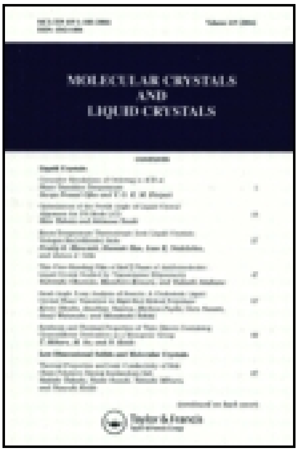

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Sine: Surface Induced Nonlinear Effects

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Sine: Surface Induced Nonlinear Effects

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Pump-probe and TIR experiments have been performed on the dye-doped nematic liquid crystal 5CB, in order to study the basic mechanisms of the extraordinarily large nonlinear response recently reported. Experimental data show that light-induced modifications of the anchoring conditions can be the origin of the observed effect. The bulk reorientation due to the collective elastic behaviour of the liquid crystal gives then rise to the nonlinearity, which occurs without a direct optical torque on the molecular director in the bulk. We have called this effect SINE (Surface Induced Nonlinear Effect).

Keywords Dye doped liquid crystals, nonlinear response, surface effect, surface director distortion

INTRODUCTION

Recent papers[1,2] have put into evidence that methyl-red (MR)-doped nematic liquid crystal films can exhibit a nonlinear refractive index change effect orders of magnitude larger than in other organic and inorganic materials. In these materials in fact, a nonlinear coefficient n_2 of the order of 1 cm^2/W has been observed without the application of a dc bias field.

The origin of this extraordinarily large nonlinearity is now subject of investigation. Thermal gradient effects are ruled out because of the measured decay time which is consistent with a director reorientation effect. On the other hand in all samples where an extraordinarily large n_2 has been observed, the occurrence of a photo-voltaic effect has been demonstrated under the same illumination conditions. In principle, the light-induced space charge field associated to this effect could play an important role in determining the observed nonlinear response, however the measured value of the photovoltage (of the order of 1 mV for cells 23 μm thick), appears to be too low to explain the nonlinearity through a photorefractive-like effect. It is the authors' opinion that, most probably, the measured voltage is an indication of the modifications induced by the light beam on the boundary surfaces, which affect the director orientation through the elasticity of the medium.

In this paper we show that a high nonlinear optical response can be obtained in dye-doped nematic liquid crystals by light-induced modifications of the anchoring conditions. We believe that this effect is the origin of the observed extraordinarily large nonlinearity in Methyl-Red (MR)-doped nematics and could be also responsible for the effects observed in other compounds. The basic idea is very simple: it is well known that the bulk orientation of a liquid crystal is strongly affected by the anchoring conditions, then any change of them induced by a light wave will produce a bulk reorientation. This reorientation affects the light propagation itself with the consequent onset of a nonlinear optical response. Moreover, since only a thin layer near the surface has to be excited to get the elastic reorientation of the whole sample, a very low intensity will be required to induce the nonlinearity.

EXPERIMENTAL

Our investigation has been carried out on MR-doped 5CB using both the pump-probe and the Total Internal Reflection (TIR) techniques.

Samples for pump-probe measurements have been prepared between ITO coated glasses, treated to have homeotropic alignment. The mixture of 5CB and MR (1% in weight) was introduced by capillarity and the good homeotropic alignment of the cell was checked by optical polarising microscopy. Cells thickness is 23, as determined by mylar spacers. Conventional pump-probe geometry was used, with a probe He-Ne laser linearly polarised parallel to the pump beam, detecting the signal transmitted by a crossed polarizer located behind the sample. The unfocussed pump beam is provided by a cw Ar ion laser (λ = 514 nm). Pump and probe beams are co-propagating at normal incidence on the sample.

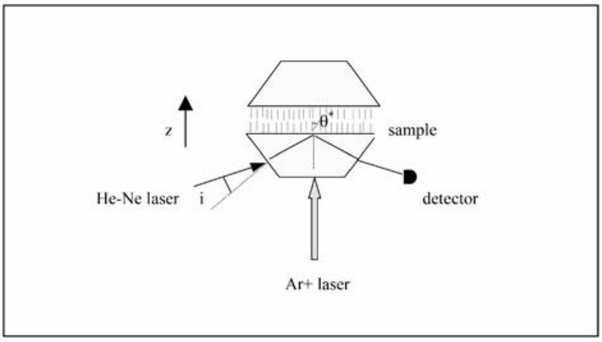

Figure 1: Experimental set-up for TIR measurements

The experimental set-up for TIR measurements is shown in fig.1. Two equal high index prisms (n = 1.94) are the substrates of the used cell. The homeotropic alignment has been realised by treating only the surface opposite to the light entrance, which affects the orientation of the whole sample. The alignment has been checked by direct vision through crossed polarisers. Sample's thickness is 23 μm. A low power He-Ne laser beam is reflected at the prism/liquid crystal interface in correspondence of the region irradiated by the pump beam, which impinges at normal incidence on the sample. The polarisation of the He-Ne has been fixed both as extraordinary and ordinary wave with respect to the initial homeotropic alignment of the sample. A polarizer parallel to the incident polarisation is also present in front of the detector. By rotating the sample around its central symmetry axis, in order to be sure that pump and probe beams are always superimposed on the sample, the reflected light versus the incidence angle is recorded and from this kind of data the surface tilt angle and the liquid crystal extraordinary index can be determined, as will be discussed in the following sections.

RESULTS AND DISCUSSION

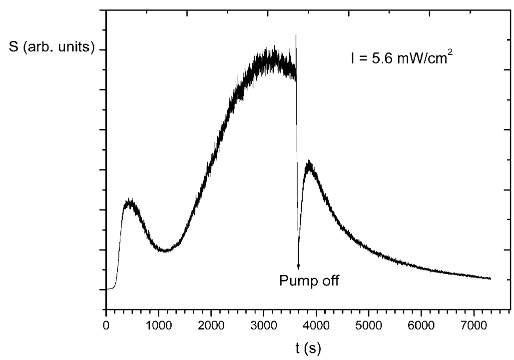

Figure 2: Signal detected during the pump-probe experiments, for a pump intensity I = 5.6 mW/cm^2

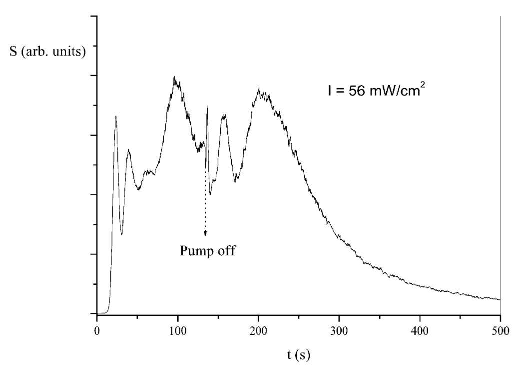

Figure 3: Signal detected during the pump-probe experiments, for a pump intensity I = 56 mW/cm^2

Figure 2 and figure 3 show the signal detected for two different values of the pump intensity, versus time. Oscillations visible both during signal's rise and relaxation, can be interpreted by taking into account that the observed signal can be written as[3]:

$$S \approx C \cdot e^{-\alpha d} \sin^2(2\phi)\sin^2\left(\frac{\delta}{2}\right) \qquad (1)$$

where C is a constant, α is he absorption coefficient at the probe wavelength, d is the sample thickness, ϕ is the angle between the probe beam polarisation and the ordinary wave vibration direction and δ is the phase shift between the e-wave and the o-wave. Signal's oscillations, which are due to the interference between the ordinary and the extraordinary waves travelling through the cell, clearly show that director reorientation occurs in a direction different from that of the probe polarisation. Moreover, experimental data tell us that $\phi \neq 0$, $\pi/2$ and this observation is in agreement with our previous experiments[4] where we observed ϕ approaching zero (director parallel to pump polarisation) for longer time exposure, correspondent to energy densities 2-3 orders of magnitude higher than in the present case.

A careful consideration of fig.2 and fig.3 reveals the occurrence of a delay between the beginning of pump irradiation and the signal's rise, which increases on reducing the pump power. The delay time is about 120 s in the case of fig. 2 (I = 5.6 mW/cm^2) and 15 s in the case of fig. 3 (I = 56 mW/cm^2). Moreover, for long illumination times a memory effect sets in and the induced reorientation may relax after a few days. These observations suggest that the onset of the phenomenon depends on the incident energy density rather than on the intensity. This makes questionable the meaning of the nonlinear refractive index n_2, since the fundamental dependence n = n(I) seems to be no more appropriate.

Experimental data can be interpreted by taking into account that a light-induced easy axis in the azimuthal plane changes the actual surface conditions, thus making unstable the initial alignment. A new director orientation is thus established trough the cell due to the elasticity of the medium. In this way it is easy to explain the observed nonlinear optical behaviour. Furthermore, the effect of the photo-voltage as basic mechanism of the nonlinearity can be dropped by a detailed analysis of the experimental data: in fact a longitudinal space charge field would stabilise the homeotropic alignment preventing any director reorientation. Measurements not reported here, actually show that the application of a dc bias field completely quenches the signal thus confirming the orientational character of the observed effect.

As a final remark, it is worth pointing out that the experiments previously performed in planar samples[4], which demonstrate the transient director sliding over an isotropic surface, have been repeated. They confirm that in a 23μm planarly aligned MR-doped 5CB cell, a reversible modification of the anchoring conditions on the illuminated surface leads to a director surface reorientation that produces a twist of 5°-10° through the cell with an incident power of 1 mW. For light impinging at normal incidence with a polarisation parallel to the planar alignment, this means an average $\delta n \approx 0.08$, which corresponds to a nonlinear refractive index $n_2 \approx 2.9$ cm^2/W. This result strongly supports our idea, since the huge nonlinear response is in this case clearly associated to a director reorientation over the surface. We believe that, in a similar way, in the homeotropic configuration the dye absorption can give rise to a transient modification of the anchoring conditions in the azimuthal plane, namely a transient increase of the azimuthal anchoring energy. This effect produces a weakening of the homeotropic anchoring and leads to an increase of the surface tilt angle θ^*.

In order to directly verify this model, TIR experiments have been performed by using the set-up shown in fig. 1. The TIR technique is in fact sensitive to surface modifications of the liquid crystal refractive index from which light-induced variations of the surface tilt angle can be derived. It is worth noting that by using an ordinary wave as probe beam no change in the reflectivity versus the incidence angle has been observed within our angular resolution (of the order of half a degree). This allows us to neglect the effect of twist in the TIR data analysis. However, we would like to point out that this observation should not be considered in contradiction with the pump-probe experimental data. In fact, even a small azimuthal rotation on the surface (not observable with our limited resolution) can be responsible for the interference effect between ordinary and extraordinary waves travelling through the cell. In what follows, only the experimental results concerning the extraordinary wave, that is the reflectivity parallel to the incidence plane, will be reported and discussed

The calculated reflectivity curve corrected for the trasmittivity of the two air-prism interfaces, is reported in the inset of fig. 4 in case of homeotropic alignment (it is worth noting that we are neglecting reflection from the second boundary which can give rise to interference patterns). The incidence angle in the abscissa is the angle at the interface air-prism (the one indicated by "i" in fig.1). For anisotropic media, the component of the reflectivity parallel to the plane of incidence can be written as[3]:

$$R = \left[\frac{n(n_o^2 \sin^2\theta + n_e^2 \cos^2\theta - n^2 \sin^2\theta_i)^{1/2} - n_o n_e \cos\theta_i}{n(n_o^2 \sin^2\theta + n_e^2 \cos^2\theta - n^2 \sin^2\theta_i)^{1/2} + n_o n_e \cos\theta_i} \right]^2 \qquad (2)$$

where θ_i is the incidence angle at the prism-liquid crystal interface, θ is the angle between the optic axis and the normal to the cell boundaries and n, n_o, n_e are the refractive indexes of the prism and of the liquid crystal, respectively. The angle θ_i can be trivially deduced for each value of i by means of the Snell law. The value of θ_i, which corresponds to the onset of total internal reflection depends on θ and can be deduced by the condition R = 1. We measure the critical angle at the air-prism interface (indicated as i_l) from which the critical θ_i can be calculated and, as a consequence, the surface tilt angle θ^* can be determined.

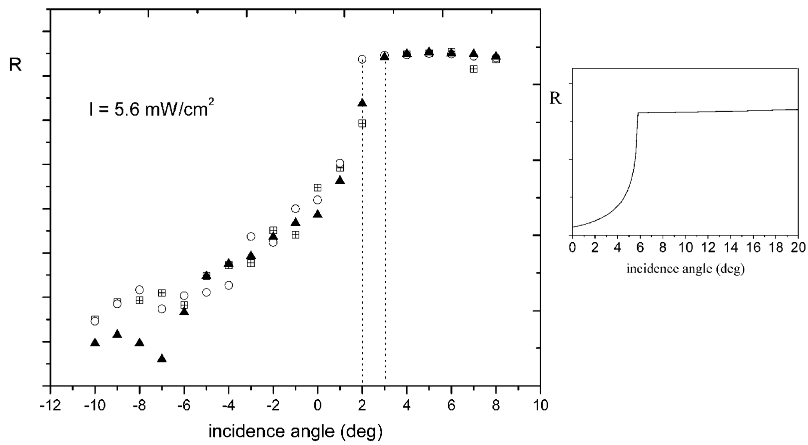

Figure 4: Reflectivity curves for an impinging pump intensity I = 5.6 mW/cm^2. Triangles: reflectivity curve before irradiation; empty circles: reflectivity curve after 60 s from the beginning of irradiation; squares: reflectivity curve after 120 s from the beginning of irradiation. The limit angle i_l for total internal reflection shifts by 1° during irradiation. The inset shows the calculated reflectivity curve corrected for the trasmittivity of the two air-prism interfaces.

Figure 4 reports three reflectivity curves detected while a pump intensity of 5.6 mW/cm^2 is impinging on the sample. The black symbol curve has been recorded before irradiating the sample with the pump beam. Total internal reflection occurs in this case for $i_l = 3°$, which corresponds to a surface tilt angle $\theta^* = 20°$. The other curves in fig. 4 have been recorded during pump irradiation. As it can be seen, the first measurement does not show any variation of i_l, while in the second the limit angle is lower by 1° ($i_l = 2°$) and the corresponding surface tilt angle is $\theta^* = 25°$. Thus light irradiation leads to a surface tilt angle change, as we expected. The delay time between the beginning of pump irradiation and this latter measurement is about 2 minutes, which is consistent with the delay observed in fig. 3 for the onset of the nonlinear response.

From the surface tilt angle change, the surface extraordinary index variation can be directly deduced by means of the well known relation[5]:

$$n_{lc} = \frac{n_o n_e}{\sqrt{n_e^2 \sin^2 \theta^* + n_o^2 \cos^2 \theta^*}} \qquad (3)$$

where n_e and n_o are the extraordinary and the ordinary indexes of 5CB and θ^* has been defined in fig. 1. This angle is zero in the unperturbed homeotropic configuration. The values $\theta^* = 20°$ and $\theta^* = 25°$ derived from data of fig. 4 correspond to $n_{lc} = 1.702$ and $n_{lc} = 1.690$ respectively, which means a light-induced surface index variation of 10^{-2}. By keeping the strong anchoring condition $\theta = 0°$ on the surface opposite to the light entrance and neglecting as a first approximation the light induced twist, the angle $\theta(z)$ can be written as[6]:

$$\theta(z) = -\theta^* (\frac{z}{d} - 1) \qquad (5)$$

With this expression for the tilt angle, the average light induced birefringence through the whole cell corresponding to a variation of θ^* from 20° to 25°, is $\delta n = 3.3 \times 10^{-3}$, which gives rise to a nonlinear refractive index $n_2 = 0.6$ cm^2/W, taking into account that the pump intensity is $I = 5.6$ mW/cm^2. This value is consistent with the extraordinarily high nonlinearity recently reported in 5CB, even if, as already pointed out, the meaning of n_2 is somewhat questionable in the case of the nonlinear response of MR-doped 5CB in the homeotropic configuration.

As a final remark it is worth noting that the observed value of 20° for the surface tilt angle before irradiation is probably due to the bad alignment of the cell that occurs because of the technical difficulty in treating the prism surfaces. Work is in progress to overcome this trouble. We believe that with a better initial homeotropic alignment, the surface tilt angle induced variations would be even larger.

CONCLUSIONS

We have reported the results of an investigation performed on the dye-doped nematic liquid crystal 5CB, in order to study the basic mechanisms of the extraordinarily large nonlinear response recently reported. Experimental data show that light-induced modifications of the anchoring conditions can be the origin of the observed effect, thus suggesting that observed strong nonlinear behaviour is actually a surface induced nonlinear effect occurring without a direct optical or electrical bulk torque on the director. We have called this effect SINE (Surface Induced Nonlinear Effect, "sine" = without in latin language) to remind these peculiarities. The discussed behaviour is typical of liquid crystals because of their collective properties, however it may fall in a new category of optical nonlinearities controlled by surface.

References

[1] I.C. Khoo, S. Slussarenko, B.D. Guenther, M. Shih, P. Chen, M.V. Wood, Opt. Lett. **23**, 253 (1998).
[2] I.C. Khoo, M. Shih, M.V. Wood, B.D. Guenther, P. Chen, F. Simoni, S. Slussarenko, O. Francescangeli, L. Lucchetti, IEEE J. Quantum Electron. **87**, 1897 (1999).
[3] M. Born, E. Wolf, *Principles of Optics* – Pergamon Press, 1959.
[4] O. Francescangeli, F. Simoni, S. Slussarenko, D. Andrienko, V. Reshetnyak, Y. Reznikov, Phys. Rev. Lett. **82**, 1855 (1999).
[5] F. Simoni, *Nonlinear Optical Properties of Liquid crystals and Polymer Dispersed Liquid Crystals* – World Scientific, Singapore 1997.
[6] L. Lucchetti, D.E. Lucchetta, O. Francescangeli and F. Simoni, Optics Express **9(2)**, 85 (2001).