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NONLINEAR EFFECTS IN NEMATICS DOPED BY DYSES AND CHIRAL AGENTS

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5.1 INTRODUCTION

This chapter presents a brief overview of our more recent results on laser-induced optical reorientation in mixtures made by adding to nematic liquid crystals small quantities of cholesteric or dye dopants. The optical properties of such mixtures are quite different from those of the pure nematic host, and a number of new phenomena have been observed and are reported here.

Mixtures of liquid crystals are widely used to improve the performance of liquid crystal cells in display technology. Nematic–nematic mixtures (NNM) may increase the working cell temperature range, cholesteric–nematic mixtures (CNM) may enhance the cell contrast, and dye–nematic mixtures (DNM) permit the making of color displays. The behavior of such mixtures in external electric fields has therefore been investigated carefully. Not so much work exists, however, on the optical reorientation in such materials. Recent experimental
investigations showed that the optical Fréedericks transition (OFT) in CNM and DNM differs, both quantitatively and qualitatively, from the same effect observed in pure nematics (1–3). In particular, the OFT in CNM has a characteristic double-threshold feature and exhibits a very large optical bistable hysteresis loop, while the OFT in DNM is characterized by a strong reduction of the threshold intensity and, in some cases, even by the reversing of the optical torque with respect to that in a pure nematic. However, the underlying mechanism is completely different in the two cases. In the CNM, the occurrence of optical bistability is due to the competition between the helical structure induced by the chiral dopant and the homeotropic anchoring conditions imposed at the sample boundary. In the DNM, the enhancement of the optical torque and its change of sign are due to a not yet well-understood phenomenon occurring at the molecular level and related to the different interactions among the nematic and the dye molecules in their ground and excited states (4). In this work, the most recent results concerning the nonlinear optical properties of these new materials will be reviewed and new results will be presented. These results show that CNM may be used for low-power nonlinear optical devices, provided that a slow response time can be tolerated.*

5.2 CHOLESTERIC–NEMATIC MIXTURES

The laser-induced optical reorientation in nematic–cholesteric mixtures was studied extensively. The cholesteric concentration was taken very low (of the order of a few percent) so that the helical pitch produced in the nematic host was of the same order of the sample thickness (approximately 100 μm). Unlike in the twisted or super-twisted cells used for displays, where planar anchoring was used, cells were coated to maintain homeotropic boundary conditions at the walls. This geometry is interesting because of the incompatibility between homeotropic alignment and the cholesteric helix. It was expected that for very low chiral concentrations (helical pitch much longer than the cell thickness), the homeotropic alignment would be stable in the whole sample. Increasing the chiral dopant concentration above a critical threshold, which is dependent on the cell thickness, yields the formation of domains where the helical structure prevails, as shown in Figures 5.1–5.3. Below the critical concentration, the alignment is homeotropic (Fig. 5.1), while a characteristic fingertip domain structure is observed at higher chiral concentrations (Fig. 5.2). Figure 5.2 was obtained at a temperature well below the clearing point of the nematic phase. For temperatures very close to (but below) the clearing point, the fingertip domains are replaced by bubbles, as shown in Figure 5.3. The critical chiral concentration where the homeotropic alignment becomes unstable is found to be quite independent of temperature in the whole nematic range. The twisted domains can be quenched to the uniform homeotropic alignment by applying

* Typical reorientational response time of these materials ranges from 0.1 to 1 s.
an external electric field (5,6). It can be shown that the transition from the homeotropic to the twisted alignment at the critical chiral concentration is first order, provided that the nematic elastic constants obey the inequality (7).

\[ k_{11} + 3k_{22} < 3k_{33} \]  

(1)

In most common nematics (e.g., 5CB and E7), \( k_{11} \approx k_{33} \approx 2k_{22} \) and inequality (1) is fulfilled, leading to a first-order transition.

Cholesteric–nematic mixtures can be reoriented by the optical field produced by continuous wave (cw) laser beams. The phenomenon of the optical Fréedericksz transition (OFT) is also observed in these materials, but it presents features quite different from the OFT in the pure nematic. In recent experiments, in fact, two characteristic thresholds in the laser intensity have been observed: the first one is second order, as in the pure nematic, and corresponds to the transition from the homeotropic undistorted state to the twisted state; the second one is first order and accompanied by a very large hysteresis loop. This second transition occurs between the low-distortion state, where twist is prevailing, to a high distortion state, where splay-bend is dominant (8). The differences are even more striking if circularly polarized light is used. The double-threshold feature is observed, in fact, only when the light elicits is the same as the elicity induced by the chiral dopant. When the two elicitities are opposite, only one second-order OFT is obtained, as in the pure nematic (9). This provides a simple method to determine the sample chirality when the helical pitch is too large to be measured by Cano’s wedge method.

The OFT in chiral-doped nematics can be described by a straightforward generalization of the continuum model used for calculating the optical reorientation induced in the pure nematic by an incident laser beam having elliptical polarization (10). The generalization consists in adding to the elastic free energy density of the sample, the chiral term

\[-\left(\frac{2\pi k_{22}}{p_0}\right)\sin^2 \theta \frac{d\phi}{dz}\]  

(2)

where \( \theta \) and \( \phi \) are the polar and azimuthal angles, respectively, of the molecular director \( \mathbf{n} \) with respect to the \( z \)-axis normal to the sample walls, and \( p_0 \) is the helical pitch induced by the chiral dopant. In the case of normal incidence of the laser beam, a straightforward linearization of the torque equations brings about the following expressions for the first OFT threshold intensity, \( I_1 \):

\[ \tilde{T}_1 = 4\tilde{\eta} \frac{\tan\left(\frac{\pi\Delta}{2}\right)}{\pi\Delta} \]  

(linear polarization)  

(3)

\[ \tilde{T}_1 = 2(1 - \tilde{\eta}^2) \]  

(circular polarization)  

(4)

where

\[ \Delta = \sqrt{T_1 + 4\tilde{\eta}^2} \]  

(5)

\[ \tilde{\eta} = \frac{2k_{22}L}{p_0k_{33}} \]  

(6)

and \( L \) is the sample thickness. The dimensionless threshold, \( \tilde{T}_1 \), is the actual threshold intensity, \( I_1 \), in units of the threshold intensity:

\[ I_{1k} = \frac{\pi^2 c k_{33} n_e^2}{n_a(n_a^2 - n_e^2)L^2} \]  

(7)

for the OFT in pure nematic. In Eq. 7, \( n_a \) and \( n_e \) are the optical refractive indices of the nematic host and \( c \) is the speed of light (cgs units are used). For common nematic liquid crystal samples having thickness of approximately 100 \( \mu \)m, \( I_{1k} \) ranges from 0.1 to 1 kW/cm\(^2\).

The experiments were performed with mixtures of nematic E7* and either

* E7 is itself a mixture of different cyanobiphenyl nematic liquid crystals.
cholesteric C15 to obtain positive chirality, or CB15 to obtain negative chirality. All chemicals were from Merck-RDH. The components were mixed up in the isotropic phase, above the clearing temperature of E7 ($\pm 60^\circ$ C). The hot mixtures were then introduced by capillarity into cells made of two parallel glass plates coated with surfactant cetyltrimethyl ammonium bromide (CTAB) for homeotropic alignment. The cells were finally cooled slowly into the nematic phase. The cholesteric dopant concentration was taken close to, but below, the critical value, so that the homeotropic alignment was stable on the whole sample area. In the experiments, the sample temperature was held fixed at 25.0 $\pm 0.1^\circ$ C by means of a stabilized oven, but the homeotropic alignment was found to be stable in the whole nematic range of E7. Samples having thicknesses of 50 $\mu$m and 110 $\mu$m were used. The critical concentration of C15 was found to be $1.75 \pm 0.01\%$ for 50 $\mu$m samples and $0.82 \pm 0.01\%$ for 110 $\mu$m samples. For CB15, the critical concentration in 50 $\mu$m samples was $0.21 \pm 0.01\%$; in 110 $\mu$m samples, the CB15 critical concentration was too low to be measured.

The OFT was investigated using a 3 W argon laser at $\lambda = 514.5$ nm in the TEM$_{00}$ mode. The laser beam was focused onto the sample to a measured $1/e^2$ radius of $82 \pm 2$ $\mu$m. The occurrence of the optical reorientation in the cell was monitored either by counting the number of rings produced by self-diffraction in the far field, or by detecting the polarization state of the light going through a 1 mm$^2$ pinhole placed at the center of the far-field pattern. The data obtained with different samples were found to be always consistent. The data reported in this work, however, refer only to 50 $\mu$m thick samples made of a mixture of E7 and CB15. The formation of fingertip or bubble domains was never observed during the optical reorientation, probably due to the small size of the illuminated region. The sample birefringence as a function of the laser intensity for linear polarization is shown in Figure 5.4. No reorientation was observed for a laser intensity below the critical value $I_1$, which is therefore identified with the threshold for the OFT. It was noted that $I_1 < 1$, as expected from Eq. 1, because the presence of the chiral agent reduces the threshold. For laser intensities above $I_1$, but below a second critical value $I_2$, the number of rings in the far field remains almost constant to a very small value (usually only a small halo, corresponding to about 0.5 ring, was observed). This small birefringence state remains stable until the second threshold, $I_2$, is reached, where a high distortion state with many diffractive rings in the far field is reached through a first-order transition. The high distortion state is stable even if the laser intensity is decreased, producing optical bistability. At the critical intensity, $I_3$, the system returns to the low distortion state, closing the bistability loop. As shown in Figure 5.4, the bistability loop is very large ($\Delta I/I$ about 20%), more than one order of magnitude broader than the hysteresis loop observed in pure nematic by applying a bias magnetic field (11). The behavior of the critical intensities, $I_1$, $I_2$, and $I_3$, as functions of the sample chirality (assumed proportional to the cholesteric concentration) is shown in Figure 5.5. The data corresponding to the first threshold, $I_1$, have been compared with theory (solid line in Fig. 5.5). The agreement is very good. No comparison with

![Figure 5.4](image1.png)

*Figure 5.4.* Number of rings in the far field as a function of the laser intensity for E7-CB15 mixture. The laser beam was linearly polarized. Chirality parameter $\bar{\eta} = 0.45$ corresponding to a helical pitch of 150 $\mu$m. Film thickness: $L = 50$ $\mu$m; temperature: 50 $^\circ$ C. $\circ$, Increasing intensity; $\bullet$, Decreasing intensity.

![Figure 5.5](image2.png)

*Figure 5.5.* The three thresholds as functions of chirality for E7-CB15 mixture. The solid line is from Eq. 3. The chirality was altered by changing the CB15 concentration. Other parameters as in Figure 5.4.
theory was made for $\tilde{I}_1$ and $\tilde{I}_3$, because it is very difficult to extend the model beyond the linear regime. It was observed, however, that the difference $\Delta I = \tilde{I}_1 - \tilde{I}_3$, and hence the width of the hysteresis loop, is an increasing function of the chirality, $\tilde{q}$. A somewhat unexpected behavior was found in the plateau region between the intensities $\tilde{I}_1$ and $\tilde{I}_2$. In this region, the formation of rings is prevented: so it should be presumed that, when the intensity is increased from $\tilde{I}_1$ to $\tilde{I}_2$, the excess energy put into the sample by the laser beam should be stored in the twist degree of freedom. If this were the case, a rotation of the polarization plane should be present in the light beyond the sample, because of Mauguin theorem (12). No polarization rotation was observed, however, in this experiment. There is no clear explanation for this. One possibility is that the optical phase retardation is fixed to $\pi$ (the number of rings is also fixed, consistently), irrespective of the incident intensity, so that the sample behaves as a $\lambda/2$ plate, rotating the polarization plane by exactly $180^\circ$. Another possibility is that the finite transverse dimensions of the excited region play a fundamental role in determining the polarization plane at the center of the far-field pattern.

Figures 5.6 and 5.7 show the sample birefringence as a function of laser intensity for right- and left-handed circular polarization. The two figures refer to samples having the same chirality parameter, $\tilde{q} = 0.45$, corresponding to a helical pitch of 150 µm. It is evident that the double-threshold feature and the hysteresis loop are observed only when the light helicity and the sample chirality have the same handedness. When they are opposite, a second-order OFT with no hysteresis is obtained, as shown in Figure 5.7. Consistent behavior was observed by changing either the light helicity or the sample chirality, passing from CB15 to C15. The effect is amazing, considering that the chiral pitch was about three times the sample thickness.

### 5.3 Dye-Nematic Mixtures

Mixtures of nematic liquid crystals and organic dyes are widely used in color display technology and also in optical applications. For example, real-time holographic recording was reported in azo-dye-doped nematic 4-cyano-4'-pentylbiphenyl (PCB) liquid crystal (13). The presence of dye may deeply alter the mechanism of laser-induced optical reorientation in the nematic host. This was first noticed by Jánossy et al. in 1990 (14), who reported a dramatic decrease of the threshold intensity of the OFT when small quantities ($\geq 1\%$) of absorbing dye were added to the nematic material. Indeed, large optical reorientations have been obtained by using laser sources in the milliwatt range, corresponding to an increase of the nonlinear optical response, with respect to the pure nematic, by more than two orders of magnitude. It is worth noting that the enhancement of the nonlinear optical response is not accompanied by an increase of the response time. This renders the dye-nematic mixtures appealing
for low-intensity nonlinear optical applications where a small amount of absorption can be tolerated. The physical mechanism producing the enhancement of the reorientational response of the nematic host is not yet well understood, but all experiments seem to confirm that it should be of molecular origin. In fact, all macroscopic material constants, except absorption, remain almost unchanged after adding the dye, as can be easily checked, for example, by comparing the electric field-induced Fréedericks transition threshold of dyed and pure nematics. Even more amazing is the fact that some dyes can reverse the sign of the optical torque on the nematic molecules (15), so that the dyed material can become self-defocusing.* Jánossy's effect was observed with two different families of dyes: azo dyes and anthraquinone dyes. Azo dyes are known to undergo cis-trans photosomerization when illuminated by green light. It was expected, therefore, that the change in the molecular conformation would affect the local orientation of the nematic, producing an extra torque proportional to laser intensity. But, quite surprisingly, although azo dyes show Jánossy's effect, anthraquinone dyes, which are known not to suffer photoinduced conformational changes, produce a much larger enhancement of the optical torque. This suggests that the molecular mechanism underlying Jánossy's effect may be different in the two cases, depending on the dye and on the nematic host. That this may be the case is also supported by a recent statistical model, showing that the enhancement of the optical torque may occur under very general circumstances: it is enough to suppose that the ground-state and excited-state dye molecules interact with the nematic molecules at differing intensities (16). The difference in the interaction strength may be not very large: about 1 kT difference over an average interaction energy of a few kT values may be enough. No more details are needed about the molecular mechanism producing the actual interaction. It is clear, therefore, why Jánossy's effect is observed in the majority of dye–nematic mixtures. Before discussing some experimental results about Jánossy's effect, a simple phenomenological model will be presented here, which, although not very accurate, grasps, in our opinion, the essence of the process. In the absence of the optical field, the dye molecules are in their ground state and their angular distribution function, \( f_0(\theta) \), has cylindrical symmetry around the direction of the nematic director \( n \) (\( f_0 \) is independent of the azimuthal angle, \( \phi \)). It may be assumed that, in the absence of direct chemical reactions, the dye–nematic interaction is quadrupole–quadrupole. Then, the average torque exerted by one dye molecule oriented along the fixed direction \( l \) on a large group of nematic molecules is given, in the mean-field approximation, by

\[
m_{c,g} = u_c(n \cdot l)(n \times l)
\]

where different coupling constants, \( u_c \) and \( u_g \), are assumed for the dye molecules in the excited and ground state, respectively. The occurrence of the director \( n \) in Eq. 8 is due to the average with respect to the directions of the nematic molecules. When the optical field is switched on, the dye molecule has a probability \( \rho(l) \) to be found in its excited state. The key point is that the excitation probability, \( \rho \), is itself anisotropic. If the incident laser beam is linearly polarized along the direction \( e \) and has intensity \( I \), this gives, at steady state and far from the dye saturation (\( \rho \ll 1 \)),

\[
\rho(l) = \left( \frac{\alpha_I}{h} \right) (e \cdot l)
\]

where \( \sigma \) is the absorption cross section of the dye molecule, \( h \) is the Planck constant, \( v \) is the optical frequency of the beam, and \( \tau \) is the average time a dye molecule stays in the excited state and in the direction \( l \). In a first approximation, we may take

\[
\frac{1}{\tau} = \frac{1}{\tau_f} + \frac{1}{\tau_p}
\]

where \( \tau_f \) is the dye fluorescence time and \( \tau_p \) is a typical rotational diffusion time. Finally, the total macroscopic average torque per unit volume exerted on the nematic by the dye molecules may be evaluated as

\[
M^{\text{dy}} = \left( \frac{N_d}{V} \right) \langle [pm(1 - \rho) + m_p] \rangle_0
\]

where \( N_d \) is the number of dye molecules in the volume \( V \), and \( \langle ... \rangle_0 \) denotes the average with respect to the distribution function, \( f_0 \). Inserting Eq. 9 into Eq. 11 and performing the average with respect to the azimuthal angle, \( \phi \), gives

\[
M^{\text{dy}} = \rho \left( \frac{\alpha_I}{h} \right) (u_c - u_g) (n \cdot e)(n \times e)
\]

where

\[
\rho = \langle \sin^2 \theta \cos^2 \theta \rangle_0
\]

and

\[
z = \left( \frac{N_d}{V} \right) \sigma \frac{z_\parallel + 2z_\perp}{3}
\]

is the isotropic part of the dye absorption coefficient. The coefficient \( \rho \) depends
on the ground-state dye distribution function, $f_0$, and, hence, on the dye order parameter in the absence of the optical field. Comparing the dye-induced torque (Eq. 12) with the usual optical torque $M^{opt} = [(n_{x}^2 - n_{y}^2)/c](n \cdot e)(n \times e)$ in the pure nematic, gives $M^{dy} = \xi M^{opt}$, with

$$\xi = \mu \left[ \frac{2\pi \tau}{h(n_{x}^2 - n_{y}^2)} \right] (n_x - n_y)$$

(15)

where $\lambda$ is the optical wavelength. It is noticed that $\xi$ may be negative if $n_x < n_y$. Inserting the typical values $\mu = 0.5$, $x = 100 \text{ cm}^{-1}$, $\lambda = 0.5 \mu \text{m}$, $\tau = 10^{-9} \text{ s}$, $n_x = 1.7$, $n_y = 1.5$, $(n_x - n_y) \approx kT \approx 4 \times 10^{-14} \text{ erg}$, we find $\xi \approx 30$, which has the right order of magnitude as the experimental value. From Eq. 15, the merit figure, $\mu$, can be introduced, defined as

$$\mu = \frac{\xi(n_{x}^2 - n_{y}^2)}{2\pi \tau n_x} = \frac{\mu\tau(n_x - n_y)}{h}$$

(16)

The advantage of this merit figure is that all quantities appearing in the second member can be measured, while the third member contains only molecular parameters. A closer inspection shows that $\mu$ is the average angular momentum transferred by one dye molecule to the nematic host in units of $h$. A more refined version of the present model, where the diffusion rotational dynamics of the dye molecules is taken into account, is given by Jánossy et al. (16). We conducted several experiments to investigate the dependence of the merit figure, $\mu$, on wavelength and on the guest–host materials. The nonlinear optical response of the mixtures was determined by measuring the nonlinear phase change suffered by the beam, either using the Z-scan technique (17) or a more sensitive interferometric technique (18). The measurements were made at different wavelengths using a dye laser to reorient the sample. A strong DC electric field was eventually applied to the sample in order to cancel out the laser-induced distortion and measure the contribution of spurious effects not related to the molecular reorientation. The isotropic absorption coefficient, $x$, was determined by measuring, for each sample, $x_0$ and $x_1$ in a separate experiment. The experimental results for D4 and AQ2 are reported in Figures 5.8 and 5.9, respectively. It can be seen that $\mu$ is large and negative in D4, but large and positive in AQ2. This is surprising, because both these two dyes are anthraquinone derivatives and both have a positive linear dichroism. Moreover, in D4 the merit figure is almost wavelength independent, according to Eq. 16, while in AQ2 it increases slightly with wavelength. For the azo dyes, it was found that methyl-red has a behavior similar to the anthraquinone dye D4, in agreement with the model presented here. Since anthraquinone dyes do not suffer cis–trans photoisomerization, it was concluded that in the optical reorientation of methyl-red, cis–trans transitions should play a little role, contrary to what was claimed by Chen and Bradly (13). In the case of para-red,
5.4 CONCLUSIONS

An overview of recent experimental studies on laser-induced reorientation in cholesteric-nematic and in dye-nematic mixtures has been presented. In both cases, the reorientation process presents significant qualitative differences with respect to the case of pure nematics. For chiral-doped nematics, the most striking effect is the occurrence of very strong intrinsic optical bistability with a large hysteresis loop. A closer inspection shows that the bistability loop occurs between a low-distortion state, where twist is prevailing, and a high-distortion state where splay-bend dominates. The low-distortion state is obtained from the initial homeotropic alignment through a second-order Fréedericksz transition and remains stable over a wide range of incident beam intensities, forming the characteristic plateau shown in Figure 5.4. Although the main features of the reorientation phenomenon, including the large optical bistability, can be accounted for by a simple plane-wave continuum model, some peculiar aspects, such as the behavior of the light polarization inside the sample, are not yet well understood.

Dye-nematic mixtures were also studied extensively by measuring their characteristic merit figure for different dyes, nematic hosts, and laser wavelengths. An organic picture of the nonlinear optical properties of these mixtures is not yet available. Several experiments, however, confirm that the observed enhancement of the nonlinear optical response should be of molecular origin. Simple considerations permit the conclusion that the enhancement is due to the extra torque originating from the dye molecules, which are driven anisotropically in their excited state by the laser beam. The optical response of the mixture may be either positive or negative (or zero, as in Dye 9), irrespective of the sign of the absorption coefficient anisotropy, $\Delta \alpha$, of the dye. The merit figure may differ by many orders of magnitude, even for dyes belonging to the same family, such as the anthraquinone dyes. For anthraquinone dyes, the effect cannot be ascribed to cis-trans isomerization. This could be true for azo dyes, but, in the few cases tested here, their behavior was very similar to anthraquinone dyes. In one azo dye (para-red), a strong enhancement of the nonlinear optical response was observed, but it seems to be of non-reorientational origin. Finally, the comparison of the merit figure of Dye 12 with different nematic hosts suggests that the cyano-biphenyl group in the nematic may have an important role. In general, however, it is probable that several different molecular mechanisms, depending on both components of the mixture, may lead to the observed enhancement of the optical reorientation efficiency.

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REFERENCES


6. TWO- AND FOUR-WAVE MIXING IN PHOTOREFRACTIVE MATERIALS FOR DYNAMIC CORRECTION OF PULSED LASER BEAMS

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6.1 INTRODUCTION

Correction of aberration of optical devices using holography was initiated in the mid-1960s (1). The principle of this type of correction remains the same in the 1990s but now we have access to new materials which allow dynamic correction.