General considerations on optical second-harmonic generation from surfaces and interfaces

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Second-harmonic generation from an interface, in relation to the second-order nonlinearities of the interface layer and the adjacent bulk, is considered. It is shown that both structural asymmetry and field discontinuity contribute to the interface nonlinearity, which, as far as second-harmonic generation is concerned, can be characterized by a local surface nonlinear susceptibility tensor. The bulk nonlinearity may also contribute to the second-harmonic signal, but is an order of magnitude weaker than the surface nonlinearity in centrosymmetric media with a large optical dielectric constant. The possibility of detecting submonolayers of adsorbates on various substrates is discussed qualitatively.

I. INTRODUCTION

Surface second-harmonic generation (SHG) was a subject of extensive study almost twenty years ago.[1–8] It was found that in a medium with inversion symmetry, the surface contribution to SHG could be comparable with or even dominant over the bulk contribution.[1–3,5,6] Jha[4] as well as Bloembergen and co-workers[5] showed that the surface contribution could originate from the discontinuity of the normal component of the electric field at the surface, resulting in a quadrupole-type surface term. One would then expect the surface SHG from a high-refractive-index material to be particularly strong and essentially independent of surface contaminants or adsorbed layers.[5–7] For cubic crystals, the SH signal would also be independent of the surface orientation.[5–7] Experimental results from various groups seemed to have supported these conclusions.[5–7]

More recently, however, experiments with better control have shown that although high-refractive-index materials do generally yield strong surface SHG, the effect of a submonolayer of adsorbates on such materials also can be easily detected,[9,10] and the reflected SH signal can be very different for different crystalline surfaces.[11,12] For this reason, surface SHG has emerged as a useful tool for studies of various types of surfaces and interfaces, including those of metals and semiconductors.[9–20] It was found that surface SHG is sensitive to submonolayers of CO or O on metals[15] and semiconductors,[17,19] and can be used to measure the in-plane symmetry of the surface layer of metals or semiconductors.[11,16,20] Adsorbates on insulating substrates can also be detected and their orientations determined.[13,14,18] Actually, the technique is applicable to the study of any interface between two media with inversion symmetry as long as it is accessible by light.

These recent results clearly suggest that there exists a surface nonlinearity characteristic of the structure and properties of the surface layer. In this surface layer, the inversion symmetry is necessarily broken, and hence its second-order nonlinearity is nonvanishing in the electric dipole approximation. But then, the structural discontinuity at the surface is also responsible for the field discontinuity at the surface that leads to the quadrupole-type surface contribution to the SHG mentioned above. Whether these two sources, structural discontinuity and field discontinuity, describe two separate contributions to the surface nonlinearity or not has caused some confusion in the literature. Here, we hope to resolve this confusion.

We shall show, with a rigorous derivation, that structural discontinuity and field discontinuity do contribute separately to the surface nonlinearity. This can be illustrated by a simple example. Imagine an interface between a liquid and a solid with matching refractive indices. Obviously, at such an interface, the field discontinuity is absent, but the structural discontinuity is still present and gives rise to a nonvanishing surface nonlinearity. The structural discontinuity here refers to the structural changes in passing from the bulk to the surface layer. These include changes in the atomic positions, symmetry, and electron density, as well as the possible appearance of adsorbates at the surface. The field discontinuity refers to the variation of the field across the surface layer. This is the result of the local-field variation across the surface layer caused by the induced dipoles in the bonding media. Physically, one can visualize this field discontinuity as extremely sharp, occurring in a few atomic or molecular layers. Thus, the nonlocal response of the surface layer to the field must be dominant and therefore the multipole expansion of this response is actually meaningless.

In the bulk of a homogeneous medium, however, the multipole expansion is generally valid. When the medium has an inversion symmetry, the electric dipole part of the second-order nonlinearity vanishes, and the electric quadrupole and magnetic dipole part is the first nonzero term in the multiple expansion. Although the nonlinearity is weak, it is easily detectable, as was first observed by Terhune *et al.* in 1962.[21] In the surface SHG experiment, the detector unavoidably collects the total SH signal contributed by both the surface and the bulk. In fact, it can be shown that as far as the signal is concerned, one can define an equivalent surface nonlinear polarization as a source for SHG to take into account contributions from both the surface and the bulk.[7,11,22,23] Difficulty may arise if one wants to separately deduce the two contributions from measurements. Only in special cases with proper combinations of beam polarizations will this be possible, as we shall see. However, a quick estimate will show that the bulk contribution, in the case of strong phase mismatch, is expected to be at most of the same order of magnitude as the surface contribution.

We should remark that the surface nonlinearity here is the total nonlinearity arising from structural and field discontinuities across the surface layer. In this respect, the thickness of the surface layer is somewhat arbitrary. Only the nonlinearity per unit surface area obtained by integrating the nonlinearity through the surface layer comes in as a measurable quantity.

In Sec. II, we shall start from general nonlocal, linear and nonlinear, response functions of a medium to a field rapidly varying in space, and formally establish the existence of a surface nonlinear susceptibility which includes both the dipole contribution from the structural asymmetry in the surface layer and the nonlocal contribution from the rapid field variation across the surface layer. Section III will then describe how the measurable SH signals are related to the surface and bulk nonlinearities. Our aim is to deduce the surface nonlinear susceptibilities from SHG, and hence learn about the surface properties. We therefore would like to find the limitation of the technique in this respect. Section IV will be devoted to a discussion of various problems. Part of the purpose of this paper is to provide some order-of-magnitude estimates on the relative importance of the bulk, surface, and adsorbates in the SHG for various types of interfaces. In the case of adsorbates at an interface, our calculations allow us to predict on which systems monolayers of adsorbates can be easily detected by SHG.

II. SURFACE NONLINEARITY

In this section, we shall show that surface optical nonlinearity at an interface between two media can be characterized by an effective local surface nonlinear susceptibility that includes both local and nonlocal responses of the interface layer to the field. We define the interface layer as follows. In the ideal case where the bulk structures of the media in the two sides of an interface extend all the way to the boundary plane,[5] the overall medium experiences only a sudden structural change at the boundary plane. In real cases, the structure of a medium at a surface or interface is always somewhat different from that of the bulk. The change usually occurs in a few atomic layers near the surface or interface. An interface layer often refers to the region where the structural change from the bulk is significant. Around this region, the optical field along the surface normal changes rapidly from its macroscopic value on one side of the interface to the macroscopic value on the other side of the interface. Then, for our purpose, the interface layer can be defined more generally as the region where both the structure and the field change significantly. The thickness of an interface layer is always much smaller than an optical wavelength. As a result, perturbation calculation can be used to deal with the response of an interface layer to an applied field.[24]

Boundary conditions require that the electrical field components along the interface ($\hat{\mathbf{x}}$-$\hat{\mathbf{y}}$) and the displacement current component along the surface normal ($\hat{\mathbf{z}}$) are continuous across the interface layer. The electric field component E_z along $\hat{\mathbf{z}}$, on the other hand, changes rapidly across the layer. The response of this layer to E_z is therefore expected to be nonlocal. Let the field at frequency ω_i be $E(\mathbf{r},\omega_i)$. We can write, in general, the linear and second-order nonlinear polarizations arising from the nonlocal response of a medium as

$$\begin{aligned}\mathbf{P}^{(1)}(\mathbf{r},\omega_i) &= \int \overleftrightarrow{\chi}^{(1)}(\mathbf{r},\mathbf{r}',\omega_i)\cdot\mathbf{E}(\mathbf{r}',\omega_i)d^3r' ,\\ \mathbf{P}^{(2)}(\mathbf{r},2\omega) &= \int\int \overleftrightarrow{\chi}^{(2)}(\mathbf{r},\mathbf{r}',\mathbf{r}'',2\omega)\cdot\mathbf{E}(\mathbf{r}',\omega)\\ &\quad\times\mathbf{E}(\mathbf{r}'',\omega)d^3r'\,d^3r'' .\end{aligned} \tag{1}$$

In the bulk, we have $\overleftrightarrow{\chi}^{(n)}$ replaced by the bulk value $\overleftrightarrow{\chi}_0^{(n)}$ which is $\overleftrightarrow{\chi}_{01}^{(n)}$ in medium 1 on the $z<0$ side and $\overleftrightarrow{\chi}_{02}^{(n)}$ in medium 2 on the $z>0$ side (see Fig. 1). In the interface layer, we have

$$\begin{aligned}\overleftrightarrow{\chi}^{(1)} &= \overleftrightarrow{\chi}_0^{(1)}+\Delta\overleftrightarrow{\chi}^{(1)} ,\\ \overleftrightarrow{\chi}^{(2)} &= \overleftrightarrow{\chi}_0^{(2)}+\Delta\overleftrightarrow{\chi}^{(2)} .\end{aligned} \tag{2}$$

We should remark that in principle, it is possible to have an interface layer of finite thickness in which $\Delta\overleftrightarrow{\chi}^{(n)}=\overleftrightarrow{0}$ and E_z varies significantly.

We realize that the macroscopic fields and polarizations are obtained from averages of corresponding microscopic quantities over a macroscopic volume. In the interface layer, both E_z and $\mathbf{P}^{(n)}$ can vary rapidly on the atomic scale. Consequently, the definition of a macroscopic quantity is somewhat arbitrary, depending on the averaging volume. However, we know that regardless of the size of the averaging volume, E_z should change smoothly across the interface layer from its macroscopic value in medium 1 to its value in medium 2, and as we shall see later, the surface optical effects generally depend only on the integrated response of the interface layer to the field, that is, $\int \mathbf{P}^{(n)}(z)dz$ integrated across the interface layer.

Let us consider second-harmonic generation from the system in Fig. 1. We write the wave equation for the second-harmonic field in the form

$$\left[\nabla\times(\nabla\times)-\left[\frac{2\omega}{c}\right]^2\overleftrightarrow{\epsilon}_0\right]\cdot\mathbf{E}(2\omega) = -4\pi\left[\frac{2\omega}{c}\right]^2\left[\int\Delta\overleftrightarrow{\chi}^{(1)}(\mathbf{r},\mathbf{r}',2\omega)\cdot\mathbf{E}(\mathbf{r}',2\omega)d^3r' + \int\overleftrightarrow{\chi}^{(2)}(\mathbf{r},\mathbf{r}',\mathbf{r}'',2\omega):\mathbf{E}(\mathbf{r}',\omega)\mathbf{E}(\mathbf{r}'',2\omega)d^3r'd^3r''\right] , \tag{3}$$

assuming that the linear dielectric constant of the bulk is local and given by

$$\overleftrightarrow{\epsilon}_0=\overleftrightarrow{1}+4\pi\int\overleftrightarrow{\chi}_0^{(1)}(\mathbf{r},\mathbf{r}')d^3r' ,$$

that is,

$$\overleftrightarrow{\chi}_0^{(1)}(\mathbf{r},\mathbf{r},\omega_i)=[\overleftrightarrow{\epsilon}_0(\omega_i)-\overleftrightarrow{1}]\delta(\mathbf{r}-\mathbf{r}')/4\pi .$$

In medium 1 $\overleftrightarrow{\epsilon}_0=\overleftrightarrow{\epsilon}_1$, and in medium 2 $\overleftrightarrow{\epsilon}_0=\overleftrightarrow{\epsilon}_2$. The Green's function $\overleftrightarrow{G}(\mathbf{r},\mathbf{r}',2\omega)$ for Eq. (3) is defined to be the solution of the equation

$$[\nabla\times(\nabla\times)-(2\omega/c)^2\overleftrightarrow{\epsilon}_0]\overleftrightarrow{G}=\delta(\mathbf{r}-\mathbf{r}')\overleftrightarrow{1} . \quad (4)$$

The explicit expression of $\overleftrightarrow{G}$ for the present problem is given in Appendix.[24] The solution of Eq. (3) can then be written formally in terms of G. We consider here a system with translational symmetry in the $\hat{\mathbf{x}}$-$\hat{\mathbf{y}}$ plane such that

$$\begin{aligned}\mathbf{E}(\mathbf{r},\omega)&=\mathscr{E}(z,\omega)\exp(ik_xx-i\omega t) ,\\ \mathbf{E}(\mathbf{r},2\omega)&=\mathscr{E}(z,2\omega)\exp(2ik_xx-2i\omega t) ,\\ \mathbf{P}^{(n)}(\mathbf{r},2\omega)&=\mathscr{P}^{(n)}(z,2\omega)\exp(2ik_xx-2i\omega t) .\end{aligned} \quad (5)$$

We then find

$$\begin{aligned}\mathscr{E}(z,2\omega)=&-\int\overleftrightarrow{G}(z,z',2\omega)\cdot4\pi(2\omega/c)^2\\ &\times\left[\int\Delta\overleftrightarrow{\chi}^{(1)}(z',z'',2\omega)\cdot\mathscr{E}(z'',2\omega)\times d^3z''+\mathscr{P}^{(2)}(z',2\omega)\right]dz'\\ \mathscr{P}^{(2)}(z,2\omega)=&\int\overleftrightarrow{\chi}^{(2)}(z,z',z'')\cdot\mathscr{E}(z',\omega)\mathscr{E}(z'',\omega)dz'dz'' .\end{aligned} \quad (6)$$

Because of the possible existence of $\Delta\overleftrightarrow{\chi}^{(2)}$ and the rapid variation of $\mathscr{E}_z$ in the interface layer, $\mathscr{P}^{(2)}$ in the interface layer could be significantly different from that in the bulk. We can decompose $\mathscr{E}(z,2\omega)$ into two parts: one associated with $\mathscr{P}(2\omega)$ in the bulk and the other with $\mathscr{P}(2\omega)$ in the interface region, remembering that the interface layer has a thickness much smaller than an optical wavelength. As shown in Appendix A, the Green's function $\overleftrightarrow{G}$ has the property that $G_{ij}(z,z')$ (for $j\neq z$) or $\epsilon_0(z')G_{iz}(z,z')$ is continuous in z' (we assume, from here on, isotropic ϵ_0 for simplicity). Therefore, in the interface layer, $G_{ij}(z,z')$ for $j\neq z$ and $\epsilon_0(z')G_{iz}(z,z')$ should assume essentially their values at $z'=0$. Equation (6) can then be written as (for $z\neq0$)

$$\begin{aligned}\mathscr{E}_i(z,2\omega)=-4\pi(2\omega/c)^2\Bigg[&\sum_{j=x,y}G_{ij}(z,0)[\mathscr{P}_{sj}^{(1)}(2\omega)+\mathscr{P}_{sj}^{(2)}(2\omega)]+\lim_{z'\to0}[\epsilon_0(z',2\omega)G_{iz}(z,z')][\mathscr{P}_{sz}^{(1)}(2\omega)+\mathscr{P}_{sz}^{(2)}(2\omega)]\\ &+\sum_{j=x,y,z}\int G_{ij}(z,z')\mathscr{P}_{vj}^{(2)}(z',2\omega)dz'\Bigg] .\end{aligned} \quad (7)$$

Here, we recognize that $\mathscr{E}_z(z,2\omega)$ varies rapidly across the interface layer, but can be related to the displacement current component $\mathscr{D}_z$ by defining a function $s(z,2\omega)$ such that

$$\mathscr{E}_z(z,2\omega)=s(z,2\omega)[\mathscr{D}_z(z,2\omega)-4\pi\mathscr{P}_z^{(2)}(z,2\omega)] .$$

Therefore, we have defined the surface polarizations $\mathscr{P}_{sj}^{(n)}$ and the volume polarizations $\mathscr{P}_{vj}^{(2)}$ as

$$\begin{aligned}\mathscr{P}_{sj}^{(1)}(2\omega)&=\int_I\Delta\chi_{jj}^{(1)}(z,z')\mathscr{E}_j(z',2\omega)dz'dz \quad \text{for } j=x,y\\ &=\int_I\epsilon_0^{-1}(z,2\omega)\Delta\chi_{jj}^{(1)}(z,z')s(z',2\omega)\mathscr{D}_z(z',2\omega)dz'dz \quad \text{for } j=z ,\\ \mathscr{P}_{sj}^{(2)}(2\omega)&=\sum_{k,l}\int_I\chi_{jkl}^{(2)}(z,z'z'')\mathscr{E}_k(z',\omega)\mathscr{E}_l(z'',\omega)dz''dz'dz \quad \text{for } j=x,y\\ &=\sum_{k,l}\int_I s(z,2\omega)\chi_{jkl}^{(2)}(z,z',z'')\mathscr{E}_k(z'\omega)\mathscr{E}_l(z'',\omega)dz''dz'dz \quad \text{for } j=z ,\\ \mathscr{P}_{vj}(z,2\omega)&=\int_B\chi_{0,jkl}^{(2)}(z,z',z'')\mathscr{E}_k(z',\omega)\mathscr{E}_l(z'',\omega)dz'\,dz'' ,\end{aligned} \quad (8)$$

where $\int_I$ and $\int_B$ denote integrations across the interface layer and in the bulk, respectively, and we assumed that $\Delta\chi_{ij}^{(1)}$ is diagonal in the coordinates specified. The more general case with $\Delta\chi_{ij}^{(1)}$ being nondiagonal is described in Appendix B. Equation (7), with the help of Eq. (8), shows explicitly that the interface layer contributes to the output SH field through $\mathscr{P}_{sj}^{(1)}$ and $\mathscr{P}_{sj}^{(2)}$, both of which are surface polarizations per unit area. This confirms our earlier assertion that optical effects depend on the integrated response of the interface layer.

Equation (6) or (7) is an integral equation which can be solved iteratively if $\overleftrightarrow{\chi}^{(1)}$ and $\overleftrightarrow{\chi}_0^{(1)}$ are known everywhere. The $\mathscr{P}_{sj}^{(1)}$ term describes the interface contribution to linear reflection and transmission. However, if we are interested only in the field generated by nonlinear wave mixing, it can be shown that the effect of the $\mathscr{P}_{sj}^{(1)}$ term on the solution is only of the order of d/λ, where d is the interface layer thickness. Consequently, we can neglect that term in Eq. (6) or (7) and write

$$\mathscr{E}_i(z,2\omega)=-4\pi(2\omega/c)^2\left[\sum_{j=x,y}G_{ij}(z,0)\mathscr{P}_{sj}^{(2)}(2\omega)+\lim_{z'\to 0}[\epsilon_0(z',2\omega)G_{iz}(z,z')]\mathscr{P}_{sz}^{(2)}(2\omega)+\sum_{j=x,y,z}\int_B G_{ij}(z,z')\mathscr{P}_{vj}^{(2)}(z',2\omega)dz'\right] . \quad (9)$$

We now focus our discussion on the surface nonlinear polarizations $\mathscr{P}_{sj}^{(2)}(2\omega)$. We can define a surface nonlinear susceptibility $\overleftrightarrow{\chi}_s^{(2)}$ by the relation

$$\mathscr{P}_{si}^{(2)}(2\omega)=\sum_{j,k}\chi_{s,ijk}^{(2)}F_j(0,\omega)F_k(0,\omega) ,$$
$$F_j(0,\omega)=\begin{cases}\mathscr{E}_j(0,\omega) & \text{for } j=x,y\\ \mathscr{D}_j(0,\omega) & \text{for } j=z .\end{cases} \quad (10)$$

This is because both the fields $\mathscr{E}_x$, $\mathscr{E}_y$ and the displacement current $\mathscr{D}_z$ are continuous and can be regarded as constant across the interface layer. On the other hand, the field component $\mathscr{E}_z(z,\omega)$ is rapidly varying across the interface layer. Let us define $\mathscr{E}_z(z,\omega)=s(z,\omega)\mathscr{D}_z(0,\omega)$, with $s(z,\omega)$ describing the rapid variation across the interface layer. Then, from Eq. (8), we find, for $i,j,k=x$ or y,

$$\begin{aligned}\chi_{s,ijk}^{(2)}&=\int_I\chi_{ijk}^{(2)}(z,z',z'')dz\,dz'dz'' ,\\ \chi_{s,zjk}^{(2)}&=\int_I[\chi_{zjk}^{(2)}(z,z',z'')s(z,2\omega)]dz\,dz'dz'' ,\\ \chi_{s,ijz}^{(2)}&=\int_I[\chi_{ijz}^{(2)}(z,z',z'')s(z'')]dz\,dz'dz'' ,\\ \chi_{s,izz}^{(2)}&=\int_I\chi_{izz}^{(2)}(z,z',z'')s(z')s(z'')dz\,dz'dz'' ,\\ \chi_{s,zzz}^{(2)}&=\int_I[\chi_{zzz}^{(2)}(z,z',z'')s(z')s(z'')s(z,2\omega)]dz\,dz'dz'' .\end{aligned} \quad (11)$$

This surface nonlinear susceptibility $\overleftrightarrow{\chi}_s^{(2)}$, which has been defined uniquely without arbitrariness,[25] fully characterizes the overall second-order nonlinearity of the interface layer.

The expressions of surface nonlinear susceptibility in Eq. (11) contains the usual dipole and multipole contributions, or in other words, the "local" contribution, which does not depend on the variation of the electric field, and the "nonlocal" contribution, which depends on the rapid variation of the electric field in the interface layer. The usual dipole or local contribution can be identified with

$$\int_I\chi_{ijk}^{(2)}(z,z',z'')\langle S(z',z'')\rangle dz'dz'' ,$$

while the multipole or nonlocal contribution can be identified with

$$\int_I\chi_{ijk}^{(2)}(z,z',z'')[S(z',z'')-\langle S(z',z'')\rangle]dz'dz'' ,$$

where $S(z',z'')$ is either 1 or $s(z')$ or $s(z')s(z'')$ in Eq. (11) and $\langle\ \rangle$ denotes the average over the interface layer. It is seen that if the interface is formed by two media with the same linear dielectric constants, then $E(z)$ is continuous across the interface with $S(z',z'')=1$, and the interface nonlinearity, if present, must originate from the dipole or local contribution.

We can relate our results to those derived by other authors.[4] In the derivation of Bloembergen *et al.*,[4] the structural deviation of the interface from the bulk is neglected with $\Delta\overleftrightarrow{\chi}^{(2)}$ taken as zero, and only the electric quadrupole and magnetic dipole contribution was considered. The sharp variation of the fundamental field component along the surface normal due to mismatch of the dielectric constants at the interface was taken to be responsible for the surface nonlinearity and that of the output field is ignored. In this approximation the expression for a bulk nonlinear polarization $\mathbf{P}^{(2)}(2\omega)$ arising from electric quadrupole and magnetic dipole contribution is $\mathbf{P}^{(2)}(2\omega)=\overleftrightarrow{\alpha}\vdots\mathbf{E}(\omega)\nabla\mathbf{E}(\omega)$, or in terms of nonlocal susceptibilities

$$P_i^{(2)}(z,2\omega)=\int\chi_{ijk}^{(2)}(z,z',z'')E_j(z',\omega)E_k(z'',\omega)dz'dz'' ,$$

with

$$\chi_{ijk}^{(2)}(z,z',z'')=\sum_l\alpha_{ijlk}(z)\delta_j(z'-z)(\delta_k')^l(z''-z) , \quad (12)$$

where δ_i is the Dirac δ function for the ith component, and $(\delta_1')^l$ is its spatial derivation along the l direction. For an isotropic medium, we have

$$P_i^{(2)}(z,2\omega)=(\delta-\beta-2\gamma)[\mathbf{E}(\omega)\cdot\nabla]E_i(\omega)+\beta E_i(\omega)[\nabla\cdot\mathbf{E}(\omega)]+\gamma\nabla_i[E^2(\omega)]$$

and

$$\begin{aligned}\alpha_{ijji}&=\delta-\beta-2\gamma ,\\ \alpha_{iijj}&=\beta ,\\ \alpha_{ijij}&=2\gamma \quad \text{for } i\neq j .\end{aligned} \quad (13)$$

Assuming an infinitely sharp interface between two isotropic media, and using Eq. (11) with

$$s(z,\omega)=\epsilon_1^{-1}(\omega)\Theta(-z)+\epsilon_2^{-1}(\omega)\Theta(z)$$

where Θ is a unit step function, we find the nonvanishing surface nonlinear susceptibility components as

$$\begin{aligned}\chi_{s,zzz}^{(2)}&=\frac{\epsilon_1^2-\epsilon_2^2}{4\epsilon_1\epsilon_2}\left[\frac{\delta_1}{\epsilon_1}+\frac{\delta_2}{\epsilon_2}\right] ,\\ \chi_{s,yzy}^{(2)}&=\chi_{s,xzx}^{(2)}=\frac{\epsilon_1-\epsilon_2}{2\epsilon_1\epsilon_2}(\beta_1+\beta_2) .\end{aligned} \quad (14)$$

[From Eqs. (11) and (12) we notice that in this ideal case, we are dealing with the product of two distribution functions $\chi^{(2)}$ and s, both of which have singularities at $z=0$.

TABLE I. Independent nonvanishing elements of $\overleftrightarrow{\chi}_s^{(2)}(2\omega)$ for surfaces of various symmetry classes (surface is in the $\hat{\mathbf{x}}$-$\hat{\mathbf{y}}$ plane).

Symmetry classes	Location of mirror plane	Independent nonvanishing elements
C_1	No Mirror	xxx, $xxy=xyx$, xyy, yxx, $yxy=yyx$, yyy, $xxz=xzx$, $xyz=xzy$, $yxz=yzx$, $yyz=yzy$, zxx, $zxy=zyx$, zyy, xzz, yzz, $zxz=zzx$, $zyz=zzy$, zzz
C_{1v}	$\hat{\mathbf{y}}$-$\hat{\mathbf{z}}$	$xxy=xyx$, yxx, yyy, $xxz=xzx$, $yyz=yzy$, zxx, zyy, yzz, $zyz=zzy$, zzz
C_2	No mirror	$xxz=xzx$, $xyz=xzy$, $yxz=yzx$, $yyz=yzy$, zxx, zyy, $zxy=zyx$, zzz
C_{2v}	$\hat{\mathbf{x}}$-$\hat{\mathbf{z}}$, $\hat{\mathbf{y}}$-$\hat{\mathbf{z}}$	$xxz=xzx$, $yyz=yzy$, zxx, zyy, zzz
C_3	No mirror	$xxx=-xyy=-yxy=-yyx$ $yyy=-yxx=-xxy=-xyx$ $xxz=xzx=yyz=yzy$, $zxx=zyy$ $xyz=xzy=-yxz=-yzx$, zzz
C_{3v}	$\hat{\mathbf{y}}$-$\hat{\mathbf{z}}$	$yyy=-yzz=-xxy=-xyx$ $xxz=xzx=yyz=yzy$ $xxz=xzx=yyz=yzy$ $zxx=zyy$, zzz
C_4, C_6	No mirror	$xxz=xzx=yyz=yzy$, $zxx=zyy$ $xyz=xzy=-yxz=-yzx$, zzz
C_{4v}, C_{6v} or isotropic	$\hat{\mathbf{x}}$-$\hat{\mathbf{z}}$, $\hat{\mathbf{y}}$-$\hat{\mathbf{z}}$	$xxz=xzx=yzy=yyz$, $zxx=zyy$, zzz

Mathematically such a problem is not well defined; the result will depend on the shape of the functions in the interface layer as the layer thickness approaches to zero. For a crude estimate, however, we can assume $s(z)$ linear in the interface.] Here, the subindices 1 and 2 refer to the two media. In this case, the electric dipole contribution to $\overleftrightarrow{\chi}_s^{(2)}$ has been neglected. When $\epsilon_1=1$ for a vacuum/matter interface, the above expressions reduce to those given by Bloembergen *et al.* in Ref. 5.

There is a total of 18 possible independent elements of the surface susceptibility tensor $\overleftrightarrow{\chi}_s^{(2)}(2\omega)$. The actual number of independent elements, however, can be drastically reduced by the symmetry of the surface or interface layer. In Table I, independent nonvanishing elements of several surface symmetry classes are listed.

III. SECOND HARMONIC GENERATION FROM AN INTERFACE

We have seen in Sec. II that both the interface and the bulk contribute to SHG from a system with an interface. In developing SHG as a surface or interface probe, we need to know how the bulk contribution limits the surface sensitivity of SHG. For clarity in later discussions, we shall first give a full expression of the SH output field from an interface. We assume, for simplicity, a plane interface bonded by two semi-infinite isotropic media. This problem has been solved by other authors with various simplification.[5,7,22,26] The results can be easily extended to more complicated systems.

Let the wave vectors of free SH waves in media 1 and 2 be $\mathbf{K}_1=K_{1x}\hat{\mathbf{x}}-K_{1z}\hat{\mathbf{z}}$ and $\mathbf{K}_2=K_{2x}\hat{\mathbf{x}}+K_{2z}\hat{\mathbf{z}}$, respectively, with $K_1^2=(2\omega)^2\epsilon_1/c^2$, $K_2^2=(2\omega)^2\epsilon_2/c^2$, and $K_{1x}=K_{2x}=2k_x$, where k_x is the x component of the fundamental wave vectors (see Fig. 1). Substitution of the expression of the Green's function in Appendix A into Eq. (7) would yield an explicit expression for the SH field $\mathscr{E}_i(z,2\omega)$. We use the notation

$$\mathscr{P}_{vj}^{(2)}=\sum_{\mathbf{Q}_1} p_{1j}(\mathbf{Q}_1)\exp(i\mathbf{Q}_1\cdot\mathbf{r})$$

in medium 1, and $\mathscr{P}_{vj}^{(2)}=\sum_{\mathbf{Q}_2} p_{2j}(\mathbf{Q}_2)\exp(i\mathbf{Q}_2\cdot\mathbf{r})$ in medium 2 with $K_x=2k_x$. We then find in medium 1

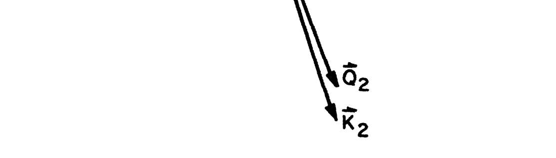

FIG. 1. Geometry of SHG from an interface (shadowed region) between two semi-infinite media. $\mathbf{k}_I$, $\mathbf{k}_R$, and $\mathbf{k}_T$ are the wave vectors for incident, reflected, and transmitted fundamental waves; $\mathbf{Q}_1$ and $\mathbf{Q}_2$ are the wave vectors for the nonlinear polarizations at 2ω induced in media 1 and 2; $\mathbf{K}_1$ and $\mathbf{K}_2$ are the wave vectors for the waves at 2ω in media 1 and 2.

$$\mathscr{E}_y(z)=4\pi(2\omega/c)^2\left[\frac{i}{K_{1z}+K_{2z}}\left[\mathscr{P}^{(2)}_{sy}+i\sum_{Q_2}\frac{p_{2y}(Q_2)}{Q_{2z}+K_{2z}}-i\sum_{Q_1}\frac{p_{1y}(Q_1)(Q_{1z}-K_{2z})}{(Q_{1z}^2-K_{1z}^2)}\right]e^{-iK_{1z}z}+\sum_{Q_1}\frac{p_{1y}(Q_1)}{Q_{1z}^2-K_{1z}^2}e^{iQ_{1z}z}\right],$$

$$\mathscr{E}_x(z)=K_{1z}Me^{-iK_{1z}z}+\frac{4\pi K_{1z}}{\epsilon_1(Q_{1z}^2-K_{1z}^2)}\sum_{Q_1}\left[K_{1z}p_{1x}(Q_1)-\frac{K_xQ_{1z}}{K_{1z}}p_{1z}(Q_1)\right]e^{iQ_{1z}z},$$

$$\mathscr{E}_z(z)=K_xMe^{-iK_{1z}z}+\frac{4\pi K_x}{\epsilon_1(Q_{1z}^2-K_{1z}^2)}\sum_{Q_1}[K_xp_{1z}(Q_1)-Q_{1z}p_{1x}(Q_1)]e^{iQ_{1z}z}-4\pi\epsilon_1^{-1}\sum_{Q_1}p_{1z}(Q_1)e^{iQ_{1z}z}, \tag{15}$$

$$M=\frac{i4\pi K_{2z}}{\epsilon_1K_{2z}+\epsilon_2K_{1z}}\left[\mathscr{P}^{(2)}_{sx}+\frac{\epsilon_2K_x}{K_{2z}}\mathscr{P}^{(2)}_{sz}-\sum_{Q_2}\frac{+K_{2z}p_{2x}(Q_2)+K_xp_{2z}(Q_2)}{iK_{2z}(Q_{2z}+K_{2z})}\right.$$
$$\left.+\sum_{Q_1}\left[\frac{\epsilon_1K_{2z}Q_{1z}-\epsilon_2K_{1z}^2}{i\epsilon_1K_{2z}(Q_{1z}^2-K_{1z}^2)}p_{1x}(Q_1)+\frac{K_x(\epsilon_2Q_{1z}-\epsilon_1K_{2z})}{i\epsilon_1K_{2z}(Q_{1z}^2-K_{1z}^2)}p_{1z}(Q_1)\right]\right],$$

where all ϵ_i's are at 2ω. Similar expressions can be obtained for $\mathscr{E}_i(z)$ in medium 2. For the vacuum/matter interface, $\epsilon_1=1$ and $\epsilon_2=\epsilon$, and the above expressions for $\mathscr{E}_i(z)$ reduce to those given in Ref. 5.

It can be seen from Eq. (15) that even if SHG in the bulk has a phase mismatch as large as $\Delta k\sim 1/\lambda$, where λ is the optical wavelength, the bulk contribution to $\mathscr{E}_i$ as compared to the interface contribution is a factor of $|\mathscr{P}_v|\lambda/2\pi|\mathscr{P}_s|$ larger. When the bulk medium has no center of symmetry, we expect $|\mathscr{P}_v|\sim|\mathscr{P}_s/d|$ with d being the interface layer thickness, and then $|\mathscr{P}_v|\lambda/2\pi|\mathscr{P}_s|\sim\lambda/2\pi d\gg 1$. This shows that in such media, SHG from the interface would be overwhelmed by that from the bulk. For this reason, surface studies with SHG are often restricted to media with centrosymmetry. In this latter case, the bulk nonlinear polarization arises from the electric quadrupole and magnetic dipole terms given in Eq. (13) for an isotropic medium. Let the incoming fundamental field from medium 1 be $\mathbf{E}_I(z,\omega)=\mathscr{E}_I(\omega)\exp(ik_xx+ik_{1z}z-i\omega t)$, which creates a reflected wave $\mathbf{E}_R(z,\omega)=\mathscr{E}_R(\omega)\exp(ik_xx-ik_{1z}z-i\omega t)$, in medium 1 and a transmitted wave, $\mathbf{E}_T(z,\omega)=\mathscr{E}_T(\omega)\exp(ik_xx+ik_{2z}z-i\omega t)$ in medium 2. Equation (15) for the SH field in medium 1 then becomes

$$\mathscr{E}_y(z,2\omega)=i4\pi\left[\frac{2\omega}{c}\right]^2\frac{1}{(K_{1z}+K_{2z})}\left[\left[2\chi^{(2)}_{s,yzy}+\frac{K_{2z}k_{2z}}{K_{1z}^2\epsilon_1'\epsilon_2'}(\epsilon_2'-\epsilon_1')(\delta_1-\beta_1-2\gamma_1)\right]\mathscr{D}_z(0,\omega)\mathscr{E}_y(0,\omega)e^{-iK_{1z}z}\right.$$
$$\left.-\frac{k_{2z}(\epsilon_2'-e_1')}{K_{1z}^2\epsilon_1'\epsilon_2'}(\delta_1-\beta_1-2\gamma_1)\mathscr{D}_z(0,\omega)\mathscr{E}_y(0,\omega)\right],$$

$$\mathscr{E}_x(z,2\omega)=K_{1z}Me^{-iK_{1z}z}-4\pi i\frac{K_x}{\epsilon_1}\gamma_1(\mathscr{E}_Ie^{ik_{1z}z}+\mathscr{E}_Re^{-ik_{1z}z})^2-4\pi i\epsilon_1^{-1}N\mathscr{D}_z^2(0,\omega),$$

$$\mathscr{E}_z(z,2\omega)=K_xMe^{-iK_{1z}z}-4\pi i\frac{2k_{1z}}{\epsilon_1}\gamma_1(\mathscr{E}_I^2e^{i2k_{1z}z}-\mathscr{E}_R^2e^{-i2k_{1z}z}), \tag{16}$$

$$M=\frac{i4\pi K_{2z}}{(\epsilon_1K_{2z}+\epsilon_2K_{1z})}\left[2\chi^{(2)}_{s,yzy}\mathscr{E}_x(0,\omega)\mathscr{D}_z(0,\omega)+\frac{\epsilon_2K_x}{K_{2z}}\left[\chi^{(2)}_{s,zzz}-\frac{\gamma_2}{\epsilon_2(\epsilon_2')^2}+\frac{\gamma_1}{\epsilon_1(\epsilon_1')^2}\right]\mathscr{D}_z^2(0,\omega)\right.$$
$$\left.+\frac{\epsilon_2K_x}{K_{2z}}\left[\chi^{(2)}_{s,zxx}-\frac{\gamma_2}{\epsilon_2}+\frac{\gamma_1}{\epsilon_1}\right][\mathscr{E}_x^2(0,\omega)+\mathscr{E}_y^2(0,\omega)]+\frac{\epsilon_2}{\epsilon_1K_{2z}}N\mathscr{D}_z^2(0,\omega)\right],$$

$$N=\tfrac{1}{2}(\epsilon_1'-\epsilon_2')\frac{1}{(\epsilon_1')^2(\epsilon_2')^2K_x}\left[\epsilon_1'\epsilon_2'\left[\frac{2\omega}{c}\right]^2-K_x^2(\epsilon_1'+\epsilon_2')\right](\delta_1-\beta_1-2\gamma_1),$$

where ϵ_i and ϵ_1' denote the dielectric constants at frequencies 2ω and ω, respectively, and $\mathscr{E}_x(0,\omega)$, $\mathscr{E}_y(0,\omega)$, and $\mathscr{D}_z(0,\omega)$ are fundamental field and displacement current components at $z=0$ given by

$$\mathscr{E}_x(0,\omega)=\mathscr{E}_{Ix}(0,\omega)+\mathscr{E}_{Rx}(0,\omega),$$
$$\mathscr{E}_y(0,\omega)=\mathscr{E}_{Iy}(0,\omega)+\mathscr{E}_{Ry}(0,\omega), \tag{17}$$
$$\mathscr{D}_z(0,\omega)=\epsilon_1'[\mathscr{E}_{Iz}(0,\omega)+\mathscr{E}_{Rz}(0,\omega)].$$

The $(\delta_1-\beta_1-2\gamma_1)$ terms in Eq. (16) arise from interference between the incident and reflected fundamental fields in medium 1.

Equation (16) shows that even if we consider the ideal case with $\overleftrightarrow{\chi}_s^{(2)}$ given by Eq. (14) and the electric dipole contribution to $\overleftrightarrow{\chi}_s^{(2)}$ neglected, the bulk contribution to SHG from centrosymmetric media is at most of the same order of magnitude as the interface contribution. In the case of media with high dielectric constants, the interface contribution should actually dominate, as we shall discuss in more detail later.

In the expressions of Eq. (16), each field component consists of two parts: one is a free wave proportional to $\exp(iK_{1z}z)$; the other is a group of driven waves with different wave vectors generated in the bulk. These two parts can be experimentally distinguished from their different directions for propagation. We are only interested in the former which contains the interface contribution. The various terms in the free wave can be distinguished by different combinations of beam polarizations and the dependence of the SH signal on the incidence angle. For example, by detecting the $\hat{\mathbf{s}}$-polarized (along $\hat{\mathbf{y}}$) SH signal with known fundamental fields along $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ for different incidence angles, the quantities $\chi^{(2)}_{s,yzy}=\chi^{(2)}_{s,xzx}$ and $(\delta_1-\beta_1-2\gamma_1)$ can be deduced separately. In many cases, such as the case of a gas for medium 1, $(\delta_1-\beta_1-2\gamma_1)$ is negligible compared to $\chi^{(2)}_{s,xzx}$. By detecting the $\hat{\mathbf{p}}$-polarized SH output (in the $\hat{\mathbf{x}}$-$\hat{\mathbf{z}}$ plane) with an $\hat{\mathbf{s}}$-polarized fundamental input, $(\chi^{(2)}_{s,zxx}-\gamma_2/\epsilon_2+\gamma_1/\epsilon_1)$ can be deduced. Finally, by detecting $\hat{\mathbf{p}}$-polarized output at 2ω with $\hat{\mathbf{p}}$-polarized input at ω,

$$[\chi^{(2)}_{s,zzz}-\gamma_2/\epsilon_2(\epsilon_2')^2+\gamma_1/\epsilon_1(\epsilon_1')^2]$$

can be deduced.

Separate determination of the surface susceptibilities $\chi^{(2)}_{s,zxx}$ and $\chi^{(2)}_{s,zzz}$ from the bulk nonlinear constants γ_1 and γ_2 seems impossible from the above results. However, it can be achieved with a more complicated arrangement. As an example, consider an air/liquid or air/solid interface. If we use two orthogonally polarized fundamental input beams with slightly different frequencies, propagating collinearly in the condensed matter (medium 2), the sum-frequency bulk nonlinear polarization will vanish according to Eq. (13). Then only the surface nonlinearity should contribute to the sum-frequency signal. By choosing different polarization contributions while keeping the polarizations of two fundamental beams orthogonal, all the nonvanishing surface susceptibility elements $\chi^{(2)}_{s,ijk}$ can be measured.

In the case of a crystalline medium, both the surface and the bulk nonlinearities could acquire some anisotropic terms but separate determination of the surface and bulk anisotropic terms is possible from measurements of SHG with a few different crystalline surfaces. This has been demonstrated in Si.[11] With a somewhat more complicated arrangement, it is also possible to eliminate the bulk anisotropic contribution while measuring the surface anisotropy. For example, for a Si(111)-1×1 or 7×7 surface, both the surface and the bulk have a $3m$ symmetry.[16] The surface and bulk anisotropic terms in the nonlinear polarizations are, respectively,

$$\mathscr{P}^{(2)}_{SA}=\chi^{(2)}_{S,xxx}\sum\hat{\xi}E_\xi(\omega)E_\xi(\omega)$$

and

$$\mathbf{P}^{(2)}_{VA}=\zeta\sum\hat{\alpha}E_\alpha\nabla_\alpha E_\alpha\ ,$$

where $\hat{\xi}$'s are along the directions of the projected [111] axes on the surface, and $\hat{\alpha}$'s are along the principal axes of the zinc-blende crystal. To make $\mathbf{P}^{(2)}_{VA}$ vanish, we can employ two counter-propagating fundamental beams in Si. A Brewster angle of incidence with $\hat{\mathbf{p}}$ polarization can be used to eliminate the interference effect due to reflection of the fundamental beam into the Si bulk. The three-fold symmetry thus observed in SHG should arise entirely from the surface anisotropy.

In practical applications of SHG as a surface probe, one would hope to use the simplest arrangement with a single fundamental pump beam. In those cases, the SH signal comprises, in general, both surface and bulk contributions. In order to deduce the interface properties from SHG, the surface nonlinearity should dominate the bulk nonlinearity or one should have the interface modulated and the corresponding change of the SH signal detected. We shall give a general discussion on this subject in Sec. IV.

IV. DISCUSSION

We are interested in deducing surface or interface information from SHG. This means that we need to be able to deduce $\overleftrightarrow{\chi}^{(2)}_S$, or $\Delta\overleftrightarrow{\chi}^{(2)}_S$ due to interface modulation, from the measured SH signal. As we have seen, the situation could be complicated by bulk contribution to SHG even in media with centrosymmetry. With a simple arrangement, it is generally not possible to completely suppress the bulk contribution. Fortunately, in all cases the bulk contribution is at most of the same order of magnitude as the surface contribution. In many cases, the surface contribution actually dominates. In developing SHG as a surface probe, it is important to have some feeling about the circumstances under which we can obtain useful information on an interface.

Let us consider interfaces between air and various types of condensed matter. The fundamental beam is incident from the air side, and we have, in Eq. (16), $\delta_1=\beta_1=\gamma_1=0$. Then, from Eq. (16), the ratio of surface to bulk contribution to the SH output field is always larger than $|\chi^{(2)}_S\epsilon_2/\gamma_2|$. For a crude estimate, if we assume an ideal interface with $\overleftrightarrow{\chi}^{(2)}_S$ given by Eq. (14) and $\delta_2\sim\beta_2\sim\gamma_2$, we find $|\chi^{(2)}_S\epsilon_2/\gamma_2|\sim\epsilon_2-1$. This shows that in the case of centrosymmetric media with high dielectric constants such as metals and semiconductors ($\epsilon_2>10$), the surface contribution to SHG should dominate. On the other hand, in the case of insulators and liquids with $\epsilon_2\sim3$, the bulk contribution may still be appreciable.

It may be useful to give some typical values of the SH signal strength for various systems. Let the pump beam be a 10-nsec laser pulse at 1.06 μm with 20-mJ energy and 1-cm^2 cross section. The SH signal from a metal or semiconductor surface is of the order of 10^3 photons per pulse.[11,15,17,22,23] This corresponds to $|\chi^{(2)}_S|$ is $\sim10^{-15}$ esu. The signal from an insulator surface is generally much weaker, or the order of 10 photons per pulse. the corresponding $|\chi^{(2)}_S|$ is $\sim10^{-16}$ esu.[14,23] The structural asymmetry of the surface layer often contributes roughly as much to $|\chi^{(2)}_S|$ as the field discontinuity at the surface. This can be demonstrated by comparing the SH signals from an air/solid interface and an index matched liquid/solid interface;[27] the field discontinuity is absent in the latter case.

Measurements of $\overleftrightarrow{\chi}_S^{(2)}$ could provide some useful information about the symmetry and electronic structure of a surface layer.[16] However, SHG as a surface tool is probably more useful for probing of surface modification. For example, melting of a surface layer can be readily detected by SHG.[20,28] It has also been established that SHG is a viable method to detect adsorbates on a wide variety of interfaces.[8–10,13–18] In these cases, one measures the change in $\overleftrightarrow{\chi}_S^{(2)}$ in response to the surface modification. By using some nulling method for background cancellation,[14] it is possible to detect a $|\Delta\overleftrightarrow{\chi}_S^{(2)}|$ appreciably smaller than $|\overleftrightarrow{\chi}_S^{(2)}|$. For this reason, SHG can be a very sensitive technique for studies of surface modification.

A submonolayer of atoms or molecules on a surface would change $\overleftrightarrow{\chi}_S^{(2)}$ to $(\overleftrightarrow{\chi}'_S)^{(2)}$. One can express $(\overleftrightarrow{\chi}'_S)^{(2)}$ as

$$(\overleftrightarrow{\chi}'_S)^{(2)}=\overleftrightarrow{\chi}_S^{(2)}+\overleftrightarrow{\chi}_A^{(2)}+\overleftrightarrow{\chi}_I^{(2)} , \qquad (18)$$

where $\overleftrightarrow{\chi}_A^{(2)}$ denotes the nonlinear susceptibility of the same layer of adsorbates placed far away from the surface, and $\overleftrightarrow{\chi}_I^{(2)}$ is the nonlinear susceptibility resulting from interaction of the layer of adsorbates with the surface. For sensitive detection of adsorbates, we need either $|\overleftrightarrow{\chi}_A^{(2)}|$ or $|\overleftrightarrow{\chi}_I^{(2)}|$ to be sufficiently large. In the case of metals and semiconductors, $|\overleftrightarrow{\chi}_S^{(2)}|$ is quite large, and therefore a layer of adsorbates that interacts with the surface and changes the surface properties is expected to also yield an appreciable $|\overleftrightarrow{\chi}_I^{(2)}|$. Thus, a submonolayer of adsorbates can be observed through $|\overleftrightarrow{\chi}_I^{(2)}|$ even though the intrinsic nonlinear susceptibility of the adsorbates $|\overleftrightarrow{\chi}_A^{(2)}|$ may be small. Indeed, it has been found that submonolayers of atoms and small molecules on metal and semiconductor surfaces can be easily detected. In the case of insulators, $|\overleftrightarrow{\chi}_S^{(2)}|$ is relatively small, and the change due to interaction with adsorbates, $|\overleftrightarrow{\chi}_I^{(2)}|$, could be even smaller. When this is the case, in order for the adsorbates to be easily detected, the intrinsic nonlinear susceptibility of the adsorbates, $|\overleftrightarrow{\chi}_A^{(2)}|$, must be sufficiently large. Again, this agrees with our general finding that irrespective of strong or weak molecule/surface interaction, only molecules with relatively large nonlinearity can be easily observed by SHG on an insulator surface. The above discussion suggests that SHG will be most useful for studying molecule/surface interaction on metal and semiconductor surfaces, and for studying behavior of individual molecules or groups of molecules on insulator surfaces.

V. CONCLUSION

We have shown from a formal derivation that both structural asymmetry and field discontinuity at an interface contribute to the second-order optical nonlinearity of the interface. If the refractive indices of the bonded media are not matched, the optical field component along the surface normal varies rapidly across the interface layer. Consequently, the optical response of the interface layer is nonlocal. It involves not only the electric dipole contribution, but also all the multipole contributions. As far as SHG from an interface is concerned, however, one can show that the nonlinear response of the interface layer can be described effectively by a local surface nonlinear polarization. The interface nonlinearity is then represented by a local (or electric dipole allowed) surface nonlinear susceptibility tensor.

Measurement of SHG from the interface allows us to deduce the surface nonlinear susceptibility. The bulk nonlinearity may complicate the measurement. It is however much weaker, especially in media with a large dielectric constant. Surface modification can be monitored by observing the induced change in the surface nonlinear susceptibility. A monolayer of atoms or molecules chemically adsorbed on centrosymmetric metals or semiconductors should be readily detectable. On insulator surfaces, on the other hand, easy detection of molecular adsorbates would require molecules with sufficiently large intrinsic nonlinearity unless chemical adsorption of the molecules results in the establishment of highly nonlinear bonds between the molecules and the surface.

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APPENDIX A

Here we give a brief description of the Green's functions used in this paper. A thorough derivation can be found in Ref. 24.

The Green's functions obey Eq. (4) in Sec. II. For the s-polarized field, Eq. (4) for the relevant Green's function G_{yy} has the form

$$\left[\frac{d^2}{dz^2}-k_x^2+(2\omega/c)^2\epsilon_0(z)\right]G_{yy}(z,z')=\delta(z-z') , \qquad (A1)$$

the solution of which is

$$G_{yy}(z,z')=\frac{1}{2iK_{2z}}(1+R_s^0)[\Theta(z-z')U_y(z)V_y(z') + \Theta(z'-z)V_y(z)U_y(z')] , \qquad (A2)$$

where

$$R_s^0=(K_{1z}-K_{2z})/(K_{1z}+K_{2z})$$

is the usual Fresnel reflection coefficient for the s-polarized light, and $U_y(z)$ and $V_y(z)$ are the two linearly independent solutions for light incident from medium 1 and medium 2, respectively. Therefore,

$$U_y(z)=\begin{cases}\exp(iK_{1z}z)+R_s^0\exp(-iK_{1z}z) , & z<0\\ \exp(iK_{2z})(1+R_s^0) , & z>0\end{cases} \qquad (A3)$$

$$V_y(z)=\begin{cases}\exp(-iK_{1z}z)(1-R_s^0) , & z<0\\ \exp(-iK_{2z}z)-R_s^0\exp(iK_{2z}z) , & z>0 .\end{cases} \qquad (A4)$$

For the p-polarized light, because E_x and E_z are coupled, the corresponding Green's functions are determined by four coupled equations presented here in the matrix form as

$$\begin{bmatrix} \frac{d^2}{dz^2}+\left[\frac{2\omega}{c}\right]^2\epsilon_0(z) & -iK_x\frac{d}{dz} \\ -iK_x\frac{d}{dz} & \left[\frac{2\omega}{c}\right]^2\epsilon_0(z)-K_x^2 \end{bmatrix} \begin{bmatrix} G_{xx}(z,z') & G_{xz}(z,z') \\ G_{zx}(z,z') & G_{zz}(z,z') \end{bmatrix} = \delta(z-z')\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} . \quad (A5)$$

The solution of Eq. (A5) is

$$\begin{aligned} G_{xx}(z,z') &= \alpha[\Theta(z-z')U_x(z)V_x(z')+\Theta(z'-z)V_x(z)U_x(z')] , \\ G_{zx}(z,z') &= -\alpha[\Theta(z-z')U_x(z)V_z(z')+\Theta(z'-z)V_z(z)U_x(z')] , \\ G_{xz}(z,z') &= -\alpha[\Theta(z-z')U_x(z)V_z(z')+\Theta(z'-z)V_x(z)U_z(z')] , \\ G_{zz}(z,z') &= -\alpha\{[\Theta(z-z')U_z(z)V_z(z)+\Theta(z'-z)V_z(z')U_z(z')]-[1/\epsilon_0(z)][c^2/\alpha(2\omega)^2\delta(z-z')]\} , \end{aligned} \quad (A6)$$

where

$$\alpha=-\frac{i(\epsilon_2K_{1z}+\epsilon_1K_{2z})}{4\epsilon_1\epsilon_2(2\omega)^2/c^2} \quad (A7)$$

and

$$U_x(z)=\begin{cases} \exp(iK_{1z}z)-R_p^0\exp(-iK_{1z}z) , & z<0 \\ (1-R_p^0)\exp(-iK_{1z}z) , & z>0 \end{cases} \quad (A8)$$

$$V_x(z)=\begin{cases} (1+R_p^0)\exp(-iK_{2z}z) , & z<0 \\ \exp(-iK_{2z}z)+R_p^0\exp(iK_{2z}z) , & z>0 \end{cases} \quad (A9)$$

and

$$\left.\begin{matrix} U_z(z) \\ V_z(z) \end{matrix}\right\} = \frac{iK_x}{(2\omega/c)^2\epsilon_0(z)-K_x^2}\frac{d}{dz}\times\left\{\begin{matrix} U_x(z) \\ V_x(z) \end{matrix}\right. . \quad (A10)$$

R_p^0 is the usual Fresnel reflection coefficient for the p-polarized light:

$$R_p^0=\frac{\epsilon_2K_{1z}-\epsilon_1K_{2z}}{\epsilon_2K_{1z}+\epsilon_1K_{2z}} . \quad (A11)$$

From these expressions, the continuity property of $G_{xx}(z,z')$, $\epsilon_0(z)G_{zx}(z,z')$, $G_{xz}(z,z')\epsilon_0(z')$, and $\epsilon_0(z)G_{zz}(z,z')\epsilon_0(z')$ at $z'=0$ used in Sec. II can easily be verified.

APPENDIX B

If $\chi_{ij}^{(1)}$ is nondiagonal in the specified (x,y,z) coordinates, we can define

$$\mathcal{E}(z)=\overleftrightarrow{S}(z)\cdot\mathcal{E}_{\text{eff}}(z)$$

with

$$\overleftrightarrow{S}=\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ s_{zx} & s_{zy} & s_{zz} \end{bmatrix}$$

and

$$\mathcal{E}_{\text{eff}}=\begin{bmatrix} \mathcal{E}_x \\ \mathcal{E}_y \\ \mathcal{D}_z \end{bmatrix} .$$

By writing

$$\overleftrightarrow{\epsilon}_0^{-1}=\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \epsilon_0^{-1}(z) \end{bmatrix}$$

we can show that Eq. (7) in the text is still valid if we define

$$\mathcal{P}_s^{(1)}(2\omega)=\int_I\overleftrightarrow{\epsilon}_0^{-1}(z,2\omega)\Delta\overleftrightarrow{\chi}^{(1)}(z,z',2\omega)\cdot\overleftrightarrow{S}(z',2\omega)\cdot\mathcal{E}_{\text{eff}}(z')dz'dz ,$$

$$\mathcal{P}_s^{(2)}(2\omega)=\int_I\overleftrightarrow{\epsilon}_0^{-1}(z,2\omega)[1-4\pi\Delta\overleftrightarrow{\chi}^{(1)}(z,z',2\omega)\cdot\overleftrightarrow{S}'(z',2\omega)]\cdot\overleftrightarrow{\chi}^{(2)}(z,z',z'')\cdot\mathcal{E}(z',\omega)\mathcal{E}(z'',\omega)dz''dz'dz$$

$$\overleftrightarrow{S}'(z',2\omega)=\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & s_{zz} \end{bmatrix} .$$

The above equations reduce to those in Eq. (8) when $\Delta\chi_{ij}^{(1)}$ becomes diagonal.

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