Sum-Frequency Vibrational Spectroscopy of a Langmuir Film: Study of Molecular Orientation of a Two-Dimensional System

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Using infrared-visible sum-frequency generation as a probe, we have obtained the vibrational spectrum of a monolayer of pentadecanoic acid on a water surface in the CH stretch region. We have monitored the molecular orientation at different surface densities. It was found that the molecules in the liquid condensed phase have their alkane chains extended and oriented nearly normal to the surface, while in the liquid expanded phase the chains are highly disordered.

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The so-called Langmuir films formed by long-chain molecules spread on water are of great interest to many researchers because of their relevance to cell membranes and molecular electronics.[1] Such systems often exhibit a gas phase at low density, a liquid expanded (LE) phase at intermediate density, and a liquid condensed (LC) phase at high density.[2] The first-order transition between the LE and LC phases is the subject of many recent investigations.[3-6] Traditionally, it was studied by surface tension and potential measurements, but new techniques probing the microscopic features of the transition have recently been developed.[3-5] Optical second-harmonic generation has found that the molecules reorient themselves upon surface compression,[4] but how the long molecular chains are extended, oriented, and aligned in the two phases has not yet been well investigated for lack of experimental tools. In this paper, we show that using our recently developed molecular surface vibrational spectroscopic technique, via infrared-visible sum-frequency generation (SFG) spectroscopy, we could deduce information about the microscopic properties of Langmuir films. This is the first application of surface SFG to the study of a molecular monolayer at an air/liquid interface.

We focused on the system of pentadecanoic acid molecules [PDA, $CH_3(CH_2)_{13}COOH$] on a water surface and found that the alkane chains are bent and disordered in the LE phase but straightened up when the molecules are compressed. As the system changes from the LE to the LC phase, a strong reorientation of the molecules perpendicular to the water surface occurs.

Analogous to second-harmonic generation, SFG is a second-order process, and hence, it is highly surface specific. It has, however, the additional advantage of being able to probe the vibrational spectra of surface monolayers.[7,8] This is achieved by our scanning the infrared (IR) frequency in SFG. A vibrational mode appears in a SFG spectrum if it is both infrared and Raman active. The resonant contribution of the νth mode to the nonlinear polarizability $\alpha_\nu^{(2)}$ for SFG can be expressed in terms of the resonant IR and Raman polarizabilities $\alpha_\nu^{(1)}$ and $\alpha_\nu^{(3)}$ as

$$|\alpha^{(2)}_{\nu,ijk}(\omega_{\rm SF}=\omega_{\rm vis}+\omega_{\rm IR})| = |\alpha^{(1)}_{\nu,kk}(\omega_{\rm IR})|^{1/2}\,|\alpha^{(3)}_{\nu,ijij}(\omega_{\rm SF}=\omega_{\rm vis}+(\omega_{\rm SF}-\omega_{\rm vis}))|^{1/2}. \tag{1}$$

This relation then relates the SFG spectrum to the corresponding infrared and Raman spectra. The overall nonlinearity $\alpha^{(2)}$ is given by

$$\alpha^{(2)}=\alpha^{(2)}_{\rm NR}+\alpha^{(2)}_{\rm R}, \tag{2}$$

where $\alpha^{(2)}_{\rm NR}$ is the nonresonant contribution and $\alpha^{(2)}_{\rm R}=\sum_\nu \alpha_\nu^{(2)}$ is the resonant contribution from all the near-resonant modes.

The surface susceptibility $\chi^{(2)}$ is then obtained from an average over the molecular orientation,

$$\chi^{(2)}_{ijk}=N_s\sum_{i'j'k'}[\alpha^{(2)}_{i'j'k'}\langle\hat{\mathbf{i}}\cdot\hat{\mathbf{i}}'\rangle\langle\hat{\mathbf{j}}\cdot\hat{\mathbf{j}}'\rangle\langle\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}'\rangle], \tag{3}$$

where N_s is the surface molecular density. When the resonant contribution of a particular mode dominates at a certain frequency, measuring the components of the surface nonlinearity allows one to determine the orientational order parameters of that mode. For an in-plane isotropic surface, the nonvanishing components of $\chi^{(2)}$ are

$$\begin{gathered}\chi^{(2)}_{zzz};\ \chi^{(2)}_{xxz}=\chi^{(2)}_{yyz};\\ \chi^{(2)}_{xzx}=\chi^{(2)}_{yzy};\ \chi^{(2)}_{zxx}=\chi^{(2)}_{zyy},\end{gathered} \tag{4}$$

where $\hat{\mathbf{z}}$ is normal to the surface. In the limit when $\omega_{\rm SF}$ and $\omega_{\rm vis}$ are both far from resonance, we have the additional relation $\chi^{(2)}_{xzx}=\chi^{(2)}_{zxx}$. Because the SFG signal is proportional to $|\chi^{(2)}|^2$, the interference of the resonant and the nonresonant parts may distort the spectrum, as in linear reflection spectroscopy or coherent anti-Stokes Raman spectroscopy.

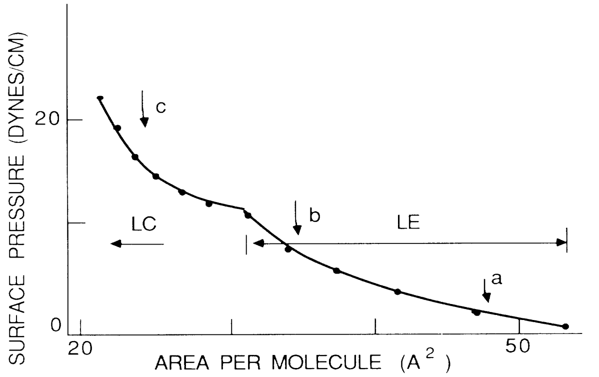

FIG. 1. Surface pressure of a monolayer of PDA on water as a function of area per molecule at $T=28.5\,^\circ\mathrm{C}$.

In the present experiment, a system of a monolayer of PDA on water was prepared by our depositing a measured amount of PDA dissolved in petroleum ether onto a thoroughly cleaned water surface ($p\mathrm{H}=2$), and waiting until the ether had evaporated. The surface pressure of the system was monitored with the Wilhelmy plate method.[2] The surface pressure as a function of area per molecule at 28.5 °C is shown in Fig. 1. For the SFG measurements, we used a visible laser beam at 532 nm and an infrared beam tunable around 3.5 μm. Both were generated by a mode-locked neodymium-doped yttrium-aluminum-garnet laser, the former by second-harmonic generation in potassium dihydrogen phosphate and the latter by parametric amplification in $\mathrm{LiNbO_3}$. The input energies were 1.5 and 0.2 mJ, respectively, in a pulse width of $\simeq 20$ psec. The visible beam was focused on the surface at an angle of 52° and the IR beam at 58° to a common area of $\simeq 0.1\ \mathrm{mm}^2$. At full monolayer coverage of PDA, the peak signal was $\simeq 500$ photons/pulse with a signal-to-noise ratio of $\simeq 10^3$. The IR frequency was calibrated to $\pm 1.5\ \mathrm{cm}^{-1}$ with use of the methane absorption spectrum, and the IR laser linewidth was $\simeq 6\ \mathrm{cm}^{-1}$. We found no surface anisotropy in the SFG, indicating an azimuthal symmetry of the molecular orientation.

We shall first focus on the spectra (Fig. 2) taken with various input polarization combinations at the highly compressed end of the LC phase (point c in Fig. 1). This allows us to identify the CH stretches in the SFG spectra. Only the terminal $\mathrm{CH_3}$ group is expected to contribute strongly; the $\mathrm{CH_2}$ groups distributed along a straight alkane chain have their contribution nearly canceled by one another for inversion symmetry.

The IR and Raman spectra of the methyl group have been extensively studied in bulk alkanes.[9] They consist of a symmetric s stretch at $\simeq 2875\ \mathrm{cm}^{-1}$ corresponding to a change of the dipole moment along the symmetric z axis of the $\mathrm{CH_3}$ group (see Fig. 2), and two nearly degenerate modes, the d_x stretch at $\simeq 2962\ \mathrm{cm}^{-1}$ and the d_y stretch at $\simeq 2954\ \mathrm{cm}^{-1}$, corresponding to changes of the dipole moment in and out of the plane of the alkane chain, respectively. An additional peak at $2935\ \mathrm{cm}^{-1}$ is usually attributed to a Fermi resonance of the s stretch with the overtones of the methyl bending modes.[10] Our spectra in Fig. 2 exhibit the $\mathrm{CH_3}$ stretch peaks in the expected regions except that the one attributed to the Fermi resonance appears to be shifted to $2940\ \mathrm{cm}^{-1}$. This relatively large shift ($\simeq 5\ \mathrm{cm}^{-1}$) is presumably the result of the high sensitivity of the Fermi resonance to the change of the environment (i.e., from bulk to surface). Thus we conclude that the methyl group indeed dominates our spectra. As expected, different input polarizations give very different intensities for the various modes and we can use this feature to determine the orientation of the methyl group. We recognize that the methyl group has an approximate C_{3v} symmetry. Then, for both s and d stretches, there are only two independent components for the nonlinear susceptibility $\alpha_v^{(2)}$ (see Table I). We note that $\alpha_v^{(2)} \propto \partial\alpha^{(1)}/\partial\mathbf{R}_v$, where $\mathbf{R}_v$ is the normal coordinate of the vth mode and $\alpha^{(1)}$ is the linear electronic polarizability. Therefore, using the known angle of 109° between the C–C and C–H bonds, we can relate for the s-stretch mode the two independent components $\alpha_{s,zzz}^{(2)}$ and $\alpha_{s,xxz}^{(2)}$ of $\alpha_s^{(2)}$,

$$\alpha_{s,zzz}^{(2)} = \cot^2(109\,^\circ)\,\alpha_{s,xxz}^{(2)}. \qquad (5)$$

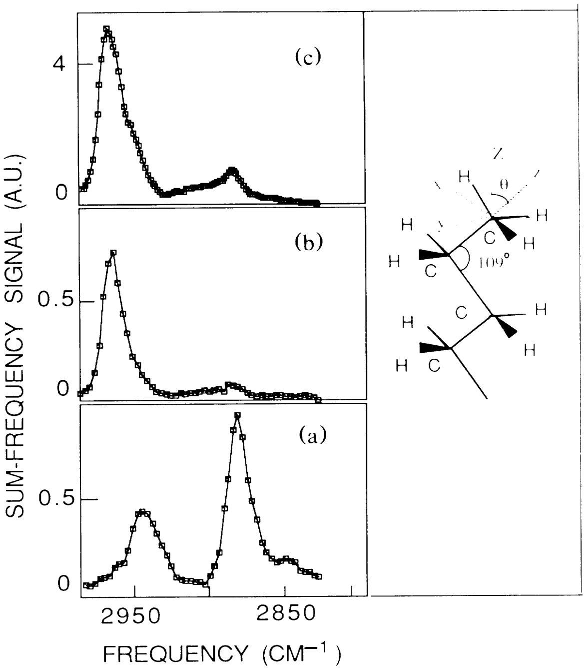

FIG. 2. SFG spectra of PDA at full monolayer coverage with various (vis; IR) polarization combinations. (a) s visible, p IR; (b) p visible, s IR; (c) p visible, p IR. The lines simply connect the experimental data points (squares). Inset: coordinate axes chosen for the methyl group.

TABLE I. Hyperpolarizability components for the various modes of the methyl group.

CH mode	ν (cm^{-1})	IR dipole moment	$\alpha^{(2)}_{\nu,ijk}(\omega_{\mathrm{SF}}=\omega_{\mathrm{vis}}+\omega_{\mathrm{IR}})$
s stretch	2875	z	α_{zzz}; $\alpha_{xxz}=\alpha_{yyz}$
d stretch	2962	x	$\alpha_{xxx}=-\alpha_{yyz}$; $\alpha_{zxx}=\alpha_{xzx}$
d stretch	2954	y	$\alpha_{xyy}=\alpha_{yxy}$; $\alpha_{zyy}=\alpha_{yzy}$

A similar method has been used to calculate the Raman depolarization ratio with reasonable success.[11] Now, with only one independent component in $\alpha_s^{(2)}$, we can easily find the orientation of the methyl group from the ratio of two components of $\chi^{(2)}$. Let θ be the angle between the C-CH$_3$ axis and the surface normal. We can show that

$$\left|\frac{\chi_{yyz}}{\chi_{yzy}}\right| = \left|\frac{\langle\cos^3\theta\rangle + 0.56\langle\sin^2\theta\cos\theta\rangle}{0.44\langle\sin^2\theta\cos\theta\rangle}\right|. \tag{6}$$

Our results in Fig. 2 yield

$$1.5 \lesssim \frac{\langle\cos^3\theta\rangle}{\langle\cos\theta\sin^2\theta\rangle} < 3, \tag{7}$$

corresponding to $39° \gtrsim \theta > 30°$ if we assume a δ function for the orientational distribution.

The above result suggests that for a full monolayer of PDA, on water, the alkane chain of the molecules stands nearly vertically on the surface as this leads to $\theta = 35°$ for the methyl group. The data are also consistent with a chain orientation that has a distribution of tilt between 10° and 0° about the surface normal. Infrared studies have shown that fatty acid on solid substrates have the chain tilted at $(25 \pm 4)°$ [12] or $\theta = (60 \pm 4)°$ for the methyl group. Fatty acid salts, however, were found to be oriented nearly normal to the substrate.[13] In the latter case, LEED studies indicate that the chains are oriented with a dominant tilt angle of 8° from the surface normal.[14] A similar analysis of our spectra could be made for the d stretch. Unfortunately, we could not resolve the d_x and d_y modes. The presence of two independent components of $\alpha_d^{(2)}$ makes an unambiguous interpretation difficult.

We now focus our attention on the spectra with different surface coverages, shown in Fig. 3. In the LC-LE coexistence region ($\simeq$23–31 Å^2/molecule), we observed strong fluctuations of the sum-frequency signal as expected. We therefore studied more specifically the LE phase, taking complete spectra close to the two ends of this phase, namely points a and b in Fig. 1. The most striking result is the appearance of a strong CH$_2$ s-stretch signal at 2850 cm^{-1} as well as a broad background also attributable to the CH$_2$ stretches in the 2930–2880-cm^{-1} range in the spectra. They must arise from a weakening of the selection rules on the CH$_2$ modes along the alkane chain. For a straight chain, near inversion symmetry leads to a near cancellation of the different CH$_2$ contributions. When this symmetry is broken the CH$_2$ modes become observable. The most likely reason for such a symmetry breaking is a *trans-gauche* transformation which effectively would lead to a kink in the hydrocarbon chain. These transformations have been proposed in many theoretical models attempting to explain the LE-LC transition.[15] The decrease of the background and the mode at 2850 cm^{-1} from point a to b then indicate that as the monolayer is compressed, the number of *trans-gauche* transformations is reduced (the chain is straightened up). The intensities of the CH$_2$ structure are related to the *trans-gauche* deformation as follows: For each deformation, there is an unpaired CH$_2$ group created. It is the combined contribution of the number of *trans-gauche* deformations and the average orientation of those groups along the chain that determines the CH$_2$ mode intensity in the spectrum. One could also argue for an increased water-alkane chain interaction. However, in view of the strong hydrophobicity of the alkane such an interaction is unlikely to reduce the chain symmetry significantly. The deformation and the orientational disordering of the chain in the LE phase are expected to lead also to a poorer orientational order of the terminal methyl group. This should show up as a decrease in the intensities of the CH$_3$ peaks as we indeed see in Fig. 3, spectra (a) and (b). Chain disordering has been observed at high temperatures ($\simeq$100 °C) in Langmuir-Blodgett films of fatty acid salts on solid substrates.[16] In contrast to our result, the

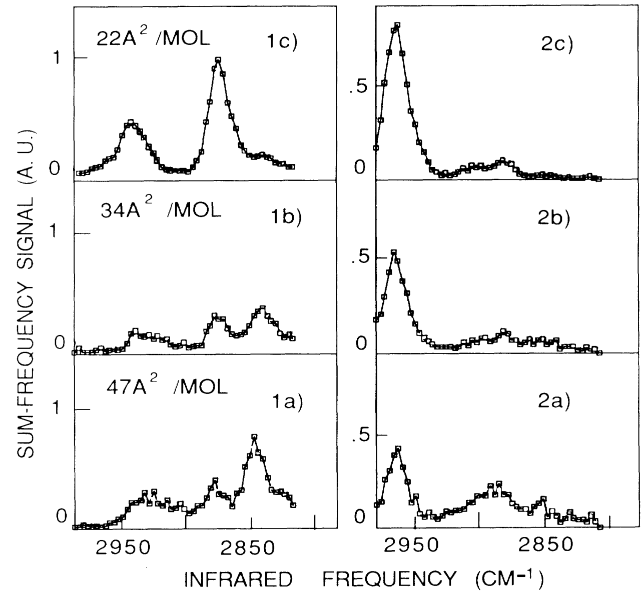

FIG. 3. SFG spectra of PDA at different surface coverages normalized per molecules. (1a)–(1c) were taken with the s-visible, p-IR polarization combination. (2a)–(2c) were taken with p visible, s IR.

higher disordering temperature of those films is probably due to their closer packing (23 Å^2/molecule) which would lead to a stronger steric interaction.

In conclusion, by the use of infrared-visible sum-frequency generation, we have obtained for the first time, with various polarization combinations, vibrational spectra of the CH stretches for PDA Langmuir monolayers on water in their LE and LC phases. From the results we have deduced that in the LC phase the long alkane chains of the PDA molecules are straight and oriented nearly normal to the water surface. In the LE phase, the chains are deformed and orientationally disordered.

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