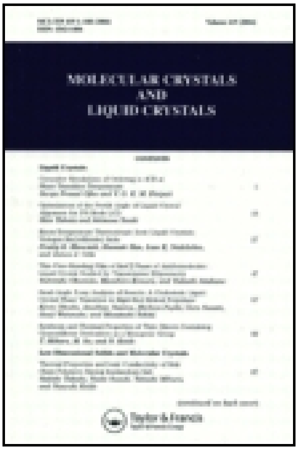

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Molecular Rotational Dynamics in Highly Ordered Smectic Mesophases

N. Kirov [a], I. Dozov [a], M. Petrov [a], M. P. Fontana [b] & B. Rosi [b]

[a] Institute of Solid State Physics, 72 boulv. Lenin, Sofia, 1784, Bulgaria

[b] Department of Physics, University of Parma, 85 M. d'Azeglio, Parma, 43100, Italy

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MOLECULAR ROTATIONAL DYNAMICS IN HIGHLY ORDERED SMECTIC MESOPHASES

N. KIROV, I. DOZOV, M. PETROV
Institute of Solid State Physics, 72 boulv.
Lenin, Sofia 1784, Bulgaria

M. P. FONTANA, B. ROSI
Department of Physics, University of Parma,
85 M. d'Azeglio, Parma 43100, Italy

Abstract The temperature dependence of the rotational diffusion coefficient $D^{r}_{\parallel}$ and biaxial orientational order parameter $\langle D^{2}_{02}\rangle$ in aligned S_B, S_C and S_A phases obtained by IR bandshape analysis is reported.

I. INTRODUCTION

The molecular dynamics in mesomorphic phases is actively investigated by neutron quasielastic scattering (NQS), nuclear magnetic resonance (NMR), electronic paramagnetic resonance (EPR), dielectric relaxation and vibrational spectroscopy. It is generally assumed that in the highly ordered smectic mesophases the molecules perform only overdamped libration around the body axes. In the less ordered smectic modifications (S_C, S_A) as well in the nematic phase the molecules perform a rotational diffusion around the long molecular axes plus long axes fluctuations. The spinning (rotation around the long molecular axes) relaxation times are in the region 5-15 ps. A much slower (50-200 ps) are the reorientational correlation times around the short molecular axes (tumbling reorientation).

However, most of the experiments were carried out at one or two fixed temperatures and the temperature behaviour of the rotational molecular mobility has not been studied in details. Moreover, often the reported relaxation times do not characterize solely the molecular reorientation but depend on orientational order parameters, some specific molecular properties and sometimes even reflect a mixture of several relaxation processes. That is why nontrivial discrepancies between the results from different techniques even for the same mesogen may be found in the literature[1].

Recently we established a new method - in which the rotational relaxation times and rotational diffusion coefficients are unambiguously determined - by studying the bandshape or the bandwidth of carefully selected vibrational modes[2]. Our results indicate that for tumbling motion in a strongly anisotropic system such as mesophase (where $D^r_\parallel \gg D^r_\perp$) the biaxial term of the nematic pseudopotential has a negligible effect on the correlation functions. On the contrary, all vibrations whose induced dipole moment makes a reasonably large angle with the long molecular axis are particularly sensitive to the deviations of the ordering potential from cylindrical symmetry[3,4].

In this paper we present new results on the rotational dynamics in some smectic phases, obtained by IR bandshape measurements. In the second paragraph we briefly summarize the relevant theory.

In the third paragraph we report the experimental conditions. In the last section we present the temperature behaviour of the spinning diffusion coefficient $D^r_{\parallel}$ and the order parameter $\langle D^2_{02} \rangle$ in S_B, S_C and S_A mesophases of two mesogens.

II. ROTATIONAL CONTRIBUTION TO TOTAL IR BANDSHAPE

In the case of a molecule with effective D_{2h} symmetry the nematic pseudopotential can be written as[3] :

$$U(\Omega) = -kTa(D^2_{00}(\Omega) + \lambda (D^2_{02}(\Omega)+D^{2\,*}_{02}(\Omega))) \tag{1}$$

For such potential $\langle D^{m\,*}_{0n} \rangle = \langle D^m_{0n} \rangle = \langle D^m_{0-n} \rangle \neq 0$ for even m and n . From NMR data for the nematic 4,4'-dimethoxyazoxybenzene (PAA) the results $\lambda \cong 0.2$ and $\langle D^2_{02} \rangle \leqq 0.035$ are reported[5].

The general expression for the rotational contribution to the total IR bandshape derived in the framework of the small-step rotational diffusion model is presented elsewhere[3,4]. Here we will give the rotational relaxation contribution for the three most important cases, ϑ and φ being the polar coordinates of the induced dipole moment in the molecular frame.

For parallel bands ($\vartheta \cong 0$):

$$\frac{d}{dt}\ln\frac{a_z(t)}{a_x(t)} = \frac{9\langle P_2 \rangle}{(1-\langle P_2 \rangle)(1+2\langle P_2 \rangle)}\, D^r_{\perp} \tag{2}$$

For depolarized modes ($\vartheta \cong 55^\circ$):

$$\frac{d}{dt}\ln\frac{a_z(t)}{a_x(t)} = \frac{18\, D_\perp^r\, x + (\langle P_2\rangle + 10x)(D_\parallel^r - D_\perp^r)}{(1-2x)(1+4x)} \tag{3}$$

For transversally polarized modes ($\vartheta \cong 90^\circ$):

$$\frac{d}{dt}\ln\frac{a_z(t)}{a_x(t)} = \frac{-9(\langle P_2\rangle - 6x)D_\perp^r + 36x(D_\parallel^r - D_\perp^r)}{(1-\langle P_2\rangle + 6x)(2+\langle P_2\rangle - 6x)} \tag{4}$$

where $x = \cos 2\varphi \langle D_{02}^2\rangle / \sqrt{6}$

For highly ordered smectic mesophases $D_\parallel^r \gg D_\perp^r$. In this case the spinning rotational diffusion coefficient $D_\parallel^r$ and $\langle D_{02}^2\rangle$ can be calculated by simpler equations:

$$\frac{d}{dt}\ln\frac{a_z(t)}{a_x(t)} = \frac{\langle P_2\rangle + 10x}{(1-2x)(1+4x)} D_\parallel^r \tag{3'}$$

$$\frac{d}{dt}\ln\frac{a_z(t)}{a_x(t)} = \frac{36x}{(1-\langle P_2\rangle + 6x)(2+\langle P_2\rangle - 6x)} D_\parallel^r \tag{4'}$$

The order parameter $\langle P_2\rangle$ should be determined independently from the value of the dichroic ratio R of a strongly longitudinally polarized band:

$$\langle P_2\rangle = \frac{R-1}{R+2} \tag{5}$$

where $$R = \frac{\int A_z(\omega)\, d\omega}{\int A_x(\omega)\, d\omega}$$

In Eqs. (2-5) $a_i(t)$ (i=x or z) is the Fourier transform of the absorption bandshape $A_i(\omega)$.

III. EXPERIMENTAL TECHNIQUES

The mesogens studied were N-(4-butoxybenzylidene) 4',n-butylaniline (BBBA) and 4,n-hexyloxyphenyl-4',n-decyloxybenzoate (HOPDOB). The relevant transition temperatures of these compounds are as follows:

$$\text{BBBA:}\quad Cr \xleftrightarrow{36.2^{o}C} S_B \xleftrightarrow{44^{o}C} S_A \xleftrightarrow{63.3^{o}C} N \xleftrightarrow{78.4^{o}C} I$$

$$\text{HOPDOB:}\quad Cr \xleftrightarrow{34.2^{o}C} S_E \xleftrightarrow{38.3^{o}C} S_B \xleftrightarrow{44.5^{o}C} S_C \xleftrightarrow{77.5^{o}C} S_A \longleftrightarrow$$

$$\xleftrightarrow{83.3^{o}C} N \xleftrightarrow{88.9^{o}C} I$$

The samples were aligned homogeneously by rubbing the cell windows. The orientation of the smectic modifications was checked by investigating the conoscopic figures. At S_A - S_C phase transition of HOPDOB the molecules start to tilt in the smectic layers. The tilt angle however is not so big - it highest value of saturation is 17°. Thus the S_C phase of HOPDOB might be considered almost uniaxial[6] and our method can be applied too.

Infrared spectra were taken with a dual spectrophotometer. Spectral resolution for most runs was set at 1 cm^{-1}. Whenever possible, the spectral range about each line was investigated over about 4-6 times full bandwidth at halfmaximum intensity. Sample thickness was chosen to yield optimum absorbance, i.e. a transmission of 30-50 %, and was approximately 12-13 microns for both samples. The temperature was controlled by a thermostat with circulating water incide a brass block which housed the sample cell. Temperature stability was better than 0.03°C.

The bands 889 cm^{-1} (benzene ring - nitrogen in-plane bending, BBBA), 693 cm^{-1} (benzene ring out-of-plane deformation, HOPDOB) and 1739 cm^{-1} (carbonyl group stretch vibration, HOPDOB) were selected to study the temperature dependence of $D^r_\parallel$ and $\langle D^2_{02} \rangle$ in the mesophases. The transition dipole moment of the mode 1739 cm^{-1} is directed along the "magic" angle, i.e. about 55° away from the long molecular axis. The band at 889 cm^{-1} (R = 2.8) is weakly longitudinally polarized (with $\vartheta \cong 36^\circ$). The benzene out-of-plane deformation is strongly transversally polarized (R=0.11 and $\vartheta \cong 87^\circ$). The orientational order parameter $\langle P_2 \rangle$ was determined independently using Eq.(5) from the dichroic ratio of the bands 1605 cm^{-1} (HOPDOB) and 1602 cm^{-1} (BBBA) assigned to benzene ring stretching vibration.

IV. RESULTS AND DISCUSSION

We do not observe any broadening of the strongly parallel bands with temperature and phase transitions, which implies that the tumbling motion is completely "frozen" in the highly ordered smectic phase. The spinning rotational diffusion, obtained by Eqs.(3',4'), in S_B, S_C and S_A phases is rather fast - $D^r_\parallel$ is about $15.\ 10^{10}\ s^{-1}$ and does not depend on the temperature (Figs. 1 and 2). In the limits of our experimental error (~10 %) there are

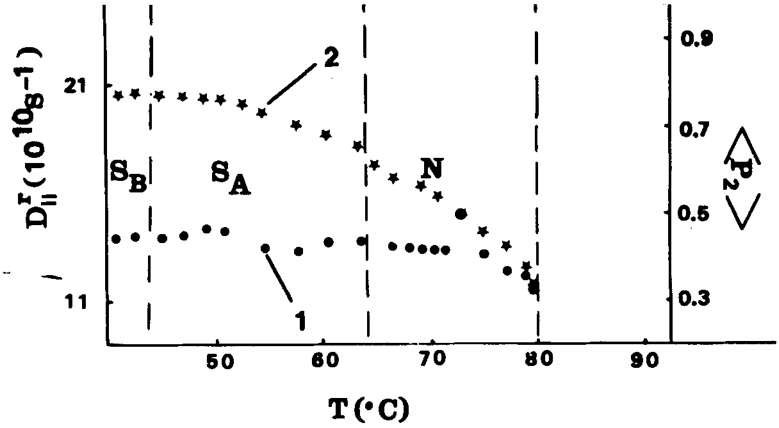

FIGURE 1. Temperature dependence of: 1 - spinning rotational diffusion coefficient $D^r_{\parallel}$; 2 - orientational order parameter $\langle P_2 \rangle$ of BBBA.

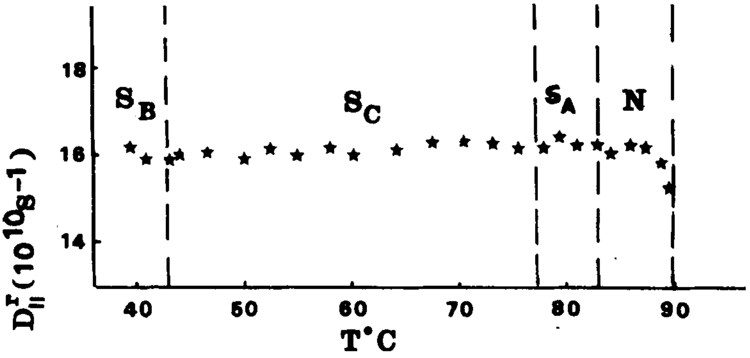

FIGURE 2. Temperature dependence of the spinning rotational diffusion coefficient $D^r_{\parallel}$ of HOPDOB.

no observable changes in the rotational molecular mobility at the phase transitions S_B - S_C, S_B-S_A and S_A - N . This is reasonable since all smectic and nematic phases are uniaxial (S_B, S_A and N) or quasiuniaxial (S_C). The slowing down of $D^r_{\parallel}$ observed in the nematic phase close to the clearing temperature was already discussed in our previous work[7].

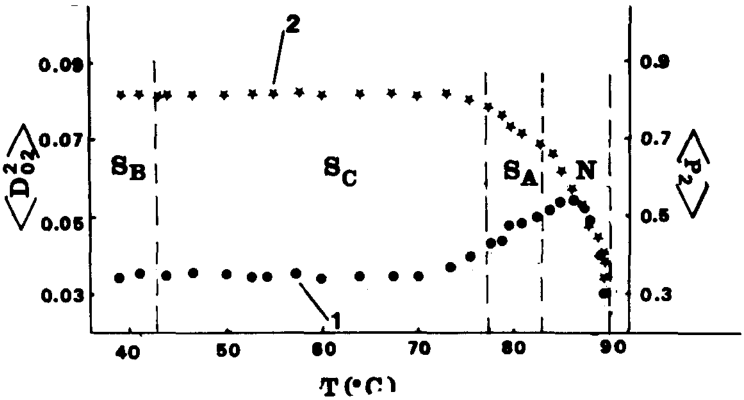

FIGURE 3. Temperature dependence of the order parameters in HOPDOB: 1 - $\langle D^2_{02} \rangle$; 2 - $\langle P_2 \rangle$

The measured temperature dependence of $\langle D^2_{02} \rangle$ has the same feature (Fig. 3) - the presence of maximum close to the clearing temperature - as that reported by other authors[8]. A more detailed comparison of the temperature dependence of $\langle D^2_{02} \rangle$ with mean field theory prediction is under study.

CONCLUSION

We report here the first acurate study of the temperature dependence of the spinning rotational diffusion coefficient $D^r_\parallel$ and the order parameter $\langle D^2_{02}\rangle$ in uniaxially aligned smectic modifications. A relatively fast reorientation around the long molecular axis exists in nematic and smectic phases and is reasonably well described via the uniaxial rotational diffusion model.

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