Center for Advanced Materials

CAM**REPORT**

Presented at the Eighth International Conference
on Laser Spectroscopy, Åre, Sweden, June 22-26, 1987

**SECOND-HARMONIC AND SUM-FREQUENCY GENERATION
FOR SURFACE STUDIES**

J.H. Hunt, P. Guyot-Sionnest and Y.R. Shen

July 1987

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory • University of California

ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISTRIBUTION STATEMENT OF THIS REPORT

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California and shall not be used for advertising or product endorsement purposes.

Lawrence Berkeley Laboratory is an equal opportunity employer.

Second-Harmonic and Sum-Frequency Generation for Surface Studies

J. H. Hunt, P. Guyot-Sionnest and Y. R. Shen

LBL--23676

DE87 014081

Department of Physics, University of California, Berkeley, and
Center for Advanced Materials, Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720 USA

Second harmonic generation (SHG) has now been well established as a versatile surface-sensitive probe [1]. It has been used to study electrochemical processes at electrode surfaces, molecular adsorption and desorption at metal and semiconductor surfaces, orientational phase transition of molecular monolayers on water, surface reconstruction and epitaxial growth, and so on. More recently, it has been employed as a tool to monitor monolayer polymerization and other surface reactions [2], to probe polar order of molecules at interfaces [3], and to measure molecular nonlinearity [4]. While most surface techniques are restricted to the solid/vacuum environment, SHG is applicable to nearly all interfaces as long as the interfaces are accessible by light. In addition, SHG has the advantages of being capable of in-situ measurements with high temporal, spatial, and spectral resolutions.

The source responsible for the SHG is the nonlinear polarization $\vec{P}^{(2)}(2\omega)$ in the medium.

$$\vec{P}^{(2)}(2\omega) = \vec{\chi}^{(2)}(2\omega) : \vec{E}(\omega) \vec{E}^*(\omega). \quad (1)$$

If the medium has an inversion symmetry, then the nonlinear susceptibility $\vec{\chi}^{(2)}$ vanishes in the electric-dipole approximation. Since the inversion symmetry is necessarily broken at an interface, this makes SHG an effective surface probe. For a monolayer of molecules at a surface, the surface nonlinear susceptibility is typically $\sim 10^{-15}$ esu, which should yield an SH signal of $\sim 10^3$ photons/pulse with a laser pulse of 10 mJ energy and 10 nsec duration impinging on a surface area of 0.2 cm².

The resonant behavior of $\vec{\chi}^{(2)}(2\omega)$ can provide spectroscopic information about a surface or molecules adsorbed at the surface. This has been demonstrated in a number of cases [5]. However, since the optical wavelengths involved in the surface SHG experiments are generally in the 0.2-1 μ m range, only electronic transitions of the molecules or surface structure can be probed. They usually have relatively broad bandwidths, making SHG not particularly useful for identification or selective monitoring of surface molecular species. Vibrational spectroscopy is more suitable for selective studies of adsorbed molecules and their interaction with the substrate. Unfortunately, vibrational modes appear in the IR range, and SHG in this part of the spectrum is not practical because of the poor sensitivity of the photodetectors. This problem can be solved by using instead of SHG, the IR-visible sum-frequency generation (SFG) [6].

In the SFG process, the IR input beam is tuned through the vibrational resonances, and the visible input beam up-converts the excitation to a sum-frequency output also in the visible, which can then be detected by photomultipliers. As a second-order process, SFG has nearly all the

MASTER

Handwritten signature

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

advantages of SHG for surface probing, but in addition, it allows the studies of surface resonant excitations in the IR. The nonlinear susceptibility responsible for the SFG can be written as

$$\chi^{(2)}(\omega_s = \omega_{vis} + \omega_{IR}) = N_s \langle \alpha^{(2)}(\omega_s) \rangle, \quad (2)$$

assuming that the local-field correction is negligible, where N_s is the surface density of molecular adsorbates, $\alpha^{(2)}$ is the nonlinear polarizability, and $\langle \rangle$ denotes an average over the molecular orientational distribution. In general, $\alpha^{(2)}$ consists of a resonant and a nonresonant part.

$$\alpha^{(2)} = \alpha_R^{(2)} + \alpha_{NR}^{(2)} \quad (3)$$

with $\alpha_R^{(2)} = \sum_v \alpha_{RV}^{(2)}$, where v indicates the v th mode near resonance. It can be shown from the microscopic expressions that

$$[\alpha_{RV}^{(2)}(\omega_s)]_{ijk} = [\alpha_{RV}^{(1)}(\omega_{IR})]_{kk} [\alpha_{RV}^{(3)}(\omega_s = \omega_{vis} + \omega_s - \omega_{vis})]_{ijij}, \quad (4)$$

where $\alpha_{RV}^{(1)}$ and $\alpha_{RV}^{(3)}$ are resonant IR and Raman polarizabilities, respectively. This points to the fact that only modes which are both IR and Raman active can contribute to the SFG spectrum [6].

As a demonstration of SFG as a surface vibrational spectroscopic tool, we have measured the C-H vibrational spectra of alcohol, methanol, and isopropanol evaporated on glass in the 3.3 to 3.5 μ m wavelength range. A mode-locked Nd:YAG laser was used to generate a visible beam at 0.532 μ m by SHG in KDP and a tunable IR beam around 3.4 μ m by parametric amplification in LiNbO₃ [6]. The beam energies were 1.5 mJ and 0.2 mJ per pulse, respectively. With the two beams simultaneously impinging on the glass surface, SFG could be detected after proper spatial and spectral filtering. Figure 1 displays the SFG spectra of the three adsorbed molecular species together with their Raman spectra from the bulk liquid [7]. The close agreement between the Raman and the SFG spectra allows us to assign unambiguously the observed peaks in the SFG spectra.

In Fig. 1(a) for methanol CH₃OH on glass, two peaks at 2840 cm⁻¹ and at 2960 cm⁻¹ correspond to the CH₃ symmetric and asymmetric stretch vibrations, respectively. In Fig. 1(b) for ethylene glycol, C₂H₄(OH)₂, the symmetric and asymmetric CH₂ stretches appear at 2875 and 2935 cm⁻¹, respectively. Finally, for isopropyl alcohol, (CH₃)₂CHOH, we assign the peak at 2885 cm⁻¹ as the CH₃ symmetric stretch, the two peaks at 2950 and 2980 cm⁻¹ as the degeneracy-lifted CH₃ asymmetric stretches, and the little bump at 2920 cm⁻¹ as the CH stretch. All the spectra were taken with the visible light s-polarized and the infrared light unpolarized. It is seen that the spectra for the three alcohols are distinctly different, and various CH stretches are clearly distinguishable.

The methanol spectrum appeared to have changed in a few hours after the sample was prepared, as shown in Fig. 2. This suggests that the methanol might have been transformed into another molecular species, presumably methoxy, CH₃O. The result is a manifestation of the capability of SFG to monitor surface molecular reactions. We have also found that after leaving the alcohol-covered samples in air for a while, the isopropyl alcohol spectrum would disappear, but the other two would not. This indicates that only isopropyl alcohol is desorbed completely from the

†Fig. 1 Sum-frequency generation spectra as a function of infra-red input frequency. The bold lines are the bulk liquid Raman spectra.

Fig. 3 SFG spectra, normalized per molecule, of a Langmuir film of pentadecanoic acid in the condensed "solid" and dilute "liquid" phases.

Fig. 2 SFG spectrum of methanol on glass of a fresh sample and an old sample. The latter was taken several hours later.

glass surface and explains why it is often used as the solvent for cleaning glass.

We have also used SFG to study monolayers of pentadecanoic acid on a water surface. Figure 3 shows two spectra of the CH stretches in the 2900 cm^{-1} region, one for the dilute liquid phase and the other for the more condensed "solid" phase. The "solid" spectrum is dominated by the CH_3 group at the end of the long chain molecule; the two peaks in the spectrum correspond to the symmetric and asymmetric CH_3 stretches. The liquid spectrum shows a new peak at 2850 cm^{-1} and a broad hump in the 2880-2930 cm^{-1} region, presumably arising from the CH_2 groups along the chain. A careful analysis of the polarization dependence of the spectra suggests that in the "solid" phase, the molecular chains are straight and normal to the surface (with perhaps an orientational distribution about the surface normal), but in the "liquid" phase, the chains may have coiled up more and orient more randomly on the water surface.

In conclusion, we have shown that while SHG has been demonstrated to be a successful surface analytical tool, SFG can be expected to be even more powerful because of its capability for IR spectroscopy measurements.

P.G-S. acknowledges support from the delegation generale de l'armement (France). This work was supported by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

1. See, for example, Y. R. Shen, *Ann. Rev. Mat. Sci.* **16**, 69 (1986); in Chemistry and Structure at Interfaces: New Laser and Optical Techniques, eds. R. B. Hall and A. B. Ellis (Verlag-Chemie, Berlin, 1986), p.151, and references therein.
2. G. Berkovic, Th. Rasing, and Y. R. Shen, *J. Chem. Phys.* **85**, 7374 (1986); R. B. Hall, A. M. DeSantolo, and S. G. Grubb, *J. Vac. Sci. Technol.*, to be published.
3. P. Guyot-Sionnest, H. Hsiung, and Y. R. Shen, *Phys. Rev. Lett.* **57**, 2963 (1986).
4. Th. Rasing, G. Berkovic, and Y. R. Shen, *Chem. Phys. Lett.* **130**, 1 (1986).
5. T. F. Heinz, C. K. Chen, D. Ricard, and Y. R. Shen, *Phys. Rev. Lett.* **48**, 478 (1982); T. L. Mazely and W. M. Hetherington, *J. Chem. Phys.* **86**, 3640 (1987).
6. X. D. Zhu, H. Suhr, and Y. R. Shen, *Phys. Rev. B* **35**, 3047 (1987); J. H. Hunt, P. Guyot-Sionnest, and Y. R. Shen, *Chem. Phys. Lett.* **133**, 189 (1987).
7. Selected Raman Spectral Data, ed. L. B. Beach (Thermodynamic Research Center Hydrocarbon Project Publications, College Station, Texas, 1983), Ser. No. 807,653,55.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.