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Sum Frequency Generation (SFG) Spectroscopy

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10 Sum Frequency Generation (SFG) Spectroscopy

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Abstract: Optical sum-frequency generation can be highly surface-specific and yet also sensitive enough to detect a submonolayer. It therefore has been developed into a powerful surface probe in recent years. The many advantages of this technique over conventional techniques allow many unique applications and have opened up many new areas of research in surface science. Selected examples covering a wide range of fields are discussed in this chapter to illustrate the power of the technique and its range of applicability. The basic theory behind the technique and the practical aspects of the experimental arrangement are also briefly described.

10.1 Introduction.

Spectroscopic studies are essential for real understanding of surfaces and interfaces. Among the existing surface spectroscopic techniques, those employing optics are particularly attractive. Unlike the others, they can be used for in-situ remote sensing of surfaces even in hostile environments and can be applied to any interfaces accessible by light. Linear optical spectroscopy has been well developed, but unfortunately it lacks the intrinsic surface specificity needed for most surface studies. Nonlinear optical spectroscopies, on the other hand, can be highly surface-specific by symmetry if the nonlinear optical process involved is of even order (1). Second-order nonlinear processes such as second harmonic generation (SHG), sum-frequency generation (SFG), and difference frequency generation (DFG) are naturally more appealing because of their simplicity and sensitivity. In this chapter, we shall focus our discussion on SFG spectroscopy (2). SHG and DFG can be regarded as special cases of SFG.

Optical SFG describes a process in which two input laser beams at frequencies $\omega_1$ and $\omega_2$ interact in a medium and generate an output at the sum frequency $\omega = \omega_1 + \omega_2$. Being second order, it is forbidden in media with inversion symmetry. At a surface or interface, however, the inversion symmetry is necessarily broken and SFG becomes allowed. This then makes SFG highly surface-specific for interfaces between two centrosymmetric media. More generally, even for media without inversion symmetry, surfaces and bulks often have different symmetries. With proper input and output beam polarizations, one can suppress the bulk contribution even if it is present (3).
Spectroscopic information can be obtained from resonant enhancement of SFG if either \( \omega_1(\omega_2) \) or \( \omega_1 + \omega_2 \) or both is tuned over resonances (Fig. 10.1). Using pulsed lasers, SFG also has the sensitivity to detect a submonolayer of atoms or molecules. These two characteristics combined make SFG a most powerful and versatile surface spectroscopic tool. Because of the intrinsic ability of SFG to discriminate against bulk contribution, the measurement of a surface spectrum is now possible even in the presence of a strong overlapping bulk spectrum. This allows surface spectroscopic studies of many hitherto unexplored systems including pure liquids and solids. As a second-order effect, SFG is sensitive to the polar orientation of molecules or groups of atoms in the molecules. Since the process is coherent and highly directional, it is capable of in-situ, remote sensing measurements in hostile environments. With ultrashort laser pulses, SFG can also be used to study surface dynamics with a subpicosecond time resolution. These unique features of SFG have led to many unique applications, opening the doors to some very exciting new areas of research in surface science.

Fig. 10.1. Schematic diagrams of resonant SFG processes: (a) \( \omega_1 \) at resonance; (b) \( \omega_1 + \omega_2 \) at resonance; (c) both \( \omega_1 \) and \( \omega_1 + \omega_2 = \omega \) at resonance.

SFG surface spectroscopy was developed as a natural extension of SHG as a surface analytical tool (1,2). Heinz et al. first demonstrated that SHG can be used for spectroscopic studies of surface monolayers (4). With two input frequencies that can be both varied, SFG is clearly more versatile than SHG. In particular, for surface vibrational spectroscopy, SHG is not applicable because the output appears in the infrared where photodetectors are generally not sufficiently sensitive for detection of a single monolayer. The situation is different with SFG. Having \( \omega_1 \) tunable in the infrared and \( \omega_2 \) in the visible, the SF output appears in the visible and can be easily detected by a photomultiplier (5).

SFG surface spectroscopy has been applied successfully to different interfacial systems,
many of which cannot be probed by other means. These include studies of free liquid interfaces, solid/solid, liquid/solid, and liquid/liquid buried interfaces, surfactant conformations, chemical vapor depositions, surface catalysis under real atmosphere, ultrafast surface dynamics, and others. In this chapter, we give a brief description of the basic theory underlying the technique and the practical aspects of the experimental arrangement. We shall discuss, with selective examples, a range of applications and show how information about an interface can be deduced from a surface SFG spectrum.

10.2. Basic Theory.

The theory of surface SFG has been worked out in detail and can be found in the literature (6). Here, because of space limitation, we can only give a sketch of the theory. We shall emphasize the physical understanding behind the theoretical derivations in our discussion.

As is well known, the source of an electromagnetic wave is generally the polarization \( \mathbf{P} \) (the oscillation dipoles per unit volume) (1). In the case of SFG, \( \mathbf{P} \) is nonlinearly induced in a medium by mixing of two input fields at \( \omega_1 \) and \( \omega_2 \) and can be described by

\[
\mathbf{P}^{(2)}(\omega_1 + \omega_2) = \chi^{(2)}(\omega_1 + \omega_2) \cdot \mathbf{E}(\omega_1) \mathbf{E}(\omega_2)
\]

Solution of the Maxwell wave equation with \( \mathbf{P}^{(2)}(\omega_1 + \omega_2) \) as the source term and with proper boundary conditions then leads to an expression for the SF output.

For a better understanding of SFG from an interface, we can divide the calculation into several logical steps. First, we consider SFG from a polarization sheet, given by

\[
\mathbf{P}^s(\omega = \omega_1 + \omega_2) = \mathbf{P}^s \delta(z) \exp(ik \cdot \mathbf{r} - i\omega t)
\]  
\[
= \chi_s^{(2)}(\omega_1) \mathbf{E}_L(\omega_1) \mathbf{E}_L(\omega_2),
\]

embedded between two semi-infinite dielectric media of dielectric constants \( \varepsilon_a \) (for \( z < 0 \)) and \( \varepsilon_b \) (for \( z > 0 \)), respectively. The pump fields in the polarization sheet are denoted by \( \mathbf{E}_L(\omega_1) \). The geometry is sketched in Fig. 10.2, with the linear dielectric constant of the polarization sheet labelled as \( \varepsilon' \). The solution of SFG from such a three-layer system is easily obtained. We find for pump waves incident from medium a, the SF output field reflected back into medium a is given by
The polarization sheet \( P^s(\omega) = \omega_1 + \omega_2 \) is imbedded in a thin layer with dielectric constant \( \varepsilon' \).

\[
E_p(\omega) = \frac{i4\pi k}{\varepsilon_b k a z + \varepsilon_a k b z} \left[ k b z P^s_x + \varepsilon_b k x (P^s_z / \varepsilon') \right] \exp(i k a \cdot \vec{r} - i \omega t)
\]

\[
E_s(\omega) = \frac{i4\pi k}{k a z + k b z} \left[ k a P^s_y \right] \exp(i k a \cdot \vec{r} - i \omega t)
\]

where \( \vec{k}_a \) and \( \vec{k}_b \) are SF wave vectors in media a and b, respectively, and the subscripts p and s denote the \( \hat{p} \)- and \( \hat{s} \)-polarized components of the field. Expressions for SF outputs from other beam geometries can also be found.

In the absence of boundary surfaces at \( z = 0 \), i.e., when \( \varepsilon_a = \varepsilon' = \varepsilon_b = \varepsilon \), Eq. (10.3) reduces to

\[
E_{p0}(\omega) = \frac{i2\pi k}{e k z} \left( k z P^s_x + k x P^s_z \right) \exp(i k \cdot \vec{r} - i \omega t)
\]

\[
E_{s0}(\omega) = \frac{i2\pi k^2}{k z} P^s_y \left( \exp(i k \cdot \vec{r} - i \omega t) \right)
\]

This is a well-known result that can be derived from the simple theory of radiation for a thin sheet of dipole oscillations embedded in an infinite, uniform dielectric medium. Comparison of the fields in Eqs. (10.3) and (10.4) yields the ratios for the three field components along \( \hat{x} \), \( \hat{y} \) and \( \hat{z} \).
We note that these L factors are identical to the transmission Fresnel coefficients relating the propagating field in medium a to the field in the polarization sheet. Physically, \( \tilde{L} = (L_{xx}, L_{yy}, L_{zz}) \) acts as a macroscopic local-field correction that accounts for the effect of boundary surfaces in coupling the radiation field in or out of the polarization sheet. We can write

\[
\tilde{E}(\omega) = \tilde{L}(\omega) \cdot \tilde{E}_o(\omega)
\]

(10.6)

with \( \tilde{E}_o \) given in Eq. (10.4).

Now the pump fields inside the polarization sheet, \( \tilde{E}_L(\omega_i) \), must also be related to the pump field incident from medium a (Fig. 10.1) by a similar Fresnel coefficient, i.e., \( \tilde{E}_L(\omega_i) = \tilde{L}(\omega_i) \cdot \tilde{E}_o(\omega_i) \). Equation (10.2) becomes

\[
\tilde{P}(\omega) = \chi_s^{(2)}(\omega = \omega_1 + \omega_2) : [\tilde{L}(\omega_1) \cdot \tilde{E}(\omega_1)] [\tilde{L}(\omega_2) \cdot \tilde{E}(\omega_2)]
\]

(10.7)

From Eqs. (10.4), (10.6), and (10.7), we can then immediately find the SF output field

\[
E_p(\omega) = i(2\pi\omega / c)(L_{xx}(\omega)\chi_s^{(2)}_{x,ijk}L_{jj}(\omega_1)L_{kk}(\omega_2)
+ (k_x(\omega) / k_{az}(\omega))L_{zz}(\omega)\chi_s^{(2)}_{y,ijk}L_{jj}(\omega_1)L_{kk}(\omega_2)]E_{aj}(\omega_1)E_{ak}(\omega_2)
\]

(10.8)

\[
E_s(\omega) = i(2\pi\omega / c)(k_y(\omega) / k_{az}(\omega))L_{yy}(\omega)\chi_s^{(2)}_{z,ijk}L_{jj}(\omega_1)L_{kk}(\omega_2)]E_{aj}(\omega_1)E_{ak}(\omega_2).
\]

The above discussion shows that we can obtain the expression without derivation for the SF output for any beam geometry as long as the expression for \( \tilde{E}_o \) in Eq. (10.4) and the proper Fresnel coefficients are known.

The SF output intensity can be readily calculated knowing \( \tilde{E}(\omega) \). For the case given by

\[
(E_p / E_{po})_x = L_{xx} = \frac{2\epsilon_a k_{az}}{\epsilon_b k_{az} + \epsilon_a k_{az}}
\]

(10.5)

\[
(E_p / E_{po})_z = L_{zz} = \frac{2\epsilon_a k_{az}(\epsilon_b / \epsilon')}{\epsilon_b k_{az} + \epsilon_a k_{az}}
\]

\[
(E_s / E_{so})_y = L_{yy} = \frac{2k_{az}}{k_{az} + k_{bz}}
\]
Eq. (10.8) (Fig. 10.1), we have

\[
I(\omega) = c e_a(\omega) \left| \mathbf{E}_a(\omega) \right|^2 / 2\pi
\]

\[
= \frac{8\pi^3 \omega^2 \sec^2 \theta_\omega}{c^2 [e_a(\omega)e_a(\omega_1)e_a(\omega_2)]^{1/2}} \left| \mathbf{e}^+(\omega) \cdot \mathbf{\chi}^{(2)}_s(\omega_1) \mathbf{e}(\omega_1) \mathbf{e}(\omega_2) \right|^2 I_a(\omega_1)I_a(\omega_2)
\]

Here, \( \theta_\omega \) is the reflection angle of the SF output, \( \mathbf{e}(\Omega) = \mathbf{\tilde{L}}(\Omega) \cdot \mathbf{\tilde{\epsilon}}(\Omega) \) with \( \mathbf{\tilde{\epsilon}}(\Omega) \) being a unit vector describing the polarization of the field at \( \Omega \), and \( I_a(\omega) \) is the input laser intensity. If the input lasers have a pulsewidth \( T \) and an overlapping beam cross-section \( A \) at the sample, then the SF output, in terms of photons per pulse, can be written as

\[
S(\omega) = I(\omega)AT / h\omega
\]

\[
= \frac{8\pi^3 \omega^2 \sec^2 \theta_\omega}{h\epsilon^3 [e_a(\omega)e_a(\omega_1)e_a(\omega_2)]^{1/2}} \left| \mathbf{e}^+(\omega) \cdot \mathbf{\chi}^{(2)}_s(\omega_1) \mathbf{e}(\omega_1) \mathbf{e}(\omega_2) \right|^2 I_a(\omega_1)I_a(\omega_2)AT
\]

So far, we have assumed that the induced polarization sheet at the boundary surface is the only source for the SFG. More generally, however, nonlinear polarizations induced in the bulks of the two media may also contribute to the SFG. It is possible to combine the surface and bulk contributions in such a way that they can be described by an effective polarization sheet with a surface polarization \( \mathbf{\tilde{\mathbf{P}}}_s^{eff} \), or an effective surface nonlinear susceptibility \( \mathbf{\tilde{\mathbf{\chi}}}^{(2)}_s^{eff} \) at the boundary (6). Then the results of Eqs. (10.8-10) are still valid if \( \mathbf{\tilde{\mathbf{P}}}^{s} \) and \( \mathbf{\tilde{\mathbf{\chi}}}^{(2)}_s \) are replaced by \( \mathbf{\tilde{\mathbf{P}}}_s^{eff} \) and \( \mathbf{\tilde{\mathbf{\chi}}}^{(2)}_{s,eff} \). Consider, for example, the case where the bulk nonlinear polarization \( \mathbf{\tilde{\mathbf{P}}}^B(\omega = \omega_1 + \omega_2) \) is negligible in medium a, but non-negligible in medium b. This is a problem that has been worked out by a number of researchers (7). The solution is described by Eqs. (10.8-10), but \( \mathbf{\tilde{\mathbf{\chi}}}^{(2)}_s \) in the equations should be replaced by

\[
(\mathbf{\tilde{\mathbf{\chi}}}^{(2)}_{s,eff})_{ijk} = \mathbf{\tilde{\mathbf{\chi}}}^{(2)}_{s,ijk} + \mathbf{\tilde{\mathbf{\chi}}}^{(2)}_{B,ijk} / \left[ k_{BZ}(\omega) + k_{BZ}(\omega_1) + k_{BZ}(\omega_2) \right] F_i(\omega)F_j(\omega_1)F_k(\omega_2)
\]

(10.11)

where \( \mathbf{\tilde{\mathbf{\chi}}}^{(2)}_B \) is the bulk nonlinear susceptibility of medium b, defined by

\[
\mathbf{\tilde{\mathbf{P}}}^B(\omega = \omega_1 + \omega_2) = \mathbf{\tilde{\mathbf{\chi}}}^{(2)}_{B} \mathbf{E}_b(\omega_1)\mathbf{E}_b(\omega_2), F_j(\Omega) = e_b(\Omega)/e' \text{ for } j = z, \text{ and } F_j(\Omega) = 1 \text{ for } j = x, y.
\]

From Eq. (10.11), we notice that for SFG to be surface-specific, we must have \( |\mathbf{\chi}^{(2)}_s| >> |\mathbf{\chi}^{(2)}_B|/2k_b(\omega) \). This inequality generally holds only if the bulk has inversion symmetry since otherwise one would find \( |\mathbf{\chi}^{(2)}_s| \sim |\mathbf{\chi}^{(2)}_B|a \) with \( a \) being the monolayer thickness. If the surface is
a simple termination of the bulk structure and both \( \chi_f^{(2)} \) and \( \chi_B^{(2)} \) arise from electric quadrupole contribution due to field gradients, we would find \( |\chi_f^{(2)}| \sim |\chi_B^{(2)}|/k \) because the fields should vary on the scale of \( 1/k \) in the bulk but on the scale of the surface layer thickness at the surface. However, \( \chi_f^{(2)} \) could be dominated by electric-dipole contribution if the surface consists of a polar layer. In such cases, the surface contribution to SFG can easily dominate over that of the bulk.

A crude estimate of the signal strength of surface SFG is in order. For a polar monolayer of molecules at an interface, the resonant \( \chi_f^{(2)} \) is typically \( 10^{-14} - 10^{-16} \) esu. If we take \( |\chi_f^{(2)}| \sim 10^{-15} \) esu, \( I_1(\omega_1) \sim I_2(\omega_2) \sim 10^{10} \) w/cm\(^2\), \( A \sim 10^{-3} \) cm\(^2\), \( T = 10 \) ps, and \( \theta_\omega \sim 45^\circ \), Eq. (10.10) predicts a signal of \( \sim 10^4 \) photons/pulse. Such a signal can be easily detected.

In the above discussion, we have assumed a three-layer model (Fig. 10.1). This is of course a simplified model. In reality, the interfacial layer should be the surface-bulk transition layer in which the structure of the medium and the fields vary continuously (6). The surface nonlinear polarization must be an integration of the bulk nonlinear polarization across the interfacial layer.

\[
P_s^i = \int_I P_i^B(z) dz \quad \text{for } i = x, y
\]

\[
P_s^z / e' = \int_I [P_z^B(z) / e(z)] dz
\]

where \( I \) denotes the interfacial layer. For the \( z \) component, we have considered \( P_z^s/e' \) instead of \( P_z^s \) since the former is the effective radiation source, as can be seen in Eq. (10.3). Because of the rapid field variation across the interfacial layer, the multipole expansion of the polarization in this region is also important. We have (1)

\[
P^B(\omega) = \bar{P}^{(2)}(\omega) - \nabla \cdot \bar{Q}^{(2)}(\omega) + i \frac{c}{2\omega} \nabla \times \bar{M}(\omega) + \cdots
\]

where \( \bar{P}, \bar{Q}, \) and \( \bar{M} \) denote electric-dipole polarization, electric-quadrupole polarization, and magnetization, respectively. As quadratic functions of the input fields, these multipoles can be expressed as
\[
\tilde{P}^{(2)}(\omega) = \tilde{\chi}_{D}^{(2)} : \tilde{E}(\omega_1) \tilde{E}(\omega_2) + \tilde{\chi}_{DQ}^{(2)} : \nabla[\tilde{E}(\omega_1) \tilde{E}(\omega_2)] \\
+ \tilde{\chi}_{DM}^{(2)} : \nabla \times [\tilde{E}(\omega_1) \tilde{E}(\omega_2)] + \cdots
\]

\[
\tilde{Q}^{(2)}(\omega) = \tilde{\chi}_{Q}^{(2)} : \tilde{E}(\omega_1) \tilde{E}(\omega_2)
\]

\[
\tilde{M}^{(2)}(\omega) = \tilde{\chi}_{M}^{(2)} : \tilde{E}(\omega_1) \tilde{E}(\omega_2).
\]

Inserting Eqs. (10.13) and (10.14) into Eq. (10.12) makes the expression of \( \tilde{P}^S \) very complicated. We shall not discuss the complications here, but simply refer the readers to Ref. 6.

In the following discussion, we shall assume that the surface polarization is dominated by the electric-dipole term \( \tilde{P}^{(2)}_D = \tilde{\chi}_D^{(2)} : \tilde{E}(\omega_1) \tilde{E}(\omega_2) \) in \( \tilde{P}^B(z, \omega) \). Note that in media with inversion symmetry, \( \tilde{\chi}_D^{(2)} \) vanishes in the bulk, but can become significant at the interface.

We now turn our attention to \( \tilde{\chi}_s^{(2)} \) or \( \tilde{\chi}_D^{(2)} \). The surface nonlinear optical susceptibility, \( \tilde{\chi}_s^{(2)} \), of an interface reflects the intrinsic property of the interface, and is the quantity we would like to measure. As seen in Eqs. (10.10) and (10.11), this is what can be achieved by SFG if the bulk contribution is negligible. Although the output intensity measurements yield only absolute values of \( \chi_{s,ijkl}^{(2)} \), output interference measurements can determine phases of \( \chi_{s,ijkl}^{(2)} \). To see what information \( \chi_{s,ijkl}^{(2)} \) may contain, we show here explicitly the microscopic expression of \( \chi_{s,ijkl}^{(2)} \) under the electric-dipole approximation.

\[
\chi_{s,ijkl}^{(2)} = \int I \chi_{D,ijkl}^{(2)} (z) dz
\]

\[
= \int d z \int d \Omega \cdot f(\Omega) \sum_{g,n,n'} \left\{ \frac{e^2}{h^2} \left[ \frac{\langle g| r_j| n' \rangle \langle n'| r_j| n \rangle \langle n| r_k| g \rangle}{(\omega - \omega_{n' g} + i\Gamma_{n' g})(\omega_2 - \omega_{n g} + i\Gamma_{n g})} \right] \\
+ \frac{\langle g| r_j| n' \rangle \langle n'| r_k| n \rangle \langle n| r_j| g \rangle}{(\omega - \omega_{n' g} + i\Gamma_{n' g})(\omega_1 - \omega_{n g} + i\Gamma_{n g})} + 6 \text{ other terms} \right\} \rho_{gg}^o \}
\]

where \( \rho_{gg}^o \) is the population in the \( \langle g \rangle \) state, \( \omega_{ng} \) and \( \Gamma_{ng} \) are the transition frequency from \( \langle g \rangle \) to \( \langle n \rangle \) and the associated damping constant, and \( f(\Omega) \) denotes the distribution function of a set of parameters, \( \Omega \), with \( \int f(\Omega) d\Omega = N(z) = \text{density of molecules at } z \). We have assumed here that the interfacial layer is composed of a set of localized, noninteracting molecules. Extension to the more general case is possible, but not essential for our discussion.
The expression in Eq. (10.15) shows that $\chi^{(2)}_{s,ijk}$ is resonantly enhanced if $\omega_1$, or $\omega_2$, or $\omega_1 + \omega_2$ approaches a resonance and the resonant enhancement of SFG naturally provides the spectroscopic information. We note that even at a resonance, the nonresonant terms in $\chi^{(2)}_{s,ijk}$ are not negligible. We can write

$$\tilde{\chi}^{(2)}_S = \chi^{(2)}_{NR} + \sum_q \frac{\tilde{A}_q}{\omega - \omega_q + i\Gamma_q}$$

(10.16a)

and according to Eq. (10.10), the SF output is

$$S \propto \left| \tilde{e}^{(2)}(\omega) \cdot \tilde{\chi}^{(2)}_S \cdot \tilde{e}(\omega_1) \tilde{e}(\omega_2) \right|^2$$

(10.16b)

where q refers to individual modes near resonance. Interference between the resonant and nonresonant terms causes the SFG spectral profile to be different from those observed in conventional spectroscopy. Similar to coherent anti-Stokes Raman spectroscopy, the profile of a resonance can appear in various different forms depending on the interference (Fig. 10.3). In

![Fig. 10.3. Possible spectral profiles of an SFG resonance with the signal proportional to $\left| \chi^{(2)}_{NR} + A/(\omega_1 - \omega_0 + i\Gamma) \right|^2$, where $\chi^{(2)}_{NR}$ is complex in general and A is real. (a) $\chi^{(2)}_{NR}$ is real and has the same sign as A. (b) $\chi^{(2)}_{NR} \ll |A / \Gamma|$. (c) $\chi^{(2)}_{NR}$ is real with a sign opposite to A. (d) $\chi^{(2)}_{NR}$ is imaginary and opposite in sign compared to $A / \Gamma$ with $|\chi^{(2)}_{NR}| > |A / \Gamma|$.

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order to deduce the parameters characterizing the resonances, Eq. (10.16) must be used to fit the observed spectrum. In some cases, however, $\chi^{(2)}_{NR}$ is negligibly small and resonances are far apart; well defined resonant peaks can then be expected in the SFG spectrum.

We conclude the theoretical discussion here by briefly discussing some other characteristic features of surface SFG spectroscopy. The technique is often used to probe low lying surface resonances. From Fig. 10.1(a) and Eq. (10.15), one may recognize that $\tilde{A}_q$ in Eq. (10.16) is proportional to the matrix element product of infrared and Raman transitions from $\langle g \rangle$ to $\langle nl \rangle$. In fact, we can write $\tilde{A}_q = M_q \bar{\mu}_q$ with $M_q$ and $\bar{\mu}_q$ being the Raman and infrared transition probability amplitudes, respectively. For $\tilde{A}_q$ to be nonvanishing, the $q$ mode must be both Raman and infrared active. This is an important selection rule for SFG spectroscopy. We also see in Eq. (10.15) that $\chi_S^{(2)}$ depends on the distribution function $f(\Omega)$, where $\Omega$ may denote the orientation and arrangement of a molecule or group of atoms in a molecule. Being a second-order process, SFG is very sensitive to polar orientations, with $\chi_S^{(2)}$ vanishing if the average orientation is nonpolar. Finally, the surface symmetry is directly reflected in the symmetry of $\chi_S^{(2)}$. The symmetry relations among $\chi_{s,ijk}^{(2)}$ lead to the vanishing of some $\chi_{s,ijk}^{(2)}$ elements and inter-dependences of others. The nonvanishing, independent $\chi_{s,ijk}^{(2)}$ elements can be determined by SFG measurements using different input/output polarization combinations. In many cases, hyperpolarizabilities $\alpha_{\xi,\eta,\zeta}^{(2)}$ of a molecule or group of atoms in a molecule at an interface are the quantities of interest. If intermolecular interaction is negligible, then $\chi_{s,ijk}^{(2)}$ and $\alpha_{\xi,\eta,\zeta}^{(2)}$ are related by a coordinate transformation linking the lab coordinates $\hat{x}, \hat{y}, \hat{z}$ and the molecular coordinates $\hat{X}, \hat{Y}, \hat{Z}$.

$$\chi_{s,ijk}^{(2)} = N_s \langle \hat{i} : \hat{\xi} \rangle \langle \hat{j} : \hat{\eta} \rangle \langle \hat{k} : \hat{\zeta} \rangle \alpha_{\xi,\eta,\zeta}^{(2)}$$ (10.17)

Here, $N_s$ is the surface density of molecules in the interfacial layer, and the angular brackets denote the orientational average or $\int d\Omega \ f(\Omega)$ in Eq. (10.15).

10.3. Experimental Arrangement.

The experimental arrangement for SFG spectroscopic measurements is usually quite simple except for the laser system. A typical setup is sketched in Fig. 10.4. The two input laser beams should be well overlapped on the sample. Since the SF output is highly directional, spatial filtering can be used to effectively discriminate against the background noise resulting
from laser scattering and fluorescence. Spectral filtering can be achieved by placing a spectrometer or a set of interference filters in the detection arm and allowing further elimination of the unwanted background light. The SF signal is finally detected by a photomultiplier connected to a gated integrator and computer system. For adjustment of input and output beam polarizations, polarizers are inserted in the optical paths before and after the sample.

The important and expensive part of the experimental setup is the laser system. For SFG spectroscopy, a tunable laser is needed. A short-pulse laser is preferred because according to Eq. (10.10), the optimized signal is inversely proportional to the pulse duration if \( I(\omega_f)T \) is the quantity that is limited by laser damage of the sample, as is usually the case. A widely tunable, high-energy, short-pulse laser is difficult to find. Fortunately, recent advances in optical parametric oscillators and amplifiers have changed the scene (8). Take the picosecond Nd:YAG-laser-pumped optical parametric generator and amplifier as an example (9). Together with sum and difference frequency generators, coherent pulses tunable from 200 nm to 20 \( \mu \)m (10) with tens to hundreds of \( \mu \)J per pulse can be obtained from a small table-top system (Fig. 10.5). Such a tunable source is fairly ideal for surface SFG spectroscopy as it can cover a wide range of electronic and vibrational transitions. Nanosecond optical parametric oscillators with sum and difference frequency generators are commercially available. They can also be used for SFG spectroscopy. Their higher energy per pulse (tens of mJ per pulse) partly offsets the loss of signal due to the longer pulse. Stimulated Raman scattering in gases has also been used to generate tunable nanosecond pulses in the infrared, and has been employed for SFG spectroscopy (11). More recently, free electron lasers have also become a viable tunable source for SFG spectroscopy as they can be tuned, in principle, throughout the mid- and far-infrared (12). In the visible range, dye lasers can still be used, but are likely to be replaced by optical parametric generators.
Fig. 10.5 Schematic of an optical parametric generator and amplifier (OPG/OPA) system using BBO crystals pumped at 532 nm. The system generates tunable picosecond pulses from 650 nm to 2.5 μm and has an output bandwidth near the transform limit. The output wavelength can be extended to UV by SFG and mid-IR by difference frequency generation (DFG) in a nonlinear crystal. Shown in the figure is a DFG stage using an AgGaS₂ crystal to extend the output to ~ 10 μm. (After J. Y. Zhang, J. Y. Huang, Y. R. Shen, and C. Chen, *J. Opt. Soc. Am. B* 10, 1758 (1993)).

As we mentioned earlier, the maximum laser flux allowed on a sample is determined by the laser damage threshold. To optimize the SF signal, the pump area on the sample surface should be as small as possible. Given the input laser powers, the signal is inversely proportional to the pump area. Scanning the tunable source may cause overlapping of the input beams on the sample surface to change. Therefore in the measurement normalization of the observed spectrum against a known reference is important.

**10.4. Applications: Selective Examples.**

The main advantage of SFG as a surface spectroscopic technique is its versatility. It can
be applied to all interfaces accessible by light. There already exist in the literature many reports on successful applications of SFG spectroscopy to a wide variety of interfacial problems. Here we have only space to discuss a selective few. We shall focus on those that are unique with SFG.

10.4.1. Surface Specificity.

We first show an example illustrating the surface specificity of SFG spectroscopy. Figure 10.6 depicts the surface vibrational spectra in the CH stretch region for three interfaces (13): hexadecane/silica, hexadecane/octadecyltrichloride (OTS) monolayer/silica, and CCl₄/OTS/silica. The (p, p, p) (SF output, visible input, and infrared input are all p-polarized) polarization combination was used. It is seen that for the hexadecane/silica interface, the SFG spectrum has hardly any detectable features even though the infrared spectrum of liquid hexadecane is known to have very strong absorption bands in this region arising from the large number of CH₂ modes in the molecule. For the hexadecane/OTS/silica interface, however, a clear SFG spectrum is observed. The three well resolved peaks at 2870, 2935, and 2965 cm⁻¹ can be identified as the symmetric stretch of CH₃, Fermi resonance between symmetric stretch and bending overtone of CH₃, and asymmetric stretch of CH₃, respectively. This spectrum obviously is originated from the OTS monolayer adsorbed at the interface. No CH₂ stretch modes are clearly present, indicating that the alkyl chains of the OTS molecules have little trans-gauche defects since for a straight chain, the CH₂ modes approximately must be either Raman or infrared active, but not both (14). That the observed SFG spectrum for the
hexadecane/OTS/silica interface must arise from the OTS monolayer is further confirmed by the observed spectrum for the CCl₄/OTS/silica interface. As seen in Fig. 10.6, the spectrum remains basically unchanged with CCl₄ replacing hexadecane.

The above example clearly illustrates the surface-specific nature of SFG. The polar orientation of the OTS molecules at the interface leads to an electric-dipole-dominated surface nonlinear susceptibility whose contribution to SFG overwhelms the electric-quadrupole bulk contribution. We shall see later many other examples demonstrating the surface specificity of SFG spectroscopy.

10.4.2. Chain Conformation and Orientation.

As seen in the above example, the unusual selection rule of SFG spectroscopy suppresses the CH₂ modes of a straight alkyl chain, permitting the CH₃ modes to be readily observable, in contrast to IR and Raman spectroscopies. Trans-gauche defects in the chains break the symmetry and make the CH₂ modes allowed. The appearance of CH₂ peaks in the SFG spectrum is therefore an indication of the existence of defects in the alkyl chains of the molecular monolayer. Because defects disturb the orientational order of the terminal CH₃ group on the chains, the CH₃ peaks are expected to decrease accordingly. Thus, the SFG spectrum can allow an evaluation of the chain conformation of a surface monolayer, which is of great importance in surfactant chemistry, biology, and other areas of science and technology. Figure 10.7 provides an example (14). The SFG spectra in the CH stretch region were taken for monolayers of pentadecanoic acid (PDA) adsorbed on water at three different surface densities: 47, 34, and 22 Å/molecule. The right and left panels correspond to two different input/output polarization combinations, (s, s, p) and (s, p, s), respectively. In the case of 22 Å/molecule, the main peaks can all be assigned to CH₃ stretch modes as we did for the peaks in Fig. 10.6. The small peaks at 2850 cm⁻¹ in the (s, s, p) spectrum and at 2890 cm⁻¹ in the (s, p, s) spectrum can be identified with the symmetric and asymmetric CH₂ stretches. The very weak strengths of the CH₂ peaks indicate that the alkyl chains of this densely packed PDA monolayer have hardly any defects. With the surface density of PDA reduced, the CH₃ peaks drop accordingly, but the CH₂ peaks become appreciably stronger. This indicates that the chains must have developed more defects as the chain density decreases. Unfortunately, quantitative calculation is not yet available to relate the SFG spectrum to the average number of defects on a chain, preventing us from a quantitative evaluation of the chain conformation.
Fig. 10.7 SFG spectra of PDA at different surface coverages normalized per molecules. 
1a)-1c) were taken with the s-visible, p-infrared polarization combination. 2a)-2c) 
were taken with p-visible, s-infrared: a) 47 Å²/molecule, b) 34 Å²/molecule, 
c) 22 Å²/molecule. (After Ref. 14.)

In the case of straightened alkyl chains, the average chain orientation can be inferred 
from the average orientation of the terminal CH₃ groups (14). The latter can be deduced from 
the polarization-dependent SFG spectra of the CH₃ modes. Consider the case where the chain 
distribution is azimuthally isotropic. Equation (10.17) gives, for the symmetric CH₃ stretch

\[
\chi_{xyz}^{(2)} = \alpha_s[(r + 1)(\cos \theta) + (r - 1)(\cos^3 \theta)]
\]

\[
\chi_{yzy}^{(2)} = \alpha_s(1 - r)(\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle)
\]  

(10.18a)

and for the asymmetric CH₃ stretch

\[
\chi_{xyz}^{(2)} = -\alpha_d(\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle)/2
\]

\[
\chi_{yzy}^{(2)} = \alpha_d(\cos^3 \theta)/2
\]  

(10.18b)
with $\alpha_s = N_s(\alpha_{zzz})_s$, $r = (\alpha_{2xx} / \alpha_{zzz})_s$, and $\alpha_d = N_d(\alpha_{zzz})_d$. Here, $\hat{z}$ is along the surface normal, $\hat{Z}$ is along the symmetry axis of the CH$_3$ group, $\theta$ is the angle between $\hat{z}$ and $\hat{Z}$, and $\alpha^{(2)}$ is the hyperpolarizability of the CH$_3$ group with $\alpha_{2xx}$, $\alpha_{zzz}$, and $\alpha_{zzz}$ being the only independent, nonvanishing elements. Experimentally, $\chi^{(2)}_{yyz}$ and $\chi^{(2)}_{zyy}$ can be deduced from the SFG spectra with (s, s, p) and (s, p, s) polarization combinations, respectively. From the ratio of $\chi^{(2)}_{yyz} / \chi^{(2)}_{zyy}$, the angle $\theta$ can be determined, assuming that the orientational distribution of $\theta$ is sharp. Application of this analysis to the spectra in Fig. 10.7 for the densely packed PDA monolayer finds that the CH$_3$ groups of the alkyl chains are tilted at $-35^\circ$ away from the surface normal, implying that the chains are oriented essentially along the surface normal (14). Wolfrum et al. used this method to determine the chain orientations of fatty alcohols and found excellent agreement with the X-ray results (15).

Long-chain surfactant monolayers adsorbed at air/liquid, liquid/liquid, and liquid/solid interfaces have been studied by a number of groups using SFG spectroscopy (14-19). Chain conformations and orientations in response to the environmental changes are information needed for the understanding of interfacial properties of such systems. In some cases, information on the spatial arrangement of the chains at an interface can also be deduced from the measurements (19).

10.4.3. Pure Liquid Interfaces.

SFG can be used to study molecular monolayers adsorbed at interfaces, but is not the only spectroscopic technique for such studies. Linear optical spectroscopy can be equally effective although the selection rules are different. This is not the case if one is interested in surface spectroscopy of pure liquids. Here, for lack of surface specificity, linear optical techniques are unable to yield a surface spectrum not dominated by bulk contribution. Raman spectroscopy has the same difficulty. SFG appears to be the only spectroscopic method that can be adopted for liquid interfacial studies.

Liquid interfaces are certainly not less important than solid surfaces, which have been extensively investigated, but they have hardly been explored experimentally at the molecular level owing to the lack of experimental tools. Unlike solids, molecules in liquids are still free to move. They can orient and arrange themselves at the surface to minimize the free energy of the system, resulting in the specific surface physical and chemical properties. We expect that molecular orientation and arrangement at a pure liquid surface can be deduced from the surface.
vibrational spectrum obtained by SFG. For illustration, we use water as an example (20).

Water is the most important liquid on earth. Many theoretical calculations have been carried out to predict water structures at various interfaces (21). The results however are rather confusing. Surface vibrational spectra, if available, can provide a meaningful check on the theory.

![SFG spectrum from the air/water interface with the (ssp) polarization combination.](image_url)

**Fig. 10.8** SFG spectrum from the air/water interface with the (ssp) polarization combination. (After Ref. 20.)

Figure 10.8 shows the SFG spectra of the air/water interface in the OH stretch region (20). The (s, p, s) spectrum is very weak with hardly discernible features. The (s, s, p) spectrum exhibits three prominent peaks at 3680, 3400, and 3200 cm\(^{-1}\); they can be identified with OH stretches associated with dangling OH bonds, OH with H bonded to a neighbor in a disordered structure, and OH with H bonded to a neighbor in a well ordered structure like ice, respectively. The one at 3680 cm\(^{-1}\) is most significant. Its presence indicates that first, the spectrum must come from the water monolayer at the surface since no dangling bonds would exist in the sublayers, and second, at least part of the surface water molecules must be oriented with one OH bond pointing out of the liquid. Quantitative measurements showed that about 25% of the water molecules in the surface monolayer have contributed one dangling bond per molecule. This is exactly what one would find on a hexagonal ice surface. Therefore, the result suggests that the surface structure of water at the air/water interface is ice-like. However, unlike ice, the tetrahedral hydrogen-bonding network is significantly disordered at the water surface, as evidenced by the strong peak at 3400 cm\(^{-1}\).
The free OH peak at 3680 cm\(^{-1}\) is completely suppressed when a monolayer of surfactant molecules adsorbs at the air/water interface (20). The adsorbed molecules must have either terminated the OH dangling bonds or rearranged the surface water molecules to eliminate the dangling bonds. We can use the surface vibrational spectrum to understand hydrophobicity and hydrophilicity at the molecular level (20). It was found that against a hydrophilic surface, the water surface spectrum has the dangling OH peak at 3680 cm\(^{-1}\) completely suppressed. Clearly, hydrophilic interaction must have terminated the dangling OH bonds. On the other hand, for a water/hydrophobic interface, the 3680 cm\(^{-1}\) peak is as pronounced as ever, indicating that the dangling OH bonds are unaffected by the presence of the hydrophobic surface. Thus the free OH peak can be regarded as a signature of the hydrophobic interface, signifying the lack of bonding interactions between water and the non-wetting surface. Two examples are presented in Fig. 10.9. In both cases, the strength of the free OH peak also provides valuable information. As for

![Fig. 10.9](image)

Fig. 10.9  SFG spectra from (A) the quartz-OTS-water interface, (B) the air-water interface, (C) the hexane-water interface, and (D) the quartz-ice interface. The SF output, visible input, and IR input were s-, s-, and p-polarized, respectively. (After Ref. 20.)

the air/water interface, it indicates that the water interfacial structure is ice-like. In the bonded OH region (3000-3600 cm\(^{-1}\)), the spectra of the two cases look different. For the water/hydrophobic solid surface, the spectrum closely resembles that of ice with the peak at 3400 cm\(^{-1}\) very much suppressed. This suggests that the interfacial ice-like structure of water is highly ordered. The result can be expected if we realize that the water surface layer, being
against a solid wall, is not so flexible and cannot allow much disordering in its hydrogen-bonding network. For the flexible water/oil interface, the spectrum resembles that of the free water surface, as one would expect.

Surface structure of water at a charged water/solid interface and its response to the bulk pH value and salt concentration have also been studied by SFG vibrational spectroscopy (20). The result shows that the surface water structure varies significantly with surface charges. This should be an important piece of information in the search for an understanding of electrochemistry. SFG is currently the most viable spectroscopic method for in-situ studies of electrochemical reactions at surfaces. It has already been used in several cases to study nonlinear response of electrode surfaces and to identify surfaces species appearing and disappearing in an electrochemical process (22).

SFG spectra for other pure liquid interfaces such as alcohols have also been reported (23). They have provided useful information about the surface structures of those liquids. It is hoped that such work will eventually lead to some general understanding of liquid surfaces and interfaces. The difficulty in the study often lies in our inability to assign and analyze the observed spectral features. Much work is needed before we can relate a surface spectrum unambiguously to a surface structure.

10.4.4. Phase Transitions of Surface Monolayers.

Surface monolayers of pure liquids or adsorbed monolayers on liquids can undergo various phase transitions. They can be probed by surface tension measurements, ellipsometry, and X-ray reflection and diffraction, but none of these techniques can provide as detailed information about the nature of the phase transitions as surface vibrational spectroscopy. We consider two cases here (24). The first one is a monolayer of long-chain alcohol (C₁₂H₂₆O) floating on water. It was found that the monolayer undergoes a freezing transition at 39°C, which is 17°C higher than the bulk alcohol freezing temperature. Ellipsometry measurements suggested that the transition is characterized by a sudden change in layer thickness (25). This is however not supported by the SFG spectra presented in Fig. 10.10 (24). It is seen that the spectra before and after the freezing transition are very much the same except that the former is 40% weaker than the latter and has a somewhat more pronounced CH₂ mode at 2840 cm⁻¹. The other peaks can all be identified to various CH₃ stretch modes as we did for the spectrum in Fig. 10.6 or 10.7. These spectra clearly indicate that both before and after the transition, the alcohol molecules are oriented perpendicular to the surface with nearly straight chains. The surface
freezing transition is characterized by a simple density increase together with a slight reduction of defects on the hydrocarbon chains.

The second case occurs in pure n-alkane (C\textsubscript{n}H\textsubscript{2n+2}) liquids. It was found that for n ≥ 16, the liquid would experience a surface monolayer freezing transition at a temperature several degrees higher than the bulk freezing temperature (26), but the nature of the transition was not completely clear. Again, the SF spectra can provide some clues (24). As shown in Fig. 10.11, the spectra before and after the surface monolayer transition are significantly different. Using the spectra in Fig. 10.7 as references, we notice that the spectra before the transition describe a surface monolayer of vertically oriented chains with an appreciable number of defects. After the transition, the monolayer becomes much better ordered, with the chains in essentially all-trans configuration. Therefore, the surface freezing transition is mainly characterized by a change in the chain configuration.
In a study of binary mixtures of CH$_3$CN and water using surface SFG spectroscopy, Zhang et al. (27) found that there are sudden changes in the stretch vibrational frequency of CN and the orientation of the symmetric axis of CH$_3$CN at the air/liquid interface when the bulk molar concentration of CH$_3$CN exceeds 0.07. At this bulk composition, CH$_3$CN presumably has reached a full monolayer at the interface. They attributed the sudden changes to an interfacial structural phase transition in which the chemical environment is drastically modified. However, this conclusion is yet to be corroborated by other experimental tests, including the question whether the changes are indeed so sudden as can be legitimately called a phase transition.

10.4.5. Surface Catalysis.

Understanding of surface catalytical reactions has long been a goal of modern surface science. Many studies of surface reactions on well defined substrate surfaces in ultrahigh vacuum (UHV) have been carried out in the past several decades. They were designed to search for a microscopic understanding of the catalytical reactions. However, surface reactions in UHV could be characteristically different from those in a real gas atmosphere. To monitor catalytical reactions in practical circumstances, one would then need in-situ surface probes that can be operative in real atmospheres. This requirement unfortunately cannot be met by the conventional surface analytical tools. Now SFG spectroscopy provides a great opportunity for such studies.

We use hydrogenation of ethylene (C$_2$H$_4$) on Pt(111) into ethane (C$_2$H$_6$) as an example (28). As proposed by Horiuti and Polanyi in 1934 (29), the process was widely believed to proceed in the steps described in Fig. 10.12(a). The C$_2$H$_4$ molecules are supposed to be di-$\sigma$ bonded to the Pt(111) surface and hydrogenated first to ethyl (C$_2$H$_5$) and then to C$_2$H$_6$ by the hydrogen atoms adsorbed on the surface. Without sufficient H on the surface, C$_2$H$_4$ tends to dehydrogenate to ethylidyne above 240 K. SFG spectroscopy in the CH stretch region can be used to identify these various species on the surface: ethylidyne is characterized by a CH$_3$ symmetric peak at 2884 cm$^{-1}$, di-$\sigma$ bonded ethylene by a CH$_2$ symmetric peak at 2904 cm$^{-1}$, and ethyl by peaks at 2860, 2920, and 2970 cm$^{-1}$. It is also possible to have ethylene $\pi$-bonded on Pt(111). The spectral feature is a weak CH$_2$ symmetric mode at $\sim$3000 cm$^{-1}$.

We can record the surface SFG spectrum in-situ during a reaction process in a real atmosphere. Figure 10.13 displays the spectra for two related cases (28). One was taken during ethylene hydrogenation at 295 K with 100 torr H$_2$, 35 torr ethylene, and 625 torr He; the process started with a bare, clean Pt(111) crystal. The other was taken under the same condition, but the
Pt(111) crystal was initially covered with ethylidyne. Gas chromatography was used to monitor the ethane production. It revealed a production rate of $11 \pm 1$ ethane molecules (from ethylene) per surface Pt atom per second in the first case and $12 \pm 1$ in the second case. This means that the production rates of the two cases are practically the same. The two spectra in Fig. 10.13 are also about the same. They show that the surface is mostly covered by ethylidyne (0.15 ML in one case and 0.21 ML in the other, with 0.25 ML being the saturation coverage), and partly covered by di-σ- and π-bonded ethylene. While the π-bonded ethylene coverages in the two cases are the same, the di-σ bonded ethylene coverages differ by a factor of 4. Since the production rates of ethane in the two cases are essentially the same, this result indicates that di-σ bonded ethylene cannot be the important intermediate species in this hydrogenation process. Ethylidyne is known to be just a spectator in the process (30). Therefore π-bonded ethylene must be the truly responsible intermediate species. The relevant steps for the hydrogenation process are described in Fig. 10.12(b). We notice that the π-bonded ethylene is not the primary adsorbed species on Pt(111) and is only weakly bonded to the surface. This is presumably the reason why ethylene hydrogenation is not sensitive to the Pt surface structure (30).

Catalytical reactions can also take place at liquid/solid interfaces. Clearly, SFG spectroscopy again will be a unique probe for this type of reactions.
Fig. 10.13  (a) SFG spectrum of the Pt(111) surface during ethylene hydrogen with 100 Torr H₂, 35 Torr C₂H₄, and 615 Torr He at 295 K. (b) The SFG spectrum under the same conditions as (a), but on a surface which was precovered in UHV with 0.25 ML of ethylidyne. (After Ref. 28.)

10.4.6. Surface States of Buried Interfaces.

SFG spectroscopy is an effective means to study buried interfaces. Liquid/solid
interfaces are good examples. The intrinsic surface specificity of SFG permits spectroscopic measurements of the interfacial layers even in the presence of strong bulk absorption in the same spectral region.

Fig. 10.14 Resonant three-wave mixing signals associated with $s_{zzz}^{(2)}$ as a function of the energy of a photon from the tunable dye laser. (a) Results for the SHG process and b) the case of SFG involving mixing the output of the dye laser with a Nd:YAG laser at 1.17 eV. The filled symbols refer to signal from the CaF$_2$/Si(111) sample, the open symbols to a Si(111) surface covered by the native oxide. The solid curve in a) is a fit to theory. (After Ref. 31.)

Here we focus our attention on solid/solid interfaces. Such interfaces are of great importance for modern electronics, but few techniques are available for their studies. SFG is currently the only spectroscopic technique applicable. Heinz et al. first used it to probe surface states of an CaF$_2$/Si(111) interface (31), which is a prototype insulator/semiconductor interface. Figure 10.14 shows the spectra obtained by SHG ($\omega_2 + \omega_1 \rightarrow 2\omega_1$) and SFG ($\omega_1 + \omega_2 \rightarrow \omega$) with $\omega_1$ scanned in the 2.2 - 2.5 eV range. The spectral features arise from one-photon resonances of $\omega_1$ with electronic transitions. The main peak at 2.4 eV can be identified as due to transitions from the occupied to the empty interface states. It marks the band gap of the interfacial electronic structure, and is very different from the band gaps of the bulk Si (1.1 eV) and CaF$_2$ (12.1 eV). The peak at 2.26 eV is believed to be associated with the $n = 1$ surface exciton, but the one at 2.32 eV is not identified.
Similar experiments were carried out by Daum et al. on SiO₂/Si interfaces (32). They observed a strong two-photon resonance at 3.3 eV and found that it arises from direct band gap transitions between valence and conduction band states associated with a few monolayers of strained Si at the interface. The same resonance was observed at clean Si(100)-(2x1) and Si(111)-(7x7) surfaces where strained Si sublayers also exist due to surface reconstructions.

Yodh and coworkers have also used SHG and SFG spectroscopy to study interface states of ZnSe/GaAs(001) heterojunctions (33). In this case, the semiconductor bulks have no inversion symmetry which makes SHG and SFG non-surface-specific in general. However, as we mentioned earlier, the symmetries of the interface and bulks are still intrinsically different, and selective input/output beam polarizations can render SHG and SFG surface-specific (3). Using this scheme, Yeganeh et al. found a two-photon resonance at 2.72 eV that can be assigned to a transition between the valence states of ZnSe and a quantum-well state on the GaAs side at the buried interface (33). The interfacial quantum well was created by interdiffusion of Zn into GaAs and Ga into ZnSe during the sample growth. This resonance is sensitive to a variety of structural phenomena; any process that modifies the band profile near the heterojunction, such as lattice strain and interfacial reconstruction, can affect the strength of the resonance.

More recently, with the same technique, the same research group has studied interface states of buried metal/GaAs junctions (34) and found that these states are sensitive to preparation of the interface. For the As-rich, Au/GaAs (n-type) interface, a one-photon resonance at 0.715 eV arising from transitions from an interface state to the conduction band states was observed. The same resonance was found in As-capped GaAs (n-type) samples. For Ga-rich Au/GaAs (n-type) interface, the spectrum exhibited two such resonances. However, no such resonance was observed in Au/GaAs (p-type) systems. These interface states have been identified as As and Ga p-like defect states associated with As and Ga atomic displacements just below the buried interface.

10.4.7. Ultrafast Surface Dynamics.

Conventional surface probes are limited in time response to the millisecond range. Therefore, ultrafast surface dynamics is a field whose exploration had to wait for the arrival of ultrashort laser pulses. Surface dynamics can now be studied with a picosecond or subpicosecond time resolution, and SHG and SFG spectroscopy is best suited for this type of work, namely, studies of transient excitations and relaxations of surface species or surface states and detection of intermediate species in surface reactions. We consider, as examples,
measurements of longitudinal and transverse relaxations of surface molecular vibrations using SFG.

Longitudinal relaxation here refers to the approach to thermal equilibrium of populations or energies in or out of the states of a system. Vibrational energy relaxations of adsorbates on substrates are often intimately connected to surface excitations and reactions. Ultrafast infrared spectroscopy has been developed for such studies, but the poor signal-to-noise ratio usually limits the investigations to samples with high surface areas, such as powder or porous materials. SFG spectroscopy permits studies of well-defined crystalline surfaces of metals and semiconductors.

Harris et al. first used the technique to study longitudinal relaxation of the symmetric CH stretch vibration of methyl thiolate (CH$_3$S) on Ag(111) (35). As sketched in Fig. 10.15, the picosecond pump and probe pulses are at the same frequency resonant with the v = 0 and v = 1 transition. The pump pulse excites some population from v = 0 to v = 1 and the time-delayed probe pulse probes via SFG the relaxation of the population difference between v = 0 and v = 1 back to equilibrium. Figure 10.16 depicts the experimental results that exhibit a bi-exponential relaxation. This suggests that an intermediate state is involved in the relaxation from v = 1 to v = 0. The population difference recovers in a time less than 100 ps, which seems to be dominated by intramolecular relaxation rather than energy transfer to electron-hole pair excitations in the Ag metal substrate. This is believed to be generally true for sufficiently large polyatomic molecules if the vibrational excitation is on an atomic group situated away from the metal.

![Fig. 10.15](image)

Fig. 10.15 Schematics describing the pump/probe processes using resonant SFG to probe (a) the population recovery and (b) the population decay from the v = 1 state after pumping of the v = 0 to v = 1 transition (indicated by the heavy arrows).
Fig. 10.16 Transient vibrationally resonant SFG signals at 300 K in experiments carried out with pulse widths (FWHM) a) $\tau_p = 2.5$ ps or b) $\tau_p = 1.0$ ps and corresponding visible-infrared cross-correlations. Solid points, normalized transient SFG signals $1 - [S(\tau_d)/S_0]^{1/2}$; solid lines, fits to transient SFG signals according to a three-level model; lines with inverted triangles, visible-infrared cross-correlation. (After Ref. 35.)

Harris and coworkers also studied CO stretch on Cu(100) using SFG (36). For such small molecules, electron-hole pair excitations become the dominant mechanism for longitudinal vibrational relaxation. A similar result was obtained by Beckerle et al. studying CO on Pt(111) (37). As a further confirmation of this picture, Peremans et al. measured the CO vibrational relaxation at a Pt(100) electrochemical interface and found that it was not affected by the interfacial electric field or environment (38).

Vibrational relaxations of adsorbates on semiconductor surfaces have also been studied, namely, Si-H and C-H stretches for H on Si and diamond, respectively (39,40). As mentioned above, the population recovery time depends on the possible existence of intermediate states in the relaxation pathway. It is therefore generally not the same as the longitudinal lifetime of the
excited state. To find the latter, a different scheme must be used. As described in Fig. 10.15, this can be achieved by time-delayed probing via SFG of the $v = 1$ to $v = 2$ transition after population is pumped from $v = 0$ to $v = 1$. The time-dependent SFG signal is directly proportional to the population in the $v = 1$ state and provides a direct measurement of the $v = 1$ lifetime. This is shown in Fig. 10.17 for the Si-H vibration of H/Si(111) (39). The measured relaxation time of $T_1 = 800$ ps at room temperature is long compared to what one would normally expect for chemisorbed molecules on semiconductors and metals. This is because the H-Si stretch vibration is effectively decoupled from the electronic excitations of Si as well as the H-Si bending vibration and surface Si phonons. The main relaxation pathway is believed to be the four-phonon energy transfer to the H-Si bending and surface Si phonon modes. A similar situation occurs for H on diamond C(111)(40), although the lifetime of the CH stretch is significantly shorter because of the more efficient coupling in relaxation.

![Graph](image)

Fig. 10.17 SFG amplitude as a function of time delay in the pump/probe experiment on the H-Si stretch vibration of H/Si(111) using the scheme described in Fig. 15 (b). The dotted line is a theoretical fit giving a relaxation time of $T_1 = 0.9$ ns. (After Ref. 39.)

Transverse (or dephasing) relaxation of a surface excitation can also be measured by SFG (41,42). It is known that for an inhomogeneously broadened transition, dephasing of an excitation can only be monitored by coherent transient processes such as photon echoes. To observe photon echoes from surface vibrations is however difficult because of the limited sensitivity of the infrared detectors. With SFG it becomes possible. Instead of waiting for the rephased oscillating dipoles to radiate the infrared photon echo, we can wave-mix the oscillating dipoles with an incoming visible laser pulse and produce an SFG signal, which is effectively an up-converted photon echo. Guyot-Sionnest used this scheme to observe photon echoes from the surface H-Si stretch vibration of H/Si(111). A dephasing time of 85 psec at 120 K was deduced.
Fig. 10.18  Logarithmic plot of the surface SFG echo signal from the stretch vibration of H/Si(111) as a function of time delay of the visible probe. The data points connected by dashed lines are shown for several delays between the two infrared pulses: 15 ps, ▲; 28 ps, ○; 42 ps, △; 55 ps, ⋆; 68 ps, □; 78 ps, O. The solid lines are theoretical fits. (After Ref. 41.)

from the measurement (Fig. 10.18); it corresponds to a homogeneous linewidth of 0.12 cm\(^{-1}\). In comparison, the observed spectral linewidth is 0.3 cm\(^{-1}\), which is obviously dominated by inhomogeneous broadening. Quadratic anharmonic coupling of the H-Si stretch vibration with Si surface phonons at ~190 cm\(^{-1}\) is believed to be mainly responsible for the dephasing.

10.5. Conclusion.

SFG is a most powerful and versatile spectroscopic technique for surface and interface studies. In many cases, it is the only technique available. A number of examples have been given in this article for illustration. As a probe that can be applied to all interfaces accessible by light, we should be able to find many more applications. Examples are interfacial biological systems, chemical vapor depositions, plasma etching, corrosion, reactions at liquid/solid interfaces, and surface dynamics at liquid interfaces. All of these are problems that can hardly be studied in-situ by other means.

As one would expect, SFG is also not a technique without difficulties. First, tunable laser sources are still limited. Although infrared tunability can be extended to ~20 μm in a table-top setup, the energy per pulse is low (~10 μJ/pulse) towards the long wavelength end, making the SFG sensitivity poor. The free electron laser allows a wavelength coverage over the entire IR range, but it is still not a facility easily available to all researchers. Second, the interpretation of
an observed SFG spectrum may not be straightforward. Like all new spectroscopies, assignment of spectral features is a delicate matter, especially when the line profiles are not the same as those appearing in the usual absorption or emission spectrum. In general, it is also necessary to be sure that the bulk contribution to the SFG spectrum is negligible. Otherwise, to obtain the surface or interfacial spectrum, the bulk contribution must be measured separately and subtracted from the observed spectrum. Finally, the attainable signal strength of surface SFG is still rather low and makes the spectroscopic measurement time consuming and difficult for routine applications.

We also note that in most surface science problems, a single probe cannot provide the complete answer. SFG spectroscopy is certainly not an exception. Complementary information obtained by other methods is often needed for a full appreciation of the SFG result. However, SFG spectroscopy does have the capability to yield some unique information about surfaces and interfaces. Judging from the growing interest in this area, it is likely to become a common tool in a surface science laboratory in the near future.

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21. See, for example, a recent article on the subject by I. Benjamin, *Phys. Rev. Lett.* 73, 2083 (1994), and references therein.


