Orientational characteristics of liquid crystals (5CB) by means of optical study

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Orientational characteristics of liquid crystals (5CB) by means of optical study

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Information on molecular dynamics of the nematic liquid crystal 4-*n*-pentyl-4'-cyanobiphenyl (5CB) doped with the dyes DMANS and DMANAB has been obtained by luminescence and Raman measurements. Temperature dependences of reorientational correlation times are not the same for different molecular motions. Mechanisms responsible for the marked deviation of the time values obtained by different optical methods are discussed.

1. Introduction

Rotation of molecules affect, to a larger or smaller extent, almost all physical properties of those substances built up from these molecules. Therefore the physical properties of these materials can be used to extract information on molecular motion. Liquid crystals are not the exception and one can find in the literature attempts at such studies by very different experimental techniques. At earlier stages, dielectric relaxation measurements [1] were applied. Later the dielectric measurements were complemented by studies over a very broad frequency region—from middle infrared [2, 3] to far infrared and the microwave [4, 5] ranges. As a natural extension of the isotropic phase studies, light scattering techniques such as Raman scattering [6, 7] were developed and applied to the liquid crystalline phase. Application of quasi-elastic scattering measurements for these purposes [8], analogous to the Rayleigh wing studies for the isotropic phase, was less prominent because of the long range character of the director fluctuations in mesophases. Much research was devoted to steady-state [9, 10] luminescence measurements, time resolved Kerr effect studies [11], neutron scattering [12] and NMR band shape analysis [13].

Among these, optical methods seem to be the most promising for molecular and structural studies of liquid crystals. In comparison with the other experimental methods, which deal either only with the collective effects in the mesophase, as, for example, dielectric relaxation, nuclear magnetic resonance, etc., or with particular molecular motions (neutron scattering), optical study gives information on both types of motion. Although these methods have been applied frequently in the past, their success in studying rotation in the mesophase still faces some problems. Many questions concerning the eigen functions for a description of molecular rotation [14]

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and the correct approximation for the functional dependence on time [15, 16] remain unsolved. Also, the relative importance of rotational motion anisotropy on the macro- or micro-scopic level [3], and of the contribution of cooperative effects [17] are not treated satisfactorily. To solve these problems computer simulations are often helpful, but at present only a few model simulations are available. Hence the development of experimental procedures for the study of molecular motion, based on a comparison of the results obtained by different techniques, are most helpful at this stage.

Recently we have shown the possibility of determining the ratio of reorientational correlation times (τ_{ij}) to the luminescence lifetime (τ_1) proceeding from the combination of polarized luminescence and resonance Raman scattering measurements [19]. These studies have been performed on liquid crystals doped with dyes. The results of these experiments can be compared with those obtained from liquid crystalline matrix studies, only under the following fundamental assumption: the dye molecule is very similar to the host molecule, and hence static and dynamic parameters are presumed to refer to the host medium itself.

Another optical method providing information on the reorientational dynamics is Fourier analysis of the vibrational–rotational Raman band-shape. This technique has been used to determine the reorientational diffusion coefficients (D_r) and reorientation times on the picosecond time scale for both infrared [2, 3] and Raman [6, 7] spectra. As shown previously [9, 18], these independent measurements give different results depending on the time scale of the experiment. The behaviours of the temperature dependences differ too and could not be explained within existing theories.

The main purpose of the present article is to compare the information on dynamic parameters of probe molecules dissolved in a nematic liquid crystalline medium obtained with the help of different time scale measurements performed for such probes and the liquid crystalline system itself. The basic theory is summarized in §2, while the experimental details are presented in §3. Finally, the temperature dependences of the reorientational correlation times and of the corresponding diffusion coefficients are discussed in the final section.

2.   Theoretical background
2.1.   *Steady-state polarized luminescence*
Information on the molecular rotational dynamics is contained in the correlation functions $\langle \Phi^l_{mn}(t) \rangle$ of the Wigner matrices $D^l_{mn}(\Omega)$ [20]

$$\Phi^l_{mn}(t) = \langle D^l_{mn}[\Omega(0)] D^l_{mn}[\Omega(t)] \rangle \tag{1}$$

However, the direct measurement of the correlation functions (1) is difficult, as the experimental results depend on many correlation functions of this type. In the nematic medium, because of the existence of long-range orientational order and the anisotropy of the molecules, the reorientational process is more complicated. The initial orientation has also to be taken into account. As a result, the number of the independent correlation functions increases. Some simplifications may be achieved by using specific models for the reorientation, for example, the small-step rotational diffusion model [20, 21] or the strong collision model [22]. Although direct measurements, such as those using time resolved luminescence spectroscopy, are very informative and suitable for investigation of the relaxation processes, such studies do not provide the whole information on the correlation function and lead to severe difficulties when the absorption and emission dipole moments are not parallel to the

molecular long axis. Moreover, they are very few in number. Dolganov *et al.* [10], have shown that the temperature dependences of reorientational correlation times agree mostly with predictions of the small-step rotational diffusion model. This model has also been used successfully to interpret many other experimental results. The theory is based on the hypothesis that the reorientation is a stochastic process which proceeds by angular jumps and for which the components of the angular momentum relax with a correlation time much smaller than the relaxation time of the angular variables. Within the framework of this theory, the intensity of the polarized luminescence components $I_{ij}(t)$ $(i,j = z, x)$ (where z, x refer to the polarization of the exciting and emitted light, respectively and y is the direction of propagation of the light beam) is given, when both the absorption (μ_a) and emission (μ_e) moments are parallel to the molecular long axes, as [20]

$$
\left.
\begin{aligned}
I_{zz} &= f_{zz}^2 f_{zz}^2 [\tfrac{1}{9} + \tfrac{4}{9}\langle P_2 \rangle + \tfrac{4}{9} R_{00}], \\
I_{xz} &= I_{zx} = f_{xx}^2 f_{zz}^2 [\tfrac{1}{9} + \tfrac{1}{9}\langle P_2 \rangle - \tfrac{4}{9} R_{00}], \\
I_{xx} &= f_{xx}^2 f_{xx}^2 [\tfrac{1}{9} - \tfrac{2}{9}\langle P_2 \rangle + \tfrac{1}{9} R_{00} + \tfrac{1}{3} R_{20}],
\end{aligned}
\right\}
\tag{2}
$$

where

$$
\left.
\begin{aligned}
R_{00} &= \frac{1}{\tau_1} \int \Phi_{00}^2(t) \exp(-t/\tau_1)\,dt, \\
R_{20} &= \frac{1}{\tau_1} \int \Phi_{20}^2(t) \exp(-t/\tau_1)\,dt,
\end{aligned}
\right\}
\tag{3}
$$

represent the extent of rotational Brownian motions during the luminescence lifetime. The factors for the local field anisotropy correction in the nematic mesophase are f_{mn}. Under the assumption of a single exponential decay of the orientational correlation functions with the correlation times τ_{00} and τ_{20}, it is possible to write R_{ij} as

$$
\left.
\begin{aligned}
R_{00} &= \langle P_2 \rangle^2 \tau_{00}/(\tau_{00} + \tau_1) + \langle P_2 \rangle^2, \\
R_{20} &= (\tfrac{1}{5} - \tfrac{2}{7}\langle P_2 \rangle + \tfrac{3}{35}\langle P_4 \rangle)\tau_{20}/(\tau_1 + \tau_{20}).
\end{aligned}
\right\}
\tag{4}
$$

The luminescence depolarization ratios (r_{ij}) are written as

$$
r_1 = \frac{1 + \langle P_2 \rangle - 2R_{00}}{1 + 4\langle P_2 \rangle + 4R_{00}}, \quad r_2 = \frac{1 + \langle P_2 \rangle - 2R_{00}}{1 - 2\langle P_2 \rangle + R_{00} + 3R_{20}},
\tag{5}
$$

where $r_1 = I_{xz}/I_{zz}$ and $r_2 = I_{zx}/I_{xx}$. The steady-state luminescence measurements provide the ratio τ_{ij}/τ_l rather than reorientational correlation times τ_{ij}. Moreover, in order to obtain these ratios, some assumptions have been made [23, 24] resulting in a constant temperature behaviour of the τ_{20}/τ_l ratio, which is far from reality. The homeotropic configuration used in these studies has its own drawbacks. First it is a difficult problem to obtain a well aligned sample which is needed especially for the polarized experiments. Secondly, we must take into account that the use of two configurations implies, in general, the study of two different samples. Comparisons of steady-state experiments with results from the time-resolved luminescence technique have been made recently [9]. The time resolved experiments do not provide accurate information about the molecular reorientational dynamics if τ_{ij} is smaller than the duration of the exciting pulse and/or τ_l. More preferable seems to be a combination of

the depolarization luminescence measurements with the Raman depolarization ratios [18]. In the case when Raman scattering is excited in resonance with a transition whose dipole moment is oriented parallel to the symmetry axis of the axially symmetrical molecules, the depolarization ratios of the totally symmetrical vibration can be described using the same expressions. A very important advantage is also the possibility of determining, from the data from resonance Raman measurements and the absorption dichroism (N), the values of the order parameters and the local field anisotropy factors. Therefore, in the present studies we chose this method for treatment of the luminescence depolarization measurements.

2.2. *Raman band-shape analysis*

Raman band-shape analysis has become a classic tool for investigation of rotational dynamics of molecules in isotropic systems [25]. In fact, comparing Fourier transforms of the normalized spectral densities of isotropic and anisotropic components of vibration–rotation Raman bands, one can obtain comprehensive information on the rotational movement of molecules

$$\left.\begin{aligned} C_{\text{iso}}(t) &= C_{\text{vib}}(t), \\[2mm] C_{\text{anis}}(t) &= C_{\text{vib}} \sum \alpha_{2m}\alpha_{2n}\langle D^2_{mn}(t)\rangle \Big/ \sum \alpha_{2m}\alpha_{2n}\langle D^2_{mn}(0)\rangle, \end{aligned}\right\} \qquad (6)$$

where

$$C(t) = \int dw I(w)\exp(-iwt)\Big/\int dw I(w),$$

$$I_{\text{iso}} = I_{\text{vv}} - \tfrac{4}{3}I_{\text{vh}}, \quad I_{\text{anis}} = I_{\text{vh}};$$

I_{vv} and I_{vh} are plane polarized Raman intensities with polarizations coincident with and orthogonal to those of the exciting light, respectively. $C_{\text{vib}}(t)$ is the autocorrelation function of molecular vibration and α_{2m} stands for the mth spherical component of the polarizability derivative in the molecule fixed frame for the normal mode under study. The orientational correlation function is composed of autocorrelation functions $\langle D^2_{mn}(t)\rangle$ of Wigner D-functions [26] which connect the molecular and laboratory frames. For axially symmetrical molecules, which are of particular interest in the present work, only D-functions with $n=m$ are non-vanishing, and by studying Raman active modes of different symmetry, one can determine all three orientational correlation functions. Only a few assumptions have to be made when deriving equation (6): the absence of correlation between vibrations and rotations and between vibrations of different molecules. It is also supposed that there is no collision-induced scattering. These approximations are usually well controlled in ordinary cases and the decoupling of the orientational correlation functions from equation (6) is straightforward.

Another case concerns anisotropic systems. First of all, the situation is substantially complicated by the reduction of orientational symmetry: the number of independent orientational correlation functions $\langle \Phi^2_{mn}(t)\rangle$ (see equation (1)) increases. Even for the simplest case of uniaxial mesophase composed of cylindrically symmetric molecules $(m=p, n=q)$, there are 9 non-vanishing functions with different non-negative m and n

[20], while the number of independent polarized Raman components is only twice greater [7] than for the isotropic liquid

$$
\left.
\begin{aligned}
C_{zz}(t) &= |\alpha_{00}|^2 + 2\sqrt{\frac{2}{3}}\,\alpha_{00}\alpha_{20}P_2 + \frac{2}{3}\sum_{m=-2}^{2}|\alpha_{2m}|^2\langle D_{0m}^2(t)D_{0m}^2(0)\rangle, \\
C_{xx}(t) &= |\alpha_{00}|^2 - \sqrt{\frac{2}{3}}\,\alpha_{00}\alpha_{20}P_2 + \frac{1}{6}\sum_{m=-2}^{2}|\alpha_{20}|^2\langle D_{0m}^2(t)D_{0m}^2(0)\rangle \\
&\quad + \frac{1}{2}\sum_{m=-2}^{2}|\alpha_{2m}|^2\langle D_{2m}^2(t)D_{2m}^2(0)\rangle, \\
C_{xz}(t) &= \frac{1}{2}\sum_{m=-2}^{2}|\alpha_{2m}|^2\langle D_{1m}^2(t)D_{1m}^2(0)\rangle, \\
C_{xy}(t) &= \frac{1}{2}\sum_{m=-2}^{2}|\alpha_{2m}|^2\langle D_{2m}^2(t)D_{2m}^2(0)\rangle,
\end{aligned}
\right\} \tag{7}
$$

where the z axis is coincident with the symmetry axis of the mesophase. Therefore, for extracting useful information, one should proceed with additional approximations.

In order to derive information about the peculiarities of the time evolution of the reorientational process, one can, for example, neglect correlation between orientation and rotation [27]. In that case, which is equivalent to the neglect of the existence of an orienting potential, orientational correlation functions become similar to those for the isotropic phase, and consequently, their number is reduced, allowing separate studies of reorientation around different molecular axes [18]. Contrarily, if one is interested only in some integral characteristics, such as reorientation times, some models can be adopted for treating the rotational process [3, 14–16]. For the comparison with steady-state luminescence measurements, which contain information only on reorientation times, it is convenient to use the approach developed in [7], on the basis of the strong collision model. In this case, reorientation is an exponential process and relaxation of each D-function is described only by one exponent [19]. Modifying the diffusion equation to account for the orienting potential and assuming that this potential is of the mean field type, one can derive explicit expressions for $\langle\Phi_{mn}^2(t)\rangle$ in terms of rotational diffusion constants. In [3, 28] it has been shown that molecular biaxiality and anisotropy of rotational friction coefficients play a minor role in the reorientational process, and therefore we shall use expressions for orientational correlation functions derived in [7] where the mentioned effects have been neglected

$$
\langle\Phi_{00}^2(t)\rangle = P_2^2 + \frac{7 + 10P_2 + 18P_4 - 35P_2^2}{35}\exp\left[-6D_r t\,\frac{7 + 5P_2 - 12P_4}{7 + 10P_2 + 18P_4 - 35P_2^2}\right],
$$

$$
\langle\Phi_{10}^2(t)\rangle = \frac{7 + 5P_2 - 12P_4}{35}\exp\left[-6D_r t\,\frac{7 + 2 \cdot 5P_2 + 8P_4}{7 + 5P_2 - 12P_4}\right], \tag{8}
$$

$$
\langle\Phi_{20}^2(t)\rangle = \frac{7 - 10P_2 + 3P_4}{35}\exp\left[-6D_r t\,\frac{7 - 5P_2 - 2P_4}{7 - 10P_2 + 3P_4}\right],
$$

where D_r is the diffusion constant for tumbling motion (other components of D-functions where the second index is non-zero depend also on the spinning diffusion

constant). Relaxation times for the first and the third correlation functions correspond to τ_{00} and τ_{20} respectively, and are obtained from the luminescence depolarization measurements in the previous section. For determination of these times from Raman measurements, it is unnecessary to obtain the Fourier transform of the Raman band contour. All necessary information can be obtained from band-width measurements [29] for suitably selected modes. For example, the band shapes of the polarized components of totally symmetric modes in molecules possessing cylindrical symmetry are dependent only on three correlation functions [7]. Such highly symmetrical modes are not affected by spinning motion and can be studied with the aim of determining τ_{00} and τ_{20}.

3. Experimental
3.1. *Band-shape analysis*

The experimental set-up for Raman studies and the preparation of liquid crystalline samples are thoroughly described elsewhere [10]. To achieve a high signal to noise ratio, Raman scattering has been excited by a rather high power (30–80 mW) of the 514 nm line. For higher excitation powers, overheating of the sample within the light beam caused a shift in the clearing point exceeding $0.2°C$ and prevented precise depolarization measurements. The slit widths of the monochromator were also chosen to be comparatively large (FWHH $2 \, cm^{-1}$) for the same reason. The setting was appropriate because we were only interested in the relative difference between the components with different polarizations. Also the probable contribution of rotational motion to the full width at half height (FWHH) of 6–$8 \, cm^{-1}$ for typical mesomorphic substances is only about 0.1–$0.3 \, cm^{-1}$ [30]. Nevertheless, sufficiently small thicknesses of the samples (3–$4 \, \mu m$) allowed us to avoid use of an extrapolation procedure to zero thickness [31]. This was especially desirable because of large uncertainties in the experimental bandwidth data which prevent accurate extrapolation.

For averaging long-term noise while accumulating the data, we combined a relatively short accumulation time interval (usually 2–5 s) at every special point with a large number of scans to make the overall accumulation time greater than 20–30 s. To make the bandwidth measurements more reliable, we used a band fitting procedure instead of direct bandwidth measurements. As in the theoretical considerations, we adopted an exponential model for orientational relaxation a lorentzian bandshape was used for fitting and these lorentzian HWHH have then been used in the analysis. Although deviations of the real band shapes from lorentzians are noticeable, the systematic errors caused by this approximation are expected to be much less than the data scattering, because of the smallness of the rotational contributions to the total bandwidth of the polarized components.

Raman bandshape of the cyano-vibration of 4-*n*-pentyl-4'-cyanobiphenyl have been studied. This vibration 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, the Raman band corresponding to it is well separated (figure 1) allowing precise bandwidth determination. Thirdly, the polarizability derivative tensor for this mode has been shown [32] to possess cylindrical symmetry with the symmetry axis parallel to the long molecular axis, with perpendicular components that are much smaller than longitudinal one. Hence, according to [29] it is sufficient to determine the difference between the bandwidths of the *zz* and *xz* components for the determination of the diffusion
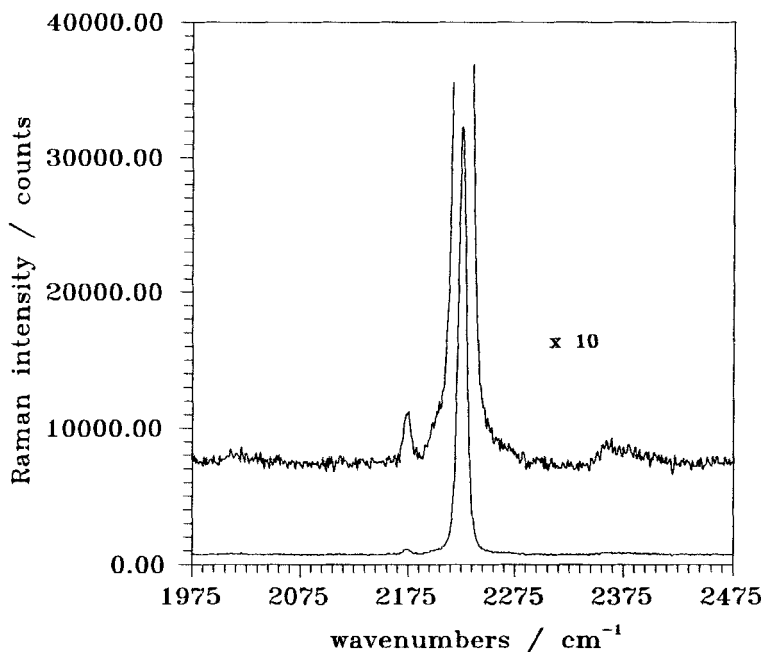
Figure 1. Raman spectrum of 5CB in the vicinity of the band at $2\,225\,\mathrm{cm}^{-1}$ (isotropic phase).

coefficient of the tumbling motion of the molecules in the mesophase

$$\left.\begin{aligned}
\delta_{xz} &= \delta_{\mathrm{vib}} + \frac{6}{\pi c} D_r (7 + \tfrac{5}{2}P_2 + 8P_4)/(7 + 5P_2 - 12P_4), \\[2mm]
\delta_{zz} &= \delta_{\mathrm{vib}} + \frac{8}{3\pi c} D_r (7 + 5P_2 - 12P_4)/(7 + 20P_2 + 8P_4).
\end{aligned}\right\} \tag{9}$$

The main band at $2225\,\mathrm{cm}^{-1}$ and small satellite at $2176\,\mathrm{cm}^{-1}$ were fitted in the spectral interval $450\,\mathrm{cm}^{-1}$ by two lorentzians to minimize the errors due to uncertainty of the background and the effect of the neighbouring bands. The resulting HWHH for different polarized components of the $2225\,\mathrm{cm}^{-1}$ band are shown in figure 2. The diffusion coefficient and orientational relaxation times computed according to equation (8) are shown in figure 3.

It should be noted that the order parameters were determined from depolarization measurements (figure 4) using formulae which take into account the diagonality of the polarizability derivative tensor in the molecule fixed frame and its axial symmetry

$$\left.\begin{aligned}
r_1 &= \frac{(n_g + n_z)^2 f_{xx}^2}{(n_g + n_x)^2 f_{zz}^2} \frac{\tfrac{1}{2}\alpha_{20}^2(\tfrac{1}{5} + \tfrac{1}{7}\langle P_2\rangle - \tfrac{12}{35}\langle P_4\rangle)}{\tfrac{1}{3}\alpha_{00}^2 + \tfrac{2\sqrt{2}}{3}\,\alpha_{00}\alpha_{20}\langle P_2\rangle + \tfrac{2}{3}\alpha_{20}^2(\tfrac{1}{5} + \tfrac{2}{7}\langle P_2\rangle + \tfrac{18}{35}\langle P_4\rangle)}, \\[3mm]
r_2 &= \frac{(n_g + n_z)^2 f_{zz}^2}{(n_g + n_z)^2 f_{xx}^2} \frac{\tfrac{1}{2}\alpha_{20}^2(\tfrac{1}{5} + \tfrac{1}{7}\langle P_2\rangle - \tfrac{12}{35}\langle P_4\rangle)}{\tfrac{1}{3}\alpha_{00}^2 - \tfrac{\sqrt{2}}{3}\,\alpha_{00}\alpha_{20}\langle P_2\rangle + \tfrac{1}{3}\alpha_{20}^2(\tfrac{2}{5} - \tfrac{2}{7}\langle P_2\rangle + \tfrac{27}{70}\langle P_4\rangle)}.
\end{aligned}\right\} \tag{10}$$

As has been observed, the neglect of the contribution of the perpendicular component of the polarizability derivative tensor in the determination of order parameters leads to large errors in diffusion coefficient calculations. Here n_x, n_z and n_g are the ordinary and extraordinary refractive indices of the liquid crystalline sample and that of the glass cell,
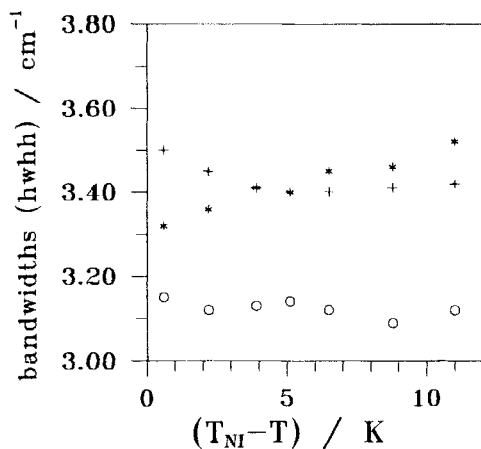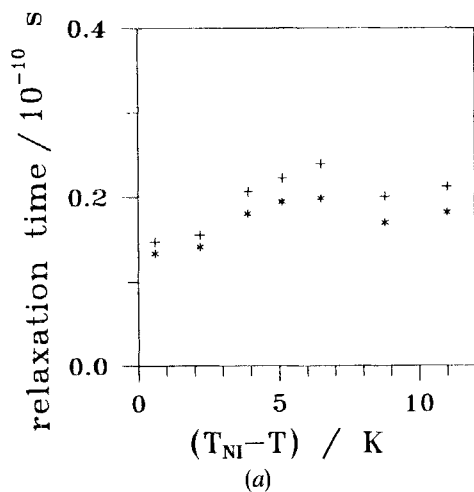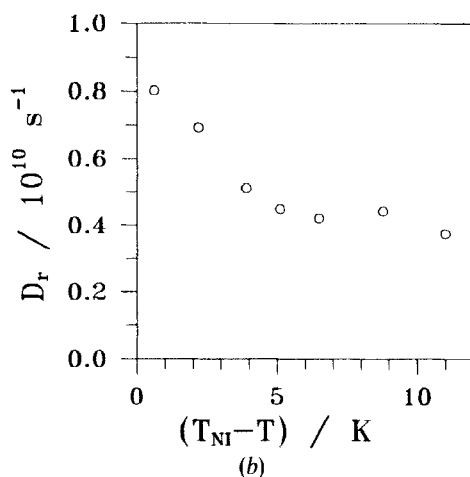
Figure 2. Temperature dependence of the bandwidths of the polarized components of the $2225\,cm^{-1}$ band of 5CB. ZZ, ($\bigcirc$); ZX, ($*$); XX, ($+$).

(a)

(b)

Figure 3. (a) Temperature dependence of the orientational relaxation times of 5CB molecules obtained from the bandwidth measurements. τ_{00}, ($+$); τ_{20}, ($*$). (b) Temperature dependence of the orientational diffusion coefficient of the 5CB molecules obtained from the bandwidth measurements.
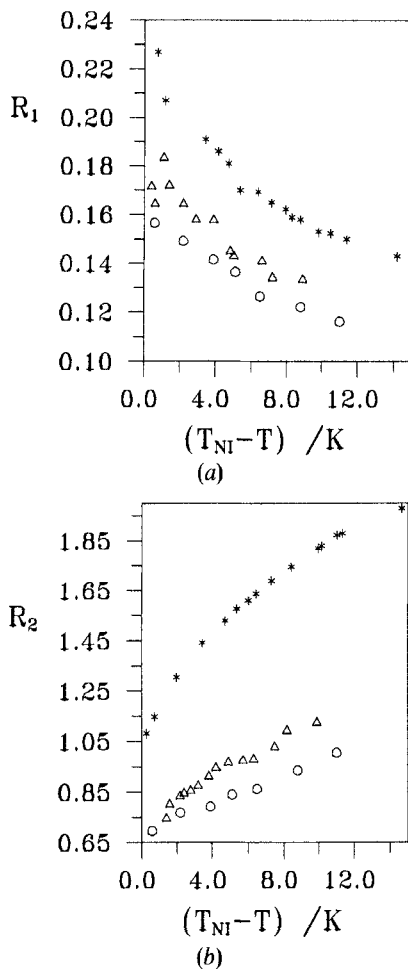
Figure 4. Temperature dependences of the depolarization ratios R_{ij}—(a) R_1, (b) R_2—for the luminescence band of DMANS molecules in 5CB ($*$), for the resonance Raman bands of DMANAB in 5CB ($\triangle$) and for the spontaneous Raman band of 5CB ($\bigcirc$).

respectively. The local field anisotropy factors f_{ii} has been taken to be the same as that of the local field acting on DMANAB dye molecules [33], which have a similar length to width ratio, as determined by the resonance Raman scattering method [34] for the matrix of 4-n-pentyl-4'-cyanobiphenyl. Partly due to performing the local field anisotropy corrections and partly due to r_1 ratios, little lower than in [32], the resulting order parameters are somewhat higher than those obtained earlier [32] for the same substance. But this difference leads to negligible shifts in the diffusion coefficient and the orientational relaxation time data, which can be compared with those determined from steady-state luminescence measurements.

3.2. *Luminescence*

For luminescence and resonance Raman depolarization studies, we used the same experimental set-up and cells as for the band shape analysis, with the only difference that here it was possible to use much larger slitwidths (5–10 cm^{-1}). Peak intensities

have been measured for the determination of the depolarization ratios by subtracting the background (also in the case of luminescence where the contribution of the background was found to be negligible). In order to test the influence of sample thickness on the result obtained, we used a variety of teflon spacers within the range $3-12\,\mu m$. We have not found any thickness dependence for our samples within this interval.

We have used two dyes the molecules of which are nematic-like, and which dissolve easily and are oriented in the nematic matrix with both absorption and emission dipole moments oriented approximately parallel to the molecular long axis [35, 36]. The depolarization ratios of the luminescence have been obtained for the first dye, namely 4-N,N-dimethylamino-4'-nitrostilbene (DMANS). The bands belonging to the stretching vibrations of the N=N ($1338\,cm^{-1}$) and NO_2 ($1396\,cm^{-1}$) groups polarized along the molecular long axis of 4-N,N-dimethylamino-4'-nitroazobenzene (DMANAB) were selected from the resonance Raman spectrum. The 4-n-pentyl-4'-cyanobiphenyl (5CB) was used as the liquid crystalline medium. Previously, it has been shown that under illumination, photophysical and photochemical processes can occur in these substances (see [37] and reference therein). To ensure conservation of the dyes during the period of the measurements, resonance Raman scattering has been excited at rather small power ($3-8\,mW$) and luminescence—at by $10-20\,\mu W$ of 514 nm light. Although degradation of the dyes under such illumination did not seem possible, this was checked by repeating the measurements of the maximum position and of the depolarization ratio. Previously we discussed the validity and errors of this method, by using the data for measurements using these two dyes [18]. It was shown that these dyes have the same values of the order parameter P_2 and similar temperature dependences of their orientational statistical parameters in a binary nematic matrix. The same features have been observed for these dyes in the 5CB matrix which is under present study.

We have mentioned the very significant role of the local field anisotropy for the interpretation of optical measurements [38], especially in the case of the depolarization ratios. Corrections of the local field anisotropy, which have been done in accordance with the data in [33], have sufficiently small deviations of the local field anisotropy factors from the smooth temperature dependence, in comparison with the previous
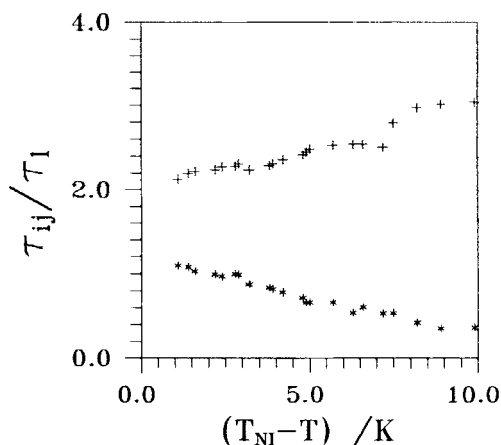

Figure 5.   Temperature dependence of the ratios τ_{00}/τ_1. (+) and τ_{20}/τ_1, (*).

data for the two component nematic matrix [18]. On the basis of the comparison of depolarization ratio data for the luminescence and resonance Raman scattering in the homogeneous geometry presented in figure 4 and the above mentioned local field anisotropy factors, we calculated the τ_{00}/τ_l and τ_{20}/τ_l ratios which are presented in the figure 5.

4. Results and discussion

As we can see in figure 5, the reorientational correlation times show distinct temperature dependences. The existence of a temperature dependence of the τ_{00}/τ_l ratio is not a new finding, but the decrease of this ratio within the mesophase, as predicted by theory, with increasing temperature, is contradictory to the results of other studies [9, 12]. The change of the τ_{20}/τ_l ratio with increasing temperature has also not been observed previously. Moreover, these two temperature dependences have different signs. The values of the reorientational relaxation times are within the interval of several nanoseconds, with $\tau_{00} \gg \tau_{20}$, as predicted by the model of small-step rotational diffusion. A time resolved study performed for DMANS in an EBBA matrix yields a value of the luminescence life time of about 2 ns [39]. We can use this value in order to evaluate the magnitude of the τ_{ij}. The deduced values of τ_{00} are about 4–6 ns and of τ_{20} about 1–3 ns, within the temperature range of the mesophase. These results correlate with the data of time resolved measurements using MBBA [10]. In this work increases in the reorientational correlation times have also been observed, similarly to the temperature dependence of the τ_{00}/τ_l ratio. This agrees with data for temperature effects on viscosity [40].

As we can see from figure 3 (a), the reorientational correlation times computed according to equation (8) are of the order of 10^{-11} s and have the same temperature dependence. We have no final explanation for the different temperature behaviour of τ_{00} and τ_{00}/τ_l obtained from the above mentioned luminescence measurements, but some reasons could be discussed. We have determined the values of τ_{ij} from the data on the D_r calculated from the equation (8). The luminescence measurements provide a direct independent determination of the τ_{ij}/τ_l ratios. One can suppose that the temperature dependence of τ_l can influence the curves in figure 5 and lead to the deviation from those in figure 3. But the temperature dependence of the luminescence life time of the DMANS molecules is very small [39]. That is why the temperature dependences of the ratios correspond to the temperature dependences of the τ_{ij}. Another advantage of the luminescence measurements is that the theoretical treatment does not require any suppositions about the intermolecular potential, while in order to obtain equation (8), some assumptions about the form of the nematic pseudo-potential have been made. The ratio of τ_{20}/τ_l to τ_{00}/τ_l to does not depend on luminescence life time and it is possible to use its temperature dependence for testing model approximations. The data in figure 6 show that this curve differs from the temperature dependence of the model parameters which have been used in equation (8).

In §3.2. we discussed the possibility of using the combination of two methods and two dyes in the nematic matrix. The data presented in figure 7 could also be considered as a confirmation of the validity of this approach. The P_2 values obtained by both the resonance Raman measurements for DMANAB in the 5CB matrix and the spontaneous Raman scattering measurements for the matrix itself coincide perfectly. The P_4 data obtained from these studies are also close to each other in the temperature region far from the transition point. The small values of P_4 for 5CB in the vicinity of the
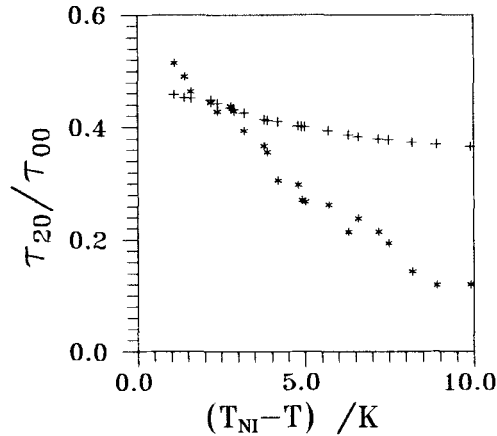
Figure 6.   Temperature dependence of the ratio τ_{20}/τ_{00} obtained from the luminescence measurements (*) and the model calculations (equation (8)) (+).
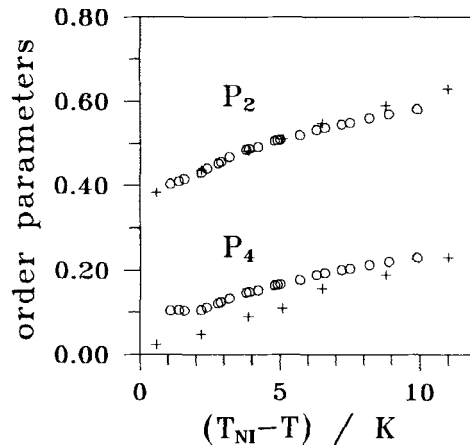

Figure 7.   Temperature dependence of the order parameters obtained from the resonance Raman measurements using DMANAB in 5CB (O) and the spontaneous Raman measurements for 5CB (+).

nematic to isotropic transition are a well-known fact [41], which can be explained by the antiferroelectric packing of the 5CB molecules.

Another reason for the above mentioned disagreement between the data on temperature dependences is the following. We compare the reorientational parameters of the molecules which have, in general, a different orientational distribution function and which can occupy different levels. The time scale of the Raman studies is very short for the transition between different orientational distribution functions, but in the case of the luminescence measurements, the information obtained depends essentially on the relation between the luminescence life time and the effective time of the reorientational processes.

The difference in time scale between values of τ_{ij} obtained from the steady-state luminescence measurements and the Raman band shape analysis is more than one order of magnitude. Previously we showed that the Raman method is sensitive only for short time scales several picoseconds because of the fast decay of the vibrational
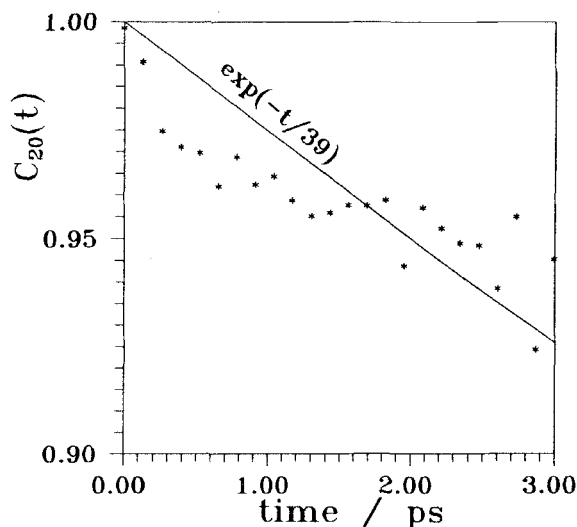
Figure 8. Orientational autocorrelation function of 5CB molecules in the isotropic phase (*) as a function of time. A solid line is obtained in the small-step rotational diffusion approximation with the relaxation time taken from Raman bandwidth measurements.

correlation function [18]. This is confirmed by a comparison of the orientational correlation function obtained from the Raman band-shape in the isotropic phase of 5CB with that predicted by the small-step diffusion model with the relaxation time calculated from the band-width measurements (figure 8). These curves are close to each other only in the picosecond interval, but at large time scales, due to non-exponential decay of the orientational correlation function, they diverge substantially. The smaller slope of the autocorrelation function at larger times is observed in the luminescence experiments, but its value could not be evaluated from Raman measurements.

It seems necessary to take into account several mechanisms or stages for the molecular reorientation process. At the first stage, the non-equilibrium orientational distribution function of the excited molecules relaxes to the distribution function characterized by the local orientational order of the near surroundings. Within this time scale, the molecular rotation looks like hindered vibration. The final relaxation to the equilibrium distribution must be realized by means of reorientations of the whole ensemble of molecules. This explanation is similar to the mechanism proposed in the model of the slowly relaxing local structure suggested by Freed *et al.* [41, 42].

As a conclusion, the temperature dependences of reorientational correlation times are not the same for different molecular motions. In order to clarify the mechanisms responsible for the marked deviation of the time values obtained by different optical methods, future experiments should be concentrated on finding substances particularly suited for the variety of techniques with different time scales; for example, substances with short luminescence life times, and time-resolved techniques with appropriate times of excitation. Of course, it seems most promising to investigate a substance [37] which permits the use of both methods and their combination, as discussed in this paper.

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