Orientation-Dependent Spin Relaxation: 
Tridical Spin Probes in Anisotropic Environments

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The theory necessary to understand the positions and widths of the lines in the electron resonance spectra of tritiloals dissolved in anisotropic environments is developed for systems with rapid molecular reorientation. Particular attention is paid to the angular variation of the linewidths and it is shown how this may be employed to determine a fourth-rank orientational order parameter for the tritioal spin probe, not available with other techniques.

INTRODUCTION

Electron resonance spectroscopy is frequently employed in the investigation of anisotropic systems such as thermotropic liquid crystals (1) and membranes (2). The value of this particular technique may not be immediately apparent because most systems of interest are diamagnetic and so must be doped with a paramagnetic spin probe. Consequently the information available from these experiments would appear to relate to the interactions between the environment and the spin probe but not to the properties of the environment itself. Thus, although certain continuum properties of the pure liquid crystal can be extracted from some experiments (3), in the majority of studies the electron resonance spectra are analyzed to yield the static and dynamic properties of the spin probe. Even though these properties must reflect the behavior of the environment, such studies are only valid if the information gained cannot be obtained for the pure system in any other way. For example, the line positions in the spectrum of the spin probe may be used to determine the second-rank orientational order parameter for the probe but this information can be obtained from nuclear magnetic resonance studies of the pure liquid crystal (1). Here the only justification for the spin probe technique would appear to be the ease of spectral analysis when compared with the difficulties often encountered in interpreting the nuclear magnetic resonance spectrum. In contrast, the linewidths in the electron resonance spectrum may be employed to obtain information not readily available for the pure system. These widths allow a determination of the fourth-rank order parameter for the spin probe as well as the correlation times describing its reorientation in the anisotropic environment (4, 5). This higher order parameter is, in principle, available from laser scattering experiments involving the pure liquid crystal (6) but in practice the validity of the results has been questioned (7). The rotational correlation times for the liquid crystal can often be inferred from dielectric relaxation experiments although the route from the frequency...
dependence of the permittivity to these imes is not straightforward (8). Since a knowledge of both the static and dynamic properties is important for a detailed understanding of liquid crystals there is some merit in the use of the spin probe technique based on the spectral linewidths.

The relevance of such studies to the behavior of the pure mesophase is clearly increased as the structure of the spin probe tends to that of the system under investigation. It is important therefore to employ a range of spin probes in order to be able to extrapolate the results to those for the pure system. Such experiments are now possible because the skill of the synthetic chemist has made available a wide range of stable nitroxide radicals. Indeed, they have been employed with considerable success in studying the dynamic and static properties of a variety of systems (9-11). However, these spin probes do suffer from one disadvantage for linewidth investigations, in that the anisotropy in the magnetic interactions is not significantly influenced by changes in the structure of the probe. Since the extent of the line broadening is directly related to the product of the rotational correlation time and the square of the magnetic anisotropy, only systems with a particular range of correlation times can be studied. This limitation has been largely overcome by the introduction of spin probes containing two or more unpaired electrons, for the anisotropic interaction between the electron spins can be varied simply by changing their separation. Bridicals have already been employed to study several anisotropic systems (12, 13) and the theory necessary to interpret both the line positions and widths has been developed (14). However, it is difficult to make an unambiguous assignment of the line-broadening processes because the widths of the spectral lines are observed, and predicted, to be the same. This problem does not occur for triradical spin probes in anisotropic environments, for the lines in the electron resonance spectra are found to exhibit quite marked variations in their widths (15-17). These variations, could, as we shall see, be employed with some confidence to determine both the higher orientational order parameter and the rotational correlation times. However, there is no theory with which to analyze the linewidths and so here we develop the necessary spin relaxation theory.

STATICs

We begin with a brief description of the theory needed to understand the line positions in the electron resonance spectrum of a triradical dissolved in a liquid crystal. Although the unpaired electrons interact with the magnetic nuclei in the triradical we shall ignore these hyperfine interactions because they complicate the calculation without contributing to the basic physics. In addition these terms will only be important when the quartet-doublet separation is comparable to the hyperfine couplings and then our theory will need to be extended (19). The scalar spin Hamiltonian for a set of three electrons is

\[ H^s = g \langle B \rangle S_0 + \frac{1}{2} J S \cdot S, \]  

[1]

where \( J \) is the scalar electron-electron exchange integral and \( S \) is the total electron spin operator (18). The eigenfunctions, \( |S, m_s \rangle \), of this spin Hamiltonian are the four components \( |3/2, m_s \rangle \) of the quartet state together with the four components of the two doublet states \( |\frac{1}{2}, m_{s1} \rangle \) and \( |\frac{1}{2}, m_{s2} \rangle \) (19). In zero magnetic field the energy separation between the quartet and doublet states is just \( \pm J/2 \).
For a fixed molecular orientation another term must be added to this spin Hamiltonian to represent the anisotropic interaction between the unpaired electrons. In principle there are other contributions originating from the anisotropy of the g tensor but these will be neglected because they are small in comparison with the electron-electron interaction. We shall find it convenient to write this additional term using irreducible spherical tensor notation (19) and so the spin Hamiltonian takes the form

$$H = H^0 + \sum \sum (-1)^{P} P^{(0), r}_{\alpha \beta} T^{(0), r}_{\alpha \beta},$$

where $D^{(0), r}_{\alpha \beta}$ denotes the pth component of the zero-field splitting tensor and $T^{(0), r}_{\alpha \beta}$ is an appropriate combination of total spin operators (4). Their matrix elements are best evaluated with the aid of the Wigner-Eckart theorem

$$\langle S', m_s|T^{(0), r}_{\alpha \beta}|S, m_s\rangle = C(S2S' ; m_s, p)|S|T^{(0), r}_{\alpha \beta} \delta_{\alpha \beta},$$

where $C(S2S' ; m_s, p)$ is a Clebsch-Gordan coefficient and $|S|T^{(0), r}_{\alpha \beta}$ is a reduced matrix element (19). When the molecule rotates, these matrix elements fluctuate in time because the zero-field tensor is written in the molecular frame; we can, however, remove this time dependence by transforming the spin operators to a space-fixed coordinate system. For uniaxial environments, such as nematic and smectic A liquid crystals, it is natural to choose the laboratory frame with the z axis parallel to the symmetry axis or director of the liquid crystal. Thus

$$H = H^0 + \sum \sum (-1)^{P} D^{(0), r}_{\alpha \beta} \langle 0|T^{(0), r}_{\alpha \beta}|0\rangle,$$

where $\langle 0|T^{(0), r}_{\alpha \beta}|0\rangle$ is a Wigner rotation matrix connecting the molecular and laboratory frames (19). The static spin Hamiltonian can be calculated from Eq [4] by taking a time average ensemble average, provided the inverse of the zero-field splitting is greater than the correlation times describing the rotational motion. We therefore find

$$\bar{H} = H^0 + \sum \sum (-1)^{P} D^{(0), r}_{\alpha \beta} \langle 0|T^{(0), r}_{\alpha \beta}|0\rangle,$$

where the averages of those rotation matrices with $q$ not equal to zero vanish because of the $D_{bl}$ symmetry of the mesophase (20). This spin Hamiltonian is identical to that for a static species whose zero-field splitting $\bar{H}$ is cylindrical symmetric about the director with

$$D^{(0), r}_{\alpha \beta} = \sum (-1)^{P} D^{(0), r}_{\alpha \beta} \langle 0|T^{(0), r}_{\alpha \beta}|0\rangle,$$

The spectroscopic properties of such a system are well understood (21) and are particularly simple when the Zeeman separations greatly exceeds the zero-field splitting, for then the nonsecular terms in the spin Hamiltonian may be ignored. This condition is likely to be satisfied by most organic radicals and so the allowed transitions within the quartet manifold are

$$\begin{align*}
|3\rangle & \rightarrow |2\rangle \rightarrow |1\rangle \\
|3\rangle & \rightarrow |2\rangle \rightarrow |0\rangle \\
|3\rangle & \rightarrow |1\rangle \rightarrow |0\rangle \\
|3\rangle & \rightarrow |1\rangle \rightarrow |0\rangle.
\end{align*}$$
just as in the isotropic phase. However, the degeneracy of the transitions is removed by the partially averaged zero-field splitting and the resonant fields are now

\[ B_{\alpha} = (\hbar \omega_0 / g_\beta) \pm 3 \vec{D} \cdot \vec{P} (\cos \gamma), \]  

\[ \delta B = \hbar \omega_0 / g_\beta. \]  

when the director makes an angle \( \gamma \) with the magnetic field \( \vec{D} \). Parallel to the director is denoted by \( \vec{D} \), and \( P (\cos \gamma) \) is the second Legendre function \( (19) \). The spectrum from the quartet state therefore contains three lines with relative intensities 3:4:3 and with an orientation-dependent separation \( \delta B \), between the outer lines given by

\[ \delta B_{\alpha} = 6 \vec{D} \cdot \vec{P} (\cos \gamma). \]  

The zero-field splitting does not affect the doublet levels because the matrix elements of \( T^{(1, 1)} \) within these states all vanish. This is readily seen because the Clebsch-Gordan coefficients, \( C(\pm 2 \pm 1, m, p) \) required in their calculation are all zero. Similarly, the doublet states are not mixed with the quartet states by the zero-field splitting terms because the reduced matrix element \( \langle 2 | T^{(1, 1)} | 1 \rangle \) is zero. The spectrum from the doublet states is therefore unaffected by the partial alignment in the anisotropic environment and so consists of a single line at

\[ B_0 = \hbar \omega_0 / g_\beta. \]  

with an intensity of 2 relative to the quartet transitions. Provided the exchange integral is considerably less than the thermal energy, the quartet and doublet states will be equally populated and so the total spectrum will contain three lines with relative intensities 1:2:1. For most organic triradicals this condition is likely to be satisfied but, if it is not, then the relative contributions to the spectrum must be evaluated by taking the appropriate Boltzmann average. In any event the angular dependence of the separation \( \delta B_{\alpha} \) will lead to \( \vec{D} \), the single independent element of the partially averaged zero-field splitting \( \vec{D} \). In general this single piece of information is insufficient to determine the ordering tensor \( \delta D_{\alpha \beta} \) and only a linear combination of the components may be obtained. However, many triradicals possess a threefold symmetry axis \((13, 13)\) and the ordering tensor for such molecules contains just one independent component; for these spin-probes the expression for \( \delta D_{\alpha \beta} \) reduces to

\[ \delta D_{\alpha \beta} \approx \delta D_{\alpha \beta} \]  

where \( \delta D_{\alpha \beta} \) is the component of the ordering matrix \((22)\) for the molecular symmetry axis. As we shall now see the analogous higher order parameter, \( P_{\alpha} \), can be obtained from the angular dependence of the linewidths.

**DYNAMICS**

The dominant spin relaxation process for our slightly idealized triradical spin probe is expected to result from the anisotropy in the zero-field splitting together with the molecular rotation. Thus changes in the molecular orientation cause the energies of the spin levels to fluctuate in time and also induce transitions between them; in this section we calculate the resultant line broadening. Of course, for flexible triradicals containing
magnetic nuclei, modulation of the exchange integral is known to constitute a powerful spin relaxation process (18). We shall not, however, be concerned with such complications.

The line shape may be calculated from Redfield’s relaxation matrix because the rate of molecular reorientation is taken to be fast (23). The calculation begins therefore with the dynamic spin Hamiltonian, which takes the form

$$H(t) = \sum_{\nu \neq \nu'} (-1)^{\nu} D^{\nu \nu'} (t) \Omega_{\nu \nu'} (t) \delta (\nu - \nu) \otimes H^{\nu \nu'}_{\nu \nu'}. \quad [13]$$

This is written for an arbitrary orientation of the director with respect to the magnetic field and the rotation matrix $\Omega_{\nu \nu'}$ connects these two frames. The dynamic spin Hamiltonian may be expressed in a simpler form

$$H(t) = \sum_{\nu} (-1)^{\nu} F^{\nu \nu} (t) T^{\nu \nu}, \quad [14]$$

where both the angular and time dependence are now contained in $F^{\nu \nu} (t)$. The advantage of this formulation is that the relaxation matrix has already been evaluated for a quartet state subject to this perturbation and found to be

$$\begin{pmatrix}
|1\rangle & |0\rangle & |{-1}\rangle \\
|0\rangle & |B \otimes 0\rangle & |0\rangle \\
|{-1}\rangle & |C \otimes A\rangle & |{-1}\rangle
\end{pmatrix} \quad [15]$$

where the basic functions correspond to the three allowed transitions (24). The matrix elements are

$$A = -\delta (l_3 + l_1 + l_2), \quad [16]$$

$$B = -\delta (l_3 + l_2 + l_3), \quad [17]$$

and

$$C = 6l_2, \quad [18]$$

where the spectral densities are defined by

$$\tilde J_\nu = \frac{1}{2} \int_{-\infty}^{\infty} \tilde F^{\nu \nu} (0) \tilde F^{\nu \nu} (t) \exp (-i \omega t ) dt, \quad [19]$$

and are orientation dependent.

The spectral lines originating from doublet state transitions are not broadened by rotational modulation of the zero-field splitting because the relevant matrix elements of $T^{\nu \nu'}$ required in calculating the Redfield matrix are all zero. Thus elements of the type $(|j, m| T^{\nu \nu'} |j, m>)$ vanish because the Clebsch-Gordan coefficient needed in Eq. [3] is zero. Similarly there is no possibility of cross relaxation between the doublet and quartet spin levels since the reduced matrix element, $(|j, m| T^{\nu \nu'} |j, m>)$, and hence the required elements $(|j, m| T^{\nu \nu'} |j, m>)$ vanish. We may therefore confine our attention to the quartet states in the line shape calculation.

For a low-passage, low-power electron resonance experiment the form of the absorption spectrum, $S(\omega)$, is (25)

$$S(\omega) = \Re \{ S_+ | M^- \rangle \langle M^- | \}, \quad [20]$$
where the matrix, $M_0$, is related to the Redfield relaxation matrix by

$$M_{0,\alpha} = (\alpha_0 - \omega)\alpha_0 + R_{\alpha}.$$  \[21\]

Here $\alpha$ corresponds to an allowed transition occurring at resonant frequency $\omega_0$; this frequency may be replaced by a resonant magnetic field because of the $1:1$ correspondence between field and frequency implied by Eqs. [8] and [9]. The $M_0$ matrix is then

$$M_0 = \begin{bmatrix} 1 & | & 0 \\ \hline | & C & 0 \\ \hline 0 & 0 & B + i(\omega_0 - \omega) \end{bmatrix}.$$  \[22\]

where

$$\delta = 3D_1P_3(\cos\gamma).$$  \[23\]

The vector $S$, is composed of the matrix elements of $S$, between the pairs of states involved in each transition. For the quartet problem the components of $\sigma$ are proportional to those of $S$, which are $[\sqrt{3}, \sqrt{3}, 2]$ for the reordered basis set used in Eq. [22]. The lineshape calculation reduces to the inversion of the $2 \times 2$ block of $M_0$, and gives

$$\mathcal{L}(\omega) = 6\text{Re} \left[ \frac{A - C - i\omega}{(A + i(\omega_0 - \omega))(A + i(\omega_0 + \omega))} \right] + 4\text{Re} \frac{1}{(B + i(\omega_0 - \omega))}.$$  \[24\]

The spectrum therefore always contains a pure Lorentzian with width $-B$ centered at $\omega_0$ and with intensity $A$; this is associated with the $|0\rangle$ transition. The lineshape for the remaining two transitions is more complicated, as we can see from the first term in Eq. [24]; there are, however, certain situations when this takes a particularly simple form. For example, when $\gamma$ is equal to the magic angle, $\cos^2(\theta)$ vanishes. This is composed of two Lorentzians with widths $-B$ and $-A + C$ with relative intensities $3:2$ just as in a normal liquid. At the other extreme, when the line separation $2\delta$ greatly exceeds the linewidth, the off-diagonal element in the $M_0$ matrix may be ignored and the lineshape is readily seen to consist of three Lorentzians centered at $\omega_0 - \delta$, $\omega_0$, $\omega_0 + \delta$ with widths $-A$, $-B$, $-A$ and relative intensities $3:4:3$. In principle the lineshape, for intermediate situations, should be calculated from Eq. [24] but, as we shall now see, this is not always necessary.

When the rate of molecular reorientation is slow, in the sense that the Zeeman splitting, $\omega_0$, greatly exceeds the inverse of the correlation time describing the motion, then the nonequilibrium contributions to the Redfield matrix may be ignored. Under these conditions the $|0\rangle$ transition at $\omega_0$ is unBroadened while the lineshape for the $|\pm\rangle$ transitions is a pair of Lorentzians at $\omega_0 \pm \delta$, each with a width

$$T^2 = -A = 6D_0.$$  \[25\]

Since the doublet transitions at $\omega_0$ are unBroadened by this spin relaxation process the width of the outer two lines is predicted to be greater than that of the central peak. The observed spectra of triuradicals dissolved in liquid crysols are found to support this prediction although at present these systems have only been studied with the director parallel to the magnetic field ($J-17$). Our calculations indicate that the difference in
width between the outer and central lines should be ascribed entirely to spin relaxation since most other line-broadening mechanisms will affect all lines equally. We are not therefore forced to make the assumption that all of the linewidth originates from a single relaxation process, as we must for biradical spin probes (c,d); consequently triradical probes may well become more important than their biradical counterparts.

The linewidth difference, \( \Delta T^* \), is just \( \delta \), and so will depend on the relative orientations of the director and magnetic field; we shall now determine the form of this angular dependence. Comparison of Eqs. (13) and (14) for the dynamic spin Hamiltonian allows us to identify the components \( P_{\perp \perp} \) and substitution into Eq. (19) for the spectral density gives

\[
J_0 = \sum_{n, r, \gamma, e} (-1)^{r+e} D^{n-r} \mu^{r} \frac{D^e}{D^{n+r}} \sum \langle a_{n-r}^{\dagger} a_{n+r} \rangle \delta \delta(t) dt.
\]

This expression may be simplified with the aid of techniques developed for similar problems involving monoradical spin probes (5,10), thus

\[
J_0 = \sum_{n, r, \gamma, e} (-1)^{r+e} D^{n-r} \mu^{r} \frac{D^e}{D^{n+r}} \sum \langle a_{n-r}^{\dagger} a_{n+r} \rangle \delta \delta(t) dt.
\]

Here the restriction of the summation to even values of \( L \) and terms with \( q \) equal to \( q' \) results from the \( D_{\perp \perp} \) symmetry of the liquid-crystal environment. The angular dependence of the linewidth difference is therefore

\[
\Delta T^* = X_0 + X_0 P_{\gamma} \cos(\gamma) + X_0 P_{\delta} \cos(\delta),
\]

where the summation stops at the fourth Legendre function because the dynamic spin Hamiltonian contains only second-rank interactions. The majority of triradical spin probes possess a threefold symmetry axis and this enables us to simplify the expression for \( J_0 \) and hence the angular linewidth coefficients, still further. This symmetry means that the ordering tensor \( \delta \delta(t) \) can be replaced by \( P_{\gamma} \delta(t) \) and terms with \( p \) not equal to \( p' \) vanish (10):

\[
J_0 = 6 \sum_{L} (-1)^{L} \frac{D^{L+1}}{D^{L}} \sum \langle a_{L}^{\dagger} a_{L} \rangle \delta \delta(t) dt.
\]

where the spectral density \( \delta \delta(t) \) is

\[
\delta \delta(t) = \frac{1}{2} \sum \langle a_{L}^{\dagger} a_{L} \rangle \delta \delta(t) dt.
\]

To proceed further in obtaining expressions for the angular linewidth coefficients we require some model of molecular reorientation in liquid crystals with which to evaluate the spectral density in Eq. (30). Two quite different approaches have been proposed (5,27); in the strong collision model the molecular orientation is allowed to change by any amount, whereas in the diffusion model only small variations are permitted. Despite
their conflicting natures both models predict similar spectral densities and so we shall illustrate the theoretical development with the strong collision model because this leads to simpler results for the angular linewidth coefficients. According to this approach the spectral densities are

$$\Phi_{\alpha\beta} = \sum_{(i)} (-1)^{i+i} C(22L';q-q') C(22L';p-p') P_{L_2} - P_{L_2} \delta_{\alpha\beta} \delta_{L_2},$$  

where $\tau_0$ is the appropriate correlation time; for example $\tau_0$ is the relaxation time for reorientation of the symmetry axis (14).

Evaluation of the Clebsch-Gordan coefficients then gives the angular linewidth coefficients as

$$X_0 = \frac{6}{5} \left( 1 \right) \left( 1 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right),$$

$$X_2 = \frac{12}{7} \left( 1 \right) \left( 1 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right),$$

$$X_3 = \frac{36}{35} \left( 1 \right) \left( 1 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right),$$

where the components of the zero-field splitting tensor are written in a coordinate system with the molecular symmetry axis as the z axis. For the majority of triadicals the zero-field splitting tensor is cylindrically symmetric about the z axis and for these spin probes the angular linewidth coefficients reduce to

$$X_0 = \frac{6}{5} \left( 1 \right) \left( 1 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right),$$

$$X_2 = \frac{12}{7} \left( 1 \right) \left( 1 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right),$$

and

$$X_3 = \frac{108}{35} \left( 1 \right) \left( 1 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right) \left( 2 \right).$$

The measurement of these coefficients then enables us to obtain two estimates of the correlation time, $\tau_0$, from $X_0$ and $X_2$ since the order parameter $P_{L_2}$ is known from the line separation and the zero-field splitting is available from solid-state studies. Armed with the correlation time we may then extract the higher orientational order parameter, $P_{L_2}$, from $X_3$. This order parameter is of considerable importance for testing molecular theories of liquid crystals and their mixtures; it may now be determined from linewidth studies of triadical spin probes with the aid of the theory which we have just developed.

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