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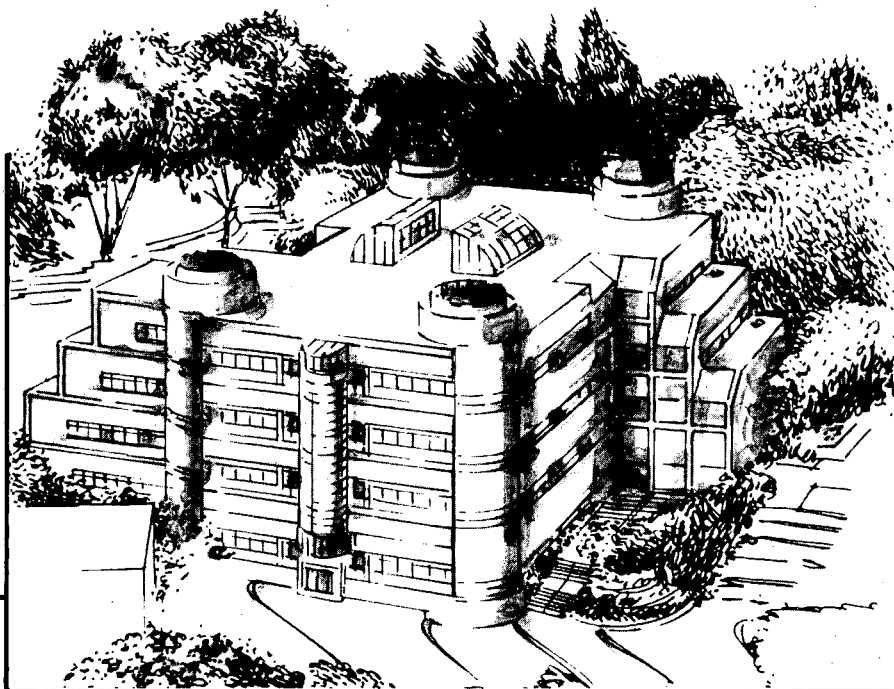
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CONFORMATION, ORIENTATION AND INTERACTION IN MOLECULAR MONOLAYERS: A SURFACE SECOND HARMONIC AND SUM FREQUENCY GENERATION STUDY

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Knowledge of the conformation and ordering of molecular monolayers is essential for a detailed understanding of a wide variety of surface and interfacial phenomena. Over the past several years, surface second harmonic generation (SHG) has proven to be a valuable and versatile probe of monolayer systems.¹ Our group has recently extended the technique to infrared-visible sum frequency generation (SFG) which has unique capabilities for surface vibrational spectroscopy.²⁻⁶ Like second harmonic generation, SFG is highly surface specific with submonolayer sensitivity at all interfaces accessible by light. The orientation of individual groups within an adsorbate molecule can be deduced by a polarization analysis of the SFG signal from the vibrational modes of the groups.

We have used SHG and SFG to study orientations and conformations of surfactant and liquid crystal (LC) monolayers and their interaction on a substrate. The interfacial properties of LC are of great interest to many researchers for both basic science understanding and practical application to LC devices. It is well known that the bulk alignment of a liquid crystal in a cell is strongly affected by the surface treatment of the cell walls. The reason behind it is not yet clear.⁷

The theoretical background and experimental arrangement of SHG and SFG have been described elsewhere.⁴ In our setup, a 30 psec. Nd:YAG mode-locked laser system together with nonlinear accessories generates a visible beam at .532μm and an infrared beam tunable about 3.4μm. Both beams are focused to a common spot of 300μm dia. The typical signal off the surface from a compact ordered alkyl chain monolayer is ~500 photons per pulse, easily detected with a photomultiplier tube.

In our experiment, we used the monolayer of pentadecanoic acid (CH₃(CH₂)₁₃COOH , PDA) on water as a standard system for the study of order in alkane chain monolayers. The SFG spectra for PDA at three different surface concentrations are presented in Fig.1. For the compact monolayer (Fig.1a), the peaks are assignable to the CH₃ symmetric stretch mode at 2875 cm⁻¹ and the CH₃ fermi resonance at 2940 cm⁻¹. An analysis of the polarization dependence of the 2875 cm⁻¹ peak gives an average tilt for the terminal methyl group of about 35° from the surface normal. This is consistent with the alkane chain being oriented perpendicular to the surface. The peaks due to the CH₂ stretch modes are hardly distinguishable. An infinite polymethylene chain in the all-trans configuration is centrosymmetric so that its vibrational modes should be strictly either Raman or infrared active.

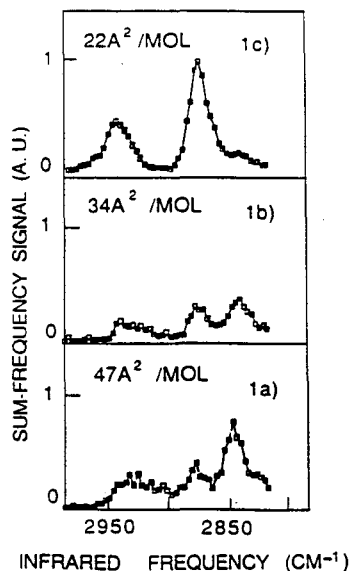


Fig.1 SFG vibrational spectra of PDA monolayers on the water surface.

- 1c) compact monolayer
- b) medium density
- a) low density

The steric interaction between alkyl chains that produces an all-trans configuration is weakened as the surface density of PDA is decreased. Indeed, as shown in Fig.1, at lower monolayer density the intensity of the CH_3 peaks becomes weaker, a sharp feature at 2850 cm^{-1} corresponding to the CH_2 symmetric stretch grows stronger and a broad background between 2880 and 2920 cm^{-1} , also attributable to CH_2 stretch modes, appears. These results are presumably due to the tilt and kink deformations of the alkyl chains.

We next studied a monolayer of *n,n*-dimethyl-*n*-octadecyl-3-aminopropyltrimethoxysilylchloride (DMOAP) deposited on glass with a surface density of about 50 \AA^2 per molecule. This system is expected to be similar to the low density case of PDA on water. Indeed, the SFG spectrum in Fig.2 (solid curve) is essentially identical to Fig.1c indicating a large degree of disorder in the alkyl chains.

The SFG spectrum for a full monolayer of liquid crystal molecules 4'-*n*-octyl-4-cyanobiphenyl (8CB) on glass, corresponding to a surface density of about 35 \AA^2 per molecule, is presented in Fig.3 (solid curve). Two peaks due to biphenyl C-H stretch modes appear at 3070 and 3050 cm^{-1} . The relative peak heights at 2875 and 2850 cm^{-1} indicate that the 8CB alkyl chains have fewer kinks than the PDA chains at the same surface density. The CH_3 modes of 8CB appear at 2884 and 2946 cm^{-1} , showing a significant shift from those of the PDA monolayer. These higher peak positions are typical of a gas phase and indicate that the 8CB chains have little interaction with each other. This is understandable from the average distance between chains of about 6 \AA and their short length. The SHG measurements determine that the biphenyl group orientation is about

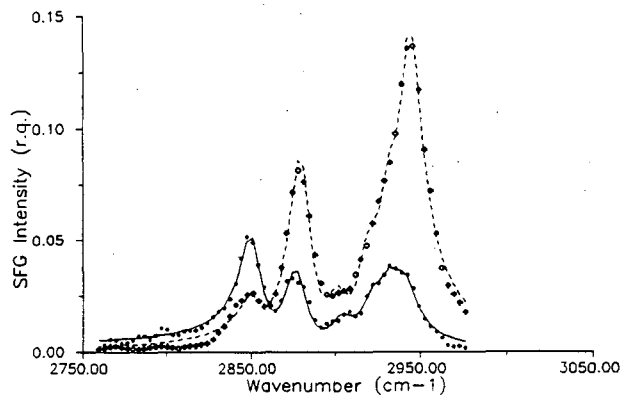


Fig.2 SFG spectrum of DMOAP monolayer (solid curve) is compared to SFG spectrum of same sample after deposition of 8CB (dashed curve).

70° from the surface normal with the alkyl chain end away from the surface.

For an 8CB monolayer on DMOAP coated glass, the DMOAP surface density is the same as described earlier, while the SHG signal calibrates the 8CB coverage to be about 70% of a full monolayer on clean glass. From the increased molecular surface density we expect greater steric hinderance of the chain conformation and stronger interaction between molecules. In Fig.2, we compare the SFG spectra of DMOAP before and after depositing 8CB and observe the 2850 cm⁻¹ oscillator strength drop by 60%. This indicates a decrease in the number of kinks in the DMOAP chain. In Fig.3 we compare the SFG spectra of 8CB on clean glass and on DMOAP coated glass and observe shifts in the C-H stretch frequencies similar to those expected in changing from a gas to a more condensed phase. This is a clear sign of the existing interaction

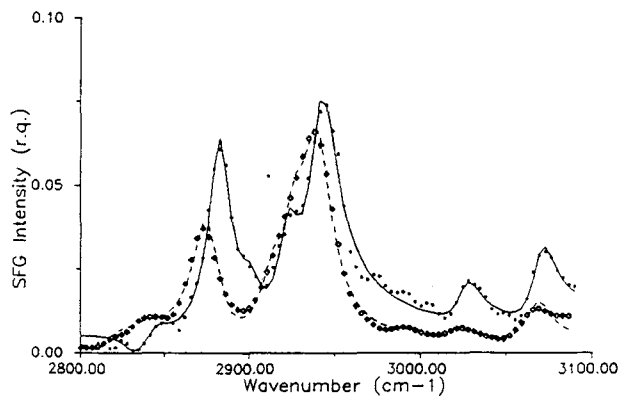


Fig.3 SFG spectrum of 8CB monolayer on clean glass (solid curve) is compared 8CB deposited on DMOAP coated surface (dashed curve).

between the 8CB molecule and the DMOAP alkyl chains.

In conclusion, we have used SFG to study the order in a silane monolayer before and after the deposition of a coadsorbed liquid crystal monolayer. We observe an increase in the order of the chain of the silane molecule induced by the interpenetration of the liquid crystal molecules. By using SHG and SFG, we have studied the orientation and conformation of the liquid crystal molecule on clean and silane coated glass surfaces. On both surfaces, the biphenyl group is tilted by 70° with the alkyl chain end pointing away from the surface. The shift in the C-H stretch frequencies in the coadsorbed system indicates a significant interaction between molecules.

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