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Publication Date

1987-12-01

Center for Advanced Materials

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Submitted to Surface Science Letters

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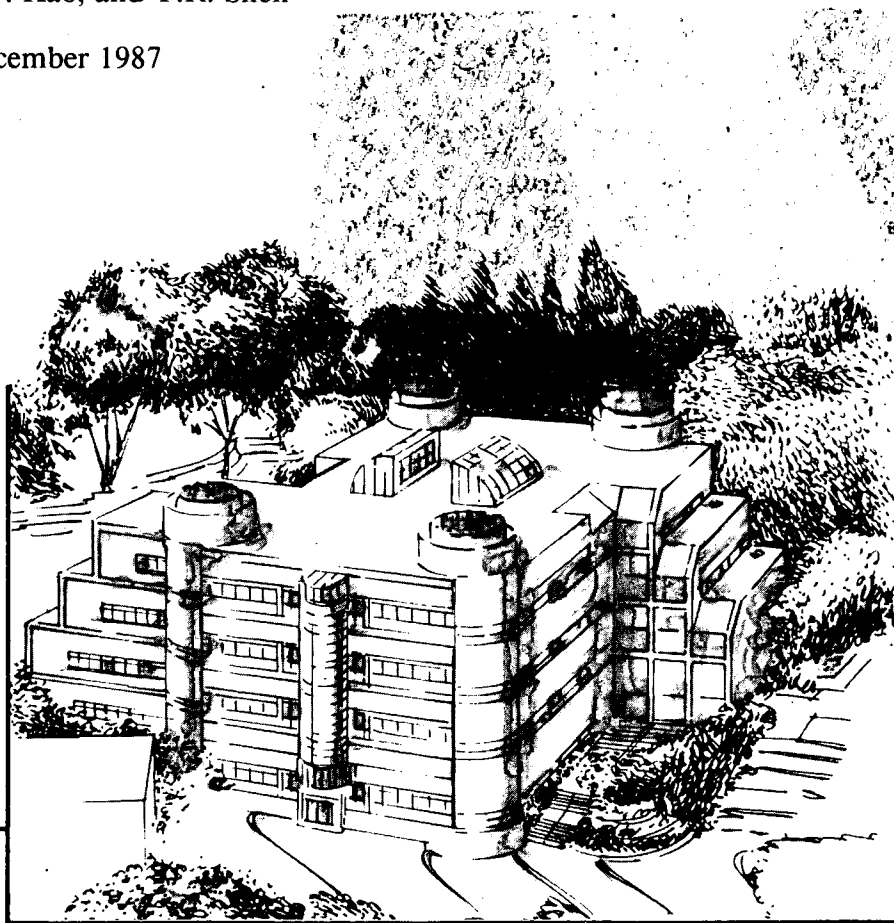
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SURFACE VIBRATIONAL SPECTROSCOPY OF MOLECULAR ADSORBATES ON METALS AND SEMICONDUCTORS BY INFRARED-VISIBLE SUM-FREQUENCY GENERATION

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ABSTRACT

We demonstrate the applicability of surface vibrational spectroscopy using infrared-visible sum-frequency generation to molecules adsorbed on metals and semiconductors. The spectra of CH stretches of octadecyltrichlorosilane on silicon and aluminum and ethylidyne on Rh(111) are presented as examples.

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Surface vibrational spectroscopy is of central importance for surface studies [1]. Most of the existing spectroscopic techniques, unfortunately, have serious limitations. Recently, we have developed a new versatile surface spectroscopic tool, infrared-visible sum-frequency generation (SFG) [2-5], that has a number of clear advantages over the existing techniques. Like optical second harmonic generation [6], SFG is highly surface-specific, and is applicable to all interfaces accessible by light. With the help of ultrashort pump pulses, it has the potential of monitoring in-situ surface dynamics, surface reactions, and intermediate transient species with picosecond time resolution. In several recent publications, we have successfully demonstrated the possibility of using SFG to obtain vibrational spectra of monolayers of molecules adsorbed at air/liquid [4], air/glass [2,3], and liquid/glass [5] interfaces. However, to many researchers, studies of molecules adsorbed on metals and semiconductors are far more interesting because of their relevance to surface catalysis and surface preparation of electronic devices. Therefore, we have also tried the technique on metals and semiconductors. In this paper, we report the preliminary results of our measurements, showing the applicability of surface SFG spectroscopy to metals and semiconductors.

The SFG signal obtained by reflection from an interface is given by

$$S = 128\pi^3(\omega_{SF}/\hbar c^3)|\hat{\epsilon}_{SF}\chi^{(2)}:\hat{\epsilon}_{ir}\hat{\epsilon}_{sf}|^2 I_V I_{ir} A T \frac{\text{photons}}{\text{pulse}}, \quad (1)$$

where $\hat{\epsilon}_i = \hat{\epsilon}_i L_i$, $\hat{\epsilon}$ is the field polarization unit vector, L_i 's are the geometric Fresnel factors, I 's are the pump laser intensities, A is the beam overlapping cross-section, T is the laser pulsewidth overlap, and

the subscripts sf, v, and ir refer to sum-frequency, visible, and infrared, respectively. The surface nonlinear susceptibility $\chi^{(2)}$ that characterizes the surface SFG process is in general composed of a resonant and a nonresonant part

$$\chi^{(2)} = \chi_{NR}^{(2)} + \chi_R^{(2)}. \quad (2)$$

In the case of surface vibrational studies of molecules on metals and semiconductors, $\chi_R^{(2)}$ comes from vibrational resonances of the molecules. Assuming Lorentzian lineshapes for the resonances, we have

$$\chi^{(2)} = \sum_{\sigma} \frac{\vec{A}_{\sigma}}{(\omega_{IR} - \omega_{\sigma} + i\Gamma_{\sigma})}, \quad (3)$$

where σ refers to the various near-resonant modes, each specified by \vec{A}_{σ} , ω_{σ} , and Γ_{σ} . The nonresonant part of $\chi^{(2)}$ can generally be written as

$$\chi_{NR}^{(2)} = \chi_{sub}^{(2)} + \chi_{mol}^{(2)} + \chi_{s-m}^{(2)},$$

in which sub, mol, and s-m denote contributions from the substrate, molecule, and substrate-molecule interaction, respectively. For metal and semiconductor substrates, $\chi_{NR}^{(2)}$ is often dominated by $\chi_{sub}^{(2)}$, although $\chi_{s-m}^{(2)}$ could also be significant. The surface of a metal or semiconductor is known to be highly nonlinear [7,8]. Thus $\chi_{NR}^{(2)}$ is large and contributes to a strong nonresonant background in the SFG spectrum. Since $\chi^{(2)}$'s are in general complex quantities, the nonresonant background may distort the resonant peaks in a complicated

way. This is different from the case of SFG spectroscopy of molecules on glass or water where the substrate susceptibilities are small and real.

Another characteristic feature of SFG on metals and semiconductors is the much weaker Fresnel factors for field polarization parallel to the surface. This is particularly true for frequencies far below the plasma resonance. Thus, with sufficiently large angles of incidence, the $\chi_{ZZZ}^{(2)}$ component appears to dominate in the SFG process, where \hat{z} is parallel to the surface normal. Being opaque to the pump laser beams, metal or semiconductor substrates also have lower damage thresholds than transparent solids due to laser heating. As a result, the SF signal is usually limited to a relatively low level by the low damage threshold.

For obtaining the spectra of octadecyltrichlorosilane (OTS) on glass, we have taken advantage of an internal reflection geometry where the infrared, visible, and sum-frequency beam angles are above the critical angle of the glass-air interface. A calculation of the relevant Fresnel factors (for the case where the infrared and visible beams are p-polarized) shows that the $\chi_{ZZZ}^{(2)}$ component will have the dominant contribution. Therefore this experimental geometry on glass probes the same component of $\chi^{(2)}$ as the experiment on metals and semiconductors.

Our experimental setup of IR-visible sum-frequency spectroscopy has been described elsewhere [3]. The visible pump pulses were fixed at 0.532 μm while the IR pump pulses were tunable around 3.4 μm . Both pulses have a pulsewidth of ~ 30 ps. For demonstration of the applicability of SF spectroscopy to metals and semiconductors we chose

to study first OTS monolayers deposited on silicon and freshly evaporated aluminum films. The samples were prepared through a self-assembly technique reported by Sagiv [9,10]. The silane monolayers produced by this technique typically have surface densities of approximately 25 \AA^2 per molecule with the molecular chain oriented essentially perpendicular to the surface.

We were interested in observing the C-H stretching vibrations of OTS in the 3 \mu m range. In spite of the low laser damage thresholds, we were able to obtain the spectra without difficulty. They are shown in Fig. 1 together with the spectra of OTS on glass. For better signal-to-noise ratio, all beams were p-polarized. The spectrum for OTS on silicon was recorded with pulse energies of 60 \mu j at 0.532 \mu m and 100 \mu j of the infrared, focused to a spot of 250 \mu m diameter on the surface. The pulsed energies were below the measured damage limit of 400 \mu j at 0.532 \mu m . The damage threshold of the infrared is much higher. In comparison, the damage threshold of our aluminum sample was considerably lower, approximately 15 \mu j at 0.532 \mu m . We obtained the spectra of OTS on aluminum with pulse energies just below the damage threshold by translating the sample by $.5 \text{ mm}$ every 500 laser shots. With a detection efficiency of about 1%, we estimate the signal level at the peak to be about 50 photons/pulse in both cases. The spectrum of OTS on glass was recorded with pulse energies of 1 m j at 0.532 \mu and 100 \mu J of the infrared. The signal at the peak was about 1500 photons/pulse.

The three spectra in Fig. 1 show the expected larger background to peak ratio for the OTS on Si and Al substrates in comparison to OTS on glass. The spectra all have in common three peaks which are

characteristic of the OTS methyl group [3,11,12]. They are the symmetric s-stretch at $\sim 2870 \text{ cm}^{-1}$, the nearly degenerate asymmetric stretches at $\sim 2965 \text{ cm}^{-1}$ and the Fermi resonance of the s-stretch at $\sim 2935 \text{ cm}^{-1}$. The difference in the relative peak heights between the three spectra might be due to different chain orientation or due to the different nonresonant substrate susceptibilities which can alter the relative peak heights as well as shift peaks and distort lineshapes. Further studies will be necessary to separate these and other effects.

We have also used SFG to obtain the vibrational spectrum of CH stretches of ethylidyne on a single crystal of Rh(111). This system is interesting because Rhodium is a versatile catalyst for hydrocarbon reactions. The sample was prepared in an ultrahigh vacuum chamber. The clean Rh(111) surface at 300°K was exposed to C_2H_4 and NO to produce an ordered monolayer of ethylidyne (C-CH_3) with approximately one CH_3 group per 25 \AA^2 [13,14]. The resulting system was highly stable even under atmospheric conditions. Thus, the sample could be transferred from the vacuum into a simple cell for easy insertion into our SFG setup. The cell was filled with N_2 in order to avoid possible detrimental effects of the real atmosphere.

To obtain the C-H vibrational spectrum from the sample by SFG, we used the same experimental arrangement described earlier except that the visible pulse energy was increased to $150 \text{ }\mu\text{J}$, which is still below the damage threshold of $\sim 200 \text{ }\mu\text{J}$ for Rh(111). Two recorded spectra are shown in Fig. 2. The first run was taken from a spot on the surface that had been irradiated by the visible laser beam for more than 4 hours. The second run was taken from a spot that had not been irradiated. No significant difference between the two spectra could be

identified. This shows that SFG can be used to obtain reproducible spectra even from a chemically active surface over the course of several hours, and suggests that nondestructive in-situ monitoring of surface chemical reactions using SFG on a picosecond time scale is possible.

The spectra in Fig. 2 show a strong nonresonant background (due to the metal substrate) and several resonant peaks. A fit using Eqs. (2) and (3) for $\chi^{(2)}$ in Eq. (1) allows us to determine the vibrational resonances. Attempts at fitting the spectra with three peaks were not successful. If we assume four peaks, the vibrational resonances are 2863, 2905, 2956, and 3035 cm^{-1} . While the 2863 peak can be assigned to the ethylidyne symmetric stretch [15], the other peaks possibly include contributions from C-H and C_2H surface species [16] and assignment of these peaks should await a more thorough study.

In conclusion, we have shown that surface vibrational spectroscopy using IR-visible SFG is indeed applicable to molecules adsorbed on metals and semiconductors. The signal-to-noise ratio in the present experiment was not optimized. By choosing a proper beam geometry, we can anticipate an improvement of one order of magnitude in our SF signal. This should make the technique extremely attractive for future dynamic studies of selective molecules adsorbed on metals and semiconductors.

We acknowledge several helpful discussions with Prof. G. A. Somorjai. PGS acknowledges support from the Delegation Generale de l'Armement; CTK gratefully acknowledges a B.P.-America Fellowship; RS acknowledges financial support from 3M. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences,

Materials Sciences Division of the U.S. Department of Energy under
Contract No. DE-AC03-76SF00098.

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Table 1. Parameters for fit of Eq. (1) to ethylidyne spectrum.

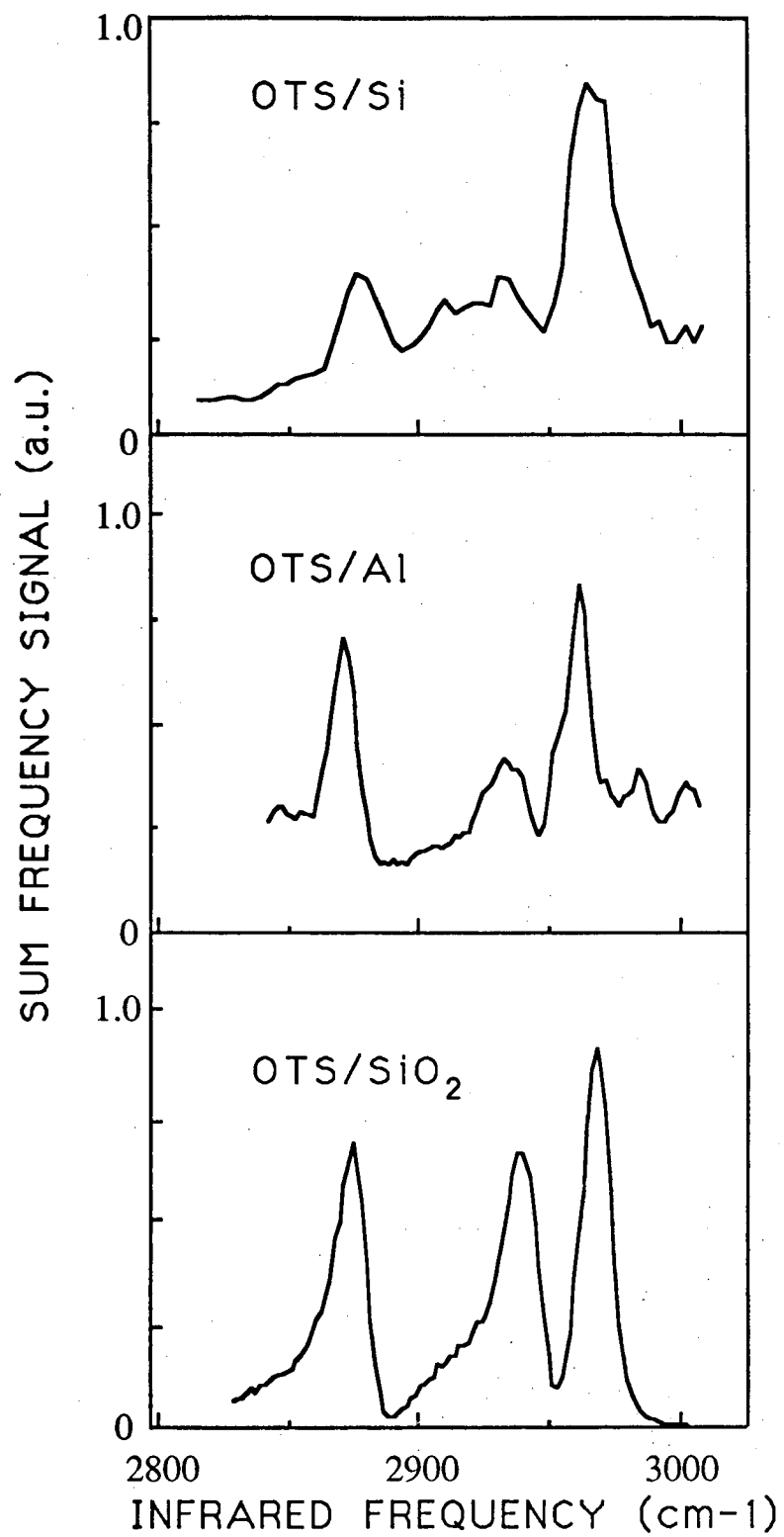
σ	A_{σ} (a.u.)	ω_{σ} (cm ⁻¹)	Γ_{σ} (cm ⁻¹)
1	19.5	2863	35
2	1.8	2905	5
3	.7	2956	1.5
4	26.4	3035	60

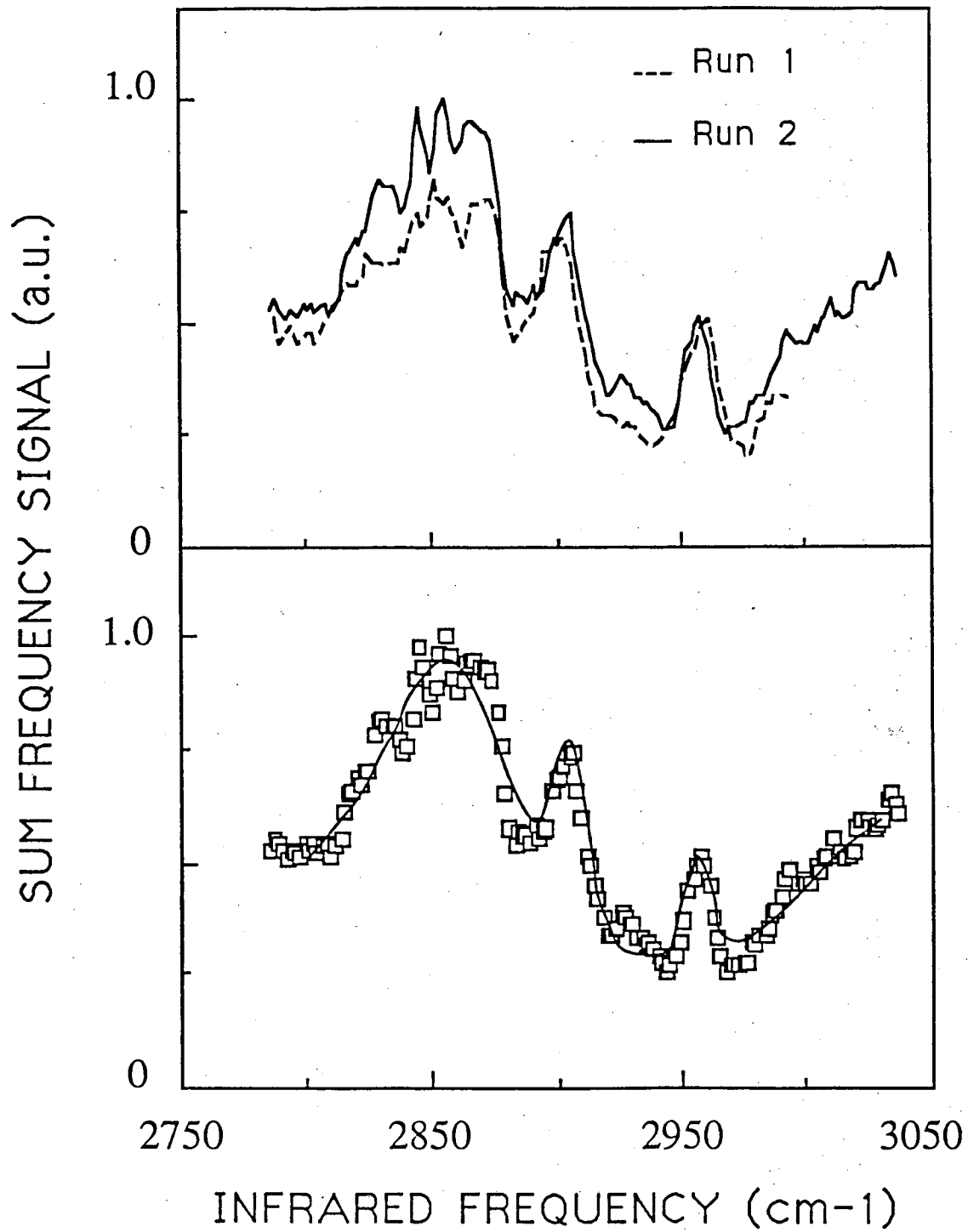
XNR = .29 + .29i

Figure Captions

Fig. 1 Sum-frequency spectra of OTS on silicon, OTS on freshly evaporated aluminum and OTS on glass, as described in the text.

Fig. 2 Sum-frequency spectra of ethylidyne on Rh(111). Top) comparison of two separate scans, run 1 - after 4 hrs of laser irradiation, run 2 - a fresh spot. Bottom) run 2 with fit to Eq. (1).





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