Surface-Enhanced Raman Scattering in Small Noble-Metal Nanoparticles

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ABSTRACT

We present a microscopic theory of quantum-size effects in surface-enhanced Raman scattering (SERS) from molecules adsorbed on small metal nanoparticles. In noble-metal nanoparticles, the confining potential has different effect on s-band and d-band electrons. Namely, the spillout of delocalized sp-electrons beyond the classical nanoparticle boundary results in an incomplete embedding of s-electron distribution in the background of localized d-electrons whose density profile follows more closely the classical shape. We demonstrate that a reduction of d-electron screening in the surface layer leads to the enhancement of the surface plasmon local field acting on a molecule located in a close proximity to metal surface. Our numerical calculations of Raman enhancement factor, performed using time-dependent local density approximation, show additional enhancement of the Raman signal which becomes more pronounced for small nanoparticles due to the larger ratio of surface layer to overall nanoparticle size.

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 fixed at 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 a microscopic theory for SERS in noble-metal particle, based on the quantum extension of two-region model [15]–[17], [21], which describes the role of the surface-layer phenomenologically while treating conduction electrons quantum-mechanically within time-dependent density functional theory. 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 QUANTUM TWO-REGION MODEL

We consider SERS from a molecule adsorbed on the surface of Ag spherical particle with radius R. For $R \ll \lambda$, the frequency-dependent potential is determined from Poisson equation,

$$\Phi(\omega, \mathbf{r}) = \phi_0(\mathbf{r}) + e^2 \int d^3r' \frac{\delta N(\omega, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \qquad (1)$$

where $\phi_0(\mathbf{r}) = -e\mathbf{E}_i \cdot \mathbf{r}$ is potential of the incident light with electric field amplitude $\mathbf{E}_i = E_i\mathbf{z}$ along the z-axis, and $\delta N(\omega, \mathbf{r})$ is the induced density (hereafter we suppress frequency dependence). There are four contributions to $\delta N(\mathbf{r})$: from valence s-electrons, $\delta N_s(\mathbf{r})$, core d-electrons, $\delta N_d(\mathbf{r})$, dielectric medium, $\delta N_m(\mathbf{r})$, and the molecule, $\delta N_0(\mathbf{r})$. The density profile of delocalized s-electrons is not fully inbedded in the background of localized d-electrons but extends over that of localized d-electrons by $\Delta \sim 1 - 3$ Å[15]–[17]. Due to localized nature of the d-electron wave-functions, we can adopt a phenomenological description by assuming a uniform bulk-like d-electron ground-state density n_d in the region confined by $R_d < R$ with a sharp step-like edge. Then the induced charge density, $e\,\delta N_d(\mathbf{r}) = -\nabla\cdot\mathbf{P}_d(\mathbf{r})$, is expressed via electric polarization vector vanishing outside of the region $r < R_d$,

$$\mathbf{P}_d(\mathbf{r}) = \frac{\epsilon_d - 1}{4\pi}\,\theta(R_d - r)\mathbf{E}(\mathbf{r}) = -\frac{\epsilon_d - 1}{4\pi e}\,\theta(R_d - r)\nabla\Phi(\mathbf{r}), \tag{2}$$

where $\epsilon_d(\omega)$ is the core dielectric function which can be taken from experiment. Similarly, dielectric medium contribution, which is nonzero for $r > R$, is given by

$$\begin{aligned} e\,\delta N_m(\mathbf{r}) &= -\nabla\cdot\mathbf{P}_m(\mathbf{r}),\\ e\,\mathbf{P}_m(\mathbf{r}) &= -\frac{\epsilon_m - 1}{4\pi}\,\theta(r - R)\nabla\Phi(\mathbf{r}), \end{aligned} \tag{3}$$

where ϵ_m is medium dielectric constant. We represent the molecule by a point dipole with dipole moment $\mathbf{p}_0 = \alpha_0\mathbf{E}$, where α_0 is the molecule polarizability tensor, so that

$$\begin{aligned} &e\,\delta N_0(\mathbf{r}) = -\nabla\cdot\mathbf{P}_0(\mathbf{r}),\\ &e\,\mathbf{P}_0(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_0)\,\mathbf{p}_0 = -\delta(\mathbf{r} - \mathbf{r}_0)\,\alpha_0\nabla\Phi(\mathbf{r}_0), \end{aligned} \tag{4}$$

where $\mathbf{r}_0$ is the vector pointing at the molecule location (we chose origin at the sphere center).

Using Eqs. (2-4), the potential $\Phi(\mathbf{r})$ in Eq. (1) can be expressed in terms of only induced s-electron density, δN_s. Substituting 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 integrating by parts, we obtain,

$$\begin{aligned} \epsilon(r)\Phi(\mathbf{r}) = \phi_0(\mathbf{r}) &+ e^2\int d^3r'\frac{\delta N_s(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\\ &+\frac{\epsilon_d - 1}{4\pi}\int d^3r'\nabla'\frac{1}{|\mathbf{r} - \mathbf{r}'|}\cdot\nabla'\theta(R_d - r)\Phi(\mathbf{r}')\\ &+\frac{\epsilon_m - 1}{4\pi}\int d^3r'\nabla'\frac{1}{|\mathbf{r} - \mathbf{r}'|}\cdot\nabla'\theta(r - R)\Phi(\mathbf{r}')\\ &-\nabla_0\frac{1}{|\mathbf{r} - \mathbf{r}_0|}\cdot\alpha_0\nabla_0\Phi(\mathbf{r}_0), \end{aligned} \tag{5}$$

where $\epsilon(r) = \epsilon_d$, 1, and ϵ_m in the intervals $r < R_d$, $R_d < r < R$, and $r > R$, respectively. Since the source term has the form $\phi(\mathbf{r}_0) = \phi(r_0)\cos\theta = -eE_i r\cos\theta$, we expand Φ and δN_s in terms of spherical harmonics and, keeping only the dipole term ($L = 1$), obtain,

$$\begin{aligned} \epsilon(r)\Phi(r) = \phi_0(r) &+ e^2\int dr' r'^2 B(r, r')\delta N_s(r')\\ &-\frac{\epsilon_d - 1}{4\pi}R_d^2\partial_{R_d}B(r, R_d)\Phi(R_d)\\ &+\frac{\epsilon_m - 1}{4\pi}R^2\partial_R B(r, R)\Phi(R)\\ &-\nabla_0[B(r, r_0)\cos\theta_0]\cdot\alpha_0\nabla_0[\Phi(r_0)\cos\theta_0], \end{aligned} \tag{6}$$

where θ_0 is the angle between molecule position and incident light direction (z-axis), and

$$B(r.r') = \frac{4\pi}{3}\left[\frac{r'}{r^2}\,\theta(r - r') + \frac{r}{r'^2}\,\theta(r' - r)\right] \tag{7}$$

is the dipole term of the radial component of the Coulomb potential.

The second terms in rhs of Eq. (6) is the s-electrons contribution to total induced potential, while the third and fourth terms originate from the scattering due to change of dielectric function at $r = R_d$ and $r = R$, respectively. The last term represents the potential of the molecular dipole. The latter depends on the molecule orientation with respect to the nanoparticle surface. In the following we assume averaging over random orientations and replace the polarizability tensor by isotropic α_0.

The values of Φ at the boundaries and at the molecule position can be found by setting $r = R_d, R, r_0$ in Eq. (6). In doing so, the total potential is expressed in terms of only s-electron induced density δN_s. Within TDLDA formalism, the latter can be related back to the potential via

$$\delta N_s(\mathbf{r}) = \int d^3r'\Pi_s(\mathbf{r}, \mathbf{r}')\Big[\Phi(\mathbf{r}') + V_x'[n(r')]\delta N_s(\mathbf{r}')\Big], \tag{8}$$

where $\Pi_s(\mathbf{r}, \mathbf{r}')$ is the polarization operator for noniteracting s-electrons, $V_x'[n(r')]$ is the (functional) derivative of the exchange-correlation potential (in the endependent-particle approximation) and $n(r)$ is electron ground-state density. The latter is calculated in a standard way using Kohn-Sham equations for jelium model, and then is used as imput in the evaluation of Π_s and V_x'. Eqs. (6) and (8) determine the self-consistent potential in the presence of molecule, nanoparticle, and dielectric medium.

3 CALCULATION OF RAMAN SIGNAL

In the conventional SERS picture, the enhancement of Raman signal from the molecule comes from two sources: far-field of the radiating dipole of the molecule in the local nanopartricle field, and the secondary scattered field of this dipole by the nanoparticle. Accordingly, we present total potential as a sum $\Phi = \phi + \phi^R$,

where ϕ^R is the potential of the radiating dipole. Since the molecular polarizability is very small, in the following we will restrict ourselves by the lowest order in α_0, i.e., ϕ is the potential in the absence of molecule and ϕ_R determines the Raman signal in the first order in α_0. Inclusion of higher orders leads to the renormalization of molecular and nanoparticle polarizabilities due to image charges; these effects are not considered here. In the same manner, the induced s-electron density can be decomposed into two contributions, $\delta N_s = \delta n + \delta n^R$, originating from the electric field of incident light and that of the radiating dipole.

Keeping only zero-order terms in Eq. (6), we have

$$\epsilon(r)\phi(r) = \bar{\phi}(r) - \frac{\epsilon_d - 1}{3}\beta(r/R_d)\phi(R_d) + \frac{\epsilon_m - 1}{3}\beta(r/R)\phi(R), \quad (9)$$

where

$$\bar{\phi}(r) = \phi_0(r) + e^2 \int dr' r'^2 B(r, r')\delta n_s(r'), \quad (10)$$

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

$$\beta(x) = x^{-2}\,\theta(x-1) - 2x\theta(1-x). \quad (11)$$

The boundary values of ϕ can be obtained by matching $\phi(r)$ at $r = R_d, R$,

$$\begin{aligned}(\epsilon_d + 2)\phi(R_d) + 2a(\epsilon_m - 1)\phi(R) &= 3\bar{\phi}(R_d)\\ (\epsilon_d - 1)a^2\phi(R_d) + (2\epsilon_m + 1)\phi(R) &= 3\bar{\phi}(R)\end{aligned} \quad (12)$$

where $a = R_d/R$. Substituting $\phi(R_d)$ and $\phi(R)$ back into Eq. (9), we arrive at

$$\epsilon(r)\phi(r) = \bar{\phi}(r) - \beta(r/R_d)\,\frac{\lambda_d}{\eta}\left[\bar{\phi}(R_d) - 2a\lambda_m\bar{\phi}(R)\right] + \beta(r/R)\,\frac{\lambda_m}{\eta}\left[\bar{\phi}(R) - a^2\lambda_d\bar{\phi}(R_d)\right], \quad (13)$$

where

$$a = R_d/R, \quad \lambda_d = \frac{\epsilon_d - 1}{\epsilon_d + 2}, \quad \lambda_m = \frac{\epsilon_m - 1}{2\epsilon_m + 1}, \quad \eta = 1 - 2a^3\lambda_d\lambda_m \quad (14)$$

It is convenient to separate out δn_s-independent contribution by writing

$$\phi = \varphi_0 + \delta\varphi_0 + \delta\varphi_s, \quad (15)$$

where $\varphi_0 = \phi_0/\epsilon(r) = -eE_i r/\epsilon(r)$,

$$\delta\varphi_0(r) = \frac{1}{\epsilon(r)}\Big[-\beta(r/R_d)\phi_0(R_d)\,\lambda_d(1 - 2\lambda_m)/\eta + \beta(r/R)\phi_0(R)\,\lambda_m(1 - a^3\lambda_d)/\eta\Big], \quad (16)$$

and

$$\delta\varphi_s(r) = \int dr' r'^2 A(r, r')\delta n_s(r'), \quad (17)$$

with

$$A(r, r') = \frac{e^2}{\epsilon(r)}\Bigg[B(r, r') - \beta(r/R_d)\Big[B(R_d, r') - 2a\lambda_m B(R, r')\Big]\lambda_d/\eta + \beta(r/R)\Big[B(R, r') - a^2\lambda_d B(R_d, r')\Big]\lambda_m/\eta\Bigg]. \quad (18)$$

Note that $\delta\varphi_s(r)$ as well as the total potential $\phi(r)$ are continuous at $r = R_d, R$.

Turning to Eq. (8), we use decompositions $\Phi = \phi + \phi^R$ and $\delta N_s = \delta n_s + \delta n_s^R$ to obtain decoupled equations for quantities of zero and first orders in α_0. Then, expanding both parts in spherical harmonics and keeping only the dipole ($L = 1$) terms, we obtain

$$\delta n_s(r) = \int dr' r'^2 \Pi_s(r, r')\Big[\phi(r') + V_x'(r')\delta n_s(r')\Big]. \quad (19)$$

Using Eqs. (15) and (17) then leads to a closed equation for δn_s,

$$\delta n_s(r) = \int dr' r'^2 \Pi_s(r, r')\Big[\varphi_0(r') + \delta\varphi_0(r')\Big] + \int dr' r'^2 \Pi_s(r, r')\Bigg[\int dr'' r''^2 A(r', r'')\delta n_s(r'') + V_x'(r')\delta n_s(r')\Bigg], \quad (20)$$

with $A(r, r')$ given by Eq. (18). The effect of d-electrons and dielectric medium is thus encoded in the functions $A(r, r')$ and $\delta\varphi_0(r)$, which reduce to $B(r, r')$ and 0, respectively, for $\epsilon_d = \epsilon_m = 1$.

Turning to the first order in α_0, the equation for ϕ^R takes the form,

$$\epsilon(r)\phi^R(r) = \bar{\phi}^R(r) - \frac{\epsilon_d - 1}{3}\beta(r/R_d)\phi^R(R_d) + \frac{\epsilon_m - 1}{3}\beta(r/R)\phi^R(R), \quad (21)$$

with

$$\bar{\phi}^R(r) = \phi_0^R(r) + e^2 \int dr' r'^2 B(r, r')\delta n_s^R(r'), \quad (22)$$

where

$$\phi_0^R(r) = -\alpha_0\nabla_0[B(r, r_0)\cos\theta_0] \cdot \nabla_0[\phi(r_0)\cos\theta_0], \quad (23)$$

is the potential of the molecular dipole in the presence of local field and $\delta n_s^R(r)$ is the induced charge of s-electrons due to molecular potential. The frequency dependence of the Raman field $\phi^R(\omega_s, r)$ is determined by

the Stokes shift $\omega_s = \omega - \omega_0$, where ω_0 is the vibrational frequency of the molecule as determined by α_0. The last two terms in Eq. (21) describe potential of molecular dipole scattered from the nanoparticle boundaries at R_d and R. For simplicity, we only consider the case when the molecule is located at the z-axis ($\theta_0 = 0$) so that molecular dipole potential is given by

$$\phi_0^R(r) = -\frac{4\pi\alpha_0}{3r_0^2}\,\beta(r/r_0)\,\frac{\partial\phi(r_0,\omega)}{\partial r_0} = -\chi(\omega)\,eE_i\Big[r\theta(r_0-r) - \frac{r_0^3}{2r^2}\,\theta(r-r_0)\Big], \quad (24)$$

where

$$\chi(\omega) = \frac{8\pi\alpha_0}{3eE_i r_0^3}\frac{\partial\phi(r_0)}{\partial r_0} \quad (25)$$

Marching ϕ^R at $r = R_d$ and $r = R_d$, we obtain

$$\phi^R = \varphi_0^R + \delta\varphi_0^R + \delta\varphi_s^R = \chi(\omega)\Big[\tilde{\varphi}_0 + \delta\varphi_0 + \delta\tilde{\varphi}_s\Big], \quad (26)$$

where

$$\tilde{\varphi}_0(r) = -\frac{eE_i}{\epsilon(r)}\Big[r\theta(r_0-r) - \frac{r_0^3}{2r^2}\,\theta(r-r_0)\Big], \quad (27)$$

$\delta\varphi_0$ is given by Eq. (16) with ω_s instead of ω and

$$\delta\tilde{\varphi}_s(r) = \int dr' r'^2 A(r,r')\delta\tilde{n}_s(r'), \quad (28)$$

where $A(r,r')$ is given by Eq. (18), with ω_s instead of ω, and $\delta\tilde{n}_s(r) = \delta n_s^R(r)/\chi(\omega)$ satisfies Eq. (20) but with $\tilde{\varphi}_0(r)$ instead of $\varphi_0(r)$ (and ω_s instead of ω). In the following we consider the case when the molecule is located at the distance of several angstroms from the nanoparticle classical boundary, so the overlap between the molecular orbitals and the s-electron wave function is small. Then we have

$$\int dr' r'^2 \Pi_s(r,r')\tilde{\varphi}_0(r') \simeq \int dr' r'^2 \Pi_s(r,r')\varphi_0(r'), \quad (29)$$

leading to $\delta\tilde{n}_s(r) \simeq \delta n_s(r)$ and, correspondingly, $\delta\tilde{\varphi}_s(r) \simeq \delta\varphi_s(r)$. The Raman signal is determined by the far-field asymptotics of $\phi^R(r)$. From Eqs. (16-18), we find for $r \gg R$

$$\delta\varphi_0(r) = \frac{eE_i}{\epsilon_m r^2}\,\alpha_d, \quad \delta\varphi_s(r) = \frac{eE_i}{\epsilon_m r^2}\,\alpha_s, \quad (30)$$

with

$$\alpha_d(\omega_s) = R^3\Big[1 - (1+\lambda_m)(1-a^3\lambda_d)/\eta\Big],$$

$$\alpha_s(\omega_s) = \frac{4\pi}{3eE_0}\Bigg[\int_0^\infty dr' r'^3\delta n_s(r') - \Big[1-(1+\lambda_m)(1-\lambda_d)/\eta\Big]\int_0^R dr' r'^3\delta n_s(r') - \Big[1-(1+\lambda_m)(1-a^3\lambda_d)/\eta\Big]R^3\int_R^\infty dr'\delta n_s(r') + \Big[(1+\lambda_m)\lambda_d/\eta\Big]\int_{R_d}^R dr'(r'^3 - R_d^3)\delta n_s(r')\Bigg], \quad (31)$$

and using Eq. (27) we obtain for the far field

$$\phi^R(r) = \frac{eE_i r_0^3}{2\epsilon_m r^2}\,\chi\Big[1 + 2(\alpha_d+\alpha_s)/r_0^3\Big]. \quad (32)$$

Turning to χ, we note that for small molecule-nanopatricle overlap, the local potential at the molecule location can be evaluated using the far-field expressions Eqs. (30). We then obtain

$$\frac{\partial\phi_0}{\partial r_0} = -\frac{eE_i}{\epsilon_m}\Big[1 + 2(\alpha_d+\alpha_s)/r_0^3\Big], \quad (33)$$

and, substituting into Eq. (32), we finally arrive at

$$\phi^R(r) = -\frac{4\pi\alpha_0 eE_i}{3\epsilon_m r^2}\Big[1+2g(\omega)\Big]\Big[1+2g(\omega_s)\Big], \quad (34)$$

with

$$g = \frac{\alpha}{r_0^3}, \quad \alpha = \alpha_d + \alpha_s. \quad (35)$$

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.

Finally, the enhancement factor is given by the ratio of Raman to incident field intensities,

$$A(\omega,\omega_s) = \Big|1 + 2g(\omega) + 2g(\omega_s) + 4g(\omega)g(\omega_s)\Big|^2. \quad (36)$$

4 NUMERICAL RESULTS

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 $\gamma_s \simeq v_F/R$. At the resonance frequency, the size-dependence of SERS is quite strong. Indeed, if molecular vibrational frequencies are smaller that 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

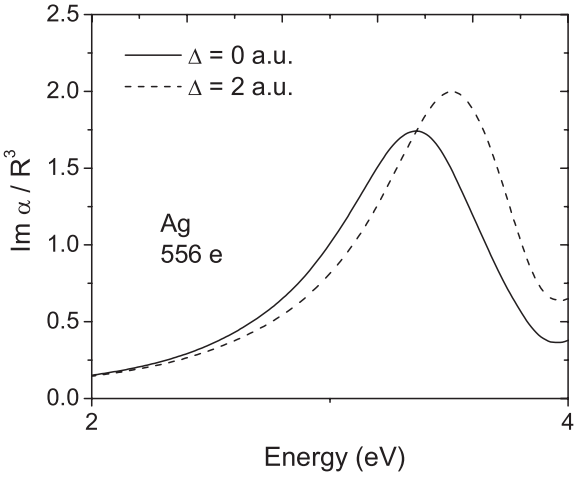

Figure 1: Calculated nanoparticle polarizability for different surface layer thicknesses

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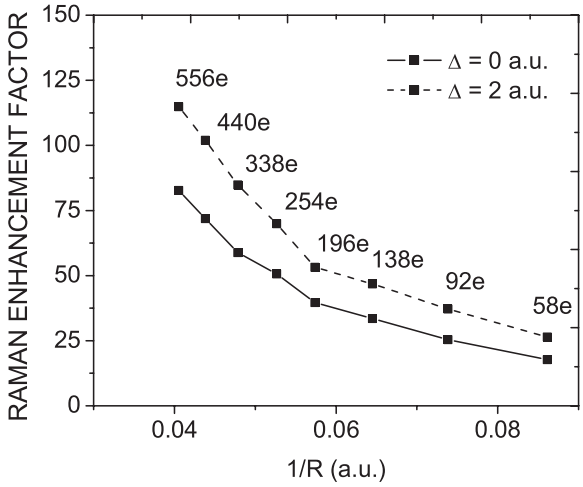

Figure 2: Size-dependence of enhancement factor for different surface layer thicknesses.

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 oveall nanoparticle size [15]–[17], such an enhancement can be condiderable for a molecule located in a close proximity to the surface. In Fig. 1 we show the calculated polarizability with and without surface layer. 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. At the same time, an increase in the peak amplitude, which accompanies the blueshift, indicates a stronger local field at resonance energy acting on a molecule in a close proximity to nanoparticle surface.

In Fig. 2 we show the results of our numerical calculations of SERS with and without surface layer thicknesses, Δ for different nanoparticle sizes. Although the overall magnitude of the enhancemet increases with Δ, a more important effect is its size-dependence. For finite Δ, the enhancement factor descreases more slowly that in the absence of the surface layer: as nanoparticle size decreases, the signals strength ratio *increases*. 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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