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Surface nonlinear optics: a historical overview

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Abstract. A comprehensive theory of the behavior of light waves at the boundary of nonlinear optical media was first presented in 1962. Observation of second harmonic reflected light quickly followed, first from media which lack inversion symmetry, but soon thereafter from silver, silicon, germanium, and ionic crystals. While it was established in the mid-sixties that second harmonic and sum frequency generation could be used to investigate specifically the structures of surfaces and interfaces of centrosymmetric materials, it was not until about 1980 that nonlinear optical spectroscopy of surfaces became well established as a separate subfield.

The availability of widely tunable dye lasers and optical parametric oscillators permit the detection of surface specific electronic and vibrational states. Polarization dependent studies yield information about the orientation of molecular monolayers and surface specific bonds. The use of picosecond and femtosecond pulse–probe techniques permits time-resolved studies of surface phase transformations, desorption, and melting. A few examples from the rapidly growing literature are selected to illustrate this historical evolution.

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1 Light waves at the boundary of nonlinear optical media

The demonstration by Franken et al. [1] of second harmonic generation (SHG) of light unleashed the development of a new branch of physics, which was soon to be designated as nonlinear optics. Also Franken had sent a preprint of his SHG paper to Wilcox, who was at that time a postdoctoral research fellow in my Harvard group. Franken and Wilcox had known each other for several years when they were graduate students of Lamb at Stanford University. I immediately recognized the potential of nonlinear optics from reading this preprint. Our group at Harvard started with theoretical investigations in the summer of 1961, since our laboratory lacked an operating ruby laser. One of our theoretical papers [2] dealt with the behavior of light waves at the boundary of a nonlinear medium. The classical laws of optical reflection and refraction were generalized to nonlinear optical response. When our laboratory acquired its first ruby laser, manufactured by Trion Inc., in 1962, the research activity in many large industrial laboratories had already grown rapidly in pursuit of new optical devices including harmonic generators, parametric oscillators, and modulators. Therefore, our laboratory concentrated at first on second harmonic generation (SHG) in optically absorbing materials, which had not yet been studied elsewhere. We measured the nonlinear optical properties of GaAs in reflection. Ducuing [3, 4] verified the predicted laws of nonlinear reflection and Chang et al. [5] measured both the real and imaginary part of the complex nonlinear susceptibility $\chi^{(2)}$.

The reflected SHG intensity from media which lack a center of inversion symmetry is generated by the harmonic polarization in a layer about one quarter optical wavelength thick in a transparent dielectric, or in the absorption depth in the case of a strongly absorbing medium. These early observations are therefore not surface specific.

SHG in a medium with a center of inversion symmetry was first observed by Terhune et al. [6] in calcite. They introduced a nonlinear term of quadrupolar origin in the form of a second harmonic polarization proportional to the product of the fundamental field and its gradient. Pershan [7] showed that in media with inversion symmetry the second harmonic polarization source term may be written in the general form,

$$P_i(2\omega) = \nabla_j[\chi^{\mathrm{Q}}_{ijkl} E_k(\omega) E_l(\omega)] \tag{1}$$

In this expression, which corresponds to Eq. (4.13) of [7], a summation over repeated indices is implied on the right-hand side. This source term in a non-absorbing dielectric is ninety degrees out of phase with the nonlinear SH polarization induced in the presence of an applied dc electric field. Bloembergen and Pershan discuss a possible interference between these two source terms as the dc field may not have the same spatial boundary condition at the edge of the crystal. The most careful observation of the quadrupole effect in the phase matched propagation geometry in calcite has been carried out by Bjorkholm and Siegman [8]. In cubic and isotropic

media with inversion symmetry the quadrupole term does not give rise to transmitted harmonic radiation as the source term in (1) has only a longitudinal component. In anisotropic media, such as calcite, the component parallel to the wave vector can couple to the extraordinary second harmonic wave.

2 SHG at interfaces between centrosymmetric media

The theoretical underpinning for SHG at interfaces between media with inversion symmetry is already contained in (1). At such an interface a discontinuity in the normal component of electric field and in the tensor components of the quadrupolar susceptibility occur. This leads to a delta-function type of contribution to the volume polarization at the surface. The addition of a thin surface dipolar layer can be taken into account by treating the thin parallel slab in the limit of vanishing thickness, already contained in the 1962 paper of Bloembergen and Pershan [2].

It may therefore be argued that the basic source terms for second harmonic generation at the surface of a medium with inversion symmetry had already been identified in 1963. At the interface of two centrosymmetric media with different linear indices of refraction, a discontinuity occurs in the normal component of the electric field. There is also a discontinuity in the tensor components of χ^{Q}_{ijkl} occurring in (1). Thus the gradient of the quadrupolar density, equivalent to an effective dipolar source, behaves as a delta-function at the surface.

The first observation of SHG in reflection from a centrosymmetric isotropic material was made by Brown et al. [9, 10]. They demonstrated SHG from silver films by a fundamental ruby laser pulse, incident at an angle of 45°. The SH beam was polarized in the plane of incidence. The linear polarization of the ruby pulse made an angle φ with the plane of incidence. As φ is varied from 0 (p-polarization) to $\pi/2$ (s-polarization), the SH intensity was found to be proportional to $\cos^4\varphi$. It was concluded that the effect was caused by conduction electrons via the discontinuity in the normal component of E.

Kronig and Bouwkamp [11] and Bloembergen [12] had already shown in 1963 that a volume term in the form of a longitudinal current proportional to $\boldsymbol{E}(\omega)\times\boldsymbol{H}(\omega)$ or to $\boldsymbol{E}\times(\nabla\times\boldsymbol{E})$ also contributes to the reflected SHG. Jha [13] discussed the relative importance of these two plasma responses. In the case $\varphi=\pi/2$, i.e. when the incident light is s-polarized parallel to the surface, only the volume contribution survives. The intensity of the reflected SHG is then only 4% of that for p-polarized incident light. The volume contribution is nevertheless not negligible in the geometry with $\varphi=0$, because the Fresnel factor which determines the strength of the fundamental field inside the metal is larger for p- than for s-polarization. Furthermore, it was shown by Bloembergen et al. [14, 15] that the electrons of the 4d-valence band make a contribution comparable to that of the conduction electrons to SHG in silver, gold, and silver–gold alloys.

They also found that SHG in reflection from silicon and germanium has the same order of magnitude and dependence on φ as in silver. In these semiconductors the contribution of the conduction electrons to the linear and nonlinear optical susceptibilities was negligible. It is possible under the admittedly poorly controlled surface conditions of these early experiments that an internal space charge field causing band bending due to trapped surface charges contributed significantly to the observed signal via electronic field induced SHG. In fact, it was observed that the signal could be modified significantly by immersing the semiconductors in an electrolyte solution with an applied dc voltage [16].

Both the linear and nonlinear susceptibilities are significantly smaller in wide band gap transparent optical materials. During the late sixties, Wang [17] succeeded in measuring SH intensities in reflection from alkali halide crystals, water and other transparent materials with inversion symmetry.

Generally, the SHG intensity at interfaces decreases as the difference between the indices of refraction on both sides of the interface becomes smaller and the discontinuity in the normal component of the E-fields disappears.

The developments of SHG at interfaces of media with inversion symmetry during the decade of the sixties are summarized in a fairly comprehensive paper by Bloembergen et al. [18]. It was followed by a decade with relatively little activity. Since 1980, the subject has experienced a period of continuous growth. For this topic one may designate the decade of the sixties as the period of "classical antiquity", the seventies as the Middle Ages, with the Renaissance starting in 1980.

Shen [19] has reviewed the progress made during the eighties. Refined theoretical analysis carefully examined the discontinuities in the normal component of the electric field $\boldsymbol{E}$, as one passes from a centrosymmetric medium with dielectric constant ε_1 through a dipolar sheet with dielectric constant ε' to a centrosymmetric medium with dielectric constant ε_2. Equation (18) of Shen's review paper [19] defines an effective surface nonlinear susceptibility tensor χ^{s}_{ijk} which clearly delineates the three effects discussed earlier in the "classical" period.

(a) The electric dipole term arises from the lack of inversion symmetry at the interface. This term may be significantly enhanced by absorbed monolayers of polar molecules.
(b) The non-local electric quadrupolar contribution to the surface nonlinearity is controlled by the strong gradient in the normal component of the electric field. This contribution is diminished when the difference in dielectric constants or indices of refraction between the two media at the interface is small.
(c) A third term results from the discontinuity in the volume quadrupole moment densities of the two bulk media defining the interface. The gradient operator in this case acts on χ^{Q}. This term, when integrated across the interface, yields the difference of two volume susceptibilities. It represents a bulk contribution which cannot be separated from the other two specific surface contributions for one single interface.

The effective nonlinear surface tensor $\chi^{\mathrm{s}}_{ijk}(2\omega)$ must reflect the symmetry characteristic of the surface. Here the index i refers to the components of the second harmonic field, and j and k to the Cartesian components of the fundamental field. For the surface of an isotropic medium, normal to the z-direction, only three independent elements exist with the following index combinations: $xxz=xzx=yzy=yyz$, $zxx=zyy$, and zzz.

The individual components can be determined by different combinations of the directions of polarization and angles of the incident beam(s) and of the second harmonic beam.

For crystal surfaces of lower symmetry one can also rotate the crystal around the surface normal to obtain information about additional tensor elements of the surface nonlinear susceptibility $\chi^{s(2)}$. These considerations can be readily extended to sum- and difference-frequency generation at surfaces. When two different beams of light are incident at frequencies ω_1 and ω_2, radiation at $\omega_1+\omega_2$ and $\omega_1-\omega_2$ will occur in specific directions, as described in [2]. The frequencies ω_1 and/or ω_2 may be varied. One may find resonances in the nonlinear surface response, characteristic of electronic surface states, surface plasmons, or of vibrational frequencies of adsorbed molecules.

3 Nonlinear surface spectroscopy

The potential of nonlinear optics as a surface-specific tool was not fully exploited until the decade of the eighties. The pioneering experiments of the sixties were all carried out with ruby laser pulses with multimode structure in both the spatial and temporal domain. More quantitative investigations with diffraction-limited and Fourier-transform-limited pulses of picosecond and femtosecond duration only became possible after the technical development of counter-propagating tunable pulsed dye-laser systems, pulsed Ti-sapphire lasers and tunable optical parametric oscillators. Pump–probe techniques with picosecond and femtosecond laser systems also enable one to investigate the dynamics of surface processes, including the absorption, desorption, and surface diffusion of atoms and molecules as well as melting and other surface phase transitions.

A significant advance in nonlinear surface spectroscopy during the decade of the seventies was the demonstration of surface plasmon resonant enhancement of nonlinear susceptibilities. Simon et al. [20] demonstrated an order of magnitude increase in SHG when a surface plasmon resonance in silver was excited. The amorphous silver layer was deposited on a totally reflecting glass prism. In this geometry resonant coupling, either at the fundamental or the second harmonic frequency, leads to a large enhancement of the field at the metallic surface. More extensive investigations on plasmon enhanced SHG structures, with further amplification and diffraction by a periodic grating, were reported by Reinisch and coworkers [21].

The same enhancement of local field factors also was largely responsible for the surface-enhanced Raman scattering, or SERS, effect. Raman scattering and coherent anti-Stokes Raman scattering from molecules adsorbed on amorphous rough silver surfaces could be enhanced sufficiently for Raman scattering from monomolecular layers to become detectable. Since the SERS effect relates to the Raman susceptibility $\chi^{(3)}$, the next higher order nonlinear susceptibility, it does not fall under the scope of this review. It has nothing to do with the breaking of inversion symmetry at the surface.

The renaissance of nonlinear optical spectroscopy since 1980 is illustrated by the following very brief selection of representative examples.

The adsorption and desorption of CO molecules on a clean crystalline Ni surface in high vacuum can be studied as the intensity of SH generated by an incident pulse decreases proportional to the degree of coverage of the adsorbed monomolecular layer [22].

Adsorption of a monolayer of oxygen on a (111) surface of a silicon crystal almost completely suppresses SHG. Heinz et al. [23] have studied SHG, the transformation from a (2×2) structure for a freshly cleaved surface to a (7×7) structure. They used a linearly polarized normally incident fundamental and observed the total SH harmonic signal and its polarized components as a function of crystal orientation. The angular variation demonstrate the change in surface symmetry from C_2 to C_3. At 275 °C, the surface phase transition takes several tens of seconds. The transition from a crystalline surface to a liquid molten surface has been investigated with femtosecond pump–probe techniques. Tom et al. [24] used a pump pulse at a wavelength of 610 nm with arbitrary polarization to melt the surface layer. A p-polarized probe pulse creates both s- and p-polarized SH before the pump pulse. After the pump pulse the s-polarized signal decays in about 100 fs, while the p-polarized SH light decays more slowly to a steady state value characteristic of liquid silicon with a 350 fs time constant. The linear reflection coefficient increases by a factor 1.8 with a comparable time constant from its crystalline state to the liquid state value. This time may therefore be characteristic for energy exchange between the hot carrier plasma and the lattice. The shorter time for the disappearance of the s-polarized light indicates that the electronic structure loses its three-fold symmetry characteristic and becomes more or less isotropic in a shorter time.

Other experiments on GaAs (Glezer et al. [25, 26]) have been used to study the phase transitions induced by a femtosecond pump pulse in more detail. The threshold for a phase transition occurs when about 10% of tetrahedral bonds are broken, or roughly 10% of the valence electrons are promoted to antibonding orbitals in the conduction band. Then a reconfiguration occurs in the electronic structure in less than 100 fs. The original non-centrosymmetric structure disappears, causing the disappearance of the originally very large SH reflected signal from the crystalline non-centrosymmetric structure. Again this time is much shorter than the time required for significant energy transfer to the lattice modes and melting. The variation of the linear dielectric function was also studied in great detail [26]. The energy band structure changes as the fluence in the pump pulse is increased. Large changes in both the real and imaginary part of the dielectric constant occur. The band gap collapses to zero as the density of the electron–hole plasma is increased. All this occurs in a time scale which is shorter by a factor of 3–10 than the time required for melting by complete energy transfer to atomic motion.

Information about the orientation of adsorbed polar molecules in monomolecular layers can also be obtained by polarization studies of SHG. Heinz et al. [27] studied SHG p-nitrobenzoic acid (PNBA) on glass. The nonlinearity is dominated by the ζ axis of large polarizability of the PNBA molecule. The ratio of two components of nonlinear susceptibility tensor $\chi^{s}_{zzz}/\chi^{s}_{zxx}$ was measured. The angle between the ζ axis and the surface normal was found to be about 70° for the PNBA layer on glass. Adding ethanol to the interface reduced this angle to about 40°, indicating the influence of solvation energy.

Heinz et al. [28] also measured the variation of SHG intensity with wavelength of a dye laser tuned from 600 to 720 nm incident on quartz crystals, covered with about half a monolayer of rhodamine 110 and rhodamine 6G respectively, which showed the different electronic excited state resonances of these molecules at the SH wavelength.

Another important example is provided by the studies of SHG in thin films of buckyball molecules C_{60}. Films have been deposited on substrates of fused quartz, single crystal silicon, copper, and others. The C_{60} film is treated as an isotropic optical medium, layered between two interfaces.

By studying the polarization dependence of the fundamental and SH light and by rotating the crystalline interface various components of the surface susceptibility tensor may be partially unraveled. In addition there is an effective volume contribution to the signal amplitude, which increases monotonically with the film thickness. Koopmans et al. [29, 30] have shown that this effective nonlinear volume polarization is of magnetic dipolar origin. Its radiation interferes in a characteristic manner with the interface substrate. Furthermore, it exhibits a resonance between 620 and 774 nm incident wavelength. The enhancement is caused by a double resonance between two successive transition with nearly equal spacing. This could be inferred from interference effects between surface and volume terms. When C_{60} is deposited on copper, significant charge transfer generates an electric dipolar surface term.

Wilk et al. [31] showed that the volume contribution of C_{60} at a fundamental wavelength of 1064 nm is an order of magnitude smaller than around 700 nm, and dominantly of electric quadrupole character. The analysis of the various components of the surface and volume contributions demonstrates the level of sophistication attained in nonlinear surface spectroscopy.

Du et al. [32] developed sum frequency generation spectroscopy for the purpose of studying vibrational resonances at molecular interfaces. They used a visible laser beam at fixed frequency and generated a variable infrared frequency with a tunable optical parametric oscillator. They obtained a very interesting result at the liquid–vapor interface of water. When the infrared frequency becomes resonant with the OH bond vibrational frequency at 3600 cm^{-1}, the reflected signal at the sum frequency increases. With polarization-dependent studies at this resonance it could be determined that the angle between the dangling OH bonds and the normal to the water surface is less than 38°. About one quarter of the water molecules at the surface have a free OH bond, independent of temperature between 20 °C and 80 °C. A single monolayer of stearyl alcohol removes the dangling bonds. The infrared spectral response loses the strong resonance at 3600 cm^{-1}, and becomes about the same as that of ice.

The SHG and SFG methods can also be used to study the effect of polymer interfaces. Several investigations have been made of oriented liquid crystal surfaces. A two-dimensional orientational phase transition as a function of density of a surfactant monolayer has been reported [33].

The investigation of chiral molecules by SHG should also be mentioned. Koroteev [34] and coworkers [35] have demonstrated SHG by a higher order $\chi^{(4)}$-type nonlinearity in optically active liquids. Verbiest et al. [36, 37] have shown that a difference in SH intensity results by irradiation with left- or right-handed circularly polarized normally incident light, on a surface of chiral molecules. They also showed that chirality can be induced by the geometry of the experiment. Consider the director of a non-chiral nematic liquid crystal, oriented parallel to surface, and incident light at an angle to the surface normal. The coordinate system defined by the wave vector of incident light, the surface normal and the director of the anisotropic liquid define a chirality, which induces a difference in SHG for right or left circularly polarized light. The properties of surfaces of magnetic materials are also of much current interest.

With these examples this brief overview of the first quarter century of the field of nonlinear surface spectroscopy is concluded. Unfortunately the bulk of the literature on this subject, which has been growing rapidly since 1980, could not be mentioned. The limited number of references quoted in this review merely serve as an introduction to the literature. The field remains quite active, as is evident from the other contributions in this special issue.

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