

Anomalous wavelength dependence of the dye-induced optical reorientation in nematic liquid crystals

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We report on Z-scan measurements of the spectral dependence of dye-induced enhancement of optical torque in nematic liquid crystals. It is found that the enhancement factor changes sign from positive to negative as photon energy increases from 2.4 to 2.7 eV. Modification of our earlier model is proposed to describe the observed spectral dependence.

Recent experiments with dye-doped nematic liquid crystals revealed that absorption has a considerable effect on the optical-field-induced director reorientation. Investigations of optical nonlinearities through the optical Freedericksz transition,^{1,2} four-wave mixing,³ and the Z-scan technique⁴ indicated a strong dye-induced amplification of the optical torque in a number of guest-host systems. The amplification factor η , defined as the ratio of the dye-induced torque to the usual dielectric torque, can be as high as 200 at dye concentrations of the order of 1%. For most dyes η is negative, i.e., the optical field tends to align the director perpendicularly to the electric-field vector. This fact is in striking contrast with the situation in transparent nematics where, because of the positive birefringence of the system, the director is aligned parallel to the electric field of the light beam.

A molecular interpretation of the observations was given in Ref. 5. In the model, the orientationally selective excitation probability of the dye molecules was taken into account and it was assumed that the mean-field potential acting on a ground-state dye molecule differs from that acting on an excited molecule. According to this model, the sign of the amplification factor is positive if the orienting potential is stronger for the excited state than for the ground state, and it is negative in the opposite situation.

In a recent study the wavelength dependence of the amplification factor was measured for two anthraquinone dyes.⁶ For one of the dyes (D4), the η coefficient proved to be proportional to the dichroism of the guest-host system. This finding could be interpreted with the help of the previous theoretical considerations. For the other dye (AQ2), however, which shows a very large positive amplification, an obvious deviation from the proportionality was found; with decreasing wavelength η decreased more rapidly than the dichroism.

In this Letter we report our findings on a guest-host system, in which the amplification factor changes from positive values to negative ones as the wavelength is decreased. The dichroism of the system, in contrast, has a large positive value in the entire wavelength range covered in the experiments. This example shows, even more clearly than the case of the AQ2-doped material, that the theoretical model has to

be modified in some way to describe correctly the wavelength dependence of the dye-induced reorientation. In this Letter, after describing the experimental results, we propose a simple extension of the model that can qualitatively explain the observed behavior.

In our experiments we investigated the guest-host system containing 0.5% of the dye 4'-dimethylaminophenyl-[1,4-phenylenebis(azo)]-(3-chloro-4-heptyloxy) benzene (R4), dissolved in the host E63 or E48 (BDH trade names). The absorption coefficients of the systems are shown in Fig. 1 as a function of the wavelength.

The optical reorientation was studied with the help of the Z-scan technique,⁷ following the procedure described in Ref. 4. The sample, a 35- μm -thick homeotropic layer sandwiched between two indium tin oxide-coated glass plates and illuminated by a focused laser beam at an angle of incidence of 45°, is translated along the beam in the vicinity of the focal point. Extraordinary polarization is applied. The intensity of the central part of the transmitted beam is monitored in the far field. In the case of self-focusing nonlinearity the detected intensity exhibits a minimum at a certain sample position between the lens and the focal point; a maximum is observed at a position behind the

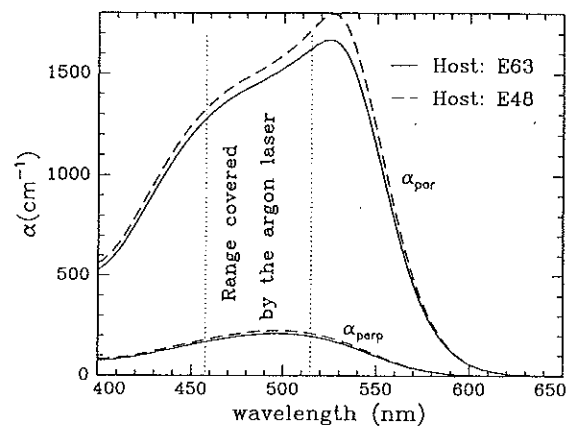


Fig. 1. Absorption coefficients of the guest-host systems; 0.5% R4 in two different hosts. The absorption coefficients were calculated from the transmission spectra of 25- μm -thick planar samples taken with ordinary and extraordinary polarizations.

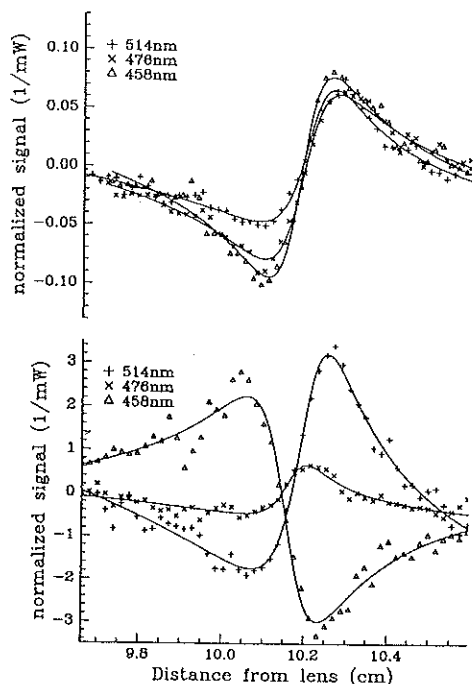


Fig. 2. Examples of Z-scan curves. Upper curves, pure E63; lower curves, 0.5% R4 in E63. The y axes show the difference between the detected signals without and with applied optical field, normalized to the average signal and the input power. (The solid curves are only a guide to the eye.)

focal point. For self-defocusing the positions of the minimum and the maximum are interchanged. To separate the orientational and thermal components of the nonlinearity, we carried out the scan both with and without a strong stabilizing low-frequency electric field. In the former case the orientational effect is suppressed.

We carried out the experiments with a Spectra-Physics Model 164 argon-ion laser, using the eight available lines, ranging from 514 to 458 nm. Z-scan curves for pure E63 and for R4-doped E63 are shown in Fig. 2. As expected, for the undoped nematic the nonlinearity is positive (self-focusing) and shows only a weak wavelength dependence. The measurements on the doped material indicate that the R4 dye induces a large positive amplification at 514 nm, yet it has little effect on reorientation at 476 nm and induces a significant negative amplification at 458 nm.

The amplification factor η can be obtained from a comparison of the Z-scan curves of the host and the dyed system. According to Ref. 4,

$$\eta = \frac{\Delta v_{\text{dye}}/P_{\text{dye}}^{\text{av}}}{\Delta v_{\text{host}}/P_{\text{host}}} - 1. \quad (1)$$

Here Δv_{host} and Δv_{dye} denote the modulation amplitude of the normalized Z-scan curve for the host and for the dye-doped nematic, respectively; P_{host} is the input power applied at the host Z-scan measurement. Furthermore

$$P_{\text{dye}}^{\text{av}} = P_{\text{dye}} \frac{1 - \exp(-\alpha d)}{\alpha d},$$

where P_{dye} is the input power for the dyed cell, α denotes the absorption coefficient for the actual polariza-

tion and angle of incidence, and d is the length of the path of the laser beam through the film. The η factor is shown as a function of the photon energy for the two hosts in Fig. 3.

To interpret the above observations, we extend in a qualitative way the model published in Ref. 5. In the original model it was assumed that the molecules underwent a transition from the S_0 ground state to the S_1 excited electronic state, without a change of the orientation of the long axis, and returned to the ground state after an average time τ had elapsed. In reality, however, the transitions are from an S_0^* level to an S_1^* level, where the asterisks indicate that a number of vibrational and rotational modes are excited (Fig. 4). The energy difference between the S_0^* and S_0 levels is of the order of the thermal energy, kT . The energy of the S_1^* level is determined by energy conservation:

$$E_{S_1^*} - E_{S_0^*} = h\nu.$$

The energy difference between the S_1^* and S_1 levels, ΔE , is therefore of the order of $h(\nu - \nu_0) - kT$, where $h\nu_0$ is the energy difference between the S_1 and S_0 levels.

The relaxation process from the S_1^* to an S_0^* level consists of two or more distinct steps. First, if ΔE is much higher than the thermal energy kT , collisions with the surrounding molecules induce transitions between different S_1^* levels. As a result, the molecule relaxes to the S_1 level (or to a level separated from S_1 only by $\approx kT$). It is known that in isotropic solutions of luminescent molecules this transition takes place in 10^{-12} s, i.e., in a very short time compared with the lifetime of the excited electronic state. Second, the molecule returns from S_1 to the ground electronic state either by direct spontaneous emission of a photon ($\tau \approx 10^{-8}$ s) or via a triplet state ($\tau \gg 10^{-8}$ s).

Regarding the nematic phase, we note that the nematic mean-field orienting potential is of the order of kT . Therefore, in the limit $\Delta E \gg kT$, one can assume that the $S_1^* \rightarrow S_1$ transition is not very different in the isotropic and nematic phases and that it also takes place in the latter phase within a few picoseconds. Furthermore, as the excess energy contained in the vibrational and rotational modes is lost in collisions

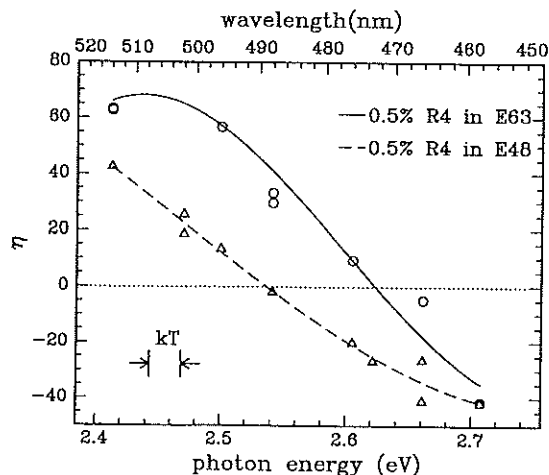


Fig. 3. Amplification factor as a function of the photon energy and wavelength. (The solid curves are only a guide to the eye.)

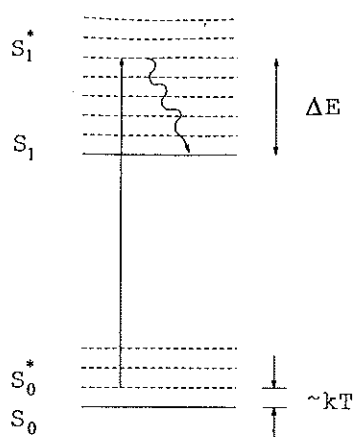


Fig. 4. Schematic energy-level system of the dye molecules.

with the surrounding host molecules, one expects that the dye molecules will be reoriented significantly during this transition. Therefore the orientation of an excited dye molecule becomes more or less independent of its initial orientation in a time interval of 10^{-12} – 10^{-11} s. In contrast, the characteristic reorientation time of the long axis of a ground-state dye molecule in the nematic field is of the order of $1/D \approx 10^{-8}$ s (D is the rotational diffusion constant). The validity of the above hypothesis might be proven by time-resolved absorption spectroscopy.

In the model published in Ref. 5, the wavelength of the optical field became a factor only through the wavelength dependence of the excitation probability of the dye molecules. However, the considerations presented above indicate a further effect. When the photon energy of the light satisfies the condition $h\nu - h\nu_0 \approx kT$, one can ignore the role of the vibrational and rotational levels, and the original theory remains valid. When the photon energy is increased, the randomization of the orientation of the excited dye molecules during the $S_1^* \rightarrow S_1$ transition becomes significant. At sufficiently high photon energies the steady-state distribution of the excited molecules can be considered isotropic and, therefore, makes no contribution to the dye-induced amplification of the optical torque. On the other hand, the absorption-induced perturbation of the ground-state dye molecules is not affected by the described process.

As shown in Ref. 5, the contribution of the ground-state molecules to η is always *negative*. One observes a positive amplification if the positive contribution from the excited dye molecules is stronger than the negative one coming from the ground-state molecules. However, according to the arguments presented above, with increasing photon energy the positive contribution of the excited molecules vanishes; hence η becomes negative. This corresponds to the observations described in Ref. 6 and in this Letter.

The experimental results shown in Fig. 3 indicate that the strength of the dye-induced optical torque depends on the composition of the host as well. At low photon energies η is considerably higher for the E63 host than for E48. At high photon energies, where η becomes negative, the deviation seems to be reduced significantly. This finding can be interpreted within the framework of our model as follows. At low photon energies the amplification factor depends on the difference between the order parameters of the excited-state and ground-state dye molecules. The (linear) absorption coefficient curves (Fig. 1) indicate that the ground-state order parameters are very close to each other in the two hosts. Therefore the higher η value observed in the case of E63 should correspond to a higher-order parameter of the *excited* R4 molecules in this host. On the other hand, at high photon energies, according to the considerations presented above, the dye-induced torque is generated by the ground-state molecules alone. As there is no significant difference in the ground-state order parameters for the two hosts, the difference of the amplification factors should vanish as well.

In conclusion, we presented an example of a nematic guest–host system, in which the optical nonlinearity associated with director reorientation changes from self-focusing to self-defocusing within the wavelength range covered by argon-ion lasers. Such systems provide an interesting possibility for switching the sign of the nonlinearity without significant modification of other parameters in the setup. In addition, the interpretation of the observed effect gives further insight into the mechanism of the dye-induced amplification of the optical torque in nematics.

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