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Surface-plasmon-polariton resonance factors in a classical calculation of surface-enhanced Raman scattering

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The effect of resonant excitation of surface-plasmon polaritons of a general metal substrate on the relatively long-range classical enhancement of the surface-enhanced Raman scattering is considered. It is shown that all the three factors in the classical enhancement arising from the presence of the metal, namely the local electric field at the molecular site at the incident frequency, the electrodynamic renormalization factor for the molecular polarizability, and the propagator for the Stokes scattered field, are modified resonantly. However, their individual impact on the total enhancement differs appreciably, depending strongly on the shape of the metal surface and the distance of the molecule from the surface. As an example, explicit results are given for a molecule adsorbed on a small sphere.

I. INTRODUCTION

The experimental discovery of very large Raman cross sections for molecules adsorbed on metals like Ag has attracted considerable theoretical attention¹⁻³ during the last few years. The enhancement factor in this surface-enhanced Raman scattering (SERS) from molecular vibrations is known^{2,4} to be a strong function of the distance d of the molecule from the metal surface. The relatively-long-range part of the enhancement is believed to be due to resonant excitation of surface-plasmon polaritons (SPP) of the metal substrate by the light wave. There is an additional short-range enhancement when the molecule is in contact with the metal surface because of modified ground-state electronic charge-density distribution and the new electronic excitation spectrum of the metal-molecule complex.

A complete calculation of the interesting short-range enhancement for the first one or two molecular monolayers necessarily involves a quantum calculation^{2,5} of the new polarizability of the modified charge distribution near the surface. On the other hand, a classical electrodynamic calculation in terms of the experimental molecular polarizability tensor $\underline{\alpha}$ of an isolated molecule is enough to find the long-range enhancement. In this paper, we address ourselves to examining the way that the

resonant excitation of SPP modifies all three factors in the classical enhancement, involving the local field at the molecular site in the absence of the molecule, the renormalized molecular polarizability, and the propagation characteristics of the scattered field in the presence of the metal surface. In particular, we will investigate whether it is possible to obtain a cancellation of resonance factors appearing in the scattering propagator (out coupling) and the renormalized molecular polarizability. For definiteness, explicit results will be presented for the case of a molecule in the presence of a small metallic sphere.

II. MATHEMATICAL FORMULATION AND RESULTS

As an approximation, let us assume that in the presence of an optical field of frequency ω , an isolated molecule can be represented by a point dipole, with induced polarization

$$\vec{P}_{\text{mol}}(\vec{r}, \omega) = \vec{p}(\omega) \delta(\vec{r} - \vec{r}_0). \quad (1)$$

The dipole moment $\vec{p}(\omega)$ can be defined either in terms of the bare polarizability and the total electric field or, more conveniently, in terms of the physical polarizability $\underline{\alpha}(\omega)$ of the molecule and the "local" field \vec{E}_M whose source lies outside the molecule. In the presence of the metallic medium

and the point dipole, the total electric field $\vec{E}(\vec{r}, \omega)$ anywhere is determined by Maxwell's equations

$$[-\nabla^2 + \vec{\nabla} \cdot \vec{\nabla} - \epsilon(\vec{r}, \omega)k^2]\vec{E}(\vec{r}, \omega) = 4\pi k^2 \vec{p}(\omega) \delta(\vec{r} - \vec{r}_0), \quad (2)$$

where $k = \omega/c$, $\epsilon(\vec{r}, \omega)$ is equal to 1 outside the metal, and where at time $t \rightarrow -\infty$, an incident light wave $\vec{E}_{\text{inc}}(\omega, \vec{r})$ is assumed to be propagating towards the system. For simplicity, the metallic medium has been represented by a local dielectric function.⁶

In terms of the Green function $\underline{G}(\vec{r}, \vec{r}_0, \omega)$ defined by

$$[-\nabla^2 + \vec{\nabla} \cdot \vec{\nabla} - \epsilon(\vec{r}, \omega)k^2]\underline{G}(\vec{r}, \vec{r}_0, \omega) = 4\pi\delta(\vec{r} - \vec{r}_0)\underline{I}, \quad (3)$$

where \underline{I} is a unit dyadic, the complete solution of (2) can be written as

$$\vec{E}(\vec{r}, \omega) = \vec{E}^{(0)}(\vec{r}, \omega) + k^2 \underline{G}(\vec{r}, \vec{r}_0, \omega) \cdot \vec{p}(\omega), \quad (4)$$

where $\vec{E}^{(0)}(\vec{r}, \omega)$ is the solution of (2) in the absence of the molecule. In other words, $\vec{E}^{(0)}(\vec{r}, \omega)$ is the usual local field (of Ref. 2) at the molecular site, *in the absence of the dipole*. Since the bare polarizability for an isolated point dipole is not a well-defined quantity, it is better to work with the "local" field \vec{E}_M instead of the total field \vec{E} . In order to introduce the "local" field \vec{E}_M in the presence of the metal, whose sources lie outside the molecule, we can indeed split the full Green's function \underline{G} as

$$\underline{G}(\vec{r}, \vec{r}_0, \omega) = \underline{G}_0(\vec{r}, \vec{r}_0, \omega) + \underline{G}_s(\vec{r}, \vec{r}_0, \omega), \quad (5)$$

where

$$\underline{G}_0(\vec{r}, \vec{r}_0, \omega) = \left[\underline{I} + \frac{1}{k^2} \vec{\nabla} \cdot \vec{\nabla} \right] \frac{e^{ik|\vec{r} - \vec{r}_0|}}{|\vec{r} - \vec{r}_0|} \quad (6)$$

is the free-space Green's function in the absence of the metal. In terms of the experimentally measured polarizability for an isolated molecule, one then has

$$\vec{p}(\omega) = \underline{\alpha}(\omega) \cdot \vec{E}_M(\vec{r}_0, \omega), \quad (7)$$

where the "local" electric field satisfies the relation

$$\vec{E}_M(\vec{r}, \omega) = \vec{E}^{(0)}(\vec{r}, \omega) + k^2 \underline{G}_s(\vec{r}, \vec{r}_0, \omega) \cdot \vec{p}(\omega), \quad (8)$$

in contrast to (4) for the total field \vec{E} . Using (7) and (8), the induced dipole moment can finally be rewritten as

$$\vec{p}(\omega) = \underline{\alpha}_{\text{eff}} \cdot \vec{E}^{(0)}(\vec{r}_0, \omega), \quad (9)$$

where

$$\underline{\alpha}_{\text{eff}}(\omega) = [I - (\omega^2/c^2)\underline{\alpha}(\omega) \times \underline{G}_s(\vec{r}_0, \vec{r}_0, \omega)]^{-1} \cdot \underline{\alpha}(\omega), \quad (10)$$

leading to the so-called "image" enhancement of the polarizability.¹ Note that the final expression for \vec{p} involves only \underline{G}_s , the physical polarizability tensor $\underline{\alpha}$, and the local field $\vec{E}^{(0)}$ at the molecular site (in the absence of the dipole).

Because of the modulation of α by the molecular vibrations, \vec{p} is a function of the normal coordinates $\vec{Q}e^{\pm i\omega_0 t}$, and can oscillate at frequencies $\omega \pm \omega_0$, where ω_0 is the vibrational mode frequency under consideration. The solution of Maxwell's equations at the Stokes frequency $\omega_s = \omega - \omega_0$ [similar to Eq. (2)], is then given by

$$\vec{E}_{\text{Stokes}}(\vec{r}, \omega_s = \omega - \omega_0) = \frac{\omega_s^2}{c^2} \underline{G}(\vec{r}, \vec{r}_0, \omega_s) \cdot \left[\vec{Q} \cdot \frac{\partial}{\partial \vec{Q}} \right] \times \underline{\alpha}_{\text{eff}}(\omega) \cdot \vec{E}^{(0)}(\vec{r}_0, \omega). \quad (11)$$

This has to be compared with the Stokes field for the same vibration in an isolated molecule:

$$\vec{E}_{\text{Stokes}}(\vec{r}, \omega_s) \Big|_{\text{isolated mol}} = \frac{\omega_s^2}{c^2} \underline{G}^{(0)}(\vec{r}, \vec{r}_0, \omega_s) \cdot \left[\vec{Q} \cdot \frac{\partial}{\partial \vec{Q}} \right] \underline{\alpha} \cdot \vec{E}_{\text{inc}}(\vec{r}_0, \omega). \quad (12)$$

Because of the presence of the metal, there are three distinct modifications in the Stokes field: (i) the incident field \vec{E}_{inc} is changed to the local field $\vec{E}^{(0)}$ at the molecular site, (ii) the free-space polarizability $\underline{\alpha}$ is renormalized to $\underline{\alpha}_{\text{eff}}$ via (10), and (iii) the scattering propagator for the Stokes field is changed from the free-space $\underline{G}^{(0)}$ to the full \underline{G} .

For a given vibrational mode, the classical enhancement factor for the Raman intensity can now be written as

$$F(\text{classical}) = \frac{\left| \underline{G}(\vec{r} \rightarrow \infty, \vec{r}_0, \omega_s) \cdot \left[\hat{Q} \cdot \frac{\partial}{\partial \vec{Q}} \right] \left[I - \frac{\omega^2}{c^2} \underline{\alpha} \cdot \underline{G}_s(\vec{r}_0, \vec{r}_0, \omega) \right]^{-1} \cdot \underline{\alpha} \vec{E}^{(0)}(\vec{r}_0, \omega) \right|^2}{\left| \underline{G}_0(\vec{r} \rightarrow \infty, \vec{r}_0, \omega_s) \cdot \left[\hat{Q} \cdot \frac{\partial}{\partial \vec{Q}} \right] \underline{\alpha} \cdot \vec{E}_{\text{inc}}(\vec{r}_0, \omega) \right|^2}. \quad (13)$$

Once the geometry of the metallic medium is specified, with

$$\epsilon(\vec{r}, \omega) = \epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$$

inside the medium, the solution of Maxwell's Eq. (2), in the absence of the dipole term, determines the local field $\vec{E}^{(0)}(\vec{r}_0, \omega)$, and the solution of (3) determines $\underline{G} = \underline{G}_0 + \underline{G}_s$ and hence, \underline{G}_s . For suitable frequencies and geometrical shapes of the metal surface, the local field $\vec{E}^{(0)}$, the Green function \underline{G}_s , and the Green function \underline{G} can each show resonant enhancement due to SPP excitation at the metal surface. The question arises whether such resonant enhancements in \underline{G} and \underline{G}_s in (13) can become large enough to cancel each other, leaving mostly the enhancement of the local field $\vec{E}^{(0)}(\vec{r}_0, \omega)$ at the molecular site.

For a plane metallic surface, it is well known that a light wave can not excite the corresponding SPP, because of its inability to satisfy momentum conservation parallel to the surface. For such a geometry, SPP wave vector \vec{K}_g parallel to the surface must satisfy the condition

$$K_g^2 = (\omega^2/c^2)\epsilon_1(\omega)/[\epsilon_1(\omega) + 1],$$

with $\epsilon_1(\omega) < -1$. Apart from a numerical factor of order unity, which is determined by the detailed symmetry of the polarizability tensor $\underline{\alpha}$ with respect to the normal vector drawn from the molecular position \vec{r}_0 to the metal surface, in this case $(\omega^2/c^2)\underline{\alpha} \cdot \underline{G}_s(\vec{r}_0, \vec{r}_0, \omega)$ is of the order $[(\epsilon - 1)/(\epsilon + 1)](\alpha/4d^3)$, where d is the distance of the molecule from the metal surface. Since $\underline{\alpha}$ is of the order of atomic volume ($1 - 10 \text{ \AA}^3$), this implies that except for d of the order of a few \AA , we may also ignore the renormalization effect on α for a plane surface. In any case, as indicated earlier, for such a small d one has to perform a quantum calculation, and the molecule should no longer be represented by a point dipole for near-field calculations.

The situation described above changes completely if the metallic surface is rough, and its departure from the plane surface ($z=0$) can be represented by a superposition of sinusoidal gratings:

$$z = \xi(x, y) = \sum_{\vec{g}} \xi_g e^{i\vec{g} \cdot \vec{r}_\perp}, \quad \vec{r}_\perp = (x, y). \quad (14)$$

In such a case, resonant excitations of SPP, with parallel wave vector

$$\vec{K}_g = \vec{k}_{||} \pm \vec{g}$$

becomes readily possible. In fact, for $\xi_g K_g \ll 1$, it is easy to show² that $\vec{E}^{(0)}(\vec{r}_0, \omega)$ has a SPP component proportional to $\xi_g K_g$ which can be excited resonantly. The resonant field enhancement with respect to $|\vec{E}_{\text{inc}}|$ in this case is given by

$$\left| \frac{\vec{E}^{(0)}(\vec{r}_0, \omega)}{\vec{E}_{\text{inc}}(\vec{r}_0, \omega)} \right| \cong 2\xi_g K_g [|\epsilon_1(\omega)|^{3/2}/\epsilon_2(\omega)] \times e^{-(K_g^2 - \omega^2/c^2)^{1/2}d} \quad (15)$$

for $\epsilon_1 \ll -1$.

At an arbitrary scattering angle, where near scattered field cannot couple out from the metal surface resonantly, one can ignore the enhancement in the scattering propagator $\underline{G}(\vec{r} \rightarrow \infty, \vec{r}_0, \omega_s)$, and the net result is same as in Ref. 2, except for a renormalization factor for the polarizability (which goes to 1 for $d \gg 20 \text{ \AA}$). However, for specific scattering angles for which the near field at frequency ω_s can couple out resonantly, one must consider the additional enhancements in both $\underline{G}(\vec{r} \rightarrow \infty, \vec{r}_0, \omega_s)$ and $\underline{G}_s(\vec{r}_0, \vec{r}_0, \omega)$ in (13). The cancellation of these two resonant factors is only partial at reasonable values of d . Inclusion of these additional resonances becomes much more important for large $\xi_g K_g$. The details of this will be published in a separate paper.

A more complete calculation of F can be made more readily for a molecule adsorbed on a metallic sphere of radius $a \ll c/\omega$. Let the origin be the center of the sphere, with the molecular position

$$\vec{r}_0 = r_0 \hat{z} = (a + d)\hat{z}, \quad d > 0.$$

In this case, the local field outside the metal is given by³

$$\vec{E}^{(0)}(\vec{r}, \omega) \cong \vec{E}_{\text{inc}}(\vec{r}, \omega) + \frac{a^3}{r^3} g(\omega, a) [3\hat{r}(\hat{r} \cdot \vec{E}_{\text{inc}}) - \vec{E}_{\text{inc}}], \quad (16)$$

where

$$g(\omega, a) \cong \left[\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2 + \frac{12}{5} \frac{\omega^2}{c^2} a^2} \right]. \quad (17)$$

Resonant enhancement of the local field becomes possible when the dipole SPP dispersion relation

$$\epsilon_1(\omega) + 2 + (12/5)\omega^2 a^2/c^2 = 0$$

is satisfied. At exact resonance

$$g(\omega, a) \cong (\epsilon - 1)/i\epsilon_2.$$

For a scalar α and the incident wave polarized along \vec{r}_0 , it can be shown that the enhancement factor (13) has the form

$$F(\text{small sphere, radius } a) = \frac{\left| 1 + 2 \left[\frac{a}{a+d} \right]^3 g(\omega_s, a) \right|^2 \left| 1 + 2 \left[\frac{a}{a+d} \right]^3 g(\omega, a) \right|^2}{\left| 1 - \frac{\alpha a}{(a+d)^4} \sum_l \frac{l(l+1)^2 [\epsilon(\omega) - 1]}{[l+1+l\epsilon(\omega)]} \frac{a^{2l}}{(a+d)^{2l}} \right|^4}. \quad (18)$$

Here, the denominator represents the renormalization factor for the polarizability, and the factors in the numerator are due to changes in the scattering propagator and the local field, respectively, because of the presence of the metal. In the final expression, Wang *et al.*^{3(b)} have ignored the renormalization denominator, whereas Gersten and Nitzan^{3(c)} have considered a more general example. In the nonretardation limit, the renormalization denominator was obtained by using the expression

$$\lim_{k \rightarrow 0} k^2 \underline{G}_s(\vec{r}, \vec{r}_0, \omega) = \vec{\nabla} \vec{\nabla}_0 \left[\sum_l \frac{4\pi l(\epsilon-1)}{(2l+1)(l+1+l\epsilon)} \frac{a^{2l+1}}{r^{l+1} r_0^{l+1}} Y_{lm}(\theta, \phi) Y_{lm}^*(\theta_0, \phi_0) \right] \quad (19)$$

and \vec{r} and \vec{r}_0 outside the metal sphere, so that

$$k^2 \underline{G}_s(r_0 \hat{z}, r_0 \hat{z}, \omega) \rightarrow \sum_l \frac{l(\epsilon-1)}{(l+1+l\epsilon)} \frac{a^{2l+1}}{r_0^{2l+4}} \left[(l+1)^2 \hat{z}\hat{z} + \frac{l(l+1)}{2} \hat{x}\hat{x} + \frac{l(l+1)}{2} \hat{y}\hat{y} \right]. \quad (20)$$

In the renormalization denominator in (18), $l=1$ term corresponds to the dipolar SPP resonance. It is important to emphasize here that this is not the leading term for small d . As in the case of the flat surface, the renormalization correction in the denominator diverges when $d \rightarrow 0$. This can be best seen by isolating the leading order divergence term varying as $1/d^3$, by decomposing the denominator in the form

$$\begin{aligned} \left| 1 - \alpha(\epsilon-1) \sum_l \frac{l(l+1)^2}{l+1+l\epsilon} \frac{a^{2l+1}}{r_0^{2l+4}} \right|^4 &= \left| 1 - \frac{\alpha(\epsilon-1)}{\epsilon+1} \left[\frac{\partial}{\partial r_0^2} \right]^2 \sum \left[1 + \frac{\epsilon}{l+1+l\epsilon} \right] \frac{a^{2l+1}}{(r_0^2)^l} \right|^4 \\ &= \left| 1 - \frac{\epsilon-1}{\epsilon+1} \frac{2\alpha a^3}{(2a+d)^3 d^3} - \frac{\epsilon}{\epsilon+1} \left[\frac{\partial}{\partial r_0^2} \right]^2 \sum_l \left[\frac{\epsilon-1}{l+1+l\epsilon} \right] \frac{a^{2l+1}}{(r_0^2)^l} \right|^4, \end{aligned} \quad (21)$$

where $r_0 = a + d$.

Note that the frequencies ω and ω_s differ by the vibrational frequency ω_0 , which may be of the order of 1000 cm^{-1} or more. Thus, except for very small ω_0 , the resonance peaks in $g(\omega_s, a)$ and $g(\omega, a)$ will occur at different values of the incident frequency ω . However, because of a finite width for the resonance in $g(\omega, a)$, there will be a substantial overlap of the structures in F as a function of ω , arising from the resonance peaks in $g(\omega, a)$ and $g(\omega_s, a)$. This is particularly true for small a , giving rise to a large net enhancement. At exact resonance,

$$|g| \simeq (\epsilon_1 - 1) / \epsilon_2$$

could be as high as 50–100 in the visible, for Ag. Except for very small d or $a + d$ the denominator in (18) is again not important. The dipolar SPP

resonant term in the denominator (the $l=1$ term, with $\epsilon_1 = -2$) may be ignored for $a + d$ greater than about 30 \AA . A significant cancellation of one of the dipolar resonances in the numerator with that of the denominator is not possible for large enough $a + d$. The higher-order resonance terms in the denominator ($l > 1$) are also insignificant for $a + d > 30 \text{ \AA}$, besides the fact that then the numerator is off resonance. The same thing is true for the resonance at $\epsilon_1 = -1$, unless d is very small. Thus, as long as d is greater than about 30 \AA , we can ignore the renormalization denominator in (18) for the calculation of the long-range part of the enhancement factor. For $d \lesssim 10\text{--}20 \text{ \AA}$, the renormalization effect (the feedback effect) can however become important. The net enhancement can be larger for the case of molecules adsorbed on a

small sphere as compared to that on a small amplitude grating. Results similar to the case of a sphere are expected to be valid also for the case of spheroidal particles.

III. CONCLUSIONS

In summary, we have presented here a general formulation for the calculation of the classical enhancement factor in SERS in the presence of SPP resonances of the metal substrate of an arbitrary shape. Because of the SPP resonance, the renormalization of molecular polarizability (the "im-

age" enhancement) becomes important at molecular distances d as large as 20 Å from the surface; i.e., in the region where the classical calculation may not be too bad. Our formulation also shows that overall physics involved in the enhancement is independent of the exact shape of the substrate, as long as SPP can be excited resonantly in that geometry. For arbitrary incident and scattering angles and polarizations, the ability to obtain resonances in the incident or the scattering channel depends, however, strongly on the morphology of the substrate.

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