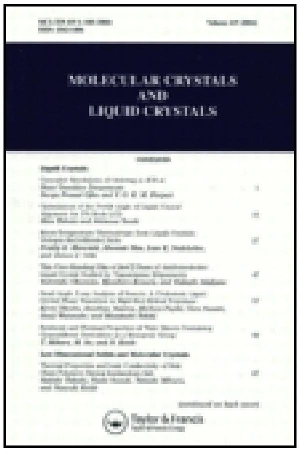

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Ronald Y. Dong [a] & G. M. Richards [a]

[a] Department of Physics and Astronomy, Brandon University, Brandon, R7A 6A9, Manitoba, Canada

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Deuterium Spin Relaxation in a Ring-Deuterated Smectic Liquid Crystal

RONALD Y. DONG† and G. M. RICHARDS

Department of Physics and Astronomy, Brandon University, Brandon, Manitoba, Canada R7A 6A9

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The phase-cycled Jeener-Broekaert sequence was used to simultaneously measure the deuterium Zeeman (T_{1Z}) and quadrupole (T_{1Q}) spin-lattice relaxation times in the mesophases of 4-n-butoxybenzylidene-4′-n-octylaniline-2,3,5,6-d_4 at a Larmor frequency of 15.4 MHz. The derived spectral densities of motion $J_1(\omega_0)$ and $J_2(2\omega_0)$ increase with decreasing temperature in the nematic, smectic A and smectic B phases and show a discontinuity similar to that of the quadrupolar splitting at the S_A to S_B phase transition. The angular dependence of T_{1Z} and T_{1Q} were measured in the smectic B phase, thus allowing us to obtain $J_1(2\omega_0)$ and $J_2(\omega_0)$. Within experimental error, the spectral densities $J_p(\omega)$ ($p = 1,2$) are in the white spectrum regime. Molecular reorientation seems to be a dominant relaxation mechanism for the aniline deuterons and is discussed in terms of a small step rotational diffusion model.

Keywords: deuterium relaxation, spectral density, angular dependence, reorientation, smectic

I. INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy has been used to provide useful information on molecular dynamics[1,2] and orientational ordering[3] of liquid crystalline molecules in anisotropic mesophases[4,5] of liquid crystals. In particular, deuterium NMR has emerged as a powerful technique in examining flexible liquid crys-

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talline molecules because their DMR spectra usually show well-resolved spectral lines which give the site specificity of the observed deuteron spin. For instance, recent DMR studies[6,7] have provided evidence in support of strong correlation between the motion of the rigid core of a flexible molecule and the macroscopic structure of the 'ordered' smectic phases (e.g. smectic E and G phases). Furthermore pulsed NMR techniques have been applied to obtain deuteron spin relaxation measurements, resulting in separation of individual spectral densities of motion in liquid crystals.[8-12] The temperature and frequency dependence of these spectral parameters contain information on the frequency spectra of fluctuations from molecular motions such as molecular tumbling and internal motions in a flexible molecule. In examining nuclear spin relaxation of flexible mesogens, their internal motions and segmental isomerization pose a formidable task. However, one can conclude from the observed site dependence of spectral densities[8,10,11] that one of the assumptions used in the current theories of nuclear spin relaxation for mesogens[13-16] is invalid; namely that the liquid crystalline molecule can be idealized as a rigid rod or disk. Besides the molecular reorientation, a collective hydrodynamic mode known as director fluctuations[13,17] is a characteristic relaxation mechanism for liquid crystals. To avoid treating the difficult problem of alkyl chain motions in 4-n-butoxybenzylidene-4′-n-octylaniline (40.8),[11]4 we have carried out DMR measurements of the Zeeman spin-lattice relaxation time T_{1Z} and the quadrupolar spin-lattice relaxation time T_{1Q} in the mesophases of a ring-deuterated 40.8. The angular dependence of these relaxation rates in the smectic B phase was also studied. 40.8 is chosen to complement our study on a similar smectic mesogen 50.7 reported earlier[12] and is particularly suitable to check models for molecular reorientation since its orientational order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ are known from Raman studies.[18]

II. THEORY

Standard NMR relaxation theory[19-21] by nuclear quadrupole interaction (assume axial symmetry) for a spin $I = 1$ gives the following expression 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 $\hat{n}$ and the external magnetic field, and the spectral densities $J_p(p\omega)$ 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. In the nematic phase, one can obtain $J_p(p\omega_0,0) \equiv J_p(p\omega_0)$ for $p = 1$ and 2 from simultaneous measurement of T_{1Z} and T_{1Q} since the director is normally aligned along the magnetic field (sample has postive $\Delta\chi$). One may however carry out relaxation measurements at θ other than zero in the nematic phase by applying an electric field to the sample for alignment and in some smectic phases without any external aligning agent. Such angular dependence study can further provide spectral densities at two other frequencies, thus allowing one to examine the frequency dependence of the derived spectral densities of motion. For a uniaxial mesophase, one can express $J_p(p\omega,\theta)$ in terms of $J_p(p\omega)$ according to

$$J_p(p\omega,\theta) = \sum_{q=-2}^{2} [d^2_{pq}(\theta)]^2 J_q(p\omega) \tag{4}$$

where

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

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

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

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

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

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

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 molecular tumbling under the restriction of an anisotropic orientational potential. The spectral densities derived from a small step rotational diffusion model[13,16] for reorientation of a symmetric top molecule in a restoring potential $U(\beta_0) = -\lambda P_2(\cos\beta_0)$ are

$$J_p(p\omega) = \sum_{q=-2}^{2} [d^2_{q0}(\beta)]^2 \kappa(p, q) \frac{\tau^2_{pq}}{1 + p^2\omega^2(\tau^2_{pq})^2} \tag{5}$$

where β is the angle between the principal quadrupole tensor axis and the molecular symmetry axis, and 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 of this axis, respectively:

$$(\tau^2_{pq})^{-1} = (D_\perp/\beta^2_{pq}) + (D_\parallel - D_\perp)q^2 \tag{6}$$

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:

$$\kappa(p, q) = \langle [D^2_{pq}(\Omega_0)]^2\rangle - |\langle D^2_{pq}(\Omega_0)\rangle|^2\delta_{p0}\delta_{q0} \tag{7}$$

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[13] in terms of order parameters $\langle P_2\rangle \equiv \langle D^2_{00}(\Omega_0)\rangle$ and $\langle P_4\rangle \equiv \langle D^4_{00}(\Omega_0)\rangle$ as reproduced in table I. It should be noted that the

TABLE I

Values of $\kappa(p,q)$ and μ_{pq}

$\lvert p\rvert$	$\lvert q\rvert$	$\kappa(p, q)$	μ_{pq}
0	0	$(1/5) + (2/7)\langle P_2\rangle + (18/35)\langle P_4\rangle - \langle P_2\rangle^2$	$(6/5) + (6/7)\langle P_2\rangle - (72/35)\langle P_4\rangle$
1	0	$(1/5) + (1/7)\langle P_2\rangle - (12/35)\langle P_4\rangle$	$(6/5) + (3/7)\langle P_2\rangle + (48/35)\langle P_4\rangle$
2	0	$(1/5) - (2/7)\langle P_2\rangle + (3/35)\langle P_4\rangle$	$(6/5) - (6/7)\langle P_2\rangle - (12/35)\langle P_4\rangle$
1	1	$(1/5) + (1/14)\langle P_2\rangle + (8/35)\langle P_4\rangle$	$(6/5) + (3/14)\langle P_2\rangle - (32/35)\langle P_4\rangle$
1	2	$(1/5) - (1/7)\langle P_2\rangle - (2/35)\langle P_4\rangle$	$(6/5) - (3/7)\langle P_2\rangle + (8/35)\langle P_4\rangle$
2	2	$(1/5) + (2/7)\langle P_2\rangle + (1/70)\langle P_4\rangle$	$(6/5) + (6/7)\langle P_2\rangle - (2/35)\langle P_4\rangle$

$\kappa(p, q)$ 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]

In evaluating the spectral densities in eq. (5), the autocorrelation function was approximated by a single-exponential, i.e.

$$G_{pq}(t) = \kappa(p, q)\exp(-t/\tau^2_{pq}) \tag{8}$$

which is valid except for high orientational order ($\langle P_2\rangle > 0.8$) and for $p = q = 1$. In general, the autocorrelation function is a sum of exponentials. In particular, $G_{11}(t)$ requires at least two exponentials in the sum.[23] As a consequence, β^2_{11} was calculated numerically and found to increase rather than decrease with increasing $\langle P_2\rangle$, as shown in the plot given in ref. (16). The increase in β^2_{11} is more dramatic than that of β^2_{22} in the plot. Using the single-exponential approximation for the autocorrelation function, Szabo[24] provides an analytical expression for the correlation times τ^2_{pq} in which β^2_{pq} is replaced by $\lambda_{pq} = \kappa(p, q)/\mu_{pq}$. For an arbitrary potential $U(\beta_0)$, μ_{pq} $q \neq 0$ cannot be all expressed in terms of $\langle P_2\rangle$ and $\langle P_4\rangle$ alone. However, for potentials that are symmetric about $\pi/2$ (i.e. the orientational distribution function satisfies $P_{eq}(\beta_0) = P_{eq}(\pi - \beta_0)$), they can be and the results are reproduced in table I. It is noted that the dependence of λ_{pq} and β^2_{pq} on $\langle P_2\rangle$ are similar except for $p = q = 1$. In fact λ_{11} behaves more like β^2_{11} when a sum of several exponentials were used for the autocorrelation function.

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 in eq. (5) can be modified for the ring deuterons to give

$$\begin{aligned} J_p(p\omega) = {} & \kappa(p, 0)[d^2_{00}(\beta')]^2[d^2_{00}(\beta'')]^2 \frac{\tau^2_{p0}}{1 + p^2\omega^2(\tau^2_{p0})^2} \\ & + 4\kappa(p, 1)[d^2_{11}(\beta')]^2[d^2_{10}(\beta'')]^2 \frac{\tau^2_{p1}}{1 + p^2\omega^2(\tau^2_{p1})^2} \\ & + 4\kappa(p, 2)[d^2_{22}(\beta')]^2[d^2_{20}(\beta'')]^2 \frac{\tau^2_{p2}}{1 + p^2\omega^2(\tau^2_{p2})^2} \end{aligned} \tag{9}$$

where β'' is the angle between the C—D bond and the para axis and β' is the angle between the para axis and the long molecular axis. When the angle β' is set to zero, the above equation reduces to eq.

(5). Treatment of segmental isomerization and internal motions in the alkyl chains of liquid crystals is still lacking. Other spin relaxation mechanisms include director fluctuations[17] and translational diffusion[15] which is an intermolecular interaction. These are not effective in relaxing the aniline deuterons investigated here.[26]

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

$$\Delta\nu_Q = (3/2)(e^2qQ/h)P_2(\cos\beta')P_2(\cos\beta'')\,\langle P_2\rangle \qquad (10)$$

where $P_2(\cos\beta) = (3\cos^2\beta - 1)/2$. The longitudinal relaxation times T_{1Z} and T_{1Q} can be conveniently determined by means of a Jeener-Broekaert pulse sequence $[(\pi/2) - \tau - (\pi/4) - t - (\pi/4)]$ with the proper phase-cycling[25] to get rid of unwanted coherences. The preparation time τ was chosen according to $(2n + 1)/2\Delta\nu_Q$. T_{1Z} and T_{1Q} can be derived from the sum $S(t)$ and difference $D(t)$ of the doublet component intensities obtained by the third monitoring pulse, respectively:

$$S(t) \propto \sqrt{2}(1 - \exp(-t/T_{1Z})) \qquad (11)$$

$$D(t) \propto -(3/2)\exp(-t/T_{1Q}) \qquad (12)$$

III. EXPERIMENTAL

The 4-n-butoxybenzylidene-4′-n-octylaniline-2,3,5,6-d_4(40.8-d_4) sample was obtained from Dr. J. W. Doane, Kent, Ohio and was degassed and sealed under vacuum using the freeze-pump-melt method in a 7.5 mm o.d. NMR tube. The transition temperatures for smectic B-smectic A, smectic A-nematic, and nematic-isotropic phase transitions were 48.8, 63.8 and 78.8° C, respectively. Deuterium spin-lattice relaxation times T_{1Z} and T_{1Q} were determined by the Jeener-Broekaert method with phase-cycling[25] at 15.4 MHz using a home-built superheterodyne coherent pulsed spectrometer and a Varian 15in. high-resolution electromagnet. The NMR spectrometer has been described elsewhere,[12] the $\pi/2$ pulse width used was 6 μs. The sample was placed in an oven whose temperature was maintained by an external bath circulator and the sample temperature was monitored by a copper-constantan thermocouple. The thermal gradient across the sample was estimated to be better than 0.3°C. The 4k quadrature FFT spectrum was achieved with a BNC12 (Nicolet) by averaging signals starting at a time τ after the third monitoring $\pi/4$ pulse over 400-800 scans at repetition times of $\geq$300 ms. The measurements of the above relaxation times had an experimental error of $\pm 5\%$.

The observed doublet splitting was used to calculate the order parameter $\langle P_2 \rangle$ shown in Figure 1 using eq. (10) with $e^2qQ/h = 183$ kHz, $\beta' = 15°$ and $\beta'' = 60°$. The β' angle between the para axis and the long molecular axis was chosen such that the $\langle P_2 \rangle$ derived from NMR and by Raman studies[18] in the smectic B phase coincided. This value was also consistent with what one would expect from molecular models.[27] As shown in figure, the value $\langle P_2 \rangle$ derived from NMR deviates from that of Raman studies in nematic and smectic A phases. We will use the $\langle P_2 \rangle$ values derived in the present study and the $\langle P_4 \rangle$ shown in the figure, which has been scaled according to $(\langle P_2 \rangle_{\mathrm{NMR}}/\langle P_2 \rangle_{\mathrm{Raman}})\ \langle P_4 \rangle_{\mathrm{Raman}}$.

In performing the angular dependence study in the smectic B phase, the NMR probe and sample assembly could be rotated about the vertical axis in the magnetic field to any angle with an accuracy of ± 1° with the aid of a goniometer. The angular dependence of T_{1Z} and T_{1Q} was measured at three different field orientations, the angles θ were 0°, 90° and 30° or 45°. The measurement at $\theta = 45°$ would reduce the errors[11] involved in calculating $J_1(2\omega_0)$ and $J_2(\omega)$ from eq. (4).

The rotational diffusion coefficients $D_\parallel$ and $D_\perp$ which appear in the

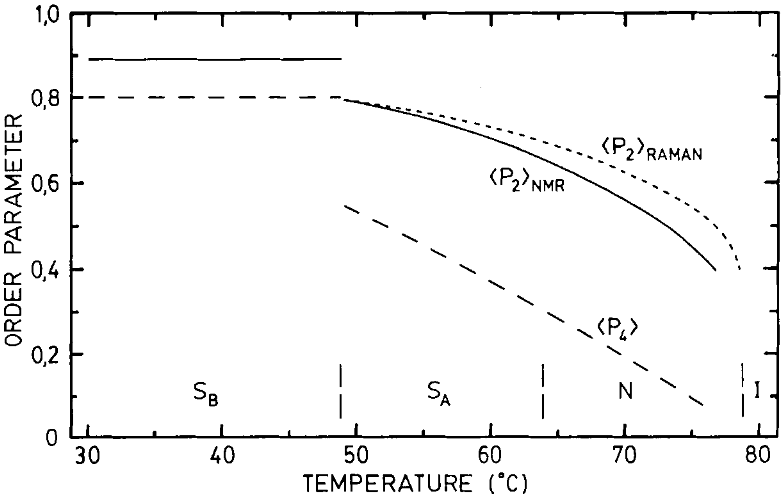

FIGURE 1 Plots of order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for 40.8 versus temperature. $\langle P_2 \rangle$ is calculated from the quadrupolar splitting, while $\langle P_4 \rangle$ is from Raman data (see text).

correlation times τ_{pq}^2 were evaluated using the small step rotational diffusion model, eq. (9). Smoothed $J_1(\omega_0)$ and $J_2(2\omega_0)$ data was used in this calculation. The equations for $J_1(\omega_0)$ and $J_2(2\omega_0)$ reduced to a quartic in R ($= D_\parallel/D_\perp$) and $D_\perp$, which was solved using two methods. The simplifying assumption that $\omega\tau_{pq}^2 << 1$ allows solution by the method of bisection. The full equation, including the frequency term, was solved using Newtons' Method.[28]

IV. RESULTS AND DISCUSSION

Using eqs. (1)–(2), one can derive from the observed relaxation rates, $J_1(\omega_0)$ and $J_2(2\omega_0)$ when the director is aligned along the external magnetic field (i.e. $\theta = 0$). These values were plotted versus the reciprocal temperature in the three mesophases (Figure 2). Also shown in the figure are the derived $J_1(2\omega_0)$ and $J_2(\omega_0)$ from the angular dependence study in the smectic B phase. Such angular dependence study was not possible in the smectic A phase because the sample director would reorient in the field. It should be noted from the figure that within experimental error no frequency dependence is apparent in the spectral densities of motion for 40.8. Barbara et al.[11] have reported deuteron spin relaxation data for 40.8 with a perdeuterated octyl chain and aniline ring at 9.2 MHz and 38.2 MHz. In comparison with our data at 15.4 MHz, both their spectral densities of the aniline deuterons are about 20–30 percent higher in all the mesophases. The discrepancy may perhaps be ascribed to impurity in their sample (whose clearing temperature is close to 75°C). Their data also suggest a slight frequency dependence (between 18 to 77 MHz) for $J_2(2\omega_0)$ and a small discontinuity in J_1 and J_2 at the smectic A and B phase transition (see also Figure 2).

The rotational diffusion coefficients $D_\parallel$ and $D_\perp$ were evaluated using eq. (9), with β_{pq}^2 given by Agostini et al.[16] Figure 3 shows the resultant plots of $D_\parallel$ and $D_\perp$ versus the reciprocal temperature for 40.8. These results were consistent with the experimental indication[11] that $\omega\tau_{pq}^2 << 1$ is applicable in all the mesophases of 40.8. In the smectic B phase both $D_\parallel$ and $D_\perp$ have a temperature dependence of Arrhenius type with roughly the same activation energy (36 kJ/mol for $D_\parallel$). At the smectic A to B phase transition, both $D_\parallel$ and $D_\perp$ show distinct decreases in magnitude, reflecting hinderance in reorientation of the long molecular axis as a result of hexagonal order within each layer in the crystalline B phase.[29] In the smectic A and nematic phases $D_\parallel$ continues to exhibit Arrhenius type behavior ($E_a = 45$ kJ/mol).

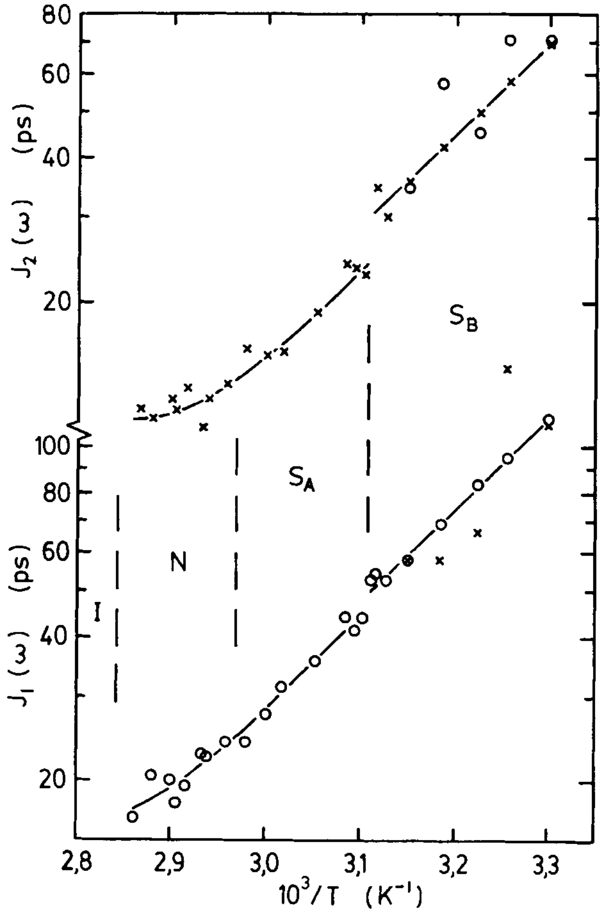

FIGURE 2 Plots of spectral densities $J_1(\omega)$ and $J_2(\omega)$ versus the reciprocal temperature in the mesophases of 40.8. ○ and × denote $\omega = \omega_0$ and $2\omega_0$, respectively.

$D_\perp$ however appears to level off in the smectic A phase and decrease in the nematic phase as T_c is approached. This behavior is not expected as the anisotropic factor R should tend to one in the isotropic phase. One possible reason for this apparent anomaly can be seen from the error bars drawn in Figure 3; these show that $D_\perp$ is particularly sensitive to slight variations in the spectral densities as the temperature approaches T_C. It is noted that R for 40.8 varies from ~15 in the smectic B phase to ~90 at the $N - I$ transition when one uses the single-exponential approximation for the autocorrelation functions proposed in ref. (16). This range of R value appears to be

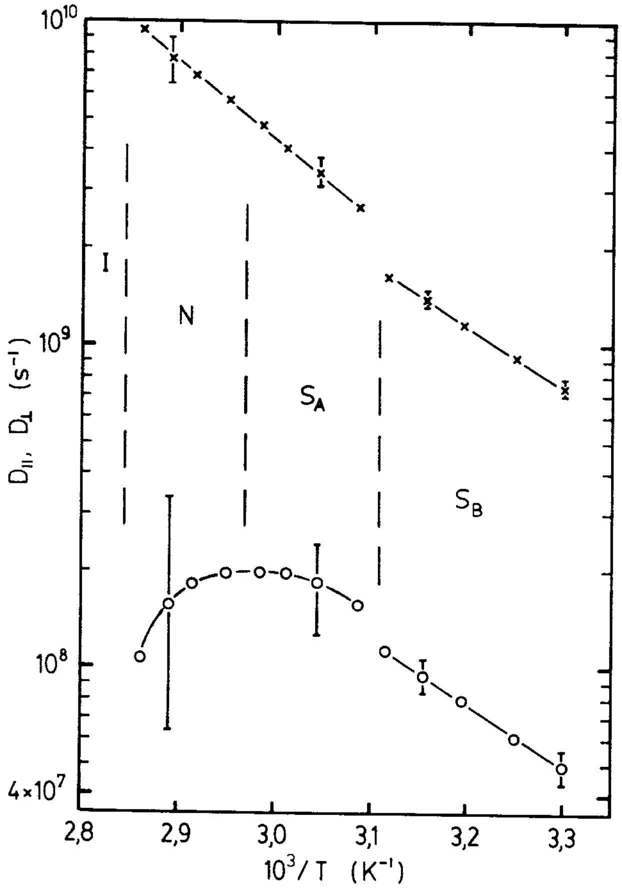

FIGURE 3 Plots of rotational diffusion coefficients versus the reciprocal temperature in the mesophases of 40.8 using τ^2_{pq} given by Agostini et al. (ref. 16). × and ○ denote $D_\parallel$ and $D_\perp$, respectively. Error bars denote ±5% variation in $J_1(\omega_0)$ and $J_2(2\omega_0)$.

reasonable for an elongated molecule reorienting in an anisotropic liquid.

A different approximation for τ^2_{pq} in the small step rotational diffusion model was proposed by Szabo,[24] and has recently been used in a ^{13}C study[30] of the nematic phase in the liquid crystal CBOOA. Keeping all parameters in eq. (9) the same and μ_{pq} as given in Table I, we have again extracted the rotational diffusion coefficients and the R value using the fast motion limit. It can be seen from Figure 4 that $D_\parallel$ decreases with temperature over the whole temperature range, with Arrhenius type behavior in the smectic phases. However,

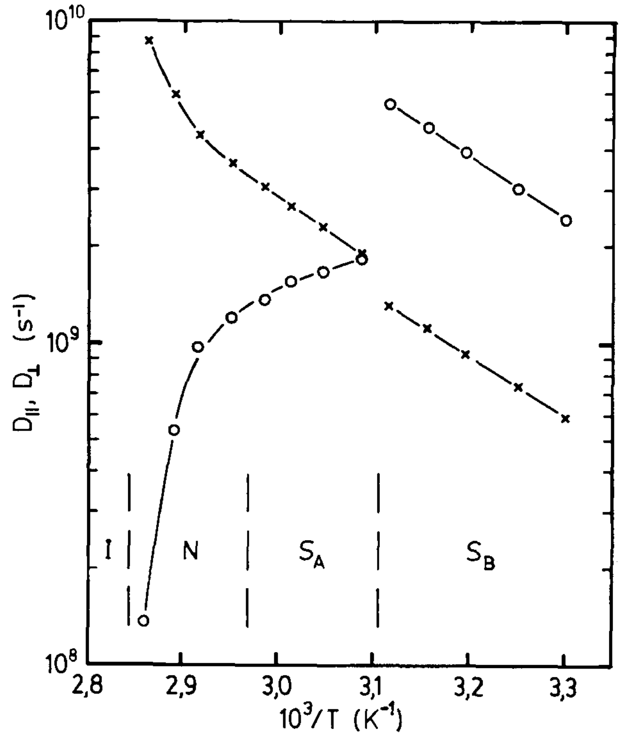

FIGURE 4 Plots of rotational diffusion coefficients versus the reciprocal temperature in the mesophases of 40.8, using τ^2_{pq} given by Szabo (ref. 24). × and ○ denote $D_\parallel$ and $D_\perp$, respectively.

$D_\perp$ increases continuously in the nematic and smectic A phases, resulting in an R value of ~1 at the smectic A-B transition. In the smectic B phase $D_\perp$ is larger than $D_\parallel$ giving an unreasonable R value of ~0.24; moreover the magnitude of $D_\perp$ is comparable to that of $D_\parallel$ in the nematic phase.

Using both the Szabo[24] and the Agostini et al.[16] estimates for τ^2_{pq}, when the full expression for eq. (9) is used an additional set of real, positive solutions for R is found. However, this set of $D_\parallel$ and $D_\perp$ values does not appear to be physically acceptable for a number of reasons. They indicate a strong frequency dependence for J_1 and J_2, in contradiction with experimental observations; $D_\parallel$ and $D_\perp$ are both low (~$10^6\,s^{-1}$ and ~$10^5\,s^{-1}$ respectively), also the rotational diffusion coefficients increased with decreasing temperature in the smectic B phase.

It would then appear that the present data is incompatible with the Szabo[24] approximation for μ_{pq} and τ^2_{pq}. The Agostini et al.[16] approximation for β^2_{pq} and τ^2_{pq} generally gives reasonable results, although it should be realized that the rotational diffusion coefficients obtained are very sensitive to the relative magnitude of the spectral densities. It is also surprising to see that $D_\parallel$ decreases faster than $D_\perp$, resulting in a decrease in R with decreasing temperature. It remains to be seen whether these rotational diffusion coefficients can be verified by direct measurements such as dielectric relaxation study.[31]

Acknowledgments

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