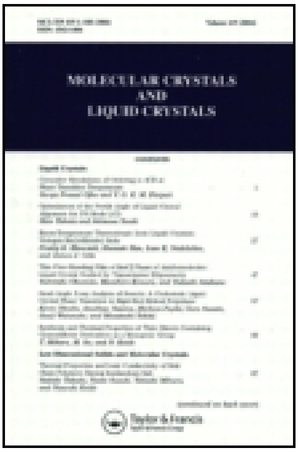

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CONFORMATIONAL OPTICAL NONLINEARITY OF NEMATIC LIQUID CRYSTAL

I.P.PINKEVICH, Yu.A.REZNIKOV, V.Yu.RESHETNYAK

Abstract The expressions for parameters of the cubic optical nonlinearity caused by light induced impurities are obtained. It is shown that the order parameter change near impurities give the main contribution to the conformational nonlinearity. The values of nonlinearity parameters are measured in MBBA by dynamic holography method.

INTRODUCTION

In the region of nematic liquid crystals (NLC) electron self-absorption the photostimulated changes in shape and structure of its molecules are possible when the latter pass to the electron-excited state . Such molecules with changed structures can be considered as light-induced impurities. As the parameters of light-induced impurity molecules (LIM) in particular the polarizability γ differ from those of own NLC molecules, then their appearance will change the magnitude of intermolecular interaction energy as well as the magnitude of the order parameter S in the vicinity of impurity.

The NLC refractive index n is defined by molecular polarizability and order parameter, and therefore both the change in γ and S will make a contribution to the change of refractive index. The additional, as compared to the isotropic liquid, contribution to Δn occurring at the expense of the change in order parameter in appearing LIM gives rise to great magnitude of nonlinearity, which appears to be of the same order as orientational nonlinearity. Systematic studies of responses of nonlinearity associated with molecular phototransformations were carried out in [2-6] The fact that the anomalously large magnitudes of the nonlinearity parameter in mesophase are associated with the change in NLC order parameter was first drawn attention to in[4] . As the above studies suggested that on phototransformation the change in molecular conformation takes place, such nonlinearity received the name conformational or LIM-nonlinearity. Here the expressions for the parameter of LIM-nonlinearity are obtained in some theoretical model framework and values of the parameters are measured bydynamic holography method.

EXPRESSIONS FOR THE NONLINEARITY PARAMETERS.

The nonlinear addition to NLC polarizability can be described by the forth rank tensor $\chi_{ijk\ell}$:

$$\Delta\alpha_{ij} \equiv \chi_{ijk\ell} E_k E_\ell \tag{1}$$

The second two indices of tensor components $\chi_{ijk\ell}$ correspond to polarization of radiation exciting LIM, and the first two indices correspond to polarization of radiation registering nonlinearity.

Proportionality of nonlinear addition $\Delta\alpha_{ij}$ to light intensity tensor $I_{k\ell} = E_k E_\ell$ means that conformational nonlinearity is described by cubic term of polarization expansion into a power series of field intensity $I_{k\ell}$. In this case appropriate changes of refractive index n for e- and o-waves are connected with components $\chi_{ijk\ell}$ as follows:

$$\Delta n^e = \frac{2\pi \chi_{33k\ell} E_k E_\ell}{n^e}, \quad \Delta n^o = \frac{2\pi \chi_{11k\ell} E_k E_\ell}{n^o}. \tag{2}$$

To obtain the values of tensor components $\chi^{(3)}$ we can use description[4] of conformational nonlinearity in the framework of light-induced temperature shift model of phase transition to isotropic liquid with LIM excitation. This model makes it possible to express the magnitudes χ_{ijkl} through measured parameters and can be described as follows.

It is well known that the addition of impurity molecules to NLC changes its phase transition temperature T_{co}[7]. The appearence of light-induced impurities in a nematic causes the same effect. In this case the curve $n(\tau_T^o \equiv T/T_{co})$ is shifted along the axis τ_T^o by the value $\Delta\tau_T$ relative to the point $\tau_T^o = 1$ (Fig.1) and thus $\Delta n = n_o(\tau_T^o) - n_o(\tau_T^o + \Delta\tau_T^o)$ (here and further the subscript 'c' corresponds to an unexcited sample).

The impure crystal average S is the universal function of τ_T independent (at low LIM concentration n') of the character and concentration of LIM and coinciding with the dependence $S_o(\tau_T^o)$ of pure NLC, but $\Delta\tau_T = (T_c - T_{co})/T_{co} \sim n'$.

Inasmuch as in mesophase the main contribution to the temperature dependence of refractive index is made by the order parameter $S(\tau_T)$, the dependence $n(\tau_T)$ can also be considered as universal for a given NLC and independent on the type of LIM. Therefore, the change in refractive index at the expense of T_{co} shift can be found using the relationship:

$$\Delta n_S^{o,e} \simeq n_o^{o,e}(\tau_T^o) - n_o^{o,e}(\tau_T^o + \Delta\tau_T^o),$$

or taking into account infinitesimal of $\Delta\tau_T$:

$$\Delta n_S^{o,e} \simeq \frac{\partial n_o^{o,e}}{\partial \tau_T^o} \Delta\tau_T . \qquad (3)$$

Thus, the magnitude Δn_S is defined by the curve shift $n_o(\tau_T^o)$ proportional to LIM concentration along the axis by the value $\Delta\tau_T$. Inasmuch as LIM concentration n' is proportional to light intensity, then according to the above consideration, Δn is proportional to $|E|^2$ and associated with cubic nonlinearity parameter $\hat{\chi}^{(3)}$. The part $\hat{\chi}^{(3)}$ stemming from the change of NLC order parameter with the appearance of LIM will be described by the appropriate cubic nonlinearity parameter $\chi^{(3)}$.

It is clear that the expression for χ^{s}_{ijkl} will take the following form:

$$\chi_{33kk} = \frac{n^e}{2\pi |E_k|^2} \frac{\partial n^e}{\partial \tau^o_T} \Delta \tau^o_T(I), \; \chi_{11kk} = \frac{n^o}{2\pi |E_k|^2} \frac{\partial n^o}{\partial \tau^o_T} \Delta \tau^o_T(I) \qquad (4)$$

These relations expressing χ^{s}_{ijkl} through the parameters being measured make it possible to draw the following conclusions about the properties of tensor $\hat{\chi}^{(3)S}$.

1. The components χ^{s}_{3311} and χ^{s}_{3333} as well as χ_{1133} and are of the same sign, and the signs themselves are defined by the character of temperature shift $\Delta\tau_T$. In most cases the addition of non-mesogenic impurities to NLC decreases the value of T_{co} and thus $\Delta\tau^o_T < 0$. Inasmuch as $\partial n^e/\partial \tau_T > 0$, $\partial n^o/\partial \tau_T < 0$ we obtain that χ^{s}_{1133}, $\chi^{s}_{1111} > 0$; χ^{s}_{3311}, $\chi^{s}_{3333} < 0$.

2. The NLC molecules usually possess positive dichroism of absorption and thus $\Delta\tau_{33} > \Delta\tau_{11}$. Inasmuch as $(\partial n^e/\partial \tau_T) > (\partial n^o/\partial \tau_T)$, this means that nonlinearity should be maximal for extraordinary writing and testing beams. Owing to the fact that the derivatives $\partial n^{o,e}/\partial \tau_T$, defined by the dependence $S(\tau_T)$ rapidly grow as they approach T_c, nonlinearity should rise with temperature. The values χ^{s}_{ijkl} specific for each NLC are determined by experimentally measured dependences $n^{o,e}(\tau_T)$ as well as LIM excitation anisotropy which is due to NLC molecular absorption dichroism.

Let us estimate the contribution of the refractive index change Δn_s to the common magnitude Δn and accordingly the values χ^{s}_{ijkl} to the total tensor $\hat{\chi}^{(3)}$

The expression for refractive index of impure NLC at $n' \ll 1$ can be written as [8]

$$(n^{o,e})^2 = 1 + 4\pi F N_o (\bar{\gamma} + g \bar{\gamma}_a S), \qquad (5)$$

where $\bar{\gamma} = (1-n')\gamma + n'\gamma'$; $\bar{\gamma}_a = (1-n')\gamma_a + n'\gamma_a'$, γ, γ_a, γ' and γ_a'

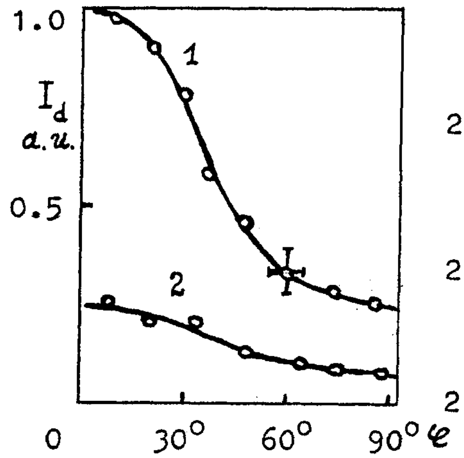

Fig.3.

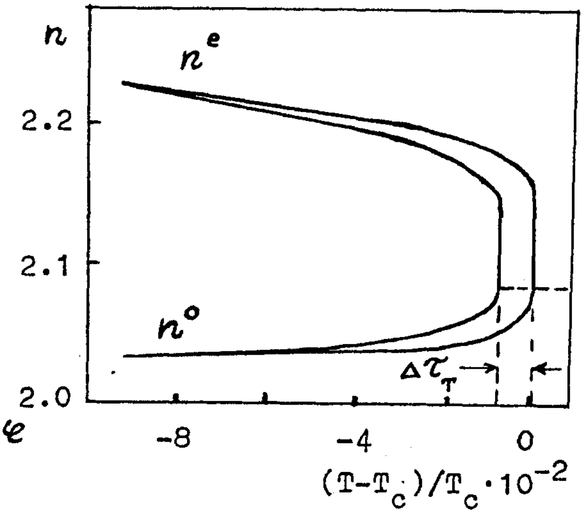

Fig.1.

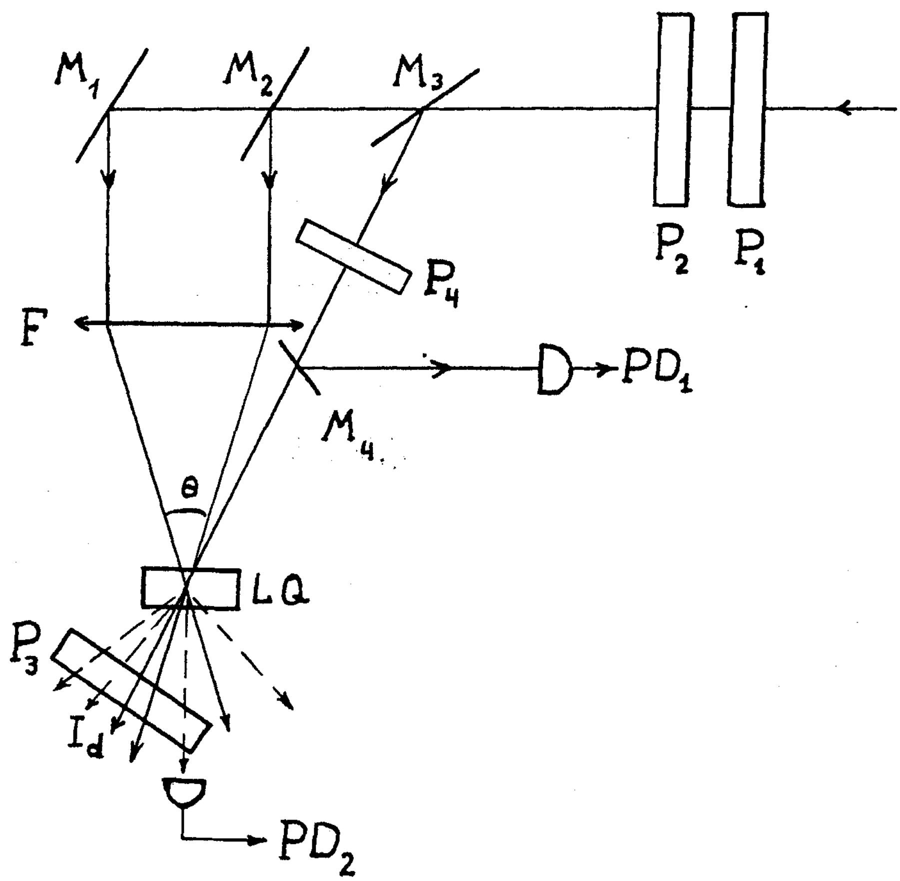

Fig.2.

are the mean polarizability and polarizability anisotropy of NLC and LIM molecules, respectively, g =-1/3 for o-wave and g =2/3 for e-wave, F is the local field factor, N_0 - number of NLC molecules Subtracting the relation for refractive index of pure NLC from this expression (in this case n' =0, $S = S_0$) we obtain:

$$\Delta n^{o,e} = 4\pi F N_0 [n' \Delta\gamma + g(\bar{\gamma}_a S - \gamma_a S_0)] , \tag{6}$$

where $\Delta\gamma = \gamma' - \gamma$.

Considering, as stated above, that the dependence coincides with the dependence $S_0(\tau_T^o)$ and expanding the function $S(\tau_T)$ into a power series we obtain that

$$S(\tau_T) = S_0(\tau_T^o) + \frac{dS_0}{d\tau_T^o} \Delta\tau_T(n').$$

Substituting the last expression into (6) and taking into account that $4\pi FN_0 = (\bar{n}^2-1)/\bar{\gamma}$, $\bar{n}^2 = n_e^2/3 + 2n_o^2/3$ we obtain:

$$\Delta n^{o,e} = (\bar{n}^2-1)n'(I)[\Delta\gamma + g\Delta\gamma_a(S_0 - 2\tau_T^o \frac{dS_0}{d\tau_T^o})]/2\gamma n^{o,e} \equiv$$

$$\equiv \Delta n_\gamma + \Delta n_S . \tag{7}$$

where $\Delta\gamma_a = \gamma_a' - \gamma_a$. The first component in this expression corresponds to the change of n which must also be observed in isotropic liquid and the second one describes an additional contribution appearing in mesophase due to orientational ordering and its change on appearing LIM.

Let us make numerical estimations. If one supposes that $\Delta\gamma_a = \Delta\gamma$, then even far off the phase transition (for example, at τ =0.96 ,that for MBBA NLC corresponds to T =22° at τ =45°) and at typical values S_0=0.6, $dS_0/d\tau_T^o$=1.5 , we obtain that $\Delta n_S/\Delta n$ =75 i.e. the contribution of order parameter is decisive.

With increasing temperature the contribution of order parameter becomes greater at the expense of growth of the derivative $\partial S_0 / \partial \tau_T^0$ as T_{co} is approached.

Thus, the change in order parameter on molecular phototransformations is likely to make the main contribution to Δn at NLC LIM-nonlinearity and we can consider at $T \approx T_{co}$ that $\Delta n \simeq \Delta n_s$, $\chi_{ijkl} \simeq \chi^s_{ijkl}$.

EXPERIMENTAL RESULTS

The relationship between all the independent tensor components χ_{ijkl} were obtained by dynamic holography technique [3]. Intensity I_d of the diffracted radiation testing the holographic grating is described by the expression

$$I_d = E^2_{di} = 2\pi L E^2_{tj} (E_{1k} E_{2k} + E_{2e} E_{1k}) (\bar{e}_{tj} \chi_{ijke} \bar{e}_{de})^2 / \lambda \qquad (8)$$

Here $\vec{e}_t$ and $\vec{e}_d$ are the unit vectors of polarization of incident and diffracted testing radiation, $E^2_t = I_t$ is the intensity of testing beam.

It is seen that the measurement of diffraction efficiency of holograms $\eta = I_d / I_t$ at various polarizations of recording E_k , E_e , testing E_j and diffracted E_i radiations makes it possible to define the relations between all the independent components $/ \chi_{ijke} /$, and knowing the holographic grating parameter we can also find their absolute values. For example, if the polarization of recording beams is directed, as well as the NLC director, along the axis z (e-wave) and the testing and diffracted beams along the axis x (o-waves), then the diffraction intensity will be defined by the component χ_{1133} .

The experimental diagram is shown in Fig.2. (F is the lens with a focal distance of 1 m, LQ is the planary oriented MBBA NLC, 50 mkm thick and the phase transition temperature T_{co} =43° M_1 - M_4 are the mirrors, P_1 - P_4 are the polaroids which make it possible to vary the radiation intensity, to establish polarization of recording and testing beams independently and also to analyze the diffracted wave polarization). To record the holograms, He-Cd-laser radiation (λ=0.44 mkm, power P =50mW) was used, which was not polarized initially. The intensities of recording beams in NLC cell ($I_0 = I_1 + I_2 \simeq 3W/cm^2$) were the same. The intensity of testing radiation was $I_t \simeq 10^{-2} I_0$. The holographic grating period Λ was equal to 10 mkm. The measurement were made at room temperature.

The dependence of testing radiation diffraction intensity with a given polarization on the angle φ between the director and the recording field intensity vector was measured experimentally.

The results are given in Fig.3, where curve 1 corresponds to the e-polarization of testing radiation, and curve 2 corresponds to o-polarization. The analysis of the state of diffracted radiation polarization has shown that it coincides with the recording radiation polarization, as it was obtained theoretically (see (4)). The relationships between the values I_d at points corresponding to angles φ=0° and φ=90°, made it possible, using expression (4), to determine the relations between all the independent components χ_{ijkl}:

$$|\chi_{1111}| \simeq 0,19 |\chi_{3333}|; \; |\chi_{1133}| \simeq |\chi_{3311}| \simeq 0,45 |\chi_{3333}|. \qquad (9)$$

The analysis of the curves obtained in Fig.3 allows us to determine if the components χ_{1111} and χ_{1133} as well as χ_{3333} and χ_{3311} coincide or differ in sign. Indeed, at $\varphi \neq 0°$ and $\varphi \neq 90°$ the polarization of testing beam contains both the ordinary and extraordinary components, and the magnitude I_d is proportional to the square of a linear combination of the corresponding components χ_{ijkl}. Thus in the case of different signs between the components χ_{3311} and χ_{3333} as well as between χ_{1133} and χ_{1111} we should find such value of φ at which the changes in refractive index will compensate each other and the intensity I_d =0. The absence of such compensation allows us to affirm that the signs χ_{3333} and χ_{3311} as well as χ_{1111} and

χ_{1133} coincide. This is consistent with our theoretical results, obtained above.

The signs of these components were measured by the method of induced nonlinear lens [10]. In the result we obtained that $\chi_{1111}>0$, $\chi_{3333}<0$ and according to the above relations between the signs χ_{1133} and χ_{1111} as well as χ_{3311} and χ_{3333}: $\chi_{1133}>0$, $\chi_{3311}<0$.

The numerical value χ_{3333} =2.6 $\cdot 10^{-3}$ $cm^3 erg^{-1}$ was obtained by measuring diffraction efficiency for the case of self-diffraction when one of the writing beams was a testing beam.

The value $\tilde{\chi}_{3333}$ depending only on NLC and LIM characteristics and not associated with the geometry of the experiment is determined by the relation $\chi_{3333}=\mathcal{L}_{33}\tilde{\chi}_{3333}$, where for our experiment the parameter $\mathcal{L}_{33}=\mathcal{D}q^2+1/\tau$ Here τ is the LIM life-time, $\mathcal{D}$ is the LIM diffusion coefficient, $q=2\pi/\Lambda$ Using the value $\mathcal{D}$ (T=25)=0.8 10 $cm^2\ s^{-1}$ measured in [11] and taking into accountthat τ =0.7 s we obtain that $\tilde{\chi}_{3333}$ =8.8$\cdot 10^{-3} cm^3 erg^{-1} s^{-1}$

It should be noted that the measured value χ_{3333} under the condition of the experiment is determined only by conformational nonlinearity and the contribution of thermal nonlinearity to $\chi^{(3)}$ is negligibly small [3]. This conclusion follows from the fact that the relaxation of holograms is described by the exponent with the characteristic time $\tau_H=1/[2(\mathcal{D}q^2+1/\tau)] \simeq 10^{-1}s$ corresponding to the magnitudes of LIM life-time and their diffusion. In the case of essential contribution of thermal nonlinearity the dependence $I_d(t)$ during the lattice relaxation should contain additional exponential term with the characteristic time $\tau_H^t=(\mathcal{D}^t q^2)^{-1}/2 \simeq 10^{-3}s$ ($\mathcal{D}^t \simeq 10^{-3} cm^2\ s^{-1}$ is the thermal diffusion coefficient) that wasn't observed in experiments.

In the result, a complete set of independent components of tensor $\tilde{\chi}_{ijkl}$ was expermentally determined for MBBA conformational nonlinearity:

$$\tilde{\chi}_{3333} = -8.8\cdot 10^{-3}\ cm^3 erg^{-1} s^{-1}, \quad \tilde{\chi}_{3311} = -3.8\cdot 10^{-3}\ cm^3 erg^{-1} s^{-1},$$
$$\tilde{\chi}_{1111} = 1.7\cdot 10^{-3}\ cm^3 erg^{-1} s^{-1}, \quad \tilde{\chi}_{1133} = 3.8\cdot 10^{-3}\ cm^3 erg^{-1} s^{-1}. \qquad (10)$$

Note that the obtained data on the values χ_{ijkl} may be used to get the information on changing the magnitude of intermolecular interaction in MBBA NLC during photoisomerization of its molecules.

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