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The local field effects in resonance Raman scattering Structural anisotropy studies in some nematic cyanophenyl derivatives

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Different methods for the determination of the local field anisotropy in liquid crystals are analysed and the problems resulting from their application are outlined. One such method, namely that based on the comparison of the polarization of resonance Raman scattering and absorption bands is studied in more detail. The method is applied to determine the structural anisotropy for the 4-*n*-pentyl-(4'-cyanophenyl) derivatives of benzene, cyclohexane and bicyclooctane. To account for the difference between the optical properties of the probe and of the solvent at the wavelength of the scattered light the local field factor is treated theoretically within the framework of an anisotropic continuous dielectric medium.

1. Introduction

Optical and spectroscopic methods have been shown to be powerful tools for studying microscopic properties of liquid crystals. With their help we can obtain information on intrinsic molecular parameters such as linear and hyperpolarizabilities, permanent electrical and magnetic multipole moments, which govern the physical properties of the mesophase and which also characterize the structure and molecular dynamics usually described by the molecular distribution and autocorrelation functions [1-3]. The main advantage of the optical methods is in their relative simplicity and their high precision as experimental tools. But it is a rather difficult task to extract from these data quantitative information on the microscopic parameters.

The main problem arising during the interpretation of all molecular optical and spectroscopic experiments is the connection between the average electric field of the incident or out-coming light wave in the medium and the local electric field acting on the molecules [3]. Compared to the case of isotropic liquids, the macroscopic anisotropy of liquid crystals substantially complicates this connection and we cannot apply here simple Lorentz or Onsager formulae [4]. On the other hand, translational and partial orientational disorder introduce the need of additional statistical averaging of the formulae for tensorial properties developed in the solid state physics. Nevertheless, during the past 20 years many efforts have been made in the theoretical description of the local field anisotropy in a mesophase.

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The first attempt was made by Maier and Saupe [5], who used for this purpose the analogy existing between solid and liquid crystals following Neugebauer's treatment. As a result the authors obtained a relation between the local field and the refractive indices together with the lattice parameters. The same lattice approach, but using the evaluation of the direct lattice sum, has been published by Dunmur [6]. He obtained the well-known formula for the local field factor $\mathbf{f}(\mathbf{E}_{\text{loc}} = \mathbf{fE})$, as a function of the depolarizing tensor \mathbf{L}

$$\mathbf{f} = [\mathbf{I} + \mathbf{L}(\boldsymbol{\varepsilon} - \mathbf{I})], \quad (1.1)$$

where $\boldsymbol{\varepsilon}$ and \mathbf{I} denote the dielectric permittivity and unit tensors, respectively.

The main drawback of these theories is that we have to decide which type of lattice is the most appropriate for the liquid crystal under study. This problem is avoided by those local field theories, which are based on the assumption that the matter surrounding the selected molecule can be treated as a continuous dielectric. These so-called cavity theories appeared as a generalization of the Onsager and Lorentz models for isotropic liquids. De Jeu and Bordewijk [7] have taken into account the macroscopic anisotropy of the mesophase and the anisotropy of the molecular polarizability and shape. Segre [8] has also considered the effect of non-coincidence of the principal axes of the ellipsoidal cavity, occupied by a molecule, with those of dielectric permittivity tensor. The final expressions obtained by these theories are similar to the formulae derived within the lattice formalism, with the only difference that the lattice parameters of the latter model are replaced by the cavity parameters of the cavity model. Therefore, we shall adopt equation (1.1) as the basic formula describing the relation between the local field and the material parameters. The only crucial point of the cavity theories concerns the way they relate the cavity parameters to those of the mesogenic molecules. In reality this cavity does not exist and so we cannot measure its dimensions. The answer to this question may be given within the molecular statistical approach. In [9] the anisotropy of the \mathbf{L} tensor in equation (1.1) has been expressed via the anisotropy of the pair distribution function in the approximation of the absence of short range orientational correlations of the neighbouring molecules and in [10] it has been shown that these correlations can be treated as corrections to the molecular polarizability in the Lorentz-Lorenz equation without changing the form of the expression for the local field. But in this case the problem of the determination of the local field or depolarizing factor anisotropy is replaced by that of the measurement of the pair distribution function, which is not easily available. Therefore, it is worthwhile to search for experimental methods which allow us to determine the local field anisotropy more directly.

Up to now different kinds of such experimental methods have been developed. For uniaxial liquid-crystalline systems (nematic, smectic A, cholesteric), neglecting short range effects, the local field tensor \mathbf{f} also possesses a symmetry axis and therefore only two of its components are independent: f_{zz} and f_{xx} for example, if z is the symmetry axis, or by using rotational invariants,

$$\bar{f} = \frac{1}{3} \text{Tr}(\mathbf{f}) \quad \text{and} \quad \Delta f = \frac{1}{3}(f_{zz} - f_{xx}). \quad (1.2)$$

If f is described by equation (1.1) then the problem is even simpler: the components of $\boldsymbol{\varepsilon}$ can be taken from dielectric or refractometric measurements and, because of the definition of \mathbf{L} , $\text{Tr}(\mathbf{L}) = 1$, only one parameter ΔL should be measured. ΔL is defined in a similar way to equation (1.2) and characterizes the structural anisotropy of the material.

Different kinds of experiments which can be used to determine ΔL are reviewed in the next section. In the third section we develop the theoretical background for an improved treatment of resonance Raman scattering experimental data and the results obtained for different systems are discussed in the fourth section. Finally a short conclusion is made on possible applications of the approach developed.

2. Analysis of experimental methods

All of the experimental methods for the determination of the local field anisotropy are based on the measurement of the local field effect on physical parameters of a probe molecule. First, we discuss such methods in which the probe molecules are the mesogenic molecules themselves.

The first attempt to determine the structural anisotropy and to account in this way for the effect of the local field anisotropy on the refractive indices in the mesophase was made in [5]. For this purpose it was proposed to use the persistence of the average molecular polarizability during the phase transition. Consequently, deriving the polarizability from the Lorentz–Lorenz equation (while using equation (1.1) for the local field factor in the mesophase) gives

$$\frac{1}{\rho_{lc}} \left[\frac{\epsilon_{zz} - 1}{\epsilon_{zz} + 2 + 6\Delta L(\epsilon_{zz} - 1)} + 2 \frac{\epsilon_{xx} - 1}{\epsilon_{xx} + 2 - 3\Delta L(\epsilon_{xx} - 1)} \right] = \frac{3}{\rho_{is}} \frac{\epsilon - 1}{\epsilon + 2}. \quad (2.1)$$

From this equation the structural anisotropy can be determined (ρ is the density).

A similar approach, but based on absorption measurements has been proposed in [11]. Taking into consideration the Kramers–Kronig relation it is clear that for absorption coefficient measurements we can rely on the constancy of the absolute value of molecular transition dipole moment. While dealing with electron absorption spectra both approaches are equivalent and both suffer from the neglect of the conformational flexibility of mesogenic molecules and the molecular interaction contribution, both of which change the molecular properties during the phase transition. They become evident in the unpredictable variations of the structural anisotropy values for different substances as can be found in various publications devoted to the refractometric method. Perhaps, even for vibrational bands this effect has been recognized in [12] because there it has been found that ΔL depends not only on the structural, but also on the optical anisotropy of the mesophase.

There has also been an attempt to use the wavelength dependence of refractive indices for the local field anisotropy determination [13]. The main idea is to find the point in the spectral dependence of the transverse component of the molecular polarizability tensor where its dispersion becomes abnormal due to the neglect of the local field anisotropy. However the occurrence of this inversion of the sign of the dispersion coefficient tells us nothing about how to determine ΔL .

Another group of experimental methods is only applicable for the determination of the local field acting on probe molecules, but not on the mesogenic molecules themselves. It is clear from the formula for the absorption dichroic ratio

$$\frac{D_z}{D_x} = \frac{n_x f_{zz}^2}{n_z f_{xx}^2} \frac{2\bar{P}_2 + 1}{1 - \bar{P}_2}, \quad (2.2)$$

that if a spherical molecule dissolved in a liquid-crystalline matrix possesses absorption dichroism then the only reason for this is the local field anisotropy [1]. In equation (2.2) \bar{P}_2 is the second rank orientational order parameter for axially symmetric absorbers

and D_i is the absorption coefficient for light polarized along axis i . Tetrahedral symmetry is enough to cause \bar{P}_2 of the probe molecules to vanish. Of course, within this method only rigid molecules can be used. In other cases the absorption dichroism can be due to the distortion of molecular symmetry [14], or due to the formation of quasi-chemical bonds with the solvent molecules [15]. But even in an ideal case we are probing by this method the local field, acting on the spherical molecule, which can differ from the field acting on those of the mesogen.

With the aim of studying the dependence of the local field anisotropy on the probing molecule shape a method based on resonance Raman measurements has been proposed [16]. As is clear, if absorption of light and resonance Raman scattering processes occur due to the transition between the same electronic levels of the molecule, then their depolarization is determined by the same orientational and local field parameters. Thus comparing

$$\left. \begin{aligned} R_1 &= \frac{I_{xz}}{I_{zz}} = \frac{(n_g + n_z)^2 f_{xx}^2}{(n_g + n_x)^2 f_{zz}^2} \frac{7 + 5\langle P_2 \rangle - 12\langle P_4 \rangle}{21 + 60\langle P_2 \rangle + 24\langle P_4 \rangle}, \\ R_2 &= \frac{I_{zx}}{I_{xx}} = \frac{(n_g + n_x)^2 f_{zz}^2}{(n_g + n_z)^2 f_{xx}^2} \frac{7 + 5\langle P_2 \rangle - 12\langle P_4 \rangle}{21 - 30\langle P_2 \rangle + 9\langle P_4 \rangle}, \end{aligned} \right\} \quad (2.3)$$

with equation (2.2) we can derive the local field anisotropy or ΔL . Here n_g is the refractive index of the glass cell. In general, in these kinds of experiments not only Raman scattering, but any two-photon process can be used. We shall not discuss here the requirements for probe molecules in this method. This information and some experimental results can be found in [17]. But it is obvious, that all processes with light absorption and emission in this method inevitably occur in the vicinity of the absorption bands of the dye dissolved in the liquid-crystalline solvent. This means, that we can no longer neglect the difference between the optical parameters of the probe and of the solvent. Consequently, in the next section we develop the theoretical background for the local field treatment during near-resonance processes and with its help we shall analyse the experimental data. We believe that these results will be helpful not only in the field of resonance Raman scattering, but in all cases when optical phenomena in liquid-crystalline media with the strongly different probe molecules are dealt with.

3. Theoretical background

The theoretical model described in this section is based on the following assumptions. The liquid-crystalline solvent is treated as a uniform anisotropic dielectric with an electric permittivity tensor ϵ_1 . Dye molecules, represented by uniform ellipsoids with an anisotropic dielectric permittivity ϵ_2 , are embedded into ellipsoidal cavities in this dielectric. In the general case, the principal axes of ϵ_1 and ϵ_2 are non-coincident, and the orientation of the ϵ_2 axes for different dye molecules is statistically distributed. For nematics, which are of the most interest to us, the ϵ_1 tensor is axially symmetric. We shall confine ourselves to the treatment of axially symmetric molecules or to such cases where their asymmetry can be neglected (for example due to molecular elongation). In this case the singlet orientational distribution function for the dye molecules can be expanded in a set of Legendre polynomials with the coefficients P_i being the conventional order parameters. The concentration of dye is expected to be so small that we can neglect its influence on the macroscopic dielectric properties of the system. Permanent molecular moments, as well as retardation effects are neglected because we are interested in the phenomena which occur at the frequency of light in

systems lacking spatial dispersion. It is obvious that within such a model we neglect all short range features of the molecular arrangement in real liquid crystals. Therefore the cavity model cannot be reliable for estimating a parameter such as ΔL , which is dependent on the pair distribution function, from the molecular model. Nevertheless, it has been proved [8] to give the correct analytical expression for the relation between the local field and structural anisotropy [9] and we hope it can be useful for treating the local field phenomena in liquid-crystalline mixtures.

For the externally applied macroscopic electric field \mathbf{E} , which is homogenous far from the cavity, the cavity field, following Bordewijk and Segre [4, 8] can be written as

$$\mathbf{E}_c = \boldsymbol{\varepsilon}_1^{1/2} \{ \boldsymbol{\varepsilon}_1 - \mathbf{L}'(\boldsymbol{\varepsilon}_1 - \mathbf{I}) \}^{-1} \boldsymbol{\varepsilon}_1^{1/2} \mathbf{E}, \quad (3.1)$$

where \mathbf{L}' is the depolarizing tensor of the cavity obtained after changing from a cartesian coordinate system with axes along the principal axes of the tensor $\boldsymbol{\varepsilon}_1$, to a new coordinate system given by

$$x'_i = (\varepsilon_{1,ii})^{-1/2} x_i. \quad (3.2)$$

Even the orientation of \mathbf{L}' differs from that of the conventional depolarizing tensor of this cavity which is related to its semi-axes a_i by

$$L_{ii} = \frac{a_1 a_2 a_3}{2} \int_0^\infty dv [(v + a_1^2)(v + a_2^2)(v + a_3^2)]^{-1/2} (v + a_i^2)^{-1}. \quad (3.3)$$

The dye molecule, being placed in the cavity, due to its polarization modifies this cavity field by the reaction field through the polarization of the environment. The resulting internal field \mathbf{E}_i induces in the ellipsoid of dielectric permittivity $\boldsymbol{\varepsilon}_2$ embedded in the dielectric medium of permittivity $\boldsymbol{\varepsilon}_1$ the dipole moment

$$\mathbf{m} = (V/4\pi)(\boldsymbol{\varepsilon}_{2,i} - \mathbf{I}) \boldsymbol{\varepsilon}_1^{1/2} \{ \boldsymbol{\varepsilon}_1 - \mathbf{L}'(\boldsymbol{\varepsilon}_1 - \boldsymbol{\varepsilon}_{2,i}) \}^{-1} \boldsymbol{\varepsilon}_1^{1/2} \mathbf{E}. \quad (3.4)$$

The additional subscript i in $\boldsymbol{\varepsilon}_2$ indicates that this expression considers only one component of the dipole moment, which is induced by the local field component parallel to one of the principal axes of the tensor $\boldsymbol{\varepsilon}_2$. However, polarization occurs due to the fact that the dye molecule possesses a polarizability and for the component of the anisotropic dielectric ellipsoid polarizability parallel to one of the principal axes of the tensor $\boldsymbol{\varepsilon}_2$ we have

$$\boldsymbol{\alpha} = (V/4\pi)(\boldsymbol{\varepsilon}_{2,i} - \mathbf{I}) \{ \mathbf{I} + \mathbf{L}(\boldsymbol{\varepsilon}_{2,i} - \mathbf{I}) \}^{-1}. \quad (3.5)$$

Thus, inserting equations (3.4) and (3.5) into $\mathbf{m} = \boldsymbol{\alpha} \mathbf{E}_{loc}$ we find

$$\mathbf{E}_{loc} = [\mathbf{I} + \mathbf{L}(\boldsymbol{\varepsilon}_{2,i} - \mathbf{I})] \boldsymbol{\varepsilon}_1^{1/2} \{ \boldsymbol{\varepsilon}_1 - \mathbf{L}'(\boldsymbol{\varepsilon}_1 - \boldsymbol{\varepsilon}_{2,i}) \}^{-1} \boldsymbol{\varepsilon}_1^{1/2} \mathbf{E}. \quad (3.6)$$

The total local field is obtained by summing the contributions of linearly independent components. It is obvious, that in the general case, when the principal axes of tensors $\boldsymbol{\varepsilon}_1$ and $\boldsymbol{\varepsilon}_2$ do not coincide, averaging of equation (3.6) over the equilibrium distribution of the dye molecules is tedious and gives us little information, because the cross-terms of the general form $\langle \mathbf{L}\boldsymbol{\varepsilon} \rangle$ appear in it and it is impossible to evaluate them or to obtain any experimental information about them. On the other hand it is impossible to compare this equation with equation (1.1). Only in the isotropic case is the solution trivial and for a spherical cavity, for example, equation (3.6) reduces to the result well-known from electrostatics

$$\mathbf{E}_{loc} = \frac{\varepsilon_1(\varepsilon_2 + 2)}{2\varepsilon_1 + \varepsilon_2} \mathbf{E}. \quad (3.7)$$

This expression is a very poor model for the treatment of liquid-crystalline behaviour, and that is why we prefer to proceed with the less rough approximation originally made by Segre [8]: we adopt the idea of the uniformity of the system and make algebraic manipulations in order to transfer from formulae dependent on the components of ϵ_2 to the tensorial representation [8]. Thus, inserting equations (3.1), (3.4) and (3.5) into

$$\mathbf{m} = \alpha(\mathbf{E} + \mathbf{R}) = \alpha(\mathbf{E}_c + \mathbf{f}\mathbf{m}), \quad (3.8)$$

we obtain the expression for the reaction field \mathbf{R} . Taking into account the fact that the local field is the sum of the cavity and reaction fields we can relate it to the average field in the medium:

$$\mathbf{E}_{\text{loc}} = \mathbf{E} + \mathbf{N}^{-1}\mathbf{f}\mathbf{P} = \{\mathbf{I} + \mathbf{L}_{\text{ef}}(\epsilon_1 - \mathbf{I})\}\mathbf{E}, \quad (3.9)$$

where the polarization \mathbf{P} due to the uniformity of the system is

$$\mathbf{P} = \frac{(\epsilon - 1)}{4\pi} \mathbf{E}, \quad (3.10)$$

and

$$\mathbf{L}_{\text{ef}} = \mathbf{L}(\epsilon_2 - \mathbf{I})(\epsilon_1 - \mathbf{I})^{-1} + \epsilon_1^{1/2}\{\epsilon_1 - \mathbf{L}'(\epsilon_1 - \mathbf{I})\}^{-1}\mathbf{L}'(\epsilon_1 - \epsilon_2)\epsilon_1^{-1/2}(\epsilon_1 - \mathbf{I})^{-1}.$$

In deriving equations (3.9) and (3.10) it was assumed that the volume of the cavity is the volume occupied by one molecule.

After averaging equation (3.9) over the equilibrium distribution of the dye molecules we obtain the local field value, which is observed in optical experiments. Because the laboratory coordinate system is fixed to the principal axes of the liquid crystal dielectric permittivity, this is equivalent to averaging \mathbf{L}_{ef} . As seen from equation (3.8), in the general case the local field, acting on an impurity molecule in the mesophase depends not only on the properties of the solvent, but also on the structural (\mathbf{L}) and optical (ϵ_2) properties of the impurity and such an averaging procedure is not straightforward. Only when $\epsilon_1 = \epsilon_2$ does $\mathbf{L}_{\text{ef}} = \mathbf{L}$, which means, that the local fields acting on the impurity and solvent molecules are similar only when both their optical properties and the geometrical parameters are identical. In all other cases the difference between the structural anisotropy for the impurity and solvent molecule, which is approximately proportional to the difference of their optical parameters, should be taken into account.

This result is illustrated by the following example. For typical liquid crystals $\Delta\epsilon_1 = 0.5$, and $\bar{\epsilon}_1 = 2.4$ in the visible range. In the experiments devoted to the determination of the local field anisotropy the probe molecules can have either almost the same optical parameters and shapes, or they can be isotropic. For simplicity in equation (3.10) we can assume L and ϵ to be statistically independent. The averaging over the orientational distribution function gives

$$L_{\text{ef}ii} = L_{ii} \frac{(\epsilon_{2ii} - 1)}{(\epsilon_{1ii} - 1)} + \frac{L'_{ii}(\epsilon_{1ii} - \epsilon_{2ii})}{[\epsilon_{1ii} - L'_{ii}(\epsilon_{1ii} - 1)](\epsilon_{1ii} - 1)}, \quad (3.11)$$

for the components and due to the axial symmetry of nematics equation (3.3) has been transformed to

$$L_{zz} = \frac{1 - e^2}{2e^3} \left[\ln \frac{1 + e}{1 - e} - 2e \right] \quad \text{with} \quad e^2 = 1 - (w/l)^2, \quad (3.12)$$

where L_{zz} is now determined only by the width-to-length ratio of the model cavity. In figure 1 we have plotted the dependence of the structural anisotropy ΔL_{ef} on this ratio

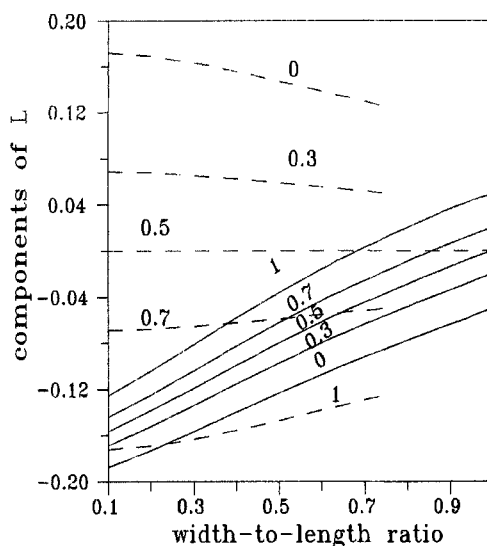


Figure 1. Calculated values of $\text{Tr}(\mathbf{L}_{\text{ef}}) - 1$ (dashed curves) and ΔL_{ef} (solid curves) versus width-to-length ratio of the model cavity according to equation (3.11). The numbers are the values of $\Delta\epsilon_2$, while $\Delta\epsilon_1 = 0.5$, $\bar{\epsilon}_1 = \bar{\epsilon}_2 = 2.4$.

for different values $\Delta\epsilon_2$ (for convenience we chose $\bar{\epsilon}_2 = 2.4$. The values at $\Delta\epsilon_2 = 0$ and the right hand side of the figure correspond to spherical probe molecules. We cannot show directly the corresponding point on the horizontal axis, because the model geometrical parameters of the cavity depend on the geometry of both the probe and the matrix molecules. But even for spherical probe molecules with $\Delta\epsilon_2 = 0$ and a width-to-length ratio equal to 1, it is obvious that $\Delta L_{\text{ef}} \neq 0$. In this case, according to the continuous dielectric model its value is dependent on the dielectric properties of the matrix. It is seen from this figure, that ΔL_{ef} can differ substantially from ΔL (they coincide in our case only at $\Delta\epsilon_2 = 0.5$) already for realistic parameters of the probe molecule. In the case, when the optical parameters of the probe molecule differ from that of the solvent, the effective structural anisotropy starts to depend not only on the molecular geometry, but also on all of the optical parameters of the system. An unsatisfactory result in this case is that $\text{Tr}(\mathbf{L}_{\text{ef}}) \neq 1$ (dashed curves in figure 1). Therefore, during the treatment of the experimental data it is recommended to take care of such effects.

4. Results and discussion

Phenomena resembling the effect described in the previous section have been observed in [17], where resonance Raman depolarization ratios have been measured for several dyes in a binary nematic mixture. In fact, as it is seen from figures 8 and 10 of [17] the values of the structural anisotropy parameter determined from these measurements are strongly dependent not only on the molecular shape, but also on the range of excitation of the scattering. On the one hand for such substances as β -carotene and DMANAB, which possess very different shapes, very similar values of ΔL have been obtained. On the other hand, for C10, the molecules of which have geometrical parameters more or less similar to those of β -carotene, while Raman scattering in it has been excited almost with off-resonance conditions, much larger values of the structural

anisotropy have been obtained. In the present work we have chosen for the experimental study of local field effects 4-dimethylamino-4'-nitroazobenzene (DMANAB), which has sufficiently rigid molecules, but rather low values of ΔL and a negligible temperature dependence.

The experimental set-up and methods are thoroughly described in [17]. All of the measurements have been performed for DMANAB dissolved in three different nematic substances with a concentration lower than 0.2 wt%: 4-*n*-pentyl-4'-cyanobiphenyl (5CB), 4-*n*-pentyl-(4'-cyanophenyl)-cyclohexane (5PCH) and 4-*n*-pentyl-(4'-cyanophenyl)-bicyclooctane (5BCO). These compounds differ only in one cyclic fragment, but they have very different optical and mesomorphic properties. DMANAB has a sufficiently strong absorption band in the visible range (see figure 2) with the transition dipole moment parallel to the long molecular axis; the temperature dependencies for its dichroic ratio are presented in figure 3. The similarity of the dichroic ratios in 5CB and 5PCH is surprising if we remember the difference in their refractive indices (see figure 4). In order to clarify the origin of such different refractive indices which can be either in dissimilar molecular properties, or in different orientational statistics, it is useful to compare the orientational properties of DMANAB in these matrices. This can be easily done on the basis of absorption dichroism measurements, but we have to choose an adequate model for the local field correction. These can be, for example, the isotropic local field approximation, when $f_{zz} = f_{xx}$, or the model proposed by Segre [8]

$$\Delta L = \bar{P}_2 \Delta L_{\text{mol}}, \quad (4.1)$$

where ΔL_{mol} is determined by the molecular shape and can be calculated with the help of equations (3.3) or (3.12). But, as we can see from figure 5, depending on the local field model chosen quantitative differences in \bar{P}_2 result and even qualitative conclusions are different. While using the Segre model for the local field we find the result, that the orientational ordering of DMANAB in 5CB and 5PCH is similar, whereas with an isotropic local field model we come to the opposite conclusion.

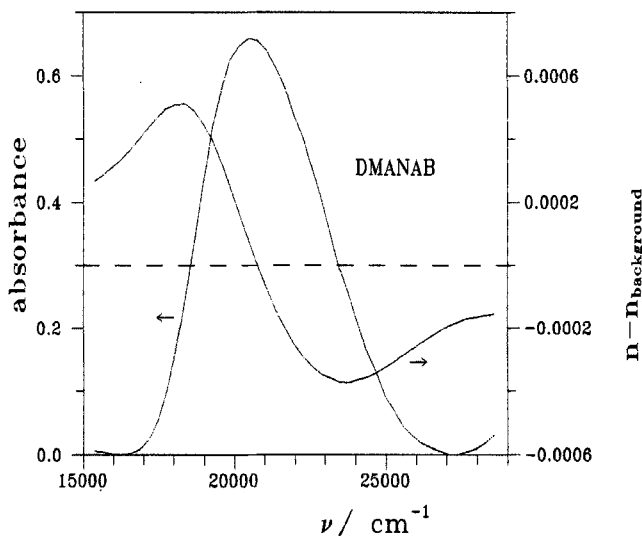


Figure 2. Absorption spectrum and dispersion of the refractive index for 0.088 wt% of DMANAB in 5CB at 40°C (the cell thickness was 32 μm).

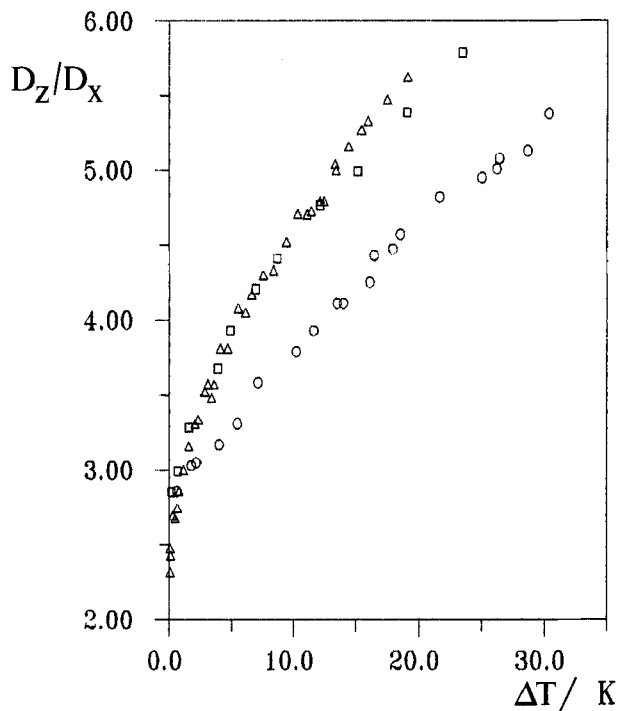


Figure 3. The temperature dependencies of the dichroic ratio D_z/D_x for DMANAB in different liquid-crystalline solvents. \circ , 5BCO; \square , 5PCH; \triangle , 5CB. $\Delta T = T_{NI} - T$.

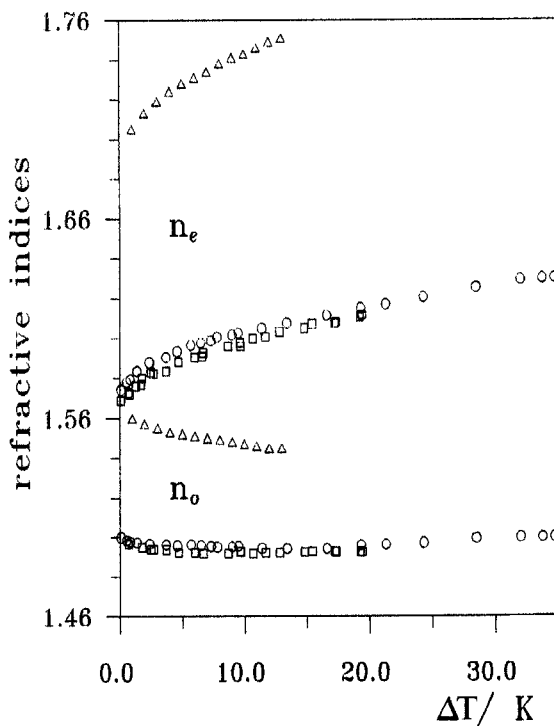


Figure 4. The temperature dependencies of the ordinary (n_o) and extraordinary (n_e) refractive indices of different liquid-crystalline solvents for $\lambda = 488$ nm (the wavelength of the absorption maximum for DMANAB). \circ , 5BCO; \square , 5PCH; \triangle , 5CB. $\Delta T = T_{NI} - T$.

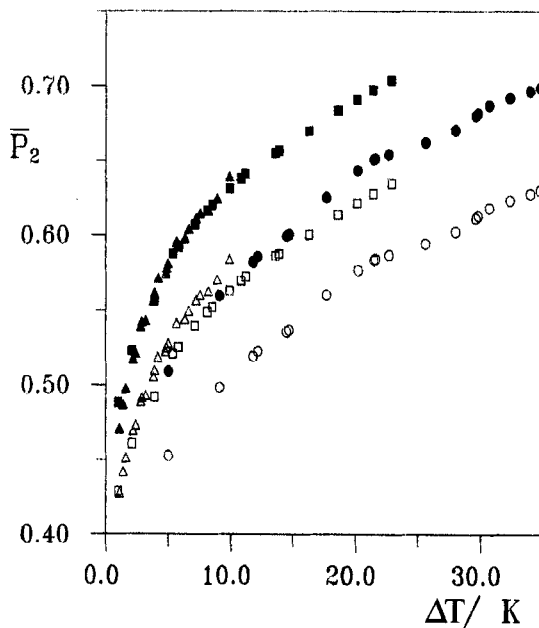


Figure 5. The orientational order parameter \bar{P}_2 for DMANAB in different nematic solvents, determined from absorption dichroism measurements within the isotropic local field approximation (open symbols) and with the Segre model [8] (filled symbols). In the latter case we used $\Delta L_{\text{mol}} = -0.112$, determined from the molecular structure of DMANAB. ●, ○, 5BCO; ■, □, 5PCH; ▲, △, 5CB. $\Delta T = T_{\text{NI}} - T$.

The importance of the local field correction, or more generally, of the contribution of the molecular interactions to the spectral properties of the mesophase can be seen not only from this particular example. Also we can compare the results obtained from absorption measurements with that from resonance Raman scattering. Another orientational order parameter \bar{P}_4 , which is necessary for the evaluation of Raman depolarization ratios can be taken from the relation

$$\ln(S_4)/\ln(S_2) = 10/3, \quad (4.2)$$

derived within the framework of the Faber model for liquid-crystalline ordering [18]. In the present experiments resonance Raman scattering was excited with 514 nm laser light and the average measured depolarization ratios for 1337 and 1393 cm^{-1} bands are presented in figure 6. In figure 7 those for the solution in 5PCH are compared with the values calculated with \bar{P}_2 taken from absorption measurements corrected for the local field according to the Segre model. Similar results have also been obtained for other solutions. As we see from figure 7, neglecting rather high order parameters (see figure 5) the calculated ratios are substantially larger than the experimental values. This means, that either \bar{P}_4 is very large, or (see equation (2.3)) that ratio the f_{zz}^2/f_{xx}^2 is not the same as in the case of absorption.

In order to account for the influence of the probe molecule parameters on the local field acting on it (see § 3), we should find some information on the dielectric permittivity (refractive indices) of the probe compound, which is not a trivial task for strongly absorbing polycrystalline substances such as dyes. In our case the dispersion of the refractive index of DMANAB within the absorption range and in the vicinity of it can

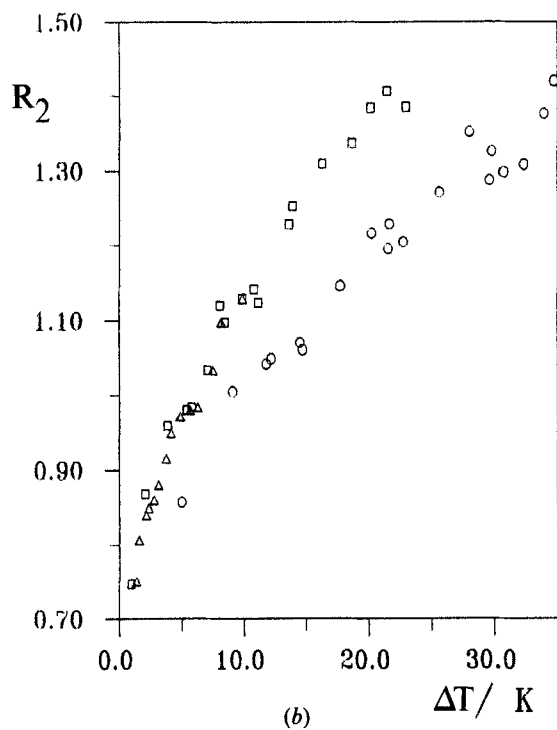
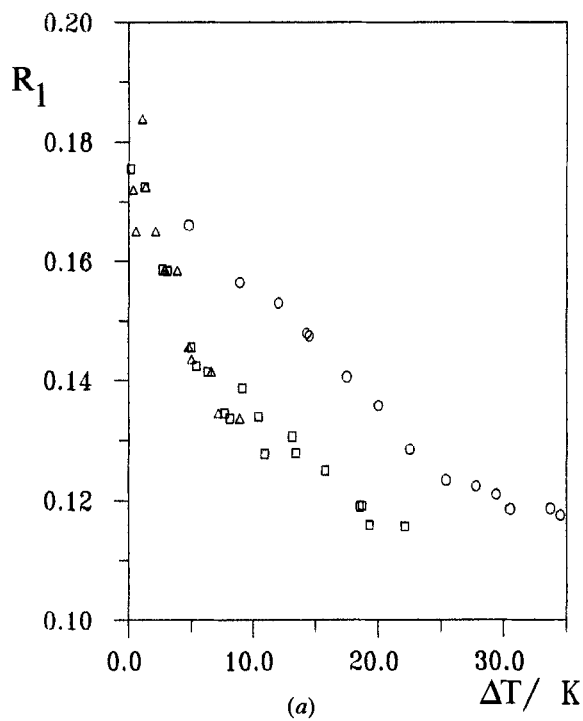


Figure 6. The temperature dependence of the resonance Raman depolarization ratios (a) R_1 and (b) R_2 for DMANAB in different liquid-crystalline solvents. \circ , 5BCO; \square , 5PCH; \triangle , 5CB. $\Delta T = T_{NI} - T$.

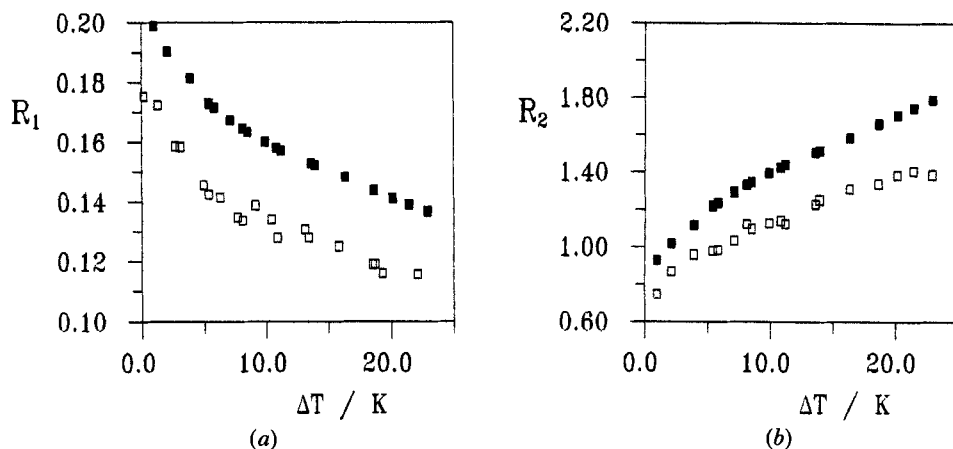


Figure 7. The temperature dependence of resonance Raman depolarization ratio (a) R_1 and (b) R_2 for DMANAB in 5PCH obtained from direct experimental measurements and evaluated from absorption dichroism measurements with the local field correction according to the Segre model. \square , experiment; \blacksquare , absorption dichroism. $\Delta T = T_{NI} - T$.

be derived from the spectral dependence of the absorbance with the Kramers–Kronig relation (see figure 2). Its absolute value can be calculated from the molar refraction of the dye in solution in the range of transparency. For DMANAB, for example, this can be done at 600 nm and for the extrapolation in the range of absorption we can neglect the dispersion of the background refractive index because the absorption band of DMANAB is well separated. It is seen from figure 2 that the dispersion of the refractive index is noticeable even for such dilute solutions. For the case of absorption dichroism measurements, when we usually deal with the peak intensities of well separated bands this dispersion can be neglected. But in resonance Raman scattering we usually deal with frequencies at the lower edge of the absorption band, where the contribution to the refractive index is largest. From the concentration dependence we conclude that in our case (the frequency of resonance Raman scattering is approximately $18\,000\text{ cm}^{-1}$) the dielectric anisotropy of the totally orientationally ordered DMANAB sample would be 1.7. This value is much higher than 0.45, which is characteristic for 5PCH at the same frequency, and as it is clear from figure 1 that the effective structural anisotropy for the dye molecules and the local field in the case of resonance Raman scattering will be substantially different from that observed in absorption.

To evaluate this difference between the effective structural anisotropy and the conventional one, and to determine the local field parameters we have to solve the problem of averaging equation (3.10). In this equation the structural and optical parameters are coupled to each other and to perform the averaging we should make a reasonable approximation concerning the connection between these parameters. Our procedure was as follows; we estimated the shape of the cavity from the molecular dimensions and with equations (3.12) and (4.1) we have calculated the depolarizing factor (the order parameters were derived from absorption dichroism measurements with the local field correction according to equation (1.1)). Using the effective value of L (see equation (3.11)) the local field factors for Raman scattering were estimated with equation (3.12). The order parameters were determined from the experimental Raman depolarization ratios. These order parameters were used for the recalculation of the

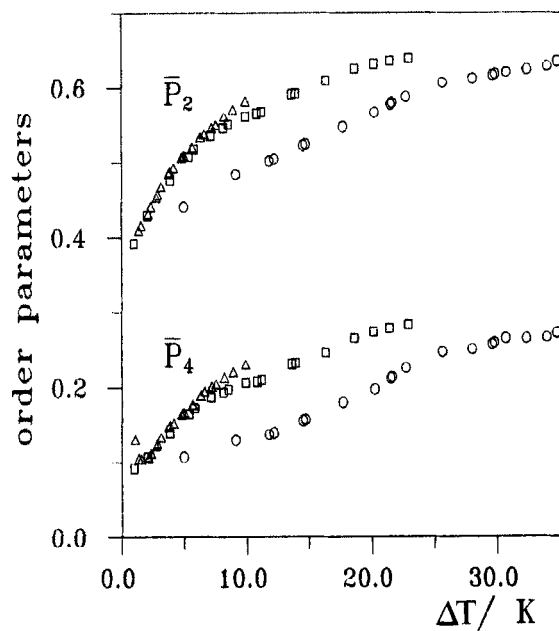


Figure 8. The temperature dependence of the orientational order parameters for DMANAB in different liquid-crystalline solvents determined from resonance Raman and absorption polarization studies. \circ , 5BCO; \square , 5PCH; \triangle , 5CB. $\Delta T = T_{NI} - T$.

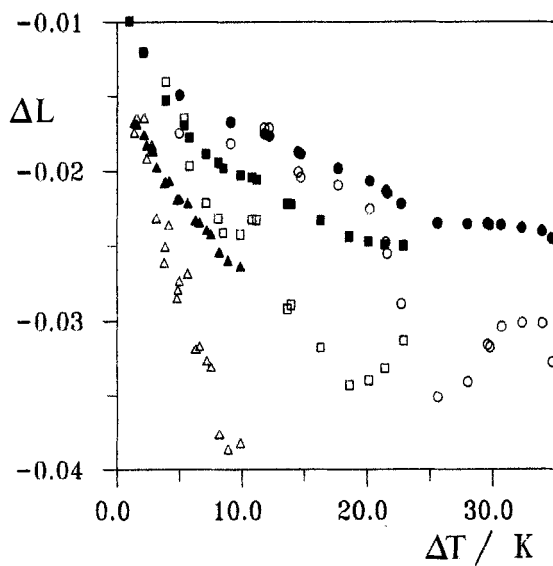


Figure 9. The temperature dependence of the structural anisotropy ΔL (open symbols) and of its effective values ΔL_{eff} (filled symbols) for DMANAB in different liquid-crystalline solvents determined from resonance Raman and absorption polarization studies. \bullet , \circ , 5BCO; \blacksquare , \square , 5PCH; \blacktriangle , \triangle , 5CB. $\Delta T = T_{NI} - T$.

depolarizing factor of the model cavity and this procedure was repeated in an iterative manner until a convergence had been achieved. The obtained orientational order parameters and structural anisotropy values are presented in figures 8 and 9.

As expected, the difference between the structural anisotropy and its effective value, which contributes to the local field in resonance Raman scattering, is sufficiently large. They also differ for different liquid-crystalline solvents. For the case of 5CB and 5PCH the origin of this discrepancy does not come from different \bar{P}_2 parameters (it is seen from figure 8 that they are very similar), but is due to the fact that the structural anisotropy is not single molecule property. From the molecular statistical point of view it is determined by the anisotropy of the pair distribution function [9]

$$\Delta L = \frac{1}{4\pi} \int \frac{d\mathbf{r}}{|\mathbf{r}|} g_2(\mathbf{r}) P_2[\cos(\mathbf{r}, \mathbf{n})], \quad (4.3)$$

and, of course, the solvent structure contributes to it. Therefore, when going from the benzene fragment to cyclohexane and further to bicyclooctane the thickness of the mesogenic molecules increases and the anisotropy of the pair distribution function is decreased in the sequence 5CB–5PCH–5BCO. This behaviour becomes apparent in the results shown in figure 9. One more feature should be emphasized: because of the conformational flexibility of the liquid-crystalline molecules, the obvious deviations of their shapes from being ellipsoidal and because of the non-uniformity of the intramolecular distribution of electron density the values of the experimentally determined structural anisotropy are substantially different from those, which can be estimated from molecular models. This conclusion is especially important for the various applications of the local field methods to treat dielectric and optical phenomena in liquid crystals.

5. Conclusions

Resonance Raman scattering and absorption polarization measurements have proved to be a very useful tool with which to study orientational statistics in the mesophase. The experiments can give information not only on the single particle distribution function (i.e. orientational order parameters), but also provide some insight into the peculiarities of the molecular arrangement (the structural anisotropy is one of the coefficients of the pair distribution function expansion in a basis set of Wigner rotation matrices). But the interpretation of the experimental data are very sensitive to the contribution of the molecular interactions, the so-called local field effects. The approach developed in this paper within the dielectric cavity concept helps to account for the local field effects in those cases where the probe molecule differs from the solvent molecules. The potential of this approach is demonstrated by results from resonance Raman scattering measurements. The method presented here should also be useful for treating the absorption dichroism of impurities with overlapping bands, when the use of the so-called background refractive index is not justified. It should be also possible to analyse within the framework of this approach the behaviour of the absorption dichroism for spherical molecules in liquid-crystalline solvents.

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