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NONLINEAR OPTICAL STUDIES OF MOLECULAR ADSORBATES

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In recent years, the possibility of employing laser interaction with surfaces as a surface diagnostic tool has attracted a great deal of attention. Optical second harmonic generation (SHG) and sum-frequency generation (SFG) have been proven to be most effective and versatile for surface and interfacial studies.¹ By symmetry, these processes are forbidden in media with centrosymmetry, and can therefore be highly surface-specific. They have the advantages of being capable of high spatial, temporal, and spectral resolutions, suitable for *in-situ*, remote sensing of samples in hostile environment, and applicable to all interfaces accessible to light. Indeed, they have been applied with great success to a large variety of surface and interfacial problems¹: probing adsorption and desorption of molecules from surfaces, measuring average molecular orientation of adsorbates, monitoring surface symmetry and surface phase transitions, conducting surface microscopy and spectroscopy, and many others. Here, we shall describe a few experiments recently carried out in our laboratory using these techniques.

We first discuss the use of SHG to study surface diffusion.² This is a subject of great importance in modern surface science, as surface diffusion often plays a major role in limiting a surface reaction.³ Research in this area is, however, still rather limited because of the lack of convenient tools.⁴ Most exciting techniques are either applicable only to metal surfaces or vulnerable to perturbation during measurements. The SHG technique has a number of important advantages over the common methods and provides many new opportunities, as we shall see.

Our technique is based on the following designed steps. First, a monolayer grating of adsorbed molecules is created on the sample surface by laser desorption using two-beam interference.⁵ Second, diffraction of surface SHG by the monolayer grating is used to probe the grating.^{2,6} Third, the smearing-up of the monolayer grating by surface diffusion is monitored by the decay of the diffracted SH signal.⁷ The results analyzed by the one-dimensional diffusion equation then yield the diffusion constant for the surface diffusion.

Our demonstrating experiment used CO on Ni(111).² The sample was in an ultrahigh vacuum chamber with a base pressure of 0.9×10^{-10} torr. The Ni surface was initially dosed with a saturated CO coverage of $\theta = \theta_s = 0.5$. The optical arrangement for the creation of a CO monolayer grating by laser desorption and the detection of the grating by SH diffraction is shown in Fig. 1. It involved a single-mode Q-switched Nd:YAG laser at $1.06 \mu\text{m}$. For the creation of a CO monolayer grating, the $1.06\text{-}\mu\text{m}$ beam was split into two and recombined at incident angles $\phi = \pm 1.50$ on the CO-covered Ni surface over an area of 2-3 mm in diameter. Desorption of CO by the spatially modulated beam intensity as a result of interference produced a monolayer grating

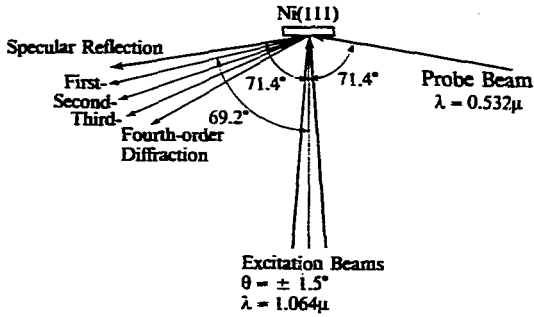


Fig. 1. Experimental arrangement for creation of a CO monolayer grating on Ni(111) by the excitation beams and detection of the grating by second harmonic diffraction of the probe beam.

with a spacing $2a = \lambda/2 \sin\theta = 20\mu\text{m}$. The grating profile was determined by the energy distribution in the two beams.³ This can be predicted if the CO desorption versus the laser pulse energy impinging on the surface is known. In our experiment, the latter relation was obtained by using SHG to probe quantitatively the remains of CO on the surface (calibrated against thermal desorption spectroscopy) after laser desorption with different energies.⁷ The monolayer grating could be probed by diffraction of surface SHG^{2,8} (Fig. 1). For this, we used the frequency-doubled beam at $0.53\mu\text{m}$ for the laser. It was incident on the sample at 71.4° and covered the entire desorption area. The n th-order diffraction of SHG with $n = 1-4$ appeared at $\Delta\theta = 2.22^\circ, 4.24^\circ, 6.10^\circ$, and 7.84° , respectively, off the specularly reflected direction. With the surface coverage given by

$$\theta(x) = \theta_0 + \sum_{n=1}^{\infty} 2\theta_n \cos(n\pi x/a) \quad (1)$$

it is easily seen that the n th-order SH diffraction signal S_n is directly proportional to θ_n^2 or more rigorously,

$$S_n \propto \int \theta_n^2 dx dy \quad (2)$$

where I_n is the probe beam intensity and $\hat{x} - \hat{y}$ is the surface plane. Therefore, knowing θ_n from laser desorption, S_n can be calculated and directly compared with experiment. For our experiment, this is presented in Fig. 2.³ The good agreement between measured and calculated results show clearly that we not only can have quantitative control over the creation of a monolayer grating by laser desorption but also can quantitatively characterize the monolayer grating using SHG.

For our surface diffusion studies,² a CO monolayer grating was first created on Ni(111) at a sufficiently low temperature ($< 200\text{K}$). The sample temperature was then raised to initiate surface diffusion of CO across the grating. This one-dimensional diffusion is expected to follow the Fick's law

$$\partial\theta/\partial t = (\partial/\partial x)(D\partial\theta/\partial x). \quad (3)$$

If the diffusion constant D is assumed to be independent of θ , then the solution of Eq. (3) yields

$$\theta_n(t) = \theta_n(0) \exp(-n^2\pi^2 D t/a^2). \quad (4)$$

We then have

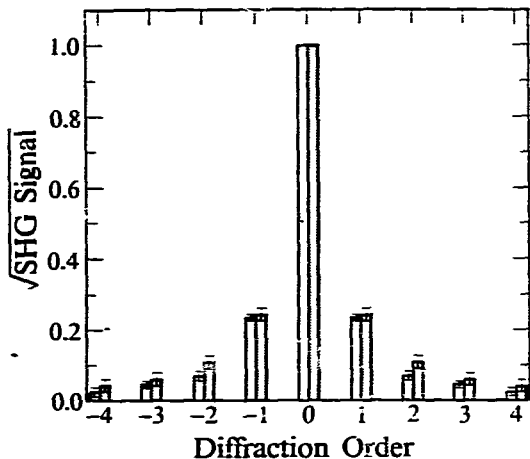


Fig. 2. Measured (unshaded) and calculated (shaded) amplitudes of various orders of second harmonic diffraction from a monolayer grating of CO on Ni(111).

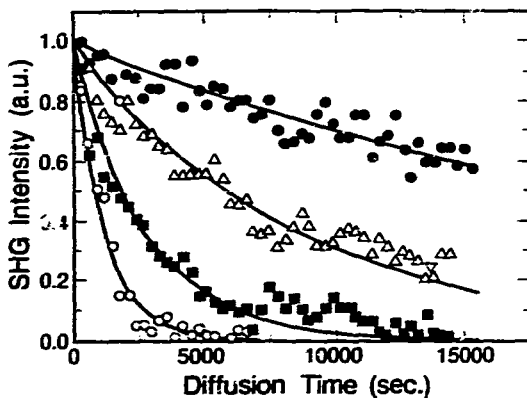


Fig. 3. Normalized first-order diffracted second harmonic signal from CO monolayer gratings on Ni(111) as functions of time at various sample temperatures. Solid circles: $T = 219\text{K}$; open triangles: $T = 247\text{K}$; solid squares: $T = 261\text{K}$; open circles: $T = 273\text{K}$. The solid curves are least square fits using single exponential functions.

$$S_n(t) = S_n(0)\exp(-2n^2\pi^2Dt/a^2). \quad (5)$$

Thus, from the measured $S_n(t)$ and the known value of a , we can obtain D . In our experiment, we monitored the first-order SH diffraction signal $S_1(t)$. The results are shown in Fig. 3 for four different sample temperatures 219, 247, 261, and 273K. The diffusion constants deduced from the data are plotted against the temperature in Fig. 4. They can be fit by the Arrhenius expression $D(T) = D_0\exp(-E_{diff}/kT)$, with $D_0 = 1.2 \times 10^{-5} \text{ cm}^2/\text{sec}$ and $E_{diff} = 6.9 \text{ KCal/mole}$. In the present case, the adsorbed CO molecules occupy the bridge sites. The above value of E_{diff} , together with the adsorption energies of CO at bridge and top sites, suggests that the pathway of CO diffusion between bridge sites on Ni(111) is via hopping over a top site.

The present technique measures macroscopic diffusion of adsorbed molecules on a surface. It has a few very attractive features. The analysis of the experimental results is simple. Anisotropy of surface diffusion can be readily measured by orienting the grating in different directions. A large dynamic range of kinetic parameters can be studied by properly adjusting the grating spacing. Finally, the technique is applicable to a large variety of surfaces and interfaces, including those of semiconductors and insulators. Moreover, it can be applied to studies of surface diffusion of energy, momentum or other types of excitations.

We now discuss the use of SFG for surface spectroscopy. It is clear that with a tunable laser, SHG can serve as a surface spectroscopic tool since resonant enhancement of SHG is expected when ω or 2ω coincides with a transition frequency. This has been demonstrated in a number of cases.^{8,9} As an example, we show in Fig. 5 the SH spectrum of a reinal monolayer on water.⁹ The 335-nm peak is due to a resonant one-photon transition; in membranes, it is shifted to the green and is responsible for the green sensitivity of the eye. The 360-nm peak arises from a two-photon resonance, which has never been observed in linear absorption measurements.

The SHG surface spectroscopy is, however, limited to probing electronic transitions in the visible because the available photodetectors in the infrared generally are not sensitive enough to detect a surface monolayer. Thus, infrared-visible SFG which is an extension of SHG, must be used in order to probe surface vibrational or electronic transitions in the infrared.¹⁰ In the process, a tunable infrared laser at ω_1 excites the resonant transition and a visible laser beam at ω_2 up-converts the signal to a sum-frequency output at $\omega_1 + \omega_2$ in the visible. The technique has been employed to obtain, for example, vibrational spectra of CH stretch modes of molecular monolayers adsorbed at various interfaces.¹¹ Here, we show one example of how it can be used to probe interaction between coadsorbed molecules.¹²

The experiment was on detecting possible interaction between cyano-biphenyl liquid crystal molecules (8CB) and surfactant molecules $\text{CH}_3(\text{CH}_2)_{17}(\text{Me})_2\text{N}^+(\text{CH}_2)_3\text{Si}(\text{OMe})_2\text{Ct}^-$ (DMOAP) coadsorbed on glass. An optical parametric amplifier pumped by a picosecond Nd:YAG laser provided the tunable infrared beam while frequency-doubling of the laser provided the visible beam. The observed spectra of a full monolayer of 8CB on clean glass and a monolayer of 8CB adsorbed on DMOAP-coated glass are depicted in Fig. 6. There is a definite shift in the positions of the C-H peaks in the two spectra. For the 8CB monolayer on clean glass, the C-H stretching frequencies are nearly the same as those of the gas phase, whereas for the 8CB monolayer on DMOAP-coated glass, they appear close to those of the condensed phase. The red shift of the peaks from one to the other is a clear indication of existing interaction between DMOAP and 8CB.

SFG surface spectroscopy has great potential for many exciting research opportunities. Infrared vibrational or electronic transitions of buried interfaces or bare surfaces can now be studied. With time-resolved SFG using picosecond or femtosecond laser pulses, surface reactions can be probed *in-situ* with the possibility of identifying intermediate species. Selective surface dynamics can also be investigated. For example, it is possible to study surface diffusion of selected molecules in the presence of other molecular species on the surface.

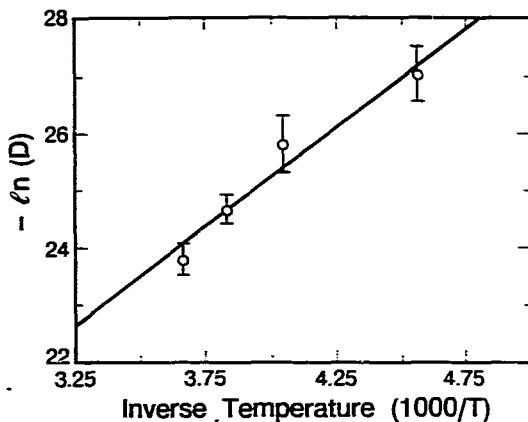


Fig. 4. The Arrhenius plot (open circles) of the diffusion constant obtained from the results of Fig. 3. The solid line is a least square fit to the data.

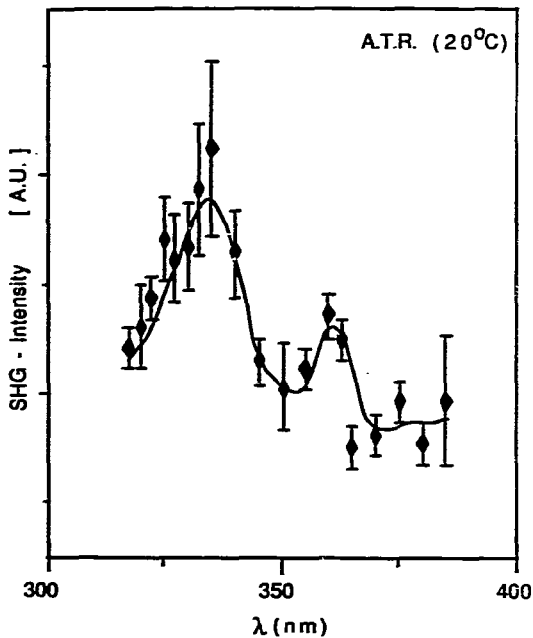


Fig. 5. Second harmonic spectrum of an all-trans retinal monolayer at an air/water interface.

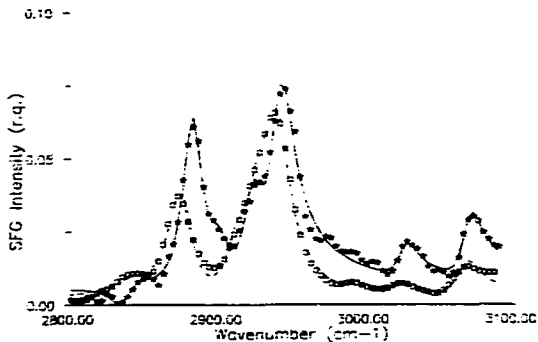


Fig. 6. Sum-frequency vibrational spectrum of an 8CB monolayer on clean glass (solid curve) is compared with that of an 8CB monolayer deposited on DMOAP-coated glass (dashed curve).

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