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Nonlinear Optical Spectroscopy for Surface Studies

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Nonlinear Optical Spectroscopy for Surface Studies

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ABSTRACT

Infrared-visible sum-frequency generation as a versatile surface vibrational spectroscopic tool is described. Applications to neat water interfaces and hydrogen adsorption on diamond are used as illustrative examples.

The development of nonlinear optical spectroscopy in the past decades has revolutionized the field of atomic and molecular sciences. One would wonder whether it can also be exploited to stimulate advances in surface science which is a field of great importance to many disciplines. It is clear that the progress of surface science and technology relies heavily on probing and characterization of surfaces and interfaces,¹ and nonlinear optical spectroscopy can certainly enhance our ability to do so. Specifically, when pulsed lasers are used for excitations with an output that is coherent and directional, nonlinear optical spectroscopic techniques possess the advantages of having very high spatial, temporal, and spectral resolutions. They allow *in-situ* remote sensing of a sample surface in a hostile environment, and are capable of probing any interface accessible by light. Surface coherent anti-Stokes Raman scattering (CARS) was first proposed as a possible nonlinear spectroscopic tool for *in-situ* surface studies.² Unfortunately, as a third-order nonlinear process, CARS is allowed by symmetry in all media and, hence, does not have the surface specificity needed for an ideal surface probe. It is then obvious that a second-order nonlinear optical process is more appropriate as a tool for surface studies, because it is forbidden in a medium with inversion symmetry, but necessarily allowed at a surface or interface.³ Indeed, optical sum frequency generation (SFG) has recently been developed into a very powerful and versatile technique for surface spectroscopy.⁴

Optical SFG describes a process in which two input laser beams at frequencies ω_1 and ω_2 interact in a medium and generate an output at the sum frequency $\omega_{\text{out}} = \omega_1 + \omega_2$. For spectroscopic studies, we let ω_1 be tunable. As it is scanned over a resonance, (see Fig. 1), the SF output should experience a resonant enhancement which provides the spectral information. The theory of surface SFG has been worked out in detail elsewhere.^{4,5} Here, we simply point out that measurements of SFG with different input/output polarization combinations often permits the deduction of the various independent nonvanishing elements of the surface nonlinear susceptibility, $\chi_{ijk}^{(2)}$. It is the dispersion of $|\chi_{ijk}^{(2)}(\omega_1)|$ as functions of ω_1 that yields the surface SFG spectra. The signal strength of surface SFG is fairly strong. With 10 - psec, 100 - uJ input pulses focused to an area of 1 mm² on a surface that has a $\chi^{(2)}$ of $\sim 10^{-15}$ esu, the estimated SF output is $\sim 10^5$ photons/pulse, which is readily detectable.

A typical experimental setup is sketched in Fig. 2.⁵ The SF output is highly directional as a consequence of wave vector matching parallel to the surface or interface. Spatial filtering can therefore be used to help discriminate the background noise arising from laser scattering or fluorescence. Either an interference filter or a spectrometer is usually employed to selectively detect the SF output and further improve the signal to background ratio. In the experiments discussed below, SFG is used for surface vibrational spectroscopy, and a tunable infrared laser-like source is needed. This can be

obtained by optical parametric amplification or difference frequency generation in appropriate nonlinear optical crystals. The IR tuning range can be extended from near infrared to $12.5\text{ }\mu\text{m}$ with AgGaS_2 , and to $18\text{ }\mu\text{m}$ with AgGaSe_2 . For even longer wavelengths, a free electron laser can be employed. As a good compromise between reasonable spectral resolution and good output signal strength picosecond, input pulses are best suited for the experiments.

We now discuss a few examples of surface vibrational spectroscopy using SFG that have recently been carried out in our laboratory. The first example is on pure liquid interfaces.^{6,7} In all respects, liquid interfaces are as important as crystalline surfaces, but so far they have hardly been explored for lack of suitable experimental techniques. Recently, using SFG, we have succeeded in obtaining the first vibrational spectra of pure liquid interfaces. Here, we consider the vapor/water interface as an example.⁷ The observed SFG vibrational spectrum from the interface is shown in Fig. 3. The sharp peak at 3680 cm^{-1} can be unequivocally assigned to the free OH stretch mode of water molecules and the broad band at lower frequencies to the hydrogen-bonded OH stretch modes.⁸ Since no water molecules in the bulk can have free OH bonds, the spectrum must come from polar-oriented water molecules at the interface. Energy consideration as well as the observation of only a single free OH peak in the spectrum suggests that the molecules are oriented with one H sticking out of the liquid. An estimate of the signal strength indicates that $\sim 25\%$ of a water monolayer has such orientation. This agrees with the prediction of a simple picture: the surface water molecules form a hydrogen bonding network with the number of hydrogen bonding maximized in a nearly tetrahedral bonding geometry; one fourth of the OH bonds is expected to be free from hydrogen bonding in this configuration. Only the spectrum with the IR input p-polarized and the visible input and SF output s-polarized appears to be easily detectable. This polarization dependence of the SFG spectrum is consistent with a relatively broad orientational distribution of the OH bonds. To make sure that the sharp peak indeed originates from free OH at the vapor/water interface, we have spread a monolayer of long-chain alcohol molecules on water and found that the peak is suppressed due to quenching of the free OH bonds by alcohol adsorption, as shown in Fig. 3.⁷ In this case, we also notice that the bonded OH spectrum becomes sparser and more ice-like. The result indicates that the alcohol monolayer has induced a more ordered structure in the water monolayer underneath. This provides a direct evidence in support of the earlier finding that ice could be nucleated by an adsorbed alcohol monolayer.⁹ The above picture of the vapor/water interface that we have deduced from the SFG spectrum agrees well with the one obtained by several authors using molecular dynamics simulation.¹⁰

As another example, we consider a water/hydrophobic quartz interface where the hydrophobicity comes from coating the quartz surface by a monolayer of octadecyltrichlorosilane (OTS). Knowledge of interfacial water structure near hydrophobic surfaces is crucial for the understanding of many important surface problems involving water. For instance, wetting or non-wetting is a daily phenomenon, but there is not yet a clear physical picture of the phenomenon at the molecular level. Figure 4 presents the SFG vibrational spectrum of the water/OTS/quartz interface. Again we notice the appearance of the sharp peak at 3680 cm^{-1} , corresponding to the presence of free OH bonds at the interface. It has nearly the same strength as that of the vapor/water interface. The result therefore suggests that the water surface structure at a hydrophobic surface is very much like that at the water/vapor interface. In this respect, vapor or air can also be regarded as hydrophobic. Thus at the molecular level, hydrophobicity can be identified by the presence of free OH bonds of water not chemically interacting with the surface of the other medium. Unlike the water/vapor interface, however, the bonded-OH spectrum in Fig. 4 is sharper and more like the one obtained from the alcohol-covered water/vapor interface in Fig. 3. Apparently, the rigid solid wall has forced the surface water layer into a more bond-ordered ice-like structure. This was actually predicted in an earlier calculation.¹¹ Oil/water interfaces are also hydrophobic. We have measured, as an example, the SFG vibrational spectrum of the water/n-hexane interface and found that it is similar to that of the water/vapor interface as expected.

SFG can also be used to study diamond film growth by chemical vapor deposition.¹² As a first step, we monitor H adsorption on diamond surfaces since H termination of the surfaces is believed to be an important intermediate stage in the growth process. Figure 5 shows the SFG spectra of the CH stretch vibration of H/C(111).¹³ Like in the case of H/Si(111),¹⁴ a single sharp peak is observed. The polarization dependence of the spectrum indicates that hydrogen atoms are adsorbed on the top sites of the C(111) surface. From the observed CH vibrational frequency, the CH bond length is estimated to be 1.1 Å. Anharmonicity in the CH vibration can also be measured by SFG. By probing the $v = 1 \rightarrow v = 2$ transition of the vibration in comparison with the $v = 0 \rightarrow v = 1$ transition. The observed anharmonic shift is in good agreement with the calculated value of Zhu and Louie.¹⁵ Preliminary experiments have also been carried out to monitor *in-situ* the molecular species appearing on C(111) when the sample is dosed by methane as well as methane plus hydrogen through a hot filament. Appearance and disappearance of CH_x peaks in the spectra in various circumstances have been observed, indicating that SFG spectroscopy is indeed a powerful means to monitor the variation of surface composition with time.

In short, we have demonstrated that surface SFG can provide some very unique opportunities for surface studies. Many research groups have already employed SFG to attack a host of interesting problems in surface science, including ultrafast surface dynamics.¹⁶ Yet there are still many other exciting new areas that could be probed by SFG. Clearly we are still at the beginning stage of exploration with SFG.

2. ACKNOWLEDGMENTS

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4. FIGURE CAPTIONS

- Fig. 1. Schematic showing the resonant sum-frequency generation process.
- Fig. 2. A typical experimental setup for infrared-visible sum-frequency generation spectroscopy.
- Fig. 3. SFG spectra, with the ssp polarization combination, of the pure water/vapor interface (dashed line) and on water surface covered by a stearyl alcohol monolayer compressed to 10 mN/m (dotted line). The infrared absorption spectrum of ice (solid line) (from E. Whallhey and J. E. Bertie, *J. Chem. Phys.* **46**, 1264 (1967)) is also shown for comparison.
- Fig. 4. SFG spectrum from a quartz/surfactant (OTS)/water interface with the ssp polarization combination.
- Fig. 5. SFG spectra of stretch vibration of a well annealed H-terminated C(111) (1×1) surface, obtained with different polarization combinations: Solid squares for the s (sum-frequency output), s (visible input), p (infrared input) polarization combination, open squares for the pss combination, and open circles for the sps combination.

Fig. 1.

Fig. 2

Fig. 3

Fig. 4

Fig. 5

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