Studies of Orientational Order of Some Nematogens by means of Raman Scattering Spectroscopy

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Z. Naturforsch. **59a,** 510 – 516 (2004); received April 11, 2004

The orientational behaviour of some liquid crystals with various molecular structures was studied by means of the Raman scattering depolarization method. The Raman scattering spectra of linearly polarized light were recorded as a function of temperature in the nematic phase. On the basis of these spectra the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as well as the molecular distribution function were determined. The obtained data were compared with those estimated on the basis of polarized light absorption and emission measurements. The influence of the molecular structure on the orientational order of liquid crystals was discussed.

Key words: Liquid Crystal; Raman Scattering; Order Parameter; Distribution Function.

1. Introduction

The mechanical, optical, electrical, and magnetic properties of liquid crystals depend on their molecular orientation [1]. Knowledge of the degree of order of liquid crystals is thus of great value not only for various aspects of the physics of these substances, but also for most of their applications.

For a system of molecules with an effective cylindrical form the orientational order can be described by a probability distribution function $f(\beta)$, where β is the angle between the long molecular axis and the major symmetry axis of the system. The distribution function can be expressed [2] as a series expansion of even Legendre polynomials, $P_{2\mathrm{L}}(\cos\beta)$, each of which is weighted by an order parameter $\langle P_{2\mathrm{L}} \rangle$, which is the ensemble average of the corresponding term:

$$f(\beta) = \sum_{L=0}^{\infty} \frac{4\mathrm{L}+1}{2} \langle P_{2\mathrm{L}}(\cos\beta) \rangle P_{2\mathrm{L}}(\cos\beta). \quad (1)$$

This expansion defines the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as follows:

$$\langle P_2 \rangle = \frac{1}{2} \left\langle 3\cos^2\beta - 1 \right\rangle, \quad \text{(2a)}$$

$$\langle P_4 \rangle = \frac{1}{8} \left\langle 35\cos^4\beta - 30\cos^2\beta + 3 \right\rangle. \quad \text{(2b)}$$

The experimental determination of the degree of order of liquid crystals has been carried out by a wide variety of methods. Most of these methods, i. e. optical birefringence and diamagnetic anisotropy measurements, infrared spectroscopy, dichroism in the visible and UV region, nuclear magnetic resonance, allow to estimate only the order parameter $\langle P_2 \rangle$. Both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ can be simultaneously obtained on the basis of X-ray diffraction [3], electron paramagnetic resonance [4], fluorescence depolarization of a guest probe dissolved in a liquid crystalline matrix [2, 5] as well as Raman scattering spectroscopy [6, 7].

The knowledge of the infinite set of $\langle P_{2\mathrm{L}} \rangle$ would completely define the molecular distribution. Knowing only the parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$, a truncated distribution function $f_4(\beta)$ may be obtained:

$$f_4(\beta) = \frac{1}{2} + \frac{5}{2} \langle P_2 \rangle P_2(\cos\beta) + \frac{9}{2} \langle P_4 \rangle P_4(\cos\beta). \quad (3)$$

However, the function with the fourth range order parameter describes better the orientational order of the liquid crystal molecules than $\langle P_2 \rangle$ only, because $\langle P_4 \rangle$ contains higher powers of the cosine of the deviation angle and therefore is more sensible to molecular fluctuations.

In this paper we present the results of the study of the orientational order for some liquid crystals with various molecular structure by using Raman scattering

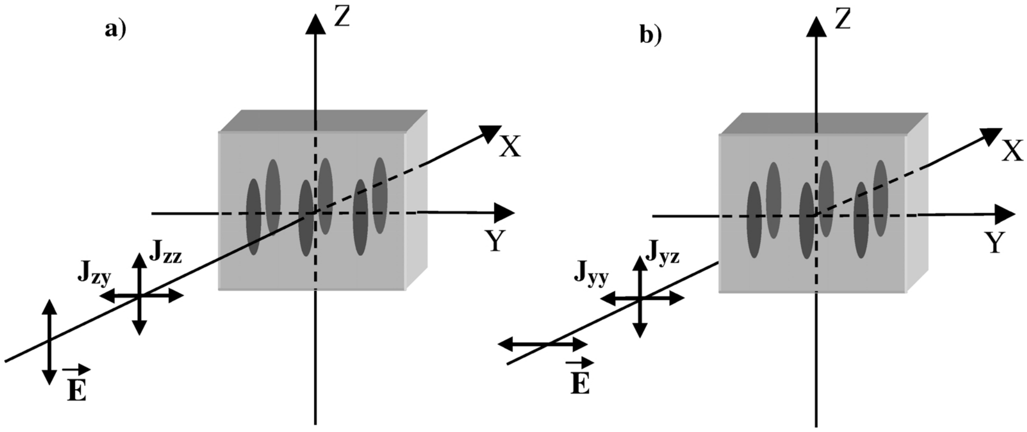
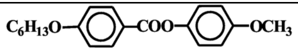
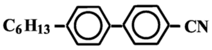
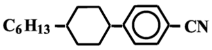
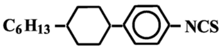
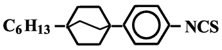
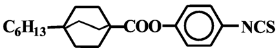


Fig. 1. Experimental geometries for measuring the scattering anisotropies R_1 a) and R_2 b). Arrows indicate the vibration direction of the electric vectors of the incident and scattered light.

Table 1. Chemical formulae and phase transition temperatures of liquid crystals investigated.

Liquid Crystals	Molecular Structure	T_{CN}/K	T_{NI}/K
1		326.8	350.8
2		287.7	302.0
3		315.2	323.3
4		285.5	315.7
5		323.7	363.1
6		324.7	378.9
7		334.2	380.9

depolarization. This method is very suitable for studying the alignment of liquid crystal molecules because Raman spectra are excited in the visible region, where liquid crystalline materials are transparent and can be recorded for localized regions of space. Moreover, the intensity of lines depends on the relative orientations of the molecule and the polarization of the exciting beam [6, 7].

2. Experimental Section

The molecular structure of liquid crystals used in this study and their crystal-nematic and nematic-isotropic phase transition temperatures, T_{CN} and T_{NI}, respectively, are given in Table 1. The compounds show only a nematic phase between the solid and isotropic states. They all were supplied by Prof. R. Dąbrowski from the Military Academy of Technology in Warsaw.

The polarized Raman scattering spectra were recorded by means of the conventional apparatus. The experiments were performed in the back scattering geometry by using two neutral UV polarizers. An ILA-120 Carl Zeiss, Jena laser, operating at 488 nm, was the exciting source. In order to reduce the local heating of the sample by the laser beam, the light power was kept at 20 mW. The measurements were made as a function of temperature over the whole nematic phase. "Sandwich" cells of 20 – 40 μm thickness were used. The planar molecular orientation was achieved by treatment of the cell glass surfaces with polyimide, and by an additional rubbing process.

Figure 1 presents the liquid crystal sample in the laboratory coordinate system. The light beam incidents along the x axis, the yz plane is the plane of the sample, and the director $\boldsymbol{n}$ coincides with the z axis. The polarized Raman scattering spectra were recorded for the sample setting where the electric vector $\boldsymbol{E}$ of the incident light was taken as the z direction (Fig. 1a) or the y direction (Fig. 1b). J_{zz}, J_{zy}, J_{yz} and J_{yy} are the appropriate scattering intensities.

On the basis of the experimentally obtained J_{ij} values the scattering anisotropies R_1 and R_2 were calculated by

$$R_1 = \frac{J_{zz} - J_{zy}}{J_{zz} + 2J_{zy}} \tag{4a}$$

for the excitation with light polarized parallel to the z

axis, and

$$R_2 = \frac{J_{yz} - J_{yy}}{J_{yz} + 2J_{yy}} \tag{4b}$$

for the excitation with light polarized parallel to the y axis. Here, the J_{ij}'s require corrections for the anisotropy of the refractive index and of the apparatus polarization.

In the Raman scattering spectrum it is always possible to find the particular vibration for which the polarizability tensor, $\hat{\alpha}$ related to the molecular frame has the diagonal form [6]

$$\hat{\alpha} = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{5}$$

For uniaxial liquid crystal molecules it is reasonable to assume that $a = b$. This value can be easily determined on the basis of scattering anisotropy measurements in the isotropic phase [6]. In the simplest case $a = b \approx 0$, and then the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ can be calculated directly on the basis of the experimentally obtained values of R_1 and R_2, using the relations

$$\langle P_2 \rangle = \frac{2 + 7R_1 - 14R_2 + 5R_1R_2}{23 - 14R_1 + R_2 - 10R_1R_2}, \tag{6a}$$

$$\langle P_4 \rangle = \frac{12 + 21R_1 - 21R_2 + 30R_1R_2}{23 - 14R_1 + R_2 - 10R_1R_2}. \tag{6b}$$

Equations (6a) and (6b) are valid if the principal axis of the normal mode of a vibration lies along the long molecular axis.

3. Results and Discussion

Figures 2–5 show the polarized components of the Raman scattering spectra of the liquid crystals **1**, **2**, **4** and **6**, as examples, recorded at 330 K (**1**, **6**) and 300 K (**2**, **4**). The spectra obtained for all liquid crystals investigated at various temperatures consist of several distinctly separated lines with different intensity. Using a fitting procedure by means of the Lorentz curve, and making the analysis of the spectra, the individual bands were attributed to appropriate vibrations. The Raman spectra of all liquid crystals contain the band lying 1590–1600 cm^{-1} away from the exciting line. This band is assigned to the C-C stretching mode of the benzene ring [8–10]. In the spectra of the liquid crystals **1** and **3**–**7** appears the band at 1239–1255 cm^{-1}, which is connected with the aromatic ring vibration [8]. This band is the most intensive one for the liquid crystals **6** and **7**. The spectra of the liquid crystal **2** reveal the presence of a band at 1283 cm^{-1} related to the C-C stretching vibration of the biphenyl ring [8, 10]. Moreover, in the Raman spectra of the liquid crystals investigated bands at 1155–1176 cm^{-1}

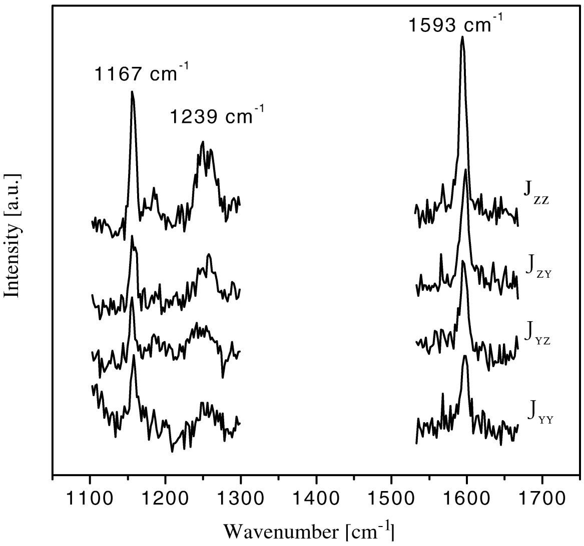


Fig. 2. Polarized components of the Raman scattering spectra J_{zz}, J_{zy}, J_{yz}, and J_{yy} of the liquid crystal **1** ($d = 20$ μm, $T = 330$ K).

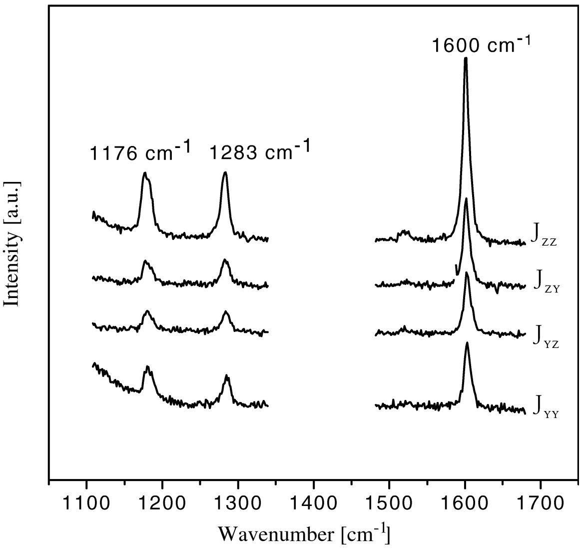


Fig. 3. Polarized components of the Raman scattering spectra J_{zz}, J_{zy}, J_{yz}, and J_{yy} of the liquid crystal **2** ($d = 20$ μm, $T = 300$ K).

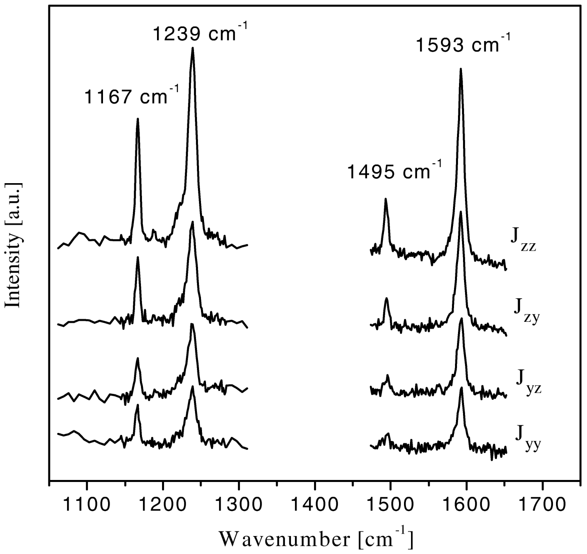


Fig. 4. Polarized components of the Raman scattering spectra J_{zz}, J_{zy}, J_{yz}, and J_{yy} of the liquid crystal **4** ($d = 20\ \mu$m, $T = 300$ K).

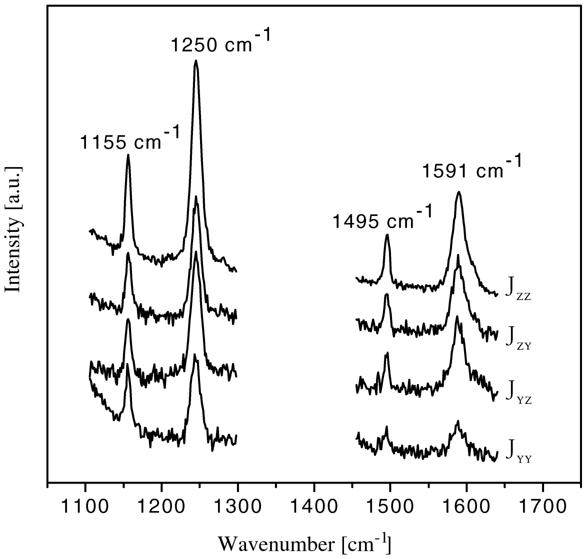


Fig. 5. Polarized components of the Raman scattering spectra J_{zz}, J_{zy}, J_{yz}, and J_{yy} of the liquid crystal **6** ($d = 20\ \mu$m, $T = 300$ K).

and at 1495 – 1518 cm^{-1} can be distinguished. The first band is assigned to the aromatic C-H in-plane deformation, whereas the latter to the C-H deformation of the alkyl chain [8, 10]. The intensity of all Raman scattering bands varies with the experimental geometry, thus they can reflect the molecular order of a liquid crystal in a thin oriented layer.

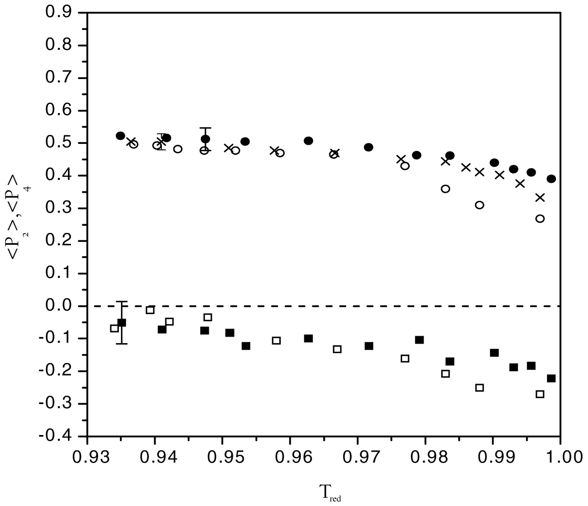


Fig. 6. Dependence of the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ on the reduced temperature $T_{\text{red}} = T/T_{\text{NI}}$ for liquid crystal **1** obtained from Raman scattering measurements (•, ■) and for liquid crystal **1** doped with DANS [12] determined from fluorescence (○, □) and absorption (× - $\langle P_2\rangle$ only) measurements.

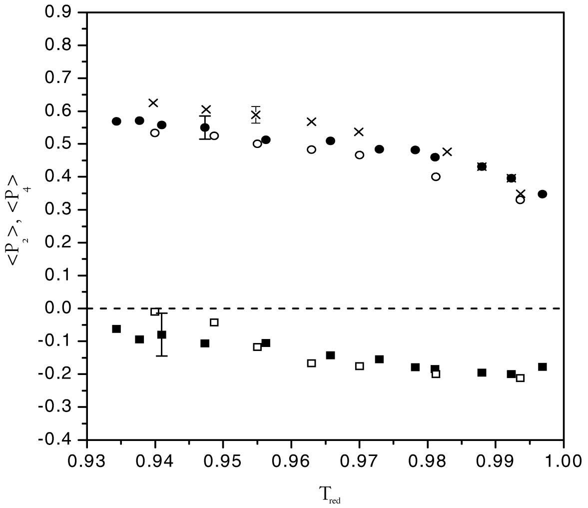


Fig. 7. Dependence of the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ on the reduced temperature $T_{\text{red}} = T/T_{\text{NI}}$ for liquid crystal **4** obtained from Raman scattering measurements (•, ■) and for liquid crystal **4** doped with DANS [12] determined from fluorescence (○, □) and absorption (× - $\langle P_2\rangle$ only) measurements.

For our further considerations we choose initially the band at 1590 – 1600 cm^{-1}, because it was very intensive in the spectra of all liquid crystals under investigation. On the basis of the band intensities at various geometry we noticed that, although the C-C stretching vibration in the aromatic ring should be symmetric for an isolated molecule, for liquid crystal molecules in the nematic phase the largest element of the polarizability tensor is α_{zz}. This means that the nematic potential privileges the vibration along the orientation direction ($\boldsymbol{n}$). Similar observations were made previously for other liquid crystals [7, 11]. Thus the assumption that the angle between the long molecular axis of the normal mode of this vibration is equal to 0° can be made with good approximation. Moreover, for this band the value of $a = b \approx -0.05$ was obtained, which is small comparing to 1. Therefore it was possible to assume $a = b = 0$ in our consideration and to use (6a) and (6b) for the calculation of the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$.

Figures 6 and 7 present the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ as functions of the reduced temperature $T_{\mathrm{red}} = T/T_{\mathrm{NI}}$ for liquid crystals **1** and **4** as examples. For the calculations, the values of the Raman scattering intensities were taken at the wavenumbers corresponding to the maxima of the band. In Figs. 6 and 7 the order parameters obtained by using other methods of polarized light spectroscopy, namely absorption and fluorescence depolarization measurements of 4-dimethylamino-4'-nitrostilbene (DANS) dissolved as a probe in the liquid crystals [12] are shown for comparison. From the results presented in Figs. 6 and 7 as well as obtained for other liquid crystals follows that the character of the order parameters changes with the temperature does not depend on the liquid crystal and the method used, although the absolute values differ somewhat. The values of the order parameter $\langle P_2\rangle$ obtained for DANS-liquid crystal mixtures from fluorescence measurements are usually lower than those obtained from absorption measurements, especially at higher temperatures. This may be due to the assumption made in considerations in [12] that $\tau_{\mathrm{R}} \gg \tau_{\mathrm{F}}$($\tau_{\mathrm{R}}$ = relaxation time, τ_{F} = fluorescence lifetime of a molecule). Meanwhile, as the temperature increases the values of both times become comparable. This can lead to a considerable misinterpretation of the fluorescence data and to cause the difference between the $\langle P_2\rangle$s obtained from fluorescence measurements and those determined by using other methods.

Raman scattering, like fluorescence, is a two-photon process, and the only difference occurs in the scale of time: while the lifetime of the molecule in the excited state is of order of $10^{-9} - 10^{-7}$ s, the Raman scattering process takes place almost immediately ($\approx 10^{-12}$ s) after absorption of the light. The results obtained in our experiments from Raman scattering measurements are very similar to those obtained by using fluorescence spectroscopy. The difference occurs solely at higher temperatures when the fluorescence depolarization due to the rotational motion plays some role. This is seen very distinctly from the data for the liquid crystal **1** in Figure 6.

Table 2. Order parameter $\langle P_2\rangle$ for liquid crystals investigated at various reduced temperatures.

Liquid Crystals	$\langle P_2\rangle$ $T_{\mathrm{red}} = 0.88$	$T_{\mathrm{red}} = 0.94$	$T_{\mathrm{red}} = 0.97$	$T_{\mathrm{red}} = 0.98$
1	–	0.51	0.49	0.46
2	–	–	0.36	0.34
3	–	–	0.43	0.38
4	–	0.55	0.49	0.46
5	0.55	0.46	0.40	0.35
6	0.48	0.41	0.32	0.30
7	0.53	0.49	0.43	0.37

For the comparison of the orienting properties of various liquid crystals used in our studies, in Table 2 the values of $\langle P_2\rangle$ obtained from Raman scattering measurements at four reduced temperatures are gathered. From the data presented in this table follows that the molecular structure of the liquid crystal significantly influences the orientational order in the thin oriented layer. The following indications can be made: 1) the order parameter of liquid crystals with the terminal –NCS group is higher than that of analogous compounds with the –CN group (compare the values of $\langle P_2\rangle$ for the liquid crystals **4** and **3**), 2) comparison of the results for the liquid crystals **2** and **3** as well as for the liquid crystals **4** and **5** indicate that the order parameter depends on the kind of the ring (benzene, cyclohexane or bicyclooctane) at the alkyl chain, 3) the bridging group –COO decreases strongly the order parameter (compare the data for the liquid crystal **6** with those for liquid crystals **5** and **7**).

In order to see what is responsible for the low values of $\langle P_2\rangle$ for the liquid crystal **6**, the order parameters were calculated additionally for the band at 1250 cm^{-1}. The results, together with the data for the band at 1591 cm^{-1}, are presented in Figure 8. It is seen that, although the values of $\langle P_2\rangle$ determined for both bands are equal within the experimental uncertainty, the values of $\langle P_4\rangle$ differ significantly: the $\langle P_4\rangle$s calculated from the band intensities at 1250 cm^{-1} are always higher than those obtained from the data for the band at 1591 cm^{-1}. Similar calculations, carried out for the liquid crystals **4**, **5** and **7**, showed the opposite relation between the $\langle P_4\rangle$ values for these two bands. However, the intensity of the band at 1239 cm^{-1} for

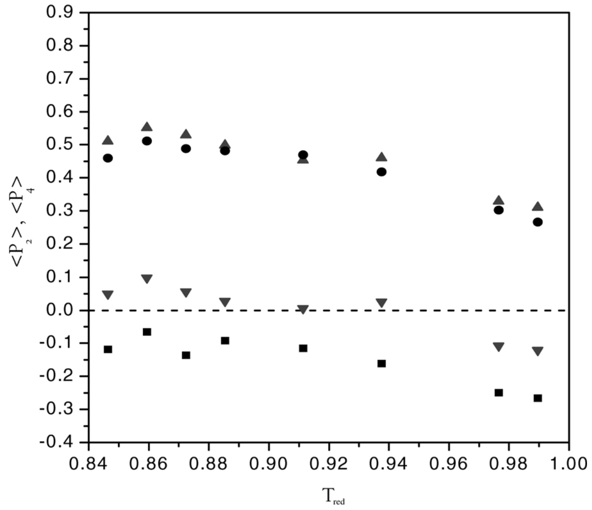


Fig. 8. Dependence of the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ on the reduced temperature $T_{\mathrm{red}} = T/T_{\mathrm{NI}}$ for liquid crystal **6** obtained from Raman scattering measurements for the bands at 1591 cm^{-1} (●, ■) and at 1250 cm^{-1} (▲, ▼).

the liquid crystal **1** is too small to obtain reasonable results.

The $\langle P_4\rangle$ values obtained in our study for all liquid crystals investigated are very low, and in most cases they are negative. These results disagree with theoretical calculations: neither the Maier-Saupe theory of the nematic phase [13], nor that of Humphries et al. [14] predict the negative value of $\langle P_4\rangle$. However, the non-typical behaviour of this parameter was observed by many author studying the orientational order in the nematic phase using Raman scattering spectroscopy [6, 7, 15–17] and the fluorescence depolarization method [2, 18–21]. Many attempts were undertaken [12, 15–17, 22, 23] to explain the observed phenomenon, but the reason of the deviation of the experimentally obtained $\langle P_4\rangle$ values from the theories was not found. Recently Jones et al. [24] measured the Raman intensities of the liquid crystal E7 (Merck) as a function of the angle of rotation around the scattering direction and noticed that the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ are sensitive functions of this angle when it is changed from 0° to 360°. They showed theoretically that, taking this dependence into account, it is possible to obtain positive values of $\langle P_4\rangle$, and that neglecting the small influence of the polarization components α_{xx} and α_{yy} can lead to misinterpretation of the results obtained from measured Raman scattering spectra. This founding requires, however, experimental confirmation.

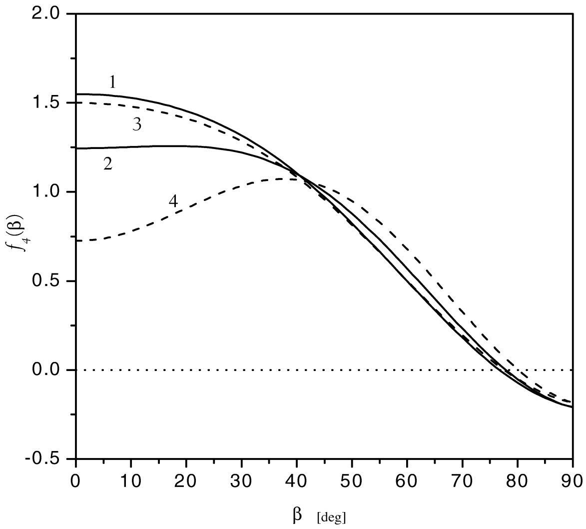


Fig. 9. The distribution function $f_4(\beta)$ for the liquid crystal **1** obtained from Raman scattering measurements (curves 1, 2) and doped with DANS determined from fluorescence measurements (curves 3, 4) [12] at $T_{\mathrm{red}} = 0.94$ (1, 3) and $T_{\mathrm{red}} = 0.98$ (2, 4).

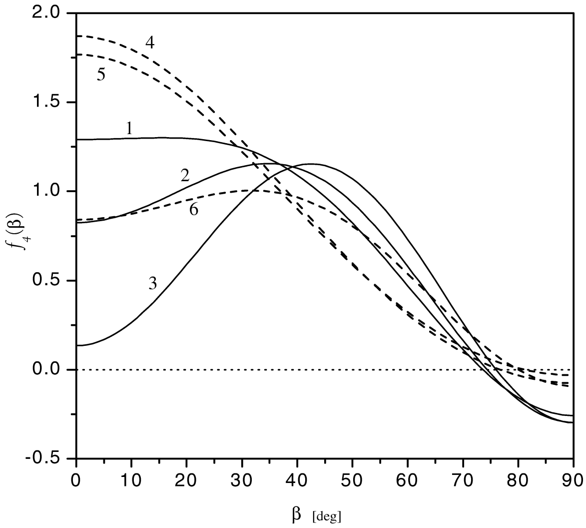


Fig. 10. The distribution function $f_4(\beta)$ for the liquid crystal **6** obtained from Raman scattering measurements for bands at 1591 cm^{-1} (curves 1, 2, 3) and at 1250 cm^{-1} (curves 4, 5, 6) at $T_{\mathrm{red}} = 0.88$ (1, 4), $T_{\mathrm{red}} = 0.94$ (2, 5) and $T_{\mathrm{red}} = 0.98$ (3, 6).

The low values of $\langle P_4\rangle$ influence the shape of the molecular distribution function $f(\beta)$, as illustrated in Figs. 9 and 10. Figure 9 presents $f_4(\beta)$ determined for two reduced temperatures on the basis of $\langle P_2\rangle$ and $\langle P_4\rangle$ calculated from the Raman scattering spectra for the liquid crystal **1** (curves 1 and 2) as well as obtained from fluorescence measurement results for the liquid crystal **1** doped with DANS given in [12] (curves 3 and 4). Comparing the curves 1 and 3 it is seen that the presence of DANS in the liquid crystal matrix has only small influence on the statistical distribution of molecules around the director at low temperatures. This confirms the assumption about the compatibility of some nematogenic liquid crystals and DANS molecules. However, at higher temperatures discrepancies occur, indicating that the assumption $\tau_R \gg \tau_F$ used in calculations of order parameters from fluorescence measurements in [12] cannot be valid in the whole temperature range. Therefore Raman scattering depolarization seems to be a more suitable method than fluorescence spectroscopy to study the orientational behaviour of nematogens.

Figure 10 shows the distribution functions $f_4(\beta)$ for the liquid crystal **6** determined at three reduced temperatures on the basis of $\langle P_2\rangle$ and $\langle P_4\rangle$ values calculated for the bands at 1250 cm^{-1} and 1591 cm^{-1}. The results indicate distinctly that in the case of this liquid crystal it cannot be assumed that the C-C stretch of the aromatic ring of all molecules occurs along the orientation direction. The presence of the –COO bridge causes probably the bending of some molecules in so far that, on average, the principal axis of the aromatic ring vibration giving the band at 1250 cm^{-1} lies more towards the director $\boldsymbol{n}$ than the principal axis of the C-C stretching. Different results obtained for the liquid crystal **6** on the basis of various Raman scattering bands illustrate simultaneously that the distribution function can give more information about the molecular orientation of liquid crystals than the $\langle P_2\rangle$ value alone: the statistical distribution of molecules around the director can be different for various compounds although the order parameter $\langle P_2\rangle$ remains constant.

Acknowledgements

This work was supported by Poznan University of Technology Research Project PB 64-016/2004-BW.

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