is large compared with the linewidth whose magnitude is of order A . In addition inspection of equations (14) and (15) for A and B reveals that B is always less than A , consequently $\delta > B$. The off-diagonal elements in \mathbf{M}_0 may therefore be ignored and the spectrum calculated from equation (17) is found to be a sum of two lorentzians separated by δ and with equal widths:

$$T_2^{-1} = -A. \quad (21)$$

For intermediate situations the entire line shape should be computed from equation (19); fortunately this is not always necessary. When the molecular motion is slow in the sense that the rotational correlation time is large compared with the inverse of the microwave frequency ω_0 , then the non-secular spectral densities J_1 and J_2 are small in comparison with the secular contribution J_0 . Under these conditions B may be ignored in comparison with A and the line shape is lorentzian for all sample orientations with a width

$$\begin{aligned} T_2^{-1} &= -A, \\ &= \frac{3}{2} J_0. \end{aligned} \quad (22)$$

In the remainder of the linewidth calculation for the electron resonance spectrum of the biradical we shall take this to be the case.

The calculation demands a knowledge of the spatial operator $F^{(2,\gamma)}$ which is obtained by a direct comparison of equations (11) and (12). This operator may then be used to evaluate the spectral density J_0 , for a particular orientation as

$$\begin{aligned} J_0 &= \sum_{p,p',q,q'} (-1)^{p+p'} D^{(2,p)} D^{(2,p')*} \mathcal{D}_{0,q}^{(2)} \mathcal{D}_{0,q'}^{(2)*} \\ &\times \frac{1}{2} \int_{-\infty}^{\infty} \{ \overline{\mathcal{D}_{q,-p}^{(2)}(0) \mathcal{D}_{q',-p}^{(2)*}(t)} - \overline{\mathcal{D}_{0,-p}^{(2)} \mathcal{D}_{0,-p'}^{(2)} \delta_{0q} \delta_{0q'}} \} dt. \end{aligned} \quad (23)$$

The simplification of this multiple summation is entirely analogous to the procedure adopted in calculating the angular dependence of the linewidth for

doublet state species [3]. Here it was shown that terms in the summation vanish unless q equals q' , because the mesophase is cylindrically symmetric, and so

$$J_0 = \sum_{L;p,p',q} (-1)^{p+p'+q} D^{(2,p)} D^{(2,p')*} C(22L;00) C(22L;q-q) P_L(\cos \gamma) \\ \times \frac{1}{2} \int_{-\infty}^{\infty} \{ \overline{\mathcal{D}_{a,-p}^{(2)}(0) \mathcal{D}_{a,-p'}^{(2)*}(t)} - \overline{\mathcal{D}_{0,-p}^{(2)} \mathcal{D}_{0,-p'}^{(2)} \delta_{0q}} \} dt, \quad (24)$$

where the product of rotation matrices has been replaced with a sum of Legendre polynomials by resorting to the Clebsch–Gordan series [12]. The summation is restricted to even values of L because of the $D_{\infty h}$ symmetry of the environment and so the angular dependence of the linewidth is found to be

$$T_2^{-1} = X_0 + X_2 P_2(\cos \gamma) + X_4 P_4(\cos \gamma). \quad (25)$$

To proceed further and obtain explicit expressions for the angular linewidth coefficients we shall require some model for the molecular reorientation process. Two quite different approaches are available although both find it particularly convenient to restrict attention to those spin probes for which the ordering tensor $\overline{\mathcal{D}_{0,p}^{(2)}}$ is cylindrically symmetric, that is the only non-vanishing component has $p=0$. Of course the magnitude of the ordering tensor is determined by the solute–solvent interactions and we can only be certain that $\overline{\mathcal{D}_{0,p}^{(2)}}$ is cylindrically symmetric when the spin probe has the same symmetry. In practice there are few spin probes with cylindrical symmetry although this does not guarantee that the ordering tensor for the remainder are not cylindrically symmetric, but now the symmetry must be established experimentally. Providing the ordering tensor is cylindrically symmetric we may replace $\overline{\mathcal{D}_{0,p}^{(2)}}$, in equation (24) for the spectral density J_0 by $\overline{P_2} \delta_{0p}$ and, more importantly, we can eliminate those terms with p not equal to p' ; the expression for X_L reduces to

$$X_L = \frac{3}{2} \sum_{p,q} (-1)^q |D^{(2,p)}|^2 C(22L;00) C(22L;q-q) j_{q-p}, \quad (26)$$

where the spectral density j_{q-p} is

$$j_{q-p} = \frac{1}{2} \int_{-\infty}^{\infty} \{ \overline{\mathcal{D}_{a,-p}^{(2)}(0) \mathcal{D}_{a,-p}^{(2)*}(t)} - \overline{P_2^2 \delta_{0p} \delta_{0q}} \} dt. \quad (27)$$

The components of the zero-field splitting tensor must now be expressed in the coordinate system which contains the symmetry axis for the ordering tensor as one of the axes. There are several variants of the first model which is based implicitly on the notion of a strong collision which results in instantaneous molecular reorientation through any angle [16]. If, on average, the time between reorientational collisions is τ then the correlation function, which is the integrand in equation (27), decays exponentially with a single time constant τ ; accordingly

$$j_{q-p} = \left\{ \sum_{L'} (-1)^{p+q} C(22L';q-q) C(22L';-pp) \overline{P_{L'}} - \overline{P_2^2 \delta_{0p} \delta_{0q}} \right\} \tau. \quad (28)$$

Of course, such an expression does not reflect the molecular anisotropy accurately since the reorientation process would be expected to be governed by several correlation times. In general, therefore, τ should depend on both p and q [2]; however, even though this assertion is theoretically reasonable, it is unacceptable on practical grounds because it would introduce too many arbitrary parameters. Thus it is difficult to relate the various correlation times $\tau_{p,q}$ in any rigorous fashion although some reduction can be achieved if the correlation times are

assumed to parallel those for a cylindrical symmetric molecule undergoing rotational diffusion in an isotropic system. Accordingly $\tau_{p,q}$ should be independent of q and depend only on the modulus of p [3]; taking the assumption further the remaining three correlation times τ_p should be quadratic in p and so related by

$$\tau_p^{-1} = \frac{\tau_0^{-1}}{4} \left\{ 4 + \left(\frac{\tau_0}{\tau_2} - 1 \right) p^2 \right\}. \quad (29)$$

Such assertions can only be justified by comparison with experiment and at present the few results available seem to support these intuitive expressions for the spectral densities in anisotropic systems. One of the major advantages of this approach is its mathematical simplicity, for example the angular linewidth coefficients are readily calculated to be

$$X_L = \frac{3}{2} \sum_p (-1)^p |D^{(2,p)}|^2 C(22L; 00) C(22L; -pp) \{ \bar{P}_L - \bar{P}_2^2 \delta_{0p} \} \tau_p. \quad (30)$$

Evaluation of the Clebsch-Gordan coefficients [12] then gives the explicit expressions for X_L as

$$X_0 = (3/10) \{ |D^{(2,0)}|^2 (1 - \bar{P}_2^2) \tau_0 + 2 |D^{(2,1)}|^2 \tau_1 + 2 |D^{(2,2)}|^2 \tau_2 \}, \quad (31)$$

$$X_2 = (3/7) \{ |D^{(2,0)}|^2 (\bar{P}_2 - \bar{P}_2^2) \tau_0 + |D^{(2,1)}|^2 \bar{P}_2 \tau_1 - 2 |D^{(2,2)}|^2 \bar{P}_2 \tau_2 \} \quad (32)$$

and

$$X_4 = (9/35) \{ 3 |D^{(2,0)}|^2 (\bar{P}_4 - \bar{P}_2^2) \tau_0 - 4 |D^{(2,1)}|^2 \bar{P}_4 \tau_1 + |D^{(2,2)}|^2 \bar{P}_4 \tau_2 \}. \quad (33)$$

As we mentioned in the Introduction, electron spin relaxation for a triplet state is identical to nuclear spin relaxation, for a nucleus of spin 1, by the quadrupole interaction [17]. Consequently a partial check of equations (31)–(33) is possible because Egozy *et al.* [18] have calculated the deuterium relaxation times, T_1 and T_2 , for perdeuterated benzene dissolved in a nematic mesophase. However, they restrict their attention to the situation when the director is parallel to the magnetic field, the field gradient at the deuterium nucleus is cylindrical symmetric and the molecular reorientation can be described by a single correlation time, as in the simple version of the strong collisional model. If we impose all of these restrictions on equations (25) and (31)–(33) then we obtain the secular contribution to the linewidth, T_2^{-1} , which has the same form as that found by Egozy *et al.* but which is twice as large. Since our results yield the correct limiting value for the secular part of T_2^{-1} when both the system and the motion is isotropic [17] we suppose their equation is in error.

At the other extreme the molecular reorientation is assumed to proceed via small angle jumps, as a consequence the dynamic properties of the system are well defined. They are obtained by solving the diffusion equation, for the conditional probability, after adding terms to allow for the ordering potential provided by the anisotropic environment [19]. According to this diffusion model the spectral densities at zero frequency are given by [20].

$$j_{qp} = \sum_{\substack{L' \neq 0 \\ L'' \text{ (even)}}} \{ (-1)^{p+q} C(2L'L''; q-q) C(2L'L''; p-p) \bar{P}_{L'} - \bar{P}_2 \bar{P}_{L'} \delta_{0p} \delta_{0q} \} \tau_{L',q,p}. \quad (34)$$

The times $\tau_{L',qp}$, which play the same role as the correlation time τ in the strong-collision model, are determined from the matrix \mathbf{R}_{qp} whose elements are defined by

$$R_{qp}^{LL'} = - \{ L(L+1) + (D_{\parallel}/D_{\perp} - 1) p^2 \} \delta_{LL} - \frac{1}{2} \sum_{L''} \lambda_{L''} \\ \times \{ L(L+1) - L'(L'+1) + L''(L''+1) \} C(L''L'L; 0p) C(L''L'L; 0q), \quad (35)$$

where \mathbf{D} is a cylindrically symmetric diffusion tensor whose symmetry axis is assumed to coincide with that of the ordering tensor. The parameters $\lambda_{L'}$ are the expansion coefficients for the orientational energy of a molecule which is

$$U(\beta) = kT \sum_{L(\text{even})} \lambda_L P_L(\cos \beta), \quad (36)$$

where β is the angle between the symmetry axis for the ordering tensor and the director. The $(2, L')$ elements of the inverse matrix \mathbf{R}_{qp}^{-1} are then $-5D_{\perp} \tau_{L', pq} / (2L' + 1)$, where D_{\perp} is the component of the diffusion tensor perpendicular to the molecular symmetry axis. The spectral densities obtained from this model obey certain symmetry rules because of the properties of the Clebsch-Gordan coefficients, in fact

$$j_{qp} = j_{-q-p} = j_{q-p} = j_{-q,p}. \quad (37)$$

We can therefore write the angular linewidth coefficients explicitly as

$$X_0 = (3/10) \{ |D^{(2,0)}|^2 (j_{00} + 2j_{10} + 2j_{20}) + 2|D^{(2,1)}|^2 (j_{01} + 2j_{11} + 2j_{21}) + 2|D^{(2,2)}|^2 (j_{02} + 2j_{12} + 2j_{22}) \}, \quad (38)$$

$$X_2 = (3/7) \{ |D^{(2,0)}|^2 (j_{00} + j_{10} - 2j_{20}) + 2|D^{(2,1)}|^2 (j_{01} + j_{11} - 2j_{21}) + 2|D^{(2,2)}|^2 (j_{02} + j_{12} - 2j_{22}) \} \quad (39)$$

and

$$X_4 = (9/35) \{ |D^{(2,0)}|^2 (3j_{00} - 4j_{10} + j_{20}) + 2|D^{(2,1)}|^2 (3j_{01} - 4j_{11} + j_{21}) + 2|D^{(2,2)}|^2 (3j_{02} - 4j_{12} + j_{22}) \}. \quad (40)$$

In the following section we shall compare the predictions of the two dynamical models with the angular linewidth coefficients measured for a nitroxide biradical dissolved in a nematic mesophase.

3. COMPARISON WITH EXPERIMENT

3.1. The experiment

The biradical spin probe employed to test the theoretical predictions was 1,4-bis(3-spiro-[2'-N-oxyl-3',3'-dimethyloxazolidine]) cyclohexane which has the

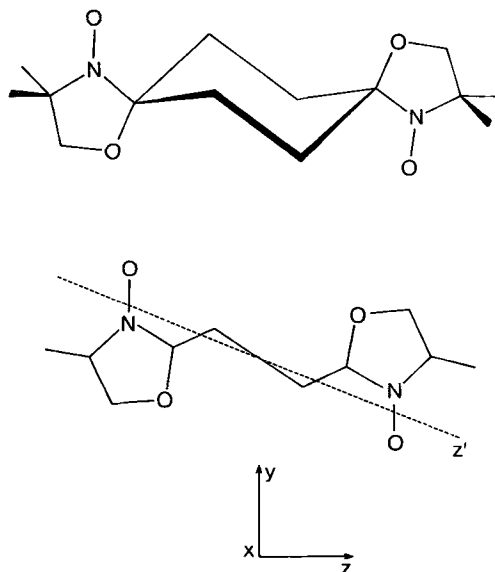


Figure 1. The molecular structure of the biradical spin probe 1,4-bis(3-spiro-[2'-N-oxyl-3',3'-dimethyloxazolidine]) cyclohexane together with a co-ordinate system in which the ordering tensor is supposed to be cylindrically symmetric.

structure shown in figure 1. The spin probe was synthesized from cyclohexan-1,4-dione using the route described by Michon and Rassat [21]. The nematogen, 4,4'-di-n-butyloxyazoxybenzene, was purchased from Eastman Kodak Ltd. and purified by recrystallization from ethanol (T_{S-N} 102°C; T_{N-I} 132°C). In the experiment the orientation of the director is controlled by an electric field, consequently the sample, made by doping the nematogen with the spin probe, was contained in a cell made from two glass plates approximately 1 cm \times 10 cm and held 125 μ m apart with a Teflon spacer. The inner surfaces of the plates were coated with tin oxide and this allows the application of an electric field perpendicular to the surface. In the absence of an electric field the director is aligned parallel to the spectrometer's magnetic field; however, the magnetic forces responsible for this alignment are overcome by a 14 kHz electric field from an applied voltage of 90 volts. Under these conditions the director is aligned perpendicular to the electric field and so parallel to the plates of the cell because the anisotropic permittivity is negative [1]. The only effect of the magnetic field now is to constrain the director to lie in the plane containing both the magnetic and electric

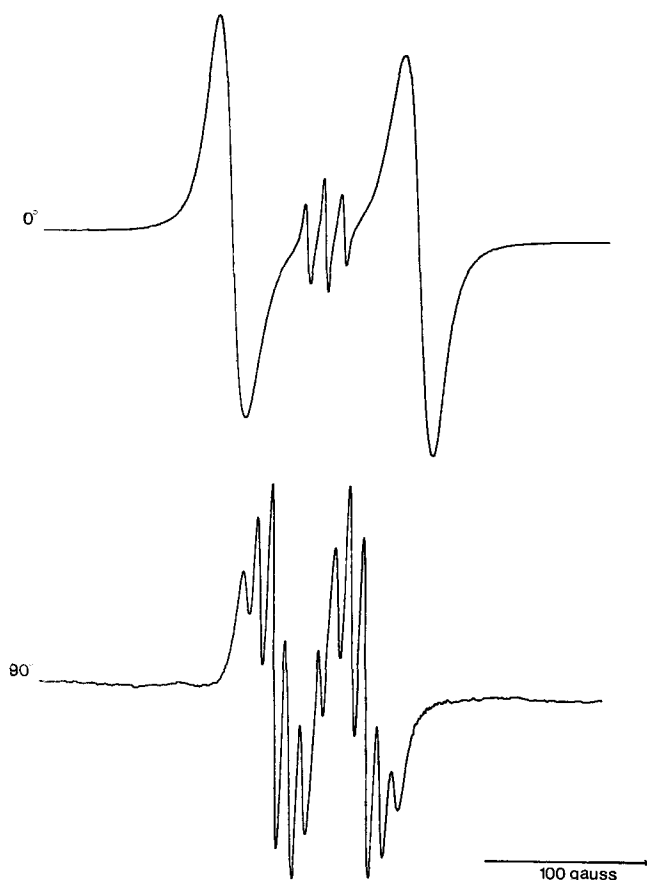


Figure 2. The electron resonance spectrum of the biradical in the nematic mesophase of 4,4'-di-n-butyloxyazoxybenzene at 104°C with the director (a) parallel and (b) perpendicular to the magnetic field.

fields. The angle γ between the director and the magnetic field is then 90° minus the angle made by the electric field with the magnetic field. The cell was mounted in a goniometer and the angular dependence of the spectrum for the spin probe in the nematic mesophase was recorded; the measurements were made at two temperatures, 127°C and 104°C . Typical spectra are shown in figure 2 for the sample at 104°C with the director parallel and perpendicular to the magnetic field; these two spectra clearly demonstrate the angular dependence of the linewidths and we shall now describe the determination of these widths.

3.2. Spectral analysis

The spectra in figure 2 are dominated by the dipolar splitting whose angular dependence is predicted by equation (6); for those orientations where the dipolar splitting is well resolved there is complete agreement between the observed and theoretical line separations. The values of \tilde{D}_\parallel determined from the angular dependence for the two temperatures are given in table 2. The spectrum, for the

| Temperature ($^\circ\text{C}$) | \tilde{D}_\parallel (MHz) | \tilde{A}_\parallel (MHz) | \tilde{A}_\perp (MHz) | $\tilde{D}_\parallel/(\tilde{A}_\parallel - \tilde{A}_\perp)$ |
|-------------------------------------|--------------------------------|--------------------------------|----------------------------|---|
| 104° | 101 | 29.2 | 47.2 | -5.6 |
| 127° | 64 | 33.7 | 44.9 | -5.7 |

Table 2. The partially averaged magnetic parameters.

director orthogonal to the magnetic field, also exhibits hyperfine structure from the two equivalent nitrogen nuclei, the spacing between the lines is just one-half the nitrogen coupling constant because the electron-electron interaction greatly exceeds the hyperfine interaction [22]. For many orientations the hyperfine splitting is not resolved but does result in inhomogeneous broadening of the spectral lines; consequently it is essential to allow for this broadening when obtaining the true linewidth. We have therefore simulated spectra which incorporate both the dipolar and hyperfine splittings, the linewidth was then varied until agreement with the observed spectrum was obtained. The angular dependence of the coupling constant, required in the simulations, is given by [1]

$$\bar{a}(\gamma) = \{\tilde{A}_\parallel^2 \cos^2 \gamma + \tilde{A}_\perp^2 \sin^2 \gamma\}^{1/2}, \quad (41)$$

since the anisotropy in the partially averaged g tensor is negligibly small. The values of the two components of the partially averaged nitrogen hyperfine tensor employed in the spectral simulations are given in table 2. Since $\bar{a}(\gamma)$ could not always be obtained from the spectrum of the biradical we have also measured the nitrogen coupling constant of the nitroxide monoradical, which is responsible for the central three lines in figure 1 (*a*). The radical is almost certainly the hydroxylamine derivative of the biradical formed by hydrogen abstraction from the solvent. In view of the great similarity of the structures of mono and biradical we expect their partially averaged nitrogen hyperfine tensors to be the same and this is found to be so when both splittings can be measured simultaneously. The linewidths obtained by matching the theoretical and experimental spectra are plotted against the director orientation in figure 3 for the sample at 104°C ; a similar angular dependence was observed at 127°C .

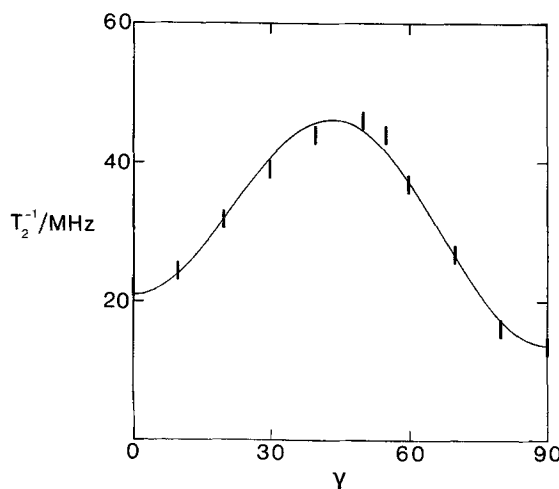


Figure 3. The angular dependence of the linewidth for the biradical dissolved in the nematic mesophase at 104°C. The solid line is the best fit to equation (25).

3.3. The molecular symmetry

The expressions obtained for the angular linewidth coefficients are only valid when the ordering tensor $\overline{\mathcal{D}}_{0,p}^{(2)}$ for the spin probe is cylindrically symmetric. The spin probe employed in the experiments does not possess cylindrical symmetry and so we must first show that $\overline{\mathcal{D}}_{0,0}^{(2)}$ is the only non-zero component of the ordering tensor. There are five unknown order parameters, and since there are only two independent pieces of experimental information (\tilde{A}_\parallel and \tilde{D}_\parallel) all we can hope to achieve is to show that they are consistent with an assumed cylindrical symmetry. The spin probe may exist in one of several conformations but solid-state electron resonance studies indicate that the equatorial–equatorial chair form of the trans isomer, shown in figure 1, is preferred [23]. Examination of molecular models then suggests that the ordering tensor for the spin probe in the nematic mesophase should be cylindrically symmetric about the z axis shown in figure 1, together with a projection formula for the conformer. Provided the assumption of cylindrical symmetry is correct then the components of the partially averaged tensors are given by

$$\tilde{D}_\parallel = (2/3)^{1/2} D^{(2,0)} \overline{P}_2 \quad (42)$$

and

$$\tilde{A}_\parallel - \tilde{A}_\perp = (3/2)^{1/2} A^{(2,0)} \overline{P}_2, \quad (43)$$

where the zeroth component of the appropriate anisotropic tensor is evaluated in the xyz coordinate system, shown in figure 1. The nitrogen hyperfine tensor, for such oxazolidines, is cylindrically symmetric about the x axis [23] and so

$$A^{(2,0)} = -(3/8)^{1/2} A_\parallel', \quad (44)$$

where A_\parallel' is the component of the anisotropic tensor along this symmetry axis. The zero-field splitting tensor is, to a good approximation, also cylindrically symmetric [21, 23] but about the z' axis which makes an angle θ with the z axis and so

$$D^{(2,0)} = (3/2)^{1/2} \frac{(3 \cos^2 \theta - 1)}{2} D_{z'z'}. \quad (45)$$

Because the symmetry axes of the two magnetic tensors are not parallel the ratio $\bar{D}_{\parallel}/(\bar{A}_{\parallel}-\bar{A}_{\perp})$ may only be independent of temperature if the ordering tensor is cylindrically symmetric. The values calculated for this ratio are essentially constant as we can see from the results given in table 2. The angle θ can be extracted from these values for $\bar{D}_{\parallel}/(\bar{A}_{\parallel}-\bar{A}_{\perp})$ since, from equations (42)–(45)

$$\frac{(3 \cos^2 \theta - 1)}{2} = - \frac{3\bar{D}_{\parallel}}{4(\bar{A}_{\parallel}-\bar{A}_{\perp})} \frac{A'_{\parallel}}{D_{z'z'}}. \quad (46)$$

Calculation of θ provides us with an additional check on the assumption of cylindrical symmetry because this angle may be estimated from molecular models. Thus the z' axis has been found to intersect the N–O bonds at about one-quarter of the bond length from nitrogen [23] and so θ should be about 20° , given our assignment of the z axis. Since θ is relatively small rather precise values of the parameters occurring in equation (46) are required to obtain a reliable estimate of this angle. The zero-field splitting tensor is known, with some accuracy, from single crystal studies and $D_{z'z'}$ is found to be 230 MHz [23]. Unfortunately the anisotropic hyperfine tensor is not known with such certainty and three reasonable values are available. The single crystal study of the biradical yields a value for A'_{\parallel} of 52.5 MHz although the accuracy is said not to be high [23]. A more reliable value of 51.1 MHz has been determined for the structurally related monoradical 2-N-oxyl, 1,1,3,3-tetramethyloxazolidine [23]. Finally A'_{\parallel} is 48.7 MHz for another monoradical, (3-spiro-[2'N-oxyl-3',3'-dimethyloxazolidine])-5 α -androstane-17 β -ol [24], which, in view of the cyclic groups, should be most closely related to the biradical. The magnitudes of θ and \bar{P}_2 obtained from the single value of $D_{z'z'}$ together with these three values of A'_{\parallel} are listed in table 3 for both temperatures. The angle θ is seen to range from 8° to 15° even though the component of the anisotropic hyperfine tensor only changes by an amount, 3.8 MHz, not greatly in excess of the experimental error in A'_{\parallel} . In view of this extreme sensitivity of the angle to A'_{\parallel} we believe the results for θ are also in accord with the assumption of a cylindrically symmetric ordering tensor. In addition we shall take θ to be 15° in subsequent calculations because this value is closest to our original estimate of 20° based on an examination of molecular models.

| A'_{\parallel} /MHz | Temperature ($^\circ$ C) | | | |
|-----------------------|---------------------------|-------------|--------------|-------------|
| | 104 $^\circ$ | | 127 $^\circ$ | |
| | θ | \bar{P}_2 | θ | \bar{P}_2 |
| 52.5 | 9 $^\circ$ | 0.46 | 8 $^\circ$ | 0.29 |
| 51.1 | 12 $^\circ$ | 0.47 | 11 $^\circ$ | 0.29 |
| 48.7 | 15 $^\circ$ | 0.49 | 15 $^\circ$ | 0.31 |

Table 3. The derived parameters θ and \bar{P}_2 .

3.4. The angular linewidth coefficients

As we have just seen, our assumption of a cylindrically symmetric ordering tensor is not unreasonable and so we may now turn to a detailed analysis of the linewidths. The first test of the theory is to see if the angular dependence of the

linewidths is in accord with that predicted by equation (25). The theoretical angular dependence of T_2^{-1} is shown as the solid line in figure 3 and is seen to be in good agreement with experiment; comparable agreement is also found for the linewidths measured at 127°C. Of course such comparisons do not provide a particularly severe test for the theory because the predicted angular dependence of the linewidth stems directly from the $D_{\infty h}$ symmetry of the anisotropic environment and the second rank nature of the zero-field splitting tensor. In fact the good agreement between theory and experiment may be taken as confirmation of our correct assignment of the dominant spin relaxation process. A more searching test of the theory is provided by an attempt to predict the observed angular linewidth coefficients X_L ; these are listed in table 4 and were obtained by fitting equation (25) for $T_2^{-1}(\gamma)$ to the experimental linewidths. There are, of course, two theoretical expressions for the coefficients X_L and one of the major objectives of any experimental linewidth investigation is to distinguish between the two extreme models for molecular reorientation. However, in this study we shall be primarily concerned with using the experimental results, which are not of high accuracy, simply to illustrate the theory.

| Temperature (°C) | X_0 (MHz) | X_2 (MHz) | X_4 (MHz) | X_0/X_2 | X_0/X_4 |
|---------------------|----------------|----------------|----------------|-----------|--------------|
| 104° | 31.4 ± 0.5 | 16 ± 1 | -26 ± 1 | 2.0 ± 0.2 | -1.21 ± 0.07 |
| 127° | 29.5 ± 0.9 | 9 ± 2 | -14 ± 2 | 3.3 ± 0.8 | -2.1 ± 0.4 |

Table 4. The angular linewidth coefficients.

We now proceed to calculate the angular linewidth coefficients using both models. To make the comparison with experiment as equitable as possible the ordering potential, given in equation (36), will be restricted to just the first term, i.e.

$$\frac{U}{kT} = \lambda_2 P_2(\cos \beta), \quad (47)$$

in both calculations. The magnitude of the single parameter λ_2 may then be calculated from the observed value of the order parameter \bar{P}_2 ; the results of this calculation are listed in table 5. Because the potential is restricted to a single term both dynamic models lead to sets of equations for X_L which contain just two arbitrary parameters. In addition the ratios X_0/X_2 and X_0/X_4 of the angular linewidth coefficients are seen to depend on the ratio of the appropriate parameters; in the case of the strong-collision model this is τ_0/τ_2 while for the diffusion model it is $D_{||}/D_{\perp}$.

| Temperature (°C) | \bar{P}_2 | \bar{P}_4 | λ_2 |
|---------------------|-------------|-------------|-------------|
| 104° | 0.49 | 0.16 | -2.3 |
| 127° | 0.31 | 0.06 | -1.4 |

Table 5. The order parameters.

We begin with the strong-collision model; the evaluation of the linewidth coefficients requires the order parameter \bar{P}_4 and this was calculated from the values for λ_2 with the results given in table 5. This procedure contrasts with previous linewidth studies employing doublet states where the angular linewidth coefficients were employed to determine \bar{P}_4 [3, 4, 7]. The components of the zero-field splitting tensor in the principal coordinate system, xyz , for the ordering tensor were found to be

$$\left. \begin{aligned} D^{(2,0)} &= 252 \text{ MHz,} \\ D^{(2,\pm 1)} &= 85 \text{ MHz} \\ \text{and} \\ D^{(2,\pm 2)} &= 12 \text{ MHz.} \end{aligned} \right\} \quad (48)$$

The two ratios of the linewidth coefficients, X_0/X_2 and X_0/X_4 , were calculated from equations (31)–(33) for a wide range of values of the relative correlation time τ_0/τ_2 in an attempt to find agreement with experiment. However, both X_0/X_2 and X_0/X_4 proved to be virtually independent of τ_0/τ_2 and it was not possible to fit the experimental results. For example, at 104°C, where the experimental data are most reliable, X_0/X_2 was predicted to change only from 2.3 to 2.2 when τ_0/τ_2 was varied from 1 to 8. This prediction is in reasonable agreement with experiment, but, in marked contrast, X_0/X_4 is calculated to be -3.7 , which is over three times the observed value. It is, of course, possible to force agreement with the experimental value of X_0/X_4 by changing the magnitude of the order parameter \bar{P}_4 , since this affects just the X_4 angular linewidth coefficient. Agreement can only be achieved when \bar{P}_4 is virtually zero; a result which is in accord with small values of \bar{P}_4 determined by Raman studies [25]. However, we suspect that the value is unreasonably small in view of the success of the single parameter potential in linewidth investigations employing doublet state spin probes [3, 4, 7]. The analysis of the angular linewidth coefficients obtained for the biradical at 127°C yielded similar discrepancies between theory and experiment.

The angular linewidth coefficients were also evaluated using the diffusion model; again the ordering potential was restricted to a single term with λ_2 taking the values given in table 5. For these relatively low values of λ_2 it was found to be adequate to truncate the series expansion of the spectral density in equation (34) after $L'' = 20$; consequently the matrix \mathbf{R}_{pq} was restricted to a maximum dimension of 20. The relative linewidth coefficients were obtained for various values of D_{\parallel}/D_{\perp} and although the results were not particularly sensitive to D_{\parallel}/D_{\perp} it did prove possible to obtain the ratios X_0/X_2 and X_0/X_4 in fair, but not complete, agreement with experiment. The best fit was found for a range of values for D_{\parallel}/D_{\perp} and these are listed in table 6, together with the predicted linewidth ratios. As we expect the agreement between theory and experiment is best for the more accurate angular linewidth coefficients measured at 104°C. The agreement for the less accurate results at 127° is not so impressive although still an improvement on the predictions of the strong-collisional model. The ratio D_{\parallel}/D_{\perp} for the components of the diffusion tensor is independent of temperature as we might anticipate [4]. We can estimate this ratio in the hydrodynamic limit if the molecular dimensions are known [4, 26]; using molecular models we gauge the major semi axis to be 12 Å while the minor semi axis is about 4.5 Å. The hydrodynamic value of D_{\parallel}/D_{\perp} is then found to be 2.7, which is about twice as large as

| Temperature (°C) | D_{\parallel}/D_{\perp} | X_0/X_2 | X_0/X_4 | D_{\perp} (Mrads ⁻¹) |
|---------------------|---------------------------|-----------|-----------|---------------------------------------|
| 104° | 1.2 | 1.8 | -1.4 | 600 |
| | 1.4 | 1.8 | -1.5 | 520 |
| | 1.6 | 1.8 | -1.6 | 540 |
| 127° | 1.2 | 2.3 | -3.4 | 720 |
| | 1.4 | 2.3 | -3.6 | 700 |
| | 1.6 | 2.3 | -3.8 | 680 |

Table 6. The diffusion model predictions.

the experimental value. It is surprising to find a value below the hydrodynamic limit because similar studies of doublet-state spin probes have yielded value in excess of this limit [4-6]. Indeed, for these systems it proved necessary to introduce an anisotropic interaction tensor κ (4) whose magnitude is related to the anisotropy in the intermolecular potential [27] to account for the deviations from the hydrodynamic limit. Of course analogous explanations cannot be invoked, for rod-like molecules, when the ratio D_{\parallel}/D_{\perp} is less than the hydrodynamic limit [4].

The diffusion model of molecular reorientation in an anisotropic medium provides an adequate description of the angular linewidth coefficients, even though the ordering potential is restricted to a single term. This limited success contrasts with the apparent failure of the strong collision model which is only able to predict the ratio X_0/X_2 when the ordering potential contains a single term. In the anisotropic system which we have studied the molecular reorientation would appear to occur via rotational diffusion although more precise results will be required before we can differentiate with complete certainty between the two models.

4. ADDITIONAL SPECTRAL FEATURES

When the director is orthogonal to the magnetic field the five nitrogen hyperfine lines associated with either component of the dipolar doublet are well resolved. Close inspection of the appropriate spectrum, shown in figure 2, reveals a minor variation in the widths of the hyperfine lines. Such asymmetric line broadening cannot be accounted for by the theory which we have just developed because the anisotropic hyperfine interaction was specifically excluded from the dynamic perturbation. However quite straightforward arguments [28] show that this line broadening can be explained by inclusion of the hyperfine term in $\mathcal{H}'(t)$, the asymmetric linewidth effect then originates from the cross term between the anisotropic hyperfine interaction and the zero-field splitting tensor. We do not feel impelled to make a more detailed analysis because this broadening is quite secondary to the other linewidth variation which we have observed.

The spectral line shape is expected to be symmetric about the base line but examination of the spectrum for the director parallel to the magnetic field shows that this is not the case. Similar asymmetry in the line shape has been observed for doublet-state spin probes dissolved in liquid crystals and has been attributed to non-uniform alignment of the director, probably caused by thermal fluctuations [29]. A slight departure from uniform alignment of the director would also be expected to produce asymmetric line shapes for biradical spin probes and we have

used spectral simulations to confirm this expectation. Of course we also expect the line shape to become asymmetric when the rate of molecular rotation is comparable to the inverse of the zero-field splitting [30]. Unfortunately it is difficult to devise experiments to distinguish between these two possible explanations of asymmetric line shapes. However, the rate of motion may be obtained from the inverse of the diffusion tensor; from the values listed in table 6 we can see that the ratio of the zero-field splitting to either component of the diffusion tensor is just less than unity. Accordingly the assumption of rapid motion should be valid for this system and the asymmetric line shape presumably originates for non-uniform alignment of the director.

5. QUADRUPOLE RELAXATION

The problem which we have just solved is formally identical to the calculation of the spin relaxation times, for a nucleus of spin 1, caused by a quadrupole interaction coupled to the molecular reorientation. Consequently our results could be of value in understanding the spin relaxation behaviour of nuclei, such as deuterium, when they are incorporated in molecules forming part of a liquid crystalline system. However, some caution must be exercised in the application of these results. For example, although the neglect of the non-secular terms in the dynamic perturbation is a good approximation for electron resonance spectroscopy such an assumption may not be valid for nuclear magnetic resonance where the operating frequency is much smaller. If the non-secular terms do have to be retained then the entire lineshape will have to be calculated from equation (19) and a simple analysis is only possible when the lines are well resolved or the transitions are completely degenerate. In addition our assignment of the dominant process responsible for changes in the molecular orientation may be quite irrelevant for nuclear magnetic resonance. This situation obtains because the quadrupole interaction is considerably smaller than the zero-field splitting and so the motion with respect to the director, which we have considered, is too fast to make a significant contribution to the nuclear spin relaxation times [31]. However, the molecular orientation is also changed by thermal fluctuations in the director and although this motion is slow on the electron resonance time scale it is sufficiently fast to influence the relaxation times in nuclear magnetic resonance [32]. Consequently the spectral densities employed in this paper would be inappropriate for calculating the deuteron relaxation times; it is however straightforward to obtain the relevant spectral densities from continuum theory [32, 33]. The calculation of the spin lattice relaxation time T_1 also presents certain difficulties especially when the two transitions are nearly degenerate. Indeed the general angular dependence of T_1 is complicated even when the spectral lines are well resolved and we shall not discuss this aspect of the problem here.

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REFERENCES

- [1] LUCKHURST, G. R., 1974, *Liquid Crystals and Plastic Crystals*, Vol. 2, edited by G. W. Gray and P. A. Winsor (Ellis Horwood Ltd.), Chap. 7.
- [2] MCFARLAND, B. G., and MCCONNELL, H. M., 1971, *Proc. natn. Acad. Sci. U.S.A.*, **68**, 1274.
- [3] LUCKHURST, G. R., and SANSON, A., 1972, *Molec. Phys.*, **24**, 1297.
- [4] LUCKHURST, G. R., SETAKA, M., and ZANNONI, C., 1974, *Molec. Phys.*, **28**, 49.
- [5] HEMMINGA, M. A., 1974, *Chem. Phys.*, **6**, 87.
- [6] SCHINDLER, H., and SEELIG, J., 1973, *J. chem. Phys.*, **59**, 1841; 1974, *Ibid.*, **61**, 2946.
- [7] LUCKHURST, G. R., and POUPKO, R., 1974, *Chem. Phys. Lett.*, **29**, 191.
- [8] KEANA, J. F. W., and DINERSTEIN, R. J., 1971, *J. Am. chem. Soc.*, **93**, 2808.
- [9] GIROUD, A. M., RASSAT, A., and SIEVEKING, H. U., 1974, *Tet. Lett.*, p. 635.
- [10] CHARVOLIN, J., MANNEVILLE, P., and DELOCHE, B., 1973, *Chem. Phys. Lett.*, **23**, 345.
SEELIG, J., and NIEDERBERGER, W., 1974, *J. Am. chem. Soc.*, **96**, 2069. LUZ, Z., HEWITT, R. C., and MEIBOOM, S., 1974, *J. chem. Phys.*, **61**, 1758.
- [11] LUCKHURST, G. R., and PEDULLI, G. F., 1971, *Molec. Phys.*, **20**, 1043.
- [12] ROSE, M. E., 1957, *Elementary Theory of Angular Momentum* (John Wiley).
- [13] LOW, W., 1960, *Paramagnetic Resonance in Solids* (Academic Press), p. 52.
- [14] BINSCH, G., 1968, *Molec. Phys.*, **15**, 469.
- [15] REDFIELD, A. G., 1965, *Adv. magn. Res.*, **1**, 1.
- [16] KAUZMANN, W., 1942, *Rev. mod. Phys.*, **14**, 12.
- [17] CARRINGTON, A., and LUCKHURST, G. R., 1964, *Molec. Phys.*, **8**, 125.
- [18] EGOZY, Y., LOEWENSTEIN, A., and SILVER, B. L., 1970, *Molec. Phys.*, **19**, 177.
- [19] BENOIT, H., 1951, *Ann. Phys.*, **6**, 561; 1952, *J. chem. Phys.*, **49**, 517.
- [20] NORDIO, P. L., and BUSOLIN, P., 1971, *J. chem. Phys.*, **55**, 5485. NORDIO, P. L., RIGATTI, G., and SEGRE, U., 1972, *J. chem. Phys.*, **56**, 2117.
- [21] MICHON, J., and RASSAT, A., 1974, *J. Am. chem. Soc.*, **96**, 335.
- [22] SLICHTER, C. P., 1955, *Phys. Rev.*, **99**, 479.
- [23] ROHDE, O., VAN, S. P., KESTER, W. R., and GRIFFITH, O. H., 1974, *J. Am. chem. Soc.*, **96**, 5311.
- [24] HUBBEL, W. L., and MCCONNELL, H. M., 1971, *J. Am. chem. Soc.*, **93**, 314.
- [25] JEN, S., CLARK, N. A., PERSHAN, P. S., and PRIESTLEY, E. B., 1973, *Phys. Rev. Lett.*, **26**, 1552.
- [26] PERRIN, F., 1934, *J. Phys., Paris*, **5**, 497.
- [27] KIVELSON, D., KIVELSON, M. G., and OPPENHEIM, I., 1970, *J. chem. Phys.*, **52**, 1810.
- [28] LEMAIRE, H., 1966, *J. Chim. phys.*, **64**, 559.
- [29] BROOKS, S. A., LUCKHURST, G. R., and PEDULLI, G. F., 1971, *Chem. Phys. Lett.*, **11**, 159.
- [30] FREED, J. H., 1972, *Electron Spin Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (Plenum Press), Chap. 14.
- [31] DOANE, J. W., and JOHNSON, D. L., 1970, *Chem. Phys. Lett.*, **6**, 291.
- [32] PINCUS, P., 1969, *Solid-St. Commun.*, **6**, 839.
- [33] DE GENNES, P. G., 1969, *Molec. Crystals Liq. Crystals*, **7**, 325.