A few selected applications of surface nonlinear optical spectroscopy

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ABSTRACT As a second-order nonlinear optical process, sum-frequency generation is highly surface-specific and accordingly has been developed into a very powerful and versatile surface spectroscopic tool. It has found many unique applications in different disciplines and thus provided many exciting new research opportunities in surface and surface-related science. Selected examples are discussed here to illustrate the power of the technique.

In recent years, we have been developing and applying modern optical techniques to surface and interface studies. The one that has attracted much attention is surface optical second harmonic generation (SHG) and sum-frequency generation (SFG) (1). This is because the technique has very high surface specificity and wide applicability. SFG is a nonlinear optical process in which two laser beams at frequencies \( \omega_1 \) and \( \omega_2 \) impinging on a medium mix and generate a sum-frequency output at \( \omega_3 = \omega_1 + \omega_2 \). SHG is a special case of SFG with \( \omega_1 = \omega_2 \). It is well known that a second-order nonlinear optical process like SHG and SFG is forbidden in a medium with inversion symmetry (2). At a surface or interface, however, the inversion symmetry is necessarily broken. This then leads to the surface specificity of SHG and SFG. More formally, SFG (or SHG) originates from a nonlinear polarization \( \hat{P}^{(2)}(\omega_3) \) induced in a medium by laser wave mixing (2):

\[
\hat{P}^{(2)}(\omega_3) = X^{(2)}(\omega_1) \hat{E}(\omega_1) \hat{E}(\omega_2)
\]

where \( \hat{E}(\omega) \) is the laser field at \( \omega \) and \( X^{(2)} \) is a tensor describing the nonlinear response of the medium to the fields. Inversion symmetry of the medium yields \( X^{(2)} = -X^{(2)} \), and therefore \( X^{(2)} \) must vanish.

Second-order nonlinear optical effects are naturally much weaker than the linear ones. Typically, \( X^{(2)} \approx 10^{-15} \) esu for a surface molecular monolayer. To generate 100 sum-frequency photons per exciting laser pulse from such a monolayer, a signal that can be readily detected, we need to have laser pulses with an energy of 10 \( \mu \)J/pulse focused to an area of 0.1 mm\(^2\) on the surface assuming a 10-ps pulsewidth, or 1 mJ/pulse focused to an area of 1 mm\(^2\) assuming a 10-ns pulsewidth (2, 3). Focusing of the laser beams is usually limited by laser damage of the surface. Since both picosecond and nanosecond pulsed lasers with the required energies per pulse are easily available nowadays in a laboratory, SHG or SFG as a surface probe can fairly routinely function with a monolayer or submonolayer sensitivity. The SHG or SFG output from a surface is coherent and highly directional in both transmitted and reflected directions as required by the boundary condition that the input and output wavevector components along the surface must be matched (4). In usual experiments, detection of the output in the reflected direction is preferred.

The SFG (or SHG) measurement on a surface allows the deduction of \( X^{(2)}(\omega_3 = \omega_1 + \omega_2) \), which is a tensor characteristic of the surface (3). For example, the symmetry of \( X^{(2)} \) provides information about the surface structural symmetry. The spatial variation of \( X^{(2)} \) over the surface directly reflects the spatial variation of the surface structure. The time variation of \( X^{(2)} \) indicates how the surface structure changes with time. Of particular importance is that \( X^{(2)} \) also carries spectroscopic information that enables us to learn microscopic details about the surface. As shown in Fig. 1, if \( \omega_1(\omega_2) \) or \( \omega_1 + \omega_2 \) or both are at resonances, then \( X^{(2)} \) will be resonantly enhanced. The resonant enhancement in \( X^{(2)} \) versus \( \omega_1 \) and \( \omega_2 \) naturally yields the spectral information (3). However, it should be pointed out that unlike ordinary absorption and emission spectroscopies, the SFG signal \( S \) is proportional to \( |X^{(2)}|^2 \) and has contributions from both real and imaginary parts of \( X^{(2)} \). Even away from resonances, \( S \) may be finite because of the presence of a nonresonant background in \( X^{(2)} \). Consequently, the spectral shape of a resonance may not look like that in an absorption or emission spectrum. Consider for example the case of \( \omega_1 \) near resonances. The SFG signal versus \( \omega_1 \) is given by (3):

\[
S(\omega_1) \propto \left| X^{(2)} \right|^2 \sum_{\omega_n} \frac{A_n}{\omega_1 - \omega_n + i \gamma_n}
\]

where \( X^{(2)} \) is the nonresonant background in \( X^{(2)} \), \( \gamma_n \), and \( A_n \) are the damping, \( n \)th resonance, and total amplitude of the \( n \)th resonance. Interferences of the various terms in Eq. 2 can severely distort the lineshapes. Only when \( X^{(2)} \) is negligibly small and resonances sufficiently far apart can we find resonant peaks similar to those in absorption spectra. However, even if an observed SFG spectrum shows unusual resonant lineshapes, it is possible to use Eq. 2 to fit the spectrum and deduce \( A_n, \omega_n, \gamma_n \) for the resonances.

SFG (SHG) as a surface analytical tool has a number of clear advantages (3). Being an optical technique, it can be used to probe all types of interfaces as long as they can be assessed by light. The unusually high surface specificity together with the monolayer sensitivity permits spectroscopic study of an interface even if the associated bulk absorbs in the same spectral region. Because the SFG output is highly directional, spatial filtering can be employed in addition to spectral filtering to supress the unwanted luminescence and scattering background noise. The technique can therefore be used for \textit{in situ} remote sensing study of a surface even in a very hostile environment. Finally, the spatial and spectral resolutions of the technique are only limited by spatial and spectral mode quality of the exciting lasers. The time resolution is limited by the laser pulse width which can be in the picosecond or femtosecond range.

Abbreviations: SHG, second harmonic generation; SFG, sum-frequency generation; OTS, octadecytrichlorosilane; DOAC, dioctadecyldimethyl ammonium chloride; (s, p), (s-output, s-visible, p-infrared); UVH, ultrahigh vacuum.
These advantages have rendered SFG (SHG) an extremely powerful and versatile tool for surface and interface studies. Applications that have already been successfully demonstrated appear in almost all areas of surface science, ranging from physics to chemistry, biology, and materials science. Many of them are highly unique, providing good opportunities to explore new areas of research in various disciplines. In the case of SFG, these include, for example, studies of buried interfaces (5–9), interfaces of pure liquids (10–13), electrochemical processes (14–17), catalytic reactions in real atmosphere (17), surface monolayer microscopy (18), ultrafast surface dynamics (19–23), and so on. Quite a few review articles have already been written on the subject (1, 3, 24–25), a number of which focus on specific areas of applications (26–28).

In this paper, I shall discuss only a selected few experiments we have performed in our laboratory with SFG surface spectroscopy. They can be taken as examples to illustrate the power and versatility of the technique. For the sake of completeness, I shall begin with a brief discussion of the experimental arrangement.

**EXPERIMENTAL**

Fig. 2 shows a schematic diagram of a typical experimental setup for SFG surface spectroscopy. Two exciting laser (or laser-like) beams at frequencies $\omega_1$ and $\omega_2$, respectively, are needed. While one can be of fixed frequency, the other must be tunable. The most convenient laser-like tunable source nowadays is the optical parametric systems (29). Together with sum- and difference-frequency generation stages, they can have a continuous tuning range from 0.2 $\mu$m to 10 $\mu$m or wider. In the longer wavelength region, however, free electron lasers are most appropriate since they can provide picosecond $\mu$J pulses readily tunable from 3 $\mu$m to 100 $\mu$m (30, 31, *). For nonlinear optical experiments, shorter laser pulses often yield larger signals. In the case of surface SFG, the output signal is proportional to $E_1E_2/\Delta T$ (3), where $E_1$ and $E_2$ are the pulse energies of the two exciting laser pulses impinging on the surface, $\Delta$ is the beam spot size on the surface, and $T$ is the laser pulsewidth. For the same pulse laser energies, the signal is inversely proportional to the pulsewidth. For this reason, although even continuous wave (cw) lasers could be used in some surface studies by SHG or SFG, ultrashort pulsed lasers are generally preferred. We also notice that the signal is inversely proportional to the beam spot size on the surface. For given laser pulse energies, the minimum beam spot size is, however, limited by laser damage of the surface. For example, the damage threshold for metal surfaces is of the order of mJ/cm$^2$, but for liquid surfaces, it can be of the order of J/cm$^2$.

Depicted in Fig. 2 is the usual geometry adopted for SFG measurements. The SFG output in the reflected direction is detected and recorded. Other geometries can of course be used, depending on the practical situation. As discussed earlier, the output signal is rather weak, often of the order of 100 photons per pulse or weaker. With the exciting laser energies at $\approx 100 \mu$J/pulse ($\approx 10^{13}$ photons/pulse), discrimination of the signal against laser scattering, and fluorescence background is not so trivial, especially if the output sum frequency is not far from the input laser frequencies. Fortunately, the SFG output is highly directional and is in a direction different from those of the reflected laser beams. Spatial filtering can therefore be used to suppress the unwanted background by many orders of magnitude. Together with spectral filtering by filters and/or monochromators, it makes the SFG output readily detectable even if the sum frequency and the laser frequency are only few hundred cm$^{-1}$ (hundredths of eV) apart. This latter case happens when SFG is used to probe surface excitations in the mid-IR range ($\omega_2$ scanned over mid-IR resonances). To measure various components of the $\chi^{(2)}$ tensor, the input laser beams must be selectively polarized and the output polarization of SFG analyzed.

The fixed laser frequency ($\omega_2$) is normally chosen to place the output sum frequency ($\omega_0$) in the visible so that the SFG output can be detected by a sensitive photomultiplier. The signal is then recorded by a gated integrator connected to a computer. For small signal levels, a photon counting mode of operation is preferred.

**SURFACE SPECTROSCOPIC STUDIES**

Nonlinear optical surface studies were first developed with SHG requiring only a single fixed-frequency laser (32). The first spectroscopic SHG measurement was performed on half monolayers of rhodamine dye adsorbed on quartz using a tunable dye laser (33). The electronic resonances of the adsorbed rhodamine molecules were probed. Both SHG and SFG spectroscopy have now been used to study electronic transitions involving surface or interface states of metals and semiconductors (5–9), in particular, buried semiconductor interfaces which are difficult to investigate by other nondestructive techniques.

In many areas of surface science and technology, surface vibrational spectroscopy is capable of providing most useful information. Known as finger prints of molecules, vibrational spectra permit identification of molecular species, their orientations and conformations, and possibly their interactions with neighbors. Surface SFG vibrational spectroscopy (Fig. 1a with $\omega_0$ scanned over vibrational resonances in the IR) has indeed been very successful in finding meaningful applications to various subfields of surface science. In particular, the unique capabilities of SFG have enabled us to explore some important areas that have been very much neglected because of lack of suitable experimental probes. A number of them that has been worked out recently in our laboratory will be discussed below.

**Surfactant Monolayers.** Surfactants play a key role in many important industrial processes—e.g., detergency, oil recovery, lubrication, painting, cosmetics, etc. (34, 35). Their formation of micelles and lamellar layers is closely related to biological membranes. Chain orientations and conformations of surfactant monolayers adsorbed at interfaces have been a subject of great interest to many researchers because they can directly affect the interfacial properties. IR and Raman spectroscopies

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(36–38) have long been used to probe vibrational spectra of surfactant monolayers. In most favorable cases, they can be free from spectral interference from the bulk, but are necessarily dominated by the CH2 modes (for surfactants with long hydrocarbon chains) from the large number of CH2 groups on the chains (36–38). SFG vibrational spectroscopy is very different. On a straight hydrocarbon chain, the distribution of CH2 groups is nearly centrosymmetric. Consequently, the CH2 modes nearly vanish, leaving the modes of the terminal CH3 group appearing dominant in the spectrum. This is shown in Fig. 3 lc and 2c for a compact monolayer of pentadecanoic acid on water (33). The peaks at 2875, 2940, and 2960 cm−1 correspond to the CH3 symmetric stretch, antisymmetric stretch, and Fermi resonance between symmetric stretch and bending modes, respectively. If trans-gauche defects on the chain set in, then the CH2 modes will become prominent in the spectrum. Examples are shown in Fig. 3 ia, 2a, 1b, and 2b for the pentadecanoic acid monolayer densities significantly reduced from the fully packed one. The peaks at 2850 and 2925 cm−1 can now be assigned to CH2 symmetric and antisymmetric stretches, respectively. This shows that the SFG vibrational spectra of the hydrocarbon chains can give a clear indication of whether the chains possess defects or not. An excessive number of defects, rendering the chains to contract into a highly compact conformation, will cause all the spectral features to diminish as a result of the establishment of a near inversion symmetry (39).

Unlike IR and Raman spectroscopies, the very high surface specificity of SFG makes the surface SFG spectra nearly free of bulk contribution even in the presence of strong bulk absorption in the same spectral region. Fig. 4 presents a clear example (40). For an octadecyltrichlorosilane (OTS) surfactant monolayer adsorbed at two different liquid/quartz interfaces (buried interfaces), CC14/OTS/quartz and hexadecane/OTS/quartz, the spectrum is completely dominated by the OTS monolayer. Only the CH3 symmetric stretch, antisymmetric stretch, and Fermi resonance modes at 2875, 2940, and 2960 cm−1, respectively, show up in the spectrum, indicating that the OTS chains are straight with little defects. In the hexadecane/OTS/quartz case, even though hexadecane liquid has very strong bulk absorption in the CH stretch region because of the large number of CH2 groups on the molecules, hardly any spectral features from hexadecane can be perceived in the spectrum of Fig. 4. As a further proof, the SFG spectrum was also taken for the hexadecane/quartz interface without the OTS monolayer. As shown in Fig. 4, no prominent spectral features can be easily identified, indicating that the spectrum due to bulk hexadecane must be very weak.

The chain conformation of a surfactant monolayer at an interface depends on the chain length, the chain density, and the interfacial environment (P. Miranda, V. Pflumio, H. Saijo, and Y.R.S., unpublished). For a fully packed chain density, the chain–chain interaction effectively keeps the chains in the all-trans configuration, which is not likely to be affected by the opposing medium. This is the case of the OTS monolayer on quartz discussed above. The spectrum of OTS shown in Fig. 4 remains essentially unchanged whether the chains are exposed to CC14, or hexadecane, or water, or air (40). The same is not true for surfactant monolayers with lesser chain densities. The reduced chain–chain interaction and the spacing between chains now allow trans-gauche defects to develop. For a given chain density, the chain conformation may depend on the fluid medium the chains are facing. From what we have observed in the cases of dioctadecyldimethyl ammonium chloride (DOAC), n,n-dimethyl-n-octadecyl-3-amino propyltrimethoxysilylchloride, and other low-chain-density (>40 Å2/molecule) surfactant monolayers adsorbed at liquid/solid interfaces, we realize that the conformational changes can be drastic (Miranda et al., unpublished).

We consider here DOAC monolayers as an example. The chain density of a full DOAC monolayer adsorbed on quartz is 3 × 1014 chains/cm2 (35 Å2/chain), about two times less than that of a full OTS monolayer. Fig. 5 shows SFG vibrational spectra in the CH stretch region of the adsorbed DOAC monolayer immersed in various liquids. In nonpolar liquid
CCl₄, the spectrum is not very different from that of a DOAC monolayer exposed in air, and is characterized by the presence of CH₃ (at 2840 and 2920 cm⁻¹) and CH₂ (at 2875 and 2940 cm⁻¹) peaks of nearly equal strengths. This indicates the existence of appreciable amount of defects on the chains. In CCl₄–CDCl₃ liquid mixtures, as the fraction of the polar component increases, the spectrum decreases in its overall intensity. Finally, in hydrogen-bonding (or associative) liquids such as water and methanol, the spectrum completely disappears. These results suggest that the number of defects on each chain must have increased significantly as the polarity or hydrogen-bonding character of the liquid increases. Presumably in a less favorable solvent, the chains like to fold into a more compact conformation to reduce their surface areas exposed to the solvent. Unfortunately, theoretical calculation that can give an observed SFG spectrum a quantitative evaluation of the corresponding chain conformation is not yet available.

Immersion of the adsorbed DOAC monolayer in alkane liquids could also have the chain conformation changed drastically (Miranda et al., unpublished). In a study using alkane of various chain lengths, we have found that the amount of defects on the DOAC chains is greatly reduced when the alkane chain length is close to that of DOAC. Fig. 6 provides an example. The spectrum of the DOAC monolayer in hexadecane shows that all the CH₂ peaks are now clearly suppressed, indicating conversion to a nearly all-trans conformation for the DOAC chains. The chain–chain interaction between DOAC and hexadecane must be responsible for the change. The same interaction may not be sufficient to eliminate the chain defects if the surfactant chain length is too short or the chain density too low (Miranda et al., unpublished).

Liquid Interfaces. For science and technology, liquid interfaces are at least as important as solid surfaces. Their properties directly influence many aspects of our life. Yet because few techniques are applicable to liquid interfaces, their experimental studies have been rather limited. In particular, on pure liquid interfaces, few spectroscopic investigations have ever been reported. Conventional spectroscopic techniques do not have the needed surface specificity and therefore the observed spectra are generally overwhelmed by the bulk contribution. In this respect, SFG is currently the only effective spectroscopic tool applicable to liquid interfaces (apart from studies of adsorbates at interfaces). We consider here a few examples of how SFG vibrational spectroscopy can be used to deduce useful information about liquid interfacial structures.

Water is the most important liquid on earth (41). Water interfaces play key roles in many important problems of science and technology, namely, wetting and drying, electrochemistry, environmental chemistry, corrosion, membrane formation, protein hydration, and so on. Despite numerous theoretical works on the subject, experimental investigations have been largely limited to the use of surface tension, surface potential, and ellipsometry measurements. Comparison between theory and experiment has failed to provide definitive information about the water interfacial structures. Now surface vibrational spectroscopy permits a change of the situation.

Depicted in Fig. 7 are the SFG spectra of the air/water interface in the OH stretch region (11). They are among the first vibrational spectra ever obtained for a neat liquid interface. The one with the (s, p, s) polarization combination is weak and shows hardly any discernible features. The (s, s, s) spectrum, on the other hand, exhibits three prominent peaks at 3680, 3400, and 3200 cm⁻¹. They can be attributed to OH stretches associated with dangling OH bonds, OH with its H connected to a neighboring molecule in a local disordered structure, and OH connected to neighbors in an ordered ice-like structure, respectively. The 3680-cm⁻¹ peak is particularly significant. Its presence indicates that the spectrum must come from the surface monolayer of water since no dangling OH bonds should exist in the sublayers. Furthermore, to account for the dangling OH bonds, at least part of the surface water molecules must be oriented with one H pointing out of the liquid. Quantitative calibration of the spectrum allowed us to find that about 25% of the water molecules in the surface monolayer must have contributed one dangling bond per molecule. This is the same as what one would find on a bulk-terminated crystalline ice surface. The result therefore suggests that the surface water structure at the air/water interface is ice-like (43). However, unlike ice, the hydrogen-bonding network of surface water is highly disordered as evidenced by the presence of the strong 3400-cm⁻¹ peak. Physically, the ice-like structure is the consequence of a tendency for the surface layer to have the maximum number of hydrogen bonds. In a recent molecular dynamics calculation, Benjamin (44) was able to reproduce the spectrum of Fig. 7 for the air/water interface fairly well.

Also shown in Fig. 7 is a spectrum of an air/water interface with a fully packed long-chain alcohol monolayer adsorbed at the interface (11). The 3680-cm⁻¹ peak is now completely suppressed as expected since the dangling OH bonds must be eliminated by the adsorption of alcohols. However, the 3400-cm⁻¹ peak also seems to have disappeared, making the spectrum resemble that of ice (shown as the dashed curve in Fig. 7). This suggests that the alcohol monolayer, is capable of
Contact with water, the surface can remain neutral or be negatively charged by deprotonation depending on the pH value of water. The vibrational spectrum of water at the interface varies accordingly, as shown in Fig. 9 (12). Both high and low pH values yield a spectrum resembling that of ice, indicating that the hydrogen-bonding network of the interfacial water layer is well ordered. Intermediate pH values lead to a spectrum representing a more disordered bonding network. This can be understood as follows. Water molecules in the interfacial layer are bonded into a more or less ice-like structure, but they also experience two oppositely orienting forces created by the surface: a hydrogen-bonding force that would orient the water molecules to have their oxygen bonded to hydrogen on the surface, and a surface field from surface charges that would orient the water molecules with their permanent dipoles facing the surface (or their oxygen pointing away from the surface). The former dominates at low pH values, while the latter dominates at high pH values. In both cases, the surface-originated orienting force helps to establish a more ordered interfacial water structure. For intermediate pH values, the two forces are of comparable magnitude but opposite in direction. Their competition in aligning the water molecules would cause disordering in the water interface structure. We note that the above picture predicts opposite average orientations of surface water molecules in the low and high pH cases. This was actually observed as a 180° phase shift in the SFG output between the two cases (12). The results here show that the surface water structure next to an electrode can be highly ordered. This finding should be important in our search for a better understanding of electrochemistry. SFG spectroscopy is also an effective probe for in-situ studies of electrochemical reactions at surfaces (14–16). It has already been used in several cases to identify molecular species appearing and disappearing at the electrode surface in an electrochemical process (14–16).

SFG spectra for other neat liquid interfaces have also been measured (48–51). They all provide useful information about the liquid interface structures. For example, n-alkane \( (\text{C}_n\text{H}_{2n+2}) \) liquids with \( n \geq 16 \) exhibit a surface monolayer
freezing transition at a temperature several degrees above the bulk freezing temperature (52-54). The surface vibrational spectra of \( n \)-alkane show clearly that the monolayer freezing transition is characterized by a conformational change of surface molecules from a configuration of vertically oriented chains with significant defects to a well-ordered nearly all-trans configuration (51). For some liquid mixtures, namely, water-ethanol and water-CH\(_3\)CN, SFG spectra also suggest the occurrence of a phase transition in the surface structure when the bulk composition is varied (55, 56). In general, one would hope that through surface vibrational spectroscopy, enough information could be obtained to permit deduction of a general understanding of liquid surfaces and interfaces. Currently the difficulty often lies in our inability to properly identify the observed spectral features. Much theoretical and experimental work is needed before we can unambiguously relate a surface spectrum to a surface structure.

**Surface Reactions and Catalysis.** *In situ* probing of adsorbates and surface reactions is another area we have found unique applications for SFG spectroscopy. There already exist many techniques for such studies in ultrahigh vacuum (UHV) (57), but few of them are applicable to samples in a real atmosphere. IR spectroscopy, for example, can be employed in some cases, but its surface sensitivity and specificity are often not sufficient. Furthermore, none of the techniques has a time resolution in the picosecond or subpicosecond range.

SFG spectroscopic studies of adsorbates on metals and semiconductors have been carried out by a number of groups (5-9, 14-16, 19-28). Here we consider adsorptions of H and CH\(_3\) on diamond C(111) studied in our laboratory (58-61). For the understanding of diamond film growth by chemical vapor deposition (62-64), a clear understanding of how H and CH\(_3\) adsorb and how CH\(_3\) converts to CH on the diamond surfaces are necessary. *In situ* surface vibrational spectra could provide the needed information. Indeed high-resolution electron energy loss spectroscopy has been employed for this purpose (65-67), but the reported spectra all show insufficient spectral resolution that could distinguish CH from CH\(_2\) and CH\(_3\). IR spectroscopy with a multiple reflection geometry could be used to yield clear, highly resolved spectra (68). Unfortunately, this requires a diamond sample of a size that is prohibitively expensive. Thus SFG vibrational spectroscopy becomes a unique tool for such studies.

Fig. 10a shows the SFG spectra of CH stretching and bending modes of H on a well-ordered C(111)-(1×1) surface (58, 59). Similar to H/Si(111), a single sharp peak appears in both the CH stretch and bend regions. This result together with the polarization dependence of the spectrum indicates that H sits nearly vertically on top of C, in agreement with the theoretical prediction (69). As in the case of H/Si(111), other properties of the CH stretch mode of H/C(111), such as anharmonicity and vibrational lifetime, could be measured and compared with theories (58, 59). The observation of the sharp CH stretch and bend peaks is actually quite important since it asserts that all H must have been adsorbed at the stable, well-ordered C(111)-(1×1) top sites with an sp\(^2\) bonding.

It can therefore be used as signature of a well-ordered, H-covered, C(111)-(1×1) surface. Such a surface, we found, can be reliably created by dosing H on C(111) at 850°C, and is believed to be the functional surface in the chemical vapor deposition (CVD) diamond growth along [111]. If the surface is contaminated or disordered with H appearing at metastable sites, the SFG spectrum would exhibit weaker and broader peaks with subsidiary features around them. One metastable site that H would first adsorb at shows up as a CH stretch peak blue-shifted by 30 cm\(^{-1}\) from the stable one (58, 59, 70) (see Fig. 10b). It can be converted to the stable CH stretch by increasing H coverage or annealing of the substrate.

On SFG spectroscopic studies of adsorption of CH\(_3\) and conversion of CH\(_3\) to CH on C(111), an example is depicted in Fig. 11 (61). In the experiment, the methyl radicals were produced by thermal decomposition of di-per-butyl peroxide [(CH\(_3\))\(_2\)OOC(CH\(_3\))\(_2\)] through a hot filament at \( \approx 800^\circ\mathrm{C} \). Their adsorption on C(111) at room temperature is evidenced by the presence of three resonant modes in the spectrum of Fig. 11, spectrum b: the CH\(_3\) symmetric stretch, antisymmetric stretch, and stretch-bend Fermi resonance at 2895, 2975, and 2935 cm\(^{-1}\), respectively. (The unusual lineshapes result from interferences between various terms in Eq. 2 as discussed in the Introduction.) To see that the adsorbed CH\(_3\) can be converted to CH, we show in Fig. 11, spectra b-g, how as the substrate temperature increases, the CH\(_3\) peaks diminish while the CH stretch peaks grow. Note that here two CH stretch peaks show up in the spectra. The high-frequency one corresponds to H adsorbed at the metastable site discussed above. It disappears by conversion into the low-frequency mode corresponding to H adsorbed at the normal well-ordered site when the substrate is annealed at high temperatures. The spectra of Fig. 11 show that conversion of CH\(_3\) to CH on C(111) begins at a temperature less than 350°C, which is many times lower than the temperature required for decomposition of CH\(_3\) in the gas phase. Obviously the observed process is surface-mediated. This suggests that CVD diamond growth via adsorption and conversion of CH\(_3\) is possible.

We should remark, however, that all the above experiments were carried out under high vacuum, and therefore the processes observed may not be the same as those occurred in a real CVD atmosphere. The same difficulty may exist in studies of surface catalytic reactions. In the past decades, a great deal of information on various surface catalytic reactions have been deduced from investigation of catalytic systems in UHV (57). One must question whether they can actually be used to understand surface catalysis in a real atmosphere. The lack of suitable techniques has so far prevented *in situ* studies in the
latter case, but now with SFG spectroscopy, they have become possible. Discussed below as an example is an experiment on hydrogenation of ethylene (C₂H₄) to ethane (C₂H₆) on Pt(111) carried out jointly with G. Somorjai's group (17).

Ethylene hydrogenation on Pt is an important catalytic reaction. The widely accepted model used to describe the reaction was first proposed by Horiuti and Polanyi in 1934 (71). According to the model (Fig. 12a), ethylene first chemisorbs on Pt by forming two σ bonds with Pt while H₂ adsorbs and dissociates into two H atoms on Pt. The di-σ-bonded ethylene then reacts with H on Pt and is stepwise hydrogenated through an ethyl (C₂H₅) intermediate to ethane. To check whether the model is correct, we need to monitor in situ the surface species during the reaction in the real atmosphere. This can be done with SFG vibrational spectroscopy. Our experiment was performed with a Pt(111) sample in a batch reactor. The gas with a fixed composition of ethylene, hydrogen, and helium was circulated constantly in a closed loop that contained a gas chromatograph for measuring the ethane production. SFG spectroscopy monitored simultaneously the appearance of various species on the Pt(111) surface.

Fig. 13 describes the SFG surface vibrational spectra of two related cases with essentially the same ethane production rate. In the first case (Fig. 13a), the atmosphere was composed of 35 torr ethylene, 100 torr H₂, and 625 torr He; the reaction started with a clean Pt(111) surface at 295 K. In the second case (Fig. 13b), the conditions were the same except that the reaction started with Pt(111) fully covered by ethylidyne. In both cases, the ethane production rate was ∼11 ethane molecules per surface Pt atom per second. The three peaks at 2875, 2910, and 3000 cm⁻¹ in the spectra of Fig. 13 have been identified as signatures for ethylidyne (C₂H₃), di-σ-bonded ethylene, and π-bonded ethylene (ethylene bonded weakly to Pt through its π orbital), respectively. Ethylidyne resulted from dehydrogenation of di-σ-bonded ethylene, but as already shown by others (72), it is only a spectator in the ethylene hydrogenation process. In our batch reactor, the various species appearing on the Pt(111) surface were all in dynamic equilibrium with species both on the surface and in the atmosphere. The spectra of Fig. 13 show that in both cases the Pt surface was covered mostly by ethylidyne at the 3-fold hollow sites (0.15 monolayer in one case and 0.25 monolayer in the other, with 0.25 monolayer being the saturation coverage) and partly by di-σ- and π-bonded ethylene. The amount of π-bonded ethylene remained unchanged in the two cases, but that of di-σ-bonded ethylene changed by a factor of 4. Since the ethane production rates in the two cases were the same, the result clearly indicates that the di-σ-bonded ethylene cannot be the surface species responsible for the catalytic reaction of

![Fig. 11. SFG spectra exhibiting the effects of surface annealing after dosing of di-tert-butylperoxide (DTBP) (through an ∼800°C hot filament) on C(111) at room temperature. Spectra: a, nearly-bare surface; b, as-dosed surface; c–g, dosed surface annealed at 350°C, 500°C, 620°C, 740°C, and 800°C, respectively. Spectra c–g have been incrementally shifted upwards by 5 units for clarity. [Reproduced with permission of ref. 61 (Copyright American Physical Society).]

![Fig. 12. (a) Horiuti–Polanyi mechanism for ethylene hydrogenation on platinum. (b) New mechanism for ethylene hydrogenation on platinum.

![Fig. 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 that was precorroded in UHV with 0.25 monolayer of ethylidyne. [Reproduced with permission from ref. 17 (Copyright 1996, American Chemical Society).]
ethylenic hydrogenation into ethane. The π-bonded ethylene is then more likely the responsible one. The corresponding relevant steps for the hydrogenation process are described in Fig. 12b. 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 why ethylene hydrogenation is not sensitive to the Pt surface structure (72–74).

The above finding suggests that the more weakly bonded surface species may actually play a dominant role in a surface catalytic reaction. If this is true in general then UHV studies of catalysis would yield very different results from those obtained in real atmosphere, because the weakly bonded species may not even appear on the surface in UHV. Catalytic reactions can also occur at liquid/solid interfaces. Being capable of probing buried interfaces, SFG spectroscopy should also be ideally suited for investigation of such reactions.

**CONCLUSION**

I have discussed here a number of selected examples to illustrate the unique applications of SFG as a surface spectroscopic tool. There are certainly many others worth discussing. As a probe that can be applied to all interfaces accessible by light, SFG is capable of finding applications in many areas—for example, studies of interfacial biological systems, reactions at liquid/solid interfaces, corrosion, etching, and chemical vapor deposition processes, surface dynamics at liquid/solid interfaces, and others. All of these are problematic of great significance but their investigations have been very limited so far because of lack of suitable techniques. SFG surface spectroscopy is likely to change the scene. Currently, the IR tuning range of a table-top SFG setup is limited to ~10 μm on the long-wavelength side, and could perhaps be extended to ~20 μm. With a free electron laser, however, the spectral range can be easily extended to cover the entire IR region. Surface vibrational spectroscopy will then become even more powerful and versatile as a surface analytical tool.

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