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Vibrational bandshape analysis and inertial-stochastic molecular motion in anisotropic ordered fluids

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Résumé. — Nous généralisons le modèle étendu de diffusion J à la dynamique des réorientations moléculaires des fluides uniaxes tels que les nématiques. En particulier nous calculons des fonctions de corrélation qui sont valables à la fois pour le régime inertiel et pour le régime stochastique de ces mouvements. Ces fonctions sont ensuite utilisées pour modéliser les fonctions de corrélations déterminées expérimentalement par analyse des formes de bandes Raman et infrarouge. Nous déterminons ainsi les paramètres du modèle, qui sont les moments d'inertie, les coefficients de diffusion de rotation et de basculement, le temps de corrélation du moment angulaire et l'angle moyen de rotation dans la phase inertielle du mouvement moléculaire. Les résultats confirment la validité du modèle J étendu pour la dynamique rotationnelle des fluides anisotropes ; ils procurent également la première vérification expérimentale de la validité du modèle de diffusion à petits sauts pour le régime stochastique.

Abstract. — We generalize the extended J -diffusion model to molecular reorientational dynamics in uniaxially aligned fluids such as nematics. In particular we calculate correlation functions valid for both the inertial and stochastic regimes of the motion. Such functions are then used to fit correlation functions determined experimentally from Infrared and Raman bandshape analysis. We determined thus the parameters of the model, namely the molecular moments of inertia, the spinning and tumbling diffusion coefficients, the angular momentum correlation time and the average rotation angle in the inertial phase of the molecular motion. The results confirm the validity of the extended J -model for the rotational dynamics in anisotropic fluids, and provide the first direct experimental verification of the validity of the small-step diffusion model to describe the stochastic regime.

1. Introduction.

Recently we have established a spectroscopic method for the simultaneous determination of the reorientational diffusion coefficients D_{\parallel} (molecular spinning) and D_{\perp} (molecular tumbling) and the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ (the lowest order coefficients in the expansion of the nematic molecular distribution function [1] in the oriented nematic phases). Reorientational correlation functions were obtained experimentally by Fourier analysis of selected molecular vibrational band in Infrared (IR) [2] or Raman [3] spectra. The static and dynamical parameters were then derived by fitting the experimental correlation functions in the time domain

$$\tau_J < t < D_{\parallel}^{-1} \quad (1)$$

with the theoretical correlation functions obtained using irreducible tensor formalism to solve the rotation-

al diffusion equation [4] within the framework of the small-step rotational diffusion model [5]. In equation (1) τ_J is the angular momentum correlation time : for $t \gg \tau_J$ both the small-step and the other well known stochastic model, the strong collision model [6], may describe equally well the rotational dynamics of the molecules.

In order to go beyond a single relaxation time approximation and to discriminate between different microscopic dynamical models for molecular reorientation, it is important to study the behaviour in the time domain $t < \tau_J$. This is however a difficult area to treat theoretically and to study experimentally, and it is even more so for complex molecular systems such as liquid crystals. Recently the $t \ll \tau_J$ limit was treated by a moment expansion of the correlation function about $t = 0$ [7]. In this paper we extend the treatment of reference [7] to cover the whole time domain, including in particular the transition ($t \sim \tau_J$) from inertial motion

to the Debye-like relaxation regime. For this we have applied the extended J -diffusion model [8] to the case of uniaxially aligned systems such as nematic phases. As in the case of isotropic liquids, we have assumed that :

- a) The molecules rotate « freely » for an average time τ_J ;
- b) Each free rotation period is terminated by a hard collision which randomizes both direction and amplitude of the angular momentum \mathbf{J} ;
- c) During the collision, which is assumed to be instantaneous (in respect to the time interval between the collisions), the molecular orientation relative to the fixed laboratory frame does not change.
- d) The angular momentum components are Markoffian variables.

Our theoretical results have been fitted to reorientational correlation functions corresponding to both spinning and tumbling fluctuations. The mesogens studied were PAA and OET ; for spinning fluctuations we used the IR absorption bands at $1\,027\text{ cm}^{-1}$ (PAA) and $1\,047\text{ cm}^{-1}$ (OET) corresponding to O-CH stretching ; for tumbling fluctuations the IR bands used were the 757 cm^{-1} and 910 cm^{-1} (PAA) and $1\,175\text{ cm}^{-1}$ (OET), which correspond to benzene ring in-plane deformations. The determinations were carried out as a function of temperature in the nematic phase ; for further experimental and data handling details we refer the reader to our paper [2].

2. Calculation of the reorientational correlation functions.

Let $P(\Omega_0/\Omega t)$ be the conditional probability for the reorientation of one molecule from Ω_0 to Ω (where Ω stands for the set of Euler angles α, β, γ) in time t . Let $P_0(\Omega_0/\Omega t)$ be the conditional probability for the reorientation of a « free » rotator (i.e. without collisions with other molecules, but in the field of the nematic pseudopotential $U(\Omega)$). The probability that precisely n molecular collisions will take place in time t is given by the Poisson distribution :

$$P(n, t) = (t/\tau_J)^n \exp(-t/\tau_J) \cdot (1/n!) . \quad (1)$$

We have then :

$$P(\Omega_0|\Omega t) = \sum_n P(n, t) n! t^{-n} P_n(\Omega_0|\Omega t) \quad (2)$$

where

$$\begin{aligned} P_n(\Omega_0|\Omega t) &= \int_0^{t_n} dt_n \int_0^{t_{n-1}} dt_{n-1} \dots \times \\ &\times \int_0^{t_1} dt_1 \int d\Omega_1 \dots \int d\Omega_n \cdot P_0(\Omega_0|\Omega_1 t_1) \\ &\times P_0(\Omega_1|\Omega_2 t_2 - t_1) \dots P_0(\Omega_n|\Omega t - t_n) \end{aligned}$$

is the partial conditional probability for the reorientation after precisely n collisions, and the factor $P(n, t) n! t^{-n} dt_1 \dots dt_n$ gives the product probability that a molecule at time t has undergone n collisions during the time intervals t_1 to $t_1 + dt_1, \dots, t_n$ to $t_n + dt_n$.

The reorientational correlation function may be obtained by a similar generalization :

$$\begin{aligned} \phi^{LM}(t) &= \langle D^{L*}(\Omega_0) D^M(\Omega) \rangle \\ &= \int d\Omega_0 f(\Omega_0) \times \\ &\times \int d\Omega D^{L*}(\Omega_0) P(\Omega_0|\Omega t) D^M(\Omega) \\ &= \sum_n P(n, t) n! t^{-n} \phi_n^{LM}(t) . \end{aligned} \quad (3)$$

In (3) $f(\Omega_0)$ is the nematic orientational distribution function, $D^L(\Omega) = D_{l', l''}^L(\Omega)$ are the Wigner matrices (where, in order to simplify the notation we designate the set of indices l', l'' with L, m', m'' with M , and the delta functions δ_{LM} stand for the product $\delta_{lm} \delta_{l' m'} \delta_{l'' m''}$) and

$$\begin{aligned} \phi_n^{LM}(t) &= \int d\Omega_0 f(\Omega_0) \times \\ &\times \int d\Omega P_n(\Omega_0|\Omega t) D^{L*}(\Omega_0) D^M(\Omega) \end{aligned} \quad (4)$$

is the partial correlation function for the reorientations which involve n collisions.

In order to calculate $\phi_n^{LM}(t)$ we shall use a Taylor expansion in the $t \approx 0$ range, following the approach of Pasini and Zannoni [7]. Since these authors have not considered the collisions between the molecules their calculated correlation functions correspond in fact to our $\phi_0^{LM}(t)$, i.e. they describe the inertial rotation of the molecules in the nematic pseudopotential $U(\Omega)$: when $t/\tau_J \rightarrow 0$, $\phi^{LM}(t) \rightarrow \phi_0^{LM}(t)$. In this limit we have :

$$\begin{aligned} \phi_0^{LM}(t) &= \phi_0^{LM}(0) + \frac{1}{2} t^2 \ddot{\phi}_0^{LM}(0) + \\ &+ \frac{1}{24} t^4 \ddot{\ddot{\phi}}_0^{LM}(t) + \dots = \\ &= a^{LM} + \frac{1}{2} b^{LM} t^2 + \frac{1}{24} c^{LM} t^4 + \dots \end{aligned} \quad (5)$$

The coefficients in this expansion for $l, m \leq 4$ are reported in reference [7]: a^{LM} depends only on the orientational order parameters $\langle P_j \rangle$, where $|l - m| < j < l + m$; b^{LM} is a similar function multiplied by kT/I_i (where i stands for \parallel (spinning) and \perp (tumbling) and I_i is the corresponding molecular moment of inertia). The coefficient c^{LM} depends also on the moments of $U(\Omega)$ and is proportional to $(kT/I_i)^2$.

In our experimental conditions $kT/I_i \ll t^{-2}$; thus we

shall be looking for a solution for $\phi^{LM}(t)$ as an expansion in the small parameter $x = b^{LM} \tau_J t$, and we shall retain only the first non-trivial term in this expansion. The inertial reorientation probability $P_0(\Omega_0/\Omega t)$ may be expressed in terms of Wigner matrices :

$$P_0(\Omega_0|\Omega t) = \sum_{HK} d^{HK}(t) \times \frac{2k+1}{8\pi^2} D^H(\Omega_0) D^{K*}(\Omega). \quad (6)$$

Due to the orthogonality of $D^L(\Omega)$, we have :

$$\phi_0^{HM}(t) = \sum_K a^{HK} d^{KM}(t) \quad (7)$$

and $d^{KM}(0) = \delta_{KM}$.

From equations (2), (4) and (6) we obtain a recursion relation for the partial correlation function :

$$\phi_n^{LM}(t) = \sum_K \int_0^t dt_n \phi_{n-1}^{LK}(t_n) d^{KM}(t-t_n). \quad (8)$$

The solution of this system is :

$$\phi_n^{LM}(t) = a^{LM} \frac{t^n}{n!} + b^{LM}(n+1) \frac{t^{n+2}}{(n+2)!} + \dots \quad (9)$$

Substituting in equation (3) we have finally :

$$\phi^{LM}(t) = a^{LM} + b^{LM}(\tau_J t - \tau_J^2 + \tau_J^2 \exp(-t/\tau_J)). \quad (10)$$

We recall that this result is valid only if $x \ll 1$. If necessary additional terms of the order of x^2 could be calculated from equation (8). In the $t \rightarrow 0$ limit equation (10) tends to the result reported in reference [7], while for $t/\tau_J \gg 1$ it reduces to the expressions obtained from the application of the small-step diffusion model to the case of nematic phase [5], provided of course that the condition $x \ll 1$ is still fulfilled. In the latter case we have :

$$D_{\parallel}^r = \tau_J \frac{kT}{I_{\parallel}}, \quad D_{\perp}^r = \tau_J \frac{kT}{I_{\perp}} \quad (11)$$

and therefore

$$\frac{D_{\parallel}^r}{D_{\perp}^r} = \frac{I_{\perp}}{I_{\parallel}} \quad (12)$$

which is an unphysical result, since the rotational diffusion coefficients must depend not only on the moments of inertia of the molecules but also on other molecular properties such as the friction coefficients [8]. In fact equation (12) is a consequence of the assumption that τ_J does not depend on the direction of \mathbf{J} in the molecular coordinate system ; we shall see in the following paragraph how the introduction of the system dynamical anisotropy will eliminate this problem.

3. Connection to the experimental correlation functions.

3.1 IR ABSORPTION. — The experimental correlation functions may be obtained by the ratio of the normalized Fourier transforms of the absorption bands for light polarized parallel $a_z(t)$ and perpendicular $a_x(t)$ to the nematic axis in the aligned samples. If θ is the angle between the long molecular axis and the induced dipole moment corresponding to the molecular vibration under study, we have (see Ref. [2], Eq. (14)) :

$$\frac{a_z(t)}{a_x(t)} = \frac{\cos^2 \theta \phi_{00}^1(t) + \sin^2 \theta \phi_{01}^1(t)}{\cos^2 \theta \phi_{00}^1(0) + \sin^2 \theta \phi_{01}^1(0)} \times \frac{\cos^2 \theta \phi_{10}^1(0) + \sin^2 \theta \phi_{11}^1(0)}{\cos^2 \theta \phi_{10}^1(t) + \sin^2 \theta \phi_{11}^1(t)}. \quad (13)$$

Substituting in equation (13) the generalized correlation functions $\phi^{LM}(t)$ as determined in equation (10), we obtain the connection with the experimental correlation functions $a_z(t)/a_x(t)$.

Two particular cases of interest here lead to substantial simplification. For a vibrational mode which is sensitive to tumbling molecular motions, we have $\theta \simeq 0$. In this case from equations (10) and (13) we obtain :

$$\ln \frac{a_z(t)}{a_x(t)} \simeq b_{\perp} \left(\tau_J t - \tau_J^2 + \tau_J^2 \exp\left(-\frac{t}{\tau_J}\right) \right) \quad (14)$$

where

$$b_{\perp} = \frac{9 \langle P_2 \rangle}{(1 - \langle P_2 \rangle)(1 + 2 \langle P_2 \rangle)} \cdot \frac{kT}{I_{\perp}}. \quad (15)$$

The other interesting particular case is that of $\theta \simeq 55^\circ$, i.e. the « magic angle » at which $P_2(\cos \theta) = 0$, where P_2 stands for the Legendre polynomial of order 2. A molecular vibration characterized by such angle is most sensitive to spinning motion [2], and the corresponding result is :

$$\ln \frac{a_z(t)}{a_x(t)} = b_{\parallel} \left(\tau_J t - \tau_J^2 + \tau_J^2 \exp\left(-\frac{t}{\tau_J}\right) \right) \quad (16)$$

where $b_{\parallel} = \langle P_2 \rangle \frac{kT}{I_{\parallel}}$.

A further simplification is obtained if we consider the strong dynamical anisotropy of the system, which allows the separation of the tumbling and spinning reorientations [11]. Thus the general dependence of τ_J on the vector \mathbf{J} may be reduced to the introduction of the two scalars τ_{\parallel} and τ_{\perp} of obvious meaning. Substituting in equations (15) and (16) we obtain :

$$\ln \frac{a_z(t)}{a_x(t)} = b_i \left(\tau_i t - \tau_i^2 + \tau_i^2 \exp\left(-\frac{t}{\tau_i}\right) \right) \quad (17)$$

for tumbling ($i = \perp$) and spinning ($i = \parallel$) motions respectively. Now the ratio of the rotational diffusion coefficients turns out to be :

$$\frac{D_{\parallel}^r}{D_{\perp}^r} = \frac{I_{\perp} \tau_{\parallel}}{I_{\parallel} \tau_{\perp}} \quad (18)$$

and the unphysical result equation (12) does not apply any longer.

3.2 RAMAN SCATTERING. — In this case equation (10) still applies ; now however the coefficients a^{LM} and b^{LM} will depend on $\langle P_2 \rangle$ and $\langle P_4 \rangle$.

If $a_{ik}(t)$ denotes the normalized Fourier transform of the polarized ($i = k$) and depolarized ($i \neq k$) components of a given Raman band in the three relevant scattering geometries (for details see our Ref. [3]), in the picosecond time domain we obtain :

$$\ln \frac{a_{xx}(t)}{a_{zz}(t)} = \frac{kT}{I} \tau \left[t - \tau + \tau \exp \left(-\frac{t}{\tau} \right) \right] \times \\ \times \left[6 \frac{7 + 2.5 \langle P_2 \rangle + 8 \langle P_4 \rangle}{7 + 5 \langle P_2 \rangle - 12 \langle P_4 \rangle} - \right. \\ \left. - \frac{8}{3} \frac{7 + 5 \langle P_2 \rangle - 12 \langle P_4 \rangle}{7 + 20 \langle P_2 \rangle + 8 \langle P_4 \rangle} \right] \quad (19)$$

where the term containing $\langle P_2 \rangle$ and $\langle P_4 \rangle$ was calculated using the methods discussed in references [1] and [3]. In equation (19) I is an effective molecular moment of inertia which, for the Raman lines we have been able to investigate, corresponds to I_{\perp} ; by the same token, $\tau = \tau_{\perp}$.

4. Experimental techniques and results.

For details on sample preparation, experimental set-up and data analysis we refer the reader to our previous publications [2] and [3]. Here we note that particular care had to be taken to obtain good spectra in the tail region of a given spectral band, since we were interested in the short and very short time behaviour of the reorientational correlation functions. Furthermore, even with good starting data, the analysis turned out to be particularly difficult in the very short time region (e.g. $t < 0.5$ ps) and the resulting correlation functions in this range turned out to be sensitive to the various phases of the data reduction process, and particularly to the background subtraction. Thus we tried to perform such crucial step as carefully as possible, trying several methods and using systematically the procedure which consistently gave the most reproducible results. In spite of all this, for some data it was impossible to go beyond the qualitative level, particularly in the case of Raman scattering.

4.1 IR ABSORPTION. — Spectra were taken with a Perkin-Elmer 180 and a Jasco 702G spectrometers. Spectral resolution was generally set at 1 cm^{-1} . We studied both PAA (4-azoxyanisole) and OET (4,n-octyl 4'-ethoxytolane) ; the more complete set of data, which we report here, refer to PAA ; in any case, the results obtained for OET were similar within our large experimental uncertainties.

We selected the lines at 757 cm^{-1} and 910 cm^{-1} (benzene in-plane deformations), and 1028 cm^{-1} (O-CH₃ stretching). The first two correspond to transition moments directed along the main molecular axis, and hence are sensitive to the tumbling molecular reorientations ; the third line instead is sensitive to spinning motion, since its transition moment points approximately 50 degrees away from the main molecular axis.

The spectrum of each line was run three times for each of the two polarizations (incoming light electric field vector oriented parallel and perpendicular to the nematic axis respectively) ; a single spectral run took approximately 30 minutes, and the results were averaged over the complete set of three runs. Thus one single experimental point (or correlation function) was obtained in about three to four hours. Our temperature stabilization over such time interval was better than 0.1 K, and was achieved using a programmable flow thermostat, with water or glycerine as the thermostatic fluid.

The reorientational correlation functions obtained for PAA at $T = 119^\circ \text{C}$ are shown in figure 1 (spinning) and 2 (tumbling). In the same figures (solid line) we show the corresponding least square theoretical fits

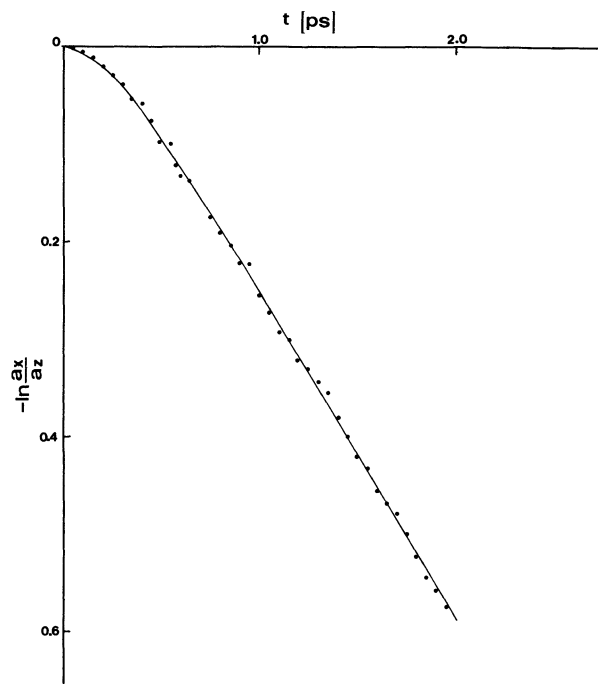


Fig. 1. — Reorientational correlation function of the IR 1028 cm^{-1} band (PAA, 119°C) ; points : experimental data ; full line : best fit obtained by equation (16).

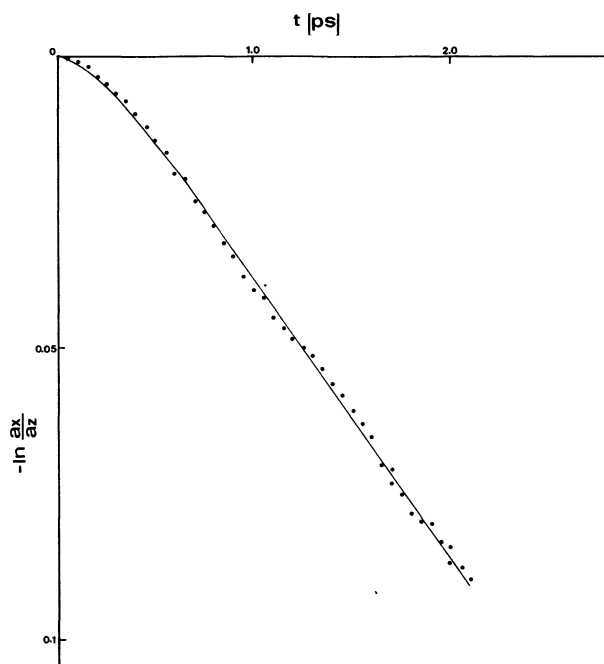


Fig. 2. — Reorientational correlation function of the IR 910 cm^{-1} band (PAA, 119°C) ; points : experimental data ; full line : best fit obtained by equation (14).

obtained using equations (14) and (16). Here we must note that the experimental points have been averaged over the small spurious oscillations due to the usual and unavoidable termination problems in the Fourier transform procedure. From fits such as those shown in figures 1 and 2 we obtained the relevant parameters for the reorientational dynamics of the molecules in the short time regime. These are summarized in table I for the four different temperatures studied.

For tumbling reorientations the relaxation time of the angular momentum, τ_\perp , is about 0.2 ps, and shows practically no temperature dependence. The corresponding values of the diffusion coefficient D_\perp^r and

their temperature dependence are similar to those already reported by us for other mesogens, in the framework of the single exponential approximation of the stochastic part of the correlation function [2]. The average angle of molecular rotation between two successive collisions, $\langle \epsilon^2 \rangle^{\frac{1}{2}}$, is also included in table I. It is worth noting that this is the first direct experimental determination of such parameter, which is crucial for the discrimination among potentially equivalent stochastic models for the reorientation. The tumbling rotation angle turns out to be of the order of a few degrees, and this clearly justifies the use of the small-step rotational diffusion model to describe rotational dynamics in the nematic phase, at least for tumbling motion. For spinning motion the values of the average angle are almost an order of magnitude higher, and this makes the use of the small-step rotational diffusion model less warranted. Within this uncertainty however, even for spinning motion this model seems to yield better results on the whole.

As stated before, the temperature dependence of the parameters is characterized by large errors and therefore the results are only qualitative ; within these limits however, the observed decrease with increasing temperature of the average spinning angle is reasonable, since our previous results [2] indicate that reorientation about the main molecular axis becomes more difficult with increasing temperature (and hence disorder).

The observed values for the moments of inertia seem reasonable. For instance, at 132°C I_\parallel and I_\perp are close to the values reported in reference [6] [$I_\parallel = 4.2 \times 10^{-45}\text{ kg.m}^2$, $I_\perp = 5.9 \times 10^{-44}\text{ kg.m}^2$]. The temperature dependence of I_\parallel and I_\perp however is somewhat unexpected, particularly for I_\perp , where the increase with decreasing temperature should be significant, i.e. outside our admittedly large experimental uncertainty. We have verified that our results are not model dependent by fitting the inertial portion of the correlation function with an order parameters-independent

Table I. — Experimental values of the dynamic parameters in the inertial and stochastic regimes.

| Band | T [K] | τ_i [10^{-12} s] | b_i [10^{24} s^{-2}] | I_i^* [10^{-45} kg.m^2] | D_i^r [10^9 s^{-1}] | $\langle \epsilon^2 \rangle^{1/2}$ [deg] |
|--|------------|-------------------------------------|--------------------------------------|---|-------------------------------------|---|
| 910 cm^{-1} $i = \perp$ | 391 | 0.21 | 0.22 | 110 (170) | 10.3 | 2.7 |
| | 395 | 0.22 | 0.22 | 110 (170) | 10.7 | 2.8 |
| | 399 | 0.25 | 0.20 | 100 (140) | 13.7 | 3.3 |
| | 405 | 0.26 | 0.23 | 45 (65) | 32.3 | 5.3 |
| $1\,028\text{ cm}^{-1}$ $i = \parallel$ | 391 | 0.26 | 1.28 | 2.2 (2.6) | 661 | 24 |
| | 395 | 0.77 | 0.49 | 5.2 (4.9) | 805 | 45 |
| | 399 | 0.73 | 0.29 | 8.0 (9.1) | 503 | 20 |
| | 405 | 0.10 | 0.52 | 2.5 (5.5) | 220 | 9 |

parabola. Although the absolute values for the moments of inertia turned out to be somewhat different (see Table I), their temperature behaviour was similar to that found by using equation (10).

For isotropic liquids, a similar temperature dependence of the moment of inertia was attributed to collective effects in the molecular motion, effects which are neglected in calculation [7] and in our own. Thus the observed temperature dependence of I_{\perp} may indicate a correlation between tumbling reorientations of different molecules; such correlation would increase with increasing molecular orientation, i.e. with decreasing temperature.

For spinning fluctuations the results are less definite and no specific conclusions may be drawn from their temperature behaviour. Qualitatively, the average value of I_{\parallel} is of the right order of magnitude, and the same is true for the other parameters, such as the angular momentum relaxation time τ_{\parallel} , which turns out to be about twice τ_{\perp} , as could be expected from the smaller steric hindrance of spinning motion of the rod-shaped molecules.

Again, the values of the diffusion coefficient D_f agree both in value and in temperature dependence with those already determined by us [2] from the exponentially decaying part of the correlation function.

4.2 RAMAN SCATTERING. — Raman spectra were taken on several mesogens in their nematic phase. Here we report as typical the results obtained for the compound 2-cyanobiphenyl 4',n-heptyloxybenzoate, which has a nematic range of 60 °C to 109 °C. We studied the band at 1603 cm⁻¹ (benzene ring stretch vibration) which is sensitive to tumbling fluctuations. The experimental apparatus consisted of a standard Raman spectrometer with microprocessor control and data acquisition. Details on this and on data analysis procedures are described in our reference [3]. In order to have better accuracy for the very short time range of the correlation functions, the band tails were obtained with comparable signal-to-noise ratio as the main band area, by using constant noise level recording. Furthermore the spectra were iterated up to 10 times; a typical run for the weaker depolarized component took up to eight hours.

Following the same procedures for background subtraction as for the IR case, we arrived at reorientational correlation functions such as that shown in figure 3, obtained at $T = 70$ °C. In order to fit the data with equation (19), we had to evaluate the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$; this we did using the method reported by Jen *et al.* [1], which makes use of the depolarization ratios ρ_1, ρ_2, ρ_3 taken in three different geometries (two corresponding to homogeneous alignment and one corresponding to the homeotropic configuration). We assumed uniaxiality of the polarizability tensor associated with the 1603 cm⁻¹ vibration.

We obtained the values of 0.64 for $\langle P_2 \rangle$ and 0.31 for

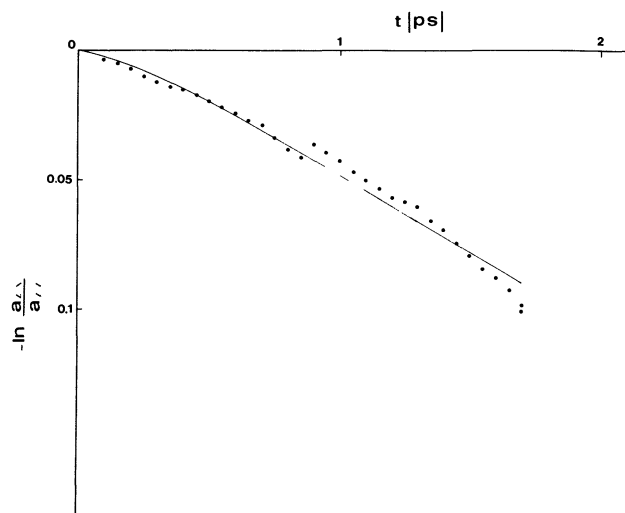


Fig. 3. — Reorientational correlation function of the Raman 1603 cm⁻¹ band (2-cyanobiphenyl, 4'n-heptyloxybenzoate); points: experimental data; full line: best fit obtained by equation (19). In this case the experimental points are the actual ones, i.e. the eventual spurious oscillations have not been smoothed out.

$\langle P_4 \rangle$ at $T = 70$ °C. Using these values in equation (19), we performed a least square fit (solid line in Fig. 3) of the experimental correlation function. From this we obtained $\tau_{\perp} = 0.2$ ps and $I_{\perp} = 1.5 \times 10^{-43}$ kg.m². Both values are very reasonable (f.i. $I_{\perp} = 5.9 \times 10^{-44}$ kg.m² for the smaller mesogen PAA [9], whereas we obtain, again for PAA, values for I_{\perp} that range between 1.1×10^{-43} kg.m² and 0.43×10^{-43} kg.m² from the IR data reported in this paper).

The tumbling rotational diffusion coefficient D_{\perp}^r turns out to be 7×10^9 s⁻¹, again in good agreement with the data obtained for other nematics [2].

Finally we evaluated the mean tumbling reorientational angle, determining the value of 2°, in good agreement with the IR data for tumbling reorientations.

The study of the temperature behavior of correlation functions in the short time limit was even more inconclusive than the IR case. Within an estimated error of about 50 %, all parameters could be considered constant.

5. Conclusive remarks.

Our generalization of the extended J -diffusion model to cover the whole range of correlations in the reorientational dynamics of single molecules in nematic phase has found semi-quantitative confirmation from our IR and Raman Fourier band analysis method. However intrinsic difficulties in data analysis make our results less cogent on a more quantitative level. Furthermore, at least for an isotropic liquid, equations such as (10) may be derived either in the framework of models similar to the one we used, or of completely different

models, e.g. reorientations under a smoothly varying random force with a correlation time $\tau_c \ll \tau_J$ [10].

Therefore, some ambiguity persists. If we look however at the complete set of data we have obtained, the substantial agreement between IR and Raman determinations, the consistency of the values obtained for the diffusive coefficients using the approach of the present Paper or that of our previous works [2, 3], our results do yield a reasonable picture of stochastic reorientations in this class of anisotropic fluids. In particular the use of the small-step diffusion model to describe molecular reorientations for times $t > \tau_J$

stands confirmed strongly for tumbling motion, and less so for spinning rotation. We should note that this is, to our knowledge, the first experimental demonstration of a specific stochastic model for reorientational dynamics in nematic phases [12].

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see also LYNDEN-BELL, R. M. and McDONALD, I. R., *Chem. Phys. Letts.* **89** (1982) 105.
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- [11] This decoupling of the angular momentum decay in the two different directions is not evident *a priori*. A complete treatment would require the introduction of this anisotropy in the model from the very beginning. Nevertheless, this would introduce big complications in our theoretical analysis, while the corresponding refinement would not be comparable with the quality of the experimental results obtainable, which give large errors even in the framework of our simplifying approximation. In spite of this, the results we have obtained are consistent, we think, with our simplification, giving it sufficient justification. We are referring in particular to the small values for the tumbling reorientational angles, which make rather improbable a tumbling reorientation strongly affecting the spinning one.
- [12] For a comprehensive review of proposed models for molecular reorientational dynamics see however also the work by J. H. Freed, in *Spin Labelling, Theory and Applications*, L. J. Berliner Ed., (Academic Press, N.Y.) 1976, Chapter 3.