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Dynamics in Dye-Doped LC Systems in Presence of Trans-Cis Isomerism

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The excitation as well as relaxation dynamics of dye-doped nematic liquid crystal cells has been explored both experimentally and theoretically. Overshoots in the build up of the probe signal diffracted from gratings written onto dye-doped liquid crystal systems have often been observed. The overshoot behaviour makes the accurate measurement of nonlinear optical (NLO) response magnitude difficult and ambiguous. Moreover, it complicates the understanding of the dynamics and the physics of the NLO processes.

On the basis of the system with trans-cis isomerisation as a mechanism of the NLO effect the quantitative model has been built to describe the experimental results which we observe.

The two unknown material parameters: diffusion coefficient and cis species lifetime are calculated from the relaxation data. A quantitative model of the signal build-up uses these parameters. The calculated dynamic behaviour based on this model correlates very well with the experimental data.

The model is used to predict the performance of the system with various dopant diffusion properties.

Keywords: dynamics; dye-doped liquid crystal; photorefractivity; trans-cis isomerism

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INTRODUCTION

Chromophore-doped liquid crystals are recognised for their extraordinary large optical nonlinearities that make them attractive for many applications in the field of photonics, in particular they may be used as materials for novel Optically Addressed Spatial Light Modulators (OASLMs) based on photorefractive orientational effects [1–5].

We have shown that azo-substituted anthraquinone (ASAQ) dye-doped liquid crystal (LC) systems are interesting materials for applications in the field of (OASLMs) [6]. The optical nonlinearity in liquid crystals is attributed to trans-cis isomerisation in the dopant molecules.

Nematic liquid crystals usually have response times of about 20–50 ms. The aim of this article is to research the dynamical response of the optical nonlinear effect in ASAQ-doped NLC systems and the possibilities of decreasing the response times to the minimum obtainable from nematic liquid crystals.

The dynamics of nonlinearity exhibited by dye-doped NLC films is complicated. Here we study the influence of operational characteristics like writing beam power, host material, device thickness and spatial frequency of the written hologram on the build up and relaxation times of the optical nonlinearity in DC161 doped devices.

Experimental Technique

The devices consist of two ITO glass slides, usually with rubbed polyimide layer as an aligning agent. The thicknesses are 5 μm, 10 μm, 14 μm, 20 μm. Several commercially available nematic LC such as 5CB, BLO48 and E7 from Merck have been doped by ASAQ dye DC161 by agitation in of the mixtures at elevated temperatures and

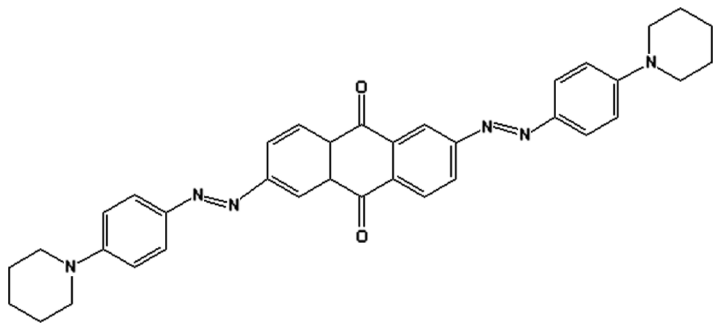

FIGURE 1 Azo-Anthraquinone dye DC161 structure.

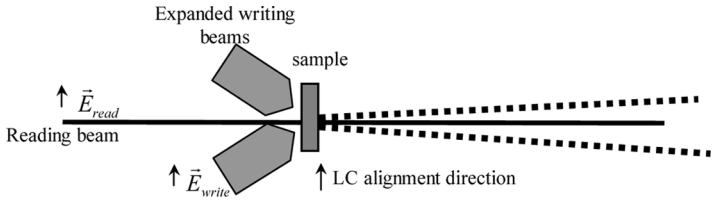

FIGURE 2 Experimental setup for holographic grating formation experiment, two-beam interference.

cycling through the isotropic-nematic transition. The dye structure is shown on Figure 1.

A holographic grating is recorded on the sample using two Ar+ laser beams ($\lambda = 514\,\text{nm}$) intersecting at a small angle and forming an interference pattern (Fig. 2). The interference pattern that is formed is a sinusoidal grating with a wavelength of 12.5 μm (corresponding to a 80 line pairs/mm (lp/mm) grating). A weak He-Ne laser beam ($\lambda = 633\,\text{nm}$, 1 mW) is used to read the recorded grating. All the beams are polarised along the director of the LC, i.e., along the alignment direction of the device. The first diffracted order is measured using a photo-multiplier and oscilloscope during switch "on" and switch "off" of the writing beams.

EXPERIMENTAL RESULTS

The typical dynamic behaviour of a dye-doped nematic device is shown in Figure 3 for the example of 1%DC161 doped 5CB. The relaxation of liquid crystal has a decaying exponential form while the build up process is more complicated.

Relaxation

First, let us concentrate on the relaxation dynamics.

The relaxation of the LC may be described by the decay constant τ_{decay} (in an exponential law $e^{-t/\tau}$). We derive the decay constant by approximating the diffracted signal dynamic behaviour with an exponential function of the form $e^{-t/\tau}$. In this case the statistical error due to the noise and fluctuations in the signal is minimised, as many data points are approximated at the same time.

It is important to note that the diffracted signal is proportional (in the first approximation) to the square of refractive index change. Thus if the relaxation of the refractive index change is described by

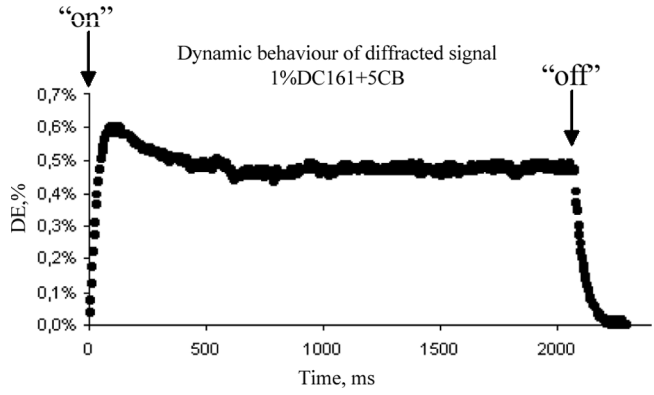

FIGURE 3 Typical dynamic behaviour of diffracted signal. Optical power of the writing beams 50 mW/cm^2; sample is 1% DC161 doped 5CB, 9 μm thick. The arrows indicate the time when the writing beams are switched "on" and "off".

the function $e^{-t/\tau}$, the diffraction efficiency relaxation would follow the $e^{-2t/\tau}$, and the resulting decay constant:

$$\tau_{DE} = \frac{\tau_{LC}}{2} \tag{1}$$

There can be two contributions to the relaxation dynamics of orientational effects in the dye-doped systems: from the *LC* and from the *dye molecules*.

The decay constant of the liquid crystal is defined by its viscous and elastic properties and is derived from the viscous, elastic and optical torque balance equation [7]. For sinusoidal optical intensity:

$$\tau_{LC} = \frac{\gamma}{K\left(\frac{4\pi^2}{\Lambda^2} + \frac{\pi^2}{d^2}\right)}, \qquad \text{and} \qquad \tau_{DE} = \frac{\gamma}{2K\left(\frac{4\pi^2}{\Lambda^2} + \frac{\pi^2}{d^2}\right)} \tag{2}$$

where γ is the effective viscosity of the LC material, K is the elastic constant; d is the LC film thickness and Λ is the fringe spacing.

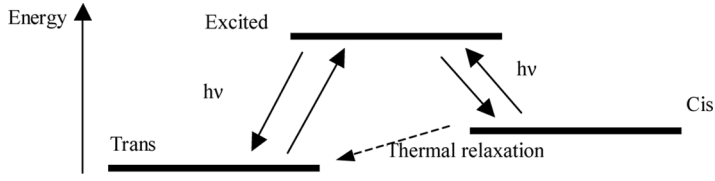

FIGURE 4 Schematic energy model of Trans-Cis photoisomerisation.

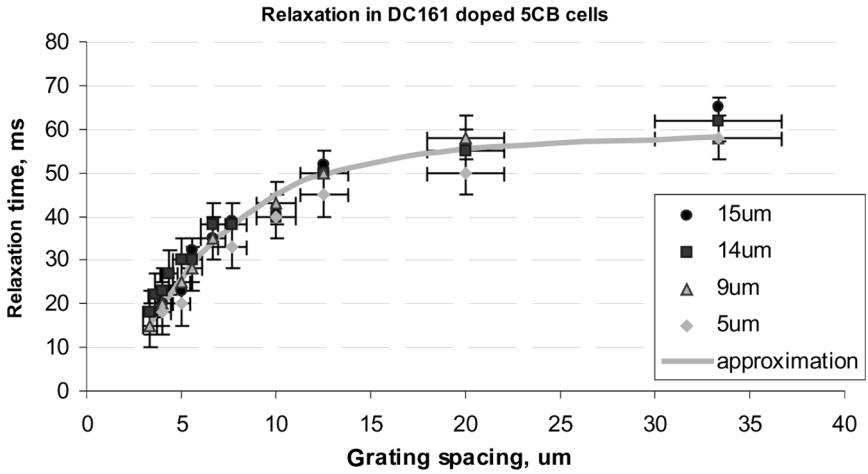

FIGURE 5 Relaxation in 5CB films doped with 1% of DC161 dye, dependence on the grating spacing. The intensity of the writing beams is 50 mW/cm^2. The solid line is a fitting curve according to the relations 6 and 1. Films with 0.5% doping level have almost identical relaxation characteristics.

The experimentally observed decay constants are longer than the ones calculated from (1 and 2). There is almost no dependence of the decay time on the sample thickness even when the grating spacing is of the order of, or larger than, the thickness (Fig. 5). Thus the relation (2) does not govern the relaxation in our systems. It will now be shown the dye diffusion is responsible for the temporal switching characteristics of the devices.

Diffusion Model

Let us consider the possible effect of the dye on the decay time. As suggested earlier [8], excited dye species will diffuse into non-illuminated regions, and the decay times will depend on this diffusion, the grating spacing and the lifetime of excited state.

Consider the dye molecule with two ground levels trans and cis (Fig. 4).

In the linear region of optical excitation, which is a good approximation for the low optical powers used, it is reasonable to assume that the population of excited states may be neglected.

For this case, the rate of change of the number of cis species at any moment would obey the relation [9]:

$$\frac{\partial N_{cis}}{\partial t} = ((N - N_{cis})\sigma_{trans}\Phi_{trans\text{-}cis} - N_{cis}\sigma_{cis}\Phi_{cis\text{-}trans})\frac{I}{h\nu} - \frac{N_{cis}}{T_{cis}} + D_y\frac{\partial^2 N_{cis}}{\partial y^2} \quad (3)$$

where:

N is the number of dye molecules per unit volume,
N_{cis} is the number of the cis species;
σ_{trans} and σ_{cis} are the cross sections of absorption of a photon with energy $h\nu$ for trans and cis isomers;
$\Phi_{trans\text{-}cis}$ and $\Phi_{cis\text{-}trans}$ are quantum efficiencies of the respective transitions;
D_y is the diffusion coefficient in the y direction;
T_{cis} is the lifetime of the cis state;
$I = I(y)$ is a periodic optical field characterised by the grating spacing Λ.

When the optical intensity is switched off this equation can be written in the form:

$$\frac{\partial N_{cis}}{\partial t} = -\frac{N_{cis}}{T_{cis}} + D_y \frac{\partial^2 N_{cis}}{\partial y^2} \tag{4}$$

Since we know that at t = 0

$$N_{cis} = N_{cis}^{\max} \sin\left(\frac{2\pi y}{\Lambda}\right) \tag{5}$$

this gives a similar relation for the relaxation constant as in [10]:

$$\tau_{dye} = \frac{1}{\left(D_y \frac{4\pi^2}{\Lambda^2} + \frac{1}{T_{cis}}\right)} \tag{6}$$

The experimentally measured relaxation times in samples of different thickness are shown in Figure 5. The relaxation time increases as the grating spacing is increased, and starts to saturate for spacing larger than 20 μm.

The experimental data has been approximated using relation (6) (solid line in Fig. 5). The following fitting parameters have been used: $D_y = 7\,\mu m^2/s$; $T_{cis} = 120\,ms$. The fact that these parameters are the same for all 5CB doped with DC161 films regardless of the dye concentration, the age of the sample, and alignment interface supports the discussed idea of dye contribution.

At a large grating spacing in thick samples the LC relaxation time might become longer than the contribution of the dye, and the relaxation dynamics will be governed by (2). The calculation shows that in 5CB devices the relaxation dynamics may be governed by the elastic properties of a liquid crystal only in devices thicker than 20 μm. The

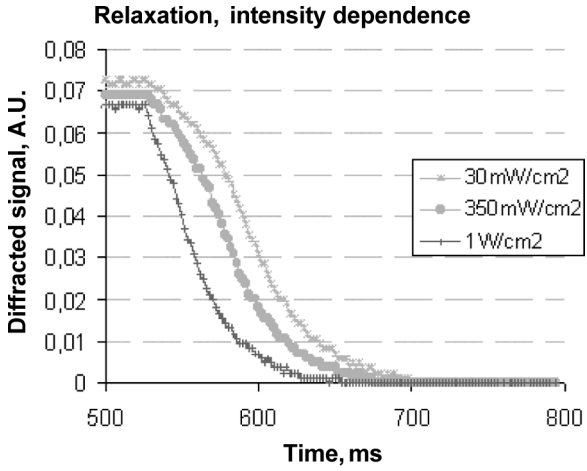

FIGURE 6 Writing beam intensity dependence of relaxation process. The device is 10 μm thick 5CB + 1% DC161.

grating spacing threshold at which this occurs decreases from $\Lambda = 50\,\mu m$ for 30 μm thick devices to about $\Lambda = 40\,\mu m$ as the device thickness is increased to over 50 μm.

We observe a dependence of relaxation time on the writing light intensity (Fig. 6).

Samples switch off faster when a higher light intensity of the writing beams has been used. For example, the decay constant τ associated with diffracted signal at writing beam intensity $30\,mW/cm^2$ is 46 ms, while the decay constant associated with $1\,W/cm^2$ is 33 ms. As the power of the light cannot influence the relaxation directly, we suggest that it can stimulate cis-trans thermal back relaxation [11].

Build Up: Rise Times and Overshoot

The rise times of the nonlinear effect depend on many parameters, including wavelength and optical power. In DC161 doped systems the fastest operation is achieved using writing beams at $\lambda = 514\,nm$. We study the dynamics of nonlinearity build up as a function of operating and device parameters, such as optical power, sample material and thickness, and grating spacing.

At high optical powers (above $30\,mW/cm^2$), an overshoot appears (Fig. 7). The initial rise time and the overshoot magnitude both depend strongly on the writing beam intensity.

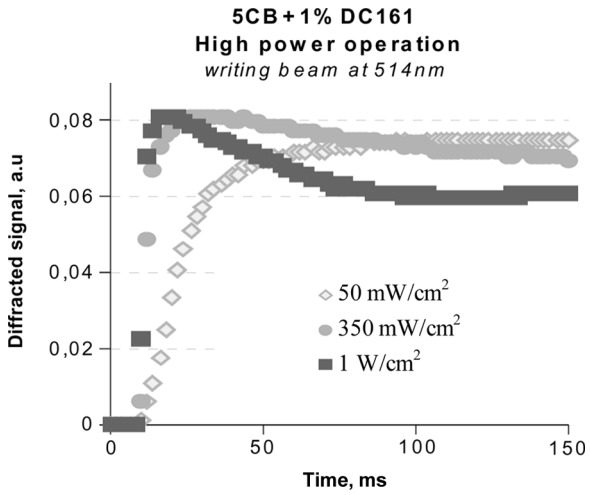

FIGURE 7 Nonlinearity build up, intensity dependence. 1% DC161 doped 5CB; thickness 10 μm. The grating spacing is 12.5 μm.

The overshoot has a peculiar behaviour. First of all, it is quite slow and cannot be attributed to thermal effect. The time scale suggests an orientational origin. Secondly, it is virtually the same in ASAQ-doped devices with different host materials, hence is not of guest-host interaction nature. The possibility of the molecules in the excited state contributing to the overall reorientation is excluded taking into consideration the time scale of the effect: the excited state lifetime in 10 ms range is highly unlikely. As will be shown below, the phenomenon can be explained by dye diffusion process similar to the phenomenon occurring during relaxation.

When the optical power is increased, the nonlinearity builds up faster (Fig. 7). The rise time can become as short as 6 ± 2 ms at $1\,W/cm^2$ (more than 10 times the difference as compared to $50\,mW/cm^2$). The possibility to shorten the initial rise times by using high optical powers is an important result for the applications.

Cis Species Build up Dynamics

The molecular motion in nematic phase (20–100 ms) is of the same order and faster than the lifetime of cis state of the dopant molecules ($T_{cis} = 120$ ms, as shown in the previous section). Therefore the molecular reorientation and resulting refractive index change (that manifests itself in diffracted signal) will follow the behaviour of the cis population dynamics.

The build up dynamics of cis species may be derived from the Eq. (3). The equation is solved numerically using *Matlab* software package. The number of cis isomers N_{cis} is calculated using the described diffusion model. Most parameters were measured experimentally. The following values have been used for the calculation:

- The value of absorption cross-section is calculated from the experimentally measured absorption coefficients of trans and cis components:

$$N\sigma_i = \alpha_i; \quad i = trans, cis \tag{7}$$

  where α_{trans} and α_{cis} are the absorption coefficients of trans and cis components [9].
- Absorption coefficients of trans and cis dye species have been measured as in [9]. In this case, we used planar samples. In this geometry optically induced reorientation of LC director is difficult to control. The reorientation of LC may lead to reorientation of dye molecules resulting in the change of absorption. Therefore, the coefficients calculated from experimental measurements in planar cells may contain a systematic error. Nevertheless, they can be a good guide when testing the model.
- Cis species lifetime: $T_{cis} = 120\,\text{ms}$ (calculated from the relaxation dynamics);
- Diffusion constant: $D_y = 7\,\mu\text{m}^2/\text{s}$ (calculated from the relaxation dynamics);
- The quantum efficiencies of transitions at excitation wavelength $\lambda = 514\,\text{nm}$ are not known and have been chosen $\Phi_{trans\text{-}cis} = 0.3$; $\Phi_{cis\text{-}trans} = 0.2$ and gave good agreement with the experimental data.
- From previous studies, Trans-cis isomerisation leads to anisotropic change in the order parameter of the liquid crystal [12]. Differentiating expression for refractive index in Jeu and Bordewijk model, one can find that the change of refractive index linearly depends on the change of the order parameter: $dn = q_1 dS$. We assume linear dependence of the LC order parameter on the number of cis isomers: $dS = q_2 N_{cis}$, which leads to the relation:

$$dn = q \cdot N_{cis} \tag{8}$$

  $q = q_1 \cdot q_2$ is the proportionality constant. The assumption about linear dependence of dS on N_{cis} may lead to overestimated efficiency for higher optical powers;
- The model does not account for the decrease of the optical power due to absorption in the sample. In order to minimise the related error we have chosen a thin $5\,\mu\text{m}$ device for comparison.

- In real optical systems when interference pattern is formed or grating is imaged onto the sample the contrast between dark and bright areas cannot be ideal. The contrast can be described by visibility function:

$$V = \frac{I_{bright} - I_{dark}}{I_{bright} + I_{dark}} \tag{9}$$

where I_{bright} and I_{dark} are optical intensities in bright and dark areas. In our model we assumed V = 0.95.

As can be seen from Fig. 8, the discussed model gives a good approximation of the complicated dynamic behaviour of dye-doped liquid crystals. An overestimated response at high powers is due to not taking into account optical intensity change as the light propagates in strongly absorbing sample, and due to assuming linear dependency of the refractive index change on the number of Cis species.

Predictions Based on the Model

Further, we have modelled the influence of the parameters that may be modified by means of chemical engineering or host material selection: diffusion and cis species lifetime on the dynamics of the system.

As can be seen from the graphs on Figure 9, by limiting diffusion it is possible to improve efficiency and dynamics. Nevertheless, the change is not as dramatic, as could be expected. Longer lifetime of molecules in Cis state also leads to increase in efficiency, but hampers the uniformity of dynamic response. Therefore, both coefficients

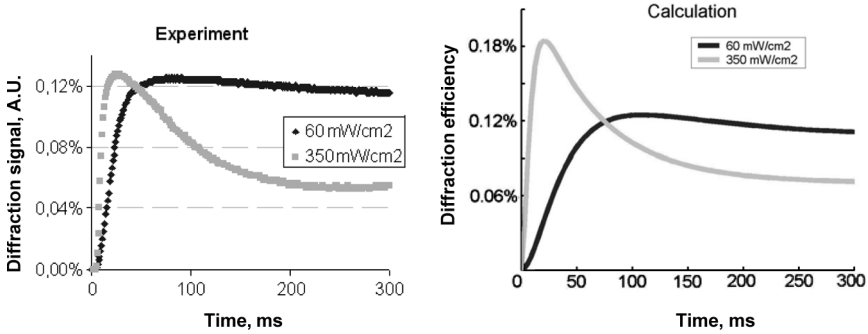

FIGURE 8 Experimentally observed (left) and calculated (right) dynamic behaviour at different optical intensities. 5 μm 1%DC161 + 5CB sample.

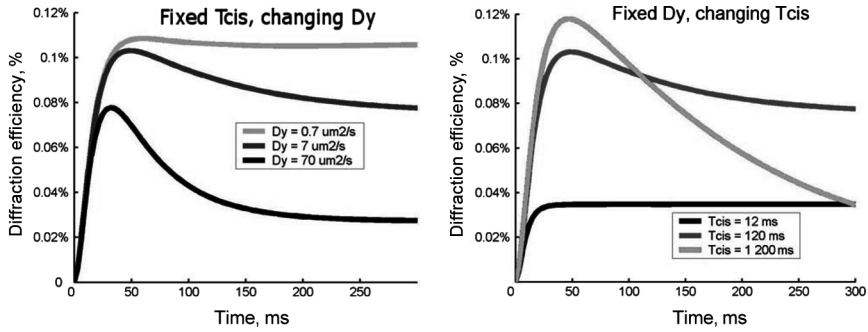

FIGURE 9 Calculated temporal dependence of diffraction efficiency on the diffusion coefficient (left) and on the lifetime of cis state (right) of dynamic behaviour of LC system doped with azo dye.

should be optimised together. For example, 20% decrease in D_y and 20% increase in Tcis would lead to 9% increase of efficiency; 2 times decrease in D_y and 2 times increase in Tcis would lead to 30% increase of efficiency.

CONCLUSIONS

Researching dye-doped nematic systems suitable for OASLMs applications we have studied relaxation and build up of nonlinearity evoked by Trans-Cis isomerisation in dopant molecules in these systems. Relaxation in the system is governed by dye (diffusion and lifetime of excited state). Diffusion leads to decrease in efficiency of the devices and leads to slowing down the relaxation and overshoots in the build up dynamics. We have described experimental results with a diffusion model and derived diffusion coefficient and lifetime in cis state of the dopant molecule from the relaxation dynamics of the system. Our model predicts that to improve switching and efficiency, diffusion coefficient D_y should be minimised, while the lifetime of excited state should be optimised for specific D_y.

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