



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials Sciences Division

Presented at the Surface Studies by Nonlinear Optical Spectroscopy Conference, Kassel, Germany, May 29–June 2, 1994, and to be published in the Proceedings

Nonlinear Optical Studies of Surfaces

Y.R. Shen

July 1994



REFERENCE COPY |
Does Not |
Circulate |
Bldg. 50 Library.
Copy 1

LBL-35991

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-35991
UC-410

Nonlinear Optical Studies of Surfaces

Y.R. Shen

Department of Physics
University of California

and

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

July 1994

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

NONLINEAR OPTICAL STUDIES OF SURFACES

Y. R. Shen

Department of Physics, University of California and
Materials Sciences Division, Lawrence Berkeley Laboratory
Berkeley, California 94720-7300

The possibility of using nonlinear optical processes for surface studies has attracted increasing attention in recent years. Optical second harmonic generation (SHG) and sum frequency generation (SFG), in particular, have been well accepted as viable surface probes.¹ They have many advantages over the conventional techniques. By nature, they are highly surface-specific and has a submonolayer sensitivity. As coherent optical processes, they are capable of *in-situ* probing of surfaces in hostile environment as well as applicable to all interfaces accessible by light. With ultrafast pump laser pulses, they can be employed to study surface dynamic processes with a subpicosecond time resolution. These advantages have opened the door to many exciting research opportunities in surface science and technology. This paper gives a brief overview of this fast-growing new area of research.

Optical SHG from a surface was first studied theoretically and experimentally in the sixties.² Even the submonolayer surface sensitivity of the process was noticed fairly early.³ The success was, however, limited because of difficulties in controlling the experimental conditions. It was not until the early 1980's that the potential of the process for surface analysis was duly recognized.⁴ The first surface study by SHG was actually motivated by the then active search for an understanding of the intriguing surface enhanced Raman scattering (SERS).⁵ It had been suspected that the enhancement in SERS mainly came from the local-field enhancement due to local plasmon resonances and pointing rod effect on rough metal surfaces. In our view, Raman scattering is a two-photon process and is therefore a nonlinear optical effect. If one

nonlinear optical effect is enhanced by local-field enhancement, so will the others be. We should then expect SHG to be also strongly enhanced on rough metal surfaces. A measurement of SHG from a roughened Ag surface indeed showed a $\sim 10^4$ enhancement in comparison to a smooth surface.⁶ The observed signal was surprisingly strong. It immediately suggests that even without surface enhancement, an adsorbed monolayer could be readily detected. The use of SHG to monitor adsorption and desorption of molecules on an electrode in an electrolytical cell was soon demonstrated.⁴ In subsequent years, a large number of experiments were performed to explore the potential of SHG as a surface tool.¹ Today, the technique together with SFG has already found such a wide range of applications that few other surface techniques can match. We note in passing that although the surface enhanced local field effect played a key role in the successful development of SHG as a surface probe, it itself has not yet had a satisfying quantitative understanding. For example, one can estimate from the simple theory that if a 10^4 enhancement in SHG from a rough metal surface is observed, then a 10^8 enhancement in degenerated four-wave mixing at the same frequency should be expected. Despite numerous experimental attempts, no such strong enhancement has ever been reported.

SHG and SFG are highly surface-specific because of their intrinsic symmetry. As second-order processes, they are forbidden in a medium with inversion symmetry, but necessarily allowed at an interface. While electric quadrupole and magnetic dipole contributions from the bulk may not be totally negligible, in many cases the surface contribution does dominate. In general, the signal of reflected or transmitted SHG or SFG from an interface between a linear and a nonlinear medium can be written as¹

$$S \propto |\mathbf{L}(\omega) \cdot \chi_{\text{eff}}^{(2)} \cdot \mathbf{L}(\omega_1) \mathbf{L}(\omega_2)|^2 \quad (1)$$

where $\mathbf{L} = (L_{xx}, L_{yy}, L_{zz})$ are the appropriate Fresnel coefficients, and $\chi_{\text{eff}}^{(2)}$ is the effective surface nonlinear susceptibility given by

$$(\chi_{\text{eff}}^{(2)})_{ijk} = (\chi_s^{(2)})_{ijk} + (\chi_B^{(2)})_{ijk} / [k_z(\omega) + k_z(\omega_1) + k_z(\omega_2)] f_i(\omega) f_j(\omega_1) f_k(\omega_2). \quad (2)$$

Here $\chi_s^{(2)}$ is the surface nonlinear susceptibility of the interface, $\chi_B^{(2)}$ is the bulk nonlinear susceptibility of the nonlinear medium, k_z is the wavevector along the surface normal in the nonlinear medium $f_j(\omega) = 1$ for $j = x, y$, and $f_j = \epsilon(\omega)/\epsilon'(\omega)$ for $j = z$ with ϵ and ϵ' being the dielectric constants of the nonlinear and the interfacial layer, respectively.

In order for SHG or SFG to be surface-specific, we must have $|\chi_s^{(2)}| \geq |\chi_B^{(2)}|/2 |k(\omega)|$. This is the case with a centrosymmetric medium (as we mentioned earlier) since $\chi_B^{(2)} = 0$ under the electric dipole approximation. In this case, if we assume that the surface is a mere termination of the bulk structure and both $\chi_s^{(2)}$ and $\chi_B^{(2)}$ come from electric quadrupole contribution responding to the spatial variation of the field, we should find $|\chi_s^{(2)}| \sim |\chi_B^{(2)}|/k$. This is because the field varies in the bulk on the scale of wavelength whereas at the surface, on the scale of surface layer thickness. However, if the surface has the structure of a polar layer so that $\chi_s^{(2)}$ is nonvanishing in the electric dipole approximation, we could find $|\chi_s^{(2)}| \gg |\chi_B^{(2)}|/k$. SHG or SFG would then effectively measure $\chi_s^{(2)}$ and appear surface-specific.

The microscopic expression of $\chi_s^{(2)}(\omega = \omega_1 + \omega_2)$ can be written as¹

$$\begin{aligned} (\chi_s^{(2)})_{ijk}(\omega = \omega_1 + \omega_2) = & -N_s \frac{e^3}{\hbar^2} \sum_{g,n,n'} \left[\frac{\langle g|r_i|n\rangle \langle n|r_j|n'\rangle \langle n'|r_k|g\rangle}{(\omega - \omega_{ng} + i\Gamma_{ng})(\omega_2 - \omega_{n'g} + i\Gamma_{n'g})} \right. \\ & \left. + \frac{\langle g|r_i|n\rangle \langle n|r_k|n'\rangle \langle n'|r_j|g\rangle}{(\omega - \omega_{ng} + i\Gamma_{ng})(\omega_1 - \omega_{n'g} + i\Gamma_{n'g})} + 6 \text{ others terms} \right] \rho_g^0 \end{aligned} \quad (3)$$

where N_s is the surface density of molecules, and ρ_g^0 is the ground state population. It is seen that $\chi_s^{(2)}$ is resonantly enhanced as ω_1 or ω_2 or $\omega_1 + \omega_2$ approaches a resonance. Thus SHG and SFG can be used for surface spectroscopy. Through resonances, selective surface species can be identified and probed, and surface resonant dynamics can be studied.

Being a rank-3 tensor, $\chi_s^{(2)}$ can reflect a surface symmetry equal to or lower than a 3-fold rotational one.⁷ With its surface sensitivity, SHG or SFG can then be used to monitor surface phase transition such as surface melting and surface reconstruction. In comparison, a linear optical technique suffers not only from its lack of surface specificity, but also from its inability to identify a surface symmetry higher than a 2-fold rotational one. Experimentally, the nonvanishing elements of $(\chi_s^{(2)})_{ijk}$ can be determined using SHG or SFG with various input/output polarization combinations and beam geometries. Chiral surfaces⁸ and magnetized surfaces⁹ can be studied by measuring their signatures embedded in $(\chi_s^{(2)})_{ijk}$. The most attractive areas of applications of SHG and SFG are on liquid surfaces¹⁰ and buried interfaces⁶ where conventional techniques have serious limitations. However, we should remark that as is usually the case, no single analytical tool can characterize a surface or interface completely. SHG or SFG is certainly not an exception.

Although SHG and SFG are powerful and versatile, they also have their limitations and difficulties like other techniques. Lest the applications of the techniques be erroneous, it is important to know these limitations. Here, we discuss briefly the most frequently encountered ones. First, we should provide a clear definition of surface or interface. In our case, a surface or interface is defined as the transition layer between two adjacent bulk media; in this layer, the induced polarization is different from the bulks because of the difference in structure or field distribution or both.¹ The layer thickness is practically of the order of one to several monolayers. The goal of our surface studies is to probe the properties of this microscopic layer. However, as mentioned before and displaced explicitly in Eq. (2), the bulk contribution to SHG or SFG in general is not negligible. In an actual experiment, proper steps must be taken to extract the desired surface signal from the measurement. Surface modulation is a commonly adopted scheme. Since SHG and SFG are particularly sensitive to surface, surface preparation is necessarily important. For example, surface contaminations or defects can drastically affect the measured signals. This was actually the difficulty encountered in the early experiments of SHG from surfaces of metals and semiconductors.^{2,3}

One useful application of SHG or SFG is to probe adsorbates on a surface or interface. One would hope that the signal could be simply related to the surface density of the adsorbates. Unfortunately, this is far from the case. The measured effective surface nonlinear susceptibility can be expressed in the form¹

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{BS}}^{(2)} + \chi_{\text{M}}^{(2)} + \chi_{\text{I}}^{(2)} \quad (4)$$

where $\chi_{\text{BS}}^{(2)}$ is the effective surface nonlinear susceptibility of the bare substrate including the bulk contribution, $\chi_{\text{M}}^{(2)}$ is the surface nonlinear susceptibility of the monolayer, and $\chi_{\text{I}}^{(2)}$ is due to interaction between the monolayer and the substrate. Only in simple cases, will $\chi_{\text{M}}^{(2)}$ and $\chi_{\text{I}}^{(2)}$ be proportional to the surface density of adsorbates N_{S} ; even then, the three terms in Eq. (4) can all be complex quantities with different phases. More generally, if the local-field correction¹¹ and the interaction between adsorbates are significant, $\chi_{\text{M}}^{(2)}$ and $\chi_{\text{I}}^{(2)}$ become complex and often unknown functions of N_{S} . In this latter case, the use of SHG and SFG to probe the adsorbates obviously needs special care. Average orientation of molecular adsorbates on a surface is, for example, a useful piece of information for many applications. This requires knowing the ratios of the nonvanishing average polarizability elements $\langle \alpha_{\xi\eta\zeta}^{(2)} \rangle$ of the adsorbed molecules. To achieve that without complication, we would like to have $\chi_{\text{M}}^{(2)}$ dominate over the other two terms in Eq. (4) and be linearly proportional to N_{S} . Even so, it is often not possible to determine all $\langle \alpha_{\xi\eta\zeta}^{(2)} \rangle$ because there may not be as many nonvanishing independent $(\chi_{\text{S}}^{(2)})_{ijk}$ as $\langle \alpha_{\xi\eta\zeta}^{(2)} \rangle$. Only in simple cases can the contributions of some elements of $\langle \alpha_{\xi\eta\zeta}^{(2)} \rangle$ to $\chi_{\text{S}}^{(2)}$ be neglected and then all the dominant $\langle \alpha_{\xi\eta\zeta}^{(2)} \rangle$ be determined. For instance, we can expect for rod-like molecules that $|\alpha_{\xi\xi\xi}^{(2)}| \gg |\alpha_{\xi\eta\eta}^{(2)}| \sim |\alpha_{\eta\xi\eta}^{(2)}| \sim |\alpha_{\eta\eta\xi}^{(2)}|$, where $\hat{\xi}$ is along the long molecular axis. For an azimuthally isotropic distribution of such molecules on a surface, we can deduce their average polar orientation by SHG measurement of the independent nonvanishing elements $(\chi_{\text{S}}^{(2)})_{zzz}$ and $(\chi_{\text{S}}^{(2)})_{zyy}$. The assumption of $\alpha_{\xi\xi\xi}^{(2)}$ dominating should be justified by the existence of the equality $(\chi_{\text{S}}^{(2)})_{zyy} = (\chi_{\text{S}}^{(2)})_{yzy}$.

There exists yet another intrinsic difficulty if the values of $(\chi_s^{(2)})_{ijk}$ are to be deduced from experiment. We need to know the dielectric constants of the bulk media and the surface layer in order to be able to calculate the Fresnel coefficients in Eq. (1). The bulk dielectric constants of a material may not be readily available, but they can at least be measured. The dielectric constant $\epsilon'(\omega)$ of the surface layer, however, is an average quantity over the layer thickness, and is not easily measurable. In an SHG or SFG experiment we can actually determine only $(\chi_s^{(2)})_{ijk} g_i g_j g_k$, but not $(\chi_s^{(2)})_{ijk}$,¹ where $g_j(\omega) = 1$ if $j = x, y$, and $g_j(\omega) = 1/\epsilon'(\omega)$ if $j = z$. This leads to some arbitrariness in the determination of the molecular orientation, for example. We should also be aware of the fact that $\epsilon'(\omega)$ is generally a tensor, and there is the usual controversy of whether the dielectric constant of a microscopic layer can be properly defined.

The most attractive feature of SHG and SFG is perhaps their capacity for surface spectroscopy.¹ The intrinsic surface specificity makes them rather unique as spectroscopic tools for studies of pure liquid and solid surfaces or interfaces. With ultrashort laser pulses, even transient surface spectroscopy can be explored. However, similar to the well-known coherent anti-Stokes Raman spectroscopy, SHG and SFG suffer from the fact that their spectral profiles represented by $|L(\omega) \cdot \chi_{\text{eff}} \cdot L(\omega_1) L(\omega_2)|^2$ are more complicated than the conventional ones. Assuming ω_1 is near resonances, we can write

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{NR}}^{(2)} + \sum_{\alpha} \frac{A_{\alpha}}{\alpha(\omega_1 - \omega_{\alpha} + i\Gamma_{\alpha})} \quad (5)$$

Clearly, the real and imaginary parts of $\chi_{\text{eff}}^{(2)}$ must both contribute to the observed spectrum, and unlike conventional spectroscopies, the nonresonant background $\chi_{\text{NR}}^{(2)}$ can be important in determining the spectral profile. Furthermore, the dispersion of $L(\omega_j)$ can also significantly alter the spectral profile. In order to deduce quantitative information about resonances, a least square fit of Eq. (1) to the experiment data is necessary.

As a spectroscopic technique, SHG or SFG is presently limited by the tuning range of available laser sources. In the infrared region where surface vibrational resonances are of great interest, the limitation is set by difference frequency generation in nonlinear media to around 12 μm . With the advent of free electron lasers, extension of the tuning range to 100 μm or longer should no longer be a problem. In the uv region, continuous tuning to several tens of nm by wave mixing should be possible.

Finally, we note that like most of other techniques, calibration is always important but difficult for SHG and SFG. For example, we can use SHG to probe *in-situ* the surface density of adsorbates, N_s , but we first need a calibration of SHG versus N_s . We can use SFG spectroscopy to monitor the change of a surface, but we need reference spectra of well-defined surfaces for quantitative interpretation. In this respect, it is usually important to have other surface techniques as complementary tools in a surface study.

In summary, there is no doubt that the SHG and SFG are powerful and versatile as surface probes, and can be exploited to explore many new areas of surface science. However, they also have limitations. For proper applications of the techniques, care must be taken in the measurement and analysis to avoid or overcome these limitations.

Acknowledgments

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

1. See, for example, Y. R. Shen, *Surface Science* **299/300**, 551 (1994); "The Principles of Nonlinear Optics," (J. Wiley, New York, 1984), Ch. 25; in *Fundamental System in Quantum Optics*, ed. by J. Dalibard et al., North Holland, Amsterdam, 1992, Course 15; Y. R. Shen, in "Frontiers in Laser Spectroscopy," *Proc. International School of Physics "Enrico Fermi,"* ed. by T. Hansch, Academic Press, NY, 1994.
2. N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, *Phys. Rev.* **174**, 813 (1968), and references therein.
3. F. Brown, and M. Matsuoko, *Phys. Rev.* **185**, 985 (1969); J. M. Chen, J. R. Bower, C. S. Wang, and C. H. Lee, *Opt. Comm.* **9**, 132 (1973); J. M. Chen, J. R. Bower, and C. S. Wang, *Jpn. J. Appl. Phys. Suppl.* **2**, 711 (1974).
4. C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, *Phys. Rev. Lett.* **46**, 1010 (1981); T. F. Heinz, C. K. Chen, D. Ricard, and Y. R. Shen, *Phys. Rev. Lett.* **48**, 478 (1982).
5. M. Fleischmann, P. J. Hendra, and A. J. McQuillan, *Chem. Phys. Lett.* **26**, 163 (1974).
6. C. K. Chen, A. R. B. de Castro, and Y. R. Shen, *Phys. Rev. Lett.* **46**, 145 (1981).
7. B. Koopmans, F. van der Wonde and G. A. Sawatzky, *Phys. Rev. B* **46**, 12780 (1992).
8. T. Petralli-Mallow et al., *J. Phys. Chem.* **97**, 1383 (1993).
9. R. P. Pan and Y. R. Shen, *Chinese J. Phys.* **25**, 175 (1987); R. P. Pan, H. D. Wei, and Y. R. Shen, *Phys. Rev. B* **39**, 1229 (1989); W. Hübner and K. H. Bennemann, *Phys. Rev. B* **40**, 5973 (1989).
10. See, for example, Q. Du, R. Superfine, E. Freysz, and Y. R. Shen, *Phys. Rev. Lett.* **70**, 2313 (1993).
11. P. Ye and Y. R. Shen, *Phys. Rev. B* **28**, 4288 (1983).

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720