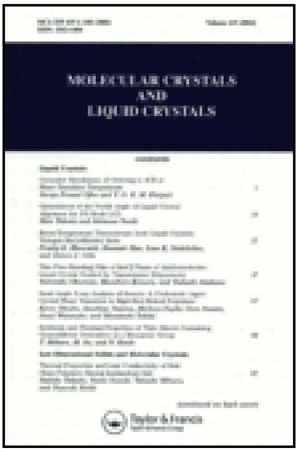

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Y. R. Shen [a], W. Chen [a], M. B. Feller [a], J. Y. Huang [a] & R. Superfine [a]

[a] Department of Physics, University of California, Berkeley, CA, 94720

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PROBING THE MECHANISMS FOR SURFACE-INDUCED ALIGNMENT OF LIQUID CRYSTALS

Y. R. SHEN, W. CHEN, M. B. FELLER, J. Y. HUANG, and
R. SUPERFINE
Department of Physics, University of California, Berkeley, CA 94720

Abstract Optical second harmonic generation is used to probe the alignment of liquid crystal monolayers on surfaces treated with different methods. The results provide definitive information about physical mechanisms responsible for the surface-induced bulk liquid crystal alignment. Infrared-visible sum-frequency generation allows the measurements of vibrational spectra of molecular monolayers at an interface. It is used to see how liquid molecules interact with long-chain surfactants to yield homeotropic bulk alignment.

Surface-induced bulk alignment is a problem of great importance in the liquid crystal (LC) field.[1] It is a process commonly adopted in the construction of almost all LC devices. Yet the physical mechanism responsible for the effect is not fully understood. For homeotropic bulk alignment, coating of surfaces by surfactants is known to be most effective. For homogeneous alignment, mechanical rubbing of surfactant- or polymer-coated surfaces or grooving of surfaces by evaporation of SiO_x, etching, or microfabrication is often used. These practices suggest that, in general, there are two possible mechanisms for the surface-induced bulk alignment. One similar to molecular epitaxy is based on short-range surface-molecule and then molecule-molecule interactions to align the bulk.[2] The other relies on minimization of long-range interaction (mainly elastic) between the surface and the bulk.[3] To see which mechanism dominates in a particular case, we need to know how the first LC monolayer at the surface is aligned. The alignment is expected to be good if the molecular epitaxy mechanism is operative, but no so if the long-range mechanism is effective. Thus experiments that allow probing of an LC monolayer at a surface are essential for a better understanding of the problem.

Recently, optical second harmonic generation (SHG) has been proven to be a powerful means for studying molecular monolayers at various interfaces.[4] It is therefore ideal to be used for the study of the LC problem we have in hand. As a second-order optical process, SHG is forbidden in a medium with inversion symmetry, but necessarily allowed at an interface. It is particularly sensitive to a polar-oriented molecular monolayer adsorbed at an interface. The azimuthal dependence of SHG with different input/output polarization combinations permits the determination of average molecular orientation and alignment in a monolayer. The technique has already been applied to the study of LC monolayers at azimuthally isotropic interfaces.[5] Here we shall review applications of the technique to the study of the orientation and alignment of LC monolayers on surfaces treated for homogeneous alignment.[6]

The experimental arrangement has been described elsewhere.[5,6] We used four different input/output polarization combinations (p-in/p-out, p-in/s-out, s-in/p-out, and s-in/s-out) and measured the azimuthal dependence of SHG from reflection by rotating the sample about its surface normal. We first studies 8CB (octyl-cyanobiphenyl) monolayers on MAP (methylaminopropyl-trimethoxy silane) -coated surfaces. With or without mechanical rubbing of the surfaces, the SHG signal is independent of the sample rotation, indicating that the monolayer orientation is azimuthally isotropic. The rubbed MAP-coated surface did yield homogeneous bulk alignment along the rubbing direction. The results therefore suggest that the alignment in this case must come from the long-range surface-bulk interaction.[3] Presumably hard rubbing created grooves on the MAP-coated surface and minimization of the overall elastic energy commanded the LC molecules to lie along the grooves.

The polymer-coated surfaces gave very different results.[6] Figure 1 depicts the azimuthal dependence of SHG in the four input/output polarization combinations from an 8CB monolayer adsorbed on a polyimide-coated surface. Without rubbing of the surface, SHG is azimuthally isotropic, reflecting the azimuthal symmetry of the monolayer orientation. With rubbing, however, the data clearly show a mirror (C_{IV}) symmetry with respect to the rubbing direction. this corresponds to a monolayer orientation with a preferred alignment along the rubbing direction. Analysis of the data in Fig. 1 allows us to find the orientational distribution of 8CB molecules in the monolayer. First, a theoretical fit of the data yields values for the independent, nonvanishing elements of the surface nonlinear susceptibility $\chi^{(2)}$ of the 8CB monolayer. Then knowing the dependence of $\chi^{(2)}$ on the molecular orientation permits the determination of several weighted averages of the polar and azimuthal angles, θ and ϕ, respectively, of the molecular orientation. By assuming a Gaussian distribution for the polar orientation and a serial distribution for the azimuthal

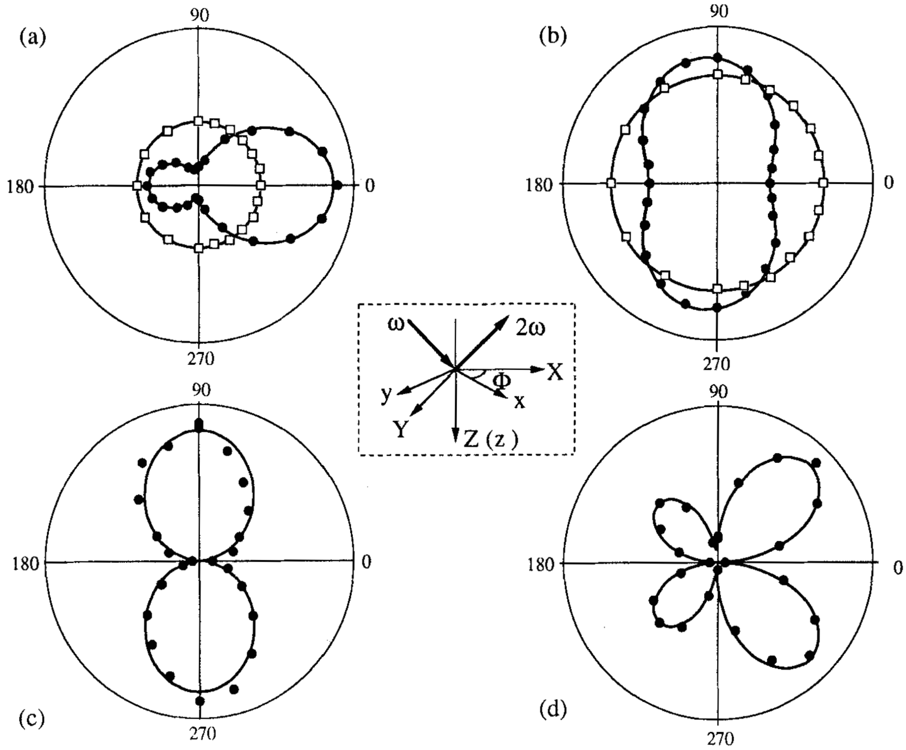

FIGURE 1 Output second-harmonic field (arbitrary units) vs sample rotation Φ from 8CB monolayers on a polyimide-coated substrate. Open squares are data from unrubbed substrates, filled circles are data from rubbed substrates, and solid lines are the theoretical fits. The input-output polarization combinations 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 $\hat{X}$ - $\hat{Z}$.

orientation, the following results are found from the data in Fig. 1.[6] For the polar orientation, the distribution is

$$P(\theta) \propto \exp[-(\theta - \langle\theta\rangle)^2/(\Delta\theta)^2]$$

with $\langle\theta\rangle = 78°$ and $\Delta\theta = 10°$. For the azimuthal orientation, the distribution is

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

The azimuthal distribution $F(\phi)$ is plotted in Fig. 2 to show explicitly the azimuthal anisotropy of the molecular orientation induced by rubbing of the polymer-coated surface.

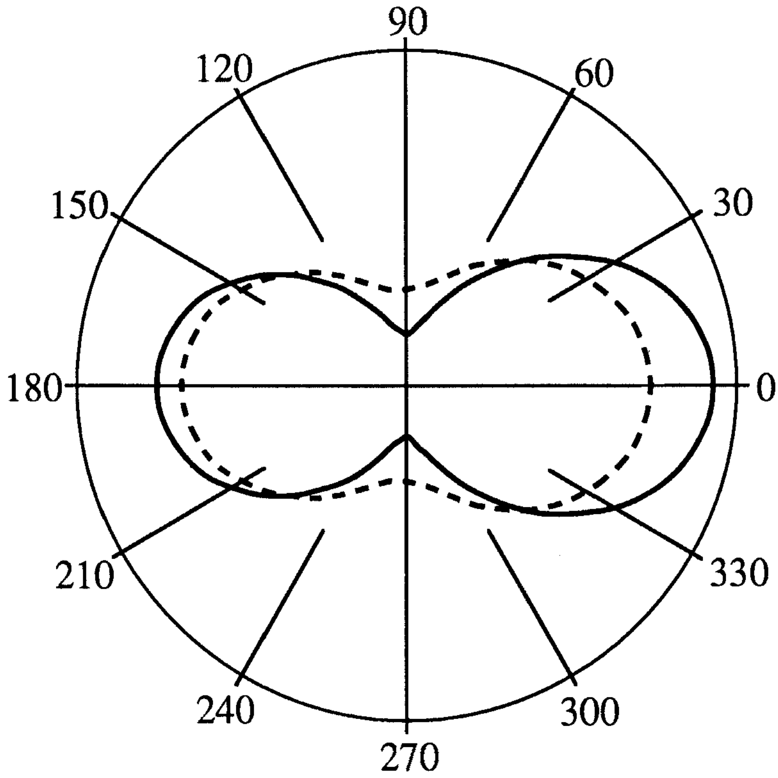

FIGURE 2 Azimuthal orientational distribution functions of an 8CB monolayer on a rubbed polyimide-coated substrate (solid line), and an 8CB interfacial layer between a rubbed polyimide-coated surface and an 8CB bulk (dashed line).

The 8CB monolayer alignment on the polyimide-coated surface along the rubbing direction indicates that the surface-induced homogeneous bulk alignment in this case must come from the molecular epitaxy mechanism. As suggested by Patel and coworkers,[2] rubbing stretches the polymer chains at the surface of the polymer film. Interaction of the LC monolayer with the stretched polymer chains then leads to an anisotropic orientational distribution of the monolayer. Correlation between LC molecules finally effects the bulk alignment.

The above interpretation is further supported by the following observations: 1) As seen by ellipsometry, there was indeed a birefringence in the polymer coating induced by rubbing.[2] 2) The observed birefringence increased with increase of the rubbing strength (defines as the pressure of the rubbing cloth on the polyimide film times the rubbing time).[7] 3) The monolayer alignment appeared more anisotropic (i.e., better alignment along the rubbing direction) with higher rubbing strength, and eventually saturated. Figure 3 illustrates the last point. The observed anisotropy in the azimuthal orientation of the 8CB monolayer is stronger with more rubbing of the polyimide coating, but saturates at ~ 10 rubbings. In all cases, the polar orientation of the monolayer appeared to be unaffected by rubbing.

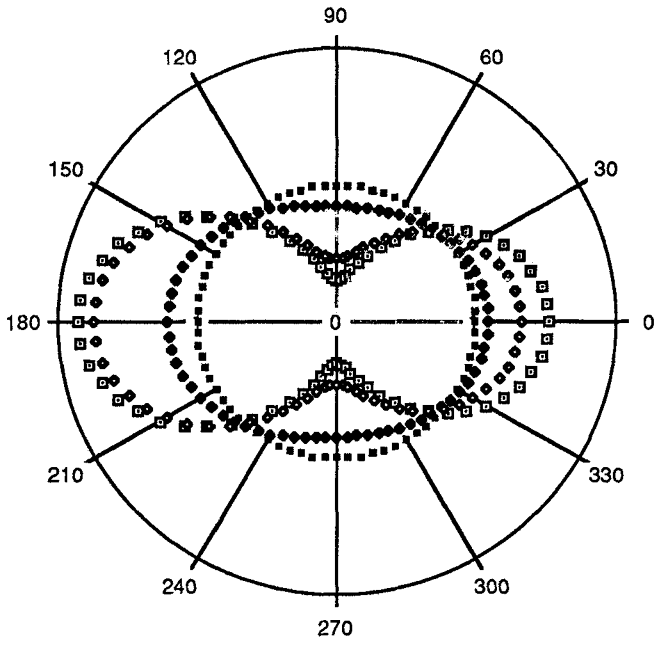

FIGURE 3 Azimuthal orientational distributions of an 8CB monolayer on polyimide-coated substrates rubbed with different strengths. Filled squares, filled diamonds, and open diamonds denote data obtained with 0, 5, and 20 rubbings of the substrates, respectively, all under the same pressure. Open squares denote hard rubbing with saturated anisotropy.

The monolayer alignment on the rubbed polyimide-coated surface showed little temperature dependence. It was also hardly affected by the presence of a bulk 8CB film in either the isotropic or the mesomorphic phase. The latter was concluded from our SHG experiment on an 8CB cell constructed with the rubbed polyimide-coated windows[6] (see Fig. 2).

Other polymers can also be used in surface coating to effectively align the adsorbed LC monolayer and hence the LC bulk.[2,8] Polyvinyl-alcohol is an example. Isotatic polystyrene aligns LC perpendicular to the rubbing direction.[8] This is presumably because LC molecules interact more strongly with the side (phenyl) groups of the stretched polymer. Unfortunately, the orientation of the LC monolayer on polystyrene is not polar, preventing us from probing the monolayer directly with SHG.

We also conducted measurements on LC monolayers on obliquely evaporated SiO_x surfaces. The results indicate that the monolayers are not aligned on such surfaces. The homogeneous bulk alignment along the SiO_x ridges in this case comes from the long-range surface-bulk elastic interaction. Surface-induced alignment of ferroelectric LC is of special interest to researchers working on surface-stabilized ferroelectric LC devices.[9] Rubbing on polymer-coated surfaces is again commonly used to homogeneously align the LC bulk. For LC molecules with large permanent dipoles, however, it has been found that the bulk smectic-A alignment is along a direction deviated from the rubbing direction,[10] for example, 7° in the case of 4'-(2s,3s)-2"-chloro-3" methylpentanoyloxyphenyl-4-decyloxythiobenzene.[11] The layer normal remains unchanged as the bulk transforms into the smectic-C* phase. It is then interesting to know whether the first LC monolayer at the surface still lies along the rubbing direction. We found from the SHG measurements that this was actually the case. The change of LC alignment from the surface to the bulk must come from minimization of the combined elastic and electromagnetic interactions.

Both polymer- and MAP-coated surfaces without rubbing yield planar bulk LC alignment (parallel to the surface but azimuthally isotropic). On the other hand, surfaces covered with long-chain surfactants such as DMOAP (n,n-dimethyl-n-octadecyl-3-aminopropyltrimethoxysilychloride) and OTS (octadecyltrichlorosilane) lead to homeotropic alignment. Obviously, the latter alignment must be effected by the long alkyl chains of the surfactants spouting from the surface. It is interesting to see how LC molecules interact with the surfactant molecules at the surface. For this, we used infrared-visible sum-frequency generation[12] to obtain vibrational spectra of surfactant and LC monolayers and monitor their changes due to LC/surfactant interaction.

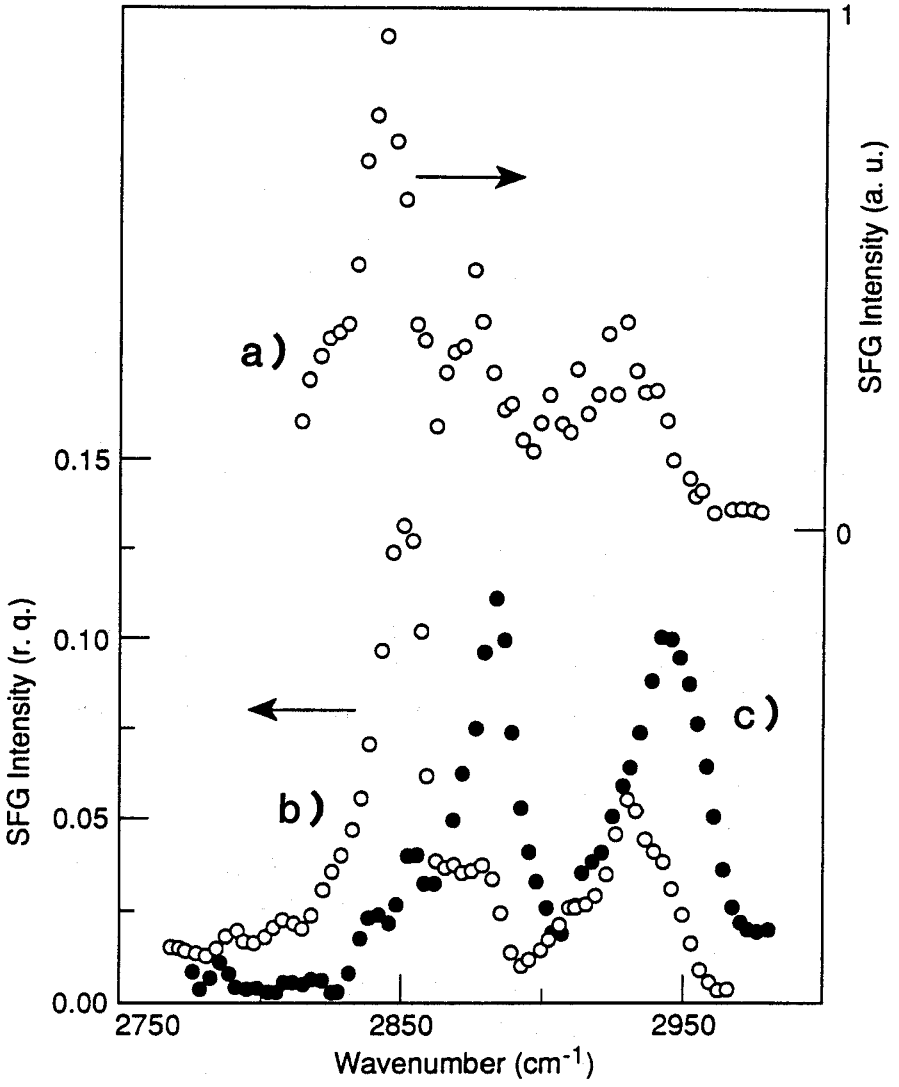

FIGURE 4 (a) SFG spectrum of a PDA monolayer on water at a density of 47 Å^2/molecule. (b) SFG spectrum of DMOAP on clean glass. (c) SFG spectrum of 0.7 monolayer of 8CB deposited on the DMOAP-covered glass.

Figure 4 shows the C-H spectra of (a) a loosely packed monolayer of PDA (pentadecanoic acid) (47 Å^2/molecules as compared to 22 Å^2/molecule for a fully packed layer), (b) a full monolayer of DMOAP (~ 45 Å^2/molecule), and (c) a 0.7 monolayer of 8CB deposited on the DMOAP monolayer.[13] The first two spectra are very similar. In each spectrum, the peak at 2850 cm^{-1} can be assigned to the CH_2 symmetric stretch mode, and the peaks at 2875 and 2940 cm^{-1} to the stretch and Fermi resonance modes, respectively, of the terminal CH_3 group.[12,13] The CH_2 peak is prominent only because the alkyl chains of the molecules are not straight and upright.[12] They have room to flap around and develop trans-gauche defects that break the symmetry and contribute to the CH_2 peak. Deposition of 8CB on the DMOAP layer changes the spectrum drastically, as seen in Fig. 4(c). The CH_2 peak is significantly reduced and the spectrum now looks more like that for a full PDA or OTS monolayer. This indicates that the interaction between 8CB and DMOAP molecules have straightened the alkyl chains of DMOAP.

From the geometry of the molecular arrangement. it is likely that the chain-chain interaction between 8CB and DMOAP molecules is most important for the observed conformational change on DMOAP. The same interaction together with the geometrical restriction aligns the second 8CB monolayer homeotropically (tails against tails with the first monolayer to offset the polar arrangement of the first monolayer). This then leads, in the molecular epitaxy sense, to the homeotropic bulk alignment. We note that as far as the arrangement of alkyl chains goes, an 8CB monolayer on DMOAP resembles to a large extent the surface covered by a monolayer of OTS; both are effective for the homeotropic bulk alignment.

In summary, we have shown with SHG and SFG measurements that a properly treated surface can effectively align the first LC monolayer anchored on it in a prescribed way. Then through correlation of LC molecules, the aligned monolayer induces a particular bulk alignment in the mesophase. In other cases, a prescribed surface morphology can also induce a particular bulk alignment via long-range interaction.

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