Electrodynamic coupling of electric dipole emitters to a fluctuating mode density within a nano-cavity

Alexey I. Chizhik,\textsuperscript{1} Ingo Gregor,\textsuperscript{1} Frank Schleifenbaum,\textsuperscript{2} Claus B. Müller,\textsuperscript{1} Christian Röling,\textsuperscript{3} Alfred J. Meixner,\textsuperscript{2} and Jörg Enderlein\textsuperscript{1}\textsuperscript{,}\textsuperscript{†}

\textsuperscript{1}III. Institute of Physics, Georg August University, 37077 Göttingen, Germany
\textsuperscript{2}Institute of Physical and Theoretical Chemistry, Eberhard Karls University, 72076 Tübingen, Germany
\textsuperscript{3}Accurion GmbH, 37079 Göttingen, Germany

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We investigate the impact of rotational diffusion on the electrodynamic coupling of fluorescent dye molecules (oscillating electric dipoles) to a tunable planar metallic nano-cavities. Fast rotational diffusion of the molecules leads to a rapidly fluctuating mode density of the electromagnetic field along the molecules’ dipole axis, which significantly changes their coupling to the field as compared to the opposite limit of fixed dipole orientation. We derive a theoretical treatment of the problem and present experimental results for rhodamine 6G molecules in cavities filled with low and high viscosity liquids. The derived theory and presented experimental method is a powerful tool for determining absolute quantum yield values of fluorescence.

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\textbf{Introduction.---} Fluorescing molecules located close to a metal surface (at sub-wavelength distance) or inside a metal nano-cavity, dramatically change their fluorescence emission properties such as fluorescence lifetime, fluorescence quantum yield, emission spectrum, or angular distribution of radiation \textsuperscript{[1,4]. This is due to the change local density of modes of the electromagnetic field caused by the presence of the metal surfaces \textsuperscript{[5]. Although a large amount of studies have dealt with the investigation of this effect, they all have considered fixed dipole orientations of the emitting molecules, so that each molecule exhibits a temporally constant mode density during its de-excitation from the excited to the ground state. However, when molecules are dissolved in a solvent such as water, their rotational diffusion leads to rapid changes of dipole orientation even on the time-scale of the average excited state lifetime. We will show here that this dramatically influences the coupling of the molecules to the local, strongly orientation-dependent density of modes and the resulting excited state lifetime. This is enormously important for applications of tunable nanocavities for fluorescence quantum yield measurements.

\textbf{Theory.---} Let us consider an ensemble of molecules within a planar nano-cavity, which had been excited by a short laser pulse into their excited state. Due to the electrodynamic coupling to the cavity, these molecules will exhibit an emission rate $K$ that depends on their vertical position within the cavity, and on the angle $\theta$ between their emission dipole axis and the vertical. In what follows, we assume that the excited state lifetime is so short that one can neglect any translational diffusion of a molecule within the cavity. However, this is in general not the case for its rotational diffusion time which can be on the same order as the excited state lifetime. Then, for a given position within the cavity, the probability density $p(\theta,t)$ to find a molecule still in its excited state at time $t$ with orientation angle $\theta$ obeys the following evolution equation

$$\frac{\partial p(\theta,t)}{\partial t} = \frac{D}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial p(\theta,t)}{\partial \theta}) - K(\theta)p(\theta,t)$$  \hspace{1cm} (1)

where the first term on the right hand side is the rotational diffusion operator \textsuperscript{[6]} multiplied with rotational diffusion coefficient $D$, and the second term accounts for de-excitation. For the sake of simplicity, we omit any explicit indication of the position dependence of the involved variables. The emission rate $K$ itself is given by a weighted average of the wavelength dependent rates $k(\theta, \lambda)$,

$$K(\theta) = \langle k(\theta, \lambda) \rangle_\lambda = \frac{\int k(\theta, \lambda) F_0(\lambda) d\lambda}{\int F_0(\lambda) d\lambda}$$  \hspace{1cm} (2)

where $F_0(\lambda)$ is the free-space emission spectrum of the molecules as a function of wavelength $\lambda$. For a planar cavity, the rates $k$ themselves can be decomposed into

$$k(\theta, \lambda) = k_\perp(\lambda) \cos^2 \theta + k_\parallel(\lambda) \sin^2 \theta$$  \hspace{1cm} (3)

where the $k_\perp(\lambda)$ and $k_\parallel(\lambda)$ are the rates for a vertically and a horizontally oriented emitter, respectively. Within the semi-classical theory of dipole emission \textsuperscript{[7]}, these rates are given by

$$k_\mu(\lambda) = k_{nr} + \frac{S_\mu(\lambda)}{S_0} k_{rad}$$ \hspace{1cm} (4)

$$= \frac{1}{\tau_0} \left[1 - \Phi + \frac{S_\mu(\lambda)}{S_0} \Phi \right]$$  \hspace{1cm} (5)
where the index $\mu$ is either $\perp$ or $\parallel$, and where $k_{nr}$ and $k_{rad}$ are the free-space non-radiative and radiative transition rates, respectively, $\tau_0$ is the free-space excited state lifetime, $\Phi$ is the intrinsic quantum yield of fluorescence, $S_\mu(\lambda)$ are the wavelength-dependent emission rates of an oscillating electric dipole with orientation $\mu$ within the cavity, and $S_0$ is the free-space emission rate, which is independent on orientation and wavelength (thus neglecting optical dispersion of the solvent). The emission rates $S\mu(\lambda)$ are calculated in a semi-classical way by firstly using a plane wave representation of the electromagnetic field of an emitting electric dipole of given orientation (and position) [8]; secondly calculating the interaction of each plane wave component with the cavity; and finally finding the emission rate as the integral of the Poynting vector of the total field over two surfaces sandwiching the emitter on both sides. An exemplary result for such a calculation is shown in Fig. 1.

The initial distribution $p(\theta, t = 0)$ right after excitation is defined by the polarization and intensity of the focused excitation light. These can be found by again expanding the electromagnetic field of the focused laser beam into a plane wave representation [9][10], and calculating the interaction of each plane wave with the cavity [11]. If one denotes the horizontal and vertical components of the excitation intensity at the position of the molecules by $I_\parallel$ and $I_\perp$, respectively, then $p(\theta, t = 0)$ is given by

$$p(\theta, t = 0) = \frac{3(I_\perp \cos^2 \theta + I_\parallel \sin^2 \theta)}{2(I_\perp + 2I_\parallel)}$$ (5)

Computational results for $I_\perp$ and $I_\parallel$ are shown in Fig. 2.

for the same cavity geometry as in Fig. 1.

Next, the solution to Eq. (1) can be found by expanding $p(\theta, t)$ into a series of Legendre polynomials $P_\ell(\cos \theta)$:

$$p(\theta, t) = \sum_{\ell=0}^{\infty} a_\ell(t) P_\ell(\cos \theta)$$ (6)

where the $a_\ell(t)$ denote time-dependent expansion coefficients. Inserting that into Eq. (1) yields an infinite set of ordinary differential equations for the $a_\ell(t)$,

$$\frac{da_\ell(t)}{dt} = -D_\ell(\ell+1)a_\ell(t) - \sum_{\ell'} M_{\ell\ell'}a_{\ell'}(t)$$ (7)

where the transition matrix $M_{\ell\ell'}$ is defined by the integrals

$$M_{\ell\ell'} = \frac{2\ell + 1}{2} \int_{-1}^{1} dx P_\ell(x)P_{\ell'}'(x)(x^2 \Delta K + K')$$ (8)

with the abbreviations $K_{\perp/\parallel} = \langle k_{\perp/\parallel}(\lambda) \rangle_\lambda$, and $\Delta K = K_{\perp} - K_{\parallel}$. By carrying out the integration, one finds that the only non-vanishing components of $M_{\ell\ell'}$ are given by

$$M_{\ell\ell'} = \begin{cases} \frac{(\ell-1)\ell}{(2\ell-3)(2\ell-1)} \Delta K & \text{for } \ell' = \ell - 2 \\ \frac{(2\ell+1)(2\ell-1)}{(2\ell+3)(2\ell+1)} \Delta K + K_{\parallel} & \text{for } \ell' = \ell \\ \frac{(\ell+1)(\ell+3)}{(2\ell+3)(2\ell+5)} \Delta K & \text{for } \ell' = \ell + 2 \end{cases}$$ (9)

From the initial condition, Eq. (5), one finds that the only non-vanishing initial values $a_\ell$ are

$$a_0(t = 0) = \frac{1}{2}$$

$$a_2(t = 0) = \frac{I_\perp - I_\parallel}{I_\perp + 2I_\parallel}$$ (10)

Although Eq. (7) represents an infinite set of differential equations, it occurs that for our experimental conditions
Finally, the observable mean fluorescence lifetime $\langle \tau \rangle$ is found as

$$\langle \tau \rangle = \int_0^\infty dt\, F(t) t / \int_0^\infty dt\, F(t)$$  (15)
The free-space lifetime. The reason for that can be understood when inspecting Figs. [1] and [2]. The focused laser beam will predominantly excite molecules with horizontal orientation (see Fig. [2], for which the emission rate can be lower than the free-space rate. If the molecules do not rotate, one can thus observe, for specific cavity size values, average lifetime values which are longer than the free-space lifetime. However, if molecular rotation is much faster than the average excited state lifetime, than the emission rate will be dominated by that for vertically oriented molecules (which is much faster than that for horizontally oriented ones, see Fig. [1]) and will always result in average lifetime values smaller then the free-space lifetime. Finally, it should be emphasized that the excellent agreement between theoretical model and experimental results offer the fascinating possibility to use lifetime measurements on dye solutions in tunable nanocavities for simple and direct determination of the fluorescence quantum yield, a quantity which is notoriously difficult to determine by other methods [15].

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early proportional to cavity length). Both curves show a strong decrease of the lifetime values with increasing cavity length. The solid lines represent fits of the theoretical model to the experimental values, where the only fit parameters have been the free space lifetime $\tau_0$, the fluorescence quantum yield $\Phi$, and the rotational diffusion time $\tau_D = 1/6D$. For the water solution, the fit values are $\tau_0 = 4.1$ ns, $\Phi = 0.93$, and $\tau_D < 50$ ps, whereas for the glycerol solution they are $\tau_0 = 3.6$ ns, $\Phi = 0.99$, and $\tau_D > 100$ ns (indicating that $D \approx 0$ on the time scale of the fluorescence lifetime). The fluorescence lifetime and fluorescence quantum yield values are in excellent agreement with published values, see [10] and citations therein. The large fit value of the rotational diffusion time for rhodamine in glycerol, which is by nearly two orders of magnitude larger than the fluorescence lifetime, indicates that rotational diffusion is practically frozen during de-excitation of the excited molecules, which is similar to the limiting case of fixed dipole orientations. Contrary, the fitted rotational diffusion value in water is significantly shorter than the lifetime, indicating a situation where the emitters perceive an environment with a rapidly fluctuating mode density of the electromagnetic field. Both situations, rapid and slow rotational diffusion, lead not only to quantitatively different results for the dependence of average lifetime on cavity size as seen in Fig. [3] but also to qualitatively different behavior: While for slow rotors, the average lifetime can exceed, for specific cavity size values, the free space lifetime (dotted lines in Fig. [3]), the average lifetime for rapidly rotating molecules will always be smaller than the free-space lifetime. The reason for that can be understood when inspecting Figs. [1] and [2].
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