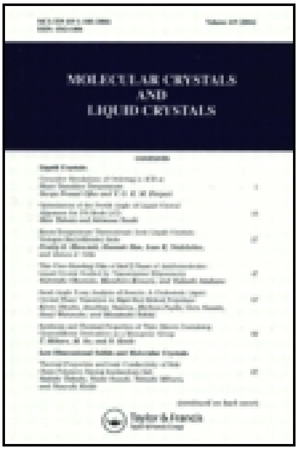

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REORIENTATION OF A NEMATIC LIQUID CRYSTAL OF DISCOTIC MOLECULES BY PHOTOINDUCED SPACE CHARGE FIELDS

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Abstract A new reorientation effect in nematic liquid crystals of discotic molecules has been observed and investigated for the first time, which occurs under the combined influence of DC-electrical and optical fields. It is shown that illumination with intensities as low as 10^{-3} W/cm^2 is sufficient for a strong photo-induced reorientation process, indicating a rather large nonlinear optical coefficient. The dependence of photo-excitation upon the applied voltage as well as from intensity and wavelength of the light wave has been investigated. Furthermore, a first model will be discussed, which explains the experimental observations to result from photo-induced space charge fields which enhance the electrical field-induced reorientation of the discotic molecules.

Keywords: *Nonlinear Optics, Electro-Optical Effects, Light-Valve, Photorefractive Effect*

INTRODUCTION

Liquid crystals of calamitic, i.e. rod-like molecules are well-established materials for electro-optical devices like flat displays, spatial light modulators, etc. Furthermore, it turned out during the last years, that these materials possess also promising nonlinear optical properties which are of interest for future applications in photonics, optical information techniques or laser optics. Much less attention has been spent, however, to check for the potential and applicability of liquid crystals consisting of disk-like molecules, which are known[1] already since 1977. It was only in the early 1990's, that electro-optical switching was investigated in discotic liquid crystals[2]. The most spectacular results with respect to opto-electronic applications were reported recently[3,4,5], where huge electrical conductivity in a magnitude not know so far from any other material was observed with photo-induced charge carriers in so-called columnar phases of discotic molecules. Nevertheless, it must be noted that no investigations concerning nonlinear optical properties of discotic liquid crystals have been performed so far to our knowledge.

The present investigations concern a new molecular reorientation effect in nematic liquid crystals of discotic molecules, which occurs under the combined application of DC-electrical fields and low power optical waves. The huge photosensitivity of the investigated discotic liquid crystals has been reported in a preliminary note recently[6], where it was stated that even illumination with a microscope lamp is sufficient to induce the effect. As will be shown below the observations can be explained by photo-excitation and separation of space charges in the presence of an electrical field which result in additional internal fields and enhanced molecular reorientation. Consequently, the new effect resembles some properties of the so-called orientational photorefractive effect known recently from dye- or fullerene-doped nematic liquid crystals of calamitic molecules[7,8] or functionalized polymers[9]. On the other hand it can also be interpreted as a liquid crystal light valve with an intrinsic photo-conductor, working similar like conventional hybrid liquid crystal light valves[10], consisting of a photo-sensitive semiconductor and an liquid crystalline electro-optical modulator.

In the following experiments the reorientation of the optical axis from an initially homeotropic to an inclined state by DC-electric fields under optical excitation is investigated. It will be shown that the induced reorientation depends clearly on the voltage as well as the light intensity. Furthermore, the wavelength dependence of the photo-excitation has been studied.

EXPERIMENTAL SETUP

Investigations have been carried out with homeotropically aligned films of 5 μm thickness. DC and AC electric fields were applied across the film with the help of transparent ITO (Indium-Tin-Oxide) electrodes which were covered by weakly rubbed polymer (PI) orientational layers. The studied liquid crystal was pentakis [(4-pentylphenyl)ethynyl] phenyl 10-carbethoxydecyl ether[11], which has a nematic liquid crystalline phase between 57 °C and 69 °C. The discotic material was not doped with any dye. The following investigations have been performed in the nematic phase at $T = 60$ °C.

Because of the homeotropic alignment the optical axis is oriented perpendicular to the glass plates. The optical properties are thereby quasi isotropic for light that propagates normally through the cell. If, however, optical axis reorientation is induced, the rubbed orientation layer leads to a preferential direction of the reoriented molecules. As a consequence the birefringence changes which can be detected with a polarized weak HeNe laser by detecting the transmitted intensity behind a crossed polarizer. It has been proved previously that the wavelength of the probe beam is not absorbed, and therefore, does not excite the liquid crystal.

The experimental setup is shown in Fig. 1. An Argon laser beam with wavelengths between 458 nm and 514 nm was used to excite the sample. The effect has been found to be independent of the Ar laser polarization. In case of molecular reorientation the effective optical axis was determined by rotating the LC-cell around the normal axis and detecting the transmitted intensity behind a crossed polarizer. It turned out that the preferred direction of the reoriented axis was given by the rubbing direction of the orientation layer. In the following experiments the induced optical axis was always adjusted 45 deg. with respect to the polarization of the laser beams.

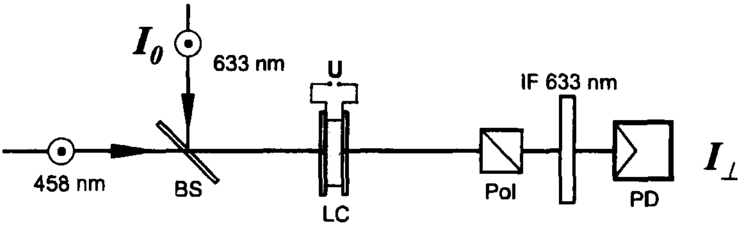

Figure 1 The birefringence was measured with a linear polarized HeNe laser. The depolarized probe beam signal at 633 nm was separated from the excitation beam by an interference filter and measured with a photodiode. An Ar laser was used for the photoenhancement of the reorientation.

EXPERIMENTAL RESULTS

Fig. 2 displays the intensity dependence of the reorientation for different wavelengths at a fixed voltage of 5 Volts. With increasing reorientation the effective birefringence increases and leads to a larger depolarized signal $I_\perp$. The effect becomes stronger if the spectral position of the excitation is closer to the absorption edge of the liquid crystal at about 460 nm.

The large sensitivity of the effect can be seen in the results shown in Fig. 3. The plotted depolarization is defined as the quotient of the intensity of the crossed polarized part compared to the intensity of the input probe beam. Laser powers of 100 μW or even less on a beam diameter of 1.1 mm are sufficient to induce a large birefringence at voltages between 1.5 V and 5 V. A typical intensity to induce a $\lambda/2$ phase shift was only $I = 4 \cdot 10^{-3}$ W/cm^2 at $\lambda = 458$ nm for an applied DC voltage of 3V. The nonlinear coefficient $\Delta n_e/I$, i.e. the induced birefringence per optical intensity is estimated to 6 cm^2/W. For comparison, nonlinear coefficients in inorganic photorefractive crystals[12,13] are in the range of 10^{-5} to 10^{-6} cm^2/W and about 10^{-3} cm^2/W for the orientational photorefractive effect in calamitic nematics[7,8].

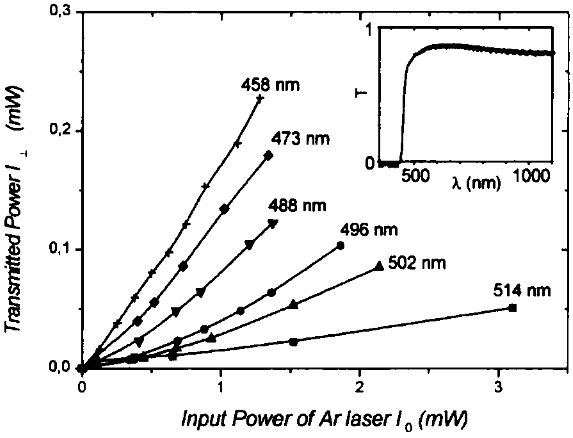

Figure 2 Dependence of the photoinduced birefringence on the wavelength of the Argon laser; inset shows the transmission spectra of the liquid crystal

It must be noted, that even for the maximum depolarization - usually corresponding to a λ/2 phase shift - only a part of about 30 % (instead of theoretically 100%) was rotated into the perpendicular state of polarization in these experiments, indicating that the reorientation of molecules is not homogeneous. This may be explained by the Gaussian intensity profile of the excitation beam as well as a not perfect quality of the orientation layer.

First investigations concerning the dynamics of the reorientation process have been performed either by gating the voltage or the laser intensity. The observed response times were running on the time scale of several seconds, which is a clear confirmation of reorientation as the nonlinear mechanism in the highly viscous liquid crystal. The difference in the phase retardation between the extraordinary and ordinary beam reaches multiples of the wavelength at higher voltages. Accordingly, the depolarization did transiently pass one or more maxima before reaching a stationary state if the voltage or the Ar laser intensity is switched on.

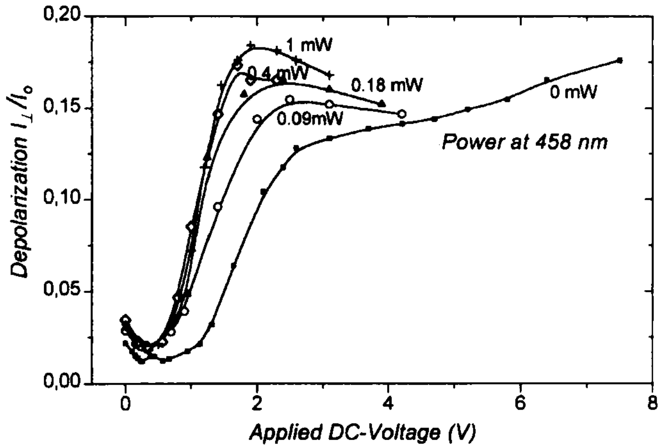

Figure 3 Argon laser illumination of the liquid crystal leads to a large enhancement of the birefringence

Finally, another interesting observation concerning the spontaneous formation of periodic index patterns at higher voltages should be mentioned. The corresponding texture observed under a polarizing microscope looks very similar to the electric field induced convective instabilities (Williams domains) in nematic liquid crystals of calamitic molecules[14,15]. The threshold voltage for this instability was also drastically reduced by illumination with an Ar laser beam at $\lambda = 458$ nm, which will be discussed in detail elsewhere.

THEORETICAL CONSIDERATIONS AND DISCUSSION

The observed reorientation effect as well as the reduction in the threshold voltage of the convective instability may be explained by assuming photo-induced space charges which enhance the effective electric field inside the liquid crystal. Alternatively, we checked that photoheating due to absorption leads only to a rather weak temperature rise of clearly less than 1 K and can be neglected. Furthermore, we found no indication that enhanced optical reorientation due to dipole-dipole interaction of excited molecules as reported[16,17] for some dye-doped liquid crystals (so-called Janossy effect) can explain the effect.

At the present stage of investigation it is reasonable to assume that illumination leads to photo-ionization of the discotic molecules, i.e. creation and separation of electron-hole pairs in the presence of applied electrical DC-fields, very similar as reported in refs. 6, 7, 8. In contrast to columnarly ordered liquid crystals, the mobility of holes is given mainly by the mobility of ions in the nematic discotic phase and therefore negligible compared to the mobility of the free electrons[3,4,5]. As a result, the electrons will be almost removed by the electric field inside the liquid crystal, whereas the holes basically remain at their positions. Even any ionic charge transport will not qualitatively influence the following theoretical model. However, the ionic transport of the positive charge carriers may be responsible for the above mentioned electro-hydrodynamical instability and pattern formation process.

As a result, illumination of the liquid crystal leads to a space charge field which enhances the electric field inside the liquid crystal. The locally increased internal electric field supports electrical torque induced molecular reorientation. Since the discotic molecules have a negative dielectric anisotropy $\varepsilon_{\parallel} - \varepsilon_{\perp} < 0$ the observed optical axis reorientation occurs. Obviously the effect requires illumination of the sample face containing the positive electrode. This was experimentally checked by changing the polarity of the applied DC-field. Furthermore the effect does not work with AC-fields.

A theoretical estimation of the space charge field starts with the rate equation for the density of charged molecules N_D^i which can be written[12,13] neglecting the thermal generation of electron-hole pairs as

$$\frac{\partial N_D^i}{\partial t} = \frac{\sigma I}{h\nu}(N_D - N_D^i) - \gamma_R N N_D^i . \tag{1}$$

The liquid crystal molecule density is denoted by N_D of which N_D^i are ionized. The cross section for photo-excitation is given by σ, the light intensity is I and $h\nu$ is the photon energy. The recombination rate is characterized by $\gamma_R N$, where N is the electron density. The steady state density of photoexited molecules can be calculated from this equation to

$$N_D^i = \frac{\sigma I N_D}{\sigma I + h\nu\gamma_R N}. \tag{2}$$

In case of weak laser intensities where saturation is avoided (i.e. $\sigma I \ll h\nu\gamma_R N$), the photo-induced space charge density $\rho = eN_D^i$ can be assumed to be proportional to the local light intensity I which decreases exponentially along the propagation direction due to absorption in the liquid crystal, hence

$$\rho(z) = \rho_0 \exp(-\alpha z). \tag{3}$$

The absorption coefficient is $\alpha = \sigma(N_D - N_D^i) \approx \sigma N_D$ and the charge density at the liquid crystal surface is given by

$$\rho_0 = \frac{e\sigma N_D}{h\nu\gamma_R N} I(0). \tag{4}$$

The change of the electric displacement $\vec{D}$ inside the liquid crystal cell $(0 \le z \le d)$ caused by the space charges may easily be obtained from the well-known equation $\nabla \cdot \vec{D} = \rho$. Assuming that ρ only depends on z (i.e. for plane optical waves), $\vec{D}$ has only a z-component given by

$$\vec{D}(z) = \frac{\rho_0}{\alpha}\left[\tfrac{1}{2} - \exp(-\alpha z) + \tfrac{1}{2}\exp(-\alpha d)\right] \cdot \vec{z}_0. \tag{5}$$

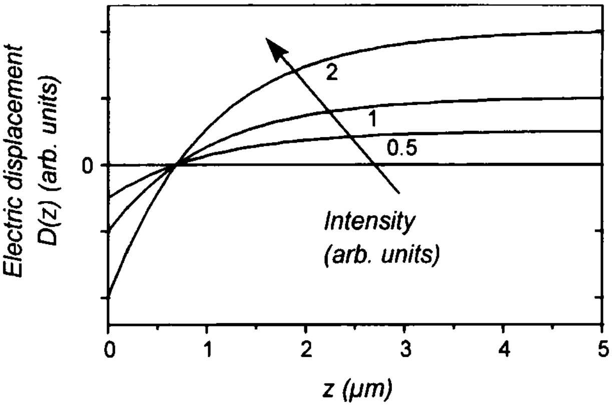

Figure 4 **Calculated change of the electric displacement across the liquid crystal cell dependent on the intensity of illumination. The absorption coefficient was assumed to 1·10^4 /cm.**

The displacement $D(z)$ according to eqn. (5) is displayed in Fig. 4 for different excitation intensities. It can be seen that the field at the sample entrance is reduced due to space charges but increased at the same time in the center of the liquid crystal film, where the reorientation of molecules takes place. The enhancement depends on the number of photo-induced charges and thus upon laser intensity. Obviously, the effect becomes also stronger with higher absorption, which explains the observed wavelength dependence.

At least, it is important to discuss some of the approximations and limitations of the presented theoretical approach. For the above calculation of $D(z)$ we have neglected the influence of molecular reorientation upon the dielectric permittivity which also affects the internal field but usually gives only a small correction. Furthermore, saturation effects and also the influence of a dark current which was in the order of 100 μA in the present experiments is not considered in this simple model. The dark current will decrease the space charge amplitude according to eqn. (4) because of a higher recombination rate. However, the spatial distribution of space charges and hence the principles of the effect will not be changed.

Although most of the material parameters which would allow for a real quantitative proof of the model are not known presently for the investigated material, we can try to estimate the density of induced space charges and the recombination rate which are required to explain the observed field enhancement. A weak laser illumination of about 10 mW/cm^2 at $\lambda = 458$ nm reduces the necessary external voltage to about 0.5 V, which means that the internal field is enhanced in a 5 μm thick cell approximately like 10^5 V/m and the photo-induced electric displacement D can be estimated to $9 \cdot 10^{-7}$ As/m^2. Using eqn. (5) the space charge amplitude ρ_0 is then calculated to 0.6 C/m^3. This corresponds to a density of charged molecules of about $4 \cdot 10^{18}$ Ions/m^3. For comparison, the molecular density of the liquid crystal is about $6 \cdot 10^{26}$ Molecules/m^3. On the other hand, comparison of the required space charge density with eqn. (4) and taking into account the measured absorption coefficient $\alpha = 2400$ cm^{-1} yields a recombination time of $\tau_R = (\gamma_R N)^{-1} = 0.6$ μs.

CONCLUSION

We have observed a very sensitive photo-induced electro-optical reorientation effect in a nematic liquid crystal of discotic molecules. A considerable reorientation was induced even with very weak light intensities of 10^{-3} W/cm^2 supported by DC-electrical fields of 0.6 V/μm. The nonlinear coefficients are as large as 6 cm^2/W and orders of magnitude stronger than the orientational photorefractive effect reported with dye- or fullerene-doped calamitic nematic liquids. Therefore, the material is very promising for various electro-optical, opto-optical and opto-electronic applications.

In a first approach, the new reorientation effect has been explained by photo-excitation and photo-ionization of the discotic molecules in the presence of applied electrical DC-fields resulting in additional space charge fields due to extremely different mobility of electrons and ions in the nematic phase of discotic molecules. The internal field enhancement is roughly estimated to result from a space charge density of about $4\,10^{18}$ Ions/m^3 at the positive electrode which drops down exponentially across the sample as the light intensity due to absorption, together with a recombination time of 1 μs or somewhat less. The developed simple model is already in very good qualitative agreement with the experimental observations, whereas a better quantitative proof requires determination of several material parameters like electrical conductivity, dielectric constants, cross section for photoionization or the electron recombination rate which are not known by now.

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