Theory of second-harmonic generation by small metal spheres

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A small metal sphere interacting with an incident electromagnetic wave will produce second-harmonic radiation in a quadrupolar mode. A hydrodynamical model for the electron gas is employed and a Green-function formalism is used to solve for the cross section for producing second-harmonic generation. Numerical results are obtained for aluminum and silver.

I. INTRODUCTION

Ever since intense sources of electromagnetic radiation have become available, interest in the nonlinear optical properties of matter has persisted. One of the most elementary manifestations of such a nonlinear property is second-harmonic generation (SHG). First-principles calculations of the effect in bulk matter have been carried out by numerous researchers. Adler[1] discussed the general symmetry properties of nonlinear media and outlined a formalism to compute the nonlinear polarization currents in polarization theory. Early theoretical studies of the nonlinear optical behavior of metallic surfaces were conducted by Jha and co-workers.[2–5] Experiments on media with inversion symmetry confirmed,[4] to within an order of magnitude, these theoretical models. In more recent years attention has turned to rough surfaces primarily because of the observation of surface-enhanced Raman scattering. Agarwal and Jha[6] have studied the surface enhancement of second-harmonic generation at a metal grating using a perturbation expansion based on an expansion in terms of the surface roughness parameter. Chen *et al.*[7] have studied the interconnection between SHG and Raman scattering. Arya[8] has developed a Green's-function formalism for treating SHG from rough metal surfaces. Boyd *et al.*[9] made a detailed study of the local-field enhancement of various solids using SHG as a probe. Recently, Keller[10] emphasized the need for including nonlocal electronic transport effects in describing SHG.

In a somewhat unrelated development there has also developed in recent years an interest in the properties of small particles. A variety of techniques have become available to prepare small particles ranging in size from what may be called just clusters of atoms to particles micrometers in size. An extensive body of work has been devoted to the study of the linear optical properties of such particles[11] but not much work has centered on their nonlinear optical properties. Agarwal and Jha[5] studied the nonlinear optical properties of spherical particles in the context of a dielectric model for the limiting case of the particle size being much smaller than the wavelength of light. In this paper we will extend their work in two directions. First we will use what is analogous to a full Mie theory and develop a formalism which is valid for all particle sizes, although for computational reasons we will restrict our attention to particles of moderate size but smaller than the wavelength of light in vacuum. Secondly, we will base our study on a more microscopic model of the particle, rather than employ simply dielectric theory. This will allow us to include screening effects, both at the level of the linear theory and the nonlinear theory. Our attention will be restricted to the study of SHG from a spherical metallic particle.

At first sight the production of SHG seems difficult, at least for centrosymmetric materials, due to the fact that symmetry considerations outlaw dipolar radiation at the second-harmonic frequency for a spatially uniform field. However, it is well known, that as the particle grows in size, higher multipolar scattering becomes more and more important. Thus, we may envisage a range of particle sizes for which quadrupolar (and higher multipolar) higher-harmonic generation becomes significant. Thus, the observation of higher-harmonic radiation could provide us with a new set of experimental techniques to help characterize and probe the properties of small particles.

In Jha's early work[2] it was found that the nonlinear polarization responsible for SHG could be written in the form

$$\mathbf{P}(2\omega)=\alpha\mathbf{E}\times\mathbf{B}+\beta\mathbf{E}\nabla\cdot\mathbf{E}\ , \tag{1.1}$$

where $\mathbf{E}$ and $\mathbf{B}$ are the electric and magnetic fields and α and β are simply related to the properties of an electron. Based on simple symmetry considerations and Maxwell's equations, it is possible to extend this formula and develop simple formulas for the multipolar moments of a small particle in terms of the incident fields.[5] We restrict our attention to SHG and let $\boldsymbol{\mu}$, $\mathbf{m}$, $\overleftrightarrow{Q}$, and $\overleftrightarrow{\chi}$ denote the electric dipole moment, the magnetic dipole moment, the electric quadrupole moment, and the magnetic quadrupole moment, respectively. Note that $\boldsymbol{\mu}$ and $\overleftrightarrow{\chi}$ are even under parity reversals, while $\mathbf{m}$ and $\overleftrightarrow{Q}$ are odd. Also note that $\boldsymbol{\mu}$ and $\overleftrightarrow{Q}$ are even under time reversal while $\mathbf{m}$ and $\overleftrightarrow{\chi}$ are odd. Thus, in a truncated hierarchy,

$$\boldsymbol{\mu}(2\omega)=\beta_E\,\nabla E^2+\gamma_E\mathbf{E}\cdot\nabla\mathbf{E}+\delta_E\nabla B^2+\epsilon_E\mathbf{B}\cdot\nabla\mathbf{B}\ , \tag{1.2a}$$

$$\mathbf{m}(2\omega)=\beta_M\mathbf{E}\times(\nabla\times\mathbf{B})+\gamma_M\mathbf{B}\times(\nabla\times\mathbf{E})+\delta_M E_i\,\nabla B_i+\epsilon_M B_i\,\nabla E_i+\nu_M\mathbf{E}\cdot\nabla\mathbf{B}+\sigma_M\mathbf{B}\cdot\nabla\mathbf{E}\ , \tag{1.2b}$$

$$\overleftrightarrow{Q}(2\omega)=\alpha_Q(E^2\overleftrightarrow{1}-3\mathbf{E}\mathbf{E})+\beta_Q(B^2\overleftrightarrow{1}-3\mathbf{B}\mathbf{B})\ , \tag{1.2c}$$

$$\overleftrightarrow{\chi}(2\omega)=\gamma\overleftrightarrow{\mathbf{I}}\mathbf{E}\cdot\mathbf{B}+\delta\mathbf{E}\mathbf{B}+\delta'\mathbf{B}\mathbf{E}\ , \tag{1.2d}$$

where $\alpha,\beta,\gamma,\delta,\ldots$ are coefficients which depend on the nature of the particle's composition.

In this paper we will consider an incident electromagnetic field which is a circularly polarized plane wave. Then, as we shall see, symmetry further requires that $\mu(2\omega)$ and $\mathbf{m}(2\omega)$ vanish. We start by developing formulas describing the linear response of the system. These are used as driving terms to generate the nonlinear response. What we will ultimately obtain are formulas for the cross section for producing second-harmonic generation.

II. THEORY

A. The model

Consider a metallic sphere of radius a interacting with an incident plane electromagnetic wave. In our previous work[12] we introduced a model in which both the electrons and ions were modeled as interacting hydrodynamic and elastic systems. For the case of SHG, however, we are likely to be concerned with photon frequencies sufficiently high that the ionic contribution will not be of significant size to warrant its inclusion in the model. Thus, we consider an electronic fluid moving in the presence of a uniform jellium background. Our goal is to solve Maxwell's equations:

$$\nabla\cdot\mathbf{E}=4\pi\rho\ , \tag{2.1a}$$

$$\nabla\cdot\mathbf{B}=0\ , \tag{2.1b}$$

$$\nabla\times\mathbf{E}+\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t}=\mathbf{0}\ , \tag{2.1c}$$

$$\nabla\times\mathbf{B}-\frac{1}{c}\frac{\partial\mathbf{E}}{\partial t}=\frac{4\pi}{c}\mathbf{J}\ , \tag{2.1d}$$

together with the hydrodynamical equation for the electrons

$$M\left[\frac{d\mathbf{v}}{dt}+\frac{\mathbf{v}}{\tau}\right]=-e\left[\mathbf{E}+\frac{\mathbf{v}}{c}\times\mathbf{B}\right]-\nabla\mu\ . \tag{2.2}$$

Here, ρ and $\mathbf{J}$ are the charge and current densities, e and m are the charge and mass of the electron, τ is the electron relaxation time, $\mathbf{v}$ is the electron velocity, and μ is the chemical potential. Thus,

$$\rho=-e(n-n_0)\ , \tag{2.3a}$$

$$\mathbf{J}=-ne\mathbf{v}\ , \tag{2.3b}$$

where n is the electron density and n_0 is the ion density. At the level of Thomas-Fermi-Dirac theory,

$$\mu=\frac{(\hbar k_F)^2}{2m}-e^2\left[\frac{3n}{\pi}\right]^{1/3}\ , \tag{2.4}$$

where $k_F=(3\pi^2 n)^{1/3}$ is the Fermi wave vector.

We shall derive our description of SHG from perturbation theory. The first-order response will be at the incident frequency ω, while the second-order response includes, in principle, contributions from both 2ω and dc effects. The latter are of no interest here so will be neglected. Thus, let

$$n-n_0=n_L+n_S+\cdots\ , \tag{2.5a}$$

$$\mathbf{v}=\mathbf{v}_L+\mathbf{v}_S+\cdots\ , \tag{2.5b}$$

$$\mathbf{E}=\mathbf{E}_L+\mathbf{E}_S+\cdots\ , \tag{2.5c}$$

$$\mathbf{B}=\mathbf{B}_L+\mathbf{B}_S+\cdots\ , \tag{2.5d}$$

where the subscripts denote the particular harmonic in question (L = linear, S = second harmonic, ...). By assumption, $|n_S|\ll|n_L|\ll n_0$, etc. Noting that the chemical potential is nonlinear in the electron density, we obtain

$$\mu=\mu_0+\chi_0 n_L+\chi_0 n_S+\chi_1 n_L^2+\cdots\ , \tag{2.6}$$

where the expansion constants are

$$\mu_0=\frac{(\hbar k_F^0)^2}{2m}-\frac{e^2}{\pi}k_F^0\ , \tag{2.7a}$$

$$\chi_0=\frac{(\hbar k_F^0)^2}{3n_0 m}-\frac{e^2K_F^0}{\pi 3\pi n_0}\ , \tag{2.7b}$$

$$\chi_1=-\frac{\mu_0}{9n_0^2}\ , \tag{2.7c}$$

and $k_F^0=(3\pi^2 n_0)^{1/3}$. Carrying out similar expansions for ρ and $\mathbf{J}$ and the various terms of Eq. (2.2) leads to a revised set of equations which may be separated into first- and second-order equations:

$$\nabla\cdot\mathbf{E}_L=-4\pi e n_L\ , \tag{2.8a}$$

$$\nabla\cdot\mathbf{B}_L=0\ , \tag{2.8b}$$

$$\nabla\times\mathbf{E}_L=\frac{i\omega}{c}\mathbf{B}_L\ , \tag{2.8c}$$

$$\nabla\times\mathbf{B}_L=-\frac{i\omega}{c}\mathbf{E}_L-\frac{4\pi e n_0}{c}\mathbf{v}_L\ , \tag{2.8d}$$

$$m\left[-i\omega+\frac{1}{\tau}\right]\mathbf{v}_L=-e\mathbf{E}_L-\chi_0\nabla n_L\ , \tag{2.8e}$$

and

$$\nabla\cdot\mathbf{E}_S=-4\pi e n_S\ , \tag{2.9a}$$

$$\nabla\cdot\mathbf{B}_S=0\ , \tag{2.9b}$$

$$\nabla\times\mathbf{E}_S=\frac{2i\omega}{c}\mathbf{B}_S\ , \tag{2.9c}$$

$$\nabla\times\mathbf{B}_S=-\frac{2i\omega}{c}\mathbf{E}_S-\frac{4\pi e}{c}(n_0\mathbf{v}_S+n_L\mathbf{v}_L)\ , \tag{2.9d}$$

$$m\left[-2i\omega+\frac{1}{\tau}\right]\mathbf{v}_S+m\mathbf{v}_L\cdot\nabla\mathbf{v}_L=-e\left[\mathbf{E}_S+\frac{1}{c}\mathbf{v}_L\times\mathbf{B}_L\right]-\chi_0\nabla n_S-\chi_1\nabla n_L^2\ . \tag{2.9e}$$

Note that the first-order equations are homogeneous equations, whereas the second-order equations are inhomogeneous with the first-order variables acting as source terms. The incident field for the linear equations enters through the boundary conditions.

B. Solution of the first-order equations

Wave equations for n_L, $\mathbf{E}_L$, and $\mathbf{B}_L$ follow directly from Eqs. (2.8):

$$(\nabla^2+k^2)n_L=0\ , \tag{2.10a}$$

$$(\nabla^2+p^2)\mathbf{E}_L=\frac{4\pi e}{k^2}(p^2-k^2)\nabla n_L\ , \tag{2.10b}$$

$$(\nabla^2+p^2)\mathbf{B}_L=0\ , \tag{2.10c}$$

where we have introduced the plasma frequency,

$$\omega_p=(4\pi n_0 e^2/m)^{1/2}\ , \tag{2.11a}$$

the Thomas-Fermi screening constant,

$$\lambda=\omega_p[m/(\chi_0 n_0)]^{1/2}\ , \tag{2.11b}$$

and

$$p=q\sqrt{\epsilon}\ , \tag{2.11c}$$

where q is the wave vector of the photon in free space, $q=\omega/c$, and

$$k=\lambda[\epsilon/(1-\epsilon)]^{1/2}\ , \tag{2.11d}$$

and ϵ is the Drude dielectric constant

$$\epsilon=1-\omega_p^2/[\omega(\omega+i/\tau)]\ . \tag{2.11e}$$

The solutions to Eqs. (2.10) which apply inside the sphere $(r<a)$ are

$$\nabla\cdot\mathbf{v}_L=\frac{i\omega}{n_0}n_L\ . \tag{2.12}$$

The solutions to Eqs. (2.10) which apply inside the sphere $(r<a)$ are

$$n_L=\sum_{l,m}C_{lm}j_l(kr)Y_{lm}(\hat{\mathbf{r}})\ , \tag{2.13a}$$

$$E_{Lr}(\mathbf{r})=\frac{1}{r}\sum_{l,m}\left[F_{lm}j_l(pr)+C_{lm}\frac{4\pi e}{k^2 r}krj_l'(kr)\right]Y_{lm}(\hat{\mathbf{r}})\ , \tag{2.13b}$$

$$\mathbf{E}_{Lt}(\mathbf{r})=\sum_{l,m}\left[\frac{R_{lm}}{\sqrt{l(l+1)}}j_l(pr)\mathbf{X}_{lm}-[l(l+1)]^{1/2}\left[\frac{1}{l(l+1)}\frac{F_{lm}}{r}\frac{\partial}{\partial r}[rj_l(pr)]+\frac{4\pi e}{k^2}C_{lm}\frac{j_l(kr)}{r}\right]\hat{\mathbf{r}}\times\mathbf{X}_{lm}\right]\ , \tag{2.13c}$$

$$B_{Lr}(\mathbf{r})=\frac{1}{qr}\sum_{l,m}R_{lm}j_l(pr)Y_{lm}(\hat{\mathbf{r}})\ , \tag{2.13d}$$

$$\mathbf{B}_{Lt}(\mathbf{r})=-\frac{1}{q}\sum_{l,m}\left[p^2F_{lm}j_l(pr)\mathbf{X}_{lm}+iR_{lm}\frac{1}{r}\frac{\partial}{\partial r}[rj_l(pr)]\right]\frac{\mathbf{r}\times\mathbf{X}_{lm}}{[l(l+1)]^{1/2}}\ , \tag{2.13e}$$

where the fields are expressed as radial and tangential fields

$$\mathbf{E}_L(\mathbf{r})=\hat{\mathbf{r}}E_{Lr}(\mathbf{r})+\mathbf{E}_{Lt}(\mathbf{r})\ , \tag{2.14a}$$

$$\mathbf{B}_L(\mathbf{r})=\hat{\mathbf{r}}B_{Lr}(\mathbf{r})+\mathbf{B}_{Lt}(\mathbf{r})\ , \tag{2.14b}$$

and $\mathbf{X}_{lm}$ are the vector spherical harmonics defined by

$$\mathbf{X}_{lm}=\frac{\mathbf{L}}{[l(l+1)]^{1/2}}Y_{lm}(\hat{\mathbf{r}})\ , \tag{2.15a}$$

where

$$\mathbf{L}=-i\mathbf{r}\times\nabla\ . \tag{2.15b}$$

The coefficients C_{lm}, F_{lm}, and R_{lm} are to be determined by matching boundary conditions on the surface of the sphere.

Let us focus our attention on an incident circularly polarized plane wave

$$\mathbf{E}=E_0(\hat{\mathbf{i}}\pm\hat{\mathbf{j}})e^{iqz}\ , \tag{2.16a}$$

$$\mathbf{B}=\mp i\mathbf{E}\ , \tag{2.16b}$$

where $\mathbf{E}_0$ is the amplitude of the electric field. For the linear fields the general solution for elliptically polarized light may be obtained by superposition, but for the nonlinear fields simple superposition does not apply and a more extensive analysis will be needed.

The fields outside the sphere $(r>a)$ are[13]

$$\mathbf{E}_L(\mathbf{r})=E_0\sum_{l,m}\delta_{m,\pm1}i^l\sqrt{4\pi(2l+1)}\left[[j_l(qr)+\tfrac{1}{2}\alpha_{lm}h_l^{(1)}(qr)]\mathbf{X}_{lm}\pm\frac{1}{q}\{\nabla\times[j_l(qr)\mathbf{X}_{lm}]+\tfrac{1}{2}\beta_{lm}\nabla\times[h_l^{(1)}(qr)\mathbf{X}_{lm}]\}\right]\ , \tag{2.17a}$$

and

$$\mathbf{B}_L(\mathbf{r})=-E_0\sum_{l,m}\delta_{m,\pm1}i^{l+1}\sqrt{4\pi(2l+1)}\left[\frac{1}{q}\nabla\times[j_l(qr)\mathbf{X}_{lm}]+\frac{1}{2q}\alpha_{lm}\nabla\times[h_l(qr)\mathbf{X}_{lm}]\pm[j_l(qr)+\tfrac{1}{2}\beta_{lm}h_l^{(1)}(qr)]\mathbf{X}_{lm}\right]\ . \tag{2.17b}$$

Again the coefficients α_{lm} and β_{lm} are to be determined by matching boundary conditions.

In the present model we have explicitly taken into account all dielectric effects in the charge and current densities, so the boundary conditions are such that E_{Lr}, $\mathbf{E}_{Lt}$, B_{Lr}, and $\mathbf{B}_{Lt}$ be continuous at $r=a$. This leads to

$$\alpha_{lm}=\frac{2}{D_l}[zj_l(x)j_l'(z)-xj_l(z)j_l'(x)]\ , \tag{2.18a}$$

$$R_{lm}=E_0\delta_{m,\pm1}\frac{i^{l+1}}{xD_l}[4\pi(2l+1)(l+1)l]^{1/2}\ , \tag{2.18b}$$

where

$$D_l=xj_l(z)h_l^{(1)'}(x)-zh_l^{(1)}(x)j_l'(z)\ , \tag{2.18c}$$

and

$$\beta_{lm}=-\frac{2}{\Delta_l}\left\{[xj_l(x)]'-j_l(x)\left[\left[\frac{x}{z}\right]^2\frac{[zj_l(z)]'}{j_l(z)}+\left[1-\frac{x^2}{z^2}\right]\frac{l(l+1)}{y}\frac{j_l(y)}{j_l'(y)}\right]\right\}, \tag{2.19a}$$

$$C_{lm}=\pm\frac{kE_0}{4\pi ex^2}\frac{\delta_{m,\pm1}}{\Delta_l j_l'(y)}i^{l+2}\sqrt{4\pi(2l+1)l(l+1)}\left[1-\frac{x^2}{z^2}\right], \tag{2.19b}$$

$$F_{lm}=\pm\frac{qE_0}{p^2x}\frac{\delta_{m,\pm1}}{j_l(z)}i^{l+2}\frac{\sqrt{4\pi(2l+1)l(l+1)}}{\Delta_l}\ , \tag{2.19c}$$

where

$$\Delta_l=[xh_l^{(1)}(x)]'-h_l^{(1)}(x)\left[\left[\frac{x}{z}\right]^2\frac{[zj_l(z)]'}{j_l(z)}+\left[1-\frac{x^2}{z^2}\right]\frac{l(l+1)}{y}\frac{j_l(y)}{j_l'(y)}\right] \tag{2.19d}$$

and $x=qa$, $y=ka$, and $z=pa$. Note that the coefficients β_{lm} and α_{lm} refer to the electric and magnetic multipoles of the sphere, respectively. The coefficients C_{lm} are related to the charge-density fluctuations. In the present model the boundary condition $v_{Lr}(a)=0$ is automatically satisfied, as would be expected for a problem in which the electrons are confined to the interior of the sphere.

In summary, Eqs. (2.13) and (2.17), in combination with Eqs. (2.18) and (2.19) provide an analytic solution to the linear problem.

C. Second-harmonic generation

In order to solve Eq. (2.9) let us introduce two auxiliary vectors

$$\xi=n_L\mathbf{v}_L\ , \tag{2.20a}$$

$$\eta=-m\mathbf{v}_L\cdot\nabla\mathbf{v}_L-\frac{e}{c}\mathbf{v}_L\times\mathbf{B}_L-\chi_1\nabla n_L^2\ . \tag{2.20b}$$

Then the wave equations for the second-harmonic fields become

$$(\nabla^2+k_2^2)n_S(\mathbf{r})=S(\mathbf{r})\ , \tag{2.21a}$$

$$(\nabla^2+p_2^2)\mathbf{B}_S(\mathbf{r})=\mathbf{T}(\mathbf{r})\ , \tag{2.21b}$$

and

$$(\nabla^2+p_2^2)\mathbf{E}_S(\mathbf{r})=4\pi e\left[\frac{p_2^2}{k_2^2}-1\right]\nabla n_S+\mathbf{U}(\mathbf{r})\ , \tag{2.21c}$$

where we have introduced a second-harmonic Drude dielectric constant

$$\epsilon_2=1-\frac{\omega_p^2}{2\omega(2\omega+i/\tau)}\ , \tag{2.22a}$$

and let

$$k_2=\lambda[\epsilon_2/(1-\epsilon_2)]^{1/2} \tag{2.22b}$$

and

$$p_2=2q(\epsilon_2)^{1/2}\ . \tag{2.22c}$$

The source terms appearing in Eq. (2.21) are

$$\mathbf{T}=\frac{4\pi e}{c}\nabla\times\xi+\frac{i\omega_p^2}{ce}\frac{\nabla\times\eta}{2\omega+i/\tau}\ , \tag{2.23a}$$

$$\mathbf{U}=i\frac{8\pi\omega e}{c^2}\xi+(2q)^2\frac{\epsilon_2-1}{e}\eta\ , \tag{2.23b}$$

$$S=-\frac{i\lambda^2}{2\omega}\frac{\nabla\cdot\xi}{1-\epsilon_2}+\chi_0^{-1}\nabla\cdot\eta\ . \tag{2.23c}$$

The radial components of $\mathbf{E}_2$ and $\mathbf{B}_2$ obey

$$(\nabla^2+p_2^2)rB_{Sr}=\mathbf{r}\cdot\mathbf{T} \tag{2.24a}$$

and

$$(\nabla^2+p_2^2)rE_{Sr}=-8\pi en_S+\mathbf{r}\cdot\mathbf{U}+4\pi e\left[\left[\frac{p_2}{k_2}\right]^2-1\right]r\frac{\partial n_S}{\partial r}\ . \tag{2.24b}$$

Equations (2.21a) and (2.24) may be solved by using the Green's function $G_\mu(\mathbf{r},\mathbf{r}')$ which satisfies

$$(\nabla^2+\mu^2)G_\mu(\mathbf{r},\mathbf{r}')=-\delta(\mathbf{r}-\mathbf{r}')\ . \tag{2.25}$$

In free space we have

$$G_\mu(\mathbf{r},\mathbf{r}')=\frac{e^{i\mu|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|}$$
$$=i\mu\sum_l j_l(\mu r_<)h_l^{(1)}(\mu r_>)\sum_m Y_{lm}^*(\hat{\mathbf{r}}')Y_{lm}(\hat{\mathbf{r}}) . \quad (2.26)$$

In order to obtain solutions that are not overly involved let us simplify matters by making two assumptions now: (a) the incident plane wave has positive helicity, i.e., $m=+1$ and (b) the linear dipole response is assumed to be much more important than higher-order multipole responses, i.e., the wavelength is not too short. In this case the subscripts l,m may be restricted to take the value 1,1 when considering the linear fields. Let

$$n_L(\mathbf{r})=n_1(r)Y_{11}(\hat{\mathbf{r}}) , \quad (2.27a)$$

$$B_{Lr}(\mathbf{r})=B_1(r)Y_{11}(\hat{\mathbf{r}}) , \quad (2.27b)$$

$$B_{L\theta}(\mathbf{r})=B_2(r)\frac{Y_{11}(\hat{\mathbf{r}})}{\sin\theta}+B_3(r)\frac{\partial Y_{11}(\hat{\mathbf{r}})}{\partial\theta} , \quad (2.27c)$$

$$B_{L\phi}(\mathbf{r})=i\left[B_2(r)\frac{\partial Y_{11}(\hat{\mathbf{r}})}{\partial\theta}+B_3(r)\frac{Y_{11}(\hat{\mathbf{r}})}{\sin\theta}\right] , \quad (2.27d)$$

$$v_{Lr}(\mathbf{r})=-iv_1(r)Y_{11}(\hat{\mathbf{r}}) , \quad (2.27e)$$

$$v_{L\theta}(\mathbf{r})=-i\left[v_2(r)\frac{Y_{11}(\hat{\mathbf{r}})}{\sin\theta}+v_3(r)\frac{\partial Y_{11}(\hat{\mathbf{r}})}{\partial\theta}\right] , \quad (2.27f)$$

$$v_{L\phi}(\mathbf{r})=v_2(r)\frac{\partial Y_{11}(\hat{\mathbf{r}})}{\partial\theta}+v_3(r)\frac{Y_{11}(\hat{\mathbf{r}})}{\sin\theta} . \quad (2.27g)$$

Here

$$n_1(r)=C_{11}j_1(kr) , \quad (2.28a)$$

$$B_1(r)=\frac{R_{11}}{qr}j_1(pr) , \quad (2.28b)$$

$$B_2(r)=\frac{p^2}{2q}F_{11}j_1(pr) , \quad (2.28c)$$

$$B_3(r)=\frac{R_{11}}{2qr}\frac{\partial}{\partial r}[rj_1(pr)] , \quad (2.28d)$$

$$v_1(r)=\frac{\omega C_{11}}{n_0 k}j_1'(kr)+\frac{eF_{11}}{m(\omega+i/\tau)}\frac{1}{r}j_1(pr) , \quad (2.28e)$$

$$v_2(r)=-\frac{eR_{11}}{2m(\omega+i/\tau)}j_1(pr) , \quad (2.28f)$$

$$v_3(r)=\frac{\omega C_{11}}{n_0k^2r}j_1(kr)+\frac{eF_{11}}{2m(\omega+i/\tau)}\frac{1}{r}\frac{\partial}{\partial r}[rj_1(pr)] . \quad (2.28g)$$

Also we write

$$\mathbf{r}\cdot\mathbf{U}=\pi(r)Y_{22}(\hat{\mathbf{r}}) , \quad (2.29a)$$

$$\mathbf{r}\cdot\mathbf{T}=\rho(r)Y_{22}(\hat{\mathbf{r}}) , \quad (2.29b)$$

$$S=\sigma(r)Y_{22}(\hat{\mathbf{r}}) , \quad (2.29c)$$

where

$$\pi(r)=\left[\frac{3}{10\pi}\right]^{1/2}\left\{\frac{8\pi\omega e}{c^2}rn_1(r)v_1-(2q)^2\frac{\epsilon_2-1}{e}\left[m\left[-rv_1\frac{\partial v_1}{\partial r}+v_1v_3+v_2^2-v_3^2\right]+\frac{er}{c}(v_2B_3-v_3B_2)+2\chi_1rn_1\frac{\partial n_1}{\partial r}\right]\right\} , \quad (2.30a)$$

$$\rho(r)=\left[\frac{3}{10\pi}\right]^{1/2}\left\{-\frac{12\pi e}{c}n_1v_2+\frac{3\omega_p^2}{ce(2\omega+i/\tau)}\left[m\left[v_1\frac{\partial v_2}{\partial r}+\frac{v_1v_2}{r}-\frac{2}{r}v_2v_3\right]+\frac{e}{c}(v_1B_3-v_3B_1)\right]\right\} , \quad (2.30b)$$

and

$$\begin{aligned}\sigma(r)=&\left[\frac{3}{10\pi}\right]^{1/2}\left[\frac{\lambda^2}{2\omega}\frac{1}{1-\epsilon_2}\left[\frac{n_1v_3}{r}-v_1\frac{\partial n_1}{\partial r}+\frac{\omega}{n_0}n_1^2\right]\right]\\&-\frac{1}{\chi_0}\left[\frac{3}{10\pi}\right]^{1/2}\left\{m\left[-v_1\frac{\partial^2}{\partial r^2}v_1-\left[\frac{\partial v_1}{\partial r}\right]^2-\frac{2}{r}v_1\frac{\partial v_1}{\partial r}+\frac{4}{r^2}v_1v_3-2\left[\frac{v_2}{r}\right]^2-4\left[\frac{v_3}{r}\right]^2+\frac{4v_1}{r}\frac{\partial v_3}{\partial r}\right.\right.\\&\left.+\frac{v_3}{r}\frac{\partial v_1}{\partial r}+\frac{2v_2}{r}\frac{\partial v_2}{\partial r}-\frac{2}{r}v_3\frac{\partial v_3}{\partial r}\right]+\frac{e}{c}\left[\frac{2}{r}(v_2B_3-v_3B_2)+B_3\frac{\partial v_2}{\partial r}+v_2\frac{\partial B_3}{\partial r}\right.\\&\left.-B_2\frac{\partial v_3}{\partial r}-v_3\frac{\partial B_2}{\partial r}+\frac{3}{r}(v_1B_2-v_2B_1)\right]\\&\left.+2\chi_1\left[n_1\frac{\partial^2}{\partial r^2}n_1+\left[\frac{\partial n_1}{\partial r}\right]^2+\frac{2n_1}{r}\frac{\partial n_1}{\partial r}-3\left[\frac{n_1}{r}\right]^2\right]\right\} .\end{aligned} \quad (2.30c)$$

Expressed in terms of $\pi(r)$, $\rho(r)$, and $\sigma(r)$, the solutions for n_S, $\mathbf{r}\cdot\mathbf{B}_S$, and $\mathbf{r}\cdot\mathbf{E}_S$ are

$$n_S=[C_{22}j_2(k_2r)+v(r)]Y_{22}(\hat{\mathbf{r}}) , \tag{2.31a}$$

$$\mathbf{r}\cdot\mathbf{B}_S=\left[\frac{1}{2q}r_{22}j_2(p_2r)+Z(r)\right]Y_{22}(\hat{\mathbf{r}}) , \tag{2.31b}$$

$$\mathbf{r}\cdot\mathbf{E}_S=[f_{22}j_2(p_2r)+k(r)+C_{22}I(r)]Y_{22}(\hat{\mathbf{r}}) , \tag{2.31c}$$

where

$$v(r)=-ik_2\int dr'r'^2j_2(k_2r_<)h_2^{(1)}(k_2r_>)\sigma(r') , \tag{2.32a}$$

$$z(r)=-ip_2\int dr'r'^2j_2(p_2r_<)h_2^{(1)}(p_2r_>)\rho(r') , \tag{2.32b}$$

$$k(r)=-ip_2\int dr'r'^2j_2(p_2r_<)h_2^{(1)}(p_2r_>)\left\{-8\pi e v(r')+4\pi e\left[\left[\frac{p_2}{k_2}\right]^2-1\right]r'\frac{\partial v(r')}{\partial r'}+\pi(r')\right\} , \tag{2.32c}$$

$$I(r)=-ip_2\int dr'r'^2j_2(p_2r_<)h_2^{(1)}(p_2r_>)\left\{-8\pi e j_2(k_2r')+4\pi e\left[\left[\frac{p_2}{k_2}\right]^2-1\right]k_2r'j_2'(k_2r')\right\} . \tag{2.32d}$$

To obtain the tangential components of $\mathbf{E}_S$ and $\mathbf{B}_S$ let us write

$$\mathbf{E}_S=E_{Sr}Y_{22}(\hat{\mathbf{r}})+\phi(r)\mathbf{X}_{22}+\psi(r)\hat{\mathbf{r}}\times\mathbf{X}_{22} , \tag{2.33a}$$

$$\mathbf{B}_s=B_{Sr}Y_{22}(\hat{\mathbf{r}})+u(r)\mathbf{X}_{22}+v(r)\hat{\mathbf{r}}\times\mathbf{X}_{22} , \tag{2.33b}$$

and

$$\phi(r)=\frac{2q}{\sqrt{6}}\mathbf{r}\cdot\mathbf{B}_S , \tag{2.34a}$$

$$\psi(r)=-\frac{i}{\sqrt{6}}\left[4\pi e r v(r)+4\pi e C_{22}rj_2(k_2r)+2E_{Sr}+r\frac{\partial}{\partial r}E_{Sr}\right] , \tag{2.34b}$$

$$u(r)=\frac{i}{2q}\left[\frac{i\sqrt{6}}{r}E_{Sr}+\frac{1}{r}\frac{\partial}{\partial r}[r\psi(r)]\right] , \tag{2.34c}$$

$$v(r)=\frac{-i}{\sqrt{6}}\left[2B_{Sr}+r\frac{\partial}{\partial r}B_{Sr}\right] . \tag{2.34d}$$

There are three coefficients, r_{22}, C_{22}, and f_{22}, to be determined by matching boundary conditions. The fields outside the sphere are given by formulas analogous to those of Eq. (2.17) but without an incident field at frequency 2ω being present. Thus, for $r>a$,

$$\mathbf{E}_S(\mathbf{r})=-(5\pi)^{1/2}\left[a_{22}h_2^{(1)}(2qr)\mathbf{X}_{22}+\frac{b_{22}}{2q}\left[\frac{i\sqrt{6}\hat{\mathbf{r}}}{r}h_2^{(1)}(2qr)Y_{22}(\hat{\mathbf{r}})+\frac{1}{r}\frac{\partial}{\partial r}[rh_2^{(1)}(2qr)]\hat{\mathbf{r}}\times\mathbf{X}_{22}\right]\right] , \tag{2.35a}$$

$$\mathbf{B}_S(\mathbf{r})=-\frac{i}{2q}\nabla\times\mathbf{E}_S(\mathbf{r}) . \tag{2.35b}$$

Again $\hat{\mathbf{r}}\cdot\mathbf{E}_S$, $\hat{\mathbf{r}}\cdot\mathbf{B}_S$, $\mathbf{E}_{St}$, and $\mathbf{B}_{St}$ must be continuous at $r=a$. We find, after some lengthy algebra, that

$$a_{22}=-\frac{2q}{p_2^2a\sqrt{30\pi}}\frac{I_1(a)}{\Delta} , \tag{2.36}$$

where

$$I_1(a)=\int_0^a dr(p_2r)^2j_2(p_2r)\rho(r) , \tag{2.37a}$$

$$\Delta=2qaj_2(p_2a)h_2^{(1)\prime}(2qa)-p_2ah_2^{(1)}(2qa)j_2'(p_2a) , \tag{2.37b}$$

and

$$b_{22}=\frac{2iq}{\sqrt{30\pi}}\frac{\Delta_b'}{\Delta_2'} , \tag{2.38}$$

where

$$\Delta_b'=\left[1+p_2a\frac{j_2'(p_2a)}{j_2(p_2a)}-\frac{6}{k_2a}\frac{j_2(k_2a)}{j_2'(k_2a)}\right]\pi(a)+\frac{4\pi eaI_3(a)}{(k_2a)^2j_2(p_2a)}+\frac{I_4(a)}{aj_2(p_2a)}-\frac{24\pi eaI_2(a)}{(k_2a)^3} , \tag{2.39a}$$

$$\Delta_2'=p_2^2\left[[2qah_2^{(1)}(2qa)]'-h_2^{(1)}(2qa)\left\{\left[\frac{2q}{p_2}\right]^2\frac{[p_2aj_2(p_2a)]'}{j_2(p_2a)}+\left[1-\left[\frac{2q}{p_2}\right]^2\right]\frac{6}{k_2a}\frac{j_2(k_2a)}{j_2'(k_2a)}\right\}\right] , \tag{2.39b}$$

and

$$I_2(a)=\int_0^a dr(p_2r)^2\frac{j_2(k_2r)}{j_2'(k_2a)}\sigma(r)\ , \tag{2.39c}$$

$$I_3(a)=\int_0^a dr(p_2r)^2[p_2rj_2'(p_2r)+j_2(p_2r)]\sigma(r)\ , \tag{2.39d}$$

$$I_4(a)=\int_0^a dr(p_2r)^2j_2(p_2r)\pi(r)\ . \tag{2.39e}$$

The integrals I_1 to I_4 are evaluated numerically.

III. RESULTS AND DISCUSSION

In the preceding section we have derived expressions for the linear and nonlinear electric and magnetic fields both inside and outside a small metallic spherical particle illuminated by an incident electromagnetic wave. The sources of the nonlinearity included the Lorentz force, the convection of electron velocity, nonlinear contributions to the electron current, and nonlinear chemical potential terms. In order to be able to compare these expressions with laboratory measurements, let us compute the cross section for SHG and compare it with the corresponding linear cross section. We define the SHG cross section as the ratio between the radiated SHG power at frequency 2ω and the incident intensity at frequency ω. Thus, putting in the atomic units explicitly,

$$\sigma_{\rm SHG}=\frac{5\pi}{8q^2}(\,|a_{22}|^2+|b_{22}|^2)\left[\frac{E_0a_0^2}{e}\right]^2a_0^2\ , \tag{3.1}$$

where e is the electron charge and a_0 is the Bohr radius. The cross section is proportional to the square of the incident electric field. It includes contributions from both the electric and magnetic quadrupole terms. The corresponding linear cross section may be written as a multipole series

$$\sigma_L=\frac{\pi}{2q^2}\sum_l(2l+1)(\,|\alpha_{l1}|^2+|\beta_{l1}|^2)\ , \tag{3.2}$$

where, in the dipole approximation, only the terms with $l=1$ are retained. This cross section will be denoted by σ_1.

In order to compare our results with those of Agarwal and Jha,[5] let us start by writing expressions for the general solution for the linear internal electric fields given by Eqs. (3.13b) and (2.13c) in the limit in which the wavelength is much larger than the particle size both inside and outside the particle ($pa \ll 1$ and $qa \gg 1$) and the screening length is much less than the particle size ($ka \gg 1$). Then our formulas reduce to that given by dielectric theory and we get the formula quoted in Ref. 5 for the internal field

$$\mathbf{E}\approx\frac{3\mathbf{E}_0}{\epsilon+2}-\frac{i}{2}\mathbf{r}\times(\mathbf{q}\times\mathbf{E}_0)\ . \tag{3.3}$$

However, for the cases of interest in this paper the above limits are not satisfied. Thus, at the resonance frequency for Al, for example, $qa=0.43$ for $a=100$ Å and $qa=0.74$ for $a=200$ Å. Typical values of pa for a 100-Å sphere are in the range 0.6 to 0.8 and typical values of ka are around 200. The fact that the values qa and pa are not too small, points to the need for using the full Mie theory in evaluating the cross sections.

Another point of comparison between our theory and the standard Mie theory involves evaluating Eq. (2.19a) explicitly. We do this for the linear theory because there it is simpler to write analytic expressions than it is to do so for the nonlinear theory. Analogous considerations hold, of course, for the nonlinear coefficient given by Eq. (2.38). The general expression for β_1 is

$$\beta_l=-2\frac{[xj_l(x)]'-j_l(x)\left\{\left[\frac{x}{z}\right]^2\frac{[zj_l(z)]'}{j_l(z)}+\left[1-\left[\frac{x}{z}\right]^2\right]\frac{l(l+1)}{y}\frac{j_l(y)}{j_l'(y)}\right\}}{[xh_l^{(1)}(x)]-h_l^{(1)}(x)\left\{\left[\frac{x}{z}\right]^2\frac{[zj_l(z)]'}{j_l(x)}+\left[1-\left[\frac{x}{z}\right]^2\right]\frac{l(l+1)}{y}\frac{j_l(y)}{j_l'(y)}\right\}}\ . \tag{3.4}$$

In the strong screening limit ($y\to\infty$) this result reduces to the Mie formula

$$\beta_l^{\rm Mie}\to-2\left[\frac{[xj_l(x)]'-j_l(x)(x/z)^2\dfrac{[zj_l(z)]'}{j_l(z)}}{[xh_l^{(1)}(x)]'-h_l^{(1)}(x)(x/z)^2\dfrac{[zj_l(z)]'}{j_l(z)}}\right]\ . \tag{3.5}$$

In Fig. 1 we plot the quantity $\sigma_{\rm SHG}/(\pi a^2E_0^2)$ for aluminum as a function of the dimensionless parameter $x=qa=\omega a/c$. Graphs are presented for several values of the sphere radius varying from 50 to 200 Å. Several features are worthy of note. At low values of x, corresponding to low frequencies, the cross sections rise rapidly with frequency, as would be expected for a sphere of finite conductivity. The bulk plasma frequency for Al corresponds to $\omega_p=2.4\times10^{16}$ rad/sec. In each case we see two resonance peaks. The low-frequency peak corresponds to the quadrupolar plasmon resonance frequency, while the higher-frequency peak occurs at the dipole plasmon resonance. In Mie theory these occur at frequencies given by the condition[5]

$$l\epsilon(\omega)+l+1+2\left[\frac{\omega a}{c}\right]^2\frac{(l+1)(2l+1)}{l(2l-1)(2l+3)}=0\ .$$

The dipole plasmon is excited for $l=1$ and the quadrupole plasmon for $l=2$. Since we are concerned with

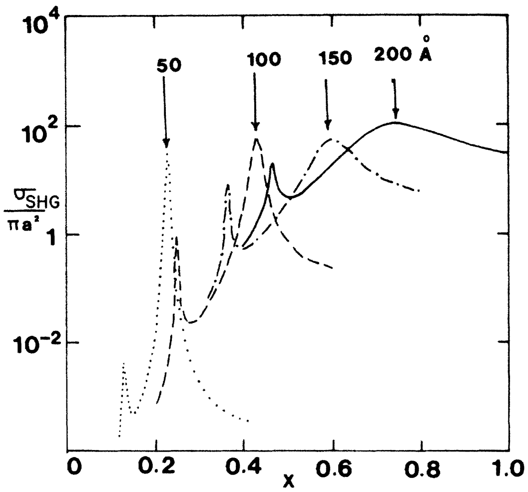

FIG. 1. Cross sections for scattering of electromagnetic radiation by aluminum spheres in units of the geometric cross section for spheres of 50, 100, 150, and 200 Å radii. Abscissa denotes the dimensionless parameter $x=\omega a/c$, where ω is the radian frequency, a is the sphere radius, and c is the speed of light. The set of curves give second-harmonic-generation cross sections corresponding to an incident electric field strength of 1 a.u. ($E_0=e/a_0^2$).

values for a which are reasonably large, the approximation $l\epsilon(\omega)+l+1=0$ is not appropriate for determining the position of the resonances.

In Fig. 2 we plot, for comparison purposes, the linear dipole and linear quadrupole cross sections as a function of $x=qa$ for spheres of the same size as in Fig. 1 (100 Å). We note that the linear quadrupole cross section is several orders of magnitude smaller than the linear dipole cross section. These results, including the screening effects, are in good agreement with the Mie scattering formulas.

In Fig. 3 curves similar to those of Fig. 1 are presented,

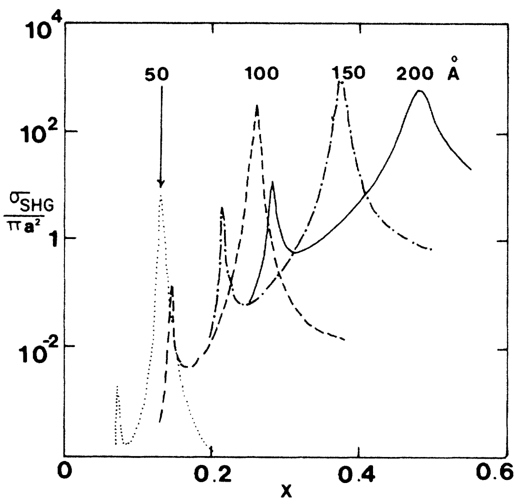

FIG. 3. Same as Fig. 1 but for silver spheres.

but this time for Ag spheres ranging in size from 50 to 200 Å. Again the nonlinear cross section displays the pronounced dipolar and quadrupolar resonances. One would naturally expect these linear resonances to play a role in the nonlinear quadrupole resonance because the nonlinear quadrupole is generated by the mixing of two dipole excitations in the field and the production of a quadrupole outgoing field.

We have not shown the differential cross sections for SHG explicitly, but these may be obtained from the total cross sections by noting that the fields have an angular dependence associated with $Y_{22}(\hat{r})$. Thus a standard quadrupole pattern is to be expected.

In Fig. 4 we compare our calculations with the calculations of Agarwal and Jha[5] for Al spheres of two sizes: $a=50$ and 100 Å. We see that for small spheres the agreement is good, whereas for large spheres there is con-

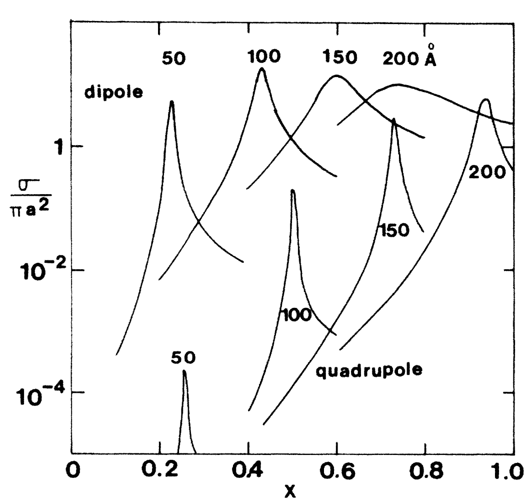

FIG. 2. Linear cross sections for dipole (electric and magnetic) and quadrupole interaction for spheres of various radii (50, 100, 150, and 200 Å).

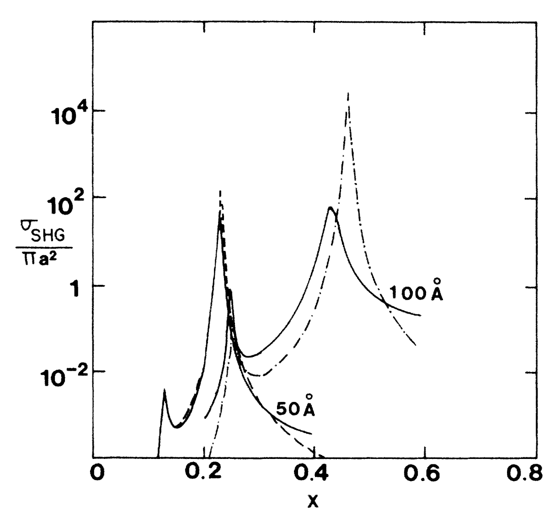

FIG. 4. Comparison of the second-harmonic cross sections as computed in this paper (solid curves) with those given by Ref. 5 (dashed curves). Curves are given for $a=50$ and 100 Å.

siderable disagreement. For larger spheres the need for a full Mie theory accounts for a considerable amount of the disagreement. Then the wavelength of the light inside the sphere becomes smaller than the radius and different parts of the sphere begin to destructively interfere in the production of both a dipole in the in field and a quadrupole in the out field. This leads to a diminished cross section.

In Fig. 5 we plot the linear dipole cross section $\sigma_1/\pi a^2$ and the cross section for second-harmonic generation $\sigma_{SHG}/\pi a^2$ as a function of sphere radius a for two fixed values of the frequency $\omega=5.0\times10^{15}$ rad/sec and $\omega=1.0\times10^{16}$ rad/sec. The curves are plotted for aluminum particles. The SHG cross section is plotted for an incident electric field strength corresponding to 1 a.u. (e/a_0^2). Values for other field strengths may be obtained by multiplying by $(E_0 a_0^2/e)^2$. For low values of a the cross section rises rapidly with size but tends to saturate when the dimensionless parameter becomes of the order of unity. For values of x larger than 1, we know that higher-order linear multipoles begin playing a more important role in scattering. Presumably the same thing will occur in the nonlinear scattering, but we have not computed higher multiples as of yet.

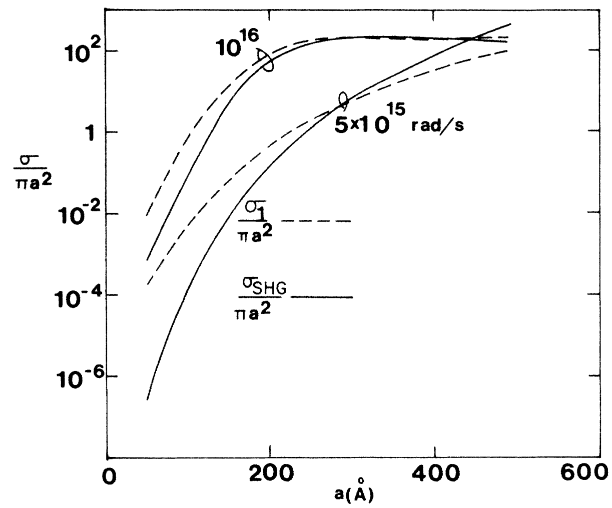

FIG. 5. Linear dipolar cross section (dashed curves) and second-harmonic cross section (solid curves) as a function of sphere radius for Al spheres. Graphs for two frequencies are given, $\omega=5\times10^{15}$ and 1.0×10^{16} rad/sec.

Let us estimate the rate of generation of SHG photons for a hypothetical experimental arrangement. Suppose we prepare a smoke of 100-Å Al particles with a concentration of 10^{12} cm^{-3}. For an incident intensity of 10^{12} W/cm^2 we have a field strength $E_0^2=8.4\times10^9$ esu^{2}cm^{-4}$=2.9\times10^{-5}$ a.u. For the quadrupolar resonance frequency in Fig. 1, $\omega=1.3\times10^{16}$ rad/sec, the flux of incident photons is 7.4×10^{29} cm^{-2}sec^{-1}. The cross section for second-harmonic generation is 6.4×10^{-15} cm^2 as compared with the cross section for linear dipole scattering which 6.3×10^{-11} cm^2. Thus, 4.7×10^{15} photons per second will be produced by frequency 2ω per sphere. Taking an illuminated volume of 10^{-5} cm^3 we would have 10^7 spheres contributing, for a net rate of 4.7×10^{22} photons per second. This number may be increased by increasing the illumination volume, the concentration of the spheres, or the intensity of the radiation.

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