Characterization of single emitters and nano-antennas
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Quantum efficiency measurement of single nanodiamond NV centers

We apply two techniques on single nanodiamond NV centers to calibrate their quantum efficiency by varying the local density of optical states at the position of the emitters. In the first technique, the local density of states (LDOS) variations are induced at a dielectric interface by using liquids to vary the refractive index. By applying this technique on nanodiamond NV centers we find that in 25 nm nanodiamonds, NV centers are essentially insensitive to the LDOS variations imposed by liquids with different refractive indices, and propose that quantum efficiencies in such nanocrystals are widely distributed between 0% and 20%. In the second technique, we nanomechanically vary the distance between a fluorescent source and a mirror, thereby varying the local density of optical states at the source position. Application of this technique to NV defects in diamond nanocrystals shows that their quantum yield can significantly differ from unity. For single NV centers in larger 100 nm nanocrystals, we show that decay rate changes can be reversibly induced by nanomechanically approaching a mirror to change the LDOS. Using this scanning mirror method, for the first time we report calibrated quantum efficiencies of NV centers, and show that different but nominally identical nanocrystals have widely distributed quantum efficiencies between 10% and 90%.
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3.1 Introduction

Due to the photostability properties of nanodiamond NV centers, these emitters are generally regarded as efficient fluorescent sources that are suitable for use as LDOS probes for integration in nanophotonic devices. However, according to chapter 2, our data indicate that NV centers even in nanocrystals as large as 100 nm across do not have unit quantum efficiency, and that there is a distribution of nonradiative and radiative rates. The general opinion in literature that NV centers must be efficient emitters is evident from several reports that claim lifetime changes for NV centers that are induced by placing nanocrystals in photonic environments of varying index and topology [1–5]. However, to our knowledge all these measurements of lifetime changes for nanodiamonds were performed by comparing the mean rate from an ensemble of single-center measurements in one system, to measurement on a different ensemble of single-centers in a second system [2, 4, 5]. Ruijgrok et al. [4] in particular report changes for a system in which the induced LDOS change is exactly known, and report changes in the mean rate consistent with those expected for unit-quantum-efficiency emitters. However, we note that in these ensemble measurements, the change of the mean decay rate was far smaller than the width of the rate distribution. Therefore, those measurements do not allow to ascertain whether for any given single NV center the rate actually varies with varying LDOS in a manner that is consistent with the expectations for efficient emitters. Therefore, it is crucial to measure quantum efficiency, radiative and nonradiative decay rates independently on individual NV centers in order to decide if/which NV centers in nanodiamonds are suitable for use as LDOS probes for integration in nanophotonic devices.

Several methods have been proposed so far for measuring the quantum efficiency of emitters. These methods are based on exposing the emitters to a known LDOS variation while measuring the decay rate from which the quantum efficiency can be extracted [6–8] as explained earlier in chapter 1. A realization of this method using liquids with different refractive indices to induce LDOS variations was pioneered by Snoeks et al [9], and later adopted by e.g. Refs. [4, 10, 11]. As an alternative, Buchler et al. pioneered a micromechanical method to vary LDOS by approaching a mirror to a single molecule. Similarly, Chizhik et al. made use of a nanomechanically tunable cavity [8]. Here we use similar methods to systematically induce variations in the LDOS experienced by individual nanodiamond NV centers.

In this chapter, we first present the results of experiments in which we measure emission rate changes of individual nanodiamonds as we controllably vary the LDOS of their environment using liquids of different refractive indices. As discussed in chapter 2, for small nanocrystals there is a decay rate distribution indicative of low-quantum-efficiency emitters. Consistent with this low quantum efficiency, using the LDOS tuning method with liquids, we find no evidence that small single NV centers are responsive LDOS probes when applying moderate LDOS variations.

Next, using a variation of the nanomechanical technique of Buchler et al. [6] we effect a Drexhage experiment [7, 12–15] to calibrate decay constants of single NV centers [16]. As in Ref. [16] we use a spherical silver mirror of several 10 µm
3.2 Liquid tuning of LDOS on single NV centers in small nanodiamonds

in diameter attached to a scanning probe. The technique relies on the shear-force mechanism to keep the mirror in near-contact with the sample and a lateral scanning procedure. We calibrate our technique on colloidal beads infiltrated with high-quantum-yield dye and on thin emissive layers. Finally, we measure the quantum efficiency of single NV centers in diamond nanocrystals. For the larger nanocrystals (100 nm diameter), we for the first time manage to induce reversible changes of up to 25% in the total decay rate of single NV centers using a calibrated LDOS change induced by a nanomechanically moved mirror. On basis of these measurements we argue that the apparent quantum efficiency of nanodiamonds in the size range 50–150 nm ranges widely from about 10% to 90%. This wide range of quantum efficiencies implies that prior to constructing a photonic structure, it is necessary to screen the nanocrystals using a calibrated quantum efficiency measurement on the single NV center level, as shown in this chapter.

The chapter is structured as follows. In section 3.2 we present the results of LDOS tuning on small nanodiamond NV centers using liquids with different refractive indices. Next, in section 3.3 we apply the technique of nanomechanical tuning of LDOS on, first, fluorescing beads and dye layers (section 3.4), and then, on large nanodiamonds containing single NV centers (section 3.3.1). Finally, we conclude our findings in section 3.4 where we give an outlook for further possible studies.

3.2 Liquid tuning of LDOS on single NV centers in small nanodiamonds

For the small nanodiamonds only the liquid tuning method could be applied due to experimental constraints. Sources are placed in close proximity to a planar interface between a dielectric and a half-space that can be filled with liquids of different refractive index. The advantage of using liquid tuning of refractive index for sources near an interface is that the LDOS changes near an interface are nearly independent of emission frequency, and are known to be excellently described by the theory explained in full by Urbach and Rikken [17]. In view of the broad emission spectrum of NV centers in diamond, it is important to apply a broadband LDOS change when seeking to measure lifetime changes. A narrowband LDOS variation as obtained with a high-Q microcavity that would for instance be tuned to the zero phonon line, would not necessarily affect the rate, but rather only the branching ratio between the zero phonon line and the rest of the spectrum.

We prepared the sample by evaporating a 60 nm thick layer of SiO$_2$ on one of the 25 nm nanodiamond samples on which we had identified single NV centers as discussed in chapter 2. This step immobilizes the nanodiamonds, and ensures that liquid application to tune LDOS does not add new chemically induced nonradiative decay channels. Next, we defined a 3 mm deep liquid reservoir on top of the sample using a ring-shaped enclosure cut from Polydimethylsiloxane (PDMS) bonded to the substrate. Figure 3.1(a) depicts a schematic of the sample. In order to investigate the decay dynamics of the NV centers in response to the LDOS variations, we randomly
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selected six NV centers from the ensemble of figure 4.3 and measured their lifetimes in three conditions: before adding any liquids where the top half space of nanodiamonds consists of air \((n = 1.00)\), after adding water with refractive index of \(n = 1.33\), and after adding isopropyl alcohol (IPA) with refractive index of \(n = 1.38\) to the liquid bath on top of the nanodiamonds. In the lower panel of figure 3.1(b) we plot the decay rate of each NV center as a black bar measured when the sample is dry. The color bars in the upper panel of figure 3.1(b) show the difference between decay rates of each NV center after and before introducing a liquid. We observe that for most centers, the decay rate either barely varies, or varies non-monotonically with applied index, although generally, one expects to observe an increase in the decay rate of a dipole emitter in a homogenous medium by increasing the refractive index of the environment due to an increase of the LDOS [17].

For comparison to the data we calculate the normalized decay rate of a dipole positioned in the middle of a 60 nm thick SiO\(_2\) slab \((n = 1.52)\) which is sandwiched between a semi-infinite slab of quartz with \(n = 1.46\) at the bottom and a semi-infinite slab with varying refractive index at the top. Figure 3.1(c) shows the calculated decay rate of the dipole as a function of the refractive index of the top layer for different dipole-moment orientations. The calculation shows that as the refractive index increases the decay rate change is expected to be monotonic and increasing and is the largest for a dipole oriented perpendicular to the interface while the change is slight for a
dipole-moment parallel to the interface. Comparing the calculated rate changes to the measured decay rates (figure 3.1(b)), we find no systematic rate variation for the NV centers within the error bars of our experimental data. The error bar for measurements on individual NV centers is composed of two contributions. First, the error bar contains the uncertainty in the fit to the fluorescence decay trace. Second, the experiment is hampered by the fact that the decay rates of some of the single nanodiamonds was observed to jump slightly between observations, even if no change in environment was applied. These jumps amount to approximately 5%, and occur on time scales of hours to days. To exclude this effect, we have measured the rate for each liquid and a reference in air on the same day for each NV center to generate the plot of rate changes in figure 3.1(b).

We find that there is no evidence that the rate of individual NV centers in 25 nm diamond nanocrystals actually varies in accordance with the known applied LDOS changes. This observation appears to be at variance with earlier work that evidenced a small change in the mean decay rate of an ensemble of NV centers in a liquid-tuning experiment [4]. As two caveats, we note that first, in that previous work it was not verified if any such change occurred for each source individually, and second, that a shortcoming of our experiment for quantitative interpretation is that for dipoles located close to an interface (as is the case here), the decay rate enhancement significantly depends on the unknown dipole-moment orientation of the emitter with respect to the interface. While the fact that we do not know the dipole orientations for each NV center makes it impossible to conclude with certainty that an LDOS effect is absent, two hypotheses for absence of an LDOS effect could be proposed. First, that the quantum efficiency of 25 nm diamond nanocrystals is low, or second, that the very high index diamond shell around the NV centers intrinsically prevents the NV center from responding to (moderate) changes in the LDOS of the environment it is supposed to probe. We exclude the latter explanation on basis of a set of finite element (COMSOL) simulations, in which we calculate the decay rate of a point dipole randomly located in a diamond nanosphere, which in turn is placed at varying distances from a planar interface with materials of various dielectric constants. We find that in all cases, the decay rate of the source simply follows the theory of Urbach and Rikken [17] for a source without dielectric shell, multiplied by a pre-factor that is essentially a quasistatic local field correction factor due to the diamond shell and is independent of the varying LDOS.

To conclude, our observation that no NV center responds to LDOS changes together with our earlier correlation plots of brightness versus decay rate (figures 4.2 and 4.3) means that the quantum efficiencies of 25 nm diamond nanocrystals are likely low. A second important conclusion is that single NV centers of 25 nm size appear unsuitable to measure LDOS changes due to the slight jumps in lifetime, unless the entire measurement scheme (including reference measurements) takes less than a few hours.
3.3 The scanning-mirror method

In this section we report on the results of the nanomechanically varying LDOS method to assess if single NV centers are suited for LDOS measurements, and to calibrate emission rates. This method has the advantage that we can apply calibrated LDOS changes rapidly so that jumps in the intrinsic rate constants can be avoided that hamper experiments where macroscopic sample changes are required to modify LDOS, as in a liquid immersion experiment. The scheme is similar to a measurement procedure reported by Buchler et al [6], based on a Drexhage experiment [7, 12–15]. In a Drexhage experiment, a mirror is used to impose a large LDOS change, and rates are measured as a function of the emitter-mirror separation. While this method is usually implemented by creating a set of macroscopic samples where mirrors are coated with spacers of calibrated thicknesses [7, 13, 14] or by creating a single sloping wedge between a mirror and an ensemble of emitters [15], Buchler et al realized a nanomechanical version that can be applied to a single emitter. Buchler et al used a silver-coated curved fiber end as a mirror attached to a piezo-stage to precisely tune the mirror distance to an underlying single emitter on the sample [6]. Here, we use a similar method in a shear-force-feedback near-field microscope. However, instead of a vertical mirror displacement, we use a lateral displacement of the curved mirror while...
staying in shear-force feedback to keep the mirror and sample substrate in near-contact. Our scheme of changing the distance between an emitter and a mirror is illustrated in Fig. 3.2(a). The interrogated source is fixed to a substrate and a large spherical mirror is laterally scanned across the sample surface while the mirror-sample distance is kept constant using shear-force feedback \[18\]. This procedure is implementable in most closed-loop scanning-probe microscopes, as opposed to calibrated retraction of the probe. In Fig. 3.2(a) two positions of the mirror with respect to an emitter are shown to illustrate the principle of changing the emitter-mirror distance by laterally moving the mirror over the sample. To fabricate the micromirror we glue polystyrene beads (diameter 45 µm, Polysciences Europe) to the cleaved end of an optical fiber with a small amount of super-glue. We subsequently evaporate a layer of 200 nm of Ag onto the sphere to obtain a spherical micromirror. The optical fiber is then glued to a quartz tuning fork, as sketched in Fig. 3.2(b, inset), which is mounted on a 3D piezo scanner, the \(z\)-axis of which is controlled through a standard shear-force feedback loop. In other words, the quartz fork is vibrated at a frequency just above its resonance using weak electric excitation, and the resultant phase response of the fork is used as input for a PID-loop that adjusts the \(z\)-piezo to approach the sample surface to within 5-15 nm. The scanning probe assembly is placed on top of the inverted confocal microscope described in chapter 2, allowing us to collect fluorescence intensity and fluorescence lifetime data as function of probe position. In particular this is achieved by fixing the sample in the confocal focus of the ps pulsed 532 nm laser, and scanning the probe sideways.

### 3.3.1 Nanomechanical tuning of LDOS on large nanodiamonds

We have applied the scanning-mirror LDOS changing technique to 100 nm nanodiamonds containing single NV centers, prepared as described in section 2.2.1, and subsequently embedded in a 200 nm thick layer of planarizing spin-on glass (FOX-14, Dow Corning). The spin-on glass immobilizes the nanocrystals, so that they are not moved during shear-force scanning. In order to vary the distance between the mirror and the emitter, we scan the mirror bead laterally on top of an identified NV center. For each position of the mirror bead, we collect the fluorescence emission of the NV center, positioned at the focus of the pump laser, through the confocal microscope setup described in section 2.2.2. By scanning the mirror bead, we obtain a confocal fluorescence intensity map as shown in figure 3.3(a). Here, each pixel represents the relative position of the mirror bead with respect to the NV center with the false color representing the collected fluorescence intensity. We clearly observe interference rings in the fluorescence intensity map. These rings mainly stem from the fact that the mirror imposes a standing-wave pattern on the 532 nm pump field, which subsequently results in a modulation of the fluorescence intensity.

For each pixel in the fluorescence intensity map, we stored absolute photon arrival times, as well as laser pulse arrival times, allowing us to extract the decay dynamics. We use a single-exponential fit to obtain the corresponding decay rate of the emitter for each mirror position, as plotted in figure 3.3(b). Here, the color scale represents the
fitted decay rate corresponding to a defined mirror position. Interestingly, we observe a radial modulation of the decay rates varying between about 0.02 ns\(^{-1}\) to 0.04 ns\(^{-1}\), which we attribute to the varying LDOS in front of the mirror. To quantify the variation as a function of the distance from emitter to mirror, we extracted the decay rates as a function of the lateral distance to the mirror central position. To this end, we bin pixels in concentric rings of equal lateral distance to the mirror center, and concatenate the photon-correlation time traces of all pixels in each bin to obtain a single fluorescence decay trace per radial distance. Using the spherical form factor of the bead, we convert lateral position of the mirror to normal distance of the mirror to emitter. The decay rate fitted to the fluorescence decay for each mirror-emitter separation is depicted in figure 3.4 (black dots). We observe a distinct oscillation of the rate around 0.028 ns\(^{-1}\), with a 15\% amplitude. To our knowledge, this is the first report of a reversible change in the decay rate of a single NV center in a calibrated LDOS experiment.

Due to the large radius of the mirror compared to its distance to emitters, it is reasonable to consider the experimental configuration as a planar glass-air-mirror system in which we vary the air thickness. For this system, the LDOS is exactly known [14, 18] for any dipole orientation and position. The LDOS is calculated according to the formalism of Amos and Barnes [14], which essentially expresses the required imaginary part of the Green function at the source position as a Sommerfeld integral over all parallel wave vectors. In particular, the local density of states normalized to that in vacuum differs for the case of dipole orientation parallel and perpendicular to the interface, taking on the values

\[
\rho_\perp(z) = \frac{3}{2} \text{Im} \int_0^\infty [1 - r^p(\kappa_\parallel, z) e^{-2i\kappa_z h}] \frac{ix^3 \kappa_\parallel}{\kappa_z} d\kappa_\parallel
\]
3.3 The scanning-mirror method

Figure 3.4: Dots: decay rate as a function of the emitter distance to mirror, extracted from the decay rate map shown in figure 3.3(b). Solid line: fitted LDOS on the measured rate oscillations with fit parameters $\gamma_r$, $\gamma_{nr}$ and a set of dipole moment orientations. The shown QE is the most-likely value.

respectively

$$
\rho_{||}(z) = \frac{3}{4} \text{Im} \int_0^\infty \left\{ [1 + r^s(\kappa_{||}, z)e^{-2i k_z h}] + (1 - \kappa_{||}^2)[1 + r^p(\kappa_{||}, z)e^{-2i k_z h}] \right\} \frac{i \kappa_{||} d\kappa_{||}}{\kappa_z}.
$$

In this formulation, the emitter is understood to be buried at a depth $h$ into the glass-air interface. The integration variable $\kappa_{||}$ represents the magnitude of the parallel wavevector normalized to the wave number $k$ in glass. The perpendicular wave vector follows as $\kappa_z = k_z / k = \sqrt{1 - \kappa_{||}^2}$. The mirror enters through the reflection coefficient $r^s$ and $r^p$. These are the $s$- and $p$-reflection coefficient for waves impinging from the glass side on the composite system of the glass-air interface at $z = 0$, plus the metallic mirror at height $z$ above the glass air interface. This composite amplitude reflection coefficient for a double interface is simply calculated from the Fresnel coefficients given tabulated optical constants and the separation $z$, according to the textbook derivation for a two-interface system

$$
r = r_{12} - \frac{(t_{12})^2 r_{23} e^{2i k_{z,2} z}}{1 - t_{12} r_{23} e^{2i k_{z,2} z}}.
$$

Here the subscript 12 is understood to refer to the glass-air interface, 23 to the air-mirror interface $s$ and $p$ superscripts are suppressed, and $k_{z,2}$ is understood to be the perpendicular wave vector in air, given the parallel wave vector $k\kappa_{||}$ in the integrand. An important realization about the integral is that it runs over both propagating, and
evanescent contributions. In particular, the contributions with $\kappa_\parallel < 1$ are contributions corresponding to propagating waves in glass. Contributions with larger $\kappa_\parallel$ contain evanescent waves, i.e., decay rate contributions due to the mirror system that do not end up in far field radiation. In part this consists of quenching by the mirror, and in part this consists of emission into surface plasmon polaritons. An important abstraction here is that the required Fresnel reflection constants are equally valid when evaluated at large parallel wavevector, i.e., for evanescent waves, and that they contribute a pole at every guided mode of the system. Given that the parallel and perpendicular dipole orientation are the principal axes for a planar geometry, the local density of states normalized to that in vacuum for a dipole at an angle $\theta$ relative to the sample normal reads

$$\rho(z, \theta) = \cos^2 \theta \rho_\perp(z) + \sin^2 \theta \rho_\parallel(z).$$

Figure 3.5 shows the calculated LDOS map of the planar glass-air-mirror system for a dipole buried in the semi-infinite glass slab and oriented parallel (a) or perpendicular (b) to the interface. The vertical axes in figure 3.5 represents the depth $h$ at which the emitter is positioned inside the glass and the horizontal axis represents the glass-mirror distance $z$ which is equal to the thickness of the sandwiched air layer. We set the emission wavelength of the dipole to 680 nm corresponding to the peak emission wavelength of the NV centers and assume dielectric constants of $\epsilon_{glass} = 1.4^2$ and $\epsilon_{Ag} = -21.04 + 0.8i$ for glass and silver mirror layers, respectively. We note that the LDOS oscillations are more pronounced for dipoles oriented parallel to the interface.

![Figure 3.5](image)

**Figure 3.5:** LDOS map of a planar glass-air-mirror as function of the distance between emitter and glass-air interface and as function of glass-mirror distance for (a) parallel, and, (b) perpendicular dipole moment orientation. The wavelength of the emission is set to 680 nm corresponding to the peak emission wavelength of the NV centers. LDOS values are normalized to the value in vacuum.

We fit the experimental decay rate data using the theoretical LDOS $\rho(z + d, \theta)$ according to $\gamma(z) = \gamma_{nr} + \gamma_r \rho(z + d, \theta)$, where $\gamma_{nr}$ is the nonradiative, and, $\gamma_r$ is the
radiative decay rate, and θ is the dipole orientation relative to the normal to the plane. A small offset d appears due to the unknown distance-of-closest approach in shear-force microscopy which is of the order of d ≈ 15 nm. The source depth h into the glass we have set to 150 nm, corresponding to the expected average depth of the NV centers into the FOX spin-on glass layer. We use as fit function γ = γ_{nr} + γ_{r} [α · ρ∥ + (1 − α) · ρ⊥], where ρ∥,⊥ (z, d, θ) is the calculated LDOS for dipoles parallel and, respectively, perpendicular to the surface and α = \cos^2 θ parametrizes dipole moment orientation θ. To be inferred from the fit to the data are α, the quantum efficiency (0 ≤ QE ≤ 1), and the total decay rate γ_{tot} in absence of the mirror. We sweep θ through its range and at each value of θ apply a maximum likelihood fitting routine to obtain the values of QE and γ_{tot}, as well as the residuals between the fitted curve and the measured dataset. By minimizing the residuals of the fit we obtain the set of most likely parameters. This gives a range of quantum efficiency values for which the fit is consistent with the data. Figure 3.6 shows the fitted values as a function of θ for the particular data set shown in figure 3.4. We find a most likely quantum efficiency of 26% and a dipole moment orientation within 20° along the sample plane. The corresponding fit to the experimental data is shown as the red solid line in figure. 3.4. According to figure 3.6 the range of quantum efficiencies consistent with the data for this NV center is bounded from below by 26%, and from above by 50%. To our knowledge this is the first experimental calibration of the quantum efficiency of a single NV center in a diamond nanocrystal. Care must be taken that a correlation exists between the dipole orientation θ, and the apparent quantum efficiency γ_{r}/(γ_{nr} + γ_{r}) returned by the fit routine, due to the fact that the LDOS for different dipole-moment orientations is similar in qualitative z-dependence, but different in oscillation contrast. In case the dipole moment orientation of the NV center is known, which could in principle be realized using Fourier microscopy [19], one can extract a more precise value for the quantum efficiency. The range of θ commensurate with the measurement uncertainty of the data in figure 3.4 is Δθ = ±45°. Even within that range of θ ± Δθ, the quantum efficiency remains bounded to QE ≤ 50%. We therefore conclude that the quantum efficiency of the individual NV defect of Fig. 3.4 does not exceed 50% and is most likely as low as 26%. We note that in contrast to the 1D dipole moment assumed here, NV centers have been reported to posses two dipole moments in a plane normal to the symmetry axis of the NV center (along \tilde{θ}) [20]. In this case the same fit function applies but with α = 1 − 1/2 cos^2 \tilde{θ}, assuming all dipole orientations within the plane are equally sampled. This re-interpretation of α does not affect the determined rate and quantum efficiency. While we indeed fit α ≥ 1/2, both the 1D and 2D model are consistent with our data.

In order to investigate the typical quantum efficiencies of NV centers, we selected five random NV centers and examined them with the moving mirror experiment as explained above. Each nanodiamond was selected to be a single NV center containing nanocrystal according to the criteria we outlined in section 2.2.3, without further post-selection for inclusion in the Drexhage experiment. Table 3.1 summarizes the confidence intervals for the fitted values of the quantum efficiencies, given that we do not know the dipole orientation a priori. The total decay rate γ_{tot}, i.e. the sum
of $\gamma_r$ and $\gamma_{nr}$ varies almost over a factor 2, and can be fitted accurately. In Table 3.1 we also report radiative and nonradiative decay rates. Values are reported as fitted to the data while fixing the dipole orientation at its most likely value, in which case the data can be fit with small error bars on $\gamma_r$ and $\gamma_{nr}$. The wide range of quantum efficiencies consistent with the data of course imply that in a completely free fit $\gamma_r$ and $\gamma_{nr}$ both have a large error bar, though their sum $\gamma_{tot}$ does not. We find that the different NV centers we probed, while having reasonably comparable brightness, in fact have widely different quantum efficiencies. For instance, NV center 4 (figure 3.7(a)) has an efficiency certainly below 14%, while NV center 5 (figure 3.7(b)) has a quantum efficiency certainly above 58%, in the range 58% to 90%. Furthermore, we note that the fits neither result in the conclusion of a fixed nonradiative rate at varying radiative rate, nor conversely in the conclusion that the radiative rate is a constant while the nonradiative rate varies. Instead, both the radiative and the nonradiative decay rates are distributed. Even with the wide error bars on quantum efficiencies, we establish that both distributions span at least around a factor two in range. Our measurements

\[ \theta \]

\begin{figure}[h]
  \centering
  \includegraphics[width=0.5\textwidth]{figure3.6.png}
  \caption{Fitted parameters QE and $\gamma_{tot}$ as a function of $\alpha$ and $\theta$.}
\end{figure}
### 3.4 Conclusions and outlook

In conclusion, we presented two techniques to quantify the quantum efficiency of single NV centers. Using liquid-tuning method on small nanodiamond NV centers, we find no evidence that small single NV centers are responsive LDOS probes when applying moderate LDOS variations, commensurate with the assumption of low quantum efficiency for NV centers in small nanocrystals. Furthermore, we presented a
technique in which LDOS variations are introduced by a nanomechanically moving mirror. Using this technique, for the first time we measured the quantum efficiency of single nanodiamond NV centers. Our measurements show that even NV centers in large nanocrystals show a wide range of quantum efficiencies when probed in a controlled LDOS experiment. For NV centers in 100 nm nanocrystals we find quantum efficiencies distributed between 10% and 90%. For the smaller nanodiamonds, the scanning mirror technique turned about to be inappropriate because the much weaker emission brightness of NV centers in nanodiamonds necessitated much higher pump powers, to a level at which our metallized microspheres melted. Accordingly, for the smaller NV centers we can only speculate about quantum efficiency. The fact that NV centers in small diamonds did not respond to LDOS changes, and that they are markedly dimmer leads us to believe that their efficiency is likely a factor of two smaller on average.

If we combine the findings of Chapter 2 and 3 together, we conclude that our quest to determine the suitability of nanodiamonds as photonic LDOS probes, or as building blocks for hybrid photonic systems has led to a disappointing conclusion. We have investigated the brightness, decay rate, and quantum efficiency of single NV centers in nanodiamonds of 25 nm, and of 100 nm median size. For both size ranges a wide distribution in brightnesses and rates is found, consistent with reports by earlier workers. We conclude that the wide distribution of rates is due to a distribution in radiative rates, nonradiative rates and quantum efficiencies. This conclusion contradicts earlier work, that interpreted the wide distribution of decay rates as mainly due to a photonic effect that causes a distribution in radiative decay rates via the LDOS. Instead, our measurements show that even NV centers in large nanocrystals show a wide range of quantum efficiencies when probed in a controlled LDOS experiment. For applications in nanophotonic experiments using single NV centers, a most problematic property is that quantum efficiency does not correlate with brightness, due to the fact that both the radiative and nonradiative rate are distributed. In other words, screening nanodiamonds to pick the best one to probe LDOS or for incorporation in a photonic device can not rely on a simple metric such as spectrum or brightness. Instead, we argue that future work in the hybrid assembly of nanodiamonds in plasmonics and photonic crystals to realize accelerated spontaneous emission decay always requires an experimental protocol in which nanodiamonds are first individually calibrated in terms of quantum efficiency. While we have shown a method for such calibration, this is a highly tedious procedure that is not easily implementable and requires dedicated near-field manipulation equipment.

In this work, we have not speculated on the origin of the apparent low quantum efficiency of single NV centers in nanodiamonds. We close with two remarks on the origin of the low apparent quantum efficiency. Firstly, we have treated the NV center as a quasi two-level system. Our experiments thus address the question what the apparent quantum efficiency is when attempting to use an NV center as a two-level LDOS probe. From the NV center spectrum it is clear that the spectrum is very wide with a large vibrational broadening spectrum. Moreover it is well known that the NV\(^-\) center is not a two level system. Instead, the NV\(^-\) has different spin sublevels,
and may experience spin-flip intersystem crossing between allowed spin transition manifolds. The rates for these transitions were recently characterized in detail for NV centers in bulk diamond in Ref. [21]. A further complication is that the NV$^-$ defect may infrequently transition to an uncharged NV center that also luminesces, yet at different rate and efficiency. The many rates involved in these transitions can further vary between NV centers due to, e.g., variations in crystal strain. A full treatment of the response of NV centers to LDOS changes would hence have to treat the full rate equations in which radiative transition rates are, and intersystem crossing rates are not, affected by LDOS. An important step beyond our work will be to perform the measurements we have described here but employing it on the most controlled diamond system available (CVD grown diamond sheets by Element Six, used in spintronic experiments) and applying the spin selective techniques reported by Robledo [21] to establish what the nonradiative and radiative rates are for each transition separately, instead of lumping rates into effective two-level parameters. While the LDOS changes we have applied using a mirror are broadband LDOS changes that modify radiative transitions roughly equally across the emission spectrum, LDOS changes that have strong spectral features could be used advantageously to enhance or suppress the importance of intersystem crossing. As further part of this proposed follow up work, we note that an independent means to obtain rates would be to fit a multi-level decay model to the temporal $g^{(2)}(\tau)$ photon-correlation. Fitting a pump intensity series of $g^{(2)}$ correlation functions measured in absence of the mirror, together with data on the concomitant saturation power and measured brightness at saturation could give more insight in the rates, complementary to our Drexhage data. Even more exciting could be to measure $g^{(2)}(\tau)$ as function of the NV-center mirror distance.

Having established that further work is required to separate the quantum efficiencies reported here into parameters per transition in a more complete level scheme, we turn to possible reasons for the below-unity values of quantum efficiency that we find. The lower brightness of the smaller NV centers, as well as their lack of response to LDOS changes suggest that the surface, i.e., surface contamination with carbon, or surface defects may play a role in providing quenching sites. Indeed, it has already been suggested for very small (5 nm) nanodiamonds that NV centers may suffer quenching due to graphite shells on the diamonds [22, 23]. While the nanodiamonds we used have been employed by several groups in spontaneous emission control experiments in untreated form, exactly as in our experiments, additional surface treatments such as by prolonged immersion in boiling sulphuric acid, or cleaning in Köningswasser have been proposed by several workers. Whether or not such treatments actually affect quantum efficiency is as yet unclear, as is whether quenching can be completely suppressed. We propose that the quantum efficiency calibration method that we demonstrated will be an indispensable tool to evaluate such cleaning methods, as well as to screen other color centers in diamond for advantageous fluorescence properties.
Appendix: calibration of nanomechanical tuning of LDOS on fluorescing beads and dye layers

In this appendix, for completeness we replicate a calibration study of our nanomechanical Drexhage measurement undertaken by M. Frimmer in our lab, and published in a joint publication in Ref. \[16\]. As calibration samples, we prepared homogeneous, 70 nm thick PMMA films doped with dye (Bodipy TR, D-6116, Invitrogen) by spincoating. The spin-coated solution was prepared by diluting 5 mg of dye in 1 ml of anisole, and subsequent 30-fold dilution of the dye solution in a 2% solution of 950 K PMMA in anisole. As second type of calibration sample we used clean cover slips with dye-doped polystyrene beads (diameter 100 nm, F8801, Invitrogen) dispersed at low concentration. We evaporated about 60 nm of SiO$_2$ on top of the sample for mechanical protection.

For the first type of calibration measurement, we use our inverted confocal fluorescence-lifetime imaging (FLIM) microscope to collect lifetime data from a single, randomly chosen, diffraction limited spot in the film while scanning the mirror in shear-force contact over the sample. For the second type of calibration measurement, we locate a single fluorescing bead in the focus and collect lifetime data while scanning the mirror. In all instances we used the picosecond pump laser (532 nm, 10 MHz), and the 100$\times$, NA=1.4 objective also used for our diamond experiments. Figure 3.8(a) shows a fluorescence intensity map obtained from a single bead while scanning the mirror, while panel (b) shows the associated fluorescence lifetime image, obtained by fitting the time traces for each pixel to single exponential decay. The circular symmetry of Figs. 3.8(a,b) is expected due to the symmetry of our micromirror with respect to its touching point with the sample. Procedurally, we exploit this symmetry by determining the center of the circular patterns in Figs. 3.8(a,b) and concatenating TCSPC data of pixels with equal distance to the center of the pattern into a single decay trace. Given the known diameter of the micromirror to convert in-plane distances into a vertical mirror-emitter separation, while assuming the shear force distance between micromirror and sample to be negligible, we obtain the decay rate as a function of distance to the mirror, shown as the full diamonds in Fig. 3.8(c). We clearly observe characteristic decay-rate oscillations in front of the mirror \[12\]. Panel (c) also obtains typical traces obtained on the dye films.

For both the film case, and the bead case we have calculated the LDOS, including the layered system we used to immobilize the beads. We find excellent agreement, assuming a unit quantum efficiency for this dye, for separations between mirror and emitters above 200 nm. At smaller separations deviations occur, which we attribute to the fact that for both films and beads, ensemble averaging over the spectral, orientational and positional ensemble of molecules is challenging to accurately replicate in the modelling. Indeed, the optimal calibration technique would be to use single emitters of known and fixed dipole orientation, as well as known quantum efficiency.
Figure 3.8: (a) Fluorescence-intensity map of dye-doped bead in laser focus as micromirror is scanned across it, showing ring-shaped intensity variations. Each pixel denotes a specific lateral position of the mirror. (b) Fluorescence-lifetime map of same measurement that yielded (a). (c) Decay rate versus mirror-sample distance, as obtained from (b) by combining pixels with identical distance to the center of the circular pattern. Full diamonds are data obtained from (b), measured on 100 nm fluorescing bead. Open symbols show results on continuous dye layers (different positions, and different micromirrors [see legend]). Solid and dashed lines are analytical calculations for dye layer and fluorescing bead, respectively. This figure is replicated from [16], presenting a calibration performed by M. Frimmer.
References


REFERENCES