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NONLINEAR OPTICAL STUDIES OF ORGANIC LIQUID INTERFACES

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Abstract. Infrared-visible sum-frequency generation is the only available technique that can generate surface vibrational spectra for liquid interfaces. Several examples from recent studies in our laboratory are used to show how the surface vibrational spectra can yield useful information about structures of liquid surfaces.

Liquid interfaces are of great importance to many disciplines in science and technology, and have been extensively studied over many decades.¹ However, they are still hardly understood because few existing surface probes are applicable to liquids, although the field abounds with theoretical calculations. The structure of a liquid interface is often most important to researchers as it dictates the physical and chemical properties of the interface. For example, the orientation of surface molecules may directly control the reactivity of a liquid interface, and the surface molecular arrangement may significantly affect the surface tension. Unfortunately, existing techniques that can yield such information about a solid surface are generally not applicable to a liquid interface. They either require a high vacuum environment or do not have sufficient surface sensitivity or specificity.² Recently, second-order nonlinear optical processes have been developed into a most powerful and versatile surface probe.³ Applications of second-harmonic generation to molecular adsorption at liquid interfaces and liquid crystal interfaces have been most successful.⁴ The technique, however, is not capable of generating a surface vibrational spectrum and therefore is limited in its ability to provide information on an interfacial structure. In this respect, the infrared-visible sum-frequency generation (SFG) is much more informative. It can yield surface vibrational spectra with different input/output polarization combinations that allows us the deduction of information about orientations of selected groups of atoms within the surface molecules.⁵ One of the unique applications of SFG spectroscopy is on liquid interfaces since it is the only technique available that can generate a surface vibrational spectrum for a liquid.⁶

As a second-order nonlinear optical effect, SFG is forbidden in media with

inversion symmetry, but necessarily allowed at an interface.³ This makes the process highly surface-specific. In a reflection geometry, the reflected SF signal from an interface is given by

$$S \propto |\tilde{\chi}_s^{(2)}|^2 \quad (1)$$

where $\tilde{\chi}_s^{(2)}$ is a surface nonlinear susceptibility, which can be written as

$$\tilde{\chi}_s^{(2)} = \tilde{\chi}_{s,NR}^{(2)} + \sum_{\alpha} \frac{\bar{A}_{\alpha}}{\omega_{IR} - \omega_{\alpha} + i\Gamma_{\alpha}} \quad (2)$$

with the subindex α denoting the infrared resonant modes. If $\tilde{\chi}_s^{(2)}$ is dominated by the interfacial layer, then the resonant modes in Eq. (2) simply reflect the vibrational resonances of the interfacial molecules. This is often the case when the molecules are polar-ordered. Generally, however, the bulk contribution to $\tilde{\chi}_s^{(2)}$ may not be neglected, and care must be taken to deduce the true surface spectrum from the measured $\tilde{\chi}_s^{(2)}$.⁷

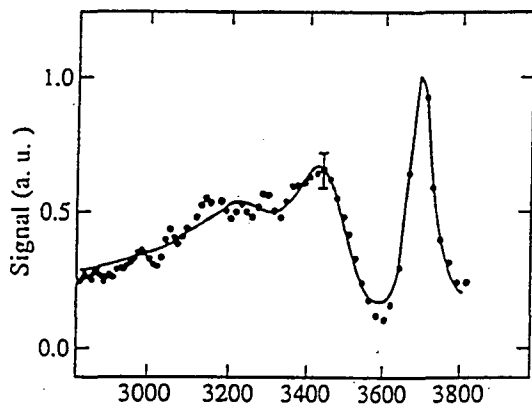


FIGURE 1. SFG spectrum of the pure water/vapor interface at 40°C with the ssp polarization combination. Solid line is a theoretical fit using Eq. (2).

We are interested in using SFG to obtain vibrational spectra of liquid interfaces, in particular, the vapor/liquid interfaces. Figure 1 displaying the ssp (SF output, visible input, and IR input being s-, s-, and p-polarized, respectively) spectrum of the vapor/water interface in the OH stretch region is a representative example.⁸ The sharp peak at 3680 cm⁻¹ can be identified as due to dangling OH bonds of the surface water molecules and the two broad peaks at 3940 and 3920 cm⁻¹ due to hydrogen-bonded OH. The fact that the entire spectrum would change significantly in response to surface

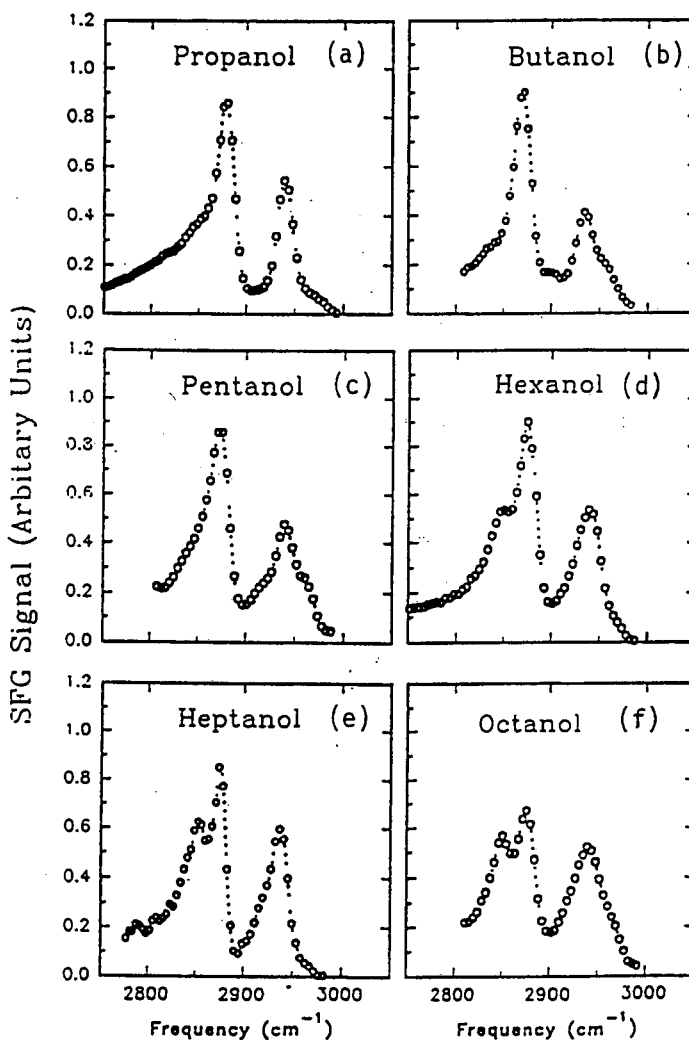
modification is a clear manifestation that it is indeed dominated by the surface structure. This therefore illustrates the surface specificity and sensitivity of the SFG

technique. In contrast, if IR reflection spectroscopy were used for the same system, one would find that the spectrum is completely dominated by the bulk water.

We now discuss some of our recent work using SFG vibrational spectroscopy to probe structures of liquid interfaces. Consider first the vapor/alcohol interfaces.⁹ Being polar and highly anisotropic, the alcohol molecules are expected to be polar-oriented at the interfaces although they must be randomly oriented in the bulk. An earlier experiment on the vapor/methanol interface shows that the methyl group of the molecules should be pointing away from the liquid at the interface.⁶ We are also interested in the conformation of the hydrocarbon chains of the surface molecules. It is known that in bulk liquid, the trans conformation probability per CH₂-CH₂ bond is about 0.7,¹⁰ and therefore the percentage of long-chain alcohol molecules having an all trans configuration must be very low. With the molecules polar-oriented at the interface, the chain conformation could be drastically different. This is indeed the case, as seen from the SFG spectra of the vapor/n-alcohol with (C₃-C₈) in Fig. 2. All spectra are dominated by the

symmetric CH₃ stretch peak at 2875 cm⁻¹ and the peak at 2940 cm⁻¹ due to Fermi resonance between the symmetric stretch and the overtones of the methyl bending modes. For hexanol, heptanol, and octanol, an additional peak at 2850 cm⁻¹ due to the CH₂ symmetric stretch also becomes visible, having its strength

FIGURE 2. SFG spectra in the CH stretching region of the vapor/liquid interfaces of (a) propanol, (b) butanol, (c) pentanol, (d) hexanol, (e) heptanol and (f) octanol, with the ssp polarization combination.



increasing with the chain length.

The spectra in Fig. 2 are characteristic of that of a surface monolayer of hydrocarbon chains.¹¹ They are dominated by the spectral features of the terminal methyl group. If the chain is in the all-trans configuration (i.e., straight with no trans-gauche defects), then by symmetry, we expect that the CH₂ groups on the chain should hardly contribute to the spectra. The weak CH₂ stretch peak observed in the spectra for the longer-chain alcohols therefore indicates the presence of trans-gauche defects in the chains of those molecules. Obviously, the probability of finding such defects is higher for longer chains as one would expect. Nevertheless, it is still much less than what one finds for the same molecules in the bulk liquid. For the shorter-chain alcohols, the surface molecules are essentially defect-free. This suggests that polar-oriented surface alcohol molecules must be well ordered (orientationally) and densely packed so that their alkane chains are nearly in the all-trans conformation as a result of steric chain-chain interaction.

The above picture of an oriented surface molecular layer at the vapor/alcohol interface raises the possibility that the molecules in the surface layer may even be bond-ordered. It is well known that fully-packed long-chain alcohol monolayers on water do possess two-dimensional crystalline phases.¹² Recently, by SFG spectroscopy, water molecules were found to form an ordered hydrogen-bonding network resembling that of ice at the vapor/water interface.⁸ We expect that the oriented alcohol molecules at the vapor/alcohol interface may also form an ordered hydrogen-bonding network much like that of solid alcohol. This appears to be true as we find from SFG that the spectra of the vapor/methanol and vapor/ethanol interfaces in the OH stretch region do resemble those of methanol and ethanol solids.

We now discuss the use of SFG vibrational spectroscopy to study the nature of monolayer phase transitions at vapor/liquid interfaces.¹³ As we mentioned earlier, alcohol monolayers on water can possess two-dimensional crystalline phases. The liquid-solid phase transition has been studied by many researchers. The recent ellipsometry work on a dodecanol monolayer on water concludes that the monolayer film thickness increases by 8 Å upon crystallization presumably because of changes in molecular orientation and conformation.¹² Our SFG surface vibrational spectra of the same system, depicted in Fig. 3, however show that, for both phases, the molecules are in the almost all-trans configuration as the spectra are clearly dominated by the CH₃ peaks with only a weak shoulder at 2840 cm⁻¹ representing the presence of some trans-gauche defects. The polarization dependence of the spectra indicates that, on average, the molecules are oriented nearly along the surface normal. On the other hand, there is a considerable increase in the SF signal strength upon crystallization, which can be

explained by a $\sim 20\%$ increase in the surface density. Thus surface density variation appears to be the main characteristic of the alcohol monolayer transition although there is an appreciable reduction of trans-gauche defects upon crystallization. The misinterpretation of the ellipsometry data is probably due to the use of liquid refractive index for the monolayer film above the transition temperature.¹² There is no reason to believe that an orientationally ordered film should have the same refractive index as the bulk liquid. In fact, the ellipsometry result can be well explained by a constant film thickness with an adjustable refractive index for the liquid phase.¹³

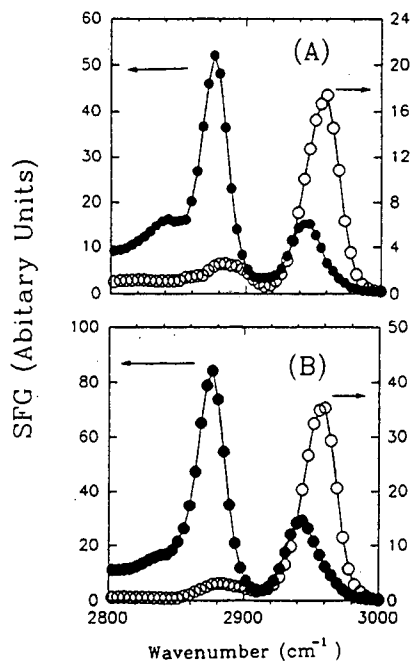


FIGURE 3. SFG spectra of a dodecanol monolayer on water surface at (A) 43°C (liquid phase) and (B) 27°C (crystalline phase). Solid circles are for the ssp polarization combination and open circles are for the sps polarization combination.

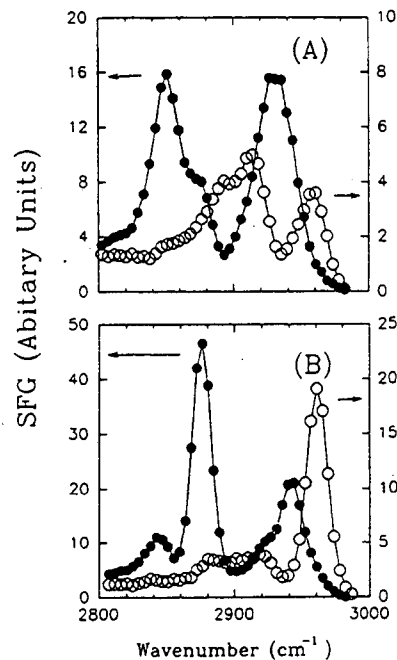


FIGURE 4. SFG spectra of n-eicosane ($nC_{20}H_{42}$) at (A) 40°C (above surface freezing) and (B) 37°C (below surface freezing). Solid circles are for the ssp polarization combination and open circles are for the sps polarization combination.

Surface monolayer phase transition can also occur at the vapor/liquid interface of a pure liquid. This has recently been discovered and studied in long-chain n-alkanes by X-ray reflection and diffraction, surface tension, and ellipsometry,¹⁴ but the nature of the liquid-solid transition is not clear. Again, SFG vibrational spectroscopy can be

used to study the system. Figure 4 describes the spectra of n-eicosane for two different polarization combinations before and after the surface monolayer freezing. For the solid phase, the spectrum is very much like that for the liquid phase of a dodecanol monolayer on water shown in Fig. 3, indicating that the surface eicosane molecules are oriented more or less along the surface normal in the all-trans configuration. Above the surface freezing transition, the spectrum is significantly different. The CH₃ peaks decrease in strength and the CH₂ stretch peaks at ~ 2850 and ~ 2920 cm⁻¹ become prominent, indicating that although the molecules are still more or less oriented vertically at the surface, they now have a significantly larger number of trans-gauche defects. Therefore, in this case, the monolayer transition is mainly characterized by a conformational change in the molecules. One might question how SFG can be an effective surface probe for a system of symmetric molecules like n-alkanes. This is because different parts of the molecules in the surface monolayer experience, in general, different local Fresnel factors. In particular, even if the molecules are in the all-trans configuration, contributions to SFG spectra from the two methyl terminal groups of the molecules do not cancel each other. The total signal strength is expected to be less than that of long-chain molecules with a single methyl terminal like alcohols. This is indeed found to be the case.

In conclusion, we remark that we have only discussed a few examples to illustrate how SFG vibrational spectroscopy is a unique powerful tool for studies of liquid interfaces. There are obviously many other interesting and important problems to be investigated. Among them, to name a few, are vapor/acid solution interfaces for atmospheric chemistry, liquid/electrode interfaces for electrochemistry, and liquid/membrane interfaces for biology.

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