

## Probing the structure of freely suspended smectic-*A* films by optical second-harmonic generation

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Optical second-harmonic generation (SHG) was used to probe the structure of freely suspended films of 4'-*n*-octyl-4-cyanobiphenyl (8CB) in the smectic-*A* phase. The intensity of the SHG from ultrathin films with thickness varying from 2 to 10 molecular layers appeared quantized, but its behavior suggested no modifications of molecular arrangement in the layers in the presence of the two "free" surfaces. A macroscopic theory for the SHG from a film with stratified nonlinear susceptibility is presented and compared with the experimental observation.

### I. INTRODUCTION

The microscopic environment of a molecule at the free surface of a liquid (i.e., liquid-vapor interface) is different from that in the bulk liquid, leading to different molecular arrangements and local macroscopic properties.<sup>1</sup> Investigations of the liquid-crystal free surface are particularly interesting because, in contrast to normal liquids, liquid crystals can possess long-range molecular-orientational ordering and perhaps a certain degree of translational ordering, which could have profound influence on the structure of the free surface. In recent years, much theoretical<sup>1-6</sup> and experimental<sup>7-9</sup> interest has been focused on the nematic or smectic ordering at a free surface. Here, we direct our attention to a less studied subject—the question of possible ferroelectric ordering at the free surface of a nonferroelectric liquid-crystalline medium.<sup>5,10</sup> Such a surface ordering could occur, for example, if the liquid-crystal molecule has a highly polar end group which tends to point into the (polar) bulk medium.

Although most liquid crystals are composed of polar molecules, they do not exhibit ferroelectricity in the nematic or smectic-*A* phase. This indicates equal probability of having the polar molecules pointing in opposite directions. For this reason, the orientational order parameter has quadrupole rather than dipole symmetry. X-ray studies of some liquid-crystal compounds with cyano (—CN) end groups strongly suggested that in a smectic-layer neighboring molecules prefer an antiparallel orientation, as illustrated in Fig. 1.<sup>11</sup> (In such molecules, the permanent dipole lies along the long molecular axis.) It is interesting to know whether such an antiparallel arrangement would be perturbed in the presence of a free surface where the molecules experience an asymmetric interaction in the direction normal to the surface.

Freely suspended films of smectic liquid crystals with two free surfaces are relatively simple and particularly interesting to be investigated.<sup>12</sup> Stable films can be made with uniform thickness consisting of two or more molecular (smectic) layers. Thus, the separation between the two free surfaces of such films can be controlled by varying the film thickness layer by layer. In thicker films, the two

"surface" layers are isolated from each other. In very thin films (close to two layers), one might expect that the surface layers could interact with each other and cause enhancement (or reduction) of any surface effects, that is, certain physical properties might display anomalous behavior as the film thickness is reduced. (For example, an anomaly in the in-plane shear modulus was observed in a two-layer smectic-*B* film.<sup>13</sup>) Therefore, whether the ferroelectric ordering could occur in the surface layers and how it changes with the film thickness should be interesting to find out.

Optical second-harmonic generation (SHG) has recently been proven to be a surface-sensitive technique that can be used to probe submonolayers of molecules.<sup>14</sup> It is also ideal as a tool to probe the ferroelectric ordering of freely suspended smectic-*A* films. Within the electric-dipole approximation, SHG is allowed in a film with dipole symmetry but forbidden in one with quadrupole symmetry (e.g., molecules orienting in an antiparallel manner). In the latter case, SHG should be dominated by electric-quadrupole and magnetic-dipole contributions.

We have used the SHG technique to study freely suspended films of 4'-*n*-octyl-4-cyanobiphenyl (8CB) in

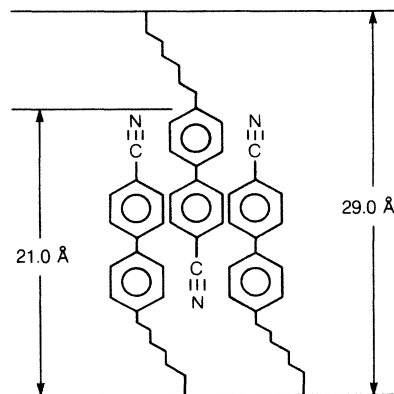


FIG. 1. Schematic depiction of local ordering in cyanobiphenyl liquid crystals, after Ref. 11. The dimensions shown correspond to that of 7CB.

the smectic-*A* phase. From the theoretical consideration we expect that the SH signal from the suspended films should be quantized, corresponding to the quantized film thickness according to the number of molecular layers in the film. It is noted that with or without ferroelectric surface layers, the signal should have different dependence on the film thickness. This property can be used to determine the existence of ferroelectric surface ordering. Our experimental results, however, show no evidence of the existence of ferroelectric ordering in the 8CB films. This is in contrast to a recent investigation of an 8CB-solid interface where ferroelectric surface ordering has been observed.<sup>15</sup>

We present in Sec. II the theory of SHG from a freely suspended smectic-*A* film. This is followed by a description of the experimental arrangement in Sec. III, and a presentation and discussion of the experimental results in Sec. IV.

## II. THEORY

### A. Nonlinear polarizations of smectic-*A* films

A coherent optical field  $\mathbf{E}$  of frequency  $\omega$  can induce in a medium a nonlinear polarization  $\mathbf{P}^{\text{NL}}$  of frequency  $2\omega$ . In the multipole expansion,  $\mathbf{P}^{\text{NL}}$  with the two leading terms is given by<sup>16</sup>

$$\begin{aligned} \mathbf{P}^{\text{NL}}(2\omega) &= \mathbf{P}^D(2\omega) + \mathbf{P}^Q(2\omega), \\ \mathbf{P}^D(2\omega) &= \vec{\chi}^D \cdot \mathbf{E}(\omega) \mathbf{E}(\omega), \\ \mathbf{P}^Q(2\omega) &= \vec{\chi}^Q \cdot \mathbf{E}(\omega) \nabla \mathbf{E}(\omega), \end{aligned} \quad (1)$$

where  $\mathbf{P}^D$  is the electric-dipole term coming from the local response and  $\mathbf{P}^Q$  includes both electric-quadrupole and magnetic-dipole contributions arising from the nonlocal response. Being a collection of oscillating dipoles, this nonlinear polarization  $\mathbf{P}^{\text{NL}}$  can radiate and generate coherent waves at the second-harmonic frequency  $2\omega$ . The nonlinear susceptibility  $\vec{\chi}^D$  is a third-rank tensor while  $\vec{\chi}^Q$  is a fourth-rank tensor. Like the linear susceptibility tensor, they should have the symmetry form invariant under symmetry operations on the medium. The  $\vec{\chi}^D$  and  $\vec{\chi}^Q$  for a smectic-*A* film are determined as follows.

The director  $\hat{\mathbf{n}}$  (average molecular orientation) in the smectic-*A* phase is perpendicular to the smectic-layer planes. In the freely suspended films, these planes are parallel to the film surfaces. A model of the smectic-*A* film is shown in Fig. 2. Each molecular layer in the film is isotropic in the  $\hat{\mathbf{x}}\text{-}\hat{\mathbf{y}}$  plane with the symmetry axis along  $\hat{\mathbf{z}}$ . As we shall see later, our experimental results indicate that all inner layers are equivalent. They are likely to have the antiparallel arrangement as in the bulk medium; in this case,  $\hat{\mathbf{n}}$  and  $-\hat{\mathbf{n}}$  are equivalent. In a surface layer, if the polar molecules prefer to orient along one direction than the other, the inversion symmetry is spoiled and a vectorial symmetry axis  $\hat{\mathbf{d}}$  can be defined. The other surface layer, by symmetry, should have a symmetry axis  $-\hat{\mathbf{d}}$ . In this model, the surface contains only one layer, since we do not expect this effect to be able to propagate more than one or two layers into the film.

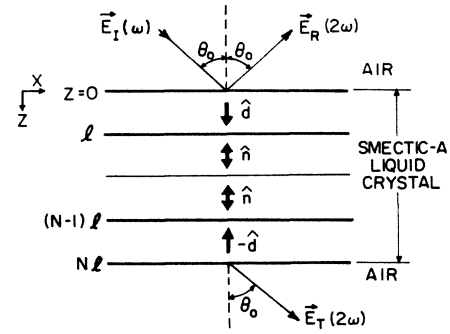


FIG. 2. Model of a smectic-*A* film with an incident wave at  $\omega$  and second-harmonic radiations in the reflected and transmitted directions.  $l$  is the smectic-layer spacing.

Nonzero tensor elements of  $\vec{\chi}^D$  and  $\vec{\chi}^Q$  for the two axial symmetries are listed in Table I. The nonzero  $\chi_{ijkl}^Q$ 's are the same for both symmetries, while in the inversion-symmetry case ( $\hat{\mathbf{n}} \equiv -\hat{\mathbf{n}}$ ),  $\chi_{ijk}^D = 0$ .

For simplicity, the polarization of the incident fundamental wave is chosen to be along the  $\hat{\mathbf{y}}$  direction (*s* wave). Since this wave is continuous across the film boundaries, the only spatial variation of the optical field comes from the variation in the phase, hence  $\nabla \mathbf{E} \rightarrow i\mathbf{k}\mathbf{E}$ , where  $\mathbf{k}$  is the wave vector inside the medium. The wave propagating in the film suffers multiple reflections from the boundary surfaces; hence the total fundamental waves in the medium consist of a forward ( $\mathbf{E}_f$ ) and a backward ( $\mathbf{E}_b$ ) traveling wave

$$\mathbf{E}_{f,b} = \hat{\mathbf{y}} E_{f,b} \exp[i(k_x x \pm k_z z - \omega t)], \quad (2)$$

with

$$E_f \propto E_I [1 + F \sin^2(N\phi/2)]^{-1/2} \quad (3)$$

and

$$E_b = -r e^{iN\phi} E_f,$$

where  $\phi = 2k_z l$ ,  $r$  is the reflection coefficient of a single reflection,  $F = 4R/(1-R)^2$ , with  $R = r^2$ , and  $E_I$  is the amplitude of the incident wave. The mixing of  $\mathbf{E}_f$  with  $\mathbf{E}_f$ ,  $\mathbf{E}_f$  with  $\mathbf{E}_b$ , and  $\mathbf{E}_b$  with  $\mathbf{E}_b$  can all contribute to SHG. In Fig. 2, only the two surface layers of the smectic-*A* film are assumed to have nonzero  $\mathbf{P}^D$  which, when summed over all the wave-mixing terms, is given by (see Table I)

$$\mathbf{P}^D = \begin{cases} +\hat{\mathbf{z}} \sum_{\alpha,\beta} P_z^D \exp[i(K_x x + K_{1z} z - 2\omega t)], & 0 < z < l \\ -\hat{\mathbf{z}} \sum_{\alpha,\beta} P_z^D \exp[i(K_x x + K_{1z} z - 2\omega t)], & [(N-1)l < z < Nl] \end{cases} \quad (4)$$

where  $P_z^D = \chi_{zyy}^D E_\alpha E_\beta$  ( $\alpha, \beta = f, b$ ),

$$K_{1z} = \begin{cases} +2k_z, & \alpha = \beta = f \\ 0, & \alpha \neq \beta \\ -2k_z, & \alpha = \beta = b \end{cases}$$

TABLE I. Distinct nonzero elements of  $\vec{\chi}^D(2\omega=\omega+\omega)$  and  $\vec{\chi}^Q(2\omega=\omega+\omega)$  for two axial symmetries.

| Tensor type     | Symmetry axis $\parallel \hat{z}$ | $\hat{d} \neq -\hat{d}$   | $\hat{n} \equiv -\hat{n}$                   |
|-----------------|-----------------------------------|---|---|
|                 | $\chi_{ijk}^D$                    |   | $zzz, zxx = zyy$<br>$xxz = xzx = yyz = yzy$ |
| $\chi_{ijkl}^Q$ |                                   | $zzzz, xxxx = yyyy$<br>$zzxx = zzyy, xzzz = yzzz, xxxy = yyxx$<br>$zxzx = zyzy, xzzz = yzyz, xyxy = yxyx$<br>$zxzx = zyzy, xzzz = yzyz, xyxy = yxyx$<br>$xxxx = xxyy + xyxy + xyxy$ |   |

and  $K_x = 2k_x$ . The nonlocal response  $\mathbf{P}^Q$  can exist in the entire film, which is given by

$$\mathbf{P}^Q = \sum_{\alpha, \beta} (\hat{\mathbf{x}} P_x^Q + \hat{\mathbf{z}} P_z^Q) \exp[i(K_x x + K_{1z} z - 2\omega t)], \quad (5)$$

where

$$P_x^Q = (i/2) K_x \chi_{xyxy}^Q E_\alpha E_\beta,$$

$$P_z^Q = (i/2) K_{1z} \chi_{zyzy}^Q E_\alpha E_\beta.$$

### B. Second-harmonic generation from a smectic-*A* film

The nonlinear polarizations in Eqs. (4) and (5) generate a reflected SH wave  $\mathbf{E}_R$  and a transmitted SH wave  $\mathbf{E}_T$ , both being linearly polarized in the  $\hat{\mathbf{x}}-\hat{\mathbf{z}}$  plane (*p* waves). Expressions of  $E_R$  and  $E_T$  can be obtained by solving the nonlinear wave equations<sup>17</sup>

$$\left[ \nabla \times (\nabla \times) - \left( \frac{2\omega}{c} \right)^2 \hat{\boldsymbol{\epsilon}} \right] \mathbf{E}(2\omega) = 4\pi \left( \frac{2\omega}{c} \right)^2 \mathbf{P}^{\text{NL}}(2\omega), \quad (6)$$

$$\nabla \cdot [\hat{\boldsymbol{\epsilon}} \mathbf{E}(2\omega)] = -4\pi \nabla \cdot \mathbf{P}^{\text{NL}}(2\omega),$$

subject to the boundary conditions that  $E_x$  and  $H_y$  be continuous. The detailed derivation is given in the appendix, where we assume the linear optical properties are uniform over the entire film with refractive indices  $n_1 \equiv n_0(\omega)$  and  $n_2 \equiv n_e(2\omega)$  for the fundamental (*s* or ordinary) and second-harmonic (*p* or extraordinary) waves, respectively. The results for the reflected SH wave  $\mathbf{E}_R(2\omega)$ , expressed as functions of the incident angle  $\theta_0$  of the pump beam [which is also the reflection angle of  $\mathbf{E}_R(2\omega)$ ] are summarized in the following.

The electric-dipole contribution to the reflected wave  $\mathbf{E}_R(2\omega)$  from the two surface layers separated by  $(N-2)$  inner layers is

$$E_R^D = \sum_{\alpha, \beta} P_z^D D [A_+ B_- e^{-iN\phi_2} (1 - e^{i\phi_+}) (1 - e^{i(N-1)\phi_+}) + A_- B_+ e^{iN\phi_2} (1 - e^{i\phi_-}) (1 - e^{i(N-1)\phi_-})], \quad (7)$$

with

$$D = \frac{4\pi K_0^2}{K_2^2 - K_1^2} \left[ \frac{K_x}{K_2} \right] (A_+^2 e^{-iN\phi_2} - A_-^2 e^{iN\phi_2})^{-1},$$

$$A_\pm = (K_{0z} \pm K_{2z}/n_2^2)/K_0,$$

$$B_\pm = (K_{2z} \pm K_{1z})/K_2,$$

$$\phi_\pm = \phi_1 \pm \phi_2; \quad \phi_1 = K_{1z}l, \quad \phi_2 = K_{2z}l,$$

where  $K_0 = 2\omega/c$ ,  $K_x = K_0 \sin\theta_0$ ,  $K_{0z} = K_0 \cos\theta_0$ ,  $K_2 = n_2 K_0$ ,  $K_{2z} = (K_2^2 - K_x^2)^{1/2}$ , and  $K_1 = (K_x^2 + K_{1z}^2)^{1/2}$ .  $K_{1z}$  is given in Eq. (4), where  $k_z$  can be expressed in terms of the incident angle  $\theta_0$  as  $k_z = (\omega/c)(n_1^2 - \sin^2\theta_0)^{1/2}$ .

The quadrupole-type contribution from all the  $N$  molecular layers in the film is

$$E_R^Q = \sum_{\alpha, \beta} D [ (P_z^Q + P_x^Q K_{2z}/K_x) A_+ B_- e^{-iN\phi_2} (1 - e^{iN\phi_+}) + (P_z^Q - P_x^Q K_{2z}/K_x) A_- B_+ e^{iN\phi_2} (1 - e^{iN\phi_-}) ]. \quad (8)$$

The total reflected second-harmonic intensity is the coherent sum of the two contributions

$$I_R(2\omega) \propto |E_R^D + E_R^Q|^2. \quad (9)$$

Usually,  $\phi_1, \phi_2, \phi_\pm \ll 1$  since the layer spacing  $l$  is small compared to the optical wavelength. Therefore, for very thin films (small  $N$ ),  $E_R^D$  and  $E_R^Q$  can be approximated by

$$E_R^D \approx -(N-1) \chi^D \sum_{\alpha, \beta} (A_+ B_- \phi_+^2 + A_- B_+ \phi_-^2) D E_\alpha E_\beta, \\ E_R^Q \approx (N/2) \sum_{\alpha, \beta} [ (\chi_1^Q/l) \phi_1 (A_+ B_- \phi_+ + A_- B_+ \phi_-) + (\chi_2^Q/l) \phi_2 (A_+ B_- \phi_+ - A_- B_+ \phi_-) ] \times D E_\alpha E_\beta, \quad (10)$$

where  $\chi^D \equiv \chi_{zyy}^D$ ,  $\chi_1^Q \equiv \chi_{zyzy}^Q$ , and  $\chi_2^Q \equiv \chi_{xyxy}^Q$ . Notice that  $E_R^D \propto (N-1)\chi^D$ , while  $E_R^Q \propto N\chi^Q/l$ . Therefore, by extrapolation of the experimental values of  $I_R(2\omega)$  to  $N=0$ , the relative value of  $\chi^D$  could, in principle, be determined.

### C. Macroscopic versus microscopic nonlinear susceptibilities

The macroscopic susceptibility tensors  $\vec{\chi}^D$  and  $\vec{\chi}^Q$  can be related to the corresponding molecular polarizability tensors  $\vec{\beta}^D$  and  $\vec{\beta}^Q$  through a statistical averaging with the proper local-field corrections,<sup>17</sup>

$$\begin{aligned}\vec{\chi}^D &= \mathcal{N} \langle \vec{\beta}^D; \vec{L}(2\omega) \vec{L}(\omega) \vec{L}(\omega) \rangle, \\ \vec{\chi}^Q &= \mathcal{N} \langle \vec{\beta}^Q; \vec{L}(2\omega) \vec{L}(\omega) \vec{L}(\omega) \rangle,\end{aligned}\quad (11)$$

where  $\vec{L}$ 's are local-field factors, which arise from molecular interaction and reflect the microscopic environment of a molecule, and  $\mathcal{N}$  is the number of molecules per unit volume. In the bulk of a liquid-crystalline medium, even if  $\beta^D \neq 0$ , the equal probability of nearby molecules oriented in opposite directions will make  $\chi^D = 0$ . At the surface, some degree of ferroelectric ordering of the molecules will lead to a nonvanishing  $\chi^D$ . Even if the molecules would orient themselves equally in opposite directions, the asymmetric environment seen by them could make  $\vec{L}$  asymmetric and hence  $\chi^D \neq 0$ .

Roughly speaking,  $|\beta^Q| \sim l |\beta^D|$ , where  $l$  is the molecular dimension. If all the molecules are pointing roughly in the same direction, we have  $|\chi^Q| \sim l |\chi^D|$ . If the molecules are oriented with more or less equal probability in opposite directions, we have  $|\chi^Q| \gg l |\chi^D|$ . Irrespective of the molecular layer being at the surface or in the bulk, the ratio  $|\chi^D/\chi^Q|$  should be a good measure of any significant ferroelectric ordering of molecules in the layer.

## III. EXPERIMENTAL ARRANGEMENT

### A. Freely suspended smectic films

The liquid crystal 8CB used in this experiment is commercially available from British Drug Houses, Inc. Its smectic-*A* phase occurs between 21.1 and 33.5°C, and the smectic-layer spacing is 31.6 Å.<sup>11</sup> Freely suspended films were prepared with a usual technique<sup>12</sup> as shown in the inset of Fig. 3. We wet the edges of a 6 mm × 6 mm hole in

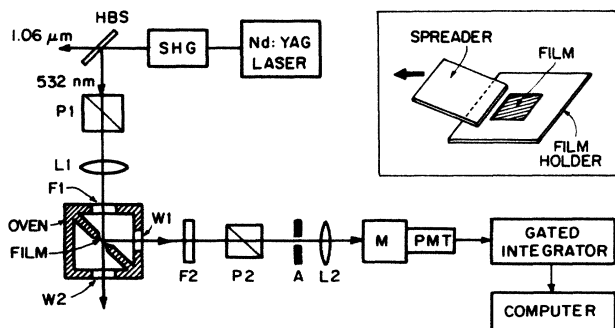


FIG. 3. Experimental arrangement. SHG—second-harmonic generator; HBS—harmonic beam separator;  $P_1, P_2$ —polarizers;  $L_1, L_2$ —lenses;  $F_1, F_2$ —color filters;  $W_1, W_2$ —windows;  $A$ —aperture;  $M$ —monochromator; PMT—photomultiplier tube. Inset illustrates the film preparation.

a 0.15 mm thick glass slide (film holder) with smectic-*A* 8CB. A second glass slide (spreader) was then drawn across the hole to form a liquid-crystal film over the hole. The angle between the spreader and film holder was about 20°. By varying the amount of material and the rate of drawing, we could prepare stable films with thickness of two to hundreds of smectic layers. The number of layers,  $N$ , contained in the film was determined by measuring the optical reflectivity of a weak He-Ne laser beam. For the thin films ( $2 \leq N \leq 10$ ) studied in this experiment, the optical reflectivity was closely proportional to  $N^2$ .<sup>18</sup> The sample film was situated in an oven with temperature stabilized at  $31.1 \pm 0.1^\circ\text{C}$ .

### B. Optical second-harmonic generation technique

The experimental arrangement is shown in Fig. 3. The excitation pulses were derived from an actively mode-locked and  $Q$ -switched Nd:YAG laser. Laser pulses at 1.06  $\mu\text{m}$  were then frequency doubled in a phase-matched KTP crystal to provide excitation pulses at 532 nm. The  $Q$ -switch was operated at a repetition rate of 0.5 KHz with each  $Q$ -switched pulse train consisting (within its 120 ns FWHM duration) of 12 pulses. An individual pulse had a  $\sim 60$  ps duration and an average energy of 30  $\mu\text{J}$ , which was focused to a  $\sim 0.1$  mm<sup>2</sup> cross-sectional area with 46° incident angle on the liquid-crystal film. The relatively low pulse energy was preferred in order to reduce the heating of the sample film by the excitation pulses. In Fig. 3, the color filter  $F_1$  was used to reject residual SH photons at 266 nm generated before the sample film, while the color filter  $F_2$  allowed the SH photons generated from the film to pass but blocked the reflected fundamental wave.  $F_1$  also served as an incident window of the sample oven. The two exit windows,  $W_1$  and  $W_2$ , are made of fused silica which is transparent in uv. In principle, SHG in either reflected or transmitted direction can be detected and similar information about the sample film can be deduced. In practice, since the SH and fundamental waves are collinear, and the reflected fundamental wave is much weaker than the transmitted one, the discrimination against the fundamental photons is easier to accomplish by detecting SH photons in the reflected direction. In the experiment,  $s$ -polarized excitation pulses could generate from a two-layer smectic film an average of 0.1 SH photons/pulse ( $p$  polarized), which could in turn generate  $\sim 0.01$  photoelectrons/pulse at the cathode of the photomultiplier tube (PMT), owing to the  $\sim 10\%$  quantum efficiency of the overall detection system. The output of the PMT was sent to a gated integrator with its gate open during each  $Q$ -switched pulse train, and the integrated signal for each pulse train was then forwarded to a microcomputer for further analysis. For the low signal level encountered in the experiment, it was convenient to analyze the result with a counting rather than an analog technique. By keeping the count rate  $\Lambda$  below 1 count per pulse train, the average number of photoelectrons  $\lambda$  emitted per pulse train can be related to  $\Lambda$  through Poisson statistics by  $\lambda = -\ln(1 - \Lambda)$ .<sup>19</sup> Large uncertainty in  $\lambda$  is expected when  $\Lambda$  is close to one.

The excitation frequency at 532 nm was chosen since

the SH frequency falls within the first electronic excitation band of 8CB and hence the SHG was resonantly enhanced (by a factor of  $\sim 10^2 - 10^3$  compared to excitation at  $1.06 \mu\text{m}$ ). The electronic transition from the ground state to the first excited state is polarized parallel to the molecular long axis.<sup>20</sup> Consequently, the 8CB molecule may be considered as quasi-one dimensional in the resonant second-order nonlinear processes.

#### IV. RESULTS AND DISCUSSION

About 50 films of thickness ranging from 2 to 10 smectic layers were studied. The measured SH signals from these films were quite reproducible. The polarizations of the SH waves were consistent with those predicted theoretically by our model for the smectic-*A* films (Fig. 2). Namely, a SH wave generated by a pure *s*- or *p*-polarized excitation wave is always *p* polarized. Figure 4 shows the square root of the measured reflected SH intensity, which is proportional to the field amplitude  $|E_R(2\omega)|$ , as a function of number of layers,  $N$ , in the film. The experimental uncertainty in  $|E_R(2\omega)|$  for a fixed  $N$  was  $\leq \pm 3\%$ . For  $N \leq 5$ ,  $|E_R(2\omega)|$  follows a linear dependence on  $N$  closely, and shows saturation for  $N > 5$ . The fit of a straight line (dashed line in Fig. 4) to the data for  $N \leq 5$  appears to yield a nonzero intercept at  $N = 0$ , with

$$|E_R(2\omega)|_{N=0} / |E_R(2\omega)|_{N=2} \approx 11\% .$$

The discrete signal levels and the linear dependence on  $N$  for small  $N$  suggest that each of the inner layers of the films contribute equally to the total SHG, and hence, they must have nearly the same structure. The relatively small offset from zero at  $N = 0$  in the signal, as shown in Fig. 4, indicates that the quadrupole contribution is dominant in the SHG from the smectic-*A* films; only a small residual  $\chi^D$  arising from the electric-dipole contribution is present in the surface layers. An estimate of the ratio  $|I\chi^D/\chi^Q|$  was obtained by fitting the calculated values of  $|E_R(2\omega)|$  [using Eqs. (7) and (8)] to the experimental data. In the calculation, we have used  $n(\omega) = 1.52$  (Ref.

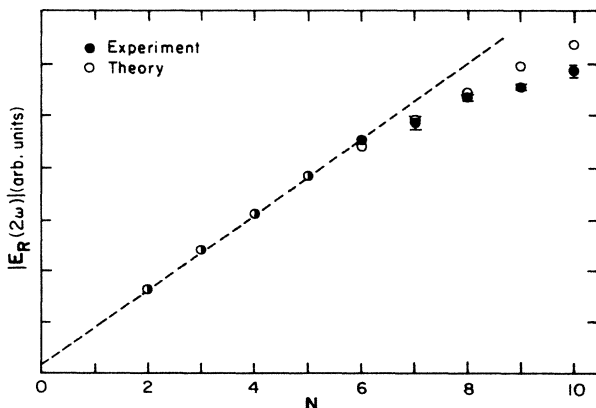


FIG. 4. Amplitude of reflected second-harmonic wave ( $|E_R(2\omega)|$ ) as a function of number of layers ( $N$ ) in the films. The incident excitation wave at  $\omega$  was *s* polarized.

21) and  $n(2\omega) \approx 1.1 + i0.18$  for the refractive indices of 8CB, where  $n(2\omega)$  was estimated from the absorption spectrum of an 8CB solution.<sup>20</sup> For simplicity, we have taken the ratio  $(\chi^D/\chi^Q)$  to be real, and let  $\chi_{xyxy}^Q = 0$  (Ref. 22) and  $\chi_{zyz}^Q = \chi^Q$ . We found  $|I\chi^D/\chi^Q| \approx 7\%$ . As shown in Fig. 4, the calculated values are in good agreement with the measured values, with an 8% discrepancy in the worst case ( $N = 10$ ). The discrepancy at large  $N$  presumably arises from the inaccuracy in the value of  $n_2(2\omega)$  chosen and the approximations we made in the analysis. Following the argument given in Sec. II C, this small value of  $|I\chi^D/\chi^Q|$  does not provide sufficient evidence for the existence of ferroelectric or ferroelectric-type molecular rearrangement in the surface layers. The small  $\chi^D$  of the surface layers could simply result from the asymmetric local field experienced by the molecules in these layers. The saturation behavior of the SH signal at large  $N$  came from two sources: (1) The amplitude of the fundamental wave within the film is modified by the multiple reflections from the boundary surfaces; it depends on the film thickness through the factor  $[1 + F \sin^2(N\phi/2)]^{-1/2}$  in Eq. (3). The generated SH wave also experiences a similar effect as represented by the factor  $D$  in Eq. (7). (2) 8CB is very absorptive in the neighborhood of the second-harmonic frequency. In thicker films, the effective interaction length was limited by the attenuation length of light.

For comparison, we have also studied SHG from the free surface and the 8CB/glass interface of an 8CB film on glass.<sup>15</sup> Our observations indicate that the antiparallel ordering persists at the free surface of 8CB, but a ferroelectric ordering shows up in the first monolayer of molecules at the 8CB/glass interface.

The fact that the ferroelectric ordering does not exist at the free surface of a smectic-*A* film may be understood through the following argument: In order to make two polar molecules orient parallel to each other, the molecules would have to displace along their axes relative to each other so that the dipole-dipole interaction energy is minimized. In a smectic surface layer, such motion is seriously restricted by the layer structure, hence the parallel arrangement is not preferred even in the presence of a surface potential. Although this restriction may be relaxed at a nematic or isotropic free surface in general, it is not the case for 8CB due to the smectic-*A* ordering induced at the free surface of such a material.<sup>7</sup> A polar potential imposed by a solid substrate, for example, is, however, possible to align the 8CB molecules in parallel, as in the case of the 8CB/glass interface studied by us.

#### V. CONCLUSION

Using an optical SHG technique, we have studied the structure of thin smectic liquid-crystal films freely suspended in air. The investigation was focused on probing the possible existence of surface-induced ferroelectric ordering, which could arise if the local molecular arrangement is perturbed by the presence of a free surface. For molecules with the normal nematic-type orientational ordering, only the electric-quadrupole or magnetic-dipole processes can contribute to the generation of SH radi-

tions; for molecules with any degree of ferroelectric ordering, the electric-dipole process is the additional contribution to SHG. Therefore, the extent of ferroelectric ordering in a medium can be determined by comparing the relative contributions from the two types of nonlinear processes to the SHG. For the freely suspended smectic-*A* films, this comparison was accomplished by studying the dependence of the SH intensity on the film thickness. Only a very small contribution from the electric-dipole process was observed, which is not necessarily due to weak ferroelectric ordering, but could result from modification of the molecular local field as a consequence of the broken symmetry at the surfaces. We conclude that, in the smectic-*A* films of 8CB, molecules in all layers have nearly the antiparallel orientational order similar to that in the bulk.

Optical SHG is a unique probe for studying the induced ferroelectric ordering in free surfaces or thin films of liquid crystals. Many fundamental questions, such as the local structure at the free surface of various liquid-crystal phases and the importance of dipole-dipole interaction in determining the surface ordering, can be answered through further experimental investigations using this relatively simple optical technique.

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#### APPENDIX: SECOND-HARMONIC REFLECTION FROM A SMECTIC-*A* FILM

Expressions for the SH waves  $E_R$  and  $E_T$  are obtained by solving the nonlinear wave equation, Eq. (6), with the source term  $P^{NL}$  given by Eqs. (4) and (5). The particular solution to Eq. (6) associated with  $P^{NL}$  is<sup>23</sup>

$$\begin{aligned} E_p &= \frac{4\pi K_0^2}{(K_1^2 - K_2^2)K_2^2} \left\{ \hat{x}(K_{2z}^2 P_x^{NL} - K_x K_{1z} P_z^{NL}) \right. \\ &\quad \left. + \hat{z}[-K_x K_{1z} P_x^{NL} + (K_2^2 - K_{1z}^2) P_z^{NL}] \right\} \\ &\quad \times \exp[i(K_x x + K_{1z} z - 2\omega t)], \\ H_p &= \hat{y} \frac{4\pi K_0}{K_1^2 - K_2^2} \\ &\quad \times (K_{1z} P_x^{NL} - K_x P_z^{NL}) \exp[i(K_x x + K_{1z} z - 2\omega t)], \end{aligned} \quad (12)$$

where the wave vectors are defined in Eqs. (4) and (7). The corresponding homogeneous solution (depicted in Fig. 5) is

$$\begin{aligned} E_{R,T} &= \hat{e}_{R,T} E_{R,T} \exp[i(K_x x \mp K_{0z} z - 2\omega t)], \\ H_{R,T} &= \hat{y} E_{R,T} \exp[i(K_x x \mp K_{0z} z - 2\omega t)], \\ E_{M,M'} &= \hat{e}_{M,M'} E_{M,M'}(z) \exp[i(K_x x \pm K_{2z} z - 2\omega t)], \\ H_{M,M'} &= \hat{y} n_2 E_{M,M'}(z) \exp[i(K_x x \pm K_{2z} z - 2\omega t)], \end{aligned} \quad (13)$$

where  $\hat{e} \perp \mathbf{K}$ . The wave amplitudes  $E_M(z)$  and  $E_{M'}(z)$  in the film are constant within the region  $0 < z < l$ ,  $l < z < (N-1)l$ , or  $(N-1)l < z < Nl$ , but discontinuous at  $z = l$  and  $z = (N-1)l$  due to the discontinuity in  $P^{NL}$ .

To solve Eq. (6), the source term  $P^{NL}$  can be divided into parts and the solution for each part be derived separately. As an illustration, we consider the solution associated with the dipole source polarization  $P_z^D(2\omega)$  [Eq. (4)] in the top surface layer ( $0 < z < l$ ). From Eq. (12), the particular solution is given by

$$\begin{aligned} E_p &= P_z^D d \left\{ \hat{x} \frac{K_{1z}}{K_2} - \hat{z} \frac{K_2}{K_x} \left[ 1 - \left( \frac{K_{1z}}{K_2} \right)^2 \right] \right\} \\ &\quad \times \exp[i(K_x x + K_{1z} z - 2\omega t)], \\ H_p &= \hat{y} n_2 P_z^D d \exp[i(K_x x + K_{1z} z - 2\omega t)], \end{aligned} \quad (14)$$

where

$$d = 4\pi K_0^2 (K_x / K_2) (K_2 - K_1)^{-1}.$$

The corresponding homogeneous wave amplitudes may be written as

$$E_{M,M'}(z) = \begin{cases} E_{a,a'}, & 0 < z < l \\ E_{b,b'} e^{\mp i K_{2z} l}, & l < z < Nl. \end{cases} \quad (15)$$

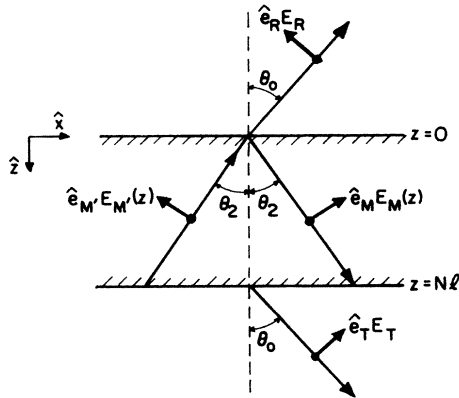
The boundary condition that the tangential components of  $\mathbf{E}$  and  $\mathbf{H}$  be continuous requires that

$$\begin{aligned} E_x(z=0) &= -E_R \cos\theta_0 = (E_a - E_{a'}) \cos\theta_2 \\ &\quad + P_z^D d (K_{1z}/K_2), \\ H_y(z=0) &= E_R = n_2 (E_a + E_{a'}) + n_2 P_z^D d, \\ E_x(z=l) &= (E_b - E_{b'}) \cos\theta_2 \\ &= (E_a e^{i\phi_2} - E_{a'} e^{-i\phi_2}) \cos\theta_2 \\ &\quad + P_z^D d (K_{1z}/K_2) e^{i\phi_1}, \\ H_y(z=l) &= n_2 (E_b + E_{b'}) \\ &= n_2 (E_a e^{i\phi_2} + E_{a'} e^{-i\phi_2}) + n_2 P_z^D d e^{i\phi_1}, \\ E_x(z=Nl) &= E_T \cos\theta_0 \\ &= (E_b e^{i(N-1)\phi_2} - E_{b'} e^{-i(N-1)\phi_2}) \cos\theta_2, \\ H_y(z=Nl) &= E_T = n_2 (E_b e^{i(N-1)\phi_2} + E_{b'} e^{-i(N-1)\phi_2}), \end{aligned} \quad (16)$$

where  $\cos\theta_2 = K_{2z}/K_2$ ,  $\phi_1 = K_{1z}l$ , and  $\phi_2 = K_{2z}l$ . Equation (16) is a set of six simultaneous linear equations that can be solved to give all the homogeneous wave amplitudes and phases. The solution for the reflected SH wave is

$$\begin{aligned} E_R^D(\text{top}) &= P_z^D D [ A_+ B_- e^{-iN\phi_2} (1 - e^{i\phi_+}) \\ &\quad + A_- B_+ e^{iN\phi_2} (1 - e^{i\phi_-}) ], \end{aligned} \quad (17)$$

where  $D$ ,  $A_\pm$ ,  $B_\pm$ , and  $\phi_\pm$  are given in Eq. (7). Following

FIG. 5. Homogeneous waves at  $2\omega$ .

similar procedures, the reflected SH wave generated by the bottom surface layer  $[(N-1)\ell < z < N\ell]$  can be obtained,

$$E_R^D(\text{bottom}) = -P_z^D D e^{i(N-1)\phi_1} [A_+ B_- e^{-i\phi_2} (1 - e^{i\phi_+}) + A_- B_+ e^{i\phi_2} \times (1 - e^{i\phi_-})]. \quad (18)$$

The net electric-dipole contribution to the reflected SH wave is

$$E_R^D = E_R^D(\text{top}) + E_R^D(\text{bottom}), \quad (19)$$

which yields Eq. (7).

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<sup>19</sup>The probability of the emission of  $n$  photoelectrons during a laser pulse train is  $P(n) = (\lambda^n/n!)e^{-\lambda}$ , hence the probability of detecting at least one photoelectron is  $\Lambda = 1 - P(0) = 1 - e^{-\lambda}$ . Equivalently,  $\lambda = -\ln(1 - \Lambda)$ .

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