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STUDY OF ROTATION DIFFUSION OF ASYMMETRIC MOLECULES IN LIQUID CRYSTALS USING DEUTERON SPIN RELAXATION

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Abstract The spectral densities of p-methoxy-benzylidene-p-n-butylaniline (1O.4) were analysed using a new global target approach and a rotational diffusion model. The correlated internal motions are described by the decoupled model. We use the Nordio model and its extention to asymmetric molecules, the Tarroni and Zannoni (TZ) model, to analyse molecular reorientations. These diffusion models are compared in the nematic phase of 1O.4 and in the nematic and smectic *A* phases of 4O.8. Both models gave similar results for 1O.4, but for 4O.8 the TZ model appears to be more suitable.

INTRODUCTION

The rotational diffusion model[1,2] has been successfully used in liquid crystals to describe symmetric-top molecules reorienting in a pseudopotential of mean torque set up by their neighbours. In reality, mesogenic molecules do not in general possess unaxial symmetry and contain flexible chains. A number of diffusion models of increasing complexity have been proposed.[3,4] In particular, an extension of the Nordio model to asymmetric molecules has recently been developed by Tarroni and Zannoni[4] (the TZ model); application of this model remains scarce. There is a recent report[5] in which the TZ model was tested by examining deuteron spin relaxation of a biaxial solute in Phase V. The same model was used by us[6] to interpret spectral densities in the nematic and smectic *A* phases of p-pentylbenzylidene-p-n-heptylaniline (5O.7). Based on the relaxation data the molecular biaxiality ξ of 5O.7 was found to be small ($\xi = -0.09$). Here the quadrupolar splittings of p-methoxy-d$_3$-benzylidene-d$_1$-p-n-butyl-d$_9$-aniline (1O.4-d$_{13}$) are used to obtain[1,7] $< P_2 >$ and $< S_{xx} - S_{yy} >$ for the 'average' conformer. These in turn determine ξ at each temperature.[4] When dealing with the dynamics of internal bond rotations, we used the decoupled model[8] in which internal rotations were assumed to be independent of the overall reorientation of the molecule. A realistic geometry was used to generate all 27 configurations in the butyl chain of 1O.4. The transition rate matrix $\underline{\underline{R}}$ that describes conformational changes in the chain is a 27×27 matrix and contains jump rate constants k_1, k_2 and k_3 for the one-, two- and three-bond motions in the chain.[8] The paper is organized into a theory section, followed by a section of analysis and discussion.

THEORY

The TZ model is briefly surveyed to write down the spectral densities used in fitting the experimental data. To evaluate the correlation functions for reorientation of asymmetric molecules, one needs to find the conditional probability by solving the rotational diffusion equation

$$\frac{1}{\rho}\,\frac{\partial \hat{P}(\Omega_0|\Omega t)}{\partial t} \;=\; \hat{\Gamma}\hat{P}(\Omega_0|\Omega t) \tag{1}$$

where the symmetrized diffusion operator $\hat{\Gamma}$ is given by Equation (14) of Ref. [4]. The rotational diffusion tensor in the molecular frame contains principal diffusion elements $D_x \equiv D_{xx}, D_y \equiv D_{yy}$ and $D_z \equiv D_{zz}$. Now $\hat{\Gamma}$ is written in terms of $\rho = (D_x + D_y)/2, \varepsilon = (D_x - D_y)/(D_x + D_y)$, and $\eta = D_z/\rho$. For uniaxial molecules, the asymmetry parameter for diffusion ε is zero and the TZ model reduces to the Nordio model $(D_x = D_y \equiv D_\perp, D_z \equiv D_{||})$. In general, the orientational correlation functions can be written as a sum of decaying exponentials[2,4]

$$g^2_{mnn'}(t) = \sum_K (\beta^2_{mnn'})_K \exp[(\alpha^2_{mnn'})_K t] \tag{2}$$

where $(\alpha^2_{mnn'})_K/\rho$, the decay constants, are the eigenvalues and $(\beta^2_{mnn'})_K$, the relative weights of the exponentials, are the corresponding eigenvectors from diagonalizing the $\hat{\Gamma}$ matrix whose elements are formed using a Wigner basis set. The solutions of the rotational diffusion equation[4] could take ranks (L) up to 40 in the basis set.

The spectral densities for the methine (C_0) deuteron of 1O.4 are due to molecular rotations and are given by

$$J^{(0)}_m(m\omega) = \frac{3\pi^2}{2}(q^{(0)}_{CD})^2 \sum_n \sum_{n'} d^2_{n0}(\beta_{M,Q}) d^2_{n'0}(\beta_{M,Q}) \sum_K \frac{(\beta^2_{mnn'})_K (\alpha^2_{mnn'})_K}{(\alpha^2_{mnn'})^2_K \;+\; m^2\omega^2} \tag{3}$$

where the $\beta_{M,Q}$ angle between the C-D bond and the molecular z_M axis is taken to be 67°. In the decoupled model, the spectral densities $J^{(i)}_m(m\omega)$ of the C_i methylene deuteron(s) for $m \neq 0$ are given by

$$J^{(i)}_m(m\omega) \;=\; \frac{3\pi^2}{2}(q^{(i)}_{CD})^2 \sum_n \sum_{n'} \sum_{j=1}^{27} \left(\sum_{l=1}^{27} d^2_{n0}(\beta^{(i)l}_{M,Q}) \exp\left[-in\alpha^{(i)l}_{M,Q}\right] x^{(1)}_l x^{(j)}_l \right)$$

$$\times \left(\sum_{l'=1}^{27} d^2_{n'0}(\beta^{(i)l'}_{M,Q}) \exp\left[in'\alpha^{(i)l'}_{M,Q} \right] x^{(1)}_{l'} x^{(j)}_{l'} \right)$$
$$\times \sum_K \frac{(\beta^2_{mnn'})_K \left[(\alpha^2_{mnn'})_K + \mid \wedge_j \mid \right]}{\left[(\alpha^2_{mnn'})_K + \mid \wedge_n \mid \right]^2 \ + \ m^2\omega^2} \tag{4}$$

where $\beta^{(i)l}_{M,Q}$ and $\alpha^{(i)l}_{M,Q}$ are the polar angles of the C_i-D bond of the l^{th} conformer in the molecular M frame (the z_M axis is along the ring *para* axis). Equation (3) can be used for the C_α deuterons of 4O.8, while a similar expression which includes internal ring rotation (D_R) can be written using the superimposed rotations model.[1]

ANALYSIS AND DISCUSSION

The global target analysis takes advantage of the fact that the target parameters of the model vary smoothly with temperature, allowing simultaneous analysis of all temperatures. From individual target analyses, we found that the rotational diffusion constants and jump constants k_1 and k_3 obey simple Arrhenius-type relations, giving

$$D_{x,y} = D^0_{x,y} \exp\left[-E^{\perp}_a / RT \right] \tag{5}$$

$$D_z = D^0_z \exp\left[-E^{\parallel}_a / RT \right] \tag{6}$$

$$k_i = k^0_i \exp\left[-E^{k_i}_a / RT \right] \tag{7}$$

where a common activation energy $E^{\perp}_a$ is assumed[6] for D_x and D_y in a first approximation, and $D^0_y = f \times D^0_x$ where f is a constant. In Equations (5) - (7), the global parameters are pre-exponentials D^0_x, D^0_z, k^0_1 and k^0_3, and their corresponding activation energies $E^{\perp}_a$, $E^{\parallel}_a$, $E^{k_1}_a$ and $E^{k_3}_a$. When such a relation does not exist for a target parameter as with k_2, it is still helpful to introduce an interpolating relation:

$$k_2 = k'_2 + k''_2 (T - T_{min}) \tag{8}$$

where the temperature T_{min} is the lowest temperature used in the global analysis.

TABLE I Interaction parameters, order parameters and effective potential coefficients of the biaxial potential at several temperatures for 1O.4.

T (K)	X_a (kJ/mol)	λ_x	$< P_2 >$	$< S_{xx} - S_{yy} >$	a_{20}	ξ
285	2.377	0.1701	0.592	0.0066	-2.91	0.0365
291	2.212	0.1752	0.559	0.0069	-2.68	0.0364
297	2.035	0.1809	0.524	0.0072	-2.46	0.0364
303	1.787	0.1871	0.472	0.0076	-2.17	0.0369
309	1.403	0.1941	0.377	0.0078	-1.70	0.0372

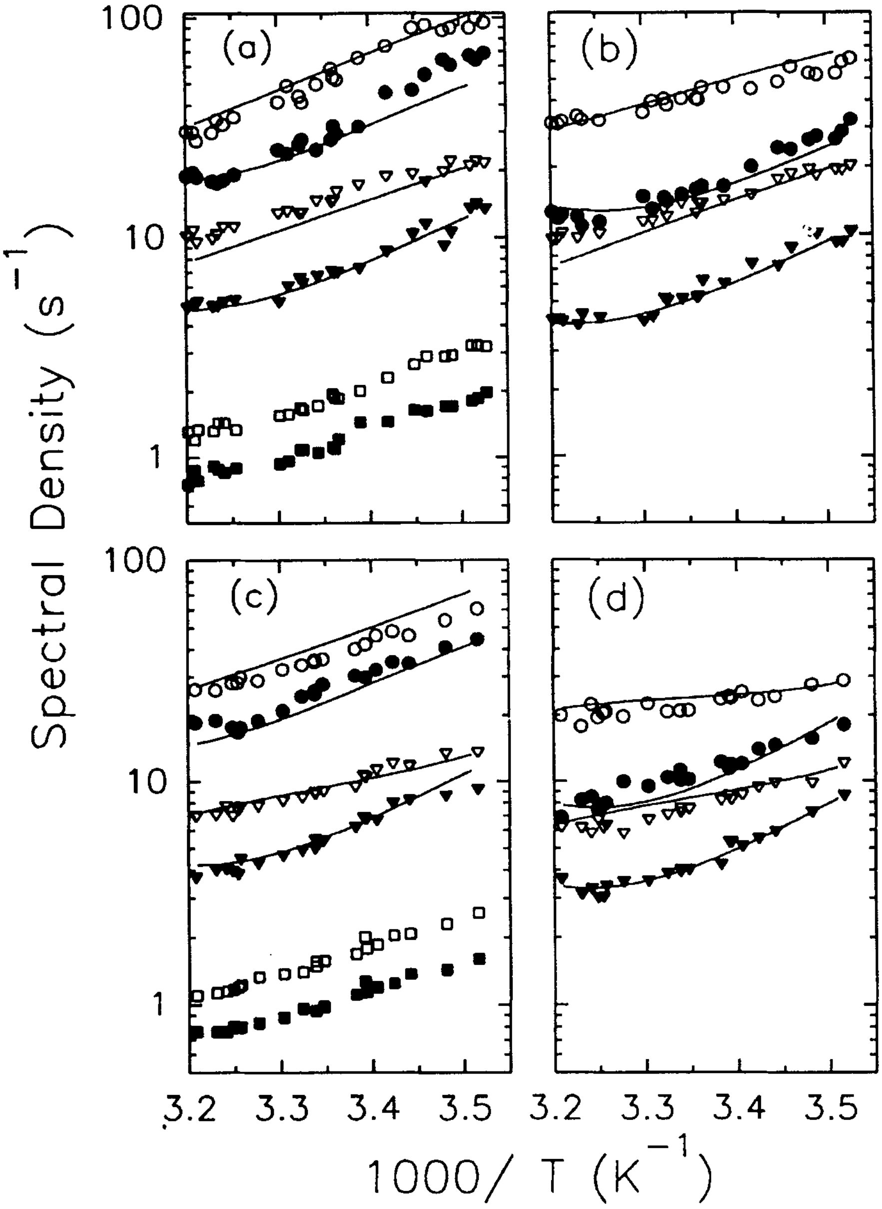

FIGURE 1 Plot of spectral densities against the reciprocal temperature in the nematic phase of 10.4-d_{13}. Open symbols denote the spectral densities $J_1(\omega)$, while closed symbols denote the corresponding $J_2(2\omega)$. Figures 1(a) and (b) are for 15.3 MHz, and figures 1(c) and (d) are for 46 MHz. In figure 1(a) and (c), ○, ● denote C_0 data, ▽, ▼ C_2 data and □, ■ C_4 data; in figures 1(b) and (d), the ○, ● denote C_1 data and the ▽, ▼ C_3 data. Solid lines are predicted using a global target analysis of data with the TZ model.

Since k_2 is weakly temperature dependent, no second order term is needed in the above relation and k_2' and k_2'' form part of the set of ten global parameters.

p-Methoxybenzylidene-p-n-butylaniline

Analysis of quadrupolar splittings to obtain the interaction parameters X_a and λ_x (TABLE I) in the potential of mean torque and the order parameters for the average conformer can be found elsewhere.[7] Using maximum entropy formalism,[4] these order parameters allow determination of the anisotropic potential coefficients a_{20} and a_{22} or $\xi = a_{22}/a_{20}$ in the second-rank biaxial potential needed in Γ (listed in Table I). We note that ξ is almost independent of temperature. The experimental $J_m^{(i)}(m\omega)$ were reported before.[7]

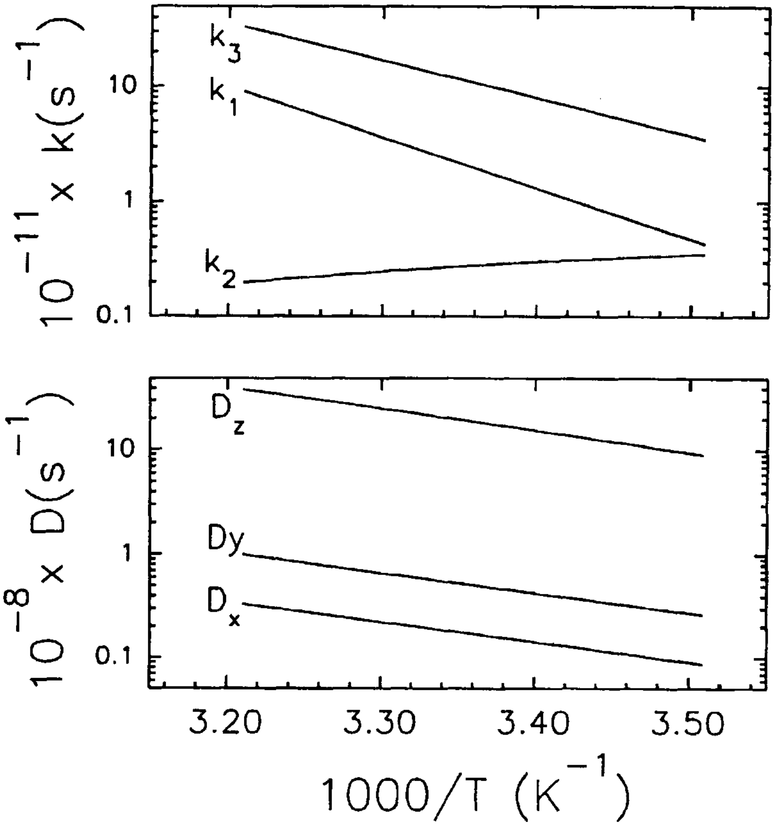

FIGURE 2 Temperature dependence of rotational diffusion coefficients and jump rate constants for 10.4, derived using TZ model with global analysis.

An optimization routine[9] (AMOEBA) was used to minimize the sum squared percent error F,

$$F = \sum_k \sum_\omega \sum_i \sum_m \left[\frac{J_m^{(i)calc}(m\omega) - J_m^{(i)}(m\omega)}{J_m^{(i)}(m\omega)} \times 100 \right]_k^2 \tag{9}$$

where the sum over k is for ten temperatures, ω for two frequencies, i for four carbons (1 methine and 3 methylene) and $m = 1$ or 2. The fitting quality factor is given by the percent mean-squared deviation,

$$Q = \frac{\sum_k \sum_\omega \sum_i \sum_m \left[J_m^{(i)calc}(m\omega) - J_m^{(i)}(m\omega) \right]_k^2}{\sum_k \sum_\omega \sum_i \sum_m \left[J_m^{(i)}(m\omega) \right]_k^2} \times 100 \tag{10}$$

The calculated and experimental spectral densities for 1O.4 are shown in Figure 1 (Q = 1.44%). In these calculations $D_y^0 = 3D_x^0$; smaller values of f gave less accurate fits and larger values gave 'non-physical' parameters with only marginal gains in fit. These results can be compared with previous global, uniaxial calculations,[10] which gave a similar Q value of 1.35%. This work used Vold's approximations to the diffusion problem in a Maier-Saupe potential which appears to give a fortuitous decrease in total error, i.e. in the present work the uniaxial model ($a_{22} = 0, f = 1$) gave Q = 1.40%. The derived temperature dependences of the rotational diffusion coefficients, D_x, D_y, and D_z are given in Figure 2, together with those of the jump rate constants of the chain, k_1, k_2 and k_3; these too are very similar to those obtained in the uniaxial case. The activation energies are $E_a^\perp = 37.0$ kJ/mol, $E_a^\parallel = 40.3$ kJ/mol, $E_a^{k_1} = 84.7$ kJ/mol, and $E_a^{k_3} = 62.6$ kJ/mol. Thus it appears that both the uniaxial Nordio model and the biaxial TZ model can adequately account for the observed spectral densities of 1O.4.

4-n-Butoxybenzylidene-4′-octylaniline

The spectral density data of 4O.8-d$_4$ has been globally analyzed based on a model which combined the TZ model and director fluctuations.[11] The 4O.8 sample was deuterated at the aniline ring and partially deuterated at the C$_\alpha$ of the octyl chain. Here the quadrupolar splitting of C$_\alpha$ is used to get $< P_2 >$ and ξ is an input in fitting the experimental spectral densities $J_m^{(R)}(m\omega)$ and $J_m^{(\alpha)}(m\omega)$ where the superscripts R and α denote ring and C$_\alpha$ deuterons. ξ was found to be 0.53 and ϵ = - 0.5 ($D_y = 3D_x$). To illustrate the fits to the experimental data, we list the results at two temperatures, one in the nematic phase and the other in the smectic A phase in TABLE II for the two deuterated sites. We note that contributions from director fluctuations (DF) have been carried to second-order as seen in the table. The calculated spectral density is the sum of contributions from director fluctuations and molecular rotations, plus a small negative cross-term when $m = 1$. The derived diffusion coefficients are: at 345 K, $D_x = 2.16 \times 10^8$ s^{-1}, $D_z = 5.54 \times 10^9$ s^{-1}, and $D_R = 4.03 \times 10^9$ s^{-1}; at 330 K, $D_x = 1.39 \times 10^8$ s^{-1}, $D_z = 4.61 \times 10^9$ s^{-1}, and $D_R = 1.97 \times 10^9$ s^{-1}. The activation energies are $E_a^{\perp} = 22.7$ kJ/mol, $E_a^{\parallel} = 11.6$ kJ/mol, and $E_a^R = 45.2$ kJ/mol. We note that the spinning motion is less hindered than the tumbling motion for 4O.8.

TABLE II Comparison between experimental and calculated spectral densities for ring and C_α deuterons of 4O.8 at two temperatures. The numbers (in s^{-1}) within brackets are for 46 MHz, while those without brackets are for 15 MHz.

	T (K)	$J_1(\omega)$	$J_2(2\omega)$	$J_1^{calc}(\omega)$	$J_2^{calc}(2\omega)$	$J_{1DF}(\omega)$	$J_{2DF}(2\omega)$
ring	345	9.95	5.9	9.6	5.99	0.87	0.035
		(8.9)	(5.9)	(9.12)	(5.96)	(0.40)	(0.018)
ring	330	15.6	8.45	16.09	7.06	0.77	0.01
		(14.5)	(8.2)	(15.6)	(7.04)	(0.31)	(0.004)
C_α	345	16.4	5.8	16.5	5.17	7.68	0.31
		(12.5)	(5.4)	(12.3)	(5.01)	(3.52)	(0.16)
C_α	330	17.6	5.6	17.2	6.44	6.76	0.09
		(12.4)	(5.13)	(13.1)	(6.37)	(2.73)	(0.03)

In conclusion, we have shown in the present study that the TZ model of treating rotational diffusion of asymmetric molecules can successfully explain the spectral density data of two liquid crystals. In addition, global target analysis provided a more direct and reliable determination of activation energies.

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