Investigation of Anisotropic Molecular Orientational Distributions of Liquid-Crystal Monolayers by Optical Second-Harmonic Generation

W. Chen, M. B. Feller, and Y. R. Shen Department of Physics, University of California, Berkeley, California 94720 (Received 30 August 1989)

We show that optical second-harmonic generation can be used to determine the anisotropic orientational distribution of a surface monolayer of molecules. The technique applied to liquid-crystal monolayers on a rubbed and unrubbed substrates indicates that two different surface-originated mechanisms are effective in aligning a liquid-crystal film: One is based on molecular interaction and the other on elastic interaction.

PACS numbers: 61.30.-v, 42.65.Ky, 68.35.Bs, 68.90.+g

The problems of interfacial properties of liquid crystals (LC) are not only of fundamental interest but also of practical importance to the design and construction of LC devices. It is well known that the bulk alignment of an LC film can be controlled by surface treatment.¹ Rubbing of polymer- or surfactant-coated substrates is a routinely used technique to obtain bulk homogeneous alignment (average molecular orientation parallel to the surface in the rubbing direction) of an LC cell. However, the mechanism involved is hardly understood. Both short-range interaction at the molecular level² and longrange elastic interaction of macroscopic nature³ have been proposed. Experimentally, ellipsometry and other linear optical methods have been used to study surfaceinduced ordering,^{4,5} but none of these techniques has enough surface specificity to directly distinguish shortand long-range surface alignment. Recently, optical second-harmonic generation (SHG) has proven to be an effective tool for probing orientation and arrangement of an adsorbed molecular monolayer.⁶ The technique has been used to study LC monolayers at various interfaces with azimuthal symmetry.⁷⁻⁹ In the present paper, we show that it can also be used to probe the anisotropic molecular alignment and deduce an approximate orientational distribution of molecules in a monolayer. Such SHG measurements applied to LC monolayers on substrates with different surface treatments then allows us to ascertain whether the surface alignment is short range or long range. We find from our experiment that a rubbed polyimide-coated surface can effectively orient an adsorbed LC monolayer towards the rubbing direction whereas a rubbed surfactant-coated substrate cannot, although both are capable of inducing a uniform homogeneous bulk alignment. This leads to the conclusion that the surface-induced homogeneous bulk alignment is via a short-range interaction in the polyimide case and via a long-range interaction in the rubbed surfactant case. We also found that the presence of an LC bulk on top of the LC monolayer could slightly alter the molecular orientation of the monolayer.

The basic theory of SHG for surface studies has already been published.⁶ For a monolayer of molecules with a dominant hyperpolarizability element $\alpha_{\xi\xi\xi}^{(2)}$ along the long molecular axis $\hat{\xi}$, the nonlinear susceptibility responsible for the SHG is given by

$$\chi_{ijk}^{(2)} = N_s \langle (\hat{\mathbf{i}} \cdot \hat{\boldsymbol{\xi}}) (\hat{\mathbf{j}} \cdot \hat{\boldsymbol{\xi}}) (\hat{\mathbf{k}} \cdot \hat{\boldsymbol{\xi}}) \rangle \alpha_{\boldsymbol{\xi}\boldsymbol{\xi}\boldsymbol{\xi}}^{(2)}, \qquad (1)$$

where N_s is the surface density of molecules, i,j,k refer to the sample coordinates (x,y,z), and the brackets denote an average over the molecular orientations. With \hat{z} defined as the surface normal, we find, for a monolayer of C_{1v} symmetry with the symmetric axis along \hat{x} , the following nonvanishing elements of $\chi^{(2)}$:

$$\chi_{zzz}^{(2)} = N_s \langle \cos^3 \theta \rangle \alpha_{\xi\xi\xi}^{(2)},$$

$$\chi_{xxx}^{(2)} = N_s \langle \sin^3 \theta \rangle \langle \cos^3 \phi \rangle \alpha_{\xi\xi\xi}^{(2)},$$

$$\chi_{zyy}^{(2)} = \chi_{yzy}^{(2)} = \chi_{yyz}^{(2)}$$

$$= N_s \langle \cos \theta - \cos^3 \theta \rangle \langle 1 - \cos^2 \phi \rangle \alpha_{\xi\xi\xi}^{(2)},$$

$$\chi_{zxx}^{(2)} = \chi_{xzx}^{(2)} = \chi_{xxz}^{(2)}$$

$$= N_s \langle \cos \theta - \cos^3 \theta \rangle \langle \cos^2 \phi \rangle \alpha_{\xi\xi\xi}^{(2)},$$

$$\chi_{zxz}^{(2)} = \chi_{zzx}^{(2)} = \chi_{xzz}^{(2)}$$

$$= N_s \langle \sin \theta - \sin^3 \theta \rangle \langle \cos \phi \rangle \alpha_{\xi\xi\xi}^{(2)},$$

$$\chi_{xyy}^{(2)} = \chi_{yxy}^{(2)} = \chi_{yyx}^{(2)}$$

$$= N_s \langle \sin^3 \theta \rangle \langle \cos \phi - \cos^3 \phi \rangle \alpha_{\xi\xi\xi}^{(2)}.$$
(2)

We have assumed here independent orientational distributions for θ and ϕ , the polar and azimuthal angles of $\hat{\xi}$, respectively. In the case of azimuthal anisotropy, we have $\langle \cos^n \phi \rangle = 0$ for odd *n* and $\langle \cos^2 \phi \rangle = \langle 1 - \cos^2 \phi \rangle = \frac{1}{2}$, and Eq. (2) reduces to only two independent nonvanishing elements $\chi_{zzy}^{(2)}$.

We can measure SHG in reflection as a function of the sample rotation Φ about its surface normal for four different input and output polarization combinations: *p*in/*p*-out, *s*-in/*p*-out, and *p*-in/*s*-out. The theory of SHG can then be used to fit the experimental data and deduce the values of $\chi_{ijk}^{(2)}$. We note that in such a fit, the number of data points greatly exceeds the number of unknowns so that the $\chi_{ijk}^{(2)}$ are highly overdetermined. A good fit with the data will therefore give us confidence in both the measurements and the deduced values of $\chi_{ik}^{(2)}$.

From the known values of $\chi_{ijk}^{(2)}$, we can determine the approximate orientational distribution of the molecules. Assuming a Gaussian distribution in θ , we can find from the ratios $\chi_{zzz}^{(2)}/(\chi_{zxx}^{(2)} + \chi_{zyy}^{(2)})$ and $\chi_{zxz}^{(2)}/(\chi_{xxx}^{(2)} + \chi_{xyy}^{(2)})$ the peak position and the width of the distribution. Then the values of the remaining $\chi_{ijk}^{(2)}$ in Eq. (2) allow us to determine the distribution function in ϕ to third order if it is expanded into a series $\sum_{n=0}^{\infty} a_n \cos(n\phi)$.

The liquid crystal used for our experiment was 4'-noctyl-4-cyanobiphenyl (8CB). Monolayers of LC were deposited on substrates by evaporation using SHG as an *in situ* monitor.⁹ SHG measurements were carried out by a frequency-doubled Q-switched mode-locked yttrium aluminum garnet laser in reflection from the LC side. The polyimide coating of approximately 0.1 μ m thick on glass substrates was prepared by spin-coating polyimide (Japanese Synthetic Rubber Co.) onto a fused-silica substrate, whereas the surfactant (methylaminopropyltrimethoxysilane, MAP) coating of approximately one monolayer was prepared by deposition from solution.¹⁰ Rubbing was done by translating a coated substrate at constant velocity and constant pressure under a rotating wheel of velvet. Without the LC monolayer, neither the polyimide- nor the surfactant-coated samples showed significant SHG.

We measured SHG from a monolayer of 8CB on rubbed and unrubbed substrates as a function of the angle Φ between the plane of incidence and the rubbing direction. The results for the case of the polyimidecoated substrates are shown in Fig. 1. From the unrubbed substrate, the signal is isotropic in Φ , indicating that the 8CB molecules adsorbed on the substrate in the form of a monolayer are oriented randomly in the azimuthal plane. In this case, the output with s polarization is forbidden. On the rubbed substrate, however, the azimuthal isotropy is broken. The data in Fig. 1 show that the orientational distribution of the molecules now only has a mirror symmetry about the rubbing direction. Obviously, rubbing has reoriented the molecules preferentially along the rubbing direction. This anisotropy remains even if the sample temperature is so high that the bulk 8CB would be isotropic. We also found that $\chi^{(2)}$ for an 8CB monolayer on the polyimide surface has the same phase as that for an 8CB monolayer on water or clean glass, meaning the polar end group (-CN) of the molecules is adsorbed to the surface of the polyimide.⁸

90 90 (b) (a) 180 180 0 ω 2ω 270 270 90 90 Z (z) 180 0 180 0 (d) (c) 270 270

FIG. 1. Output second-harmonic field (arbitrary units) vs sample rotation Φ from 8CB monolayers on a polyimide-coated substrate. Open squares are data from unrubbed substrates, filled circles are data from rubbed substrates, and solid lines are the theoretical fits. The input-output polarization combinations are (a) *p*-in/*p*-out; (b) *s*-in/*p*-out; (c) *s*-in/*s*-out; (d) *p*-in/*s*-out. Inset: Coordinates (x, y, z) used in the analysis in relation to the fixed laboratory coordinates (X, Y, Z=z). The plane of incidence is $\hat{X} \cdot \hat{Z}$.

The theoretical fits to the data are also presented in

Fig. 1. The values of $\chi_{ijk}^{(2)}$, up to an overall phase factor, deduced from the fits are $\chi_{zzz}^{(2)} = 1.1$ and $\chi_{xyy}^{(2)} = 3.7$ for the unrubbed case and $\chi_{zzz}^{(2)} = 0.8$, $\chi_{xxz}^{(2)} = 1.7$, $\chi_{zyy}^{(2)} = 1.8$, $\chi_{zxx}^{(2)}$ = 3.7, $\chi_{zxz}^{(2)} = 0.15$, and $\chi_{xyy}^{(2)} = 0.37$ for the rubbed case, in units of 10^{-15} esu with an accuracy of 5%. Using these values of $\chi_{ijk}^{(2)}$, and assuming a Gaussian molecular orientational distribution in θ , we find the peak position and the width of the distribution to be $\theta_0 = 78^{\circ}$ and $\sigma = 10^{\circ}$, respectively, for the rubbed case and $\theta_0 = 78^{\circ}$ for the unrubbed case with σ assumed the same. In the latter case, if the orientational distribution is assumed to be a δ function, then the molecules should have a tilt angle of $\theta = 69^{\circ}$. On the rubbed surface, the molecular orientational distribution in ϕ can be determined to third order in the form

$$f(\phi) = [1 + 0.13\cos(\phi) + 0.69\cos(2\phi) + 0.03\cos(3\phi)]/2\pi$$

This function is plotted in Fig. 2, showing explicitly the anisotropic azimuthal orientational distribution of the 8CB monolayer. Rubbing causes the molecule to lie preferentially parallel and antiparallel to the rubbing direction, more antiparallel than parallel.

We conducted similar measurements on 8CB monolayers deposited on MAP-coated substrates, rubbed and unrubbed. The SH signal showed an isotropic dependence on Φ in both cases. The above results clearly indicate that the polyimide-coated surface has an effective short-range orienting force on the LC molecules while the MAP-coated surface does not. As suggested by Geary *et al.*,² molecular interaction between LC molecules and polyimide should be responsible for the orientation; rubbing orients the polymer at the surface and hence the LC molecules adsorbed it.

We are also interested in whether the presence of the LC bulk affects the orientation of the LC monolayer on the rubbed polyimide-coated substrate. For this, we measured reflected SHG from an 8CB film sandwiched between two rubbed polymide-coated glass plates. In the



FIG. 2. Azimuthal orientational distribution functions of an 8CB monolayer on a rubbed polyimide-coated substrate (solid line), and an 8CB interfacial layer between a rubbed polyimide-coated surface and an 8CB bulk (dashed line).

nematic phase, the 8CB film had a homogeneous alignment parallel to the rubbing direction. We now have both the 8CB bulk and the 8CB interfacial layer contributing to the SHG. The bulk contribution is of electric quadrupole character, and can be obtained separately from the measurements on a freely suspended film or an air/8CB interface.^{8,11} The contribution from the interfacial layer, and hence its values of $\chi_{ijk}^{(2)}$ in Eq. (2), can then be evaluated from the measured SHG from the cell. Finally, information about the orientational distributions of 8CB in the interfacial layer in θ and ϕ can be deduced from $\chi_{ijk}^{(2)}$.

Our experimental results from the 8CB cell are shown in Fig. 3 together with the theoretical fits. With the bulk in the isotropic phase, SHG as a function of the sample rotation Φ still exhibits a clear anisotropy, which must arise from the C_{1v} symmetry of the orientation distribution of 8CB in the interfacial layer. The relatively poor quality of the s-in/s-out data is due to the intrinsic low signal level of this polarization combination and multiple scattering from the 8CB bulk. A detailed calculation¹² showed that the 8CB monolayer is still responsible for the anisotropy. Assuming a Gaussian distribution in θ for the monolayer, we find in the present case $\theta_0 = 71^\circ$ and $\sigma = 4^\circ$, and

$f(\phi) = [1 + 0.06\cos(\phi) + 0.43\cos(2\phi) - 0.01\cos(3\phi)]/2\pi,$

which is also plotted in Fig. 2. Compared to the singlemonolayer case, the distributions in θ and ϕ are somewhat changed. The LC bulk appears to have loosened



FIG. 3. Output second-harmonic field (arbitrary units) vs sample rotation Φ from an 8CB cell made with rubbed polyimide-coated substrates. Open circles are data from the cell in the isotropic phase, filled triangles are data from the cell in the nematic phase, and solid lines are the theoretical fits for the isotropic case. The input-output polarization combinations are (a) *p*-in/*p*-out; (b) *s*-in/*p*-out; (c) *s*-in/*s*-out; (d) *p*-in/*s*-out.

the grip of the surface on the adsorbed LC molecules, making them tilted further away from the surface and azimuthally less influenced by the rubbing. With the bulk switched to the nematic phase, SHG vs Φ exhibits additional anisotropy due to the bulk homogeneous alignment. The deduced values of $\chi_{ijk}^{(2)}$ for the interfacial monolayer, however, do not change significantly, indicating no appreciable reorientation of the monolayer induced by the bulk transition. Anisotropy of the interfacial layer remained even at temperatures 20 °C above the isotropic-nematic transition.

Similar measurements on an 8CB cell made of rubbed MAP-coated substrates showed anisotropic SHG only when the bulk was in the nematic phase. Again, in this case, rubbing does not induce any alignment in the interfacial monolayer.

The results presented here lead us to the following conclusions. Two different surface-orienting mechanisms are effective in aligning a bulk LC. One is short range via molecular interaction. Homogeneous alignment by a rubbed polymer-coated surface is an example. The other is long range via elastic interaction. Homogeneous alignment by a rubbed MAP-coated surface is an example. Rubbing presumably creates grooves on the surface and the bulk alignment of the LC molecules along the grooves could lower the elastic energy in the interfacial region.³ In conclusion, we remark that the technique of surface SHG used here to probe the orientational anisotropy of LC monolayers can certainly be employed to study anisotropy of other molecular monolayers such as

Langmuir films at air/liquid interfaces and Langmuir-Blodgett films at air/solid interfaces.

This work was supported by National Science Foundation-Solid State Chemistry-Grant No. DMR-8717137. M.B.F. acknowledges receipt of an AT&T Bell Laboratories Pre-Doctoral Fellowship. We would like to thank K. H. Yang of IBM for providing the polyimide solution.

¹See, for example, J. Cognard, Mol. Cryst. Liq. Cryst. 51, 1 (1982).

²J. M. Geary, J. W. Goodby, A. R. Kmetz, and J. S. Patel, J. Appl. Phys. **62**, 4100 (1987).

³D. W. Berreman, Phys. Rev. Lett. **28**, 1683 (1972); Mol. Cryst. Liq. Cryst. **23**, 215 (1973).

⁴T. J. Sluckin and A. Poniewierski, in *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, New York, 1986), Chap. 5, and references therein.

⁵W. Chen, L. J. Martinez-Miranda, H. Hsiung, and Y. R. Shen, Phys. Rev. Lett. 62, 1860 (1989).

⁶See, for example, Y. R. Shen, Annu. Rev. Mater. Sci. 16, 69 (1986); Nature (London) 337, 519 (1989).

⁷Y. R. Shen, Liq. Cryst. 5, 635 (1989).

⁸P. Guyot-Sionnest, H. Hsiung, and Y. R. Shen, Phys. Rev. Lett. **57**, 2963 (1986).

⁹C. S. Mullin, P. Guyot-Sionnest, and Y. R. Shen, Phys. Rev. A **39**, 3745 (1989).

¹⁰F. J. Kahn, Appl. Phys. Lett. **22**, 386 (1973).

¹¹H. Hsiung and Y. R. Shen, Phys. Rev. A 34, 4303 (1986).

¹²M. Feller, W. Chen, and Y. R. Shen (to be published).