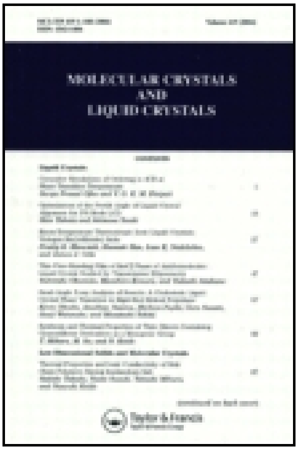

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Spectral Density of Motion in a Reentrant Nematic by Deuterium NMR

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We report on a deuterium spin relaxation study of a 26 wt.% sample of perdeuterated hexyloxycyanobiphenyl (6OCB-d_{21}) in octyloxycyanobiphenyl as a function of temperature at a Larmor frequency of 13.81 MHz. The binary mixture exhibits the following phase sequence: isotropic—nematic—smectic A—reentrant nematic—crystal. The DMR spectrum of this sample is relatively well-resolved and permits the measurement of the Zeeman (T_{1Z}) and quadrupole (T_{1Q}) spin-lattice relaxation times for several distinct deuterons in 6OCB-d_{21}. The present study considers only the ring deuterons. In fact, there are two sets of ring deuterons and we restrict our study to the set with the smaller quadrupolar splitting to avoid spectral overlap from the methyl deuterons. These relaxation times were simultaneously measured by the phase-cycled Jeener-Broekaert sequence, and the spectral densities $J_p(p\omega)$ ($p = 1,2$) were found to increase continuously with decreasing temperature. Molecular reorientation seems to be a dominant relaxation mechanism for the ring deuterons and is discussed in terms of a small step rotational diffusion model.

I. INTRODUCTION

The reentrant phenomenon was discovered in liquid crystals in 1975 when Cladis[1] observed that a smectic A phase could undergo a phase transition to a nematic phase on lowering the temperature in a mixture of two para-cyano substituted compounds. Later it was also observed in a pure compound[2] at high pressure and finally even in pure compounds at atmospheric pressure. Numerous studies,[3] both experimental and theoretical, have been carried out to elucidate the nature of reentrant mesophases. Among the reentrant systems, one common system is the binary mixture[1] of hexyloxycyanobiphenyl (60CB) and octyloxycyanobiphenyl (80CB) which has been extensively studied using various experimental techniques.[4-8] Deuterium NMR has been used to investigate[4,5] subtle changes in the orientational order parameters at the transition from the smectic A (S_A) to the reentrant nematic (RN) phase in this mixture. Thus far molecular dynamics[7] in reentrant mesophases has received little attention. Recently pulsed NMR techniques have been successfully applied to deuterons in deuterated liquid crystals[9-12] in order to determine individual spectral densities of motion. These spectral densities can be measured as a function of temperature and frequency. They contain information on the frequency spectra of fluctuations arising from motions such as director fluctuations,[13] molecular tumbling and internal motions in an anisotropic potential. Here we report on a DMR spin relaxation study of a 26 wt.% solution of perdeuterated 60CB (60CB-d_{21}) in 80CB. The DMR spectrum of this sample[4] is relatively well-resolved and permits the measurement of the Zeeman (T_{1Z}) and quadrupole (T_{1Q}) spin-lattice relaxation times for several distinct deuterons in 60CB-d_{21}. The present study considers only the ring deuterons, since a treatment of internal rotations and segmental isomerization in an alkyl chain for spin relaxation in liquid crystals is still lacking. For 60CB-d_{21}, there are two sets of ring deuterons and we restrict this study to the set with the smaller quadrupolar splitting to avoid spectral overlap from the methyl deuterons.[4] It was argued before[14] that molecular reorientation rather than director fluctuations appears to play a dominant role in relaxing ring deuterons. The derived spectral densities as a function of temperature are discussed using a small step rotational diffusion model[15-17] of a symmetric top.

II. BASIC THEORY

From the standard NMR relaxation theory[18-20] by nuclear quadrupole interaction (assume axial symmetry) for a spin I = 1, one has the following expressions for T_{1Z} and T_{1Q},

$$T_{1z}^{-1}(\theta) = A[J_1(\omega_0,\theta) + 4J_2(2\omega_0,\theta)] \tag{1}$$

$$T_{1Q}^{-1}(\theta) = 3AJ_1(\omega_0,\theta) \tag{2}$$

where $A = (3\pi^2/2)(e^2qQ/h)^2$, e^2qQ/h is the quadrupolar coupling constant, $\omega_0/2\pi$ is the Larmor frequency, θ is the angle between the director n and the external magnetic field, and the spectral densities $J_p(p\omega)$ for $\theta = 0$ (i.e. $J_p(p\omega_0,0) \equiv J_p(p\omega_0)$) are given by

$$J_p(p\omega) = \int_0^\infty G_p(t)\cos(p\omega t)dt \tag{3}$$

where $G_p(t)$ is the autocorrelation function of second rank tensor components which appear in the relaxation Hamiltonian and the subscript p refers to a projection index of the corresponding component. One can derive these spectral densities of motion (for $p=1$ and 2) from simultaneous measurement of T_{1Z} and T_{1Q} at one particular Larmor frequency. To account for the variation of spectral densities with temperature and frequency, one has to examine the various relaxation mechanisms which are responsible for the spin-lattice relaxation of nuclear spins. One of the important relaxation processes is restricted molecular tumbling in an anisotropic orientational potential.

Under the assumption that the phenyl ring rotation about the para axis is fast and is uncoupled to the overall molecular reorientation, the spectral densities for the ring deuterons derived from a small step rotational diffusion model[15-17,21] for a symmetric top reorienting in a restoring potential $U(\beta_0) = -\lambda P_2(\cos\beta_0)$ are given by

$$\begin{aligned} J_p(p\omega) = {} & \kappa(p,0)[d^2_{00}(\beta')]^2[d^2_{00}(\beta'')]^2 \frac{\tau^2_{p0}}{1 + p^2\omega^2(\tau^2_{p0})^2} \\ & + 4\kappa(p,1)[d^2_{11}(\beta')]^2[d^2_{10}(\beta'')]^2 \frac{\tau^2_{p1}}{1 + p^2\omega^2(\tau^2_{p1})^2} \\ & + 4\kappa(p,2)[d^2_{22}(\beta')]^2[d^2_{20}(\beta'')]^2 \frac{\tau^2_{p2}}{1 + p^2\omega^2(\tau^2_{p2})^2} \end{aligned} \tag{4}$$

where β'' is the angle between the C-D bond and the para axis, β' is the angle between the para axis and the long molecular axis, and

$$[d^2_{00}(\theta)]^2 = (3\cos^2\theta - 1)^2/4$$

$$[d^2_{10}(\theta)]^2 = (3\sin^2 2\theta)/8$$

$$[d^2_{11}(\theta)]^2 = (1 - 3\cos^2\theta + 4\cos^4\theta)/4$$

$$[d^2_{12}(\theta)]^2 = (1 - \cos^4\theta)/4$$

$$[d^2_{20}(\theta)]^2 = (3\sin^4\theta)/8$$

$$[d^2_{22}(\theta)]^2 = (1 + 6\cos^2\theta + \cos^4\theta)/16$$

The correlation times τ^2_{pq} are given in terms of an axially symmetric diffusion tensor whose principal components are $D_\parallel$ and $D_\perp$, the rotational diffusion coefficients of the molecule about the molecular symmetry axis and perpendicular to this axis, respectively:

$$(\tau^2_{pq})^{-1} = (D_\perp/\beta^2_{pq}) + (D_\parallel - D_\perp)q^2 \tag{5}$$

The parameters β^2_{pq} depend on the orientational order of the phase. Plots of β^2_{pq} versus the order parameter $\langle P_2\rangle$ were given in Ref. (16). The $\kappa(p,q)$ are mean square of the Wigner rotation matrices:

$$\kappa(p,q) = \langle[D^2_{pq}(\Omega_0)]^2\rangle - \left|\langle D^2_{pq}(\Omega_0)\rangle\right| 2\delta_{p0}\delta_{q0} \tag{6}$$

where Ω_0 are the Euler angles describing the instantaneous orientation of the molecule in the liquid crystalline coordinate system. These quantities account for effects of static order in mesophase and can be expressed[15] in terms of order parameters $\langle P_2\rangle \equiv \langle D^2_{00}(\Omega_0)\rangle$. It should be noted that the $\kappa(p,q)$ values with $q \neq 0$ depend on the anisotropic rotational diffusion factor $R = D_\parallel/D_\perp$ and on the form of the restoring potential.[22]

The deuterium NMR spectrum of a single ring deuteron consists of a quadrupolar doublet whose splitting $\Delta\nu_Q$ is given by

$$\Delta\nu_Q = (3/2)(e^2qQ/h)P_2(\cos\beta')P_2(\cos\beta'')\,\langle P_2\rangle \tag{7}$$

where $P_2(\cos\beta) = (3\cos^2\beta - 1)/2$. In using the small step rotational diffusion model, one requires the order parameter $\langle P_4\rangle$ which cannot be measured by NMR. Raman studies[23] have been used to measure both the $\langle P_2\rangle$ and $\langle P_4\rangle$ in liquid crystals. These order parameters have been reported[24] for 8OCB but not for the binary mixture. Therefore we have adopted the restricted cone model[25] for the purpose of calculating $\langle P_4\rangle$ only. In this model, all orientations of a rigid rod are equally probable within a cone of semiangle θ_0 and simple algebraic expressions can be written for $\langle P_2\rangle$ and $\langle P_4\rangle$:

$$\langle P_2\rangle = (1/2)\cos\theta_0(1 + \cos\theta_0) \tag{8}$$

$$\langle P_4\rangle = (1/8)\cos\theta_0(1 + \cos\theta_0)(7\cos^2\theta_0 - 3) \tag{9}$$

This procedure was used in a recent ^{13}C study[26] of a liquid crystal.

III. EXPERIMENTAL

The sample was the same as that used in an earlier study.[4] The transition temperatures of the sample were about 78, 46 and 28°C for $I \rightarrow N, N \rightarrow S_A$ and $S_A \rightarrow RN$ transitions, respectively. The sample temperature was monitored by a copper-constantan thermocouple.

The deuterium spin-lattice relaxation measurements were made at 13.81 MHz with a Bruker SXP spectrometer equipped with a 1180 (Nicolet) FFT accessory. The external magnetic field was "locked" at 21.14 kG and its field homogeneity was maximized by proper trimming with shim coils. The longitudinal relaxation times T_{1Z} and T_{1Q} were determined by means of a Jeener-Broekaert pulse sequence $[(\pi/2) - \tau - (\pi/4) - t - (\pi/4)]$ with the proper phase-cycling[27] to get rid of unwanted coherences. The preparation time τ was chosen according to $(2n+1)/\Delta\nu_Q$. T_{1Z} and T_{1Q} were derived from the sum and difference of the doublet component intensities obtained by the third monitoring pulse, respectively. DMR spectra were obtained by averaging signals from about 900 sweeps. These measurements had an experimental error of about 5%. The transverse relaxation times were measured with quadrupolar echo experiments. Since they involve a much larger error due to some experimental difficulties, we have not derived the spectral density $J_0(0)$.

IV. RESULTS AND DISCUSSION

Quadrupolar splittings for various deuterons of 6OCB-d$_{21}$ in the binary mixture of 26 wt.% 6OCB/8OCB were reported[4] earlier. $\Delta\nu_Q$ for the ring deuterons (say ring A) with a smaller doublet splitting was used to calculate $\langle P_2\rangle$ using Eq. (7). One encounters the difficulty of not knowing the exact molecular geometry in extracting $\langle P_2\rangle$ from $\Delta\nu_Q$. Fortunately it was observed[5] that $\Delta\nu_Q$ for pure 6OCB (or 8OCB) is similar to that of 6OCB (or 8OCB) in the binary mixture over the same temperature range. Using $e^2qQ/h = 183$ kHz and $\beta'' = 60°$, we have chosen an effective value of 32.6° for β' such that the $\langle P_2\rangle$ values (see Figure 1) derived from $\Delta\nu_Q$ between $15° \geqslant T_{NI} - T \geqslant 0°$ coincide with that of 8OCB from Raman data.[24] The β' value appears to be large for the angle between the para axis and the long molecular axis,

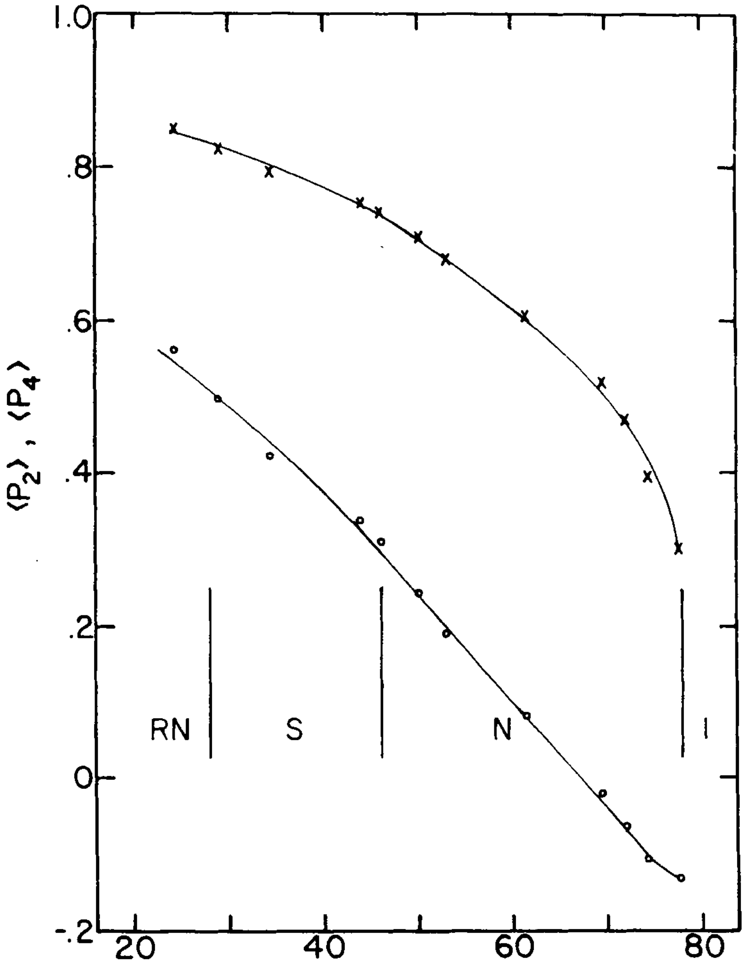

FIGURE 1 Plots of order parameters for 60CB/80CB mixture versus temperature. $\langle P_2 \rangle$ is calculated from the quadrupolar splitting, while $\langle P_4 \rangle$ is calculated using the restricted cone model (see text). *x* and 0 denote $\langle P_2 \rangle$ and $\langle P_4 \rangle$, respectively.

but this is necessary to make $\langle P_2 \rangle$ not close to one in the RN phase and not below 0.3 at the clearing temperature. It is also used later in Eq. (4) for consistency. Using the restricted cone model (Eq. (8–9)), $\langle P_4 \rangle$, was evaluated from $\langle P_2 \rangle$, as shown in Figure 1. In comparison with $\langle P_4 \rangle$ of 80CB, the $\langle P_4 \rangle$ values at temperatures just below T_{NI} are less negative. The negative or low $\langle P_4 \rangle$ value has been ascribed[28] to "dimerization" (see below) in para-cyano substituted compounds which would suggest that 6OCB/8OCB may have less dimerization than pure 8OCB.

The spectral densities of motion, $J_1(\omega_0)$ and $J_2(2\omega_0)$, for the ring A deuterons were calculated from T_{1Z} and T_{1Q} using Eqs. (1–2) and $A = 0.5 \times 10^{12} \mathrm{s}^{-2}$. These are plotted versus the reciprocal temperature in the N,S_A, and RN phases in Figure 2. Both spectral densities are seen to increase continuously with decreasing temperature, even

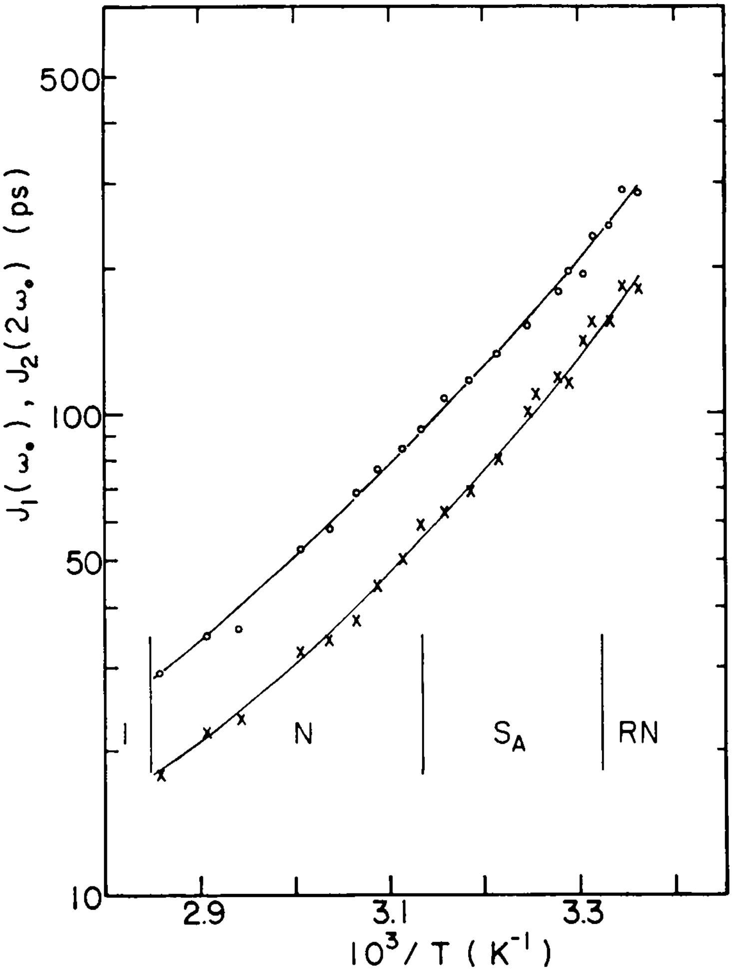

FIGURE 2 Plots of the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ versus the reciprocal temperature. 0 and x denote $J_1(\omega_0)$ and $J_2(2\omega_0)$, respectively. Lines a guide through points only.

at phase transitions. The rotational diffusion coefficients $D_{\|}$ and $D_{\perp}$ were evaluated using Eqs. (4) and (5), with β^2_{pq} given by Agostini *et al.*[16] and $\kappa(p,q)$ given by Freed.[15] The equations for $J_1(\omega_0)$ and $J_2(2\omega_0)$ reduced to a quartic in $R(=D_{\|}/D_{\perp})$ and $D_{\perp}$, which was solved[29] by either the method of bisection (when $\omega\tau^2_{pq} \leq 1$ in the fast motion limit) or Newton's method. In the N and S_A phases, it was found that the fast motion limit applies, while the full equation was needed in the RN phase as the motion is in the intermediate motion regime.

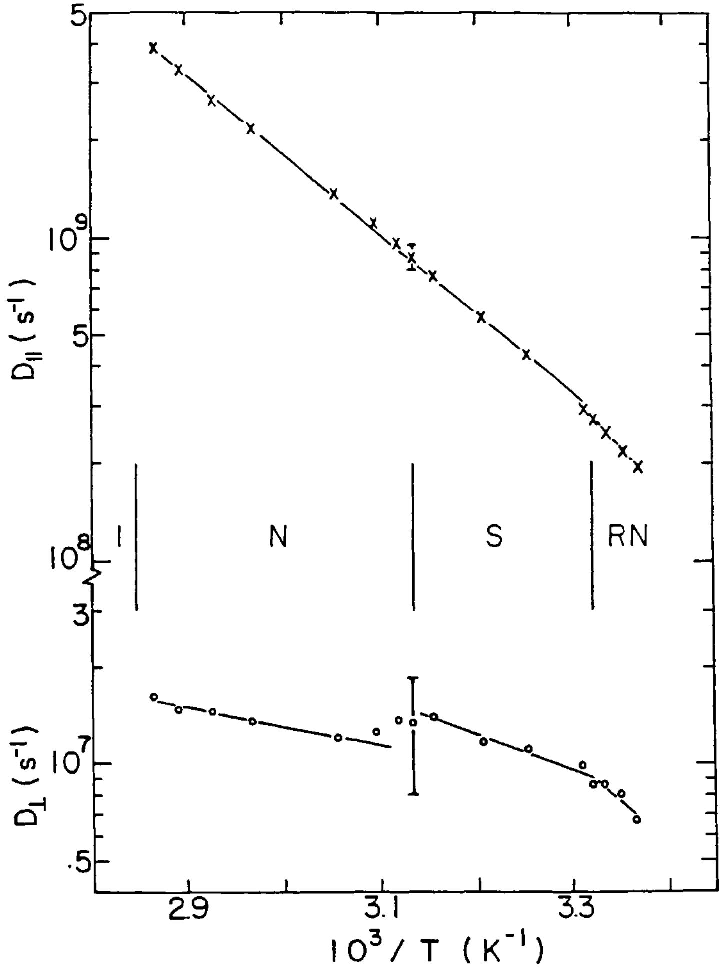

FIGURE 3 Plots of rotational diffusion coefficients $D_{\|}$ and $D_{\perp}$ versus the reciprocal temperature.

The derived rotational diffusion coefficients are plotted versus the reciprocal temperature in Figure 3. As seen in the figure, $D_{\parallel}$ follows an Arrhenius temperature behavior with an activation energy E_a of 47.5 kJ/mole in the N and S_A phases and shows a slightly higher E_a in the RN phase. The behavior of $D_{\perp}$ is rather different, since the E_a's are different in the various phases, with a progressively larger value in lower temperature phases (11 kJ/mole, 20 kJ/mole and 46 kJ/mole in N, S_A and RN phases, respectively). There seems to be a discontinuity of $D_{\perp}$ at the N-S_A transition but not at the S_A-RN transition. As noted for other liquid crystals,[29] we note that the error bars for $D_{\perp}$ are much larger than those of $D_{\parallel}$ and depend on the accuracy of the relaxation data. The anisotropic factor R varies from 240 at the clearing temperature to about 30 in the RN phase. The range of RN phase in the binary mixture is small and therefore one cannot determine its E_a value for $D_{\perp}$ with great certainty. However, the observed doubling in the E_a value at the phase transitions is interesting. The para-cyano substituted compounds show strongly antiparallel dipole association. At the S_A-RN transition, pairing favors the nematic phase, depairing favors the S_A phase.[30] In other words, there is saturation of dimer formation in the RN phase. In the S_A phase, the partial bilayer structure does not allow effective packing of dimers within each layer, and therefore allows easy flipping of a molecule around a short axis. This could explain why the E_a value for $D_{\perp}$ is much larger in the RN phase.

In summary, molecular reorientation seems to be a dominant relaxation mechanism for the ring deuterons of the binary mixture of 6OCB-d_{21}/8OCB. The spectral densities of motion can be quantitatively interpreted using a small step rotational diffusion model of a symmetric top. The derived rotational diffusion coefficients may be useful for shedding light on the height of nematic barrier.[31]

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