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BY SECOND HARMONIC GENERATION

Y.R. Shen

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A FEW RECENT EXPERIMENTS ON SURFACE STUDIES BY
SECOND HARMONIC GENERATION

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Surface second harmonic generation (SHG) has recently been shown to be a viable tool for surface studies.¹ It is sensitive to submonolayers of molecules on surfaces and has many obvious advantages in comparison with the conventional surface tools. Being optical, it is nondestructive, capable of in-situ remote sensing, and applicable to any interface accessible by light. The time response of SHG is nearly instantaneous. Therefore, the technique also has the potential of being useful for surface dynamic studies with extremely high time resolution. Thus, surface SHG can provide many unique opportunities in surface science research. In the past several years, we have already succeeded in demonstrating that the technique can be used to monitor molecular adsorption and desorption at a variety of interfaces,² to probe the spectrum of submonolayers of molecules adsorbed on surfaces,³ to measure the orientation and distribution of adsorbed molecules,^{3,4} to study surface reconstruction and phase transformation of semiconductors,⁵ and so on. In this paper, we describe a few additional experiments that we have recently carried out in our laboratory to further explore the applicability of surface SHG.

Let us first give a sketch of the underlying theory. We consider an interface formed by two bulk media with centrosymmetry. Because of the broken symmetry at the interface, the second-order nonlinearity of the interface layer becomes nonvanishing (under the electric-dipole approximation). We can use a surface nonlinear susceptibility tensor $\chi_s^{(2)}$ to describe the interface nonlinearity which includes both local and nonlocal responses of the interface layer to the incoming field.⁶ Since the layer thickness is generally much smaller than an optical wavelength, the dipoles nonlinearly induced in the layer can be considered as forming a surface polarization sheet at the interface boundary. This surface polarization acts as the source for generating the second harmonics. It can be shown that the SH signal generated from a surface polarization at 2ω induced by a laser pulse incident at an angle θ with intensity $I(\omega)$, cross-section A , and pulsewidth T , is given approximately by

$$S(2\omega) = [32\pi^3 \omega \sec^2 \theta / Mc^3 \epsilon(\omega) \epsilon^{1/2}(2\omega)] |\chi_s^{(2)}|^2 I^2(\omega) AT \text{ photons/pulse. (1)}$$

However, the second-order nonlinearity of the centrosymmetric bulk is not strictly vanishing because of the higher-order multipole contributions, and its effect on the surface SHG may not be negligible.⁷ Fortunately, in most cases of practical interest, the bulk contribution to SHG is

either much smaller or can be subtracted from the surface contribution. Measurement of $\chi_s^{(2)}$ then allows us to deduce useful information about the interface layer.

Equation (1) shows that the SH signal should increase with increase of I, A, and T, but is eventually limited by surface optical breakdown. If we assume that the threshold energy for breakdown for a short-pulse excitation is $(IT)_{th} \sim 1 \text{ J/cm}^2$, then the maximum SH signal is given by⁸

$$S_{\max} \sim 10^{27} |\chi_s^{(2)}|^2 A/T \text{ photons/pulse.} \quad (2)$$

With $A \sim 0.1 \text{ cm}^2$, $T \sim 10 \text{ nsec}$, and a minimum detectability of 1 photon/pulse, we should be able to measure a $\chi_s^{(2)}$ as small as $\sim 3 \times 10^{-18} \text{ esu}$. Since $\chi_s^{(2)} = N_s \alpha^{(2)}$, where N_s is the number of surface atoms or molecules per cm^2 , and $\alpha^{(2)}$ is the nonlinear polarizability which has a value $\gtrsim 10^{-29} \text{ esu}$ for the more highly nonlinear molecules, the above estimate suggests that surface SHG has the sensitivity to detect $N_s \lesssim 3 \times 10^{11} \text{ molecules/cm}^2$. Note that the surface density of a monolayer is of the order of $10^{14} - 10^{15} \text{ molecules/cm}^2$.

One may ask whether a CW laser will also be intense enough as a pump source for surface SHG. In this case, the pump intensity is limited by laser-induced surface melting, which has a threshold power P_{th} roughly proportional to $A^{1/2}$ for sufficiently small A. If we assume $P_{th}/A^{1/2} \sim 10^4 \text{ W/cm}$ (as for Si), the maximum signal is

$$S_{\max} \sim 10^{36} |\chi_s^{(2)}|^2 \text{ photons/sec,} \quad (3)$$

independent of A.⁸ The minimum detectable $|\chi_s^{(2)}|$ is again around $3 \times 10^{-18} \text{ esu}$. The above estimate suggests that in some cases where $|\chi_s^{(2)}|$ is large ($\gtrsim 10^{-15} \text{ esu}$), even a CW diode laser with a power of $\sim 10 \text{ mW}$ should be powerful enough to detect a monolayer of molecules by SHG. In a recent experiment,⁸ using a 20-mW diode laser at 780 nm focused to a spot of $\sim 10^{-6} \text{ cm}^2$ on a silver electrode in an electrolytical cell, we were able to monitor the adsorption and desorption of monolayers of AgCl and pyridine. As shown in Fig. 1, the SH signal ($\sim 4000 \text{ photons/sec}$)

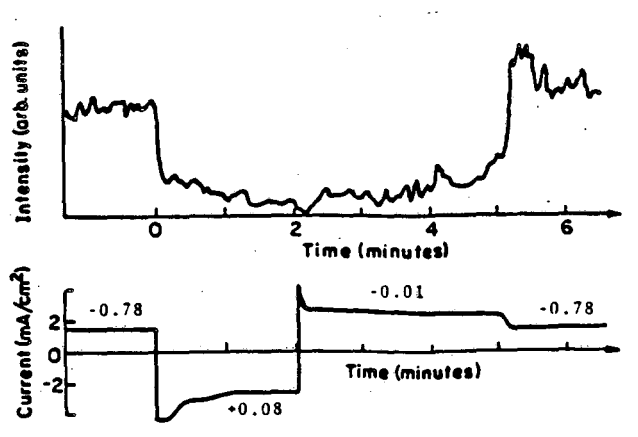


Fig. 1: Top trace: SH intensity vs. time from an Ag electrode in an electrolytic cell with 0.1 M KCl and 0.1 M pyridine. Bottom trace: cell current vs. time. This bias potentials (-0.78 , $+0.08$, -0.01 v) are relative to a standard calomel electrode. (After Ref. 8.)

drops abruptly at $t = 0$ when pyridine is desorbed from Ag. The residual signal at $t > 0$ arises from AgCl layers formed on Ag. Since SHG is only sensitive to the first one or two surface AgCl layers, the signal does not vary appreciably with the multiplayer formation or reduction of AgCl

on Ag. The reduction of AgCl is complete at $t = 5$ min, and with the bias potential changed to -0.78 v, the monolayer of pyridine is again adsorbed on Ag, leading to a sudden rise in the SH signal.

Both Eq. (2) and Eq. (3) also suggest that one can detect a monolayer of molecules in an area of $\lesssim 10^{-7}$ cm² by SHG. Thus, surface SHG is potentially useful as a surface microscopic technique which is capable of probing the distribution of a surface monolayer of molecules.⁸ Figure 2 depicts the result of our first attempt in this respect. The SHG was used to map out a laser-ablated hole in a monolayer of dye molecules adsorbed on a fused quartz plate. With the probe laser focused to a 8- μ m spot, the surface scan could indeed display the hole with a resolution of ~ 10 μ m, as seen in Fig. 2.

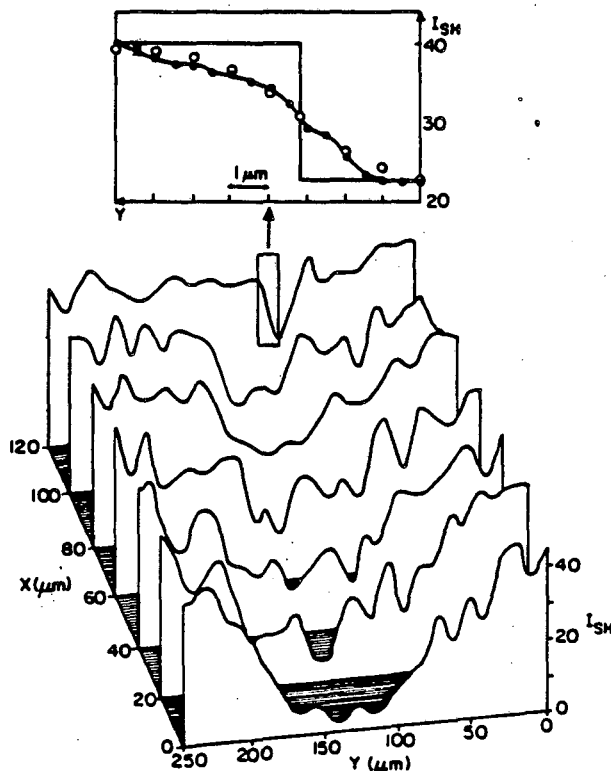


Fig. 2. SH image of an ablated hole in a rhodamine 6G dye monolayer. Inset: a high resolution scan of the region bracketed by the rectangle. Circles are a theoretical fit assuming a step change in the layer. (After Ref. 8.)

Surface SHG is a viable method to monitor adsorption and desorption of molecules on well-defined metal and semiconductor surfaces in ultra-high vacuum (UHV).^{2,5,9} Figure 3 is an example, showing how the SHG responds to the adsorption of CO on Cu(100).¹⁰ The sample properly cleaned and kept at 140°K in UHV was allowed to be exposed to CO, and SHG with a Nd:YAG laser beam was used to monitor the adsorption of CO. It is known that at $T = 140^\circ\text{K}$, CO adsorbs on Cu(100) only at the top sites. The adsorption kinetics is then likely to obey the simple Langmuir model.¹¹ This was actually the case. As shown in Fig. 3, the experimental data can indeed be fit very well by a theoretical calculation following the Langmuir model. From the fit, the sticking coefficient of CO on Cu(100) can be deduced.

As a monitoring tool, surface SHG has the advantage of being nearly instantaneous in response, and is therefore ideal for surface dynamic studies. In the case of studying surface adsorbates, one may need to

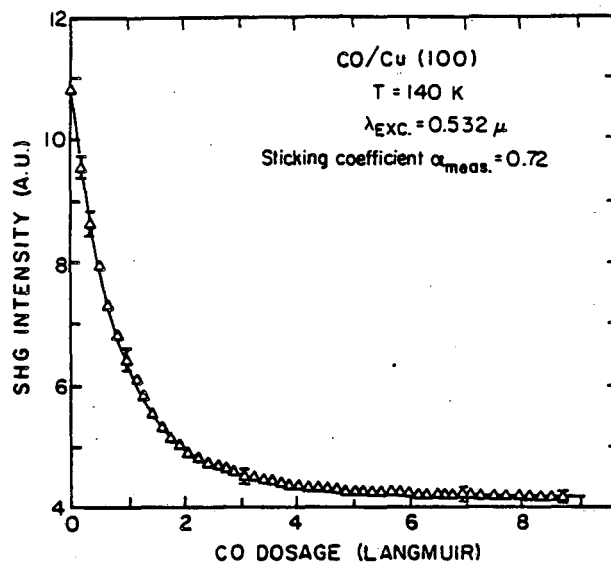


Fig. 3. SHG as a function of CO dosage on Cu(100) at 140 K. The solid theoretical curve, derived from the Langmuir kinetic model with the surface coverage given by $\theta = \theta_s[1 - \exp(-\alpha D)]$ and the SH signal by $S = |A + B\theta/\theta_s|^2$, is used to fit the experimental data. Here, D denotes the CO dosage, and α , A , and B are constants. (After Ref. 10.)

know the absolute surface coverage of the adsorbates. This requires calibration of the surface SH signal. In a UHV chamber, the surface SHG can be calibrated against the thermal desorption spectroscopy (TDS).¹⁰ The latter measures $\partial\theta/\partial t = (\partial\theta/\partial T)(\partial T/\partial t)$ when the surface temperature is increased at a given rate. Here, θ denotes the surface coverage. A normalized integration of the thermal desorption spectrum gives

$$\int_{T_1}^T \frac{\partial\theta}{\partial T} dt / \int_{T_1}^T \frac{\partial\theta}{\partial T} dT = 1 - \theta(T)/\theta_s, \quad (4)$$

where θ_s is the saturated surface coverage. If, during the thermal desorption, the surface is simultaneously monitored by SHG, then $\theta(T)/\theta_s$ derived from TDS can be used to calibrate the SH signal. We again take CO on Cu(100) as an example. In this case, the one-to-one correspondence between θ and the SH signal was already established by the good agreement between the experimental result and the Langmuir kinetic model shown in Fig. 3. Therefore, we could convert $\theta(T)/\theta_s$ obtained from TDS into a curve of SHG versus T , which could then be compared with the direct measurement of the SHG. As shown in Fig. 4, the agreement is excellent, indicating that TDS can indeed be used as a calibration for SHG from adsorbates. We note that while both TDS and SHG can monitor the surface coverage, the former technique has a much longer response time compared with the latter.

Surface SHG has also been used to study monolayers of molecules at a liquid/air interface.^{2,4} In a recent experiment, we have used it to probe the so-called liquid expanded (LE) - liquid compressed (LC) transition of a Langmuir film floating on a water surface.¹² The system is usually prepared by first spreading a monolayer of molecules on a water surface. The molecules can then be swept together by a moving barrier. A measurement of the surface tension (π) as a function of the surface area per molecules (A) at a constant temperature yields the π - A isotherm for the two-dimensional system. Analogous to the P - V curve for a three-dimensional system, the π - A curve for such a two-dimensional system may also undergo the gas-liquid and liquid-solid transitions.¹² It has been

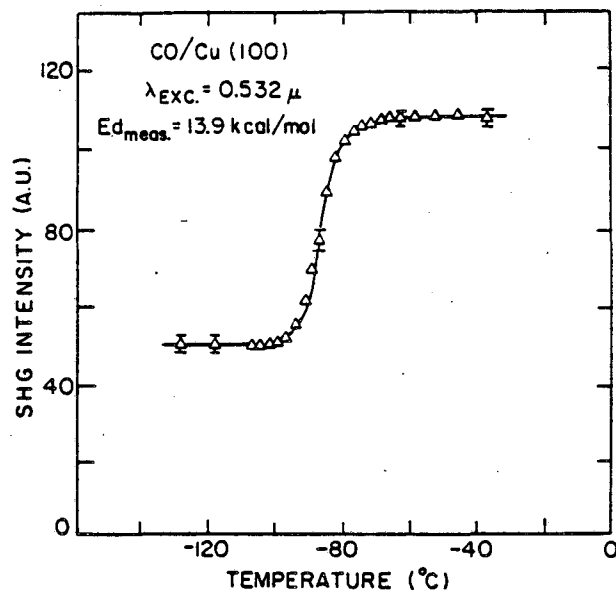


Fig. 4. SHG from CO on Cu(100) as a function of desorbing temperature. The solid curve is calculated from thermal desorption spectra data, and the triangular points are obtained from direct measurements. (After Ref. 10.)

found by many researchers that in some cases, the π -A curve may even exhibit an additional phase transition in the liquid phase, designated as the LE-LC transition.¹² Fattic acid on water is a well-known example. This is illustrated in Fig. 5, where the onset of the LE-LC transition is marked by a kink in the π -A curve.¹³ Although many careful π -A measurements and theoretical calculations on the system have been reported, the

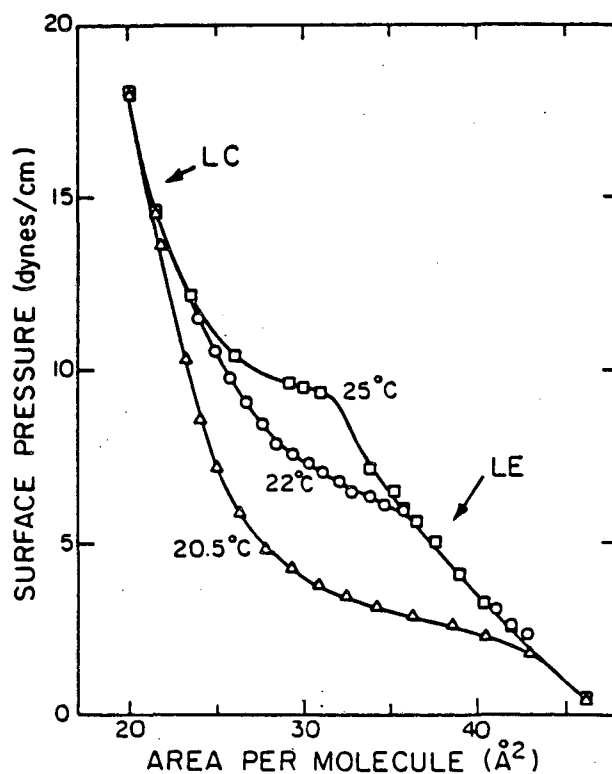


Fig. 5. Surface pressure of PDA as a function of area per molecule on a water surface of pH = 2 for various temperatures. (After Ref. 13.)

nature of this LE-LC transition is not yet well understood. Some authors suggested that the transition should be marked by a sudden change in the molecular orientation, but no direct measurement of the molecular orientation has even been reported. Whether the transition is of first or second order is also not clear, since most researchers failed to observe a clear LE-LC coexistence region (characterized by a flat section) on the π -A curve.

The surface SHG allows us to measure directly an averaged molecular orientation. The basic principle is as follows. The second-order surface nonlinear susceptibility $\chi^{(2)}$ of a layer is related to the second-order nonlinear polarizability $\bar{\alpha}^{(2)}$ of the molecules by

$$\chi^{(2)} = N_s \langle \vec{G} \rangle : \bar{\alpha}^{(2)}, \quad (5)$$

where N_s is the number of molecules per cm^2 , \vec{G} is a tensor describing the transformation from the molecular coordinates to the lab coordinates, and the angular brackets denote an average over the molecules. If $\bar{\alpha}^{(2)}$ is dominated by a single element $\alpha_{z'z'z'}^{(2)}$, with z' chosen to be along a certain axis attached to the molecule, then we can easily show

$$\frac{\chi_{zzz}^{(2)}}{\chi_{zxx}^{(2)}} = \frac{2\langle \cos^3 \theta \rangle}{\langle \sin^2 \theta \cos \theta \rangle}. \quad (6)$$

Here, z' is parallel to the surface normal, and θ is the angle between z' and z . Thus, a measurement of $\chi_{zzz}^{(2)}/\chi_{zxx}^{(2)}$ gives a weighted average of the molecular orientation.

For the case of pentadecanoic acid (PDA) $[\text{CH}_3(\text{CH}_2)_{13}\text{-COOH}]$ in Fig. 5, we have found that the second-order polarizability is dominated by the C-OH bond in the molecule. By measuring $\chi_{zzz}^{(2)}/\chi_{zxx}^{(2)}$ for PDA monolayers on water at different surface molecular densities N_s and assuming a δ -function for the molecular orientational distribution, we obtained the results in Fig. 6.¹³ It is seen that θ approaches zero at low N_s and 60° at high N_s . This is understandable because the C-OH bond, being polar, likes to dip normally into the water. As the surface density of molecules increases, the steric interaction between molecules tends to align the main body of the molecules along the surface normal. Consequently, at high surface densities, the C-OH bond is expected to tilt at an angle $\theta \sim 60^\circ$ from the surface normal.

Figure 6 also shows that at the surface density where the LE-LC transition first sets in, a kink in the θ versus N_s curve appears. The value of θ at this point is around 45° , and does not seem to vary with temperature even though the transition point (A_C, π_C) does change appreciably with temperature. The results indicate that associated with the LE-LC transition, there must be a change in the molecular orientation, in addition to a change in the surface density.

Analysis of the SH data also enable us to answer the question of whether the LE-LC transition is first or second order. It is known that the local-field effect arising from induced dipole-induced dipole interaction can affect SHG from a PDA monolayer. Depending on whether the layer is heterogeneous (in the coexistence region of the first-order transition) or homogeneous (for the second-order transition), the local-field effect should be different. Our calculation assuming a heterogeneous layer in the transition region showed a much better agreement with the observed SH data. This indicates that the LE-LC transition must be of the first order.

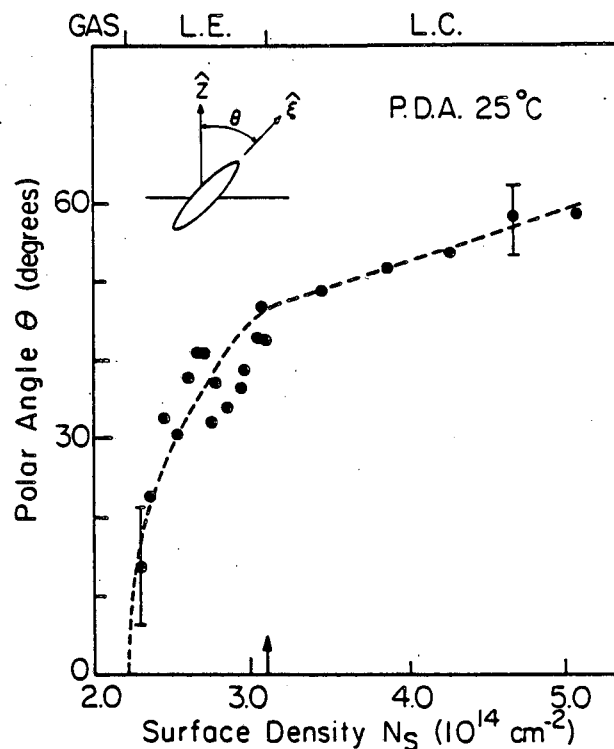


Fig. 6. Tilt angle θ between the C-OH bond in PDA and the surface normal as a function of surface density for PDA on water at 25°C. The dashed line is an extrapolation through the data points. (After Ref. 13.)

The experiments described above are just a few examples illustrating how surface SHG can be used to probe adsorbates at various interfaces. There are undoubtedly many other possible applications one can think of. Among them, the potential use of the technique to study surface dynamics is very exciting. The possibility of using surface SHG to study coating, epitaxial growth, corrosion, and catalysis is equally fascinating.

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REFERENCES

1. See, for example, Y. R. Shen, *Annual Rev. Material Sciences* 16 (to be published).
2. C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, *Phys. Rev. Lett.* 46, 1010 (1983), T. F. Heinz, H. W. K. Tom, and Y. R. Shen, *Laser Focus* 19, 101 (1983); H. W. K. Tom, C. M. Mate, X. D. Zhu, J. E. Crowell, T. F. Heinz, G. Somorjai, and Y. R. Shen, *Phys. Rev. Lett.* 52, 348 (1984).
3. T. F. Heinz, C. K. Chen, D. Ricard, and Y. R. Shen, *Phys. Rev. Lett.* 48, 478 (1982).
4. H. W. K. Tom, T. F. Heinz, and Y. R. Shen, *Phys. Rev. A* 28, 1883 (1983); Th. Rasing, Y. R. Shen, M. W. Kim, P. Valint, and J. Bock, *Phys. Rev. A* 31, 537 (1985).
5. T. F. Heinz, M. M. T. Loy, and W. A. Thompson, *Phys. Rev. Lett.* 54, 63 (1985).
6. P. Guyot-Sionnest, W. Chen, and Y. R. Shen (to be published).

7. See, for example, Y. R. Shen, "The Principles of Nonlinear Optics," (J. Wiley, New York, 1984), Chapter 25.
8. G. T. Boyd, Y. R. Shen, and T. W. Hansch, Optics Lett. (to be published).
9. H. W. K. Tom, X. D. Zhu, Y. R. Shen, and G. A. Somorjai, in "Proc. XVII Internatl. Conf. on Physics of Semiconductors" (Springer-Verlag, Berlin, 1984), p.99.
10. X. D. Zhu, Y. R. Shen, and R. Carr, Surf. Sci. 163, 114 (1985).
11. See, for example, I. Langmuir, J. Am. Chem. Soc. 28, 28 (1918).
12. See, for example, G. M. Bell, L. L. Coombs, and L. J. Dunne, Chem. Rev. 81, 15 (1981).
13. Th. Rasing, Y. R. Shen, M. W. Kim, and S. Grubb (to be published).

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