Optical Second Harmonic Generation as a Probe of Surface Chemistry

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I. Introduction

Optical second harmonic generation (SHG) is the nonlinear conversion of two photons of frequency \( \omega \) to a single photon of frequency \( 2\omega \) which, in the electric dipole approximation, requires a noncentrosymmetric medium. The ability of noncentrosymmetric crystals to produce SHG has led to their implementation as frequency doublers in a wide variety of laser systems. SHG can also be obtained from the break in symmetry that occurs at the interface between two centrosymmetric media. Since only the first few atomic or molecular monolayers on either side of the interface participate in this symmetry breaking, the SHG process can be used as a highly surface-selective optical probe of interfacial phenomena.1

Shortly after the initial SHG measurements of Franken et al. in 1961,2 the sensitivity of SHG to the interface between two centrosymmetric media was experimentally demonstrated by Brown, Parks, and Sleeper.3 In a series of papers, Bloembergen and co-workers determined the theoretical equations that govern SHG from surfaces in a reflection geometry,4,5 from a thin slab of nonlinearly active material,4 and finally from the interface of two centrosymmetric media.6 In the last case, it was assumed that the discontinuity in the electric fields at the interface led to a quadrupolar term in the nonlinear polarization that resulted in SHG from the interface. However, in 1969 Brown and Matsuoka demonstrated that the SHG from a silver surface was highly sensitive to the presence of adsorbed layers.7 In this work, Brown and Matsuoka proposed that the observed sensitivity was due to an additional surface dipole term in the nonlinear polarization. Rudnik and Stern subsequently presented a new theoretical description of SHG from interfaces between centrosymmetric media in which the surface sensitivity of SHG was primarily attributed to the symmetry-breaking nature of the surface rather than the quadrupolar effects of the previous theories.8 From these initial works, SHG has evolved into a powerful surface technique that has been widely applied. The extensive application of SHG to the study of surfaces is a direct result of its tremendous sensitivity and selectivity to the interfacial region.

This review presents an extensive overview of the current literature on the application of SHG to the study of surface chemistry. A number of fine reviews on the different aspects of SHG at surfaces have appeared in the past few years.9-21 We have chosen to concentrate on the most recent works in the field (primarily after 1988) and to present some examples of chemical processes at interfaces that have been studied with the surface SHG technique. Our presentation will include a discussion of some general theoretical concepts that are used to interpret the results of the SHG experiments, along with a brief summary of the experimental requirements for surface SHG measurements. The various examples of surface SHG studies have been divided according to the type of chemical information obtained from the particular experiment.

II. Sources of SHG at Interfaces

The generation of second harmonic light at frequency \( 2\omega \) from an interface can be described using a model of the sample as a collection of \( N \) electrons, each in a slightly anharmonic potential field, under the influence of an external fundamental light field of frequency \( \omega \).22 For metals, this model can be used to approximate the response from the nearly free electrons at the surface (an extension of Drude theory). For a monolayer of molecules adsorbed to a surface, this model can be viewed as a very simple picture of the valence electrons that lead to the molecular nonlinear optical response. A description of the motion \( x(t) \) for one of the electrons is given in the following equation:

\[
\dot{x} + \omega_0^2 x + \xi x^2 = \frac{e}{m} \{E(\omega) \cos(\omega t)\}
\]

where \( \omega_0 \) and \( \xi \) are the resonant frequency and anharmonicity of the potential field, \( E(\omega) \) is the magnitude of the oscillating electric field associated with the incident fundamental light, and all other symbols have their usual meaning. The motions of the collection of electrons under the influence of this oscillating electric field give rise to a macroscopic time-dependent polarization \( P(t) = \Sigma_N x(t) \). The Fourier component of this polarization at frequency \( 2\omega \), \( P^{(2)}(2\omega) \), is responsible for the SHG from the sample and is proportional to the square of the amplitude of the incident electric field:

\[
P^{(2)}(2\omega) = \chi^{(2)} E^2(\omega)
\]

The proportionality constant \( \chi^{(2)} \) is called the second-order nonlinear susceptibility, and is given in this simple
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description by the following equation:

\[
\chi^{(2)} = \frac{N e^4}{2m^2 (\omega_0^2 - \omega^2)^2 (\omega_0^2 - 4\omega^2)}
\]  (3)

Note that \( \chi^{(2)} \) has several important properties:

(i) \( \chi^{(2)} \) is proportional to the anharmonicity constant \( \omega \). This is the realization of the symmetry requirements for SHG in the electric dipole approximation. If \( \omega \) is zero, the potential becomes symmetric and there is no SHG. For metals, theoretical calculations have shown that the magnitude of \( \chi^{(2)} \) from the interface depends critically on the shape of the electron density profile at the surface.23-38 For molecular systems, only those molecules which have an asymmetric electron density distribution (either inherent or induced by adsorption to a surface) will be capable of yielding a surface second harmonic response.

(ii) \( \chi^{(2)} \) has resonances at frequencies \( \omega_0 \) and \( (1/2)\omega_0 \). The second harmonic response from a metal surface when both the fundamental and second harmonic frequencies are below the plasma frequency \( \omega_0 \) is sometimes referred to as "nonresonant SHG" in reference to the weak wavelength dependence expected for the SHG from the surface.19 At frequencies above \( \omega_0 \), resonance effects should be observed in the surface second harmonic response. In addition, real metals possess complex band structures that contain optical interband transitions and surface-state excitations which can also potentially lead to resonant enhancement effects and wavelength dependencies in the surface second harmonic response.37,39-45

When in resonance with an electronic transition in an adsorbed molecule, the SHG from the interface is often dominated by adsorbate contributions to \( \chi^{(2)} \). This molecular surface second harmonic response is sometimes referred to as "resonant SHG".46 The magnitude and polarization dependence of the resonant SHG response from a monolayer of adsorbed molecules depends upon the average molecular orientation at the surface and the intrinsic nonlinear optical response of the molecules. This response is described by the molecular nonlinear polarizability tensor \( \beta \) and can be calculated theoretically.1,47-49

(iii) In this model, \( \chi^{(2)} \) is proportional to \( N \), the number of electrons in the system. For molecules, this means that \( \chi^{(2)} \) of an adsorbed monolayer will depend linearly on the surface concentration. Similarly for metals, the \( \chi^{(2)} \) of the surface will be directly related to the surface concentration of free electrons. An extension of this relation is that the SHG should vary inversely with the work function of the metal surface. A number of authors have exploited this relation in a semiquantitative fashion.39,50-54 In general, it is observed that adsorbates which donate electrons to the metal surface (e.g., hydrogen, alkali metals) increase the surface second harmonic response, whereas adsorbates which accept electrons from the metal surface (e.g., oxygen) generally decrease the amount of SHG from the surface.

When the preceding derivation of the surface nonlinear susceptibility \( \chi^{(2)} \) is generalized for application to three-dimensional systems, \( \chi^{(2)} \) becomes a third-rank tensor. The second harmonic intensity \( I(2\omega) \) from any interface in either reflection or transmission geometry is proportional to the square of \( \chi^{(2)} \):

\[
I(2\omega) = \frac{32\pi^3 e^2 \theta_\omega}{c^3} |e(2\omega)\cdot e(\omega)^2 f(\omega)|^2 (4)
\]

where \( \theta_\omega \) is the angle from the surface normal at which the SHG signal occurs, the vectors \( e(\omega) \) and \( e(2\omega) \) describe the fundamental and second harmonic light.
fields at the surface, and all other symbols have their usual meaning. This equation has been derived by Heinz and by Mizrahi and Sipe.

As implied in eq 4, the surface nonlinear susceptibility $\chi^{(2)}$ is a third-rank tensor which in general can have 18 distinct nonzero complex elements, $\chi_{IJK}$, where $I$, $J$, and $K$ refer to Cartesian axes defined with the surface normal as the $+Z$ direction. For most systems, the number of nonzero elements is greatly reduced by the surface symmetry. For example, if the surface is rotationally isotropic about the surface normal, as in the case of a nonchiral liquid surface, there are only three distinct independent nonzero tensor elements: $\chi_{ZXX} = \chi_{XXZ} = \chi_{YZZ}$, and $\chi_{XYZ} = \chi_{XYZ} = \chi_{YZX}$. For single-crystal metal or semiconductor surfaces, additional tensor elements are allowed and SHG experiments can be used to probe the average surface symmetry as described below.

The description of the surface nonlinear susceptibility discussed above is valid only in the electric dipole approximation. It should be noted that the SHG signal from an interface arises from the sum of surface electric dipole, bulk magnetic dipole, bulk electric quadrupole, and higher order contributions. Although the additional terms cannot be neglected a priori, it is often assumed or determined experimentally that they do not contribute significantly to the surface second harmonic response. However, in certain cases the contributions of the higher order surface and bulk terms to the overall nonlinear polarizability are important; these cases have been discussed in the literature.

### III. General Experimental Considerations

Since the second harmonic response of an interface is proportional to the square of the incident light intensity, surface SHG measurements normally employ high-powered pulsed-laser systems. A schematic of the typical experimental apparatus used in surface SHG studies is shown in Figure 1. A nanosecond or picosecond pulsed laser is usually the source of the fundamental light. The output of the laser is polarized, filtered to remove any extraneous second harmonic light, and sometimes focused onto the sample. Typical power densities on the surface range from $10^4$ to $10^8$ W cm$^{-2}$, depending on the nonlinear susceptibility and damage threshold of the surface. The SHG created at the surface is analyzed with a second polarizer and separated from the fundamental light by filters and a small monochromator. The second harmonic photons are detected with a photomultiplier tube and the overall second harmonic intensity is measured with either a boxcar averager or gated photon counting electronics. Conversion efficiencies are normally very small, on the order of 10$^{-12}$%. Thus, the observed SHG signal from surfaces typically ranges from 5 to 50 000 photons s$^{-1}$, depending on the laser and surface employed. A small piece of the fundamental beam is often diverted to a reference channel that creates an SHG signal from a second source. The output of the reference channel is used to normalize the surface SHG signal and remove the effects of any fluctuations in the laser power during the course of the experiment.

Surface SHG experiments can be performed in either a reflection or transmission geometry. (The latter, of course, will only work for transparent substrates.)

![Figure 1. The SHG experimental apparatus.](image)

Typical angles of incidence for the fundamental beam range from 30° to 70° with respect to the surface normal. For an isotropic surface, no SHG is observed at an incident angle of 0° (normal incidence). The second harmonic created at the interface is phase matched to the incident fundamental light in the plane of the surface. Therefore, for surfaces in air or in UHV, the SHG beam is coincident with the reflected fundamental beam; however, for more dispersive media the two beams need not be collinear. A more complicated phase-matching arrangement arises if the SHG experiment is performed with two fundamental beams. Additional experimental details specific to a particular surface SHG measurement are elaborated separately in the following sections.

### IV. SHG Measurements of Surface Chemistry

The sensitivity and selectivity of the SHG technique has led to its application in the study of surface chemistry for a large number of interfacial systems. The surface nonlinear susceptibility, $\chi^{(2)}$, is directly related to the structure of the interface and can be determined from measurements of the magnitude, polarization dependence, and phase of the SHG from the surface. What is measured in most surface SHG experiments is a change in $\chi^{(2)}$ upon adsorption to some new value $\chi'^{(2)}$. This change can be formally separated into two parts:

$$\chi'^{(2)} = \chi^{(2)} + \chi_{A}^{(2)} + \Delta \chi_{I}^{(2)}$$

where $\chi_{A}^{(2)}$ is the inherent nonlinear susceptibility of the adsorbate and $\Delta \chi_{I}^{(2)}$ is the change in nonlinear susceptibility of the surface due to any interactions with the adsorbate. SHG experiments utilizing either
\( \chi_A^{(2)} \) or \( \Delta \chi^{(2)} \) have been applied to metal, semiconductor, oxide, polymer, and liquid surfaces. These experiments can be categorized by the type of information obtained from the surface SHG studies: (i) adsorption strength and surface coverage, (ii) molecular orientation, (iii) surface symmetry, (iv) interfacial electric field strength, and (v) reaction kinetics and surface diffusion.

A. Adsorption and Surface Coverage Measurements

Most surface SHG experiments monitor the adsorption of a species to an interface via changes in the surface second harmonic response. While these changes can always be used in a qualitative manner to observe an adsorption process, in some cases the SHG measurements can be used as a quantitative measure of adsorption strength and surface coverage. In these instances the modifications to the surface nonlinear susceptibility are related to changes in the relative surface coverage, \( \theta \), where \( \theta = \Gamma / \Gamma_p \), the adsorbate surface coverage divided by the maximum surface coverage observed for the species. For systems where the nonlinear optical response of an adsorbate dominates the surface SHG, \( \theta \) is monitored via \( \chi_A^{(2)} \). At other interfaces the relative surface coverage of an adsorbed species is probed indirectly via changes in the surface nonlinear susceptibility (\( \Delta \chi^{(2)} \)). The various classes of interfaces at which the adsorption and reaction of surface species have been monitored with SHG experiments are examined separately in further detail below.

1. Metal Surfaces in UHV

The original SHG measurements of adsorption to metal surfaces in vacuum were performed by Brown and Matsuoaka in 1989, who reported that the amount of SHG from a silver surface changed dramatically upon adsorption of contaminants. Over a decade later, Tom et al. published the first application of SHG measurements to single-crystal metal surfaces in UHV; in these studies, the authors used SHG to investigate the adsorption of O, CO, and Na onto Rh(111) surfaces. Since these initial efforts, the application of SHG to studies of adsorption at metal surfaces in UHV has expanded considerably and to date includes studies of adsorption onto Ag, Cu, Pt, Pd, Ni, Al, Re, and Rh.

The SHG from the surface of metals is almost always dominated by the nonlinear polarizability of the free and bound metal electrons at the interface. Any changes in the amount of surface SHG upon adsorption of a molecule or atom onto the metal surface are usually related to changes in the nonlinear optical response of the surface electronic states. A number of researchers have attempted detailed theoretical descriptions of the changes in the SHG response of the surface upon chemisorption, but have only produced qualitative results. Most experimental studies still rely on empirical models similar to the anharmonic oscillator theory described in section II. As mentioned in that section, in some instances the SHG signal can be related to the free-electron surface density and the work function of the metal surface.

Whatever the mechanism, the changes observed in the SHG from a metal surface upon adsorption can be formally described as a change in the surface nonlinear susceptibility, \( \Delta \chi^{(2)} \). If the changes are sufficiently small, then \( \Delta \chi^{(2)} \) will depend linearly on the relative surface coverage \( \theta \) of the adsorbed species. An example of this relationship can be seen in Figure 2, in which the SHG signal from a Ni(110) surface is plotted as a function of CO surface coverage. The solid line in Figure 2 is a fit of the experimental data using the assumption of a linear decrease in \( \chi^{(2)} \) with increasing \( \theta_{CO} \). Further theoretical and experimental work is needed in this area to relate the SHG measurements in a detailed fashion to the electronic structure of the metal surface.

2. Metal–Electrolyte Interfaces

At solid–liquid interfaces, the unique symmetry requirements of the SHG process result in a surface selectivity (as well as sensitivity) that is not attainable with any linear spectroscopic method. For this reason, SHG is an ideal spectroscopic technique for examining electrochemical interfaces and has been employed to study the adsorption of molecules, ions, metal atoms, and reaction intermediates at metal electrodes. SHG has also been used to characterize the surface enhancement of electromagnetic fields at roughened noble metal electrodes; these experiments are not covered in this review.

SHG measurements of surface symmetry, surface reconstruction, and electrostatic fields at metal electrodes are discussed separately in sections C and D.

As in the UHV studies, the SHG from the metal–electrolyte interface is dominated by the nonlinear optical response of the metal surface. Changes in the metal surface nonlinear susceptibility (\( \Delta \chi^{(2)} \)) due to adsorption are used to indirectly monitor the relative surface coverage of chemisorbed species. In the absence of any specific electronic resonances, the chemisorption of species which increase the surface density of free electrons results in an increase in the surface SHG. In contrast, adsorbates which decrease the surface free-electron density lead to a reduction of the SHG from the interface. This indirect method of monitoring chemisorption limits the chemical selectivity of these
At potentials above 0.4 V vs SCE, Figure 3a shows a decrease in the SHG from the platinum surface due to the formation of an oxide or OH monolayer. This decrease in surface SHG is consistent with the results of UHV experiments of oxygen adsorption onto Pt(111) surfaces. The formation of oxides has also been found to affect the SHG signal from Ag, Au, Cu, Fe, and Ni electrodes.

At potentials between 0.0 V and 0.4 V, chlorine ions are chemisorbed onto the platinum electrode. The amount of SHG observed in Figure 3a at these potentials depends upon the amount of chloride chemisorbed onto the surface. Figure 3b plots the relative surface coverage of chloride ($\theta_{Cl}$) at 0.2 V determined from the SHG experiments as a function of chloride concentration in solution. The surface coverage of chloride was obtained by assuming a linear relationship between $\Delta \chi_2$ and $\theta_{Cl}$, and that $\theta_{Cl} = 1$ at the highest solution concentration. Bromide and iodide adsorption onto Pt electrodes has also been monitored with SHG measurements. In addition, anionic adsorption has been studied extensively at Ag, Cu, and Au electrodes.

### 3. Semiconductor Surfaces

SHG experiments employing GaAs and Si crystals in a reflection geometry represent some of the earliest examples of surface SHG measurements. The analysis of the second harmonic response in these early experiments aided in the development of the macroscopic theoretical description of nonlinear optical effects at interfaces. The first systematic application of SHG to the study of adsorption at semiconductor surfaces was performed by Chen et al., who monitored the adsorption of alkali metals onto Ge in UHV. Since those initial experiments, the vast majority of SHG measurements of adsorption onto semiconductor surfaces has been performed on Si surfaces. Specific works have included studies on the chemisorption of H, P, B, Ba, Ge, Ga, As, and Au onto Si surfaces in UHV. Several authors have also studied the formation and removal of oxide layers on Si. In addition, Heinz et al. have used SHG measurements to probe the CaF$_2$-Si interface. SHG measurements have also been used to study adsorption onto Ge and noncentrosymmetric GaAs surfaces. In the majority of these measurements, adsorption was monitored through the contributions of $\Delta \chi_2$ to the surface nonlinear susceptibility.

### 4. Oxide and Insulator Surfaces

In contrast to metal and semiconductor surfaces, it is often the case for insulating oxide surfaces (e.g., fused silica) that the inherent nonlinear susceptibility of the surface is small. In these systems, the molecular SHG from an adsorbate, $\chi_d^{(2)}$, can dominate the surface susceptibility; this is particularly true if the adsorbed molecules are specifically designed with a large nonlinear polarizability and if the SHG is resonantly enhanced by the selection of fundamental or second harmonic wavelengths near a molecular electronic transition. The SHG from these surfaces will be proportional to the square of the surface concentration of the adsorbed molecules, as long as the average molecular orientation and the molecular nonlinear polarizability of the adsorbate does not change as a function of surface coverage.
The use of resonant SHG as a quantitative measure of molecular adsorption on oxide surfaces was first demonstrated by Heinz et al. for the adsorption of p-nitrobenzoic acid at the fused silica–ethanol interface. Subsequent studies of adsorption have been performed for a variety of molecules at fused silica surfaces in air, ethanol, chloroform, and chloroform. In addition to silica surfaces, SHG has also been employed to monitor adsorption onto a variety of other insulator surfaces.

In some cases the surface nonlinear susceptibility depends on the surface coverage of an adsorbed molecule in a more complicated fashion. For example, it has been shown for large dye molecules that molecular aggregation within the monolayer leads to large local field effects which result in a nonlinear dependence of on the surface coverage. In addition, for molecules with small nonlinear polarizabilities, or in cases where the molecular response is not resonantly enhanced, the small amount of SHG from the substrate surface cannot always be neglected.

In some instances the second harmonic response of the surface is dominated by of the substrate. As in the case of metal or semiconductor surfaces, molecular adsorption must then be monitored through . This type of measurement has been utilized to study the adsorption of water onto alkali halide crystals and the adsorption of polymers onto mica surfaces.

A topic related to the adsorption of molecular monolayers on oxide surfaces is the preparation of noncentrosymmetric thin films for nonlinear optics. Two excellent books discussing the design of molecules for such systems have recently been published. Films of these molecules are typically prepared on nonconducting substrates, such as fused silica, by a Langmuir–Blodgett dipping process or by spreading from a liquid-air interface followed by a rubbing procedure. These films can range in thickness from submonolayer up to microns. Since the preparation of nonlinear optical materials is reviewed elsewhere, we will not discuss the properties of these films in any detail. However, interfacial SHG measurements of adsorption and surface coverage have been used to monitor the formation of a wide variety of monolayers of these materials, as well as the extent of molecular orientation and order within the monolayers.

5. Liquid–Air Interfaces

One interface for which a wealth of new information has been obtained with surface SHG measurements is the liquid–air interface. The first observation of SHG from a liquid–air interface was by Wang in 1969, and the first quantitative measurements of surface coverage and molecular orientation on monolayers at the water–air interface were performed by Rasing et al. on Langmuir films. Since these initial experiments, SHG has been used extensively to examine the adsorption equilibrium between solute molecules at the interface and in the bulk liquid. As in the case of oxide surfaces, the contributions of the organic adsorbates to the surface nonlinear susceptibility usually dominate the surface second harmonic response. A typical example of an SHG measurement of surface coverage at a liquid–air interface is shown in Figure 4.

![Figure 4](image-url)

**Figure 4.** The square root of the second harmonic intensity, from a water–air interface as a function of propylphenol concentration in the aqueous phase. The solid line is the best fit to a Langmuir isotherm for adsorption of propylphenol to the interface. Results of this type can be used to determine the energetics of adsorption; in this case, the free energy of adsorption is determined to be ~5.8 kcal/mol. (Reprinted from ref 210. Copyright 1991 American Institute of Physics.)

In this work by Castro et al., the authors examined the adsorption of a series of alkylphenol and alkyllaniline molecules to the water–air interface. The dependence of on the bulk concentration of an adsorbate was used to determine the adsorption isotherm, and thus the free energy of adsorption to the interface. Similar experiments have been performed for other molecules at liquid–air interfaces.

The molecular specificity provided by has led to the application of SHG in the study of chemical transformations at interfaces. Changes in the molecular nonlinear polarizability upon the reaction of an adsorbed molecule will result in changes in the surface second harmonic response. Xiao et al. have observed changes in the SHG from hemicyanine and nitrostilbene monolayers at the water–air interface as a function of the pH in the bulk aqueous phase; the results of this work are plotted in Figure 5. The changes in the SHG from the interface as a function of pH are attributed to the protonation/deprotonation of the acid–base sites.
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Figure 6. The square root of the second harmonic intensity, $\sqrt{I_{SHG}}$ (filled squares), and the interfacial tension (open squares) from an electrified water–1,2-dichloroethane interface as a function of the applied potential $E_a - E_w$. The solid lines are drawn to show the trends in the data. The dichloroethane contains 20 μM of an anionic surfactant 2-(N-octadecylamino)naphthalene-6-sulfonate (ONS) which adsorbs to the liquid–liquid interface. The increase in the SHG is due to the potential-dependent adsorption of ONS to the interface and is accompanied by a decrease in the interfacial tension. These results were used quantitatively to obtain thermodynamic information on the adsorption of ONS. (Reprinted from ref 60. Copyright 1993 American Chemical Society.)

on the molecules. Reactions of this type result in changes in the electronic structure of the molecule and shifts in the strength and position (energy) of the charge-transfer bands. These shifts lead to dramatic variations in the amount of SHG observed from the interface. The populations of protonated and deprotonated species are easily monitored with the surface SHG signal, thus allowing for the elucidation of pH differences between the surface region and the bulk solution. Several other pH-dependent studies of this type have appeared recently.156,222-224 Studies involving the use of time-resolved SHG measurements to probe the kinetics of surface reactions have also been reported and will be discussed in section E.

6. Liquid–Liquid Interfaces

Molecular adsorption to liquid–liquid interfaces can also be monitored with the SHG from the interface. The first detailed SHG study of a liquid–liquid interface was performed by Grubb and co-workers for the adsorption of an anionic surfactant at the decane–water and water–carbon tetrachloride interfaces.225 Subsequent studies have been performed at water–heptane interfaces,226 silver metal liquidlike films at water–organic interfaces,227 and most recently, liquid–liquid electrochemical interfaces.60 An example of the information that can be obtained from the liquid–liquid electrochemical interface is shown in Figure 6, which plots the potential dependent SHG from an anionic surfactant at the water–1,2-dichloroethane interface.60 At potentials where the dichloroethane side of the interface is negatively charged, the anionic surfactant is strongly adsorbed to the interface, and a large SHG signal is observed. Conversely, when the dichloroethane side of the interface is positively charged, the surfactant is driven away from the interface, resulting in a complete loss of the surface SHG signal. An analysis of the SHG results, in conjunction with surface tension measurements, can provide a very accurate description of the interfacial energetics. In addition to adsorption measurements, surface reactions can be followed through the changes in the surface SHG signal. This has been demonstrated for a photoinduced electron transfer reaction at a liquid–liquid interface.228

B. Molecular Orientation Measurements

In addition to the numerous applications of interfacial SHG to the study of molecular adsorption, SHG experiments have been frequently utilized to determine the average orientation of molecules adsorbed at surfaces. For systems where the SHG from the interface is dominated by molecular contributions to the surface nonlinear susceptibility $\chi^{(2)}$, the average orientation of the molecules at the interface can be obtained from measurements of the polarization dependence and phase of the molecular SHG. The current methodology for these molecular orientation measurements is an extension of the original experiments by Heinz et al. in the early 1980s.46,112

The SHG molecular orientation measurement incorporates three main steps: first, the magnitudes and relative phases of the surface nonlinear susceptibility tensor elements are measured; second, the nonlinear response of an individual molecule is calculated or assumed; and third, the average molecular orientation at the interface is calculated through the appropriate equations relating the experimentally measured macroscopic surface nonlinear response to the expected microscopic molecular nonlinear response. In some cases, an additional step involving the measurement of the phase of the surface second harmonic response with respect to the fundamental light fields can be used to ascertain the absolute molecular direction of the molecules adsorbed onto the surface.

1. Molecular Orientation Determination Methodology

The average molecular orientation within an adsorbed monolayer is determined from the polarization dependence of the surface SHG signal $I(2\omega)$. This polarization dependence is stated formally in eq 4 and depends upon the relative magnitudes and phases of the elements of the surface nonlinear susceptibility tensor $\chi^{(2)}$ as well as the input and output polarization vectors $e(\omega)$ and $e(2\omega)$.

$$I(2\omega) \propto \left| \alpha_1 x_{XXZ} \sin^2 \gamma \right|^2 I(\omega)^2$$

Explicit equations for the polarization vectors for a variety of experimental geometries can be found in papers by Heinz,112 Sipe,60 and Marlow113 and are based on the Fresnel factors for the interface.

If the SHG from the adsorbed monolayer is invariant during rotation of the surface about the surface normal (the $Z$ axis), then the molecules within the laser spot are randomly oriented about the surface normal and $\chi^{(2)}$ has only three unique elements: $x_{XXX}$, $x_{XZX}$, and $x_{XXZ}$. The intensity of the $s$-polarized (perpendicular to the plane of incidence) and $p$-polarized (parallel to the plane of incidence) SHG signal ($I_s(2\omega)$ and $I_p(2\omega)$, respectively) can be directly related to these elements:
The nonlinear response is governed only by the lowest energy. In many of the molecular orientation studies to date, this rather complicated equation has been approximated by assuming that the molecular nonlinear response is governed only by the lowest energy.

Using perturbation theory, the components of $\beta$ can be expressed in terms of the molecular energies and wave functions. In many of the molecular orientation studies to date, this rather complicated equation has been approximated by assuming that the molecular nonlinear response is governed only by the lowest energy.
semiempirical \( \pi \)-electron wave functions obtained from a Pople-Pariser-Parr SCF-CI methodology.\(^{48,233-237}\) Although the calculations show that at visible wavelengths \( \beta_{zzz} \) is the largest \( \beta \) tensor element, there is also a nonnegligible contribution from \( \beta_{zxx} \). It has been shown that both of these tensor elements must be included in the molecular orientation calculation for \( p \)-nitrophenol in resonant SHG experiments and that their relative magnitudes can be obtained from the experimentally measured \( \chi^{(2)} \) elements (see below).\(^{49,226}\)

Once it has been determined which elements of the molecular nonlinear polarizability dominate the molecular nonlinear response, these elements can be related to the experimentally determined tensor elements of \( \chi^{(2)} \) through a coordinate transformation from the molecular coordinate system to that of the surface. This mathematical relationship allows for the calculation of the average molecular orientation on the surface and is given by\(^{222}\)

\[
\chi_{ijk} = N_s \sum (R_{i,R,j,R,k}) \beta_{ijk} = N_s \sum (F_{ijk}(\phi, \theta, \alpha)) \beta_{ijk} \quad (10)
\]

where \( N_s \) is the surface concentration of adsorbed molecules, and \( (R_{i,R,j,R,k}) \) is the ensemble average of the product of three direction cosines, \( R_{X,Y} \), between the laboratory and molecular coordinate systems. The product of direction cosines can be expressed as a function \( F_{ijk}(\phi, \theta, \alpha) \), where the molecular angles \( \phi, \theta, \) and \( \alpha \) are defined relative to the space fixed coordinates as shown in Figure 9. For most molecular monolayers, the SHG from the surface does not depend upon the azimuthal angle \( \phi \). In this case the molecules are oriented randomly about the surface normal and \( F_{ijk} \) can be integrated over \( \phi \), leaving a function of \( \theta \) and \( \alpha \). Further simplification of the function \( F_{ijk} \) is possible and depends upon which \( \beta_{ijk} \) tensor elements dominate the molecular nonlinear response.

For example, in the molecular orientation calculation for a monolayer of \( p \)-nitrophenol adsorbed at the fused silica-air interface,\(^{49}\) eq 10 can be used to relate the measured values of the elements of \( \chi^{(2)} \) to the molecular \( \beta \) elements. The ratio of the two dominant elements \( \beta_{zxx}/\beta_{zzz} \) derived from this equation is given in eq 11:

\[
\frac{\beta_{zxx}}{\beta_{zzz}} = \frac{2 \chi_{xxx} - \chi_{xxz}}{\chi_{zzz} + 2 \chi_{xzx}} \quad (11)
\]

The values of the tensor elements determined from the data in Figure 7 lead to a \( \beta_{zxx}/\beta_{zzz} \) of \(-0.31\). If it is further assumed that there is a random distribution in the angle \( \alpha \) for the adsorbed \( p \)-nitrophenol molecules, then a molecular orientation parameter \( D \) can be derived from eq 10:

\[
D = \frac{\langle \cos^2 \theta \rangle}{\langle \cos \theta \rangle} = \frac{\chi_{zzz} - \chi_{xxz} + \chi_{xxx}}{\chi_{zzz} + 3 \chi_{xzx} - \chi_{xxz}} \quad (12)
\]

Using the values of the tensor elements determined from Figure 7, a value of 0.33 is obtained for \( D \). This \( D \) corresponds to an average angle \( \theta \) of \( 55^\circ \) if all of the molecules are sitting on the surface with the same orientation. A concurrent study by Bell et al. on \( p \)-nitrophenol at water-air and water-heptane interfaces arrived at a similar result.\(^{226}\) A more involved interpretation of \( D \) that assumes a Gaussian distribution of molecular angles \( \theta \) has also been discussed.\(^{49,238}\)

The equations for the orientation parameter \( D \) in cases where other \( \beta \) tensor elements are dominant have been presented in other review articles.\(^{239}\)

### 2. Examples of Molecular Orientation Measurements

As noted above, the original SHG orientation measurements were performed on a rhodamine dye adsorbed at the fused silica-air interface.\(^{49}\) By assuming a single dominant molecular nonlinear polarizability element, an orientation parameter of \( D = 0.69 \), corresponding to an average angle \( \theta \) of \( 34^\circ \), was calculated from the polarization dependence of the surface SHG. Several similar studies on large dye molecules have appeared in the literature.\(^{49,240}\) Orientation measurements which assume the presence of two molecular nonlinear polarizability tensor elements have been performed on monolayers of the dye molecule methylene blue at fused silica-air\(^{160}\) and metal-electrolyte\(^{59}\) interfaces. An interesting extension of the SHG orientation methodology has been reported by Peterson and Harris,\(^{241}\) in which UV-vis spectroscopy was coupled with SHG orientation studies of rhodamine B monolayers at a fused silica-air interface in order to elucidate the average orientation of dimers adsorbed onto the surface.

Orientation studies of large dye molecules are complicated by the close proximity of several molecular electronic resonances to the fundamental and second harmonic wavelengths. The contributions of multiple electronic transitions in \( \beta \) make the molecular nonlinear polarizability tensor analysis more difficult, but lead to large resonance enhancement of the surface SHG response. The difficulties associated with the larger molecules are avoided in orientation studies of small aromatic molecules like \( p \)-nitrophenol. As shown in the \( \beta \) calculation in Figure 8, these molecules can be studied with lasers that provide for resonance enhancement at the second harmonic only. Although the surface SHG signal may be smaller, the orientation analysis of the SHG is often simplified by the presence of only one dominant molecular nonlinear polarizability tensor element, \( \beta_{zzz} \). Molecules of this nature include \( p \)-nitrobenzoic acid,\(^{102}\) \( p \)-nitroaniline, and many others. Many orientation measurements utilizing these small molecules have been performed at fused silica-air,\(^{49,238}\) water-air,\(^{176,208,209,211,212,218,225,226,229,242-244}\) and a variety of other interfaces.\(^{233,226}\)
3. SHG Phase Measurements of Absolute Molecular Orientation

In addition to the measurement of the orientation parameter \( D \) from the polarization dependence of the surface SHG, measurements of the phase of the surface second harmonic response can be used to deduce the absolute direction of the adsorbed molecules on the surface. As first demonstrated by Kemnitz et al., \(^{245}\) these experiments entail the measurement of the phase of a surface susceptibility tensor element (usually \( \chi_{xxxz} \)) with respect to the phase of the incident fundamental light fields via an interference method. The phase measurements involve the insertion of a second source of SHG, usually a thin piece of \( z \)-cut quartz, into the beam reflected from the sample surface. The residual fundamental light in the beam will generate SHG in the \( z \)-cut quartz that is shifted in phase from the SHG generated at the sample surface. By translating the \( z \)-cut quartz along the beam path, an interference pattern is produced which includes the desired information on the phase relationship between the surface nonlinear susceptibility and the fundamental light fields. In order to ascertain the phase shift of this interference pattern with respect to the input fields, the system must first be calibrated by replacing the sample with a second piece of \( z \)-cut quartz of known orientation and repeating the above interference measurements.\(^{245}\) Comparison of the observed phase with that predicted from the molecular nonlinear polarizability calculations results in the determination of the absolute molecular direction for the molecules adsorbed to the interface. The original absolute orientation determination was made with phase measurements of the SHG from phenol molecules adsorbed to the water–air interface\(^{246}\) and has since been applied to adsorbates at other interfaces.\(^{49,546}\)

As a representative example of this type of measurement, Figure 10a plots the \( \chi_{xxxz} \) interference curves for the SGH from a \( p \)-nitrophenol monolayer adsorbed at the air–water interface (open squares) and a quartz reference (filled squares).\(^{49}\) The quartz reference in these experiments is known to generate SHG with a phase of \(-90^\circ\) with respect to the incident light fields. Therefore, the interference measurements for \( p \)-nitrophenol show that at this fundamental wavelength (610 nm), the tensor element \( \chi_{xxxz} \) is \(+70^\circ\) out of phase with respect to the incident light fields. Figure 10b plots the theoretically expected phase of the nonlinear susceptibility element \( \chi_{xxxz} \) for a monolayer of \( p \)-nitrophenol adsorbed with the orientation shown in the figure (the \( \text{OH} \) group down). These results were calculated from the elements of \( \beta \) that are expected to contribute to the molecular SHG in this wavelength region. As seen in the figure, the phase of \( \chi_{xxxz} \) is calculated to be \(180^\circ\) below resonance, \(90^\circ\) on resonance, and \(0^\circ\) above resonance. In contrast, if the molecule were oriented with its nitro group down, the phase of \( \chi_{xxxz} \) would range between \(0^\circ\) and \(180^\circ\) with a value of \(-90^\circ\) on resonance. A phase of \(+70^\circ\) (from Figure 10a) for \( \chi_{xxxz} \) indicates that the \( p \)-nitrophenol molecules are oriented with the \( \text{OH} \) group pointing down, into the water.

A different interferometric method for determining absolute molecular orientation has been developed by Sato et al. and involves the interference of the SHG from two monolayers adsorbed on opposite faces of a fused silica substrate.\(^{247,248}\) The advantage of this method is that the reference sample is another adsorbed layer of the same (or related) molecule; therefore, the phase characteristics of the two monolayers can be matched very closely and lead to a simple interpretation of the data. The sample geometry and experimental setup used in this type of SHG measurement are shown in Figure 11. By collecting the SHG in transmission through the sample as a function of the angle of incidence, an interference pattern is produced which contains the desired phase relationship between the SHG from the monolayers on either side of the substrate. An example of such an experiment is shown in Figure 12, in which the interference patterns for the two types of hemicyanine monolayer systems shown in Figure 11a are compared to illustrate the utility of the method.

C. Surface Symmetry Measurements

A third major application of surface SHG measurements has been the determination of surface symmetry
monolayers of nonlinearly active hemicyanine molecules
schematic diagram of the two samples used to generate the
sides of a centrosymmetric substrate. Part a shows the
the absolute orientation of molecules deposited on opposite
to one another, one set being noncentrosymmetric and the other
centrosymmetric. Part b shows the experimental geometry used to measure the
SHG interference patterns from the two samples described
in part a. The SHG at 2ω is collected in transmission through the sample as a function of the angle of tilt off normal incidence.

Figure 11. The general experimental methodology used by Sato et al. [1445] for SHG interference measurements to determine the absolute orientation of molecules deposited on opposite sides of a centrosymmetric substrate. Part a shows the schematic diagram of the two samples used to generate the SHG interference patterns. The type A sample has two monolayers of nonlinearly active hemicyanine molecules (denoted as ) aligned in the same direction (the monolayer is nonlinearly inactive), and the type B sample has the nonlinearly active molecules aligned in opposite directions. Part b shows the experimental geometry used to measure the SHG interference patterns from the two samples described in part a. The SHG at 2ω is collected in transmission through the sample as a function of the angle of tilt off normal incidence.

Figure 12. The SHG interference patterns for hemicyanine dye monolayer samples of type A (—) and type B (—) as described in Figure 11a as a function of the incident angle on the surface. The two interference patterns are observed to be 180° out of phase due to the inversion of the hemicyanine dye orientation on the surface in type A with respect to type B systems. The arrows indicate the theoretical maxima for films of type A. (Reprinted from ref 248. Copyright 1991 Elsevier Sequoia.)

at single-crystal metal and semiconductor surfaces. As noted above, the number of the 18 possible unique tensor elements that can be observed in a particular SHG experiment will depend upon the average symmetry of the surface. Table 1 lists some simple surfaces for a face-centered cubic single crystal, the inherent symmetry of each surface, and the unique nonzero elements expected. More complete listings of the allowed tensor elements for different crystal faces and surface symmetries have been tabulated elsewhere. [14,17,18,56]

Table 1. The Nonzero Elements of χ(2) Expected for Crystal Faces of Given Symmetry [14,17,18,56]

<table>
<thead>
<tr>
<th>Crystal face</th>
<th>Symmetry</th>
<th>Nonzero χ(2) elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>C4v</td>
<td>XZZZ, XXXX, XXXZ</td>
</tr>
<tr>
<td>111</td>
<td>C4v</td>
<td>XZZZ, XXXX, XXXX, XXX</td>
</tr>
<tr>
<td>110</td>
<td>C4v</td>
<td>XZZZ, XXXX, XXXX, XYZ</td>
</tr>
</tbody>
</table>

The relative magnitudes and phases of the various χ(2) tensor elements expected for a given single-crystal surface can be determined via SHG rotational anisotropy measurements as depicted in Figure 13. In these experiments, the SHG from the surface is measured at a fixed angle between 30° and 70°, and the SHG is collected in reflection as a function of crystal rotation about the surface azimuthal angle φ. The rotational anisotropy patterns obtained with different input and output polarizations are used to probe the various nonlinear susceptibility tensor elements of a particular single-crystal surface.

Figure 13. The experimental geometry employed in SHG rotational anisotropy experiments on single-crystal surfaces. The fundamental laser beam is incident on the sample at an angle between 30° and 70°, and the SHG is collected in reflection as a function of crystal rotation about the surface azimuthal angle φ. The rotational anisotropy patterns obtained with different input and output polarizations are used to probe the various nonlinear susceptibility tensor elements of a particular single-crystal surface.

SHG rotational anisotropy measurements are particularly useful for the study of single-crystal metal surfaces in electrochemical environments, as there are exceedingly few techniques that can monitor surface symmetry in situ. The processes of surface disordering, overlayer chemisorption, and surface reconstruction can all potentially lead to changes in the average surface symmetry of an electrode. These symmetry modifications will create new χ(2) tensor elements, and result in changes in the observed SHG rotational anisotropy. G. Richmond and co-workers at the University of Oregon have pioneered the application of this technique to the study of single-crystal metal electrode surfaces [10,12,17]. Figure 14 depicts SHG rotational anisotropy measurements by Koos and Richmond [111] from a Au(111) electrode with an adsorbed monolayer of Cu, Ag, Tl, or Pb atoms. The process of spontaneous metal monolayer adsorption is denoted by electrochemists as underpotential deposition (upd) and can be used to modify the catalytic properties of an electrode surface.
At a single-crystal metal electrode, changes in the surface electronic structure due to the presence of the upd monolayer can lead to changes in the relative magnitudes of the various elements of the surface nonlinear susceptibility ($\Delta r_e$). By measuring the SHG rotational anisotropy, a complete description of the form, magnitude, and phase of $\Delta r_e$ is obtained.\textsuperscript{17,19}

SHG measurements have also been applied to single-crystal Pt electrodes to ascertain the average surface symmetry.\textsuperscript{117-119,266} Figure 15, parts a and b, depict SHG rotational anisotropy measurements (plotted in polar coordinates) for Pt(111) and Pt(110) electrodes that are covered with an ordered monolayer of chemisorbed monatomic iodine.\textsuperscript{119,266} The anisotropy plots clearly reflect the symmetry of the two surfaces, $C_{3v}$ for the Pt(111) surface and $C_{2v}$ for the Pt(110) surface.

While the differences in the SHG anisotropies from iodine-coated Pt(111) and Pt(110) electrodes arise from the symmetry differences of the metal substrates, different structures of a chemisorbed overlay on the same single-crystal surface can also lead to changes in the overall surface symmetry. These reductions in surface symmetry upon adsorption can be monitored either with SHG rotational anisotropy experiments\textsuperscript{73,117,118} or with normal-incidence SHG polarization anisotropy measurements.\textsuperscript{80,302,265}

The experimental geometry for normal-incidence polarization anisotropy measurements is depicted schematically in Figure 16a. In these experiments, the input polarization is varied from 0° to 360°, while the output polarization is fixed along one of two perpendicular crystal axes. The use of a normal-incidence geometry greatly simplifies the tensor analysis, especially for surfaces of lower symmetry. The absence of any Z component in the fundamental and second harmonic light fields restricts the surface SHG to only those surface tensor elements without a Z subscript (e.g., $XXY$).

An example of a normal-incidence SHG measurement is shown in Figure 16b, which plots the SHG signal from an iodine-coated Pt(111) electrode during the potential dependent surface phase transition from a (3 × 3) to a (ν3 × ν3)$\sqrt{3}$R19.1° iodine monolayer.\textsuperscript{265} The second harmonic intensity doubles as the symmetry of the electrode surface changes from $C_{3v}$ to $C_{3}$ due to the change in the structure of the chemisorbed monolayer. In contrast, the iodine surface coverage is found to change by less than 2% during this transition, as determined by integration of the current in the cyclic voltammogram (also shown in Figure 16b). These results clearly demonstrate the surface sensitivity of the SHG normal-incidence measurements.

The reconstruction of single-crystal metal surfaces can also be observed via the concomitant changes in surface symmetry.\textsuperscript{108,262,263,264} For example, SHG rotational anisotropy measurements of surface reconstruction as a function of applied potential have been performed on Au(111) electrodes by Pettinger and coworkers.\textsuperscript{113} Figure 17 plots the changes they observed in the symmetry of the SHG rotational anisotropy patterns due to a $\sqrt{3}$ × $\sqrt{3}$ reconstruction of the Au(111) electrode. In addition, reconstruction changes in surface symmetry with applied potential, the adsorption of overlayers onto single-crystal electrodes can also lead to a reconstruction of the surface. The adsorbate-induced reconstruction of electrode surfaces has also been monitored with SHG rotational anisotropy measurements.\textsuperscript{108,113}
overlayers on a Pt(111) electrode. Part a shows the experimental geometry for normal-incidence SHG measurements. This geometry is used to significantly reduce the number of tensor elements contributing to the SHG from the surface by eliminating all those that require an electric field in the Z direction (the surface normal). Part b shows the normal-incidence SHG (--;-) and cyclic voltammogram (--;--) as a function of potential (vs SSCE) for a Pt(111) electrode in contact with a 0.1 M potassium iodide solution in the region of the phase transition between the (√7 × √7)R19.1° and 3 × 3 iodine monolayers. The (√7 × √7)R19.1° monolayer exists on the surface at potentials below 0.2 V, while the 3 × 3 surface is found on the surface at potentials above 0.3 V. The use of the normal-incidence geometry results in a large change in the surface SHG signal, even though the surface coverage of chemisorbed iodine only changes by 2%. (Reprinted from ref 265. Copyright 1991 Elsevier Sequoia.)

SHG symmetry measurements at single-crystal surfaces are complicated by the fact that the SHG signal is summed in a coherent fashion over all of the domains present within the laser spot on the surface. Thus, in principle, a surface which contains equal amounts of surface domains of a lower symmetry can lead to SHG rotational anisotropy patterns that indicate a higher average surface symmetry. For example, a surface with exactly equal amounts of two domains of C3v symmetry will lead to an SHG anisotropy pattern corresponding to an average surface symmetry of C3v. More effective use of the SHG rotational anisotropy measurements in a surface symmetry determination can be made if a single-crystal surface with unequal amounts of equivalent domains is employed. The use of a stepped or vicinal single-crystal surface in SHG rotational anisotropy measurements has recently been demonstrated as a method of obtaining such a surface.267-270

D. Electric Field Measurements

In the presence of an externally applied static electric field, a bulk centrosymmetric medium can become SHG active as a result of either molecular realignment or the polarization of bonds in the sample. This process is denoted as electric field induced second harmonic generation (EFISH) and has been observed in solids,271,272 liquids,273,274 and gases.275 The static electric field at an interface can also lead to an additional surface second harmonic response. In 1967, Lee et al. proposed an EFISH mechanism to explain the dependence of the surface SHG from Ag and Si electrodes on an externally applied potential.275 The contribution of the EFISH process to the surface SHG can be written as an additional term, \( P^{(2)}_E(2\omega) \), in the surface nonlinear polarization:

\[
P^{(2)}_E(2\omega) = \chi^{(3)}:E_{dc}E(\omega)E(\omega)
\]

where \( \chi^{(3)} \) is the third-order nonlinear susceptibility that relates three electric fields, two at frequency \( \omega \) and one at zero frequency, to the surface nonlinear polarization at frequency \( 2\omega \). In cases where the electric fields exist over an extended distance, eq 13 must be integrated over the entire interfacial region. Equation 13 predicts that in the absence of other sources, the intensity of the SHG from an interface will vary as the square of the static electric field. Thus, for cases where \( P_d \) dominates the surface nonlinear polarization, surface SHG measurements can be used to monitor the static electric fields at an interface. EFISH measurements of interfacial electric fields have been employed at metal37,84,85,87,88,90,94,96,124,125,276 semiconductor277 and oxide surfaces.278

EFISH measurements of the electrostatic fields at an electrochemical interface are particularly important since chemical processes at an electrode surface are, of course, controlled primarily by the externally applied electric field. For a metal electrode in contact with a solution of high electrolyte concentration, the electric field exists only at the metal surface. From Gauss' law, the static electric field at the electrode should be directly proportional to the surface charge density \( \sigma \). In 1984, Corn et al. suggested that, in the absence of specific adsorption, the potential dependent SHG from Ag electrodes could be used to monitor the surface charge density as a function of applied potential.84,85 The potential at which \( \sigma = 0 \) is denoted as the potential of zero charge (pzc); determination of the pzc with SHG measurements has been performed at several electrochemical interfaces.84,85,86,88,124,125,276 An example of this type of measurement by Guyot-Sionnest and Tadjeddine126 on a Ag(111) electrode in a KClO4 solution is depicted in Figure 18. The SHG shown in the figure is plotted as a function of applied potential, and exhibits a minimum at ~0.7 V vs SCE. The observed minimum is identical to the pzc for the electrode as obtained from differential capacitance measurements.

EFISH measurements of electric fields have also been applied to the oxide–water interface, although the intensity of the SHG from this surface is much smaller than that observed at a metal electrode. For example, Ong et al. have measured the change in SHG from the silica–water interface as a function of bulk pH.278 The results of this experiment are plotted in Figure 19, and show that the SHG from the interface increases dramatically with increasing bulk pH. The changes in the SHG from the interface were determined to arise from an EFISH mechanism involving the alignment of the water molecules in the diffuse double layer as a result of the charging of the silica surface by the deprotonation of –SiOH groups.
Figure 17. SHG rotational anisotropy patterns from a Au(111) electrode showing the effects of surface reconstruction on the surface symmetry. The solid lines are fits to theoretical equations. The three SHG rotational anisotropies in the left-hand column correspond to polarization combinations of p-in/p-out, p-in/s-out, and s-in/s-out for the unreconstructed Au(111) surface, which exhibits $C_{3v}$ symmetry. The three SHG rotational anisotropies in the right-hand column were obtained at a potential where the Au(111) surface is believed to reconstruct to a $\sqrt{3} \times 3$ monolayer that has $C_s$ symmetry. (Reprinted from ref 113. Copyright 1992 Elsevier Sequoia.)

E. Time-Resolved Studies

One of the most useful properties of the SHG from an interface is its nearly instantaneous response time. This attribute, coupled with the fact that pulsed lasers are usually employed in surface SHG experiments, has provided a relatively simple method for making time-resolved measurements of surface processes. The utility of SHG as a time-resolved method has been demonstrated at an unparalleled number of interfaces on time scales ranging from tens of seconds down to hundreds of femtoseconds. Some examples of time-resolved SHG studies include adsorption and desorption kinetics at semiconductor, insulator, and metal surfaces; surface diffusion measurements at liquid, metal, and semiconductor interfaces; surface-phase transformation measurements on Si and Langmuir-Blodgett films; underpotential deposition reaction kinetics at electrochemical interfaces; and the reorientation of molecules at silica-air and liquid-air interfaces.

Figure 20 depicts an example of a time-resolved SHG measurement by Castro et al. of the ultrafast orientational changes that occur in a monolayer of rhodamine 6G at a water-air interface during relaxation to the ground state following optical excitation. The authors have monitored the picosecond time evolution of two separate tensor elements, $\chi_{zxx}$ and $\chi_{xxz}$. The polarization dependence of the return of the surface SHG to its original value indicates that the orientation of rhodamine 6G in the excited state is different from that in the ground state. Additional experiments which compared the effects of linearly polarized and circularly polarized excitation indicated that the authors were observing out-of-plane rotations in the reorientation of the dye molecules at the surface.
Figure 18. The square root of the SHG signal (solid line) as a function of applied potential (vs SCE) for a Ag(111) electrode in 0.1 M KClO₄ at a fundamental wavelength of 1064 nm. The minimum occurs very near the potential of zero charge (pzc) for this electrode (arrow). The potential dependence of the second harmonic response expected if an EFISH process at the metal–electrolyte interface is the dominant source of surface SHG is plotted in the figure as the dashed curve. (Reprinted from ref 126. Copyright 1990 American Institute of Physics.)

Figure 19. The square root of the surface SHG (denoted as the SH electric field) from a fused silica–water interface as a function of pH. The increase in SHG with increasing pH is attributed to an EFISH mechanism in which the static electric field in the diffuse double layer produces a preferential orientation of the water molecules at the interface. The static electric fields at the interface are controlled by the surface concentration of deprotonated surface silanol groups. The deprotonation of these surface species is a function of pH, and the curve in the figure indicates that there are two types of silanol species present on the surface. (Reprinted from ref 278. Copyright 1992 Elsevier Science Publishers.)

In addition to directly monitoring changes in the magnitude and polarization dependence of the SHG from an interface, more elaborate techniques have also been implemented in time-resolved surface SHG measurements. For example, SHG studies of surface diffusion and desorption kinetics on metal and semiconductor surfaces in UHV have employed transient gratings to create diffracted surface SHG signals. The experimental geometry used in these studies is shown schematically in Figure 21. Two beams from a high-powered pump laser are overlapped at a surface to create a spatially modulated intensity pattern which, through desorption, produces a spatially modulated adsorbate surface coverage. A second laser beam is then used to probe the surface by collecting the SHG response that is diffracted from the adsorbate grating. Because the SHG is only from the surface, the time dependence of the diffracted SHG beam intensity can be used to monitor surface diffusion kinetics. These SHG measurements were first applied by Zhu et al. to study the diffusion of CO on Ni(111) surfaces. Another example of such a measurement is shown in Figure 22, in which Reider et al. produced a monolayer grating of adsorbed hydrogen on a reconstructed Si- (111) surface. By assuming a linear relationship between the surface concentration of adsorbed hydrogen and the surface nonlinear susceptibility, the authors...
be noted that SHG is only the simplest of a variety of nonlinear optical experiments that can be performed at surfaces. Sum frequency generation, difference frequency generation, and five-wave mixing experiments all possess the same surface selectivity inherent in the SHG measurements, and therefore can potentially all serve as highly valuable optical probes of surface phenomena.

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VII. References
