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Surface-Enhanced Photoabsorption and Photoyield in Small Spheres

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Calculations of the photoabsorption and photoyield of small metal spheres are reported for photon energies below the plasmon energy. It is found that the excitation of electron-hole pairs due to the presence of the surface results in (1) enhancements in the photoabsorption rates and photoyields that are typically $10-10^2$ and (2) similar enhancements in the threshold photoyields of small spheres relative to plane surfaces in agreement with recent experimental results.

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In recent years the spatial variation of the photon field at the metal surface has been identified as an important element in photoemission experiments.[1-5] This variation is associated with excitation of plasmons and electron-hole (e-h) pairs by p polarized incident light. Theoretical work has progressed from the inclusion of plasmons via an additional boundary condition[6] to the unified treatment of plasmons and e-h pairs with an infinite surface barrier[7-9] to use of a realistic surface potential.[10]

To date almost all calculations have been carried out for plane surfaces. However, small particles (e.g., 15–50-Å radii) are of interest in a number of contexts, particularly in atmospheric physics. Recent experiments by Schmidt-Ott, Schurtenberger, and Siegmann[11] (SSS) have served to focus attention on the very unusual optical properties of such particles. They find that the photoelectric yields at threshold of small particles of Ag, Au, MoO_3, and WO_3 are much larger ($\sim 10-10^2$) than the yields from plane surfaces of the same materials. There has also been evidence that the surface-enhanced Raman effect, currently of great interest, is associated with surface roughness which in a very crude sense can be simulated by spherical particles at the metal surface. Thus the study of small particles may ultimately be relevant to that phenomenon.

In a classic work Mie[12] treated the transverse modes of the sphere. More recently a semiphenomenological paper by Ruppin[13] included the excitation of plasmons in the spirit of Melnyk and Harrison[6] for plane surfaces. The purpose of the present work is to include for the first time e-h pair excitations on an equal footing with plasmons and transverse modes. We find that the e-h pair excitations can dominate the absorption and photoelectric yield of a small sphere. An examination of the experimentally determined dielectric functions, $\epsilon_1(\omega)$, and the threshold energies of the materials observed by SSS shows that the enhanced photoyields cannot be due to the well-known peak in the optical absorption of a sphere predicted by Mie theory to be at the energy determined by $\epsilon_1(\omega)+2=0$. This is simply because the thresholds for these materials do not lie sufficiently near the "Mie peaks."

The probability per unit time for photoexcitation, P_E, is given by the Fermi golden rule. With the aid of Maxwell's equations it can be reexpressed as $P_E = \int d^3r\, P_E(\vec{r})$, where

$$P_E(\vec{r}) = \mathrm{Re}\nabla\cdot[E(\vec{r})\times H(\vec{r})^*], \qquad (1)$$

where $\vec{E}$ and $\vec{H}$ are the total electric and magnetic fields in the solid. This establishes the connection between the quantum mechanical and classical electrodynamic formulations. The optical adsorption is $\alpha = P_E/I_0$, where I_0 is the incident flux. The photoelectric yield at threshold is given by the three-step model:

$$Y = \int d^3r\, P_E(\vec{r}) P_T(\vec{r}) P_{ES}(\vec{r})/I_0, \tag{2}$$

where $P_E(\vec{r})$ is the probability that an electron is photoexcited at point $\vec{r}$, $P_T(\vec{r})$ is the probability that the electron reaches the surface without inelastic scattering having started from the point $\vec{r}$, and $P_{ES}(\vec{r})$ is the probability that it escapes from the solid. If $P_E(\vec{r})$ is assumed constant it can be shown that the ratio of sphere to plane yield is at most 4 and the enhanced yields seen by SSS cannot be due to escape and transport factors, in agreement with comments by those authors.

We next evaluate $P_E(\vec{r})$, Eq. (1), for the case of a sphere. This requires the use of Maxwell's equations and the associated boundary conditions $\vec{E}_\parallel$ and $\vec{H}_\parallel$ continuous. In addition Gauss's law, $\nabla \cdot \vec{E} = 4\pi\rho_I$, where ρ_I is the induced charge, yields the boundary condition $\vec{E}_\perp$ continuous. The conditions $\vec{H}_\parallel$ and $\vec{E}_\perp$ continuous are derived with the assumption that J_I, the induced current, and ρ_I are finite at the boundary as must be the case. Since $\nabla \cdot J_I = 4\pi\rho_I$ the boundary conditions on $\vec{H}_\parallel$ and $\vec{E}_\perp$ have equal validity even though $\vec{E}_\perp$ continuous has been traditionally ignored as was the excitation of plasmons by p-polarized light, an effect which follows directly from Gauss's law. This point has been discussed in detail[6] and Kliewer[8] finds that $\vec{E}_\perp$ is continuous in his microscopic treatment of a plane surface.

The electric and magnetic fields $\vec{E}$ and $\vec{H}$ are obtained from the vector potential $\vec{A}$ which satisfies[9]

$$\nabla\times\nabla\times\vec{A} - (\omega/c)^2 \overleftrightarrow{\epsilon}\cdot\vec{A} = 0, \tag{3}$$

where $\overleftrightarrow{\epsilon}$ is the dielectric tensor of the solid including surface effects. It has been shown[7,9] that for the case of a plane surface with specular reflection, the solution for $\vec{A}$ in the solid can be obtained from a solution of the model problem,

$$\nabla\times\nabla\times\vec{A} - (\omega/c)^2 \overleftrightarrow{\epsilon}_0\cdot\vec{A} = \vec{J}, \tag{4}$$

where $\overleftrightarrow{\epsilon}_0$ is the *bulk* dielectric function of the solid and $\vec{J}$ is a current determined by $\vec{A}$ and located at the surface of the solid.[7]

In order to find $\vec{A}$ for the sphere we make the *Ansatz* that $\vec{A}$ satisfies Eq. (4) where $\vec{J}$ is a general current at the sphere surface. Because $\vec{A}$ must satisfy the three boundary conditions discussed above, the specification of the amplitude of the incident light is sufficient to determine both the fictitious current $\vec{J}$ and $\vec{A}$. This procedure is capable of reproducing all relevant results obtained by previous workers: For the case of the plane surface it yields the results of Kliewer and Fuchs[7] and Kliewer,[8] for a sphere it gives the results of Ruppin[13] if we use a dielectric function that describes plasmon and transverse excitations and Mie[12] theory if it describes transverse excitations only.

The solution of Eq. (4) proceeds by expanding $\vec{A}$ in a set of basis states, $\vec{L}_i$, $\vec{M}_i$, $\vec{N}_i$, where i specifies a set of quantum numbers and the basis vectors all satisfy[14]

$$\nabla^2\vec{C} + k^2\vec{C} = 0, \tag{5}$$

where $\vec{C} = \vec{C}(\vec{r}, k)$ stands for $\vec{L}_i$, $\vec{M}_i$, or $\vec{N}_i$. $\vec{L}_i$ represents a longitudinal mode while $\vec{M}_i$ and $\vec{N}_i$ are transverse. Explicit expressions for $\vec{L}_i$, $\vec{M}_i$, and $\vec{N}_i$ in spherical coordinates are given by Stratton.[14] The dielectric tensor $\overleftrightarrow{\epsilon}_0$ in Eq. (4) is a nonlocal operator which we take to be the Lindhard dielectric tensor.[15] It can be shown that[16]

$$\overleftrightarrow{\epsilon}_0\cdot\vec{M}(\vec{r},\vec{k}) = \epsilon_t(k)\vec{M}(\vec{r},\vec{k}), \tag{6a}$$

$$\overleftrightarrow{\epsilon}_0\cdot\vec{N}(\vec{r},\vec{k}) = \epsilon_t(k)\vec{N}(\vec{r},\vec{k}), \tag{6b}$$

$$\overleftrightarrow{\epsilon}_0\cdot\vec{L}(\vec{r},\vec{k}) = \epsilon_l(k)\vec{L}(\vec{r},\vec{k}), \tag{6c}$$

where $\epsilon_t = \epsilon_t(k,\omega)$ and $\epsilon_l = \epsilon_l(k,\omega)$ are the transverse and longitudinal Lindhard dielectric functions. A general form for the surface current, $\vec{J}$, in terms of vector spherical harmonics is

$$J(\vec{r}) = \delta(r - R)\sum_i\{\alpha_i\hat{r}Y_i + \beta_i\vec{r}\times\nabla Y_i + \gamma_i\hat{r}\times(\vec{r}\times\nabla)Y_i\}, \tag{7}$$

where Y_i is a spherical harmonic. Writing

$$\vec{A}(\vec{r}) = \int dk \sum_i [a_i\vec{M}_i + b_i\vec{N}_i + c_i\vec{L}_i] \tag{8}$$

and using Eqs. (5), (6), (7), and (8) in Eq. (4) yields equations for $\{a_i, b_i, c_i\}$ of Eq. (8) in terms of $\{\alpha_i, \beta_i, \gamma_i\}$ of Eq. (7). In particular the $\{a_i, b_i, c_i\}$ for a given angular momentum, l, only couple to $\{\alpha_i, \beta_i, \gamma_i\}$ of the same angular momentum. The incident plane wave and the reflected wave are also written in terms of $\vec{M}_i$, $\vec{N}_i$ (Ref. 14) and the three boundary conditions are then used to determine the $\{a_i, b_i, c_i\}$ in terms of the amplitude of the incoming plane wave and thus a solution for $\vec{A}$ is obtained.

The absorption is given by $\alpha = P_E/I_0$. After taking the limit $k_0R \ll 1$, where R is the radius of the

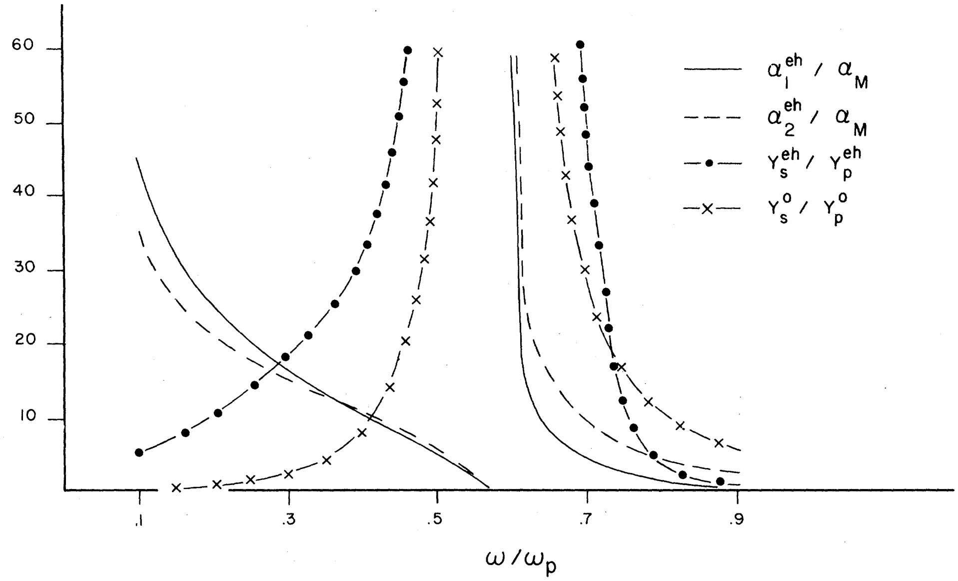

FIG. 1. α_1^{eh}/α_M is the ratio of the absorption of a sphere including electron-hole pair excitations, Eq. (9), to the classical absorption of a sphere calculated from Mie theory which only includes transverse modes. α_2^{eh}/α_M is the same ratio but with use of Eq. (10) instead of Eq. (9). Y_s^{eh}/Y_p^{eh} is the ratio of the yield at threshold of a sphere to that of a plane including electron-hole pair excitations in the calculations. Y_s^{0}/Y_p^{0} is the same ratio including only transverse modes. The calculations are for the case $r_s = 4$, $\lambda = 21.2$ Å, and $\omega_p\tau = 10^3$.

sphere, we have

$$\alpha = -2\sum_{l=1}^{\infty}(k_0R)^{2l-1}[(2l-1)!!]^{-2}\,\mathrm{Im}[1-(2/\pi)\Delta_l^*]^{-1}, \tag{9a}$$

$$\Delta_l = (l+1)[Q_l^{(1)}Q_l^{(3)} - Q_l^{(2)}Q_l^{(2)}]/[(l+1)Q_l^{(2)} - Q_l^{(3)}], \tag{9b}$$

$$Q_l^{(i)} = R\int_0^\infty dq[\epsilon_l^{-1}(q)-1]f_l^{(i)}(qR),$$
$$f_l^{(1)}(\rho) = [j_l(\rho)]^2,\quad f_l^{(2)}(\rho) = j_l(\rho)\rho j_{l-1}(\rho),\quad f_l^{(3)}(\rho) = [\rho j_{l-1}(\rho)]^2, \tag{9c}$$

where k_0 is the wave vector of the incident light. For a small sphere $k_0R \ll 1$ (this implies typically $R \lesssim 10^2$–10^3) and the term $l=1$ dominates. Note that k_t, the transverse wave vector in the sphere, does not appear explicitly in Eq. (8) but does enter via the relationship $\epsilon_t(0) = (k_t/k_0)^2 = \epsilon_t(0)$.

After this work was completed we received a preprint from Dasgupta and Fuchs[17] in which they present formulas for the absorption of a sphere in the nonretarded limit which include the effects of e-h pair excitations. In obtaining numerical results they specifically include plasmons and neglect e-h pairs and find numbers very close to those of Ruppin.[13] Dasgupta and Fuchs give two different approximations for the adsorption, both of which yield very similar numerical results. Their first expression for α can be obtained within our *Ansatz*, Eq. (7), by the choice $\alpha_i = 0$, the use of only two boundary conditions, $\vec{E}_\parallel$ and $\vec{H}_\parallel$ continuous, and in the limit $k_0R \ll 1$. Their second approximation for α can also be obtained within our *Ansatz* by the replacement of $\alpha_i\delta(r-R)\hat{r}$ in Eq. (7) by $\alpha_i\theta(R-r)(R/r^2)\hat{r}$, where $\theta(x)$ is 0 for $x<0$ and 1 for $x>0$. Their expression is obtained in the limit $k_0R \ll 1$,

$$\alpha = 4k_0R\,\mathrm{Im}\frac{[\epsilon_t(0)-1](T-S)}{[\epsilon_t(0)+2]T + 2[\epsilon_t(0)-1]S}, \tag{10a}$$

where

$$T = \int_0^\infty d\rho[\epsilon_l^{-1}(\rho/R) - \epsilon_l^{-1}(0)]j_1(\rho)^2, \tag{10b}$$

$$S = \int_0^\infty d\rho[\epsilon_l^{-1}(\rho/R) - \epsilon_l^{-1}(0)]\rho j_1'(\rho)j_1(\rho). \tag{10c}$$

A plot of the absorption of a sphere as given by Eq. (9) and by Eq. (10) relative to the absorption as calculated by Mie theory, α_M, is shown in Fig. 1 for the case where $r_s = 4$ and a phenomenological lifetime[8,18] is $\omega_p\tau = 10^3$, where ω_p is the plasmon frequency. The results are relatively insensitive to the choice of r_s and R. The decrease in α/α_M with increasing ω is related to the peak in α_M (Ref. 13) at $\omega_p/\sqrt{3}$. The similarity of the two curves indicates that the numerical results are somewhat insensitive to the precise choice of $\vec{J}$.

The enhancement in the yields observed by SSS were in fact obtained by comparing the small-sphere yields to those of cylindrical wires of large radius. The yield for a cylinder has not been calculated and we approximate it by that of a plane surface with light incident at 45°. The yield at threshold is then given by Eq. (2) with use of the theory of Kliewer[8] for $P_E(\vec{r})$. The yield for a sphere can be obtained from Eq. (2) and use of our procedure to calculate $P_E(\vec{r})$. At threshold $P_T P_{ES} \propto (1/r)^2$ if the photoexcited electron is treated semiclassically. In a proper quantum mechanical approach the excited electron would be described by a wave packet. We simply assume that in a small sphere the photoexcited electron is uniformly distributed and so approximate $P_T P_{ES}$ by its average over the sphere. This procedure underestimates the yield since the fields E and H are largest at the sphere center. The resulting yield is then proportional to the absorption, $Y = (3\lambda/R)[1 - \exp(-2R/\lambda)]\alpha$. The ratio of the sphere yield with α from Eq. (9) to the yield for the plane is shown in Fig. 1 for an escape depth of $\lambda = 21.2$ Å (the results are relatively insensitive to λ and other parameters are the same as used in the graphs of α/α_M). The ratio of the sphere to plane yield leaving e-h production out of the calculation is also shown in Fig. 1. The yield curves in Fig. 1 refer to the threshold yield because the threshold expression was used for P_{ES} in Eq. (2). For any material, the threshold energy is determined by the work function, φ, and the yield curves are valid only near threshold, $\omega \simeq \varphi$. These yield curves imply that e-h pair excitation has a far greater effect on the yield of a sphere than on the yield of a plane surface. This is directly related to the existence of resonant behavior[13] in the sphere adsorption for $\omega > \omega_p$ due to the excitation of plasmons with wave vectors that satisfy a resonant condition. Below ω_p plasmons cannot be excited; however, e-h pair excitations involve a range of wave vectors, some of which will satisfy the conditions for a resonance.

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