Optically induced molecular reorientation and third-order nonlinear optical processes in nematic liquid crystals

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We report some quantitative studies of four-wave mixing in aligned nematic-liquid-crystal films. Using an unfocused cw laser of 200 mW power, at an estimated intensity of 5 W/cm^2, we have observed a conversion efficiency of 10^{-2}. The third-order nonlinear polarization that is responsible for this wave-mixing process is attributed to the optically induced molecular reorientation. A quantitative calculation of the wave-mixing efficiency and the intensity dependence is presented. It is shown that the experimental results are in good agreement with the theoretical predictions.

INTRODUCTION

The theory and practice of degenerate four-wave mixing have been standardized for many years.[1-3] In essence, four-wave mixings hinge on the nonlinear third-order polarization of the medium, which may arise from electronic or orientational contributions. In recent years, liquid-crystalline media have received considerable attention because of their large optical nonlinearities, which are due to their large anisotropies.[4-10] Measurements by Wong and Shen[4] have shown that the Kerr constant of MBBA (*p*-methoxybenzylidene-*p*-butylaniline), for example, can be almost 100 times that of CS_2, a well-known liquid of large optical nonlinearity. In recent developments of nonlinear optical devices, these large nonlinearities have been fruitfully utilized. Self-focusing,[5] optical second- and third-harmonic generation,[6,7] nonlinear Fabry-Perot action[8], and most recently, degenerate four-wave mixing have been demonstrated.[9,10] The nonlinearities come from the orientational contribution, which has been shown to be principally due to the collective molecular orientational fluctuation. An important point to note about these studies is that they are all performed in the isotropic phase. Typically, the conversion efficiency, which is proportional to the square of the laser intensities, was found to be on the order of 10^{-4}, for laser intensities on the order of tens of MW/cm^2.

It was suggested by Herman and Serinko [Phys. Rev. A 19, 1757 (1979)] that larger wave-mixing efficiency could be obtained in the nematic phase, if one makes use of a dc field to bring the nematic crystal to near a critical orientational transition (the so-called Freedericks transition).[11] This was verified in some of our recent studies.[12] Above the Freedericks transition, we have observed the predicted probe beam-amplification process, as well as the diffraction of a fourth wave in the phase-matched direction. These processes occur in the low optical intensity region, which is defined by $\frac{1}{2}(\Delta\epsilon/4\pi)E_{op}^2 \ll \frac{1}{2}\Delta\chi H_{dc}^2$ or $\frac{1}{2}(\Delta\epsilon/4\pi)E_{dc}^2$, where E_{op} is the electric-field strength of the optical field, E_{dc} and H_{dc} are the dc electric and magnetic field, respectively, and $\Delta\epsilon$ and $\Delta\chi$ are the anisotropies in the permittivity and the permeability, respectively. In this paper, we report some quantitative studies of degenerate four-wave mixing in aligned nematic in which the nonlinearity is purely *optically* induced. Our theoretical analysis is analogous to Herman and Serinko's, but there are important details which we will point out.

THEORETICAL ESTIMATE

Without much loss of generality, we consider the scattering geometry as depicted in Fig. 1. The sample is homeotropically aligned with the director axis pointing in the Z direction. The incident optical waves are polarized in the x direction and are almost normally incident on the face of the sample. These two beams are crossed at a small angle defined by their respective propagation vector $\vec{k}_1$ and $\vec{k}_2$. For this geometry, the Maxwell equation $D=\epsilon E$ may be solved to give an effective dielectric constant ϵ_{eff} (cf. Herman and Serinko):

$$\epsilon_{eff}=\frac{\epsilon^2-(\frac{1}{2}\Delta\epsilon)^2}{\epsilon-\frac{1}{2}\Delta\epsilon\cos 2\theta}\;,\quad \epsilon=\tfrac{1}{2}(\epsilon_\perp+\epsilon_\parallel)\;, \tag{1}$$

where $\Delta\epsilon=\epsilon_\parallel-\epsilon_\perp$, with $\epsilon_\parallel$ and $\epsilon_\perp$ being the dielectric

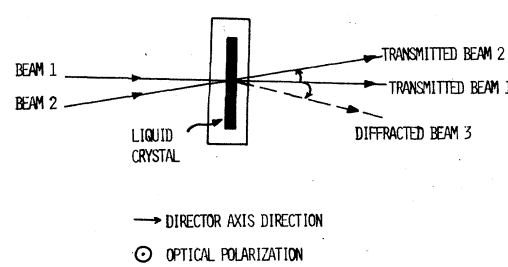

FIG. 1. Scattering geometry.

constant for optical field polarization parallel and perpendicular to the director axis (optical axis) of the nematic crystal. θ is the tilt angle of the director axis with respect to the Z axis. In the absence of the optical field, $\theta = 0$ and $\epsilon_{eff} = \epsilon_{\perp}$. When subjected to perturbation by an optical field of strength greater than the Freedericks field, θ will assume a new, finite value. (This is, in fact, shown to be the case in our experiment, as we will discuss in a later section.) Our main task is to determine the nonlinearity in ϵ_{eff} (i.e., the E^2_{op} dependent part) that is associated with this director-axis reorientation.

For optical fields whose associated electric field strength is not too much greater than the dc Freedericks field, we expect the induced molecular reorientation to be small, i.e., θ is small throughout the bulk of the sample. In that case, Eq. (1) reduces to

$$\epsilon_{eff} = \epsilon_{\perp}\left(1 + \frac{\Delta\epsilon\theta^2}{2\epsilon_{\parallel}}\right). \tag{2}$$

This shows that the optically induced dielectric constant change is given by

$$\delta\epsilon = \frac{\epsilon_{\perp}\Delta\epsilon\theta^2}{2\epsilon_{\parallel}} . \tag{3}$$

To solve for θ, we quote here the well-known sine-Gorden equation[13] obeyed by θ

$$\xi^2 \frac{\partial^2\theta}{\partial_Z 2} + \sin\theta\cos\theta = 0 , \tag{4}$$

where

$$\xi^2 = E^{-2}_{op}(4\pi K/\Delta\epsilon) .$$

This equation is obtained by minimizing the free energy of the system which, in the present context, is given by

$$F = \frac{1}{2}K\left(\frac{\partial\theta}{\partial Z}\right)^2 - \frac{1}{2}\frac{\Delta\epsilon}{4\pi}E^2_{op}\sin^2\theta . \tag{5}$$

K is the elastic constant, assumed equal for the three types of distortion (i.e., bend, splay, and twist). This one-constant approximation has been shown to give a fairly accurate numerical estimate of MBBA's responses.[14] E_{op} is the electric field of the incident optical waves

$$\begin{aligned}\vec{E}_{op} &= \vec{E}_1 + \vec{E}_2 \\ &= \hat{e}E_1 \exp i(\vec{k}_1 \cdot \vec{r} - wt) \\ &\quad + \hat{e}E_2 \exp i(\vec{k}_2 \cdot \vec{r} - wt) + \text{c.c.}\end{aligned} \tag{6}$$

We note here that if $\Delta\epsilon$ is negative (which is the case in purely dielectric MBBA), then Eqs. (5) or (4) shows that the applied field will tend to stabilize the orientation in the $\theta = 0$ direction (i.e., the initial configuration). In optical fields, $\Delta\epsilon$ is positive, and the system will stabilize under optical perturbation with θ assuming a finite value for E_{op} greater than the equivalent dc Freedericks field. It is important to note here that because the molecules orientational responses are slow, only the slowly varying (in fact, time-independent) terms $E_1E_2^*$ and $E_1^*E_2$ matter in Eqs. (4) and (5). In general, the solutions to Eq. (4), subjected to the boundary condition for homeotropic sample (i.e., $\theta = 0$ at $Z = -d$ and $Z = d$) are generalized Jacobian sine-amplitude functions,[14] and have been discussed in great detail elsewhere. These analytical solutions, however, do not allow easy identification of the various nonlinear optical processes associated with mixings of the optical electric field. A quick estimate of the third-order nonlinearity, nevertheless, can be made if we consider an approximate solution of Eq. (4). Assuming that "hard" boundary conditions exist (i.e., $\theta = 0$ at $Z = 0$ and $Z = d$, even in the presence of the optical field) an approximate solution[15] of (4) is

$$\theta = \theta_{max}\sin\frac{\pi Z}{d} , \tag{7}$$

where d is the sample thickness. θ_{max} is the maximum angle of inclination of the director axis with respect to the Z axis and, by symmetry, occurs at $Z = d/2$. Several approximate forms of θ_{max} have been used in the literature. In general, if "hard" boundary conditions are assumed, the solutions predict the existence of a critical value E_F (i.e., the Freedericks field). For applied field strength below E_F, $\theta_m = 0$. Above E_F, θ_{max} is given approximately by

$$\theta_{max} \cong 2\left(\frac{E^2_{op} - E^2_F}{E^2_F}\right)^{1/2} , \tag{8}$$

where $E^2_F = (\pi/d)^2 4\pi K/\Delta\epsilon$. This form of approximate solution is slightly different from that assumed by Herman and Serinko, but it follows more naturally from the quadratic dependence of the free energy (5) as well as the Torque balance equation (4) on E's. Equation (8) predicts a sharp cut off at $E = E_F$. In practice, several factors (including slight variation in the boundary conditions, nonuniformity of the field, presence of contaminants and ions, etc.) will introduce a round off near E_F. This has been shown to be the case in most experiments, and in our experiment as we will show presently.

Putting (8) into (3), one gets

$$\delta\epsilon = \epsilon_{\perp}\frac{\Delta\epsilon}{\epsilon_{\parallel}}\frac{E^2_{op}}{E^2_F}\sin^2\left(\frac{\pi Z}{d}\right) . \tag{9}$$

The nonlinear third-order polarization is thus given by

$$p^{(3)}=\frac{\epsilon_\perp \Delta\epsilon E_{op}^3}{4\pi\epsilon_\parallel E_F^2}\sin^2\left(\frac{\pi Z}{d}\right) . \tag{10}$$

The term in (10) responsible for the wave-mixing process of interest comes from

$$p^{(3)}=\frac{\epsilon_\perp \Delta\epsilon}{4\pi\epsilon_\parallel E_F^2}\sin^2\left(\frac{\pi Z}{d}\right)E_1^2E_2^*\exp[i(2\vec{k}_1-\vec{k}_2)\cdot\vec{r}] . \tag{11}$$

This polarization generates a diffracted wave in the phase-matched direction $\vec{k}_3=2\vec{k}_1-\vec{k}_2$. The magnitude of the diffracted wave E_3 may be found by integrating the Maxwell wave equation

$$\nabla^2 E_3-\frac{1}{C^2}\frac{\partial^2 E_3}{\partial_t^2}=\frac{4\pi}{C^2}\frac{\partial^2}{\partial_t^2}(P_L+p^{(3)}) , \tag{12}$$

where P_L is the linear polarization associated with E_3. Following the usual wave-mixing calculation,[2] this gives

$$E_3=E_1^2E_2\left(\frac{\epsilon_\perp\Delta\epsilon k d}{\epsilon_\parallel 2E_F^2}\right), \tag{13}$$

where $k=|k_3|$. This expression for the diffracted-wave intensity is similar to that derived by Herman and Serinko for the case of optical plus dc magnetic field induced nonlinearity, with the appropriate replacement of $\frac{1}{2}\Delta\chi H_F^2$ by $\frac{1}{2}(\Delta\epsilon/4\pi)E_F^2$. An important point to note here is that in our case we are studying purely optically induced effects associated with high optical strength [i.e., with $\frac{1}{2}(\Delta\epsilon/4\pi)E_{op}^2>\frac{1}{2}(\Delta\epsilon/4\pi)E_F^2$]. On the other hand, the magneto-optical effect as studied by Herman and Serinko deals with the low optical intensity limit $[\frac{1}{2}(\Delta\epsilon/4\pi)E_{op}^2\ll\frac{1}{2}\Delta\chi H_F^2\equiv\frac{1}{2}(\Delta\epsilon/4\pi)E_F^2]$ and requires the presence of the dc magnetic field H ($>H_F$).

From Eq. (13), the intensity of the diffracted wave is thus given by

$$I_3=I_2I^2\left(\frac{10^7 k d^3\Delta\epsilon^2\epsilon_\perp}{\pi^2 K C\epsilon_\parallel}\right)^2 , \tag{14}$$

where we have defined all intensities in unit of W/cm^2, and have made use of $E_F^2=(\pi/d)^2 4\pi K/\Delta\epsilon$. Putting in $k=2\pi(\lambda)^{-1}$ for $\lambda=5145$ Å, $\epsilon_\parallel\simeq\epsilon_\perp$, $d=75$ μm, $\Delta\epsilon=0.1$ and $K=5\times10^{-7}$ dynes, one finally gets

$$I_3\approx 8\times10^{-4}I_1^2I_2 . \tag{15}$$

It is important to note here that the numerical factor in (15) depends on the form of the approximate solution for θ that one chooses. Furthermore, there are uncertainties associated with the values for K and $\Delta\epsilon$. In practice, therefore, Eq. (15) should be regarded as only an order of magnitude estimate of the wave-mixing efficiency.

For the purpose of brevity, we have not included here calculations of the scattering for other optical polarizations and scattering geometry. In any case we do not expect the basic mechanism underlying the wave-mixing process under study here to be drastically different for other scattering and polarization setups.

EXPERIMENTAL RESULTS

At this point, some remarks on light scattering in the nematic phase of liquid crystal are in order. It is well known that because of the higher degree of order, and thus a much higher light scattering cross section, nematics are turbid in appearance, and scatter an incident laser light wildly. Alignment of the molecules to minimize these spurious side scatterings is therefore extremely crucial, especially when our final objective is to demonstrate the use of nematic films as practical holographic and imaging media. It is found that, in general, the least spurious side scattering occurs for nematics that are aligned homeotropically (i.e., the director axis is perpendicular to the face of the cell), with the incident light almost normal to the face of the film, and the polarization perpendicular to the director axis.

In our experiment, homeotropic samples are made using a surfactant treatment, and checked by a conoscopic optical interference method.[16] The liquid crystal used was MBBA (which is nematic at room temperature), with a sample thickness of 75 μm. As a first check of the optical field induced molecular orientation, the conoscopic interference set up as shown in Fig. 2 is used, with the argon laser and the He-Ne laser polarized in the same direction. When the argon laser

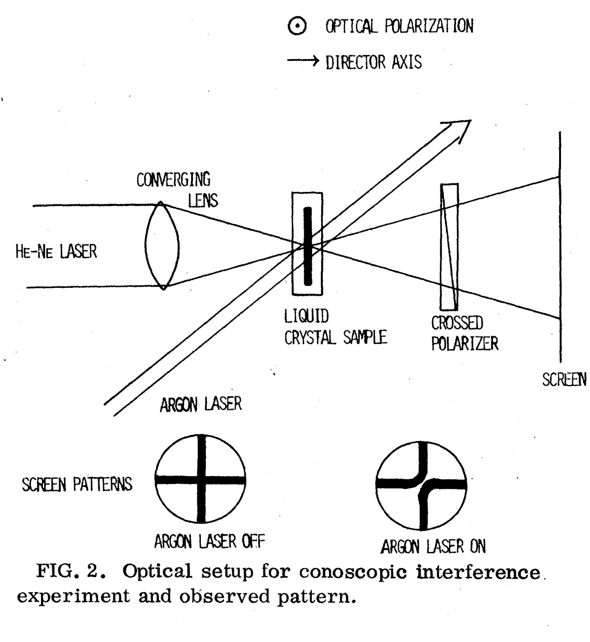

FIG. 2. Optical setup for conoscopic interference experiment and observed pattern.

is on, it was observed that indeed the interference pattern changed to one corresponding to a tilted director-axis configuration, when the incident argon-laser intensity exceeded 4.5 W/cm^2. At this intensity, the associated electric-field strength E_{op} is estimated to be about 57 V/cm. In a separate experiment, we have performed a series of conoscopic interference experiments in which samples of various thickness were subject to dc electric field applied perpendicular to the director axis. The corresponding Freedericks fields E_F's were measured. For a sample thickness of 75 μm, the de Freedericks field was found to be about 60 V/cm, which is in good agreement with the optical field strength mentioned above. A point to note is that these dc and optical field strengths for inducing molecular reorientation are much smaller than those values given in the theoretical expression for E_F. Using known values of $K=5\times10^{-7}$ dynes, $\Delta\epsilon\approx0.1$ and $d=75$ μm, E_F is estimated to be 600 V/cm. This discrepancy can be attributed to various factors, including nonideal boundary conditions, presence of contaminants or free ions (e.g., coming from the surfactant) that tend to change the elastic constant K or the anisotropy $\Delta\epsilon$ or $\Delta\chi$.

The four-wave-mixing scattering geometry is shown in Fig. 1. Both incident beams were derived from the 5145-Å line of a argon-ion laser operating in the single-frequency mode. These beams were crossed at a small angle of about 0.6°. The beams were almost normally incident on the face of the sample, with the polarization about perpendicular to the director axis. The diameter of these beams was estimated to be 2 mm. At an incident beam 1 power of 200 mW (5 W/cm^2 in intensity) and beam 2 of 120 mW, an easily visible diffracted beam was produced in the phase-matched direction. As the angle of crossing for the incident beams was varied, the diffracted-beam direction varied accordingly. The crossing angle could be increased up to 1° and the diffracted beam was still visible. The power of the diffracted beam was measured to be 5×10^{-2} mW. An interesting point to note is that the beam waist of this beam was considerably smaller than those of the incident beam. When expanded and then projected on a screen, the beam waist was measured to be roughly one-third that of the incident beams. The conversion efficiency, namely I_3/I_2, was thus estimated to be 0.5×10^{-2}. This is in good order-of-magnitude agreement with the theoretical value estimated from Eq. (14), which gives 2×10^{-2} for the conversion efficiency.

To check the four-wave-mixing nature of the observed effect, we first established that the generation of the diffracted beam required the simultaneous presence of both beams 1 and 2, by successive blocking of these incident beams. A more quantitative measurement is the intensity dependence. Since I_2 is derived from the same laser that provided I_1, we expect I_3 to be proportional to the third power of the laser intensity and is linear in I_2. The dependence on the laser intensity was checked by simply raising and lowering the laser intensity, while the dependence on I_2 is checked by introducing neutral density filters in the path of I_2. Figures 3 and 4 show the observed intensity dependence. I_3 obeys the predicted intensity dependence very closely.

FURTHER REMARKS

The interaction of liquid crystals with optical and dc fields is a complex issue. In the study described above, we have singled out but one of the effects associated with these complex electro- and magneto-optical effects. For the case of purely optical perturbation, although we have removed many complications associated with dc fields, there exists a host of optical effects that remain to be solved. It is conceivable that various other polarization and scattering geometries may be tested to gain more quantitative characterization of the process. We have, instead, studied effects associated with high optical intensities. Previous studies[5] have shown that because of the large nonlinearity of liquid crystal, self-focusing, and the associated irregular beam intensity, distribution will occur at a high optical intensity. To qualitatively investigate this, we have expanded all the beams after the cell and study the beam intensity

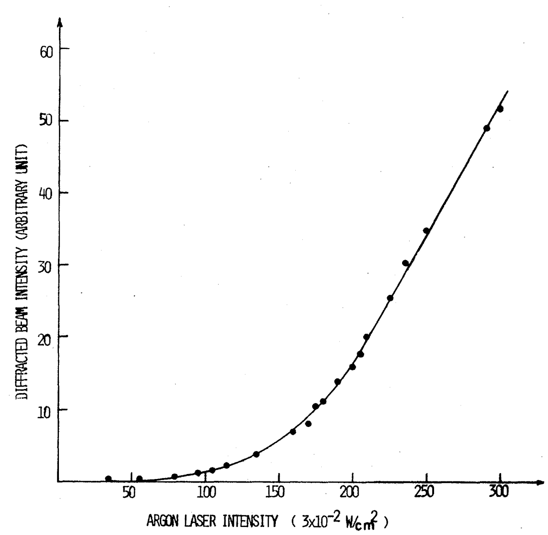

FIG. 3. Cubic dependence of the diffracted-beam intensity on the argon-laser intensity.

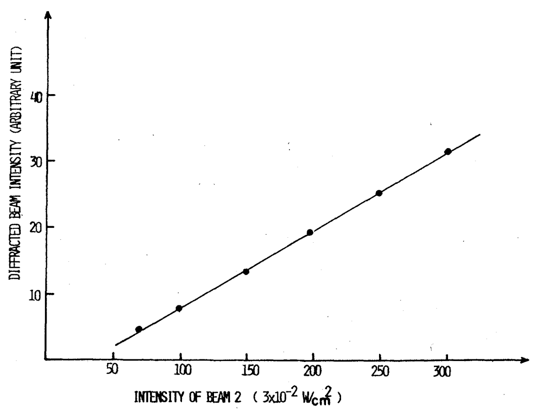

FIG. 4. Linear dependence of diffracted intensity on beam 2 intensity.

profile. No unusual intensity distribution was observed up to the maximum power output of the laser (with an estimated incident optical intensity I_1 of 20 W/cm^2). To raise the intensity, the incident beams were lightly focused. At an estimated incident optical intensity I_1 of 100 W/cm^2, an irregular transmitted intensity distribution profile began to appear. At the same time, the diffracted-beam profile was also distorted, and second- and sometimes third-order diffracted beams began to appear. At these intensities, side scatterings from the main beams, which otherwise occur as a relatively faint background, also began to increase to comparable intensity as the diffracted beam. This study, while qualitative, shows that there exists a good working range of optical intensities in which the wave-mixing process may be optimized without complication from high intensity effects.

Our study also clearly indicates the possibility for further fundamental and also applied studies. Using a pulsed laser, or by modulating either beam 1 or 2, one could study the orientational relaxation rate of the molecules in the nematic phase, and perhaps gain further insights into the phase-transition aspect of nematics. From a more applied standpoint, it is obvious that the degenerate four-wave-mixing process under study could be utilized in real time holographic imaging and optical modulation devices. We have, for example, successfully attempted wave-front conjugation.[17] The possibility of high-resolution imagery is also being tested.

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