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Director fluctuations and anisotropic reorientation of a liquid crystal: A deuterium NMR study

Ronald Y. Dong[1,2] and X. Shen[2]
[1]*Department of Physics and Astronomy, Brandon University, Brandon, Manitoba, Canada R7A 6A9*
[2]*Physics Department, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2*

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The spectral densities of motion were determined by deuteron NMR relaxation measurements in the nematic and smectic-*A* and -*C* phases of 4-*n*-pentyloxybenzylidene-d_1-4′-heptylaniline and 4-*n*-pentyloxybenzylidene-4′-heptylaniline-2,3,5,6-d_4 at two different Larmor frequencies. These spectral densities can only be interpreted by invoking director fluctuations and molecular reorientation as relaxation mechanisms for the deuteron spins at the methine and ring sites. We compared the model of Nordio and co-workers [Nordio and Busolin, J. Chem. Phys. **55**, 5485 (1971)] and the third-rate model of molecular reorientation [Vold and Vold, J. Chem. Phys. **88**, 1443 (1988)] and found that the third-rate model is more appropriate in the present study. Rotational diffusion constants were determined as a function of temperature in the mesophases of 4-*n*-pentyloxybenzylidene-4′-heptylaniline.

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I. INTRODUCTION

Molecular dynamics of liquid crystals have been studied by many experimental techniques [1]. Among these, nuclear-spin-relaxation techniques [2] appear to be most promising in revealing different motional degrees of freedom in liquid crystals. Mesogenic molecules usually contain a rigid core and one or more pendant alkyl chains. In recent years considerable efforts, both experimental and theoretical, have been focused on the role of internal rotations on the NMR observables, notably the observed deuteron quadrupolar splittings and spin-lattice relaxation rates at different sites of a deuterated mesogen. The study of internal dynamics is, however, complicated by anisotropic molecular rotations and collective excitations that are due to elastic deformations in a liquid-crystal sample. The collective modes are commonly known as director fluctuations [3] and are responsible for the characteristic frequency dependence in the spin-lattice relaxation rate. NMR field-cycling experiments [4] have demonstrated their dominant role in the kHz frequency regime. In the MHz region, the sluggish rotational diffusion of molecules tends to mask the effects of director fluctuations on deuteron spin relaxation. Furthermore, there remains controversy on how to account for possible couplings between director modes and reorientation of an individual molecule. When time-scale separation of these motions is invalid, a generalized Langevin equation approach [5] is needed to handle the coupling between these motions. It is important to model molecular reorientation and collective motion of molecules before examining multiple internal degrees of freedom in their flexible alkyl end chains. The present study is aimed as a guide in our studies of internal dynamics of nematogens 4-*n*-pentyl-4′-cyanobiphenyl (5CB) [6] and 4-methoxybenylidene-4′-butylaniline (MBBA) (1O.4) [7]. Here we will not address internal dynamics of the alkyl chains in 4-*n*-pentyloxybenzylidene-4′-heptylaniline (5O.7), but will focus on the linkage methine deuteron (5O.7-d_1) and the aniline ring deuterons (5O.7-d_4), both of which are located in the central core of the molecule. The spectral densities of motion, determined from deuteron NMR relaxation measurements, were reported [8,9] at a Larmor frequency of 15.3 MHz. Our spectral density data at a single frequency could not distinguish between two different motional models of molecular rotation: the small-step rotational diffusion model of Nordio and co-workers [10] and the "third-rate" model of Vold and Vold [11]. While the mechanism of director fluctuations was used [8] in conjunction with the model of Nordio, the third-rate model seems to adequately explain the spectral densities of the methine and ring deuterons at 15.3 MHz without any contribution from director fluctuations. Of course, the derived motional parameters of the third-rate model hinge on the assumption that both $J_1(\omega_0)$ and $J_2(2\omega_0)$ are independent of the Larmor frequency at and below 15.3 MHz. However, the earlier analyses with the model of Nordio and co-workers assumes that $J_1(\omega_0)$ is frequency dependent due to the contribution from director fluctuations. Here we examine the role of director fluctuations through direct measurements of the spectral densities at 15.3 and 46 MHz. We have repeated the measurements at 15.3 MHz with much improved signal-to-noise ratio. Moreover, we aim at distinguishing the two motional models of molecular reorientation.

Molecular reorientation of liquid-crystal molecules has been considered by many authors [10–12]. The small-step rotational diffusion model proposed by Nordio and co-workers [10] has been widely used. It described reorientation of a symmetric-top molecule in a potential of mean torque of the Maier-Saupe type and employs a rotational diffusion tensor that is diagonal in a molecule-fixed frame. Strictly speaking, such a rotational diffusion tensor is only appropriate in isotropic liquids. Freed and co-workers [12] account for the viscosity anisotropy of the mesophase by diagonalizing the rotational diffusion tensor of the symmetric-top in a laboratory (director) frame. The third-rate model extends the above model of Freed by superimposing fast rotations about the long

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molecular axis onto the reorientation of the symmetric top in the director frame. This superimposed model is based on the assumption of statistical independence between these two motions. Both the model of Nordio and co-workers and the third-rate model have been used to discuss spin relaxation by molecular reorientation in liquid crystals, but a clear demonstration of which is more appropriate is still lacking [11,13,14]. In this paper, we compare these models by examining the temperature and frequency dependences of spectral densities obtained from the molecular core of 5O.7. We defer our study of the low-temperature smectic phases to a future report. In Sec. II, the theory required to interpret the spectral density data is outlined and the reader is asked to refer to the original literature for details. In Sec. III, the experimental method is given. The last section describes the results and their interpretations in terms of model parameters such as rotational diffusion constants and the standard prefactor A_{DF} for director fluctuations.

II. THEORY

The evolution of a spin system is governed by a spin Hamiltonian. In the Hamiltonian, there are fluctuating terms because of the rotational and/or collective motions of liquid-crystal molecules. From the standard spin-relaxation theory [15] for deuterons ($I=1$), the Zeeman and quadrupolar spin-lattice relaxation rates are given in terms of spectral densities $J_{m_L}(m_L\omega)$ by

$$\begin{aligned} T_{1Z}^{-1}&=J_1(\omega_0)+4J_2(2\omega_0) , \\ T_{1Q}^{-1}&=3J_1(\omega_0) , \end{aligned} \tag{1}$$

respectively. The spectral density is simply the Fourier transform of the autocorrelation function $G_{m_L}(t)$

$$J_{m_L}(m_L\omega)=\frac{3\pi^2}{2}(q_{\mathrm{CD}})^2\int_0^\infty G_{m_L}(t)\cos(m_L\omega t)dt , \tag{2}$$

where $q_{\mathrm{CD}}=e^2qQ/h$ ($\eta=0$ is assumed) is the nuclear quadrupole coupling constant and $G_{m_L}(t)$ may be evaluated in terms of the Wigner rotation matrix $D^2_{m_L m_M}(\Omega_{LM})$ in the fluctuating Hamiltonian

$$\begin{aligned} G_{m_L}(t)=\sum_{m_M} &[d^2_{m_M 0}(\beta_{M,Q})]^2 \\ &\times\langle\{D^2_{m_L m_M}[\Omega_{LM}(0)]-\overline{D^2_{m_L m_M}}\} \\ &\times\{D^{2*}_{m_L m_M}[\Omega_{LM}(t)]-\overline{D^{2*}_{m_L m_M}}\}\rangle . \end{aligned} \tag{3}$$

Now Ω_{LM} ($\equiv\alpha,\beta,\gamma$) denotes the Euler angles that transform between a molecular frame (M) attached to the molecular core and the laboratory frame (L), $\beta_{M,Q}$ is the angle between the C—D bond and the z_M axis of the molecular frame, and m_L and m_M are the projection indices for a tensor of rank two in the laboratory and molecular z axis, respectively. The autocorrelation functions are generally given by a sum of decreasing exponentials [10]. In the third-rate model, the γ angle in Ω_{LM} describes fast rotations of the molecule about its long z_M axis, while the α and β angles describe molecular reorientation in the director frame. Under the assumption of statistical independence between the γ motion and molecular reorientation (α and β motions) and using a set of diffusion rate constants D_γ, D_α, and D_β to characterize these motions, one obtains multiexponential correlation functions [11]

$$\begin{aligned} G_{m_L}(t)=\sum_{m_M} &c_{m_L m_M}[d^2_{m_M}(\beta_{M,Q})]^2 \\ &\times\sum_j a^{(j)}_{m_L m_M}\exp[-t/\tau^{(j)}_{m_L m_M}] , \end{aligned} \tag{4}$$

where $a^{(j)}_{m_L m_M}$ represent normalized relative weights of each exponential decay, $c_{m_L m_M}$ are the mean-square averages of the Wigner rotation matrices and equal to $\langle|D^2_{m_L m_M}|^2\rangle-\overline{(D^2_{0,0})}^2$, the correlation times $\tau^{(j)}_{m_L m_M}$ are

$$(\tau^{(j)}_{m_L m_M})^{-1}=k_{m_M}+[6D_\beta+m_L^2(D_\alpha-D_\beta)]/b^{(j)}_{m_L m_M} , \tag{5}$$

and the $a^{(j)}_{m_L m_M}$, $b^{(j)}_{m_L m_M}$, and $c_{m_L m_M}$ coefficients are all functions of the nematic order parameter $\langle P_2\rangle$. k_{m_M} reflects the nature of the γ motion and can be expressed in terms of p and D_γ as

$$\begin{aligned} k_0&=0 , \\ k_1&=D_\gamma , \\ k_2&=(3p+1)D_\gamma , \end{aligned} \tag{6}$$

where $0\le p\le 1$ with $p=0$ corresponding to the strong collision limit and $p=1$ to small-step rotational diffusion about the z_M axis. The spectral densities of the methine deuteron are given by

$$J^{(0)}_{m_L}(m_L\omega)=\frac{3\pi^2}{2}[q^{(0)}_{\mathrm{CD}})^2\sum_{m_M}c_{m_L m_M}[d^2_{m_M 0}(\beta^{(0)}_{M,Q})]^2\sum_j a^{(j)}_{m_L m_M}(\tau^{(j)}_{m_L m_M})^{-1}/[(m_L\omega)^2+(\tau^{(j)}_{m_L m_M})^{-2}] , \tag{7}$$

where the superscript (0) is used to label the methine site. For the γ motion, we adopt $p=0$ in Eq. (6). $\beta^{(0)}_{M,Q}$ is taken [8] to be 68°. The aniline ring deuterons have internal rotations about its para axis described by a diffusion constant D_R. Using the superimposed rotations model [16,17] for internal rotations about an axis, the spectral densities of the ring deuterons are

$$J^{(R)}_{m_L}(m_L\omega)=\frac{3\pi^2}{2}(q^{(R)}_{\mathrm{CD}})^2\sum_{m_M}\sum_{m_R}c_{m_L m_M}[d^2_{m_R 0}(\beta^{(R)}_{R,Q})]^2[d^2_{m_M m_R}(\beta_{M,R})]^2$$
$$\times\sum_j a^{(j)}_{m_L m_M}[(\tau^{(j)}_{m_L m_M})^{-1}+(1-\delta_{m_R 0})D_R]$$
$$\times\{(m_L\omega)^2+[(\tau^{(j)}_{m_L m_M})^{-1}+(1-\delta_{m_R 0})D_R]^2\}^{-1}\ , \quad (8)$$

where the ring rotation is assumed to be free and in the strong collision limit, $\beta^{(R)}_{R,Q}=60°$ and $q^{(R)}_{\mathrm{CD}}=q^{(0)}_{\mathrm{CD}}=q_{\mathrm{CD}}=185$ kHz. The $\beta_{M,R}$ angle is between the para axis of the aniline ring and the long molecular (z_M) axis. For simplicity, the z_M axis is assumed to lie close to the para axis, making $\beta_{M,R}\simeq 0$ and $d^2_{m_M m_R}(\beta_{M,R})=\delta_{m_M m_R}$. The $\langle P_2\rangle$ value needed for a, b, and c coefficients may be obtained from the doublet splitting of the methine deuteron [18]

$$\Delta\nu=\tfrac{3}{4}q^{(0)}_{\mathrm{CD}}(3\cos^2\beta^{(0)}_{M,Q}-1)\langle P_2\rangle\ . \quad (9)$$

This is an approximation as a chain-deuterated 5O.7 sample is unavailable at present. Ideally one must consider all possible configurations [7,19] of the molecule in order to calculate the orientational order of an "average" conformer.

If the model of Nordio and co-workers is used to describe small-step rotational diffusion of the molecule, the rotational diffusion tensor is now diagonalized in a molecular frame and its principal values $D_\parallel$ and $D_\perp$ are rotational diffusion constants of the molecule about the z_M axis and of the z_M axis, respectively. The correlation times that appear in Eq. (4) become

$$(\tau^{(j)}_{m_L m_M})^{-1}=[6D_\perp+m_M(D_\parallel-D_\perp)]/b^{(j)}_{m_L m_M}\ . \quad (10)$$

In the model of Nordio and co-workers, the spectral densities of the methine and ring deuterons are again given by Eqs. (7) and (8), respectively, in which $\tau^{(j)}_{m_L m_M}$ are now given by Eq. (10).

In addition to molecular reorientation and ring rotation, director fluctuations may also contribute to the spectral densities of motion. When fluctuations in the nematic director are assumed to give small amplitudes, $J_{m_L}(m_L\omega)$ is zero unless $m_L=1$. Furthermore, if director fluctuations are slow in comparison with molecular reorientation, the coupling between these two types of motion would only produce a small cross term [20,21]. In the "single"-constant approximation, the contribution to $J_{1\mathrm{DF}}(\omega)$ from director fluctuations is given by

$$J_{1\mathrm{DF}}(\omega)=a_{\mathrm{DF}}[P_2(\cos\beta)]^2\times\left[U(\omega_c/\omega)\omega^{-1/2}-\frac{\sqrt{8}}{\pi}\frac{\omega_c^{1/2}}{D_i}\right]\ , \quad (11)$$

where the second term is the negative cross term obtained by Freed [20], D_i is equal to D_β or $D_\perp$ depending on the model of molecular reorientation, β is $\beta^{(R)}_{R,Q}$ or $\beta^{(0)}_{M,Q}$, the prefactor a_{DF} in $s^{-3/2}$ is

$$a_{\mathrm{DF}}=\frac{3\pi^2}{2}(q_{\mathrm{CD}})^2\frac{3kT\langle P_2\rangle^2}{4\sqrt{2}\pi K(D_t+K/\eta)^{1/2}}\ , \quad (12)$$

η and K are one constant approximation to the anisotropic viscosities and elastic constants of the medium, D_t is the averaged translational self-diffusion constant, ω_c is a high-frequency cutoff frequency, and $U(\omega_c/\omega)$ is the cutoff function [22]. $U(\omega_c/\omega)$ is unity at low frequency and becomes small for the Larmor frequency much larger than ω_c. The cutoff function is taken as one here and $\omega_c/2\pi=200$ MHz may be used for the highest-frequency director modes. Usually the angular factor $[P_2(\cos\beta)]^2$ is included in the prefactor. Here we write it explicitly in Eq. (11) because the β angle is different for the two types of deuterons, but note that A_{DF} used [4] by Noack and co-workers is

$$A_{\mathrm{DF}}=[P_2(\cos\beta)]^2 a_{\mathrm{DF}}/\sqrt{2\pi}\ . \quad (13)$$

III. EXPERIMENT

Two samples of 5O.7 were used. The 5O.7-d$_1$ sample is labeled at the methine site and has a nematic-isotropic transition temperature $T_c=77.6$ °C, while the 5O.7-d$_4$ sample is labeled at the aniline ring and has a $T_c=76.2$° C. The transition temperatures of 5O.7-d$_1$ are close to the literature values [23] for 5O.7 [the smectic-G (Sm-G) to smectic-B (Sm-B) transition at 38 °C, the Sm-B–Sm-C transition at 52 °C the Sm-C-Sm-A transition at 55 °C, the Sm-A to nematic (N) transition at 64 °C, and the N to isotropic (I) transition at 78 °C]. When comparing the data of 5O.7-d$_1$, and 5O.7-d$_4$, we scale the temperatures to give a common T_c of 77.6 °C. In this study, we report measurements of the Zeeman and quadrupolar spin-lattice relaxation times T_{1Z} and T_{1Q} of the methine and ring deuterons at two different Larmor frequencies. A home-built superheterodyne coherent pulse NMR spectrometer was operated at 15.3 MHz using a Varian 15 in electromagnet and at 46.05 MHz using a 7.1-T Oxford superconducting magnet. The sample was placed in a NMR probe whose temperature was regulated by air flow with a Bruker BST-1000 temperature controller or by an external oil bath circulator. The temperature gradient across the sample was estimated to be better than 0.3 °C. The $\pi/2$ pulse width of ca. 4.5 μs was produced by an Amplifier Research Model 200L power amplifier. Pulse control, signal collection, Fourier transformation, and data processing [24] were done by a General Electric 1280 computer. The broadband Jeener-Broekaert (JB) sequence with the appropriate phase cycling of radiofrequency and receiver phases [25] was used to simultaneously measure T_{1Z} and T_{1Q}. The pulse sequence was modified using an additional monitoring $\pi/4$ pulse to minimize any long-term instability of the spectrometer. This pulse was phase cycled to have net effect of subtracting the equilibrium magnetization (M_∞) signal from the JB signal. Signal collection was started ca. 10 μs after each monitoring $\pi/4$ pulse, and averaged over 128–640 scans at 46 MHz and 1280–2048 scans at 15.3 MHz. The larger number of scans was required for 5O.7-d$_1$. The experimental uncertainty in the spin-lattice relaxation times was estimated to be ±5% or better. The quadrupolar splittings of the methine deuteron were determined from deuteron NMR spectra obtained by Fourier transforming the free-induction-decay (FID) signal after a $\pi/2$ pulse. These splittings have an experimental error of better than ±1%.

IV. RESULTS AND DISCUSSION

Figures 1 and 2 show the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ of 5O.7-d$_1$ and 5O.7-d$_4$, respectively, as a function of temperature in the nematic, smectic-A and -C phases at two Larmor frequencies 15.3 and 46 MHz. As seen from these figures, $J_1(\omega)$ is larger than $J_2(2\omega)$. Both $J_1(\omega)$ and $J_2(2\omega)$ increase with decreasing temperature and show no apparent discontinuities at the N–Sm-A and Sm-A–Sm-C phase transitions. The $J_2(2\omega)$ of both the methine and ring deuterons are within experimental errors independent of the Larmor frequency, while their J_1's are frequency dependent. Such frequency dependences have been obtained from deuterated solute diethynyl-benzene (DEB-d$_2$) dissolved in liquid crystals Merck Phase V [26] and 4O.8 [27]. We found that molecular reorientation alone cannot account for the different frequency dependences of $J_1(\omega_0)$ and $J_2(2\omega_0)$. Furthermore the frequency dependence in $J_1(\omega_0)$ of the methine deuteron is substantially larger than that of the ring deuterons. These observations lead us to believe that director fluctuations must contribute to $J_1(\omega_0)$ in the studied MHz region. In particular we note in Eq. (11) that contribution of director fluctuations depends on the angular factor $P_2(\cos\beta)$. Since the value of $P_2(\cos\beta)$ varies rapidly near the magic angle (54.7°), we anticipate quite different effects on the experimental $J_1(\omega_0)$ of the methine and ring deuterons.

We adopt a model in which both the director fluctuations and internal and/or reorientation motions are effective relation mechanisms. The experimental spectral densities can be calculated from

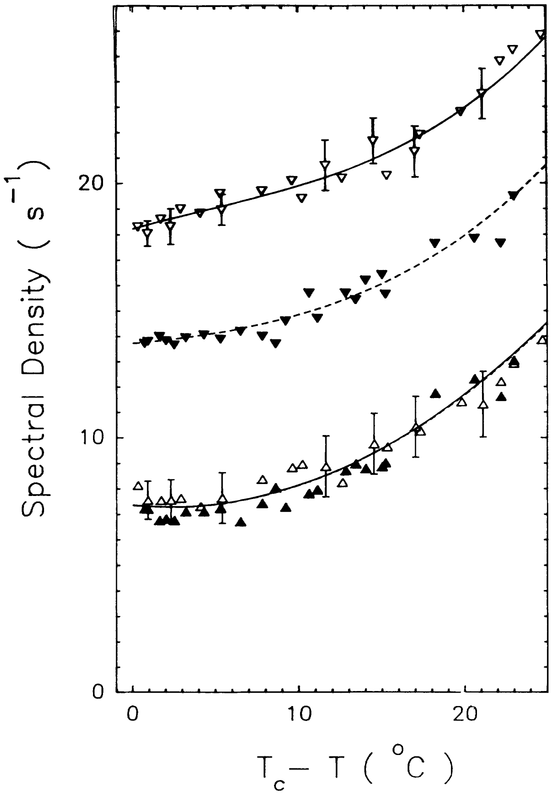

FIG. 1. Plots of spectral densities versus T_c-T in the nematic, smectic-A and -C phases of 5O.7-d$_1$. ∇ and △ denote $J_1(\omega_0)$ and $J_2(2\omega_0)$, respectively. Open symbols denote data at 15.3 MHz, while closed symbols denote data at 46.05 MHz. Solid and dashed curves are theoretical spectral densities based on the third-rate model of molecular reorientation and director fluctuations.

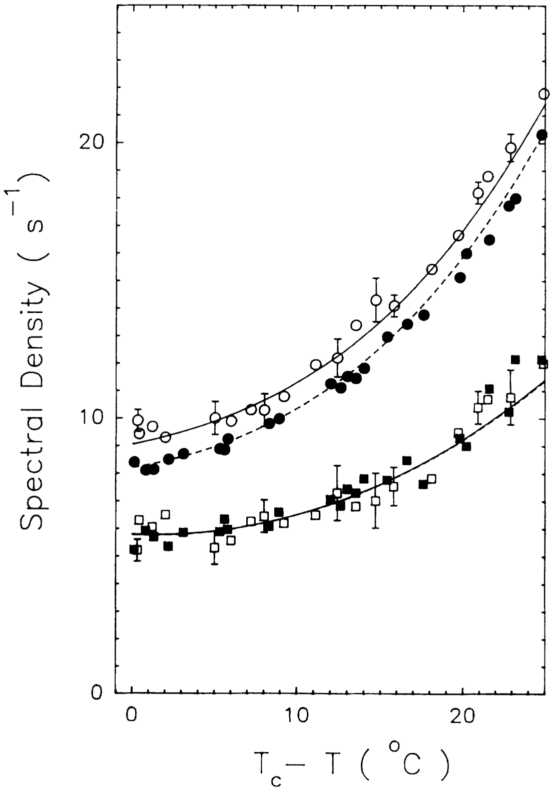

FIG. 2. Plots of spectral densities versus T_c-T in the nematic, smectic-A and -C phases of 5O.7-d$_4$. ○ and □ denote $J_1(\omega_0)$ and $J_2(\omega_0)$, respectively. Open symbols denote data at 15.3 MHz, while closed symbols denote data at 46.05 MHz. Solid and dashed curves are theoretical spectral densities based on the third-rate model of molecular reorientation and director fluctuations.

$$\begin{aligned} J_1^{(i)}(\omega_0) &= J_{1R}^{(i)}(\omega_0) + J_{1\mathrm{DF}}^{(i)}(\omega_0) , \\ J_2^{(i)}(\omega_0) &= J_{2R}^{(i)}(2\omega_0) , \end{aligned} \tag{14}$$

where the subscript R denotes the contributions from molecular rotation and the corresponding spectral densities can be evaluated using either the third-rate model or the model of Nordio and co-workers. We have tried both models of molecular reorientation and found that the third-rate model in conjunction with director fluctuations can successfully interpret the spectral densities measured in the present study. Thus the analyses based on the third-rate model will be given first.

In the third-rate model, there are three model parameters D_α, D_β, and D_γ in the correlation times given by Eq. (5). To evaluate them at each temperature, $\langle P_2 \rangle$ is first calculated from the quadrupolar splitting of the methine deuteron using Eq. (9). $a_{m_L m_M}^{(j)}$, $b_{m_L m_M}^{(j)}$ and $c_{m_L m_M}$ are obtained according to table 1 of Ref. 11. Two additional model parameters D_R and a_{DF} are needed to account for internal ring rotation and director fluctuations. At each temperature, there are eight measured spectral densities (two J_1's and two J_2's at each frequency) from which five model parameters can, in principle, be determined. For simplicity, we will neglect the small negative cross term in Eq. (11) for the moment. Given the model parameters, we compute the theoretical spectral densities of the methine and ring deuterons at each Larmor frequency using Eqs. (7), and (8), and (11) in Eq. (14). In deriving the model parameters, smoothed lines through the data in Figs. 1 and 2 were used. A minimization routine (AMOEBA) [28] was used to search for best values of the model parameters by minimizing the sum squared error F

$$F = \sum_i \sum_{m_L} [J_{m_L}^{(i)\mathrm{calc}}(m_L\omega_0) - J_{m_L}^{(i)\mathrm{expt}}(m_L\omega_0)]^2 .$$

The fitting quality factor Q is given by the percentage mean-squared deviation,

$$Q = 100F / \sum_i \sum_{m_L} [J_{m_L}^{(i)\mathrm{expt}}(m_L\omega_0)]^2 .$$

Our attempt on minimizing F by varying D_α, D_β, D_γ, D_R, and a_{DF} was met with limited success. We found that a_{DF} remains more or less constant (with an average value of 1.45×10^6 s$^{-3/2}$) over the temperature range of 25 °C and the temperature dependences of all the diffusion constants except that D_β obeys a thermally activated behavior. In other words, D_β decreases with increasing temperature, which seems quite unphysical. Thus, the four spectral densities (two J_1's and two J_2's) measured at two frequencies are still insufficient to yield physical results for all the unknown model parameters. To reduce the number of unknowns, we may assume $D_\alpha = D_\beta = D$ as a first approximation. By repeating the above analyses, we found that D, D_γ, and D_R now show expected temperature behaviors and a_{DF} is essentially constant at the above value of 1.45×10^6 s$^{-3/2}$. It would seem reasonable to fix a_{DF} and to allow the four diffusion constants to vary at each temperature. We repeated the analyses with slightly different a_{DF} values and found that a value of 1.38×10^6 s$^{-3/2}$ works over the studied temperature range except within few degrees of T_c where the a_{DF} value decreases to 1.25×10^6 s$^{-3/2}$ at T_c. The corresponding A_{DF} value for the ring deuterons is 8594 s$^{-3/2}$ (7813 s$^{-3/2}$ at T_c). No A_{DF} value has been obtained for 5O.7 from NMR field-cycling experiments and a direct comparison with the above A_{DF} values was not possible. However, A_{DF} is proportional to the square of the spectral splitting (e.g., dipolar splitting for a pair of ring protons or quadrupolar splitting for a ring deuteron) and one may estimate the A_{DF} value of the ring deuterons in 1O.4 to be close to 7940 s$^{-3/2}$ which was determined from the ring protons [4] at $T_c - T = 10$ °C in 1O.4-d$_{13}$. Therefore, the A_{DF} values used here appear to be reasonable. In Table I we summarize the results of our four-parameter fit of the experimental spectral densities to the third-rate model of molecular reorientation. Theoretical spectral densities for the two deuterated sites are shown in Figs. 1 and 2 by solid and dashed curves for 15.3 and 46 MHz, respectively. We found that the agreement between experiment and theory is rather good in the N, Sm-A, and Sm-C phases of 5O.7. It is important to note that director fluctuations make a large contribution to the observed J_1's. For example, in the middle of the N-phase director fluctuations account for about 60% and 47.5% of the experimental methine $J_1(\omega_0)$ at 15.3 and 46 MHz, respectively, and about 21% and 13% of the experimental ring J_1 at these frequencies. These percentages decrease in the smectic phases as contribution to J_1 due to molecular reorientation increases with decreasing temperature. We plot the rotational diffusion constants versus the reciprocal temperature in Fig. 3. The γ motion appears to noticeably show a pretransitional behavior at T_c. All the diffusion constants increase with increasing temperature

TABLE I. Results of four-parameter minimization of sum squared error between experimental spectral density data to the third-rate model of molecular reorientation. Director fluctuations (a_{DF}) contribute to J_1's whose values are fixed.

T (°C)	$\langle P_2 \rangle$	a_{DF} (s$^{-3/2}$)	D_α (s^{-1})	D_β (s^{-1})	D_γ (s^{-1})	D_R (s^{-1})	Q
76.5	0.38	1.25×10^6	2.14×10^9	1.13×10^9	6.47×10^9	2.07×10^9	0.005
74.5	0.44	1.30×10^6	2.22×10^9	1.16×10^9	6.45×10^9	1.61×10^9	0.005
72.5	0.49	1.38×10^6	2.05×10^9	1.14×10^9	7.25×10^9	1.02×10^9	0.026
70.0	0.53	1.38×10^6	2.09×10^9	0.91×10^9	7.49×10^9	0.89×10^9	0.040
67.5	0.57	1.38×10^6	1.96×10^9	0.82×10^9	7.39×10^9	0.67×10^9	0.018
62.5	0.67	1.38×10^6	1.63×10^9	0.68×10^9	6.87×10^9	0.44×10^9	0.005
57.5	0.74	1.38×10^6	1.39×10^9	0.58×10^9	5.80×10^9	0.17×10^9	0.049
52.5	0.78	1.38×10^6	1.18×10^9	0.45×10^9	4.71×10^9	0.09×10^9	0.065

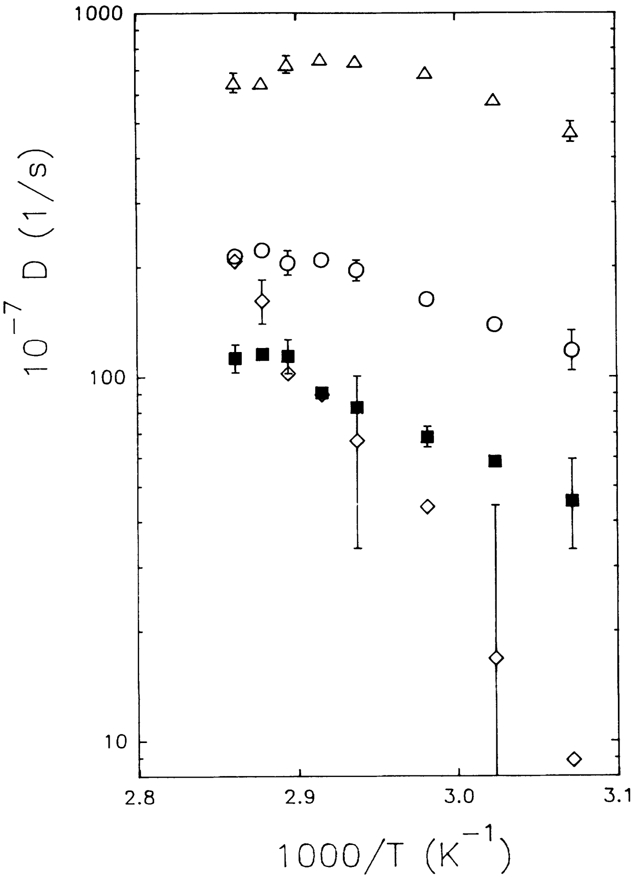

FIG. 3. Plots of rotational diffusion constants D_α (○), D_β (■), D_γ (△), and D_R (◇) versus the reciprocal temperature. Error bars are estimated by doubling the F value obtained in the minimization (see the text).

except those close to T_c. As may be seen in Figs. 1 and 2, the smoothed lines from which the spectral density data were obtained for model calculations are less reliable near T_c. The apparent pretransitional behaviors may be deceptive because of the larger uncertainty in the derived model parameters than what the error bars indicate in Fig. 3. The error bars are estimated by varying the model parameter under consideration while keeping the other three model parameters identical to those for minimum F, to give a doubling in the F value. The activation energy E_a for the α, β, and ring motions is 25 kJ/mol, 40 kJ/mol, and 120 kJ/mol, respectively. The apparent E_a for the γ motion is ca. 21 kJ/mol. We found that the γ motion is fastest, followed by the α motion and the β motion. The rate of aniline ring rotation is comparable to the α and β motions in the nematic phase and becomes slower in the smectic phases. The high activation energy for D_R may be an indication that ring flips may become hindered as temperature is lowered into the S_B phase. Another possibility is that D_R has the largest error bar, especially at low temperatures where its small values make it unimportant in comparison with the correlation times of molecular reorientation. We have tried to include the negative cross term in Eq. (11) keeping the same a_{DF} values and found that the Q factors at several temperatures deteriorate by at least a factor of 10. Furthermore, the derived values of D_β and D_γ decrease with increasing temperature. Thus, the cross term is either inappropriate or the assumption of 200 MHz for the cutoff frequency is incorrect for 5O.7.

Finally, we would like to comment on the model of Nordio and co-workers. In a recent study of internal dynamics [7] in 1O.4-d_{13}, we found that the model of Nordio and co-workers is inferior in comparison with the third-rate model. A similar case can be made here except the evidence is not as compelling. Since the contribution from director fluctuations should be same regardless of which model of molecular reorientation is used, the same a_{DF} values are used in conjunction with the model of Nordio and co-workers. There are two model parameters $D_\parallel$ and $D_\perp$ which appear in the correlation times [Eq. (10)] plus D_R for internal ring rotations. A three-parameter fit of the experimental methine and ring data to the model of Nordio and co-workers produces similar Q's as in Table I. The results are summarized in Table II. Although the Q factors are comparable to those for the third-rate model, the prediction that the tumbling motion is faster than the spinning motion of the molecule ($D_\perp > D_\parallel$) for the entire studied temperature range, is unlikely to be correct for a rodlike molecule like 5O.7. Furthermore, $D_\perp$ exhibits a wrong temperature dependence. We therefore have to rule out the model of Nordio and co-workers for 5O.7. It would be useful to have chain deuterated 5O.7 to further support this finding. It is noted that an earlier application [8] of the model of Nordio and co-workers to 5O.7 made use of single exponential autocorrelation functions. Such an assumption must be used with caution [29].

In conclusion, director fluctuations are important in relaxing deuteron spins of 5O.7 in the nematic, smectic-A, and -C phases. This is apparently not the case [7] in

TABLE II. Results of three-parameter minimization of sum squared error between experimental spectral density data to the model of Nordio and co-workers. a_{DF} values are identical to those given in Table I.

T (°C)	$D_\parallel$ (s^{-1})	$D_\perp$ (s^{-1})	D_R (s^{-1})	Q
77.5	2.80×10^9	2.93×10^9	1.94×10^9	0.019
72.5	2.10×10^9	4.92×10^9	1.74×10^9	0.064
67.5	1.59×10^9	5.51×10^9	1.43×10^9	0.073
62.5	0.88×10^9	6.15×10^9	1.05×10^9	0.062
57.5	0.39×10^9	6.21×10^9	0.47×10^9	0.145
52.5	0.17×10^9	5.43×10^9	0.15×10^9	0.084

1O.4 at 15.3 MHz because of its lower clearing temperature. For example, at $T_c - T = 25\,^\circ\mathrm{C}$, the J_1 of methine deuteron in 1O.4 is a factor of 4 larger than that of 5O.7. Thus the contribution from molecular reorientation is dominant in 1O.4, at least at temperatures not close to T_c. Both 1O.4 and 5O.7 appear to favor the third-rate model of molecular reorientation.

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