



# Modification of optical absorption of molecule near metallic nanoparticles



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## ABSTRACT

We provide an analytical model for the enhancement of optical absorption of active molecules when they are placed in the vicinity of metal nanoparticles of subwavelength dimensions. Through Mie theory, in the context of plane wave expansion (PWE) of a single sphere, we have shown that for a fully random molecular orientation, the absorption enhancement factor is equal to the local field intensity enhancement factor and depends strongly on the nanoparticle size-enabling optimization and separation between the object and metal sphere. With this understanding to the modified absorption, we call for further efforts in the engineering of the perfect absorber.

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## 1. Introduction

The optical properties of various optically active objects of similar dimensions such as atoms, molecules, or quantum dots (QDs) are dramatically changed when they are adsorbed on rough metal surfaces, metal island films, or metal particles [1–10]. The best-known example is surface-enhanced Raman scattering (SERS), in which the Raman scattering of molecules is enhanced by millions of times compared with free molecules. Recently, there has been a great deal of interest in enhancing the efficiency of spontaneous emission (fluorescence) using the surface plasmon polariton (SPP) in the vicinity of a metal–dielectric boundary [11–19]. Metallic nanostructures have been theoretically proposed as candidates to strongly drive spontaneous emission, various experimental works have indeed confirmed enhanced fluorescence close to metal nanoparticles [17–19], allowing in turn for single molecule spectroscopy. The strong modifications are conceptually well understood as a product of surface plasmons (SPs) that induce strong localized electric fields near the surface of nanostructured metals.

In this paper, we turn our attention to the reverse problem, i.e. enhancement of the absorption by molecules placed in the vicinity of metal nanoparticles. This problem is important for two reasons, first it had been proposed to use metal nanoparticles to enhance

the efficiency of photo-detectors [20,21] and solar panels [22,23], and second, absorption is the first step in the photoluminescence emission of photoluminescence (PL) sensors and thus enhanced absorption means improved sensitivity [24]. Through Mie theory, in the context of plane wave expansion (PWE) of a single sphere, we have shown that for a fully random molecular orientation, the absorption enhancement factor is equal to the local field intensity enhancement factor. The absorption properties of molecules are strongly modified in the vicinity of metallic objects which is particularly true when the excitation wavelength is close to the electromagnetic resonances of the system in particular localized surface plasmon resonances for metals.

## 2. Numerical model and simulations

A scattering process consists of an incident beam of photons giving rise to scattered radiation. We estimate the scattered radiation can be classically described as emission from a dipole and start with the case of elastic (Rayleigh) scattering, whereby scattering occurs at the same frequency as the incident radiation. The response to the incident radiation can then be described, by analogy with the static case, within linear response function theory. Excitation by an incident field  $E$  at frequency  $\omega$  results in an induced dipole  $p = \hat{\alpha}(\omega) \cdot E$  oscillating at the same frequency  $\omega$ . Within the classical phenomenological approach, the power absorbed  $P_{Abs}$  by the molecule is equal to the power absorbed by this induced dipole, i.e.

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$$P_{Abs} = \frac{\omega}{2} \text{Im}(E^* \cdot p) = \frac{\omega}{2} \text{Im}(E^* \cdot \hat{\alpha}(\omega) \cdot E) \quad (1)$$

The most common type of linear polarizability tensor is the uni-axial tensor along an axis  $e_m$  (attached to the molecule). For simplicity, we will restrict ourselves to this case, which simplifies greatly the surface selection rules factor. We therefore take  $\hat{\alpha} = \alpha e_m \otimes e_m$ , where  $\alpha$  is the scalar polarizability (implicitly at frequency  $\omega$ ). Then the absorbed power can then be simplified to

$$P_{Abs} = \frac{\omega}{2} \text{Im}(\alpha) |e_m \cdot E|^2 \quad (2)$$

As we already know, Maxwell’s equations for media, on which most of classical EM treatment is based, relate to the macroscopic electromagnetic fields, i.e. average fields over relatively small volumes. But at the molecular (or atomic) level, the microscopic fields are different and usually much more complicated than these average fields. The difference between macroscopic and microscopic fields is often referred to as the local field correction (local field referring in this context to the microscopic field). It is a well-understood effect in the framework of the optical properties of dielectric media; a correction factor for local fields must be applied to optical polarizability. For our purpose here, the microscopic electric field is related to the macroscopic one, in the case of a dielectric liquid of refractive index  $n = \sqrt{\epsilon}$ , by  $E_{micro} = L^{1/4} E_{macro}$ , where  $L^{1/4} = (\epsilon + 2)/3$  [26].

So for a molecule with fully random orientation in free-space, excited with a plane wave with electric field amplitude  $E_{inc}$ , we can then deduce the absorbed power  $P_{Abs}^M = (L^{1/2} \omega/2) |E_{inc}|^2 \text{Im}(\alpha)/3$ . Where we have included explicitly the local field correction and where the factor of 1/3 arises from the orientation averaging ( $\langle |e_m \cdot E| \rangle = 1/3$ ). Since the power density for excitation is  $S_{inc} = (n \epsilon_0 c/2) |E_{inc}|^2$ , we also deduce the free-space absorption cross-section as  $\sigma_{Abs}^M = P_{Abs}^M/S_{inc} = (L^{1/2} \omega/n \epsilon_0 c) \text{Im}(\alpha)/3$ .

The same expressions can be written for a fixed molecule close to surfaces. The field felt by the molecule is  $\hat{E}_{Loc} = E_{Loc} \hat{e}_{Loc}$ , where  $\hat{e}_{Loc}$  is, by definition, a unit vector, characterizing the local field polarization. The local field intensity enhancement factor then takes the form  $M_{Loc}(\omega) = |\hat{E}_{Loc}(\omega)|^2 = |E_{Loc}(\omega)|^2$ .

We write the resulting absorption enhancement factor defined as  $M_{Abs}(\omega) = P_{Abs}/P_{Abs}^M = \sigma_{Abs}/\sigma_{Abs}^M$ , i.e.  $M_{Abs}(\omega) = M_{Loc}(\omega) T_{Abs}$ , with  $T_{Abs} = 3 |e_m \cdot \hat{e}_{Loc}(\omega)|^2$ , and  $M_{Loc}(\omega) = |E_{Loc}|^2/|E_{inc}|^2$  is the local field intensity enhancement factor.  $T_{Abs}$  is the absorption equivalent of the surface selection rules factor. Note that for a fully random molecular orientation,  $\langle T_{Abs} \rangle = 1$  and therefore  $\langle M_{Abs} \rangle = M_{Loc}$ .

A general divergence-less solution of the vector wave equations can be written in spherical coordinates as an infinite series of a complete set of vector spherical harmonics as  $E(r) = E_0 \sum_0^\infty \sum_{m=-n}^{m=n} a_{nm} M_{nm}^{(i)}(k, r) + b_{nm} N_{nm}^{(i)}(k, r)$ , where the wave vector is given by  $k^2 = (\epsilon^2/c^2) \epsilon(\omega)$ .  $a_{nm}$  and  $b_{nm}$  can be any complex coefficients.  $E_0$  is an electric field amplitude (arbitrary at this stage) to make these coefficients non-dimensional. The vectors  $M_{nm}^{(i)}(k, r)$  and  $N_{nm}^{(i)}(k, r)$  are vector spherical harmonics (VSHs). Then we can use this expansion formalism to solve the EM problem of a single sphere excited by an incident wave with a given electric field  $E_{inc}(r)$  at frequency  $\omega$ , and the unknown coefficients must then be determined by imposing two independent EM boundary conditions at the sphere surface. The local field can be calculated at any point outside the sphere, then the modified absorption properties can be analysed.

### 3. Results and discussions

Fig. 1 shows the illustration of the enhancement of optical absorption by a molecule placed at distance  $d$  from the metallic nanoparticle. The property of the modified absorption is illustrated

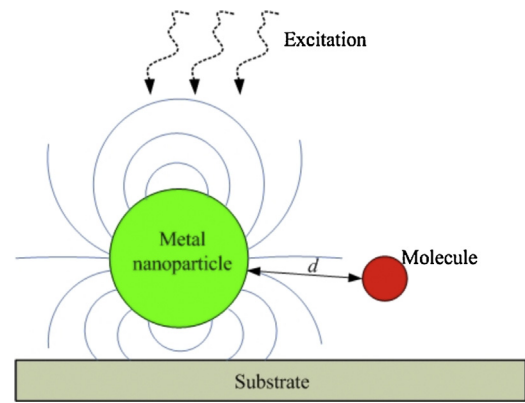


Fig. 1. Illustration of the enhancement of optical absorption by a molecule placed at distance  $d$  from the metallic nanoparticle.

in Fig. 2 by considering the wavelength dependence of  $M_{Abs}$  at a specific point at a distance  $d = 5$  nm from the surface of a sphere. We compare the results for two different cases: a nonabsorbing dielectric nanoparticle ( $\epsilon = 2.25$ ) and a silver nanoparticle. In both of the cases, the radius of the particle is  $r = 25$  nm. In our simulation, based on the Drude model, a good parameterization of the optical properties of silver in the visible, near-IR, and near-UV range is given by [27]

$$\epsilon_{Ag}(\lambda) = \epsilon_\infty \left( 1 - \frac{1}{\lambda_p^2 \left( \frac{1}{\lambda^2} + \frac{i}{\mu_p \lambda} \right)} \right),$$

where  $\epsilon_\infty = 4$ ,  $\lambda_p = 282$  nm;  $\mu_p = 17,000$  nm and  $\lambda$  is the wavelength. The real and imaginary parts of the dielectric function of silver are shown in Fig. 3.

Large local field intensity enhancement is possible close to the surface of a metallic object which is associated with a coupling to localized surface plasmon (LSP) resonances, as evidenced by the resonant response as a function of wavelength. The electric field  $E_{Loc}$  at the molecule position can be very different, both in magnitude and orientation, to the incident field  $E_{inc}$ . The presence of the metal nanoparticles in this case acts as funnel to concentrate the electromagnetic fields on the surface. Under the right conditions, huge local field enhancements can be obtained which is the type of enhancement that people are looking to exploit in SERS. Because of the huge local field enhancements, the properties of optical

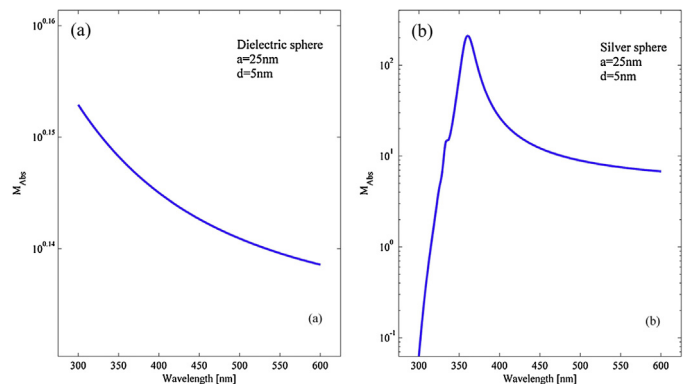


Fig. 2. Absorption enhancement factor calculated for a molecule which is placed at a distance  $d = 5$  nm from the surface of nanoparticles using Mie theory. (a) For a glass sphere, there is a small enhancement, hardly dependent on wavelength. (b) For a silver sphere,  $M_{Abs}$  varies widely with wavelength, showing resonances associated with the localized surface plasmon resonances of the silver sphere. Large enhancements are predicted at the main resonance ( $\lambda = 360$  nm).

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