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Surface-enhanced second-harmonic generation at a metallic grating

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The theory of surface-enhanced second-harmonic generation at a metallic grating is developed. Using the form of the nonlinear source polarization given by Bloembergen *et al.* [Phys. Rev. 174, 813 (1968)], we solve Maxwell's equations to obtain the fields at the second-harmonic frequency. The calculations are done up to second order in the surface-roughness parameter. These perturbation expressions are used to evaluate numerically the second-harmonic intensity, in various directions, produced by a plane wave incident on a metallic grating. The resonant enhancement in the second-harmonic intensity due to surface-plasmon excitation at fundamental frequency ω is discussed and the results compared with some recent experimental observations. The second-harmonic fields are also shown to get enhancement due to excitation of surface plasmons at 2ω; these, however, correspond to local-field enhancements at 2ω and are evanescent in nature.

I. INTRODUCTION

The optical second-harmonic generation (SHG) at a metal surface[1,2] and the nonlinear interaction of prism-coupled optical surface waves[3] excited on a plane metallic surface have been studied for a long time. With the experimental observation of the enhanced Raman cross sections for molecules adsorbed on a rough metal surface like Ag, there has been a revival of interest in investigating such enhancements for other processes[4] in general, and SHG in particular.[5-7] In the processes involving only the metal, such an enhancement is due to the resonant excitation of surface-plasmon polaritons (SPP) in the metal substrate[8,9] and the consequent field enhancement at the appropriate frequency.

Chen *et al.*[5] were the first to observe enhanced SHG from silver particles on a rough silver surface due to the local-field enhancement by a factor of about 20 at the fundamental frequency. Although our recent theory[6] for SHG involving SPP excitations in small metallic spheres is consistent with these results, a detailed numerical comparison has not been possible because of the relatively complex substrate used in the experiment. More recently, Wokaun *et al.*[7] have been able to correlate their observations of surface-enhanced second-harmonic generation (SEHG) on silver and gold island films and regular arrays of silver particles with the corresponding observations of the surface-enhanced Raman scattering (SERS).

Keeping in view the importance of the role played by well-characterized metallic grating experiments of Tsang *et al.*[8] in the study of SERS, in this paper we address ourselves to the calculation of optical harmonic fields generated at a metallic grating. Although, the theory is first developed for an arbitrary surface, only the case of a sinusoidal grating with two-dimensional wave vector $\vec{g}$ (in the xy plane) and amplitude $\xi \ll \lambda/2$ (the wavelength of the second-harmonic wave) is considered explicitly. These results are correct to order ξ^2/λ^2 and may be generalized, if necessary, to a statistically rough surface. The enhancement in the second-harmonic intensity arises from the resonant excitation of SPP either at the incident frequency ω or at the second-harmonic frequency 2ω. To show the nature of the resonances in detail, numerical results for SH intensity as functions of the incident angle θ are presented for the typical case of Ag.

In Sec. II of this paper, we present the mathematical formulation of the problem at hand for a general metal surface defined by the functional equation $f(x,y,z)=0$. The metal occupies the domain $f>0$, and the fundamental wave of frequency ω and wave vector

$$\vec{k}_0=(\vec{\kappa},[(\omega^2/c^2)-\kappa^2]^{1/2}\hat{z})$$

is incident from the region $f<0$. Here $\vec{\kappa}$ is the wave vector in the xy plane, with

$$|\kappa| = |(\omega/c)\sin\theta| \; .$$

We later specialize to the special case of a small-amplitude sinusoidal grating of wave vector $\vec{g}$, with

$$f = z + \xi \sin gy = 0 \; .$$

To order ξ^2, the second-harmonic (SH) field is calculated in Sec. III. In the vacuum (domain $f<0$), the possible parallel wave vectors (in the xy plane) of the SH field are $2\vec{\kappa}$, $2\vec{\kappa}\pm\vec{g}$, and $2\vec{\kappa}\pm 2\vec{g}$, which arise from the bilinear combinations of the fundamental frequency field with parallel wave vectors $\vec{\kappa}$, $\vec{\kappa}\pm\vec{g}$, and $\vec{\kappa}\pm 2\vec{g}$. The equations giving the SH fields with parallel wave vectors $2\vec{\kappa}$, $2\vec{\kappa}\pm\vec{g}$, and $2\vec{\kappa}\pm 2\vec{g}$ are formulated.

In Sec. IV, the SH intensity is calculated explicitly in the directions $\vec{Q}_{R\pm}$, with the parallel wave vectors $2\vec{\kappa}\pm\vec{g}$, and the corresponding normal wave vectors $[4\omega^2/c^2-(2\vec{\kappa}\pm\vec{g}\,)^2]^{1/2}$. For $\vec{\kappa}$ parallel to $\vec{g}$, this is equivalent to the directions given by reflection angles $\theta_{R\pm}$, with

$$\tan\theta_{R\pm} = (\sin\theta \pm gc/2\omega) \times \{[1-(\sin\theta\pm gc/2\omega)^2]^{1/2}\}^{-1} \; .$$

The p components of the second-harmonic fields are shown to contain two resonant denominators

$$|\vec{\kappa}\pm\vec{g}\,|^2 - (\omega^2/c^2)\{\epsilon(\omega)/[\epsilon(\omega)+1]\}$$

and

$$|2\vec{\kappa}\pm\vec{g}\,|^2 - (4\omega^2/c^2)\{\epsilon(2\omega)/[\epsilon(2\omega)+1]\} \; .$$

The resonant enhancement of SH radiation is due to the vanishing of the denominator

$$\kappa_\pm^2 - (\omega^2/c^2)\{\epsilon(\omega)/[\epsilon(\omega)+1]\} \; , \quad \vec{\kappa}_\pm = \vec{\kappa}\pm\vec{g}$$

for certain directions of incidence and the direction and the magnitude of the periodicity of the grating. Numerical results for such enhancements are presented for a fixed ω but for different directions of incidence of the field at fundamental frequency. In Sec. V, we consider the other important case of SHG in the primary direction of reflection, i.e., in the direction determined by the reflection angle $\theta_R=\theta$, the incident angle. Surface-plasmon excitation both at ω and 2ω leads to dispersionlike resonances in the intensity as a function of incident angle. Relevant background material needed to perform perturbation theory is discussed in Appendixes A, B, and C.

II. NONLINEAR SOURCE POLARIZATION AND BASIC FIELD EQUATIONS

It is well known[2] from the work of Bloembergen *et al.* that an electromagnetic field at ω, when incident on a metallic medium, leads to a nonlinear polarization at 2ω:

$$\vec{P}_{NL}(\vec{r},2\omega) = \gamma\vec{\nabla}[E^2(\vec{r},\omega)] + \beta\vec{E}(\vec{r},\omega)\vec{\nabla}\cdot\vec{E}(\vec{r},\omega) \; . \tag{2.1}$$

The general form of the parameters γ and β are known in the literature.[1,2] In the special case when the contribution of valence electrons is negligible, then these are related to the conduction-electron mass m and charge e by

$$\beta = \frac{e}{8\pi m\omega^2} \; , \quad \gamma = e[1-\epsilon(2\omega)]/8\pi m\omega^2 \; . \tag{2.2}$$

Here $\epsilon(2\omega)$ is the dielectric function of the metal at 2ω. The special form (2.2) is not used until we do numerical work in Secs. IV and V. In (2.1) $\vec{E}$ is the field at the fundamental frequency. Having the form of the source polarization, one can derive the equations for the field at 2ω. Let the metal surface be defined by $f(x,y,z)=0$ and let us assume that the medium occupies the domain $f(x,y,z)>0$; the region $f(x,y,z)<0$ is the vacuum region. The field distribution at ω will have the form (η representing the step function)

$$\vec{E}(\vec{r},\omega) = \vec{E}^{(+)}(\vec{r},\omega)\eta(f) + \vec{E}^{(-)}(\vec{r},\omega)\eta(-f) \; , \tag{2.3}$$

where $\vec{E}^{(+)}$ and $\vec{E}^{(-)}$ represent, respectively, the fields inside and outside the medium. From (2.3), $\vec{\nabla}\cdot\vec{E}$ can be calculated to be

$$\begin{aligned}\vec{\nabla}\cdot\vec{E}(\vec{r},\omega) &= (\vec{\nabla}\cdot\vec{E}^{(+)})\eta(f) + (\vec{\nabla}\cdot\vec{E}^{(-)})\eta(-f) \\ &\quad + \vec{E}^{(+)}\cdot\vec{\nabla}\eta(f) + \vec{E}^{(-)}\cdot\vec{\nabla}\eta(-f) \\ &= \vec{E}^{(+)}\cdot\vec{\nabla}\eta(f) + \vec{E}^{(-)}\cdot\vec{\nabla}\eta(-f) ,\end{aligned} \tag{2.4}$$

since each of the fields $\vec{E}^{\pm}$ is transverse. Introducing the unit normal $\vec{n}$ to the surface $f=0$ by

$$\vec{n} = -\vec{\nabla}f/|\vec{\nabla}f| \; , \tag{2.5}$$

we can rewrite (2.4) as

$$\vec{\nabla}\cdot\vec{E}(\vec{r},\omega) = |\vec{\nabla}f|\,\delta(f)(\vec{n}\cdot\vec{E}^{(-)} - \vec{n}\cdot\vec{E}^{(+)})_{f=0} \; . \tag{2.6}$$

On using the continuity of the normal component of electric induction, (2.6) finally reduces to

$$\vec{\nabla}\cdot\vec{E}(\vec{r},\omega)=|\vec{\nabla}f|\,\delta(f)(\vec{n}\cdot\vec{E}^{(+)})_{f=0}[\epsilon(\omega)-1]\ . \tag{2.7}$$

Thus the second term in (2.1) represents the surface polarization and the first term is the volume contribution to nonlinear polarization. Following Bloembergen *et al.* one can now obtain the equations for the electric field for a medium occupying an arbitrary domain:

$$\vec{\nabla}\times\vec{\nabla}\times\vec{E}(\vec{r},2\omega)-\frac{4\omega^2}{c^2}\epsilon(2\omega)\vec{E}(\vec{r},2\omega)=\frac{16\pi\omega^2\gamma}{c^2}\vec{\nabla}[E^2(\vec{r},\omega)]\ ,\quad f>0 \tag{2.8}$$

$$\vec{\nabla}\times\vec{\nabla}\times\vec{E}(\vec{r},2\omega)-\frac{4\omega^2}{c^2}\vec{E}(\vec{r},2\omega)=0\ ,\quad f<0\ . \tag{2.9}$$

In view of the form of the surface polarization the boundary conditions are found to be (i) tangential $\vec{E}(\vec{r},2\omega)$ should be continuous across $f=0$, i.e., $\vec{n}\times\vec{E}(\vec{r},2\omega)$ continuous across $f=0$,

$$\vec{n}\times\vec{E}(\vec{r},2\omega)\,|_{-}^{+}=0\ , \tag{2.10}$$

and (ii) the magnetic field boundary condition, which depends on the presence of sources at surface, leads to

$$\vec{n}\times[\vec{\nabla}\times\vec{E}(\vec{r},2\omega)]\,|_{-}^{+}=\frac{16\pi\omega^2}{c^2}\beta[\epsilon(\omega)-1]\{\vec{n}\times[\vec{n}\times\vec{E}(\vec{r},\omega)]\}\vec{n}\cdot\vec{E}(\vec{r},\omega)\,|_{+}\ , \tag{2.11}$$

where we have used the usual notation

$$\phi(\vec{r},2\omega)\,|_{-}^{+}\equiv\lim_{f\to 0+}\phi(\vec{r},2\omega)-\lim_{f\to 0-}\phi(\vec{r},2\omega)\ . \tag{2.12}$$

The general solution of (2.8) can be written as

$$\vec{E}(\vec{r},2\omega)=\vec{F}_T(\vec{r},2\omega)+\vec{A}\ ,\qquad \vec{A}=-\frac{4\pi\gamma}{\epsilon(2\omega)}\vec{\nabla}[E^2(\vec{r},\omega)] \tag{2.13}$$

where $\vec{F}_T(\vec{r},2\omega)$ is the solution of the homogeneous equation

$$\vec{\nabla}\times\vec{\nabla}\times\vec{F}_T(\vec{r},2\omega)-\frac{4\omega^2}{c^2}\epsilon(2\omega)\vec{F}_T(\vec{r},2\omega)=0\ . \tag{2.14}$$

We will denote the solution of (2.9) by $\vec{F}_R(\vec{r},2\omega)$. This gives the field distribution at 2ω outside the medium $f<0$. One obviously also has the transversality conditions

$$\vec{\nabla}\cdot\vec{F}_T(\vec{r},2\omega)=0\ ,\quad \vec{\nabla}\cdot\vec{F}_R(\vec{r},2\omega)=0\ . \tag{2.15}$$

We have so far considered the general equations describing second-harmonic generation. It is possible to solve the above equations for simple geometries, for example, when $f(x,y,z)\equiv z$, i.e., a metallic medium occupying a semi-infinite domain. We have considered solutions for spherical geometries in our earlier Communication.[6] Since the surface-enhanced second-harmonic generation has been done in situations involving surface roughness, we must solve the above equations when the surface is rough. In such a situation a general solution is not possible. One can, however, develop a perturbation theory[10,11] in powers of the surface-roughness parameter.

We now assume that the roughness is in the form of a sinusoidal grating, i.e.,

$$z=-\xi\sin gy\ ,\quad \xi\frac{\omega}{c}\ll 1\ . \tag{2.16}$$

We can now write a power-series expansion

$$\vec{F}_{\begin{Bmatrix}T\\R\end{Bmatrix}}(\vec{r},2\omega)=\sum_n \xi^{(n)}\vec{F}^{(n)}_{\begin{Bmatrix}T\\R\end{Bmatrix}}(\vec{r},2\omega)\ , \tag{2.17}$$

where each term in view of (2.14) and (2.15) satisfies

$$\vec{\nabla}\cdot\vec{F}^{(n)}_{\begin{Bmatrix}T\\R\end{Bmatrix}}=0\ ,$$

$$\left[\nabla^2+\frac{4\omega^2}{c^2}\epsilon(2\omega)\right]\vec{F}^{(n)}_T=0\ , \tag{2.18}$$

$$\left[\nabla^2+\frac{4\omega^2}{c^2}\right]\vec{F}^{(n)}_R=0\ .$$

It should be borne in mind that since the boundary conditions involve the values at the surface, further Taylor-series expansions like the following are needed:

$$\vec{F}^{(n)}(x,y,-\xi\sin gy,2\omega)=\vec{F}^{(n)}(x,y,0,2\omega)-\xi\sin gy\frac{\partial\vec{F}^{(n)}}{\partial z}(x,y,0,2\omega)+\frac{\xi^2\sin^2 gy}{2}\frac{\partial^2\vec{F}^{(n)}}{\partial z^2}(x,y,0,2\omega)+\cdots \quad (2.19)$$

Similarly one must carry out the perturbation expansion of $\vec{A}$, which is defined by Eq. (2.13). Moreover, the vector $\vec{n}$ is also to be expanded in a Taylor series:

$$\vec{n}=-\hat{z}-\xi g\cos gy\hat{y}+\tfrac{1}{2}\xi^2(g^2\cos^2 gy)\hat{z}+\cdots \quad (2.20)$$

The next step in the calculation consists of substituting these perturbation expansions in Eqs. (2.10) and (2.11) and equating the equal powers of ξ. Note that the boundary conditions (2.10) and (2.11) can now be written as

$$\vec{n}\times[\vec{F}_T(x,y,-\xi\sin gy)+\vec{A}(x,y,-\xi\sin gy)-\vec{F}_R(x,y,-\xi\sin gy)]=0\ , \quad (2.21)$$

$$\vec{n}\times[\vec{\nabla}\times\vec{F}_T(x,y,-\xi\sin gy)-\vec{\nabla}\times\vec{F}_R(x,y,-\xi\sin gy)] = -\frac{16\pi\omega^2}{c^2}\beta[\epsilon(\omega)-1]\{\vec{n}\times[\vec{n}\times\vec{E}_T(x,y,-\xi\sin gy)]\}[\vec{n}\cdot\vec{E}_T(x,y,-\xi\sin gy)]\ . \quad (2.22)$$

Further simplification can be made depending on the form of the incident electromagnetic field.

III. PERTURBATIVE EQUATIONS FOR THE SECOND-HARMONIC FIELDS

In this section we use the formalism of Sec. II to obtain the explicit form of the fields at the second-harmonic frequency for the case when the incident electromagnetic field on the metallic surface is a plane wave propagating in the direction $\vec{K}_0$. We denote the component of $\vec{K}_0$ parallel to the flat surface $z=0$ by $\vec{\kappa}$ and along z by w_0. One, of course, has $\kappa^2+w_0^2=\omega^2/c^2$. For this purpose we need the perturbation expansions for fields at the fundamental frequency ω. In order that our paper be self-contained, we have listed such expressions in Appendix C. It would be clear from the structure of fields at ω, i.e., from Eqs. (C3), (C4), (C9), and (C13) that the second-harmonic fields in various orders of roughness will have the structure

$$\vec{F}_T^{(0)}(\vec{r})=\vec{F}_T^{(0)}e^{i\vec{Q}\cdot\vec{r}}\ ,\quad \vec{Q}=(2\vec{\kappa},\Lambda) \quad (3.1)$$

$$\vec{F}_T^{(1)}(\vec{r})=\vec{F}_{T+}^{(1)}e^{i\vec{Q}_+\cdot\vec{r}}+\vec{F}_{T-}^{(1)}e^{i\vec{Q}_-\cdot\vec{r}}\ ,\quad \vec{Q}_\pm=(2\vec{\kappa}\pm\vec{g},\Lambda_\pm) \quad (3.2)$$

$$\vec{F}_T^{(2)}(\vec{r})=\vec{F}_{T0}^{(2)}e^{i\vec{Q}\cdot\vec{r}}+\cdots\ , \quad (3.3)$$

where ellipses denote the fields with wave vectors whose components parallel to the plane $z=0$ are $2\vec{\kappa}\pm 2\vec{g}$. In Eqs. (3.1)–(3.3), the z component of the propagation vector is given by

$$4\kappa^2+\Lambda^2=\frac{4\omega^2}{c^2}\epsilon(2\omega)\ ,\qquad (2\vec{\kappa}\pm\vec{g})^2+\Lambda_\pm^2=\frac{4\omega^2}{c^2}\epsilon(2\omega)\ . \quad (3.4)$$

The second-harmonic fields outside the medium also have a similar structure:

$$\vec{F}_R^{(0)}(\vec{r})=\vec{F}_R^{(0)}e^{i\vec{Q}_R\cdot\vec{r}}\ ,\quad \vec{Q}_R=(2\vec{\kappa},\Lambda_R) \quad (3.5)$$

$$\vec{F}_R^{(1)}(\vec{r})=\vec{F}_{R+}^{(1)}e^{i\vec{Q}_{R+}\cdot\vec{r}}+\vec{F}_{R-}^{(1)}e^{i\vec{Q}_{R-}\cdot\vec{r}}\ ,\quad \vec{Q}_{R\pm}=(2\vec{\kappa}\pm\vec{g},\Lambda_{R\pm}) \quad (3.6)$$

$$\vec{F}_R^{(2)}(\vec{r})=\vec{F}_{R0}^{(2)}e^{i\vec{Q}_R\cdot\vec{r}}+\cdots\ , \quad (3.7)$$

where ellipses have the same meaning as in (3.3) and where

$$\Lambda_R=-\left[\frac{4\omega^2}{c^2}-4\kappa^2\right]^{1/2}\ ,\qquad \Lambda_{R\pm}=-\left[\frac{4\omega^2}{c^2}-(2\vec{\kappa}\pm\vec{g})^2\right]^{1/2}\ . \quad (3.8)$$

We have to now substitute expressions (3.1)–(3.8), (C3), (C9), and (C11)–(C17) in the boundary conditions (2.21) and (2.22). After considerable algebraic effort one finds that (2.21) leads to the set of equations (up to second order in the surface-roughness parameter ξ)

$$\hat{z}\times(\vec{\mathbf{F}}_T^{(0)}-\vec{\mathbf{F}}_R^{(0)})=\frac{4\pi\gamma i}{\epsilon(2\omega)}(\vec{\mathscr{E}}_T^{(0)}\cdot\vec{\mathscr{E}}_T^{(0)})(\hat{z}\times 2\vec{\kappa}) , \tag{3.9}$$

$$\begin{aligned}\hat{z}\times(\vec{\mathbf{F}}_{T\pm}^{(1)}-\vec{\mathbf{F}}_{R\pm}^{(1)})=&-\frac{g}{2}\hat{y}\times(\vec{\mathbf{F}}_T^{(0)}-\vec{\mathbf{F}}_R^{(0)})\pm\tfrac{1}{2}\hat{z}\times(\Lambda\vec{\mathbf{F}}_T^{(0)}-\Lambda_R\vec{\mathbf{F}}_R^{(0)})\\&+\frac{4\pi i\gamma}{\epsilon(2\omega)}\{2(\vec{\mathscr{E}}_T^{(0)}\cdot\vec{\mathscr{E}}_{T\pm}^{(1)})[\hat{z}\times(2\vec{\kappa}\pm\vec{g})]\mp w(\vec{\mathscr{E}}_T^{(0)}\cdot\vec{\mathscr{E}}_T^{(0)})(\hat{z}\times 2\vec{\kappa})+g(\vec{\mathscr{E}}^{(0)}\cdot\vec{\mathscr{E}}^{(0)})(\hat{y}\times\vec{\mathbf{K}})\} ,\end{aligned} \tag{3.10}$$

$$\begin{aligned}\hat{z}\times(\vec{\mathbf{F}}_{T0}^{(2)}-\vec{\mathbf{F}}_{R0}^{(2)})=&-\frac{g}{2}\hat{y}\times(\vec{\mathbf{F}}_{T+}^{(1)}+\vec{\mathbf{F}}_{T-}^{(1)}-\vec{\mathbf{F}}_{R+}^{(1)}-\vec{\mathbf{F}}_{R-}^{(1)})+\frac{g^2}{4}\hat{z}\times(F_T^{(0)}-F_R^{(0)})+\frac{\hat{z}}{4}\times(\Lambda^2\vec{\mathbf{F}}_T^{(0)}-\Lambda_R^2\vec{\mathbf{F}}_R^{(0)})\\&-\frac{\hat{z}}{2}\times(\Lambda_+\vec{\mathbf{F}}_{T+}^{(1)}-\Lambda_-\vec{\mathbf{F}}_{T-}^{(1)}-\Lambda_{R+}\vec{\mathbf{F}}_{R+}^{(1)}+\Lambda_{R-}\vec{\mathbf{F}}_{R-}^{(1)})\\&+\frac{4\pi i\gamma}{\epsilon(2\omega)}\left\{(\hat{z}\times 2\vec{\kappa})\left[2\vec{\mathscr{E}}_T^{(0)}\cdot\vec{\mathscr{E}}_{T0}^{(2)}+2\vec{\mathscr{E}}_{T+}^{(1)}\cdot\vec{\mathscr{E}}_{T-}^{(1)}-\left[w^2+\frac{g^2}{4}\right]\vec{\mathscr{E}}_T^{(0)}\cdot\vec{\mathscr{E}}_T^{(0)}\right]\right.\\&\quad+\{(w+w_+)(\vec{\mathscr{E}}_T^{(0)}\cdot\vec{\mathscr{E}}_{T+}^{(1)})[\hat{z}\times(2\vec{\kappa}+\vec{g})]-(+\rightarrow-)\}\\&\quad\left.+g\hat{x}[(w+w_+)(\vec{\mathscr{E}}_T^{(0)}\cdot\vec{\mathscr{E}}_{T+}^{(1)})+(+\rightarrow-)]\right\} ,\end{aligned} \tag{3.11}$$

where $(+\rightarrow-)$ implies the terms with all $\vec{g}\rightarrow-\vec{g}$. The magnetic field boundary condition (2.22) leads to even more complicated equations:

$$\hat{z}\times(\vec{\mathbf{Q}}\times\vec{\mathbf{F}}_T^{(0)}-\vec{\mathbf{Q}}_R\times\vec{\mathbf{F}}_R^{(0)})=-\frac{16\pi i\omega^2}{c^2}\beta[\epsilon(\omega)-1]\mathscr{E}_{Tz}^{(0)}\hat{z}\times(\hat{z}\times\vec{\mathscr{E}}_T^{(0)}) , \tag{3.12}$$

$$\begin{aligned}&\hat{z}\times(\vec{\mathbf{Q}}_\pm\times\vec{\mathbf{F}}_{T\pm}^{(1)}-\vec{\mathbf{Q}}_{R\pm}\times\vec{\mathbf{F}}_{R\pm}^{(1)})\\&=-\frac{g}{2}\hat{y}\times(\vec{\mathbf{Q}}\times\vec{\mathbf{F}}_T^{(0)}-\vec{\mathbf{Q}}_R\times\vec{\mathbf{F}}_R^{(0)})\pm\tfrac{1}{2}\hat{z}\times(\Lambda\vec{\mathbf{Q}}\times\vec{\mathbf{F}}_T^{(0)}-\Lambda_R\vec{\mathbf{Q}}_R\times\vec{\mathbf{F}}_R^{(0)})\\&\quad-\frac{16\pi i\omega^2}{c^2}\beta[\epsilon(\omega)-1]\left[\mathscr{E}_{Tz}^{(0)}\hat{z}\times[\hat{z}\times(\vec{\mathscr{E}}_{T\pm}^{(1)}\mp w\vec{\mathscr{E}}_T^{(0)})]+\mathscr{E}_{T\pm z}^{(1)}\hat{z}\times(\hat{z}\times\vec{\mathscr{E}}_T^{(0)})\right.\\&\quad\left.+\frac{g}{2}\mathscr{E}_{Ty}^{(0)}\hat{z}\times(\hat{z}\times\vec{\mathscr{E}}_T^{(0)})+\frac{g}{2}\mathscr{E}_{Tz}^{(0)}[\hat{z}\times(\hat{y}\times\vec{\mathscr{E}}_T^{(0)})+\hat{y}\times(\hat{z}\times\vec{\mathscr{E}}_T^{(0)})]\right] ,\end{aligned} \tag{3.13}$$

$$\begin{aligned}&\hat{z}\times(\vec{\mathbf{Q}}\times\vec{\mathbf{F}}_{T0}^{(2)}-\vec{\mathbf{Q}}_R\times\vec{\mathbf{F}}_{R0}^{(2)})\\&=\frac{\hat{z}}{4}\times(\Lambda^2\vec{\mathbf{Q}}\times\vec{\mathbf{F}}_T^{(0)}-\Lambda_R^2\vec{\mathbf{Q}}_R\times\vec{\mathbf{F}}_R^{(0)})-\frac{g}{2}\hat{y}\times(\vec{\mathbf{Q}}_+\times\vec{\mathbf{F}}_{T+}^{(1)}+\vec{\mathbf{Q}}_-\times\vec{\mathbf{F}}_{T-}^{(1)}-\vec{\mathbf{Q}}_{R+}\times\vec{\mathbf{F}}_{R+}^{(1)}-\vec{\mathbf{Q}}_{R-}\times\vec{\mathbf{F}}_{R-}^{(1)})\\&\quad-\frac{\hat{z}}{2}\times(\Lambda_+\vec{\mathbf{Q}}_+\times\vec{\mathbf{F}}_{T+}^{(1)}-\Lambda_-\vec{\mathbf{Q}}_-\times\vec{\mathbf{F}}_{T-}^{(1)}-\Lambda_{R+}\vec{\mathbf{Q}}_{R+}\times\vec{\mathbf{F}}_{R+}^{(1)}+\Lambda_{R-}\vec{\mathbf{Q}}_{R-}\times\vec{\mathbf{F}}_{R-}^{(1)})\\&\quad-\frac{16\pi i\omega^2}{c^2}[\epsilon(\omega)-1]\beta\left[\vec{\mathbf{z}}\times\left\{\vec{\mathbf{z}}\times\left[-\left[w^2+\frac{g^2}{2}\right]\mathscr{E}_{Tz}^{(0)}\vec{\mathscr{E}}_T^{(0)}+\frac{g}{2}(\mathscr{E}_{T+y}^{(1)}+\mathscr{E}_{T-y}^{(1)})\vec{\mathscr{E}}_T^{(0)}\right.\right.\right.\\&\quad+\frac{g}{2}\mathscr{E}_{Ty}^{(0)}(\vec{\mathscr{E}}_{T+}^{(1)}+\vec{\mathscr{E}}_{T-}^{(1)})+\mathscr{E}_{Tz}^{(0)}\vec{\mathscr{E}}_{T0}^{(2)}+\mathscr{E}_{T0z}^{(2)}\vec{\mathscr{E}}_T^{(0)}+\mathscr{E}_{T+z}^{(1)}\vec{\mathscr{E}}_{T-}^{(1)}\\&\quad+\mathscr{E}_{T-z}^{(1)}\vec{\mathscr{E}}_{T+}^{(1)}+\tfrac{1}{2}\mathscr{E}_{Tz}^{(0)}[(w+w_+)\vec{\mathscr{E}}_{T+}^{(1)}-(w+w_-)\vec{\mathscr{E}}_{T-}^{(1)}]\end{aligned}$$

$$+\tfrac{1}{2}\vec{\mathscr{E}}_T^{(0)}[(w+w_+)\mathscr{E}_{T+z}^{(1)}-(w+w_-)\mathscr{E}_{T-z}^{(1)}]\Bigg]\Bigg\}+\frac{g^2}{2}\mathscr{E}_{Tz}^{(0)}\hat{y}\times(\hat{y}\times\vec{\mathscr{E}}_T^{(0)})$$

$$+\hat{z}\times\left[\hat{y}\times\left[\frac{g^2}{2}\mathscr{E}_{Ty}^{(0)}\vec{\mathscr{E}}_T^{(0)}+\frac{g}{2}\vec{\mathscr{E}}_T^{(0)}(\mathscr{E}_{T+z}^{(1)}+\mathscr{E}_{T-z}^{(1)})+\frac{g}{2}\mathscr{E}_{Tz}^{(0)}(\vec{\mathscr{E}}_{T+}^{(1)}+\vec{\mathscr{E}}_{T-}^{(1)})\right]\right]$$

$$+\hat{y}\times\left[\hat{z}\times\left[\frac{g^2}{2}\mathscr{E}_{Ty}^{(0)}\vec{\mathscr{E}}_T^{(0)}+\frac{g}{2}\vec{\mathscr{E}}_T^{(0)}(\mathscr{E}_{T+z}^{(1)}+\mathscr{E}_{T-z}^{(1)})+\frac{g}{2}\mathscr{E}_{Tz}^{(0)}(\vec{\mathscr{E}}_{T+}^{(1)}+\vec{\mathscr{E}}_{T-}^{(1)})\right]\right]\Bigg] . \quad (3.14)$$

The solution of the above vectorial equations would yield all the fields at the second-harmonic frequency. Note that in each order we have equations with very similar structure, though the form of the inhomogeneous term in each order is different. In Appendix B we show how such equations can be generally solved and how one can obtain the s and p components of such fields.

If we now assume that the incident field at the fundamental frequency ω is p polarized, i.e., it has the structure [cf. Eq. (A2)]

$$\vec{E}^{(i)}(\vec{r},\omega)=\frac{(\hat{z}\times\vec{\kappa})\times\vec{K}_0}{\kappa k_0}\mathscr{E}_p^{(i)}e^{i\vec{\kappa}\cdot\vec{r}+iw_0 z}\ ,\quad \vec{K}_0=(\vec{\kappa},w_0)\ ,\quad w_0^2=k_0^2-\kappa^2\ ,\quad k_0=\omega/c \quad (3.15)$$

then the zero-order transmitted and reflected fields have only p components. On using (3.9), (3.12), and (B5)–(B8) we obtain for the zero-order fields at 2ω:

$$F_{Tp}^{(0)}=16\pi i k_0\kappa[\epsilon(2\omega)]^{1/2}[\Lambda+\Lambda_0\epsilon(2\omega)]^{-1}(\mathscr{E}_{Tp}^{(0)})^2\left[\frac{\gamma}{\epsilon(2\omega)}+\frac{\beta(\epsilon-1)\Lambda_0 w}{2k_0^2\epsilon}\right] , \quad (3.16)$$

$$F_{Rp}^{(0)}=16\pi i k_0\kappa[\Lambda+\Lambda_0\epsilon(2\omega)]^{-1}(\mathscr{E}_{Tp}^{(0)})^2\left[\gamma-\frac{\beta(\epsilon-1)\Lambda w}{2k_0^2\epsilon}\right] , \quad (3.17)$$

$$F_{Ts}^{(0)}=F_{Rs}^{(0)}=0\ ,\quad \epsilon=\epsilon(\omega)\ . \quad (3.18)$$

Thus the zero-order field at 2ω is only p polarized which is due to our assumption that the incident radiation at ω was p polarized. The intensity of second-harmonic generation in the direction $\vec{Q}_R$ is $|F_{Rp}^{(0)}|^2$. This result when written in terms of various angles agrees with that of Bloembergen *et al.*[2]

IV. INTENSITY OF SECOND-HARMONIC FIELD OUTSIDE THE METAL IN THE DIRECTION OF FIRST-ORDER DIFFRACTION

We now consider the features of the second-harmonic generation in the direction in which first-order diffraction (at 2ω) takes place, i.e., we will consider second-harmonic fields, outside the metal, with propagation vectors

$$\vec{Q}_{R\pm}=(2\vec{\kappa}\pm\vec{g},-[(4\omega^2/c^2)-(2\vec{\kappa}\pm\vec{g})^2]^{1/2})\ .$$

For this purpose we will assume that the incident field at the fundamental frequency is p polarized, i.e., it has the structure (3.15). We will show that SHG in these directions can have several orders of enhancement due to surface-plasmon–polariton excitation inside the medium. The actual value of enhancement depends on the relative direction of $\vec{g}$ and $\vec{\kappa}$ and the closeness of the incident angle to the angle at which surface-plasmon polaritons are excited. The expressions for the first-order fields at the second harmonic are obtained from the solutions of (3.13) and (3.10) and by noting that the zero-order fields at both fundamental and second-harmonic frequency are p polarized. The first-order fields that appear in (3.13) and (3.10) at ω have both s and p components. Using now Eqs. (B5)–(B8) of Appendix B and various relations given in Appendix A, a rather involved algebra leads to the following explicit results for the s and p components of the fields at 2ω:

$$F_{T\pm p}^{(1)} = -\frac{2k_0[\epsilon(2\omega)]^{1/2}}{|2\vec{\kappa}\pm\vec{g}|}[\Lambda_{0\pm}\epsilon(2\omega)+\Lambda_\pm]^{-1}\left[\Phi_\pm^{(1)}-\frac{\Lambda_{0\pm}}{4k_0^2}\psi_\pm^{(1)}\right], \quad (4.1)$$

$$F_{R\pm p}^{(1)} = -\frac{2k_0}{|2\vec{\kappa}\pm\vec{g}|}[\Lambda_{0\pm}\epsilon(2\omega)+\Lambda_\pm]^{-1}\left[\epsilon(2\omega)\Phi_\pm^{(1)}+\frac{\Lambda_\pm}{4k_0^2}\psi_\pm^{(1)}\right], \quad (4.2)$$

$$F_{T\pm s}^{(1)} = \frac{1}{|2\vec{\kappa}\pm\vec{g}|}(\Lambda_{0\pm}+\Lambda_\pm)^{-1}(-\Lambda_{0\pm}\Omega_\pm^{(1)}+\chi_\pm^{(1)}), \quad (4.3)$$

$$F_{R\pm s}^{(1)} = \frac{1}{|2\vec{\kappa}\pm\vec{g}|}(\Lambda_{0\pm}+\Lambda_\pm)^{-1}(\Lambda_\pm\Omega_\pm^{(1)}+\chi_\pm^{(1)}), \quad (4.4)$$

where

$$\Phi_\pm^{(1)} = \mp\frac{\Lambda^2(4\kappa^2\pm 2g\kappa_y)}{8\kappa k_0[\epsilon(2\omega)]^{1/2}}F_{Tp}^{(0)} \pm \frac{\Lambda_R^2(4\kappa^2\pm 2g\kappa_y)}{8\kappa k_0}F_{Rp}^{(0)} + \frac{\kappa}{2k_0}(2g\kappa_y \pm g^2)\left[\frac{1}{[\epsilon(2\omega)]^{1/2}}F_{Tp}^{(0)}-F_{Rp}^{(0)}\right]$$
$$+\frac{4\pi i\gamma}{\epsilon(2\omega)}|2\vec{\kappa}\pm\vec{g}|^2\left[\pm w(\mathscr{E}_{Tp}^{(0)})^2-\frac{(\vec{\kappa}\cdot\vec{\kappa}_\pm)ww_\pm+\kappa^2\kappa_\pm^2}{k_0^2\epsilon\kappa\kappa_\pm}2\mathscr{E}_{Tp}^{(0)}\mathscr{E}_{T\pm p}^{(1)} \pm \frac{2wg\kappa_x}{k_0\sqrt{\epsilon}\kappa\kappa_\pm}\mathscr{E}_{Tp}^{(0)}\mathscr{E}_{T\pm s}^{(1)}\right], \quad (4.5)$$

$$\Omega_\pm^{(1)} = \frac{g\kappa_x}{k_0}\left[\kappa\left[\frac{1}{[\epsilon(2\omega)]^{1/2}}F_{Tp}^{(0)}-F_{Rp}^{(0)}\right] \pm \frac{\Lambda^2 F_{Tp}^{(0)}}{4\kappa[\epsilon(2\omega)]^{1/2}} \mp \frac{\Lambda_R^2 F_{Rp}^{(0)}}{4\kappa}\right], \quad (4.6)$$

$$\chi_\pm^{(1)} = \frac{k_0\kappa_x g}{\kappa}[-\Lambda[\epsilon(2\omega)]^{1/2}F_{Tp}^{(0)}+\Lambda_R F_{Rp}^{(0)}]$$
$$+\frac{16\pi i\omega^2}{c^2}\frac{\beta(\epsilon-1)g\kappa_x}{k_0^2\epsilon}\left\{\pm\frac{w_\pm\kappa}{\kappa_\pm}\mathscr{E}_{Tp}^{(0)}\mathscr{E}_{T\pm p}^{(1)}+\kappa^2(\mathscr{E}_{Tp}^{(0)})^2 \pm \frac{w}{\kappa}\left[\left[\frac{gw\kappa_y}{2\kappa}\pm w\kappa\right](\mathscr{E}_{Tp}^{(0)})^2-\kappa_\pm\mathscr{E}_{Tp}^{(0)}\mathscr{E}_{T\pm p}^{(1)}\right]\right.$$
$$\left.+\frac{\kappa k_0\sqrt{\epsilon}}{\kappa_\pm g\kappa_x}\mathscr{E}_{Tp}^{(0)}\mathscr{E}_{T\pm s}^{(1)}(2\kappa^2+g^2\pm 3g\kappa_y)\right\}, \quad (4.7)$$

$$\psi_\pm^{(1)} = \frac{(4\kappa^2\pm 2g\kappa_y)k_0}{2\kappa}\{\pm[\epsilon(2\omega)]^{1/2}\Lambda F_{Tp}^{(0)} \mp \Lambda_R F_{Rp}^{(0)}\}$$
$$+\frac{16\pi i\omega^2}{c^2}\beta(\epsilon-1)\left\{\mp\frac{g\kappa\kappa_x}{k_0\sqrt{\epsilon}\kappa_\pm}\mathscr{E}_{Tp}^{(0)}\mathscr{E}_{T\pm s}^{(1)}+(\mathscr{E}_{Tp}^{(0)})^2\frac{(2g\kappa_y\pm g^2)\kappa^2}{2k_0^2\epsilon}+\frac{\kappa w_\pm(2\kappa^2+g^2\pm 3g\kappa_y)}{k_0^2\epsilon\kappa_\pm}\mathscr{E}_{Tp}^{(0)}\mathscr{E}_{T\pm p}^{(1)}\right.$$
$$\left.-\frac{w(4\kappa^2\pm 2g\kappa_y)}{2k_0^2\epsilon\kappa}\left[(\mathscr{E}_{Tp}^{(0)})^2\left[\frac{gw\kappa_y}{2\kappa}\pm w\kappa\right]-\kappa_\pm\mathscr{E}_{T\pm p}^{(1)}\mathscr{E}_{Tp}^{(0)}\right]\right\}. \quad (4.8)$$

Though the expressions for $F_{R\pm p}^{(1)}$, $F_{R\pm s}^{(10}$, etc. are quite cumbersome, two important features of these fields should be noted. The p component of these fields contain two resonant denominators:

$$D(2\omega)=[\Lambda_{0\pm}\epsilon(2\omega)+\Lambda_\pm], \quad D(\omega)=[w_{0\pm}\epsilon(\omega)+w_\pm]. \quad (4.9)$$

The vanishing of these denominators can be shown to be equivalent to the relations

$$D(\omega)=0 \Longrightarrow \kappa_\pm^2=\frac{\omega^2}{c^2}\frac{\epsilon(\omega)}{\epsilon(\omega)+1}, \quad (4.10)$$

$$D(2\omega)=0 \Longrightarrow |2\vec{\kappa}\pm\vec{g}|^2=\frac{4\omega^2}{c^2}\frac{\epsilon(2\omega)}{\epsilon(2\omega)+1}. \quad (4.11)$$

The relations (4.10) and (4.11) are just the dispersion relations for surface-plasmon polaritons at the frequencies ω and 2ω, respectively. It is thus clear that if the incident angle, frequency, and the relative direction of $\vec{\kappa}$ and $\vec{g}$ and magnitude of g are such that (4.10) is satisfied, then the surface polaritons inside the medium are excited resonantly and the fields at the second-harmonic frequency are resonantly enhanced, resulting in surface-enhanced second-harmonic generation. The s components of the fields have only the resonant denominator at the fundamental frequency.

The vanishing of the denominator $D(2\omega)$, which leads to the surface-plasmon polaritons at the frequency 2ω, can happen only under the usual conditions, on ϵ and wave vector, for the existence of surface-plasmon polaritons in planar geometries (half-space). Such surface-plasmon polaritons have a wave-vector component, parallel to plane $z=0$, $2\vec{\kappa}\pm\vec{g}$ and will be excited provided that (assuming real dielectric function) $\epsilon(2\omega)<-1$ and $|2\vec{\kappa}+\vec{g}|^2>4\omega^2/c^2$. If $|2\vec{\kappa}\pm\vec{g}|^2>4\omega^2/c^2$, then the corresponding z component of the propagation vector $\Lambda_{0\pm}=[4\omega^2/c^2-|(2\vec{\kappa}\pm\vec{g})|^2]^{1/2}$ will be purely imaginary, leading to decaying waves in the z direction. This implies that for those angles of incidence for which, say, $|2\vec{\kappa}+\vec{g}|^2>4\omega^2/c^2$, the second-harmonic field with propagation vector

$$(2\vec{\kappa}+\vec{g},-[(4w^2/c)-|2\vec{\kappa}+\vec{g}|^2]^{1/2})$$

will be evanescent in nature. Thus the second-harmonic radiation in the directions of first-order diffraction will be observable in the far zone only if the incident angles satisfy $|2\vec{\kappa}\pm\vec{g}|<4\omega^2/c^2$. When $|2\vec{\kappa}\pm\vec{g}|^2>4\omega^2/c^2$, the second-harmonic fields will only exist in the neighborhood of the surface. There may be situations involving the interaction of the atoms and molecules near the metal surface, where such second-harmonic fields, which though evanescent in nature are resonantly enhanced, could be important.

The intensities of the second-harmonic radiation can now be written as

$$I_{\pm p}=|F_{R\pm p}^{(1)}|^2\,,\quad I_{\pm s}=|F_{R\pm s}^{(1)}|^2\,. \tag{4.12}$$

We will now show the variation of the SH intensity with respect to the incident angle. We assume that the radiation at the frequency corresponding to 1.17 eV be incident on the silver grating surface. The frequency chosen corresponds to the one used in the experiment[5] of Chen *et al.* The dielectric function at the fundamental ($\omega=1.17$ eV) and the second harmonic has the values[12]

$$\epsilon(\omega)=(0.04+7.5i)^2\,,$$
$$\epsilon(2\omega)=(0.054+3.4i)^2\,. \tag{4.13}$$

Thus the dielectric function has a large negative real part both at ω and 2ω and hence in principle it will be possible to excite surface plasmons at ω and 2ω depending on the incident wave vector and grating periodicity. We show in Fig. 1 the intensities

$$I_{\pm p}/(\xi k_0)^2(e/8\pi m\omega^2)^2(\mathscr{E}_p^{(i)})^4\,,$$

in arbitrary units, as a function of the angle of incidence when the incident angle is such that $\vec{\kappa}\,||\,\vec{g}$, i.e.,

$$\vec{\kappa}\cdot\vec{g}=\kappa_y g=\kappa\sin\theta g\,.$$

The second-harmonic intensity

$$|F_{Rp}^{(0)}|^2/(e/8\pi m\omega^2)^2(\mathscr{E}_p^{(i)})^4$$

in the absence of grating structure is also shown. The resonant enhancement of the second-harmonic radiation is shown separately. For this case, the g value has been taken to be such that both (4.10) and (4.11) could be satisfied for the direction Q_+, and hence in Fig. 1, I_{+p} shows resonant enhance-

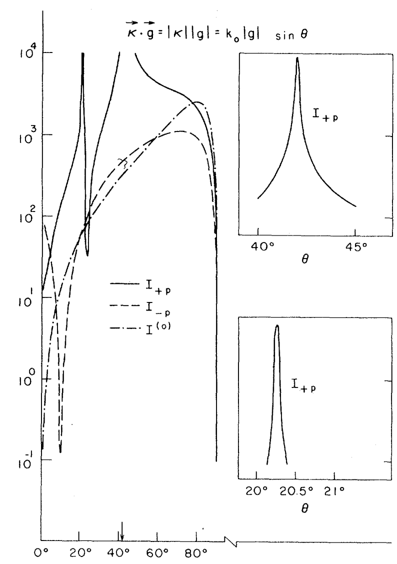

FIG. 1. Second-harmonic generation in the direction of first-order diffraction at 2ω, as a function of the angle of incidence θ of the p-polarized plane wave at ω. The azimuthal angle of incidence is taken to be $\pi/2$ so that $\vec{\kappa}$ is parallel to the direction of grating periodicity. The intensities are in arbitrary units—the plots represent $I_{\pm p}/(\xi k_0)^2(\mathscr{E}_p^{(i)})^4\beta^2$ and $I_{0p}/\beta^2(\mathscr{E}_p^{(i)})^4$, respectively [$\beta$ given by (2.21)], with $I_{\pm p}=|F_{R\pm p}^{(1)}|^2$ [Eq. (4.2)], $I_{0p}=|F_{RP}^{(0)}|^2$ [Eq. (3.17)]. The two insets show the behavior of second-harmonic radiation in the range where surface-plasmon polaritons are excited.

ments corresponding to both (4.10) and (4.11), whereas I_{-p} has no resonances. The peak positions are easily obtained by substituting (4.13) in (4.10) and (4.11). For this particular geometry $I_{\pm s}=0$. The enhancement factors are of the order of $(10^5-10^4)(\xi k_0)^2 \sim 10^3$ for $\xi k_0 \sim 0.1-0.3$. The resonant enhancements, which are roughly of the order of $|\mathrm{Re}\epsilon(\omega)/\mathrm{Im}\epsilon(\omega)|^2$, in the second-harmonic intensity due to surface-plasmon— polariton excitation are in broad agreement with the experiment of Chen *et al.*

In Fig. 2, we present the behavior of the second-harmonic radiation when the incident wave vector is such that $\vec{\kappa}\cdot\vec{g}=0$. The right-hand side of Fig. 2 gives the dependence of second-harmonic radiation for angles of incidence close to surface-plasmon—polariton excitation. All the components $I_{\pm p}$ and $I_{\pm s}$ have resonant denominators corresponding to the excitation of surface-plasmon polaritons at the fundamental frequency. As Fig. 2 shows, the enhancement of second-harmonic radiation is not so pronounced as in the case $\vec{\kappa}\times\vec{g}=0$. Our analysis thus indicates that the enhancement of second-harmonic radiation due to surface-plasmon—polariton excitation is quite sensitive to the relative directions of incidence and the

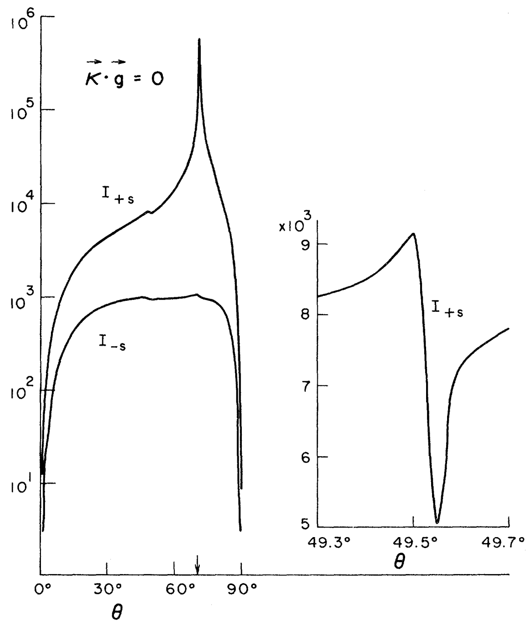

FIG. 2. Behavior of $I_{\pm s}/(\xi k_0)^2(\mathscr{E}_p^{(i)})^4\beta^2$ as a function of angle of incidence where $\vec{\kappa}$ is perpendicular to $\vec{g}$. The resonant region for I_{+s} is shown separately on the right. I_{-s} also exhibits a dispersionlike structure similar to I_{+s}, in the resonant region.

grating periodicity. The cusplike behavior of I_{+s} occurs at incident angle given by

$$|2\vec{\kappa}+\vec{g}|^2=4\omega^2/c^2 ,$$

i.e., at the point (shown by an arrow in Fig. 2) where the character of the second-harmonic field changes to being evanescent in nature [cf. the paragraph preceding (4.12)].

V. EFFECT OF METALLIC GRATING ON THE INTENSITY OF SECOND-HARMONIC GENERATION IN THE PRIMARY DIRECTION OF REFLECTION

We now examine what happens to the roughness induced second-harmonic generation in the direction

$$\vec{Q}_R \equiv (2\vec{\kappa}, -2[(\omega^2/c^2)-\kappa^2]^{1/2}) ,$$

i.e., in the direction in which second-harmonic-generated radiation propagates in the absence of surface roughness. One would expect large variations in the second-harmonic intensity in the direction $\vec{Q}_R$, if the incident angle is such that the surface-plasmon polaritons are excited in the medium. Up to second order[13] in ξ, the total intensity in the direction $\vec{Q}_R$ will be

$$I=|F_{Rp}^{(0)}|^2+2\xi^2\,\mathrm{Re}(F_{Rp}^{(0)}F_{0Rp}^{(2)*})$$

$$=|F_{Rp}^{(0)}|^2[1+2\xi^2\,\mathrm{Re}(F_{0Rp}^{(2)}/F_{Rp}^{(0)})] \qquad (5.1)$$

$$=I^{(0)}+I_0^{(2)} . \qquad (5.2)$$

We will now study the behavior of the quantity $I_0^{(2)}$ as a function of incident angle in the region of the angles for which surface-plasmon—polariton excitation is possible. The second-order fields are to be obtained from (3.11) and (3.14) and the results of Appendixes A and B. This involves considerable algebra and we quote only the final result, which is quite complex:

$$I_0^{(2)}=|F_{Rp}^0|^2 2\xi^2 k_0^2\,\mathrm{Re}\left[\frac{\epsilon(2\omega)\Phi+\dfrac{\Lambda}{4k_0^2}\psi}{\epsilon(2\omega)\Phi^{(0)}+\dfrac{\Lambda}{4k_0^2}\psi^{(0)}}\right] , \qquad (5.3)$$

where

$$\Phi^{(0)}=-\frac{16\pi i\gamma\kappa^2}{\epsilon(2\omega)}(\mathscr{E}_{Tp}^{(0)})^2\,,\quad \psi^{(0)}=\frac{32\pi i w\kappa^2}{\epsilon}\beta(\epsilon-1)(\mathscr{E}_{Tp}^{(0)})^2\,, \tag{5.4}$$

$$\begin{aligned}
\Phi=-\frac{\kappa}{4k_0}\Bigg[&\frac{\Lambda(\Lambda^2+g^2)}{[\epsilon(2\omega)]^{1/2}}F_{Tp}^{(0)}-\Lambda_R(\Lambda_R^2+g^2)F_{Rp}^{(0)}\Bigg]\\
&+\Bigg[\frac{|2\vec{\kappa}+\vec{g}\,|}{2k_0[\epsilon(2\omega)]^{1/2}}(g\kappa_y+\tfrac{1}{2}\Lambda_+^2)F_{T+p}^{(1)}-\frac{|2\vec{\kappa}+\vec{g}\,|}{2k_0}(g\kappa_y+\tfrac{1}{2}\Lambda_{R+}^2)F_{R+p}^{(1)}-\frac{g\Lambda_+^2(2\kappa_y+g)}{4k_0[\epsilon(2\omega)]^{1/2}|2\vec{\kappa}+\vec{g}\,|}F_{T+p}^{(1)}\\
&\quad+\frac{g\Lambda_{R+}^2(2\kappa_y+g)}{4k_0|2\vec{\kappa}+\vec{g}\,|}F_{R+p}^{(1)}-\frac{g\kappa_x\Lambda_+}{|2\vec{\kappa}+\vec{g}\,|}F_{T+s}^{(1)}+\frac{g\Lambda_{R+}\kappa_x}{|2\vec{\kappa}+\vec{g}\,|}F_{R+s}^{(1)}-\begin{Bmatrix}+\to-\\ g\to-g\end{Bmatrix}\Bigg]\\
&+\frac{16\pi i\gamma\kappa^2}{\epsilon(2\omega)}\Bigg[\Bigg[w^2+\frac{g^2}{4}\Bigg](\mathscr{E}_{Tp}^{(0)})^2-2\mathscr{E}_{Tp}^{(0)}\mathscr{E}_{0Tp}^{(2)}-\frac{2(\vec{\kappa}_+\cdot\vec{\kappa}_-)}{\kappa_+\kappa_-}\mathscr{E}_{T+s}^{(1)}\mathscr{E}_{T-s}^{(1)}\\
&\qquad-2\frac{w_+w_-(\vec{\kappa}_+\cdot\vec{\kappa}_-)+\kappa_+^2\kappa_-^2}{k_0^2\epsilon\kappa_+\kappa_-}\mathscr{E}_{T+p}^{(1)}\mathscr{E}_{T-p}^{(1)}-4g\kappa_x\Bigg[\frac{w_+\mathscr{E}_{T-s}^{(1)}\mathscr{E}_{T+p}^{(1)}}{k_0\sqrt{\epsilon}\kappa_+\kappa_-}-\begin{Bmatrix}+\to-\\-\to+\end{Bmatrix}\Bigg]\\
&\qquad+\Bigg[(w+w_-)\Bigg[\frac{(\vec{\kappa}\cdot\vec{\kappa}_-)ww_-+\kappa^2\kappa_-^2}{k_0^2\epsilon\kappa\kappa_-}\mathscr{E}_{Tp}^{(0)}\mathscr{E}_{T-p}^{(1)}+\frac{g\kappa_x\mathscr{E}_{Tp}^{(0)}\mathscr{E}_{T-s}^{(1)}}{k_0\sqrt{\epsilon}\kappa\kappa_-}\Bigg]-\begin{Bmatrix}+\to-\\ g\to-g\end{Bmatrix}\Bigg]\Bigg]\,,
\end{aligned} \tag{5.5}$$

$$\begin{aligned}
\psi=\kappa k_0\{&\Lambda^2[\epsilon(2\omega)]^{1/2}F_{Tp}^{(0)}-\Lambda_R^2F_{Rp}^{(0)}\}\\
&-\Bigg[\Lambda_+k_0[\epsilon(2\omega)]^{1/2}\frac{4\kappa^2+2g\kappa_y}{|2\vec{\kappa}+\vec{g}\,|}F_{T+p}^{(1)}-\frac{k_0\Lambda_{R+}(4\kappa^2+2g\kappa_y)}{|2\vec{\kappa}-\vec{g}\,|}F_{R+p}^{(1)}+\frac{g\kappa_x\Lambda_+^2}{|2\vec{\kappa}+\vec{g}\,|}F_{T+s}^{(1)}\\
&\quad-\frac{g\kappa_x\Lambda_{R+}^2}{|2\vec{\kappa}+\vec{g}\,|}F_{R+s}^{(1)}+g\kappa_x|2\vec{\kappa}+\vec{g}\,|(F_{T+s}^{(1)}-F_{R+s}^{(1)})-\begin{Bmatrix}+\to-\\ g\to-g\end{Bmatrix}\Bigg]\\
&+\frac{16\pi i\omega^2}{c^2}(\epsilon-1)\beta\Bigg[-\frac{2w}{(k_0^2\epsilon)}(g^2\kappa_y^2+w^2\kappa^2)(\mathscr{E}_{Tp}^{(0)})^2+\frac{4w\kappa^2}{k_0^2\epsilon}\mathscr{E}_{Tp}^{(0)}\mathscr{E}_{T0p}^{(2)}\\
&\qquad+\Bigg[\mathscr{E}_{Tp}^{(0)}\frac{\mathscr{E}_{T+p}^{(1)}\kappa}{k_0^2\epsilon}\Bigg[2g\kappa_y\kappa_+-\frac{(\vec{\kappa}\cdot\vec{\kappa}_+)ww_+\kappa_yg}{\kappa^2\kappa_+}+\frac{(\vec{\kappa}\cdot\vec{\kappa}_+)w_+(w+w_+)}{\kappa_+}+w(w+w_+)\kappa_+\\
&\qquad\quad-\frac{ww_+g(g+\kappa_y)}{\kappa_+}\Bigg]+\frac{\mathscr{E}_{Tp}^{(0)}\mathscr{E}_{T+s}^{(1)}\kappa_x}{k_0\sqrt{\epsilon}\kappa_+}\Bigg[\frac{g^2\kappa_yw}{\kappa}-\kappa g(w+w_+)-wg\kappa\Bigg]-\begin{Bmatrix}+\to-\\-\to+\\ g\to-g\end{Bmatrix}\Bigg]\\
&+\frac{2g\kappa_x}{k_0\sqrt{\epsilon}}\Bigg[\frac{\kappa_+}{\kappa_-}\mathscr{E}_{T-s}^{(1)}\mathscr{E}_{T+p}^{(1)}-\frac{\kappa_-}{\kappa_+}\mathscr{E}_{T+s}^{(1)}\mathscr{E}_{T-p}^{(1)}\Bigg]+\frac{\mathscr{E}_{T+p}^{(1)}\mathscr{E}_{T-p}^{(1)}}{k_0^2\epsilon}\Bigg[\frac{\kappa_+w_-}{\kappa_-}(2\kappa^2-2g\kappa_y)+\frac{\kappa_-w_+}{\kappa_+}(2\kappa^2+2g\kappa_y)\Bigg]\Bigg]\,.
\end{aligned} \tag{5.6}$$

The notation $\{{}^{+\to-}_{-\to+}\}$ ($\{{}^{\pm\to\mp}_{g\to-g}\}$) means terms obtained by changing the subscripts (and by changing the sign of any g's appearing explicitly).

We now have the complete expression, although complicated, for the roughness-induced second-harmonic generation in the direction $\vec{Q}_R$. The behavior of $I_0^{(2)}$ in arbitrary units,

$$I_0^{(2)}/\xi^2 k_0^2 (e/8\pi m\omega^2)^2 (\mathscr{E}_p^{(i)})^4 ,$$

is shown in Fig. 3 for the range of incident angles at which surface-plasmon polaritons can be excited[14] (cf. insets in Fig. 1). Various parameters have been chosen as in Sec. IV. It will be seen that $I_0^{(2)}$ displays a sharp dispersionlike structure for values of κ for which (4.10) or (4.11) could be satisfied. The resonances in $I_0^{(2)}$ arise from the resonant denominator in terms like $F_{R+p}^{(1)}$, $\mathscr{E}_{T+p}^{(1)}$, etc. It is clear from Fig. 3 that the measurements of the variation of SH intensity in the direction in which the second-harmonic radiation in the absence of roughness propagates will be quite interesting as it shows a dispersionlike resonance.

It may be noted that for the sake of illustrating the main features of the theory we have considered the case of SHG at the surface of a metallic grating. The results obviously could be generalized to more complicated surfaces, which, of course, makes the field expression even more complicated. The case of a statistical rough surface[11] with the assumption of uncorrelated Fourier components, i.e., when

$$z = -\xi \int F(\vec{\kappa}) e^{i\vec{\kappa}\cdot\vec{r}} d^2\kappa , \tag{5.7}$$

with

$$\langle F(\vec{\kappa}) F^*(\vec{\kappa}') \rangle \sim \delta(\vec{\kappa}-\vec{\kappa}') P(\vec{\kappa}) , \tag{5.8}$$

can be obtained from the foregoing results by averaging the final results of Secs. IV and V over the distribution $P(\vec{g})$.

Thus to conclude we have presented within the framework of Maxwell's equations, using the nonlinear source polarization in the metal, a complete theory of surface-enhanced second-harmonic generation. We have calculated the resonant enhancements in SHG explicitly due to SPP excitation. The only assumption of the theory is the smallness of the surface-roughness parameter, which is generally quite all right and which if one wishes could be relaxed if one resorts to extensive computer calculations. The generalizations to other nonlinear optical processes such as frequency mixing at a rough metallic surface would be examined in the future. It should also be interesting to examine the effects of hydrodynamic dispersion or the electron-hole excitations on the surface-enhanced second-harmonic generation.

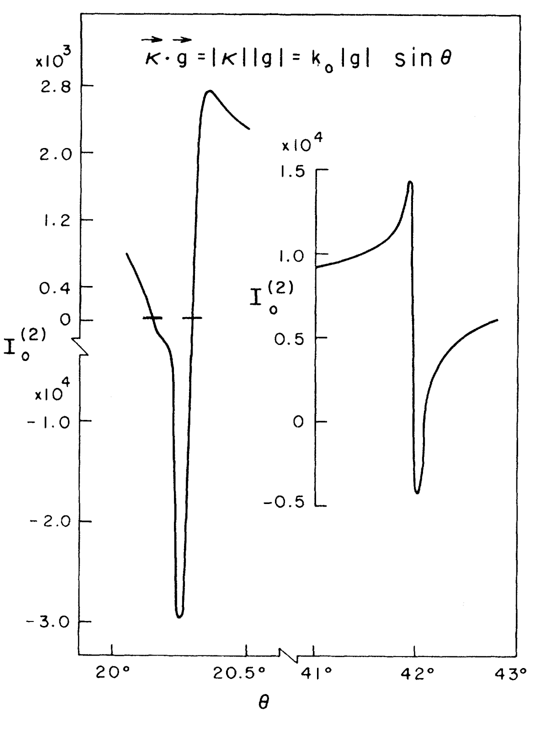

FIG. 3. Behavior of the roughness-induced second-harmonic generation in the primary direction of reflection, i.e., $I_{0p}^{(2)}/\xi^2 k^2 (\mathscr{E}_p^{(i)})^4 \beta^2$, in arbitrary units, as a function of angle of incidence. The two dispersion-shaped resonances represent the excitation of surface-plasmon polaritons at the fundamental and the second-harmonic frequency, respectively.

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APPENDIX A: RESOLUTION OF A PLANE WAVE INTO ITS s AND p COMPONENTS

In this appendix, we describe briefly the various relations among the cartesian and s and p components of a plane wave. Such relations will be used extensively in our calculations. Consider a plane wave with propagation vector $\vec{k} = (\vec{\kappa}, w)$ and frequency ω propagating in a medium with dielectric function $\epsilon(\omega)$, i.e.,

$$\vec{E}(\vec{r},\omega) = \vec{\mathscr{E}}(\vec{\kappa}) e^{i\vec{\kappa}\cdot\vec{r} + iwz} ,$$
$$\kappa^2 + w^2 = \frac{\omega^2}{c^2}\epsilon(\omega) = k^2 , \tag{A1}$$

where $\vec{\kappa}$ is a two-dimensional vector. We further assume that the waves are transverse; then the vector $\vec{\mathscr{E}}(\vec{\kappa})$ can be decomposed in terms of two unit vectors perpendicular to the direction of propagation:

$$\vec{\mathscr{E}}(\vec{\kappa})=\frac{\hat{z}\times\vec{\kappa}}{\kappa}\mathscr{E}_s+\frac{(\hat{z}\times\vec{\kappa})\times\vec{k}}{\kappa k}\mathscr{E}_p \ . \qquad (A2)$$

For propagation in a vacuum, as, for example, would be the case for reflected fields, one sets $\epsilon=1$. It is clear from (A2) that the Cartesian components of $\vec{\mathscr{E}}$ are related to s and p components by

$$\mathscr{E}_x=-\frac{\kappa_y}{\kappa}\mathscr{E}_s+\frac{w\kappa_x}{k\kappa}\mathscr{E}_p \ ,$$
$$\mathscr{E}_y=+\frac{\kappa_x}{\kappa}\mathscr{E}_s+\frac{w\kappa_y}{k\kappa}\mathscr{E}_p \ , \qquad (A3)$$
$$\mathscr{E}_z=-\frac{\kappa^2}{k\kappa}\mathscr{E}_p \ .$$

It is also clear from (A2) that

$$\mathscr{E}_s=\frac{1}{\kappa}(\vec{\kappa}\times\vec{\mathscr{E}})_z \ , \quad \mathscr{E}_p=-\frac{k}{\kappa}\mathscr{E}_z \ . \qquad (A4)$$

In a nonmagnetic medium, the magnetic field is given by

$$\vec{H}(\vec{r},\omega)=\vec{\mathscr{H}}(\vec{\kappa})e^{i\vec{\kappa}\cdot\vec{r}+iwz} \ ,$$
$$\vec{\mathscr{H}}(\vec{\kappa})=(\vec{k}\times\vec{\mathscr{E}})c/\omega \qquad (A5)$$
$$=\frac{\hat{z}\times\vec{\kappa}}{\kappa}\mathscr{H}_s+\frac{(\hat{z}\times\vec{\kappa})\times\vec{k}}{k\kappa}\mathscr{H}_p \ ,$$

where on simplification we get the relations among the s and p components of electric and magnetic fields

$$\mathscr{H}_s=\sqrt{\epsilon}\mathscr{E}_p \ , \quad \mathscr{H}_p=-\sqrt{\epsilon}\mathscr{E}_s \ . \qquad (A6)$$

APPENDIX B: GENERAL SOLUTION OF THE VECTORIAL INHOMOGENEOUS EQUATIONS INVOLVING REFLECTED AND TRANSMITTED FIELDS

In the main text of this paper, we have seen that the fields at the second-harmonic frequency to various orders in the surface-roughness parameter can be obtained provided we know the general solution of the following inhomogeneous equations [cf. Eqs. (3.9)–(3.14)]:

$$\hat{z}\times[\vec{U}(\vec{\kappa})-\vec{V}(\vec{\kappa})]+\hat{z}\times\vec{A}(\vec{\kappa})=0 \ ,$$
$$\hat{z}\times(\vec{K}_U\times\vec{U}-\vec{K}_V\times\vec{V})+\hat{z}\times\vec{B}(\vec{\kappa})=0 \ , \qquad (B1)$$

with

$$\vec{K}_U\cdot\vec{U}=0 \ , \quad \vec{K}_V\cdot\vec{V}=0 \ ,$$
$$\vec{K}_U=(\vec{\kappa},w_U) \ , \quad \vec{K}_V=(\vec{\kappa},w_V) \ . \qquad (B2)$$

Equations (B1) can be written as (with || denoting x or y component)

$$\vec{U}_{||}+\vec{A}_{||}=\vec{V}_{||} \ ,$$
$$\vec{\kappa}(U_z-V_z)-w_U\vec{U}_{||}+w_V\vec{V}_{||}+(\hat{z}\times\vec{B})_{||}=0 \ , \qquad (B3)$$

whereas (B2) leads to

$$U_z=-\frac{1}{w_U}(\vec{\kappa}\cdot\vec{U}) \ , \quad V_z=-\frac{1}{w_V}(\vec{\kappa}\cdot\vec{V}) \ . \qquad (B4)$$

It is now a simple matter to solve (B3) and (B4) for the cartesian components of $\vec{U}$ and $\vec{V}$. Once Cartesian components are known, then (A4) can be used to obtain s and p components of U and V. The results are found to be

$$U_s=\frac{1}{\kappa(w_U-w_V)}\hat{z}\cdot[w_V(\vec{\kappa}\times\vec{A})+\vec{\kappa}\times(\hat{z}\times\vec{B})] \ , \qquad (B5)$$

$$V_s=\frac{1}{\kappa(w_U-w_V)}\hat{z}\cdot[w_U(\vec{\kappa}\times\vec{A})+\vec{\kappa}\times(\hat{z}\times\vec{B})] \ , \qquad (B6)$$

$$U_p=-\frac{k_U}{\kappa}(w_Uk_V^2-w_Vk_U^2)^{-1}$$
$$\times[w_V\vec{\kappa}\cdot(\hat{z}\times\vec{B})+k_V^2(\vec{\kappa}\cdot\vec{A})] \ , \qquad (B7)$$

$$V_p=-\frac{k_V}{\kappa}(w_Uk_V^2-w_Vk_U^2)^{-1}$$
$$\times[w_U\vec{\kappa}\cdot(\hat{z}\times\vec{B})+k_U^2(\vec{\kappa}\cdot\vec{A})] \ . \qquad (B8)$$

These solutions to Eqs. (B1) and (B2) are extensively used in the text.

APPENDIX C: SUMMARY OF THE VARIOUS ORDER FIELDS AT THE FUNDAMENTAL FREQUENCY ω

The fields produced by a plane wave incident on a rough surface can be calculated by a variety of methods and these are now well known. Since our calculations of the second-harmonic generation at a rough surface involve the fields at the fundamental frequency rather extensively, we present, in what follows for the sake of completeness, the expressions for such fields. We assume as in the text, that the roughness is in the form of a sinusoidal grating, i.e., the equation of the surface is given by $z=-\xi\,\mathrm{sing}y$. We assume a plane wave with propagation vector $\vec{K}_0=(\vec{\kappa},w_0)$ incident on such a medium

$$\vec{E}^{(i)}(\vec{r},\omega)=\vec{\mathscr{E}}^{(i)}e^{i\vec{\kappa}\cdot\vec{r}+iw_0z},$$

$$\kappa^2+w_0^2=\frac{\omega^2}{c^2}=k_0^2, \tag{C1}$$

$$\mathscr{E}^{(i)}=\frac{\hat{z}\times\vec{\kappa}}{\kappa}\mathscr{E}_s^{(i)}+\frac{(\hat{z}\times\vec{\kappa})\times\vec{K}_0}{\kappa k_0}\mathscr{E}_p^{(i)}. \tag{C2}$$

Then the zero-order transmitted and reflected fields would be given as usual by Fresnel formulas, which in our present notation read as

$$\vec{E}_T^{(0)}(\vec{r},\omega)=\vec{\mathscr{E}}_T^{(0)}e^{i\vec{\kappa}\cdot\vec{r}+iwz},$$

$$\kappa^2+w^2=\frac{\omega^2}{c^2}\epsilon(\omega), \tag{C3}$$

$$\vec{E}_R^{(0)}(\vec{r},\omega)=\vec{\mathscr{E}}_R^{(0)}e^{i\vec{\kappa}\cdot\vec{r}-iw_0z},$$

$$\vec{K}'=(\vec{\kappa},-w_0), \tag{C4}$$

$$\vec{\mathscr{E}}_T^{(0)}=\frac{\hat{z}\times\vec{\kappa}}{\kappa}\mathscr{E}_{Ts}^{(0)}+\frac{(\hat{z}\times\vec{\kappa})\times\vec{K}}{\kappa k}\mathscr{E}_{Tp}^{(0)}, \tag{C5}$$

$$\vec{\mathscr{E}}_R^{(0)}=\frac{\hat{z}\times\vec{\kappa}}{\kappa}\mathscr{E}_{Rs}^{(0)}+\frac{(\hat{z}\times\vec{\kappa})\times\vec{K}_0'}{\kappa k_0}\mathscr{E}_{Rp}^{(0)}, \tag{C6}$$

$$\mathscr{E}_{Ts}^{(0)}=\frac{2w_0}{w+w_0}\mathscr{E}_s^{(i)},$$

$$\mathscr{E}_{Tp}^{(0)}=\frac{2w_0\sqrt{\epsilon}}{w_0\epsilon+w}\mathscr{E}_p^{(i)}, \tag{C7}$$

$$\mathscr{E}_{Rs}^{(0)}=\frac{w_0-w}{w+w_0}\mathscr{E}_s^{(i)},$$

$$\mathscr{E}_{Rp}^{(0)}=\frac{w_0\epsilon-w}{w_0\epsilon+w}\mathscr{E}_p^{(i)}. \tag{C8}$$

In view of the grating structure of the surface roughness, the first-order fields will have the structure

$$\vec{E}_T^{(1)}(\vec{r},\omega)=\vec{\mathscr{E}}_{T+}^{(1)}e^{i\vec{K}_+\cdot\vec{r}}+\vec{\mathscr{E}}_{T-}^{(1)}e^{i\vec{K}_-\cdot\vec{r}}, \tag{C9}$$

where

$$\vec{K}_\pm=(\vec{\kappa}_\pm,w_\pm),$$

$$\vec{\kappa}_\pm=\vec{\kappa}\pm\vec{g},\quad \kappa_\pm^2+w_\pm^2=k_0^2\epsilon(\omega). \tag{C10}$$

The fields $\vec{\mathscr{E}}_{T\pm}^{(1)}$ can be resolved into s and p components as in (A2) with $\vec{\kappa}\to\vec{\kappa}_\pm$ and $\vec{K}\to\vec{K}_\pm$. One finds that

$$\mathscr{E}_{T\pm p}^{(1)}=\pm\frac{(\epsilon-1)}{2\kappa\kappa_\pm}\mathscr{E}_{Tp}^{(0)}\{\kappa^2k_0^2(w_\pm+w_{0\pm})^{-1}+w_{0\pm}(w_{0\pm}\epsilon+w_\pm)^{-1}[w(\vec{\kappa}\cdot\vec{\kappa}_\pm)-\kappa^2w_\pm]\}$$
$$+\frac{(\epsilon-1)}{2\kappa\kappa_\pm}w_{0\pm}\mathscr{E}_{Ts}^{(0)}[(w_{0\pm}\epsilon+w_\pm)^{-1}(\vec{\kappa}\times\vec{g})k], \tag{C11}$$

$$\mathscr{E}_{T\pm s}^{(1)}=\frac{(\epsilon-1)wk_0\mathscr{E}_{Tp}^{(0)}(\vec{g}\times\vec{\kappa})}{2\kappa\kappa_\pm\sqrt{\epsilon}(w_\pm+w_{0\pm})}\pm\frac{(\epsilon-1)k_0^2(\vec{\kappa}\cdot\vec{\kappa}_\pm)}{(w_\pm+w_{0\pm})\kappa\kappa_\pm}\mathscr{E}_{Ts}^{(0)}. \tag{C12}$$

In our calculations in the text we do not need the first-order reflected fields and hence such fields are not listed here.

The fields to second order in the surface-roughness parameter will have the structure

$$\vec{E}_T^{(2)}(\vec{r},\omega)=\vec{\mathscr{E}}_{T0}^{(2)}e^{i\vec{K}\cdot\vec{r}}+\vec{\mathscr{E}}_{T++}^{(2)}e^{i\vec{K}_{++}\cdot\vec{r}}+\vec{\mathscr{E}}_{T--}^{(2)}e^{i\vec{K}_{--}\cdot\vec{r}}, \tag{C13}$$

$$\vec{K}_{\pm\pm}=(\vec{\kappa}\pm2\vec{g},w_{\pm\pm}),\quad w_{\pm\pm}^2=-(\kappa\pm2g)^2+k_0^2\epsilon. \tag{C14}$$

Only the second-order field with propagation vector $\vec{K}=(\vec{\kappa},w)$ is of interest. Using Eq. (2.12) of Ref. 13 one can show that

$$\vec{\mathscr{E}}_{T0}^{(2)}\equiv\left[-\overleftrightarrow{1}+\frac{\vec{K}_0\vec{K}}{\vec{K}\cdot\vec{K}_0}\right]\cdot\{\tfrac{1}{2}(w-w_0)(\vec{\mathscr{E}}_{T+}^{(1)}-\vec{\mathscr{E}}_{T-}^{(1)})-\tfrac{1}{4}[g^2+\tfrac{1}{2}(w-w_0)^2]\vec{\mathscr{E}}_T^{(0)}\}, \tag{C15}$$

where $\overleftrightarrow{1}$ is the unit dyadic. The s and p components of $\vec{\mathscr{E}}_{T0}^{(2)}$ can be obtained by expressing each of the fields $\vec{\mathscr{E}}_{T\pm}^{(1)}$ and $\vec{\mathscr{E}}_T^{(0)}$ in terms of their s and p components and Eqs. (A1)−(A4) with the results

$$\mathscr{E}^{(2)}_{T0p}=\tfrac{1}{4}[g^2+\tfrac{1}{2}(w-w_0)^2]\mathscr{E}^{(0)}_{Tp}-\tfrac{1}{2}\frac{w-w_0}{\kappa}(\kappa_+\mathscr{E}^{(1)}_{T+p}-\kappa_-\mathscr{E}^{(1)}_{T-p})$$
$$+\frac{1}{2}\frac{(w-w_0)w_0}{\vec{K}\cdot\vec{K}_0}\left[-\frac{k(\vec{g}\times\vec{\kappa})}{\kappa}\left[\frac{\mathscr{E}^{(1)}_{T+s}}{\kappa_+}+\frac{\mathscr{E}^{(1)}_{T-s}}{\kappa_-}\right]+\frac{w\kappa_+^2-w_+(\vec{\kappa}\cdot\vec{\kappa}_+)}{\kappa\kappa_+}\mathscr{E}^{(1)}_{T+p}\right.$$
$$\left.-\frac{w\kappa_-^2-w_-(\vec{\kappa}\cdot\vec{\kappa}_-)}{\kappa\kappa_-}\mathscr{E}^{(1)}_{T-p}\right], \tag{C16}$$

$$\mathscr{E}^{(2)}_{T0s}=\tfrac{1}{4}[g^2+\tfrac{1}{2}(w-w_0)^2]\mathscr{E}^{(0)}_{Ts}-\frac{1}{2}\frac{w-w_0}{\kappa}\left[\frac{\vec{\kappa}\cdot\vec{\kappa}_+}{\kappa_+}\mathscr{E}^{(1)}_{T+s}-\frac{\vec{\kappa}\cdot\vec{\kappa}_-}{\kappa_-}\mathscr{E}^{(1)}_{T-s}\right]$$
$$-\tfrac{1}{2}(\vec{\kappa}\times\vec{g})\frac{w-w_0}{\kappa k}\left[\frac{w_+}{\kappa_+}\mathscr{E}^{(1)}_{T+p}+\frac{w_-}{\kappa_-}\mathscr{E}^{(1)}_{T-p}\right]. \tag{C17}$$

We have now complete expressions for fields (inside the medium) at the fundamental frequency ω up to second order in surface-roughness parameter ξ. These expressions can be further simplified depending on the directions of polarization and the propagation of the incident plane wave. In the text we consider the interesting case when the incident radiation is p polarized.

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