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Single emitters coupled to plasmonic nano-antennas: angular emission and collection efficiency

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Abstract. We study the angular emission of a single emitter near a metallic nanoparticle by experiments and numerical calculations. In the experiments, a single fluorescent molecule is controllably scanned near an optical monopole antenna. Large changes in the angular emission of the molecule occur due to the coupling to the particle. Both the polarization and intensity of the angular emission show a distinct dependence on the particle plasmon resonance and on the relative positions and orientations of the emitter and particle. These changes strongly modify the collection efficiency, particularly for objectives of limited numerical aperture; it is important to take the collection system into account fully in the interpretation of enhanced fluorescence and when comparing measurements on ensembles to reference situations. Unlike for ensembles, by addressing a single emitter of well-defined orientation the angular emission is naturally separated from absolute intensities. By dynamically controlling the emitter position a clean reference is then established. This allows all results to be interpreted directly as the coupling of an emitter dipole moment to the dipolar plasmon mode of the antenna. The emitter couples to the antenna mode, which in turn couples to the radiation field, thus determining the angular emission.

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1. Introduction

1.1. Nanoparticles as optical antennas

Metallic nanoparticles support plasmon resonances that interact strongly with optical fields and for this reason are explored for a wide range of applications. Of special interest is the general ability of such particles to confine far-field radiation in a localized, sub-diffraction limited, volume. When used as such, metallic nanoparticles are now commonly referred to as optical antennas [1]–[6], in analogy to the antennas used at radio and microwave frequencies.

If a single quantum system, e.g. a molecule, atom or quantum dot, here referred to as an emitter, is coupled to such an optical antenna, the antenna acts as a resonator mediating between the radiation field and the emitter [1, 7]. As long as the coupling to the antenna mode is significantly stronger than the direct coupling to the far field, the antenna mode determines the interaction of the emitter with radiation. The nano-antenna then acts as an interface between the optical far and near fields, indeed in direct analogy to the function of radio antennas.

1.2. Optical antennas and excitation–emission rates

The coupling of an emitter to an antenna alters its transition rates. The absorption of radiation can be enhanced; an electromagnetic field that is locally enhanced at the emitter position increases the excitation rate [2, 5, 8, 9]. In emission, the coupling to the antenna mode decreases the excited-state lifetime by increasing decay rates [2, 3, 9, 10]. This can be understood as an enhancement of the electric local density of states. Since both radiative and non-radiative (losses in the metal) decay rates are altered, the final efficiency of the coupled system can be enhanced, but also decreased (quenched), depending on the balance of the intrinsic quantum efficiency of the emitter and the relative changes in radiative and non-radiative rates [2, 3]. Due to the
resonant response of the metallic nanoparticles, the spectral dependence of both excitation and emission are affected as well \[11\]. In experiments, it is difficult and in many cases impossible, to separate the effects of all these different contributions on a final obtained intensity signal. Even more, for an ensemble of emitters randomly distributed near an antenna, the averaging over both position and orientation complicates a clear-cut interpretation of the results and disentangling all contributions is the subject of several recent studies \[3\], \[12\]–\[14\].

1.3. Optical antennas and angular emission

Recently, we have experimentally shown that the angular emission of a single molecule, i.e. the far-field electric field amplitude, phase and polarization as a function of angle, can be controlled by coupling to resonant modes of optical antennas \[7\], \[15\]. This redirection of emission introduces yet another aspect, in addition to modification of transition rates, for emitters coupled to nanoparticles. Previous work recognized that the angular emission is modified in an inhomogeneous environment \[2\], \[16\]–\[19\], including effects on the emitted polarization \[20\]. Also, changes in the angular emission of an ensemble of emitters near optical antennas have been reported \[12\], \[13\], \[21\], \[22\], however, in such experiments changes in angular emission are not separated from changes in excitation rates and quantum efficiencies of the individual emitters.

The importance of the angular emission is manifold. Firstly, the direction of emission has immediate consequences for the collection efficiency. Secondly, it is common to rely on the emitted far field to determine the characteristics and position of emitters and nanoparticles, either by direct imaging, defocused imaging \[23\], \[24\] or by polarization measurements \[25\], \[26\]. Thirdly, the excitation is related to the emission by reciprocity and the angular excitation is thus expected to be affected in a similar way. Finally, control of angular excitation or emission can be exploited in sensing or switching.

Here we study, experimentally and theoretically, the angular emission of single emitters coupled to resonant optical antennas. Firstly, we theoretically treat the dependence of both the coupling and the angular emission on the antenna plasmon resonance. By varying the length of a dipole antenna, it is shown that the angular emission is rotated with increasing coupling strength, until at resonance the dipolar antenna mode fully determines the angular emission. Secondly, we present experimental and calculated results on the coupling and angular emission as a function of the emitter position and orientation relative to the antenna. In our experiments, single fluorescent molecules with differently oriented dipole moments, are controllably scanned near an optical monopole antenna one at a time. By detecting the emission polarization, we demonstrate how the angular emission is modified by coupling to the antenna. Thirdly, we investigate the collection efficiency for various emitter–antenna geometries. It is shown that, especially for limited collection angles (NA smaller than 1), strong variations in the collection efficiency occur that depend on the position of the emitter and on the relative orientations of the antenna and emitter. These results show that the collection efficiency has to be taken into account in order to interpret an observed enhancement of fluorescence intensity and in the definition of a reference situation in experiments on ensembles of emitters. For a single emitter of well-defined orientation and controlled position, the angular emission is naturally decoupled from absolute intensities and a clear reference is obtained. Importantly, this allows all results presented to be interpreted directly and to be explained in a straightforward way as the coupling of the emitter dipole to dipolar antenna plasmon modes; direct insight into the role of the antenna plasmon resonance in the emission process is gained.
2. Calculation of decay rates and angular directivity

To determine the emission rates and directivity for various emitter–antenna configurations, we have developed a general approach to calculate the electromagnetic field produced by a single emitter in proximity to a metallic nanoparticle. Full-3D finite integration technique (FIT) calculations are performed, based on a commercially available package (Computer Simulation Technology GmbH, Germany) \[27, 28\]. The electronic transition of the quantum emitter is approximated as a pure electrical dipole and represented by a classical point dipole, oscillating at the emission frequency with constant oscillator strength. In this way, by calculating the resulting classical electromagnetic field, transition rates and field amplitudes relative to a reference situation are obtained. Here, an emitter in vacuum ($\varepsilon = 1$) is used as a reference for the calculations. If these calculations are to be compared with any experimental values, a reference measurement is required for the experiment as well.

The following parameters are obtained from the calculated electromagnetic field. The relative radiative decay rate $K_{\text{rad}}$:

$$ K_{\text{rad}} = \frac{\iiint P(\varphi, \theta) \, d\Omega}{\iiint P_0(\varphi, \theta) \, d\Omega}, $$

(1)

where $P(\varphi, \theta)$ and $P_0(\varphi, \theta)$ are the angular emitted power for the system under study and for the reference dipole emitter in vacuum, respectively. The angles $\varphi$ and $\theta$ are the usual azimuthal and polar angles in spherical coordinates and the integration is performed over full space. $K_{\text{rad}}$ is related to the radiative mode density and, in the case of coupling to an antenna mode, is a measure of the coupling strength. The non-radiative decay rate, $K_{\text{nr}}$, is taken as:

$$ K_{\text{nr}} = \frac{P_{\text{diss}}}{\iiint P_0(\varphi, \theta) \, d\Omega}, $$

(2)

where $P_{\text{diss}}$ is the total power dissipated in the metal. $K_{\text{nr}}$ depends on a combination of losses, determined by both the losses of the antenna mode and losses due to the fields induced directly in the metal by the emitter. The total efficiency for emission into the far field (commonly called quantum efficiency) is:

$$ \eta_q = \frac{K_{\text{rad}}}{K_{\text{tot}}}. $$

(3)

The total decay rate, $K_{\text{tot}} = K_{\text{rad}} + K_{\text{nr}}$, is proportional to the inverse of the relative excited state lifetime. The intrinsic quantum efficiency (or yield) of the emitter is assumed to be unity.

To characterize the angular dependence of the emitted intensity, the angular directivity $D(\varphi, \theta)$ is defined as:

$$ D(\varphi, \theta) = \frac{4\pi P(\varphi, \theta)}{\iiint P(\varphi, \theta) \, d\Omega}. $$

(4)

Normally, only a fraction of the total angular emission is collected. For a detection system with a numerical aperture $\text{NA} = n \sin \theta_{\text{NA}}$, where $n$ is the refractive index of the medium in which the far-field emission is considered, the collection efficiency, $\eta_{\text{coll}}$, is given by:

$$ \eta_{\text{coll}} = \frac{2\pi \theta_{\text{NA}}}{\iiint D(\varphi, \theta) \sin(\theta) \, d\theta \, d\varphi / 4\pi}. $$

(5)
Figure 1. A horizontal dipole emitter (red arrow) coupled to a vertical dipole antenna of variable length $L$. (a) Overview, diameter $D = 30$ nm, wavelength $800$ nm, $\varepsilon_1 = 1$, $\varepsilon_m = -26.3 + 1.85i$ (gold), $d = 4.5$ nm. (b) The radiative decay rate $K_{\text{rad}}$ as a function of the antenna length $L$. The antenna is resonant for $L \approx 150$ nm.

3. The role of the plasmon resonance in the angular emission

First we address the dependence of the coupling and the resulting angular emission on the plasmon resonance of the antenna. To this end, the angular emitted power is calculated while tuning the antenna length ($L$). Figure 1(a) shows an overview of the system considered. A horizontally oriented dipole emitter is placed near a vertically oriented gold antenna with a diameter of 30 nm. The emitter is coupled to the antenna by placing it at a position of high mode density. The wavelength is 800 nm and as the dielectric constant for gold, $\varepsilon = -26.3 + 1.85i$ is taken.

Figure 1(b) shows $K_{\text{rad}}$ as a function of the antenna length. The strength of the coupling reaches a maximum of $K_{\text{rad}} \sim 500$ times the vacuum rate at the dipolar resonance length of $L \approx 150$ nm. Figure 2 shows the corresponding angular directivity for the emitter coupled to antennas of different length. In all cases, dipolar emission patterns are obtained, with a maximum directivity of 1.5. As the resonant length is approached, the emission direction steadily rotates from the pattern of the emitter itself toward a dipolar pattern that is perpendicularly oriented. This can be explained as follows. The source of angular emission is a combination of the horizontal dipole moment of the emitter, plus the transverse response of the antenna, and the vertical dipole moment of the antenna mode. As the antenna is tuned to resonance, the coupling of the emitter to the vertical antenna mode is increased. The balance progressively shifts from the emitter dipole toward the perpendicular oriented antenna dipole, until the antenna mode dominates and fully determines the angular emission [7]. Clearly, coupling to a metallic nanoparticle can result in a strong redirection of angular emission. In the case studied here, the emission pattern is directly related to the coupling strength (figure 1(b)) and is ultimately totally rotated by 90°.
Figure 2. The angular directivity $D(\phi, \theta)$ for the configuration in figure 1(a), for different antenna length $L$. The dipolar patterns progressively rotate with increased length, i.e. increased coupling strength.

4. Position and orientation dependence of coupling and angular emission

Next, we study experimentally and theoretically the effect of the position and orientation of the emitter on the coupling and on the angular emission.

4.1. Calculations for two antennas

In order to reproduce the experimental conditions described below (section 4.2), calculations are done for aluminium ($\varepsilon = -37.8 + 10.8i$ at 570 nm) optical antennas above a glass substrate ($\varepsilon = 2.25$). The antenna consists of cylindrical body and hemispherical ends with a radius of 20 nm. Two situations are considered: a vertical antenna placed 4 nm above a glass substrate (figure 3(a)) and a horizontal antenna placed directly on a glass substrate (figure 3(b)). The emitter is embedded in the substrate 6 nm below the interface and scanned laterally under the antenna. The orientation of the emitter dipole, relative to the surface normal, is given by the angle $\theta_{\text{dip}}$ and the collection of emission is considered in a solid angle of $2\pi \theta_{\text{NA}}$.

From the calculations, we obtain the angular emission pattern of an emitter with given orientation ($\theta_{\text{dip}}$) and at a given distance ($x$) from the antenna. For a selection of emitter orientations, $\theta_{\text{dip}} = 90^\circ$, $60^\circ$, $30^\circ$ and $0^\circ$, both $K_{\text{rad}}$ and the degree of polarization (DOP) are shown in figure 4 as function of emitter position $x$. The DOP is a practical observable in experiments to detect molecular orientation and changes in angular emission [7]. The emission is collected with a lens with a certain collection angle $\theta_{\text{NA}}$ and then split into two orthogonal polarizations (e.g. along the $x$- and $y$-directions) [29]. The DOP is then calculated as:

$$DOP = \frac{I_x - I_y}{I_x + I_y},$$

where $I_x$ and $I_y$ are the intensities in the two orthogonal polarization channels. For a vertical, i.e. perpendicular to the substrate, interface, the emitting dipole moment (an emitter or an antenna mode), $DOP = 0$ is to be expected. For a horizontal dipole, oriented along $x$, a DOP close to 1 is to be expected. Due to polarization mixing by the collection lens, for higher collection angles $\theta_{\text{NA}}$, the DOP for a horizontal dipole is slightly smaller than 1 [30].

Figure 3. Schematics of the configurations calculated. A dipole emitter (red arrow) is scanned along $x$ under (a) a vertical or (b) horizontal dipole antenna. The orientation of the emitter is given by $\theta_{\text{dip}}$. The wavelength is 570 nm, $\varepsilon_1 = 1$, $\varepsilon_2 = 2.25$ (glass), $\varepsilon_3 = -37.8 + 10.8i$ (aluminium). Emission is considered into a solid angle of $2\pi \theta_{\text{NA}}$ into the glass half-space. (a) For the vertical antenna: $d_1 = 4 \text{ nm}$, $d_2 = 6 \text{ nm}$, $L = 150 \text{ nm}$ and $D = 40 \text{ nm}$. (b) For the horizontal antenna: $d_2 = 6 \text{ nm}$, $L = 130 \text{ nm}$ and $D = 40 \text{ nm}$.

The strong distance dependence of $K_{\text{rad}}$ in the vicinity of the antennas shows the near-field nature of the coupling. For example, a horizontal emitter ($\theta_{\text{dip}} = 90^\circ$) does not couple to the vertical antenna mode (figure 4(a)) right under the antenna apex (i.e. $K_{\text{rad}}$ is minimum for $x = 0$), because the mode field and molecular dipole moment are perpendicular to each other [31], while 20 nm to the side of the apex, the coupling is maximum. The near-field coupling has a two-fold implication. Firstly, emitters of all orientations can be coupled to the antenna mode. Secondly, emitters with different orientations reach the maximum coupling at different positions.

The DOP values far away from the antenna ($x = 300 \text{ nm}$) correspond to undisturbed emitters. Close to the antenna the DOP is strongly influenced by the coupling. At the positions where the coupling is effective (high $K_{\text{rad}}$), the emission is expected to be dominated by the antenna mode and to be nearly independent of the molecular orientation. Indeed, for emitters of all orientations at positions of high $K_{\text{rad}}$, the DOP for the vertical antenna approaches zero (figure 4(a)) [7], whereas for the horizontal antenna the DOP approaches the highest values (figure 4(b)), as expected for vertical and horizontal dipole moments, respectively. This is most clearly seen for emitters oriented perpendicular to the antennas. An additional distinct jump in the DOP curve for the horizontal antenna is observed as the horizontal ($\theta_{\text{dip}} = 90^\circ$) emitter is moved under the antenna. This feature is not due to coupling to the antenna mode as $K_{\text{rad}}$ is not enhanced and is instead attributed to the change of the material above the emitter to metal.
4.2. Single-molecule experiments

In the experiment, single molecules with different orientations are dynamically coupled to a vertical optical monopole antenna, as previously introduced [5, 32]. The antenna is placed next to the 100 nm aperture of a conventional aperture-NSOM fibre probe [33]. The above simulations for the vertical antenna (figures 3 and 4) are a valid approximation of this experiment as the monopole antenna used in the experiments can be seen as half a dipole antenna with the other half replaced by a reflection in the conducting plane of the NSOM tip [5]. The antenna is illuminated through the aperture, by coupling a laser beam of controlled polarization, power (1 mW) and wavelength (514 nm) into the fiber [32].

Samples containing single fluorescent molecules are prepared by dissolving 0.5% poly(methyl methacrylate) (PMMA) in toluene and adding carbocyanine (DiIC18) dye molecules at approximately $10^{-8}$ molar concentration. The solution is spin-coated onto plasma-etched glass substrates. Samples are dried at ambient conditions. This procedure results in randomly-placed isolated molecules embedded in a 20 nm thick PMMA layer. The molecules have a random but fixed orientation.

The sample is raster scanned under the antenna probe with a near-field scanning optical microscope whereas a constant sample–antenna distance is kept by a shear-force feedback.
Figure 5. The fluorescence intensity $I_f$ (experimental), radiative decay rate $K_{rad}$ (calculated), and degree of polarization DOP (experimental and calculated) for three molecules with different orientations $\theta_{dip}$ when scanned along $x$ (figure 3). The insets are 2D fluorescence maps obtained by raster scanning the molecule under the antenna. The color coding represents the polarization direction of the emission. Red is along $x$ and green along $y$. Collection objective: NA = 1.3 ($\theta_{\text{NA}} = 60^\circ$).

system [34]. The resulting fluorescence (wavelength $\sim$570 nm) is collected by a 1.3 NA oil-immersion objective. After filtering the laser light, the fluorescence is split in its two orthogonal polarization directions by a polarizing beam splitter. Each branch is detected by a separate avalanche photodiode. In this way, both fluorescence intensity and DOP are determined for each position of the molecule relative to the antenna.

By scanning a molecule under the antenna, a fluorescence map is obtained. The insets in figure 5 show the response of three molecules, each with a different orientation. A color coding is used to distinguish between the two polarization directions; red along the $x$-direction, green along the $y$-direction. A characteristic pattern consisting of a narrow spot and, depending on the molecular orientation, also a large spot to the right of it is seen. The small spot is the highly localized interaction of the molecule with the antenna mode. The large spot is the response of the molecule to the residual field from the aperture that consists of the field components that do not couple to the antenna mode [35]. This residual component is mostly oriented parallel to the substrate plane and the resulting large spot is only observed for molecules with a dipole with a significant horizontal component.

Far below saturation, the collected fluorescence intensity ($I_f$) is equal to the excitation rate times the total efficiency for emission and collection:

\[
I_f = (\mathbf{E} \cdot \mathbf{p})^2 \eta_q \eta_{\text{coll}},
\]

where $\mathbf{E}$ is the electric field vector at the position of the molecule and $\mathbf{p}$ is the transition dipole moment for the molecular excitation. The detection efficiency of the collected fluorescence

is assumed to be constant and is left out of the equation. \(E\) depends on the details of the illumination and its projection on \(p\) determines the excitation rate. Note that the excitation rate, quantum efficiency and collection efficiency are all on equal footing; a measurement of the fluorescence intensity does not give access to these parameters separately. In general, either a comparison of the measured \(I_f\) to calculations, that fully take into account the experimental illumination and collection, or additional assumptions are needed in order to obtain information on the underlying parameters, and thus on the functioning of the antenna.

From the fluorescence maps, we obtain \(I_f\) and the DOP as a function of the distance to the antenna \((x)\) for individual molecules (figure 5). The \(I_f\) traces show that the narrow response to the antenna mode is confined within 25 nm. By comparing the experimental traces \(I_f(x)\) and DOP\((x)\) to calculations (figure 5), the molecular orientation can be estimated.

The \(I_f(x)\) traces are compared to the calculated \(K_{\text{rad}}(x)\), the measure for the coupling strength. The behavior of the two parameters shows a qualitatively similar behavior. This suggests that their position dependences are related, which can be understood as follows. Firstly, if the antenna mode is responsible for both the excitation and the enhancement of emission, which is true if the field enhancement is substantial and the emission and excitation couple to the same mode (small Stokes shift), then both the excitation rate and \(K_{\text{rad}}\) depend equally on the spatial profile of the antenna mode. Secondly, if \(\eta_q\) and \(\eta_{\text{coll}}\) do not vary significantly over the narrow distance of interaction, they do not influence the intensity trace (equation (7)). Here, a large detection NA (see also the results of section 5) and a 10 nm space between the antenna and molecule make this assumption plausible. Under these two assumptions the shape of the \(I_f\) and \(K_{\text{rad}}\) curves are approximately equivalent. This is of course not true when the molecule is excited by the more complicated residual aperture field instead of the antenna mode, hence \(K_{\text{rad}}\) cannot describe \(I_f\) for the aperture case.

In the case of the DOP\((x)\), the comparison between experiments and calculations is direct and quantitative. Reliable DOP values can be obtained only when the molecules emit sufficiently above background. All molecules show the redirection effect expected for a vertical antenna; when there is a strong coupling to the antenna mode, the vertical dipole moment of the antenna determines the interaction with the radiation field and the DOP is close to 0. When the molecule is moved away, the DOP quickly changes in a more complicated way. The DOP far away from the antenna is mainly determined by the orientation of the emission dipole moment of the molecule. Good agreement is found between the calculations and the experimental data. Possible causes for the minor deviations observed are: imperfections in the antenna probes, an influence of the aluminium-covered tip and the assumption in the calculations that the complete intensity in the back focal plane is detected (equation (5)).

A well-defined reference situation is important for two reasons: to determine the emitter orientation and to be able to interpret the effect of the antenna. Firstly, it is not possible to determine the orientation of a molecule near an antenna directly by a single measurement of the emission polarization. The far-field emission contains a mix of information on the positions and orientations of both the antenna and the molecule. For a strong coupling to the antenna mode, the far field is dominated by the antenna, making it hard to determine the position and/or orientation of the molecule. Secondly, although in principle any measurement can be used as a reference to test part of the theory [4, 36, 37], only measurements for the same (or equivalent) emitter(s) with and without (or close to and far from) the antenna yield direct quantitative information on the effect of the antenna on the emitter, and thus on the antenna function. Here, by scanning a single molecule with a fixed orientation near the antenna, such that the molecular position...
is controlled, information about both the position and orientation of the molecules is retrieved. In this way, a clear reference is established. By detecting both total intensity and polarization, we obtain experimental insight into how the angular emission is redirected as the molecule is coupled to the antenna mode.

5. The collection efficiency

Having established experimentally that the angular emission changes by coupling to a metal nanoparticle, the question arises how this influences the actual amount of signal collected. To answer this question, we calculate the collection efficiency $\eta_{\text{coll}}$ as a function of the position for the two antenna configurations shown in figure 3 for both a large ($\theta_{\text{NA}} = 60^\circ$ and NA = 1.3) and a small ($\theta_{\text{NA}} = 20^\circ$ and NA = 0.5) collection angle. We consider two molecular orientations, horizontal and vertical, since they show the extreme behaviors.

Additionally, we define $F = K_{\text{rad}} \cdot \eta_{\text{coll}}^2$ as a figure of merit for the relative detected fluorescence intensity. We justify this definition as follows. Firstly, equation (7) shows that the fluorescence depends on the excitation rate, which depends on the illumination. In order to keep our definition general, we assume illumination by independent, i.e. mutually incoherent, plane waves. Making the approximation that excitation and emission occur at the same wavelength, the relative excitation rate for illumination from all angles is then given by $K_{\text{rad}}$. For illumination through an objective of limited NA, we obtain: $K_{\text{rad}} \eta_{\text{coll}}$. By not specifying phase relations, we avoid the definition of a specific illumination and the introduction of the relative position of the antenna/emitter from the optical axes of the objective as an additional spatial degree of freedom. Secondly, the fluorescence depends on the efficiency of emission, $\eta_{\text{q}}$, and collection, $\eta_{\text{coll}}$. Here, for simplicity, we will neglect changes in $\eta_{\text{q}}$ to obtain the above definition of $F$.

5.1. Vertical antenna

In figure 6(a), $\eta_{\text{coll}}$ is displayed for a horizontally and vertically oriented emitter against the emitter position $x$ with respect to a vertical antenna, for both $\theta_{\text{NA}} = 20^\circ$ and $60^\circ$. Positions of special interest are: far away from the antenna (the reference), positions of high $K_{\text{rad}}$ (where the coupling is strong) and positions of high $F$ (high expected fluorescence signal).

The collection efficiency varies with position and shows a different behavior for the two orientations. The relative magnitude of the variations is much larger for the low NA = 0.5 than for the high NA = 1.3. For NA = 0.5, the most striking feature is the decrease by a factor 3 of $\eta_{\text{coll}}$ for the horizontal emitter as it approaches the antenna and $K_{\text{rad}}$ increases (the dotted vertical lines indicate the maxima of $K_{\text{rad}}$, for the complete curves refer to figure 4). These observations are explained as follows. For low NA, $\eta_{\text{coll}}$ is expected to be relatively low for a vertical dipole compared to a horizontal one, as can be seen from the values far from the antenna ($x = 300$ nm). For high NA, the two orientations are collected with a similar high efficiency. The coupling of the horizontal emitter to the vertical antenna dipole mode thus results in a stark decrease in collection efficiency in the case of NA = 0.5, but not for NA = 1.3. For the vertical emitter, the coupling to the vertical antenna leaves the angular emission relatively unchanged. Variations not related to the near-field coupling are observed ($K_{\text{rad}}$ not increased); the side-by-side parallel dipole moments interact and interfere over larger distances.

The resulting $F$ values for both emitter orientations are shown in figure 6(b). For NA = 1.3, $F$ is strongly enhanced by the coupling to the antenna; the increase of $K_{\text{rad}}$ and a relatively
unaltered $\eta_{\text{coll}}$ result in an increased fluorescence. In contrast, for a low NA, the antenna mode is not effectively excited nor collected, i.e. $\eta_{\text{coll}}$ is very small, and the $F$ values are small compared to the horizontal emitter at $x = 300$ nm. No (significant) enhanced fluorescence is observed in this case.

To quantify the relative weight of the two emitter orientations in the total fluorescence for each position, we define a parameter $S$:

$$S = \frac{F_x - F_z}{F_x + F_z}, \quad (8)$$

where $F_x$ and $F_z$ are the $F$ values for the horizontal and vertical emitters, respectively. For $\text{NA} = 0.5$, horizontal emitters represent the dominant contribution, as $S$ is larger than 0.5 for all $x$ and reaches a maximum of 0.99, which corresponds to a $F_x/F_z$ ratio of roughly 250 times.
More interesting is the situation for NA = 1.4, for which $S \approx 0.5$ far from the antenna but drops significantly close to it, due to the stronger coupling to the antenna mode of the vertical emitter. Thus, far away horizontal emitters add most to the obtained fluorescence but close to the antenna the main contribution comes from vertically oriented emitters.

5.2. Horizontal antenna

For an antenna placed horizontally on a substrate the situation is different (figure 7), the largest modifications of $\eta_{\text{coll}}$ now happen for the vertical emitter. For NA = 0.5, the $\eta_{\text{coll}}$ for the vertical emitter is increased by a factor of 20 as it is coupled to the antenna. The vertical emitter couples to the horizontal antenna dipole mode, which is effectively collected even for a low NA. For a horizontal emitter, an abrupt jump not related to the coupling is seen when the emitter is moved under the antenna; the metal above the emitter strongly diminishes the emission to the upper half-space, which is not collected.

Since the horizontal antenna is effectively excited and collected for both high and low NA, the curves of $F$ are similar in shape to $K_{\text{rad}}$ (figure 4) for both NAs and show a significant enhancement. The coupling is more efficient for the vertical emitter, for which $F$ is enhanced more than for the horizontal one. The relative importance of the vertically oriented emitters is increased for positions close to the antenna (low values of $S$, where $F$ is large). In contrast, at $x = 300$ nm horizontal emitters are more effectively collected, especially for low NA, where $S$ approaches 1 as $F$ is up to 40 times larger for the horizontal emitter than for the vertical.

5.3. On the definition of a reference for an ensemble measurement.

We have shown that the relative strength of the detected fluorescence of the two dipole orientations, $S$, varies with position (figures 6(b) and 7(b)). This observation has interesting implications for the definition of a reference situation in experiments on ensembles of emitters. A well-defined reference system is, as noted before, crucial to obtain quantitative information on the characteristics of the antenna, i.e. its effects on emitters. If an ensemble far away from the antenna is used as a reference for an ensemble close to the antenna, emitters with different orientations contribute differently to the total fluorescence intensity for both cases. In general, one is thus not observing the subsets of emitters in the reference case and the case under study with the same weight. If those subsets have different properties, as for example, is the case with lifetime and angular emission of emitters with different orientations and positions near a dielectric interface, the relation of the reference values to the obtained values is not trivially defined. For an ensemble measurement, full calculations that take into account the complete experimental conditions, i.e. including the illumination and collection, are thus required in order to quantitatively interpret the results. This is not the case for experiments on single emitters; measurements of the angular emission and lifetime of a single emitter are naturally independent of the absolute fluorescence intensity and a clear reference can be established.
Figure 7. Case of a horizontal antenna. (a) Collection efficiency $\eta_{\text{coll}}$ for a horizontal ($\theta_{\text{dip}} = 90^\circ$) and a vertical ($\theta_{\text{dip}} = 0^\circ$) emitter as a function of the distance $x$ to the antenna. Vertical dotted lines indicate the maxima of $K_{\text{rad}}$, see full curves in figure 4(b). (b) Figure of merit for the observed fluorescence, $F = K_{\text{rad}} \eta_{\text{coll}}^2$, and relative weight $S$ for horizontal and vertical emitters as a function of $x$. Left for $\theta_{\text{NA}} = 20^\circ$ (NA = 0.5) and right for $\theta_{\text{NA}} = 60^\circ$ (NA = 1.3).

6. Conclusions

In conclusion, the angular emission of an emitter can be drastically altered by coupling to the plasmon resonance of a metallic nanoparticle. The coupling and the resulting angular emission depend on the relative positions and orientations of both emitter and particle. The observed changes in angular emission significantly influence the collection efficiency, especially for low numerical apertures, showing that in order to quantitatively interpret intensity measurements the collection system and changes in angular emission have to be taken into account fully. Unlike for measurements on ensembles, studying a single emitter, which is controllably moved near a resonant optical antenna, decouples the angular emission from absolute intensities and
establishes a well-defined reference. Therefore, the results can be interpreted directly in a straightforward way as the coupling of an emitter dipole moment to a resonant antenna mode dipole; direct insight is gained into the process of angular redirection. The results show that the particle plasmon resonance acts as an intermediate resonator between the emitter and the radiation field, or between near and far fields, confirming that a metallic nanoparticle truly functions as the optical equivalent of an antenna.

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References

[27] CST-Microwave-Studio, www.cst.com


