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Effects of extraneous surface charges on the enhanced Raman scattering from metallic nanoparticles

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Motivated by recent experiments on surface enhanced Raman scattering (SERS) from colloidal solutions, we present here a simple model to elucidate the effects of extraneous surface charges on the enhanced Raman signal. The model is based on the well-established Gersten-Nitzan model coupled to the modified Mie scattering theory of Bohren and Hunt in the long wavelength approximation. We further introduce corrections from the modified long wavelength approximation to the Gersten-Nitzan model for the improvement of its accuracy. Our results show that the surface charge will generally lead to a blueshift in the resonance frequency and greater enhancements in the SERS spectrum. Possible correlations with the recent experiments are elaborated. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4809524>]

INTRODUCTION

Surface enhanced Raman scattering (SERS) remains one of the most studied dramatic surface processes since its first discovery almost four decades ago.¹ The two well-known mechanisms – electromagnetic and chemical enhancements – have been studied by many researchers over the years with significant advances made both experimentally and theoretically.^{2,3} While the specific account for each experimental observation of SERS depends on many factors ranging from the molecular properties to the substrate characteristics, one dominant undisputable mechanism will be from the surface plasmon resonance (SPR) of the free electrons in the roughened metallic substrate. This mechanism alone can lead to several orders of magnitude enhancement upon the right condition. Moreover, most earlier theoretical accounts of this SPR mechanism have been limited to an (classical) electrodynamic formulation where the metallic substrate is assumed to be neutral and characterized by a macroscopic complex dielectric function. Although more sophisticated quantum theories have been developed recently including approaches based on density functional theory⁴ or density matrix formulation,⁵ the possible effects from a net extraneous charge on the metal surface have seldom been investigated to our knowledge. Note that such effects are not the same as those due to charge transfer between the adsorbate and the metal surface leading to the so-called chemical enhancement of SERS,² in which case neutrality is maintained for the whole molecule-substrate system.

In a few recent experiments with SERS from a metallic colloid, however, the aforementioned charge effects have been studied via the monitoring of the zeta potential of the colloidal metal particles.^{6,7} While in the work of Alvarez-Puebla *et al.*,⁶ SERS from different analytes such as pyridine

is observed to be strongest when the electrostatic repulsion is minimized between the molecule and the particle; in the work of Zhang *et al.*,⁷ methyl orange (MO) is observed to undergo very different SERS process when it is adsorbed to positively charged colloidal silver particles compared to the case with negatively charged particles, with the SERS signal much stronger in the former case. This latter observation is accounted for by referring to the different orientations of the transition molecular dipole in the two cases – being almost normal to the metal surface in the positively charged case and almost tangential to the surface in the negatively charged case. In addition, the shifts in the absorption spectra with the molecule adsorbed to the two differently charged particles are also very different and are understood to be caused by relatively strong interaction between MO and the positively charged surface compared to the negative one.

Given the status of SERS studies as briefly summarized above, we are thus motivated to theoretically investigate the effects due to extraneous surface charge on the metallic particles, with focus on the electromagnetic enhancement of the process. One of the early successful SERS models was due to Gersten and Nitzan who had considered a simple surface structure in the form of a (neutral) spherical/spheroidal island and used classical electrodynamics to derive the enhanced Raman cross section for a molecular dipole adsorbed on such an island.⁸ It is the purpose of our present work to present an extended Gersten-Nitzan (GN) model for SERS to incorporate the effects due to extraneous charges on the metal islands. This is achieved with an application of the extended Mie theory of Bohren and Hunt (BH)⁹ in the long wavelength limit together with the idea of introducing an effective dielectric function for the charged metal particle. We shall first give a brief account on both the GN and BH theories before we present numerical studies on these charge effects.

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EXTENDED GN MODEL

In one of the early and pioneering theoretical works towards the understanding of the electromagnetic (EM) mechanism of SERS, Gersten and Nitzan⁸ studied the interaction between a molecular dipole and a surface protrusion modeled as a spheroidal island and conclude that the SERS enhancement can be caused by the following three factors: the lightening-rod effect due to the “sharpness” of the protrusion; the image effect from the field induced by the dipole; and the surface plasmon (SP) effect from the metallic structure. As a model study of the charge effects, here we shall assume the simplest geometry for the metallic structure taken it as a spherical particle (applicable especially to colloids) and focused on only the image and SP effects. To this end, the SERS enhancement factor (R) takes a simple form in the long-wavelength limit. For the two orthogonal (radial and tangential) orientations of the molecular dipole with respect to the spherical metal nanoparticle (MNP), we have the maximum possible values for R given by^{8,10}

$$R_{\perp} = \left| \frac{1}{1 - \alpha_M G_{\perp}} \left(1 + \frac{2\alpha_1}{(a+d)^3} \right) \right|^4, \quad (1)$$

$$R_{\parallel} = \left| \frac{1}{1 - \alpha_M G_{\parallel}} \left(1 - \frac{\alpha_1}{(a+d)^3} \right) \right|^4, \quad (2)$$

where α_M is the molecular polarizability, and the functions $G_{\perp}$ and $G_{\parallel}$ in the “image terms” are given by

$$G_{\perp} = \sum_{n=1}^{\infty} \alpha_n \frac{(n+1)^2}{(a+d)^{2(n+2)}}, \quad (3)$$

$$G_{\parallel} = \sum_{n=1}^{\infty} \alpha_n \frac{n(n+1)}{2(a+d)^{2(n+2)}}. \quad (4)$$

Note that α_n and a are the multipolar polarizability and the radius of the sphere, respectively, and d is the distance between the molecule and the MNP surface. Note also that in the long-wavelength approximation, the SP resonance is mainly from the dipole response of the MNP to the external field. In general, it is well-known that unless at very close distance (in which case quantum effects can become significant), the SP effect will dominate the enhancement factor over the image field.^{2,3}

To extend the above GN model to include the extraneous surface charges, one cannot simply start with the GN formalism which employs solving boundary value problems in the realm of strict electrostatics. The reason is that in the presence of free surface charges, a surface current will be generated when an external field is applied which must be accounted for through a modification of the continuity of the tangential magnetic fields ($\vec{H}$) across the boundary.⁹ Within a fully electrodynamic generalization of the Mie scattering theory via the incorporation of such a modified boundary condition, Bohren and Hunt have obtained the following modified Mie coefficients for the EM scattering from a charged sphere

(in vacuum):⁹

$$a_n = - \frac{\psi'_n(x)\psi_n(mx) - \psi_n(x)[m\psi'_n(mx) - i\tau\psi_n(mx)]}{\xi'_n(x)\psi_n(mx) - \xi_n(x)[m\psi'_n(mx) - i\tau\psi_n(mx)]}, \quad (5)$$

$$b_n = - \frac{\psi_n(x)\psi'_n(mx) - \psi'_n(x)[m\psi_n(mx) + i\tau\psi'_n(mx)]}{\xi_n(x)\psi'_n(mx) - \xi'_n(x)[m\psi_n(mx) + i\tau\psi'_n(mx)]}, \quad (6)$$

where ψ_n , ξ_n are the Riccati-Bessel functions, $x = ka$ is the size parameter of the sphere, $m = \sqrt{\epsilon}$ is the refraction index of the (nonmagnetic) sphere, and $\tau = \frac{4\pi}{c}\sigma_S(\omega)$ with $\sigma_S(\omega)$ the surface conductivity. Note that Gaussian units have been used. In the following, we shall apply the results in Eqs. (5) and (6) in the long-wavelength limit to obtain modifications to the GN model via the introduction of an “effective dielectric function.”

In the limit when we have both $x \ll 1$ and $|m|x \ll 1$, the small argument limits of the various Bessel functions lead to the following results for the Mie coefficients:

$$a_n \rightarrow O(x^{2n+3}), \quad (7)$$

$$b_n \rightarrow \frac{i(n+1)/n}{(2n-1)!!(2n+1)!!} \times \frac{[\epsilon + i(n+1)\tau/x] - 1}{[\epsilon + i(n+1)\tau/x] + (n+1)/n} x^{2n+1}. \quad (8)$$

When these results are compared to the response of a (neutral) metal sphere in the quasistatic approximation where it is completely governed by the multipolar polarizability of the sphere (assumed in vacuum):¹¹

$$\alpha_n = \frac{\epsilon - 1}{\epsilon + (n+1)/n} a^{2n+1}, \quad (9)$$

we conclude that the surface charge effects can be accounted for in this limit by simply introducing the following effective dielectric function:

$$\beta_n = \epsilon + i(n+1)\tau/x. \quad (10)$$

Hence we obtain the extended GN model with the results in Eqs. (1) and (2) remain valid, provided that one replaces the dielectric function (ϵ) of the metal sphere which appears in all the multipole polarizability α_n (including those in the functions $G_{\perp}$ and $G_{\parallel}$) by the one as defined in Eq. (10).

Furthermore, in order to improve on the electrostatic approximations in the GN model, we shall also go beyond the results in Eqs. (1) and (2) to include corrections from the so-called modified long wavelength approximation (MLWA).^{12,13} The main mechanism of this MLWA is to incorporate the lowest order corrections due to the finiteness of the wavelength to the electrostatic depolarizing fields inside a polarizable sphere to include (i) the dynamic depolarization due to retardation and (ii) the radiation damping field acting on the induced dipoles in the sphere. Despite the fact that such modifications will be limited only to the dipole polarizability of the sphere (since the above two effects (i) and (ii) are accounted for via the full dynamical fields of the induced electric dipoles within the sphere^{12–15}), the MLWA has been

checked to be generally accurate when compared to exact calculations for metal particles up to sizes of ~ 100 nm for optical wavelengths.¹⁶ Note that the MLWA yields more accurate results mainly in the account of the dipole SP resonance and can become inaccurate at off-resonance frequencies. Hence, with our focus on the SP resonance, we shall replace all the sphere dipole polarizability within the MLWA (with the incorporation of the surface charges) in Eqs. (1)–(4) by the following expression:^{12,13}

$$\alpha_1 = \frac{\beta_1 - 1}{3 + \eta(\beta_1 - 1)} a^3, \quad (11)$$

where $\eta = 1 - x^2 - i2x^3/3$ and β_1 is obtained from Eq. (10). Note that Eq. (11) leads back to the simple electrostatic result for $\lambda \rightarrow \infty$ and $x \rightarrow 0$. We shall perform numerical studies in the following with and without the MLWA correction and shall make comparison of the field enhancement factors (i.e., without the image factors) in Eq. (1) and (2) against the results calculated using the full Mie theory to provide an access of the accuracy of the simple MLWA.

NUMERICAL RESULTS

Here we present some numerical studies of the effects due to both the extraneous charges and the MLWA on the SERS enhancement ratio in Eq. (1) and (2) for a molecular dipole located in the proximity of a silver sphere. The molecular polarizability is taken to be $\alpha_M = 1 \text{ nm}^3$, and the dielectric function of silver is parametrized by the following Drude model:¹⁷

$$\varepsilon = \varepsilon_{Ag}(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\Gamma)}, \quad (12)$$

where $\omega_p = 1.36 \times 10^{16} \text{ s}^{-1}$ and $\Gamma = \Gamma_B + A v_F/a$ with $\Gamma_B = 2.56 \times 10^{13} \text{ s}^{-1}$, $v_F = 1.38 \times 10^8 \text{ cm/s}$ and the coefficient A in the term accounting for surface damping is simply taken as unity.⁴ We shall first consider a really small sphere of 5 nm in radius to ensure the accuracy of the electrostatic GN model without the MLWA. To account for the surface charge effect in the effective dielectric function, we apply a result derived for the surface conductivity in Refs. 9 and 18, and obtain the following:

$$\tau = ix \frac{\omega_s^2}{\omega(\omega + i\gamma_s)}, \quad (13)$$

where $\gamma_s = k_B T/\hbar$ and $\omega_s^2 = Nq_s^2/m_s a^3$ are the damping frequency and surface plasma frequency of the excess surface charges, respectively, with mass m_s and charge q_s for a single charge, and the total excess charge number N . Note that since this effect due to q_s always enters with q_s in quadratic form, the sign of the charge (positive or negative) will make no difference as far as this optical effect is concerned. The total excess charge number can also be related to the electrostatic potential by $\Phi = Nq_s/a$. In the following computations, we have fixed the temperature at $T = 300 \text{ K}$.

Figure 1 shows the SERS enhancement ratio (R) for both a radial and a tangential dipole, respectively, from which one sees the tangential dipoles (Fig. 1(b)) in general experience an enhancement of an order smaller as expected. For either ori-

FIG. 1. The SERS enhancement ratio R of (a) radial and (b) tangential molecules near a silver sphere of the radius $a = 5 \text{ nm}$ with surface charges: $q_1 = 5 \times 10^{-16} \text{ C}$, $q_2 = 8.33 \times 10^{-16} \text{ C}$, $q_3 = 1.67 \times 10^{-15} \text{ C}$, and $q_4 = 2.5 \times 10^{-15} \text{ C}$. The distance between the molecule and the sphere is fixed at $d = 5 \text{ nm}$.

entation, the molecule will experience greater enhancements with the increase of the surface charge for the MNP, with an increasing blueshifted resonance at the same time. This can be understood from the effective dielectric function in Eq. (10). First of all, it is not difficult to derive the modified resonance frequencies from Eqs. (9), (10), and (12) to be given by the following expression:

$$\omega_n = \omega_p \sqrt{\frac{n}{2n+1}} \sqrt{1 + (n+1) \frac{\omega_s^2}{\omega_p^2}}, \quad (14)$$

from which a blueshift is clearly revealed due to the term with the surface plasmon frequency. This can be interpreted as an effective increase in the plasma frequency of the metal due to the presence of the extraneous charges since this frequency is known to increase with the free electron density of the metal. Although only the dipole resonance is shown in Fig. 1, it is clear from Eq. (14) that the blueshift in resonance frequency will even be more significant for higher multipole SP's. In addition, it is easy to show that the imaginary part of β_n given by both Eqs. (10) and (12) is a decreasing function in frequency and hence when the resonance frequency is blueshifted, this imaginary part will become more insignificant close to resonance. Such decrease in loss accounts for the increasing peak enhancement ratios in Fig. 1 as the surface charge (potential) increases. Note that in this figure (and in both Figs. 2 and 5(b)), we have considered a rather broad range of the surface charge values for our model calculations so that the effects can be more manifestly displayed. One can of course limit this range to more realistic values (as done in Fig. 3) and expect similar qualitative effects to emerge with the presence of the extraneous surface charges.

Figure 2 shows how the enhancement varies as the molecule is moved away from the (charged) MNP. Here we only show the results for a radial dipole, where in Fig. 2(a), the enhancement ratio is shown for both with and without

FIG. 2. (a) The distance dependence of the SERS enhancement ratio R for radial molecule near a silver sphere of radius $a = 5$ nm with the surface charges: $q_a = 5 \times 10^{-16}$ C and $q_b = 10^{-15}$ C. The solid and dashed curves represent the results with and without the image-field effects, respectively. The frequency for each curve is chosen to be at the respective resonance. (b) The ratio R for the charged sphere with surface charges q_a and q_b to that for the uncharged sphere. The image-field effects are included.

FIG. 3. (a) The two strongest modes of the Raman spectrum of a free pyridine molecule at an incident wavelength of 357 nm as obtained in Ref. 4. (b) SERS spectrum of pyridine at a separation of 1 nm from a neutral ($q = 0$) and charged ($q = 2.78 \times 10^{-17}$ C and $q = 5.56 \times 10^{-17}$ C) silver spheres of radius 5 nm at an incident wavelength 357 nm.

the image effect, and for two values of surface charges with $q_b = 2q_a$. It is observed that while the image effect becomes really prominent only at very close molecule-MNP distances as expected due to the smallness of the molecular polarizability, the charged MNP's will have this image effect of less relative significance for a given molecule-MNP distance. This is understandable since the extraneous charge contributes to a monopole potential which will overshadow all the higher order image potentials. Incidentally, it is of interest to note that the rate of decrease in the enhancement as the molecule is moved farther turns out to be greater for the charged MNP's. Figure 2(b) shows the enhancement ratio from a charged MNP relative to that from an uncharged one. It is observed that the increase in enhancement due to the surface charge saturates as the molecule is moved away from the MNP, with the less-charged MNP saturating sooner with the increase in molecule-MNP separation.

In order to demonstrate any measurable effects in real experiments from the extraneous surface charges, we next apply our model to simulate a real SERS spectrum. We shall limit ourselves to a phenomenological approach and shall focus on the two strongest Raman modes of the pyridine molecule in the vicinity of a wave number ~ 1000 cm⁻¹ which were among the first observed SERS modes in the 1970s.¹ To simulate these modes, we shall follow Ref. 4 and use two Lorentzian profiles (with the same full-width at half-maximum of 10 cm⁻¹) to model the results obtained there with all the Raman cross sections normalized to the higher peak which is at a wavenumber of 1026 cm⁻¹. The weaker peak among these two strongest modes was obtained in Ref. 4 to be at 983 cm⁻¹. Figure 3(a) shows the spectrum simulated for a free pyridine molecule, while Fig. 3(b) shows the corresponding SERS spectra for the same molecule fixed at a distance of 1 nm from both an uncharged and a charged silver MNP of 5 nm in radius. A radial orientation for the molecule is assumed, and the same optical constants for silver and an incident wavelength of 357 nm are used as in Ref. 4, with the latter set to be close to the surface plasmon resonance of the MNP. From the results in Fig. 3(b), it is seen that while an enhancement of the order 10^2 is achievable with an uncharged silver MNP, an order of 10^3 is possible with the presence of a modest amount of surface charge of the order $\sim 10^{-17}$ C. Thus the effects revealed from our model should be realizable by conducting a SERS experiment using the pyridine – silver MNP system, where the amount of surface charge can be controlled via an applied voltage of the order ~ 10 –100 V.

Finally we present an assessment on the accuracy of the GN model (with surface charge) via a comparison of the field enhancement factors calculated from electrostatics and those from a full dynamic Mie theory (see the Appendix). Note that since the image enhancement from a full dynamic theory will be rather complicated and becomes insignificant for large molecule-MNP distances at which retardation effects really become important, here we only focus on the field enhancement in the following comparison. We have confirmed that while the GN model is accurate for sphere radius below ~ 20 nm, it can be rather inaccurate close to the dipole SP resonance frequencies. Figure 4 shows the field enhancement results for a radial dipole at a distance of 5 nm from a

FIG. 4. The enhancement ratio of the 4th-power electric field, $|E/E_0|^4$, at the position of the molecule near a neutral sphere of radius (a) $a = 5$ nm and (b) $a = 10$ nm at a distance $d = 5$ nm. The results are obtained from the GN model and Mie theory as indicated in the figure.

neutral sphere of 5 nm radius (Fig. 4(a)) and one of 10 nm radius (Fig. 4(b)), respectively. It is clear that for the 10 nm sphere, the GN model is already rather inaccurate as far as the dipole SP resonance is concerned. Similar discrepancy between the GN and Mie results can be demonstrated for a charged MNP using the results in the Appendix.

Hence in order to improve the accuracy of our extended GN model, we propose to apply the MLWA (Eq. (11)) to *both* the image and field enhancement factors in Eq. (1) and (2). Figure 5(a) shows the field enhancement factor calculated for a 10 nm sphere from all the three models: GN, MLWA, and Mie; from which the MLWA result is seemed to be pretty accurate in its account for the dipole SP resonance. Thus, using the MLWA, we have re-computed the results in Fig. 1(a) for a 10 nm MNP. Figure 5(b) shows these more accurate SERS enhancement ratios for different charged MNP's from which we observe that, while the charge-induced blueshifts are still revealed, the difference in the magnitudes for resonance enhancements are not as large as the sphere charge increases. The reason is that the radiation damping term (i.e., the term $-i2x^3/3$ in the quantity η in Eq. (11)) overshadows the surface charge effects (i.e., the term via τ) resulting in a less distinct peak enhancement among the different charged spheres. Note that although the MLWA leads to more accurate results for spheres of greater sizes, it can "overcorrect" the dipole polarizability and lead to even worse results than those from the static GN model. For example, we have observed that the GN model is actually more accurate than the MLWA for the 5 nm sphere. Hence, before one can derive an "all-dynamic" model incorporating both the image and field enhancements,

FIG. 5. (a) Same as Fig. 4(b), but including the MLWA results. (b) Same as Fig. 1(a), but for a sphere of radius $a = 10$ nm using the MLWA theory.

one must apply either the GN or the MLWA model, both with cautions. In addition, we also note that the charge effects (relative to a neutral MNP) for a fixed surface potential decreases with the increase of the MNP size as expected.

CONCLUSION

Since the first theoretical work by Bohren and Hunt⁹ on an extension of the Mie theory to incorporate the effects of the extraneous surface charges, recent subsequent works have studied such charge effects on scattering,^{18,19} absorption,²⁰ near field,²¹ and anomalous optical resonances²² from these nano particles (metallic as well as nonmetallic). In this work, we have extended the study of the corresponding effects to spectroscopy (SERS) being motivated by recent SERS experiments with colloidal particles which are most of the time charged.^{6,7} Using simple electromagnetic models, we have observed that this charge effect will in general lead to blueshifted resonances and greater enhancements. We have also simulated the SERS spectral of a real molecule (pyridine) at a silver MNP and demonstrated the possibility of observing such extraneous charge effects. However, these charge effects in the recent experiments^{6,7} are far more complicated than we can completely account for using our simple electromagnetic model since the bonding between the SERS molecules and the MNP are completely beyond what we can treat in our simple approach. Moreover, the electromagnetic effects we have elucidated are not dependent on the sign of the surface charges due to the quadratic dependence of the surface conductivity on the extraneous charge⁹ as discussed above. Hence while we were motivated by these recent experiments,^{6,7} our

model studied in this paper is strictly limited to physisorbed molecules on a MNP. Nevertheless, we believe that the results we obtained should be verifiable from specially designed single molecule – single MNP experiments,²³ and we have taken the first step to theoretically study these surface charge effects on surface enhanced spectroscopy.

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APPENDIX: DYNAMIC FIELD ENHANCEMENT FACTORS

Here we give a brief summary of the results for the field enhancement factor calculated in the extended Mie theory of Bohren and Hunt.⁹ Consider a sphere of radius a located at the origin and illuminated by a plane wave propagating along the z direction with x polarization, i.e.,

$$\mathbf{E}_{inc} = E_0 e^{ikr \cos \theta} \mathbf{e}_x. \quad (\text{A1})$$

For a radially oriented molecule with its position fixed at a distance d from the sphere, the maximum enhancement of the Raman signal can be achieved at $x = a + d$ on the x axis. The field at the position of the molecule is given by the Mie theory,⁹ and thus the field enhancement ratio can be obtained in the form:

$$\left| \frac{E}{E_0} \right|^4 = \left| 1 + \sum_{n=1}^{\infty} i^{n+1} b_n (2n+1) P_n^1(0) \frac{h_n(\rho)}{\rho} \right|^4, \quad (\text{A2})$$

where $\rho = k(a+d)$, b_n is given in Eq. (6) and the Legendre and Hankel functions are standard. Similarly, for a tangential molecule we choose the position of the molecule be at $y = a + d$ on the y axis and obtain the maximum possible enhancement ratio to be

$$\left| \frac{E}{E_0} \right|^4 = \left| 1 - \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} \times \left\{ a_n P_n'(0) h_n(\rho) - i b_n P_n^1(0) \frac{[\rho h_n(\rho)]'}{\rho} \right\} \right|^4, \quad (\text{A3})$$

where $P_n'(\cos \theta) \equiv dP_n^1(\cos \theta)/d\theta$. The results in (A2) and (A3) are used to compare with those from the other approximate theories in Figs. 4 and 5(a).

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