

# Comparison of plasmon enhanced fluorescence and Raman processes near metal nanoparticles

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## Abstract

Fluorescence and Raman spectroscopy are both precise and versatile techniques for indentifying small quantities of chemical and biological substances. One way to improve the sensitivity and specificity of these measurement techniques is to use enhancement of optical fields in the vicinity of metal nanoparticles. We present a comparative study on the enhancement of Fluorescence, normal and resonance Raman processes by a single metal nanoparticle. Taking an analytical approach, we explain the physics behind the quenching effect observed in both fluorescence and resonance Raman measurements but not in normal Raman scattering. We establish limits for attainable enhancement, and outline the path to optimization of all three processes.

## 1. Introduction

Metal nanostructures are known to enhance various optical properties of objects of nanometer scale or smaller. While spectacular results have been observed in a variety of phenomena in the laboratories, the only widespread practical application remains the one in Surface Enhances Raman Scattering (SERS) sensing - first demonstrated in 1970's [1]. Subsequent work [2] has compared the enhancements of normal (non-resonance) Raman, resonance Raman, and fluorescence, and has observed degrees of enhancement that vary by many orders of magnitude. The difference had been generally attributed to the fluorescence lifetime quenching [3] near the metal surface. This quenching effect has been explored recently to reveal the ultrafast processes of single molecules on metal surface [4] and to quantify resonance Raman cross sections of dyes with SERS [5]. The absence of commensurate quenching for normal Raman scattering, however, has never been explained in a straightforward way. The goal of this paper is to provide such a straightforward and accessible explanation as well as to outline ways for optimizing enhancement of fluorescence and Raman for sensing applications. This work is based on a recently developed comprehensive model of optical properties enhancement by metal nanoparticles [6]. In this work, we extend this model to include the effect of high order SP modes [7] and apply it to fluorescence, normal Raman, and resonance Raman to demonstrate that emission into non-radiative higher order modes does quench fluorescence and resonance Raman while it has no measurable effect on normal Raman.

## 2. Fluorescence enhancement

We have previously established the SP modes of a single metal nanosphere and their associated properties [6,7]. Under the electro-static approximation, a single metal nanosphere with a radius  $a$  being placed in a dielectric media with the dielectric constant  $\epsilon_D$ , supports infinite number of SP modes,

each characterized by an associated Legendre polynomial of index  $l$  ranging from 1 to  $\infty$ . Among all the SP modes, only the dipole mode,  $l = 1$ , with nonzero dipole moment, couples to the external fields, and therefore decays radiatively. Simultaneously, all the modes also experience non-radiative decay due to the imaginary part of the metal dielectric function at roughly the same rate equal to the metal damping rate. Furthermore, each mode is characterized by an effective volume  $V_{eff,l} = \frac{4\pi a^3}{(l+1)^2 \epsilon_D}$  - the lower is effective volume the higher is the field concentration, thus higher order non-radiative modes "hugging" the surface tend to interact stronger with molecules that are closer to the surface but the strength of interaction falls off quickly away from the surface.

The result of fluorescence enhancement for a molecule with  $\sigma_{abs} = 0.1 \text{ nm}^2$  and  $\eta_{rad} = 0.01$ , placed in the vicinity of an Au sphere surrounded by air is shown in Fig. 1 where the optical excitation is assumed to be in resonance with the dipole mode  $\omega_{ex} = \omega_1 = 2.562 \text{ eV}$ , and the emission frequency is down shifted by 100 meV to be at  $\omega_S = 2.462 \text{ eV}$ . We can see that the fluorescence enhancement factor exhibits strong dependence upon both the nanoparticle size and the separation between the molecule and particle. Without accounting for higher order modes, it is always better to have molecules positioned as close as possible to the metal sphere in order to take advantage of the large Purcell factor as well as the large field of the dipole mode. But with high order modes taken into account, energy of the molecule placed too close to the metal sphere also gets coupled into these nonradiative modes, and simply dissipates as metal loss. As a result, an optimized separation can be found to allow for significant coupling into the dipole mode while adequately suppresses the luminescence quenching by high order modes.

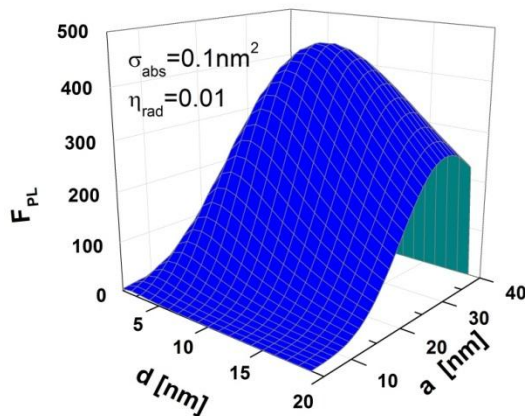


Fig.1 Fluorescence enhancement dependence on the Au nano-sphere radius  $a$  and on the molecule-sphere separation  $d$  for a molecule with  $\sigma_{abs} = 0.1 \text{ nm}^2$  and  $\eta_{rad} = 0.01$ . The optical excitation is in resonance with the dipole mode  $\omega_{ex} = \omega_1 = 2.562 \text{ eV}$ , and the PL emission is at  $\omega_S = 2.462 \text{ eV}$ .

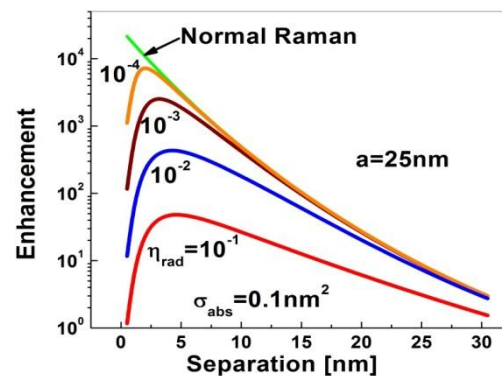


Fig.2 Comparison between Raman and PL enhancement for a range of molecules with  $\sigma_{abs} = 0.1 \text{ nm}^2$  and  $10^{-4} \leq \eta_{rad} \leq 10^{-1}$  for an Au sphere of radius  $a = 25 \text{ nm}$ . Excitations for both processes are at the dipole mode resonance  $\omega_{ex} = \omega_1 = 2.562 \text{ eV}$ , and PL and Stokes Raman emission are both at  $\omega_{PL} = \omega_S = 2.462 \text{ eV}$ .

### 3. Normal Raman enhancement

For comparison we considered the situation where the optical excitation of the Raman process is the same as fluorescence at the dipole mode resonance, and the Raman Stokes emission has the same shift of 100 meV from its excitation (assuming molecular vibration mode energy of 100 meV). For an Au sphere of 25 nm, Figure 2 compares the Raman enhancement to that of fluorescence for a range of molecules with their absorption cross section fixed at  $\sigma_{abs} = 0.1 \text{ nm}^2$  while their original radiative efficiency  $\eta_{rad}$  varies from  $10^{-1}$  to  $10^{-4}$ . Not surprisingly, the Raman enhancement consistently outperforms that of PL which exhibits various degrees of quenching effect depending on the original radiative efficiency, but no quenching whatsoever for Raman process. Indeed, one can think of Raman process as a PL with extremely low efficiency, hence SP enhancement of Raman enhancement is the absolute upper limit of the enhancement of PL.

#### 4. Resonance Raman enhancement

When the excitation frequency becomes very close to the molecular resonance, the broadening of the molecular transition must be taken into account. As the electric field of the SP dipole mode resonantly excites the dipole moment (polarization) of the molecule, this polarization decays according to a dephasing time of  $T_2$  in the absence of the metal nanoparticle. In the presence of metal particles the molecular polarization can decay due to the emission into the higher order modes at the excitation frequency, in addition to its original de-phasing. As a result, the total de-phasing rate (broadening) can increase, particularly when emission into the higher order modes becomes comparable to the de-phasing time  $T_2$ , and quenching is observed.

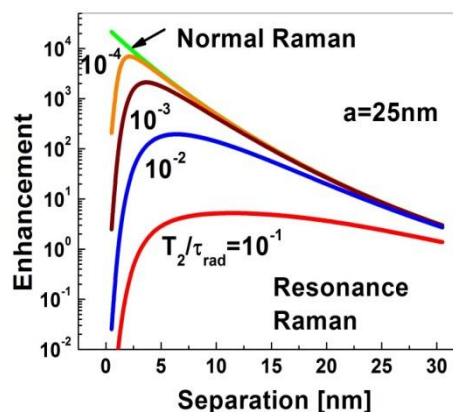


Figure 3. Quenching of resonance Raman for a range of molecules with  $T_2/\tau_{rad}$  ratio varying from  $10^{-4}$  to  $10^{-1}$  near an Au sphere of radius  $a = 25$  nm, compared with normal Raman enhancement.

Figure 3 illustrate the quenching effect in resonance Raman scattering, we fixed the radius of the Au sphere at 25 nm, but varied the spatial separation between the molecule and metal sphere, for a range of molecules with the ratio  $T_2/\tau_{rad}$  varying from  $10^{-1}$  to  $10^{-4}$ . As expected, the normal Raman enhancement consistently outperforms that of resonance Raman.

#### 5. Conclusions

Using a physically transparent analytical model, we have studied the enhancement of fluorescence, normal non-resonance Raman, and resonance Raman processes near metal nanoparticles. We have confirmed and explained the fundamental difference that makes normal Raman enhancement typically much stronger than fluorescence enhancement. We have shown that unlike fluorescence, normal Raman process does not get quenched at the surface. From the practical point of view our results indicate that the spectacular SERS-like enhancement of fluorescence is unattainable except for the molecules whose original luminescence efficiency is very low and show how this limited enhancement can be optimized. We have also analyzed the enhancement of resonance Raman scattering, and showed that for molecules with reasonably narrow linewidth on which the resonantly enhanced Raman can be observed, quenching can indeed take place as well.

#### References

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