

Nonlinear spectroscopic study of coadsorbed liquid-crystal and surfactant monolayers: Conformation and interaction

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(Received 16 April 1990)

We have used optical second-harmonic generation and infrared-visible sum-frequency generation to study liquid-crystal monolayers on clean glass and on surfactant-treated glass. The results provide insight into the competing effects of polar adsorption sites and surfactant alkyl chains in aligning the bulk liquid crystal.

The interfacial properties of liquid crystals (LC) are of great interest to many researchers for basic science understanding and for practical application to LC devices.^{1,2} It is well known that the bulk alignment of a LC in a cell is strongly affected by the surface treatment of the cell walls. Until recently, a detailed understanding of this phenomena has been impeded by a lack of microscopic probes of the interface. Over the past several years, surface second-harmonic generation (SHG) has proven to be a valuable and versatile probe of monolayer systems.^{3,4} This technique has been extended to infrared-visible sum-frequency generation (SFG) that has unique capabilities for surface vibrational spectroscopy.⁵⁻¹⁰ The purpose of the present study is to use SHG and SFG simultaneously to obtain information about the orientation and conformation of the LC and surfactant alkyl chains in pure monolayers and their interaction in mixed monolayers.

We examine monolayers of the liquid crystal 4'*n*-octyl-4-cyanobiphenyl (8CB) on clean glass and on glass coated with one of two surfactants: *n*-methylaminopropyltrimethoxysilane [MeNH(CH₂)₃Si(OMe)₃, MAP], known to induce bulk LC alignment parallel to the surface as in the clean-glass case, and *n,n*-dimethyl-*n*-octadecyl-3-aminopropyltrimethoxysilychloride [CH₃(CH₂)₁₇(Me)₂N⁺(CH₂)₃Si(OMe)₃Cl⁻, DMOAP] for homeotropic bulk alignment.¹ The two surfactants both have a MAP head group that attaches to the glass. In addition, DMOAP has an 18 carbon alkyl chain that extends away from the surface. In a previous SHG experiment,¹¹ a surprising result was found: The 8CB core had the same orientation on all three surfaces, even though they produced different bulk alignments. In this study, using SFG spectroscopy, we have found that 8CB deposited on MAP leaves the surfactant monolayer relatively unchanged, consistent with a picture of 8CB adsorbing on top of the MAP molecules. In contrast, the adsorption of 8CB on DMOAP penetrates the DMOAP monolayer and reduces the conformational defects in the DMOAP alkyl chains. This then allows us to identify the two competing effects in the surface alignment of the bulk LC.

For surface SHG and SFG, the signal is proportional to the square of the effective surface nonlinear polarization²

$$\mathbf{p}^{(2)}(\omega_s) = \vec{\chi}^{(2)}(\omega_s = \omega_1 + \omega_2) : \mathbf{E}(\omega_1) \mathbf{E}(\omega_2), \quad (1)$$

with $\omega_1 = \omega_2$ for SHG. In the case of a monolayer of mol-

ecules with appreciable second-order polarizability deposited on a centrosymmetric insulator, the monolayer dipole susceptibility often dominates other contributions in SHG and SFG. The surface susceptibility $\vec{\chi}^{(2)}$ can then be related to the nonlinear molecular polarizability $\vec{\alpha}^{(2)}$ by a coordinate transformation averaged over the molecular orientational distribution

$$\chi_{ijk} = N_s \sum_{l,m,n} \langle (\hat{i} \cdot \hat{l})(\hat{j} \cdot \hat{m})(\hat{k} \cdot \hat{n}) \rangle \alpha_{lmn}, \quad (2)$$

where N_s is the surface molecular density and the angular brackets denote the orientational average. The independent elements of $\vec{\chi}^{(2)}$ can be deduced by measuring the signal for different polarizations of the incident and output beams. Then if $\vec{\alpha}^{(2)}$ is known, the parameters of an orientational distribution can be determined.¹²

In the case of infrared-visible SFG, the nonlinear polarizability near vibrational resonances can be written as

$$\vec{\alpha} = \vec{\alpha}_{nr} + \vec{\alpha}_r, \quad \vec{\alpha}_r = \sum_q \frac{\vec{a}_q}{\omega_q - \omega_{ir} - i\Gamma_q}, \quad (3)$$

where \vec{a}_q , ω_q , and Γ_q are the strength, frequency, and damping constant of the q mode, respectively. The resonant enhancement of $\vec{\alpha}$ as ω_{ir} scans over ω_q then yields the surface-vibrational spectrum observed by SFG.

The experimental setup has been described elsewhere.⁵ In the present experiment, the laser system produced visible pulses at 0.532 μm and tunable infrared pulses around 3.3 μm , with energies at the sample of 0.6 and 0.2 mJ, respectively. Both had a pulse width of ~ 20 ps and a repetition rate of 10 Hz. The two beams were overlapped on the surface with beam diameters of 700 μm for the visible and 250 μm for the infrared beam. A 7° angular separation between the input beams was used to permit the separation of the SHG and the SFG signals. Both signals were simultaneously measured in separate detection arms. The tunable infrared source was calibrated to 1.5 cm^{-1} with a polystyrene reference and all spectra were normalized to the SFG spectrum from crystalline quartz. The peak positions, strengths, and widths of a resonance can be determined by a fit of the SFG spectrum to Eq. (3). The typical signal levels per pulse from a surface monolayer of 8CB were about 200 photons for SHG and about 100 photons for SFG on resonance. Our samples were prepared on fused quartz substrates which had been cleaned in

chromic acid and rinsed in distilled water. DMOAP and MAP were chemisorbed from solution and polymerized according to the literature.² The 8CB monolayers on various surfaces were deposited by evaporation from a heated drop of LC held above the substrate with SHG used as an *in situ* monitor.¹¹

We will focus on the SFG spectra associated with χ_{yyz} in the CH stretch region because it has been shown to be most sensitive to the conformation of the alkyl chain.⁷ They have been obtained with polarizations *s*, *s*, and *p* for the SF, visible and infrared beams, respectively. The spectrum for MAP-treated glass (MAP-G) (Fig. 1) is relatively weak with only broad features. Since χ_{yyz} here is most sensitive to the symmetric stretch of CH₂ and CH₃ and should increase with higher polar ordering of these groups along the surface normal, the weakness of the SFG signal indicates that the average orientation of the symmetry axes of the CH₂ and CH₃ groups are tilted far away from the surface normal. MAP is known to attach to the glass surface through a covalent bond between the surfactant Si atom and the surface silanol group. The NH group is expected to hydrogen bond to the surface leaving the CH₂ chain lying along the surface.¹³ A congested spectrum is expected since the CH₂ and CH₃ groups have overlapping resonances between 2850 and 2950 cm⁻¹. A more detailed analysis of the spectral features is, however, difficult because of the lack of ir and Raman studies on this molecule.

In contrast, a significantly stronger spectrum is obtained for DMOAP on glass (DMOAP-G), as displayed in Fig. 2(b). Three prominent peaks at 2848, 2880, and 2933 cm⁻¹ are present. The surprising part of the result is that the spectrum looks very much like that of a half-packed pentadecanoic acid [PDA, CH₃(CH₂)₁₃COOH] monolayer on water, as shown in Fig. 2(a) for comparison. It was found in a previous study⁷ that the SFG spectrum of $|\chi_{yyz}|^2$ for a fully packed PDA monolayer exhibits only peaks at 2875 and 2940 cm⁻¹, assigned to the symmetric stretch and Fermi resonance of the terminal methyl group. As the monolayer becomes less dense, these two peaks lose intensity while a peak at 2850 cm⁻¹,

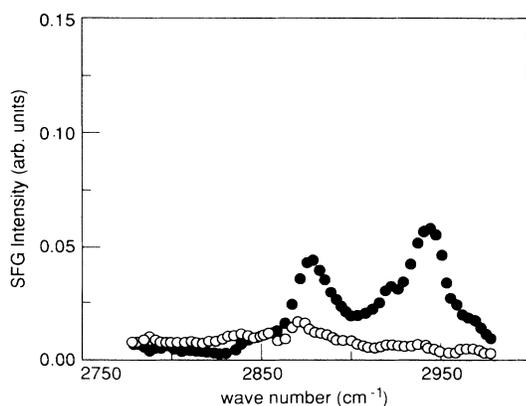


FIG. 1. SFG spectrum of MAP on clean glass (open circles) compared with the spectrum of the same sample taken after deposition of 0.70 monolayer of 8CB (solid circles). Spectra are normalized to quartz reference.

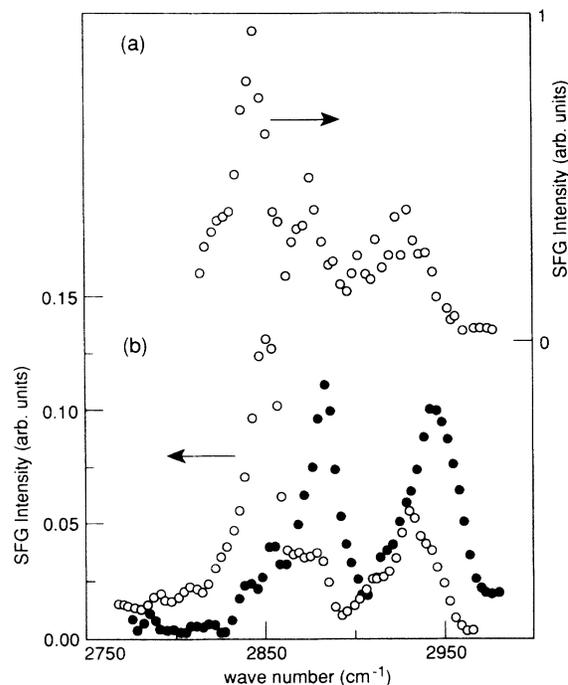


FIG. 2. (a) Spectrum of the PDA monolayer on water surface at a density of 47 Å² molecules. (b) Comparison of the SFG spectrum of DMOAP on clean glass (open circles) and the spectrum of the same sample after deposition of 0.7 monolayer of 8CB (solid circles).

assigned to the CH₂ symmetric stretch mode, increases and dominates the spectrum at a surface density corresponding to 47 Å² per alkyl chain. This is because for a full PDA monolayer, all the alkyl chains are straight and upright on the surface so that by symmetry only the terminal CH₃ group contributes to the SFG spectrum, but as the monolayer expands, the chains acquire trans-gauche defects, break the symmetry, and contribute to the CH₂ stretch resonances in the SFG spectrum. We notice that the head group of DMOAP may occupy a surface area of about 40–50 Å². The chain density of a compact DMOAP layer is then about the same as that of a half-packed PDA monolayer and the spectra of the two should be very similar if they are dominated by the contribution from the chains. The apparent lack of contribution from the DMOAP head group can be explained by the local-field (dielectric shielding) effect which reduces the field seen by the head group buried beneath the alkane chains by about 2.3, as compared to an exposed head group.

We now discuss the SFG spectra of 8CB monolayers on various surfaces. For a full 8CB monolayer on clean glass (8CB-G), the spectrum is shown in Fig. 3. The surface density here is the same as that of a full monolayer on water as measured by SHG and corresponds to 35 Å² per molecule.¹¹ Two peaks at 3070 and 3050 cm⁻¹ can be assigned to C-H stretch modes of the biphenyl core.¹⁴ The peaks at 2875 and 2940 cm⁻¹ are associated with the symmetric stretch and Fermi resonance of the terminal methyl group, respectively. The weak peak at 2850 cm⁻¹ is due to the symmetric stretch of CH₂ groups in the alkyl

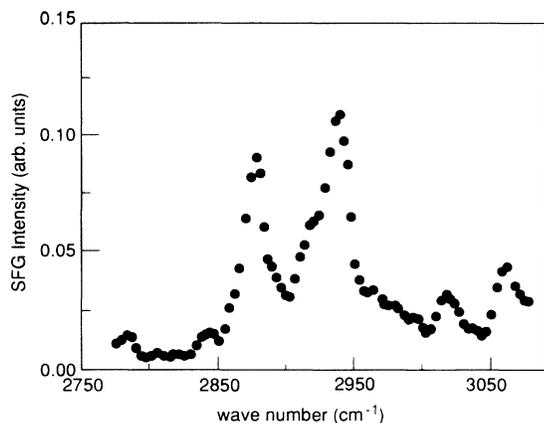


FIG. 3. SFG spectrum of the 8CB monolayer on clean glass. Note the change in the horizontal scale.

chain and the shoulder at 2920 cm^{-1} is due to either asymmetric stretches or Fermi resonances of symmetric stretches of the same CH_2 groups. The weakness of the 2850 cm^{-1} peak indicates that the 8CB alkyl chain is relatively straight. Furthermore, SHG measurements with different input-output polarizations showed that the biphenyl core of 8CB is tilted at 70° from the surface normal with the cyano group attached to the surface.¹¹ They, however, cannot determine the orientation of the molecule with respect to rotation about the biphenyl symmetry axis. In a recent experiment reported elsewhere,¹⁵ we have measured the phase of χ_{yyz} for SFG at the 2875-cm^{-1} resonance. The result shows that the methyl group, and hence the alkyl chain, must point away from the surface.

For 8CB monolayers deposited on the surfactant-treated glass, our SHG measurements confirmed that the tilt of the biphenyl core on either MAP- or DMOAP-coated glass was 70° , the same as 8CB on clean glass.¹¹ The saturation coverage, as determined by SHG, was found to be 70% of the full monolayer on clean glass. The SFG spectrum for an 8CB monolayer on MAP-coated glass is presented in Fig. 1 together with the spectrum for MAP only. It appears very similar to that for 8CB on clean glass in Fig. 3. In fact, the spectral intensity, about one-half that of 8CB-G, can be explained as originating solely from the 0.70 monolayer of 8CB with little contribution from the surfactant. This suggests that the MAP contribution must have been reduced by the dielectric shielding effect of the 8CB layer on top of MAP.

In the case of 8CB deposited on DMOAP-coated glass (8CB-D), the SFG spectrum, given in Fig. 2(b) together with that for DMOAP only, shows clear evidence of interaction between 8CB and DMOAP. The strong peak at 2850 cm^{-1} in the DMOAP-G spectrum is greatly reduced in the 8CB-D spectrum. The ratio of the susceptibility of the 2850-cm^{-1} mode before and after the deposition of 8CB is 19. This is far too large to be attributed to changes in the local field, which, at most, can account for

a change on the order of the 8CB dielectric constant, about 2.5. The spectrum of 8CB-D in the spectral region above 2850 cm^{-1} can be understood from $|\chi_{yyx}(\omega_{\text{ir}})|^2$, with $\chi_{yyz}(\omega_{\text{ir}})$ obtained from the sum of the susceptibility of DMOAP-G and that of 8CB-G weighted for the lower coverage. In the present case, the 8CB molecules must have penetrated the alkyl chain layer to adsorb on the head groups of DMOAP or glass. Thus, no dielectric shielding of the spectral contribution from the alkyl chain methyl group of DMOAP by the 8CB layer can be expected. The most likely explanation for the decrease at 2850 cm^{-1} is that the increase in steric interaction would remove trans-gauche defects in the DMOAP chains and hence reduce the CH_2 peak at 2850 cm^{-1} , as has been demonstrated in the previous study on PDA monolayers.⁷

Our results here provide insight into the microscopic mechanisms responsible for the effect of the surface treatment on the bulk LC alignment. In the case of glass treated with surfactant octadecyltrichlorosilane (OTS), deposited 8CB forms a nonpolar rather than a polar layer and the bulk alignment is perpendicular to the surface.¹¹ OTS has the same long alkyl chain as DMOAP but has a much simpler and smaller head group in that it bonds to the surface through the Si atom that terminates the alkyl chain. The SFG spectrum of a full monolayer of OTS on glass is nearly identical to that of a full PDA monolayer, indicating that the chains are well ordered and that the monolayer is compact.⁹ We can consider DMOAP as an intermediate case between clean glass, MAP, and OTS. Both DMOAP and OTS lead to homeotropic alignment of the LC bulk, while clean glass and MAP yield parallel alignment. Clean glass, MAP-G, and DMOAP-G allow the adsorption of a polar layer of 8CB, but OTS does not.¹¹ The similarity of DMOAP-G to clean glass and MAP-G is due to the large head group of DMOAP, which spaces the chains and permits access of 8CB to surface polar sites. However, once 8CB fills in the DMOAP chains, the subsequent 8CB sees a compact alkyl monolayer similar to OTS. It appears that in order for the monolayer surface treatment to induce parallel alignment of the bulk LC, the second 8CB layer must have access to the biphenyl cores of 8CB molecules bound at surface polar sites. Though DMOAP permits the presence of these strongly bound molecules, its long alkyl chain prevents their biphenyl cores from interacting with subsequent layers.

In conclusion, we have demonstrated that SHG and SFG can provide a detailed picture of the interfacial structure of LC systems. We have observed the existence of interaction between the LC monolayer and the surfactant-treated glass which reveals the importance of the competing effects of surface polar adsorption sites and surfactant alkyl chains in aligning the bulk LC.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

- ¹J. Cognard, *Alignment of Nematic Liquid Crystals and their Mixtures* (Gordon and Breach, London, 1982).
- ²F. J. Kahn, *Appl. Phys. Lett.* **22**, 386 (1973).
- ³Y. R. Shen, *Ann. Rev. Phys. Chem.* **40**, 327 (1989).
- ⁴Y. R. Shen, *Nature (London)* **337**, 519 (1989).
- ⁵X. D. Zhu, H. Suhr, and Y. R. Shen, *Phys. Rev. B* **35**, 3047 (1987).
- ⁶J. H. Hunt, P. Guyot-Sionnest, and Y. R. Shen, *Chem. Phys. Lett.* **133**, 189 (1987).
- ⁷P. Guyot-Sionnest, J. H. Hung, and Y. R. Shen, *Phys. Rev. Lett.* **59**, 1597 (1988).
- ⁸A. L. Harris, C. E. D. Chidsey, N. J. Levinos, and D. N. Loiacono, *Chem. Phys. Lett.* **141**, 350 (1987).
- ⁹P. Guyot-Sionnest, R. Superfine, J. H. Hunt, and Y. R. Shen, *Chem. Phys. Lett.* **144**, 1 (1988).
- ¹⁰R. Superfine, P. Guyot-Sionnest, J. H. Hunt, C. T. Kao, and Y. R. Shen, *Surf. Sci.* **200**, L445 (1988).
- ¹¹C. S. Mullin, P. Guyot-Sionnest, and Y. R. Shen, *Phys. Rev. A* **39**, 3745 (1989).
- ¹²W. Chen, M. Feller, and Y. R. Shen, *Phys. Rev. Lett.* **63**, 2665 (1989).
- ¹³G. S. Caravajal, D. E. Leyden, G. R. Quintig, and G. E. Mariel, *Anal. Chem.* **60**, 1776 (1988).
- ¹⁴L. J. Bellamy, *The Infrared Spectra of Complex Molecules* (Wiley, New York, 1975).
- ¹⁵R. Superfine, J. Huang, and Y. R. Shen (unpublished).