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HIGHLY NONLINEAR OPTICAL EFFECTS IN LIQUID CRYSTALS

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Résumé - Le champ optique d'un laser continu est assez fort pour induire un grand changement de l'indice de réfraction d'un cristal liquide. La transition structurelle induite par un champ optique peut avoir lieu. La grande nonlinéarité optique peut mener à des phénomènes d'optique nonlinéaire intéressants.

Abstract - CW laser fields are strong enough to induce a large refractive index change in a liquid crystal. Optical-field-induced structural transition can occur. The large optical nonlinearity can lead to some unusual highly nonlinear optical phenomena.

In recent years, applications of nonlinear optical effects based on optical-field-induced refractive indices such as phase conjugation and optical bistability have attracted a great deal of attention. An application is often most appealing if it is operative with CW laser beams. This would require a nonlinear medium with an extremely large nonlinearity. Several such media have recently been found. Photo-refractive materials (BaTiO₃, Bi₁₃GeO₂₀) can have large optical-field-induced refractive indices \( \Delta n \) through induced redistribution of charges trapped at various sites in the crystals. Direct-gap semiconductors can have large \( \Delta n \) through saturation in absorption either at the band edge (InSb) or at an exciton transition line (GaAs, GaAs-GaAs superlattice). Among fluids, liquid crystals appear to have by far the largest \( \Delta n \) because of the extremely strong optical-field-induced collective molecular reorientation in the media. In some cases, \( \Delta n \) as large as 0.1 can be obtained with a laser intensity of \(< 100 \text{ W/cm}^2\). In this paper, we shall review the theory and experiment on the optical nonlinearities of nematic liquid crystals via molecular reorientation. We shall also discuss several unusual nonlinear optical effects we have recently observed in nematic liquid crystal films. These include optical-field-induced transition, multiple diffraction rings, multi-order degenerate wave mixing, and optical bistability and self-oscillation in a Fabry-Perot cavity.

In a fluid with anisotropic molecules, the laser-induced molecular reorientation is often the dominant mechanism for \( \Delta n \). Liquid crystals are in general highly nonlinear because of their unusually large molecular anisotropy. Then, in the mesophases, as a result of the cooperative behavior of molecules, they have even more stronger optical nonlinearity than in the isotropic phase. This is analogous to the case of ferromagnetism versus paramagnetism. The former having the spins strongly correlated yields a much larger induced magnetization in an applied magnetic field than the latter. To see how strong an optical field is needed to induce a significant \( \Delta n \) in a liquid crystal, we know that a dc field of \( \sim 1 \text{ esu} \) can induce a \( \Delta n \) of about 0.01 to 0.1. As far as molecular reorientation is concerned, an optical field is more or less equivalent to a dc field in the absence of strong permanent dipoles on the molecules. Therefore, the laser beam intensity required to induce a \( \Delta n \) of 0.01-0.1 should be of the order of 100 W/cm². Such a field can be easily obtained by weakly focusing a CW laser beam.

In the detailed calculation, the equation of motion governing the molecular reorientation can be derived from the free energy density \( F \). For a nematic film, we
have

\[ F = \frac{1}{2}[K_{11}(\mathbf{V} \cdot \mathbf{n})^2 + K_{22}(\mathbf{n} \cdot \mathbf{V} \times \mathbf{n})^2 + K_{33}(\mathbf{n} \times \mathbf{V} \times \mathbf{n})^2 - 2S\mathbf{n}_r/c] \]  

(1)

where \( \mathbf{n} \) is the director describing the average direction of molecular orientation, \( K_{ij} \) are the Frank elastic constants, \( S \) is the magnitude of the Poynting vector, and \( c/\mathbf{n}_r \) is the ray velocity. We assume the geometry in Fig. 1 with \( \mathbf{n} \) being a function of \( z \) only. If the angle \( \alpha \) is small (< 30°), \( S \) can be approximated as a constant.

\[ \Delta n_e(z) = \frac{n_o n_{em}}{\left[ n_{em}^2 \cos^2(\theta + \alpha) + n_o^2 \sin^2(\theta + \alpha) \right]^{1/2}} - \frac{n_o n_{em}}{\left[ n_{em}^2 \cos^2 \alpha + n_o^2 \sin^2 \alpha \right]^{1/2}} \]

(5)

and the corresponding induced phase shift across the sample is

\[ \Delta \phi = \int_{-d/2}^{d/2} \frac{\omega dn_e(z)}{c \cos(\theta + \alpha)} \, dz \]

(6)

where \( n_o \) and \( n_e \) are the ordinary and extraordinary refractive indices, respectively, with \( n_{em} \) being the maximum of \( n_e \).

A special case of interest occurs when the linearly polarized laser beam is normally incident on the sample. From Eq. (4), it can be shown that if the laser intensity \( I = c n_o |E|^2/8\pi \) is less than a threshold value.
no molecular reorientation can be induced by the field. This is analogous to the dc case, known as the Freedericksz transition, where the molecular reorientation sets in only when the dc field parallel to the sample surface exceeds a certain threshold value. Physically, the Freedericksz transition appears because only if the field is strong enough, can the decrease in electromagnetic energy due to molecular reorientation overcome the corresponding increase in elastic energy. It can be taken as a second-order structural transition, in which the average molecular orientation changes from a homeotropic arrangement to a spatially varying arrangement. In fact, even the transition dynamics exhibit the critical slowing-down behavior as it approaches $I_{th}$.

The present case of optical Freedericksz transition is probably the only well-proven example of a nonthermal laser-induced transition.

Figure 1 shows the theoretical calculation and experiment measurement of the induced phase shift $\Delta \Phi$ by an $\Delta \tau^+$ laser beam in a 250 $\mu$m thick sample of 4-cyano-4'-pentylbiphenyl (5CB). Several incident angles are considered, and the phase shift is measured by a He-Ne beam probing only the axial region. It is seen that in the normally incident case ($\alpha = 0$), there is indeed a sharp threshold for the induced phase shift. For obliquely incident beams, the increase of the phase shift with laser intensity is more gradual. As shown in Fig. 1, the theory is in good agreement with the experiment. The observed $I_{th}$ is $155$ W/cm$^2$, while using the measured values of $n_0 = 1.54$, $n_{em} = 1.73$, and $K_{33} = 0.85 \times 10^{-6}$ dyn, in the literature for 5CB, we find from Eq. (7) $I_{th} = 164$ W/cm$^2$. The dynamic behavior of the Freedericksz transition is characterized by the switch-on time $\tau_{on}$ and the switch-off time $\tau_{off}$:

$$
\tau_{on} = \frac{y^+ I_{th} d^2}{\pi^2 K_{33}} (I - I_{th})^{-1},
$$

$$
\tau_{off} = \frac{y^+ d^2}{\pi^2 K_{33}}
$$

where $y^+$ is a Leslie viscosity coefficient. The critical slowing-down behavior of $\tau_{on}$ is clearly shown in Fig. 2, where the quantitative fit between theory and experiment is demonstrated. The value of $\tau_{off}$ is independent of I, and is found to be $\sim 65$ sec.

Figure 1 shows that for a pump intensity of 200 W/cm$^2$ with $\alpha \leq 10^\circ$, the induced phase shift across a 250-$\mu$m film is as large as $\Delta \Phi \approx 60 \pi$, which corresponds to an average $\langle \Delta n \rangle \approx 0.08$. This is compared to $\Delta n \sim 2 \times 10^{-11}$ in the well-known Kerr liquid CS$_2$ with the same intensity. Actually, even much lower laser intensity can be used to induce the same $\Delta \Phi$ if a dc bias field, either electric or magnetic, is applied to the sample. As we know, the dc field and the optical field are equivalent in orienting the molecules. Thus, for example, in 5CB a magnetic field of 500 Oe along $\hat{x}$ is roughly equivalent to a laser field of $\sim 1$ esu ($I = 250$ W/cm$^2$). Application of the magnetic field effectively shifts the origin to the right on the $I$ axis. Then, as shown in Fig. 1, with a bias field of 400 Oe, a normally incident laser intensity of only $\sim 25$ W/cm$^2$ is sufficient to induce a $\Delta \Phi \sim 60 \pi$.

Besides $\Delta n$ due to molecular reorientation, we should also mention the thermally in-
duced $\Delta n$ due to laser heating. The residual absorption in a liquid crystal can be quite large. For example, an $\text{Ar}^+$ laser intensity of $\sim 350 \text{ W/cm}^2$ in 5CB can raise the sample temperature by $\sim 2^\circ \text{K}$. This leads to $(\Delta n_0)_T \sim +3 \times 10^{-3}$ and $(\Delta n_0)_T \sim -1 \times 10^{-2}$, which are appreciable.\textsuperscript{11} Since the heating results from linear absorption, $\Delta n_T$ is proportional to the laser intensity. The response time of $\Delta n_T$ is of the order of 0.01 sec, which is short compared to the orientational relaxation time.

We now consider the various nonlinear optical phenomena that can arise from the induced $\Delta n$ in a nematic liquid crystal film. They can be highly nonlinear because $\Delta n$ is a highly nonlinear function of the laser field, and the usual perturbation calculation is not applicable. Fortunately, the main effect of $\Delta n$ is on the phase shift, and in propagating across a thin film, the intensity variation with the propagation distance can be neglected. If in addition, the polarization of the pump field does not change, the calculation is relatively simple and manageable.

The first case we would like to discuss is what would happen when a CW laser beam passes through a homeotropic nematic film of a few hundred $\mu \text{m}$ thick. Nothing would, of course, happen if the laser intensity is weak, except a linear diffraction effect on the beam. When the intensity is sufficiently high, however, the output displays a multiple diffraction ring pattern. This was first reported by Zolot'ko et al.\textsuperscript{12} An example is shown in Fig. 3, which is obtained with an $\text{Ar}^+$ laser beam of $\sim 150 \text{ W/cm}^2$ normally incident on a homeotropic 5CB film of 340 $\mu \text{m}$ thick.\textsuperscript{13} Actually, as described in Fig. 4, there is an intensity threshold below which no ring pattern is observed. This threshold is found to be the same as for $I_{\text{th}}$ for the Fredericksz transition. Also the increase of the number of rings (up to $\sim 70$) with intensity closely resembles that of the induced phase shift $\Delta \phi$ in Fig. 1. These results indicate that $\Delta \phi$ due to molecular reorientation must be responsible for the ring pattern.

![Fig. 3. Typical diffraction ring pattern.](image)

![Fig. 4. The number of observed rings N as a function of laser intensity I is shown by the filled circles. The open circles show the prediction from simultaneous birefringence measurements, and the solid line is the theoretical curve.](image)
It turns out that the observation can be easily understood from the spatial self-phase modulation effect.\textsuperscript{13} A pump beam with a Gaussian intensity profile should induce a phase shift $\Delta \psi$ with a bell-shaped transverse profile as sketched in Fig. 5.

![Fig. 5. Profile of induced phase retardation. Light diffracted at $p_1$ and $p_2$ has the same wave wave vector and interferes.](image)

For each point, say $p_1$, on the curve, there always exists another point $p_2$ with the same slope. Since $\partial (\Delta \psi) / \partial p$ is just the transverse wavevector $k_p$, the radiation fields from the regions around $p_1$ and $p_2$ have the same wavevector, and should interfere. Maximum constructive and destructive interferences occur for $\Delta \psi(p_1) - \Delta \psi(p_2)$ = $m \pi$ with $m$ being even and odd integers, respectively. The result is then the appearance of the ring pattern. The total number of rings is given by $N \equiv \Delta \phi_0 / 2\pi$, where $\Delta \phi_0$ is the induced phase shift on the beam axis, and the diameter of the outermost ring is determined by $[\partial (\Delta \psi) / \partial p]_{\text{max}}$ at the inflection point. Indeed, in Fig. 4, $N$ versus $I$ calculated from the laser-induced phase shift $\Delta \phi_0$ due to molecular reorientation describes the experimental data fairly well. The wavefront distortion giving rise to the ring pattern also leads to self-focusing of the beam.\textsuperscript{14} This is manifested by the fact that the thin nematic film behaves like a lens in focusing the beam.

A second case of interest is on degenerate wave mixing through $\Delta n$ in a homeotropic nematic film.\textsuperscript{15,16} We consider two input beams with wavevectors $k_1$ and $k_2$ and frequency $\omega$ interfering in the medium as shown in Fig. 6. The resulting spatial variation of intensity induces a three-dimensional grating structure of $\Delta n(x,z)$ in the

![Fig. 6(a). Experimental geometry.](image)

![Fig. 6(b). Diffracted beam powers of various orders. Solid lines are theoretical curves.](image)
medium through molecular reorientation. We can use a bias magnetic field to in-
crease $\Delta n(x,z)$. In this case, the initial molecular orientation is $\theta_0(z)$, as deter-
mind from minimization of the free energy $\mathcal{F}$ in the absence of the optical field.
With the optical field, the orientation becomes\(^\text{\textsuperscript{16}}\)

$$\theta(x,z) = \theta_0(z) + \theta_1(z) + \theta_2(z)\cos(2\pi x / \lambda)$$

where $\lambda = \lambda / 2\sin(\theta/2)$ is the grating period, and $\theta_1(z)$ and $\theta_2(z)$ can be obtained from minimization of $\mathcal{F}$. If the optical field is weak compared to the bias magnetic
field in their effects on the molecular reorientation, then

$$\theta_2(z) / \theta_0(z) = \text{constant}$$

where $\gamma$ is a constant, $\alpha = (K_{33}n^2/d^2 + \Lambda \Delta \chi_{\text{m}}H^2)/K_{11}$, and $\Lambda$ depending on $\theta_0$ is of the order of 1. Equation (10) shows that the depth of the grating decreases with de-
creasing grating period, because the optical orientation of molecules acts against the
elastic and magnetic forces which favor a uniform alignment. Assuming $K_{33}n^2/d^2 > \Lambda \Delta \chi_{\text{m}}H^2$ and $K_{33} = K_{11}$, we find that the limiting grating period is $\lambda = 2d$, below
which the grating depth decreases rapidly. The local refractive index seen by an
extraordinary probe beam is

$$n(x,z) = n_0(z) + \Delta n(x,z)$$

$$\Delta n(x,z) = n_2(z)\cos(2\pi x / \lambda)$$

where $n_0(z)$ is proportional to $\theta_0(z)$ and hence to $(I_1I_2)^{1/2}$.

The existence of an induced $\Delta n$ grating makes degenerate wave mixing possible in the
medium. In particular, when the probe beam propagates along $-k_2$, a phase-conjugated
output appears along $-k_2$. Wavefront reconstruction of an aberrated beam by phase
conjugation in a nematic film can be easily observed.\(^\text{15}\) However, because of the de-
pendence of the grating depth on $\lambda$, the restoration of the image will not be very
good if the aberrated input has a broad angular distribution.

Actually, the diffraction of the probe beam from the induced grating in the above
case can be of multiple orders.\(^\text{16}\) The grating is a thin phase grating, as it satis-
fies the criterion $2\pi^2 (n_0n_2)(d/\lambda)^2 < 1$, where $n_0$ and $n_2$ are averages of $n_0$ and $n_2$ over $z$, but the phase amplitude can still be large, and therefore multiple-order
diffraction can occur. The transmitted probe field at the exit plane of the sample is given by

$$\xi_2(x,y)\exp[ik_2\cdot r + i\Delta\phi(x,z) - i\omega t]$$

with $\Delta\phi(x,z) = (\omega/\gamma)\Delta n(x,z)d$. The far-field pattern that can exhibit many diffraction orders is then derived from the
Fourier integral of the field over the exit plane. In the infinite plane wave ap-
proximation for both the pump and probe beams, it reduces to the
Raman-Nath diffraction problem, and the solution can be written in terms of Bessel functions of vari-
ous orders. A practical example of multiple-order nonlinear optical diffraction in
a nematic 5CB film with a 1.45 K\text{OE} bias field is shown in Fig. 6.\(^\text{16}\) Two CW Ar+
laser beams interfere in a 250 $\mu$m thick film to induc a 71-$\mu$m grating. The two
pump beams also act as the probe beams and generate the diffracted beams. Up to 6
orders of diffraction can be discerned by eye at a beam intensity of $\sim 100 \text{ W/cm}^2$.
By taking into account the Gaussian transverse profile of the beams in the calcula-
tion, the theory fits the experimental data very well.

The third case we shall discuss here is the problem of a nonlinear Fabry-Perot (FP)
interferometer in which the nonlinear medium is a thin nematic film.\(^\text{17}\) Because of the
large induced $\Delta\phi$ even at relatively low laser intensities, the bistable operat-
ing characteristics of the interferometer can be easily observed with a proper ini-
tial phase setting. In fact, as the laser intensity is increased, higher-order bi-
stable loops can be expected. An experimental demonstration is shown in Fig. 7,
which is obtained with a FP interferometer composed of an 83 $\mu$m homeotropic film of
5CB sandwiched between two mirrors of reflectivities 55% and 75% at 5145 $\text{A}$. A bias
magnetic field of 1.5 K\text{OE} is used to increase the optical nonlinearity, so that the
multiple bistable loops can be seen even with a laser intensity $I \lesssim 50 \text{ W/cm}^2$. The
Multiple bistable loops with $|\mathbf{B}| = 1.3$ KOE. Inset shows bistable loops and onset of oscillation for $|\mathbf{B}| = 1.6$ KOE.

Fig. 7a. Oscillatory output observed with pinhole for $|\mathbf{B}| = 1.55$ KOE and $I_{in} = 70$ W/cm$^2$, together with fit from computer simulation.

Observation is made with a linearly polarized Ar$^+$ laser beam nearly normally incident on the cell.

An interesting phenomenon occurs when the laser intensity becomes higher than a certain value $I_{osc}$. It is found that the output will then break into oscillation, as shown in Fig. 7. The oscillation is periodic and lasts indefinitely. This is the result of two opposing mechanisms with very different response times contributing to $\Delta \eta$. In our case, the two mechanisms are first, the molecular reorientation, which is strong and slow with a time constant of the order of seconds (in a bias magnetic field), and second, the laser heating, which is much weaker but faster with a time constant of $\sim 0.01$ sec. We can use Fig. 8 to explain the observed oscillation. In the steady state, the round-trip phase shift including the laser-induced contribution is given by

$$
\phi = \phi_0 + \phi_0 + \phi_T,
\phi_0 = K_\alpha \mathcal{J} I_{in}, \quad \phi_T = K_\alpha \mathcal{J} I_{in}
$$

where $\phi_0$ is the intensity-independent round-trip phase shift, $K$ is a constant depending on the FP parameters, $K_\alpha$ and $\mathcal{J}$ are the coefficients governing $\Delta \eta$ due to molecular reorientation and laser heating, respectively, in the first-order approximation, and $\mathcal{J}$ is the transmission coefficient of the interferometer. In Fig. 8, Eq. (12) describes a straight line. The operating point of the interferometer is then determined by one of the crossing points of the line with the FP transmission curve, depending on the history. It varies with the input intensity, and leads to the bistable loops of output versus input.

However, the operating point, say $0$ in Fig. 8, is really stable only if it is also stable against fast fluctuations to which the thermally induced $\Delta \eta$ can respond but not the reorientation. Otherwise, in a time short compared to the orientational relaxation time, the operating point would move to either $A$ or $B$ as if only the thermal effect contributed to $\Delta \eta$. This short-time instability starts the oscillation. The operating point first moved from $0$ to $A$ (or $B$), and the laser intensity in the cavity, $I_{cav}$, decreases (or increases). Then, the reorientational mechanism begins to respond to the lower (or higher) $I_{cav}$ and decrease (or increase) $\phi_0$. It moves the operating point from $A$ to $C$ (or $B$ to $C'$) by shifting the dashed line in Fig. 8 to the left (or right). After $C$ (or $C'$), the operating point has to switch to $D$ (or $D'$), governed by the thermal effect. The resulting increase (or decrease) of $I_{cav}$ now increases (or decreases) $\phi_0$ through reorientation, and shifts the operating point from $D$ to $C'$ (or $D'$ to $C$), where it will switch to $D'$ (or $D$) and move towards...
A (or B). It then repeats the cycle ACDC'D'A, and the oscillation goes on indefinitely. The period of oscillation should be of the order of the orientational relaxation time.

![Diagram](image)

The above picture predicts that oscillation would occur if the dotted line in Fig. 3 has a slope less negative than the tangent to the FP transmission curve at the inflection point. The threshold intensity for oscillation is then determined from

$$|K_T I_{osc}|^{-1} = |\frac{\partial T}{\partial \phi}|_{max} = \frac{F}{\pi}$$

where $F$ is the finesse of the interferometer. Below $I_{osc}$, no oscillation can occur for any value of $\phi$. The parameters for the oscillation in Figs. 7b are $K = 7$, $F = 31$, and $\alpha = 0.0013 \text{ cm}^2/\text{W}$, which yield $I_{osc} = 50 \text{ W/cm}^2$. This is compared to a measured $I_{osc}$ of 63 W/cm². The observed period of oscillation is 1.2 sec, which is indeed comparable to the orientational relaxation time of 1.6 sec. A detailed calculation using the dynamic equations for molecular reorientation and laser-induced heat diffusion together with the equation for FP transmission can actually reproduce the oscillation in Fig. 7b fairly well.

The few cases presented here are only simple examples of the many possible highly nonlinear optical effects that can occur in mesomorphic liquid crystals. One can imagine other cases such as an ordinary pump wave obliquely incident on a homeotropic nematic film, or a pump wave propagating in a homogeneously aligned nematic film. That the beam polarization varies with the propagation distance in the liquid crystal makes the problems more complicated, as the high nonlinearity may drastically affect the variation of the polarization. Nonlinear optical effects in other mesophases can also be interesting. For example, the cholesteric pitch may be modified by two counter-propagating circularly polarized waves, and laser-induced transitions between various phases may happen. Theoretical and experimental exploration in this area should be most interesting and rewarding.

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1. See, for example, papers in this proceedings.
7. See, for example, P. Sheng, in "Introduction to Liquid Crystals," ed. by E. B. Priestley, P. J. Wojtowicz, and P. Sheng (Plenum, New York, 1975) p.103.