

Surface Nonlinear Optics: A Historical Perspective

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Invited Paper

Abstract—A historical review is given on the development of surface second-harmonic and sum-frequency generation and their applications as analytical tools to surface science.

Index Terms—Nonlinear optics, surfaces and interfaces, second harmonic generation, sum-frequency generation, sum-frequency vibrational spectroscopy, surface structures.

I. INTRODUCTION

THE BEST STORY one can tell is often the story about one's personal experience and involvement. In my case, it is the story of surface nonlinear optics. As commonly known, nonlinear optics is the first and the largest field created by the invention of laser. It has many branches and surface nonlinear optics is just one of them. Research in this subfield has been both exciting and rewarding as it deals with not only interesting basic physics but also useful applications to an immense area of surface science and technology. In recent years, this subfield has grown rapidly. Nonlinear optical techniques developed as surface probes have gained increasing popularity in the surface science community. Now is probably a good time to look back and provide a historical review on the field. I had the good fortune to be involved in surface nonlinear optics from the very beginning and more recently have invested 20 plus years in it. Therefore, I find it a pleasure to contribute to this special issue of the IEEE JOURNAL OF SELECTED TOPICS IN QUANTUM ELECTRONICS (JSTQE) a personal account of the development of the field. As is often the case, discovery and advances of the field did not follow a prescribed course.

Nonlinear optics was born as soon as the ruby laser was invented. Franken and coworkers in their seminal contribution first demonstrated optical second-harmonic generation (SHG) and sum-frequency generation (SFG) in quartz crystals [1]. Soon after followed the classical paper of Armstrong *et al.* [2] that provided a theoretical foundation for wave mixing in nonlinear media. Inclusion of proper boundary conditions in the theory is clearly important, as noticed and worked out by Bloembergen and Pershan in a subsequent paper [3]. Then, with their formalism, nonlinear wave transmission and reflection at an interface could be properly described. Experiments of SHG

in reflection from semiconductor surfaces were immediately performed to prove the theoretical predictions [4]. Around the same time, measurements of SHG from metal surfaces were also reported [5]. However, during that period, our knowledge of surface science was very limited. An interface was always taken simply as a plane where the truncated bulk structures of two neighboring media meet. Even so, it was already realized that because of the broken symmetry at an interface, surface nonlinearity and bulk nonlinearity of a medium should be different. First, the rapid variation of optical fields across an interface may induce a strong electric quadrupole (more generally, multipole) contribution to the surface nonlinearity. Second, the structural discontinuity at an interface can introduce surface states that may yield a significant electric-dipole contribution to the surface nonlinearity. For electric-dipole-allowed wave mixing processes in bulk media, surface nonlinearity can often be neglected, but this is not true if the processes are electric-dipole forbidden. As pointed out in the early papers by Bloembergen [6], the latter is the case for metals, liquids, as well as semiconductors that possess inversion symmetry.

Early experiments by Bloembergen and coworkers on reflected SHG from Si and Ge [7] and by Brown and coworkers on reflected SHG from silver [5] contrived to probe the origin of surface nonlinearity turned out to be misleading and inconclusive. In those experiments, the samples were not in ultrahigh vacuum, so that surface contamination was a problem but it was inadvertently ignored. The measurement of SHG from Si was certainly affected by the oxide layer grown on the surface. In the case of SHG from silver, Brown and Matsuoka [8] actually observed that a freshly evaporated silver film in vacuum generated a signal four times larger than that from a film long exposed to air. Stern and coworkers, however, observed almost just the opposite [9]. Clearly, surface contamination was the culprit of the confusing results. In retrospect, these results were the first indication that SHG may have the monolayer sensitivity required for an effective surface probe.

Interpretations of the early experimental results were not satisfactory either, because not all important contributions to surface nonlinearity were taken into account. For example, the structural difference between surface and bulk of a medium was ignored. The surface nonlinearity of a metal was often assumed to come entirely from free electrons in the metal [10]. Furthermore, the valence-band electron contribution through interband transitions was neglected. The theory of SHG from a medium with inversion symmetry was actually well established by the paper of Bloembergen *et al.* [11]. In that work, the surface

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or interface was treated as a thin layer with optical constants different from the bulk. This is still the basic model we follow today. On surface nonlinearity, unfortunately, little effort was spent to push for a better understanding, although Rudnick and Stern [12] later did consider nonlinearity of a metal in some detail. It seemed that at the time, the general interest was to prove theoretical predictions on SHG rather than to use SHG to probe the nonlinear optical property of a medium. Thus when Chen *et al.* [13] reported in Optics Communications in 1973 their observations of a high sensitivity of SHG in detecting Na atomic adsorption on clean Ge in ultrahigh vacuum, the paper hardly received any attention. They also did not pursue the subject further. Apparently, the time was not yet ripe for the development of SHG as a surface probe. While some researchers might have recognized the high surface sensitivity of SHG, they probably were not sure about its relevance, and the lack of understanding of surface nonlinearity prevented further development. If a careful analysis of surface nonlinearity had existed at the time, the situation certainly would have been very different. SHG in reflection from insulating solids and liquids had also been studied, but again, only surface nonlinearity resulting from field discontinuity across an interface was considered in the analysis [14].

Around 1970, surface plasma waves had become a subject of interest as they could be used to probe metal surfaces [15]. The existence of surface electromagnetic (em) waves was predicted by Sommerfield [16] in 1909. It requires a medium with a sufficiently negative optical dielectric constant, as is the case with metals at frequencies sufficiently below the plasma frequency. The success in nonlinear optics at that time naturally called for its extension to the surface waves. SHG by surface plasma wave was readily observed by Simon *et al.* [17], and so were other wave mixing processes involving surface em waves [18]. Again, work was mainly concerned with demonstration of the effects. Possible applications of nonlinear optics with surface em waves are actually limited. The inherent strong attenuation of such waves renders frequency conversion inefficient. That surface em waves only exist at specific interfaces and that their fields penetrate several hundred monolayers deep into the bulk make surface wave mixing not generally useful for surface studies.

Then came the discovery of surface-enhanced Raman scattering (SERS) by Fleischman *et al.* in 1974 [19]. It was shown that the Raman output from molecular adsorbates on a roughened silver surface could be $\sim 10^6$ times stronger than that from a smooth surface. This attracted great interest from many chemists and physicists in the late 1970's as they foresaw a tremendous potential of the effect for applications. It was believed that the enhancement came partly from molecule-surface interaction and partly from the local-field enhancement due to the local plasma resonance and pointing rod effect associated with the rough surface structure [20]. Which one was more important was hard to say because the two mechanisms could not be separated in SERS. At this point, familiarity with nonlinear optics was useful. In nonlinear optics, Raman scattering can be considered a two-photon process, i.e., a nonlinear optical effect. A simple idea was naturally born: If one nonlinear optical effect experiences local-field enhancement, so will the others.

An appreciable local-field enhancement in SERS suggests an equally appreciable local-field enhancement in SHG from a roughened silver surface. A subsequent experiment by Chen *et al.* [21] showed that this was indeed the case. Unlike SERS, SHG could be generated from a bare silver surface. Then the observed enhancement must result entirely from the enhanced local fields. On the other hand, like SERS, SHG could also be used to detect adsorption and desorption of molecules on a roughened metal surface. The experiment was carried out by Chen *et al.* on the Ag electrode in an electrochemical cell [22]. The signal was surprisingly strong. In fact, it was later shown that a 20-mW cw laser was already sufficiently strong to be able to monitor the oxidation-reduction cycle at the Ag electrode in an electrochemical process [23]. This immediately suggested that with a pulsed laser, SHG from an adsorbed monolayer of molecules could be readily detected even without any surface enhancement. It was then clear that SHG would be useful as a surface probe. This conclusion would have been reached much earlier if the surfaces probed in the earlier SHG measurements had been better characterized. But as is often the case in the progress of science, it had to wait for another event to happen first, in our case, the discovery of SERS. Ironically, in these crucial measurements [22], [23], the surfaces involved were not only poorly characterized but also not well defined in geometry.

I note in passing that one would expect the local-field enhancement to show up in all nonlinear optical effects on roughened metal surfaces. According to theory, the enhancement factor could be orders of magnitude higher for higher order nonlinear optical processes. For example, if the enhancement of SHG on a roughened Ag surface is 10^4 , then the enhancement of a degenerate four-wave mixing at the same input frequency on the same surface should be 10^8 . However, despite numerous attempts, no such strong enhancement of higher order processes has been observed. It is a mystery remaining to be solved.

The awareness of the submonolayer sensitivity of SHG prompted us to start a series of experiments to explore the potential of SHG as a surface probe as well as a reexamination of the theory of SHG in reflection and transmission. Several good Ph.D. theses came out of the work in our laboratory [24]–[27]. They set the foundation for SHG and sum-frequency generation (SFG) as surface analytical tools. Copies of these theses are still in demand these days. The basic symmetry argument for the surface specificity of SHG and SFG was known. The processes are electric-dipole forbidden in a medium with inversion symmetry [1], [2], but are necessarily allowed at an interface. However, the electric-quadrupole and magnetic-dipole contributions from the bulk to SHG may not be negligible. Generally, for any medium, surface and bulk have different structural symmetries. Therefore, the interfacial layer should be characterized by linear and nonlinear optical constants different from those of the bulk media. One can follow the derivation of Bloembergen *et al.* [11] and find the SHG or SFG output in terms of the surface and bulk optical constants. Comparison between theory and experiment hopefully would allow deduction of the surface nonlinear optical susceptibility, and hence, information about the interfacial structure. Unfortunately, this is true only when the bulk contribution to SHG or SFG is negligible. In general,

surface information can only be obtained from SHG or SFG measurements by perturbing the surface in a controlled way.

The first series of experiments in the early 1980's designed to explore the potential of SHG as a surface probe went successfully. It was demonstrated by Heinz and coworkers [28] that SHG could be used to obtain spectral and orientational information about a monolayer of organic molecules adsorbed on a substrate. Adsorption of molecules from solution at a solid/liquid interface was also measured. Through the observed azimuthal anisotropy of SHG, the structural symmetry of a surface could be deduced. The first such experiments using oxidized Si surfaces did exhibit anisotropic SHG in response to the Si crystallographic orientation, but the signal came at least partly from the bulk [29]. Later, experiment by Heinz *et al.* on clean Si(III) surfaces proved unambiguously the capability of SHG to probe the crystalline surface symmetry [30]. From detailed analysis of the experimental results, we learned to refine the theory of SHG in many respects [24], [25], [27], [31], [32]. These were key steps necessary to establish SHG as a surface probe. To an outside spectator, they probably appeared like nothing but a rehash or extension of the old surface SHG work. This was indeed once the comment of an eminent solid-state physicist.

After the first period of works between 1981–1983, the potential of surface SHG became obvious. As an optical technique, it could be used to probe any interface accessible by light. Yet, to attract the attention of researchers in the surface community, extra steps must be taken. First, one must prove that the technique would work on a well-defined surface system. This means that it must be a crystalline surface well characterized in ultra-high vacuum (UHV). Second, one would need a reputable scientist in surface science to endorse the work, i.e., to collaborate on the work. We were fortunate to be able to persuade Gabor Somorjai to collaborate with us and lend us an UHV chamber. Harry Tom and coworkers in our laboratory spent the Christmas and New Year vacation of 1983 on the experiment to demonstrate that SHG was an effective tool to study kinetics of O, CO, and Na adsorption on a well-characterized Rh(III) [33]. Later, measurements were extended to benzene and pyridine adsorption on Rh(III) [25], and oxygen adsorption and desorption kinetics on Si(III) [34]. With the additional works of many others in UHV [30], [35], SHG as a surface probe was finally established, but we had to face yet another critical comment: "Adsorption and desorption can be measured by conventional techniques. Can SHG yield any new information?"

One can argue that SHG has advantages over conventional techniques on adsorption and desorption measurements, but there were of course also new frontiers of surface science SHG could explore. Many were in areas where traditional surface science techniques had difficulties. Here are a few examples. With pulsed lasers, kinetics of surface structural transformation [30], including surface melting on the ~ 1 -ps time-scale [36], could be monitored. The ability to probe buried interfaces allowed the study of electrochemical processes involving surface reconstruction of an electrode and crystalline overlayer deposition at an electrode [37]. Measurement of tensorial components of the surface nonlinear susceptibility permitted determination of polar molecular orientation at an interface [28]. Applications to liquid interfaces were particularly in-

teresting. The technique allowed studies of both soluble and insoluble molecular monolayers adsorbed at, for example, a water interface probing phenomena such as two-dimensional phase transition [38], surface ionization [39], surface molecular relaxation [40], and monolayer polymerization [41]. It also provided an effective means to study surface-induced alignment of liquid crystals [42]. With SHG, surface microscopy also became possible [23], [43].

Surface spectroscopy with submonolayer sensitivity is obviously important for many areas of science and technology. With tunable lasers, SHG can yield surface-specific monolayer spectroscopy if sufficiently sensitive photo detector for the SH output is available. This generally limits SHG to the visible/near visible region where electronic transitions take place. Surface vibrational spectroscopy, which is more desirable for its better ability to selectively detect surface species, seems to be out of the reach of SHG. Can we find a way to solve the problem? The answer is perhaps obvious to many people: simply extend SHG to SFG.

Instead of a single input laser beam in SHG, two input beams are now required for SFG vibrational spectroscopy, one tunable in the infrared and the other at a fixed wavelength in the visible. The sum-frequency (SF) output now appears in the visible and can be detected by a sensitive photomultiplier. When the infrared input scans over surface vibrational resonances, SFG from the surface must respond correspondingly with resonant enhancement. This then yields the vibrational spectrum for the surface. To convert SHG to SFG in the laboratory is however not a trivial matter. This was particularly difficult in the early 1980's when coherent tunable infrared sources were not on the market. We built in Yuan T. Lee's laboratory our first LiNbO₃ optical parametric oscillator pumped by a Q-switched Nd:YAG laser. Harry Tom used it to try out SFG spectroscopic measurement on a monolayer of p-nitrobenzoic acid (PNBA) on quartz in the CH stretch region. The experiment was not conclusive because a CH spectrum was observed even before the PNBA monolayer was deposited [25]. We realized that the spectrum must have come from hydrocarbon contaminants on the quartz surface. Lee's world-famous molecular beam laboratory had several large mechanical pumps constantly in operation to keep the beam machines working, so that the air in the room was always badly contaminated by hydrocarbons. The next attempt by X.D. Zhu and Hajo Suhr of our group was to use a discretely tunable CO₂ infrared laser in synchronization with a Q-switched Nd:YAG laser for SFG study of a coumarin 504 dye monolayer on quartz in the 10- μ m range [44]. This time the experiment was successful, but only after consuming four partly broken commercial (Tachisto, Inc.) CO₂ TEA lasers. The real success came later when we finally completed our home-built mode-locked Nd:YAG laser and the associated optical parametric generator/amplifier system [45]. The setup was then reliable enough for us to routinely generate SFG vibrational spectra from surface monolayers [46]. In the meantime, Alex Harris at Bell Labs also succeeded in obtaining surface SFG spectra with his tunable IR beam generated by dye-laser-pumped stimulated Raman scattering in a metal vapor cell [47].

I should mention that stimulated Raman gain process has also been proposed and demonstrated for monolayer spectroscopy

[48]. The technique requires two input laser beams, one fixed in frequency and the other tunable. The former could be the pump and the latter the probe monitoring the Stokes Raman gain. Heritage and Allara were able to obtain a monolayer spectrum for p-nitrobenzoic acid on sapphire [48]. However, the signal-to-noise ratio was marginal even with the use of two extremely stable cw mode-locked dye lasers and a low-noise detection system. Small residual absorption and thermal fluctuations in the substrate could easily smear the spectrum. This inherent difficulty of the technique arises from the fact that stimulated Raman process is not surface-specific and makes it not so appealing. Consequently, there has been no follow-up on this technique.

Since the late 1980's, SFG spectroscopy has been developing fairly rapidly. As a surface spectroscopic tool, it is clearly more powerful than SHG. Except for the more complex experimental arrangement, it has essentially all the advantages SHG has. The vibrational spectra can provide much more information about surface molecules and surface structures. Selected peaks in the spectra allow us to focus on selected atomic groups in molecules appearing at the surface. Like any other spectroscopic technique, the difficulty of SFG vibrational spectroscopy (SFG-VS) often lies in understanding the spectra, including the proper assignment of vibrational resonances. Even so, the power of the technique is well proven and SFG-VS is now well accepted by the surface science community. It is probably interesting to see where the SFG spectroscopy plays a unique role. I will give a very brief survey here.

Surfactant monolayers at various interfaces (important for many areas of science and technology ranging from bioscience to cleaning, lubrication, cosmetics and oil recovery) appear to be the most popular systems studied by SFG-VS [49], [50]. The advantage is that the spectrum in the CH stretch region is very sensitive to the confirmation of the alkyl chains in the surfactant molecules. Dictated by symmetry consideration, only the modes from the terminal methyl (CH_3) groups appear prominently in the spectrum if the chains are straight (all-trans). Then the chain orientation can be deduced from the polarization dependence of the CH_3 spectrum. The modes from the methylene (CH_2) groups become significant when the trans-gauche (folding) defects on the chains set in. The chain confirmation is important because it basically controls the surface characteristics of the surfactant-coated substrate in the given environment. In most of the applications, SFG-VS is unique because of its surface specificity. Bulk absorption will have little effect on the surface spectrum as long as it does not block the input beams. For example, the SFG spectrum of an interfacial surfactant monolayer can be measured even in the presence of a high-bulk concentration of alkyl chains [51]. Thus experimental investigations of molecular adsorption from solution at liquid/solid, liquid/liquid, and liquid/vapor interfaces [51], surface compositions of liquid mixtures, and surface phase transformations [52] all become possible. Surface reactions and catalysis is an area of particular importance that can benefit from SFG-VS [53]. Catalytic reactions have been well studied in UHV, but the results are not necessarily the same as those obtained under high-gas pressure used in industrial practices. This "pressure gap" problem has been bothering many researchers. SFG-VS, being capable of probing

a surface in an ambient atmosphere, can now offer a solution. Another unique application of SFG-VS is in the area of ultrafast surface dynamics. With the help of picosecond laser pulses, surface vibrational excitations and relaxations, for example, can be investigated [54]. Among other applications, perhaps most worth mentioning is the ability of SFG-VS to probe surface structures of bulk media. These include not only vapor/liquid [55] and vapor/solid interfaces [56], but also liquid/liquid [57], liquid/solid [58], and solid/solid [59] interfaces. Surprisingly, so far SFG-VS has been the only spectroscopic technique available for vibrational spectroscopic studies of liquid interfaces. It has produced the first vibrational spectra of water interfaces, from which we learned that water molecules at an interface tend to organize themselves into a more or less ordered hydrogen bonding network [58], [60]. Phase measurement of the SFG output also allows the determination of absolute polar orientation of a surface atomic group, i.e., whether the group points into or out of the bulk [55], [61].

Many applications of SFG-VS require that the bulk contribution to SFG be negligible. However, as mentioned earlier, this is not true in general. For SFG in transmission, the bulk contribution is generally nonnegligible even if it is electric-dipole forbidden. For SFG in reflection, because of the much shorter effective coherent length, the bulk contribution is greatly reduced and in many cases, can indeed be neglected. The importance of bulk contribution to SFG can be estimated from measurements of SFG in both transmission and reflection [55], [62]. Our limited experience so far is that for centrosymmetric molecular liquids and solids, the bulk contribution to reflected SFG is negligible.

Today, after nearly 40 years since SHG and SFG were discovered and the underlying theory formulated, we finally have the processes well established as surface analytical tools. A growing number of researchers have adopted the techniques. Requirement of laser expertise to set up an SFG-VS system may have intimidated the traditional surface scientists, but such a system now exists commercially [63]. Not all the unique applications of surface SHG and SFG have been carefully explored. Examples are the possible uses of SHG and SFG to probe interfaces of nanostructures [64], SFG-VS to study biological samples, time-dependant SFG-VS to follow a surface catalytic reaction [65], and doubly resonant SFG-VS to investigate coupling of vibrational modes with electrons at a surface. Undoubtedly, the existence of a wide variety of possible applications is the great virtue of SHG and SFG. It guarantees an increasingly productive role for these techniques in surface science. That they can lead to the opening of a large number of new areas of research in surface science is certainly most satisfying. What we describe in this review is just one of the many examples of how the development of laser science has served other scientific communities.¹

¹I have omitted in this article some other topics of surface nonlinear optics and their relations to surface science because of my lack of involvement in their development. Among those that have attracted much attention are multiphoton photoemission (see, for example, R. Haight, *Surf. Sci. Reports*, vol. 21, p. 277, 1995) and femtosecond surface reaction dynamics (see, for example, J. A. Misewich, T. F. Heinz, P. Weizand, and A. Kalamarides, in *Laser Spectroscopy and Photochemistry of Metal Surfaces*, ed. H. L. Dai and W. Ho, Eds. (World Sci., Singapore, 1995), p. 764; H. W. K. Tom and J. A. Prybyla, *Laser Spectroscopy and Photochemistry of Metal Surfaces*, p. 827).

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Y. R. Shen, photograph and biography not available at the time of publication.