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Molecular Fluorescence in the Vicinity of a Charged Metallic Nanoparticle

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Citation Details

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Abstract: The modified fluorescence properties of a molecule in the vicinity of a metallic nanoparticle are further studied accounting for the possible existence of extraneous charges on the particle surface. This is achieved via a generalization of the previous theory of Bohren and Hunt for light scattering from a charged sphere, with the results applied to the calculation of the various decay rates and fluorescence yield of the admolecule. Numerical results show that while charge effects will in general blue-shift all the plasmonic resonances of the metal particle, both the quantum yield and the fluorescence yield can be increased at emission frequencies close to that of the surface plasmon resonance of the particle due to the suppression of the nonradiative decay rate. This provides a possibility of further enhancing the particle-induced molecular fluorescence via the addition of surface charge to the metal particle.

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1. Introduction

Since the first discovery of surface-enhanced Raman scattering (SERS) four decades ago and the subsequent understanding of the phenomenon to be largely caused by the resonant excitation of the surface plasmons in metallic nano structures, it has been widely recognized that such plasmonic enhancement can be applied to almost any molecular spectroscopy [1]. In particular, the modified fluorescence properties of molecules in the vicinity of a metallic nanoparticle (MNP) have been actively studied by many researchers in recent years [2–4]. It has been established that depending on many factors such as the emission frequency, the orientation of the emitting dipole, the distance of the molecule from the MNP, the geometry and material of the MNP, etc., the molecule fluorescence can both be enhanced and suppressed in the presence of the MNP. In general, for a radial-oriented emitting molecular dipole at a certain optimal distance from the MNP, fluorescence can be significantly enhanced when the emission frequency is close to the dipole surface plasmon resonance of the particle.

Theoretically, both quantum and classical theories have been developed in the literature [1]. In the quantum approach, density functional theory is often applied to treat both the molecule and the MNP; whereas for MNP of greater size or in case of molecule being far from the MNP, classical electrodynamics can also be applied which models the system as an oscillating dipole interacting with a metallic sphere which is characterized by a dielectric function. In this latter approach, further simplifications can be obtained via the long wavelength approximation when the characteristic dimensions are much smaller than the optical wave length. In addition, hybrid quantum/classical formulations are also available such as that adopting the multi-scale Maxwell-Schrodinger equation [1, 5], and that introducing quantum effects of the MNP through a nonlocal dielectric response function [6]. Moreover, all the existing studies so far have been limited to neutral MNP's and hence the possible effects due to the presence of a net extraneous charge on the particle have seldom been investigated in this context when a light source (i.e. the fluorescing molecule) is in close proximity. Nevertheless, the classic Lorenz-Mie scattering theory has indeed been generalized to allow for the presence of extraneous charge by Bohren and Hunt [7] and far-field scattering from such a sphere has been studied actively in the literature in recent years [8–11]. In addition, although to a lesser extent, experimental study on light scattering from charged particle has also been carried out with noticeable difference observed from millimeter-wave scattered by neutral versus charged water droplets [12]; with the observed results being consistent with the generalized theory [7].

The original motivation towards the study of far-field scattering from a charged sphere is mainly from the fact that naturally existing particles are very often non-neutral due to the production process of these particles. Examples range from cosmic dust in space to particles in the Earth environment (e.g. droplets from ocean spray, ice crystals in stormy atmosphere, etc.). In the laboratory, one can easily prepare colloidal solutions which end up with the particles in the solution being charged. Previous works have studied such charge effects on scattering [7, 8], absorption [9], near field [10], and anomalous optical resonances [11]; with the general conclusion that the deviation from a neutral sphere is significant only for particle size small compared to the wave length, except for the distribution of fields near the sphere [10] in which case discrepancy also shows up for much larger spheres. Note that all these previous studies have a "far excitation source" with an incident plane wave, and most of them have focused on non-metallic charged particles.

In a recent study [13], we have taken a first step in applying this extended Lorenz-Mie theory [7] to investigate the extraneous charge effects on MNP-enhanced molecular spectroscopy. In particular, we have studied the effects on SERS and have concluded that such effects will in general lead to blue-shifted resonances [14] and greater enhancements. Moreover, our theory was not a fully-electrodynamic one due to the complexity of the SERS problem which involves the modeling of the scattering of incident plane waves from a dipole-sphere system. We were then limited to merging the electrodynamic theory of Bohren and Hunt [7] with the static model of Gersten and Nitzan [15], with improvement of the model's accuracy relative to a full electrodynamic approach via implementation of the modified long wavelength approximation [16].

It is the purpose of this paper to launch our spectroscopic study on another very important process: molecular fluorescence, which for applications is no less significant than SERS. In particular, we shall study the charge effects on the MNP-modified fluorescence for molecules in close proximity to the particle. Since in fluorescence, unlike Raman scattering, the emission process is completely independent of the initial absorption (i.e. both photons are not linked to each other in a coherent and instantaneous way) [17], we shall see that the modeling for the MNP-modified fluorescence process is simpler than that for SERS and we can also implement a fully-electrodynamic model. However, in order to incorporate the charge effects, we have to first extend the theory of Bohren and Hunt [7] to have the incident plane wave replaced by a localized source in the form of an emitting dipole in the proximity of the charged sphere. For the neutral sphere case, this extension has been accomplished by Ruppin [18] in his study of molecular decay rates near a spherical particle. In the following, we shall first extend Ruppin's theory to allow for the presence of surface charge on the sphere, in a way parallel to that of Bohren and Hunt [7] in their generalization of the Lorenz-Mie theory to charged sphere. Following this we shall apply our extended Ruppin theory to the study of the modifications of molecular fluorescence in the vicinity of a charged MNP.

2. Theory

2.1 Generalization of Ruppin's theory to a charged sphere

In Ruppin's theory, the full electrodynamics of the scattering of a harmonically emitting dipole from a sphere has been worked out with the scattered and transmitted fields (into the sphere) expanded in terms of the vector spherical waves and the well-known Mie coefficients [18]. In deriving his solutions, Ruppin had applied the ordinary boundary conditions with the tangential components of *both* the electric and magnetic fields to be continuous:

$$\mathbf{n} \times (\mathbf{E}_1 - \mathbf{E}_2) = \mathbf{0}, \tag{1}$$

and

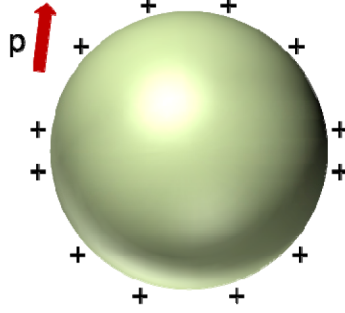$$\mathbf{n} \times (\mathbf{H}_1 - \mathbf{H}_2) = \mathbf{0}. \tag{2}$$

Fig. 1. Schematic of the dipole-sphere system with extraneous surface charges.

However, in the presence of extraneous surface charges on the sphere, shown in Fig. 1, the condition in Eq. (2) must be modified to account for the free current ($\mathbf{K}$) arising from the interaction of these charges with the external field:

$$\mathbf{n} \times (\mathbf{H}_1 - \mathbf{H}_2) = \mathbf{K}. \tag{3}$$

To study how this will modify Ruppin's results, it turns out that it is not necessary to solve the boundary value problem with a dipole source starting from the beginning, since the same problem with an incident plane wave has already been worked out in the literature [7].

In their pioneering work, Bohren and Hunt had extended the classic Mie theory for an incident plane wave with the boundary conditions (1) and (3) implemented and correlated by introducing a parameter known as surface conductivity via Ohm's law: $\mathbf{K} = \sigma_S \mathbf{E}_{1t} = \sigma_S \mathbf{E}_{2t}$. The results from this generalized Lorenz-Mie theory [7] show that all one has to do for the charged sphere scattering is to replace the various Mie coefficients to include the contributions from this surface conductivity. For example, the standard Mie scattering coefficients will now take the following form [7]:

$$a_n = -\frac{\psi_n'(x)\psi_n(mx) - \psi_n(x)\left[m\psi_n'(mx) - i\tau\psi_n(mx)\right]}{\xi_n'(x)\psi_n(mx) - \xi_n(x)\left[m\psi_n'(mx) - i\tau\psi_n(mx)\right]}, \tag{4}$$

$$b_n = -\frac{\psi_n(x)\psi_n'(mx) - \psi_n'(x)\left[m\psi_n(mx) + i\tau\psi_n'(mx)\right]}{\xi_n(x)\psi_n'(mx) - \xi_n'(x)\left[m\psi_n(mx) + i\tau\psi_n'(mx)\right]}, \tag{5}$$

where ψ_n and ξ_n are the Riccati-Bessel functions, $x = ka$ is the size parameter of the sphere, $m = \sqrt{\varepsilon}$ is the refraction index of the (nonmagnetic) sphere, and $\tau = 4\pi\sigma_S(\omega)/c$ with c the speed of light.

Now the observation is that in Ruppin's original solution to the dipole-sphere problem, the fields are all expanded in terms of the vector spherical waves modulated by a dipole source term. When the conditions (1) and (2) are matched across the sphere boundary, the expansion coefficients are found to be the same as those in the original plane wave Lorenz-Mie theory [18]. Hence if one were to generalize the theory of Bohren and Hunt [7] to the case of an emitting dipole interacting with a charged sphere, one can imagine that the same algorithm as Ruppin's can simply be applied leading to identical results as in Ruppin's theory with the standard Mie coefficients replaced by those in Eqs. (4) and (5) to account for the effects of the surface charges. We thus in the following simply apply Ruppin's results together with Eqs. (4) and (5) to study the charge effects on molecular fluorescence near a non-neutral MNP.

2.2 Calculation of fluorescence characteristics

As explained above, fluorescence is governed by two relatively independent processes (absorption and emission), one can thus introduce a MNP-modified fluorescence rate as follows [19]:

$$\gamma_F = \left| \frac{E}{E_0} \right|^2 \left(\frac{\gamma_r}{\gamma_r + \gamma_{nr}} \right), \tag{6}$$

where $\left| E / E_0 \right|^2$ is the field enhancement ratio and

$$Y = \frac{\gamma_r}{\gamma_r + \gamma_{nr}} \tag{7}$$

is the quantum yield of the molecule in the presence of the MNP. Note that $\left| E / E_0 \right|^2$ also describes the excitation probability of the molecule in the absence of saturation of fluorescence, and Y indicates the probability of receiving the emitted photons in the far field (radiation efficiency), where γ_r and γ_{nr} are the radiatve and nonradiative decay rates, respectively.

Since for a dipole-sphere system, the quantities in Eqs. (6) and (7) have all been worked out in the literature starting from Ruppin's work [18] for an uncharged sphere, we simply collect some of these in the following [18, 20, 21], where we have assumed the molecular intrinsic quantum yield to be unity for simplicity [19]. For a radial oriented dipole, we have:

$$\frac{E}{E_0} = 1 + \sum_{n=1}^{\infty} i^{n+1} b_n (2n+1) P_n^1(0) \frac{h_n(x_d)}{x_d}, \tag{8}$$

$$\gamma^{\perp} = 1 + \frac{3}{2} \operatorname{Re} \sum_{n=1}^{\infty} n(n+1)(2n+1) b_n \left(\frac{h_n(x_d)}{x_d} \right)^2, \tag{9}$$

$$\gamma_r^{\perp} = \frac{3}{2} \sum_{n=1}^{\infty} n(n+1)(2n+1) \frac{\left| j_n(x_d) + b_n h_n(x_d) \right|^2}{x_d^2}, \tag{10}$$

and

$$\gamma_{nr}^{\perp} = \frac{3x}{2x_d^2} \sum_{n=1}^{\infty} n(n+1) \left| \beta_n h_n(x_d) \right|^2 \left[(n+1)I_{n-1} + nI_{n+1} \right], \tag{11}$$

where $\gamma^{\perp} = \gamma_r^{\perp} + \gamma_{nr}^{\perp}$ is the total decay rate (all normalized to the free decay value), which can also be obtained from the mechanical oscillator model in linear systems [21]. The other quantities including the special functions and Mie coefficients are in obvious notations with $x_d = kd$ and d being the distance of the molecule from the sphere center [18]. Note that the Mie coefficient b_n is simply the one in Eq. (5) without the surface charge term, and I_n is a result from an integral obtained previously in the form $I_n = \operatorname{Im} \left[x_1^* j_{n-1}^*(x_1) j_n(x_1) \right]$ with $x_1 = \sqrt{\varepsilon} ka$ [21].

Similarly, for a tangential oscillating dipole, we have:

$$\frac{E}{E_0} = 1 + \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} \left\{ a_n P'_n(0) h_n(x_d) + i b_n P_n^1(0) \frac{\left[x_d h_n(x_d) \right]'}{x_d} \right\}, \tag{12}$$

$$\gamma^{\parallel} = 1 + \frac{3}{4} \operatorname{Re} \sum_{n=1}^{\infty} (2n+1) \left[a_n h_n^2(x_d) + b_n \left(\frac{\xi'(x_d)}{x_d} \right)^2 \right], \tag{13}$$

$$\gamma_r^{\parallel} = \frac{3}{4} \sum_{n=1}^{\infty} (2n+1) \left\{ \left| j_n(x_d) + a_n h_n(x_d) \right|^2 + \frac{1}{x_d^2} \left| \psi_n'(x_d) + b_n \xi_n'(x_d) \right|^2 \right\}, \tag{14}$$

and

$$\gamma_{nr}^{\parallel} = \frac{3x}{4} \sum_{n=1}^{\infty} \left\{ (2n+1) \left| \alpha_n h_n(x_d) \right|^2 I_n + \left| \frac{\beta_n \xi_n'(x_d)}{x_d} \right|^2 \left[(n+1)I_{n-1} + nI_{n+1} \right] \right\}, \tag{15}$$

where again $\gamma^{\parallel} = \gamma_r^{\parallel} + \gamma_{nr}^{\parallel}$ is the total decay rate [21].

It is then straightforward to apply the above results to the case of a charged sphere except for the nonradiative rates in Eqs. (11) and (15). For the other results, one simply uses the modified Mie scattering coefficients in (4) and (5) into the results in Eqs. (8)-(10) and Eqs. (12)-(14) to study the charge effects. However, in the presence of free surface charges on the MNP, there will emerge an additional Joule heating loss term in the calculation of the nonradiative rate due to the surface current given by the following angular integral on the sphere: $\int d\Omega \sigma_S \left| E_t(a,\theta,\varphi) \right|^2$, where E_t is the tangential electric field at the surface of the MNP, which is rather complicated if one follows Ruppin's work [18] to solve it explicitly in terms of the various modified Mie coefficients (in addition to those in Eqs. (4) and (5)). However, we have proven rigorously in a recent work that the decomposition of the total decay into radiative and nonradiative rates remains valid in a general way as long as the system is restricted to linear response [22], hence we shall simply calculate the "charge-modified" nonradiative rates in the following by taking the difference between the total and the radiative rates: $\gamma_{nr} = \gamma - \gamma_r$. Note that the previous calculations [21] which lead to an explicit independent confirmation of such decomposition of the total decay cannot be applied in a straightforward way to the present case since unlike the bulk conductivity which is proportional to the imaginary part of the dielectric function, the surface conductivity is a model-dependent parameter and does not relate to the material properties of the MNP in a unique way [7]. However, in light of our previous work in [22], we can still apply such decomposition to the present case even if an independent confirmation of its validity is not available.

3. Numerical results

We have performed some numerical studies of the charge effects on the MNP-modified fluorescence for a molecule in the vicinity of a silver sphere with the same dielectric function given in [13], in which a fit to the Drude function with limitation of the mean free path is adopted in the following way:

$$\varepsilon = \varepsilon_{Ag}(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\Gamma)}, \tag{16}$$

where $\omega_p = 1.36 \times 10^{16} \ \text{s}^{-1}$ and $\Gamma = \Gamma_B + Av_F/a$ with $\Gamma_B = 2.56 \times 10^{13} \ \text{s}^{-1}$, $v_F = 1.38 \times 10^8$ cm/s and the coefficient A in the term accounting for surface damping is simply taken as unity. In order to manifest these effects, we have considered relatively large values of surface charge density and small MNP size of 5 nm radius, though our formalism is fully dynamic and applicable to particles of any size. We expect the qualitative feature of the effects will remain if realistic values of the charge turn out to be smaller, and also for larger MNP sizes. The molecule is located at 1 nm from the MNP surface for all spectral calculations.

We first study the effects on the various decay rates of the molecule. Figure 2 shows the normalized total decay rate as a function of emission frequency. It is interesting to observe

that for the neutral (q_0) case, the strongest induced decay emerges at higher multipole ($\ell = 3$) SP resonance instead of the dipole SP resonance ($\omega / \omega_p \sim 0.57$) due to the dominance of nonradiative transfer at such close molecule-sphere distance (see below). As extraneous charge is added to the sphere, the total molecular decay is in general suppressed with the resonance blue-shifted (due to an effective increase of free charge density and hence the plasmon frequency [13, 14]), and a larger number of multipolar resonance being manifested. In addition, we see that the decay rates for tangential dipoles (Fig. 2(b)) are smaller than those for radial dipoles (Fig. 2(a)) as expected, even in the presence of extraneous charges on the MNP.
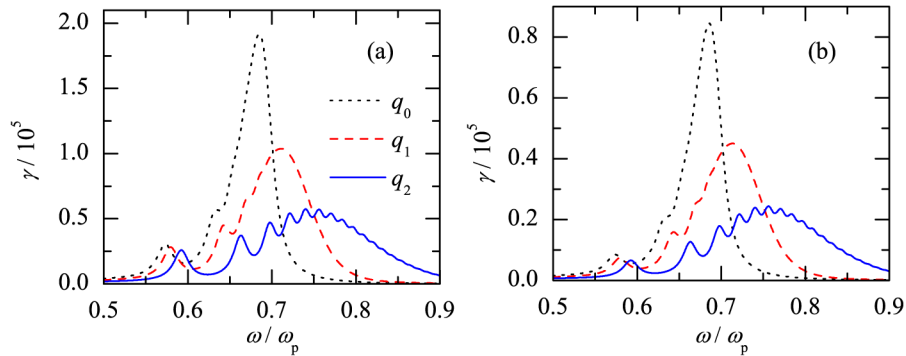
Fig. 2. The spectrum of the normalized total decay rate as a function of the emission frequency of the molecule with (a) radial and (b) tangential orientation for the molecule at a distance of 1 nm from a silver sphere of radius 5 nm. The extraneous surface charges on the silver sphere are $q_0 = 0$, $q_1 = 1.67 \times 10^{-16}$ C, and $q_2 = 5 \times 10^{-16}$ C as indicated in the figure.
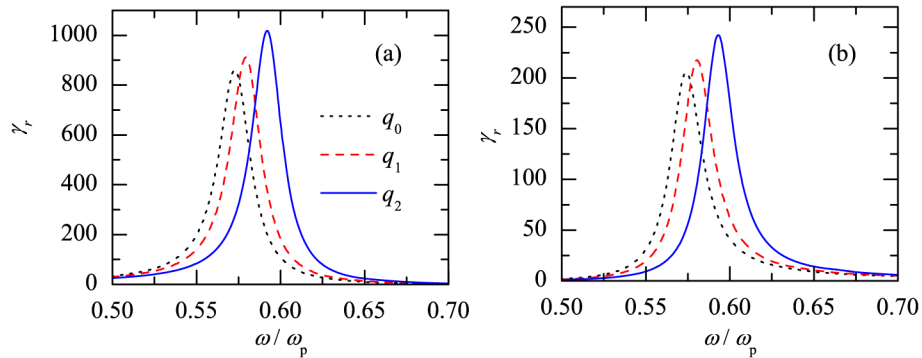

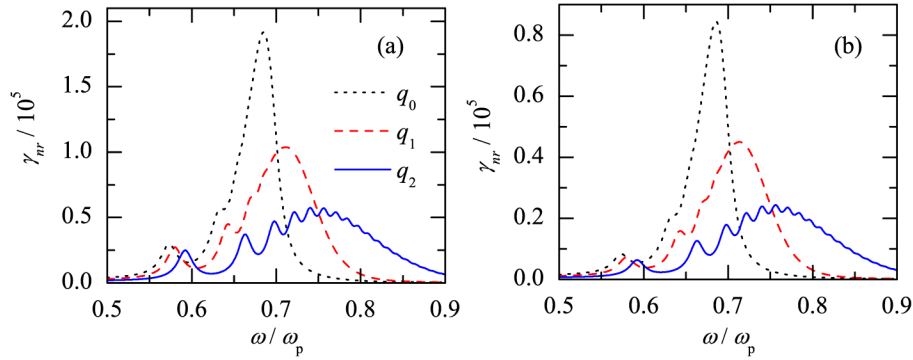Fig. 3. Same as Fig. 2, but for the normalized radiative decay rate.

Fig. 4. Same as Fig. 2, but for the normalized nonradiative rate.

In order to understand the results better, we have decomposed the total decay into radiative and nonradiative rates and plotted in Figs. 3 and 4, respectively. Figure 3 shows the expected result with the enhanced radiative rate due exclusively to the dipole surface plasmon resonance of the MNP. Moreover, while the charge-induced blue shifted resonances and the molecular orientation effects are as observed in the total decay rate, it is seen that the extraneous charge will now *increase* the radiative rate at resonance due to greater effective oscillating dipole moment for the MNP. This will be significant for enhancement of fluorescence as we shall see in the following.

In Fig. 4, it is clearly seen that the total decay in Fig. 2 is indeed dominated by nonradiative transfer from the molecule to the MNP at such close distance (1 nm). It is now obvious that the suppression in molecular decay and the emergence of multipolar resonances in the presence of extraneous charge is largely due to nonradiative transfer between the molecule and the MNP. This can be understood as a "screening effect" from the added free charges, in the presence of which electromagnetic fields penetrating into the MNP will be weakened by the surface current produced by these charges. A diminution in these fields in the MNP leads to smaller Joule loss and hence smaller nonradiative transfer. Furthermore, the multipolar resonances become more significant due to near field interaction and are consistent with the previous results which had shown the prominence of the charge effects on near fields [10]. In addition, it is also worth noted that the molecular orientation effect in this case is not as dramatic as that for the radiative rate in which the enhanced rate due to dipole surface plasmon resonance is more significantly lowered for tangential oriented dipoles. Again, we shall see that these results will have significant effects in the MNP modified fluorescence for the admolecule.
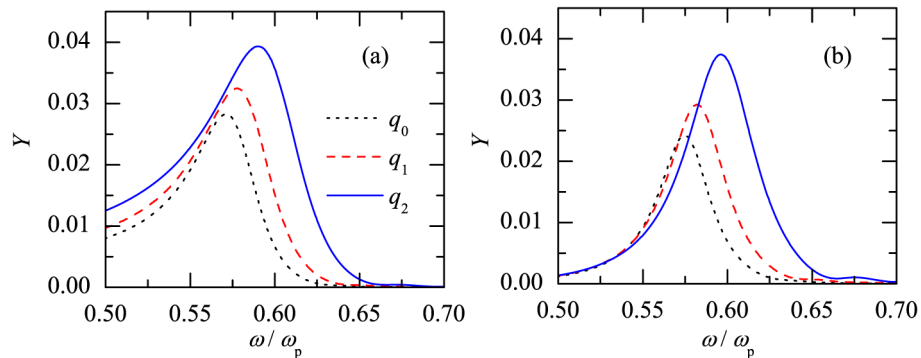

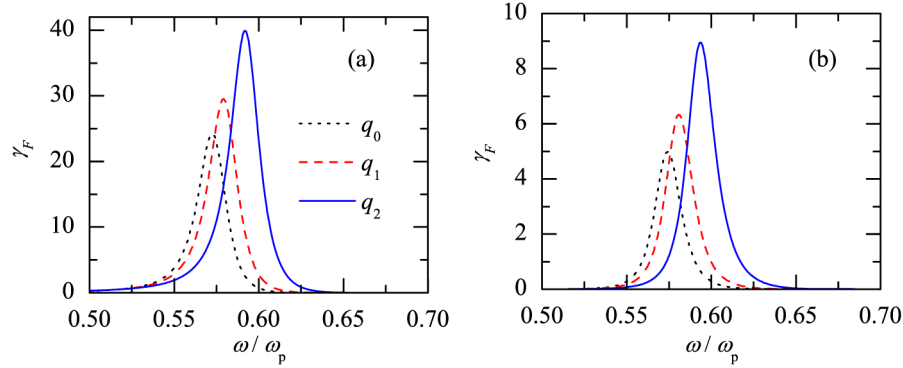Fig. 5. Same as Fig. 2, but for the quantum yield.

Fig. 6. Same as Fig. 2, but for the normalized fluorescence rate.

To have more definitive conclusion about the overall effects on the fluorescence of the molecule, we plot in Figs. 5 and 6 the quantum yield (Eq. (7)) and fluorescence rate (Eq. (6)) of the molecule in the presence of a charged MNP. Figure 5 shows that despite the rather different results for the various decay rates for the two different oriented molecules, the overall quantum yields are very similar and rather small (a few percent) for such a close molecule-MNP distance due to the dominance of the nonradiative rates. However, the addition of charges to the MNP will mostly lead to an increase of the yield (except for a small range of frequency due to the blue-shift effect). This is expected since we have already demonstrated in the above the decrease in nonradiative and increase in radiate rates due to charge effects, together with the fact that the radiative rate is much smaller than that of the nonradiative. Such charge-induced enhancement of MNP modified fluorescence is even more apparent from Fig. 6 where we have plotted the fluorescence rates, in which the enhancement at the dipole surface plasmon resonance is definite with the increase of surface charge of the MNP. More interestingly, we see that in spite of very close quantum yield values for the two different oriented molecules shown in Fig. 5, the enhanced fluorescence rate is several times greater in the case with radial molecular dipoles. This reveals that the enhanced field in the radial dipole case must be much stronger which is expected if one simply compares the relative orientations of the image dipoles between the radial and the tangential molecules, where in one case the image is parallel to and in the other case anti-aligned with the source (molecular) dipole. In addition, it is worth noting that such MNP enhanced fluorescence is in general much more modest as compared to SERS [13] as is well explained in the literature [23].
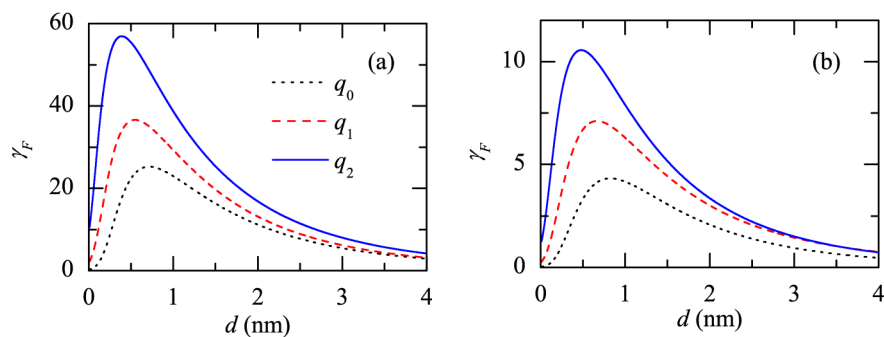

Fig. 7. Normalized fluorescence rate as a function of distance from the silver surface. The molecule is along (a) radial and (b) tangential directions. The emission frequencies are set at each of the dipole resonance for the cases q_0, q_1, and q_2 with values equal to $0.57\omega_p$, $0.58\omega_p$, and $0.58\omega_p$, respectively. Other parameters are the same as in Fig. 2.

Finally, we study the dependence of the enhanced fluorescence on the molecule-MNP distance d. It has been established that due to the competing nature of the field enhancement and the nonradiative decay as a function of this distance, there exists an optimal location for the molecule to experience the greatest overall fluorescence enhancement [19]. This happens since at very close distances, the nonradiative transfer is too large and at far distances, the enhanced field becomes too weak. In Fig. 7, we have plotted the fluorescence rate (Eq. (1)) as a function of d for the three differently charged MNP's at fixed emission frequencies equal to the respective dipole surface plasmon resonance for each sphere (Fig. 6). The results show that while for such a small MNP (5 nm radius) the optimal distances are all within 1 nm, this distance *decreases* as the charge of the MNP is increased. This is again conceivable as a consequence of the decrease in nonradiative rate due to the charge effects, so that one does not need to go too far from the sphere to have this rate significantly decreased. Furthermore, one sees that this optimal distance is not sensitive to the different orientations of the molecular dipoles.

4. Conclusion

We have in this work studied the effects on the MNP-induced plasmonic enhancement of fluorescence due to the presence of extraneous charges on the particle. While it is very common for naturally-occurring particles to carry net charges, most of the previous studies on the modified optical effects due to these charges have been limited to nonmetallic particles and pure optical phenomena (e.g. absorption, scattering, extinction, etc.). We have thus in a recent work [13] and in this work attempted to initiate studies of these surface charge effects on spectroscopy focused on plasmonic enhanced molecular spectroscopy at a MNP. The most interesting result obtained here is the further enhancement of molecular fluorescence due to the presence of these extraneous charges on the MNP, and this is assured due to the following three factors: the increase in radiative rates, the decrease in nonradiative rates, and the increase in the enhanced fields. Moreover, we have to admit that experimental observation of these charge effects in optical processes has so far been limited [12] and can be complicated by many other factors such as the deviation from perfect sphericity of the particle. Nevertheless, we believe the present findings will be useful for future experimental improvements of plasmonic enhanced fluorescence using MNP's.