Enhanced fields on large metal particles: dynamic depolarization

M. Meier and A. Wokaun

Physical Chemistry Laboratory, Swiss Federal Institute of Technology, CH 8092 Zurich, Switzerland

Received June 30, 1983

Influences of particle size on surface-enhancement processes are discussed in terms of a simple physical model. When the size of a silver sphere is increased, the magnitude of the enhancement exhibits a slight increase followed by a strong decrease. Simultaneously the plasmon resonance is shifted and severely broadened. To interpret these effects, a self-consistent calculation of the particle polarization is performed. Initial increase in magnitude and shift of the resonance are due to dynamic depolarization, whereas the decrease in magnitude and broadening are caused by radiation damping. The importance of higher-order multipoles is assessed by analyzing their contributions separately.

Recent observations of surface-enhanced optical processes[1] (e.g., Raman scattering, absorption, and nonlinear frequency mixing) have been followed by a strong theoretical interest in the origin of amplified electromagnetic fields at the surface. Although early theoretical models[2] have focused on small metal particles in the Rayleigh limit, many experiments have been performed on surfaces with roughness on a 1000-Å scale, i.e., comparable with a wavelength.

In a recent Letter, Barber *et al.*[3] presented spectacular and unexpected results for fields on the surface of large silver ellipsoids, which they obtained by numerical solution of the electromagnetic-field equations. The present Letter, which was motivated by the work of Barber *et al.*,[3] addresses the following topics: (1) The effects observed in Ref. 3 are illustrated for the simpler case of silver spheres and are discussed in terms of multipole contributions. (2) By using a self-consistent calculation of the polarization, the shift and the broadening of the particle plasmon resonance are found to be due to dynamic depolarization and radiation damping terms. (3) Conclusions are confirmed by comparing the results with a power-series expansion of the Mie-scattering coefficient. (4) Our findings are tied to earlier discussions in the literature, including the original work of Mie.[4]

Effects of particle size have been discussed in terms of Mie theory[4–6] and of radiation damping.[7] Barber *et al.*[3] have calculated the magnitude of the electric field, averaged over the surface of large 2:1 aspect-ratio silver spheroids, by numerical solution of Maxwell's equations.

They find a slight (0.5%) increase in the local intensity enhancement when the particle's semimajor axis a is increased from the electrostatic limit to $a = 4$ nm. For larger particles, the resonance shifts to longer wavelengths and is strongly broadened, with a concomitant drastic decrease in the enhancement. As the results represent an exact numerical solution, they do include the effects of higher-order multipoles. A separate quadrupole resonance becomes visible for large particles.

As analytical work becomes involved for spheroids when the particle dimensions exceed the electrostatic limit, we have decided to base our discussion on the analogous effects observed for spherical particles. We calculate the squared magnitude $|E_R|^2$ of the radial electric field, averaged ($\langle \ldots \rangle$) over the surface. Rather than series expansions[8,9] we use exact expressions[5] of the Mie-scattering coefficients ${}^eB_1$ and ${}^eB_2$, representing dipole- and quadrupole-moment contributions to the scattering. Higher-order multipoles are neglected.

Results for $\langle |E_R|^2 \rangle$ are shown in Fig. 1(a). Interpolated data[10] for the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ of silver have been used. Starting from the electrostatic solution at $q = 0$, the maximum enhancement is seen first to increase with particle radius a. At $a = 12.5$ nm, the intensity enhancement is 7.8% larger than the electrostatic limit; examination of Fig. 1(a) reveals that this maximum occurs at $\lambda = 357$ nm, which is slightly longer than the electrostatic value, $\lambda = 355$ nm. For larger particles the enhancement strongly decreases; it shifts to longer wavelengths and is broadened. This behavior is in qualitative agreement with the results of Barber *et al.*[3] A second maximum at shorter wavelengths is seen for $a > 30$ nm.

The phenomena seen in Fig. 1(a) are traced back to multipoles by plotting their contributions separately. Because of the orthogonality of the spherical harmonics, dipole and quadrupole contributions to the averaged magnitude are additive, $\langle |E_R|^2 \rangle = \langle |E_{R,\mathrm{Dip}}|^2 \rangle + \langle |E_{R,Q}|^2 \rangle$. The dipolar intensity is plotted in Fig. 1(b): It exhibits the same characteristic features as in Fig. 1(a). The quadrupolar resonance, shown in Fig. 1(c) on an expanded scale, occurs at shorter wavelengths [$\epsilon_1(\omega) \simeq -3/2$]. In the Rayleigh limit $q = ka = 0$, the quadrupole is not excited. With increasing particle size, excitation becomes more efficient; at the same time the resonance is shifted to longer wavelengths and is increasingly damped by stronger radiation, similar to the behavior of the dipole. The maximum of $\langle |E_{R,Q}|^2 \rangle$ occurs at $a = 65$ nm and $\lambda = 360$ nm. By comparing the three parts of Fig. 1 one can see that the surface field is

0146-9592/83/110581-03$1.00/0 © 1983, Optical Society of America

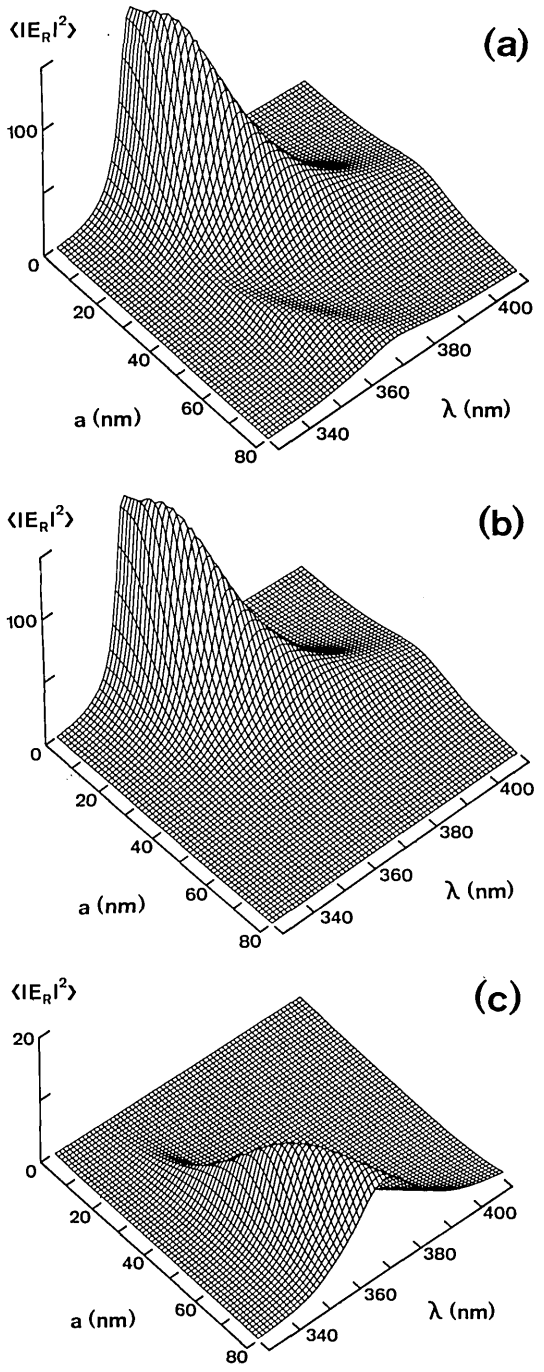

Fig. 1. Electric-field enhancement on the surface of silver spheres. The radial surface field E_R is normalized by the incident field E_0. The squared magnitude of E_R/E_0, averaged over the surface, is shown as a function of particle radius a and wavelength λ. (a) Total squared field $\langle|E_R|^2\rangle = \langle|E_{R,\mathrm{Dip}}|^2\rangle + \langle|E_{R,Q}|^2\rangle$. The absolute maximum occurs at $a = 12.5$ nm and $\lambda_{\max} = 357$ nm (electrostatic limit $a = 0$: $\lambda_{\max} = 355$ nm). (b) Dipolar contribution $\langle|E_{R,\mathrm{Dip}}|^2\rangle$. (c) Quadrupolar contribution $\langle|E_{R,Q}|^2\rangle$. The vertical scale has been expanded by a factor of 5 compared with that of (a) and (b).

dominated by the dipolar contribution. We note that resonance shift and broadening are exhibited by the dipolar Mie coefficient ${}^eB_1$ by itself and are *not* influenced by higher-order multipoles; as mentioned, the surface-averaged multipole contributions are additive.

For a qualitative understanding of the magnitude, shift, and broadening of the dipolar resonance, the polarization of a sphere is now determined using a self-consistent derivation and is related to a power-series expansion of the Mie-scattering coefficient ${}^eB_1$.

The polarization $\mathbf{P}$, assumed to be homogeneous over the volume of the sphere, is calculated from

$$4\pi\mathbf{P} = (\epsilon - 1)(\mathbf{E}_0 + \mathbf{E}_{\mathrm{dep}}), \tag{1}$$

where $\mathbf{E}_0$ is the externally applied field and $\mathbf{E}_{\mathrm{dep}}$ is a depolarization field generated by the polarized matter surrounding the center. The field $\mathbf{E}_{\mathrm{dep}}$ is determined by (1) assigning a dipole moment $\mathrm{d}\mathbf{p}(\mathbf{r}) = \mathbf{P}\mathrm{d}V(\mathbf{r})$ to each volume element $\mathrm{d}V(r, \theta, \varphi)$, (2) calculating the retarded dipolar field $\mathrm{d}\mathbf{E}_{\mathrm{dep}}$ generated by $\mathrm{d}\mathbf{p}(\mathbf{r})$ at the center, and (3) integrating over the volume of the sphere. As components perpendicular to $\mathbf{E}_0$ cancel on integration, only the parallel component $\mathrm{d}E_{\mathrm{dep},\parallel}$ must be considered. It is given by[11]

$$\mathrm{d}E_{\mathrm{dep},\parallel} = \left[\frac{1}{r^3}(3\cos^2\theta - 1) + \frac{k^2}{2r}(\cos^2\theta + 1) + i\frac{2}{3}k^3\right]\mathrm{d}p_{\parallel}(\mathbf{r}), \tag{2}$$

where the retarded dipolar field has been expanded up to power k^3.[11] Integration over the sphere (radius a) yields

$$\mathbf{E}_{\mathrm{dep}} = \left(-\frac{4\pi}{3} + k^2\frac{4\pi}{3}a^2 + i\frac{2}{3}k^3\frac{4\pi}{3}a^3\right)\mathbf{P}. \tag{3}$$

Inserting this result into Eq. (1) and solving for $\mathbf{P}$, one obtains

$$\mathbf{P} = \frac{3}{4\pi}\frac{(\epsilon - 1)}{(\epsilon + 2) - (\epsilon - 1)q^2 - (\epsilon - 1)i\frac{2}{3}q^3}\mathbf{E}_0 \qquad (q = ka). \tag{4}$$

A qualitative discussion of the effects seen in Figs. 1(a) and 1(b) is now possible with the help of Eq. (4), as the surface field $E_{R,\mathrm{Dip}}$ is determined by the polarization. The term $-(\epsilon - 1)i\frac{2}{3}q^3$ in the denominator of Eq. (4) is the radiation-damping correction to the electrostatic solution, introduced in Ref. 7. It accounts for damping of the dipole by radiative losses and results in broadening and strongly decreased magnitude of the resonance enhancement for *large* particle volumes.

The second term in the denominator of Eq. (4), $-(\epsilon - 1)q^2$, which may be identified with a dynamic depolarization,[12] has not been obtained in Ref. 7. This term causes the appearance of an enhancement maximum at a small but finite volume and is responsible for the shift of the resonance at larger volumes. For relatively small volume, the q^3 proportional term in Eq. (4) can be neglected; hence $\mathbf{P} = (3/4\pi)(\epsilon - 1)\mathbf{E}_0/[(\epsilon + 2) - (\epsilon - 1)q^2]$. Particle plasmon resonance occurs when the real part of the denominator vanishes such that $\mathbf{P}_{\mathrm{res}} = (3/4\pi)(\epsilon_{\mathrm{res}} - 1)\mathbf{E}_0/[\epsilon_2(1 - q^2)]$. It is clearly seen that increasing the particle dimensions (q) effectively reduces the intrinsic material damping ϵ_2, whereby the magnitude of the polarization increases. For larger volumes, this reduction in damping is overcome by the q^3 proportional radiation-damping term. Thus, at a small but finite value of q, a maximum in enhancement results, as is

seen both in the results of Barber *et al.*[3] and in Fig. 1.

Next the influence of the dynamic depolarization term on the position of the plasmon resonance is considered. For resonance we have the condition of vanishing denominator of Eq. (4), $\epsilon_1(\omega)(1 - q^2) + (2 + q^2) + \epsilon_2 2/3 q^3 = 0$. Obviously increasing q requires a more negative value of $\epsilon_1(\omega)$ to fulfill the condition. The decrease of $\epsilon_1(\omega)$ toward the red spectral region results in the strong red shift of the dipolar plasmon resonance discussed above. The shift of the resonance frequency by the q^2 term corresponds to the notion of dynamic depolarization.[12]

To conclude our argument, we relate Eq. (4), derived by self-consistent reasoning, to a power-series expansion of the Mie coefficient ${}^eB_1$. For small particles ($q \ll 1$), the coefficient is related to the polarization by ${}^eB_1 = iq^3(4\pi/3)(P/E_0)$. Starting from the exact solution for ${}^eB_1$, one obtains by straightforward, though tedious, expansion of the Bessel and Neumann functions up to order q^3

$$ {}^eB_1 = iq^3 \frac{(\epsilon - 1)(1 - q^2/10)}{(\epsilon + 2) - (7/10\epsilon - 1)q^2 - (\epsilon - 1)i2/3q^3} . \quad (5) $$

An analogous expression for ${}^eB_2$ has also been derived. Obviously there exists a similarity, but not an equivalence, between Eqs. (4) and (5). Differences are a factor $(1 - q^2/10)$ in the numerator of Eq. (5) and a different prefactor of the q^2 term in the denominator.

To understand the origin of these differences, we recall that a homogeneous polarization **P** throughout the sphere was assumed in the derivation of Eq. (4). Thus the retardation of the *exciting* field across the particle diameter has so far been neglected (while the retardation of the depolarizing fields was included[11]). By direct integration, it can be shown that the applied field $\mathbf{E}_0$ in Eq. (1) should be replaced by $\mathbf{E}_0(1 - q^2/10)$ to account for retardation. This immediately generates the desired factor $(1 - q^2/10)$ in the numerator of Eq. (4). Second, the self-consistent procedure should be modified to account for the varying phase of the polarization throughout the particle. We have not carried out this correction, as we feel the limits of our simple physical picture have been reached; however, it is easily seen that the correction would affect the q^2 term in the denominator of Eq. (4) and eventually produce agreement with the power-series expansion of the Mie-scattering coefficient, Eq. (5).

The resonance shifts discussed above had already been predicted by Mie in his original paper[4] on scattering by colloidal particles. A red shift of the absorption or scattering maximum with increasing particle volume was obtained from numerical evaluation of the scattering coefficient, while no physical interpretation was given. Shifts of the particle resonances were mentioned again by Doyle and Agarwal,[9] who calculated the extinction by metal spheres, including a size-dependent dielectric constant for small particles. Kerker *et al.*,[6] using Mie theory, have predicted a red shift of the surface-enhanced Raman-scattering excitation maximum with particle size. In Refs. 4 and 9 quantities proportional to the particle volume (e.g., the scattering coefficient ${}^eB_1$) were calculated. The q^3 prefactor [see Eq. (5)] results in a strong overall increase when q is increased from 0. Thus the *maximum* in the *local field* at the surface, occurring at small but finite q, had not been noticed until the work of Barber *et al.*[3]

Doyle and Agarwal[9] have pointed out that caution must be exercised to avoid division by small quantities[8] when one uses power-series expansions of Mie coefficients near resonance. Much confusion encountered in comparing results in the literature[6,8,9] is caused by the fact that certain terms can be manipulated at will in a fraction of two power series.[13]

We have calculated the enhanced fields on metal spheres of varying radius a as a function of frequency. A maximum in local intensity enhancement is obtained for small but finite a ($a = 12.5$ nm for silver). For larger particles the resonance shifts to the red, decreases in magnitude, and is strongly broadened. These effects have been given a simple physical interpretation in terms of dynamic depolarization[12] and radiation-damping terms, obtained by a self-consistent solution for the polarization. The validity of the interpretation is confirmed by comparison with a power-series expansion of the Mie-scattering coefficient.

The authors thank R. R. Ernst and U. P. Wild for encouragement and continued interest in this work and for the use of computing facilities. Financial support by the Swiss National Science Foundation and the Branco Weiss Foundation is gratefully acknowledged.

References

1. R. K. Chang and T. E. Furtak, eds., *Surface Enhanced Raman Scattering* (Plenum, New York, 1982).
2. S. L. McCall, P. M. Platzman, and P. A. Wolff, Phys. Lett. A **77,** 381 (1980); J. I. Gersten and A. Nitzan, J. Chem. Phys. **73,** 3023 (1980).
3. P. W. Barber, R. K. Chang, and H. Massoudi, Phys. Rev. Lett. **50,** 997 (1983).
4. G. Mie, Ann. Phys. **25,** 377 (1908).
5. M. Born and E. Wolf, *Principles of Optics*, 6th ed. (Pergamon, Oxford, 1980).
6. M. Kerker, D.-S. Wang, and H. Chew, Appl. Opt. **19,** 4159 (1980).
7. A. Wokaun, J. P. Gordon, and P. F. Liao, Phys. Rev. Lett. **48,** 957 (1982).
8. R. Gans and H. Happel, Ann. Phys. **29,** 277 (1909).
9. W. T. Doyle and A. Agarwal, J. Opt. Soc. Am. **55,** 305 (1965).
10. P. B. Johnson and R. W. Christy, Phys. Rev. B **6,** 4370 (1972).
11. Radial and tangential fields produced by a retarded dipole $[p] = pe^{ikr}$ are given by[5] $E_R = 2\cos\theta([p]/r^3 + [\dot{p}]/cr^2)$ and $E_\theta = \sin\theta([p]/r^3 + [\dot{p}]/cr^2 + [\ddot{p}]/c^2r)$. By expanding e^{ikr}, retaining terms up to order k^3, and using $E_\parallel = E_R \cos\theta - E_\theta \sin\theta$, one obtains Eq. (2).
12. The term $\propto q^2$ in the denominator of Eq. (4) is called "dynamic depolarization" because (1) it is obtained only in a dynamic calculation ($q > 0$) and (2) the coefficient of $(\epsilon - 1)$ is real, corresponding to a change in the effective particle depolarization factor A [see, e.g., C. J. F. Böttcher, *Theory of Electric Polarization*, 2nd ed. (Elsevier, Amsterdam, 1973)], Vol. 1.
13. Consider a fraction of the form of Eq. (5), $f = (1 + a_2q^2 + a_3q^3)/(1 + b_2q^2 + b_3q^3)$. Expanding by $(1 + c_2q^2)$, one obtains $f = [1 + (a_2 + c_2)q^2 + a_3q^3]/[1 + (b_2 + c_2)q^2 + b_3q^3]$, correct to order q^3.