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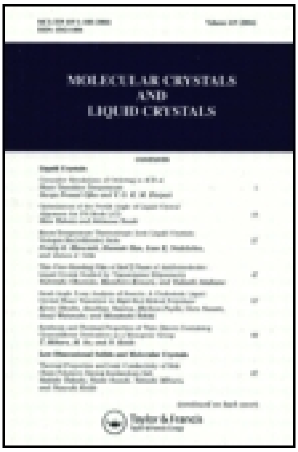

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Transient Modulation of Order Parameter and Optical Non-Linearity in a Chiral Nematic Liquid Crystal

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Light-stimulated transformation of a molecule in a liquid crystal (LC) greatly affects the ordering of its nearest neighbors. At early stage of excitation this local order parameter modification is characterized with extremely short times, while a minor concentration of photo-modified molecules could contribute a lot into modulation of refractive indices of LC. Dispersion of optical activity at the edge of the selective reflection band of a chiral LC enhances significantly the nonlinear optical response. Combination of these effects has a strong potential in different aspects of optical signal processing, all-optical switching and photonics.

Keywords Chiral nematics; dynamic gratings; nonlinear optics; optical activity; order parameter; photonic band gap

1. Introduction

Many phenomena are driven by a reversible modification of molecular properties taking place in a molecule that has absorbed a photon. A simple example is photo-induced isomerization, as that occurring in many azodyes. The sole electronic excitation can also drive an effective photo-induced molecular reorientation, if associated with a significant variation of intermolecular forces. Besides electronic excitation, another general consequence of photon absorption is a relatively large vibrational excitation of the molecule. This occurs already when the molecule is in its photoexcited electronic state, due to the Franck-Condon effect: a significant fraction of the photon energy is immediately converted to vibrational energy. Moreover, the vibrational excitation grows much stronger when the molecule nonradiatively relaxes back to its electronic ground state: in this case the absorbed energy is entirely converted into vibrational energy with transverse relaxation time $T_2 = 10^{-(12 \div 14)}$ s [1,2]. The energy is then rapidly redistributed among many different degrees of freedom of the molecule and of its neighboring molecules. One can then approximately describe this process as a “local heating”, which may be very large (of the order of

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several hundred Kelvin, as estimated by dividing the absorbed energy by the heat capacity of a molecular volume of the medium).

The possibility of photo-induced molecular reorientation driven by this local heating effect was proposed by Albrecht in the mid-1950s [3]. Albrecht's idea was that local heating may strongly enhance rotational diffusion leading, thus, to a partial or total orientational randomization. For instance, the characteristic time ($\tau_{rot} \approx 2\,\mathrm{ns}$) of this orientational motion in 5CB liquid crystal was determined from the decay of the fluorescence polarization [4].

The process of the initial energy transfer from a light-excited molecule to its neighbors was thoroughly studied by Terazima *et al.* [5,6]. Investigations of the radiationless relaxation of light-excited molecules, carried out by means of the method of optical-heterodyne-detected transient gratings, have shown that thermal energy was first transferred to several solvent molecules effectively coupled to the solute (the directly energy accepting (DEA) solvents) [5]. In organic solvents, such thermal randomization of the first-solvent-shell molecules appeared to take place within picoseconds [6]. The orientational ordering existing in the liquid crystalline state, which is drastically dependent on the intermolecular interaction, should also be greatly affected by the energy pumping. This local transient change of the LC order parameter should, in turn, cause noticeable changes of refractive indices of LC.

This effect possesses a lot of analogies with the conformational nonlinearity [7], according to which the change of the local order parameter, ΔS, resulting from molecular transformations, contributes foremost into the refractive index change. It was shown that changes of the refractive indices due to the order parameter modulation, δn^S, were several times greater than that coming from the polarizability changes of the photo-transformed molecule, δn^γ, even for the temperatures being rather far from the phase transition: $\delta n^S \gg \delta n^\gamma$. With the increasing temperature the contribution of the order parameter would grow larger [7].

Liquid crystals are widely considered as promising materials for nonlinear optics and all-optical switching due to their large birefringence and easy susceptibilities to perturbation by external fields. It is the reorientation of the LC director that is widely employed in a vast majority of different applications providing the switching times from sub-milliseconds and longer. Only recently light-induced changes of the LC order parameter have drawn particular attention in all-optical switching processes [8], where it was considered preserving its local thermodynamic equilibrium.

Changes of the refractive indices caused by the fast transient modulation of the LC order parameter should grow much more profound if accompanied with a distributed optical feedback occurring in a chiral nematic LC (CLC). If the wavelength of light is close to the spatial periodicity in CLC a bright effect of selective reflection of light (SR), i.e., a natural forbidden frequency gap, appears. Being extraordinary strong, the optical activity of CLC reveals also a very large dispersion at the edge of the SR band [9]. Modulation of the optical activity may essentially enhance the nonlinear response, substantially contributing to the efficiency of diffraction, or even be the only nonlinear optical mechanism [10].

Effect of the transient modulation of the LC order parameter in chiral nematic LC's was investigated from the standpoint of diffraction grating recording. Theoretical modeling has provided a good agreement with the experimental data; the studied phenomena reveal a strong potential in different aspects of optical signal processing, all-optical switching and photonics.

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2. Experimental Methods

Two types of cyanobiphenyl-based liquid crystalline mixtures were used in the work: a standard E7 composition and a 5CB-based system [11], the helical structure in which was induced with the help of chiral compounds (respectively, commercially available CB15 and (3b)-cholest-5-en-3-yl 4-butoxybenzoate). Apparently the same helical period (SR maximum at ~560 nm, Fig. 1) appeared with the introduction of 40.2% CB15 into E7 and of the 18% of the chiral dopant in the second mixture. Since both LC mixtures were insensitive to laser radiation under conditions of the experiment, some derivatives of ketocyanide dyes [11] were introduced into LC compounds (concentration was in the range 1–2 w.%) to facilitate the energy pumping into the system.

Cells used in the experiments consisted of glass substrates, the inner surfaces of which were covered with rubbed PI providing a uniform planar texture; the gap in different cells was established with teflon spacers (from 1–2 up to 20 μm). Liquid crystalline mixtures were introduced into cells in the isotropic state by capillary forces and naturally cooled down to the room temperature. The exact procedures of cell preparation and details of the properties of LC systems were reported elsewhere [11–13].

Transformations of the polarization state of the linearly polarized light passed through the cell comprising CLC layer were carried out within the spectral range from 425 till 600 nm. A narrower region, however, adjacent to the leftwing edge of the SR band and coinciding with wavelength of the second harmonic of Nd:YAG laser (532 nm), was of the particular interest. For the determination of the polarization plane orientation (or the semimajor axis of the light polarization ellipse in the case of elliptically polarized light) the intensity of light is usually measured for four different orientations of the analyzer, which is rotated by the step of 45° [14]. The analyzer and the CCD-spectrometer were held together in our case because of polarization sensitivity of the latter and, instead, the pair ‘polarizer – hot stage’ was

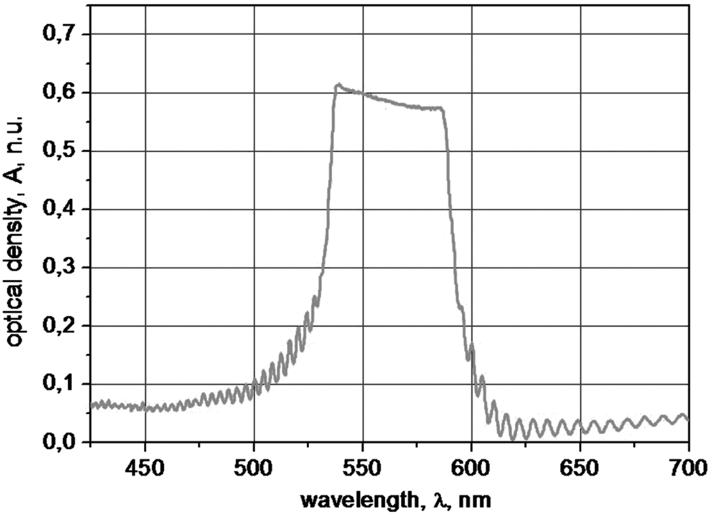

Figure 1. Selective reflection band for the mixture E7 + 40.2 w.% of CB15; cell gap was 20 μm.

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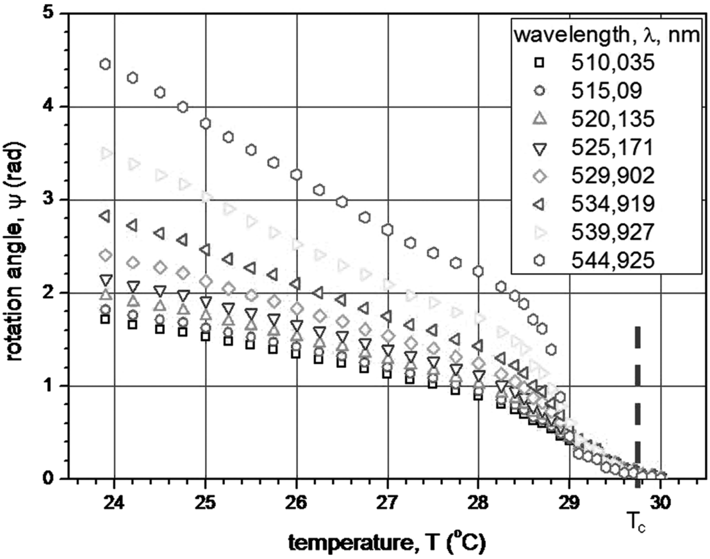

Figure 2. Angles of polarization rotation, ψ, *vs.* temperature at different selected wavelengths for the mixture E7 + 40.2 w.% of CB15; cell gap was 20 μm.

turned. The angle between transmission axes of the analyzer and polarizer has been, thus, consecutively adjusted as: $\theta_i = 0$, 45, 90 and 135°, and the sets of four intensity spectra, $I_i(\lambda)$, were recorded for each temperature ($I_1 \div I_4$ correspond, respectively, to the analyzer orientation angles $\theta_1 \div \theta_4$).

Diffracting gratings were induced in an ordinary two-beam-coupling scheme with the help of the second harmonic of Q-switched Nd:YAG laser pulses (wavelength – 532 nm, fwhm pulse duration of 15 ns). A simple photo-diode measuring system was described elsewhere [12,13].

3. Results and Discussion

3.1. *Optical Activity near Selective Reflection Band*

Polarized spectra $I_i(\lambda)$ were recorded for the cells with the E7/CB15 mixture in the temperature range $23.5 \div 30$°C; the temperature step, being 0.25°C up to 28°C, was than reduced to 0.1°C. The Stokes parameters were determined and the angles of polarization rotation in dependence on the light wavelength and temperature were calculated (Fig. 2). Rotation angle values in Figure 2 represent the orientation of the bigger axis of polarization of the light passed through the CLC layer with respect to the initial polarization plane orientation of the incoming linearly polarized wave. The helical pitch in the E7/CB15 mixture appeared to be temperature independent in the range from the room temperature till the transition to the isotropic phase (approximately 30°C).

It is seen that the heating of the cell by slightly greater than five degrees results in the significant decrease of the angle of polarization plane rotation for the light at different wavelengths. For the wavelength falling close to the SR band the change of the polarization orientation has surmounted several radians. The temperature

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dependence generally consists of a practically linear part at lower temperatures and a steeper region at elevated temperatures nearby the phase transition (Fig. 2).

At the particular wavelength corresponding to the second harmonic of the Nd:YAG laser (Fig. 3) the slope of the linear low-temperature part of the ψ-T dependence is characterized with $\frac{\partial\psi}{\partial T} \approx -0.3\,\frac{\mathrm{rad}}{\mathrm{K}}$, while in the vicinity of the phase transition it is three times as large ($\frac{\partial\psi}{\partial T} \approx -1\,\frac{\mathrm{rad}}{\mathrm{K}}$).

3.2. *Self-Diffraction at Pulsed Laser Excitation*

Strong self-diffraction has been observed at the excitation of gratings in thin layers (1–4 μm) of dye-doped cyanobiphenyl-based CLC mixtures by means of 15-ns laser pulses (the second harmonic of Nd:YAG laser, 532 nm). Diffraction efficiency of 13% for the first diffracting beam has been achieved for 2-micron cells with 2 w.% dye concentration under the average light intensity of about $0.8 \div 1\,\mathrm{MW/cm^2}$.

The dependences of self-diffraction efficiency on the grating period obtained in a single-pulse operating mode are presented in Figure 4. A well-seen suppression of the diffracting light intensity was observed at shorter grating periods.

In general, the decrease of the diffraction efficiency at shorter grating periods was not that deep under the pumping light intensities lower than $1\,\mathrm{MW/cm^2}$ and has grown essentially pronounced with the increasing pumping light intensities.

3.3. *Transient Modulation of the Order Parameter*

Reduction of the efficiency of self-diffraction as presented in Figure 4 is usually attributed to some diffusive processes washing off the grating. Since this happens during the laser pulse duration (15 ns), it is likely to be a density wave propagating

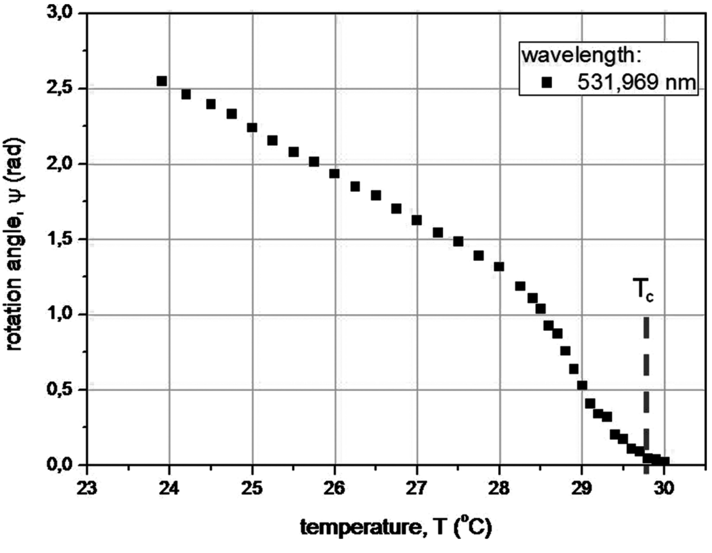

Figure 3. Temperature dependence of angle of polarization rotation, ψ, at the wavelength of the second harmonic of Nd:YAG laser for the E7/CB15 mixture.

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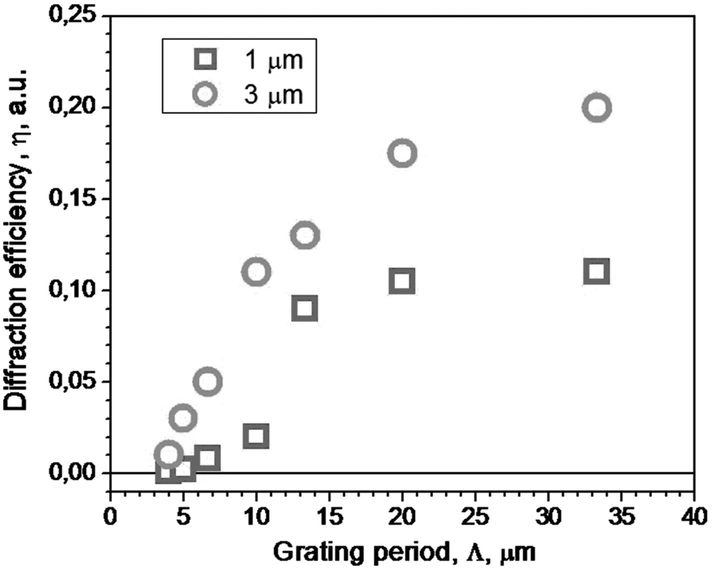

Figure 4. Dependence of efficiency of self-diffraction in chiral nematic LC doped with 1% of dye (arbitrary units) on grating period. Cell gap: (red) squares −1 μm, (green) circles −3 μm.

with the speed of sound [15]. The latter could be estimated from the experiment and the value obtained, $V \approx \frac{\Lambda}{t_{ns}} \sim 1.3 \cdot 10^3 \frac{\mathrm{m}}{\mathrm{s}}$, appeared to be in a fair agreement with the reported data [15]. If the grating period is small enough or under greater power densities, when the excess of absorbed energy is sufficient to overheat the LC layer, the orientation disordering and the mesophase destruction spread outside the grating fringes and suppress, consequently, the grating modulation amplitude.

On the basis of the Maier-Meyer theory the influence of a small concentration of light-transformed molecules ($C \ll 1$) on the LC refractive index values was taken into account and attributed to the variation of the LC order parameter [7], which was caused by the change of the intermolecular interaction potential. Strong local heating and the consecutive thermal orientational randomization of the molecules surrounding the excited dye molecule should also result in noticeable changes of refractive indices due to the temperature dependence of the LC order parameter.

Modifying the model of conformational nonlinearity [7] one can estimate the effect of thermal randomization on the refractive indices as:

$$\delta n_{o,e} = -g\frac{(\tilde{n}^2 - 1)\gamma_a}{2n_{o,e}\gamma}\alpha(\lambda, I)C_d S \tag{1}$$

where $\tilde{n}^2 = \frac{2}{3}n_o^2 + \frac{1}{3}n_e^2$, $n_o(n_e)$ is the ordinary (extraordinary) refractive index of LC medium, $g = -1/3$ for the ordinary and $g = 2/3$ for the extraordinary wave, γ, γ_a represent the average polarizability and the anisotropy of polarizability of the LC, and the dye concentration is C_d. Efficiency of the LC order parameter modulation is taken into account by the yield factor $\alpha(\lambda, I)$, which depends on the wavelength and intensity of light and some experimental parameters as well (type of a dye,

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solute-solvent interaction, parameters of excitation, temperature dependence of the order parameter etc.). For instance, strong absorption and radiationless energy relaxation, accompanying multiple consecutive acts of excitation of a single dye molecule, will pump energy sufficient for the order parameter reduction over a comparatively large region around the dye molecule. Thus, at the 15 ns pumping this thermal effect could be stronger by, at least, the order of magnitude in comparison to the conformational nonlinearity, in which the estimated refractive index modulation was of the order of $\sim 10^{-3}$ [7].

To elucidate the role of the LC order parameter the E7/CB15 mixture was used, the helical pitch of which appeared to be temperature independent within the experimental temperature range. The mixture, thus, could work for a model for manifestation of the influence of the LC order parameter changes on the optical properties of a chiral LC.

As seen from Figure 2 and 3, the modulation of the optical activity of CLC layer with the temperature change appeared to be several times less effective at lower temperatures than when the cell was heated up close to the clearing point. This is a natural consequence of the nonlinear temperature dependence of the LC order parameter. Though being short, the nanosecond pulse, nevertheless, lasts much longer than the times characteristic of the thermal randomization of the first-solvent-shell molecules that take place within picoseconds [2]. As a result, at nanosecond excitation with moderate pulse energies the pumped energy is distributed over larger volumes and the growth of the local temperature could not reach the phase transition temperature, at which the contribution of the LC order parameter modulation should be decisive.

The case is different when the duration of the pumping is slightly longer than the characteristic time of thermal randomization of the DEA solvents. Almost all energy is, then, accommodated by the nearest environment of the dye molecule that is enough for a complete destruction of the ordering. Although the relative volume involved is quite small the overall immediate effect could be greater. This mechanism is virtually supported with the experiments on diffraction gratings recording on the same LC mixtures with the picosecond excitation, where the efficiency of nonlinear optical response appeared to be a couple of orders of magnitude larger than that with nanosecond excitation if referred to the pumped energy [11].

Very large dispersion of the optical activity of a CLC layer at the edge of the SR band should also contribute to the diffraction efficiency due to the modulation of the optical activity resulted from local changes of the LC order parameter. Usually, the optics of helically winded media is quite complicated. In the very simple consideration of light diffraction on thin CLC layers, however, it is possible to limit the account of light-induced changes in CLC with the only two parameters: optical activity of the LC layer (resulting in the modulation of the light polarisation plane orientation, $\Delta\psi$, of the outgoing wave) and the average refractive index of the medium (accounted for the modulation of the usual phase retardation, $\delta = 2\pi\Delta nd/\lambda$) [13]. The intensity of light wave diffracting on such a grating was shown to be:

$$I_n \sim J_n^2(\chi_+) + J_n^2(\chi_-) \qquad (2)$$

where $\chi_\pm = \delta \pm \Delta\psi$. The optical activity modulation contributes additionally to the efficiency of diffraction and very rough estimations show that this additional contribution is to be at least of the same magnitude as coming from the phase retardation δ.

4. Conclusions and Perspectives

Distortion of the orientational ordering of LC molecules resulted from the fast energy transfer from the light-excited dye molecule into its nearest environment was shown to cause a profound modulation of refractive indices of LC. These transient local order parameter changes, characterized with extremely short times, were employed for the dynamic grating recording at pulsed laser excitation and provided the effective nonlinear optical response.

Due to the strong dispersion of optical activity at the edge of the SR band of the CLC the modulation of the LC order parameter results in the additional contribution enhancing the nonlinear optical response.

One of the particularly promising peculiarities of the use of chiral LC for different aspects of optical signal processing and photonics, is the possibility to make optical read-out spectrally independent from the pumping by a proper adjustment of the helical pitch and selection of a dye. It could be useful for a fast control of optical signals of very high intensity, for instance, in the IR range. Combination of the fast nonlinear mechanism and the distributed optical feedback in such systems could be considered for a possible application for all-optical wavelength conversion, all-optical switching or incoherent-to-coherent light transformation.

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