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NONLINEAR OPTICAL DETECTION OF ADSORBED MONOLAYERS

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The study of molecular adsorbates on surfaces is one of the central activities in surface science. This topic derives its importance from the critical dependence of the physical and chemical properties of a surface on the presence of adsorbates. A variety of techniques has been developed to probe the adsorbates [1]. These include, for example, photoemission spectroscopy, low-energy electron diffraction, extended X-ray absorption fine structure spectroscopy, tunneling spectroscopy, and infrared absorption and emission spectroscopy. Each technique, however, has certain limitations in its range of applicability. In many cases, only adsorbates at a gas/solid interface can be probed. In other cases, an ultra-high vacuum or a low temperature environment is required. New surface probes which are complimentary or superior to the existing ones are clearly needed.

In the last few years, applications of lasers to surface studies have attracted increasing attention. Several techniques have been invented for the investigation of molecular adsorbates. Laser detection of molecules scattered or desorbed from surfaces can provide information about the molecule-substrate interaction [2]. Laser-induced desorption and surface photoacoustic spectroscopy can yield vibrational spectra for adsorbed molecules [3]. Some nonlinear optical techniques have also been developed as effective surface probes. Raman gain spectroscopy with tunable cw mode-locked laser pulses has provided vibrational spectra of adsorbed molecular monolayers [4]. Surface coherent anti-Stokes Raman spectroscopy appears to have the sensitivity for detecting submonolayers of adsorbed molecules [5]. More recently, second harmonic generation has been found to be a simple, but versatile, method for studying adsorbed monolayers [6]. These purely optical techniques offer some new possibilities in the study of molecular adsorbates. In this paper, we shall review recent progress in the development of second harmonic generation as a surface probe.

The second harmonic (SH) radiation from a medium arises from the induced second-order polarization $P^{(2)}(2\omega)$ in the medium:

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

From symmetry considerations, if the medium has a center of inversion, the nonlinear susceptibility $\chi^{(2)}$ vanishes in the electric-dipole approximation. Electric-quadrupole and magnetic-dipole contributions to $\chi^{(2)}$ exist, but they are generally very much weaker than the electric-dipole contributions. Thus, in a bulk medium with inversion symmetry, little SHG is expected. The surface layer, however, is intrinsically non-centrosymmetric, and therefore SHG from this region is always allowed. Even though the total number of atoms or mole-

cles in the surface layer is small, the SH signal from the surface can be larger than or comparable with that from the bulk. For this reason, SHG is highly surface-specific and can be used to study interfaces between any two centrosymmetric media. In particular, this technique can be applied to the study of monolayers and submonolayers of molecules adsorbed at an interface.

Let us consider the simple case of a monolayer of noninteracting molecules adsorbed at a smooth interface. In this case, we can write the surface nonlinear susceptibility of the adsorbed molecules as a sum of the nonlinear polarizabilities of individual molecules over a unit surface area:

$$\chi_s^{(2)} = \sum_{i=1}^{N_s} \alpha_i^{(2)}. \quad (2)$$

This expression shows that $\chi_s^{(2)}$ is nonvanishing only if (a) the individual molecules have no inversion symmetry so that $\alpha_i^{(2)} \neq 0$, and (b) the arrangement of molecules also lacks inversion symmetry so that $\sum \alpha_i^{(2)} \neq 0$. For asymmetric molecules, a nonvanishing $\chi_s^{(2)}$ can result from the alignment of adsorbate molecules on the surface. For centrosymmetric molecules, $\chi_s^{(2)}$ can also be nonvanishing provided that the molecule-substrate interaction breaks the inversion symmetry of the molecules, thus yielding an effective $\alpha_i^{(2)}$. In general such an interaction consists of an electromagnetic part, which can be expressed in terms of local-field corrections, and a chemical part, which induces a modification of the electronic charge distribution around the adsorbed molecules.

To see whether the SH signal from a single monolayer is detectable, we use the following estimate. For a typical asymmetric molecule, the magnitude of $\alpha^{(2)}$ is of the order of 10^{-30} esu. The corresponding $|\chi_s^{(2)}|$ for an isolated layer of aligned molecules with a surface coverage of $N_s = 10^{14}/\text{cm}^2$ is then $|\chi_s^{(2)}| = N|\alpha^{(2)}| \sim 10^{-16}$ esu. The SH signal from such a surface layer of molecules can be calculated from the solution of Maxwell equations for radiation from a sheet of oscillating dipoles as [7]

$$S(2\omega) = \frac{2 \cdot 10^3 \pi^3 \omega}{3c} |\chi_s^{(2)}|^2 I^2(\omega) AT \times 10^{17} \text{ photons/pulse} \\ \sim I^2(\omega) AT \text{ photons/pulse}. \quad (3)$$

Here, the laser intensity $I(\omega)$ is in MW/cm^2 , the beam cross-section A is in cm^2 , the laser pulsewidth T is in nsec, and we have assumed a pump wavelength of $1.06 \mu\text{m}$. For $I(\omega) = 10 \text{ MW}/\text{cm}^2$, $A = 1 \text{ cm}^2$, and $T = 10 \text{ nsec}$, we find an output signal of $S(2\omega) \sim 10^3$ photons/pulse. This is certainly strong enough to be readily detectable.

In the above estimate, we have neglected the possible enhancement of SHG from the molecule-substrate interaction through $\alpha^{(2)}$, and from macroscopic local-field corrections. The latter can be formally taken into account by attaching a macroscopic local-field correction factor $L(\omega)$ to each field amplitude $E(\omega)$ [8]. It happens that on some surfaces $L(\omega)$ can be quite appreciable. This is particularly true for rough metal surfaces, for which $|L(\omega)|$ on the tip of a rough structure can be enhanced through the local plasmon resonance and the lightning-rod effect. At a silver surface, for example, $|L(\omega)|$ can exceed 50 at the tip of an ellipsoid. Such a large value for $L(\omega)$ can lead to a huge enhancement in the surface SHG, since its intensity is proportional to $|L^2(2\omega)L^4(\omega)|$ averaged over the surface. An experiment on a

rough silver surface has indeed shown an increase of $\sim 10^4$ in the SH output compared to that from a smooth surface [10]. This makes the detection of molecules adsorbed on a rough silver surface particularly easy despite the angularly diffused nature of the SH radiation.

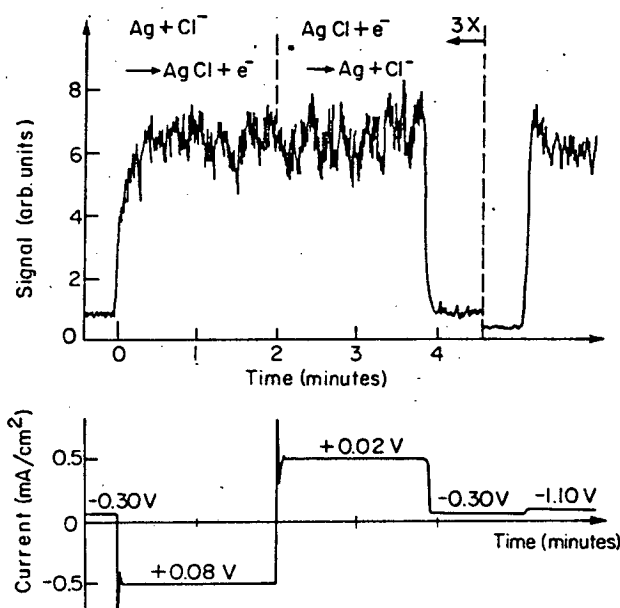


Fig.1 Variation of current and second harmonic output during and after an electrolytic cycle. The voltages listed in the lower curve refer to the voltage at the silver electrode with respect to the standard reference electrode. Pyridine (0.05M) was added to the 0.1M KCl solution following the completion of the electrolytic cycle

As an example, Fig. 1 shows how SHG can be used to monitor molecular adsorption and desorption on a roughened silver electrode during an electrolytic cycle [6]. In a 0.1M KCl electrolyte, the surface of the Ag electrode is first oxidized to AgCl and then reduced again to pure Ag. The SH signal rises sharply when the first monolayer of AgCl is formed and drops precipitously when the last layer of AgCl is reduced. During the cycle when many layers of AgCl are present on the electrode, the signal does not change significantly. This is a clear manifestation of the surface-specific character of SHG. If pyridine is added to the electrolytic solution, then the pyridine molecules are expected to be adsorbed onto the electrode under negative bias voltages. This behavior can be seen in the surface SHG, as illustrated in Fig. 1. Figure 2 shows the dependence of the SH signal on the reverse bias applied to the Ag electrode. The SH signal from the pyridine layer was found to be $\sim 8 \times 10^5$ photons/pulse, for pump excitation over an area of 0.2 cm² by 10 nsec, 0.2 mJ laser pulses at 1.06 μ m. Such a signal strength suggests the possibility of detecting as little as one hundredth of an adsorbed pyridine monolayer. This example indicates the potential of SHG for *in-situ* studies of electrochemical processes.

From the scientific point of view, the study of molecular adsorption on a smooth surface is perhaps of greater interest, since such surfaces permit better characterization. Although SHG from smooth surfaces does not enjoy any strong local-field enhancement, it does produce a coherent and highly directional output, which allows the use of spatial filtering to improve the signal-to-noise ratio. To demonstrate that SHG can be sensitive enough for detection of submonolayers of adsorbates on smooth surfaces and for submonolayer spectroscopy, we consider the case of a half monolayer of rhodamine dye molecules ($\sim 5 \times 10^{13}$ molecules/cm²) adsorbed on fused quartz [11]. As shown in Fig. 3(a), the $S_0 \rightarrow S_2$ electronic transitions of rhodamine 6G and 110 are in

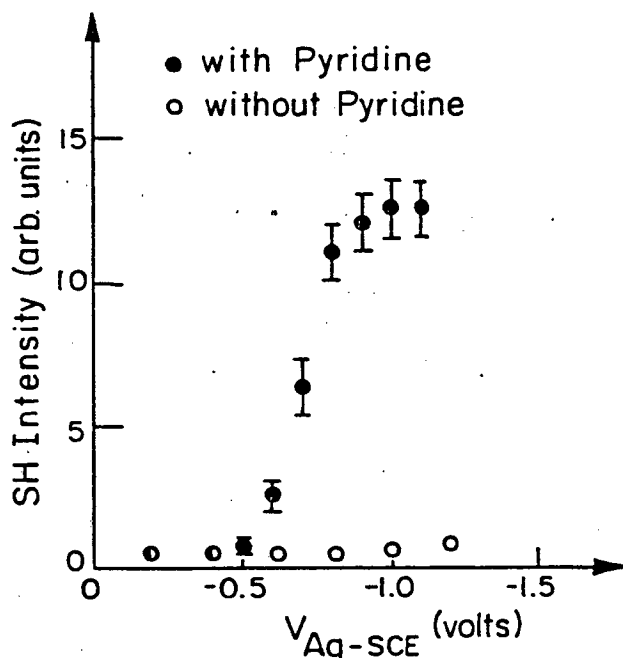


Fig.2 Second harmonic signal versus the bias voltage at the silver electrode V_{Ag-SCE} (with respect to the standard reference electrode) following an electrolytic cycle, with 0.05M pyridine and 0.1M KCl dissolved in water

the $30,000\text{ cm}^{-1}$ range, which can be reached by a two-photon excitation of a dye laser. The SHG from the dye molecules is expected to exhibit a resonant peak when twice the input laser frequency is scanned over the transition. This was indeed observed experimentally. The data in Fig. 3(b) show the two well-resolved resonances for the different dyes. The resonant SH signals were found to be $\sim 10^4$ photons/pulse for a 10 nsec laser pulse of $\sim 1\text{ mJ}$ focused to $\sim 10^{-3}\text{ cm}^2$. The signal was more than 2 orders of magnitude stronger than the SH output from the bare fused quartz substrate. This indicates that SHG should be sensitive enough for spectroscopic measurements of less than one tenth of a dye molecular monolayer.

In addition to spectroscopic applications, surface SHG can also be used to obtain information about the orientation of the molecules adsorbed on a surface [12]. This technique is based on the fact that the polarization dependence of the surface SHG is dictated by the symmetry of $\chi_S^{(2)}$ and by the ratios of the nonvanishing components of $\chi_S^{(2)}$, which in turn are governed by the average molecular orientation. We have applied this property of surface SHG to the case of p-nitrobenzoic acid (PNBA) adsorbed on fused quartz in ethanol. This example also demonstrates the fact that first, surface SHG is not limited to the study of large molecular adsorbates; and second, surface SHG can be used to study adsorbates not only at a gas/solid interface, but at any interface between two transparent centrosymmetric media. In this case, the adsorbed PNBA layer was formed and probed *in situ* at the interface between a fused quartz window and a dilute solution of PNBA in ethanol. The SH signal from the adsorbed PNBA molecules was found to be independent of the rotation of the substrate about its normal. This implies that the surface arrangement of PNBA is isotropic.

The PNBA molecules are known to adsorb on the quartz substrate in the configuration sketched in Fig. 4. In regard to the nonlinear polarizability of the molecules, the dominant component of $\alpha^{(2)}$ is $\alpha_{\xi\xi\xi}^{(2)}$, where ξ is directed along the principal molecular axis. The other nonvanishing elements $\alpha_{\xi\xi\xi}^{(2)} = \alpha_{\xi\xi\xi}^{(2)}$ and $\alpha_{\xi\xi\xi}^{(2)}$, with ξ in the molecular plane, were estimated to be an order

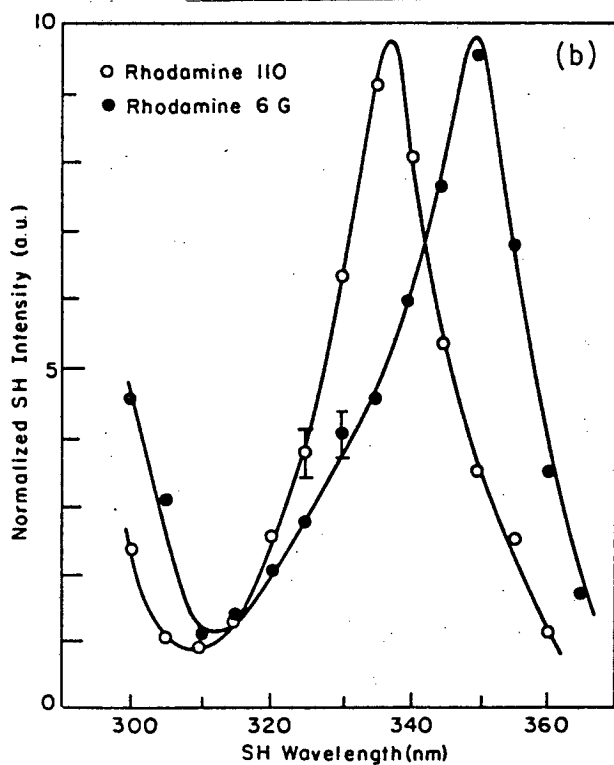
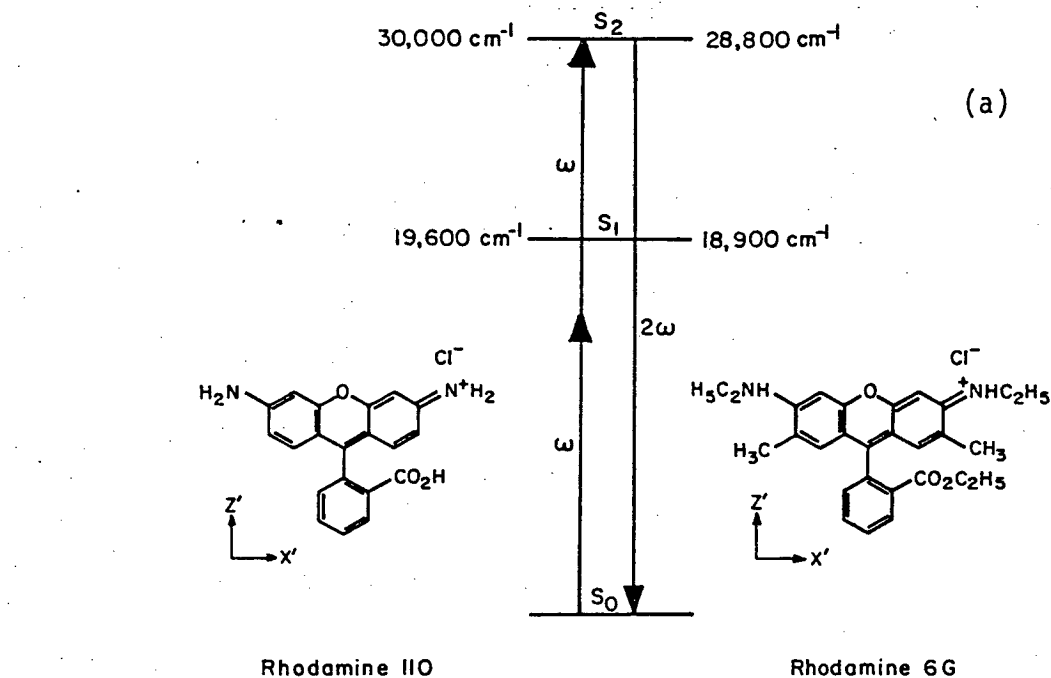
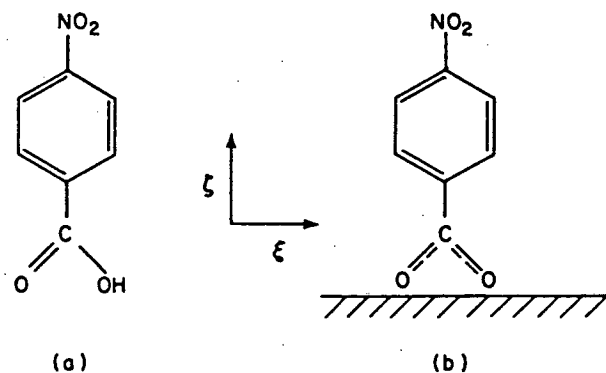


Fig.3 Resonant second-harmonic generation in rhodamine 6G and rhodamine 110. (a) indicates the structures and energy levels of the two dyes, as well as the resonant SHG process. (b) shows the experimental results for surface SHG by the dye molecules adsorbed on fused quartz at submonolayer coverages. The normalized SH intensity is given as a function of the SH wavelength in the region of the $S_0 \rightarrow S_2$ transition

Fig.4 Molecular structure of p-nitrobenzoic acid (PNBA). (a) describes the free molecule, and (b) the chemisorbed species



of magnitude smaller than $\alpha_{\zeta\zeta\zeta}^{(2)}$ [13]. The orientation of the isotropically distributed molecules can then be specified by the tilt angle θ of the molecular axis $\hat{\zeta}$ away from the surface normal \hat{z} . If the interaction between molecules can be neglected, the nonvanishing elements of $\chi_S^{(2)}$ should then be directly proportional to $\alpha_{\zeta\zeta\zeta}^{(2)}$ with some weighted averages of θ acting as the constants of proportionality:

$$\begin{aligned} \left(\chi_S^{(2)}\right)_{zzz} &= N_S \alpha_{\zeta\zeta\zeta}^{(2)} \langle \cos^3 \theta \rangle \\ \left(\chi_S^{(2)}\right)_{zii} &= \left(\chi_S^{(2)}\right)_{izi} = \frac{1}{2} N_S \alpha_{\zeta\zeta\zeta}^{(2)} \langle \sin^2 \theta \cos \theta \rangle, \end{aligned} \quad (4)$$

where $i = x$ or y . Information about the molecular orientation can now be obtained from a simple ratio of the two independent components of $\chi_S^{(2)}$

$$\frac{\left(\chi_S^{(2)}\right)_{zzz}}{\left(\chi_S^{(2)}\right)_{izi}} = 2 \left[\frac{\langle \cos \theta \rangle}{\langle \cos \theta \sin^2 \theta \rangle} - 1 \right]. \quad (5)$$

If the orientational distribution is a sharply peaked function, the above equation reduces to

$$\left(\chi_S^{(2)}\right)_{zzz} / \left(\chi_S^{(2)}\right)_{izi} = 2(1/\sin^2 \theta - 1), \quad (6)$$

and then, the orientational angle θ is specified by a measurement of $\left(\chi_S^{(2)}\right)_{zzz} / \left(\chi_S^{(2)}\right)_{izi}$. Experimentally, this can be done by a polarization null method in which a proper laser and SH polarization combination is used to obtain a vanishing $\left(\chi_S^{(2)}\right)_{\text{eff}}$ given by

$$\left(\chi_S^{(2)}\right)_{\text{eff}} = a \left(\chi_S^{(2)}\right)_{zzz} + b \left(\chi_S^{(2)}\right)_{izi} = 0, \quad (7)$$

where a and b are known coefficients. This result is independent of the laser intensity, and is therefore free of the influence of laser fluctuations.

The value of θ for adsorbed PNBA in ethanol was measured by the above-mentioned scheme to be $\sim 40^\circ$. Within our experimental accuracy, this value of θ was found to be the same for three different input laser wavelengths at 0.532, 0.683, and 1.064 μm . Since the true molecular orientation should certainly be independent of the laser wavelength used in the measurement, this result shows the reliability of the present method. It also suggests that the microscopic local field corrections, neglected in Eqs. (2) and (4) and the ensuing analysis by assuming no molecular interaction, are justified in the present case; otherwise, dispersion in the local fields would certainly lead to different deduced values of θ for different input frequencies. The value of θ for PNBA at an air/fused quartz interface was also measured and was found to be $\sim 70^\circ$. That the molecules adsorbed on fused quartz are more inclined towards the surface normal in liquid than in air can be qualitatively understood by the dielectric or solvation effect of the liquid on PNBA.

As a viable method to detect adsorbates at a liquid/solid interface, SHG can also be used to measure the adsorption isotherm of the adsorbates [12], i.e., to determine the surface coverage of the substrate by molecular adsorbates in equilibrium with the molecules in solution at various concentrations. We again use the adsorption of PNBA on fused quartz in ethanol as an example. Figure 5 shows the adsorption isotherm measured by SHG. At low surface coverage, the substrate contribution to SHG was comparable to the SH signal from the adsorbed PNBA. Fortunately, it could be separately measured and sub-

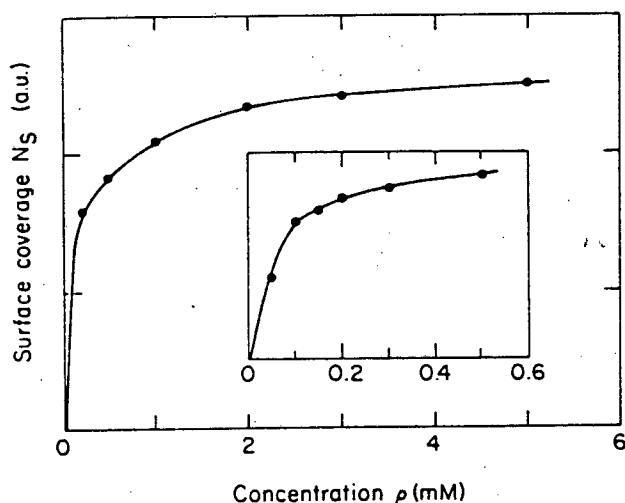


Fig.5 Isotherm for the adsorption of PNBA on fused quartz out of an ethanolic solution. The behavior for lower concentrations of dissolved PNBA is shown in the inset

strated away since SHG is a coherent process which generates signals with well-defined phases. From the slope of the isotherm at low concentration, we can estimate an adsorption free energy at infinite dilution of $\sim 8\text{kcal/mole}$ for PNBA on fused quartz in ethanol [14].

We have shown that SHG can indeed be a useful method for studies of molecular adsorbates. The main advantages of the technique over other more conventional techniques are the much simpler experimental setup, the possibility of *in-situ* measurements of adsorbates at any interface between two centrosymmetric media, and the ability to measure the average orientations of the adsorbates. Moreover, by means of transient spectroscopy with ultrashort laser pulses, we should be able to probe the dynamic properties of adsorbates in the picosecond and subpicosecond time domain. The field, however, is still in its infancy. Some important aspects of the technique are not yet well understood. For example, the microscopic local-field corrections for surface SHG could be very important in the case of adsorbates with high surface coverage on metals and semiconductors, but little theoretical work on this problem is available. How the sensitivity of the technique is limited by the substrate contribution to SHG and whether there are other factors limiting the technique are also questions that still need to be explored.

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