

¹⁹H. K. Mao, R. M. Hazen, P. M. Bell, and J. Wittig, Annual Report of the Director of the Geophysical Laboratory, Carnegie Institution, 1979-1980 (unpublished), p. 380.

²⁰R. B. Roof, R. G. Haire, D. Schiferl, L. A. Schwalbe, E. A. Kmetko, and J. L. Smith, *Science* **207**, 1353 (1980).

²¹O. K. Andersen and O. Jepsen, *Physica (Utrecht)* **91B**, 317 (1977).

²²J. Wittig, in *Proceedings of the Conference on High-Pressure and Low-Temperature Physics, Cleveland, 1977*, edited by C. W. Chu and J. A. Woollam (Plenum, New York, 1978).

²³L. Liu, *J. Phys. Chem. Solids*, **36**, 31 (1975).

Surface-Enhanced Photoabsorption and Photoyield in Small Spheres

David R. Penn and R. W. Rendell

Electron Physics Group, National Bureau of Standards, Washington, D. C. 20234

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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 condition⁶ to the unified treatment of plasmons and $e-h$ pairs with an infinite surface barrier⁷⁻⁹ 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 Siegmann¹¹ (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, MoO₃, and WO₃ 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 Mie¹² treated the transverse

modes of the sphere. More recently a semiphenomenological paper by Ruppin¹³ included the excitation of plasmons in the spirit of Melnyk and Harrison⁶ 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 re-expressed as $P_E = \int d^3r P_E(\vec{r})$, where

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

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:

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

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 detail⁶ and Kliewer⁸ 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 satisfies⁹

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

where $\vec{\epsilon}$ 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 ob-

tained from a solution of the model problem,

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

where $\vec{\epsilon}_0$ 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 Fuchs⁷ and Kliewer,⁸ for a sphere it gives the results of Ruppin¹³ if we use a dielectric function that describes plasmon and transverse excitations and Mie¹² 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 satisfy¹⁴

$$\nabla^2 \vec{C} + k^2 \vec{C} = 0, \quad (5)$$

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 $\vec{\epsilon}_0$ in Eq. (4) is a nonlocal operator which we take to be the Lindhard dielectric tensor.¹⁵ It can be shown that¹⁶

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

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

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

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

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

where Y_i is a spherical harmonic. Writing

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

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 $k_0 R \ll 1$, where R is the radius of the

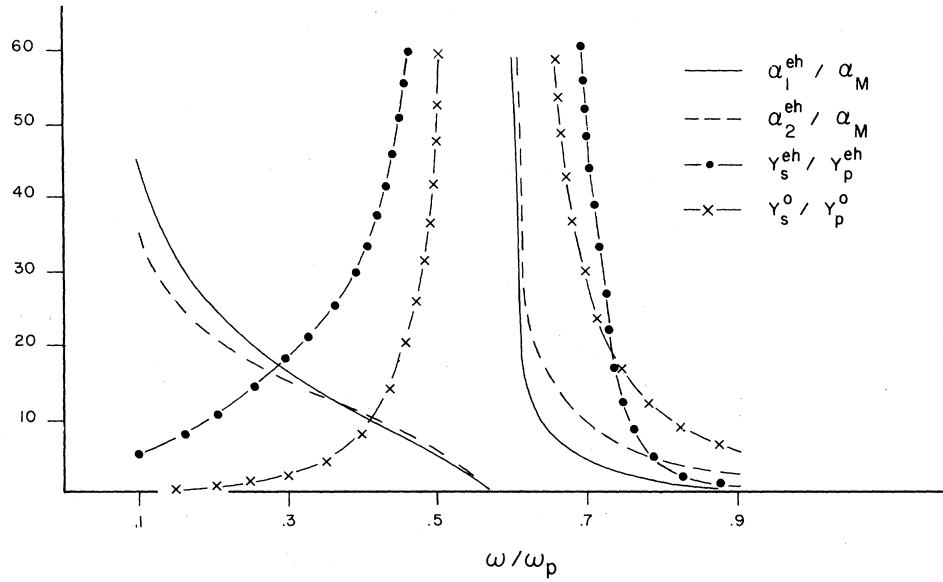


FIG. 1. α_1^{eh}/α_M is the ratio of the absorption of a sphere including electron-hole pair excitations, Eq. (9), to the classical absorption of a sphere calculated from Mie theory which only includes transverse modes. α_2^{eh}/α_M is the same ratio but with use of Eq. (10) instead of Eq. (9). Y_s^{eh}/Y_p^{eh} 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 $r_s = 4$, $\lambda = 21.2 \text{ \AA}$, and $\omega_p \tau = 10^3$.

sphere, we have

$$\alpha = -2 \sum_{l=1}^{\infty} (k_0 R)^{2l-1} [(2l-1)!!]^{-2} \text{Im}[1 - (2/\pi) \Delta_l^*]^{-1}, \quad (9a)$$

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

$$Q_l^{(i)} = R \int_0^{\infty} dq [\epsilon_i^{-1}(q) - 1] f_l^{(i)}(qR), \quad (9c)$$

$$f_l^{(1)}(\rho) = [j_l(\rho)]^2, \quad f_l^{(2)}(\rho) = j_l(\rho) \rho j_{l-1}(\rho), \quad f_l^{(3)}(\rho) = [\rho j_{l-1}(\rho)]^2,$$

where k_0 is the wave vector of the incident light. For a small sphere $k_0 R \ll 1$ (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 Fuchs¹⁷ 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 Rupp.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, $\vec{E}_{||}$ and $\vec{H}_{||}$ continuous, and in the limit $k_0 R \ll 1$. 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 $k_0 R \ll 1$,

$$\alpha = 4k_0 R \text{Im} \frac{[\epsilon_t(0) - 1](T - S)}{[\epsilon_t(0) + 2]T + 2[\epsilon_t(0) - 1]S}, \quad (10a)$$

where

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

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

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 numer-

ical 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 Kliewer⁸ 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 $\lambda = 21.2 \text{ \AA}$ (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, $\omega \simeq \phi$. 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 behavior¹³ 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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¹M. Anderegg, B. Feuerbacher, and B. Fitton, Phys. Rev. Lett. **27**, 1565 (1971).

²J. K. Sass, H. Laucht, and K. L. Kliewer, Phys. Rev. Lett. **35**, 1461 (1975).

³H. Peterson and S. B. M. Hagstrom, Phys. Rev. Lett. **41**, 1314 (1978).

⁴H. J. Levinson, E. W. Plummer, and P. J. Feibelman, Phys. Rev. Lett. **43**, 952 (1979).

⁵Guy Jezequel, Phys. Rev. Lett. **45**, 1963 (1980).

⁶A. R. Melnyk and M. J. Harrison, Phys. Rev. B **2**, 835 (1970).

⁷K. L. Kliewer and R. Fuchs, Phys. Rev. **172**, 607 (1968).

⁸K. L. Kliewer, Phys. Rev. B **14**, 1412 (1976).

⁹G. Mukhopadhyay and S. Lundquist, Physica Scripta **17**, 69 (1978).

¹⁰P. J. Feibelman, Phys. Rev. Lett. **34**, 1092 (1975), and Phys. Rev. B **12**, 1319 (1975).

¹¹A. Schmidt-Ott, P. Schurtenberger, and H. C. Siegmann, Phys. Rev. Lett. **45**, 1284 (1980).

¹²G. Mie, Ann. Phys. (Leipzig) **25**, 377 (1908).

¹³R. Rupp, Phys. Rev. **11**, 2871 (1975).

¹⁴J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941), p. 414.

¹⁵J. Lindhard, Danske Vid. Selsk. Mat.-Fys. Medd. **28**, No. 8 (1954).

¹⁶D. R. Penn and R. W. Rendell, to be published.

¹⁷B. Dasgupta and R. Fuchs, Phys. Rev. B **24**, 554 (1981).

¹⁸N. D. Mermin, Phys. Rev. B **1**, 2362 (1970).