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RESONANCE SPECTRA OF A PARAMAGNETIC PROBE DISSOLVED IN A VISCOUS MEDIUM

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ABSTRACT

A model is presented in which one calculates the paramagnetic resonance (epr) spectrum of vanadyl acetylacetonate (VAAC) dissolved in either a liquid crystal or isotropic solvent. It employs density matrix formulation in the rotating reference frame. The molecules occupy several discrete angles with respect to the magnetic field and can relax to neighboring positions in a characteristic time $\tau(\theta)$. The form of $\tau(\theta)$ is found from a diffusion approach, and the magnitude of $\tau(\theta)$ is a measure of how freely the VAAC probe tumbles in the solvent. Spectra are predicted for values of τ between 10^{-11} sec and 10^{-7} sec. The epr spectrum, in the isotropic case, is obtained by summing the contributions from the allowed angles weighted by the polar volume element, sin θ. When applying the model to the nematic liquid crystal case it is also necessary to multiply by the Saupe distribution function. For this case, $\tau(\theta)$ is obtained from the diffusion approach in which two diffusion constants are employed to reflect the difference in the parallel and perpendicular components of the viscosity. An attempt will be made to correlate the diffusion constant with the viscosity via the Einstein relation.

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Electron paramagnetic resonance (epr) has been used to measure the ordering of the probe molecule vanadyl acetylacetonate (VAAC) ($I = 7/2$ $S = 1/2$) when dissolved in liquid crystal media.[1-4] These media inhibit the tumbling of the probe molecule to various extents depending upon the temperature and solvent material. If the probe is not completely free to tumble, then the epr spectra will be affected. The assumption that the spatial and temporal averages are equal breaks down, and the epr data must be interpreted in this light. The end cases of extremely fast and slow tumbling have been discussed in the literature[3,4] and are well understood. The intermediate case is more difficult, however. Other authors[5,6] have successfully dealt with the intermediate case for isotropic liquids. The model which we are presenting is easily adapted to both nematic liquid crystal and isotropic solvents. The technique is also easier to deal with from a computational point of view.

In this model the molecules are assigned a discrete number of allowed angular positions. These positions are described by angles θ_1, θ_2, etc. measured from the preferred direction in the case of a liquid crystal solvent and from the polar axis for the case of an isotropic liquid. Both axes correspond to the direction of applied magnetic field. A molecule in the θ_n

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position can only relax to the θ_{n-1} or the θ_{n+1} position with a characteristic time $\tau(\theta)$. The choices of θ's and τ's are described below. The starting Hamiltonian in laboratory coordinates is given by[4]

$$\mathcal{H} = g\beta H_z S_z + aI\cdot S + \frac{1}{3}(\Delta g\beta H_z + bI_z)(3\cos^2\theta-1)S_z - \frac{b}{12}(3\cos^2\theta-1)(S_+I_- + S_-I_+) \tag{1}$$

where g, a and $\Delta g, b$ are the isotropic and anisotropic portions of the "g" and hyperfine tensors, respectively. S and I refer to the electronic and nuclear spin operators. Equation (1) can be rewritten as

$$\mathcal{H} = \alpha S_z + A(\theta)\, I_z S_z + \frac{a}{2}(S_+I_- + S_-I_+) - B(\theta)(S_+I_- + S_-I_+) \tag{2}$$

where

$$\alpha = \left[1 + \frac{1}{3}\frac{\Delta g}{g}(3\cos^2\theta-1)\right] g\beta H_z,$$

$$B(\theta) = \frac{b}{12}(3\cos^2\theta - 1)$$

and

$$A(\theta) = a + \frac{1}{3}b(3\cos^2\theta-1)$$

An rf field is applied

$$H_1 = \omega_1(S_x\cos\omega t - S_y\sin\omega t) \tag{3}$$

Using the density matrix notation in the rotating frame we have

$$\dot{\rho}_r = -i\hbar^{-1}[\mathcal{H}_r(\theta), \rho_r] \tag{4}$$

where

$$\mathcal{H}_r = \mathcal{H}_o + \mathcal{H}_1 \tag{5}$$

and

$$\begin{aligned} \mathcal{H}_o &\equiv (\alpha-\omega)S_z + A(\theta)S_zI_z - \omega I_z + \frac{a}{2}(S_+I_- + S_-I_+) - B(\theta)(S_+I_- + S_-I_+), \\ H_1 &\equiv \omega_1 S_x \end{aligned} \tag{6}$$

Let $\rho_r = \rho_o + \rho_1$, where ρ_o is zero order in ω_1 and ρ_1 is linear in ω_1. In addition for a steady state solution $\dot{\rho}_r = 0$. Substituting into (4) and retaining terms up to first order in ω_1

$$0 = -i\hbar^{-1}[\mathcal{H}_o(\theta), \rho_1] - i\hbar^{-1}[\mathcal{H}_1, \rho_o] \tag{7}$$

A term of the form $-\frac{\rho_i(\theta)}{T_2}$ must be included to represent relaxation of the molecule due to random perturbations and a term, $-\frac{1}{\tau(\theta)}$, to represent relaxation to other angles. The form of $\tau(\theta)$ is obtained using a diffusion approach. The θ component of the diffusion equation for the isotropic solvent is

$$(D\nabla^2 V)_{\theta \text{ component}} = \frac{D}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta \frac{\partial V}{\partial\theta}\right] = \frac{D}{r^2}\left[\cot\theta \frac{\partial V}{\partial\theta} + \frac{\partial^2 V}{\partial\theta^2}\right], \tag{8}$$

where V is an arbitrary scaler field. Let

$$\Delta = \theta_{i+1} - \theta_i$$

then

$$\frac{\partial V}{\partial\theta} = \frac{V(\theta_{i+1}) - V(\theta_{i-1})}{2\Delta} \tag{9}$$

and

$$\frac{\partial^2 V}{\partial\theta^2} = \frac{V(\theta_{i+1}) - 2V(\theta_i) + V(\theta_{i-1})}{\Delta^2} \tag{10}$$

so that equation (8) becomes

$$(D\nabla^2 V)_{\theta \text{ component}} = -\frac{1}{\tau}\left[2V(\theta_i) - V(\theta_{i+1})\left\{1 + \frac{\Delta}{2}\cot\theta_i\right\} - V(\theta_{i-1})\left\{1 - \frac{\Delta}{2}\cot\theta_i\right\}\right] \tag{11}$$

where

$$\frac{1}{\tau} = \frac{D}{r^2\Delta^2}$$

Using the format of (11)

$$\frac{1}{\tau(\theta_i)} \equiv \frac{1}{\tau}\left[2\rho(\theta_i) - \rho(\theta_{i+1})\left\{1 + \frac{\Delta}{2}\cot\theta_i\right\} - \rho(\theta_{i-1})\left\{1 - \frac{\Delta}{2}\cot\theta_i\right\}\right]. \tag{12}$$

Equation (7) is now modified to become, for the $i^{\underline{th}}$ position,

$$0 = -i\hbar^{-1}\left[\mathcal{H}_o(\theta_i),\rho_1(\theta_i)\right] -i\hbar^{-1}\left[\mathcal{H}_1(\theta_i),\rho_o(\theta_i)\right]$$

$$- \frac{\rho_i(\theta_i)}{T_2} - \frac{1}{\tau}\left[2\rho_1(\theta_i) - \rho_1(\theta_{i+1})\left\{1 + \frac{\Delta}{2}\cot\theta_i\right\}\right.$$

$$\left. -\rho_1(\theta_{i-1})\left\{1 - \frac{\Delta}{2}\cot\theta_i\right\}\right]. \qquad (13)$$

$[\mathcal{H}_1,\rho_o]$ can be evaluated as

$$\frac{1}{2}\,\frac{\omega_1\omega_o}{kT}\,[S_+ - S_-], \qquad (14)$$

where $\omega_o \equiv g\beta H_z$. Equation (13) now becomes

$$\left[\mathcal{H}_o(\theta_i),\rho_1(\theta_i)\right] - \frac{i\rho_i(\theta_i)}{T_2} - \frac{i}{\tau}\left[2\rho_1(\theta_i) - \rho_1(\theta_{i+1})\left\{1 + \frac{\Delta}{2}\cot\theta_i\right\}\right.$$

$$\left. -\rho_1(\theta - 1)\left\{1 - \frac{\Delta}{2}\cot\theta_i\right\}\right] = -\frac{1}{2}\,\frac{\omega_1\omega_o}{kT}\,(S_+ - S_-), \qquad (15)$$

where $\mathcal{H}_o$ is now in radians $\sec^{-1}$.

It is now necessary to choose values of θ_i. In order to avoid computational difficulties, $\theta = 0$, i.e., $\cot\theta = \infty$, will be avoided. We choose $\theta_1 = \pi/34$ and $\Delta = \pi/17$. This gives 9 allowed positions in the first quadrant with $\theta_9 = \pi/2$. Since the equations are independent of ϕ, $\rho(\theta_i) = \rho(\theta_{-i})$. We also assume that the molecules cannot be distinguished end from end and this yields $\rho(\theta_i) = \rho(\pi + \theta_i)$. This makes the four quadrants equivalent so that we will restrict ourselves to the first quadrant. Equation (15) then is really a series of 9 equations corresponding to the 9 allowed positions.

The absorption is proportional to

$$M_y = \mathrm{Tr}\,\rho_1(\theta_i)\,S_y = -\frac{i}{2}\,\mathrm{Tr}\,\rho_1(S_+ - S_-). \qquad (16)$$

VAAC has a nuclear spin of 7/2, thus its epr spectrum consists of eight lines. The line corresponding to $m_I = 7/2$ is obtained as

$$\text{absorption} = \mathrm{Im}\sum_{\theta_i} \langle 7/2,1/2|\rho(\theta_i)|7/2,-1/2\rangle \sin\theta_i \qquad (17)$$

The forms for the other values of m_I's are similar. The $m_I = 7/2$'s line is coupled to the $m_I = 5/2$'s line via the I_- operator so that it is necessary to solve an 18 x 18 matrix to obtain the $\langle 7/2,1/2|\rho(\theta_i)|7/2,-1/2\rangle$ elements. A 36 x 36 matrix is required for all of the other lines except $m_I = -7/2$ since these lines couple to the higher and lower hyperfine lines via the $I_\pm$ operators. T_2 is obtained from the experimental line width, and τ is varied from approximately 10^{-12} sec for the free tumbling case to approximately 10^{-7} sec for the slow tumbling case. An attempt will be made to correlate the diffusion constant D with the viscosity via the Einstein relation

$$D = \frac{kT}{6\pi a\eta} \tag{18}$$

where η is the viscosity and a is the effective radius.

Three changes must be made to apply this model to a nematic liquid crystal. First, in equation (17) the $\langle m_I,1/2|\rho(\theta_i)|m_I,-1/2\rangle$ summation must be multiplied by the Saupe distribution function $\exp(-q\cos^2\theta/kT)$ as well as the polar volume element. Second, the form of the relaxation time must be changed to reflect the fact that the viscosities are different in the parallel and perpendicular directions. Once again, taking the diffusion approach

$$V_D = D_1\left(\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2}\right) + D_2\frac{\partial^2 V}{\partial z^2} \tag{19}$$

and proceeding in a manner similar to the isotropic case one obtains

$$\begin{aligned}\frac{1}{\tau(\theta)} = \frac{1}{\tau}\Bigg[&2\rho(\theta_i)\left\{1 + \frac{D_2-D_1}{D_1}\sin^2\theta_1\right\} - \rho(\theta_{i+1})\left\{1 + \frac{D_2-D_1}{D_1}\sin^2\theta_i + \frac{\Delta}{2}\cot\theta_i\right.\\ &\left. + \frac{\Delta}{2}\frac{D_2-D_1}{D_1}\sin 2\theta_i\right\} - \rho(\theta_{i-1})\left\{1 + \frac{D_2-D_1}{D_1}\sin^2\theta_i - \frac{\Delta}{2}\cot\theta_i\right.\\ &\left. - \frac{\Delta}{2}\frac{D_2-D_1}{D_1}\sin 2\theta_i\right\}\Bigg]\end{aligned} \tag{20}$$

This reduces to the isotropic case for $D_1 = D_2$. Third, $\tau(\theta)$ must be multiplied by the Saupe function to reflect the different populations at the different angular positions.

The epr spectra will be studied as a function of both the order parameter and the relaxation time, and an effort will be made to separate the effects of these two parameters on the data. We will also attempt to correlate the diffusion constants D_1 and D_2 with the perpendicular and parallel components of the viscosity via the Einstein relation.

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