A Quantum Mechanical Theory for Single Molecule−Single Nanoparticle Surface Enhanced Raman Scattering

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Single molecule−single nanoparticle surface enhanced Raman scattering event is analyzed using a quantum mechanical approach, resulting in an analytical expression for the electromagnetic enhancement factor that succinctly elucidates the fundamental aspects of SERS. The nanoparticle is treated as a dielectric spherical cavity, and the resulting increase in the spontaneous emission rate of a molecule adsorbed onto the surface of the nanoparticle is examined. The overall enhancement in Raman scattering is due to both the increased local electromagnetic field and the Purcell effect. The predictions of the present model are in agreement with the simulation results of the classical model.

Introduction

Since its first discovery in 1977, surface enhanced Raman scattering (SERS) has drawn much attention due to its ability to extract structural information of the molecules with an enhanced detection signal.[1,2] Single molecule−single nanoparticle SERS processes were first demonstrated in 1997.[3,4] The so-called "hot sites", which may be a single spherical nanoparticle (NP) or aggregates of NPs, showed a dramatically enhanced Raman scattering cross section, 10^{-16} cm²/molecule, as compared to that for the traditional Raman scattering, 10^{-30}−10^{-25} cm²/molecule, namely a SERS enhancement factor as high as ~10^{14}.[2] In spite of this remarkable finding, no widely accepted theoretical explanation has, however, been hitherto available for the single molecule−single nanoparticle SERS process.

It is generally believed that electromagnetic (EM) enhancement is the single most important mechanism responsible for the SERS enhancement.[5−12] As a result, most theoretical studies to date have concentrated on elucidation of the EM enhancement, in which the classical Mie scattering theory was almost exclusively employed to study the local EM field, or the surface plasmon wave.[13] A drawback of this classical EM approach is, due to the complexity of the Mie scattering, that numerical calculation was mostly unavoidable, making it difficult to derive an analytical expression for the SERS enhancement factor. Consequently, comprehensive discernment of the various physical processes underlying SERS has been elusive. Recently, V. S. Zuev and co-workers derived an analytical expression for the single molecule−single nanowire SERS process using a quantum mechanical approach.[14] Their analytical expression, however, was applicable only to nanowires (NWs) with a height equal to the half wavelength of the incident photon. Furthermore, to obtain the analytical expression, they assumed that the direction of the incident optical field was either parallel or orthogonal to the NW axis, thus limiting the applicability of the expression to a very special case. Since most single-

molecule-detection experiments have been carried out using NPs, which may be more accurately approximated by spheres than by cylinders, there still is a need, and it is worthwhile, to formulate a theory based on quantum mechanics for the single molecule−single nanoparticle SERS process. The present work is to satisfy such a need.

Derivation

The underlying theoretical approach of the present work may be summarized as follows: the incident optical field excites surface plasmon waves on the NP surface, which in turn greatly enhances the local EM field. The NP acts as a microcavity which, owing to the Purcell effect, increases the density of the optical field modes. The much-enhanced local field and optical mode density, dictated by Fermi's golden rule, together give rise to an increase in the spontaneous emission rate of a molecule adsorbed onto the NP. As a result, the Raman scattering cross section, stimulated by both the incident and emitted photon, is greatly enhanced. In putting together these fundamental physical processes to formulate a theory, we first use the classical EM approach to approximate the surface plasmon wave, then the Purcell effect to calculate the optical mode density per unit energy ρ_E. Fermi's golden rule is then invoked to derive the enhancement factor for the spontaneous emission rate and Raman cross section. The results are finally combined to produce an analytical expression for the single molecule−single nanoparticle-SERS EM enhancement factor.

Although the metal NPs, used in practice and to be considered here, are in general irregular, they may very well be approximated by metal spheres with a radius a, which may be conveniently normalized to the incident optical field wavelength λ as $a_0 = 2\pi a/\lambda$. As will be discussed later, the shape of the NP, unlike its size, does not greatly affect the enhancement factor. Also, in spite of the fact that Mie scattering has been traditionally used as a means to solve the surface plasmon wave at the NP surface stimulated by the incident optical field,[13] one must note that in reality the size of a SERS-active NP is much smaller than the incident optical wavelength.[2,3] As a result, as shown by the familiar radar cross-section (RCS) plot for metal-

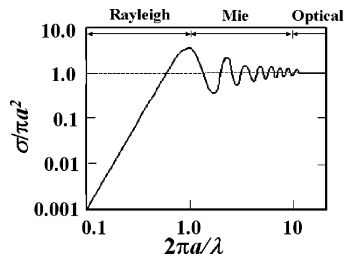* To whom correspondence should be addressed. E-mail: kevinkim@uiuc.edu.

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Figure 1. Dependence of the radar cross-section (RCS), σ, on the radius, a, of the spherical metal scatterer. λ is the incident photon wavelength.
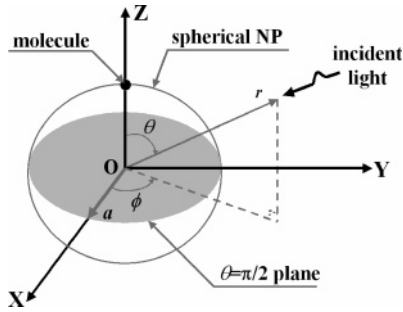

Figure 2. Spherical coordinates used in the present work.

sphere scattering reproduced, for convenience, in Figure 1,[15] the SERS process falls in the Rayleigh region, not the Mie region. In the Rayleigh region, the RCS increases monotonously with the NP radius for a given optical wavelength. Therefore, a SERS-active NP may be regarded as a spherical cavity uniformly excited by the incident photons. The EM field inside and outside the NP may then be determined as those of a cavity, instead of a general scattering object. As will be shown below, such approximation not only greatly simplifies the surface plasmon wave problem, but it is also valid as long as the radius-to-wavelength ratio is reasonably small compared to the Rayleigh limit, $2\pi a/\lambda = 1$.

The spherical coordinates used in this work to describe the single-molecule−single-nanoparticle SERS process are shown in Figure 2. For simplicity, the position of the molecule is taken as the north pole. The r, θ, and ϕ are the variables for the distance, zenith, and azimuth, respectively. The photon is incident from the angle θ. In general, the stimulated surface plasmon wave is in the principal (lowest) transverse magnetic (TM) mode, i.e., the TM_0 mode, which in this work may be approximated by the following fields directly derived from Maxwell's equations. For the TM_0 mode both the fields inside and outside of the spherical cavity have ϕ symmetry. The field inside the sphere is a standing wave with a finite value at the center of the sphere, and the field outside the sphere is a rapidly decaying wave traveling in the $+r$ direction. Thus, the vector potential inside the sphere may be written as

$$\vec{A}^{\text{inside}} = \hat{r} B \hat{J}_1(\beta_{\text{in}}r)P_1^0(\cos\theta) = \hat{r} B \hat{J}_1(\beta_{\text{in}}r)(\cos\theta) \quad (1)$$

where $\hat{r}$ is the unit vector in the radial direction, β_{in} the wavenumber of the surface wave inside the sphere, $\hat{J}_1$ the first-kind spherical Bessel function of the first order, P_1^0 the associated Legendre function of the first kind, and B the amplitude constant that will be calculated later. The vector potential of the field outside the sphere is

$$\vec{A}^{\text{outside}} = \hat{r} R_A B \hat{h}_1^{(2)}(\beta_{\text{out}}r)P_1^0(\cos\theta) =$$
$$\hat{r} R_A B \hat{H}_1^{(2)}(\beta_{\text{out}}r)(\cos\theta) \quad (2)$$

where R_A is the relative amplitude constant, $\hat{H}_1^{(2)}$ the second-kind spherical Hankel function of the first order, and β_{out} is the wavenumber of the surface wave outside the sphere. Knowing the vector field, the electric field E and the magnetic field H can be directly calculated. By matching the boundary conditions we find

$$R_A = \frac{\hat{J}_1'(\beta_{\text{in}}a)}{\hat{H}_1^{(2)'}(\beta_{\text{out}}a)} \frac{\beta_{\text{in}}}{\beta_{\text{out}}} \quad (3)$$

where

$$\beta_{\text{in}} = \frac{2\pi f}{c}\sqrt{\epsilon_{\text{r,in}}}$$

$$\beta_{\text{out}} = \frac{2\pi f}{c}\sqrt{\epsilon_{\text{r,out}}}$$

$$\frac{\beta_{\text{in}}}{\beta_{\text{out}}} = \sqrt{\frac{\epsilon_{\text{r,in}}}{\epsilon_{\text{r,out}}}} \quad (4)$$

Here $\epsilon_{\text{r,in}}$ and $\epsilon_{\text{r,out}}$ are the dielectric constants inside and outside the sphere, respectively. Denoting the wavenumber of the incident optical field as $k_0 = 2\pi/\lambda$, the real and imaginary part of the normalized wavenumber of the surface wave, $h_0 = \beta_{\text{in}}/k_0$, can be calculated. The amplitude constant B can be calculated according to the following relationship:

$$\int_V \left(\frac{1}{2}\epsilon\vec{E}^2 + \frac{1}{2}\mu\vec{H}^2\right)dV = \hbar\omega \quad (5)$$

where ϵ is the local permittivity and μ is the local permeability (in the present case μ is always equal to the vacuum permeability μ_0). Equation 5 is a simple physical statement that, due to energy conservation, the total electromagnetic energy stored in the entire space is equal to the incident photon energy. In principle, both the fields inside and outside the sphere need to be considered in the integration of eq 5. However, since the field outside the sphere decays very rapidly, the field is mainly confined to inside of the sphere, and one may use the ideal spherical-cavity model to approximate the integration in eq 5.[16] In the actual calculation we also make use of the condition that the stored electric field energy is equal to the stored magnetic field energy. Detailed calculations can be found in 10.4.3 of ref 16. As a result, the square of the amplitude constant may be obtained as

$$B^2 = \frac{0.1554\hbar\omega\mu a}{\pi} \quad (6)$$

Since the EM fields inside and outside the NP have been completely determined, we are now ready to calculate the spontaneous photon emission rate of the adsorbed molecule (considered as an atom in the following quantum mechanical approach). The single-photon transition probability of an atom interacting with an optical field is given by Fermi's golden rule as

$$w_{n|0} = \frac{2\pi}{\hbar}|H_{n|0}|^2\rho_E \quad (7)$$

where $H_{n|0}$ is the matrix element of the Hamiltonian operator representing the interaction between the photon field and the

atom, and ρ_E the density of the optical field modes per unit energy. The interaction Hamiltonian is

$$\hat{H} = -\frac{e}{m}(\vec{p}\vec{A}) \tag{8}$$

where $\vec{p}$ is the electron momentum, e the electron charge, m the electron mass, and $\vec{A}$ the vector potential of the field:

$$\vec{A}(\vec{r},\vec{t}) = (a_\lambda + a_\lambda^+)\vec{A}_\lambda(\vec{r}) = (a_\lambda + a_\lambda^+)\vec{A}_\lambda^{\text{outside}}(\vec{r}) \tag{9}$$

where a_λ and a_λ^+ are the photon annihilation and creation operator, respectively. Therefore,

$$H_{n|0} = -\frac{e}{m}\int \Psi_a^* \Psi_{n\lambda}^* (\vec{p}(a_\lambda + a_\lambda^+))\vec{A}_\lambda(\vec{r})\Psi_b\Psi_{n\lambda'}\,dV \tag{10}$$

where ψ_λ and $\psi_{\lambda'}$ are the wave functions of the radiation field, ψ_a and ψ_b the wave functions of a free atom, and dV a volume element. Assuming that the vector field does not change much in the regions of the space where ψ_a and ψ_b take on appreciable values and taking into consideration only the spontaneous emission, one may calculate the matrix element $H_{n|0}$:

$$H_{n|0} = i\sqrt{\frac{1}{2}}e\omega x_{ab}\vec{A}_\lambda^{\text{outside}}(\vec{r}) \tag{11}$$

where x_{ab} is the matrix element of a molecule oscillating in an external optical field satisfying $\int\Psi_a^*\vec{p}\,\Psi_b dV = i\omega m x_{ab}$. Note that eq 11 is a general expression independent of the shape of the NP.

One may now apply the above results to a special case involving a spherical NP. Upon substitution of eq 2 into eq 11, one obtains at $r = a$, assuming that the molecule is very close to the NP surface:

$$|H_{n|0}|^2 = \frac{e^2\omega^2}{2}|x_{ab}|^2|R_A|^2|B|^2[\hat{H}_1^{(2)}(\beta_{\text{out}}a)]^2(\cos^2\theta) \tag{12}$$

Clearly, when θ is 0 or π (i.e., in the direction along the incident optical field), $|H_{n|0}|^2$ takes on the maximum value, and it is 0 when θ is $\pi/2$ or $3\pi/2$ (i.e., in the direction perpendicular to the incident optical field).

To calculate ρ_E one makes use of the relationship $\rho_E = Q_{\text{eff}}/(\hbar\omega)$ provided by the Purcell effect, where Q_{eff} is the effective quality factor of the spherical cavity describing its energy conservation ability. In the present case, since noble metals are usually used for SERS, the propagation loss is dominant in the calculation of the quality factor. For a spherical cavity one may use[14]

$$Q_{\text{effective}} = Q_{\text{propagation}} = Re\{h_0\}/Im\{h_0\} \tag{13}$$

which can be determined straightforwardly from the solution of the field internal to the NP. Note that sphere is the shape most effective for energy conservation. If the shape of the cavity changes or the irregularities are considered, one needs to modify the quality factor to account for the shape effect by introducing Q_{shape}, so that the total effective quality factor is $Q_{\text{effective}} = (Q_{\text{propagation}}^{-1} + Q_{\text{shape}}^{-1})^{-1}$, which will be smaller than that of an ideal sphere with the same volume.

Substituting eqs 12 and 13 into eq 7, one may obtain the spontaneous emission rate of a molecule on the NP surface into the TM$_0$ mode surface wave of the NP as

$$w_{n|0}^{(\text{TM}_0)} = F_1 \cdot F_2 \tag{14}$$

where[17]

$$F_1 = \frac{1}{4\pi\epsilon_0\epsilon_{\text{r,out}}}\frac{4}{3}\frac{e^2\omega^3}{\hbar c^3}|x_{ab}|^2 \tag{15}$$

represents the spontaneous emission rate of a dipole into the free space or without the NP, where ϵ_0 is the vacuum permittivity and

$$|F_2| = \frac{3\pi^2\epsilon_0\epsilon_{\text{r,out}}c^3}{\hbar\omega^2}|B|^2|R_A|^2|\hat{H}_1^{(2)}(\beta_{\text{out}}a)|^2(\cos^2\theta)\cdot Q_{\text{eff}} \tag{16}$$

is the EM enhancement factor for the spontaneous emission rate due to the NP, where Q_{eff} can be approximated by eq 13 and $|B|^2$ by eq 7.

In the above derivation comprising eqs 7−16, we considered the interaction of only one photon (the incident photon) with the atom. Therefore, the resulting enhancement factor is due only to a single incident photon, $F_{2,\text{incident}}$. In reality, however, the emitted photon will also contribute to the enhancement exactly the same way the incident photon does, i.e., through surface plasmon wave and Purcell effect. As a result, the emitted photon gives rise to an enhancement factor, $F_{2,\text{emitted}}$. These two enhancement factors take on the same expression as in eq 16 but with slightly different wavelengths due to the Raman shift. The total enhancement for the SERS cross-section, therefore, is $|F_{2,\text{incident}} \times F_{2,\text{emitted}}|$. Ignoring the small difference in the two wavelengths, the SERS enhancement factor for the Raman scattering cross-section is simply $|F_2|^2$, or

$$|F_2|^2 = \frac{9\pi^4\epsilon_0^2\epsilon_{\text{r,out}}^2c^6}{\hbar^2\omega^4}|B|^4|R_A|^4|\hat{H}_1^{(2)}(\beta_{\text{out}}a)|^4(\cos^4\theta)\cdot Q_{\text{eff}}^2 \tag{17}$$

To the best of our knowledge, eq 17 is the first analytical expression of the enhancement factor for the single molecule−single nanoparticle SERS process for a spherical NP. A quick examination of eq 17 reveals that the enhancement factor is proportional to the fourth power of the electric field strength, i.e., $|E|^4$, which has been well accepted.[2,8]

Discussion

The most important aspect of eq 17 is that it enables one to estimate the EM enhancement factor for any metallic NP excited at any optical wavelength and any incident angle, as long as the NP radius is reasonably smaller than the photon wavelength ($a < \lambda/2\pi$). The optical wavelength used in ref 4 is 830 nm. From Table 1 of ref 18, the permittivity of a silver NP may be interpolated to be $-27.3886 + 2.7677i$.[18] As a result, the maximum SERS enhancement factor for a silver NP of 75 nm radius can be calculated to be 4.3×10^5 at $\theta = 0$ or π for the photon wavelength of 830 nm used in ref 4. This value of the enhancement factor is in the same order of magnitude with the prediction of the classical model.[5]

In general, EM enhancement alone cannot account for the high enhancement of $\sim 10^{14}$ observed of the "hot sites". In fact, one of the main conclusions of M. Kerker and co-workers was that for the single molecule−single nanoparticle case the maximum enhancement factor is $\sim 10^6$ and, even then, "only for the particle radii ≤5nm".[5] So there must be other mechanisms responsible for the enhancement exhibited by the "hot

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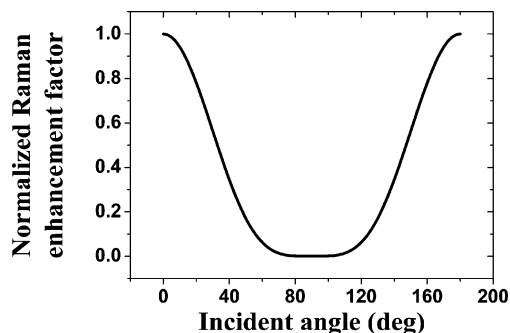
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Figure 3. Normalized SERS enhancement factor as a function of the incident angle of the optical field. Note that the $\cos^4 \theta$ dependence remains the same regardless of the optical wavelength or NP radius.

Figure 4. SERS enhancement factor as a function of nanoparticle radius at three different incident optical wavelengths: 514.5, 540.0, and 580.0 nm.

sites". Many reasons have been put forth to explain the enhancement factor as high as $\sim 10^{14}$, including chemical enhancement, resonance Raman effect, molecule location effect, and NP aggregation effect. Chemical enhancement may play an important role in the selectivity of SERS, but it is by itself too small (estimated to be $10-100^2$) and may not be always present in the SERS effect. Resonance Raman effect has been shown to be not always necessary to exhibit the ultrahigh enhancement factor[4] and was estimated to be on the order of 10^4-10^5 only.[2] Molecule location effect was examined in the framework of the classical electromagnetic theory[8] with a conclusion that the maximum enhancement factor achievable through electromagnetics is of the order of 10^{11}, which was obtained only at the interstitial sites between the particles and at the locations outside the sharp surface protrusions. NP aggregation effect might be the most convincing explanation presented so far. Michaels et al. reported that, "Ag nanoparticles that yield surface-enhanced Raman scattering (SERS) of single molecules of rhodamine (R6G) are all compact aggregates consisting of a minimum of two individual particles."[19] A most recent work also showed that high EM enhancement factors are only achievable with aggregation of particles, and that a factor as high as of 10^{13} "can be achieved with an array of dimers of truncated tetrahedra".[20]

Plotted in Figure 3 is the SERS enhancement factor as a function of the incident angle θ of the optical field according to eq 17. The strong dependence on the incident angle, ($\cos^4 \theta$), shown in this figure agrees well with the strong polarization dependence previously reported.[1,2] Equation 17 also shows that the $\cos^4 \theta$ dependence on the incident angle is independent of the optical wavelength and nanoparticle size. This angular sensitivity may be one of the reasons why stable SERS with high enhancement factor is difficult to obtain.

The analytical expression in eq 17 also implies that the enhancement factor depends weakly on the NP shape, which explains why the "hot sites" can have very different shapes. For example, the "hot sites" shown in Figure 2 of ref 3 consists of spherical NP, single nanocylinder, and aggregated NPs. The reason is that, while more irregular shape may lead to a stronger local EM field, it may also give rise to a smaller effective quality factor as indicated by the discussion following eq 13. Since both the shape and quality-factor effects contribute to SERS, they tend to cancel each other. Therefore, NP shape is not as critical a factor for SERS as its size. One also observes from eq 17 that the enhancement factor is proportional to the fourth power of the local electric field strength, but only to the second power of the quality factor, suggesting that irregularities in NP shape would still give rise to a comparatively high enhancement factor. In this case, the enhancement factor would critically depend on the location of the adsorbed molecule on the NP
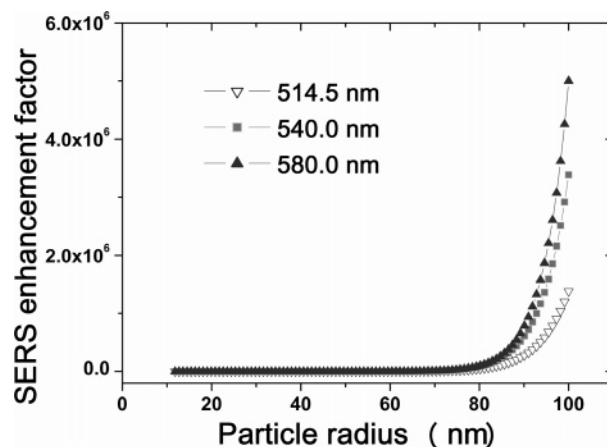
surface which is very difficult to control. One may state that the spherical-cavity model developed in this work should provide, as the first-order approximation, a good estimate of the enhancement factor for most practical experimental situations.

Plotted in Figure 4 as a function of NP radius are the SERS enhancement factors for three different incident photon wavelengths, all of which exhibit a monotonous increase. This may seem intuitively contradictory because the smaller the radius, the stronger the electric field. However, one must note that, while proportional to the fourth power of the electric field, the SERS enhancement factor is also dependent on other factors that are functions of the radius. A physical explanation for the monotonous increase may be that enhancement of scattering depends more on the photon energy "intercepted" by the NP so that in a certain size range, the larger the NP, the stronger the SERS enhancement. In fact, the spontaneous emission rate of the NPs in the same size range shows a similar size dependence as that reported by L. Rogobete et al.[21]

We speculate that the upper limit of the monotonous increase in the enhancement factor as a function of NP radius is approximately the Rayleigh scattering limit, $a = \lambda/2\pi$, above which the enhancement factor will decrease because of the oscillation introduced by Mie scattering. This provides an estimate of the optimal NP radius of $\sim a = \lambda/2\pi$. While it is not readily possible to directly relate Rayleigh images to SERS images (Figure 8 in ref 2), one must recognize that SERS is a very sensitive process requiring extremely careful experimentation. On the other hand, S. R. Emory et al. did observe a simple linear relationship between the particle size of the "hot sites" and the excitation photon wavelength, which qualitatively agrees with our result.[22] Figure 4 further implies that for a molecule exhibiting multiple SERS peaks, the one corresponding to the longest wavelength is most enhanced.

The dependence of the enhancement factor on the particle radius and incident photon wavelength as predicted by the present model is quite different from the results of M. Kerker et al.[5] which consisted of more complex relationships; however, in general, they obtained a larger enhancement factor for a smaller radius (Figures 2, 4, and 5 in ref 5). In fact, their results would predict much smaller "hot site" sizes than the actual. One possible explanation could be that the single molecule−single nanoparticle SERS process involves sizes in quantum mechanical regime and is thus dictated by certain quantum mechanical phenomena that may not be fully describable with the classical theories alone. On the other hand, the classical

model should correctly account for the collective phenomena in the SERS process.

Summary

A theory for the single molecule−single nanoparticle SERS process has been formulated for a spherical NP, giving rise to an analytical expression for the enhancement factor. The predictions of the theory were compared with the existing experimental and computer-simulation results with satisfactory agreement. The present theory further elucidates the fundamental aspects of the SERS process, such as the dependence on the incident angle of the photon, the linear dependence of the "hot site" size on the incident photon wavelength, the relatively weak influence of NP shape, and the dependence on the NP radius and optical wavelength.

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