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Plasmonics enhancement of a luminescent or Raman-active layer in a multilayered metallic nanoshell

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Abstract

Expressions for the enhancement of the far-field scattering cross section of a luminescent or Raman-active compound contained within a multilayered nanosphere are derived, where the active compound resides between an outer metallic shell and a metallic core. The quasi-static approximation is assumed for silver and gold particles using a Lorentz–Drude model of the dielectric function. An attempt has also been made to account for the effect of electron scattering from the boundaries of the shell on the enhancement calculation.

1. Introduction

Plasmonics refers to the research area of enhanced electromagnetic fields in the vicinity of metallic thin films and nanostructures, which has led to the development of extremely sensitive optical detection techniques. These include surface plasmon resonance (SPR), localized surface plasmon resonance (LSPR), surface-enhanced Raman scattering (SERS), and surface-enhanced fluorescence (SEF), also called metal-enhanced fluorescence. When a metallic nanostructured surface is irradiated by an incident electromagnetic field (e.g., laser light), conduction electrons are displaced into frequency oscillation equal to that of the incident light. These oscillating electrons, called “surface plasmons,” produce a secondary electric field, which adds to the incident field. When these oscillating electrons become spatially confined, as is the case for isolated metallic nanospheres or otherwise roughened metallic surfaces (nanostructures), there is often a characteristic frequency at which there is a resonant response of the collective oscillations to the incident field. This condition yields intense localized fields that can interact with molecules in contact with or near the metal surface. Our laboratory has developed the SERS substrate technology for chemical sensing and biosensing [1–3] and has investigated theoretical modeling of plasmonics-active nanostructures including spheroidal nanoshells [4], oblate spheroids [5], and linear chains of nanospheres [6]. Other researchers have investigated the properties of multilayered nanoshells, especially their tunability and the more complex resonance modes that can arise

[7–11]. For example, the mixing of different modes in multilayered shells can be understood qualitatively by the plasmon hybridization model of Radloff and Halas [11].

It is well known that optically induced plasmon resonances within a nanoparticle can enhance the far-field Raman scattering or fluorescence emission of molecules residing on the surface or inside the particle. Here we consider a spherical shell consisting of two layers and a core (Fig. 1). The outer layer and core are assumed to be metal, and the intermediate layer is filled with a luminescent or Raman-active compound. Our objective in this paper is to compute the enhancement of either the fluorescence emission or Raman-active response of active molecules residing in the intermediate layer due to the enhanced electric field between the metallic outer layer and core. To compute the enhancement, we derive the far-field scattering cross section of the luminescent or Raman-active layer in the absence of the metal core and outer shell and again with the core and outer shell present, and take their ratio. We compute the enhancement for two cases: (1) with both the metallic outer shell and core present, and (2) with only the metallic core present. Although the analysis is more complex for a multilayered shell, the fourth-power enhancement effect also arises here as a consequence of the fact that the emitting molecule effectively interacts twice with the particle. The first interaction gives rise to a plasmon-resonance amplification of the incident light impinging upon the molecule due to the presence of the particle. The second interaction occurs when the emitted light from the molecule is enhanced once more due to the plasmon resonance. The usual assumption, which is made here, is that the frequency difference between the incident and emitted light is sufficiently small to be amplified by the plasmon resonance both times. The scattered electric field is then squared in computing the far-field cross section, which gives rise to the fourth-power effect; that is, the scattering intensity is proportional to the fourth power of the incident electric field.

We also examine the so-called size effect in computing the enhancement. This is a correction to the dielectric model of the metal that attempts to account for electron scattering from the boundaries of the shell. The size effect becomes important when the electron mean-free path becomes comparable to the shell thickness or core radius. The effect can be modeled as an additional contribution to the imaginary part of the dielectric function, which can significantly dampen the plasmon resonance for particles of the order of tens of nanometers or smaller [12–15].

We first compute the response of a single molecule in the active layer by calculating its scattering cross section measured in the radiation zone of the shell. The responses of many molecules distributed uniformly throughout the volume of the active layer are then computed by integrating the scattering cross section over the volume of this layer. The integration of the cross sections is appropriate since the molecules radiate incoherently. In the following analysis, we assume the quasi-static approximation, which holds when the shell is much smaller than an optical wavelength. Our analysis is an extension of one given by Wang and Kerker [16] who considered the response of a single luminescent layer coating a metallic core. Here we show that the presence of an outer metallic layer over the active layer and core gives rise to stronger enhancement and introduces a second, red-shifted dipolar mode. In this analysis, we do not attempt to account for nonradiative decay channels, such as ohmic losses of the emitted light in the metallic layers [17,18]. Thus, fluorescence

quenching is not accounted for here. As a result, the computed enhancement may be considered an upper bound on fluorescent enhancement. For Raman-active compounds, however, this is not expected to introduce a noticeable error in our enhancement calculation.

In our analysis, we model the molecule as a point electric dipole with polarizability tensor α . Thus, the local electric field induces an effective dipole moment in the molecule given by $\mathbf{p}(\mathbf{r}_i, \tilde{\omega}) = \alpha \cdot \mathbf{E}(\mathbf{r}_i, \omega)$, where $\mathbf{r}_i$ is the coordinate of the molecule and $\tilde{\omega}$ is the frequency of molecular emission, which for an inelastic interaction will differ from the incident frequency, ω . Our approach is to first compute the local field $\mathbf{E}(\mathbf{r}_i, \omega)$ incident on the molecule in the presence of the metal shell and core, from which the field is derived arising from the induced molecular dipole moment $\mathbf{p}(\mathbf{r}_i, \tilde{\omega})$. This field in turn interacts again with the shell and core. The external field in the radiation zone is then computed by solving the relevant boundary value problem for the molecular field. Finally, the enhancement is computed by evaluating the cross section with and without the metal outer layer and core present.

2. Analysis

The dielectric constants of the host, the first, and the second layers, and the core are, respectively, $\epsilon_0, \epsilon_1, \epsilon_2$, and ϵ_3 . The radii of the layers and core are r_1, r_2 , and r_3 (Fig. 1). In the quasi-static approximation, we assume a uniformly incident electric field of magnitude E_0 , which is directed along the z axis. This requires linearly-polarized light whose propagation direction is perpendicular to the z axis. The electric field is given by the negative of the gradient of a potential. The potential functions associated with the field external to the particle, inside the two layers, and the core are denoted, respectively, by ψ_0, ψ_1, ψ_2 , and ψ_3 , and are of the form

$$\psi_0 = (-E_0 r + B_0/r^2) \cos \theta, \quad (1)$$

$$\psi_1 = (A_1 r + B_1/r^2) \cos \theta, \quad (2)$$

$$\psi_2 = (A_2 r + B_2/r^2) \cos \theta, \quad (3)$$

$$\psi_3 = A_3 r \cos \theta, \quad (4)$$

where A_j and B_j are constants to be determined by the boundary conditions. The electric field in each of these regions is computed from $\mathbf{E} = -\nabla \psi$, giving

$$\mathbf{E}_0 = \hat{r}(E_0 + 2B_0/r^3) \cos \theta + \hat{\theta}(-E_0 + B_0/r^3) \sin \theta, \quad (5)$$

$$\mathbf{E}_1 = \hat{r}(-A_1 + 2B_1/r^3) \cos \theta + \hat{\theta}(A_1 + B_1/r^3) \sin \theta, \quad (6)$$

$$\mathbf{E}_2 = \hat{r}(-A_2 + 2B_2/r^3)\cos\theta + \hat{\theta}(A_2 + B_2/r^3)\sin\theta, \quad (7)$$

$$\mathbf{E}_3 = -\hat{r}A_3\cos\theta + \hat{\theta}A_3\sin\theta, \quad (8)$$

where $\hat{r}$ and $\hat{\theta}$ are unit vectors. The boundary conditions at the three interfaces are

$$\psi_0|_{r=r_1} = \psi_1|_{r=r_1}, \quad (9)$$

$$\epsilon_0 \frac{\partial \psi_0}{\partial r} \bigg|_{r=r_1} = \epsilon_1 \frac{\partial \psi_1}{\partial r} \bigg|_{r=r_1}, \quad (10)$$

$$\psi_1|_{r=r_2} = \psi_2|_{r=r_2}, \quad (11)$$

$$\epsilon_1 \frac{\partial \psi_1}{\partial r} \bigg|_{r=r_2} = \epsilon_2 \frac{\partial \psi_2}{\partial r} \bigg|_{r=r_2}, \quad (12)$$

$$\psi_2|_{r=r_3} = \psi_3|_{r=r_3}, \quad (13)$$

$$\epsilon_2 \frac{\partial \psi_2}{\partial r} \bigg|_{r=r_3} = \epsilon_3 \frac{\partial \psi_3}{\partial r} \bigg|_{r=r_3}. \quad (14)$$

Substituting the potentials into the boundary conditions gives the following set of linear equations for the coefficients:

$$\begin{aligned} -E_0 r_1 + B_0 r_1^2 &= A_1 r_1 + B_1 / r_1^2, \\ \epsilon_0(-E_0 - 2B_0/r_1^3) &= \epsilon_1(A_1 - 2B_1/r_1^3), \\ A_1 r_2 + B_1 / r_2^2 &= A_2 r_2 + B_2 / r_2^2, \\ \epsilon_1(A_1 - 2B_1/r_2^3) &= \epsilon_2(A_2 - 2B_2/r_2^3), \\ A_2 r_3 + B_2 / r_3^2 &= A_3 r_3, \quad \epsilon_2(A_2 - 2B_2/r_3^3) = \epsilon_3 A_3. \end{aligned}$$

Or in matrix form:

$$\begin{bmatrix} 1/r_1^2 & -r_1 & -1/r_1^2 & 0 & 0 & 0 \\ -2\epsilon_0/r_1^3 & -\epsilon_1 & -2\epsilon_1/r_1^3 & 0 & 0 & 0 \\ 0 & r_2 & 1/r_2^2 & -r_2 & -1/r_2^2 & 0 \\ 0 & \epsilon_1 & -2\epsilon_1/r_2^3 & -\epsilon_2 & 2\epsilon_2/r_2^3 & 0 \\ 0 & 0 & 0 & r_3 & 1/r_3^2 & -r_3 \\ 0 & 0 & 0 & \epsilon_2 & -2\epsilon_2/r_3^3 & -\epsilon_3 \end{bmatrix} \begin{bmatrix} B_0 \\ A_1 \\ B_1 \\ A_2 \\ B_2 \\ A_3 \end{bmatrix} = \begin{bmatrix} r_1 E_0 \\ \epsilon_0 E_0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}. \quad (15)$$

This system can be inverted analytically for the coefficients A_j and B_j , but it is simpler to solve the system using a linear system solver after the parameters $r_1, r_2, r_3, \epsilon_0, \epsilon_1, \epsilon_2$, and ϵ_3 have been specified.

We now consider one molecule in the luminescent layer, which we model as a classical electric dipole with polarizability tensor α . If this molecule is located at the point $\mathbf{r}_i = (r_i, \theta_i, \phi_i)$, then the dipole moment induced in the molecule by the local electric field $\mathbf{E}_2(\mathbf{r}_i)$ is given by

$$\mathbf{p}_i = \alpha \cdot \mathbf{E}_2(\mathbf{r}_i). \quad (16)$$

For simplicity, we assume an isotropic molecular polarizability [19] given by $\alpha = \alpha(\hat{r}\hat{r} + \hat{\theta}\hat{\theta} + \hat{\phi}\hat{\phi})$. In this case, from Eq. (16),

$$\mathbf{p}_i = \alpha E_{2r}(\mathbf{r}_i)\hat{r} + \alpha E_{2\theta}(\mathbf{r}_i)\hat{\theta}, \quad (17)$$

where from Eq. (7),

$$E_{2r}(\mathbf{r}_i) = (-A_2 + 2B_2/r_i^3)\cos\theta_i, \quad (18)$$

$$E_{2\theta}(\mathbf{r}_i) = (A_2 + B_2/r_i^3)\sin\theta_i. \quad (19)$$

The potential produced by the polarized molecule is given by

$$\psi_i(\mathbf{r}) = -\mathbf{p}_i \cdot \nabla \left(\frac{1}{R} \right) = \mathbf{p}_i \cdot \nabla_i \left(\frac{1}{R} \right), \quad (20)$$

where $R = |\mathbf{r} - \mathbf{r}_i|$, and the subscript on ∇_i means that the gradient is computed with respect to $\mathbf{r}_i$. We now use the expansion [20]

$$\frac{1}{R} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{2l+1} \frac{r_i^l}{r^{l+1}} Y_{lm}^*(\theta_i, \phi_i) Y_{lm}(\theta, \phi), \text{ for } r_i < r, \quad (21)$$

$$\frac{1}{R} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{2l+1} \frac{r^l}{r_i^{l+1}} Y_{lm}^*(\theta_i, \phi_i) Y_{lm}(\theta, \phi), \text{ for } r < r_i, \quad (22)$$

where $Y_{lm}(\theta, \phi)$ are the spherical harmonics given by [21]

$$Y_{lm}(\theta, \phi) = \left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!} \right]^{1/2} P_l^m(\cos\theta) e^{im\phi}, \quad (23)$$

with $Y_{l,-m}(\theta, \phi) = (-1)^m Y_{lm}^*(\theta, \phi)$. From Eqs. (17) and (20), we have

$$\psi_i(\mathbf{r}) = \alpha \left[E_{2r}(\mathbf{r}_i) \frac{\partial}{\partial r_i} \left(\frac{1}{R} \right) + E_{20}(\mathbf{r}_i) \frac{1}{r_i} \frac{\partial}{\partial \theta_i} \left(\frac{1}{R} \right) \right]. \quad (24)$$

Now substituting Eqs. (21) and (22) into Eq. (24), we can write

$$\psi_i(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l u_{lm} \frac{1}{r^{l+1}} Y_{lm}(\theta, \phi), \text{ for } r_i < r, \quad (25)$$

$$\psi_i(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l v_{lm} r^l Y_{lm}(\theta, \phi), \text{ for } r < r_i, \quad (26)$$

where

$$u_{lm} = \frac{4\pi\alpha r_i^{l-1}}{(2l+1)} \left[E_{2r}(\mathbf{r}_i) l Y_{lm}^*(\theta_i, \phi_i) + E_{20}(\mathbf{r}_i) \frac{\partial}{\partial \theta_i} Y_{lm}^*(\theta_i, \phi_i) \right], \quad (27)$$

$$v_{lm} = - \frac{4\pi\alpha}{(2l+1)r_i^{l+2}} \left[E_{2r}(\mathbf{r}_i) (l+1) Y_{lm}^*(\theta_i, \phi_i) - E_{20}(\mathbf{r}_i) \frac{\partial}{\partial \theta_i} Y_{lm}^*(\theta_i, \phi_i) \right]. \quad (28)$$

The potential ψ_i originating from the molecule interacts with the layered shell and the resulting potentials in the layers may be written

$$\tilde{\psi}_0 = \sum_{l=0}^{\infty} \sum_{m=-l}^l \tilde{B}_{lm}^{(0)} \frac{1}{r^{l+1}} Y_{lm}(\theta, \phi), \quad (29)$$

$$\tilde{\psi}_1 = \sum_{l=0}^{\infty} \sum_{m=-l}^l \left[\tilde{A}_{lm}^{(1)} r^l + \tilde{B}_{lm}^{(1)} \frac{1}{r^{l+1}} \right] Y_{lm}(\theta, \phi), \quad (30)$$

$$\tilde{\psi}_2 = \sum_{l=0}^{\infty} \sum_{m=-l}^l \left[\tilde{A}_{lm}^{(2)} r^l + \tilde{B}_{lm}^{(2)} \frac{1}{r^{l+1}} \right] Y_{lm}(\theta, \phi) + \psi_i, \quad (31)$$

$$\tilde{\psi}_3 = \sum_{l=0}^{\infty} \sum_{m=-l}^l \tilde{A}_{lm}^{(3)} r^l Y_{lm}(\theta, \phi), \quad (32)$$

where the coefficients $\tilde{A}_{lm}^{(j)}$ and $\tilde{B}_{lm}^{(j)}$ are obtained by applying the boundary conditions. The application of the boundary conditions and the use of the orthogonality of $Y_{lm}(\theta, \phi)$ give the following system of equations for the coefficients:

$$\begin{aligned}
& \tilde{B}_{lm}^{(0)}/r_1^{l+1} \\
&= \tilde{A}_{lm}^{(1)}r_1^l + \tilde{B}_{lm}^{(1)}/r_1^{l+1} \\
&\quad - \epsilon_0 \tilde{B}_{lm}^{(0)}(l \\
&\quad + 1)/r_1^{l+2} \\
&= \tilde{\epsilon}_1 [\tilde{A}_{lm}^{(1)}lr_1^{l-1} \\
&\quad - \tilde{B}_{lm}^{(1)}(l \\
&\quad + 1)/r_1^{l+2}] \tilde{A}_{lm}^{(1)}r_2^l \\
&\quad + \tilde{B}_{lm}^{(1)}/r_2^{l+1} \\
&= \tilde{A}_{lm}^{(2)}r_2^l + \tilde{B}_{lm}^{(2)}/r_2^{l+1} \\
&\quad + u_{lm}/r_2^{l+1} \tilde{\epsilon}_1 [\tilde{A}_{lm}^{(1)}lr_2^{l-1} \\
&\quad - \tilde{B}_{lm}^{(1)}(l \\
&\quad + 1)/r_2^{l+2}] = \tilde{\epsilon}_2 [\tilde{A}_{lm}^{(2)}lr_2^{l-1} - \tilde{B}_{lm}^{(2)}(l \\
&\quad + 1)/r_2^{l+2} \\
&\quad - u_{lm}(l \\
&\quad + 1)/r_2^{l+2}] \tilde{A}_{lm}^{(2)}r_3^l \\
&\quad + \tilde{B}_{lm}^{(2)}/r_3^{l+1} \\
&\quad + v_{lm}r_3^l = \tilde{A}_{lm}^{(3)}r_3^l \tilde{\epsilon}_2 [\tilde{A}_{lm}^{(2)}lr_3^{l-1} \\
&\quad - \tilde{B}_{lm}^{(2)}(l \\
&\quad + 1)/r_3^{l+2} \\
&\quad + v_{lm}lr_3^{l-1}] \\
&= \tilde{\epsilon}_3 \tilde{A}_{lm}^{(3)}lr_3^{l-1}.
\end{aligned}$$

In these equations, we denote by $\tilde{\epsilon}_1$, $\tilde{\epsilon}_2$, and $\tilde{\epsilon}_3$ the dielectric functions evaluated at the emission frequency, which for an inelastic interaction (Raman or fluorescence) will differ from the frequency of the stimulating radiation. When computing the scattered field at a distance significantly greater than the diameter of the particle, the dipole terms dominate, i.e., we can neglect all terms for which $l > 1$ in the above equations. Setting $l = 1$ results in a system identical to Eq. (15) but with a different right-hand side and with ϵ_1 , ϵ_2 , and ϵ_3 replaced by $\tilde{\epsilon}_1$, $\tilde{\epsilon}_2$, and $\tilde{\epsilon}_3$:

$$\begin{bmatrix}
1/r_1^2 & -r_1 & -1/r_1^2 & 0 & 0 & 0 \\
-2\epsilon_0/r_1^3 & -\tilde{\epsilon}_1 & 2\tilde{\epsilon}_1/r_1^3 & 0 & 0 & 0 \\
0 & r_2 & 1/r_2^2 & -r_2 & -1/r_2^2 & 0 \\
0 & \tilde{\epsilon}_1 & -2\tilde{\epsilon}_1/r_2^3 & -\tilde{\epsilon}_2 & 2\tilde{\epsilon}_2/r_2^3 & 0 \\
0 & 0 & 0 & r_3 & 1/r_3^2 & -r_3 \\
0 & 0 & 0 & \tilde{\epsilon}_2 & -2\tilde{\epsilon}_2/r_3^3 & -\tilde{\epsilon}_3
\end{bmatrix}
\begin{bmatrix}
\tilde{B}_{1m}^{(0)} \\
\tilde{A}_{1m}^{(1)} \\
\tilde{B}_{1m}^{(1)} \\
\tilde{A}_{1m}^{(2)} \\
\tilde{B}_{1m}^{(2)} \\
\tilde{A}_{1m}^{(3)}
\end{bmatrix}
=
\begin{bmatrix}
0 \\
0 \\
u_{1m}/r_2^2 \\
-2\tilde{\epsilon}_2 u_{1m}/r_2^3 \\
-r_3 v_{1m} \\
-\tilde{\epsilon}_2 v_{1m}
\end{bmatrix}. \quad (33)$$

Now let T_{ij} denote the elements of the inverse of the 6 by 6 matrix on the left of Eq. (33). We wish to compute the (dipole) potential external to the shell generated by the molecule. This potential is given by Eq. (29) with $l = 1$:

$$\tilde{\psi}_0 = \frac{1}{r^2} \sum_{m=-1}^1 \tilde{B}_{1m}^{(0)} Y_{1m}(\theta, \phi), \quad (34)$$

where from the inverse of Eq. (33),

$$\tilde{B}_{1m}^{(0)} = (T_{13}/r_2^2 - 2\tilde{\epsilon}_2 T_{14}/r_2^3) u_{1m} - (r_3 T_{15} + \tilde{\epsilon}_2 T_{16}) v_{1m}. \quad (35)$$

For brevity, define

$$p \equiv T_{13}/r_2^2 - 2\tilde{\epsilon}_2 T_{14}/r_2^3, \quad (36)$$

$$q \equiv -r_3 T_{15} - \tilde{\epsilon}_2 T_{16}, \quad (37)$$

so that $\tilde{B}_{1m}^{(0)}$ may be written

$$\tilde{B}_{1m}^{(0)} = p u_{1m} + q v_{1m}. \quad (38)$$

Note that p and q are functions only of r_1 , r_2 , r_3 , $\tilde{\epsilon}_1$, $\tilde{\epsilon}_2$, and $\tilde{\epsilon}_3$ and are independent of the coordinates of the molecule, but the quantities u_{1m} and v_{1m} defined by Eqs. (27) and (28) depend on the molecular coordinates.

From Eq. (23) and recalling that $P_1^0(\cos\theta_i) = \cos\theta_i$ and $P_1^1(\cos\theta_i) = -\sin\theta_i$, we have

$$Y_{10}(\theta_i, \phi_i) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta_i, \quad (39)$$

$$Y_{11}(\theta_i, \phi_i) = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta_i e^{i\phi_i}, \quad (40)$$

$$Y_{1,-1}(\theta_i, \phi_i) = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta_i e^{-i\phi_i}. \quad (41)$$

On setting $l = 1$ in Eqs. (27) and (28) and substituting for the fields $E_{2r}(\mathbf{r}_i)$ and $E_{2\theta}(\mathbf{r}_i)$ from Eqs. (18) and (19), we obtain

$$u_{10} = -\alpha \left(\frac{4\pi}{3}\right)^{1/2} \left[A_2 + \frac{B_2}{r_i^3} - \frac{3B_2}{r_i^3} \cos^2\theta_i \right], \quad (42)$$

$$v_{10} = -\alpha \left(\frac{4\pi}{3} \right)^{1/2} \frac{1}{r_i^3} \left[A_2 + \frac{B_2}{r_i^3} + 3 \left(\frac{B_2}{r_i^3} - A_2 \right) \cos^2 \theta_i \right], \quad (43)$$

$$u_{11} = -\frac{3a}{2} \left(\frac{8\pi}{3} \right)^{1/2} \frac{B_2}{r_i^3} \sin \theta_i \cos \theta_i e^{-i\phi_i}, \quad (44)$$

$$v_{11} = -\frac{3a}{2} \left(\frac{8\pi}{3} \right)^{1/2} \frac{1}{r_i^3} \left(A_2 - \frac{B_2}{r_i^3} \right) \sin \theta_i \cos \theta_i e^{-i\phi_i}, \quad (45)$$

$$u_{1,-1} = \frac{3\alpha}{2} \left(\frac{8\pi}{3} \right)^{1/2} \frac{B_2}{r_i^3} \sin \theta_i \cos \theta_i e^{i\phi_i}, \quad (46)$$

$$v_{1,-1} = \frac{3\alpha}{2} \left(\frac{8\pi}{3} \right)^{1/2} \frac{1}{r_i^3} \left(A_2 - \frac{B_2}{r_i^3} \right) \sin \theta_i \cos \theta_i e^{i\phi_i}, \quad (47)$$

Recall that the dipole potential external to the shell generated by the molecule is given by Eq. (34). From Jackson [22] we obtain the following relation between $\tilde{B}_{1m}^{(0)}$ and the Cartesian components of the dipole moment:

$$p_x = -\left(\frac{3}{8\pi} \right)^{1/2} \left(\tilde{B}_{11}^{(0)} - \tilde{B}_{1,-1}^{(0)} \right), \quad (48)$$

$$p_y = -i \left(\frac{3}{8\pi} \right)^{1/2} \left(\tilde{B}_{11}^{(0)} + \tilde{B}_{1,-1}^{(0)} \right), \quad (49)$$

$$p_z = \left(\frac{3}{4\pi} \right)^{1/2} \tilde{B}_{10}^{(0)}. \quad (50)$$

Substituting $\tilde{B}_{1m}^{(0)} = pu_{1m} + qv_{1m}$ from Eq. (38) and substituting the expressions for u_{10} , u_{11} , $u_{1,-1}$, v_{10} , v_{11} , and $v_{1,-1}$, we find

$$p_x = \frac{3\alpha}{r_i^3} \left(pB_2 + qA_2 - \frac{qB_2}{r_i^3} \right) \sin \theta_i \cos \theta_i \cos \phi_i, \quad (51)$$

$$p_y = -\frac{3\alpha}{r_i^3} \left(pB_2 + qA_2 - \frac{qB_2}{r_i^3} \right) \sin \theta_i \cos \theta_i \sin \phi_i, \quad (52)$$

$$p_z = -\alpha \left(p + \frac{q}{r_i^3} \right) \left(A_2 + \frac{B_2}{r_i^3} \right) + \frac{3\alpha}{r_i^3} \left(pB_2 + qA_2 - \frac{qB_2}{r_i^3} \right) \cos^2 \theta_i. \quad (53)$$

The differential scattering cross section evaluated in the radiation zone can be expressed in terms of the dipole moment $\mathbf{p}$ as follows [23]:

$$\sigma_d(\hat{n}_i, \hat{n}_s) = |f(\hat{n}_i, \hat{n}_s)|^2, \quad (54)$$

where

$$f(\hat{n}_i, \hat{n}_s) = \frac{k^2}{4\pi\epsilon_0} [\mathbf{p} - \hat{n}_s(\hat{n}_s \cdot \mathbf{p})], \quad (55)$$

$k = \omega/c$ is the wavenumber of the host, and $\hat{n}_i$ and $\hat{n}_s$ are unit vectors in the direction of the incident and scattered radiation. Substituting Eq. (55) into Eq. (54), we find that

$$\sigma_d(\hat{n}_i, \hat{n}_s) = \frac{k^4}{(4\pi\epsilon_0)^2} [|\mathbf{p}|^2 - |\hat{n}_s \cdot \mathbf{p}|^2]. \quad (56)$$

Now suppose that the direction of propagation of the incident light is along the x axis so that the electric field is polarized in the z direction. We shall further assume that the scattered field is measured in the forward direction. In this case $\hat{n}_s = \hat{x}$, and Eq. (56) reduces to

$$\sigma_d = \frac{k^4}{(4\pi\epsilon_0)^2} [|p_y|^2 + |p_z|^2]. \quad (57)$$

If we now assume that the volume of the luminescent shell is filled uniformly with active molecules, the total cross section from all the molecules can be computed by integrating the cross section $\sigma_d(\mathbf{r}_i)$ over the volume of this layer. The average cross section is given by

$$\bar{\sigma}_d = \frac{1}{V_2} \int_{V_2} \sigma(\mathbf{r}_i) d^3\mathbf{r}_i = \frac{1}{V_2} \int_{r_3}^{r_2} r_i^2 dr_i \int_0^{2\pi} d\phi_i \int_0^\pi d\theta_i \sin\theta_i \sigma_d(r_i, \theta_i, \phi_i), \quad (58)$$

where $V_2 = 4\pi(r_2^3 - r_3^3)/3$ is the volume of the luminescent layer. Now for brevity, define the angular integrals

$$J_y(r_i) \equiv \int_0^{2\pi} d\phi_i \int_0^\pi d\theta_i \sin\theta_i |p_y|^2, \quad (59)$$

$$J_z(r_i) \equiv \int_0^{2\pi} d\phi_i \int_0^\pi d\theta_i \sin\theta_i |p_z|^2, \quad (60)$$

so that Eq. (58) may be written

$$\bar{\sigma}_d = \frac{k^4}{V_2(4\pi\epsilon_0)^2} \int_{r_3}^{r_2} [J_y(r_i) + J_z(r_i)] r_i^2 dr_i. \quad (61)$$

Performing the integrals in Eq. (59) and (60), we obtain

$$J_y(r_i) = \frac{12\pi\alpha^2}{5r_i^6} \left| pB_2 + qA_2 - \frac{qB_2}{r_i^3} \right|^2, \quad (62)$$

$$J_z(r_i) = 4\pi\alpha^2 \left\{ \left| \left(p + \frac{q}{r_i^3} \right) \left(A_2 + \frac{B_2}{r_i^3} \right) \right|^2 + \frac{9}{5r_i^6} \left| pB_2 + qA_2 - \frac{qB_2}{r_i^3} \right|^2 - \frac{2}{r_i^3} \operatorname{Re} \left[\left(p + \frac{q}{r_i^3} \right) \times \left(A_2 + \frac{B_2}{r_i^3} \right) \left(pB_2 + qA_2 - \frac{qB_2}{r_i^3} \right)^* \right] \right\}. \quad (63)$$

These expressions can be expanded, and the integration with respect to r_i in Eq. (61) can be performed analytically, but we have found it simpler to perform the integration numerically.

3. Computing the Enhancement

In our simulations, we employed the following Lorentz–Drude dispersion model for the dielectric function of silver and gold:

$$\epsilon(\omega) = 1 + \sum_{k=1}^6 \frac{\Delta\epsilon_k}{-a_k\omega^2 - ib_k\omega + c_k}, \quad (64)$$

where ϵ_k , a_k , b_k , and c_k are constants that provide the best fit for either metal [24]. The values of these constants for silver and gold have been found by fitting data from the *Handbook of Optical Constants of Solids*, edited by E. D. Palik [25]. It is important to note that the latter model is derived from bulk data and fails to take into account electron scattering from the boundaries of the shell. The latter effect tends to dampen the plasmon resonances when the particle size is comparable to or smaller than the electron mean-free path length [12–15]. As a result, it is likely that some published enhancement calculations that have neglected this “size” effect have significantly overestimated the true enhancement for particles smaller than 50 nm. This has also been suggested by Khlebtsov *et al.* [14]. Moroz [15] has recently examined three models that attempt to account for the size effect in a spherical shell. Of these three, he claims that the so-called billiard, or Lambertian, scattering model is in best agreement with preliminary experimental results. This formula adds a correction to the imaginary part of the dielectric model. If we denote the dielectric constant derived from bulk data by ϵ_b , given in our case by Eq. (64), Moroz’s correction takes the following form [15]:

$$\epsilon = \epsilon_b + i\Delta\epsilon, \quad (65)$$

where

$$\Delta\epsilon = \frac{\omega_p^2 v_f}{\omega^3 L}. \quad (66)$$

Here ω_p is the plasmon frequency of the metal, v_f is its Fermi velocity, and L is given by the formula

$$L = \frac{4r_1}{3} \frac{(1 - q^3)}{(1 + q^2)}, \quad (67)$$

where $q \equiv r_2/r_1$.

In our simulations, we employed this correction and used the following parameters fitted from Palik's data [25]: $\omega_p = 8.826$ eV for gold and $\omega_p = 8.806$ eV for silver. The Fermi velocities used were $v_f = 1.40 \times 10^6$ m/s and $v_f = 1.39 \times 10^6$ m/s for gold and silver, respectively [26]. The dielectric constant of the active layer was taken arbitrarily to be 4.5, which is approximately that of silica.

We should emphasize that the enhancement magnitude at the plasmon peaks depends sensitively on the values of the parameters used in Eq. (64), particularly on the value of the imaginary part of the dielectric constant, which controls the damping and thus the Q of the plasmon resonance. Small changes in this value can give rise to quite large changes in the calculated enhancement at the plasmon resonance frequencies. To add further uncertainty to the calculation, a variety of other dispersion models have appeared in the literature, including a somewhat different Lorentz–Drude model [27] and a modified Debye model [28], and these models can give rise to noticeably different predictions for the enhancement. A final caveat is that the enhancement also depends fairly sensitively on the dielectric constant of the active layer. The cumulative affect of these uncertainties is that the enhancement magnitude at the plasmon peak should be regarded as an order-of-magnitude estimate, although the locations of the peaks are less sensitive to the model parameters and thus somewhat more reliable.

To estimate the enhancement, we compute the integrated cross section (58) as a function of frequency, first with the metallic outer layer and metallic core present, and again in the absence of the outer layer and core (i.e., with only the active layer present). The enhancement is then given by the ratio of these two values, that is, in the case of gold, $\bar{\sigma}_{Au}/\bar{\sigma}_0$, where $\bar{\sigma}_{Au}$ and $\bar{\sigma}_0$ are the integrated cross sections with and without the gold present. As noted, we assume a frequency-independent dielectric constant for the active layer ($\epsilon_2 = 4.5$).

We compute the enhancement for two different configurations: (1) when the outer shell and core are both present, and (2) when only the core is present. Figure 2(a) shows the calculated enhancement for silver with the outer metallic layer and core both present, while Fig. 2(b) shows the enhancement when only the core is present. Note the difference in the vertical scale. Figures 3(a) and 3(b) show the analogous enhancements for gold. In these calculations, we first set $r_1 = 20$ nm, $r_2 = 15$ nm, and $r_3 = 10$ nm. To demonstrate the effect

of the size correction, Figs. 4 and 5 display the same calculation with all dimensions doubled, that is, with $r_1 = 40$ nm, $r_2 = 30$ nm, and $r_3 = 20$ nm. Note, in comparing Figs. 2 and 3, the noticeable increase in enhancement for the larger particle size. We point out that the dependence of the enhancement on the particle scale enters only through the correction term in Eq. (65). Without this term, the enhancement is scale invariant in the quasi-static approximation. That is, in the absence of the size correction in Eq. (65), the enhancement would remain the same if we were to multiply all dimensions by the same factor.

The above calculations were obtained by averaging the cross sections of molecules uniformly distributed throughout the active layer. One would expect that the enhancement will be larger for molecules closer to the core than to the outer layer boundary, because the electric field is larger near the core. A calculation of the enhancement of a single molecule whose location varies with radius between the core radius and inner surface of the outer layer ($r_3 - r - r_2$) is shown in Fig. 6. The enhancement was computed for a wavelength of 417 nm, the peak enhancement wavelength for the silver layer–core system. This demonstrates that the enhancement increases as the molecule moves closer to the core, as anticipated.

Finally, it is instructive to show the real and imaginary parts of the z component of the electric field along the z axis through the center of the particle. In Fig. 7, the real and imaginary parts are displayed as solid and dashed curves, respectively, for the silver shell–core particle. In the quasi-static approximation, the real and imaginary parts of the field arise solely because the dielectric function is complex. Figures 7(a) and 7(b) are profiles computed for two wavelengths, one at the peak of the high energy mode ($\lambda = 417$ nm) and again at the peak of the low energy mode ($\lambda = 875$ nm). The plasmon induced by the incident light can be related to the surface charge density at the interfaces of the shell. The surface charge density is, in turn, proportional to the jump or discontinuity in the normal component of the electric field across each boundary. At resonance, it can be argued that most of the energy resides in the imaginary part of the electric field, which is evident from Figs. 7(a) and 7(b). If we examine the sign of the jump in the imaginary part of the electric field across each interface, we see that the charge polarity on the boundaries for the two different modes is consistent with the predictions of the plasmon hybridization model of Radloff and Halas [11] for low and high energy modes.

4. Conclusion

Our objective has been to estimate the enhancement of the far-field Raman or fluorescence response of an active layer in a multilayered nanoshell residing between a metallic core and an outer metallic layer. We compute the enhancement for two cases: with the outer layer and core present, and with only the core present. The presence of the outer layer generates a second, lower energy plasmon resonance, which produces a second dipolar mode in the near infrared. The enhancement also depends sensitively on the size of the particle when the particle diameter and/or shell thickness is of the same order as the electron mean-free path length. To illustrate this sensitivity, we computed the enhancement for two sizes differing by a factor or two.

In the calculations presented here, we have used a Drude–Lorentz model derived from fitting the model parameters to the data found in [25] for silver and gold and have assumed a constant (frequency independent) dielectric function for the active compound. Due to the sensitivity of our results to the parameters of the dielectric model, the enhancement magnitudes should be regarded as qualitative, although other features should hold, such as the locations of the dipolar resonances and that the presence of an outer plasmon-active metal layer noticeably increases the far-field fluorescence or Raman-active enhancement.

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Fig. 1.
Outer layer and core are metallic and the intermediate layer contains a luminescent or Raman-active compound.

Fig. 2.

(a) Enhancement with the silver outer shell and core present with $r_1 = 20$ nm, $r_2 = 15$ nm, and $r_3 = 10$ nm; (b) enhancement with the silver core only present. Note that the enhancement is significantly greater with the outer shell present and the appearance of the second, lower-energy mode.

Fig. 3.

(a) Enhancement with the gold outer shell and core present with $r_1 = 20$ nm, $r_2 = 15$ nm, and $r_3 = 10$ nm; (b) enhancement with the gold core only present. Note that for gold, the lower-energy mode dominates, although the higher-energy mode still exceeds that for the core-only system.

Fig. 4.
Continues on facing page.

Fig. 5. Repeat of Fig. 3 with all dimensions doubled ($r_1 = 40$ nm, $r_2 = 30$ nm, $r_3 = 20$). (a) Enhancement with the gold outer shell and core present; (b) enhancement with the gold core only present.

Fig. 6.

Far-field enhancement of a single molecule whose radial position varies within the active layer over the interval $r_3 \leq r \leq r_2$ along the z axis at wavelength 417 nm. The silver shell-core particle is assumed with $r_1 = 20$ nm, $r_2 = 15$ nm, and $r_3 = 10$ nm.

Fig. 7.

(a) Plot of the profile of the electric field along the axis of a silver shell-core particle at the wavelength 417 nm (the peak of the higher energy plasmon mode). The solid and dashed curves are the real and imaginary parts of the axial component of the electric field, respectively. (b) Plot of the profile of the electric field along the axis of the particle at the wavelength 875 nm (the peak of the lower energy plasmon mode). The jump in the field at each boundary is proportional to the surface charge density on that interface.