Radiation Damping in Surface-Enhanced Raman Scattering

A. Wokaun, J. P. Gordon, and P. F. Liao
Bell Laboratories, Holmdel, New Jersey 07733
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Theoretical calculations are presented which show that the enhancement predicted by the particle plasmon model of surface-enhanced Raman scattering is limited by radiation damping. The damping becomes more severe as particle size increases, while the enhancement produced by small particles is limited by surface scattering. Good agreement between theory and experimental measurements of the wavelength dependence of surface-enhanced Raman scattering on lithographically produced microstructures is found when radiation damping is taken into account.

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Among several theoretical models[1] aimed at explaining the phenomenon of surface-enhanced Raman scattering (SERS), the electromagnetic particle plasmon model[2-7] has been successful in accounting for a number of observations. Experimental investigations have verified several predictions of the model, e.g., the distance dependence[8] and its resonance nature,[7] as well as its connection with optical properties.[9] Observations of other surface-enhanced electromagnetic processes, as, e.g., second-harmonic generation[10] and one- or two-photon dye luminescence,[11] further establish the presence of an amplified local field. However, the simple particle plasmon model[3-5] is not valid either if the particles are very small, such that the electron mean free path is determined by surface scattering, or if the particle dimensions become comparable to an optical wavelength. In this paper we address these limitations to the model by discussing both the effects of radiation damping, which becomes important for large particles, and surface scattering. These phenomena provide limits to the enhancement process. A comparison of recent experimental measurements of SERS on lithographically produced silver particle surfaces[7] with the particle plasmon model including radiation damping yields good agreement.

Usually the effects of radiation resistance can be safely neglected in molecular scattering problems. However, the prediction of enhancements by factors of 10^{11} from molecules on high-aspect-ratio silver spheroids[4] raises the question whether radiation reaction fields must be taken into account at this level of local field amplification. We find, when the particle plasmon model is extended to include the effect of radiative loss, that radiation resistance strongly limits the enhancement for large particles. The damping due to radiation can decrease the enhancement by many orders of magnitude and causes a significant broadening of the particle plasmon resonance which is responsible for the enhancement. For small particles, on the other hand, enhancement is limited by plasma damping due to surface scattering.

Consider an isolated metal particle of volume V placed in an external electromagnetic field E_0 of frequency ω_0, with Raman scattering molecules adsorbed to the surface. The particle is characterized by the bulk dielectric function $\epsilon(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega)$, and modeled as a spheroid with the electric field applied along one of the principal axes $j=x$, y, or z. The total dipole induced in the particle is given by

$$P_j(\omega_0)=\chi_{jj}(\omega_0)V[E_{0,j}+i(2k_0^3/3)P_j(\omega_0)], \quad j=x,y,z, \tag{1}$$

where $\chi_{jj}(\omega)$ is a diagonal element of the spheroid's susceptibility tensor. While $\overleftrightarrow{\chi}(\omega)$ is calculated[2-7] in the electrostatic approximation, assuming $V/\lambda^3 \ll 1$, the second term in Eq. (1) accounts for the energy loss of the particle due to radiation, by introducing a radiation reaction field[12] $\vec{E}_r=i2k^3\vec{P}(\omega)/3$ ($k=\omega/c$). This definition is chosen such that the work done by $\vec{E}_r$ on the dipole $\vec{P}$ equals the radiated energy.[12] Equation (1) can be rewritten in terms of an effective susceptibility $\overleftrightarrow{\chi}_{\text{eff}}(\omega)$,

$$P_j(\omega_0)=\chi_{\text{eff},jj}(\omega_0)VE_{0,j}=\frac{\chi_{jj}(\omega_0)}{1-i2k_0^3\chi_{jj}(\omega_0)V/3}VE_{0,j}. \tag{2}$$

The correction term in the denominator of Eq. (2) is strongly frequency dependent because of the factors k^3 and $\chi_{jj}(\omega)$; the latter becomes large exactly at the particle plasmon resonances which are the origin of the electromagnetic enhancement.[3] To calculate the enhancement, we require the field $\vec{E}_{\rm out}$ outside the particle surface, which polarizes the adsorbed molecules. At the tip of the spheroid, this field is given by[13]

$$E_{{\rm out},j}(\omega_0)=\epsilon(\omega_0)E_{in,j}(\omega_0)=\frac{\epsilon(\omega_0)}{\epsilon(\omega_0)-1}\,\frac{4\pi}{V}\,P_j(\omega_0)=f(\omega_0)E_{0,j}\,,$$

where $\vec{E}_{\rm in}$ is the uniform field inside the particle, and $f(\omega)$ is the local field enhancement factor. Using the expression[13]

$$\chi_{jj}(\omega)=(4\pi)^{-1}[\epsilon(\omega)-1]/\{1-[1-\epsilon(\omega)]A_j\}$$

for the susceptibility of ellipsoidal particles, we arrive at the result

$$|f(\omega)|^2=\frac{|\epsilon(\omega)|^2}{\{1-[1-\epsilon_1(\omega)]A_j+\epsilon_2(4\pi^2V/3\lambda^3)\}^2+\{\epsilon_2A_j+[1-\epsilon_1(\omega)](4\pi^2V/3\lambda^3)\}^2}\,, \tag{3}$$

where the depolarization factor[13] $0<A_j<1$ characterizes the particle eccentricity. The scattered intensity at the Raman frequency ω_R is enhanced[3-7] by $|f(\omega_0)f(\omega_R)|^2$.

For the important example of silver, ϵ_2 is small throughout the visible spectrum, and the peak enhancement is found by maximizing Eq. (3) with respect to $\epsilon_1(\omega)$. The analytic expression for $\epsilon_1(\omega_{\rm res})$ is lengthy and will not be reproduced here. For ϵ_2, $V/\lambda^3\ll 1$, $|f(\omega)|^2$ reaches its maximum for $1-[1-\epsilon_1(\omega_{\rm res})]A_j\approx 0$. Using this condition in Eq. (3) we see that radiation damping must be taken into account whenever $[1-\epsilon_1(\omega)]\times(4\pi^2V/3\lambda^3)\approx\epsilon_2A_j$.

In Fig. 1 we illustrate the dependence of $|f(\omega_{\rm res})|^2$ on the particle volume, V/λ^3, for silver particles of three different aspect ratios.[14] Note that the Raman enhancement will be approximately proportional to $|f(\omega_{\rm res})|^4$. For $V/\lambda^3=10^{-4}$, $|f(\omega_{\rm res})|^2$ is larger by 10^2 for a 4:1 spheroid than for a sphere. As stated before,[4,15] this difference is due to the concentration of the electric field around the tips of the spheroid which results in a larger enhancement for molecules adsorbed at this area of the surface. The dashed curves in Fig. 1 include the effects of radiation damping and clearly demonstrate the reduction in maximum enhancement with increasing particle volume. The difference between various shapes is virtually eliminated for larger volumes. However, the dipolar approximation implicit in the derivation of Eq. (3) may no longer be valid. As pointed out by Kerker, Wang, and Chew,[6] the difference between the dipole model and an exact solution for a sphere, including all higher-order multipole modes, amounts to about 5% in $|f|^2$ at $V/\lambda^3=1.35\times10^{-4}$.

The reduction in peak enhancement $|f(\omega_{\rm res})|^2$ is accompanied by a substantial broadening and distortion of $|f(\omega)|^2$. The broadening can be expressed as the deviation from resonance $\Delta\epsilon_1=\epsilon_1(\omega)-\epsilon_1(\omega_{\rm res})$ for which $|f(\omega)|^2$ drops to half its peak value and is approximately given by the expression[16]

$$\Delta\epsilon_1\approx\epsilon_2+\frac{Vk^3/6\pi}{A^2+(Vk^3/6\pi)^2}\,.$$

For $V/\lambda^3=2\times10^{-3}$ we find[14] $\epsilon_1(\omega_{\rm res})=-2.15$, -4.94, -12.96 and $\Delta\epsilon_1=0.59$, 1.20, 4.82 for $a/b=1$, 2, 4, respectively. The width and shape of the Raman

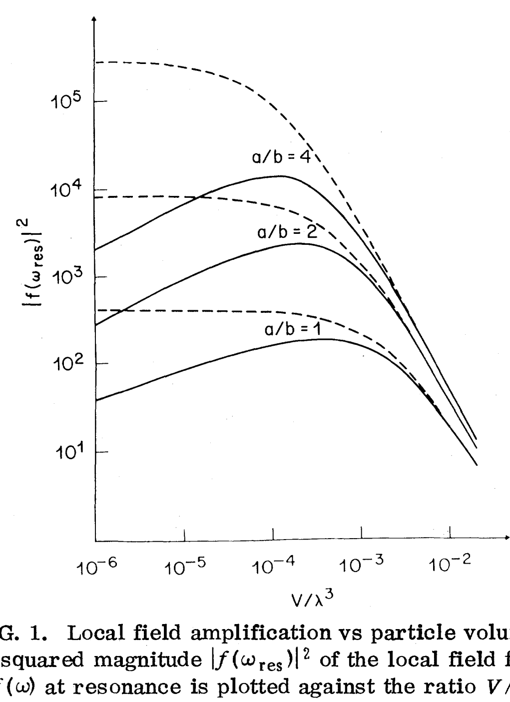

FIG. 1. Local field amplification vs particle volume. The squared magnitude $|f(\omega_{\rm res})|^2$ of the local field factor $f(\omega)$ at resonance is plotted against the ratio V/λ^3, for silver particles of various aspect ratios a/b (Ref. 14). The dashed curves only include the influence of radiation damping; the solid curves are obtained when the "surface scattering size effect" [Eq. (4)] on the dielectric constant is included.

enhancement $|f(\omega_0)f(\omega_R)|^2$ are of course dependent on the Stokes shift, $\omega_0 - \omega_R$.

Recently the wavelength dependence of SERS was measured on a lithographically prepared silver particle surface.[7] Such samples provide an opportunity to check the theory as they are composed of uniformly sized and shaped isolated silver particles supported on SiO_2 posts. The $\approx 2145\text{-cm}^{-1}$ stretch vibration of CN^- adsorbed on the particles was measured. A clear excitation resonance was observed which gave a peak enhancement of $\approx 10^7$. In Fig. 2 we reproduce the experimental data[7,17] for particles which in a first approximation appeared to have $\approx 3{:}1$ aspect ellipsoidal shape. The solid line in Fig. 2 is a fitted theoretical line shape $|f(\omega_0)f(\omega_R)|^2$, with use of Eq. (3). The depolarization factor A (and therefore the aspect ratio) and the volume V of the ellipsoid are treated as free parameters in our theory, which includes the full wavelength dependence of ϵ. The ellipsoid dimensions which gave the fit shown in Fig. 2 were $2a = 200$ nm, $2b = 55$ nm, only slightly different from the measured dimensions[7] of approximately 300 nm by 100 nm. This difference may be due to deviations of the true particle shape from ellipsoidal, the presence of the supporting substrate, and the interactions between particles[9]; however, the fitted dimensions are certainly of the correct order of magnitude. The peak enhancement predicted by the theory is $\approx 10^6$ and hence reasonably consistent with the experimental data.

In addition to producing a width of the resonance curve that is in agreement with experiment, the inclusion of radiation damping also results in the proper line shape. Both the experimental data and the solid theoretical curve show the same asymmetry; both are skewed towards lower energies. In contrast if we ignore the fact that the particle dimensions do not strictly satisfy the small-particle approximation implicit in the simplest electromagnetic models, and hence neglect radiation damping, we obtain a curve which contains two narrow peaks separated by the Raman shift of 2144 cm^{-1} and corresponding to enhancement of the incoming and scattered waves. Although a single peak could be obtained by imposing a broad distribution of particle aspect ratios (average aspect of 3.5 and standard deviation[18] of 0.78), we see that by simply including radiation damping, as Fig. 1 shows is mandatory for the sized particles used in the experiment, one obtains the correct width, amplitude, and shape of the resonance. No additional major assumptions appear necessary to explain the data.

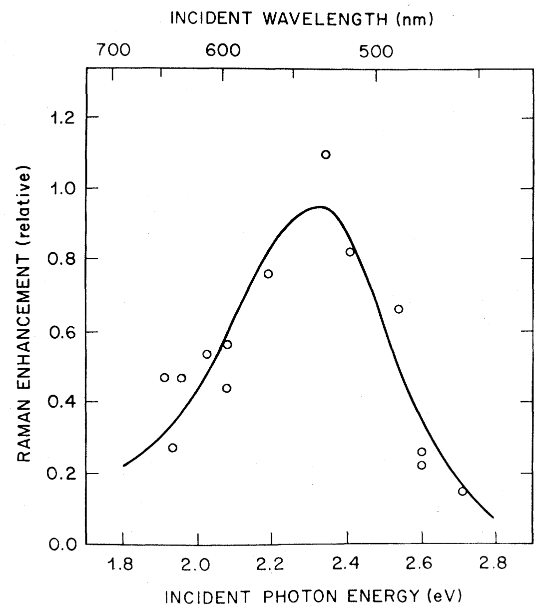

FIG. 2. Wavelength dependence of SERS (2144 cm^{-1}) from CN^- adsorbed on Ag spheroids of $\approx 3{:}1$ aspect ratio, supported by a microlithographic array of SiO_2 posts. The solid curve represents a least-squares fit including radiation damping. Note that the asymmetry of the wavelength dependence is reproduced by theory when radiation damping is included.

The radiation damping can be reduced by using very small particles. However, it is known that size effects associated with surface scattering then begin to affect the magnitude of ϵ_2. Roughly the effect can be approximated by writing ϵ_2 as[19]

$$\epsilon_2(\omega) = \frac{\omega_p^{\,2}}{(\omega^2 + \omega_c^{\,2})}\left(\frac{\nu_F}{l_\infty} + \frac{\nu_F}{b}\right) + \epsilon_2^{\text{bound}}. \tag{4}$$

The first term in Eq. (4) is the Drude expression for the free-electron contribution to the loss, with the plasma frequency ω_p. The collision frequency[19] $\omega_c = \nu_F(l_\infty^{-1} + b^{-1})$ (ν_F is the Fermi velocity) accounts for collisions within the material (l_∞ mean free path in the bulk) and with the particle boundaries (short axis b). The second term in Eq. (4) represents the contribution of bound electrons.

In Fig. 1 the solid curves show the enhancement factor $|f(\omega_{res})|^2$ including both surface scattering and radiation damping. The highest enhancement is found for particle volumes in the range $V/\lambda^3 \approx 10^{-4}$ although the precise value for the optimum volume depends on particle shape. This volume range corresponds to particles of approximately 250-Å radius. Such particle sizes have indeed been found to give the largest enhancement[9,20] for SERS on silver island films.

We have presented a theory which demonstrates the important role of radiation damping in limiting the maximum achievable enhancement for SERS by the particle plasmon effect. We have also discussed the effect of surface scattering which limits the enhancement from small particles. We note that a complete solution to the particle plasmon enhancement effect can in principle be obtained from a complete Mie scattering theory of SERS. Such a solution is quite involved for ellipsoids and has only been determined for spheres.[6] Our inclusion of radiation damping is the lowest-order correction to the electrostatic theory; it is a simple and transparent way to account for the physics of changes in the plasmon resonance. Comparison of the theoretical amplitude and wavelength dependence with measurements made on lithographically prepared silver particle surfaces gives good agreement. The comparison was only made possible by the uniformity of such surfaces, which allows one to observe a single plasmon resonance.

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[17]The solid line drawn in Fig. 2 of Ref. 7 is merely a guide to the eye.

[18]This standard deviation is somewhat larger than that quoted in Ref. 7, where only the width of the experimental resonance data was approximately fitted and deviations in the red wing of the curve were ignored.

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