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Surface-mediated electroclinic effect in a chiral nematic liquid crystal

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Optical phase-shift measurements are reported for a homeotropically aligned chiral nematic liquid crystal subject to an applied ac electric field E. A change in phase shift linear in E was observed, with a characteristic relaxation time $\tau \approx 0.01$ s. The effect vanished for the nonchiral (racemic) version of the material. The data, taken together with the symmetry, are consistent with an electroclinic effect at the surface, such that the induced molecular tilt propagates elastically into the bulk.

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In 1977 Caroff and Meyer demonstrated the existence of an electroclinic effect above the smectic-A–smectic-C^* transition in liquid crystals composed of chiral molecules [1,2]. In this effect an electric field E is applied parallel to the plane of the smectic layers, coupling to the molecular dipole moment. Since chiral molecules lack inversion symmetry, a nonzero molecular tilt $\theta \propto E$ is obtained. This effect has been studied in bulk in the smectic-A (Sm-A) and other layered phases [3–5], and has even been shown to exist in the nematic phase as well [6–12]. Very recently several groups have begun to investigate electroclinic phenomena induced by and at an interface [13–17]. It was found, for example, that the director orientation of a chiral Sm-A material at a rubbed polymer interface can deviate from the rubbing direction by several degrees [15–17]. Since the rubbing direction locally establishes D_∞ symmetry, a surface field can then couple to the polarization and induce a tilt relative to the rubbing direction in the plane of the interface. This is one example of a surface electroclinic effect.

The subject of this paper, however, is another type of interfacial electroclinic phenomenon whereby the interface itself, rather than some rubbing direction, establishes a preferred axis. We recently showed [18] that an interface can locally impose a reduced symmetry which, under appropriate conditions, can give rise to a spontaneous polarization. In that work we noted that a chiral nematic liquid crystal oriented perpendicular to the interface has an infinitefold rotation axis; if the molecule were then to tilt relative to the interface normal, this symmetry operation would vanish. A tilt of this sort can be obtained, for example, with a strong magnetic field. On tilting, the local symmetry is similar to that of the Sm-C^* case (albeit lacking even the twofold rotation axis perpendicular to the molecule). In such a situation a component of electric polarization exists parallel to and near the interface and perpendicular to the molecule; this was demonstrated in Ref. 18. Now consider the case for which the magnetic field is zero and the chiral nematic molecules remain normal to the interface. An in-plane electric field can then couple to the molecular dipole and *induce* a tilt at the surface, a situation analogous to the bulk electroclinic effect in the Sm-A phase above the Sm-A–Sm-C^* transition [1–5]. For electric fields of sufficiently low frequency, the surface tilt propagates elastically into the interior of the sample and gives rise to an observable bulk deformation. In this paper we report on optical phase-shift measurements performed as a function of electrical-field driving frequency ω in a chiral nematic liquid crystal. Our central result is a linear dependence of the phase-shift variation $\delta\alpha$ on E. In addition, the magnitude of the effect decreases rapidly with frequency for $\omega > \omega_r$, where ω_r^{-1} is a relaxation time for the long-wavelength elastic deformations in the sample.

An indium-tin-oxide- (ITO-) coated glass slide, approximately 20 Ω/□, was chemically etched to leave two parallel conducting strips separated by a distance $l = 1.9$ mm to facilitate application of an electric field in the plane of the glass. By conformal mapping techniques one can show [19] that the electric field in the center of an *infinitely long* strip is $E = 2V_{\rm app}/\pi l$, where $V_{\rm app}$ is the voltage difference between the two electrodes; for electrodes of finite extent w (i.e., $w = 12.5$ mm, the width of the glass), the field will be slightly reduced. The ITO slide as well as an ordinary glass microscope slide were treated with the sufactant hexadecyltrimethyl ammonium bromide for homeotropic alignment. They were then placed together, separated by Mylar spacers of nominal thickness 5 μm, and adjusted under monochromatic light to achieve maximum parallelism. The cell was then epoxied, and its thickness was determined using an interference scheme [20]. Two such cells were made, one containing the chiral mixture SCE12 (British Drug House) and having a thickness $d = 6.43 \pm 0.02$ μm, and the other containing the racemic version SCE12R and having a thickness $d = 8.20 \pm 0.02$ μm. Both materials were kindly supplied by EM Industries and used without further purification. The chiral cell was placed in an oven, temperature controlled to 10 mK, and tilted by an angle of 45° with respect to an incoming beam from a He-Ne laser, as shown in Fig. 1. So as to maintain an approximately uniform electric field across the profile of the laser spot, the beam was focused to a diameter of 500 μm at the sample. The sample was then situated between a pair of crossed polarizers making an angle 45° with respect to the z axis. The recollimated light impinged on a photodiode detector, whose output was fed into a lock-in amplifier referenced to the (angular) frequency ω of the electric field.

The sample was brought into the nematic phase at a temperature $T = T_{NA} + 7.8\,^\circ$C where the nematic-Sm-A

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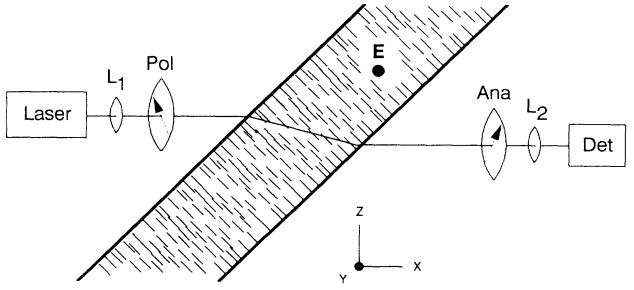

FIG. 1. Schematic representation of the optical arrangement. L_1 and L_2 are the focusing and recollimation lenses, respectively. Pol is the polarizer, Ana is the analyzer, and Det is the detector.

transition temperature $T_{NA}=79.3\,^{\circ}\mathrm{C}$. The ac electric field was ramped from zero to 20 V rms over approximately 120 s, a sufficiently slow change in amplitude to facilitate frequency locking of the lock-in amplifier. The output from the lock-in amplifier, which is proportional to the ω component of voltage $\delta V_{\mathrm{det}}(\omega)$ at the detector, was computer recorded. Note that $\delta V_{\mathrm{det}}(\omega)$ exhibited a frequency-dependent phase delay relative to the ac voltage, and in fact only the *magnitude* $|\delta V_{\mathrm{det}}(\omega)|$ was recorded. Because of the very slow frequencies used (ν as small as 1.5 Hz), it was necessary to measure the applied voltage V_{app} with a lock-in amplifier as well, whose output was computer recorded simultaneously with the detector signal. Thus, the quantity $|\delta V_{\mathrm{det}}(\omega)|/V_{\mathrm{det}}^{\mathrm{dc}}$ was measured versus V_{app}, where $V_{\mathrm{det}}^{\mathrm{dc}}$ is the dc output from the detector; a typical example is shown in Fig. 2. In light of this apparent linear behavior, measurements were made as a function of frequency for both chiral and racemic samples, and the slopes $d[|\delta V_{\mathrm{det}}(\omega)|/V_{\mathrm{det}}^{\mathrm{dc}}]/dV_{\mathrm{app}}$ are shown in Fig. 3.

Intensity changes at the detector come about from molecular reorientations. Since $\delta V_{\mathrm{det}}(\omega)\propto E$, our first

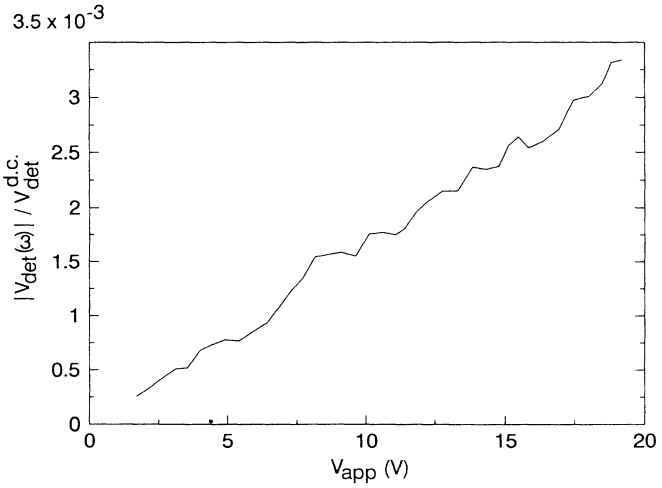

FIG. 2. Typical trace of $|\delta V_{\mathrm{det}}(\omega)|/V_{\mathrm{det}}^{\mathrm{dc}}$ vs applied voltage V_{app}. (This trace was taken at $\omega=15.7\ \mathrm{s}^{-1}$.)

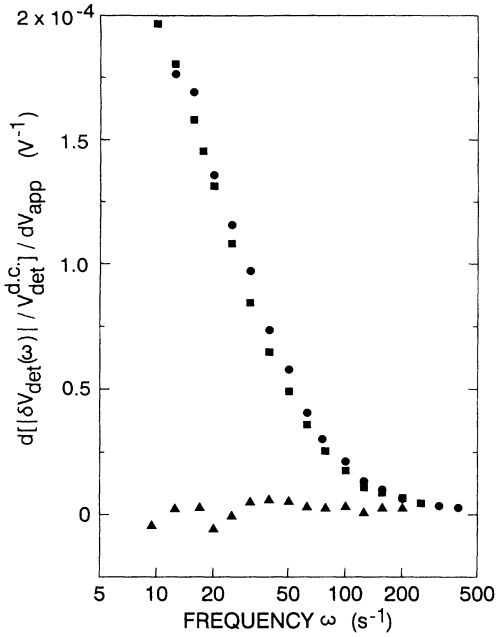

FIG. 3. $d[|\delta V_{\mathrm{det}}(\omega)]/V_{\mathrm{det}}^{\mathrm{dc}}]/dV_{\mathrm{app}}$ vs ω for two sets of chiral data (■ and ●). The racemic mixture (▲) shows a null result.

conclusion is that the electric field couples linearly to a molecular polarization, and that our apparatus is not sensitive to phenomena which scale as E^2. We can therefore exclude, for example, phenomena such as field-induced biaxiality as a contributor to the signal [21]. In addition, director reorientations in which $\delta\mathbf{n}$ is parallel to the electric field cannot, for reasons of symmetry, contribute to the detector signal at frequency ω. This would exclude phenomena such as flexoelectricity [22] and couplings to $\langle P_1(\cos\theta)\rangle$ [23–26]. The only distortions consistent with the data involve a molecular tilt in the x-z plane. For reasons of symmetry this must be either a nematic electroclinic effect (NECE) [6,7] or a surface-induced electroclinic phenomenon, both requiring chirality. Further confirmation of these two possible mechanisms can be seen in the apparent null result obtained from the racemate, as shown in Fig. 3. We shall proceed assuming a surface effect, and show that a NECE is inconsistent with the dynamic data.

The experiment was arranged to measure an optical phase shift $\alpha\equiv k_0\int[n_e^{\mathrm{eff}}d\xi_e - n_o d\xi_o]$, where k_o is the wave vector of the light, n_o and n_e^{eff} are the ordinary and angle-dependent extraordinary refractive indices, and, noting that there are two angles of refraction for the two polarization states, $d\xi_o$ and $d\xi_e$ are the appropriate differential path lengths of the light through the sample. The intensity I at the detector is approximately proportional to $\sin^2(\alpha/2)$ (see below). For a small, spatially uniform molecular tilt $\delta\theta$ in the x-z plane, one finds a corresponding change in the phase shift

$$\delta\alpha = k_o\int[\delta n_e^{\mathrm{eff}}d\xi_e + n_e^{\mathrm{eff}}\delta(d\xi_e)]\,, \tag{1}$$

where both $\delta n_e^{\mathrm{eff}}$ and $\delta(d\xi_e)$ are linear in $\delta\theta$ for the

geometry in Fig. 1. [For the general case, $\delta\theta$, and thus δn_e^{eff} and $\delta(d\xi_e)$, can be functions of position.] As long as α is not nearly a multiple of π, the change in detector intensity δI is linear in $\delta\theta$. This method was used, for example, to determine the magnetically and electrically induced tilt susceptibility in the bulk smectic-A phase just above the smectic-C transition temperature [1,2,27–29]. Owing to the symmetry of the system, for the case at hand only the *interfacial layers* will respond to the electric field and tilt in the x-z plane by some polar angle $\delta\theta$. The molecules in the interior then elastically couple to the interfacial molecules, and undergo a tilt as well. For sufficiently low frequencies $\omega \ll \omega_r$, where ω_r^{-1} is some characteristic relaxation time for the smallest q mode ($q_{\min}=\pi/d$), the director orientation remains uniform throughout the sample (tilting by an angle $\delta\theta$). Thus, both δn_e^{eff} and $\delta(d\xi_e)$ in Eq. (1) are expected to be proportional to $\delta\theta$, and the differential optical phase shift $\delta\alpha$ will be proportional to $\delta\theta$ as well.

From the data in Fig. 3 we can make an order-of-magnitude estimate of the effect. We first note that

$$\frac{|\delta V_{\text{det}}|}{V_{\text{det}}^{\text{dc}}}=\frac{\delta I}{I}\approx\frac{\frac{1}{2}(\delta\alpha)\sin\alpha_o}{\sin^2(\frac{1}{2}\alpha_o)}. \tag{2}$$

For the sample in question we used a Pockels cell to determine the zero-field phase shift $\alpha_o=1.51$ rad. Note that Eq. (2) is *not* an exact equality because the intensity is not, in fact, quite equal to $\sin^2(\frac{1}{2}\alpha_o)$. Since the sample is tilted with respect to the incoming beam, the two polarization states have different transmission coefficients at the interfaces. Thus, there is always a dc component of the intensity at the detector, independent of α_o. Nevertheless, since we estimate this correction to be about 0.3% of $\sin^2(\frac{1}{2}\alpha_o)$ at $\alpha_o\approx 1.5$, for all intents and purposes we can assume that Eq. (2) is exact. We therefore find $\delta\alpha \approx 0.9|\delta V_{\text{det}}(\omega)|/V_{\text{det}}^{\text{dc}}$. (A similar result was obtained for the racemic sample, indicating that *if* an electroclinic effect were to exist in the racemate, it would have been observable optically.) Also, since $n_e^{\text{eff}}=[(\cos\phi/n_o)^2+(\sin\phi/n_e)^2]^{-1/2}$, where n_e is the liquid crystal's extraordinary refractive index and $\phi(=\phi_o+\delta\theta)$ is the angle between the (extraordinary) light propagation direction and the molecular director, we find for small $\delta\theta$

$$\delta n_e^{\text{eff}}=\frac{1}{2}\left[\left(\frac{\cos\phi_o}{n_o}\right)^2+\left(\frac{\sin\phi_o}{n_e}\right)^2\right]^{-3/2}\times\left[\frac{1}{n_o^2}-\frac{1}{n_e^2}\right]\sin(2\phi_o)\delta\theta.$$

Using an Abbe refractometer we determined $n_o=1.479$ and $n_e=1.641$ at the sample temperature for light of wavelength $\lambda=6328$ Å. Working in the limit of $\omega\ll\omega_r$, such that the tilt angle $\delta\theta$ is nearly uniform throughout the sample, we find from Snell's law that $\phi_0=28°$. Thus, $n_e^{\text{eff}}=1.51$, $\delta n^{\text{eff}}=0.12\delta\theta$, and $\xi_e=d/\cos\phi_o=7\times10^{-6}$ m [cf. Eq. (1)]. For the second term in Eq. (1) we find

$$\delta\xi_e=d\sec\phi_o\tan(\phi_o)\delta\theta=(4\times10^{-6}\text{ m})\delta\theta.$$

Therefore, $\delta\alpha=68\delta\theta$. From Fig. 3 we can estimate that $d[|\delta V_{\text{det}}(\omega)|/V_{\text{det}}^{\text{dc}}]/dV_{\text{app}}$ extrapolates to approximately 4×10^{-4} V^{-1} as $\omega\to 0$. Then from $\delta\alpha\approx 0.9|\delta V_{\text{det}}(\omega)|/V_{\text{det}}^{\text{dc}}$ above, we find that $d(\delta\alpha)/dV_{\text{app}}\approx 4\times10^{-4}$ V^{-1} and $d(\delta\theta)/dV_{\text{app}}\approx 6\times10^{-6}$ V^{-1} in the limit of low driving frequency. Assuming that the field $E=2V_{\text{app}}/\pi l$, we finally find that $d(\delta\theta)/dE=2\times10^{-8}$ m/V. This is at least 3 orders of magnitude larger than the NECE at comparable temperatures [6], and similar in magnitude to the ordinary electroclinic effect in the Sm-A phase near the Sm-C^* phase transition [30]. We note that for a given applied electric field, the equilibrium magnitude of the electroclinic effect at the surface is determined by a competition between the electroclinic torque and the restoring torque, the latter arising from the effective surface anchoring energy $F_S=\frac{1}{2}W(\delta\theta)^2$ [31]. Thus $d(\delta\theta)/dE$ is inversely proportional to the anchoring strength coefficient W. This situation is analogous to the ordinary bulk electroclinic effect in the Sm-A phase, in which the restoring torque comes from maintaining the director perpendicular to the smectic layer, and the associated energy is $F_b=\frac{1}{2}D(\delta\theta)^2$. When the coefficient D vanishes at the Sm-A–Sm-C^* transition, the magnitude of the ordinary electroclinic effect diverges [1,2].

At driving frequencies comparable to and greater than ω_r, the modes of smallest q suffer a phase delay relative to the ac field. In this case the elastically coupled tilt $\delta\theta$ is no longer uniform, but instead becomes a function of position in the sample, i.e., $\delta\theta(\xi_e)$. Taking $\delta\theta_q^o$ as a spatial Fourier component of the field-driven interfacial layers at frequency ω, the torque equation

$$K_3q^2[\delta\theta_q-\delta\theta_q^o\cos(\omega t)]+\eta(d\delta\theta_q/dt)=0$$

can easily be solved for each q mode and reinverted to give $\delta\theta(\xi_e)$. The contribution to $\delta\alpha$ from the first term in Eq. (1) can then be determined; it is proportional to E, and thus to $\delta\theta_{\text{surf}}$ at the surface. The second term in Eq. (1) is by no means trivial, however, since the path of light propagation $\delta\xi_e$ depends in a complex way on the rapidly spatially varying profile of $\delta\theta(\xi_e)$. Nevertheless, it is also proportional to $\delta\theta_{\text{surf}}$. Further complicating the situation is a contribution from the bulk nematic electroclinic effect. At low frequencies this is small compared to the surface driven effect, although it may make a measurable contribution to the total signal at higher frequencies (see Fig. 3). In light of these considerations a formal fit of Fig. 3 to Eq. (1) is not practical.

Nevertheless, we can still glean important quantitative information from the data. The quantity ω_r can be estimated by noting that it is expected to be of order $K_3q_{\min}^2/\eta$, where η is the viscosity (0.01 to 0.03 kg m^{-1} s^{-1}, corresponding to 0.1–0.3 P) and K_3 is the bend elastic constant (typically about 10^{-11} N). For the lowest-energy mode $q_{\min}=\pi/d\approx 5\times10^5$ m^{-1}; thus $\omega_r\approx 100$ s^{-1}. Since the Fourier contributions to $\delta\theta$ and thus δn_e^{eff} scale as q^{-1} for this square-well geometry, $q_{\min}$ will be the most important contributor to $\delta\alpha$; thus, if the bulk interior is elastically driven by the surfaces as our model suggests, then Fig. 3 should exhibit a relaxation frequency of order of magnitude $\omega_r\approx 100$ s^{-1}. This is indeed the case. This is a particularly important result because it

demonstrates that the electric field couples to the bulk through an indirect elastic mechanism, rather than through a direct electrical mechanism as in the nematic electroclinic effect. *If* the coupling were direct, then relaxation frequencies of $10^7\ s^{-1}$ might be expected, similar to those found for the nematic electroclinic effect [8]. The data, however, are inconsistent with such a rapid response, and it is therefore clear that the bulk response is elastic in nature.

In summary, we observed a change of the optical phase shift that was linear in applied field in a homeotropic chiral nematic sample. In light of the frequency response and the absence of this effect in a racemic mixture, we conclude that a linear electroclinic effect obtains at the surface, and that the bulk interior elastically follows the surface.

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