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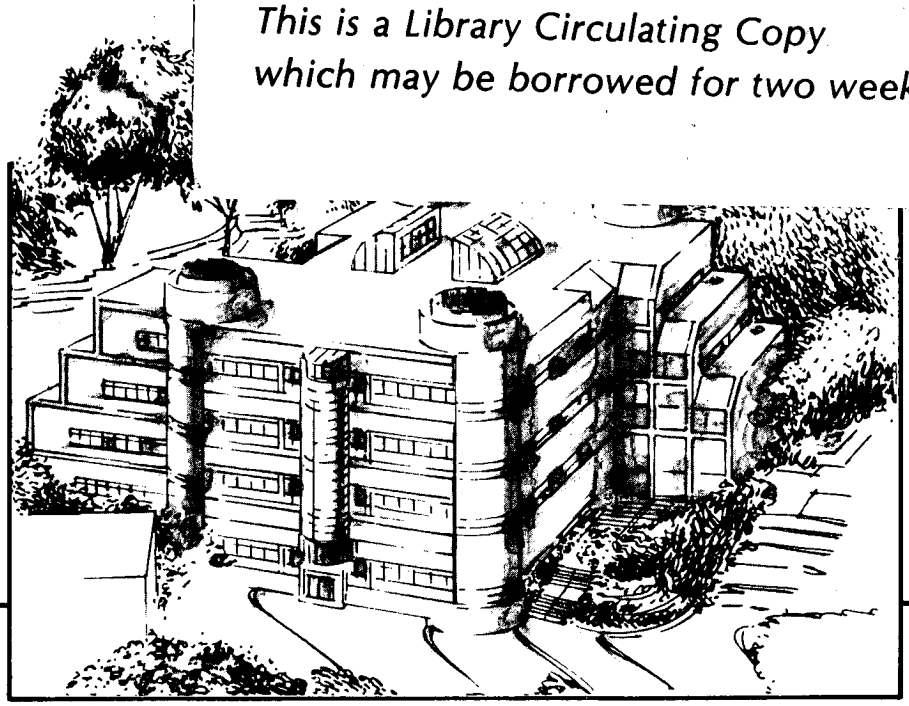

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SUM-FREQUENCY GENERATION FOR SURFACE VIBRATIONAL SPECTROSCOPY

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ABSTRACT

Infrared-visible sum-frequency generation can be used for surface vibrational spectroscopy of molecules adsorbed at various interfaces. The highly surface-specific nature of the technique is demonstrated.

In recent years, optical second harmonic generation (SHG) has been proven to be a useful tool for surface and interface studies.[1] The technique is based on the principle that a second-order optical process is highly surface-specific since it is forbidden in a medium with inversion symmetry but is necessarily allowed on a surface. Compared with conventional surface probes, it has quite a number of unique advantages. In particular, the technique can be employed for in-situ, remote sensing of a surface in a hostile environment, and can be applied to all types of interfaces accessible by light. With the help of ultrashort laser pulses, it can even be used to probe ultrafast surface dynamics and reactions. By scanning the pump laser frequency, spectroscopic studies of surfaces and interfaces by SHG also become possible. Unfortunately, the SH signal from a surface is often weak, so that a photomultiplier is usually required for its detection. This then limits the applicability of the technique to SHG with an output wavelength $\lambda_{2\omega} \lesssim 1$ μm. Therefore, only surface electronic transitions can be probed. The large bandwidths of electronic transitions make selective detection of adsorbed molecular species rather difficult. For the latter purpose, surface vibrational spectroscopy is needed.

We have recently succeeded in developing the IR-visible sum-frequency generation (SFG) technique for surface vibrational spectroscopy.[2] It is a simple extension of SHG; instead of the two input frequencies ω_1 and ω_2 being the same, we now have $\omega_1 \neq \omega_2$ (Fig. 1). One is tunable in the infrared and the other is in the visible, resulting in an output also in the visible. Scanning of the infrared

frequency then allows us to probe vibrational resonances by SFG. Like SHG, SFG is surface-specific and sensitive.

As seen in Fig. 1, the resonant SFG can be considered as a combined process of infrared and Raman excitations between the ground and excited states. Thus the resonances to be probed must be both infrared and Raman active. The SFG output is given by

$$S \propto |\chi_s^{(2)}(\omega_1 + \omega_2)|^2 \tag{1}$$

where the surface nonlinear susceptibility $\chi_s^{(2)}$ can be explicitly written as

$$\overleftrightarrow{\chi}_s^{(2)} = \overleftrightarrow{\chi}_{s,nr}^{(2)} + \sum_i \frac{\overleftrightarrow{A}_i}{(\omega_1 - \omega_i + i\Gamma_i)} . \tag{2}$$

Here, $\overleftrightarrow{\chi}_{s,nr}^{(2)}$ is the nonresonant part of $\overleftrightarrow{\chi}_s^{(2)}$, and $\overleftrightarrow{A}_i$, ω_i, and Γ_i are the strength, frequency, and damping coefficients of the ith resonance, respectively. The expression in Eq. (2) resembles that for coherent antiStokes Raman scattering (CARS).[3] One should therefore expect that SFG has the same general spectral shapes as CARS. For molecules adsorbed on a substrate, $\overleftrightarrow{\chi}_{s,nr}^{(2)}$ has, in general, contributions from both the molecules and the substrate. In cases where the substrate contribution dominates, the relative sign between $\overleftrightarrow{\chi}_{s,nr}^{(2)}$ and $\overleftrightarrow{\chi}_{s,r}^{(2)}$ (from molecules) is a direct indication of the polarity of the molecules with respect to the substrate.

Demonstrative experiments of SFG surface spectroscopy have been carried out in the 10 μm and 3 μm regions.[2] In the latter case, picosecond tunable infrared pulses can be generated by optical parametric amplification in $LiNbO_3$ crystals pumped by picosecond Nd:YAG laser pulses at 1.06 μm. The same laser can provide picosecond green pulses at 0.53 μm from a frequency doubler. The infrared and green pulses are then overlapped on the surface to be investigated and the resultant SF output is generated in the directions specified by the wavevector relation $\vec{k}_{1,\parallel} + \vec{k}_{2,\parallel} = \vec{k}_{sf,\parallel}$, where the subscript $\parallel$ denotes wavevector components parallel to the surface. After proper filtering, the SF output is detected by a photomultiplier connected to a gated integrator. With such a setup, the spectrum of allowed CH stretch vibrations of a polar-oriented molecular monolayer in the neighborhood

of 3 μm can be readily detected.

To show the potential of this new spectroscopic technique,[3-6] we consider here, as an example, the application of the technique to monolayers of surfactant molecules adsorbed at liquid/solid interfaces.[4] Figure 2 describes the SFG spectra of three systems: (1) a hexadecane/fused silica interface, (2) a monolayer of octadecyltrichlorosilane (OTS) molecules adsorbed at a hexadecane/fused silica interface, and (3) a monolayer of OTS adsorbed at a $CC\ell_4$/fused silica interface. In the first case, no identifiable spectral feature is present even though in linear IR spectroscopy, one would expect strong peaks in this region arising from the many CH stretch vibrations on hexadecane. Here, the overall contribution of the CH stretches in the SFG spectrum vanishes because the hexadecane molecules are randomly oriented in the liquid phase. The spectra of cases (2) and (3) are nearly identical, both being the spectra of an ordered monolayer of OTS. The results clearly demonstrate the surface specificity of the technique.

By comparison with the Raman spectrum of OTS in solution, the three peaks in the spectra of Fig. 2 can be assigned to the CH_3 symmetric stretch (2875 cm^{-1}), the asymmetric stretch (2964 cm^{-1}), and the Fermi resonance between the s-stretch and the overtone of the CH bending mode (2942 cm^{-1}). These spectra resemble those of other long-chain molecules, such as pentadecanoic acid, on water in a full monolayer form.[5] They indicate that the OTS molecules have their long alkane chains straightened and aligned normal to the interfaces.

Different input-output polarization combinations can lead to SFG spectra with very different relative peak strengths. This suggests that the spectra can be used to deduce information about the orientation of the adsorbed molecules.[5] An example is shown in Fig. 3 for OTS monolayers at $CC\ell_4$/silica and CH_3OH/silica interfaces.[4] The strengths of the three peaks of OTS are clearly different for different polarization combinations. From the ratio of the s-stretch intensities of the (s_{vis}, p_{IR}) and (p_{vis}, s_{IR}) polarization combinations in Fig. 3(2) and 3(3), we can calculate the average tilt angle θ between the symmetry axis of the CH_3 terminal group and the surface normal. We

find $50° < \theta < 40°$, indicating that the alkane chain is inclined at no more than 15° from the surface normal. This is consistent with the usual picture that the chain is along the surface normal; the apparent larger tilt obtained here is presumably due to roughness of the silica surface.

Figure 3b also exhibits an additional peak at 2834 cm^{-1}, which can be identified as the CH_3 s-stretch mode of methanol. Since no SF signal should be expected from the bulk methanol as suggested by the experiment on hexadecane mentioned earlier, we must attribute this peak to the methanol adsorbates at the interface. It suggests that some methanol molecules must have adsorbed at the interface with some degree of polar ordering. The relative strength of the CH_3 s-stretch mode of OTS in Fig. 3(2b) and 3(3b) however indicates that the OTS orientation at the interface is not affected by the presence of methanol.

From the above examples, it is clear that SFG surface spectroscopy has an enormous potential for surface studies. The technique is also capable of subpicosecond time resolution. It can therefore be used for research on ultrafast surface dynamics and reactions with selective detection of molecules. This opens the door to many interesting research opportunities in many branches of surface science. The future is only limited by one's imagination.

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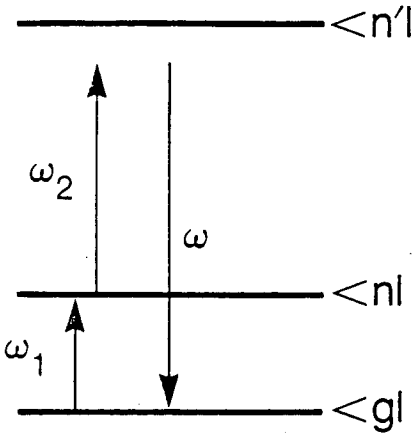

Fig. 1 Schematic of a sum-frequency generation process in which ω_1 is a tunable IR frequence near resonance.

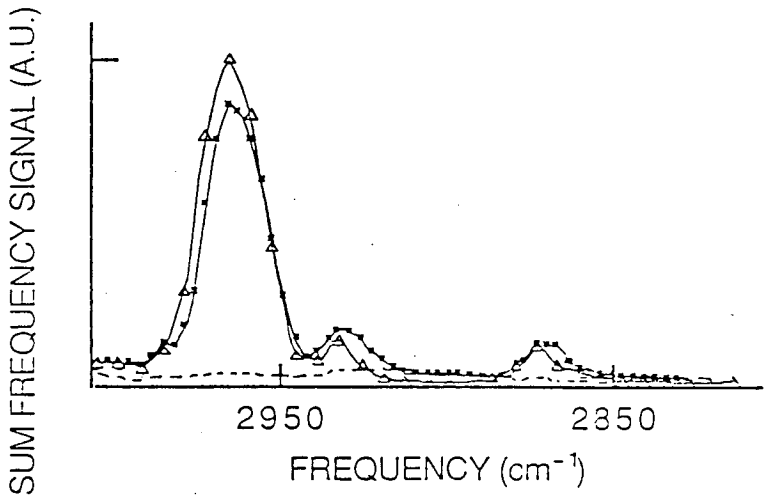

Fig. 2 SFG spectra at three different interfaces in the (p_{vis}, p_{IR}) polarization combination. Dashes: hexadecane/silica interface. Solid squares: OTS at $CC\ell_4$/silica interface. Triangles: OTS at hexadecane/silica interface.

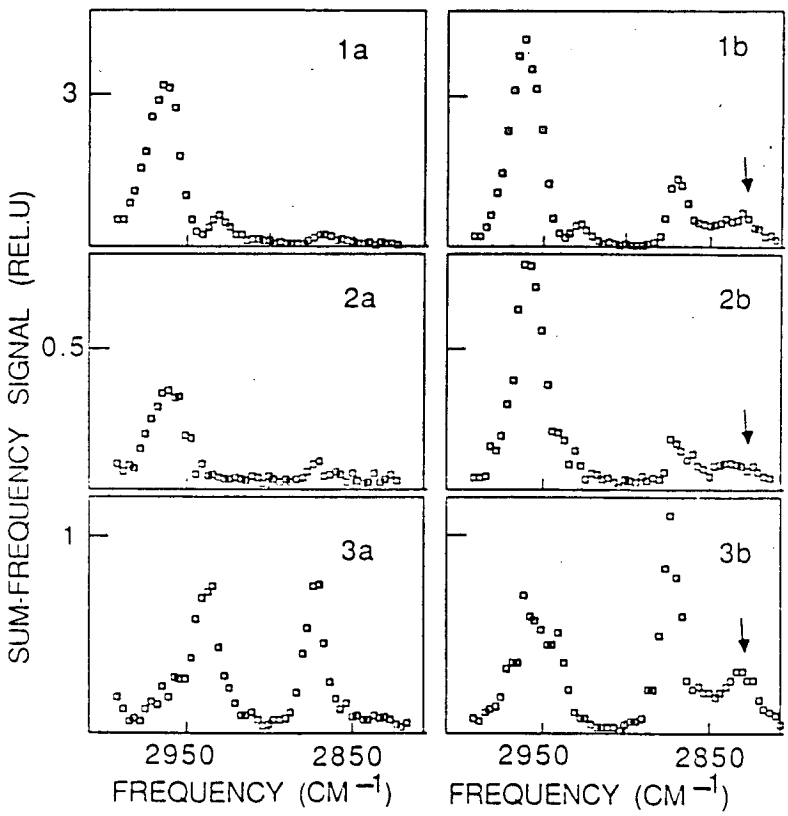

Fig. 3 SFG spectra at (a) the $CC\ell_4$/OTS/silica interface and (b) the CH_3OH/OTS/silica interface. The different panels refer to different polarization combinations: (1) (p_{vis}, p_{IR}); (2) (p_{vis}, s_{IR}); (3) (s_{vis}, p_{IR}). The arrows in (b) indicate the methyl s-stretch mode of the adsorbed methanol molecules.

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