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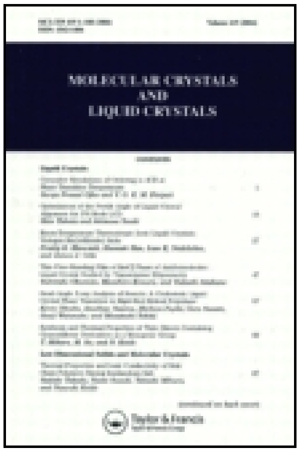

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Local Field Determination by Resonance Raman Scattering

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LOCAL FIELD DETERMINATION BY RESONANCE RAMAN SCATTERING

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Abstract The results of the local field anisotropy determination by the combination of resonance Raman scattering and absorption experiments are presented.

INTRODUCTION

Resonance Raman scattering (RRS) of light, as well as non-resonance spontaneous Raman scattering, has been shown to be very useful in the studies of orientational ordering in liquid crystals[1]. While in the RRS method one can deal only with the dye molecules, this method is more appealing because of the more concrete form of the Raman tensor (tensor of the polarizability derivatives with respect to the normal coordinate of the vibration). This fact enabled the authors of [1] to determine the order parameters P_2 and P_4 for beta-carotene molecules in MBBA matrix from RRS measurements.

THE BACKGROUND OF THE METHOD

In a more recent applications of the RRS method it has been found that P_2 values obtained by this

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method [2] differ from the order parameters determined from the absorption dichroism studies, while in both cases the transition under investigation is between the same molecular levels. It should be noted that in [1,2] the difference of the local field from the field of the incident light wave has not been taken into account.

As all other liquid crystalline properties the local field is anisotropic. Approximating mesogenic molecule by the polarizability, placed in the ellipsoidal cavity in the anisotropic dielectric, Segre[3] obtained following equations connecting the local and averaged fields:

$$\begin{aligned} \underline{F}_x &= \frac{1}{3}\left(n_x^2 + 2 + P_2(m_{zz} - m_{xx})(n_x^2 - 1)\right)\underline{E}_x = f_{xx}\underline{E}_x \\ \underline{F}_z &= \frac{1}{3}\left(n_z^2 + 2 - 2P_2(m_{zz} - m_{xx})(n_z^2 - 1)\right)\underline{E}_z = f_{zz}\underline{E}_z \end{aligned} \qquad (1)$$

where n_i are the refractive indices and z-axis is directed along the optical axis of the dielectric; m_{ii} - depolarizing factor, dependent on the shape of the cavity:

$$m_{zz} = \frac{l^2 - 1}{2l^3}\left(\ln\frac{1+l}{1-l} - 2l\right), \quad l = \sqrt{1 - \left(\frac{a}{c}\right)^2}, \qquad (2)$$

where a and c are the semi-axes of the cavity. Taking into account the local field anisotropy RRS depolarization ratios and dichroic ratios for the absorption bands can be expressed in the form

$$R_1 = \frac{I_{xz}}{I_{zz}} = \frac{f_{xx}^2}{f_{zz}^2}\,\frac{1}{3}\,\frac{7 + 5P_2 - 12P_4}{7 + 20P_2 + 8P_4}, \qquad (3)$$

$$R_2 = \frac{I_{zx}}{I_{xx}} = \frac{f_{zz}^2}{f_{xx}^2}\,\frac{1}{3}\,\frac{7+5P_2-12P_4}{7-10P_2+3P_4}\ , \tag{4}$$

$$N = \frac{n_z}{n_x}\,\frac{f_{zz}^2}{f_{xx}^2}\,\frac{1+2P_2}{1-P_2}\ . \tag{5}$$

The first/second subscript behind I stands for the direction of the polarization of the scattered/incident light wave. As it is seen from relations (3)-(5), in order to determine P_2 and P_4 only from RRS or only from dichroism measurements one is needed in independently measured f_{ii}. There are many models and approximations for the treatment of the local field in liquid crystals. For example, the semi-axes of the cavity for the calculations in (2) can be taken to be equal to the molecular length and width. However, real molecular shapes are not ellipsoidal and consequently the real local field differs from that in expressions (1). In fact the simplest molecular-statistical result for the local field factor is[4]

$$f_{ii} = 1+L_{ii}(n_i^2-1), \quad L_{zz}+2L_{xx}=1, \tag{6}$$

where L_{ii} are the components of the Lorentz tensor-factor which is related to the pair distribution function.

As one can see, there are three unknowns in expressions (3)-(6), namely, P_2, P_4 and $L_{zz}-L_{xx}$ (n_i are measured independently). These unknowns can be computed from experimental values of the depolarization ratios and absorption dichroism

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for an electronic transition of the dye in liquid crystalline matrix. For example, from the data of the pioneer work[1] we obtained the following estimates for beta-carotene in MBBA matrix at $T^*=.95$: $P_2=.72$, $P_4=.36$, $L_{zz}-L_{xx}=-.30\pm.06$. These values of the order parameters are substantially larger than those obtained in [1] without local field corrections.

EXPERIMENTAL

Here we present the results of the measurements similar to [1] for the 490 nm absorption band of p-dimethylamino-p'-nitroazobenzene (DMANAB) in binary nematic mixture

$C_7H_{12}(C_6H_4)COO(C_6H_4)C_4H_9$	37 %	
$CH_3O(C_6H_4)COO(C_6H_4)C_5H_{11}$	63 %	
$(CH_3)_2N(C_6H_4)N=N(C_6H_4)NO_2$	0.08 %	DMANAB

The measurements were performed in 180°-geometry with Spex-Ramalog spectrometer. An ILA-120 argon ion laser operating at 488 nm was the exciting source. Absorption spectra were recorded with Specord M40 spectrophotometer. Homogeneous alignment was achieved by evaporation of the SiO_x on the glass slides. Thickness of the liquid crystalline samples was varied from 10 μm to 30 μm. The incident intensity of the exciting beam was varied from 5 mW to 40 mW in order to provide equal overheating (approximately 4°) of the samples with different thickness. The refractive indices of the mixture in the range of transparency

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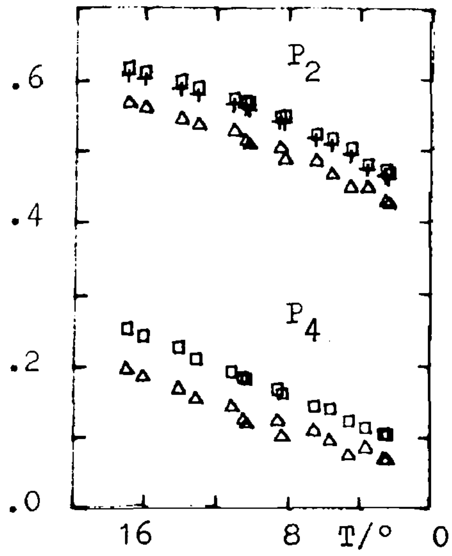
were measured with an IRF-454B Abbe refractometer and in the absorption range - were calculated from interference spectra.

RESULTS AND DISCUSSION

The strongest bands in the RRS spectrum of DMANAB are those located near 1338 cm^{-1} and 1396 cm^{-1}. The results of the computation of the order parameters and structural anisotropy with equations (3)-(6) from the measurements of the RRS depolarization for these two bands and absorption dichroism for the 490 nm band of the dye in the nematic phase are shown in Figures 1 and 2. Ob-



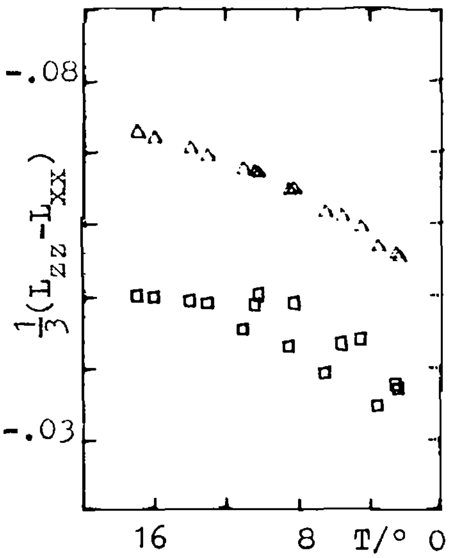


FIGURE 1. The order parameters only from RRS (△) and absorption measurements (+) and from eqs.(3)-(6) (□).

FIGURE 2. Structural anisotropy from eqs.(3)-(6) (□) and by the Segre model (△).

viously, local field corrections result in substantional increase of the computed P_2 and P_4, while the sensitivity of the RRS and absorption ratios to the local field anisotropy is different and, in principle, unpredictable.

In Figure 2 one can see also the factors of structural anisotropy computed from molecular dimensions (c=18.3 Å, a=5.5 Å) comparing equations (6) and (1) with the help of equation (2) (P_2 have been taken from Figure 1). Obviously, the estimates of $\frac{1}{3}(L_{zz}-L_{xx})$ from the Segre model are rather arbitrary, while the scattering of the data is smaller.

In conclusion it should be noted that in contrast to other methods for the local field anisotropy determination in our method all necessary measurements can be done at the same temperature and for the transitions between the similar electronic levels. This results in the minimization of the errors due to various hypotheses concerning the insensitivity of the molecular and local mesophase structure to the temperature.

REFERENCES

1. Y. Nakajima, H. Yoshida, S. Kobinata and S. Maeda, J.Phys.Soc.Japan, 49, 1140 (1980).
2. S. Kobinata, T. Kobayashi, H. Yoshida, A. D. L. Clandani and S. Maeda, J.Mol.Struct., 146, 373 (1986).
3. U. Segre, Mol.Cryst.Liq.Cryst., 90, 239 (1983).
4. A. A. Minko, V. I. Naumenko, S.Ye. Yakovenko, Optika i spektroskopiya, 60, 341 (1986).

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