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SURFACE STUDIES USING OPTICAL SECOND-HARMONIC GENERATION

H.W.K. Tom, T.F. Heinz, and Y.R. Shen

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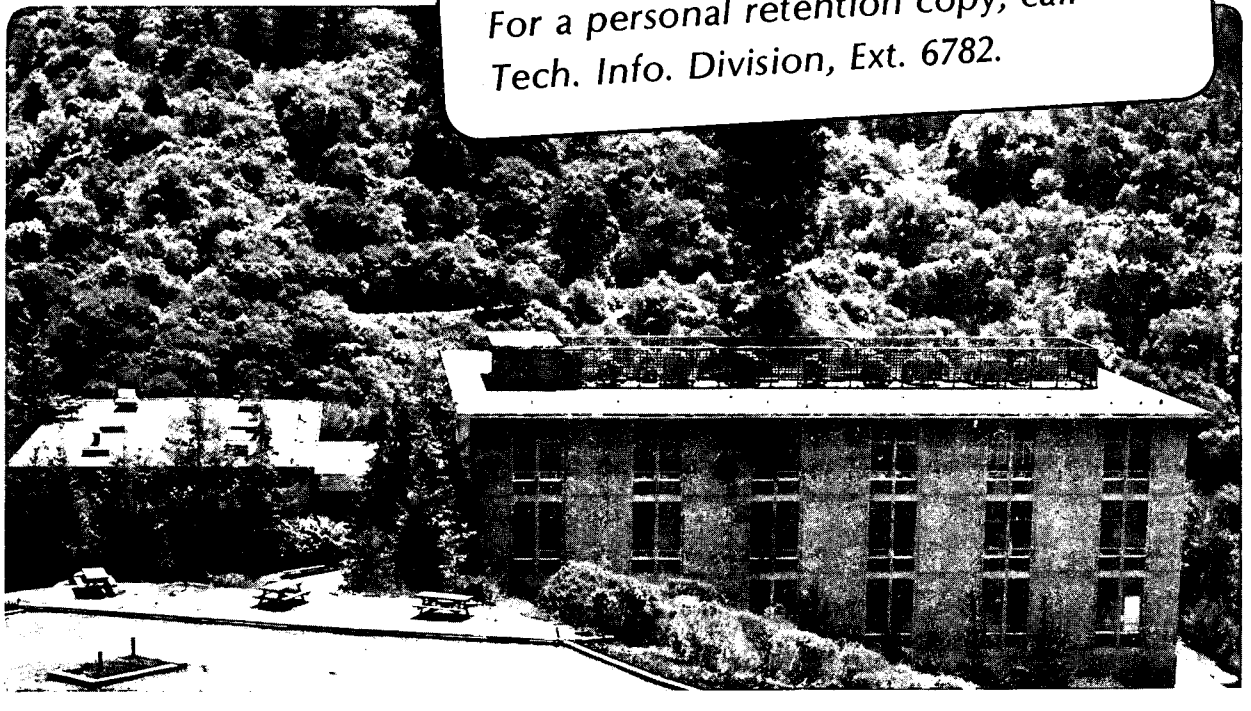

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SURFACE STUDIES USING OPTICAL SECOND-HARMONIC GENERATION*

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Optical second-harmonic generation (SHG) from a system of two centrosymmetric media arises largely from the interface between the media. This interfacial-specificity allows SHG to be a useful probe of a variety of surface properties including: surface adsorbate coverage, adsorbate orientation and arrangement on the substrate, the site of adsorption and surface structural symmetry. The versatility and sensitivity of SHG as a surface probe is illustrated with examples drawn from our most recent work.

Recently, there has been a great deal of interest in surface phenomena ranging from the fundamental interest in two-dimensional physics, surface diffusion, and surface chemistry to the more applied interest in the interfaces used in catalysis and the semiconductor electronics industry. To understand the physics and chemistry of surface phenomena it is first necessary to characterize it — to observe the composition, electronic properties and structure of the surface in question. To this end, several techniques[1] using either massive particle scattering or optical scattering have been developed. In vacuum environments, one may use the probes that employ particle scattering. These have excellent surface specificity. To probe the more practical case of an interface between two dense media, however, one must employ optical techniques. Because optical penetration depths are typically hundreds of Angstroms, linear optical scattering lacks surface specificity and requires special care in the detection scheme.[2] Here, we discuss the use of a nonlinear optical probe, namely second-harmonic generation (SHG), which, like linear optical probes, may be used at interfaces between dense media, but which, like particle scattering, may be inherently specific to interfaces on the order of 10 Å thick. Unlike linear optical probes, however, no sophisticated detection scheme is required for SHG. The typical SHG set up is shown in Fig. 1.

Since the first reports of SHG sensitivity to submonolayer coverages of adsorbates,[3] SHG has been developed into an extremely versatile surface probe. Here, we discuss the physical mechanism of SHG sensitivity to the surface and its electronics properties and then show how this sensitivity may probe not only surface adsorbate coverage, but also adsorbate bonding sites,[4] surface structural symmetry,[5] and the molecular orientation of adsorbates.[6] Examples are drawn from our recent work using SHG to study atoms and molecules adsorbed on a variety of substrates at air-solid and liquid-solid interfaces as well as under ultrahigh vacuum conditions.

SHG Surface Sensitivity

The intrinsic surface specificity enjoyed by SHG is due to a symmetry-related suppression of SHG from the surrounding bulk media. This is most easily recognized by the form of the nonlinear polarization. Consider an interface between two centrosymmetric media which is excited by an intense electric field $\vec{E}(\omega)$ at fundamental frequency ω. $\vec{E}(\omega)$ will induce a nonlinear source polarization at the SH frequency, $\vec{P}^S(2\omega)$, by which the SH radiation from the system will be fully described via Maxwell's equations. $\vec{P}^S(2\omega)$ may be expanded in a power series of $\vec{E}(\omega)$ as follows:

$$\vec{P}^S(2\omega) = \overleftrightarrow{\chi}^{(1)}\vec{E}(2\omega) + \overleftrightarrow{\chi}^{(2)}:\vec{E}(\omega)\vec{E}(\omega) + \overleftrightarrow{\chi}^{(2)}_{NL}:\vec{E}(\omega)\overleftrightarrow{\nabla}\vec{E}(\omega) + \ldots \quad (1)$$

The first term on the right is just the linear susceptibility at 2ω and is ordinarily incorporated into the dielectric constant. The second term is the usual local relationship between $\vec{P}^S(2\omega)$ and $\vec{E}(\omega)$. A polarization of this form can only arise from the interface because $\overleftrightarrow{\chi}^{(2)}$ is a third-rank tensor and must vanish in the centrosymmetric media surrounding the interface. The third term in the series is the largest nonlocal relationship between $\vec{P}^S(2\omega)$ and $\vec{E}(\omega)$ and because $\overleftrightarrow{\chi}^{(2)}_{NL}$ is a fourth-rank tensor, this term is the largest $\vec{P}^S(2\omega)$

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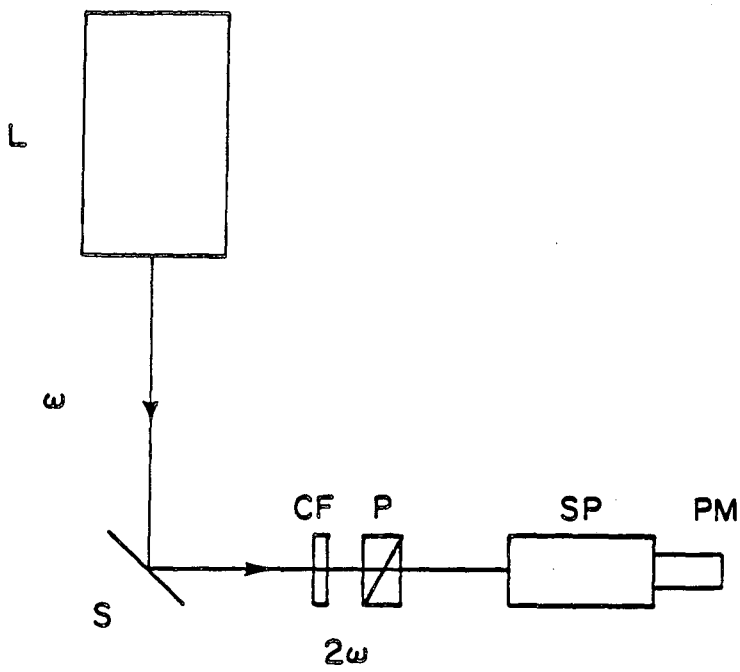

Fig. 1. SHG setup. Excitation laser pulses at fundamental frequency ω are incident on the sample interface at ~ 45° and the SHG signal at frequency 2ω is generated in the reflected direction. Typically 100 SH photons/pulse are generated with ~ 7 ns excitation pulses from a Nd^{3+}:YAG laser with fluences < 50 mj/cm². After passing through appropriate cut-off filters an optional polarizer and a spectrometer, the SH photons are detected with a photomultiplier and processed with gated electronics.

allowed in the centrosymmetric bulk media surrounding the interface. Because the third-rank (surface) term is expected to be a factor of $(ka)^{-1}$ (where k is the wavevector and a is an atomic dimension) larger than the fourth-rank (bulk) term, the surface contribution to the SH radiation is not overwhelmed, and is, in fact, expected to be comparable[7] to the bulk contribution even after taking into account the difference between the surface area and bulk volume giving rise to the radiation. Such an intrinsic suppression of the bulk contribution does not occur from linear or third-order optical processes. Because a large share of the SHG from a system of two dense media arises from the interface, SHG should be especially sensitive to changes to the surface composition and structure.

Because SHG's surface sensitivity requires a breaking of inversion symmetry, SHG is sensitive to the entire non-centrosymmetric interfacial region, including not only the narrow region of material made discontinuous by the discontinuity in the incident electric field $\underset{\sim}{E}(\omega)$ (on the order of a Thomas-Fermi screening length ~ 10A) but also regions affected by surface adsorbates, subsurface impurities, surface electronic states and surface structural disorder or reconstruction.

SHG Sensitivity to Surface Adsorbates

The SHG sensitivity to changes on the surface is due to more than just the suppression of the bulk contribution; it is also due to the sensitivity of optical radiation in the visible and uv to probe the valence electronic structure which may participate in surface bonding. The SH intensity from the surface will be proportional to $|\overleftrightarrow{\chi}^{(2)}|^2$ where the nonlinear susceptibility of the layer $\overleftrightarrow{\chi}^{(2)}$ is the sum over all surface sites of the nonlinear polarizability (defined per site) $\overleftrightarrow{\alpha}^{(2)}(2\omega)$. The latter may be derived by second-order time-dependent perturbation theory:

$$\alpha^{(2)}_{ijk}(2\omega) = \sum_{\substack{g \\ n',n\neq g}} \rho_{gg} \left\{ \frac{\langle g|p_i|n\rangle\langle n|p_j|n'\rangle\langle n'|p_k|g\rangle}{(2\omega - \omega_{ng} + i\Gamma_{ng})(\omega - \omega_{n'g} + i\Gamma_{n'g})} \right.$$

$$+ \frac{\langle g|p_k|n\rangle\langle n|p_j|n'\rangle\langle n'|p_i|g\rangle}{(2\omega + \omega_{n'g} + i\Gamma_{n'g})(\omega + \omega_{ng} + i\Gamma_{ng})} - \frac{\langle g|p_k|n\rangle\langle n|p_j|n'\rangle\langle n'|p_i|g\rangle}{(2\omega - \omega_{n'n} + i\Gamma_{n'n})}$$

$$\left. \times \left(\frac{1}{\omega + \omega_{ng} + i\Gamma_{ng}} + \frac{1}{\omega - \omega_{n'g} + i\Gamma_{n'g}} \right) \right\} + \{\text{same with } j \leftrightarrow k\}. \qquad (2)$$

Here $\langle n'|\vec{p}|n\rangle$, $\omega_{n'n}$ and $\Gamma_{n'n}$ denote the dipole moment, frequency and linewidth of a transition from $|n\rangle$ to $|n'\rangle$ and the sum is over intermediate states $|n\rangle$ and $|n'\rangle$ and over the occupied states $|g\rangle$ of the system weighted by the density matrix element ρ_{gg}. Because of the resonant denominators, $\tilde{\alpha}^{(2)}(2\omega)$ is especially sensitive to electronic states near resonance with ω or 2ω. It follows that SHG will be sensitive to the adsorption of molecules with free molecule transitions in resonance with 2ω. In earlier work, we used the frequency dependence of $\tilde{\alpha}^{(2)}(2\omega)$ to obtain the spectrum of the $S_0 \rightarrow S_2$ transition of Rh 6G and 110 molecules adsorbed to a fused silica substrate. In addition, however, $\tilde{\alpha}^{(2)}(2\omega)$ will also be sensitive to changes in the electronic structure of the combined substrate-molecule system upon adsorption. For example, an oxygen atom would not be expected to have a substantial intrinsic nonlinear polarizability. Yet as seen in Fig. 2, the SHG from the Rh(111) surface changes dramatically upon exposure to O_2[4] and subsequent O atom adsorption to the surface. The SHG reaches a saturation value when the O-atom coverage saturates. By changing the electronic states from those of the bare metal substrate, the adsorbed O atom induces a change in the nonlinear polarizability of the surface site $\Delta\tilde{\alpha}^{(2)}(2\omega)$.

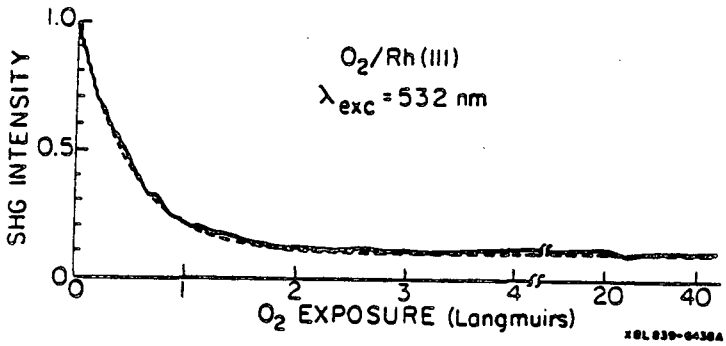

Fig. 2. SHG intensity from the Rh(111) surface as a function of O_2 exposure, 1 Langmuir = 10^{-6} torr-sec. The (2 X 2) LEED pattern of O on Rh(111) was observed at ≈ 20 L. (—— expt., --- theor. fit)

Incidentally, the data presented in Fig. 2 was the first in which a quantitative relationship between the SHG intensity and the adsorbate coverage was established on a well-characterized system. The dashed line is the fit of the SHG data to $|\chi^{(2)}|^2$ where $\chi^{(2)}$, the nonlinear susceptibility of the surface layer has the simple form $\chi^{(2)} = A + B\theta/\theta_{sat}$. Here, A and B are constants incorporating the polarizabilities of the bare and O-covered Rh sites, θ is the fractional coverage of O on Rh(111) surface atoms, and θ_{sat} is the saturation value of θ. The O_2 adsorption on Rh(111) was shown to follow Langmuir kinetics by Auger Electron Spectroscopy[9] so $\theta/\theta_{sat} = 1 - \exp(kPt)$ where P is the O_2 pressure, t is time and k is a constant related to the sticking coefficient. In deriving this form for $\chi^{(2)}$, one assumes that the chemisorption of O atoms occurs at equivalent sites and is independent of θ. Then $\Delta\tilde{\alpha}^{(2)}(2\omega)$ upon O atom adsorption is also independent of θ. These assumptions are completely consistent with Langmuir kinetics. The fit is obtained with B/A = 1.06 exp(160°) and a sticking coefficient for O_2 equal to 1 assuming $\theta_{sat} = 0.5$. The latter is in excellent agreement with Ref. 9.

We note that in this and other similar measurements the SHG technique allows a non-destructive and relatively fast (in this case, 0.1 s limited by the laser repeat time) *in situ* measurement of adsorption and desorption processes. As such a probe, SHG promises to be a useful supplement to the relatively large number of surface probes already available in ultrahigh vacuum environments. In non-vacuum environments, of course, SHG enjoys a more unique position.

Sensitivity to Adsorbate Bonding Site

It follows from the sensitivity of $\tilde{\alpha}^{(2)}(2\omega)$ to electronic properties that SHG will be sensitive not only to adsorbate coverage but also to composition if $\Delta\tilde{\alpha}^{(2)}(2\omega)$ is different for two adsorbates. Similarly, SHG may be sensitive to the site of bonding if the electronic properties of the bonds are different. This sensitivity was demonstrated recently for the case of CO adsorbed to Rh(111) at top- and bridge-sites. As shown in Fig. 3, the SHG from Rh(111) covered with CO molecules follows two smooth dependences on CO coverage. For coverages $\theta < 1/3$ CO bonds to top-sites only and the smooth curve is the fit to the data using $\chi^{(2)}$ of the form $A + B\theta$. For CO coverages $1/3 < \theta < 3/4$, CO bonds to top- and bridge-sites with a final distribution of $\theta = 1/2$ on top-sites and $\theta = 1/4$ on bridge-sites. Over this region $\Delta\alpha^{(2)}(2\omega)$ is different from the value for top-sites alone and the smooth curve is the fit to the data using a $\chi^{(2)}$ of the form $A + 1/3B + C(\theta - 1/2)$ where C is the new parameter and A and B are the same constants determined for bonding at top-sites. That C and B are different proves SHG is sensitive to the two bonding sites.

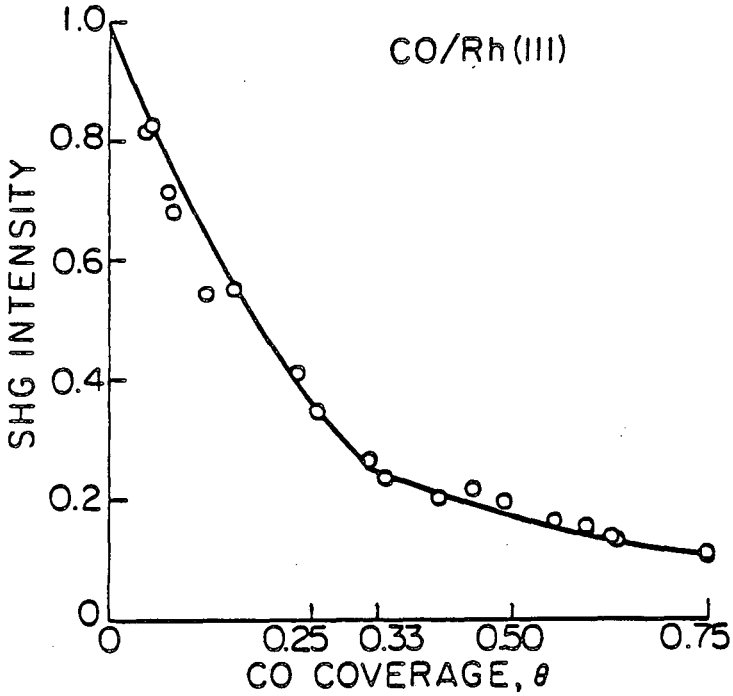

Fig. 3. SHG intensity from the Rh(111) surface as a function of CO coverage which was determined by thermal desorption yield and calibrated with the [($\sqrt{3} \times \sqrt{3}$)R30°, θ = 1/3] and the [(2 × 2), θ = 3/4] LEED patterns. (o expt.; —— theor. fit)

Sensitivity to Surface Symmetry

SHG sensitivity to electronic properties rests not only in the energy denominators of $\overleftrightarrow{\alpha}^{(2)}(2\omega)$ but also in its tensorial properties. Because the elements of $\overleftrightarrow{\alpha}^{(2)}(2\omega)$ bear direct relation to the direction of electronic wave functions through the dipole matrix elements in Eq. (2), the nonlinear susceptibility of the surface layer $\overleftrightarrow{\chi}^{(2)}$ will also reflect surface symmetries. An optical means of detecting surface order or symmetry can be an exciting new tool for monitoring the growth of epitaxial layers and surface structural transitions.

Of course $\overleftrightarrow{\chi}^{(2)}$ is a material parameter which must have the symmetry of the surface and bulk. However, the anisotropy due to surface symmetry may be too small to use SHG as a probe of symmetry. Recently, the SHG from crystalline Si surface[11,12] was shown to exhibit strong anisotropy as the crystal was rotated about its normal. We showed[5] that this anisotropy could be explained completely by choosing the appropriate symmetries for the surface and bulk susceptibilities with the forms given in Eq. (1). For the (100) surface with 4 m symmetry, the surface has only 3 independent elements of surface susceptibility $\overleftrightarrow{\chi}^{(2)}$: $\chi^{(2)}_{\perp\perp\perp}$, $\chi^{(2)}_{\perp\parallel\parallel}$ and $\chi^{(2)}_{\parallel\parallel\parallel}$, which are all independent of the crystal rotation about its normal. The subscripts $\perp$ and $\parallel$ refer to directions perpendicular and parallel to the surface. For the (111) surface with 3 m symmetry, the surface has the same three isotropic elements of $\overleftrightarrow{\chi}^{(2)}$ as the (100) face plus one anisotropic element, $\chi^{(2)}_{\zeta\zeta\zeta}$, which depends on the rotation angle of the surface. The $\hat{\zeta}$-direction is along the axis of projection of the principle bulk axes on the surface plane. As for the bulk, the susceptibility $\overleftrightarrow{\chi}^{(2)}_{NL}$ has only two elements for SHG excited with a single plane wave. The form for the component of the nonlocal polarization along a principle axis i is

$$P^{(2)}_{NL,i} = \gamma \nabla_i (\vec{E} \cdot \vec{E}) + \zeta E_i \nabla_i E_i .$$

Using these forms for $\overleftrightarrow{\chi}^{(2)}$ and $\overleftrightarrow{\chi}^{(2)}_{NL}$ one can derive the form of the SHG as a function of rotation angle for any geometry of excitation. The SHG intensity for any excitation geometry is proportional to the square of an effective scalar susceptibility $|\chi^{(2)}_{eff}|^2$ where $\chi^{(2)}_{eff}$ may be written $\chi^{(2)}_{eff} = \chi^{(2)}_{iso} + \chi^{(2)}_{anis}\, f(\psi)$. The subscripts refer to an isotropic and anisotropic amplitude, respectively, and $f(\psi)$ is a function of angle ψ of rotation about the surface normal.

For certain excitation and SHG polarization directions the isotropic amplitude is zero and only the anisotropic elements of the susceptibilities: $\chi^{(2)}_{\zeta\zeta\zeta}$ for the (111) surface and ζ for the bulk contribute to the SHG. We see SHG in such a condition ($\hat{p}$-polarized excitation and $\hat{s}$-polarized SH) in Figs. 4a and 4b for the (100) and (111) faces as the crystals are rotated angle ψ about their normals. The solid lines are the data and the dashed lines are the fit of the SHG data to $|\chi^{(2)}_{eff}|^2$ with $\chi^{(2)}_{eff}$ of the form:

$$\chi^{(2)}_{eff} = a\zeta \sin 4\psi \quad \text{for the (100) face} \tag{3a}$$

$$\chi^{(2)}_{eff} = b(\chi^{(2)}_{\xi\xi\xi} + c\zeta)(3\cos^2\psi \sin\psi - \sin^3\psi) \quad \text{for the (111) face.} \tag{3b}$$

Here, $\psi = 0$ was determined by x-ray diffraction and the constants a, b, and c are specified by geometry and the dielectric constants of Si. Note the manifestation of the 4 m and 3 m symmetries in these forms which have been derived using the surface and bulk polarizations specified above.

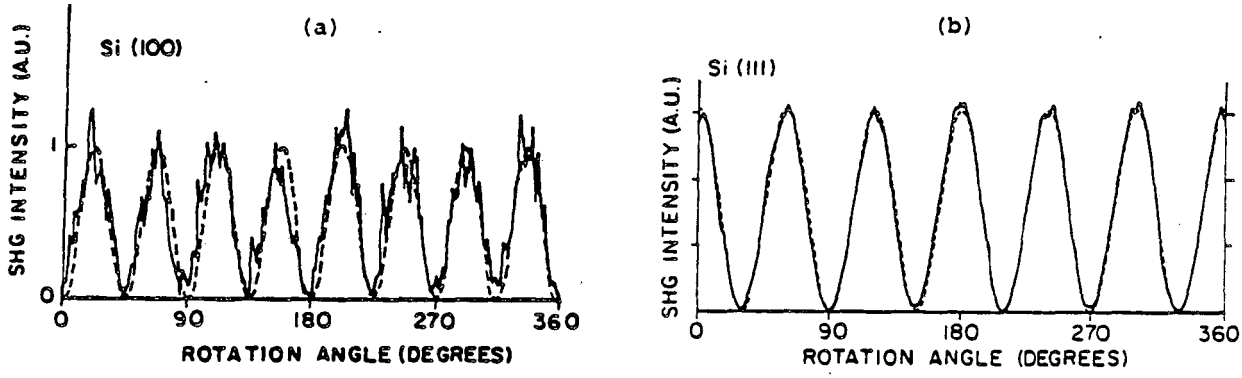

Fig. 4. $\hat{s}$-polarized SHG intensity vs. angle of rotation from the a) Si(100) and b) Si(111) surfaces with $\hat{p}$-polarized excitation at 45° angle of incidence.

For general excitation and SHG polarization directions a combination of the isotropic and anisotropic elements of susceptibilities contribute to the SHG. As shown in Fig. 5, the SHG from the (111) face for $\hat{p}$-polarized input and $\hat{p}$-polarized output has equal contributions from isotropic and anisotropic susceptibilities as the rotation angle is varied. The dashed line is the fit of the SHG data to $|\chi^{(2)}_{eff}|^2$ using:

$$\chi^{(2)}_{eff} = A + B(\chi_{\xi\xi\xi} + c\zeta)(3\sin^2\psi \cos\psi - \cos^3\psi)$$

where A is a fully specified combination of the isotropic susceptibilities. That $\chi^{(2)}$ drops to zero at = 90°, 210°, and 330° indicates $A = -B(\chi_{\xi\xi\xi} + c\zeta)$.

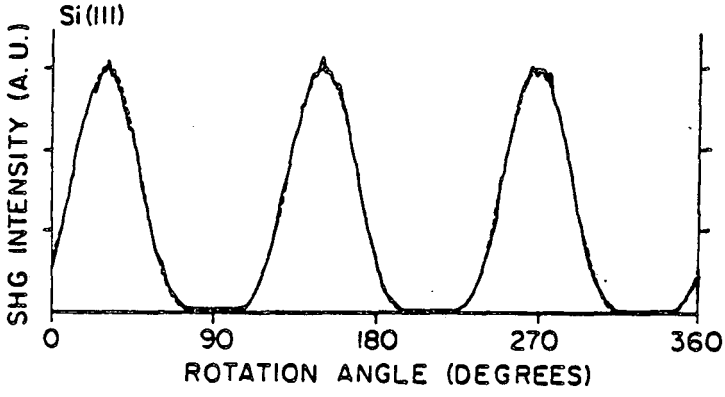

Fig. 5. $\hat{p}$-polarized SHG intensity vs. angle of rotation for the Si(111) surface with $\hat{p}$-polarized excitation at 45° incidence.

C. V. Shank et al. recently reported a time-resolved investigation of the transition from structural order to disorder of a Si(111) surface after irradiation by an intense pump laser pulse. They probed the surface order by monitoring the rotational anisotropy of the SHG excited by a weak time-delayed probe beam. For $\hat{p}$-polarized pump pulses below the damage threshold, the $\hat{p}$-polarized SHG always showed rotational anisotropy similar to that shown in our Fig. 5. However, for pump pulses exceeding the damage threshold, rotational anisotropy vanished after ~ 3 psec leaving only an isotropic contribution to the SHG. This indicated the transition to disorder proceeded in ~ 3 psec. Had they used the $\hat{s}$-polarized SHG from their $\hat{p}$-polarized probe pulse (as in Fig. 4b) they would have observed a background free monitor of the surface order, i.e., the purely rotationally anisotropic SHG signal would have vanished after ~ 3 psec. The work of C. V. Shank et al. demonstrates the extension of SHG to the study of fast-time scale photo-induced surface phenomena.

Sensitivity to Molecular Orientation

The interaction between a substrate and adsorbates can be greatly elucidated by knowing the orientation and arrangement of the adsorbates. Arrangement can be probed via surface probes of symmetry such as LEED and, by extension of the previous section, with the rotational anisotropy of SHG. The tilt angle of a molecule with respect to the surface may also be deduced by surface-related selection-rule effects on vibrational spectra,[13] LEED,[14] and SHG. In contrast to the first two techniques, SHG probes orientation by measuring directly the average orientation of the dipole matrix elements of molecules on the surface. More precisely, by measuring the susceptibility of the adsorbed molecular layer, $\overleftrightarrow{\chi}^{(2)}$, one will obtain an average of $\overleftrightarrow{\alpha}^{(2)}(2\omega)$ over all molecular orientations where the tensor $\overleftrightarrow{\alpha}^{(2)}(2\omega)$ is referenced to molecular coordinates.

To illustrate how this might work, we treat the case of a layer of uniaxial molecules distributed isotropically in the plane of the substrate with some distribution of tilt angle θ. The largest element of $\overleftrightarrow{\alpha}^{(2)}(2\omega)$ will be $\alpha^{(2)}_{\hat{\zeta}\hat{\zeta}\hat{\zeta}}$ where the $\hat{\zeta}$-axis is the unique molecular axis. In this case, the summation over all molecules leaves the layer susceptibility $\overleftrightarrow{\chi}^{(2)}$ with this simple form:

$$\chi^{(2)}_{\perp\perp\perp} = N\alpha^{(2)}_{\xi\xi\xi}\langle\cos^3\theta\rangle$$
$$\chi^{(2)}_{\parallel\perp\parallel} = \chi^{(2)}_{\perp\parallel\parallel} = \tfrac{1}{2}N\alpha^{(2)}_{\xi\xi\xi}\langle\cos\theta\ \sin^2\theta\rangle$$

where subscripts $\perp$ and $\parallel$ refer to directions perpendicular and parallel to the surface, N is the molecule surface density, the brackets indicate the average over the distribution function of θ and the trigonometric functions are simply the projections of the molecular $\hat{\zeta}$-axis on the $\perp$ and $\parallel$ directions. By measuring a ratio of the elements of $\overleftrightarrow{\chi}^{(2)}$ we obtain a ratio of the moments of θ with no dependence on $N\alpha_{\xi\xi\xi}$. Such a ratio may be measured directly by measuring the output polarization (the ratio of $\hat{p}$- to $\hat{s}$-polarization) of SHG for a given input polarization beam.

For a particular geometry we obtained the ratio $R = \langle\sin^2\theta\ \cos\theta\rangle/\langle\cos\theta\rangle$ for monolayer and submonolayers of a uniaxial molecule, p-nitrobenzoic acid (PNBA: HOOC NO_2), adsorbed at the air/silica interface and at the PNBA-ethanol solution/interface.[6] Previous workers[15] have established that PNBA adsorbs via the COO^--group to fused silica, and the $\hat{\zeta}$-axis runs through the COO^-- and NO_2-groups which strongly polarize the π-electrons of the benzene ring. We found R = 0.88 and 0.33 at the air/silica and liquid/silica interfaces, respectively, which would imply θ = 70° and 40° for the two interfaces if the θ-distribution were infinitely narrow. For comparison purposes, even for a θ-distribution which were Lorentzian and 15° FWHM, the center of the distributions would lie at θ = 76° and 37°. The relatively flat orientation of PNBA on the air/silica interface may be due to the relatively strong static dipole-dipole interaction between molecules which would favor a flat orientation and to chemical interactions between the NO_2-group and the silica which would pull the molecule toward the substrate. The more upright orientation of PNBA at the ethanolic solution/silica interface may be due to a weakening of the dipole-dipole interaction by the ethanol which has a DC dielectric constant of 24 and to the interaction of the ethanol with the NO_2-group suppressing interactions between NO_2 and silica.

Conclusion

The potential for using SHG as a surface probe has been explored in a number of experiments on various surfaces. It's reliability has been established in SHG studies of well-characterized surfaces. The intrinsically fast time response of SHG allows it to be used in studies of surface dynamics on time scales limited only by the laser repetition time. In a pump-probe time sequence SHG may be used to study photo-induced surface dynamics on time scales limited only by laser pulsewidths. The frequency dependence of SHG may be used to study surface electronic structure at visible and uv wavelengths. The application of SHG to exciting new surface science problems looks most fruitful.

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