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Sum-frequency generation on isotropic surfaces: General phenomenology and microscopic theory for jellium surfaces

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The theory of sum-frequency generation (SFG) upon reflection from isotropic media is considered. The emitted SFG radiation is expressed in terms of four bulk (quadrupole-allowed) and four surface nonlinear polarizabilities. These parameters are evaluated for the jellium surface.

I. INTRODUCTION

Optical second-order nonlinear phenomena[1,2] (three-wave mixing, $\omega_1 + \omega_2 = \omega_3$) are particularly suitable for studies of boundaries of centrosymmetric media because of their intrinsic surface (interface) sensitivity.[2,3] The degenerate ($\omega_1 = \omega_2$) three-wave mixing, surface second-harmonic generation (SHG), has been a focus of many experimental[2,3] and theoretical[4–12] studies during the last three decades. SHG has been shown to be a powerful tool to study symmetry, electronic and magnetic properties, fast surface dynamics, and other characteristics of surfaces and buried interfaces. The SHG spectroscopy, i.e., measurements of the SHG intensity in a wide frequency range, is especially effective because it allows one to probe different electronic resonances of surfaces and interfaces. Since 1987 the nondegenerate ($\omega_1 \neq \omega_2$) three-wave mixing, sum-frequency generation (SFG) spectroscopy, has also been introduced in surface science by Shen *et al.*[13] and Harris *et al.*[14] One of the fundamental frequencies is often chosen to be in the middle infrared range,[13–22] which allows one to obtain information about vibrations of adsorbed molecules, while keeping the intrinsic surface sensitivity of the three-wave mixing. SFG has other advantages in comparison with SHG. For example, the resonant structure of the SHG response can be caused by resonances at either the fundamental or the second-harmonic frequency. The possibility of independent variations of two fundamental frequencies in SFG allows the origin of surface resonances to be clarified.[23] An interesting application of doubly resonant infrared-visible SFG (two frequencies coincide with molecular resonances) has been recently proposed to study electron-vibration coupling in adsorbates.[24]

One of the most difficult problems in applications of the nonlinear optical techniques for surface-science studies is the lack of detailed microscopic understanding of the physical processes that are involved in the nonlinear interactions at boundaries. On metal surfaces, for example, it took more than 20 years for both theory and experiment to converge their results for SHG even for simple metal surfaces. Theoretical results by Weber and Liebsch,[9] Chizmeshya and Zaremba,[10] and Liebsch and Schaich[11] on jellium surfaces have demonstrated importance of the normal component (χ_{zzz}) of the surface nonlinearity in SHG. This element has been found to be the most surface sensitive among the isotropic surface terms. Experimental results by Murphy *et al.*[25] and Janz *et al.*[26] on well-characterized clean Al surfaces were found to agree with the most accurate theoretical models.[9–11] Also, the effect of alkali-metal overlayers and some other adsorbed species on the SHG response from simple metal surfaces has been qualitatively understood[27,28] within the jellium model. Recently, a similar semiquantitative agreement was achieved in interpretation of the rotational anisotropy of SHG on Al surfaces.[29] The important result of recent developments in theory of SHG on metal surfaces is that the leading isotropic term, χ_{zzz}, and the anisotropic term, χ_{xxx}, are sensitive to different aspects of the surface structure,[9–11,29] which allows SHG to be used for a selective characterization of metal surfaces. In spite of a rather large amount of remaining problems that must be solved, the progress in this field is obvious. In contrast, the theoretical description of SFG upon reflection from the boundary of centrosymmetric media is still in its infancy. Theoretical results may help to understand better the experimental data, to raise important questions, and to optimize future experiments. First of all, it is necessary to develop a general phenomenological theory of SFG. Using this theory, it should be possible to conduct measurements with the aim of finding the actual magnitude of different nonlinear polarizability components for real systems. As the second step, the microscopic calculations of these nonlinear parameters should be performed in order to find the relation of these parameters to the surface microscopic structure.

This paper is an attempt to provide such a systematic theoretical investigation of SFG, in the present case to SFG at isotropic surfaces. The theoretical considerations can be extended later to more sophisticated surface calculations, which may include the anisotropic surface properties and other physical effects. The paper consists of two main parts. A general phenomenological consideration of SFG is presented in Sec. II. The radiated SFG outgoing field is expressed in terms of the surface and bulk nonlinear polarizabilities. Based on the most recent developments of the microscopic theory of SHG, these

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nonlinear parameters are evaluated in Sec. III for the jellium surface. The results are illustrated in Sec. IV on a practical example, and the conclusions and outlook are given in Sec. V.

II. PHENOMENOLOGICAL TREATMENT OF SFG

Figure 1 shows the reflection geometry that is commonly used in SFG experiments. Two laser beams of frequencies ω_1 and ω_2 are incident on the surface at angles θ_1 and θ_2. We assume that the upper medium is linear with dielectric constant $\epsilon(\omega) = 1$, so that the nonlinear interactions take place only in the lower media and the interface region. For compactness, the dielectric constants in the bulk of the nonlinear medium at the fundamental frequencies ω_1, ω_2, and the sum frequency $\omega_3 = \omega_1 + \omega_2$ are denoted as ϵ_1, ϵ_2, and ϵ_3, respectively. Both fundamental beams and the surface normal are considered to be in the same plane (plane of incidence). The linear and nonlinear properties are assumed to be uniform in the direction parallel to the surface plane, so that the reflection condition for the outgoing wave at ω_3 is[1–3]

$$\omega_3 \sin\theta_3 = \omega_1 \sin\theta_1 + \omega_2 \sin\theta_2 \,, \tag{2.1}$$

where θ_3 is the reflection angle shown in Fig. 1. Note the difference in definition of the sign of incident and reflected angles. While θ_1 and θ_2 are positive on the left-hand side, θ_3 is positive on the right-hand side.

This section is divided into two parts. In the first the bulk (quadrupole-allowed) nonlinear polarizabilities are introduced phenomenologically for the isotropic media. The outgoing field, which arises from the bulk, is calculated as a function of linear [the dielectric function $\epsilon(\omega)$] and nonlinear parameters. The second part is devoted to the discussion of the surface contribution to SFG. The surface nonlinear parameters are introduced and the radiated field at the sum frequency is evaluated.

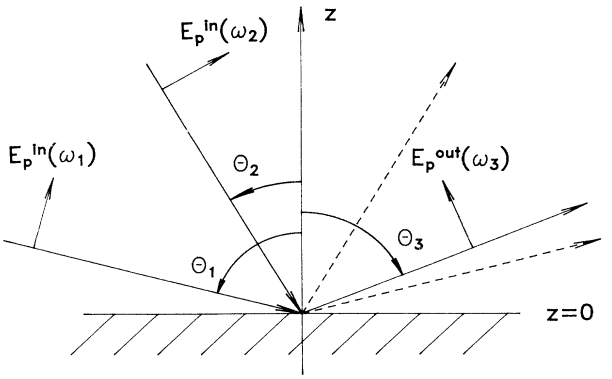

FIG. 1. Sketch of sum frequency generation in reflection from an interface between a linear medium at $z > 0$ and a nonlinear centrosymmetric medium at $z < 0$. The directions of the electric field for *p*-polarized components of two (incident) fundamental and (outgoing) SFG beams are shown. Dashed arrows display the directions of mirror reflection of the fundamental beams.

A. Bulk SFG contribution

In the uniform bulk, i.e., deep enough into the nonlinear medium, the effect of the surface on optical polarizabilities can be neglected and the medium considered as infinite. In most cases, the bulk optical response can be written in terms of the multipole expansion because of a slow variation of optical fields within the nonlocal length. For the nonlinear polarization at the SFG frequency $\mathbf{P}^B(\omega_3)$ this expansion takes the form[2]

$$\begin{aligned} P_i^B(\omega_3) = {} & \chi^d_{ijk}(\omega_1,\omega_2) E_j(\omega_1) E_k(\omega_2) \\ & + \chi^Q_{ijkl}(\omega_1,\omega_2) E_j(\omega_1) \nabla_k E_l(\omega_2) \\ & + \chi^Q_{ijkl}(\omega_2,\omega_1) E_j(\omega_2) \nabla_k E_l(\omega_1) + \cdots \,, \end{aligned} \tag{2.2}$$

where $\chi^d_{ijk}(\omega_1,\omega_2)$ is the dipole (local) second-order polarizability, $\chi^Q_{ijkl}(\omega_1,\omega_2)$ describes the quadrupole (first order in nonlocality) contribution, etc. Note the difference in dipole and quadrupole terms in Eq. (2.2): In $\chi^d_{ijk}(\omega_1,\omega_2)$ the field indices and the frequency arguments can be interchanged, i.e., $\chi^d_{ijk}(\omega_1,\omega_2) \equiv \chi^d_{ikj}(\omega_2,\omega_1)$. On the other hand, the same role cannot be applied to the quadrupole term because of the presence of the gradient operator. For centrosymmetric media, the first term in Eq. (2.2) vanishes because of symmetry, but the second one can contribute to $\mathbf{P}^B(\omega_3)$.[2,3]

The fundamental field in the nonlinear medium can be taken as a sum of plane waves

$$\mathbf{E}(\mathbf{r},\omega_\alpha) = \mathbf{E}^T_\alpha \, e^{i\mathbf{q}_\alpha \cdot \mathbf{r}} \,, \tag{2.3}$$

where $\alpha = 1, 2$. The components of the (generally complex) amplitudes $\mathbf{E}^T_\alpha$ and (complex) wave vectors $\mathbf{q}_\alpha$ of the transmitted waves in Eq. (2.8) are given by the usual Fresnel expressions (for metals at frequencies not equal to the bulk plasma frequency)

$$E^T_z(\omega_\alpha) = F_p(\omega_\alpha)\, \sin\theta_\alpha \, E^{\rm in}_p(\omega_\alpha) \,, \tag{2.4a}$$

$$E^T_x(\omega_\alpha) = F_p(\omega_\alpha)\, s_\alpha \, E^{\rm in}_p(\omega_\alpha) \,, \tag{2.4b}$$

$$E^T_y(\omega_\alpha) = F_s(\omega_\alpha)\, E^{\rm in}_s(\omega_\alpha) \,, \tag{2.4c}$$

$$q_{\alpha,x} = \frac{\omega_\alpha}{c} \sin\theta_\alpha, \tag{2.4d}$$

$$q_{\alpha,z} = -\frac{\omega_\alpha}{c} s_\alpha, \tag{2.4e}$$

where

$$F_p(\omega_\alpha) = \frac{2\cos\theta_\alpha}{\epsilon_\alpha \cos\theta_\alpha + s_\alpha} \,, \tag{2.4f}$$

$$F_s(\omega_\alpha) = \frac{2\cos\theta_\alpha}{s_\alpha + \cos\theta_\alpha}\,, \tag{2.4g}$$

$$s_\alpha = \sqrt{\epsilon_\alpha - \sin^2\theta_\alpha}\,. \tag{2.4h}$$

The wave in the reflected direction, which is radiated by a given polarization $\mathbf{P}^B(\omega)$ in the bulk of a semi-infinite medium, was first calculated by Bloembergen and Pershan.[1] Following Ref. 1, the reflected wave at the SFG frequency can be written as[30]

$$E_p^{\text{out}}(\omega_3) = \frac{4\pi}{\sqrt{\epsilon'}}\,\frac{1}{\epsilon_3\cos\theta_3 + s_3}\left\{P_\parallel^B \sin\theta_3 + P_\perp^B \frac{\epsilon_3(\omega_1 s_1 + \omega_2 s_2)/\omega_3 - \epsilon' s_3}{\epsilon_3 - \epsilon'}\right\}, \tag{2.5a}$$

$$E_s^{\text{out}}(\omega_3) = \frac{4\pi}{\epsilon_3 - \epsilon'}\,\frac{(\omega_1 s_1 + \omega_2 s_2)/\omega_3 - s_3}{s_3 + \cos\theta_3}\,P_y^B \tag{2.5b}$$

for p-polarized and s-polarized SFG, respectively. Here

$$\epsilon' = \left(\frac{c}{\omega_3}\right)^2 ||\mathbf{q}_1 + \mathbf{q}_2||^2 = \frac{(\omega_1\sin\theta_1 + \omega_2\sin\theta_2)^2 + (\omega_1 s_1 + \omega_2 s_2)^2}{\omega_3^2}\,, \tag{2.5c}$$

$||\mathbf{q}_1 + \mathbf{q}_2||$ denotes the (complex) length of $\mathbf{q}_1 + \mathbf{q}_2$. The bulk SFG source (2.2) is decomposed into three parts,

$$\mathbf{P}^B(\omega_3) = \mathbf{P}_y^B(\omega_3) + \mathbf{P}_\parallel^B(\omega_3) + \mathbf{P}_\perp^B(\omega_3)\,, \tag{2.6}$$

where $\mathbf{P}_y^B(\omega_3)$ is normal to the plane of incidence, $\mathbf{P}_\parallel^B(\omega_3)$ and $\mathbf{P}_\perp^B(\omega_3)$ are in the plane of incidence with $\mathbf{P}_\parallel^B \times (\mathbf{q}_1 + \mathbf{q}_2) = 0$ and $\mathbf{P}_\perp^B \cdot (\mathbf{q}_1 + \mathbf{q}_2) = 0$.

In order to complete the phenomenological theory of SFG, the results of Ref. 1 presented above must be supplemented as follows. The symmetry arguments should be applied to the bulk quadrupole-allowed nonlinear polarizabilities (2.2) and three components of the nonlinear source (2.6) must be calculated. Here only isotropic media are considered. The present results can be easily generalized to cubic crystals [similar to work in SHG (Refs. 31–33)]. For isotropic media the independent nonvanishing elements of χ_{ijkl}^Q are given by[2]

$$\chi_{ijij}^Q(\omega_1,\omega_2) = D_2\,, \tag{2.7a}$$

$$\chi_{ijji}^Q(\omega_1,\omega_2) = \overline{D}_2\,, \tag{2.7b}$$

$$\chi_{iijj}^Q(\omega_1,\omega_2) = \widetilde{D}_2\,, \tag{2.7c}$$

$$\chi_{ijij}^Q(\omega_2,\omega_1) = D_1\,, \tag{2.7d}$$

$$\chi_{ijji}^Q(\omega_2,\omega_1) = \overline{D}_1\,, \tag{2.7e}$$

$$\chi_{iijj}^Q(\omega_2,\omega_1) = \widetilde{D}_1\,, \tag{2.7f}$$

for all i and j except $i = j$. Nonlinear parameters D_α, $\overline{D}_\alpha$, and $\widetilde{D}_\alpha$ are introduced for compactness. The diagonal elements are

$$\chi_{iiii}^Q(\omega_1,\omega_2) = D_2 + \overline{D}_2 + \widetilde{D}_2\,, \tag{2.7g}$$

$$\chi_{iiii}^Q(\omega_2,\omega_1) = D_1 + \overline{D}_1 + \widetilde{D}_1\,. \tag{2.7h}$$

Thus, taking the fundamental fields as a sum of plane waves (2.3), the quadrupole bulk polarization $\mathbf{P}^B$ at ω_3 can be written in the vector form as

$$\begin{aligned}\mathbf{P}^B(\mathbf{r},\omega_3) = {} & i\,e^{i(\mathbf{q}_1+\mathbf{q}_2)\cdot\mathbf{r}} \\ & \times\Big\{D_1\,\mathbf{q}_1\,(\mathbf{E}_1^T\cdot\mathbf{E}_2^T) + D_2\,\mathbf{q}_2\,(\mathbf{E}_1^T\cdot\mathbf{E}_2^T) \\ & +\overline{D}_1\,(\mathbf{E}_2^T\cdot\mathbf{q}_1)\,\mathbf{E}_1^T + \overline{D}_2\,(\mathbf{E}_1^T\cdot\mathbf{q}_2)\,\mathbf{E}_2^T \\ & +\widetilde{D}_1\,\mathbf{E}_2^T\,(\mathbf{q}_1\cdot\mathbf{E}_1^T) + \widetilde{D}_2\,\mathbf{E}_1^T\,(\mathbf{q}_2\cdot\mathbf{E}_2^T)\Big\}\,.\end{aligned} \tag{2.8}$$

Since $(\mathbf{q}_\alpha\cdot\mathbf{E}_\alpha^T) = 0$, the last two terms in Eq. (2.8) do not contribute to the nonlinear source $\mathbf{P}(\omega_3)$ and the nonlinear coefficients $\widetilde{D}_\alpha$ will not appear below. It should be noted that for collinear SHG interactions (single fundamental plane wave at ω) the $\overline{D}_\alpha$ polarizabilities also do not contribute to the nonlinear source (2.8). In SFG, however, $\mathbf{q}_1$ is not parallel to $\mathbf{q}_2$ even if $\theta_1 = \theta_2$ because of the refraction index dispersion. Therefore, the $\overline{D}_\alpha$ terms (if they are nonzero) are able to contribute to the nonlinear polarization $\mathbf{P}^B(\omega_3)$.

We note that a noncollinear excitation SHG geometry can be used (two fundamental waves of the same frequency, but at two different incident angles θ_1 and θ_2). In such a case there would be two reflected SHG waves at θ_1 and θ_2 and one wave at θ_3 in between θ_1 and θ_2 due to the cross interaction with both fundamental waves. Measuring the SHG intensity at θ_3 can open additional possibilities (in comparison with those in usual collinear SHG experiments) because of the possibility to independently change two fundamental field polarizations, etc. On the other hand, it seems to the present author that the theoretical support for such experiments is still missing. The present results can also be used directly for noncollinear SHG experiments.

After some manipulation with (2.8) and (2.4), the amplitudes of the components (2.6) of the nonlinear polarization can be written as

$$\begin{aligned}P_{\parallel,pp}^B = A_{pp}\Big\{&(D_1 + D_2)\omega_1\omega_2 V^2 + (\epsilon_1\omega_1^2 D_1 + \epsilon_2\omega_2^2 D_2)V \\ &-(\overline{D}_1 + \overline{D}_2)\omega_1\omega_2 W^2\Big\}/\sqrt{\epsilon'}\,,\end{aligned} \tag{2.9a}$$

$$\begin{aligned}P_{\perp,pp}^B = A_{pp}W\Big\{&(D_2 - D_1 + \overline{D}_2 - \overline{D}_1)\omega_1\omega_2 V \\ &-\overline{D}_1\omega_1^2\epsilon_1 + \overline{D}_2\omega_2^2\epsilon_2\Big\}/\sqrt{\epsilon'}\end{aligned} \tag{2.9b}$$

for p-polarized waves at both ω_1 and ω_2 (p-ω_1, p-ω_2) with $P_{y,pp}^B = 0$,

$$\begin{aligned}P_{\parallel,ss}^B = A_{ss}\Big\{&(D_1 + D_2)\omega_1\omega_2 V \\ &+D_1\omega_1^2\epsilon_1 + D_2\omega_2^2\epsilon_2\Big\}/\sqrt{\epsilon'}\,,\end{aligned} \tag{2.9c}$$

$$P^B_{\perp,ss} = A_{ss}(D_2 - D_1)\omega_1\omega_2 W/\sqrt{\epsilon'} \tag{2.9d}$$

for s-ω_1, s-ω_2 with $P^B_{y,ss} = 0$, and, finally,

$$P^B_{y,ps} = A_{ps}\omega_3\omega_2 W\overline{D}_2 \tag{2.9e}$$

for p-ω_1, s-ω_2 with $P^B_{\parallel,ps} = P^B_{\perp,ps} = 0$. In Eqs. (2.9) the following notations are introduced:

$$A_{\beta\gamma} = \frac{i}{c\omega_3} F_\beta(\omega_1)\, F_\gamma(\omega_2)\, E^{\rm in}_\beta(\omega_1)\, E^{\rm in}_\gamma(\omega_2)\ , \tag{2.10a}$$

$$V = s_1 s_2 + \sin\theta_1 \sin\theta_2\ , \tag{2.10b}$$

$$W = s_1 \sin\theta_2 - s_2 \sin\theta_1\ , \tag{2.10c}$$

where β and γ in (2.10a) denote corresponding polarization. The expression for s-ω_1, p-ω_2 can easily be found from (2.9e) after changing the sign of W and replacing $\overline{D}_2$ by $\overline{D}_1$. We also note that in collinear SHG $P^B_{\perp,pp} = P^B_{\perp,ss} = P^B_{y,ps} = 0$.

Equations (2.9) and (2.5) provide the relation between the radiated field at $\omega_3 = \omega_1 + \omega_2$ and the bulk quadrupole parameters D_1, D_2, $\overline{D}_1$, and $\overline{D}_2$ for any combination of fundamental and SFG polarization, angles of incidence, etc.

B. Surface SFG contribution

Near the surface, the inversion symmetry is broken and the first term in Eq. (2.2) can contribute to the nonlinear polarization at ω_3. Moreover, the fundamental fields vary very rapidly, so that the multipole expansion in the form of Eq. (2.2) cannot be used because the multipole terms are no longer small. The nonlinear interactions at the surface are therefore very much stronger than those in the bulk.[34] On the other hand, the strong surface nonlinear polarization $\mathbf{P}^S(\omega_3)$ is essential only within a thin layer of thickness d^S that obeys the inequality $d^S \ll \lambda_0$. Here λ_0 is the shortest of the wavelengths (or penetration depths) of the fundamental and SFG waves in the nonlinear medium. The SFG field, which is radiated by $\mathbf{P}^S$, can then be found approximately to first order in the small parameter (d^S/λ_0). To calculate the SFG field radiated by the surface polarization, one has to solve the Maxwell equations for the electric and magnetic field at $\omega_3 = \omega_1 + \omega_2$,

$$\nabla \times \mathbf{B}(\omega_3) = -\frac{i\omega_3}{c}\Big[\mathbf{E}(\omega_3) + 4\pi\mathbf{P}^L(\omega_3) + 4\pi\mathbf{P}^S(\omega_3)\Big], \tag{2.11a}$$

$$\nabla \times \mathbf{E}(\omega_3) = \frac{i\omega_3}{c}\mathbf{B}(\omega_3)\ , \tag{2.11b}$$

where $\mathbf{P}^L(\omega_3)$ is the linear induced polarization at ω_3, and $\mathbf{P}^S(\omega_3)$ behaves as a δ function at the boundary.

An important point for the solution of Eqs. (2.11) is that the magnetic field $\mathbf{B}(\omega_3)$ is finite, i.e., has no δ-like feature at the boundary.[35] In contrast, there is a strong normal electric field $E^{\rm dl}_z = -4\pi(P^L_z + P^S_z)$ at the boundary. One can show[35] that apart from this field, the fields $[\mathbf{E}(\omega_3) - \hat{z}E^{\rm dl}_z(\omega_3)]$ and $\mathbf{B}(\omega_3)$ are of order $\sim (d^S/\lambda_0)E^{\rm dl}_z$. The screening effects are then very important for radiation of light by the normal surface polarization[6,9,11] $P^L_z + P^S_z$, while their role is very much weaker for tangential components.

In this way one can find the proper solution of Eqs. (2.11) with the nonlinear source strongly localized at the interface. For the amplitude of the radiated p- and s-polarized field $E^{\rm out}_3$ in the free half-space one has[32]

$$E^{\rm out}_{3,p} = \frac{4\pi i\omega_3}{c}\,\frac{\mathcal{P}_z\epsilon_3\sin\theta_3 - \mathcal{P}_x s_3}{\epsilon_3\cos\theta_3 + s_3}, \tag{2.12a}$$

$$E^{\rm out}_{3,s} = \frac{4\pi i\omega_3}{c}\,\frac{\mathcal{P}_y}{s_3 + \cos\theta_3}, \tag{2.12b}$$

respectively, where $\vec{\mathcal{P}} = \int_I[\mathbf{P}^S(\omega_3) + \mathbf{P}^L(\omega_3)]\,dz$ is the screened surface SFG polarization, integrated over the surface region I.

It is useful to introduce an effective surface nonlinear polarizability χ^S_{ijk} which relates the integrated surface polarization $\vec{\mathcal{P}}$ to the fundamental fields at the boundary. Since the normal components of the fundamental fields change significantly at the surface due to screening effects, one should take the "surface" fundamental fields just above or below the surface screening region to obtain an unambiguous definition of χ^S_{ijk}. Following the tradition used in studies of SHG,[3] we take here the fundamental fields inside the nonlinear medium, which are given by Eqs. (2.4a)–(2.4c). Thus, the definition of χ^S_{ijk} is

$$\mathcal{P}_i(\omega_3) = \chi^S_{ijk}(\omega_1,\omega_2)\, E^T_{1,j}E^T_{2,k}, \tag{2.13}$$

where the field components are given by (2.4) and all screening effects are incorporated into χ^S_{ijk}. For the isotropic surface the symmetry-allowed elements of χ^S_{ijk} are[2]

$$\chi^S_{zzz}, \tag{2.14a}$$

$$\chi^S_{xxz} = \chi^S_{yyz}, \tag{2.14b}$$

$$\chi^S_{xzx} = \chi^S_{yzy}, \tag{2.14c}$$

$$\chi^S_{zxx} = \chi^S_{zyy}. \tag{2.14d}$$

After some straightforward algebra the surface contribution becomes

$$E^{\rm out}_{ppp}(\omega_3) = \frac{4\pi i\omega_3}{c}\,\frac{F_p(\omega_1)F_p(\omega_2)F_p(\omega_3)}{2\cos\theta_3}E^{\rm in}_p(\omega_1)E^{\rm in}_p(\omega_2) \times\left\{\chi^S_{zzz}\,\epsilon_3\sin\theta_1\sin\theta_2\sin\theta_3 + \chi^S_{zxx}\,\epsilon_3 s_1 s_2\sin\theta_3 - \chi^S_{xxz}\,s_1\sin\theta_2 s_3 - \chi^S_{xzx}\,\sin\theta_1 s_2 s_3\right\}, \tag{2.15a}$$

$$E^{\rm out}_{ssp}(\omega_3) = \frac{4\pi i\omega_3}{c}\,\frac{F_s(\omega_1)F_s(\omega_2)F_p(\omega_3)}{2\cos\theta_3}E^{\rm in}_s(\omega_1)E^{\rm in}_s(\omega_2)\,\chi^S_{zxx}\epsilon_3\sin\theta_3, \tag{2.15b}$$

$$E^{\rm out}_{pss}(\omega_3) = \frac{4\pi i\omega_3}{c}\,\frac{F_p(\omega_1)F_s(\omega_2)F_s(\omega_3)}{2\cos\theta_3}E^{\rm in}_p(\omega_1)E^{\rm in}_s(\omega_2)\,\chi^S_{xzx}\sin\theta_1, \tag{2.15c}$$

and $E^{\rm out}_{pps} = E^{\rm out}_{psp} = E^{\rm out}_{spp} = E^{\rm out}_{sss} = 0$, where the first subscript in $E^{\rm out}_{\beta\gamma\delta}$ stands for polarization of the fundamental wave at ω_1, the second at ω_2, and the third for polarization of the reflected SFG wave at ω_3. The Fresnel factors $F_\beta(\omega_\alpha)$ are given by (2.4f) and (2.4g). $E^{\rm out}_{sps}$ can be found from Eq. (2.15c) after cyclic permutation of indices 1 and 2, and replacement of χ^S_{xzx} by χ^S_{xxz}.

The reflected outgoing field at the sum frequency $\omega_3 = \omega_1 + \omega_2$ is then given by the sum of the bulk (2.5) and surface (2.15) contributions. For isotropic surfaces the SFG intensity is determined in general by four bulk (quadrupole-allowed) nonlinear susceptibilities and four surface second-order parameters. In contrast, in collinear SHG experiments the nonlinear isotropic response depends on only one bulk and three surface terms.[2,3,8]

III. SFG ON THE JELLIUM SURFACE

In this section the bulk and surface nonlinear parameters, which are phenomenologically introduced in the preceding section, are evaluated for the jellium surface. These results can be used presumably for semiquantitative estimations of isotropic SFG for simple metals like Al (Refs. 25 and 26) and may also be relevant as an order-of-magnitude estimate for nonresonant SFG in reflection from metals with a much more complex structure.[18,19,21,22] In the latter case numerical values of the nonlinear parameters can differ significantly, however, and should therefore be measured experimentally.

We start with the hydrodynamic equation of motion of the classical free-electron gas[4–6,10]

$$\frac{\partial\mathbf{v}}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{v} = -\mathbf{E}(\mathbf{r},t) - \frac{1}{c}\,\mathbf{v}\times\mathbf{B}(\mathbf{r},t), \tag{3.1}$$

where $\mathbf{v}$ is the electron gas velocity at the point $\mathbf{r}$ and the time t. We use atomic units ($\hbar = 1$, the electron mass and charge are equal to 1 and -1, respectively) unless otherwise noted. Since the fundamental fields

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_1(\mathbf{r})\,e^{-i\omega_1 t} + \mathbf{E}_2(\mathbf{r})\,e^{-i\omega_2 t} + \text{c.c.}, \tag{3.2a}$$
$$\mathbf{B}(\mathbf{r},t) = \mathbf{B}_1(\mathbf{r})\,e^{-i\omega_1 t} + \mathbf{B}_2(\mathbf{r})\,e^{-i\omega_2 t} + \text{c.c.}, \tag{3.2b}$$

are small in respect to the atomic field, Eq. (3.1) can be solved using a perturbation approach. Following the usual way,[4] the second-order correction $\mathbf{v}_3(\mathbf{r})$ to $\mathbf{v}(\mathbf{r},t)$ at $\omega_3 = \omega_1 + \omega_2$ can be found,

$$\begin{aligned}\mathbf{v}_3(\mathbf{r}) &= \frac{i}{\omega_1\omega_2\omega_3}\left\{(\mathbf{E}_1\cdot\nabla)\mathbf{E}_2 + (\mathbf{E}_1\cdot\nabla)\mathbf{E}_2\right\} - \frac{1}{\omega_1\omega_3 c}[\mathbf{E}_1\times\mathbf{B}_2] - \frac{1}{\omega_2\omega_3 c}[\mathbf{E}_2\times\mathbf{B}_1]\\ &= \frac{i}{\omega_1\omega_2\omega_3}\nabla[\mathbf{E}_1(\mathbf{r})\cdot\mathbf{E}_2(\mathbf{r})].\end{aligned} \tag{3.3}$$

The nonlinear current at ω_3 is given by

$$\mathbf{j}(\omega_3) = -(n_0\mathbf{v}_3 + n_1\mathbf{v}_2 + n_2\mathbf{v}_1), \tag{3.4}$$

where n_0 is the electron density without the fields (3.2), $\mathbf{v}_\alpha$ and $n_\alpha = (1/i\omega_\alpha)\mathrm{div}(n_0\mathbf{v}_\alpha)$ are, respectively, the velocity and density of electrons, linearly induced at ω_α ($\alpha = 1,2$). One obtains for the nonlinear SFG polarization

$$\mathbf{P}(\omega_3) = \frac{1}{-i\omega_3}\mathbf{j}(\omega_3) = \frac{n_0}{\omega_1\omega_2\omega_3^2}\,\nabla(\mathbf{E}_1\cdot\mathbf{E}_2) + \frac{1}{\omega_1\omega_2^2\omega_3}\,\mathbf{E}_1\mathrm{div}(n_0\mathbf{E}_2) + \frac{1}{\omega_1^2\omega_2\omega_3}\,\mathbf{E}_2\mathrm{div}(n_0\mathbf{E}_1). \tag{3.5}$$

In the bulk ($n_0 = \bar{n} = \text{const}$) the last two terms do not contribute to $\mathbf{P}^B(\omega_3)$ since $\mathrm{div}\mathbf{E}_\alpha = 0$ at frequencies far from the plasma frequency. Comparing Eq. (3.5) with (2.2) and (2.7), the bulk quadrupole phenomenological parameters for jellium are

$$\overline{D}_1 = \overline{D}_2 = 0, \tag{3.6a}$$

$$D_1 = \frac{\bar{n}}{\omega_1\omega_2\omega_3^2}\,d(\omega_2,\omega_1), \tag{3.6b}$$

$$D_2 = \frac{\bar{n}}{\omega_1\omega_2\omega_3^2}\,d(\omega_1,\omega_2), \tag{3.6c}$$

with

$$d(\omega_1,\omega_2) = d(\omega_2,\omega_1) = 1. \tag{3.6d}$$

The dimensionless parameters (3.6d), which are trivial in the present simple model, are introduced here since they can differ from 1 in more sophisticated theories [due to lattice effects, for example, as it has been found earlier[36] for the SHG parameter $d(\omega)$].

At the boundary both n_0 and the normal components of the fundamental fields change dramatically, and it is necessary to describe correctly the surface profile along z. Moreover, as mentioned in Sec. II B, the screening effects for the normal polarization $P_z^S(\omega_3)$ should be taken into account. Therefore, calculation of χ^S_{zzz} requires more detailed study. Other elements [(2.14b)–(2.14d)] of the surface SFG polarizability, however, can be found directly from Eq. (3.5). Since the tangential components of the fundamental fields $\mathbf{E}_{\|}(\omega_\alpha)$ are not screened at the jellium surface, $\vec{\mathcal{P}}(\omega_3)$ is small when only $\mathbf{E}_{\|}(\omega_\alpha)$ is present. Thus,

$$\chi^S_{zxx}(\omega_1,\omega_2) = 0, \tag{3.7}$$

i.e., the same as the jellium result for SHG.[4,5] For the tangential SFG surface polarization one has

$$\begin{aligned}\mathbf{P}^S_{\|}(\mathbf{r},\omega_3) = {} & \frac{1}{\omega_1\omega_2^2\omega_3}\,\mathbf{E}_{1,\|}\frac{\partial}{\partial z}\left(n_0 E_{2,z}\right)\\ & + \frac{1}{\omega_1^2\omega_2\omega_3}\,\mathbf{E}_{2,\|}\frac{\partial}{\partial z}\left(n_0 E_{1,z}\right),\end{aligned} \tag{3.8}$$

which can be easily integrated over the surface screening region, since $\mathbf{E}_{\|}(\omega_\alpha)$ is not screened at the boundary. Thus,

$$\chi^S_{xxz}(\omega_1,\omega_2) = \frac{\bar{n}}{\omega_1\omega_2^2\omega_3}\,b(\omega_1,\omega_2)\,, \tag{3.9a}$$

$$\chi^S_{xzx}(\omega_1,\omega_2) = \frac{\bar{n}}{\omega_1^2\omega_2\omega_3}\,b(\omega_2,\omega_1)\,, \tag{3.9b}$$

where for jellium

$$b(\omega_1,\omega_2) = b(\omega_2,\omega_1) = -1\,. \tag{3.9c}$$

The physical origin of χ^S_{xxz} and χ^S_{xzx} can be seen in Eq. (3.4). The integrated screening surface charges $\sigma_\alpha = \int dz\, n_\alpha(z)$ are mainly determined by the bulk dielectric constants ϵ_α. These surface charges are moved in the tangential direction by the unscreened fundamental fields $\mathbf{E}_{\|}(\omega_{\alpha'})$, where $(\alpha,\alpha') = (1,2)$ or $(2,1)$, so that the contribution given by (3.9) is not sensitive to details of the surface structure.

As mentioned above, the calculation of χ_{zzz} requires more detailed study. We use here the earlier results for the second-order response of the jellium surface to a static electric field applied along z. Using the local-density approximation (LDA), Weber and Liebsch,[9] for example, have calculated the density profiles $n(z)$ at neutral $n_0(z)$ and slightly charged $n(z,\sigma)$ jellium surfaces. At small surface charges σ, the profile $n(z)$ can be written as a function of the surface charge in the form[9]

$$n(z,\sigma) = n_0(z) + \sigma\, n^{(1)}(z) + \sigma^2\, n^{(2)}(z) + \cdots, \tag{3.10a}$$

where

$$n^{(1)}(z) = \frac{1}{2\sigma}\left[n(z,\sigma) - n(z,-\sigma)\right], \tag{3.10b}$$

$$n^{(2)}(z) = \frac{1}{2\sigma^2}\left[n(z,\sigma) + n(z,-\sigma) - 2n(z,0)\right] \tag{3.10c}$$

describe the linear and second order induced changes in the electronic density. One can assume that the surface charge σ, which is induced by an external normal electric field, depends on time as

$$\sigma(t) = \sigma_1 e^{-i\omega_1 t} + \sigma_2 e^{-i\omega_2 t} + \text{c.c.}\,, \tag{3.11}$$

where the frequencies ω_α are low enough so that the electron density profile responds on $\sigma(t)$ adiabatically according to Eq. (3.10a). Keeping terms up to the second order in $\sigma(t)$, we write the time-dependent profile as

$$\begin{aligned} n(z,t) = {} & \Big[n_0(z) + 2(\sigma_1\sigma_1^* + \sigma_2\sigma_2^*)n^{(2)}(z)\Big] + \Big\{\sigma_1 n^{(1)}(z)e^{-i\omega_1 t} + \sigma_2 n^{(1)}(z)e^{-i\omega_2 t}\\ & + \sigma_1^2 n^{(2)}(z)e^{-2i\omega_1 t} + \sigma_2^2 n^{(2)}(z)e^{-2i\omega_2 t} + 2\sigma_1\sigma_2 n^{(2)}(z)e^{-i(\omega_1+\omega_2)t} + 2\sigma_1\sigma_2^* n^{(2)}(z)e^{-i(\omega_1-\omega_2)t} + \text{c.c.}\Big\}\\ = {} & n_{\text{dc}}(z) + \Big\{n_{\omega_1}(z)e^{-i\omega_1 t} + n_{\omega_2}(z)e^{-i\omega_2 t} + n_{2\omega_1}(z)e^{-2i\omega_1 t} + n_{2\omega_2}(z)e^{-2i\omega_2 t}\\ & + n_{\omega_1+\omega_2}(z)e^{-i(\omega_1+\omega_2)t} + n_{\omega_1-\omega_2}(z)e^{-i(\omega_1-\omega_2)t} + \text{c.c.}\Big\}\,. \end{aligned} \tag{3.12}$$

Thus, Eq. (3.12) establishes the time-independent profile n_{dc}, the low-frequency linear-induced response n_{ω_α} of the jellium surface, and the low-frequency nonlinear SHG $n_{2\omega_\alpha}$, SFG $n_{\omega_1+\omega_2} \equiv n_{\omega_3}$, and differential-frequency responses $n_{\omega_1-\omega_2}$. Note that the factors 2 in $n_{\omega_1+\omega_2}$ and $n_{\omega_1-\omega_2}$ are absent in $n_{2\omega_\alpha}$. The normal component of the integrated nonlinear polarization is determined by the first moment[9] of n_{ω_β},

$$\mathcal{P}_z(\omega_\beta) = -\int_{-\infty}^{+\infty} dz\, z\, n_{\omega_\beta}(z)\,, \tag{3.13}$$

where $\omega_\beta = 2\omega_\alpha$ for SHG and $\omega_\beta = \omega_3$ for SFG. Weber and Liebsch[9] have also calculated the adiabatic ($\omega \to 0$) value of the dimensionless SHG parameter $a(\omega)$, which is introduced via

$$\mathcal{P}_z(2\omega_\alpha) = \frac{a(\omega_\alpha)}{4\bar{n}}\,\sigma_\alpha^2\,, \tag{3.14}$$

where $\bar{n}$ is the bulk electron density. The adiabatic value of $a(\omega)$ was subsequently calculated by Kiejna[37] within the model of a stabilized-jellium surface. Using (3.12), (3.14), and the relation between the screening charge $\sigma_\alpha = (\epsilon_\alpha - 1)E^T_{\alpha,z}/4\pi$ and the screened field $E^T_{\alpha,z}$ in the interior of the jellium, one has for SFG

$$\begin{aligned}\mathcal{P}_z(\omega_3) &= \frac{a(\omega_1,\omega_2)}{4\bar{n}}\,2\sigma_1\sigma_2\\ &= a(\omega_1,\omega_2)\,\frac{(1-\epsilon_1)(1-\epsilon_2)}{2\,(4\pi)^2\,\bar{n}}\,E^T_{1,z}E^T_{2,z}\\ &= a(\omega_1,\omega_2)\frac{\bar{n}}{2\omega_1^2\omega_2^2}\,E^T_{1,z}E^T_{2,z}\,,\end{aligned} \tag{3.15}$$

where the Drude form of the jellium dielectric function is used in the last step, and at $\omega_1 \to 0$, $\omega_2 \to 0$ the dimensionless SFG parameter $a(\omega_1,\omega_2)$ coincides with the adiabatic value of the SHG parameter $a(\omega)$. The study of the frequency dependence of the SHG $a(\omega)$ parameter by Liebsch and Schaich[11] within the time-dependent local-density approach showed that the values of $a(\omega)$ are close to their adiabatic limits at $2\omega \lesssim 2$ eV. $a(\omega)$ changes at higher frequencies and exhibits a feature for 2ω near the threshold for electron emission and a second one for 2ω near $0.8\omega_p$, where $\omega_p = \sqrt{4\pi\bar{n}}$ is the bulk plasma frequency. One can therefore expect that the adiabatic values of the SFG $a(\omega_1,\omega_2)$ parameter can also be used at $\omega_3 \lesssim 2$ eV.[38]

One can make contact of $a(\omega_1,\omega_2)$ with the position of the image plane[39] $d_\perp(\omega)$ on slightly charged jellium surfaces. $d_\perp(\omega)$ corresponds to the position of the center of mass of the surface screening charge $\sigma_\omega = \int_{-\infty}^{+\infty} n_\omega(z)\,dz$, induced by the normal component of the optical field,[39]

$$d_\perp(\omega) = \int_{-\infty}^{+\infty} dz\, z\, n_\omega(z)/\sigma_\omega\,. \tag{3.16}$$

Gies and Gerhardts,[40] for example, have calculated the image plane position $d_\perp(\omega)$ as a function of the static surface charge σ_0. In the infrared-visible SFG studies, the infrared frequency $\omega_{\rm IR}$ is usually much lower than any resonant frequencies of the jellium surface, and the effect of the fundamental field at $\omega_{\rm IR}$ can be treated approximately as the adiabatic charging of the jellium surface. Using (3.13) and (3.16), one can then find the normal surface polarization $\mathcal{P}_z$ at the SFG frequency $\omega_{\rm SF} = \omega_V + \omega_{\rm IR}$ for low $\omega_{\rm IR}$ and *any* frequency ω_V of the visible fundamental component

$$\begin{aligned}\frac{\mathcal{P}_z(\omega_{\rm SF})}{E^T_z(\omega_V)E^T_z(\omega_{\rm IR})} &= -\frac{\partial\, d_\perp(\omega_V,\sigma_0)}{\partial\sigma_0}\,\frac{(1-\epsilon_V)(1-\epsilon_{\rm IR})}{(4\pi)^2}\\ &= -\frac{\partial\, d_\perp(\omega_V,\sigma_0)}{\partial\sigma_0}\,\frac{\bar{n}^2}{\omega_V^2\omega_{\rm IR}^2}\,,\end{aligned} \tag{3.17}$$

where $\epsilon_V = \epsilon(\omega_V)$, $\epsilon_{\rm IR} = \epsilon(\omega_{\rm IR})$. Therefore, using (3.15), the SFG dimensionless parameter $a(\omega_V,\omega_{\rm IR})$ at low $\omega_{\rm IR}$ is related to $d_\perp(\omega,\sigma_0)$ via

$$a(\omega_V,\omega_{\rm IR} \to 0) = -2\bar{n}\,\frac{\partial\, d_\perp(\omega_V,\sigma_0)}{\partial\sigma_0}\,. \tag{3.18}$$

Note that in Eq. (3.18) σ_0 is the *number* density and, therefore, the surface is charged *negatively* for $\sigma > 0$. Unfortunately, Gies and Gerhardts[40] have calculated $d_\perp(\omega,\sigma_0)$ only for too strongly charged jellium surfaces and it is therefore impossible to evaluate the derivative $\partial d_\perp(\omega,\sigma_0)/\partial\sigma_0$ with sufficient accuracy from the results published in Ref. 40.

The magnitude of the normal component of the surface SFG polarizability (2.14a) is then determined by

$$\chi^S_{zzz}(\omega_1,\omega_2) = a(\omega_1,\omega_2)\frac{\bar{n}}{2\omega_1^2\omega_2^2}\,, \tag{3.19}$$

where $a(\omega_1,\omega_2)$ coincides with the adiabatic value of $a(\omega)$ when $\omega_1 \to 0$, $\omega_2 \to 0$, or can be found from (3.18) when only one of the frequencies is low. We note that the estimate (3.19) of $\chi_{zzz}(\omega_1,\omega_2)$ for SFG at the degeneracy limit ($\omega_1 \to \omega$, $\omega_2 \to \omega$) is twice as large as the SHG value $\chi^S_{zzz}(\omega) = a(\omega)\bar{n}/(4\omega^4)$, which determines the normal component of the screened SHG polarization, excited by the normal component of the fundamental field,[3,9]

$$\mathcal{P}_z(2\omega) = \chi^S_{zzz}(\omega)\,E^T_z(\omega)E^T_z(\omega)\,. \tag{3.20}$$

Furthermore, one can compare the SFG terms (3.9) with the corresponding SHG values. To do this, one must introduce the SHG $\chi^S_{xxz}(\omega)$ and $\chi^S_{xzx}(\omega)$ elements in the same way as for the SFG values. Since the definition of the surface nonlinear polarizability in the form of Eq. (2.13) implies the summation over *all* indices j and k, the x component of the surface current for SHG is given by

$$\begin{aligned}\vec{\mathcal{P}}_x(2\omega) &= \chi^S_{xxz}(\omega)\mathbf{E}^T_x E^T_z + \chi^S_{xzx}(\omega)E^T_z\mathbf{E}^T_x\\ &\equiv 2\chi^S_{xxz}(\omega)\mathbf{E}^T_x E^T_z\\ &= b(\omega)\frac{\bar{n}}{2\omega^4}\mathbf{E}^T_x E^T_z\,,\end{aligned} \tag{3.21}$$

where we have made use of the fact that $\chi^S_{ijk}(\omega) \equiv \chi^S_{ikj}(\omega)$ for SHG. The jellium value[5] for $b(\omega)$ is -1, i.e., the same as for $b(\omega_1,\omega_2)$. Thus, $\chi^S_{xxz}(\omega) = \chi^S_{xzx}(\omega) = b(\omega)\bar{n}/(4\omega^4)$ elements for SHG, introduced in the same way as for SFG,[41] a factor of 2 smaller than the corresponding SFG terms (3.9) in the degeneracy limit.[2]

To clarify the problem of "discontinuity" we note that, in the limit SFG→SHG, the fundamental field at ω is $\mathbf{E}(\omega) = \mathbf{E}_1(\omega_1 \to \omega) + \mathbf{E}_2(\omega_2 \to \omega)$ or, if $\mathbf{E}_1 = \mathbf{E}_2$, is twice as large as the field that is used in expressions for SFG. Since the SHG response is proportional to the second power of the fundamental field amplitude, the nonlinear polarization at 2ω, given by (3.20) and (3.21), is *larger* by a factor of $2^2/2 = 2$ than the SHG limit of the corresponding SFG polarization (3.9) and (3.19). The reason for this factor is that the SFG term does not include the second-harmonic polarization, excited by the $\mathbf{E}_1(\omega_1)$ and $\mathbf{E}_2(\omega_2)$ fields. If one adds the $2\omega_1$ and $2\omega_2$ contributions, the *physically meaningful* quantities are, of course, continuous in the degeneracy limit. This point can be seen clearly in Eq. (3.12). From this consideration, it is clear that the SHG and SFG polarizabilities establish relations between *different physical quantities.* For SFG the $\chi^S(\omega_1,\omega_2)$ tensor is the coefficient between the product of two *different* components $\mathbf{E}(\omega_1)$ and $\mathbf{E}(\omega_2)$ of the fundamental field, and the sum-frequency polarization, which describes only *a part* of the nonlinear source in the degeneracy limit. In contrast, the SHG $\chi^S(\omega)$ tensor establishes the relation between the product of two *identical* fundamental fields $\mathbf{E}(\omega)$ and the *whole* nonlinear SHG source.

This problem of "discontinuity" can be formally solved by redefining the surface nonlinear terms. Eq. (2.13) may be replaced by

$$\begin{aligned}\mathcal{P}_i(\omega_3) = {}&\bar{\chi}^S_{ijk}(\omega_1,\omega_2)\,E^T_{1,j}E^T_{2,k}\\ &+\bar{\chi}^S_{ijk}(\omega_2,\omega_1)\,E^T_{2,j}E^T_{1,k}\,,\end{aligned} \tag{3.22}$$

where two terms on the right-hand side are equivalent since $\bar{\chi}^S_{ijk}(\omega_1,\omega_2) \equiv \bar{\chi}^S_{ikj}(\omega_2,\omega_1)$, and the summation over the indices j and k is implied [see also the definition of the bulk quadrupole second-order polarizability (2.2), which is "continuous" in the SHG limit]. Thus, the SFG surface nonlinearity $\bar{\chi}^S(\omega_1,\omega_2)$ introduced via Eq. (3.22) is half as large [with respect to that introduced via Eq. (2.13)] and coincides with the SHG value in the degeneracy limit. In the present work, however, the ("discontinuous") definition in the form of Eq. (2.13) is used for the surface terms.

Using the estimates of the quadrupole bulk (3.6) and dipole surface (3.7), (3.9), and (3.19) nonlinear terms, one can calculate the normalized SFG intensity

$$\mathcal{R}_{\beta\gamma\delta} = \frac{I_\delta(\omega_3)}{I_\beta(\omega_1)I_\gamma(\omega_2)} = \frac{2\pi}{c}\left|\frac{E^{\rm out}_\delta(\omega_3)}{E^{\rm in}_\beta(\omega_1)E^{\rm in}_\gamma(\omega_2)}\right|^2, \tag{3.23}$$

where β, γ, and δ denote corresponding polarization. In Eq. (3.23) we have used the fact that the real fields are introduced here as shown in Eq. (3.2). Using the results of the general phenomenological treatment of SFG, presented in Sec. II, one has

$$\begin{aligned}\mathcal{R}_{ppp} = \mathcal{A}_{ppp}\Big|&\epsilon_3\sin\theta_1\sin\theta_2\sin\theta_3\,a(\omega_1,\omega_2)\\ &-\frac{2s_3}{\omega_3}(\omega_1 s_1\sin\theta_2+\omega_2 s_2\sin\theta_1)\,b(\omega_1,\omega_2)\\ &+\frac{2\omega_1\omega_2}{\omega_3^2}\,V\sin\theta_3\,d(\omega_1,\omega_2)\Big|^2,\end{aligned} \tag{3.24a}$$

$$\mathcal{R}_{ssp} = \mathcal{A}_{ssp}\left|\frac{2\omega_1\omega_2}{\omega_3^2}\sin\theta_3\,d(\omega_1,\omega_2)\right|^2, \tag{3.24b}$$

$$\mathcal{R}_{pss} = \mathcal{A}_{pss}\left|\frac{2\omega_2}{\omega_3}\sin\theta_1\,b(\omega_1,\omega_2)\right|^2, \tag{3.24c}$$

where

$$\begin{aligned}\mathcal{A}_{\beta\gamma\delta} = {}&\frac{(2\pi)^3e^6\omega_3^2}{m^4c^3}\\ &\times\left|\frac{F_\beta(\omega_1)F_\gamma(\omega_2)F_\delta(\omega_3)}{2\cos\theta_3}\,\frac{\bar{n}}{\omega_1^2\omega_2^2}\right|^2,\end{aligned} \tag{3.24d}$$

$F_\beta(\omega_\alpha)$ and V are given by (2.4f), (2.4g), and (2.10b). In Eqs. (3.24) we have made use of the fact that for jellium $b(\omega_1,\omega_2) = b(\omega_2,\omega_1)$ and $d(\omega_1,\omega_2) = d(\omega_2,\omega_1)$. We have converted Eq. (3.24d) into conventional units for convenience. All other coefficients in (3.24a)–(3.24c) are dimensionless and, therefore, $\mathcal{R}_{\beta\gamma\delta}$ can be found from (3.24) either in esu or atomic units.[42]

IV. PRACTICAL EXAMPLE

In order to discuss the present results in more detail, we consider a particular example with $\omega_1 \equiv \omega_V = 2$ eV ($\lambda_V = 620$ nm) and $\omega_2 \equiv \omega_{\rm IR} = 0.2$ eV ($\nu_{\rm IR} = 1600$ cm^{-1}), which are close to typical experimental parameters.[13–22] The subscript "1" is replaced in the following by "V," "2" by "IR," and "3" by "SF." For jellium with $r_s = 3$ a.u. [$\bar{n} = 3/(4\pi r_s^3)$], one has $\epsilon_V = -20$, $\epsilon_{\rm IR} = -2000$, and $\epsilon_{\rm SF} = -16$. Figure 2(a) shows the dependence of $\sqrt{\mathcal{R}_{\beta\gamma\delta}}$ on the angle of incidence θ for collinear excitation of SFG ($\theta_V = \theta_{\rm IR} = \theta_{\rm SF} = \theta$). For $a(\omega_V,\omega_{\rm IR})$ the adiabatic value of -11.3 of Kiejna[37] is used (this value is also quite close to $a(\omega \to 0) = -12.9$ as calculated by Weber and Liebsch[9]). According to (3.6d) and (3.9c), $d(\omega_V,\omega_{\rm IR}) = 1$ and $b(\omega_V,\omega_{\rm IR}) = -1$. As can be seen in Fig. 2(a), the intensity of *ppp* SFG is the largest one at almost all θ. SFG with *ssp*, *pss*, and *sps* polarization combinations has practically the same intensity when $\theta_V = \theta_{\rm IR}$. In order to see the effect of a noncollinear SFG excitation ($\theta_V \neq \theta_{\rm IR}$), the dependencies of the normalized SFG intensity against $\theta_V = \theta$ for fixed $\theta_{\rm IR} = 60°$ and against $\theta_{\rm IR} = \theta$ for fixed $\theta_V = 60°$ are shown in Figs. 2(b) and 2(c), respectively. Since one of the angles of incidence is now fixed, the dependencies are no longer symmetric about $\theta = 0$, and the *ssp*, *pss*, and *sps* SFG intensities differ when $\theta_V \neq \theta_{\rm IR}$.

In order to analyze *ppp* SFG in greater detail, we show in Fig. 3 the corresponding angular dependencies of three different terms in Eq. (3.24a). When $\theta_V = \theta_{\rm IR} = \theta$ [Fig. 3(a)], the angular dependencies of different terms are similar to the angular dependencies of the corresponding terms in SHG upon reflection from the jellium surface.[11] As in SHG, the bulk contribution (the d term) and the tangential surface contribution (the b term) have practically the same angular dependencies, whereas the normal surface contribution (the a term) has a sharper maximum at large θ and decreases more rapidly towards smaller angles. In order to understand this similarity, it should be noted that all three frequencies (ω_V, $\omega_{\rm IR}$, $\omega_{\rm SF}$) that are used in this example are significantly lower than the plasma frequency $\omega_p = 9.1$ eV for the jellium with $r_s = 3$. In such a case $|\epsilon_\alpha| = |1-(\omega_p/\omega_\alpha)^2| \gg 1$. Thus, taking $s_\alpha \approx \sqrt{\epsilon_\alpha} \approx i\omega_p/\omega_\alpha$, Eq. (3.24a) can be approximated as

$$\mathcal{R}_{ppp} \approx \mathcal{A}_{ppp}\,|4\epsilon_{\mathrm{SF}}|^2 \left| \frac{1}{4}\sin\theta_V \sin\theta_{\mathrm{IR}} \sin\theta_{\mathrm{SF}}\, a(\omega_V,\omega_{\mathrm{IR}}) - \frac{\sin\theta_V + \sin\theta_{\mathrm{IR}}}{2}\, b(\omega_V,\omega_{\mathrm{IR}}) + \frac{\sin\theta_{\mathrm{SF}}}{2}\, d(\omega_V,\omega_{\mathrm{IR}}) \right|^2 . \qquad (4.1)$$

For $\theta_V = \theta_{\mathrm{IR}} = \theta$ the expression in $|\cdots|^2$ has exactly the same structure as the corresponding jellium expression[11] for SHG at $2\omega \ll \omega_p$. This result is essential, because different components of the Fresnel fields (2.4a), (2.4b), and (2.4c) for visible and IR light differ significantly since $|\epsilon_{\mathrm{IR}}| \gg |\epsilon_V| \gg 1$. Inside the jellium, for example, the tangential component $E_x^T(\omega_\alpha)$ of the fundamental field is of order $2E_p^{\mathrm{in}}(\omega_\alpha)/\sqrt{\epsilon(\omega_\alpha)} \propto \omega_\alpha$, whereas the normal component is much smaller $E_z^T(\omega_\alpha) \approx 2E_p^{\mathrm{in}}(\omega_\alpha)\sin\theta_\alpha/\epsilon(\omega_\alpha) \propto \omega_\alpha^2$. This significant difference in the Fresnel fields is, however, compensated by the frequency dependence of the nonlinear polarizabilities (3.6), (3.9), and (3.19).

Equation (4.1) can also help to understand the features of the angular dependencies shown in Figs. 3(b) and 3(c). In particular, the b contribution disappears in the counterpropagation geometry ($\theta_V = -\theta_{\mathrm{IR}}$). The d contribution depends mainly on the direction of the SFG reflected beam, i.e., θ_{SF}. Since $\omega_{\mathrm{IR}} \ll \omega_V$, θ_{SF} [Eq. (2.1)] and hence the bulk contribution [Fig. 3(c)] depends only slightly on θ_{IR}. It is important that ppp SFG is the result of interference between the terms shown in (3.24a) and (4.1). In particular, due to this interference, $\mathcal{R}_{ppp}$ vanishes at certain angles (Fig. 2) at which the radiated field E_p^{out} changes its sign. An important question is also the frequency dependence of $\mathcal{R}_{\beta\gamma\delta}$. Within the same approx-

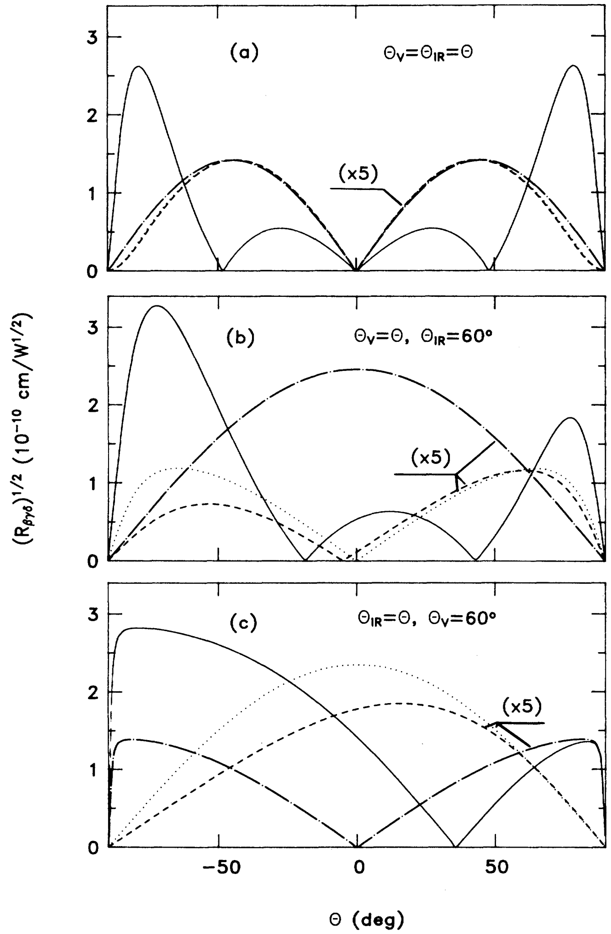

FIG. 2. The normalized SFG amplitudes $\sqrt{\mathcal{R}_{\beta\gamma\delta}}$ versus angles of incidence θ_V and θ_{IR}. (a) Both angles $\theta_V = \theta_{\mathrm{IR}} = \theta$ are changed, (b) $\theta_V = \theta$ is changed, $\theta_{\mathrm{IR}} = 60°$, (c) $\theta_{\mathrm{IR}} = \theta$ is changed, $\theta_V = 60°$. The polarization combination $\beta\gamma\delta = ppp$ (solid lines), ssp (dashed), pss (dotted), and sps (dotted-dashed). The scale for ssp, pss, and sps polarization is changed by a factor of 5. $\omega_V = 2$ eV, $\omega_{\mathrm{IR}} = 0.2$ eV, $r_s = 3$ a.u.

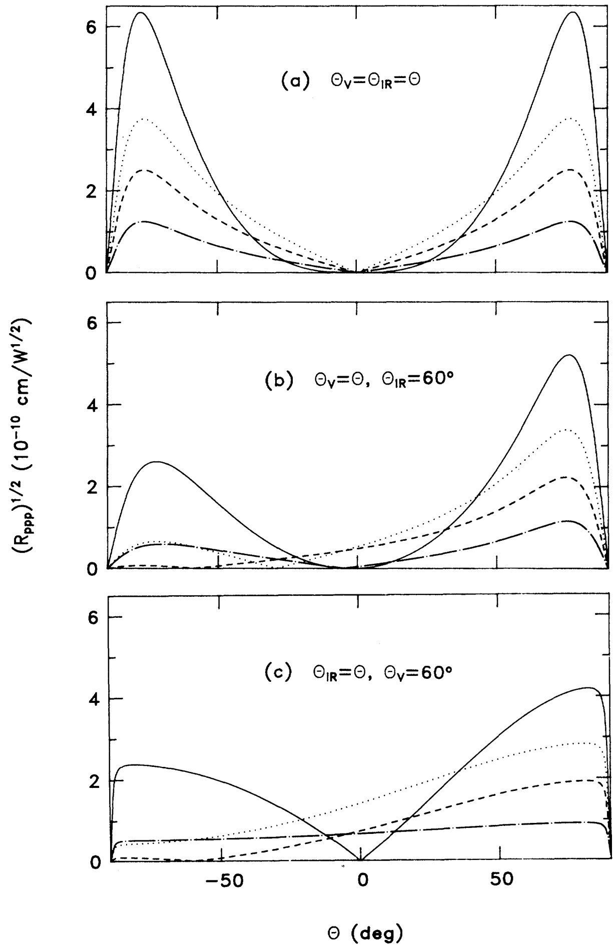

FIG. 3. The angular dependencies of amplitudes of different contributions to $\sqrt{\mathcal{R}_{ppp}}$ in Eq. (3.24a). Panels (a), (b), and (c) correspond to those in Fig. 2. Solid lines show the a-term contribution; dashed, b; dotted-dashed, d. The dotted lines present the sum of the b and d contributions.

imation that is used in (4.1) and for not very large angles θ_α [so that $\sqrt{|\epsilon_\alpha|}\cos\theta_\alpha \gg 1$ in Eqs. (2.4f) and (2.4g)], one has for jellium $\mathcal{R}_{\beta\gamma\delta}(\omega_V, \omega_{\rm IR}) \propto (\omega_V + \omega_{\rm IR})^2 = \omega_{\rm SF}^2$.

V. CONCLUSION AND OUTLOOK

A general phenomenological theory of SFG upon reflection from surfaces of isotropic media has been developed, and the relation of the emitted SFG radiation with four bulk and four surface nonlinear polarizabilities has been established. Using the latest developments of the microscopic theory of SHG, these nonlinear parameters are estimated for the jellium surface. The angular dependencies of the SFG intensity are calculated and discussed for a particular example.

It is necessary to point out that several effects that can be of importance for SFG on metal surfaces have not been considered. In particular, a more precise evaluation of $\chi_{zzz}(\omega_1, \omega_2)$ for the jellium surface may be necessary if the fundamental frequencies cannot be considered to be small. Even more serious problems may arise from the fact that the nonlinear parameters of real metals can differ significantly from the corresponding jellium values. For example, it has been found that the adiabatic value of $a(\omega \to 0)$ for silver surfaces is a factor of 2 (Ref. 43) or 3 (Ref. 44) smaller than the corresponding jellium result. χ_{zzz} also depends on the surface orientation, as it was found in SHG for Al single crystals.[25,26] In addition, lattice effects result in new anisotropic nonlinear surface[29] and bulk[36] contributions, which have angular dependencies, different from those presented in Figs. 2 and 3.

It should be noted that the metal surface is typically covered by an overlayer of adsorbed molecules in SFG experiments. The presence of such an overlayer greatly affects the second-order nonlinear SFG from metal substrates. The effective repulsion between the molecular and metal electrons pushes the latter electrons into the metal, and the electronic density profile is usually steeper and less polarizable.[28] One can therefore expect that, if ω_V, $\omega_{\rm IR}$, and $\omega_{\rm SF}$ do not coincide with electronic and vibration resonances of adsorbed molecules, the value of $a(\omega_V, \omega_{\rm IR})$ is decreased due to molecular adsorption on the metal surface.[45]

On the other hand, the direct contribution to SFG of adsorbed molecules may also be important, especially when one or both fundamental frequencies coincide with molecular resonances. The study of such a contribution requires a more detailed consideration, which is beyond the scope of the present work. However, one can formulate a simple approximate selection rule for the resonant molecular contribution, which is especially strong at IR frequencies because $\epsilon(\omega)$ of metals diverges at low frequencies. Since the Fresnel field *outside* the metal substrate with high refractive index (where the adsorbed molecules are located) is mainly oriented in the normal direction ($E_{\perp,\alpha} \sim \sqrt{|\epsilon_\alpha|}\, E_{\parallel,\alpha}$), the molecular contribution to the χ^S_{zzz} element can be expected to be the largest. Further study of this contribution is necessary. In particular, the local-field effects can be of importance.[46] A special treatment would be needed in the case when the metal electrons are directly involved in adsorbate vibrations.[47] We are currently studying some of these effects on SFG.

It is necessary to point out that in many SFG experiments performed to date, the main focus was on the vibration resonant contribution from adsorbed molecules. On the other hand, as is clear from the previous results for SHG and the present results for SFG, the nonresonant SFG response from metal surfaces (e.g., the χ_{zzz} term) depends very sensitively on the surface electronic structure. In this sense, the nonresonant part of the SFG response possesses similar information to SHG, and a more detailed analysis of *both vibration resonant and nonresonant* SFG parts may provide more information about the surface under study. An exciting example of such a complex use of the SFG technique was given recently by Yeganeh *et al.*[20]

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