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Modeling of dynamics in liquid crystals from deuterium NMR

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We present a superimposed rotations model that incorporates a three-site jump model to describe the *trans-gauche* isomerism of a hydrocarbon chain and a small step rotational diffusion model to describe the reorientation of a mesogen in an ordering potential. The model can be used to interpret the spectral densities of motion measured in liquid crystals by deuterium NMR relaxation studies. Under the simplifying assumption that rotation about each carbon-carbon bond is free, the jump model reduces to the free rotation model. Both the jump model and the free rotation model are examined using the reported J_1 and J_2 values in the literature for the nematogen 5CB- d_{15} . Analytical solutions of rotational diffusion constants by numerical computation are given. The temperature dependence of these rotational diffusion constants provides the activation energies for these diffusion processes. In conjunction with the free rotation model, we found that the contribution to spin relaxation due to director fluctuations appears to show an odd-even effect along the pentyl chain of 5CB.

I. INTRODUCTION

The anisotropic magnetic interactions of a nuclear spin may be time dependent owing to spatial motion of the spin-bearing molecule. Detailed motional information can be derived from the nuclear spin relaxation study and in some cases it may be obtained using nuclear magnetic resonance line shape analysis. Internal motions of flexible macromolecules in solution have been studied in the past, both theoretically and experimentally.¹⁻⁵ High resolution ^{13}C NMR was shown to be extremely useful because of its ability to give resolved resonant lines that correspond to various carbon sites in a large molecule. In consequence, one may separately determine the relaxation rates of carbons at different parts of a macromolecule. This technique has been used^{6,7} to investigate spin relaxation in liquid crystals. Site specificity can also be achieved in liquid crystals⁸⁻¹⁴ by means of deuterium NMR spectroscopy. DMR has the additional advantage of not requiring high power proton decoupling and can also directly measure the spectral densities of motion for deuterons at various sites. Therefore, both ^{13}C and deuterium NMR may be used to study the internal dynamics of hydrocarbon chains in liquid crystals. It is necessary to devise models of internal/overall motions to account for the NMR data obtained at different magnetic field strengths and temperatures.

Various models of segmental motions in a hydrocarbon chain have been theoretically treated for molecules in solution. These models of multiple internal rotations were used to account for their ^{13}C relaxation rates. One simple model involves a stochastic rotation diffusion about each carbon-carbon bond; this occurs if the potential barrier between several equilibrium positions is smaller than kT . When the potential barriers are larger than kT , rotational jumps occur among a few equilibrium positions. For flexible molecules in solution, one may use random jumps of a C-C bond between three (t , g^+ , g^-) sites given by the rotameric model.¹⁵ The potential energy of a *trans* (t) conformer is about 2.1 kJ/mol below that of the *gauche* states (g^+ , g^-) which are assumed to be equivalent (Fig. 1). The jumps between g^+ and g^-

were considered to be unlikely in the calculations of London and Avitabile.² However, Tsutsumi⁴ included these types of jumps in his treatment of a molecule having one bond about which internal rotation occurs. The above models assumed that rotations about different bonds are independent. This simplifying assumption was removed by Wittebort and Szabo.³ They explicitly considered all energetically allowed conformations of a macromolecule in solution, so as to describe concerted or correlation motions about different bonds.

Though the chain motions of liquid crystalline molecules in anisotropic phases have been extensively studied in recent years by pulsed deuterium NMR⁸⁻¹⁴ relaxation techniques, quantitative analysis of these NMR data in the anisotropic mesophases is still just beginning. For instance, it is not clear how the orientational ordering potential affects the internal dynamics of flexible mesogens, although the observed quadrupolar splittings along a hydrocarbon chain have been successfully modeled^{16,17} using the rotameric model of Flory.¹⁵ A small step rotational diffusion model that describes the overall reorientations of a molecule oriented in an ordering potential $U(\beta) = -\lambda P_2(\cos \beta)$ had been proposed some 15 years ago by Nordio *et al.*¹⁸ to interpret ESR linewidth.¹⁹ This model has been successfully applied to liquid crystalline molecules in studies of dielectric relaxation,²⁰ fluorescence depolarization,²¹ IR and Raman band shapes,²² and DMR relaxation.^{13,23} It appears that spin relaxation due to overall reorientations of liquid crystalline molecules can be explained by the small step rotation diffusion model. However, theoretical treatment of spin relaxation due to internal molecular dynamics in a flexible mesogen remains a challenging problem. Recently a superimposed rotations model has been used to describe internal phenyl ring rotation¹³ and segmental motions¹⁴ in liquid crystals. Beckmann *et al.*¹⁴ have used this model to study deuterium Zeeman spin-lattice relaxation rates in the nematic phase of 4-*n*-pentyl- d_{11} -4'-cyanobiphenyl- d_4 (5CB- d_{15}). In this paper we outline a three-site jump model superimposed on a small step rotation diffusion of molecules in a

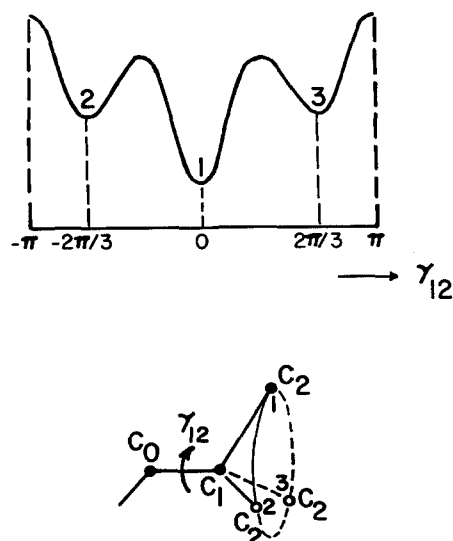


FIG. 1. Model of rotation about a bond by jump among three sites and a potential energy curve of these sites.

Maier-Saupe-type ordering potential. As a limit, we obtain the superimposed rotations model used by Beckmann *et al.* in which rotation about each C-C bond in a hydrocarbon chain covers the entire 360° range. Numerical calculations based on these models are given using the measured spectral densities of 5CB- d_{15} at 30.7 MHz.^{8,9} These calculations are used to evaluate possible contribution from director fluctuations²⁴ to the spin relaxation rates of the chain deuterons. Some preliminary data of chain deuterated 5CB (5CB- d_{11}) at 15.4 MHz is also given.

II. THEORY

The nuclear spin relaxation rates are governed by the nature of molecular motion and the form of the time-dependent part of the nuclear spin Hamiltonian $H(t)$. In an anisotropic fluid-like liquid crystal, the time average spin Hamiltonian $\overline{H(t)}$ is a nonzero constant and can therefore be subtracted from $H(t)$ to give the time-dependent Hamiltonian

$$H'(t) = \sum_{m_L} \sum_{m_M} (-1)^{m_M} F_{-m_M}^{(2)} T_{m_L}^{(2)} \times [D_{m_L m_M}^2(\alpha, \beta, \gamma) - \overline{D_{m_L m_M}^2}], \quad (1)$$

where $F_{m_M}^{(2)}$ is the m_M component of the tensor describing the spatial part of the magnetic interaction in a molecular fixed frame, $T_{m_L}^{(2)}$ is the m_L component of the spin operator in the laboratory frame, and m_M and m_L take on the values 0, ± 1 , and ± 2 . The time dependence of the Hamiltonian $H'(t)$ is solely due to the Wigner rotation matrices $D_{m_L m_M}^2$ which contain the Euler angles $\Omega_{LM}(\alpha, \beta, \gamma)$ in the transformation between the laboratory (nematic director) frame and a molecular reference frame. The above spin Hamiltonian is applicable to the magnetic dipolar interaction within a molecule and to the interaction of the nuclear quadrupole moment with the electric field gradients at the nucleus. We

restrict below to deuteron spin ($I = 1$) whose electric quadrupole tensor, in the case of axial symmetry (e.g., C-D bond), is given by

$$F_{m_M}^{(2)} = \sqrt{\frac{3}{8}} \frac{e^2 q Q}{\hbar} \delta_{m_M, 0}.$$

If the motion of molecules is fast such that motional narrowing applies, the perturbation approach of Redfield's relaxation theory may be used to relate nuclear spin relaxation rates to the nature of molecular motion via the spectral densities

$$J_{m_L}(m_L \omega) = \frac{3\pi^2}{2} \left(\frac{e^2 q Q}{h} \right)^2 \int_0^\infty G_{m_L}(t) \cos(m_L \omega t) dt, \quad (2)$$

which is a one-sided Fourier transform of the autocorrelation function

$$G_{m_L}(t) = \langle [D_{m_L 0}^2(0) - \overline{D_{m_L 0}^2}] \times [D_{m_L 0}^{2*}(t) - \overline{D_{m_L 0}^{2*}}] \rangle. \quad (3)$$

Equation (3) is written for the case in which the C-D bond coincides with the z_M axis of the molecular frame. From the standard spin relaxation theory²⁵ for $I = 1$, m_L takes on the value of 1 for the spin-lattice relaxation time (T_{1Q}) of quadrupolar order, while for the Zeeman spin-lattice relaxation time (T_{1z}), m_L takes on the values of 1 or 2. Thus, one obtains

$$T_{1z}^{-1} = J_1(\omega_0) + 4J_2(2\omega_0), \quad (4)$$

$$T_{1Q}^{-1} = 3J_1(\omega_0). \quad (5)$$

To calculate the spectral densities of motion, one has to adopt a certain motion model.

To simplify our discussion, let us choose 5CB as a model liquid crystal. Assume that the molecule is made up of rigid subunits and there are no correlations between the rotations about different C-C bonds; label R is for the phenyl ring containing deuterons and $i = 1$ to 5 for the CD_2 and CD_3 groups. For example, if rotation about each C-C bond is assumed to completely cover a 360° range, then the $i = 3$ carbon occupies an eclipsed² and a *trans* configuration with equal probability. This is not the case in reality and a jump model is probably more appropriate. The internal rotation of the phenyl rings is assumed to consist of free rotation about the para axes. We assume that z_M , the axis of the molecular reference frame (and the principal axis of the rotation diffusion tensor of the mesogen), is fixed to the core, i.e., the cyanobiphenyl group as indicated in Fig. 2, and that the

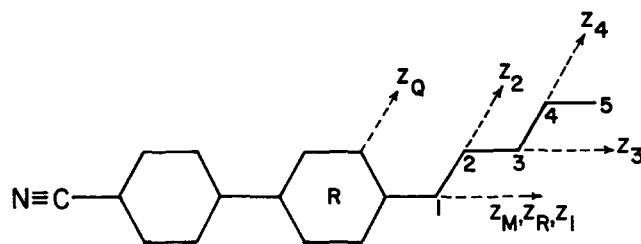


FIG. 2. Sketch of 5CB and the location of molecular reference frame and internal rotation axes.

TABLE I. Values of \bar{P}_2 ,^a \bar{P}_4 ,^b and $\lambda_{m_L m_M}^{(2)}$ ^c used in numerical computation of rotational diffusion constants for 5CB ($T_{NI} = 308.1$ K).

$T(K)$	\bar{P}_2	\bar{P}_4	$\lambda_{10}^{(2)}$	$\lambda_{11}^{(2)}$	$\lambda_{12}^{(2)}$	$\lambda_{20}^{(2)}$	$\lambda_{22}^{(2)}$
307.6	0.377	0.094	0.160	0.148	0.138	0.125	0.206
303.7	0.508	0.166	0.144	0.131	0.123	0.108	0.218
302.1	0.533	0.182	0.140	0.127	0.120	0.106	0.220
292.1	0.625	0.246	0.122	0.110	0.106	0.092	0.228

^a Calculated from $\Delta v_i = (3/2)(e^2 q Q_i / h) P_2(\cos \beta_{i,Q_i}) \bar{P}_2$.

^b Calculated using Gaussian integration and mean field theory.

^c Interpolated from plots of $\beta_{m_L m_M}^{(2)}$ vs \bar{P}_2 of Ref. 26.

reorientation of this frame is decoupled from the internal conformational changes. The internal rotation axis linking fragments i and $i-1$ is used to define the z_i axis of the i th subunit while its y_i axis is taken to be orthogonal to z_i and z_{i+1} axes. As seen in the diagram, z_M , z_R , and z_1 lie along the para axis of the cyanobiphenyl group. Since $\beta_{i,i+1}$ is a time-independent angle between the internal rotation axes z_i and z_{i+1} and the Euler angle $\alpha_{i,i+1} = 0$ by definition, the time dependence of internal motion is due to the $\gamma_{i,i+1}$ angles. The indices on the Euler angles denote coordinate transformation between the i th and the $(i+1)$ th frames. The principal axis system for the electric quadrupole tensor of the deuterons attached to the i th carbon atom is denoted by Q_i . Because of the axial symmetry of the electric quadrupole tensor, the z_Q axis lies along a C-D bond to a good approximation. In writing down the autocorrelation function for a ring deuteron, one has to carry out successive coordinate transformations from the Q_R system to the molecular reference frame and from the latter frame to the laboratory frame giving

$$G_{m_L}^{(R)}(t) = \sum_{m_M} \sum_{m_R} [d_{m_R 0}^2(\beta_{R,Q_R})]^2 [d_{m_M m_R}^2(\beta_{M,R})]^2 \times \kappa(m_L, m_M) g_R(t) \exp(-t/\tau_{m_L m_M}^{(2)}), \quad (6)$$

where β_{R,Q_R} is the angle between the C-D bond and the para axis, $\beta_{M,R}$ is the angle between the z_M and z_R axes,

$$g_R(t) = \langle \exp\{-im_R[\gamma_{M,R}(t) - \gamma_{M,R}(0)]\} \rangle \quad (7)$$

and

$$(\tau_{m_L m_M}^{(2)})^{-1} = (D_{\perp} / \lambda_{m_L m_M}^{(2)}) + m_M^2 (D_{\parallel} - D_{\perp}). \quad (8)$$

The term $\lambda_{m_L m_M}^{(2)}$ in Eq. (8) depends on the potential of mean torque and is given by Agostini *et al.*²⁶ for a Maier-Saupe-type potential. These terms are determined by the order parameter \bar{P}_2 (Table I) which can be calculated from the quadrupolar splitting of C_1 deuterons. D_{\parallel} and D_{\perp} are the diffusion constants for rotation of the molecule about the z_M axis and rotation of the z_M axis, respectively. The

$\kappa(m_L, m_M)$ terms in Eq. (6) are the mean square averages of the Wigner rotation matrices

$$\kappa(m_L, m_M) = \langle [D_{m_L m_M}^2(\Omega_{LM})]^2 \rangle - \langle D_{m_L m_M}^2(\Omega_{LM}) \rangle^2 \delta_{m_L,0} \delta_{m_M,0}, \quad (9)$$

and depend²⁷ on \bar{P}_4 as well as \bar{P}_2 ; this fourth-rank order parameter (Table I) is calculated²⁸ with the Maier-Saupe potential. The internal correlation function $g_R(t)$ describes the ring rotation through an angle $\gamma_{M,R}$ and is assumed¹⁴ to be independent of the values of m_R except when $m_R = 0$, i.e.,

$$g_R(t) = \begin{cases} \exp(-t/\tau_R) & \text{if } m_R \neq 0 \\ 1 & \text{if } m_R = 0 \end{cases}$$

where $\tau_R = 1/D_R$ and D_R is the rotation diffusion constant for ring rotation. Another form of $g_R(t)$,

$$g_R(t) = \exp(-m_R^2 D_R t),$$

may even be a better approximation.²⁹ Using the former $g_R(t)$ and $\beta_{M,R} = 0$ (Fig. 2), one obtains from Eq. (2) the spectral densities for the ring deuterons in the fast motion limit

$$\begin{aligned} J_{m_L}^{(R)}(m_L \omega_0) &= \frac{3\pi^2}{2} \left(\frac{e^2 q Q_R}{h} \right)^2 \{ \kappa(m_L, 0) [d_{00}^2(\beta_{R,Q_R})]^2 \tau_{m_L 0}^{(2)} \\ &+ 2\kappa(m_L, 1) [d_{10}^2(\beta_{R,Q_R})]^2 [(\tau_{m_L 1}^{(2)})^{-1} + \tau_R^{-1}]^{-1} \\ &+ 2\kappa(m_L, 2) [d_{20}^2(\beta_{R,Q_R})]^2 [(\tau_{m_L 2}^{(2)})^{-1} + \tau_R^{-1}]^{-1} \}. \end{aligned} \quad (10)$$

The fast motion limit for molecular reorientations and internal motions in liquid crystals is well justified by other techniques like neutron scattering and dielectric relaxation measurements.^{30,31}

When the hydrocarbon chain undergoes *trans-gauche* isomerism, the autocorrelation function for the C_n deuterons can be obtained by successive transformations from the local n th frame through the $(n-1)$ th frames to the molecular reference frame to give²

$$\begin{aligned} G_{m_L}^{(n)}(t) &= \sum_{m_1} \sum_{m_2} \sum_{m'_2} \cdots \sum_{m_n} \sum_{m'_n} d_{m_n 0}^2(\beta_{n,Q_n}) d_{m'_n 0}^2(\beta_{n,Q_n}) \cdots d_{m_1 m_2}^2(\beta_{1,2}) d_{m'_1 m'_2}^2(\beta_{1,2}) \\ &\times \exp\left[-i \frac{2\pi}{3} (m_n - m'_n)\right] \kappa(m_L, m_1) \langle \exp\{-i[m'_n \gamma_{n-1,n}(t) - m_n \gamma_{n-1,n}(0)]\} \rangle \cdots \\ &\times \langle \exp\{-im_1[\gamma_{M,1}(t) - \gamma_{M,1}(0)]\} \rangle \exp(-t/\tau_{m_L m_1}^{(2)}), \end{aligned} \quad (11)$$

where $\beta_{M,1} = 0$ has been used and the internal correlation functions $g_i(t)$ are explicitly given. [This equation reduces to one similar to Eq. (6) which makes use of $\delta_{m,m'}$ in the free rotation model.] The factor $\exp[-i(2\pi/3)(m_n - m'_n)]$ arises² from rotation about the C_n-C_{n-1} bond by an azimuthal angle of $2\pi/3$ such that the C-D bond occupies the position of the C_n-C_{n+1} bond in Fig. 2. It is postulated that each carbon-carbon bond can exist in and jump between only three states (t, g^+, g^-), two of which are equivalent. The rate of jump motion of a bond i (C_i-C_{i+1} bond or C_i-D bond) is given by a set of coupled rate equations^{2,4}

$$\frac{dP^i(t)}{dt} = W^i P^i(t), \quad (12)$$

where $P^i(t)$ is the time-dependent probability of occupation of one of three sites by bond i (Fig. 1) and W^i the matrix of kinetic coefficients:

$$W^i = \begin{pmatrix} -2W_{1i} & W_{2i} & W_{2i} \\ W_{1i} & -(W_{2i} + W_{3i}) & W_{3i} \\ W_{1i} & W_{3i} & -(W_{2i} + W_{3i}) \end{pmatrix},$$

the eigenvalues of which are $\Lambda_{1i} = 0, \Lambda_{2i} = (-W_{2i} + 2W_{1i})$ and $\Lambda_{3i} = -(W_{2i} + 2W_{3i})$. W_{1i} is the jump rate of the i th bond from $t \rightarrow g^+$ or g^- , W_{2i} is the jump rate from g^+ or g^- to t , and W_{3i} is the jump rate between g^+ and g^- . The ratio of jump rates $W_{1i}/W_{2i} = \sigma_i$ is the relative probability of the bond i in a *gauche* state vs a *trans* state. The jump between g^+ and g^- is allowed but is sterically less favorable. Thus W_{3i} is proportional² to the square of σ_i . We have chosen to write $W_{1i} = \sigma_i D_i/3$ and $W_{3i} = \sigma_i^2 D_i/3$ such that when $\sigma_i = 1$, the internal correlation function for the i th bond reduces to that of the free rotation model¹⁴ with D_i being the rotational diffusion constant of the i th bond about the internal z_i axis. The equilibrium probability of occupation in the *trans* state is $P_t = 1/(2\sigma_i + 1)$, while that of the *gauche* plus or minus is $P_{g^\pm} = \sigma_i/(2\sigma_i + 1)$. One would also need the conditional probability $P(j, t | j', 0)$ where j and j' are one of the three states since

$$\begin{aligned} & \langle \exp\{-i[m'\gamma(t) - m\gamma(0)]\} \rangle \\ &= \sum_{\gamma_0} \sum_{\gamma} P(\gamma_0) P(\gamma, t | \gamma_0, 0) \exp[-i(m'\gamma - m\gamma_0)], \end{aligned} \quad (13)$$

where γ and γ_0 can take 0 or $\pm 2\pi/3$. There are nine conditional probabilities which can be obtained from the solutions of Eq. (12). Equation (13) has been evaluated by London and Avitabile² with the assumption of $W_3 = 0$ and is given in terms of 5×5 matrix $A_{m,m'}$. By adopting the simplifying assumption of $\delta_{m,m'}$ in Eq. (11), one obtains⁴

$$\begin{aligned} G_{m_L}^{(n)}(t) &= \sum_{m_1} \cdots \sum_{m_n} [d_{m_n,0}^2(\beta_{n,Q_n})]^2 \cdots [d_{m_1,m_2}^2(\beta_{1,2})]^2 \\ &\times \kappa(m_L, m_1) (g_1(t) - [g_1(t) - 1]\delta_{m_1,0}) \cdots \\ &\times (g_n(t) - [g_n(t) - 1]\delta_{m_n,0}) \exp(-t/\tau_{m_L m_1}^{(2)}), \end{aligned} \quad (14)$$

where

$$\begin{aligned} g_i(t) &= \left(\frac{\sigma_i - 1}{2\sigma_i + 1} \right)^2 + \frac{9\sigma_i}{2(2\sigma_i + 1)^2} \\ &\times \exp[\Lambda_2 t] + \frac{3\sigma_i}{2(2\sigma_i + 1)} \exp[\Lambda_3 t], \end{aligned} \quad (15)$$

with $\Lambda_2 = -(2\sigma_i + 1)D_i/3$ and $\Lambda_3 = -(2\sigma_i^2 + 1)D_i/3$. Using $g_1(t)$ given by Eq. (15), one has

$$\begin{aligned} J_{m_L}^{(1)}(m_L \omega_0) &= \frac{3\pi^2}{2} \left(\frac{e^2 q Q_1}{h} \right)^2 \left(\kappa(m_L, 0) [d_{00}^2(\beta_1, Q_1)]^2 \tau_{m_L 0}^{(2)} \right. \\ &+ \sum_{m_1=1,2} 2\kappa(m_L, m_1) [d_{m_1,0}^2(\beta_{1,Q_1})]^2 \left\{ \left(\frac{\sigma_1 - 1}{2\sigma_1 + 1} \right)^2 \tau_{m_L m_1}^{(2)} \right. \\ &+ \frac{9\sigma_1}{2(2\sigma_1 + 1)^2} \left[(\tau_{m_L m_1}^{(2)})^{-1} + \frac{2\sigma_1 + 1}{3} D_1 \right]^{-1} \\ &\left. \left. + \frac{3\sigma_1}{2(2\sigma_1 + 1)} \left[(\tau_{m_L m_1}^{(2)})^{-1} + \frac{2\sigma_1^2 + 1}{3} D_1 \right]^{-1} \right\} \right). \end{aligned} \quad (16)$$

Despite the assumption of $\delta_{m,m'}$, this model is still cumbersome to numerically compute $J_{m_L}^{(n)}(m_L \omega_0)$ because of the form of $g_i(t)$. In this paper, we examine the effect of jump model on the spectral densities by allowing only one bond to jump.⁴ In the limit that $\sigma_i = 1$ (free rotation model), all the jump rates become equal and the $g_i(t)$ reduce to a single exponential

$$g_i(t) = \exp[-D_i t]. \quad (17)$$

This makes numerical computation easier. In particular, the spectral densities for the C_1 deuterons are given by Eq. (10) with the scripts R being replaced by 1. For a deuteron on carbon C_2 , one requires an additional geometric factor of $[d_{m_1 m_2}^2(\beta_{1,2})]^2$ and another internal correlation function $g_2(t)$ in $G_{m_L}^{(2)}(t)$. Thus, one can substitute Eqs. (14) and (17) into Eq. (2) to give $J_{m_L}^{(n)}(m_L \omega_0)$, which is too lengthy to reproduce here.

Director fluctuations (DF), a collective mode involving elastic deformations in liquid crystals, can also contribute²⁴ to the spectral densities of motion. In an earlier study³² of deuterium T_{1z} in MBBA- d_{13} , it was shown that DF may be required to explain the spin relaxation rates for the butyl chain deuterons. However, it remains unclear how the contribution of DF varies along the chain in relation to those contributions due to internal dynamics and molecular reorientation. This question can now be fully examined since the contribution to spectral densities can be evaluated for segmental motions in terms of a particular motional model. For the sample with the equilibrium director \hat{n} oriented parallel to the external magnetic field and in the small amplitude approximation for fluctuations of the director, one finds that the only nonzero contribution by DF to the spectral densities is $J_1(\omega_0)$. Furthermore, DF produces a characteristic frequency dependence that is instrumental for its detection in liquid crystals using proton spin relaxation studies.³³ In this approximation, $J_2^{(n)}(2\omega_0)$ can only be interpreted by internal dynamics and molecular reorientation. Thus one may attribute frequency dependence of $J_1^{(n)}(\omega_0)$ to DF but no frequency dependence to $J_2^{(n)}(2\omega_0)$. Here we ignore any refinement to the DF theory for spin relaxation, such as high

frequency cutoff³⁴ in the mode spectrum and cross term^{27,35} between DF and molecular reorientation. We use the one-constant approximations and examine the role of internal dynamics on DF along a flexible chain. For a deuteron located on a rigid core of a mesogen such as the cyanobiphenyl group in 5CB, one has

$$G_1^{\text{DF}}(t) = \frac{3(\bar{P}_2)^2}{2} \langle \delta \hat{n}(0) \delta \hat{n}(t) \rangle [d_{00}^2(\beta)]^2, \quad (18)$$

where β is the angle between the C–D bond and the z_M axis of molecular reference frame. The corresponding spectral density is given by

$$J_1^{\text{DF}}(\omega_0) = A_{\text{DF}} [d_{00}^2(\beta)]^2, \quad (19)$$

where

$$A_{\text{DF}} = \frac{3\pi^2 (e^2 q Q)^2}{2 \left(\frac{h}{\hbar} \right)} \frac{3kT(\bar{P}_2)^2}{4\sqrt{2\pi\omega_0 K(D + K/\eta)^{1/2}}}. \quad (20)$$

A_{DF} depends on the Larmor frequency, the average Frank elastic constant K , the average translational diffusion constant D , the average viscosity constant η , etc., and can be used as a fitting parameter. Equation (19) with the appropriate quadrupolar coupling constant is applicable to the phenyl deuterons and the methylene deuterons of C_1 in 5CB. Because of the geometric factor $[d_{00}^2(\beta)]^2$, DF contributes much smaller to $J_1^{(R)}(\omega_0)$ than to $J_1^{(1)}(\omega_0)$. To calculate the DF contribution to $J_1^{(n)}(\omega_0)$ for $n \geq 2$, one may use the superimposed rotations model in which rotation about each carbon–carbon bond is free. Equation (18) for a deuteron on the C_n atom of a hydrocarbon chain becomes

$$G_1^{(n)\text{DF}}(t) = \frac{3(\bar{P}_2)^2}{2} \langle \delta \hat{n}(0) \delta \hat{n}(t) \rangle \times [d_{00}^2(\beta_{n,Q_n})]^2 \cdots [d_{00}^2(\beta_{M,1})]^2. \quad (21)$$

Thus, the contribution to $J_1^{\text{DF}}(\omega_0)$ reduces by a geometric factor of $[d_{00}^2(\beta_{i-1,i})]^2$ each time an additional C–C bond intervenes before the subunit containing the C_n deuterons. This simple extension³⁶ appears to drastically reduce the effect of DF for deuterons further down the chain, thus further refinement may be necessary.

III. NUMERICAL RESULTS AND DISCUSSION

To test the above motional models for liquid crystals, we used the spectral densities $J_1^{(n)}(\omega_0)$ and $J_2^{(n)}(2\omega_0)$, measured in the nematic phase^{8,9} of 5CB- d_{15} at 30.7 MHz. Both $J_1^{(n)}(\omega_0)$ and $J_2^{(n)}(2\omega_0)$ were reported to be frequency dependent. Though the frequency dependence of $J_1^{(n)}(\omega_0)$ may be accounted for by director fluctuations, the frequency dependence of $J_2^{(n)}(2\omega_0)$ is harder to reconcile at this time. Preliminary data from our laboratory on 5CB- d_{11} at 15.4 MHz seems to indicate that the frequency dependence of $J_2^{(n)}(2\omega_0)$ is much smaller. In any case, we will ignore this difficulty and assume that DF plays no role in $J_2^{(n)}(2\omega_0)$. Both $J_1^{(n)}(\omega_0)$ and $J_2^{(n)}(2\omega_0)$ decrease monotonically from the ring down to the methyl end group of the chain. This feature is not uncommon among liquid crystals.^{10,11}

There are two model parameters, D_{\parallel} and D_{\perp} , to describe reorientation of the core of a mesogen in an ordering potential $U(\beta)$. From Eq. (10), the spectral densities $J_1^{(R)}(\omega_0)$

and $J_2^{(R)}(2\omega_0)$ involve another parameter D_R to describe the internal ring rotation. In the jump model, the spectral densities $J_1^{(1)}(\omega_0)$ and $J_2^{(1)}(2\omega_0)$ from Eq. (16) involve two additional parameters D_1 and σ_1 besides D_{\parallel} and D_{\perp} . Since there are only four measured values of spectral densities [$J_1^{(R)}(\omega_0)$, $J_2^{(R)}(2\omega_0)$, $J_1^{(1)}(\omega_0)$, and $J_2^{(1)}(2\omega_0)$] at present, it is difficult to determine all the above model parameters. To analytically solve for the four unknowns (D_{\parallel} , D_{\perp} , D_R , D_1), we are forced to make the following simplifying assumptions: that rotation about the phenyl- C_1 bond is free (i.e., $\sigma_1 = 1$) and that DF contributes negligibly to $J_1(\omega_0)$ s at 30.7 MHz. These assumptions may be removed when additional information is experimentally available. For numerical computation, we used 185 and 168 kHz for the quadrupolar coupling constant of the phenyl and methylene deuterons, respectively. The bond angles in 5CB were taken to be $\beta_{R,Q_R} = 60^\circ$, $\beta_{i,i+1} = 113.5^\circ$, and $\beta_{i,Q_i} = 107.5^\circ$. Since $J_1^{(R)}(\omega_0)$ can be written into a quadratic equation in D_R , one can solve for D_R from this equation. Substituting D_R into $J_2^{(R)}(2\omega_0)$ gives an equation involving only D_{\parallel} and D_{\perp} . By carrying out the same procedure for the C_1 deuterons, one obtains two complicated equations in D_{\parallel} and D_{\perp} , the solutions of which are obtained numerically using Newton's method.³⁷ The following calculations were based on limited data^{8,9} obtained at four temperatures for the spectral densities of 5CB. Figure 3 summarizes the results for D_{\parallel} , D_{\perp} , D_R , and D_1 . It is interesting to note that the activation energy E_a for D_{\perp} (33.5 kJ/mol) is higher than the E_a for D_{\parallel} (13.5 kJ/

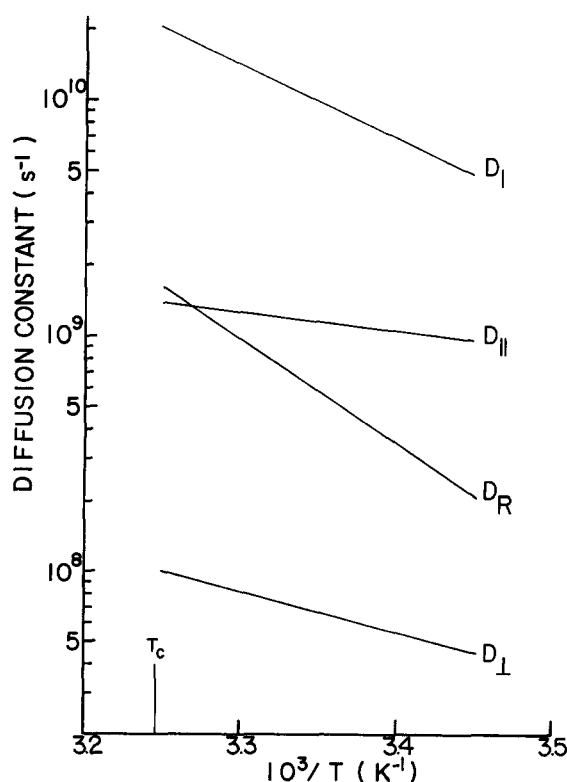


FIG. 3. Plots of rotational diffusion constants (D_{\parallel} , D_{\perp} , D_R , and D_1) vs the reciprocal temperature in the nematic phase of 5CB. These were derived without director fluctuations.

mol) as expected. Furthermore, the inclusion of D_R is necessary to give a more reasonable anisotropy factor $R = D_{\parallel}/D_{\perp}$ of about 14 near the clearing temperature.²³ It would appear that the correlation time for ring rotation in 5CB is intermediate to those for rotation about the long molecular axis and rotation of this axis.

Let us turn to the three-site jump model for the hydrocarbon chain in which only one C–C bond is allowed⁴ to jump. If the C₂–C₃ bond is considered first, $J_1^{(2)}(\omega_0)$ and $J_2^{(2)}(2\omega_0)$, obtained from Eqs. (2), (14), and (15), involve two more parameters σ_2 and D_2 . Since D_{\parallel} , D_{\perp} , and D_1 were already obtained, one can find D_2 using a particular value of σ_2 from $J_1^{(2)}(\omega_0)$ or $J_2^{(2)}(2\omega_0)$ by the method of bisection.³⁷ σ_2 is determined when the same value of D_2 is obtained from the measured spectral densities of the C₂ deuterons. For example, at 302.1 K, σ_2 and D_2 were found to be 0.49 and $4.1 \times 10^9 \text{ s}^{-1}$, respectively. In the limit that the rotation of the C₂–C₃ bond is free, one finds that the value of D_2 obtained from J_1 is slightly lower than that ($D_2 = 1.87 \times 10^9 \text{ s}^{-1}$) obtained from J_2 . This discrepancy in the values of D_2 can be reconciled by an experimental error of $\pm 5\%$ in J_1 and/or J_2 . Since the free rotation model seems to work well for the C₂–C₃ bond, one can consider the next bond (C₃–C₄) using the jump model. At the same temperature, $\sigma_3 = 4.15 \times 10^{-2}$ and $D_3 = 6.88 \times 10^{10} \text{ s}^{-1}$ give $J_1^{(3)}(\omega_0) = 11(11.5) \text{ s}^{-1}$ and $J_2^{(3)}(2\omega_0) = 5.6(5.19) \text{ s}^{-1}$. The numbers in parentheses are experimental values of Beckmann *et al.*⁸ The corresponding W_{13} , the jump rate for the C₃–C₄ bond from t to g^+ or g^- , is $9.5 \times 10^8 \text{ s}^{-1}$ in comparison with W_{12} of $6.7 \times 10^8 \text{ s}^{-1}$ at the same temperature. It is interesting to note that the free rotation model always gives a lower rotational diffusion constant in comparison to the jump model. Thus one may use the jump model to account for both J_1 and J_2 , but it fails to provide an explanation for any observed frequency dependence in J_1 or J_2 . Moreover, for critical testing of this model, one must carry out an elaborate computation involving more than one bond jumping in the chain.

Since the free rotation model appears to work for the C₂–C₃ bond, let us examine the applicability of this simple model to the rest of the pentyl chain before using more elaborate models. Using the free rotation model, two values of the rotational diffusion constant D_n may be obtained from J_1 and J_2 . It was found that D_n ($n = 3$ to 5), determined from J_1 , was consistently lower than that from J_2 . Since J_2 is not affected by DF, the rotational diffusion constants obtained from J_2 were used to calculate rotational diffusion constant of the subsequent chain carbon–carbon bond. We found that the temperature dependence of D_2 , D_3 , and D_4 is not Arrhenius (e.g., D_3 increases with decreasing temperature). Their values are smaller than D_1 and are in the range between 10^9 and 10^{10} s^{-1} . D_5 is larger (of the order of 10^{11} s^{-1}) because it describes rotational diffusion of the methyl group about the last C–C bond in the pentyl chain. We found that this simple model fails to simultaneously explain the experimental $J_1^{(n)}(\omega_0)$ and $J_2^{(n)}(2\omega_0)$ values for $n = 3$ to 5. Indeed it fails to predict large enough J_1 values, and the contribution to J_1 by DF may be required and/or a more realistic model such as the jump model for internal rotation is needed. However, the inclusion of DF has the advantage of giving frequency

dependence to J_1 s, but it would of course alter the values of D_{\parallel} and D_{\perp} .

Let us consider DF as an additional spin relaxation mechanism to the superimposed (free) rotations model. Using the measured values of K ³⁸ and of η ³⁹ for 5CB, A_{DF} was calculated, using Eq. (20), to be around 100 s^{-1} at 30.7 MHz. We used a single average value of $D(4.5 \times 10^{-11} \text{ m}^2/\text{s}$ at 296.5 K) for the entire nematic range, that was measured by quasielastic neutron scattering.⁴⁰ It is noted that in the present case A_{DF} cannot be used as an adjustable parameter if the spectral densities of the ring and C₁ deuterons are only measured at a single Larmor frequency. It was necessary to vary A_{DF} from its theoretical value to give a reasonable temperature dependence for D_{\parallel} , D_{\perp} , and D_R (see Fig. 4). The fitted value is lower than the theoretical value (Fig. 5) because a larger value of A_{DF} would produce an unphysical (i.e., negative) D_R value. The fitted A_{DF} value may be verified by the corresponding spectral densities measured at another frequency. On subtracting J_1^{DF} from the experimental J_1 , we find that the value of D_{\perp} increases by roughly a factor of 2, the values of D_R and D_1 (Fig. 5) decrease somewhat and the value of D_{\parallel} remains essentially the same. In addition, D_1 depends weakly on temperature, while D_R has a much larger activation energy. The geometric factor $[d_{00}^2(\beta_{i-1,i})]^2$ in Eq. (21) that accounts for the variation of DF down the chain would not give the same rotational diffusion constant from $(J_1^{(n)} - J_1^{(n)DF})$ and $J_2^{(n)}$ for the chain deuterons. Instead we use

$$J_1^{(n)DF}(\omega_0) = W(n) \times J_1^{(1)DF}(\omega_0),$$

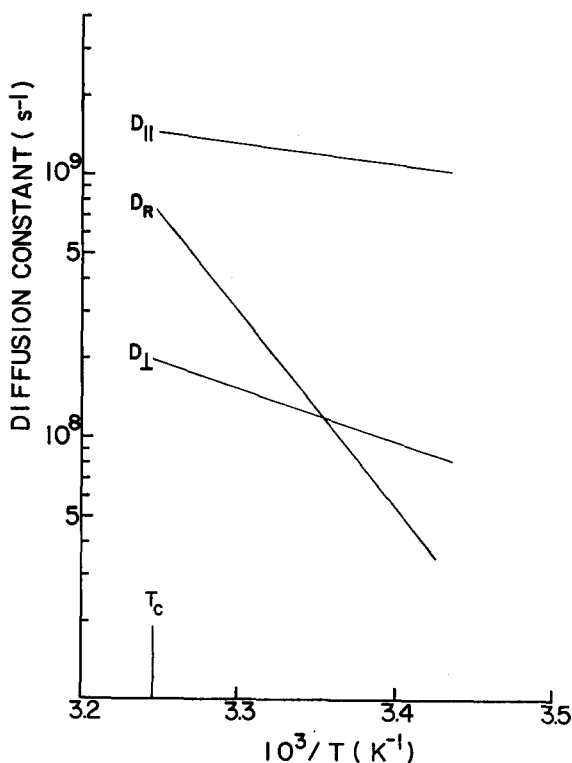


FIG. 4. Plots of rotational diffusion constants (D_{\parallel} , D_{\perp} , and D_R) vs the reciprocal temperature in the nematic phase of 5CB. These were derived with director fluctuations contributing to J_1 .

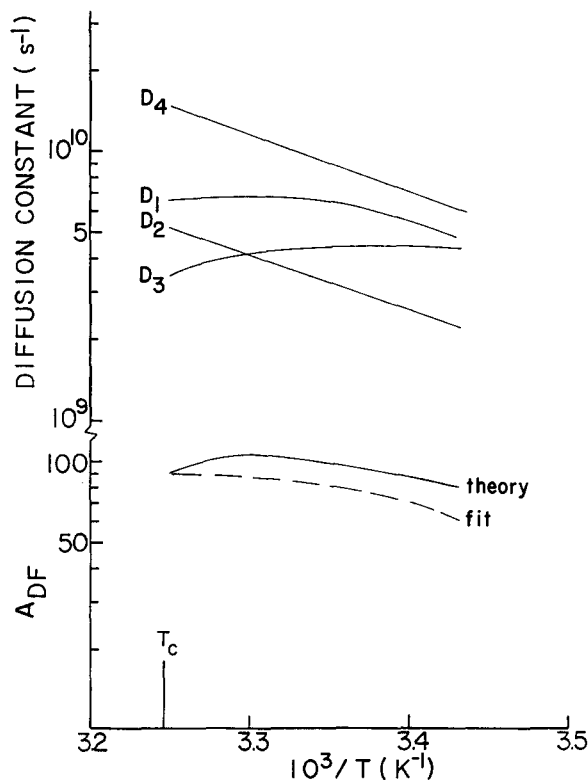


FIG. 5. Plots of rotational diffusion constants (D_n , $n = 1$ to 4) vs the reciprocal temperature in the nematic phase of 5CB. These were derived with director fluctuations whose constant A_{DF} is also given.

where $W(n)$, the derived "geometric factor," is obtained from the required magnitude of $J_1^{(n)DF}(\omega_0)$. The resultant D_2 , D_3 , and D_4 values are also shown in Fig. 5. D_5 (not shown in figure) is still of the order of 10^{11} s^{-1} . The activation energies for D_2 and D_4 are roughly the same ($E_a = 40 \text{ kJ/mol}$), while D_3 still increases slightly with decreasing temperature. More experimental data is necessary to verify whether the observed alteration in the temperature behavior of these rotational diffusion constants down the chain is genuine. Figure 6 shows the resultant variation of $W(n)$ along the chain at 302.1 and 303.7 K, as well as the predicted and experimental values of $J_1^{(n)}(\omega_0)$ at 15.4 MHz. The agreement between the predicted and experimental J_1 at 15.4 MHz, using the fitted A_{DF} and $W(n)$ derived from 30.7 MHz, is quite good. Also shown in the diagram is $(J_1 - J_1^{DF})$ which is the calculated contribution from molecular reorientation and segmental motions. The observed odd-even alternation in the geometric factor $W(n)$ is consistent with the n dependence of the statistical average of the direction cosine between the core axis and the last terminal C-C bond in $n\text{CB}$.⁴¹ Thus $J_1^{(n)DF}(\omega_0)$ appears to exhibit an odd-even effect along the butyl chain of 5CB.

In conclusion, we have used Nordio's model to describe the overall motion of a mesogen in a Maier-Saupe-type potential. The three-site jump model is given to describe chain isomerization. Due to the lack of sufficient experimental data, a more elaborate computation has not been attempted. We found that the rotational diffusion constant was always larger using the jump model (in which only one C-C bond

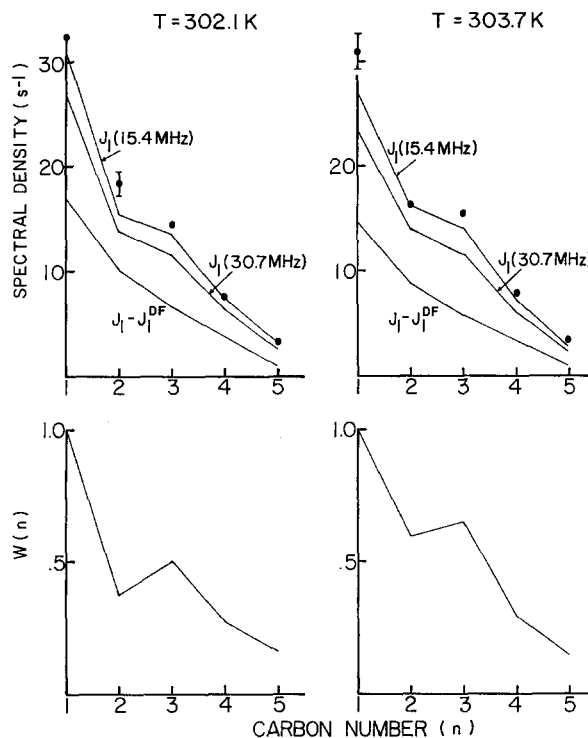


FIG. 6. Plots of spectral density J_1 at 30.7 and 15.4 MHz ($J_1 - J_1^{DF}$), and $W(n)$ as a function of carbon number n for the chain. ● denotes preliminary data at 15.4 MHz in 5CB- d_{11} .

jumps) than the free rotation model. The free rotation model for internal chain motions could not explain both measured spectral densities J_1 and J_2 . This difficulty could be resolved by the inclusion of director fluctuations in spin relaxation. The superimposed rotations model uses a basic assumption that rotations about each C-C bond are independent of each other. This assumption has proved to be inappropriate in modeling the quadrupolar splittings in liquid crystals, hence its validity for molecular dynamics may be doubtful and requires further investigation. It is important to measure spectral densities as a function of frequency and temperature in order to check more realistic models that inevitably involve additional model parameters. It is also noted that good spectral density data is necessary, since the derived rotational diffusion constants are very sensitive to the accuracy of the measured spectral densities of motion.

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¹D. Wallach, J. Chem. Phys. **47**, 5258 (1967); Y. K. Levine, N. J. M. Bird-sall, A. G. Lee, J. C. Metcalfe, P. Partington, and G. C. K. Roberts, *ibid.* **60**, 2890 (1974).

²R. E. London and J. Avitabile, J. Am. Chem. Soc. **99**, 7765 (1977).

³R. J. Wittebort and A. Szabo, J. Chem. Phys. **69**, 1722 (1978).

⁴A. Tsutsumi, Mol. Phys. **37**, 111 (1979).

- ⁵B. Perly, C. Chachaty, and A. Tsutsumi, *J. Am. Chem. Soc.* **102**, 1521 (1980).
- ⁶H. Hutton, E. Bock, E. Tomchuk, and R. Y. Dong, *J. Chem. Phys.* **68**, 940 (1978).
- ⁷R. J. Wittebort, R. Subramanian, N. P. Kulshreshtha, and D. B. DuPre, *J. Chem. Phys.* **83**, 2457 (1985).
- ⁸P. A. Beckmann, J. W. Emsley, G. R. Luckhurst, and D. L. Turner, *Mol. Phys.* **50**, 699 (1983).
- ⁹C. R. J. Counsell, J. W. Emsley, G. R. Luckhurst, D. L. Turner, and J. Charvolin, *Mol. Phys.* **52**, 499 (1984).
- ¹⁰D. Goldfarb, R. Y. Dong, Z. Luz, and H. Zimmermann, *Mol. Phys.* **54**, 1185 (1985).
- ¹¹T. M. Barbara, R. R. Vold, and R. L. Vold, *J. Chem. Phys.* **79**, 6338 (1983); T. M. Barbara, R. R. Vold, R. L. Vold, and M. E. Neubert, *ibid.* **82**, 1612 (1985).
- ¹²R. Y. Dong and K. R. Sridharan, *J. Chem. Phys.* **82**, 4838 (1985); R. Y. Dong, *J. Magn. Reson.* **66**, 422 (1986).
- ¹³R. Y. Dong, *Mol. Cryst. Liq. Cryst.* **141**, 349 (1986).
- ¹⁴P. A. Beckmann, J. W. Emsley, G. R. Luckhurst, and D. L. Turner, *Mol. Phys.* **59**, 97 (1986).
- ¹⁵P. J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience, New York, 1969).
- ¹⁶E. T. Samulski and R. Y. Dong, *J. Chem. Phys.* **77**, 5090 (1982).
- ¹⁷J. W. Emsley, G. R. Luckhurst, and C. P. Stockley, *Proc. R. Soc. London Ser. A* **381**, 117 (1982); C. J. R. Counsell, J. W. Emsley, N. J. Heaton, and G. R. Luckhurst, *Mol. Phys.* **54**, 847 (1985).
- ¹⁸P. L. Nordio and P. Busolin, *J. Chem. Phys.* **55**, 5485 (1971); P. L. Nordio, G. Rigatti, and U. Segre, *ibid.* **56**, 2117 (1972).
- ¹⁹G. R. Luckhurst and A. Sanson, *Mol. Phys.* **24**, 1297 (1972); C. F. Polnaszek and J. H. Freed, *J. Phys. Chem.* **79**, 2283 (1975); C. F. Polnaszek, G. V. Bruno, and J. H. Freed, *J. Chem. Phys.* **58**, 3185 (1973).
- ²⁰P. L. Nordio, G. Rigatti, and U. Segre, *Mol. Phys.* **25**, 129 (1973).
- ²¹A. Szabo, *J. Chem. Phys.* **72**, 4260 (1980); C. Zannoni, *Mol. Phys.* **38**, 1813 (1979).
- ²²I. Dozov, N. Kirov, and M. P. Fontana, *J. Chem. Phys.* **81**, 2585 (1984); N. Kirov, I. Dozov, and M. P. Fontana, *ibid.* **83**, 5267 (1985).
- ²³R. Y. Dong and G. M. Richards, *Mol. Cryst. Liq. Cryst.* **141**, 335 (1986); R. Y. Dong, G. M. Richards, J. S. Lewis, E. Tomchuk, and E. Bock, *ibid.* **144**, 33 (1987).
- ²⁴P. Pincus, *Solid State Commun.* **7**, 415 (1969).
- ²⁵J. P. Jacobsen, H. K. Bildsoe, and K. Schumburg, *J. Magn. Reson.* **23**, 153 (1976); S. B. Ahmad, K. J. Packer, and J. M. Ramsden, *Mol. Phys.* **33**, 857 (1977); R. R. Vold and R. L. Vold, *J. Chem. Phys.* **66**, 4018 (1977).
- ²⁶G. Agostini, P. L. Nordio, G. Rigatti, and U. Segre, *Atti. Accad. Naz. Lincei Mem. Cl. Sci. Fiz. Mat. Nat. Sez. 2a* **13**, 1 (1975); P. L. Nordio and U. Segre, in *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic, New York, 1979), pp. 411–426.
- ²⁷J. H. Freed, *J. Chem. Phys.* **66**, 4183 (1977).
- ²⁸G. R. Luckhurst, in *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic, New York, 1979), pp. 85–119.
- ²⁹D. E. Woessner, *J. Chem. Phys.* **37**, 647 (1962).
- ³⁰K. Chledowska, D. Chrusciel, J. Chrusciel, B. Janik, J. A. Janik, J. M. Janik, J. Krawczyk, and K. Otnes, *Liq. Cryst.* **1**, 127 (1986).
- ³¹C. Druon and J. M. Wacrenier, *J. Phys. Lett.* **45**, L169 (1984); L. Benguigui, *Phys. Rev. A* **28**, 1852 (1983).
- ³²R. Y. Dong, J. Lewis, E. Tomchuk, and E. Bock, *J. Chem. Phys.* **69**, 5314 (1978).
- ³³C. G. Wade, *Annu. Rev. Phys. Chem.* **38**, 47 (1977).
- ³⁴J. W. Doane, C. E. Tarr, and M. A. Nickerson, *Phys. Rev. Lett.* **33**, 620 (1974).
- ³⁵P. Ukleja, J. Pirs, and J. W. Doane, *Phys. Rev. A* **14**, 414 (1976).
- ³⁶N. J. Heaton, Ph.D. thesis, University of Southampton, 1986.
- ³⁷C. F. Gerald and P. O. Wheatley, *Applied Numerical Analysis* (Addison-Wesley, Reading, MA, 1984).
- ³⁸M. J. Bradshaw, E. P. Raynes, J. D. Bunning, and T. E. Faber, *J. Phys. (Paris)* **46**, 1513 (1985).
- ³⁹A. G. Chmielewski, *Mol. Cryst. Liq. Cryst.* **132**, 339 (1986).
- ⁴⁰A. J. Leadbetter, F. P. Temme, A. Heidemann, and W. S. Howells, *Chem. Phys. Lett.* **34**, 363 (1975).
- ⁴¹S. Kobinata, T. Kobayashi, H. Yoshida, A. D. L. Chandani, and S. Maeda, *J. Mol. Struct.* **146**, 373 (1986).