Surface Polar Ordering in a Liquid Crystal Observed by Optical Second-Harmonic Generation

P. Guyot-Sionnest, H. Hsiung, and Y. R. Shen

Department of Physics, University of California, Berkeley, California 94720

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Using optical second-harmonic generation as a probe, we have observed polar ordering of 4′-*n*-octyl-4-cyanobiphenyl (8CB) molecules in a monolayer at an 8CB-glass interface, but nonpolar ordering at the free surface of 8CB as well as in the bulk with the molecules forming quadrupole-type pairs. The surface polar ordering was independent of temperature and unaffected by the phase transitions in the bulk 8CB.

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Molecular ordering at a surface or interface of a liquid crystal (LC) may be significantly different from that in the bulk. This is a problem not only of fundamental interest, but also of practical importance in the design and construction of many LC devices.[1] In the past, x-ray[2,3] and ellipsometric[4-6] techniques have been used to determine smectic or nematic ordering at surfaces of liquid crystals. None of these methods, however, is capable of detecting the presence of polar ordering (defined as molecules aligned with heads pointing in the same direction) of molecules in surface monolayers. In this paper, we show that optical second-harmonic generation (SHG) is sensitive to such a polar ordering and can be used to probe a surface monolayer. We find that a polar ordering does occur in a surface LC monolayer at a LC-glass interface, but no such ordering is present at the free LC surface (air-LC interface).

The possibility of having surface polar ordering in LC's was first discussed by Meyer and Pershan[7] and later by Parsons.[8] It is well known that in the bulk of a LC in its isotropic, nematic, or smectic-*A* phase, the head of an asymmetric rodlike molecule has equal probabilities of pointing in opposite directions, leading to a macroscopic structure which is centrosymmetric. At the free surface or an interface, however, the asymmetric environment may impose a preferential direction on the molecular alignment, and give rise to a net polar order of the LC molecules. Optical SHG is an ideal tool to study such an ordering because within the electric-dipole approximation, a second-order nonlinear optical process is forbidden in a centrosymmetric medium but allowed when a polar symmetry emerges. In particular, the technique has been proven to be an effective surface probe with a submonolayer sensitivity.[9]

Let us first discuss briefly the underlying theory for SHG in reflection from a LC film. Consider a LC composed of rodlike, asymmetric molecules, such as 4′-*n*-octyl-4-cyanobiphenyl (8CB). The long molecular axis of an individual molecule is assumed to be along $\hat{\xi}$. If the second-harmonic frequency 2ω of the pump beam is in resonance with a transition mainly along $\hat{\xi}$ (for example, the 270-nm transition of 8CB[10]), then the nonlinear polarizability tensor $\boldsymbol{\alpha}^{(2)}(2\omega=\omega+\omega)$ characterizing the induced dipole at 2ω on the molecule is dominated by a single component $\alpha^{(2)}_{\xi\xi\xi}$.[11] In the bulk 8CB, neighboring molecules prefer an antiparallel orientation with overlapping cores[12] (Fig. 1). The induced dipoles at 2ω on the pair of molecules nearly cancel each other. As a unit, they give rise to an electric quadrupole

$$\mathbf{q}^{(2)}(2\omega=\omega+\omega)=\boldsymbol{\alpha}_Q^{(2)}:\mathbf{E}(\omega)\mathbf{E}(\omega). \tag{1a}$$

The electric-quadrupole polarizability $\boldsymbol{\alpha}_Q^{(2)}$ has a dominant component

$$\alpha^{(2)}_{Q,\xi\xi\xi\xi}=\xi_0\alpha^{(2)}_{\xi\xi\xi} \tag{1b}$$

that does not vanish when it is averaged over the molecular orientation distribution, where ξ_0 is the effective distance along $\hat{\xi}$ between the two induced dipoles on the two molecules. We have neglected the intrinsic quadrupole contributions from individual molecules, expecting them to be smaller.

We now assume that at the surface or interface of a LC, there exists a layer in which N_S molecules per unit area exhibit polar ordering. In the bulk, molecules form pairs with antiparallel orientations and there are $N_B/2$ pairs per unit volume. The macroscopic surface and bulk susceptibilities, $\boldsymbol{\chi}_S^D/\mathrm{cm}^2$ for the surface layer and $\boldsymbol{\chi}_B^Q/\mathrm{cm}^3$ for the bulk, respectively, can be obtained through a statistical averaging of $\boldsymbol{\alpha}^{(2)}$ and $\boldsymbol{\alpha}_Q^{(2)}$ over the molecular orientation distribution:

$$\begin{aligned}\chi^D_{S,ijk}&=N_S\langle\boldsymbol{\alpha}^{(2)}\rangle_{ijk}\cong N_S\alpha^{(2)}_{\xi\xi\xi}\langle(\hat{\xi}\cdot\hat{\imath})(\hat{\xi}\cdot\hat{\jmath})(\hat{\xi}\cdot\hat{\mathbf{k}})\rangle,\\ \chi^Q_{B,ijkl}&=(N_B/2)\langle\boldsymbol{\alpha}_Q^{(2)}\rangle_{ijkl}\cong(N_B/2)\xi_0\alpha^{(2)}_{\xi\xi\xi}\langle(\hat{\xi}\cdot\hat{\imath})(\hat{\xi}\cdot\hat{\jmath})(\hat{\xi}\cdot\hat{\mathbf{k}})(\hat{\xi}\cdot\hat{\mathbf{l}})\rangle.\end{aligned} \tag{2}$$

The superscripts D and Q on χ_S and χ_B are used to remind us that the dipole contribution dominates in the surface layer [the quadrupole contribution is neglected in χ_S in Eq. (2)] and the quadrupole contribution dominates in the bulk. For simplicity, the local-field correction factors[13] have been omitted in Eq. (2).

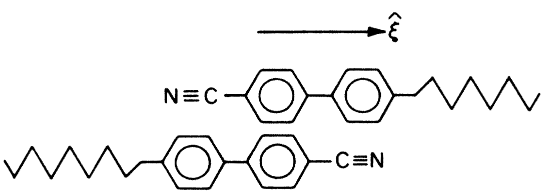

FIG. 1. Schematic depiction of an antiparallel 8CB molecular pair.

The local induced nonlinear polarization $\mathbf{P}^{\mathrm{NL}}$ at 2ω is then given by

$$\mathbf{P}^{\mathrm{NL}}(2\omega) = [\delta(z)\boldsymbol{\chi}_S^D - \nabla\cdot\boldsymbol{\chi}_B^Q]:\mathbf{E}(\omega)\mathbf{E}(\omega) \quad \text{for } z \geq 0, \tag{3}$$

where $z=0$ refers to the boundary surface. The output of SHG in the reflected direction can be obtained by solution of the wave equation with $\mathbf{P}^{\mathrm{NL}}$ as the source term. It has been shown that the result is equivalent to that generated by a surface layer with an effective surface nonlinear susceptibility $\boldsymbol{\chi}^{\mathrm{eff}}$, which is a linear combination of $\boldsymbol{\chi}_S^D$ and $\boldsymbol{\chi}_B^Q$.[14] Measurements of SHG in reflection allow us to determine $\boldsymbol{\chi}^{\mathrm{eff}}$. For a medium with an azimuthal symmetry along $\hat{\mathbf{z}}$, as in the cases we shall consider, the nonzero components of $\boldsymbol{\chi}^{\mathrm{eff}}$ are

$$\begin{aligned} \chi_{zzz}^{\mathrm{eff}} &= \chi_{S,zzz}^D/\eta_{S,zzz} - \chi_{B,zzzz}^Q/\eta_{B,zzz}, \\ \chi_{zii}^{\mathrm{eff}} &= \chi_{S,zii}^D/\eta_{S,zii} - \chi_{B,zzii}^Q/\eta_{B,zii}, \\ \chi_{iiz}^{\mathrm{eff}} &= \chi_{izi}^{\mathrm{eff}} = \chi_{S,iiz}^D/\eta_{S,iiz} - \chi_{B,ziiz}^Q/\eta_{B,iiz}, \end{aligned} \tag{4}$$

where $i=x,y$; $\boldsymbol{\eta}_S$ and $\boldsymbol{\eta}_B$ are the dielectric screening factors that effectively account for the radiation efficiencies of the surface dipole and bulk quadrupole, respectively. We have $\eta_{ijk} \equiv \eta_i(2\omega)\eta_j(\omega)\eta_k(\omega)$, with $n_l(\omega) = \varepsilon_z(\omega)\delta_{lz} + \delta_{lx} + \delta_{ly}$. In Eq. (4), while $\boldsymbol{\eta}_S$ and $\boldsymbol{\eta}_B$ may have a possible phase difference (usually small), $\boldsymbol{\chi}_S^D$ and $\boldsymbol{\chi}_B^Q$ are either in phase or 180° out of phase. In forming a pair in the bulk, the two molecules usually have their polar heads closer together than the tails, as illustrated by the example in Fig. 1. It is then easy to see that χ_S^D and χ_B^Q will have opposite signs if the polar-ordered molecules in the surface layer have their polar heads pointing away from the bulk, and vice versa.

Since the molecular orientation distribution can be affected by temperature, $\boldsymbol{\chi}_S^D$ and $\boldsymbol{\chi}_B^Q$ should, in general, be functions of temperature. The temperature dependence of $\boldsymbol{\chi}_S^D$ is unknown *a priori*, but that of $\boldsymbol{\chi}_B^Q$ can be determined from the bulk orientational order parameters. For example, from Eq. (2), we can show that

$$\chi_{B,zzyy}^Q \approx (\tfrac{1}{2}N_B)\xi_0\alpha_{\xi\xi\xi}^{(2)} \times \tfrac{1}{15}[1 + \tfrac{5}{7}\langle P_2(\cos\theta)\rangle - \tfrac{12}{7}\langle P_4(\cos\theta)\rangle], \tag{5}$$

where θ is the angle between $\hat{\boldsymbol{\xi}}$ and $\hat{\mathbf{z}}$, P_n denotes the nth-order Legendre polynomial, and $\langle P_2\rangle$ and $\langle P_4\rangle$ are usually defined as the order parameters for LC.[15] Both order parameters vanish in the isotropic phase, and normally, $\langle P_4\rangle < \langle P_2\rangle$.[16]

We used 8CB as the sample in our experiment. This material exhibits smectic-*A*, nematic, and isotropic phases with transition temperatures at $T_{AN} = 33.5\,^\circ\mathrm{C}$ and $T_{NI} = 40.5\,^\circ\mathrm{C}$. We have studied SHG from (1) an 8CB monolayer on water, (2) an 8CB monolayer on a glass substrate coated with surfactant *n*,*n*-dimethyl-*n*-octadecyl-3-aminopropyl-trimethoxysilyl chloride (DMOAP), (3) an 8CB-air interface (i.e., free surface), and (4) an 8CB-DMOAP-coated-glass interface. The glass substrate was a fused-silica optical flat with a $\sim\lambda/10$ flatness. The monolayers were prepared by spreading of a proper amount of a dilute 8CB-petroleum-ether solution on water or glass, followed by evaporation of the solvent. The uniformity of such a monolayer was confirmed by probing with SHG at different spots on the surface. For the interfaces, we simply prepared a sufficiently thick 8CB film on a horizontal glass plate; a large single domain of homeotropic alignment could be induced by the DMOAP coating on the glass.[17] If the laser beam at ω was obliquely incident on the film from the air side and SHG in reflection was measured, then only SHG from the free surface was studied because the film thickness ($\sim\frac{1}{4}$ mm) far exceeded the optical-absorption length ($\sim 0.1\ \mu$m) at 2ω so that the presence of the 8CB-glass interface could not be felt. If the laser beam came from the glass side, then SHG from the 8CB-glass interface could be studied. In all cases, the background SHG from the water and the DMOAP-coated glass substrate were both negligible.

The magnitude of $\boldsymbol{\chi}^{\mathrm{eff}}$ was deduced from the intensity of the SH signal; its phase was determined from an interference of the SH output with that generated from a crystalline quartz plate inserted in the reflected beam path. The excitation laser pulses at 532 nm were derived from a frequency-doubled Nd-doped yttrium aluminum garnet laser. Each pulse had a duration of 60 ps and an energy of 30 μJ, and was focused to an area of ~ 0.5 mm^2 on the sample surface.

Consider first the SHG measurements of 8CB monolayers with a surface density $N_S \sim 3\times10^{14}\ \mathrm{cm}^{-2}$. On the water surface, the molecules tend to have their hydrophilic polar groups (-CN) in water and the hydrophobic hydrocarbon tails up in air.[11] From the measured values of $\chi_{ijk}^{\mathrm{eff}}$, and with use of Eqs. (2) and (4) (with $\boldsymbol{\chi}_B^Q = 0$), we could deduce $\alpha_{\xi\xi\xi}^{(2)} = 2.5\times10^{-29}$ esu[18] and an average tilt angle of the molecules $\langle\theta\rangle = 71° \pm 2°$ from the surface normal, in agreement with Ref. 11. We found very similar results for an 8CB monolayer on a DMOAP-coated glass substrate. The $\chi_{ijk}^{\mathrm{eff}}$ of such a monolayer was exactly in phase with that of an 8CB monolayer on water, and the two also have roughly the same magnitude ($\chi_{zyy}^{\mathrm{eff}} \simeq 1.0\times10^{-15}$ esu). This indicates that the 8CB molecules should have their -CN terminal attached to the glass, as was proposed by Meiboom and Sammon.[19] The molecular-tilt angle was found to be $\langle\theta\rangle = 67° \pm 2°$. This may seem surprising since the DMOAP-coated surface was supposed to align molecules preferentially normal to the surface. However, it can be understood if we realize that the tilt would reduce the dipole-dipole interaction between the polar heads of 8CB molecules. The results for the 8CB monolayer on glass were independent of temperature over a wide range (20–60 °C).

Consider next SHG in reflection from the free surface of 8CB. The corresponding χ^{eff}_{ijk} deduced from the measurements appeared to be in phase with that of the 8CB monolayer on water, but its magnitude was significantly smaller. In addition, it exhibited a strong temperature dependence with a jump at the bulk transition point T_{NI}. As an example, the temperature dependence of χ^{eff}_{zyy} is shown in Fig. 2; other components behaved similarly. The behavior can be easily understood if the bulk quadrupole contribution happened to be the only source of the SHG in this case, i.e., $\chi^{\text{eff}}_{ijk} = -\chi^{Q}_{B,zijk}/\eta_{B,ijk}$. First, from our theoretical discussion earlier, the SH output from $\chi^{Q}_{B,zijk}$ here should indeed be in phase with that from $\chi^{D}_{S,ijk}$ of a monolayer on water. Second, the observed jump in $\boldsymbol{\chi}^{\text{eff}}$ at T_{NI} can be explained as resulting from the jumps in $\langle P_2\rangle$ and $\langle P_4\rangle$ in χ^{Q}_{B} of Eq. (5). In Fig. 2, a theoretical plot of Eq. (5) which uses the experimental values of $\langle P_2\rangle$ and $\langle P_4\rangle$ from Constant and Decoster[20] actually describes the data very well.[21] As a further check, the value of χ^{Q}_{B} deduced for the smectic phase was found to agree well with that deduced from SHG from freely suspended 8CB films.[22] The effective distance ξ_0 between the molecules forming the quadrupole pair determined from χ^{Q}_{B} and $\alpha^{(2)}_{\xi\xi\xi}$ by use of Eq. (2) was ~15 Å. This roughly corresponds to the dimension of the molecular core from which the optical nonlinearity originates.[11,23]

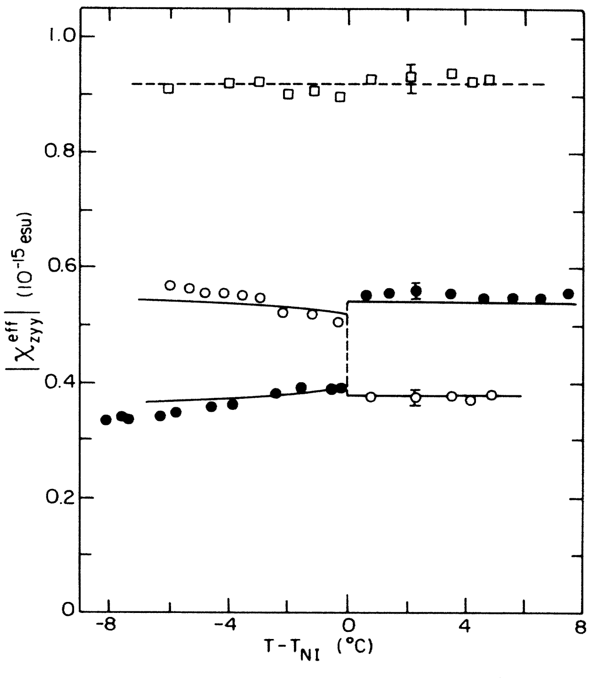

FIG. 2. Effective nonlinear susceptibility $|\chi^{\text{eff}}_{zyy}|$ as a function of temperature for (a) the 8CB free surface (open circles), (b) the 8CB-glass interface (closed circles), and (c) the algebraic sum of (a) and (b) (squares). The solid curves are theoretical curves described by Eqs. (4) and (5).

From SHG at the 8CB-glass interface, the χ^{eff}_{ijk} deduced showed a temperature dependence exactly opposite to that of the free surface (Fig. 2). With the bulk contribution being the same in both cases, the difference must be due to the presence of a polar-ordered molecular layer at the interface. As expected from the monolayer case, the molecules in the interface layer should have their -CN groups oriented preferentially towards the glass substrate. A pump beam incident from the glass side sees a $\boldsymbol{\chi}^{\text{eff}}$ given by Eq. (4) with $\chi^{D}_{S,ijk}/\eta_{S,ijk}$ and $\chi^{Q}_{B,zijk}/\eta_{B,ijk}$ 180° out of phase. The value of $|\chi^{D}_{S}/\eta_{S}|$ could then be obtained by the simple addition of $|\chi^{\text{eff}}|$ of the free surface $(=|-\chi^{Q}_{B}/\eta_{B}|)$ to that of the 8CB-glass interface $(=|x^{D}_{S}/\eta_{S}-\chi^{Q}_{B}/\eta_{B}|)$. The value of $|\chi^{D}_{S}/\eta_{S}|$ so obtained was independent of temperature and nearly equal to that of an 8CB monolayer on glass. This shows that only the first monolayer of 8 CB at the interface assumed a polar ordering, a result of the short-range nature of the polar interaction between the substrate and the molecules.

The temperature independence of $\boldsymbol{\chi}^{D}_{S}$ also indicates that the ordering of the 8CB monolayer at the interface is governed by the short-range substrate-molecule interaction. This type of polar ordering could be a rather common phenomenon occurring at the LC-glass interface for LC molecules with a polar end. How the surface polar ordering affects the LC alignment (homeotropic or planar) remains to be explored, though one experimental observation merits attention here: At several isotropic 5CB-glass interfaces, substrate-induced orientational ordering appeared to have a temperature-independent surface order parameter.[4,5] This "hard" boundary condition could be linked to the surface polar ordering observed here. Finally, we remark that the surface ordering discussed here is not the same as the surface flexoelectric or order-electric polarization discussed in the literature.[24] The latter should be strongly temperature dependent as a result of the coupling to the nematic order.

In summary, the measurements of the magnitude and phase of the SH radiations generated from the surfaces and monolayers of 8CB have led us to conclude rather unambiguously that a monolayer with polar ordering existed at the 8CB–DMOAP-coated-glass interface, but the free surface of 8CB remained nonpolar. A simple model was able to explain our experimental data quantitatively. Both the optical technique and the analysis can be easily generalized to the study of other LC surfaces and interfaces.

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