

Controlling Single Molecule Fluorescence Lifetime Through Slabs of Metallic and Negative Index Materials

L. S. Froufe-Pérez* and R. Carminati

Laboratoire d'Énergétique Moléculaire et Macroscopique, Combustion; Ecole Centrale Paris, Centre National de la Recherche Scientifique, 92295 Châtenay-Malabry Cedex, France.

*Author e-mail address : luis.froufe@em2c.ecp.fr

Abstract : The fluorescence dynamics of a single emitter can be controlled at large distances through slabs of metallic and negative-index materials. This is achieved by positioning a metallic nanoparticle in the vicinity of the emitter image.

1. Introduction

The advent of near-field optics techniques has made possible the detection and spectroscopy of single molecules in complex environments, with a lateral resolution below 100 nm. Near-field optics also stimulated the use of sharp metallic tips or nanoparticles to modify the lifetime and to enhance (or quench) the fluorescence of single molecules. The role of such nanoantennas is twofold: an enhancement of the exciting local intensity, and a modification of the radiative emission rate, both in amplitude (Purcell effect [1]) and angular dependence. A drawback when using metallic objects is the presence of absorption, which creates additional non-radiative channels. In the case of small nanoparticles, we have studied recently the trade-off between radiative and non-radiative processes using a dipole-dipole model [2]. This study has shown that the non-radiative decay rate follows a R^{-6} dependence at short range, where R is the distance between the emitter and the center of the nanoparticle, whereas the distance dependence of the radiative decay rate is more subtle. It is chiefly dominated by a R^{-3} dependence, a R^{-6} dependence being visible at plasmon resonance. This distance dependence might be used to control fluorescence lifetimes and fluorescence signals emitted by single molecules. Nevertheless, substantial influence of the nanoparticle on the emitter dynamics is obtained at distances on the order of a few nanometers. This can be a severe limitation, e.g., when the molecule is embedded in a substrate or in a biological medium.

On the other hand, it has been shown [3] that spontaneous emission lifetime of a single emitter is also greatly modified in the presence of a slab made of different materials. Again, substantial changes occur when the emitter is placed at distances of a few ten nanometers from the surface of the slabs, and hence, practical limitations are of the same kind as in the case of using a nanoparticle to modify fluorescent emission.

In this work, we study theoretically and numerically the possibility of controlling the spontaneous decay rate and the fluorescence signal of a single molecule at large distance (in the micron range), through a film made of either a metallic or a negative-index material working in the so-called perfect-lens regime [4]. It has been shown recently that images with sub-wavelength resolution can be produced through such films [5]. We extend this idea to the control of spontaneous emission by placing the emitter on one-side of the slab, and a metallic nanoparticle on the other side. When the particle is brought close to the focus of the image of the single molecule, both systems are coupled and substantial modification of the emitter spontaneous emission is observed. Although the nanoparticle is placed in vacuum above a flat interface, with the molecule at large distance, in the superlens regime the effect on the molecule is similar to that obtained with a nanoparticle placed at a few nanometers.

2. Model and results

We consider a slab of material of width w (see inset in Fig. 1) with electric permittivity $\epsilon(\omega)$ and magnetic permeability $\mu(\omega)$ at the transition frequency ω . The emitter is modelled through its transition dipole \mathbf{p} . This emitter is placed at a distance Z_s from the closest face of the slab. Analogously, a nanoparticle of radius a is placed on the other side of the slab at a distance Z_p from the surface. The radial positions of both emitter and nanoparticle can be chosen arbitrarily.

The normalized spontaneous emission rate Γ/Γ_0 is given by $\Gamma/\Gamma_0=1+(6\pi/k)\text{Im}\{\mathbf{u}\cdot\mathbf{S}(Z_s,Z_s,\omega)\cdot\mathbf{u}\}$, where Γ_0 is the decay rate of the emitter and k is the wavenumber in the medium where the particle is placed. $\mathbf{S}(Z_s,Z_s,\omega)$ stands for the modification of the free space Green tensor due to the presence of the slab and the nanoparticle, and \mathbf{u} is the direction of the transition dipole.

In the case where the particle is small enough so that it can be treated in the electric dipole approximation (see e.g. [2]), the Green tensor of the full system can be computed exactly, accounting for multiple scattering between slab interfaces and the nanoparticle. This is done by using an angular spectral decomposition and appropriate Fresnel coefficients for the transmitted and reflected fields at the slab interfaces.

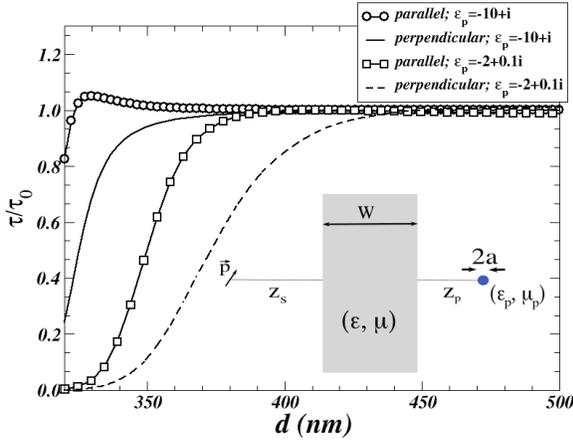


Fig. 1: lifetimes (normalized to its value in vacuum) for transition dipoles, parallel or perpendicular to a perfect left-handed material slab with $\epsilon=-1$ and $\mu=-1$, as a function of the distance between emitter and particle. In all cases $a=10\text{nm}$, $Z_s=100\text{nm}$ and $w=100\text{nm}$, the transition wavelength is $\lambda=500\text{nm}$. The two sets of curves (see legends) correspond to a metallic particle out of resonance (circles and continuous line) with $\epsilon_p=-10+i$, and a particle at resonance, with $\epsilon_p=-2+0.1i$ (in both cases $\mu_p=1$, sub-index p stands for particle's properties). Both emitter and nanoparticle lie in the same line perpendicular to the slab. Inset: Scheme of the system under consideration.

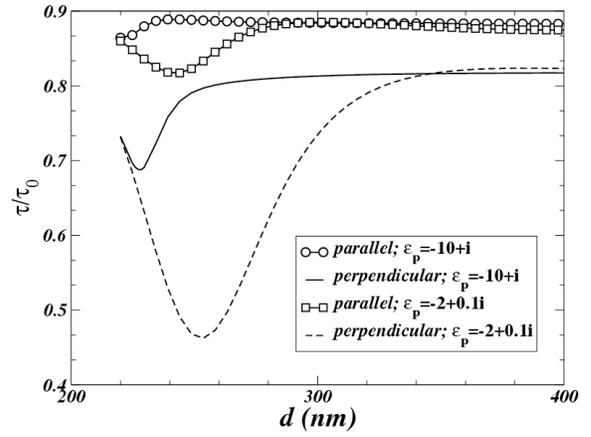


Fig. 2: lifetimes (normalized to its value in vacuum) for transition dipoles, parallel or perpendicular to a left-handed material slab with some absorption, $\epsilon=-1+0.01i$ and $\mu=-1+0.01i$; as a function of the distance between emitter and particle (placed on the other side of the slab). The remaining parameters are the same as in figure 1.

In figure 1, we plot the spontaneous emission lifetimes of an emitter 100 nm above a slab (100 nm in width) made of perfect left-handed material, with $\epsilon=-1$ and $\mu=-1$. In this case strong focusing effects are expected to happen in the other side of the slab. Hence, a small particle placed near the focus of the perfect lens, will change the lifetime to a large extent. Furthermore, if the small particle exhibits a resonance (e.g. plasmon resonance), the effect will be larger. As can be seen in Fig.1, for a particle out of resonance (circles and continuous lines), the lifetime for both parallel and perpendicular orientations of the transition dipole, decreases rapidly at distances of the order of 350 nm from the source. For a particle at resonance ($\text{Re}(\epsilon_p)=-2$ for spherical particles) the effect is even more pronounced, starting the lifetime to fall at distances of the order of 400 nm. With this example, we demonstrate that fluorescence decay rates can be enlarged by an important amount using this geometry and suitable materials, even at distances of the order of the wavelength.

Obviously there are strong practical limitations to implement this set-up experimentally, mainly due to the lack of suitable metamaterials at optical frequencies. But it seems reasonable to obtain a left-handed material with some losses, or index mismatches in general, at optical frequencies. In this case, perfect lensing is known to be destroyed, at least partially, due to absorption. In our work we demonstrate that, even in this case, lifetime can still be notably modified, although the effect is weaker than in the lossless case, and the distance between source and particle should be slightly smaller. As can be seen in figure 2, this is the case for a system like the one considered above, but with some degree of absorption in the left-handed material slab, modelled through a small positive imaginary part in both the permeability and permittivity.

In the case of metallic slabs (relative permeability $\mu=1$), easier to realize in actual experiments, we have also observed changes in the lifetime when the material is chosen such that the transition wavelength coincides with a surface plasmon excitation on the slab surfaces. This situation is very close to the one considered in reference [5].

3. Conclusions

We provide numerical examples illustrating the result, which to our knowledge has never been discussed so far, that the lifetime of fluorescent emission can be dramatically changed at distances even comparable to the wavelength. This hold for the case of perfect lenses, although the effect is achieved even in the presence of index mismatches or even using metallic slabs. We investigate the potential of this novel scheme for the control of fluorescent emitters embedded in dense media without direct physical access (e.g. nanophotonics devices or biological samples).

4. References

- [1] E.M. Purcell, "Spontaneous emission probabilities at radio frequencies", *Phys. Rev.* **69**, 681 (1946).
- [2] R. Carminati, J. J. Greffet, C. Henkel, and J. M. Vigoureux, "Radiative and non-radiative decay of a single molecule close to a metallic nanoparticle", *Opt. Comm.* **261**, 368 (2006).
- [3] Raphael Ruppini and Olivier J. F. Martin, "Lifetime of an emitting dipole near various types of interfaces including magnetic and negative refractive materials". *J. Chem. Phys.* **121**, 11358 (2004).
- [4] J. B. Pendry, "Negative refraction makes a perfect lens", *Phys. Rev. Lett.* **85**, 3966 (2000)
- [5] T. Taubner, D. Korobkin, Y. Urzhumov, G. Shvets and R. Hillenbrand, "Near-field microscopy through a SiC superlens", *Science* **313**, 1595 (2006).