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Theory of Optical Harmonic Generation at a Metal Surface*†

SUDHANSHU S. JHA‡
Department of Physics, Stanford University, Stanford, California
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It is shown that a light wave of the high intensity obtainable from lasers produces a sufficiently strong nonlinear polarization on a reflecting metal surface to result in an observable amount of second harmonic generation. The analysis is based upon a self-consistent set of Maxwell's equations and the classical Boltzmann equation, respectively, for the electromagnetic fields and the distribution function of the conduction electrons. The conduction electrons are considered to be completely free except for a potential barrier at the metal surface, and the equations are solved for the fields varying with the frequency ω of the incident wave, and also for the fields varying with the frequency 2ω in the approximation where the surface barrier can be taken as a step potential. The effect of the incident light wave is treated as a perturbation to the motion of the electrons and the frequency ω is assumed to be less than half the plasma frequency ω_p so that neither the fundamental nor the second harmonic wave can lead to plasma resonance. The part of the polarization varying as $e^{-2i\omega t}$ which is quadratic in the incident field is found to have the form

$$\mathbf{P}_2(\mathrm{NL})=\alpha(\mathbf{E}_1\times\mathbf{H}_1)+\beta\mathbf{E}_1\mathrm{div}\mathbf{E}_1,$$

where $\mathbf{E}_1$ and $\mathbf{H}_1$ are, respectively, the electric and magnetic fields varying as $e^{-i\omega t}$ and where the magnitudes of the coefficients α and β have been determined. Since div $\mathbf{E}_1$ differs from zero only near the surface of the metal, the second term in $\mathbf{P}_2$ (NL) can be considered as a surface contribution in contrast to the volume contribution of the first term. It is shown that these two terms give rise to comparable effects of second harmonic generation. The ratio of the average energy flux reflected with frequency 2ω from the surface to the incident flux is found to be of the order of magnitude $(e|E_{\mathrm{inc}}|/mc\omega_p)^2$, where E_{inc} is the amplitude of the incident electric vector.

1. INTRODUCTION

In recent years light beams of very high intensity have become available. These beams induce a nonlinear polarization and produce second harmonic waves in the interior or at the surface of the medium. The observations[1] of the optical harmonics have been, however, limited to insulators and semiconductors and no experimental work has yet been reported on the second harmonic generation at a metal surface. Except for thin foils there is no transmission of waves through a metal in the visible and lower frequency region and one has to observe the harmonics in the reflected beam. Also, it is more difficult to perform this type of experiment on metals because of excessive heating of the surface by the laser beam. Nevertheless, the order of magnitude of the nonlinear polarizability is such that with proper precautions one should be able to detect the doubling of frequency in the light reflected from a metal surface. In fact, we will describe an experiment being carried out at Stanford in this direction in the last section of this paper.

A classical calculation by Kronig and Boukema[2] and a quantum-mechanical calculation by Cheng and Miller[3] have been published for the nonlinear conductivity tensor of a free-electron gas. They obtained identical results in the limit where the Fermi velocity v_f of the metal electron is small compared to the velocity of light c and where the energy of the photon quanta $\hbar\omega$ is small compared to the rest energy mc^2 of the electrons. Both of these calculations do not take the boundary effects into account. On the other hand, the surface of the metal plays an important role in the reflection of light and it will be shown in the following treatment of the problem that it is, in an essential manner, determined by the existence of the surface. We will show in the following classical calculation that the component of the nonlinear polarization varying as $e^{-2i\omega t}$ has the form

$$\mathbf{P}_2(\mathrm{NL})=\alpha(\mathbf{E}_1\times\mathbf{H}_1)+\beta\mathbf{E}_1\,\mathrm{div}\mathbf{E}_1\,, \tag{1.1}$$

where $\mathbf{E}_1$ and $\mathbf{H}_1$ are the components of the electric and magnetic fields, respectively, varying as $e^{-i\omega t}$. This form satisfies the general symmetry requirements discussed by Adler.[4] The first term in Eq. (1.1) is identical with the results of the earlier calculations.[2,3] The second term is a new term which is nonzero only near the surface but which affects the nature of second harmonic waves even away from the surface and must be taken into account.

In this paper we consider a semi-infinite metal filling the half-space $x_1\geqslant 0$, so that the x_2-x_3 plane is the surface involved in the reflection of light of (circular) frequency ω. Here x_1, x_2, and x_3 mean x, y, and z components, respectively, of the coordinate vector $\mathbf{x}$. We use in this work potentials rather than fields $\mathbf{E}$ and $\mathbf{H}$, in the gauge where the time-dependent part of the scalar potential is taken to be zero. We first assume a

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† Based in part on a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
‡ Present address: Tata Institute of Fundamental Research, Bombay, India.
[1] P. A. Franken, A. E. Hill, and G. Weinreich, Phys. Rev. Letters **7**, 118 (1961); J. Ducing and N. Bloembergen, *ibid.* **10**, 474 (1963); P. A. Franken and J. F. Ward, Rev. Mod. Phys. **35**, 23 (1963).
[2] R. Kronig and J. I. Boukema, Konikl. Ned. Akad. Wetenschap. Proc. Ser. B **66**, 8 (1963).
[3] H. Cheng and P. B. Miller, Phys. Rev. **134**, A683 (1964).
[4] E. Adler, Phys. Rev. **134**, A728 (1964).

general form of the vector potential $\mathbf{A}$ and of the time-independent scalar potential Φ_0 and try to find the solution of the classical many-body problem given by the Boltzmann equation for the electrons in the metal in the presence of these unknown potentials. In the absence of the external light wave, the electrons in the metal are considered to be free except for a barrier potential at the surface. The solution of the Boltzmann equation gives the distribution function $f(x_j,v_j,t)$, where $f(x_j,v_j,t)d^3xd^3v$ represents the number of electrons at time t in the six-dimensional volume element d^3xd^3v of the coordinate $\mathbf{x}$ and velocity $\mathbf{v}$ space.[4a] From this function the expression for the current density containing the assumed form of the potentials can be calculated. Since this expression enters into Maxwell's equations for $\mathbf{A}$, a set of self-consistent differential equations for the vector potential is thus obtained. In Sec. 2 we will derive this set of differential equations.

The time between collisions of an electron in a metal at room temperature, e.g., in silver, is of the order[5] 10^{-14} sec and longer at lower temperatures, while the period $2\pi/\omega$ of a light wave in the optical frequency region is of the order 10^{-15} sec. Thus, the period of the light wave can reasonably well be considered to be short compared to the time between collisions of an electron, and it is permissible to neglect such collisions in calculating the potentials varying with optical frequencies. In the microwave region, where $2\pi/\omega$ is long compared to the collision time, it is necessary to retain the collision term in the Boltzmann equation. Reuter and Sondheimer[6] have calculated the part of the field varying with the incident frequency ω in the microwave region by taking a simple form for the collision term.

With the above assumption in the optical region about the collision term, the general solution for the time-varying components of f is found in Sec. 3 by solving the Boltzmann equation. This solution is approximated to the limit where the distance d, within which the surface barrier potential varies, can be considered to be small compared to v_f/ω. It is shown in Appendix I that this is equivalent to taking a step potential at $x_1=0$. Two more distinct simplifications occur in this problem. The first is due to the fact that the amplitude of the incident light wave can be assumed to be sufficiently small so that it can be treated by a perturbation method and the other is due to the smallness of the Fermi velocity v_f compared to the velocity of light c. With these approximations we solve for the potential varying with frequency ω in Sec. 4. Denoting the plasma frequency by ω_p, it is found that, for $\omega<\omega_p$ and $x_1\gg v_f/\omega$, the solution inside the metal is damped at all angles of incidence, exactly as given by Fresnel formulas.[7,8] The solution for $x_1\ll v_f/\omega$ differs appreciably from Fresnel formulas, especially for the component of the vector potential that is normal to the surface.

In Sec. 5 a solution for the potential varying with frequency 2ω is found that is correct outside the metal and for $x_1\gg v_f/\omega$ inside the metal. In Sec. 6 we derive the expressions for α and β of Eq. (1.1) and discuss our results.

2. SELF-CONSISTENT DIFFERENTIAL EQUATIONS

Let us assume that a metal slab occupies the half-space $x_1\geqslant 0$ and that after the time $t=-\infty$, a light wave of frequency ω has started to act. Choosing a convenient gauge the incident light wave is represented by a vanishing scalar potential and by a vector potential

$$\mathbf{A}_{\rm inc}=\mathbf{D}_1\exp\left[i\omega\left(\frac{\cos\theta}{c}x_1-\frac{\sin\theta}{c}x_2\right)\right]e^{-i\omega t}+\text{c.c.},\qquad(2.1)$$

where the Cartesian components of $\mathbf{D}_1$ are given by

$$\mathbf{D}_1=(A_p\sin\theta,A_p\cos\theta,A_s).\qquad(2.2)$$

Here, and later in the text, the symbol c.c. means the complex-conjugate term corresponding to the first term on the right. To emphasize the fact that, at time $t=-\infty$, the metal is not interacting with the light wave we may imagine that ω has an arbitrarily small positive imaginary part in the first term of Eq. (2.1).

By penetrating into the metal the light wave will interact with the electrons and ions in the metal, which in turn will produce a field as a result of their induced motion. Thus, a self-consistent field will be set up inside and outside the metal. In the gauge where the time-dependent part of the scalar potential is zero, let this field be represented by a vector potential $\mathbf{A}$ and a time-independent scalar potential Φ_0, where the electric and magnetic fields are, respectively, given by

$$\mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}-\nabla\Phi_0\qquad(2.3)$$

and

$$\mathbf{H}_1=\nabla\times\mathbf{A}.\qquad(2.4)$$

Since there is no zero-frequency component in the incident light wave, the deviation of the time-independent part of the scalar potential Φ_0 from the undisturbed value is expected to be at most of second order in $\mathbf{D}_1$. Maxwell's equations satisfied by $\mathbf{A}$ and

[4a] Recently it was pointed out by Professor Bloembergen and Professor Shen at the Puerto Rico Conference on the Physics of Quantum Electronics (unpublished) that the nonlinear polarizability of silver ion core at the surface should also be considered. Like our surface term this was shown to give a $\cos^4\Theta$ dependence to the reflected intensity and thus the volume contribution may still be separated.

[5] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1960), pp. 238–240.

[6] G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) **A195**, 336 (1949).

[7] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Company, Inc., New York, 1941), Chap. IX.

[8] L. I. Schiff and L. H. Thomas, Phys. Rev. **47**, 860 (1935).

Φ_0, are

$$\frac{\partial}{\partial x_j}\left(\frac{\partial A_j}{\partial x_k}-\frac{\partial A_k}{\partial x_j}\right)+\frac{1}{c^2}\frac{\partial^2 A_k}{\partial t^2}=\frac{4\pi}{c}J_k \tag{2.5}$$

and

$$-\frac{1}{c}\frac{\partial}{\partial t}\frac{\partial A_k}{\partial x_k}-\frac{\partial^2\Phi_0}{\partial x_k\partial x_k}=4\pi\rho, \tag{2.6}$$

where $\mathbf{J}$ and ρ are the current and charge densities, respectively. In Eqs. (2.5) and (2.6), j and k represent different Cartesian components, each taking the values 1, 2, or 3 corresponding to the x, y, and z components, respectively, and here as well as later in the text, repeated indices imply summations over those indices. In our formulation of the problem, the motion of the ions due to their large mass, as well as their polarization, are neglected and their presence is taken into account only in as far as it causes a neutralizing positive charge density, assumed to be static and uniform. Thus, in terms of the distribution function $f(x_j,v_j,t)$ for the electrons the components of the current density are given by

$$J_k=-e\int d^3v\, v_k f(x_j,v_j,t) \tag{2.7}$$

and the charge density is given by

$$\rho=-e\int d^3v\, f(x_j,v_j,t)+en, \tag{2.8}$$

where n is the unperturbed density of the electrons and en is the charge density of the ions.

The distribution function $f(x_j,v_j,t)$ satisfies the Boltzmann equation

$$\frac{\partial f}{\partial t}+v_j\frac{\partial f}{\partial x_j}-\frac{1}{m}\frac{dU}{dx_1}\frac{\partial f}{\partial v_1}+\frac{F_j}{m}\frac{\partial f}{\partial v_j}=\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}, \tag{2.9}$$

where

$$F_j=-\frac{e}{c}\frac{\partial A_j}{\partial t}-\frac{e}{c}v_k\left(\frac{\partial A_k}{\partial x_j}-\frac{\partial A_j}{\partial x_k}\right)+e\frac{\partial\Phi_0}{\partial x_j} \tag{2.10}$$

is the force due to the vector potential $\mathbf{A}$ and the scalar potential Φ_0. In Eq. (2.9), $U(x_1)$ is the surface-barrier potential that will be approximated later on by a step potential at $x_1=0$, and $(\partial f/\partial t)_{\text{coll}}$ is the collision term for the electrons. As explained in Sec. 1, we will neglect this collision term in the calculation of the potentials in the optical frequency region.

Equations (2.5)–(2.10) form a set of self-consistent differential equations for $\mathbf{A}$, Φ_0, and f. This set of equations must be solved with the conditions that, for $t\rightarrow-\infty$, the distribution function f approaches f^0, the unperturbed equilibrium distribution function for the electrons, and that the incoming wave in the solution for $\mathbf{A}$ for $x_1<0$ is represented by Eqs. (2.1) and (2.2).

3. SOLUTION OF THE BOLTZMANN EQUATION

When the collision term of the Boltzmann equation (2.9) is neglected, it becomes

$$\frac{\partial f}{\partial t}+v_j\frac{\partial f}{\partial x_j}-\frac{1}{m}\frac{dU}{dx_1}\frac{\partial f}{\partial v_1}=-\frac{F_j}{m}\frac{\partial f}{\partial v_j}. \tag{3.1}$$

Let

$$f=\sum_q f_q(x_j,v_j)e^{-iq\omega t} \tag{3.2}$$

and

$$F_j=\sum_q F_{jq}(x_j,v_j)e^{-iq\omega t}, \tag{3.3}$$

where q assumes all positive and negative integer values including zero and where, because of the reality conditions, the complex conjugates f_q^* and F_{jq}^* must be such that

$$f_q^*=f_{-q} \tag{3.4}$$

and

$$F_{jq}^*=F_{j,-q}. \tag{3.5}$$

The expansion of the electromagnetic force F in Eq. (3.3) is implied by a corresponding expansion of the vector potential $\mathbf{A}$ of the form

$$A_j=\sum_q a_{jq}(x_j,v_j)e^{-iq\omega t} \tag{3.6}$$

with

$$a_{jq}^*=a_{j,-q}. \tag{3.7}$$

Because of the dependence on x_2 of the incident wave of Eq. (2.1), f_q, F_{jq}, and a_{jq} can be assumed to be given by

$$f_q,\, F_{jq},\, a_{jq}\sim\exp\left(-iq\omega\frac{\sin\theta}{c}x_2\right). \tag{3.8}$$

Then, from Eq. (3.1), one obtains

$$-i\omega_q f_q+v_1\frac{\partial f_q}{\partial x_1}-\frac{1}{m}\frac{dU}{dx_1}\frac{\partial f_q}{\partial v_1}=K_q(x_1,x_2,x_3,v_j), \tag{3.9}$$

where

$$\omega_q=q\omega(1+(v_2/c)\sin\theta) \tag{3.10}$$

and

$$K_q=-\frac{1}{m}\sum_p F_{jp}\frac{\partial f_{q-p}}{\partial v_j}. \tag{3.11}$$

In the Appendix I of this paper, it is shown that we can replace the surface barrier potential $U(x_1)$ by a step potential at $x_1=0$, provided that

$$\omega d/v_f\ll 1, \tag{3.12}$$

where d is the distance within which $U(x_1)$ varies near the surface. Ordinarily in a metal, $d\cong 10^{-8}$ cm and $v_f\cong 10^8$ cm/sec, so that it is necessary to assume $\omega\ll 10^{16}$ sec^{-1}. Under this assumption it is further shown in the Appendix I that the solution of Eq. (3.9) can be written as

$$f_q(x_j,v_j)\equiv f_q^-(x_j,v_j)$$
$$=\int_{-\infty}^{x_1}\frac{dx_1'}{v_1}\exp i\left(\omega_q\frac{(x_1-x_1')}{v_1}\right)K_q(x_1',x_2,x_3,v_j) \quad (3.13)$$

for $v_1<0$ and

$$f_q(x_j,v_j)\equiv f_q^+(x_j,v_j)$$
$$=\int_0^{x_1}\frac{dx_1'}{v_1}\exp\left(i\omega_q\frac{(x_1-x_1')}{v_1}\right)K_q(x_1',x_2,x_3,v_j)$$
$$+\exp\left(i\omega_q\frac{x_1}{v_1}\right)f_q^-(0,x_2,x_3,-v_1,v_2,v_3) \quad (3.14)$$

for $v_1>0$.

The incident light wave varying with frequency ω and with the amplitude $\mathbf{D}_1$ given by Eqs. (2.1) and (2.2) is treated here as a perturbation including only the lowest terms in $\mathbf{D}_1$. It may thus be assumed that

$$f_0=f^0+O(D_1^2)\,, \quad (3.15)$$
$$f_1=O(D_1)\,, \quad (3.16)$$
$$f_2=O(D_1^2)\,, \quad (3.17)$$
$$F_{j0}=O(D_1^2)\,, \quad (3.18)$$
$$F_{j1}=O(D_1)\,, \quad (3.19)$$
$$F_{j2}=O(D_1^2)\,, \quad (3.20)$$

etc., where O stands for "terms of the order of $\cdots$." Thus, to the lowest order perturbation calculation of potentials in the powers of D_1, it follows from Eq. (3.11) that

$$K_1=-(1/m)F_{j1}(\partial f^0/\partial v_j) \quad (3.21)$$

and

$$K_2=-\frac{1}{m}F_{j2}\frac{\partial f^0}{\partial v_j}-\frac{1}{m}F_{j1}\frac{\partial f_1}{\partial v_j}\,. \quad (3.22)$$

The unperturbed distribution function f^0 satisfies the equation

$$v_j\frac{\partial f^0}{\partial x_j}-\frac{1}{m}\frac{dU}{dx_1}\frac{\partial f^0}{\partial v_1}=0\,, \quad (3.23)$$

which has the general solution

$$f^0=f^0(E)\,, \quad (3.24)$$

where

$$E=\tfrac{1}{2}mv_jv_j+U(x_1)\,, \quad (3.25)$$

so that

$$\partial f^0/\partial v_j=mv_j(\partial f^0/\partial E)\,. \quad (3.26)$$

Using this special property of f^0 as well as Eqs. (2.10), (3.3), and (3.6), one can then simplify the expressions for K_1 and K_2 to find,

$$K_1=(ei\omega/mc)a_{j1}(\partial f^0/\partial v_j) \quad (3.27)$$

and

$$K_2=(2ei\omega/mc)a_{j2}(\partial f^0/\partial v_j)$$
$$+\left\{\left(\frac{ei\omega}{mc}\right)a_{j1}+\frac{e}{mc}v_k\left(\frac{\partial a_{k1}}{\partial x_j}-\frac{\partial a_{j1}}{\partial x_k}\right)\right\}\frac{\partial f_1}{\partial v_j}\,, \quad (3.28)$$

where the Lorentz term in the force appears only in the expression for K_2.

If the electrons are treated as a degenerate Fermi gas at zero temperature, one has for $x_1>0$

$$f^0=n/(4/3)\pi v_f^3\,,\quad \text{for velocity } v\leqslant v_f \quad (3.29)$$

and

$$f^0=0\quad \text{for velocity } v>v_f\,. \quad (3.30)$$

With a step potential of sufficient height, there are no electrons for $x_1<0$, and thus $f^0=0$ in this region. The function f^0 has been normalized in Eqs. (3.29) and (3.30) in such a way that

$$\int d^3v\, f^0=4\pi\int_0^\infty v^2dv\, f^0=n\,. \quad (3.31)$$

Starting with a given f^0, Eqs. (3.27), (3.28), (3.13), and (3.14) determine the solutions for the part of the distribution function f varying with frequencies ω and 2ω in terms of the unknown vector potentials. We will use these to calculate the components of the current varying with frequencies ω and 2ω in the next two sections and solve the differential equations for the unknown vector potentials corresponding to Maxwell's equation (2.5).

4. SOLUTION FOR THE FIELDS VARYING WITH FREQUENCY ω

From Eqs. (2.5), (2.10), (3.2), (3.3), and (3.6) one obtains for the quantities a_{k1},

$$\frac{\partial^2 a_{j1}}{\partial x_j\partial x_k}-\frac{\partial^2 a_{k1}}{\partial x_j\partial x_j}-\frac{\omega^2}{c^2}a_{k1}=\frac{4\pi}{c}j_{k1}\,, \quad (4.1)$$

where j_{kq} is defined in terms of the current vector $\mathbf{J}$ as

$$J_k=\sum_q j_{kq}e^{-iq\omega t}\,, \quad (4.2)$$

and where

$$j_{k1}=-e\int_{v_1<0}d^3v\, v_kf_1^- -e\int_{v_1>0}d^3v\, v_kf_1^+ \quad (4.3)$$

in terms of the solution for f_1 given by Eqs. (3.13) and (3.14).

Outside the metal, for $x_1<0$, there is no current and the solution of Eq. (4.1) can be written as

$$a_{k1}=\left[D_{k1}\exp\left(i\omega\frac{\cos\theta}{c}x_1\right)+G_{k1}\exp\left(-i\omega\frac{\cos\theta}{c}x_1\right)\right]$$
$$\times\exp\left(-i\omega\frac{\sin\theta}{c}x_2\right) \quad (4.4)$$

where the incoming wave corresponds to the incident wave given by Eqs. (2.1) and (2.2), and where

$$G_{11}=-G_{21}\tan\theta. \qquad (4.5)$$

To obtain the classical Drude solution[9] for the problem of reflection of light from a metal surface, we can assume that for $x_1 \gg v_f/\omega$, where the electrons are not subjected to the influence of the surface barrier, the exponential of the form $\exp(i\omega(x_1-x_1')/v_1)$ in Eqs. (3.13) and (3.14) varies rapidly with v_1 except for small values of $|x_1-x_1'|$. Thus it gives an essential contribution to j_{k1} only for $x_1'=x_1$. Similarly the exponential of the form $e^{i\omega_1 x_1/v_1}$ gives any appreciable contribution to the current only near $x_1=0$. Then to the lowest order in v_f/c one finds from Eqs. (3.13), (3.14), (3.27), (3.31), and (4.3)

$$j_{k1}=-(e^2n/mc)a_{k1}, \quad \text{for} \quad x_1 \gg v_f/\omega. \qquad (4.6)$$

This procedure is, however, not valid near the surface. The normal component of the current can be shown to differ in this region considerably from the above expression. On the other hand, the knowledge of its value is not required for calculating the potentials away from the surface, if one uses the familiar procedure of deriving the Fresnel formulas where the inside and outside solutions are matched at $x_1=0$ to satisfy the following boundary conditions: (i) the tangential components of the electric field are continuous, i.e., a_{21} and a_{31} are continuous; and (ii) the tangential components of the magnetic field are continuous, i.e., $\partial a_{31}/\partial x_1$ and $\partial a_{21}/\partial x_1+(i\omega\sin\theta/c)a_{11}$ should be continuous. Applying this procedure one then obtains from Eqs. (4.1), (4.4), (4.6), and conditions (i) and (ii),

$$a_{k1}=C_{k1}e^{-\gamma_1 x_1}\exp\left(-i\omega\frac{\sin\theta}{c}x_2\right) \qquad (4.7)$$

for $x_1>0$, where

$$\gamma_1=(\omega/c)(\omega_p^2/\omega^2-\cos^2\theta)^{1/2}, \qquad (4.8)$$

$$C_{21}=(-c\gamma_1/i\omega\sin\theta)C_{11}, \qquad (4.9)$$

$$C_{11}=\frac{-2A_p\omega^2\sin\theta\cos\theta}{(\omega_p^2-\omega^2)\cos\theta-i\omega c\gamma_1}, \qquad (4.10)$$

$$C_{31}=\frac{2A_s\omega^2\cos\theta}{\omega^2\cos\theta+i\omega c\gamma_1}, \qquad (4.11)$$

$$G_{21}=C_{21}-A_p\cos\theta, \qquad (4.12)$$

and

$$G_{31}=C_{31}-A_s, \qquad (4.13)$$

and where ω_p is the plasma frequency of the electron gas given by

$$\omega_p=(4\pi ne^2/m)^{1/2}. \qquad (4.14)$$

[9] H. Sonnenberg and H. Heffner (private communications).

For a typical metal like silver, $n\simeq 6\times 10^{22}$ per cc, so that $\omega_p\simeq 10^{16}$ sec^{-1}. In order to obtain an exponentially damped solution in Eq. (4.7) for all angles θ, we see from Eq. (4.8) that the frequency ω should satisfy the relation $\omega \leqslant \omega_p$. We assume here that this is true in our case. To find the order of magnitude of γ_1 given by Eq. (4.8) we will consider ω and ω_p to be of the same order of magnitude so that γ_1 may be assumed to be of the order ω/c.

To know how the classical Drude solution differs from the correct solution near the surface, we can start with the Drude solution (4.7) and obtain f_1 and j_{k1} from Eqs. (3.13), (3.14), (3.27), and (4.3). With this known form for j_{k1} in Eq. (4.1), a_{k1} can be obtained by solving this differential equation. A better accuracy is obtained by a continued iteration procedure, but here we give the results of only the first iteration. With the omission of all terms that are negligible for $v_f/c \ll 1$, one thus obtains

$$a_{11}=\left\{C_{11}e^{-\gamma_1 x_1}+\frac{2\omega_p^2}{\omega^2}\frac{C_{11}}{n}\int_{v_1>0}d^3v \times e^{(i\omega/v_1)x_1}v_1\frac{\partial f_0}{\partial v_1}\right\}\exp\left(-i\omega\frac{\sin\theta}{c}x_2\right), \qquad (4.15)$$

$$a_{21}=C_{21}e^{-\gamma_1 x_1}\exp\left[-i\frac{\omega}{c}(\sin\theta)x_2\right], \qquad (4.16)$$

$$a_{31}=C_{31}e^{-\gamma_1 x_1}\exp\left[-i\frac{\omega}{c}(\sin\theta)x_2\right], \qquad (4.17)$$

with

$$\frac{\partial a_{21}}{\partial x_1}=\left\{-\gamma_1 C_{21}e^{-\gamma_1 x_1}-\frac{2\omega_p^2\sin^2\theta}{c^2\gamma_1 n}C_{21} \times\int_{v_1>0}d^3v\, e^{(i\omega/v_1)x_1}v_1\frac{\partial f^0}{\partial v_1}\right\}\exp\left(-i\omega\frac{\sin\theta}{c}x_2\right). \qquad (4.18)$$

Since the above solutions hold even near the surface, the boundary conditions at $x_1=0$ to be used for the differential equation (4.1) are

(i) a_{11}, a_{21} and a_{31} should be continuous; and

(ii) $\partial a_{21}/\partial x_1$ and $\partial a_{31}/\partial x_1$ should be continuous.

With $\mathbf{C}_1$ and $\mathbf{G}_1$ given by Eqs. (4.5), (4.9), and (4.10)–(4.13), it can indeed be shown that our new solutions satisfy the above boundary conditions. These new solutions given by Eqs. (4.15)–(4.18) inside the metal differ from the Drude solution only within a distance of the order v_f/ω from the surface. From the results of Eqs. (4.4), (4.5), and (4.7)–(4.13) one can show that the normal component a_{11} is discontinuous for the

Drude solution at $x_1=0$ such that

$$\frac{\partial a_{j1}}{\partial x_j}=\frac{\omega_p^2}{\omega^2}C_{11}\delta(x_1)\exp\left(-i\omega\frac{\sin\theta}{c}x_2\right), \quad (4.19)$$

whereas from the more exact solutions in Eqs. (4.15)–(4.18) one finds the normal component a_{11} to be continuous and

$$\frac{\partial a_{j1}}{\partial x_j}=-\frac{2\omega_p^2}{i\omega}\frac{C_{11}}{n}\int_{v_1>0}d^3v \times e^{(i\omega/v_1)x_1}\frac{\partial f^0}{\partial v_1}\exp\left(-i\omega\frac{\sin\theta}{c}x_2\right). \quad (4.20)$$

As a check we should mention here that integrals over x_1 of the right-hand sides of the above equations reflect the fact that

$$\int\delta(x_1)dx_1=1. \quad (4.21)$$

Since the reflection coefficient, defined as the ratio of the average energy flux reflected from the surface to the incident flux, is equal to the ratio of $G_{j1}^*G_{j1}$ and $D_{j1}^*D_{j1}$, its value remains the same as in the classical Drude case. For both the cases where the incident light is polarized either parallel ($A_s=0$) or perpendicular ($A_p=0$) to the plane of incidence one finds total reflection for $\omega_p^2/\omega^2>\cos^2\theta$.

5. SOLUTION FOR THE FIELDS VARYING WITH FREQUENCY 2ω

Similar to Eq. (4.1), the differential equation satisfied by the quantities a_{k2} can be written as

$$\frac{\partial^2 a_{j2}}{\partial x_j\partial x_k}-\frac{\partial^2 a_{k2}}{\partial x_j\partial x_j}-\left(\frac{4\omega^2}{c^2}\right)a_{k2}=\frac{4\pi}{c}j_{k2}, \quad (5.1)$$

where

$$j_{k2}=-e\int_{v_1<0}d^3v\, v_kf_2^- -e\int_{v_1>0}d^3v\, v_kf_2^+, \quad (5.2)$$

and where the functions $f_2^\pm$ can be obtained from Eqs. (3.13) and (3.14) in terms of K_2 which is given by Eq. (3.28). The expression for K_2 contains two terms, the first term involving the unknown potential a_{j2} of the same form as that of K_1 in Eq. (3.27) and the second term involving a_{j1} and f_1 which are known from the solutions of the previous section. Therefore the current j_{k2} contains a homogeneous or linear term which is very similar to the current j_{k1} and an inhomogeneous or nonlinear term. In this section we are interested in the solutions for a_{k2} only for $x_1\gg v_f/\omega$ and therefore with Eqs. (3.13), (3.14), (3.28), (3.31), and (5.2) and the considerations leading to Eq. (4.6) we may approximate the linear part of the current as

$$j_{k2}(\mathrm{L})=-(e^2n/mc)a_{k2}. \quad (5.3)$$

As explained in Sec. 5, in the limit of $v_f/c\ll 1$, this is equivalent to ignoring only a surface current in the x_1 direction. The nonlinear part of the current can be calculated from Eqs. (5.2), (3.13), and (3.14) when one uses the second term of Eq. (3.28) for K_2 and the Drude solution given by Eqs. (4.7)–(4.11) for a_{k1}. Using the general properties of f^0 given in Sec. 3, one then finds in the limit,

$$j_{k2}{}^{(v)}(\mathrm{NL})=\frac{-e^3n}{2i\omega m^2c^2}\left(\frac{\partial a_{j1}}{\partial x_k}-\frac{\partial a_{k1}}{\partial x_j}\right)a_{j1} \quad (5.4)$$

in the interior of the metal provided that $x_1\gg v_f/\omega$. This expression shall be called the volume term and is entirely due to the Lorentz term in the force. But now we find that apart from the normal component of the current there are appreciable tangential components near the surface. These tangential components, to the lowest order in v_f/c, can be written by using Eqs. (5.2), (3.13), (3.14), (3.28), and (4.7)

$$j_{22}{}^{(s)}(\mathrm{NL})=\frac{-2e^3}{m^2c^2}a_{21}C_{11}\times\int_{v_1>0}d^3v\, e^{i\omega x_1/v_1}\frac{\partial f^0}{\partial v_1}\exp\left(-i\omega\frac{\sin\theta}{c}x_2\right) \quad (5.5)$$

and

$$j_{32}{}^{(s)}(\mathrm{NL})=\frac{-2e^3}{m^2c^2}a_{31}C_{11}\times\int_{v_1>0}d^3v\, e^{i\omega x_1/v_1}\frac{\partial f^0}{\partial v_1}\exp\left(-i\omega\frac{\sin\theta}{c}x_2\right). \quad (5.6)$$

In deriving the above results we have used the fact that a nonlinear current varying as $e^{(i\omega x_1/v_1)}$ gives a contribution of the order v_1/c to the potentials as compared to a current varying as $e^{-\gamma_1 x_1}$ where $\gamma_1\sim O(\omega/c)$. This can be seen by examining Eq. (5.1). By comparison to Eq. (4.20), we may also write,

$$j_{22}{}^{(s)}(\mathrm{NL})=(e^3ni\omega/m^2c^2\omega_p^2)a_{21}(\partial a_{j1}/\partial x_j) \quad (5.7)$$

and

$$j_{32}{}^{(s)}(\mathrm{NL})=(e^3ni\omega/m^2c^2\omega_p^2)a_{31}(\partial a_{j1}/\partial x_j). \quad (5.8)$$

It is shown in the Appendix II that to calculate the potentials in the interior and outside the metal, a knowledge of the exact variation of the above terms in Eqs. (5.7) and (5.8) near the surface is not needed and that one can replace in these equations the Drude expression (4.19) for $\partial a_{j1}/\partial x_j$ instead of using Eq. (4.20). Then, using Eqs. (5.1)–(5.4), (5.7), (5.8), and (4.19) to find a_{k2}, one has to solve the differential equations

$$\frac{\partial^2 a_{j2}}{\partial x_j\partial x_k}-\frac{\partial^2 a_{k2}}{\partial x_j\partial x_j}-\frac{4\omega^2}{c^2}a_{k2} =\frac{-4\pi ne^2}{mc^2}a_{k2}-\frac{4\pi ne^3}{2i\omega m^2c^3}\left(\frac{\partial a_{j1}}{\partial x_k}-\frac{\partial a_{k1}}{\partial x_j}\right)a_{j1} \quad (5.9)$$

for $x_1>0$, and

$$\frac{\partial^2 a_{j2}}{\partial x_j \partial x_k}-\frac{\partial^2 a_{k2}}{\partial x_j \partial x_j}-\frac{4\omega^2}{c^2}a_{k2}=0\,,\quad \text{for}\quad x_1<0 \tag{5.10}$$

and match the solution at $x_1=0$, such that

(i) a_{22} and a_{32} are continuous;

$$\text{(ii)}\quad \left.\frac{-\partial a_{32}}{\partial x_1}\right|_{x_1=0^+}+\left.\frac{\partial a_{32}}{\partial x_1}\right|_{x_1=0^-}=\frac{-4\pi n e^3}{m^2c^3 i\omega}C_{31}C_{11}\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right); \tag{5.11}$$

$$\text{(iii)}\quad -\left\{\frac{\partial a_{22}}{\partial x_1}-\frac{\partial a_{12}}{\partial x_2}\right\}_{x_1=0^+}+\left\{\frac{\partial a_{22}}{\partial x_1}-\frac{\partial a_{12}}{\partial x_2}\right\}_{x_1=0^-}=\frac{-4\pi n e^3}{m^2c^3 i\omega}C_{21}C_{11}\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right). \tag{5.12}$$

These boundary conditions are equivalent to the conditions that the tangential components of the electric field $\mathbf{E}_2$ should be continuous and that the tangential components of the magnetic field $\mathbf{H}_2$ should have a discontinuity at the surface which is equal to $4\pi/c$ times the corresponding tangential component of the current at the surface. Since we do not need the exact value of the normal component of the current at the surface, this procedure implies that we may write in Eq. (5.1),

$$j_{k2}=\frac{-e^2n}{mc}a_{k2}-\frac{e^3n}{2i\omega m^2c^2}\left(\frac{\partial a_{j1}}{\partial x_k}-\frac{\partial a_{k1}}{\partial x_j}\right)a_{j1}+\left(\frac{e^3ni\omega}{m^2c^2\omega_p^2}\right)a_{k1}\frac{\partial a_{j1}}{\partial x_j}\,. \tag{5.13}$$

It should be pointed out here that the last term on the right-hand side of Eq. (5.13) represents the surface current and goes to zero if the incident light is polarized perpendicular to the surface. The solution for a_{k2} with these conditions can then be shown to be

$$a_{k2}=C_{k2}e^{-\gamma_2 x_1}\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right)-\frac{4\pi c}{(\omega_p^2-4\omega^2)}\left(\frac{e^3n}{4i\omega m^2c^2}\right)\times\frac{\partial}{\partial x_k}\left[C_{j1}C_{j1}e^{-2\gamma_1 x_1}\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right)\right],\quad \text{for}\quad x_1>0 \tag{5.14}$$

and

$$a_{k2}=G_{k2}\exp\left(-2i\omega\frac{\cos\theta}{c}x_1\right)\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right),\quad \text{for}\quad x_1<0 \tag{5.15}$$

where

$$\gamma_2=\frac{2\omega}{c}\left(\frac{\omega_p^2}{4\omega^2}-\cos^2\theta\right)^{1/2}, \tag{5.16}$$

$$C_{12}=\frac{-2i\omega\sin\theta}{c\gamma_2}C_{22}\,, \tag{5.17}$$

$$G_{12}=-G_{22}\tan\theta\,, \tag{5.18}$$

$$G_{32}=C_{32}=\left(\frac{-4\pi n e^3}{m^2c^2 i\omega}\right)\frac{C_{31}C_{11}}{c\gamma_2-2i\omega\cos\theta}\,, \tag{5.19}$$

$$G_{22}=\left(\frac{-2\pi n e^3}{m^2c^2 i\omega}\right)\frac{c(\cos\theta)(2\gamma_2C_{21}C_{11}-(i\omega/c)(\sin\theta)C_{j1}C_{j1})}{(\omega_p^2-4\omega^2)\cos\theta-2i\omega c\gamma_2}\,, \tag{5.20}$$

and

$$C_{22}=\left(\frac{-4\pi n e^3}{m^2c^2 i\omega}\right)\frac{\gamma_2 c(\cos\theta)\{C_{21}C_{11}+[\omega^2(\sin\theta)/(\omega_p^2-4\omega^2)\cos\theta]C_{j1}C_{j1}\}}{(\omega_p^2-4\omega^2)\cos\theta-2i\omega c\gamma_2}\,. \tag{5.21}$$

We shall now proceed to determine the ratio of the average energy flux reflected with frequency 2ω from the surface to the incident flux given by

$$R^{(2)}=4G_{j2}{}^*G_{j2}/D_{j1}{}^*D_{j1}\,. \tag{5.22}$$

For this purpose one has to use Eqs. (5.18)–(5.22), (4.5), (4.9)–(4.13), and (2.2). If the incident light is polarized parallel to the plane of incidence, i.e., if $A_s=0$, we find

$$R_{\text{par}}{}^{(2)}=|eE_p/mc\omega_p|^2\mathfrak{F}(\theta,\omega_p/\omega)\,, \tag{5.23}$$

where E_p given by

$$E_p = (i\omega/c)A_p \tag{5.24}$$

is the maximum amplitude of the incident electric field and where

$$\mathfrak{F}\left(\theta,\frac{\omega_p}{\omega}\right)=\frac{16\sin^2\theta(\cos^4\theta)\{(\omega_p^2/\omega^2-1)+4(\omega_p^2/4\omega^2-\cos^2\theta)^{1/2}(\omega_p^2/\omega^2-\cos^2\theta)^{1/2}\}^2}{((\omega_p^2/\omega^2)\cos^2\theta-4\cos2\theta)((\omega_p^2/\omega^2)\cos^2\theta-\cos2\theta)^2},\quad \text{for}\quad \omega_p^2\geqslant 4\omega^2\cos^2\theta. \tag{5.25}$$

In the following discussion, the special case of plasma resonance which occurs if $\omega=\omega_p$ or $\omega=2\omega_p$ is excluded. It follows in this case from Eqs. (4.8) and (5.16) that $\gamma_1=0$ or $\gamma_2=0$ indicating the absence of damping of the single or double frequency wave in the metal so that the boundary conditions for large values of x_1 become important. This situation cannot arise, however, if $\omega<\omega_p/2$ and we shall assume this condition to be fulfilled, considering that it is justified for the incident light in the infrared region. Then it is seen from Eq. (5.25) that

$$\mathfrak{F}(\theta,\omega_p/\omega)\rightarrow 0,\quad \text{if}\quad \theta\rightarrow \tfrac{1}{2}\pi \tag{5.26}$$

and

$$\mathfrak{F}(\theta,\omega_p/\omega)\rightarrow 0,\quad \text{if}\quad \theta\rightarrow 0. \tag{5.27}$$

If the incident light is polarized perpendicular to the plane of incidence, i.e., if $A_p=0$, there is no effect of the surface current and one obtains

$$R_{\text{perp}}^{(2)}=|eE_s/mc\omega_p|^2h(\theta,\omega_p/\omega), \tag{5.28}$$

where

$$E_s=(i\omega/c)A_s, \tag{5.29}$$

and where

$$h\left(\theta,\frac{\omega_p}{\omega}\right)=\frac{16\sin^2\theta\cos^4\theta}{(\omega_p^2/\omega^2)\cos^2\theta-4\cos2\theta}\quad \text{for}\quad \omega_p^2\geqslant 4\omega^2\cos^2\theta. \tag{5.30}$$

Again

$$h(\theta,\omega_p/\omega)\rightarrow 0,\quad \text{if}\quad \theta\rightarrow\tfrac{1}{2}\pi \tag{5.31}$$

and

$$h(\theta,\omega_p/\omega)\rightarrow 0,\quad \text{if}\quad \theta\rightarrow 0. \tag{5.32}$$

If the incident light is unpolarized, i.e., with $A_p=A_{\text{inc}}\cos\varphi$ and $A_s=A_{\text{inc}}\sin\varphi$ if one averages over all the orientations of the angle φ, one finds

$$\begin{aligned} R_{\text{unpol.}}^{(2)}=&(eE_{\text{inc}}/mc\omega_p)^2\sin^2\theta\cos^4\theta\\ &\times\Bigg[\frac{6\{(\omega_p^2/\omega^2-1)+4(\omega_p^2/4\omega^2-\cos^2\theta)^{1/2}(\omega_p^2/\omega^2-\cos^2\theta)^{1/2}\}^2}{((\omega_p^2/\omega^2)\cos^2\theta-4\cos2\theta)((\omega_p^2/\omega^2)\cos^2\theta-\cos2\theta)^2}\\ &+\frac{6}{((\omega_p^2/\omega^2)\cos^2\theta-4\cos2\theta)}+\frac{8}{((\omega_p^2/\omega^2)\cos^2\theta-\cos2\theta)}\\ &-\frac{4((\omega_p^2/\omega^2)\cos^2\theta-2\cos^4\theta+\cos2\theta)\{((\omega_p^2/\omega^2)-1)+4((\omega_p^2/\omega^2)-\cos^2\theta)^{1/2}((\omega_p^2/4\omega^2)-\cos^2\theta)^{1/2}\}}{((\omega_p^2/\omega^2)\cos^2\theta-\cos2\theta)^2((\omega_p^2/\omega^2)\cos^2\theta-4\cos2\theta)}\Bigg], \end{aligned} \tag{5.33}$$

where

$$E_{\text{inc}}=(i\omega/c)A_{\text{inc}}. \tag{5.34}$$

It is seen that $R_{\text{unpol.}}^{(2)}$ likewise vanishes for $\theta=0$ and $\theta=\frac{1}{2}\pi$.

6. DISCUSSION

It was pointed out in Sec. 1 that second harmonic generation by reflection on a metal surface can be ascribed to a nonlinear polarization of the form of Eq. (1.1)

$$\mathbf{P}_2(\text{NL})=\alpha(\mathbf{E}_1\times\mathbf{H}_1)+\beta\mathbf{E}_1\operatorname{div}\mathbf{E}_1.$$

In order to verify that the preceding calculations lead to this form one has to consider the expression for the nonlinear current density $j_{k2}(\text{NL})$ which can be obtained from Eq. (5.13) as

$$j_{k2}(\text{NL})=\frac{-e^3n}{2i\omega m^2c^2}\left(\frac{\partial a_{j1}}{\partial x_k}-\frac{\partial a_{k1}}{\partial x_j}\right)a_{j1}+\frac{e^3i\omega n}{m^2c^2\omega_p^2}a_{k1}\frac{\partial a_{j1}}{\partial x_j}. \tag{6.1}$$

Using the relations

$$\mathbf{H}_1=\nabla\times\mathbf{a}_1 \tag{6.2}$$

and

$$\mathbf{E}_1=(i\omega/c)\mathbf{a}_1 \tag{6.3}$$

the nonlinear current density can be written in the vector form

$$j_2(\text{NL})=\frac{e^3n}{2m^2c\omega^2}(\mathbf{E}_1\times\mathbf{H}_1)-\frac{ie^3n}{m^2\omega_p^2\omega}\mathbf{E}_1\operatorname{div}\mathbf{E}_1. \tag{6.4}$$

On the other hand, the polarization $\mathbf{P}_2$ and the current density $\mathbf{j}_2$ varying as $e^{-2i\omega t}$ are related to each other by the relation

$$\mathbf{P}_2=-(1/2i\omega)\mathbf{j}_2. \tag{6.5}$$

Combining Eqs. (6.4) and (6.5) the nonlinear polarization appears indeed in the form, given above with the coefficients

$$\alpha=ie^3n/4m^2c\omega^3 \tag{6.6}$$

and

$$\beta=e^3n/m^2\omega_p^2\omega^2. \tag{6.7}$$

The corresponding first and second terms in the nonlinear polarization were shown in Sec. 5 to represent volume and surface contributions, respectively. The latter was neglected in the calculations of Kronig and Boukema[2] and of Cheng and Miller[3] so that their result is equivalent to replacing Eq. (6.7) by $\beta=0$. Correspondingly, Eq. (5.23) for the reflectivity of the second harmonic wave for light polarized in the plane of incidence is replaced by

$$R_{\mathrm{par}}{}^{(2)}=|eE_p/mc\omega_p|^2W(\theta,\omega_p/\omega), \tag{6.8}$$

where

$$W\left(\theta,\frac{\omega_p}{\omega}\right)=\frac{16\sin^2\theta\cos^4\theta(\omega_p{}^2/\omega^2-1)^2}{((\omega_p{}^2/\omega^2)\cos^2\theta-4\cos2\theta)((\omega_p{}^2/\omega^2)\cos^2\theta-\cos2\theta)^2},\quad \text{for}\quad \omega_p{}^2\geqslant4\omega^2\cos^2\theta. \tag{6.9}$$

By comparison of these equations with the more rigorous Eqs. (5.23) and (5.25) of Sec. 5, it it seen that the surface term is by no means negligible and leads to a considerable modification of the results, obtained from its omission. It can be shown, however, that the omission of the surface term does not change the expression for the reflectivity of the second harmonic wave $R_{\mathrm{per}}{}^{(2)}$, given by Eqs. (5.28)–(5.30), for light polarized perpendicular to the plane of incidence.

While the results derived in this paper lend themselves readily to numerical evaluation, it has to be emphasized that they were derived under certain simplifying assumptions which are not rigorously justified under actual experimental circumstances. In view of the importance of surface effects mentioned above, this holds particularly for the description of the surface barrier by a step potential. As explained in Sec. 3 and the Appendix I of this paper this description is valid only if the frequency ω of the incident light satisfies the condition

$$\omega\ll v_f/d, \tag{6.10}$$

where d is the distance over which the surface potential varies appreciably and where v_f is the Fermi velocity. In reality, d must be expected to be of atomic dimension, i.e., $d\simeq10^{-8}$ cm, and $v_f\simeq10^8$ cm/sec, so that the condition of Eq. (6.10) is satisfied for a frequency

$$\omega\ll10^{16}\ \mathrm{sec}^{-1}. \tag{6.11}$$

Since the right-hand side of this inequality is of the order of magnitude of optical frequencies, our results can claim only qualitative validity for incident light in the visible region. On the other hand, these results may be expected to lead to reliable numerical values for $\omega\simeq10^{15}$ sec^{-1}, i.e., for infrared incident light, used in the experiment discussed below.

It is to be further noted that the applicability of our results to visible and ultraviolet light is questionable for other reasons too. Indeed, with the excitation frequency of the ions and of higher conduction bands lying in this region, the neglect of ion polarization and of band structure of the conduction electrons is no longer justified. Instead, they will have an appreciable influence upon second harmonic generation of visible light which would be difficult experimentally to separate from the effect, treated in this paper.

This effect, however, may be expected to be dominant under the conditions of an experiment which is at present being carried out at Stanford by Sonnenberg and Heffner[9] and to which, in conclusion, the results of Eqs. (5.23)–(5.25) shall be applied.[10] In this experiment, the incident light consists of a beam, polarized parallel to the plane of incidence, from a neodymium-doped glass laser with a wavelength of 1.06 μ and a corresponding circular frequency $\omega=1.74\times10^{15}$ sec^{-1}, and is reflected from a silver mirror. With $n\simeq6.10\times10^{22}$ cm^{-1} for the conduction electrons in silver and $\omega_p\simeq1.35\times10^{16}$ sec^{-1} from Eq. (4.14), one obtains

$$\frac{\omega_p}{\omega}\simeq8,\quad\left(\frac{mc\omega_p}{e}\right)\simeq8\times10^8\ \mathrm{esu}$$

and, hence, from Eq. (5.23),

$$R_{\mathrm{par}}{}^{(2)}=\left|\frac{E_p}{8\times10^8\ \mathrm{esu}}\right|^2\mathfrak{F}\left(\theta,\frac{\omega_p}{\omega}\right). \tag{6.12}$$

For $(\omega_p/\omega)=8$, $\mathfrak{F}(\theta,\omega_p/\omega)$, given by Eq. (5.25), is plotted in Fig. 1 shown for different θ. In the same figure we have plotted $\mathfrak{F}(\theta,\omega_p/\omega)$ for $\omega_p/\omega=3$ for comparison. As ω_p/ω increases, the peak of the function $\mathfrak{F}(\theta,\omega_p/\omega)$ is seen to shift towards $\theta=90°$. For order-of-magnitude calculations we may take the optimum value of $\mathfrak{F}(\theta,\omega_p/\omega)$ to lie between 1–10. This means that for incident laser beam of moderate flux density with E_p of the order of 2.5×10^4 V/cm or 80 esu, the fraction of the

[10] Recently it has been pointed out by Professor Bloembergen and Professor Shen that ion cores at the surface may be the main source for the harmonic intensity. The author is grateful to them for sending this information.

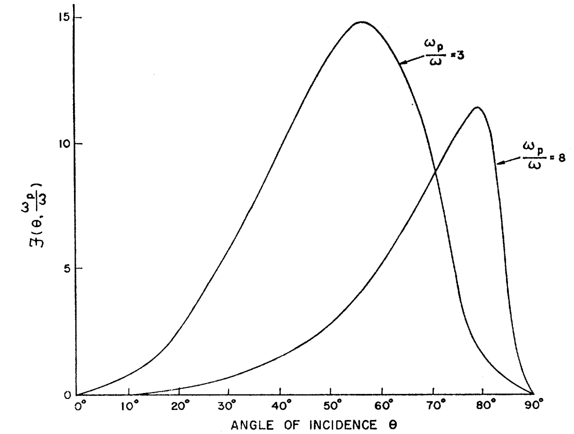

FIG. 1. Angular dependence of the reflection coefficient $R_{\text{par}}^{(2)}$.

power of the incident wave reflected in the second harmonic wave is of the order

$$R_{\text{par}}^{(2)}=\left(\frac{8\times 10\text{ esu}}{8\times 10^8\text{ esu}}\right)^2=10^{-14}. \tag{6.13}$$

The effect, so far observed,[9] seems to be consistent with this result. This efficiency can be increased if without damaging the metal surface it is possible to apply more intense laser beams which are readily available.

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APPENDIX I

Since the x_2 and x_3 dependence of f_q is already assumed to be known, Eq. (3.9) is a differential equation for f_q in the variables x_1 and v_1 only, whereas the other two variables v_2 and v_3 enter only as parameters. Thus, while Eq. (3.9) is being solved the variables x_2, x_3, v_2, and v_3 may be suppressed. In terms of two new variables given by a time τ and the constant of motion for the unperturbed electron

$$\bar{v}_1=[v_1^2+(2/m)U(x_1)]^{1/2}, \tag{I.1}$$

let

$$x_1=x_1(\tau,\bar{v}_1) \tag{I.2}$$

and

$$v_1=v_1(\tau,\bar{v}_1), \tag{I.3}$$

where

$$\partial x_1/\partial\tau=v_1 \tag{I.4}$$

and

$$\partial v_1/\partial\tau=-(1/m)(dU/dx_1). \tag{I.5}$$

If we define

$$f_q[x_1(\tau,\bar{v}_1),v_1(\tau,\bar{v}_1)]=\varphi_q(\tau,\bar{v}_1) \tag{I.6}$$

and

$$K_q[x_1(\tau,\bar{v}_1),v_1(\tau,\bar{v}_1)]=\xi_q(\tau,\bar{v}_1), \tag{I.7}$$

Eq. (3.9) can be transformed into

$$-i\omega\varphi_q+\partial\varphi_q/\partial\tau=\xi_q. \tag{I.8}$$

The solution of Eq. (I.8) for $q\neq 0$, which goes to zero for $\tau\rightarrow-\infty$, can be written as

$$\varphi_q=\int_{-\infty}^{\tau}d\tau' e^{i\omega_q(\tau-\tau')}\xi_q(\tau',\bar{v}_1). \tag{I.9}$$

In order to find f_q from Eq. (I.6) one requires the knowledge of the functional dependence of x_1 and v_1 on τ and $\bar{v}_1$ and hence from Eq. (I.5) that of U on x_1. The function $U(x_1)$ varies from zero to a value of the order of mv_f^2 within a distance d near the surface. Therefore, the average time τ^* taken by an electron between entering the surface barrier region and coming out of it after being reflected by the wall can be estimated to be of the order of d/v_f. Since the time τ enters according to Eq. (I.9) in the combination $\omega_q\tau$ and since ω_q is of the order ω, it is possible to replace $U(x_1)$ by a step potential at $x_1=0$ for which $\tau^*=0$, provided that

$$\omega d/v_f\ll 1. \tag{I.10}$$

Under this assumption we may write

$$\text{for}\quad \tau<0,\quad v_1=-\bar{v}_1\quad\text{negative} \tag{I.11}$$

$$x_1=-\bar{v}_1\tau \tag{I.12}$$

$$\text{and for}\quad \tau>0,\quad v_1=\bar{v}_1\quad\text{positive} \tag{I.13}$$

$$x_1=\bar{v}_1\tau. \tag{I.14}$$

Now Eq. (I.9) can be transformed back to the variables x_1 and v_1 to obtain the results of Eqs. (3.13) and (3.14) of the text.

APPENDIX II

Due to the rapid variation of the exponential $e^{i\omega x_1/v_1}$ in $j_{22}^{(s)}(\text{NL})$ and $j_{32}^{(s)}(\text{NL})$ given by Eqs. (5.5) and (5.6), respectively, the contribution of these terms to the current j_{k2} of Eq. (5.2) is appreciable only near the surface. Considering only the case where $k=3$, Eqs. (5.2)–(5.4), (5.6), and (4.7) lead to the result

$$j_{32}=\frac{-e^3n}{mc}a_{32}-\frac{2e^3}{m^2c^2}C_{31}C_{11}\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right)\times\int_{v_1>0}d^3v\, e^{-\gamma_1x_1}e^{i\omega x_1/v_1}\frac{\partial f^0}{\partial v_1}. \tag{II.1}$$

Using the above expression for the current in Eq. (5.1), one thus finds

$$a_{32}=C_{32}e^{-\gamma_2 x_1}\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right)+\frac{8\pi e^3}{m^2c^3}C_{31}C_{11}\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right)\times\int_{v_1>0}d^3v\frac{e^{i\omega x_1/v_1}e^{-\gamma_1 x_1}(\partial f^0/\partial v_1)}{(i\omega/v_1-\gamma_1)^2-\gamma_2^2}\quad\text{(II.2)}$$

for $x_1>0$, where

$$\gamma_2=(2\omega/c)(\omega_p^2/4\omega^2-\cos^2\theta)^{1/2}.\quad\text{(II.3)}$$

Since γ_1 and γ_2 are of the order of ω/c we may write, to the lowest order in $v_{f/c}$,

$$a_{32}=C_{32}e^{-\gamma_2 x_1}\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right)+\frac{8\pi e^3}{m^2c^3(i\omega)^2}C_{31}C_{11}\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right)\times\int_{v_1>0}d^3v\, v_1^2e^{i\omega x_1/v_1}e^{-\gamma_1 x_1}\frac{\partial f^0}{\partial v_1}.\quad\text{(II.4)}$$

From Eq. (5.1) the solution for a_{32} for $x_1<0$, where there is no current and no incident wave of this frequency, is given by

$$a_{32}=G_{32}\exp\left(-2i\omega\frac{\cos\theta}{c}x_1\right)\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right).\quad\text{(II.5)}$$

Applying the boundary conditions that a_{32} and $\partial a_{32}/\partial x_1$ are continuous at $x_1=0$, we find

$$C_{32}-G_{32}=\frac{8\pi e^3}{m^2c^3(i\omega)^2}C_{11}C_{31}\int_{v_1>0}d^3v\, v_1\frac{\partial f^0}{\partial v_1}\quad\text{(II.6)}$$

and

$$C_{32}-G_{32}\frac{2i\omega\cos\theta}{c\gamma_2}=\frac{8\pi e^3}{m^2c^3}\frac{C_{11}C_{31}}{i\omega\gamma_2}\int_{v_1>0}d^3v\, v_1\frac{\partial f^0}{\partial v_1},\quad\text{(II.7)}$$

where we have neglected γ_1 in comparison to ω/v_1 in the right-hand side of Eq. (II.7).

By examining Eqs. (II.6) and (II.7) we observe that the right-hand side of Eq. (II.6) is of the relative order v_f/c compared to that of Eq. (II.7). Therefore, to the lowest order in v_f/c, we may write the boundary conditions (II.6) and (II.7) as

$$C_{32}=G_{32}\quad\text{(II.8)}$$

and

$$\gamma_2C_{32}-G_{32}\frac{2i\omega\cos\theta}{c}=\frac{-4\pi e^3n}{m^2c^3i\omega}C_{11}C_{31},\quad\text{(II.9)}$$

where we have used the result

$$\int_{v_1>0}d^3v\, v_1\frac{\partial f^0}{\partial v_1}=-\frac{n}{2}.\quad\text{(II.10)}$$

These same relations for C_{32} and G_{32}, which determine the solutions in the interior of the metal and outside the metal, can be obtained if we write for the expression $j_{32}^{(s)}(\text{NL})$

$$j_{32}^{(s)}(\text{NL})=\frac{-e^3n}{m^2c^2i\omega}C_{31}C_{11}\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right)\delta(x_1)\quad\text{(II.11)}$$

instead of its form given by the second term of Eq. (II.1). To verify this, one can solve the differential equation for a_{32} given by Eq. (5.1) for $x_1<0$ and $x_1>0$ separately and then apply the following boundary conditions at $x_1=0$:

(i) a_{32} should be continuous (II.12)

and

$$\text{(ii)}\quad -\frac{\partial a_{32}}{\partial x_1}\bigg|_{x_1=0^+}+\frac{\partial a_{32}}{\partial x_1}\bigg|_{x_1=0^-}=\frac{4\pi}{c}\left(\frac{-e^3n}{m^2c^2i\omega}C_{31}C_{11}\right)\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right).\quad\text{(II.13)}$$

This means that it is permissible to use Eq. (II.11), i.e., to consider the surface term $j_{32}^{(s)}(\text{NL})$ to have a delta-function character, in order to obtain the solution in the interior and outside the metal. Similarly for the surface term $j_{22}^{(s)}(\text{NL})$ given by Eq. (5.6) we may write

$$j_{22}^{(s)}(\text{NL})=\frac{-e^3n}{m^2c^2i\omega}C_{21}C_{11}\times\exp\left(-2i\omega\frac{\sin\theta}{c}x_2\right)\delta(x_1).\quad\text{(II.14)}$$

Since for the Drude solution, $\partial a_{j1}/\partial x_j$ given by Eq. (4.19) has a delta-function character at $x_1=0$, we may replace (II.11) and (II.12) by

$$j_{32}^{(s)}(\text{NL})=\frac{e^3ni\omega}{m^2c^2\omega_p^2}a_{32}\frac{\partial a_{j1}}{\partial x_j}\bigg|_{\text{Drude}}\quad\text{(II.15)}$$

and

$$j_{22}^{(s)}(\text{NL})=\frac{e^3ni\omega}{m^2c^2\omega_p^2}a_{22}\frac{\partial a_{j1}}{\partial x_j}\bigg|_{\text{Drude}}.\quad\text{(II.16)}$$