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978-1-107-09884-8 - Fundamentals of Sum-Frequency Spectroscopy
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Historical perspective

Optical sum-frequency generation (SFG) is a nonlinear optical process in which mixing of two input beams of different frequencies in a medium generates a coherent sum-frequency output from the medium. Measurement of SFG from a medium allows deduction of nonlinear response coefficients that characterize the medium. Sum-frequency spectroscopy is among the most powerful and versatile nonlinear optical techniques that have been developed for material studies, and has been adopted by researchers in many disciplines. It has had a wide range of applications on characterization of both surface and bulk of materials, although most of them focus on surfaces and interfaces. Because surface and bulk generally have different structural symmetries, their SFG response coefficients are different. If the bulk response is strongly suppressed by symmetry, then SFG may be dominated by the surface response. In such cases, SFG becomes highly surface-specific, and SF spectroscopy can serve as an effective surface probe. It has created many unique opportunities for surface and interface studies. We note that second-harmonic generation (SHG) is a special case of SFG with the two inputs having the same frequency. Presented in this chapter is a brief description of how the technique has been developed into maturity over the years.

1.1 Early development of second-harmonic generation as a surface probe

Although the use of SHG as a surface probe did not begin until 1981, and SFG not until 1987, the two processes have been known since 1961–2. Immediately after the first ruby laser was built, Franken and co-workers reported the observation of SHG and SFG in quartz.[1,2] This marked the birth of nonlinear optics. The ensuing classical paper by Armstrong et al., published in 1962, soon set the theoretical foundation for nonlinear optics.[3] While formulating nonlinear wave mixing processes, Bloembergen and Pershan recognized the importance of the boundary effects. They extended the laws of reflection and refraction to nonlinear wave

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propagation in a subsequent paper,[4]and experiments of SHG were then performed in Bloembergen's lab to verify the predictions.[5] In dealing with nonlinear wave propagation, the surface of a medium was simply treated as a truncated plane of the bulk. Later, attention was soon shifted toward the existence of surface nonlinearity different from that of the bulk. It was realized that the rapid variation of the field across a boundary surface and the presence of surface states could contribute to the surface nonlinearity.[6] Bloembergen and Chang pointed out that for media with inversion symmetry, such as liquids, metals, and some semiconductors, surface nonlinearity might not be neglected.[7] He and his co-workers developed a three-layer model, treating the interface as a thin layer between two media, to describe SHG from an interfacial system.[6] This is the model we still follow nowadays.

Early experiments of Brown and co-workers on reflected SHG from Ag[8] and Bloembergen and co-workers on reflected SHG from Si and Ge[9] led to confusing results. Measurements were carried out in air, and surface contamination was a problem. For example, the surface of Si was certainly covered by a layer of oxide that could significantly modify the surface nonlinearity. Brown and Matsuoka later did an experiment with a freshly evaporated Ag film in vacuum and found that the reflected SHG was four times stronger than that with the sample in air,[10] but Stern and co-workers observed just the opposite.[11,12]

Interpretations of the early experimental results were generally not satisfactory either because our knowledge on surface nonlinearity versus surface structure was quite limited at the time. Structural difference between surface and bulk was generally ignored. Surface nonlinearity of a metal was assumed to come from free electrons in the metal; contribution from interband transitions was neglected.[12] Apparently, there was not much interest in exploring the use of SHG for surface studies. Focus was on verification of theoretical predictions on SHG from an interface and on application of SHG to probe bulk structural properties, such as monitoring paraelectric–ferroelectric transitions.[13] In 1973, Chen et al. reported observation of Na atomic adsorption on a clean Ge sample in ultrahigh vacuum by reflected SHG.[14] It suggested that SHG could have sub-monolayer sensitivity to detect atomic adsorption on a surface. Unfortunately, they did not pursue the subject further, and their paper in Optics Communications received little attention.

The next phase of active research on surface SHG began in 1981 after surface enhanced Raman scattering (SERS) from molecules on roughened Ag was discovered.[15] It was believed that the major part of the enhancement came from local field enhancement through local surface plasmon excitation and the minor part from resonance enhancement at the charge-transfer band formed by molecule–metal interaction, but the two mechanisms were not separable in SERS.[16] It was then realized that SHG and Raman scattering should experience similar local field enhancement. While SERS is proportional to the product $|E_l E_s|^2$ of the incoming

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laser field E_l and the scattered field E_s, SHG is proportional to $|E_l|^4$.[17] The local field enhancement of the two cases must be nearly the same if both E_l and E_s are close to the local surface plasmon resonance. Unlike SERS, reflected SHG from a bare Ag surface can be readily detected, and therefore used to separately probe the local field enhancement. Indeed, in SHG from a bare roughened Ag surface, Chenson Chen et al. found a local field enhancement of ~10^4, which agreed with the estimate of local field enhancement in SERS.[18] Like SERS, SHG was able to monitor molecular adsorption and desorption on a Ag electrode during an electrochemical cycle.[18,19] Even centrosymmetric molecules that supposedly have vanishing SH nonlinear response under the electric-dipole approximation could be detected.[20] The signal was surprisingly strong. In one experiment, a 20 mW cw laser was shown to be sufficient for the SHG measurement.[21]Based on the observed strength, a simple calculation led to the conclusion that even without surface enhancement, a surface monolayer could be easily detected if a pulsed laser were used. This immediately suggested that SHG could be adopted as a general surface probe. The conclusion could have been obtained earlier if the early SHG experiments were better characterized.

In subsequent years, research efforts were spent on developing SHG as a surface analytical tool. Tony Heinz and Harry Tom's PhD thesis projects,[22,23]as well as a number of others,[24–27] on the topic paved the way both theoretically and experimentally. In a series of experiments, it was shown that SHG could allow measurement of the electronic spectra of adsorbed molecular monolayers on substrates,[28] arrangement and orientation of adsorbed molecules,[29] and adsorption isotherm of molecules adsorbed from solution.[29] They demonstrated that SHG was effective to probe adsorbed molecules at any interface accessible by light. The possibility of using SHG to probe surfaces of bulk materials was also considered.[30] It was found that in media with inversion symmetry like Si, the bulk contribution to SHG, although electric-dipole forbidden, could be larger than or comparable to the surface contribution. However, surface and bulk contributions could be separated if they have different symmetries that reflect their different structural symmetries.[30] A later experiment by Heinz et al. at IBM showed that contribution from the Si (111)-(7×7) reconstructed surface actually dominated over that of the bulk in the reflected SHG, and transition from the (7×7) surface structure to (1×1) could be monitored by SHG.[31] Searching for better understanding of the experimental results during this period also led to refinement of the underlying theory for surface SHG.[32–34]

That SHG has sub-monolayer sensitivity and there are more nonlinear response coefficients than the linear ones characterizing a medium, basically guarantees it to be a useful surface probe. However, in order for the surface science community to accept a new technique, it would take some extra effort. In the 1980s, basic

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surface science research heavily focused on well-defined crystalline surfaces in ultrahigh vacuum. To convince the community that SHG would be useful as a surface probe, it was necessary to show that the technique could be applied to well-characterized surfaces in ultrahigh vacuum. To help increase credibility of the work, Gabor Somorjai, an eminent surface scientist, was persuaded to collaborate in the project. Tom, Heinz, and others spent the Christmas and New Year holidays of 1983 in Somorjai's lab carrying out a successful experiment to demonstrate that SHG could indeed be used to study adsorption kinetics of CO, O_2, and Na on Rh (111).[35] The experiment was later extended to adsorption of other molecules on Rh (111) and adsorption and desorption of oxygen on Si (111).[36] Thus, SHG as a surface tool was firmly established, but a critical comment surfaced: "Adsorption and desorption can be easily measured by other techniques. Can SHG yield any new information?"

Being a laser spectroscopic technique, SHG certainly has many advantages over conventional surface tools. It has high spatial, spectral, and temporal resolution as a probe. Its highly directional output allows remote sensing of a surface. Most importantly, it can be applied to any interface accessible by light. Accordingly, SHG provided many new opportunities in different areas of surface science where conventional techniques have difficulty in assessing. For example, it was shown that polar orientation of adsorbed molecules could be determined by polarization-dependent SHG;[37] dynamics of surface structural change and phase transformation could be monitored by time-resolved SHG;[38] spatial variation of surface structure can be imaged by SHG microscopy;[21] and molecular adsorbates at liquid interfaces,[39,40] as well as charging of such interfaces,[41,42] could be studied by SHG. On spectroscopic measurement, SHG with a tunable input could address electronic transitions of surface molecules.[28] However, electronic resonance bands are often too broad to distinguish molecular species. In order to identify or selectively probe surface molecules or structures, vibrational spectra known as finger prints of molecules are needed. Unfortunately, SHG is not sensitive in the IR range because of the limited sensitivity of available IR detectors. An obvious solution is to extend SHG to IR-visible SFG. Like SHG, SFG can be surface-specific, but in addition, its tunable IR input allows probing of vibrational resonances.

1.2 Early development of sum-frequency spectroscopy for surface studies

In the early 1980s, optical parametric systems as IR tunable coherent sources were not common in research labs. In the first demonstration of IR-visible sum-frequency vibrational spectroscopy (SFVS) carried out on a courmarine 514 dye monolayer on Si, Zhu et al. used a CO_2 TEA laser discretely tunable at ~10 μm in

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synchronization with a frequency-doubled Nd:YAG laser at 0.53 μm.[43] Several vibrational modes of coumarine were clearly observed. However, the CO_2 laser was not very reliable, making the experiment extremely difficult. Actually, the first attempt of SFVS was carried out earlier by Harry Tom with a continuously tunable optical parametric oscillator pumped by a Q-switched Nd:YAG laser and a frequency-doubled output also from the laser. The oscillator was built by Tom in Y. T. Lee's world-renowned molecular beam laboratory for molecular spectroscopic studies. To test the idea of SFVS, Tom tried the measurement on a monolayer of p-nitrobenzoic acid (PNBA) on fused quartz. However, he could observe a CH stretching spectrum even when the silica substrate was supposedly clean. It was not understood where the spectrum came from; so the result was not published but only reported in his PhD thesis.[23] Later, it was realized that the spectrum might have originated from hydrocarbon contaminants on the silica surface because there were quite a few mechanical pumps in Lee's lab pumping the molecular beam machines and the atmosphere must have been polluted by oil vapor.

Development of SFVS as a practical surface-specific spectroscopic probe only started after a dedicated picosecond optical parametric generator/amplifier system pumped by a mode-locked Nd:YAG laser was built.[26] The first measurement of SF vibrational spectra, reported by Hunt et al. in 1987 using the system,[44] was conducted on adsorbed hydrocarbon molecular monolayers on glass and water in the CH stretching region. In subsequent experiments, Guyot-Sionnest et al. demonstrated that SFVS could be used to probe orientation and conformation of adsorbed molecules, adsorption isotherms of molecules at liquid/solid interfaces, structural variation of adsorbed molecular monolayers exposed to different environments, and interactions between molecules at interfaces.[45] They showed, from the spectral changes, that the two-dimensional phase transitions of a Langmuir monolayer were correlated with conformational changes of molecules.[46] Alex Harris and co-workers at Bell Labs developed a SFVS system based on a picosecond tunable IR dye laser pumped by a mode-locked Nd:YAG laser. They succeeded in detecting SF vibrational spectra of CH stretches of adsorbed molecules on metals, and performed the first set of time-resolved SFVS measurements to study vibrational relaxation of adsorbed molecules.[47] Towards the end of the 1980s, the first ever vibrational spectra of a neat liquid interface obtained by SFVS were reported on the air/methanol interface by Superfine et al.[48] In the experiment, it was demonstrated that the bulk contribution to the reflected SFG was negligible and observed reflected SF spectra were indeed the true surface spectrum of the methanol interface. Phase of the SF output was also measured to show that the surface methanol molecules are polar-oriented with their methyl groups pointing toward the air.[49]

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1.3 Maturing of SHG and SFG for surface studies

While SFG was being developed, SHG as a surface tool bloomed because of the much simpler experimental setup. Possibilities of applying the technique to liquid, liquid crystal, and polymer interfaces were demonstrated. It was used to probe phase transitions of adsorbed monolayers on water,[39,50] charging at water interfaces,[41,42] adsorbed molecules at liquid/liquid interfaces,[51] surface and bulk structures of ordered liquid crystal films,[52,53] anisotropy of surface monolayer[54] and surface-induced alignment of liquid crystal films,[55,56] and monolayer polymerization.[57] Richmond, Furtak, and co-workers used SHG to study electrochemical processes at crystalline metal electrodes in electrochemical cells and deduce information about the structures of the metal electrode surface and the deposited overlayers.[58–60] Eisenthal and co-workers pioneered a number of SHG studies on water interfaces.[61] They also initiated application of SHG to colloidal particles in solution, monitoring the transport kinetics of molecules across the membrane of liposomes.[62] Although SHG experiments were generally carried out at interfaces of materials with inversion symmetry, it was demonstrated that it could also be employed to study surfaces of materials without inversion symmetry if surface and bulk had distinctly different symmetry.[63] Use of SHG to probe surface magnetism was proposed,[64] and later realized experimentally.[65]

Requirement of a coherent tunable IR source in the SFVS setup must have appreciably slowed down the development of SFVS. Home-built SFVS systems were not easy to obtain for many labs. But as soon as commercial SFG systems became available,[66] SFVS took off. Optical parametric systems these days can have a tuning range from 16 to 0.21 μm.[67] Being able to assess vibrational resonances, SFVS is much more powerful than SHG for selective probing of molecules at interfaces and structures of interfaces. Having two independent input beams greatly facilitates beam arrangement, allows measurement of more response coefficients that characterize a medium, and provides opportunity for double resonances to further enhance the selectivity of the process. As will be discussed in various chapters of this book, SFVS has found wide applications, many of which are highly unique. Molecular adsorption at interfaces can now be studied in greater detail, including surface reactions and kinetics. Much interest has been on surfactant monolayers with long alkyl chains presumably because of their importance to technology and biology (Chapter 6). Structure and symmetry of bare solid surfaces or buried solid interfaces, as well as their changes under perturbation, can be probed (Chapter 7). The possibility of recording vibrational spectra of liquid interfaces has created a great deal of excitement, especially after the first measured vibrational spectra of water interface were reported. Ions emerging at water interfaces and electric double layer formation near charged interfaces have been

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extensively investigated (Chapter 8). As in the case of liquids, SFVS also offers the only opportunity to probe the surface and interfacial structures of polymers at the molecular level through their vibrational spectra. Surface modification either by design or in response to environmental changes can be detected from the spectral changes. The technique also provides a means to monitor functionality of an interface in an organic or polymeric device (Chapter 9). Attempts to use SFVS to deduce information on adsorption of macro- or bio-molecules on substrates and properties and functions of lipid bilayers have also had some success (Chapter 10). On other applications, SF spectroscopy has been shown to be able to probe molecular chirality in both electronic and vibrational transitions. It has a sensitivity significantly better than the conventional circular dichroism technique, and therefore could provide opportunities for novel research on molecular chirality (Chapter 11). SHG has also been developed for label-free microscopy complementary to two-photon fluorescence microscopy and for probing interfaces of colloidal particles in solution. SHG/SFG has become an effective tool to study electrochemistry at the molecular level and ultrafast surface dynamics on the fs–ps time scale (Chapter 12).

There have also been significant advances in SF spectroscopic techniques (Chapter 4). First, a broadband scheme for SFVS was developed using a KHz femtosecond Ti:sapphire laser as the pump source.[68] It drastically reduces the data collection time and facilitates recording of spectra. Next, a scanning phase-sensitive (PS) SFVS scheme that enabled measurement of both intensity and phase spectra of the nonlinear response coefficients was demonstrated.[69] It allows direct and unambiguous characterization of resonances in observed spectra. Later, the PS technique was incorporated into the broadband scheme,[70] and time-resolved PS-SFVS was made possible.[71] On basic understanding of SFG (or SHG), theoretical effort has been focused on clarifying the confusion whether bulk contribution to reflected SFG from an interfacial system can be neglected or not (Chapter 3). For SFG to be used as a surface probe, one must be sure that the bulk contribution is negligible. In many cases, this has been proven to be true, but it is not necessarily so in general.

1.4 Prospects

We can anticipate that SF spectroscopy will become more popular in the coming years as laser technology further advances. The technique is clearly unique for probing liquid interfaces and polymer interfaces, which are two important areas of modern science and technology. It is also unique for studying surface and interfacial reactions, especially at buried interfaces. Other potentially important applications to biological interfaces, chiral materials, and solids will certainly be further explored.

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While SHG/SFG has become a mature technique for material studies, there is still much room for improvement. First of all, the IR spectral range needs to be further extended. Currently, it is limited to ≤16 μm, restricting most applications to materials composed of light elements. Although IR free electron lasers are capable of covering the entire far IR region, they are not easily accessible. Optical damage of materials is another problem. It limits the intensity of input pulses impinging on a material, and hence the SF output signal and the sensitivity of SFVS. Shorter input pulses with higher rep rates will help. For the broadband SFVS scheme, it will be preferable to have shorter femtosecond tunable IR pulses. They will provide a broader bandwidth to facilitate spectral recording in addition to better time resolution for ultrafast surface dynamic studies. Current setups of SFVS appear to be bulky and difficult to move around. High rep-rate fiber lasers as pump sources may improve the situation. Other technical areas that still need more development are phase sensitive SFVS for buried interfaces, doubly resonant (DR) SFVS, and phase sensitive DR-SFVS. Accessing a buried interface by light is difficult if the media on both sides of the interface are strongly absorbing. Methods need to be developed for SFVS to be able to study thin-film buried interfaces with little complication.

Possible bulk contribution to reflected SFG is generally still a concern because part of it is intrinsically not separable from surface contribution unless the two have distinguishable symmetries and spectra. Experience is being accumulated to learn whether SFG is surface-specific for certain types of interfacial systems. For example, SF spectroscopy of surfaces of isotropic media with molecules well polar-oriented is highly surface-specific. For nonpolar media with molecules well-oriented along the surface normal, SFVS with S, S, and P polarizations for IR input, visible input, and SF output, respectively, also appears highly surface-specific. On the other hand, there are cases where the electric-quadrupole bulk contribution is clearly not negligible. This often happens when the observed spectrum is weak. To be sure whether SFG is surface-specific or not, additional measurement has to be performed. If theoretical estimates on the strength of bulk electric-quadrupole contribution are available, they can provide guidelines for proper design of a surface SFG experiment. Generally, theoretical help will be very much needed in our understanding of SF spectra, especially on interpretation of spectral features.

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