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New method and results of Raman studies of non-diffusional reorientational dynamics of molecules in the nematic phase

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The method of differential Raman spectroscopy is developed to the case of uniaxial liquid crystals, increasing the precision of the determination of relative broadening and splitting of the polarized components of Raman bands in liquid crystals. With the help of the new technique and on the basis of a more general treatment of rotational broadening of Raman bands, some typical liquid crystal materials, namely, 4-pentyl-4′-cyanobiphenyl (5CB) and *trans*-4-pentyl-(4-cyanophenyl)cyclohexane (5PCH) have been studied. It is shown that for a particular form of intramolecular vibration (for example the cyano stretching mode), it is possible to determine all independent orientational autocorrelation functions without applying model considerations of the rotational motion in the nematic phase. The deviations of the results of these studies from a simple diffusional model of orientational relaxation in the short-time limit are discussed.

1. Introduction

Recently [1] we reported results of the comparative study of molecular reorientational dynamics by different spectroscopic methods. Band-shape analysis of spontaneous Raman spectra resulted in reorientation times which appeared to be much smaller than would have been expected from comparison of the depolarization ratios of luminescence and resonance Raman bands. It has been argued that this discrepancy originates from the non-exponential decay or from decay that is not one-exponential of the orientational autocorrelation function in the short-time limit.

In the overwhelming majority of publications devoted to the study of rotational dynamics of mesogen molecules (see, for example, [2–5]) the diffusional model is adopted as sufficiently adequate and at the same time simple. There are manifold arguments for this statement based either on comparison of molecular dimensions and the density of the system, or on comparison of the reorientational frequency and the mean frequency of the classical free rotor [6]. In addition, this model enables a fairly good description of spectroscopic data obtained by NMR [2], polarized fluorescence [5] and other techniques (we do not consider here such phenomena as dielectric relaxation or quasi-elastic light scattering, where many-particle movement can be observed). We do not attempt to refute these results. The overall reorientation of mesogen molecules occurs by small-step diffusion and magnetic relaxation experiments, which are usually performed in the fast motion limit, and luminescence experiments, for which the probe molecules are chosen with a lifetime comparable with the time of the reorientation, confirm this assumption.

Raman band shape, which we intend to discuss here, is determined by the product of the autocorrelation functions of relaxation of internal vibrational movement $\langle Q(0)Q^*(t)\rangle$ and of transition polarizability reorientation $\langle \alpha(0)\alpha^*(t)\rangle$ in the case of statistical independence of these movements [7]:

$$I_{\mathrm{ij}}(\omega) = A(\omega_0 - \Omega)^4 (2\pi)^{-1} \int_{-\infty}^{\infty} \langle \alpha_{\mathrm{ij}}(0)\alpha_{\mathrm{ij}}^*(t)\rangle \times \langle Q(0)Q^*(t)\rangle \exp(-i\omega t)\,\mathrm{d}t \qquad (1)$$

where ω_0 and ω are the frequencies of the incident and the scattered light which have the polarizations j and i,

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respectively; $Q(T)$, Ω and $\alpha(t)$ are the normal coordinate, the frequency and the transition polarizability tensor of the internal molecular vibration under study; A contains all specific experimental and local field factors, such as incident light intensity, solid angle, in which the scattered light is collected etc. The vibrational autocorrelation functions for mesogen molecules normally relax after the time interval of about 1–2 ps [8], while the reorientation time according to independent experimental estimates [1, 2, 5] is of the order of nanoseconds. Hence, at the outset, according to equation (1), Raman band shape analysis, being insensitive to the overall reorientation process, is sensitive even to the peculiarities of molecular orientational relaxation in the very beginning. This explains why deviations from diffusional motion, which are substantial only in the time region $t < 0{\cdot}1$ ps, could be observed in reorientational autocorrelation functions derived from vibrational spectra of mesogens [1, 8, 9].

The two above mentioned features: the non-exponential decay of the orientational autocorrelation functions and the smallness of the contribution of rotational movement to the vibrational spectra substantially complicate their study in mesophases by Raman spectroscopy. As compared to isotropic systems, there is a much larger number of independent autocorrelation functions [2] and to reduce the number of variables one has to specify a model for molecular rotation [3, 4]. In the present paper we make an attempt to solve these problems. We develop an experimental method which enables study of very small differences between various polarized Raman components, and hence enables a precise evaluation of the rotational contribution. Further, we show that for particular form of vibration it is possible to determine all independent autocorrelation functions without applying model considerations to the rotational motion.

The paper is arranged as follows. In § 2 which follows, we outline basic equations which are necessary for an understanding of our experimental approach. In § 3, experimental details and test measurements confirming the validity of such a method are described. In § 4, on the basis of the experimental data for some mesogens, we analyse the predictions of different diffusional models for anisotropic systems with the object of clarifying the origin of the observed phenomena. Finally, we briefly summarize the conclusions.

2. Theoretical background

Orientational autocorrelation functions of transition polarizability $\langle \alpha(0)\alpha(t)\rangle$ depend upon both the components of the transition polarizability tensor of the particular intramolecular mode in the molecular fixed frame and the reorientational movement of the molecule. Writing explicitly the transformation of the components of the transition polarizability tensor due to molecular rotation, one can obtain formulae for $I_{ij}(\omega)$ or its Fourier transform $\langle \alpha_{ij}(0)\alpha_{ij}^*(t)\rangle$ in terms of molecular orientational autocorrelation functions. For the case of a uniaxial mesophase constituted of cylindrically symmetric molecules, there are four independent, polarized Raman components and if we denote the symmetry axis of the mesophase as the z axis, then we can obtain [4]

$$\left.\begin{aligned}
\langle \alpha_{zz}(0)\alpha_{zz}^*(t)\rangle &= \tfrac{1}{3}|\alpha_{00}|^2 + 2\,\frac{\surd 2}{3}\,\alpha_{00}\alpha_{20}\langle P_2\rangle \\
&\quad + \frac{2}{3}\sum_{m=-2}^{2} |\alpha_{2m}|^2 \langle D_{0m}^2(t) D_{0m}^{2*}(0)\rangle, \\
\langle \alpha_{xx}(0)\alpha_{xx}^*(t)\rangle &= \tfrac{1}{3}|\alpha_{00}|^2 - \frac{\surd 2}{3}\,\alpha_{00}\alpha_{20}\langle P_2\rangle \\
&\quad + \frac{1}{6}\sum_{m=-2}^{2} |\alpha_{20}|^2 \langle D_{0m}^2(t) D_{0m}^{2*}(0)\rangle \\
&\quad + \frac{1}{2}\sum_{m=-2}^{2} |\alpha_{2m}|^2 \langle D_{2m}^2(t) D_{2m}^{2*}(0)\rangle, \\
\langle \alpha_{xz}(0)\alpha_{xz}^*(t)\rangle &= \frac{1}{2}\sum_{m=-2}^{2} |\alpha_{2m}|^2 \langle D_{1m}^2(t) D_{1m}^{2*}(0)\rangle, \\
\langle \alpha_{yx}(0)_{yx}^*(t)\rangle &= \frac{1}{2}\sum_{m=-2}^{2} |\alpha_{2m}|^2 \langle D_{2m}^2(t) D_{2m}^{2*}(0)\rangle.
\end{aligned}\right\} \qquad (2)$$

here $\langle P_2\rangle$ is the order parameter; α_{2m} is the mth spherical component of the transition polarizability in the molecular fixed frame for the normal mode under study (we use here irreducible spherical components as defined in [10], which are somewhat different from the definition used in [4]). Their transformation in the laboratory fixed frame is described by the Wigner D-functions [10] $D_{mn}^2(t)$ of rank 2, which in this representation constitute molecular orientational autocorrelation functions. Keeping in mind that for rod-like molecules functions with m and $-m$ are equivalent [2], one can conclude that in this, relatively simple case, which is however sufficiently adequate for many nematic phase systems, 9 different non-vanishing autocorrelation functions influence Raman band shape. For molecular vibrations along the symmetry axis, only D-functions with $m = 0$ are non-vanishing (such highly symmetrical modes are not affected by spinning motion), and these three orientational autocorrelations functions, as well as the vibrational one, can be extracted from the band shape of such Raman active modes using the relations

$$\left.\begin{aligned}
\langle\alpha_{zz}(0)\alpha_{zz}^{*}(t)\rangle &= \tfrac{1}{3}|\alpha_{00}|^2 + 2\,\frac{\sqrt{2}}{3}\,\alpha_{00}\alpha_{20}\langle P_2\rangle + \tfrac{2}{3}|\alpha_{20}|^2\\
&\quad\times[(\tfrac{1}{5}+\tfrac{2}{7}\langle P_2\rangle+\tfrac{18}{35}\langle P_4\rangle-\langle P_2\rangle^2)C_{20}(t)\\
&\quad+\langle P_2\rangle^2],\\
\langle\alpha_{xx}(0)\alpha_{xx}^{*}(t)\rangle &= \tfrac{1}{3}|\alpha_{00}|^2 - \frac{\sqrt{2}}{3}\,\alpha_{00}\alpha_{20}\langle P_2\rangle + \tfrac{1}{2}|\alpha_{20}|^2\\
&\quad\times\{\tfrac{1}{3}[(\tfrac{1}{5}+\tfrac{2}{7}\langle P_2\rangle+\tfrac{18}{35}\langle P_4\rangle\\
&\quad-\langle P_2\rangle^2)C_{20}(t)+\langle P_2\rangle^2]\\
&\quad+(\tfrac{1}{5}-\tfrac{2}{7}\langle P_2\rangle+\tfrac{3}{35}\langle P_4\rangle)C_{22}(t)\},\\
\langle\alpha_{xz}(0)\alpha_{xz}^{*}(t)\rangle &= \tfrac{1}{2}|\alpha_{20}|^2(\tfrac{1}{5}+\tfrac{1}{7}\langle P_2\rangle-\tfrac{12}{35}\langle P_4\rangle)C_{21}(t),\\
\langle\alpha_{yx}(0)\alpha_{yx}^{*}(t)\rangle &= \tfrac{1}{2}|\alpha_{20}|^2(\tfrac{1}{5}-\tfrac{2}{7}\langle P_2\rangle+\tfrac{3}{35}\langle P_4\rangle)C_{22}(t),
\end{aligned}\right\}\quad(3)$$

where for a cylindrically symmetric transition polarizability tensor

$$\begin{matrix}\alpha & 0 & 0\\ 0 & \alpha & 0\\ 0 & 0 & 1-2\alpha\end{matrix}\qquad(4)$$

both spherical components

$$\alpha_{00} = -\frac{1}{\sqrt{3}},\ \alpha_{20} = -\frac{\sqrt{2}}{\sqrt{3}}(1-2\alpha),\qquad(5)$$

can be determined from depolarization measurements on the isotropic phase. $C_{\mathrm{L}m}(t) = \Phi^{\mathrm{L}}_{m0}(t)/\Phi^{\mathrm{L}}_{m0}(0)$ stands for the normalized orientational autocorrelation functions defined similarly to [2, 5] by

$$\Phi^{\mathrm{L}}_{m0}(t) = \langle D^2_{2m}(t)D^{2*}_{2m}(0)\rangle - \langle D^2_{2m}\rangle\langle D^{2*}_{2m}\rangle.\qquad(6)$$

For $|\langle D^2_{mn}(0)\rangle|^2$ we use expressions from [5]. The order parameters and α can be determined from measurements of the depolarization ratios of the same band; formulae for integral intensities in terms of these values are readily obtained by putting $t = 0$ in relations (3) and substituting them into equation (1).

It is worth mentioning that in deriving (3), no model approximations have been used concerning the character of the molecular motion, or the kind of orienting potential acting on the molecule in the mesophase. This enables one to test experimentally different models, or to compare the effect of different approximations. For example, in the small-step diffusion approximation, the band-shape is of Lorentzian type, the bandwidth being directly related to the relaxation time: $\delta = (1/\pi c\tau)$ where c is the velocity of light. In this case straightforward differentiation of the product of the autocorrelation functions in (1) with substitution of (3) in the limit $t = 0$ gives

$$\left.\begin{aligned}
\delta_{zz} &= \delta_{\mathrm{vib}} + \frac{4}{9\pi c\tau_{20}}\,\frac{7+10\langle P_2\rangle+18\langle P_4\rangle-35\langle P_2\rangle^2}{7+20\langle P_2\rangle+8\langle P_4\rangle},\\
\delta_{xx} &= \delta_{\mathrm{vib}} + \frac{4}{9\pi c\tau_{20}}\,\frac{7+10\langle P_2\rangle+18\langle P_4\rangle-35\langle P_2\rangle^2}{7-10\langle P_2\rangle+3\langle P_4\rangle}\\
&\quad+\frac{1}{3\pi c\tau_{22}},\\
\delta_{xz} &= \delta_{\mathrm{vib}} + \frac{1}{\pi c\tau_{21}},\\
\delta_{yz} &= \delta_{\mathrm{vib}} + \frac{1}{\pi c\tau_{22}},
\end{aligned}\right\}\quad(7)$$

where

$$\tau_{\mathrm{L}m} = \int_0^\infty C_{\mathrm{L}m}(t)\,\mathrm{d}t,\qquad(8)$$

and for the sake of simplicity we put $\alpha = 0$ in (4) (cf. [4]). While deriving formulae (7), an exponential form was assumed for $C_{\mathrm{L}m}(t)$, but no specifications have been made concerning the functional form or the nature (short-range or mean-field) of the nematic orienting potential in the mesophase, thus enabling testing of these models.

3. Experimental

As it is clear from the previous section, from a theoretical point of view, there are no limitations upon deriving orientational autocorrelation functions for mesogen molecules or reorientation times from experimental data. The problem is that the smallness of the rotational contribution (0·2–0·5 cm^{-1} [1, 4, 8]) to the total bandwidth (the full width at the half height (FWHH) is about 6–8 cm^{-1} for typical mesogenic substances) leads to large uncertainties in its determination. Consequently, operating with many components, as is necessary in order to extract correlation functions according to formulae (3) or (7), one only accumulates errors. This is especially true for components with very low intensity (for stretching vibrations, I_{yx} can be 10–50 times smaller than I_{zz}). The situation is even worse due to the necessity to record Raman spectra over a very large spectral interval (300–500 cm^{-1}) in order to fulfil the requirements for the correct background subtraction [11]. Within such limits, it is impossible to use high-precision spectrometers, and the reproducibility of universal Raman spectrometers is usually worse than 0·2 cm^{-1}, i.e. is of the order of the rotational contribution.

To overcome these difficulties, we used the fact that in order to study molecular rotational movement one does not need absolute accuracy. It is clear from (3) and (7) that only within one set of measurements must the relative accuracy be as high as possible. Consequently we have modified the method of differential Raman spectroscopy [12] in order to carry out experiments with liquid crystals.

We used a conventional experimental set-up for the Raman studies [13], but we changed the registration procedure: the intensities of all polarized components were measured synchronously. This means that for every point of a spectrum the number of photon counts was determined for each polarized component by rotating the analyser and reorienting the liquid crystalline optic axis with the externally applied electric field, and only after this, was the position of the monochromator changed. The procedure was repeated at each spectral point. Certainly, this does not improve the precision of the monochromator positioning, but the relative accuracy of the bandwidth and band position determination for different components can be as high as 0·01 cm^{-1}, which is a gain of a factor of 10 as compared to the conventional technique.

All experimental details and preparation of liquid crystal samples are thoroughly described elsewhere [1, 13]. For achieving high signal-to-noise ratio, the slit-width of the monochromator has been chosen to be comparatively large: HWHH = 2·7 cm^{-1}. Although this can be supposed to be appropriate, because we are interested only in the relative difference of the components with different polarization, nevertheless the effect of the slit-width has been checked. In experiments with the slit-width varying from 2·8 to 6 cm^{-1}, almost no variations have been observed in the difference between the bandwidths with different polarization.

As is clear from the idea of the differential method, the spectra with different polarizations were recorded in one scan. For noise averaging, we accumulated the photon counts during 2–20 s, depending on the intensity of the component. In test experiments, the bandwidth appeared to be independent of the accumulation time (at least within the limits 0·5–30 s). The bandwidth measurements were also performed with different spectral intervals for fitting or Fourier transform. The absolute bandwidth values changed by 10 per cent while we varied the spectral interval of fitting from 150 to 500 cm^{-1}, but the results for the $\delta_{vh} - \delta_{vv}$ remained identical within experimental error.

In our experiments the liquid crystal samples have a planar alignment and 4 differently polarized components (both, incident and scattered light can be polarized parallel or perpendicular to the liquid crystalline director) can be determined for such a geometry. Furthermore, under the external electric field, the liquid crystal was reoriented and 2 more polarized components (with the incident light perpendicular and the scattered light parallel or perpendicular to the incident light polarization) could be measured. Only 4 of these components are linearly independent (see equations (3)), but this offers the possibility of checking directly both the effect of the depolarization due to elastic light scattering on the long-wave fluctuations of the director [14] and the effect of incomplete reorientation of the liquid crystal in the external field.

Although the Raman band intensity varies as the second power of the cell thickness, sufficiently thin samples (4–6 μm) were nevertheless used in order to avoid an extrapolation procedure of the results to zero thickness. This was especially desirable because the large uncertainties in the experimental bandwidth data prevent accurate extrapolation. With cells of this thickness, the residual difference between the bandwidths of the similar components obtained with different geometries was smaller than the scattering of the data and therefore was neglected. The external electric field applied for the reorientation of the liquid crystal sample (rectangular a.c. with a frequency 1 kHz) was chosen to be large enough (10 V amplitude for 5CB and 14 V for 5PCH) for no observable birefringence or change of the depolarization ratios to be noticed. The differences between the bandwidths of the similar components obtained with and without the external field were within the scatter of the data.

For the studies of molecular orientational dynamics, we have chosen two substances: 4-pentyl-4′-cyanobiphenyl (5CB) and *trans*-4-pentyl-(4-cyanophenyl)cyclohexane (5PCH), which have almost identical structures, but somewhat different viscosities. The cyano-vibration in both of them seems to be very appropriate for molecular rotation studies for several reasons. This mode is characteristic and well localized in the molecule and is unaffected by molecular conformational flexibility. Secondly, Raman band corresponding to it is well separated allowing precise band-shape analysis. Thirdly, the polarizability derivative tensor for this mode has been shown [15, 16] to possess axial symmetry relative to the molecular long axis and, with perpendicular components that are much smaller than the longitudinal one, this enables usage of formulae (7). The procedure used for the measurement of depolarization ratios, refractive indices and local field anisotropy, necessary for the determination of the order parameters, is described elsewhere [1, 17].

4. Discussion

Orientational autocorrelation functions for 5CB and 5PCH at several temperatures in the isotropic and the nematic phases, obtained with the help of formulae (3), are represented in figures 1 and 2. To make quantitative comparisons, it is more convenient to deal with the bandwidths and their temperature dependence. The results of the relevant measurements for both substances are presented in figure 3.

4.1. *Determination of orientational correlation times*

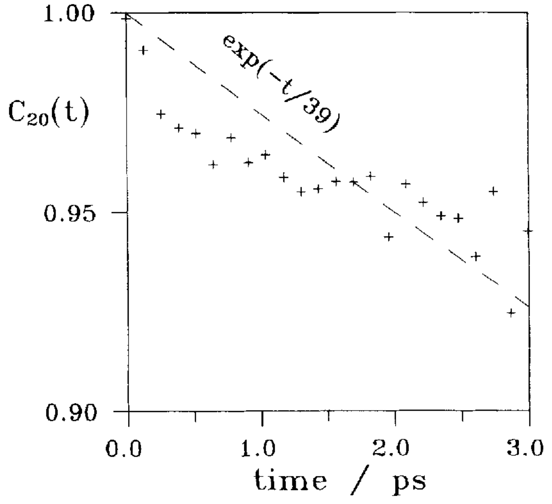
It is evident that the rotational contribution has the same order of value for both substances, and therefore the orientational relaxation times determined from these measurements with formulae (7) are depicted in figure 4 only for one of the substances. Besides the self-consistency of the temperature behaviour of the relaxation times $\tau_{20} > \tau_{21} > \tau_{22}$ so derived (all of them decreasing with temperature increase), one can notice that the scattering of the τ_{20} values is very high (some points are far beyond the borders of the plot). This is caused by the smallness of the contribution of τ_{20} to the bandwidth. For example, for 5PCH at $\Delta T = 11{\cdot}7$ (according to (7))

$$\delta_{yx} - \delta_{zz} = \frac{1}{\pi c}\left[\frac{1}{\tau_{22}} - 0{\cdot}107\frac{1}{\tau_{20}}\right],$$

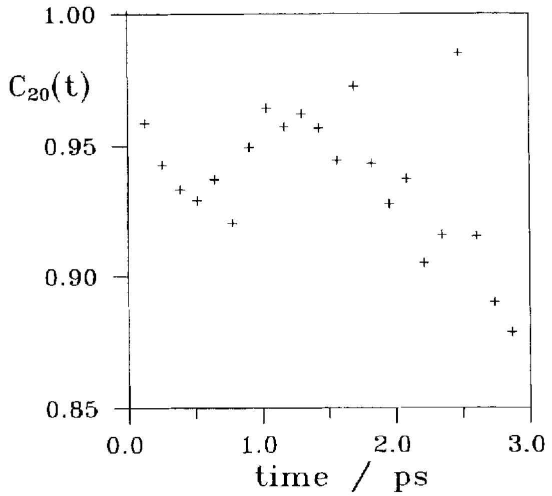
$$\delta_{xz} - \delta_{zz} = \frac{1}{\pi c}\left[\frac{1}{\tau_{21}} - 0{\cdot}107\frac{1}{\tau_{20}}\right],$$

$$\delta_{xx} - \delta_{zz} = \frac{1}{\pi c}\left[0{\cdot}333\frac{1}{\tau_{22}} + 0{\cdot}160\frac{1}{\tau_{20}}\right].$$

As a result, the relative accuracy of determining τ_{21} and τ_{22} is the same as for $\delta_{xz} - \delta_{zz}$ and $\delta_{yx} - \delta_{zz}$, respectively, while for τ_{20} it is at least 4 times worse. This is also true for the relevant autocorrelation functions (see figures 1 (*b*) and 2 (*b*)). Consequently the value of τ_{20} determined from these measurements is strongly influenced by various approximations, utilized during derivation of (7). For example, if to account for a finite value of α in (4) (relevant equations for bandwidths are presented in Appendix A), the values of τ_{20} are drastically changed and become unrealistically small in comparison with other τs (see figure 5), indicating a failure of some other model assumption (see further discussion).



(*a*)



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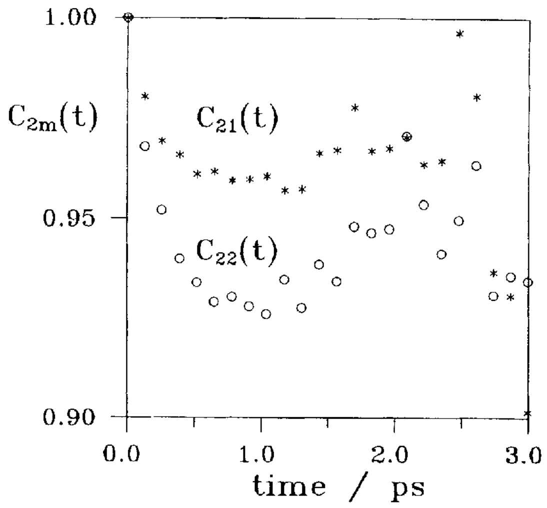

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Figure 1. Orientational autocorrelation functions for 5CB in the (*a*) isotropic and in the (*b*, *c*) nematic phases at $\Delta T = 7$ K, obtained on the basis of formulae (3): (+) τ_{20}, (*) τ_{21}, (○) τ_{22}. The dashed line (see figure 1 (*a*)) represents the autocorrelation function obtained from the bandwidth measurements.

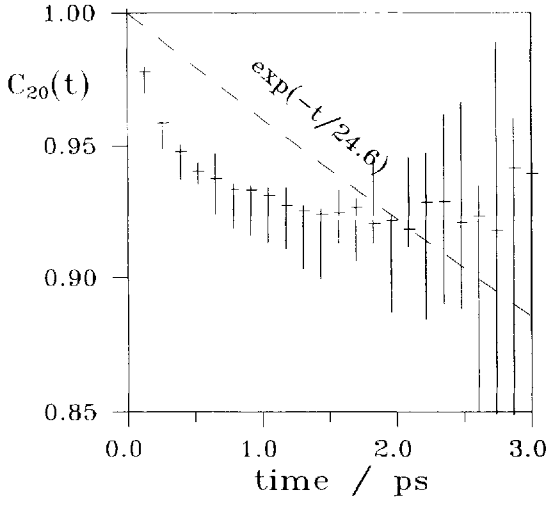
4.2. *Analysis of the small-step diffusion approximation*

The relative insensitivity of the τ_{2m} with $m \neq 0$ to the already adopted approximations makes it possible to use them for checking some models of the molecular movement in the mesophase. In [3, 4] orientational correlation times for D-functions of different symmetry were derived using the small-step diffusion model for molecular orientational relaxation in the mean-field nematic orienting potential:

$$\left.\begin{aligned}\tau_{20} &= \frac{7 + 10\langle P_2\rangle + 18\langle P_4\rangle - 35\langle P_2\rangle^2}{6D_r(7 + 5\langle P_2\rangle - 12\langle P_4\rangle)},\\ \tau_{21} &= \frac{7 + 5\langle P_2\rangle - 12\langle P_4\rangle}{6D_r(7 + 2{\cdot}5\langle P_2\rangle + 8\langle P_4\rangle)},\\ \tau_{22} &= \frac{7 - 10\langle P_2\rangle + 3\langle P_4\rangle}{6D_r(7 - 5\langle P_2\rangle - 2\langle P_4\rangle)}.\end{aligned}\right\} \qquad (9)$$

Although the resulting expressions are dependent not only on the order parameters, but also on the rotational diffusion coefficient D_r, which is the parameter of the model, one can test the dependence of the ratios of different τ_{2m} on the orientational ordering. It is evident from figure 6 (*a*), that the experimental ratios τ_{21}/τ_{22} for 5PCH agree well with the model predictions (somewhat worse agreement is observed for 5CB). This facilitates more reliable determination of the tumbling rotational diffusion coefficient (see figure 6 (*b*)) within the model. On the other hand, the experimental value of τ_{20} is much lower than that predicted by (9).

While deriving equations (7) (or (A1)) and (9), several approximations have been made, which can substantially influence the resulting values of the orientational relaxation times [4]: (i) the orientational diffusion coefficient D_r is independent of molecular orientation, i.e. macroscopic anisotropy of the D_r is neglected; (ii) the molecules are rigid; (iii) the molecules possess cylindrical symmetry; (iv) the orienting potential is treated in the mean-field approximation.



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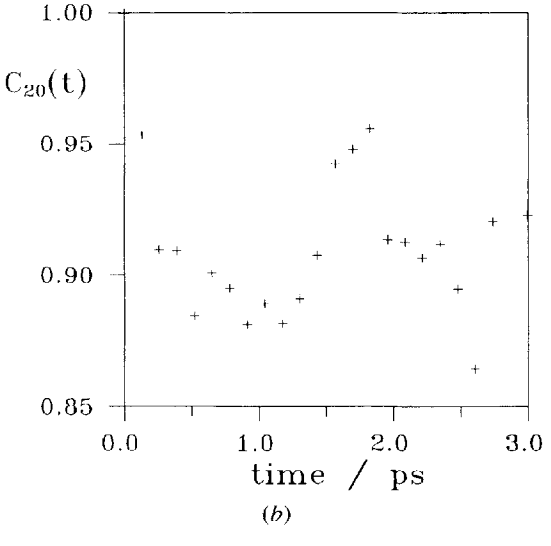

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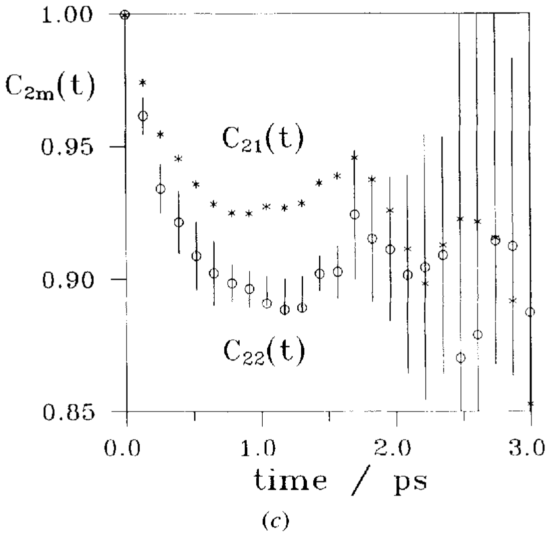

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Figure 2. Orientational autocorrelation functions for 5PCH in the (*a*) isotropic and in the (*b*) nematic phases at $\Delta T = 5$ K, obtained on the basis of formulae (3). The notations are similar to those for figure 1. Vertical lines represent the error bars.

The influence of the anisotropy of the rotational diffusion tensor on the orientational relaxation times has been considered in [18], taking, as an example, τ_{1m} derived from IR band-shape analysis. Following the derivation used in [18], one can readily obtain relevant expressions connecting τ^a_{2m}, predicted by the diffusion model which accounts for the diffusion tensor anisotropy, with τ_{2m}, given by formulae (9):

$$\left.\begin{aligned} \frac{1}{\tau^a_{20}} &= \frac{1}{\tau_{20}}, \\ \frac{1}{\tau^a_{21}} &= \frac{1}{\tau_{21}} - \frac{3D_r\delta\varepsilon P_2}{(1+2\delta\varepsilon P_2)(1-\delta\varepsilon P_2)}, \\ \frac{1}{\tau^a_{22}} &= \frac{1}{\tau_{22}} - \frac{12D_r\delta\varepsilon P_2}{(1+2\delta\varepsilon P_2)(1-\delta\varepsilon P_2)}, \end{aligned}\right\} \qquad (10)$$

where $\delta\varepsilon = (\varepsilon_{zz} - \varepsilon_{xx})/(\varepsilon_{zz} + 2\varepsilon_{xx})$ is the relative anisotropy of the rotational friction tensor introduced in [18] for a perfectly aligned nematic. As is seen from (10), accounting for the angular dependence of the orientational diffusion coefficient D_r leads to an increase of τ_{21} and τ_{22} relative to τ_{20}. Nevertheless, in order to achieve experimentally observed ratios τ_{20}/τ_{22}, one has to assume an extremely anisotropic rotational friction tensor ($\delta\varepsilon = 1$). On the other hand, recalculation of the relaxation times according to (10) makes τ_{21}/τ_{22} strongly different from the experimental value. At reasonable values of the rotational

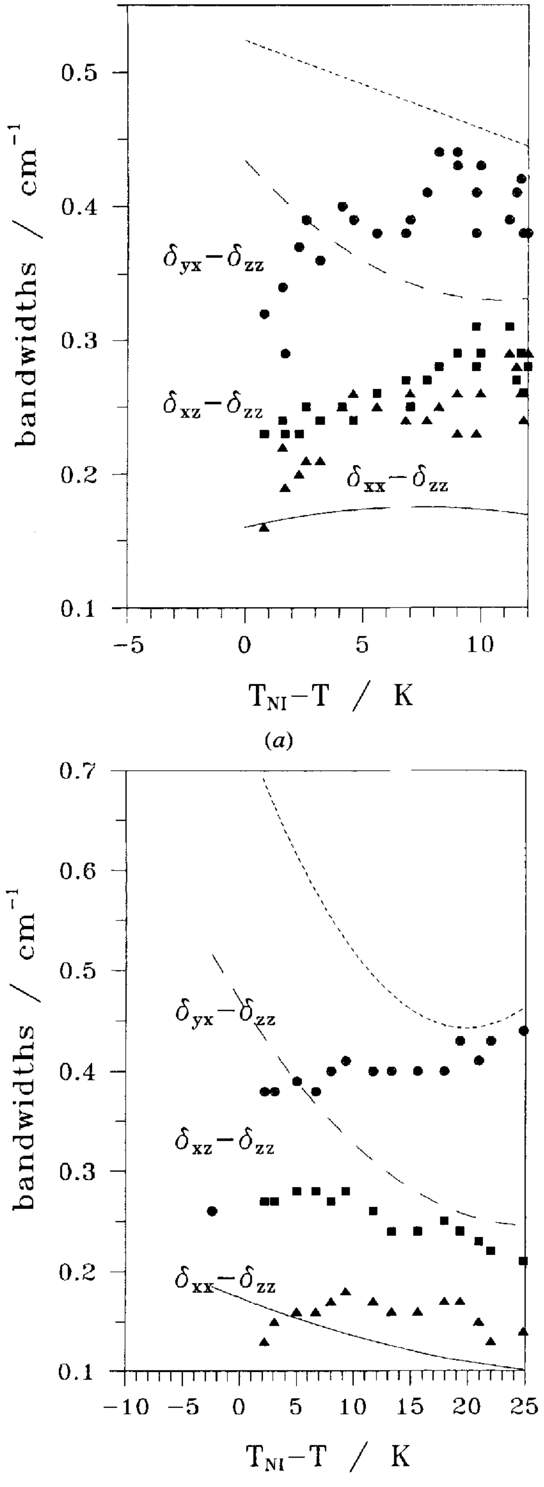


Figure 3. The temperature dependence of the bandwidths of the polarized components determined relative to the *zz* component for (*a*) 5CB and (*b*) 5PCH. The curves represent the values predicted by the small-step diffusion model [4]: (-----) $\delta_{yx}-\delta_{zz}$, (— — —) $\delta_{xz}-\delta_{zz}$, (———) $\delta_{xx}-\delta_{zz}$. The scatter of the experimental points shows the uncertainties of the measurements.

friction tensor anisotropy, its influence is relatively small and it cannot explain the experimental results.

To analyse the effect of molecular biaxiality, it is more convenient to discuss this directly in terms of the rotational broadening of the Raman bands. Looking at figure 3, one can tell that the diffusional model underestimates the rotational contribution onto the *xx* component and somewhat overestimates it for the *yx* and *xz* components. This effect is independent of whether the molecule is considered to possess cylindrical symmetry or not. Just as tumbling motion mainly contributes to the I_{ij} components with $i \neq j$, in the lack of cylindrical symmetry, the diffusional model predicts that spinning motion will even increase the difference between the bandwidths of these components and I_{xx}.

Concerning the other two approximations mentioned before, it is very difficult to teach some definite conclusions. One can only argue that both the molecular flexibility and the realistic dynamics of the molecular interaction potential can cause the molecular reorientation to be substantially different from a simple diffusion model. Correlation functions depicted in figures 1 and 2 give some evidence that the short-time molecular dynamics, at least, are non-diffusional. Correlation times derived from the Raman band shapes mainly reflect this short-time relaxation (compare corresponding exponents in figures 1 (*a*) and 2 (*a*) with experimental points) and, due to this, they are strongly different from the values obtained from luminescence depolarization measurements [1].

4.3. *Other models*

To explain this short-time evolution of the correlation functions, it is useful to compare it with the predictions of other models. In [19], the J-diffusion model, developed originally for isotropic liquids [20], has been generalized to the nematic case. Thus, inertial effects have been taken into account to fit the gaussian-type time evolution of the autocorrelation functions at $t = 0$. Unfortunately, with this simple model, it is also impossible to fit the correlation functions represented in figures 1 and 2. According to the J-diffusion model [19, 20], both in isotropic liquids and nematics, the second derivative of the autocorrelation function is always negative, while in figures 1 and 2 one can easily see regions with a positive curvature of the experimental autocorrelation functions. As can be shown within the formalism of the memory functions approach [8, 21], a more correct model must take into account non-Markovian behaviour of the molecular angular velocity.

Some such models of rotational movement of non-spherically symmetric molecules have been developed for isotropic liquids. According to the cage model [22, 23], it is supposed that the molecule has several stable orientations, i.e. potential minima of orientational energy. The

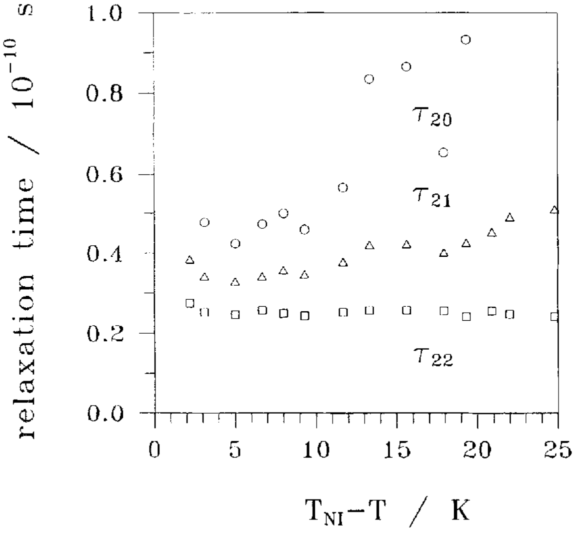


Figure 4. The temperature dependence of the orientational autocorrelation times for 5PCH obtained with formulae (7) ($\alpha = 0$ approximation) from the experimental data of figure 3.

height of the barriers separating the minima must be larger than kT to ensure oscillatory movement of the molecule. The molecule is subject to a random force due to surroundings, and hence its libration is damped. When the energy fluctuations reach the height of the potential barrier, the molecule leaks out of the well into a neighbouring well. For the two-dimensional system of this kind, the equations for rotational movement have been solved [23], resulting in the orientational autocorrelation function

$$\begin{aligned}\rho_{mn}(t) &= \langle \exp[in\theta(0) - im\theta(t)]\rangle \\ &= \exp(-2\gamma t)\delta_{mn}\left(\exp\left[-\frac{kTn^2}{b}\{1-u_{11}(t)\}\right]\right. \\ &\quad \left.-\exp\left[-\frac{kTn^2}{b}\right]\times\left\{1-\exp\left[2\gamma t\cos\frac{2\pi n}{N}\right]\right\}\right), \qquad (11)\end{aligned}$$

where

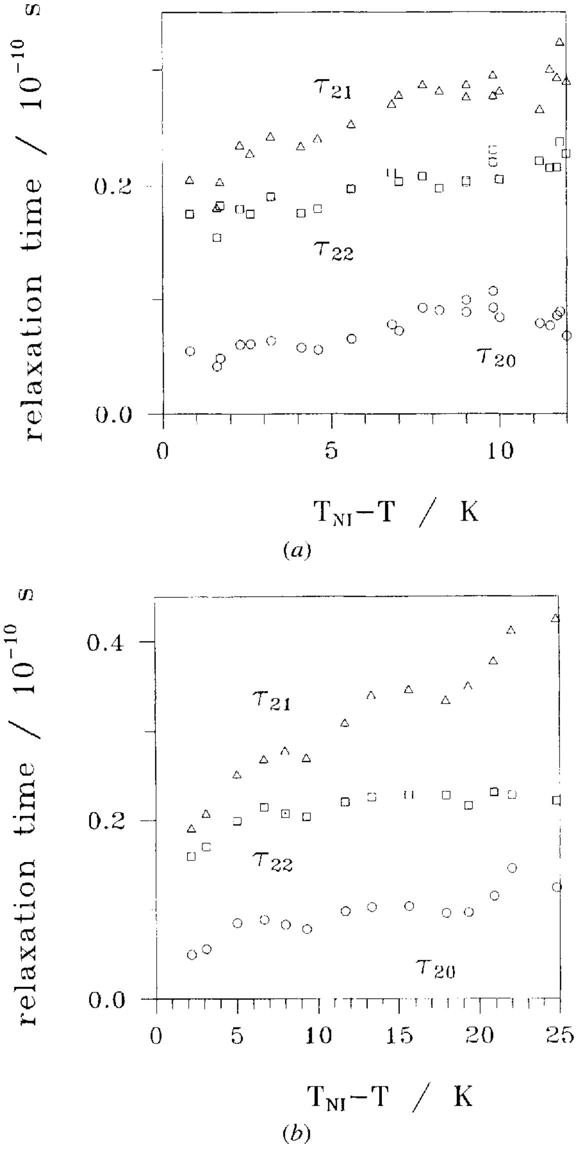
$$u_{11}(t) = \exp\left(-\frac{\eta t}{2}\right)\left[\cos\Omega t + \frac{\eta}{2\Omega}\sin\Omega t\right]$$

and

$$\Omega = \left(\frac{b}{I} - \tfrac{1}{4}\eta^2\right)^{1/2},$$

where I is the molecular moment of inertia, b is the force coefficient of the well potential $V(\theta) = (b/2)\theta^2$ and N is the number of wells. The rate of escape from the well γ can be related to these parameters and the damping factor η.

In the itinerant oscillator model [24], a non-spherical molecule librates inside a cage of neighbouring molecules. The cage in its turn performs a rotary Brownian motion.



(*a*)

(*b*)

Figure 5. The temperature dependence of the orientational autocorrelation times for (*a*) 5CB and (*b*) 5PCH obtained with formulae (A 1) from the experimental data of figure 3 (the values of α_{20}/α_{00} are 1·17 and 1·038 for 5CB and 5PCH, respectively; these are derived from the depolarization measurements made with the isotropic phase and are consistent with the data of [15, 16].

Analytical solution for disks in two dimensions have the form of equation (11). This equation combines resonance and diffusion phenomena, as can be readily seen by putting $t \ll \gamma$, or $t \gg \eta$. Extrapolation of its long-time part to $t = 0$ crosses the y axis at $\ln(\rho_{mn}(t)) = -(kTn^2)/b$, that is below zero, similarly to experimental curves. In general, at definite values of the model parameters, it can fit experimental curves. Unfortunately, analytical solutions have been found for two-dimensional models only. In order to assign some physical meaning to the parameters

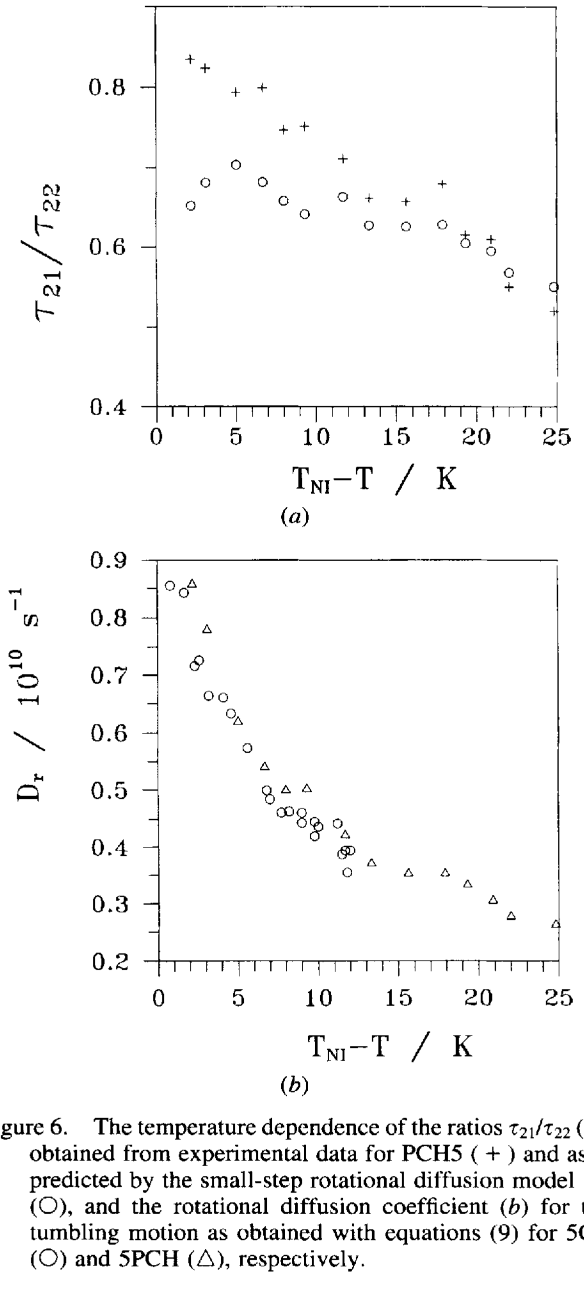


Figure 6. The temperature dependence of the ratios τ_{21}/τ_{22} (*a*), obtained from experimental data for PCH5 (+) and as is predicted by the small-step rotational diffusion model [4] (○), and the rotational diffusion coefficient (*b*) for the tumbling motion as obtained with equations (9) for 5CB (○) and 5PCH (△), respectively.

derived from such comparisons with experimental data, one has to consider a three-dimensional model and account for the macroscopic orienting potential in the mesophase.

5. Conclusions

In conclusion, we can summarize by saying that the experimental method developed in this work, i.e. modification of differential Raman spectroscopy to the case of liquid crystals, has enhanced the performance of the spectroscopic methods. The precision of the determination of the relative broadening and splitting of the polarized components of Raman bands in liquid crystals can be substantially increased. With the help of the new technique and on the basis of a more general treatment of rotational broadening of Raman bands, some typical liquid crystal materials have been studied. It is shown that for a particular shape of intramolecular vibration, it is possible to determine all independent autocorrelation functions without applying model considerations of the rotational motion. The results of these studies have proved the importance of non-diffusional behaviour of orientational autocorrelation functions in the short-time limit. To understand its origin and to build up an adequate model of molecular rotation in the mesophase, one must take account of realistic dynamics of the intermolecular potential and probability of molecular flexibility.

This work was performed within the framework of the co-operation between the Belorussian State University in Minsk and the Ruhr University in Bochum.

Appendix A

Following the derivation of (7) and differentiating formulae (3), one can obtain

$$\left.\begin{aligned}
\delta_{zz} &= \delta_{\text{vib}} + \frac{1}{\pi c \tau_{20}} \\
&\quad \times \frac{2a^2(7 + 10\langle P_2\rangle + 18\langle P_4\rangle - 35\langle P_2\rangle^2)}{35 + 70\surd(2)a\langle P_2\rangle}, \\
&\qquad + 2a^2(7 + 10\langle P_2\rangle + 18\langle P_4\rangle) \\
\delta_{xx} &= \delta_{\text{vib}} + \frac{1}{\pi c} \\
&\quad \times \frac{\tfrac{1}{2}a^2[(7 + 10\langle P_2\rangle + 18\langle P_4\rangle - 35\langle P_2\rangle^2)\,\tau_{20}^{-1} + 3(7 - 10\langle P_2\rangle + 3\langle P_4\rangle)\tau_{22}^{-1}]}{35 - 35\surd(2)a\langle P_2\rangle}, \\
&\qquad + a^2(14 - 10\langle P_2\rangle + 13{\cdot}5\langle P_4\rangle) \\
\delta_{xz} &= \delta_{\text{vib}} + \frac{1}{\pi c \tau_{21}}, \\
\delta_{yx} &= \delta_{\text{vib}} + \frac{1}{\pi c \tau_{22}}.
\end{aligned}\right\} \quad (\text{A } 1)$$

Orientational relaxation times determined from the bandwidth measurements with formulae (A 1) are depicted in figure 5. From these relations, for example, for 5PCH at $\Delta T = 11{\cdot}7$ K we have

$$\delta_{yx} - \delta_{zz} = \frac{1}{\pi c}\left[\frac{1}{\tau_{22}} - 0{\cdot}078\,\frac{1}{\tau_{20}}\right],$$

$$\delta_{xz} - \delta_{zz} = \frac{1}{\pi c}\left[\frac{1}{\tau_{21}} - 0{\cdot}078\,\frac{1}{\tau_{20}}\right],$$

$$\delta_{xx} - \delta_{zz} = \frac{1}{\pi c}\left[0{\cdot}189\,\frac{1}{\tau_{22}} + 0{\cdot}073\,\frac{1}{\tau_{20}}\right].$$

One can conclude that by taking into account the non-vanishing value of transverse components of the transition polarizability, the accuracy of determination of τ_{20} is even worse than when neglecting it.

References

[1] Ratchkevitch, V. S., Yakovenko, S. Ye., and Pelzl, J., 1993, *Liq. Crystals*, **15,** 591.

[2] Nordio, P. L., and Segre, U., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), Chap. 19 and 20.

[3] Dozov, I., Kirov, N., and Fontana, M. P., 1984, *J. chem. Phys.*, **81,** 2585.

[4] Kirov, N., Dozov, I., and Fontana, M. P., 1985, *J. chem Phys.*, **83,** 5267.

[5] Zannoni, C., 1979, *Molec. Phys.*, **38,** 1813.

[6] Moro, G., and Nordio, P. L., 1979, *Chem. Phys.*, **43,** 303.

[7] Nafie, L. A., and Peticolas, W. L., 1972, *J. chem. Phys.*, **57,** 3145.

[8] Yakovenko, S. Ye., Naumenko, V. I., Minko, A. A., and Ksenophontova, N. M., 1982, *Zh. Prikl. Spektrosk.*, **37,** 420.

[9] Kirov, N., Dozov, I., Fontana, M. P., and Rosi, B., 1987, *J. Phys., France*, **48,** 457.

[10] Varshalovich, D. A., Moskalev, A. N., and Khersonskii, V. K., 1988, *Quantum Theory of Angular Momentum* (World Scientific), Chap. 1–4.

[11] Van Woerkom, P. C. M., de Bleijser, J., de Zwart, M., Burgers, P. M. J., and Leyte, J. C., 1974, *Ber. Bunsenges phys. Chem.*, **12,** 1303.

[12] Kiefer, W., 1977, *Advances in Infrared and Raman Spectroscopy*, Vol. 3, edited by R. J. H. Clark and R. E. Hester (Heyden and Son, London), p. 1.

[13] Yakovenko, S. Ye., Ignatovich, R. R., Mueller, S., and Pelzl, J., 1991, *Liq. Crystals*, **10,** 821.

[14] Jen, S., Clark, N. A., Pershan, P. S., and Priestley, E. B., 1977, *J. chem. Phys.*, **66,** 4635.

[15] Miyano, K., 1978, *J. chem. Phys.*, **69,** 4807.

[16] Seeliger, R., Haspeclo, H., and Noack, F., 1983, *Molec. Phys.*, **49,** 1039.

[17] Yakovenko, S. Ye., Ignatovich, R. R., Mueller, S., and Pelzl, J., 1992, *Liq. Crystals.*, **12,** 973.

[18] Dozov, I., and Kirov, N., 1989, *J. chem. Phys.*, **90,** 1099.

[19] Pasini, P., and Zannoni, C., 1984, *Molec. Phys.*, **52,** 749.

[20] Gordon, R. G., 1966, *J. chem. Phys.*, **44,** 1830.

[21] Evans, G. J., and Evans, M. W., 1976, *J. chem. Soc. Faraday Trans. II*, **72,** 1169.

[22] Lassier, B., and Brot, C., 1969, *Discuss. Faraday Soc.*, **48,** 39.

[23] Praestgraad, E., and Van Kampen, N. G., 1981, *Molec. Phys.*, **43,** 33.

[24] Wyllie, G., 1971, *J. Phys. C.*, **4,** 564.