LASER-INDUCED BULK EFFECTS IN NEMATIC LIQUID CRYSTALS DOPED WITH AZO-DYES

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The photoinduced trans-cis equilibrium in nematic liquid crystals is discussed. It is suggested that photoisomerisation leads to an anomalous angular dependence of the dye-induced optical torque.

INTRODUCTION

Light-induced effects in absorbing liquid crystals attracted a considerable interest in recent years. Beside thermal effects, there are a number of additional phenomena connected with excitations of liquid crystal molecules or of dye-dopants added to a liquid crystalline host. Photoinduced conformational transformations, such as trans-cis isomerization of azo compounds, can change the orientational order parameter[1], influence the chiral properties in smectic C phase[2], cause phase transitions[3,4] or textural instabilities[5]. Light irradiation can modify also the conductivity of the liquid crystal, leading to photorefractive-like behaviour of the system[6,7]. Dye-induced enhancement of the optical torque[8,9,10] is a further example of the rich variety of processes taking place in the presence of absorption. In addition to the bulk effects, it is also possible to control the surface orientation of a liquid crystal through optical excitation of molecules attached to the surface[11,12].

The present paper deals with optical effects connected to trans-cis isomerisation in nematic liquid crystals. In the first part, we discuss the nature of trans-cis equilibrium and show that the steady-state cis concentration depends on the angle between the polarisation direction of the illuminating beam and the director. The polarisation dependence implies that in a plane-parallel cell of a nematic, for the extraordinary ray the cis concentration is a function of the angle of incidence of the light beam. We demonstrate this angular dependence experimentally.

In the second part, we describe optical reorientation in a nematic, doped with azo dyes. It is plausible to assume that the trans and cis isomers contribute with different enhancement factors to the dye-induced optical torque. As the fraction of the cis isomers depends on the angle of incidence, an angular dependence of the enhancement factor is expected. In particular, if the optical torque generated by the trans and cis isomers are of different signs, the resultant optical torque may change sign as the angle of incidence is varied. Such a behaviour was, in fact, reported by Barnik et al.[13] using a di-azo dye. We present similar experimental results and from the data we evaluate the ratio of the enhancement factors of the trans and cis isomers.

ANGULAR DEPENDENCE OF PHOTOINDUCED TRANS-CIS EQUILIBRIUM IN NEMATICS

Photoisomerisation of azobenzene derivatives is a well-known process that has been studied in the past extensively[14]. In thermal equilibrium the molecules adopt the trans configuration, i.e. the chemical bonds linking the central azo group to the two aromatic rings are parallel. Light irradiation converts a fraction of the molecules to the cis form, changing the angle between the bonds

by 120 degrees. The two isomers (trans and cis) differ in a number of chemical and physical properties, e.g. in their absorption spectra.

We discussed in detail the trans-cis equilibrium in nematic liquid crystal in another publication [15]. Here we only summarise the main results.

In steady state, there is a dynamical equilibrium between trans-cis and cis-trans transitions. The former transitions are induced by light only, the latter ones can be induced both by light and thermal excitations. Quantitatively, one can write

$$\frac{I\overline{\sigma}_T}{h\nu}\Phi_{TC}(1-X) = (\frac{I\overline{\sigma}_C}{h\nu}\Phi_{CT} + \frac{1}{\tau})X \tag{1}$$

where X is the fraction of dye-molecules in the cis form (hence $1-X$ is the fraction of the trans isomers); I is the light intensity; $\overline{\sigma}_T$ and $\overline{\sigma}_C$ is the cross section of absorption of a photon with $h\nu$ energy for a trans and cis isomer respectively, averaged over the orientatonal distribution of the relevant isomer; Φ_{TC} and Φ_{CT} is the quantum efficiency of the trans-cis and cis-trans transition resp., finally τ is the time constant of thermal cis-trans transitions. From Eq./1/, we obtain

$$X = \frac{X_S}{1 + I_S / I} \tag{2}$$

where I_S is an intensity parameter:

$$I_S = \frac{\tau}{\overline{\sigma}_T\Phi_{TC} + \overline{\sigma}_C\Phi_{CT}} \tag{3}$$

and X_S is the saturation value of the cis fraction for intensities much higher than I_S:

$$X_S = \frac{A\overline{\sigma}_T}{\overline{\sigma}_C + A\overline{\sigma}_T} \quad \text{with} \quad A = \Phi_{TC} / \Phi_{CT}. \tag{4}$$

As discussed in Ref. [15], in nematics due to the high rotational mobility of the molecules, the orientational distribution of the trans and cis isomers are

basically in thermodynamical equilibrium. Under such circumstances, the average cross sections can be given in the form

$$\overline{\sigma}_T = \sigma_T^{perp} + \sigma_T^{an} \cos^2 \Psi, \quad \overline{\sigma}_C = \sigma_C^{perp} + \sigma_C^{an} \cos^2 \Psi. \tag{5}$$

where Ψ is the angle between the polarisation direction of the exciting light beam and the nematic director. The σ quantities depend on the orientational distribution of the dye; in particular σ_T^{an} and σ_C^{an} is proportional to the orientational order parameter of the trans and cis isomers respectively.

Combining Eqs.(4) and (5), one obtains

$$X_S = A \frac{\sigma_T^{perp} + \sigma_T^{an} \cos^2 \Psi}{\sigma_C^{perp} + A\sigma_T^{perp} + (\sigma_C^{an} + A\sigma_T^{an}) \cos^2 \Psi} \tag{6}$$

with $\sigma_T^{an} = \sigma_T^{par} - \sigma_T^{perp}, \sigma_C^{an} = \sigma_C^{par} - \sigma_C^{perp}$. For ordinary polarisation $\Psi = \pi/2$, hence X_S is independent from the direction of light propagation. On the other hand, for extraordinary polarisation, the Ψ angle varies from 0 to $\pi/2$ as the propagation direction is changed, hence an angular dependence of X_S is expected.

A direct experimental verification of the above prediction is given in Fig.1. In the experiment a 50μm thick homeotropic layer of the nematic mixture E63, doped with 0.5% of R4 (4'-dimethylaminophenyl- [1,4-phenylenebis(azo)] - 3-chloro-4-heptyloxy benzene), was investigated. The transmission of a weak probe beam is shown without and with a pump beam, for different angles of incidence and polarisation directions of the pump beam. As it can be seen from the figure, the transmission increased when the exciting light beam was switched on, indicating the formation of cis isomers. Saturation of the transmission increase was observed already at intensity levels as low as a few mW/mm^2. For normal incidence, naturally, no difference was found between the two polarisation direction of the pump beam. As the angle of incidence was increased, the transmission change induced by the o-ray remained   unchanged,

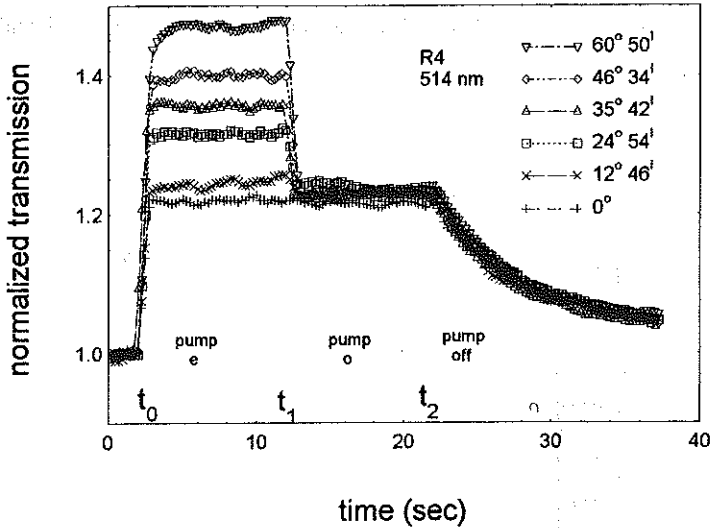while the change generated by the e-ray showed marked variation, namely it increased.

FIGURE 1. Probe transmission as a function of time. The pump beam was switched on at t_0 with extraordinary polarisation, at t_1 it was turned to ordinary polarisation, at t_2 it was switched off. Pump power 6 mW, spot radius 1 mm. Angle of incidence of probe beam 47°, e-polarisation.

From pump-probe measurements, the parameters involved in the model can be determined using the procedure described in Ref.[15]. With the help of this method, for R4 at 514nm we obtained A=0.35, $N\sigma_T^{perp} = 92cm^{-1}$, $N\sigma_T^{par} = 819cm^{-1}$, $N\sigma_C^{perp} = 90cm^{-1}$, $N\sigma_C^{par} = 186cm^{-1}$ (N is the number of dye molecules in unit volume). In Fig.2, X_S is shown as a function of Ψ computed according to Eq. (6), using the above data.

In the case of a homeotropic sample, the angle Ψ can be expressed through the angle of incidence of the light beam, β, with the help of the relation

$$\cos^2 \Psi = \frac{n_o^2 \sin^2 \beta}{n_e^4 - (n_e^2 - n_o^2) \sin^2 \beta}$$

where n_e and n_o is the extraordinary and ordinary refractive index respectively. In Fig.2. X_s is also shown as a function of β, assuming n_e=1.75 and n_o=1.52 (values for E63).
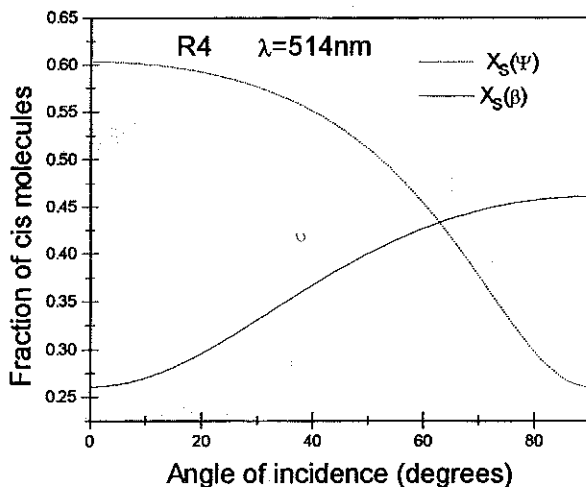

FIGURE 2. Fraction of the cis molecules for R4 as a function of the angle of incidence.

OPTICAL REORIENTATION IN THE PRESENCE OF TRANS-CIS PHOTOISOMERIZATION

It is well known that small amounts of dye-dopants can amplify the optical reorientation process in nematics significantly[8-10]. The strength of the effect can be characterised by a dye-specific enhancement factor, η, defined as the ratio of the dye-induced optical torque to the normal optical torque acting in the pure

host material. In the case of azo-dyes, the trans and cis isomers can be regarded as two separate dopants which contribute independently to the dye-induced part of the torque. Taking into account that the enhancement factor is proportional to the dye concentration, one can write

$$\eta = \eta_T (1 - X) + \eta_C X \qquad (7)$$

where η_T and η_C is the trans and cis enhancement factor respectively.

In the previous section it was shown that for the R4 dye the cis concentration saturates already at light intensity levels below a few mW/mm^2. In typical optical reorientation experiments the light intensity is much higher than this value, therefore in Eq.(7) one can substitute X by its saturation limit, X_S. In this limit Eq.(7) can be rewritten in the form

$$\eta(\Psi) = \eta_T (1 - X_S(\Psi)) + \eta_C X_S(\Psi) \qquad (8)$$

where $X_S(\Psi)$ is given by Eq. (6). Thus the dye-induced amplification of the optical reorientation in the presence of photoisomerization can be described by an enhancement factor which varies with the direction of light propagation.

We suggest that the angular dependence of the η factor explains the peculiar behaviour reported by Barnik et al. in connection with an azo dye-doped nematic[13]. They found self-defocusing orientational nonlinearity when the angle of incidence of the light beam was below a critical value; above the critical angle self-focusing was observed. A similar observation can be seen in Fig.3 for the R4 dye, where Z-scan curves[16] are shown at different angles of incidence. As the angle of incidence increases, the nonlinearity changes from self-defocusing (peak before valley) to self-focusing (valley before peak). The critical angle is around 35°. The change of sign of the nonlinearity indicates the change of sign of the net optical torque: defocusing corresponds to the rotation of the director towards the wave vector (negative optical torque), focusing implies that the director rotates towards the electric field vector of the light beam (positive optical torque).
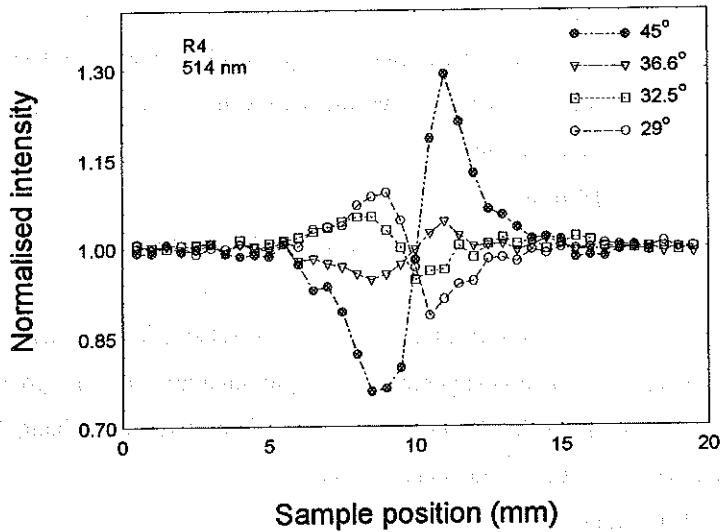
L. SZABADOS *et al.*

FIGURE 3. Z-scan curves for different angle of incidences for R4. Input power 0.4 mW.

From the above findings we conclude that η changes from negative to positive values as the angle of incidence, β, is increased. On the other hand, it is known from the results presented in Fig.2 that the cis concentration increases with increasing β. These facts imply a negative η_T and a positive η_c value.

The crossover from positive to negative η values occurs at a critical cis concentration where the condition

$$\eta_T (1 - X_{cr}) + \eta_c X_{cr} = 0 \qquad (9)$$

is fulfilled. We note that the condition for zero net optical torque is slightly different, because the normal optical torque has to be taken into account as well. The latter condition can be written as

$$\eta_T (1 - X'_{cr}) + \eta_c X'_{cr} = -1. \qquad (10)$$

If, however, η_T and $\eta_C >> 1$, i.e. the optical torques induced by the trans and cis isomers separately are both much stronger than the normal optical torque, one can assume that X_{cr} and $X_{cr}^{'}$ are approximately equal. With this assumption

$$X_{cr} \approx X_{cr}^{'} = X_S(\Psi(\beta_{cr})) \tag{11}$$

where β_{cr} is the critical angle of incidence at which no optical reorientation is observed. With $\beta_{cr} = 35^{o}$, from the data presented in Fig.2, we get $X_{cr} \approx 0.35$, and from Eq.(9)

$$\eta_T = \frac{X_{cr}}{(1 - X_{cr})}\eta_C \approx -0.54\eta_C$$

The above interpretation of the anomalous angular dependence of the orientational nonlinearity accounts also for the accompanying bistable behaviour, described by Terskov et. al.[17]. Because of the change of sign of η with Ψ, the director configurations both at $\Psi = \pi/2$ and at $\Psi = 0$ are stable with respect to the optical torque. The former case implies a negative, the latter one a positive optical torque; the two configurations correspond to different cis concentrations. In the limit of high intensities both configurations can be realised by changing the direction of light propagation in an appropriate way[17].

Finally, we note that all parameters involved in the model depend on the wavelength of the exciting light beam, hence the cross-over point depends on the wavelength too. Therefore one may also observe a change of sign of the orientational nonlinearity at fixed angle of incidence when the wavelength is varied. In fact, such observations were reported earlier[13,18].

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