

Effects of quantum tunneling in metal nanogap on surface-enhanced Raman scattering

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The quantum tunneling effects between two silver plates are studied using the time dependent density functional theory. Our results show that the tunneling depends mainly on the separation and the initial local field of the interstice between plates. The smaller separation and larger local field, the easier the electrons tunnels through the interstice. Our numerical calculation shows that when the separation is smaller than 0.6 nm the quantum tunneling dramatically reduces the enhancing ability of interstice between nanoparticles. © 2009 American Institute of Physics.

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Metal nanogaps offering strong surface plasmon couplings have very rich physical properties. The related studies have been very hot topics in the field of plasmonics, e.g., single molecule surface-enhanced Raman spectroscopy,^{1,2} optical nanoantennas,³ and high-harmonic generation.⁴ The electromagnetic (EM) enhancement near the metal surface, which is caused by the resonant excitation of surface plasmon,⁵ is the dominating reason for the surface-enhanced Raman scattering (SERS).^{1,6} Huge SERS with single molecule sensitivity can be obtained when molecules are located in the nanogap between two metallic nanostructures.^{1,2,7-9} A lot of efforts have been made to seek extreme sensitive SERS substrates.¹⁰⁻¹²

Theoretically, people have used many methods based on the classical electrodynamics¹³⁻¹⁵ to estimate the SERS enhancement. These classical results indicate that the smaller the nanogap, the higher the enhancement. However, as the separation decreases to 1 nm, the dispersive current would partly become electron tunneling current, which can reduce the EM enhancement substantially.¹⁶ A recent experiment on the four-wave mixing at coupled gold nanoparticles clearly demonstrated that the quantum tunneling (QT) effect becomes significant for the distance smaller than 0.2 nm,¹⁷ and a recent study of the plasmon resonance of a nanoparticle dimer gave quantum description of such a phenomenon.¹⁸ It is well known that the EM enhancement is the main contribution to SERS. Its enhancement factor is proportional to the fourth power of the local field enhancement, i.e., M^4 , where $M = |E_{\text{loc}}|/|E_0|$ with E_{loc} and E_0 being the local enhanced electric field and the incident electric field, respectively. Therefore, even for small QT effects on M , after a fourth power, the influence to SERS could be huge. In this letter we investigate the effects of QT on SERS with the time dependent density functional theory.¹⁹ Our studies are able to quantify these effects and point out at exactly what conditions the QT has to be taken into account.

As the “hot spot,” where the SERS is strongest, is localized in a very small volume in the interstice between particles, it is convenient to investigate the QT effect between two closely placed plates instead of two nanoparticles. As

shown in Fig. 1, in the vicinity of the hot spot (shaded area), two plates are not much different from two nanospheres. Besides we use two approximations for our numerical calculations. (1) In the generalized Mie theory, the electric current inside nanosphere is set to be zero¹³ so we can regard the silver plates as equipotential bodies at all time in our calculation. (2) The laser field is treated as a static electric field, and the QT effect in an oscillating field can be described by the results of static field in one period of laser. With these simplifications, when the separation d is not very small, the electric tunneling effect can be studied by the method developed by Simmons,²⁰ which regard electrons are tunneling through a voltage barrier. We find that Simmons' method is not proper when the distance $d < 1$ nm. For example, at $d = 0.6$ nm, the mean barrier height becomes negative at low voltage limit, indicating the failure of this method.

In this work we adopt a more sophisticated method, the time dependent density functional theory¹⁹ with the jellium model, where the ionic lattice is treated as a uniform positive charge background. In this method, we solve self-consistently a set of time dependent Schrödinger equations

$$i \frac{\partial}{\partial t} \psi_k = \left[-\frac{1}{2} \frac{\partial^2}{\partial x^2} + V_{\text{eff}}(x, t) + V_{\text{ext}}(x, t) \right] \psi_k, \quad (1)$$

where we have used the atomic units and ψ_k denotes a quantum state inside the Fermi surface of the silver plate. $V_{\text{ext}}(x, t)$ is the external potential coming from the laser field and its induced field. $V_{\text{eff}}(x, t)$ is the effective potential felt

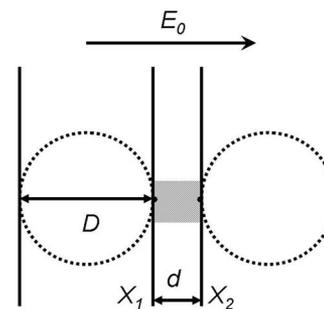


FIG. 1. Schematic drawing of the hot spot between two silver nanospheres. As the hot spot (shaded area) is small, its local field is almost identical to the one computed by replacing the sphere with a plate. E_0 is the incident laser field.

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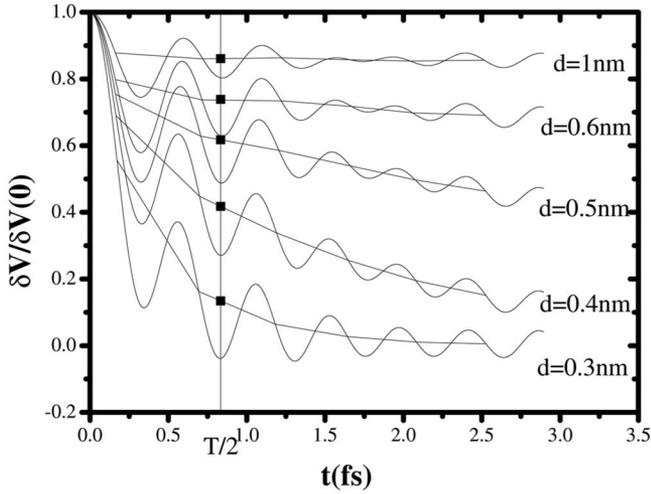


FIG. 2. Time evolutions of the potential difference δV between the silver plates for different separations $d=0.3, 0.4, 0.5, 0.6,$ and 1 nm. $D=6$ nm; $E_0=2.74 \times 10^5$ V/m; $M=1000$. Dashed lines are for the averaged $\delta \bar{V}$.

by an electron through Coulomb interaction and correlation and exchange. In our approach, we use Crank–Nicholson method²¹ to update the wave function. To quantify the QT effects on the SERS, we monitor time evolution of the potential difference δV between the two silver plates. We compute δV with the formula

$$\delta V(t) = V_{\text{eff}}\left(\frac{x_l^l + x_r^r}{2}, t\right) - V_{\text{eff}}\left(\frac{x_l^l + x_l^r}{2}, t\right), \quad (2)$$

where $x_{r,l}^l$ and $x_{r,l}^r$ are coordinates of the left and right surfaces of the right (left) plate.

Let us now turn on the laser field. The electrons inside each silver plate will start moving instantly to counter the applied electric field so that the total electric field inside each plate is zero. At the same time, an enhanced field is induced in the hot spot. Afterward, the electrons will start to tunnel between the two silver plates under the following external potential

$$V_{\text{ext}}(x, t) = \begin{cases} E_0 x & x < X_1, \\ E_{\text{loc}}(x - X_1) + E_0 X_1 & X_1 \leq x \leq X_2, \\ E_0(x - d) + E_{\text{loc}} d & x > X_2. \end{cases} \quad (3)$$

The initial electron state for the Schrödinger equations in Eq. (1) is the state where the electrons have moved to counter-balance the incident laser field. To obtain this initial state, we compute with the method developed by Schulte²² the ground state of the metallic plate under the following external potential

$$V^0(x) = \begin{cases} 0 & x < x^l, \\ E_0(x - x^l) & x^l < x < x^r, \\ E_0 D & x > x^r, \end{cases} \quad (4)$$

where x^l and x^r are the left and right surfaces of the plate and D is the width of the plate.

Figure 2 shows the calculated time evolution of the potential difference δV between the two plates separated by $d=0.3-1$ nm. The strength of the incident electric field is $E_0=2.74 \times 10^5$ V/m, corresponding to a laser with power $P=100$ μ W and focal spot ~ 1 μ m. In most SERS experiments, even for single molecule detection, a much smaller

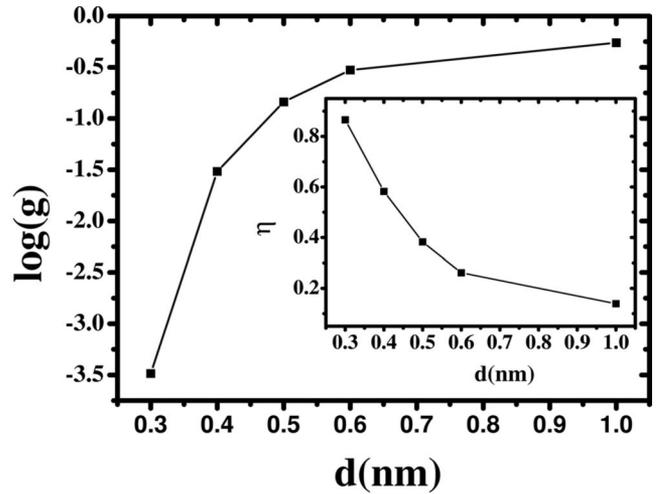


FIG. 3. $\log(g)$ as a function of the separation d . $D=6$ nm; $E_0=2.74 \times 10^5$ V/m. $M=1000$; $\lambda=500$ nm. The inset shows the decay rate η of δV .

$P \sim 1$ μ W is used.^{1,2} The diameter of nanoparticle is $D=6$ nm. Note that we have calculated for three different diameters $D=4, 5,$ and 6 nm and the results are almost identical. This indicates that the physical process in the hot spot is not sensitive to geometric features that are far away, further justifying our replacement of the spheres with the plates.

We see in Fig. 2 that δV decays while oscillating with a frequency close to the bulk plasma frequency. The decay gets severe as the separation becomes smaller. This kind of decay can be intuitively understood by viewing the system as a bad capacitor that leaks current.

To measure the decay, or the QT suppression of the enhanced field, we introduce a decay rate defined by

$$\eta = 1 - \delta \bar{V}\left(\frac{T}{2}\right) / \delta V(0), \quad (5)$$

where T is the typical optical period of the incident laser, e.g., $T=1.67$ fs for a laser wavelength $\lambda=500$ nm. Note that $\delta \bar{V}(T/2)$ is not the value of δV but the averaged value of δV over one oscillation period at $t=T/2$. Consequently, the reduction of SERS enhancement factor is

$$g = \left[\tilde{E}_b\left(\frac{T}{2}\right) / E_b(0) \right]^4 = (1 - \eta)^4, \quad (6)$$

where E_b is the electrical field strength between two plates. As the distance d decreases, the potential difference decays with time dramatically. At $d=0.3$ nm, the local field is reduced by $\sim 86.6\%$ after half optical period ($\lambda=500$ nm), that is, the SERS enhancement is 3.1×10^3 times smaller than the one obtained from classical theory. By contrast, at $d=1$ nm, there is only one time decrease of SERS enhancement factor. This means that the enhancement can be sustained if the separation is larger than 1 nm. The factor g for different separations are plotted in Fig. 3, where we see η (also g^{-1}) decreases dramatically as d increases. Specifically, when the separation is smaller than 0.6 nm, the reduction of the SERS enhancement by the QT becomes significant.

It is evident that both the enhancement factor M and the laser power P can affect the QT via the enhanced local field E_{loc} , which is proportional to $M\sqrt{P}$. We find through numerical calculations that for the range of laser power commonly

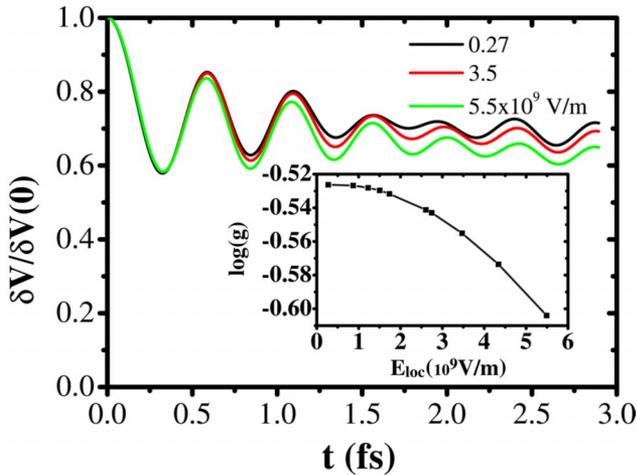


FIG. 4. (Color online) Time evolutions of the potential difference δV between the silver plates for different enhanced local electric fields E_{loc} . $d=0.6$ nm; $D=6$ nm. The inset shows $\log(g)$ as a function of the local electric field E_{loc} . $d=0.6$ nm; $D=6$ nm.

used in experiment, the deciding factor is $M\sqrt{P}$, not individual values of M and P . For example, we find that the time evolution of δV for $P=10$ mW, $M=100$, and $P=100$ μ W, $M=1000$ is almost the same (not shown). This means that we need to consider only the enhanced local field E_{loc} . Figure 4 shows the time evolutions of δV for different E_{loc} at $d=0.6$ nm and $D=6$ nm. We see clearly that larger local field induce larger QT, which in turn reduces the enhancement. As shown in the inset in Fig. 4, The factor g increases slowly when $E_{\text{loc}} < 2 \times 10^9$ V/m, and reaches a nonzero constant when E_{loc} goes to 0. This can be explained by the fact that when the tunneling is small, we still have the linear current-voltage relation,²⁰ $J(t) = \beta \delta V(t)$. From this relation, we obtain $\delta V(t) = \delta V(0)e^{-d\beta t}$. Therefore, when $\delta V(0) \rightarrow 0$, we have the minimal decay rate $\eta = 1 - \delta V(T/2) / \delta V(0) \rightarrow 1 - e^{-d\beta T/2}$.

We emphasize that the reduced SERS calculated by us is not necessarily the overall SERS of a molecule placed in the nanogap. With a molecule in the gap, the situation can become much more complex: (1) the oscillatory tunneling current can be coupled to the molecule inelastically, generating additional Raman signals;^{23,24} (2) the chemical enhancement can also be affected by the QT.²⁵ Thus the reduced EM enhancement might be compensated or even overcompensated

by these two factors. More studies are needed to clarify the issue.

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