Single-molecule spontaneous emission close to absorbing nanostructures

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The spontaneous emission of a single molecule is substantially modified close to a metallic nanostructure. We study the spectral behavior of the radiative and nonradiative decay rates and of the local-field factor in the vicinity of a plasmon resonance. We show that the highest fluorescence enhancement is obtained for an emission wavelength redshifted from the plasmon resonance, and that quenching always dominates at plasmon resonance. These results may have experimental implications in spectroscopy and monitoring of elementary light sources. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1812592]

The spontaneous emission of a single atom (or molecule) depends on the local electromagnetic field, and therefore on the environment.[1] This effect has been extensively studied in chemical physics, through the interaction of molecules with surfaces.[2] The development of near-field optics has made possible the detection and spectroscopy of single molecules with a lateral resolution below 100 nm.[3,4] These results stimulated theoretical studies of single-molecule emission in nanoscopic environments,[5–9] and single emitters have been used to probe complex structures[10–12] or to image local electromagnetic fields at the nanometer scale.[3,13] Near-field optics also stimulated the use of sharp metallic tips, producing highly localized and bright fields, to modify the lifetime[14] and to enhance the fluorescence of single molecules.[15,16] Modifying and/or amplifying in a *controlled* way the spontaneous emission of single atoms or molecules using simple nanostructures would be a breakthrough in nano-optics, e.g., for *in situ* spectroscopy and biological applications or for the design of single-photon sources based on pulsed excitation of a single atom.[17]

Metallic tips or particles are expected to enhance the local field at the molecule location. This results in an increase of the exciting intensity and a modification of the spontaneous emission rate (Purcell effect). Both effects may combine to produce an enhancement of the fluorescence rate. Nevertheless, the presence of a metallic object close to the emitter creates new *nonradiative* channels due to light absorption inside the metal.[18] Understanding and modeling the trade-off between radiative and nonradiative processes is a key issue for both the fundamental and practical aspects of fluorescence enhancement using metallic tips or particles. Important progress was achieved with the work reported in Ref. 18. It was shown using an electrostatic model that the fluorescence enhancement in the presence of absorption is substantially lower than that in an ideal situation. Nevertheless, many important questions remain unanswered: (1) What is the role of plasmon resonances inside the metallic nanostructure? (2) What is the influence of the transition dipole orientation and the molecule–object distance? (3) Do the illumination and detection directions matter? (4) Why does the signal depend so much on the tip quality? It is the purpose of this letter to address these questions, using a quantitative study based on numerical simulations.

The transition dipole of a fluorescent molecule located at a distance greater than a few nanometers from interfaces can be treated as a classical harmonic damped dipole **p** oscillating at a frequency ω. The normalized decay rate Γ (or the fluorescence lifetime $\tau = 1/\Gamma$) can be calculated from the electric-field susceptibility, which describes the electromagnetic response of the environment.[2,19] In the presence of absorption, a key point is to calculate separately the radiative decay rate Γ_R (proportional to the radiated power) and the nonradiative decay rate Γ_{NR} (proportional to the power absorbed by the environment). These quantities enter the expression of the fluorescence signal through the apparent quantum yield $\eta = \Gamma_R/(\Gamma_R + \Gamma_{NR})$ (we shall assume that the intrinsic quantum yield of the emitter is unity for simplicity). Indeed, far from saturation, the (one-photon) fluorescence signal in the presence of an absorbing tip or particle writes[18] $S = C\eta(\omega_{fluo})\sigma_{abs}(\omega_{abs})|K(\omega_{abs})|^2 I_{exc}(\omega_{abs})T$, where ω_{abs} and ω_{fluo} are the absorption and emission frequencies of the molecule, respectively, $\sigma_{abs}(\omega_{abs})$ is the absorption cross section of the molecule in vacuum, $I_{exc}(\omega_{abs})$ is the exciting (pumping) intensity in vacuum, C is a constant factor which depends on calibration, and T is the integration time of the detector. $K(\omega_{abs})$ is the local-field factor, defined by $|\mathbf{E}_{loc}(\omega_{abs})| = K(\omega_{abs})|\mathbf{E}_{exc}(\omega_{abs})|$, with $\mathbf{E}_{loc}$ the local field at the molecule location in the presence of the tip, and $\mathbf{E}_{exc}$ the exciting field in vacuum [$I_{exc}(\omega_{abs}) = |\mathbf{E}_{exc}(\omega_{abs})|^2$]. The expression of the signal shows that the key quantity which governs the fluorescence enhancement is the product $\eta(\omega_{fluo})|K(\omega_{abs})|^2$.

In order to compute the decay rates Γ_R and Γ_{NR} and the local-field factor, we use a numerical approach based on a surface-integral formalism, which has proven to handle near-field calculations around resonant particles with great accuracy.[20] We consider a dipole emitter located at a distance $z = 5$ nm from a silver tip of parabolic shape with a height $h = 200$ nm and a radius of curvature $R = 10$ nm. For the sake of computer time, we have considered a two-dimensional geometry (the system is invariant along the y direction). The

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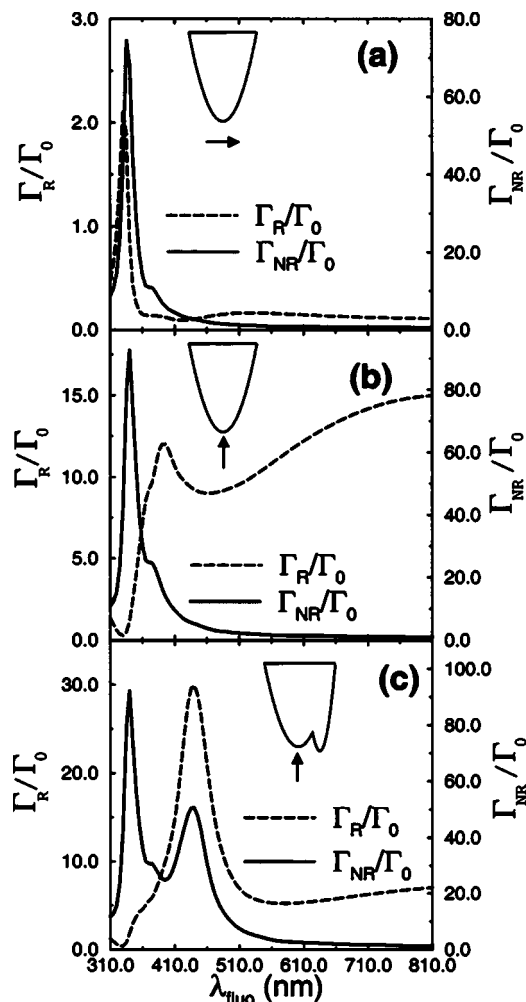
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3863

FIG. 1. Normalized decay rates Γ_R and Γ_{NR} vs the emission wavelength. Silver tip with radius of curvature 10 nm and height 200 nm (tip geometry in the inset). Tip–molecule distance 5 nm. (a) Perfect tip, dipole along the x direction. (b) Perfect tip, dipole along the z direction. (c) Tip with a surface defect (radius of curvature 4 nm, height 10 nm), dipole along the z direction.

dipole and the electric field lie in the x–z plane (p polarization).

We show in Fig. 1 the normalized radiative and nonradiative decay rates, versus the emission wavelength λ_{fluo} of the molecule. Figures 1(a) and 1(b) correspond to a perfect tip, with a transition dipole oriented along the x and z directions, respectively. Figure 1(c) corresponds to a tip with a surface defect, and a transition dipole oriented along the z direction. In Fig. 1(a), both Γ_R and Γ_{NR} exhibit a peak at the plasmon resonance wavelength $\lambda_0 = 396$ nm. Note that except at the plasmon resonance, $\Gamma_R < 1$, which shows that the molecule emits less than in free space. The situation is different in Fig. 1(b), for a transition dipole aligned with the tip axis. The maximum of Γ_R is slightly redshifted from the plasmon resonance, and the peak enhancement is about five times larger than for an x-oriented dipole. The nonradiative decay rate Γ_{NR} remains essentially the same. This shows that close to a plasmon resonance, the maxima of Γ_R and Γ_{NR} may be located at different wavelengths for a z-oriented dipole.[21] At the plasmon resonance, both Γ_R and Γ_{NR} are enhanced, but the enhancement is much larger for Γ_{NR}. In terms of quantum yield, this is a serious drawback. Finally, we observe that for wavelengths larger than the plasmon resonance wavelength,

one always has $\Gamma_R > 1$, although Γ_{NR} strongly decreases. In this spectral region, the quantum yield is maximum.

It has been found experimentally that the measurements often depend on the tip used. We have assumed that this behavior could be attributed to surface defects which modify the tip shape. We see in Fig. 1(c) that the presence of a surface defect strongly modifies the spectral behavior of Γ_R and Γ_{NR}. A second redshifted resonance peak is visible. It leads to an enhancement of Γ_R on the order of 30, which is much higher than that obtained with the perfect tip in the same conditions. We have also found that the coupling between the emitting molecule and this resonance depends on the orientation of the transition dipole (strong coupling for the z orientation, almost no coupling for the x orientation). This example shows that the spectral behavior of a tip in real experimental conditions is difficult to predict, because a non-regular tip may exhibit a strong resonance at a wavelength which is substantially different from the wavelength of the plasmon resonance of the perfect tip (here the spectral shift is $\Delta\lambda = 54$ nm).

The spectral behavior of the apparent quantum yield can be deduced from that of Γ_R and Γ_{NR} (not shown for brevity). We have observed that: (1) the z orientation always ensures a higher quantum yield; (2) the quantum yield is always low at plasmon resonance, and strongly increases for larger wavelengths; (3) for a given emission wavelength, when the tip–molecule distance decreases, one always reaches a regime in which the apparent quantum yield tends to zero. We have also observed that the presence of a surface defect on the tip does not qualitatively change the behavior of the quantum yield.

In order to discuss the excitation of the molecule, the key quantity is the intensity of the local-field factor $|K|^2$. It is displayed in Fig. 2 versus the molecule absorption wavelength, for a transition dipole oriented along the z direction. Two directions of the illuminated beam (assumed to be a plane wave) are considered. We see that (1) the local-field factor exhibits a resonance (the peak value is slightly redshifted compared to the plasmon resonance wavelength defined by the peak value of Γ_{NR}), and (2) the illumination direction plays a major role on the local-field enhancement. This can be understood as follows. In the emission situation, a single molecule behaves as a nano-antenna, whose emission pattern strongly depends on the environment.[7,22] The reciprocity theorem[23] states that a direction giving rise to a lobe in the emission situation corresponds to an illumination direction leading to an enhanced local-field factor in the excitation situation. Although not shown for brevity, we have observed that the presence of a surface defect [as that in Fig. 1(c)] substantially modifies the emission pattern, and thus the optimal illumination direction for the local-field enhancement. This is a crucial point for experiments, in which the tip shape is not always well-controlled. Finally, we note that the intensity of the local-field factor that we obtain is on the order of 40. This value strongly depends on the tip shape, and looking for specific shapes producing high field enhancement was beyond the scope of our study. Xie's group has worked along this direction recently.[24]

Finally, we show in Fig. 2(b) the fluorescence enhancement factor $\eta|K|^2$, for a two-level molecule with a transition dipole along the z direction. The influence of the resonance at $\lambda \simeq 410$ nm in the local-field factor is visible. The level of enhancement strongly depends on the illumination direction

is along the direction of the tip axis (i.e., when it points toward object). (6) The tip shape strongly influences its properties. This may explain why experiments on single-molecule detection are so dependent on the tip quality.
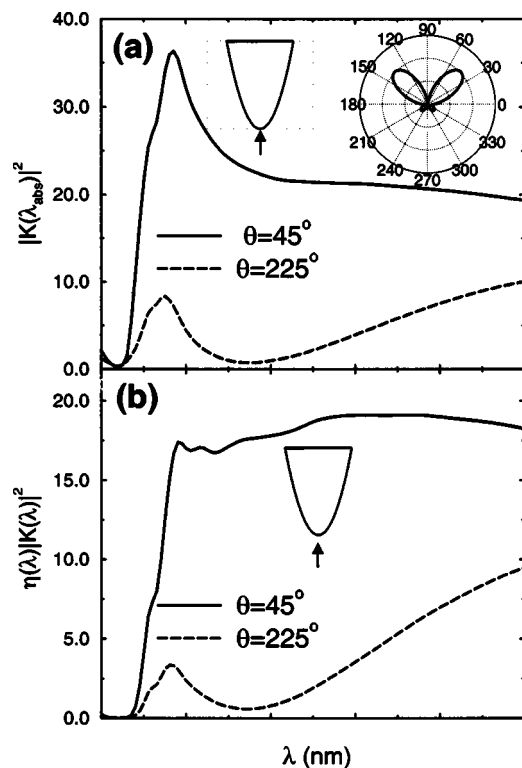
FIG. 2. (a) Intensity of the local-field factor $|K|^2$ vs the absorption wavelength of the molecule, for two illumination directions. Transition dipole along the z direction. Inset: radiation pattern for an emitting molecule vs the observation angle (emission wavelength 396 nm). (b) Fluorescence enhancement factor $\eta|K|^2$, for a two-level molecule (identical absorption and emission wavelengths).

(the emission signal is integrated over all directions in these calculations), a consequence of the antenna behavior described previously. We see that the fluorescence enhancement line shape is chiefly given by the line shape of the local-field enhancement factor. In fact, the influence of the quantum yield is substantial at the plasmon wavelength only, where the signal vanishes (fluorescence quenching), due to high absorption inside the metallic tip.

In summary, we have studied single-molecule fluorescence close to absorbing nano-objects, and discussed several key issues. (1) Close to a plasmon resonance, the radiative and nonradiative rates may have their peak values at different wavelengths. (2) The apparent quantum yield tends to zero at the plasmon-resonance frequency or when the distance to the object tends to zero. (3) The local-field factor and the fluorescence enhancement are maximum at a wavelength slightly redshifted compared to the plasmon wavelength. (4) The peak value strongly depends on the illumination-detection directions. (5) The fluorescence enhancement factor is much higher when the transition dipole

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