Finite-Size Effects and Surface-Enhanced Raman Scattering from Molecules Adsorbed on Noble-Metal Nanoparticles

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ABSTRACT

We study the role of a strong electron confinement on the surface-enhanced Raman scattering from molecules adsorbed on small noble-metal nanoparticles. We describe a novel enhancement mechanism which originates from the different effect that confining potential has on s-band and d-band electrons. We demonstrate that the interplay between finite-size and screening effects in the nanoparticle surface layer leads to an enhancement of the surface plasmon local field acting on a molecule located in a close proximity to the metal surface. Our calculations show that the additional enhancement of the Raman signal is especially strong for small nanometer-sized nanoparticles.

Keywords: nanoparticles, Raman scattering, surface plasmon

1 INTRODUCTION

An recent interest in single-molecule surface-enhanced Raman scattering (SERS) stems from the discovery of enormously high (up to $10^{15}$) enhancement of Raman spectra from certain (e.g., Rhodamine 6G) molecules adsorbed on the nanoparticle surfaces in gold and silver colloids [1]–[3]. Major SERS mechanisms include electromagnetic (EM) enhancement by surface plasmon (SP) local field near the metal surface [4]–[8] and chemical enhancement due to dynamical charge transfer between a nanoparticle and a molecule [9]–[12]. Although the origin of this phenomenon has not completely been elucidated so far, the EM enhancement was demonstrated to play the dominant role, especially in dimer systems when the molecule is located in the gap between two closely spaced nanoparticles [10]–[13].

An accurate determination of the SERS signal intensity for molecules located in a close proximity to the nanoparticle surface is a non-trivial issue. The classical approach, used in EM enhancement calculations [4]–[8], is adequate when nanoparticle-molecule or interparticle distances are not very small. For small distances, the quantum-mechanical effects in the electron density distribution can no longer be neglected. These effects are especially important in noble-metal particles where the SP local field is strongly affected by highly-polarizable (core) d-electrons. In the bulk part of the nanoparticle, the (conduction) s-electrons are strongly screened by the localized d-electrons. However, near the nanoparticle boundary, the two electron species have different density profiles. Namely, delocalized s-electrons spill over the classical boundary [14], thus increasing the effective nanoparticle radius, while d-electron density profile mostly retains its classical shape. The incomplete embedding of the conduction electrons in the core electron background [15]–[18] leads to a reduced screening of the s-electron Coulomb potential in the nanoparticle surface layer. The latter has recently been observed as an enhancement of the electron-electron scattering rate in silver nanoparticles [19], [20].

Here we study the role of electron confinement on SERS from molecule adsorbed on the surface of small Ag particles. To this end, we develop an EM theory for SERS in noble-metal particle, based on the two-region model [15]–[17], [21], which describes the role of the surface-layer phenomenologically. We find that the reduction of screening near the surface leads to an additional enhancement of the Raman signal from a molecule located in a close proximity to the nanoparticle. In particular, we address the dependence of SERS on nanoparticle size and show that the interplay of finite-size and screening effects is especially strong for small nanometer-sized particles.

2 TWO-REGION MODEL

We consider SERS from a molecule adsorbed on a spherical nanoparticle with radius $R$. For sufficiently small $R$, the retardation effects are negligible and the frequency-dependent potential is determined from the Poisson equation,

$$\Phi(\omega, \mathbf{r}) = \phi_0(\mathbf{r}) + \sqrt{\frac{\varepsilon_{\infty}}{\varepsilon}} \delta N(\omega, \mathbf{r}) \cdot \mathbf{E}_0 \cdot \mathbf{r} \frac{\mathbf{r}}{|\mathbf{r}-\mathbf{r}'|},$$

where $\phi_0(\mathbf{r}) = -e \mathbf{E}_0 \cdot \mathbf{r}$ is the potential of the incident light with electric field amplitude $E_0 = E_0 \hat{z}$ along the z-axis, and $\delta N(\omega, \mathbf{r})$ is the induced charge density (hereafter we suppress frequency dependence). In noble-metal particles, there are four contributions to $\delta N(\mathbf{r})$ originating from the valence $s$-electrons, $\delta N_s(\mathbf{r})$, the core $d$-electrons, $\delta N_d(\mathbf{r})$, the dielectric medium, $\delta N_m(\mathbf{r})$,
and the molecule, $\delta N_0(r)$. The density profile of delocalized s-electrons is not fully embedded in the background of localized d-electrons but extends over that of localized d-electrons by $\Delta \sim 1 - 3$ Å [15]–[17]. Here we adopt the classical two-region model with d-electron density extending up to $R_d = R - \Delta$, where $\Delta$ is the thickness of the surface layer without d-electron population. The induced density is expressed as

$$\delta N(r) = -\nabla \cdot P(r),$$

where the electric polarization vector $P(r) = P_d + P_s + P_m + P_0$ can be related back to the potential via

$$P_d(r) = -\frac{\epsilon_d - 1}{4\pi} \theta(R_d - r) \nabla \Phi(r),$$
$$P_s(r) = -\frac{\epsilon_s - 1}{4\pi} \theta(R - r) \nabla \Phi(r),$$
$$P_m(r) = -\frac{\epsilon_m - 1}{4\pi} \theta(r - R) \nabla \Phi(r),$$
$$P_0(r) = -\delta(r_r) \alpha_0 \nabla \Phi(r_0).$$

(2)

Here the step functions $\theta(x)$ enforce the appropriate boundary conditions, $\epsilon_d$ and $\epsilon_m$ are the core and medium dielectric functions, respectively, and

$$\epsilon_s(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma},$$

(3)

is the Drude dielectric function of s-electrons, $\omega_p$ being the bulk plasmon frequency. The width $\gamma = \gamma_0 + \gamma_s$ includes contribution of the bulk-like electron-phonon scattering, $\gamma_0$, and of the electron surface scattering, $\gamma_s = g_s \nu_F/R$, where $\nu_F$ is the Fermi velocity and $g_s$ is a numerical factor ($g_s \approx 1$ in noble-metal particles). The molecule is represented by a point dipole with polarization $\alpha_0$ located at $r_0$ (we chose origin at the nanoparticle center).

To obtain a self-consistent equation for the potential $\Phi(r)$, we substitute the above expressions into $\delta N = \delta N_s + \delta N_d + \delta N_m + \delta N_0$ in the rhs of Eq. (1) and, after integrating by parts, obtain,

$$\epsilon(r)\Phi(r) = \phi_0(r) - \nabla_0 \frac{1}{|r - r_0|} \cdot \alpha_0 \nabla \Phi(r_0)$$
$$+ \int d^3r' \frac{1}{|r - r'|} \cdot \nabla' \chi_0 \theta(R_d - r')$$
$$- \chi_0 \theta(R - r') - \chi_0 \theta(r' - R) \Phi(r'),$$

(4)

where $\epsilon(r) = \epsilon_d + \epsilon_s - 1$, $\epsilon_s$, and $\epsilon_m$ are the s, d, and m intervals, respectively, and $\chi_0$ is the corresponding susceptibilities. Since the incident field has the form $\phi(r_0) = \phi(r_0) \cos \theta = -E_0 \cos \theta$, we expand $\Phi$ and in terms of spherical harmonics and, after retaining only the dipole term ($L = 1$), obtain,

$$\epsilon(r)\Phi(r) = \phi_0(r) - \frac{\epsilon_d - 1}{4\pi} R_d^2 \partial_{R_d} B(r, R_d) \Phi(R_d)$$
$$+ \frac{\epsilon_s - \epsilon_d}{4\pi} R^2 \partial_{R_d} B(r, R) \Phi(R)$$
$$- \alpha_0 \nabla_0 B(r, r_0) \cdot \nabla \Phi(r_0),$$

(5)

where

$$B(r, r') = \frac{4\pi}{3} \left[ \frac{r'}{r^2} \theta(r - r') + \frac{r}{r'^2} \theta(r' - r) \right]$$

(6)

is the dipole term of the radial component of the Coulomb potential, and we assumed that the molecule is located on the z axis.

The second and third terms in rhs of Eq. (5) originate from the scattering due to change of dielectric function at $r = R_d$ and $r = R$, respectively, while last term represents the potential of the molecular dipole. The values of $\Phi$ at the boundaries and at the molecule position can be found by setting $r = R_d$, $R$, $r_0$ in Eq. (5). In doing so, one determines a closed-form expression for the self-consistent potential in the presence of molecule, nanoparticle, and dielectric medium.

3 RAMAN SCATTERING

In the electromagnetic mechanism of SERS, the enhancement of the Raman signal comes from the far-field of the radiating molecular dipole and secondary field of this dipole scattered by the nanoparticle. In order to extract the Raman contribution, present the self-consistent potential as a sum $\Phi = \phi + \phi^R$, where $\phi^R$ is the potential of the radiative dipole. Since the molecular polarizability is very small, we restrict ourselves by the lowest order in $\alpha_0$; in this case $\phi$ is the potential in the absence of molecule and $\phi^R$ determines the Raman signal in the first order in $\alpha_0$. Inclusion of higher orders in $\alpha_0$ leads to renormalization of molecular and nanoparticle polarizabilities due to image charges; these effects are not considered here.

Keeping only zero-order terms in Eq. (5), we find

$$\phi = \phi_0 + \delta \phi,$$

(7)

where $\phi_0 = \phi_0/\epsilon(r) = -E_0 r/\epsilon(r)$, and

$$\delta \phi(r) = \frac{1}{\epsilon(r)} \left[ -\beta(r/R_d) \phi_0(R_d) \frac{\lambda_d(1 - 2\lambda_m)}{1 - 2\alpha^3 \lambda_d \lambda_m} \right.$$
$$+ \beta(r/R) \phi_0(R) \frac{\lambda_m(1 - a^3 \lambda_d)}{1 - 2a^3 \lambda_d \lambda_m} \right].$$

(8)

Here $\beta(r/R) = \frac{3}{4\pi} R^2 \partial_{R} B(r, R)$ is given by

$$\beta(x) = x^{-2} \theta(x - 1) - 2x \theta(1 - x),$$

(9)

and

$$\lambda_d = \frac{\epsilon_d - 1}{\epsilon_d + 3\epsilon_s - 1}, \quad \lambda_m = \frac{\epsilon_m - \epsilon_s}{2\epsilon_m + \epsilon_s}.$$

(10)

The spatial dependence of the nanoparticle-induced potential, $\delta \phi$, is thus determined by $\beta(x)$. Inside the particle, the potential linearly increases for $r < R_d$, while exhibiting a more complicated behavior in the surface.
layer, \( R_d < r < R \). Outside of the nanoparticle, the induced potential falls off quadratically,

\[
\delta \varphi(r) = \frac{E_0 \alpha}{\epsilon_m r^2}, \quad r > R, \tag{11}
\]

with \( \alpha(\omega) \) is the particle polarizability

\[
\alpha(\omega) = R^3 \left[ 1 - \frac{(1 + \lambda_m)(1 - a^3 \lambda_d)}{1 - 2a^3 \lambda_d \lambda_m} \right]. \tag{12}
\]

In the absence of the surface layer, \( R_d = R \), we recover the usual expression for the polarizability in the presence of d-electrons and dielectric medium,

\[
\alpha^0 = R^3 \frac{\epsilon_s + \epsilon_d - 1 - \epsilon_m}{\epsilon_s - \epsilon_d - 1 + 2\epsilon_m}, \tag{13}
\]

with resonance peak at the SP energy \( \omega_M = \frac{\omega_p}{\sqrt{\epsilon_s + 2\epsilon_m}} \).

In the presence of the surface layer, the SP energy experiences a blueshift [15], [16] due an effective decrease in the d-electron dielectric function in the nanoparticle (see Fig. 3). At the same time, an increase in the peak amplitude (see Fig. 3), which accompanies the blueshift, indicates a stronger local field at resonance energy acting on a molecule in a close proximity to nanoparticle surface.

![Figure 1: Calculated nanoparticle polarizability for different surface layer thicknesses.](image)

The Raman signal is given by the self-consistent field of the radiating dipole, \( \tilde{\phi}^R \), determined from Eq. (5) in the first order in \( \alpha_0 \),

\[
\epsilon(r) \phi^R(r) = \phi^R_0(r) + \frac{\epsilon_m - 1}{3} \beta(r/R_d) \phi^R(R_d)
+ \frac{\epsilon_m - 1}{3} \beta(r/R) \phi^R(R), \tag{14}
\]

where

\[
\phi^R_0(r) = -\beta(r/r_0) \frac{4\pi a_0}{3r_0} \frac{\partial \phi(r_0)}{\partial r_0} = S \phi_0, \tag{15}
\]

is the potential of the molecular dipole in the presence of local field, and we introduced notations

\[
S(\omega) = \frac{8\pi a_0}{3\epsilon_0 r_0^3} \frac{\partial \phi(r_0)}{\partial r_0} \tag{16}
\]

and

\[
\tilde{\phi}_0(r) = -E_1 \left[ r \theta(r_0 - r) - \frac{r^3}{2r_0^3} \theta(r - r_0) \right]. \tag{17}
\]

Note that while the frequency dependence of the local potential, \( \phi(r_0) \), given by Eqs. (7,11), is that of the incident field, \( \omega \), the Raman field, \( \phi^R(r) \), depends on the Stokes-shifted frequency, \( \omega_s = \omega - \omega_0 \), where \( \omega_0 \) is the molecular vibrational frequency determined by \( \alpha_0 \).

The last two terms in Eq. (14) describe potential of molecular dipole scattered from the d-electron and s-electron distribution boundaries and can be determined by matching \( \phi^R \) at \( r = R_d \) and \( r = R \). We now notice that, at these values of \( r < r_0 \), we have \( \phi_0(r) = \phi_0(r) \), so the Raman potential is found as

\[
\phi^R = S(\omega)[\tilde{\phi}_0 + \delta \varphi(\omega_s)], \tag{18}
\]

where \( \tilde{\varphi}_0(r) = \tilde{\varphi}_0(r)/\epsilon(r) \) and \( \delta \varphi(r) \) is given by Eq. (8) but with \( \omega_s \) instead of \( \omega \). For the far field \( (r > r_0) \), we then obtain

\[
\phi^R(r) = \frac{E_0 r_0^3}{2\epsilon_m r^2} S(\omega) \left[ 1 + g(\omega_s) \right], \tag{19}
\]

where

\[
g = \frac{\alpha}{\epsilon_0} = \left( \frac{R}{r_0} \right)^3 \frac{1 - (1 + \lambda_m)(1 - a^3 \lambda_d)}{1 - 2a^3 \lambda_d \lambda_m} \tag{20}
\]

with \( \lambda \) given by Eq. (10). The expression for \( S(\omega) \) in Eq. (raman-far-field) can obtained in the same manner from Eqs. (7,11) by substituting the nanoparticle electric field at the molecule location,

\[
E(r_0) = -\frac{\partial \phi_0}{\partial r_0} = \frac{E_0}{\epsilon_m} \left[ 1 + 2g(\omega) \right], \tag{21}
\]

into Eq. (16). We finally arrive at

\[
\phi^R(r) = \frac{4\pi a_0 E_0}{3\epsilon_m r^2} \left[ 1 + 2g(\omega) \right] \left[ 1 + 2g(\omega_s) \right]. \tag{22}
\]

The above expression generalizes the well-known classical result [4], [5] to the case of noble-metal particle with different distributions of d-electron and s-electron densities. The surface-enhanced Raman field retains the same functional dependence on the nanoparticle polarizability, however the latter contains all the information.
about the surface layer effect. Note that the form (22) of the Raman field remain unchanged even for a non-classical distribution of the electron densities provided that the electronic wave-functions in the nanoparticle do not overlap with the molecular orbitals.

Finally, the Raman enhancement factor is given by

\[
A(\omega, \omega_s) = \left| 1 + 2g(\omega) + 2g(\omega_s) + 4g(\omega)g(\omega_s) \right|^2.
\] (23)

4 DISCUSSION

For large nanoparticle with \( R \sim 100 \) nm, the classical EM theory provides an enhancement of the Raman signal as large as \( 10^6 \)–\( 10^7 \) [6]. In reality, the EM enhancement is inhibited by various factors. In noble-metal particles, the interband transition between d-electron and s-electron bands reduce the SP oscillator strength leading to a weakening of the local fields. For nanoparticle radius below 15 nm, finite-size effects become important. The SP resonance damping comes from the electron scattering at the surface leading to the size-dependent SP resonance width \( \gamma_s \simeq \nu_F / R \). At the resonance frequency, the size-dependence of SERS is quite strong. Indeed, if molecular vibrational frequencies are smaller than the SP width, the enhancement factor decreases as \( A \propto R^4 \) for small nanoparticles, resulting in several orders of magnitude drop in the Raman signal.

Our main observation is that, in small nanoparticle, the local field enhancement due to reduced screening in the surface layer can provide an additional enhancement of the Raman signal. Although the thickness of the surface layer (0.1-0.3 nm) is small as compared to overall nanoparticle size [15]–[17], such an enhancement can be considerable for a molecule located in a close proximity to the surface. In Fig. 4 we show the results of our numerical calculations of the Raman enhancement factor for various surface layer thicknesses, \( \Delta \). Although the overall magnitude of the enhancement increases with \( \Delta \), a more important effect is its size-dependence. For finite \( \Delta \), the enhancement factor decreases more slowly that in the absence of the surface layer: as nanoparticle size decreases from \( R = 5 \) nm to \( R = 1 \) nm, the signals strength ratio between \( \Delta = 0.3 \) nm and \( \Delta = 0 \) nm increases from \( \simeq 1.5 \) to \( \simeq 4.0 \). The reason is that, as the nanoparticle becomes smaller, the fraction of the surface layer increases, and so does the contribution of the unscreened local field into SERS.

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Figure 2: Raman enhancement factor as a function of nanoparticle size for different surface layer thicknesses.