



The fluorescence rate of a single molecule close to a spherical metallic nanoparticle



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ABSTRACT

The theoretical study of fluorescence rate of a single molecule close to a spherical metallic nanoparticle is presented. The dielectric function of the metallic nanoparticle and its polarizability is analyzed when the radii of the nanoparticle is rather small. Based on dipole–dipole model, the distance dependence of the excitation rate, radiation rate, nonradiation rate and quantum yield of the emitter molecule are derived out. The results show that the quantum yield is rather small at the vicinity of the metallic nanoparticle surface.

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1. Introduction

Since the pioneering work of Purcell, it has been demonstrated that the emission rate of a single emitter such as molecule depends on the environment. It was realized that the fluorescence rate of a single molecule close to a metal surface can be enhanced [1,2]. Metallic nanoparticle (NP) are known to enhance various optical properties of objects of similar or smaller dimensions placed in the vicinity of the emitter. The spontaneous emission and radiative or nonradiative decay of a single emitter close to a metallic NP have been researched. Analytical theoretical studies of the fluorescence rate of a single molecule close to a metallic nanoparticle have been developed [3,4]. The fluorescence rate is a two-step process which includes the excitation rate and the emission probability represented by the quantum yield. So, the fluorescence rate of a single molecule close to a metallic NP involve two parts, one of them is the excitation rate and another is the quantum yield. Both the excitation rate and the quantum yield will be changed due to the presence of the metallic NP.

The underlying theoretical approach of the present work include: the incident optical field excites vibrating electric dipole on the metallic nanoparticle surface, which in turn greatly impact the local electromagnetic (EM) field; The much-influence local field

and optical mode density together lead to change in both excitation rate and the spontaneous emission rate of a fluorescence molecule near the metallic NP. As a result, the fluorescence rate is greatly influenced. In putting together these fundamental physical processes to formulate a method, we use the classical EM approach to calculate the excitation rate and the quantum yield. The results are finally combined to calculate fluorescence rate of a single molecule close to a spherical silver metallic nanoparticle.

2. Excitation enhancement factor

Let us consider a molecule located at \mathbf{r}_m and represented by a two-level system with transition dipole moment \mathbf{p} and transition frequency ω . A single spherical silver nanoparticle with diameter $2a$ is located at some place, the distance between molecule and NP center is z ($z = a + d$, d is the distance between the molecule and the NP surface) and the axis connecting molecule and particle center is denoted as the z axis (see Fig. 1). The system is irradiated by a plane wave polarized along the z axis. For a small NP ($a \ll \lambda$, λ is the wavelength of the incidence plane wave), the scattered field along the z axis will also be z polarized and therefore molecules oriented perpendicular to the z axis will not be excited. Furthermore, for such molecule orientations there is no enhancement of the irradiative decay rate [5]. It therefore suffices to consider molecules oriented along the z axis.

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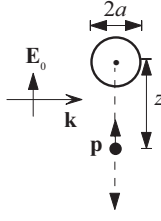


Fig. 1. The location relation between the fluorescence molecule and the spherical metallic nanoparticle.

The fluorescence enhancement by metallic NP is processed as following: First, the incident optical excitation of frequency ω_{ex} is coupled exclusively into the dipole SP mode as all the higher-order modes are not coupled with external fields; In the second step, a molecule placed at position \mathbf{r}_m is excited and make a transition from its ground state to excited state. We will talk about the excitation first.

2.1. The polarizability of the metallic nanoparticle

The dipole \mathbf{p} is induced by the local field considering the external field \mathbf{E}_{exc} and the self-field \mathbf{E}_{self} according to

$$\mathbf{p} = \alpha_0(\omega)(\mathbf{E}_{exc} + \mathbf{E}_{self}) \quad (1)$$

where $\alpha_0(\omega) = 4\pi a^3((\varepsilon(\omega) - 1)/(\varepsilon(\omega) + 2))$ is the quasi-static polarizability, $\varepsilon(\omega)$ is the frequency-dependent dielectric function of the metallic NP.

The effective polarizability α associate the incident field with $\mathbf{p} = \alpha(\omega)\mathbf{E}_{exc}$. So the effective polarizability α can be expressed as

$$\alpha(\omega) = \frac{\alpha_0(\omega)}{1 - i((k^3\alpha_0(\omega))/6\pi)} \quad (2)$$

When $\lambda \gg a$, $\alpha \approx \alpha_0 = 4\pi a^3((\varepsilon(\omega) - 1)/(\varepsilon(\omega) + 2))$.

From Fig. 2 we can know that effective polarizability α approach the quasi-static polarizability α_0 when the metallic NP is small enough.

2.2. The dielectric function of the metallic nanoparticle

The polarizability of the metallic NP $\alpha(\omega)$ is related to the dielectric function $\varepsilon(\omega)$. The dielectric function of a metal like Ag is physically described using Drude model [6]

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (3)$$

This is the Drude model for the optical properties of a free-electron metal. The plasma frequency is given by ω_p and the

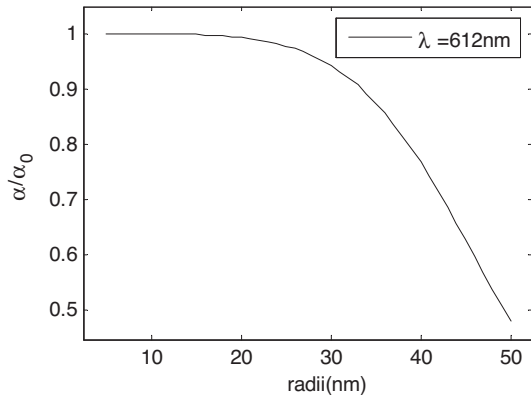


Fig. 2. Normalized polarizability versus the radii of the metallic NP.

damping constant is γ . Based on the experimental data [7] the entire dielectric function was fit over the full range of interest, 0.5–3.5 eV. The resulting parameters were $\omega_p = 9.17$ eV and $\gamma = 0.021$ eV.

In metallic NP system, it is necessary to consider the reduced mean-free path of the electrons due to electron-interface scattering. This factor can be taken into account by using a modified collision frequency, the dielectric function of the metallic NP can be written as

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega(\gamma + (v_F/a))} \quad (4)$$

where v_F denote the Fermi velocity of the electronics, a is the radii of the metallic NP.

2.3. The excitation rate

The excitation rate depend on the local excitation field $\mathbf{E}(\mathbf{r}_m, \omega)$. In fact, the excited rate $\Gamma_{exc} \propto |\mathbf{p} \cdot \mathbf{E}|^2$.

Assuming that the environment does not affect the molecule's polarizability the normalized excitation rate can be expressed as

$$\frac{\Gamma_{exc}}{\Gamma_{exc}^0} = \left| \frac{\mathbf{n}_p \cdot \mathbf{E}(\mathbf{r}_m)}{\mathbf{n}_p \cdot \mathbf{E}_0(\mathbf{r}_m)} \right|^2 \quad (5)$$

where Γ_{exc}^0 is the excitation rate in the free space, \mathbf{n}_p is a unit vector pointing in direction of electric moment of the emitter molecule \mathbf{p} .

In our case, $a \ll \lambda$, the metallic NP can be considered as an oscillating electric dipole, electric dipole is giving by $\boldsymbol{\mu} = \varepsilon\varepsilon_0\alpha\mathbf{E}_0$, α is the polarizability. In the presence of metallic NP, the radiation field of a dipole can be written as [8].

$$\mathbf{E} = \frac{1}{4\pi\varepsilon_0\varepsilon_D} \{k^2(\mathbf{n} \times \boldsymbol{\mu}) \times \boldsymbol{\mu} \frac{e^{ikr}}{r} + [3\mathbf{n}(\mathbf{n} \cdot \boldsymbol{\mu}) - \boldsymbol{\mu}] \left(\frac{1}{r^3} - \frac{ik}{r^2} \right) e^{ikr}\} \quad (6)$$

In our system (see Fig. 1), The distance between molecule and NP center is $z(z = a + d)$, and the axis connecting molecule and particle center is denoted as the z axis, \mathbf{n} is unit vector in the direction of the location of the oscillating electric dipole. In the presence of metallic NP, the total field at the position of the molecule can be expressed as

$$\mathbf{E}(\mathbf{r}_m) = \mathbf{E}_0 + \frac{1}{2\pi\varepsilon_0\varepsilon_D} \boldsymbol{\mu} \left(\frac{1}{z^3} - \frac{ik}{z^2} \right) e^{ikz} \quad (7)$$

So, the normalized excitation rate is written as

$$\left| \frac{\mathbf{n}_p \cdot \mathbf{E}(\mathbf{r}_m)}{\mathbf{n}_p \cdot \mathbf{E}_0(\mathbf{r}_m)} \right|^2 = \left| 1 + 2a^3 \frac{\varepsilon - \varepsilon_D}{\varepsilon + 2\varepsilon_D} \left(\frac{1}{z^3} - \frac{ik}{z^2} \right) e^{ikz} \right|^2 \quad (8)$$

If $z \ll \lambda$

$$\frac{\Gamma_{exc}}{\Gamma_{exc}^0} = \left| 1 + 2 \frac{\varepsilon - \varepsilon_D}{\varepsilon + 2\varepsilon_D} \frac{a^3}{z^3} \right|^2 \quad (9)$$

3. Calculation of the quantum yield

The excitation energy of a molecule can be dissipated either radiatively or non-radiatively. Radiative relaxation is associated with emission of a photon whereas nonradiative relaxation can have various path-ways such as coupling to vibrations, energy transfer to the environment. In most case, we desired to maximize the radiative output of a quantum emitter system. A useful method for describing this output is the quantum yield defined as

$$Q = \frac{\Gamma^R}{\Gamma^R + \Gamma^{NR}} \quad (10)$$

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