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EFFECTS IN NEMATIC CELLS WITH BROKEN CENTROSYMMETRY

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Abstract Unipolar electro-optic and nonlinear optical effects are observed in a nematic liquid crystal cell with broken inversion symmetry. The cell is bounded by two plates which produce electric surface polarizations normal to the plates. When the two surfaces are different a unipolar electrooptic effect is observed: the electric field-induced director distortions occur only for one polarity of the field and not for the opposite polarity ("optical diode" effect). Another manifestation of the symmetry breaking is strong second harmonic generation by the cell.

INTRODUCTION

Uniform nematic liquid crystals are centrosymmetric. Even when the nematic molecules possess permanent electric dipoles, molecular rotation and head-to-tail association lead to quadrupolar bulk arrangement on the average. Optical effects, such as electric field modulation of the intensity of light transmitted through a nematic cell, do not depend on the polarity of the applied voltage. Spatial boundaries of finite nematic samples break this symmetry in two ways. First, the absence of inversion symmetry at interface leads to an electric polarization $\mathbf{P}_s$ of the surface layer [1-7]. For instance, when the liquid crystal molecules have a longitudinal dipole moment and orient themselves normally to the substrate (homeotropic orientation), ferroelectric order of these molecules might be the reason for a non-zero $\mathbf{P}_s$ [2], as confirmed by second-harmonic generation experiments [5]. Surface polarization can be strong enough to respond to an externally applied electric field by causing director reorientation even when other mechanisms (e.g., flexoelectric and dielectric) suppress reorientation [8]. Second, even when the surface polarization $\mathbf{P}_s = \mathbf{0}$, but the nematic cell is bounded by two different plates, the inversion symmetry of the sample is broken. Two groups [3,9] have described a polar flexoelectric effect caused exclusively by the difference in the anchoring strengths at two polymer layers which align the liquid crystal tangentially. In this Letter we report on experimental observation of electro-optical and nonlinear optical effects in nematic cells with double symmetry breaking: first, both plates of the cell set homeotropic orientation to cause local surface electric polarization and second, the plates are chemically different to avoid cancellation of the two surface polarizations: $\mathbf{P}_{s1} \neq -\mathbf{P}_{s2}$. Figure 1a illustrates a particular case with $\mathbf{P}_{s1} = \mathbf{P}_{s2}$. We describe two consequences of

this geometry: (a) a unipolar electrooptic or "optical diode" effect, in which an electric field of one polarity blocks the light coming through the cell (Fig.1a) but the field of opposite polarity makes the cell transparent (Fig.1b); (b) a second harmonic generation.

UNIPOLAR ELECTROOPTIC EFFECT

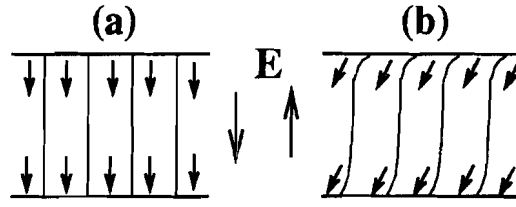

FIGURE 1 Nematic cell with homeotropic anchoring and different surface polarization layers; electric field of negative polarity stabilizes the initial state (a), while positive field causes director distortions (b).

We have studied the nematic liquid crystal 5CB (EM Industries, Inc.). 5CB molecules have a permanent dipole moment $\mu \approx 4.9D$ (as determined by measurements in different solvents [10]) directed essentially parallel to the long axis (towards the aliphatic end) of the molecule. The nematic phase of 5CB has a positive dielectric anisotropy, $\epsilon_a = \epsilon_{||} - \epsilon_{\perp} \simeq 14$ at room temperature [11]. Glass plates with transparent conducting layers ($In_2O_3 : Sn$ and In_2O_3) were treated to provide homeotropic orientation. Both organic and inorganic materials were used: (a) silicon elastomer $(CH_3)_3SiO[(CH_3)_2SiO]_nSi(CH_3)_3$, $n \sim 25000$, coated over $In_2O_3 : Sn$ (SE); (b) octadecyltrichlorosilane (OTS) over $In_2O_3 : Sn$; (c) In_2O_3; (d) $In_2O_3 - SiO_2 - NiO$; (e) lecithin L-α-phosphatidylcholine over $In_2O_3 : Sn$. The cells were filled with 5CB in the isotropic phase, then cooled to room temperature at which all experiments were performed.

We used two cell geometries. For transmitted light experiments flat cells were used; the thickness (in the range $20 - 60\mu m$) was determined by mylar spacers. For reflected light experiments and combined reflectance-transmittance experiments, wedge cells were constructed to separate the beams reflected from different interfaces.

To study the unipolar effect, a sample placed between crossed polarizers was probed with modulated light from a He-Ne laser while a D.C. voltage was applied to the cell. With normally incident light, the intensity $I \sim sin^2\Phi/2$ of the transmitted light is determined by the phase retardation Φ . With no field applied, only an ordinary wave propagates, $\Phi = 0$, and $I = 0$ (in practice, non-zero residual transmittance caused by imperfections of alignment, fluctuations, etc., can still be observed). If the electric field causes director deviations from the normal orientation, then $\Phi \neq 0$, and $I > 0$.

Figures 2 and 3 demonstrate the unipolar "optical diode" effect, i.e., a unipolar optical response of nematic cells assembled of two differently treated plates to produce homeotropic alignment. The effect is observed both for inorganic (Fig.2) and organic (Fig.3) coatings. In Fig. 2, when the In_2O_3-coated surface served as an anode, the applied voltage was plotted as positive. For positive polarity, the intensity of the transmitted light starts to increase at $U_1 \approx 2.2V$. For negative polarity, no significant changes occur till the voltage decreases to $U_2 \approx -4.2V$.

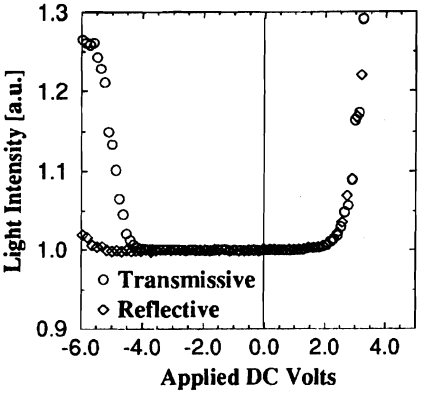

FIGURE 2 Intensity of the transmitted and reflected light as the function of DC voltage applied to a homeotropic nematic layer placed between $In_2O_3 - SiO_2 - NiO$ and In_2O_3 surfaces. In_2O_3 is the reflecting surface.

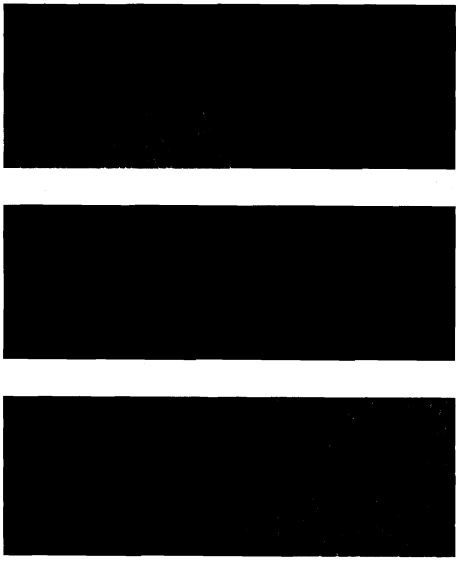

FIGURE 3 Textures of the unipolar response of the nematic film to a DC voltage of $-2V$ (top); $0V$ (middle) and $2V$ (bottom).

The two thresholds differ not only in the values of U_1 and U_2 , but also in the behavior of beam reflected from the In_2O_3-surface. For positive polarity, at $U_1 \approx 2.2V$, the intensity of the reflected light intensity changes dramatically while for negative polarity it practically does not changes in the range from 0 to $-5V$. Therefore, the low-voltage polarity at $U_1 \approx 2.2V$ is accompanied by significant surface reorientation of the director. Figure 3 gives textural illustration of the "optical diode" effect. In this case one half of each plate with ITO electrode was covered with a lecithin layer. The second half remained non-treated. The cell was assembled in such a manner that the lecithin sides faced the non-treated sides, i.e., the cell represented two asymmetric sub-cells of opposite polarity. Polarizing-microscope pictures clearly show a unipolar "optical diode" effects of different polarities in these two subcells.

The experimental features of the observed phenomena are similar to those of the surface-polarization instability described previously for the homeotropic symmetric cells [8,10]. The difference is that the response of the asymmetric cell is unipolar. Below we describe the unipolar character of the electrooptic response following the surface torque equations approach [4]. For the sake of simplicity, non-uniform distribution of the electric field across the cell, finite electric resistance of the orienting substrates, finite electroconductivity are neglected; These and other factor have been discussed in details in Refs. [6,10] for symmetric cells.

Consider a nematic slab between two plates with coordinates $z = 0$ and $z = d$. Both plates orient $\mathbf{n}$ along the z axis. The field $\mathbf{E}$ is along the z axis.

The dielectric coupling $\sim [-\frac{1}{2}\epsilon_0\epsilon_a(\mathbf{E}\cdot\mathbf{n})^2]$ stabilizes the homeotropic orientation, since $\epsilon_a > 0$ for 5CB; here ϵ_0 is the permittivity of free space and $\mathbf{n}$ is the nematic director. If the cell thickness d is much larger than the dielectric coherence length

$1/q$, $q = |E|\sqrt{\epsilon_0\epsilon_a/K}$ (K is the Frank elastic constant in the one-constant approximation) then **n** in the center of the cell is parallel to the field, the distortions near the two surfaces can be considered as independent. The free energy is minimized by solving the linearized Euler-Lagrange equations, which give[4] $\theta(z) = \theta_1 exp(-zq)$ for the lower surface and $\theta(z) = \theta_2 exp[(z-d)q]$ for the upper one.

The torque balance at the two plates gives [4, 13]:

$$(Kq + W_1 - eE + 2P_{s1}E)\theta_1 = 0 \quad at \quad z = 0 \tag{1}$$

$$(Kq + W_2 + eE + 2P_{s2}E)\theta_2 = 0 \quad at \quad z = d \tag{2}$$

where e is the flexoelectric coefficient, W_i ($i = 1, 2$) are the surface anchoring coefficients.

We consider the surface polarization $\mathbf{P_s} = \mathbf{n}P_s cos\theta$ in the form suggested by Monkade, Martinot-Lagarde and Durand [4] in the model of ferroelectric ordering of the longitudinal molecular dipoles [2]. The torque $2P_{si}E\theta_i$ from surface polarization stabilizes homeotropic orientation if **E** is parallel to $\mathbf{P_{si}}$, and destabilizes the homeotropic orientation if $\mathbf{P_{si}}$ and **E** are anti-parallel. The quantities P_{si} and E in Eqs.1 and 2 are positive when the corresponding vectors are directed along the z axis. Another destabilizing torque can arise from the flexoelectric effect, via the electric polarization $\mathbf{P_f}$ resulting from curvature distortions. A surface tilt gives rise to the flexoelectric polarization $\mathbf{P_f} \sim (-e\theta\frac{d\theta}{dz})$ in the bulk and results in the surface torques $-eE\theta_1$ and $eE\theta_2$. With $e > 0$ and $E > 0$ the flexoelectric mechanism causes distortions only at the lower plate "1".

Finally, surface anchoring tends to keep the nematic molecules in the homeotropic orientation; hence the surface anchoring torques $W_i\theta_i$ in (1) and (2) are always positive.

Torque balance at the surface described by in Eqs.1 and 2 requires that nonzero surface tilt θ_1 and θ_2 appear when the electric field exceeds the threshold

$$E_1 = \frac{W_1}{e - 2P_{s1} \mp \sqrt{\epsilon_0\epsilon_a K}}, \quad E_2 = \frac{W_2}{-e - 2P_{s2} \mp \sqrt{\epsilon_0\epsilon_a K}} \tag{3}$$

where the sign "-" should be taken for $E_{DC} > 0$ and the sign "+" for $E_{DC} < 0$. For symmetric cells with $W_1 = W_2$ and $P_{s1} = -P_{s2}$, Eq.3 recovers previous results [13].

Eq. 3 shows that the surface polarization asymmetry, $P_{s1} \neq -P_{s2}$, leads to unipolar effects. For example, a positive electric field would cause director tilt $\theta_1 \neq 0$, if $P_{s1} < (e - \sqrt{\epsilon_0\epsilon_a K})/2$ and $(-e - \sqrt{\epsilon_0\epsilon_a K})/2 < P_{s2} < (-e + \sqrt{\epsilon_0\epsilon_a K})/2$. However, a negative electric field would produce no effect at all; $\theta(z) = 0$ everywhere in the cell for $P_{s1} < (e - \sqrt{\epsilon_0\epsilon_a K})/2$ and $P_{s2} < (-e + \sqrt{\epsilon_0\epsilon_a K})/2$. The intensity I of light transmitted through the cell between crossed polarizers is thus expected to be polarity dependent. For a negative field, the cell blocks light and $I = 0$, but for a positive field $E_{DC} > E_{DC,1} > 0$, it transmits light with intensity $I \sim sin^2\Phi/2 > 0$, where $\Phi \sim \theta^2(E) > 0$. This behavior is qualitatively seen in the experiments, where both the different $\mathbf{P_{s,i}}$ and W_i contribute to the unipolar response of the cells.

Second-harmonic generation experiments, described below, give an additional evidence of the net polarization in the asymmetric cells.

SHG EXPERIMENTS

The experimental setup for SH measurements is shown in Fig. 4. The laser source is a mode locked YAG laser with 38 ps pulsewidth and 20 mJ per pulse. The fundamental wavelength is 1.06 μm. A polarizer (P) and $\lambda/2$ waveplate (WP) are used to control the intensity, and a positive lens (L) is placed before the sample so that the intensity can be changed by moving the sample. An optical monochromator (MC) and two spectral filters (SF) in front of a photomultiplier (PMT) block background radiation except the 532 nm second harmonic signal. The cutoff wavelength of the PMT is 860 nm.

Wedge-shaped cells were constructed with 5CB between *Lecithin* and *Silicone Elastomer* coated glass plates, with sample thickness of $12\mu m$ and $24\mu m$ at the ends. The SH intensity was found to be independent of the sample thickness, with comparable intensity in the transmitted and reflected beams. The transmitted beam is essentially collinear with the fundamental, differring in direction by less than 0.5° Phase matching appeared to be collinear for a wide range of angles of incidence of the fundamental beam.

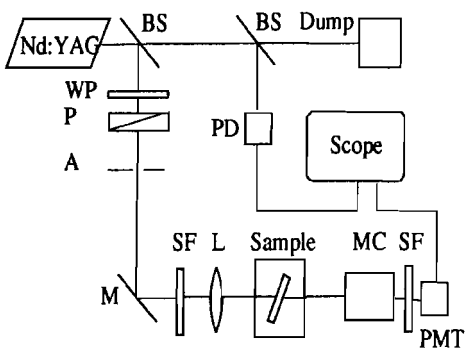

FIGURE 4 Experimental setup for surface SHG.

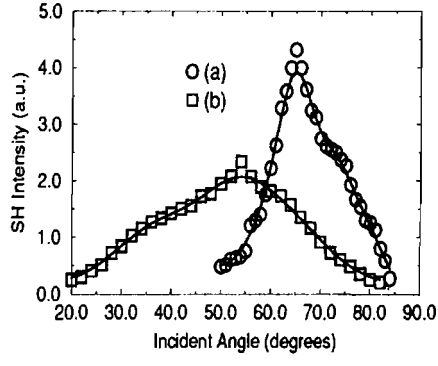

FIGURE 5 Angular dependence of SH signal from (a) wedged and (b) planar sample.

Fig. 5 shows the angular dependence of SHG signal obtained from the wedged sample. The maximum is at $\sim 65°$, with a spread of $\sim 15°$. A somewhat different angular dependence is shown by a $25\mu m$ plane parallel sample with *Silicone Elastomer* and *Octadecyltrichlorosilane* surface treatments, also shown in Fig. 5. Here the maximum is at $\sim 54°$, with a spread of $\sim 40°$. The SH signal energy was approximately $2nJ$ per pulse. The SH signal was found to be plane polarized in the same direction as the fundamental.

Cells where both plates were coated with lecithin were also studied; here the SH intensity was at least an order of magnitude smaller than in the cells with different surface treatment on the two plates.

Although the details of the mechanisms giving rise to SHG in asymmetric cells are not yet completely understood, the relatively large SH signal observed is consistent with net electric polarization and broken inversion symmetry in asymmetric samples.

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