Photonic Effects for Magnetic Dipole Transitions

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Supporting Information

**ABSTRACT:** The radiative transition probability is a fundamental property for optical transitions. Extensive research, theoretical and experimental, has been conducted to establish the relation between the photonic environment and electric dipole (ED) transition probabilities. Recent work shows that the nanocrystal (NC)-cavity model accurately describes the influence of the refractive index $n$ on ED transition rates for emitters in NCs. For magnetic dipole (MD) transitions, theory predicts a simple $n^3$ dependence. However, experimental evidence is sparse and difficult to obtain. Here we report Eu$^{3+}$-(with distinct ED+MD transitions) and Gd$^{3+}$-(MD transitions) doped $\beta$-NaYF$_4$ NC model systems to probe the influence of $n$ on ED and MD transition probabilities through luminescence lifetime and ED/MD intensity ratio measurements. The results provide strong experimental evidence for an $n^3$ dependence of MD transition probabilities. This insight is important for understanding and controlling the variation of spectral distribution in emission spectra by photonic effects.

The spontaneous emission rate of an emitter is governed by Fermi’s golden rule. Both transition dipole moments and photon density of states resonant with transitions affect the emission rate. The transition dipole moment depends on wave functions of initial and final states. For electric dipole (ED) transitions, the electromagnetic field strength interacting with the transition is influenced by the local environment and a local field correction factor $\chi$ is required. The transition probability $k_{\text{ED}}$ is given by

$$k_{\text{ED}} = k_{\text{ED}}^0 n^2 \chi^2$$

where $k_{\text{ED}}$ is the radiative decay rate of ED transition for the emitter in a dielectric medium with the refractive index $n$ and $k_{\text{ED}}^0$ is the decay rate in vacuum ($n = 1$). The transition rate $k$ is proportional to the local density of states (LDOS) and can be modified by tuning the dielectric medium surrounding the emitter.\(^1\) The distance over which dielectric properties affect transition rates is of the order of the wavelength of the light emitted (hundreds of nanometers).\(^2\) Extensive theoretical work has resulted in a variety of models for $\chi$. The most prominent are the virtual\(^3\) and real cavity\(^4\) models which predict

$$k_{\text{ED}} = k_{\text{ED}}^0 \left( \frac{n^2 + 2}{3} \right)^2$$

$$k_{\text{ED}} = k_{\text{ED}}^0 \left( \frac{3n^4}{2n^2 + 1} \right)^2$$

For emitters doped in a nanocrystal (NC), the refractive index of the NC ($n_{\text{NC}}$) must be taken into consideration, giving rise to the NC-cavity model:\(^10\)

$$k_{\text{ED}} = k_{\text{ED}}^0 n^2 \chi_{\text{NC}}^2$$

The validity of the NC-cavity model was recently demonstrated by our group.\(^1\)\(^1\)\(^1\)\(^1\)\(^1\)\(^1\)

In contrast to extensive research on photonic effects on ED transition rates, research on the influence of the local surroundings on magnetic dipole (MD) transitions is very limited. No local field effects are expected since the magnetic susceptibility (in a nonmagnetic medium) is the same as for vacuum, and thus a simple cubic dependence (reflecting the variation of photon density of states with $n$) is predicted:\(^13\)

$$k_{\text{MD}} = k_{\text{MD}}^0 n^3$$

where $k_{\text{MD}}$ and $k_{\text{MD}}^0$ are the radiative decay rates of the MD transition for the emitter in a dielectric medium with refractive index $n$ and in vacuum, respectively. Experimental results on the variation of MD transition rate with $n$ are sparse as pure MD transitions are not often observed. In 1995, Rikken\(^14\) and later in 2002, Werts\(^15\) reported on the influence of $n$ on MD transition probabilities. Rikken studied Eu$^{3+}$ complexes with different MD ($^{5}D_0\rightarrow^{3}F_4$) and ED ($^{5}D_0\rightarrow^{7}F_2$ and $^{5}D_0\rightarrow^{7}F_{4}$) transitions. For the complexes dissolved in solvents with different $n$, the influence of $n$ on the MD transition rates was measured and explained using the $n^3$ dependence. A good agreement was obtained taking into account partial quenching and a $k_{\text{MD}}^0$ of 10 s$^{-1}$ for the $^{3}D_0\rightarrow^{3}F_4$ transition. This rate is, however, significantly lower than the theoretically calculated $k_{\text{MD}}^0$ of 14.4 s$^{-1}$.\(^16\) In the work by Werts, radiative lifetimes of...
Eu\textsuperscript{3+}\textsuperscript{5D0} emission in a variety of materials were compared and related to the \textsuperscript{5D0}−\textsuperscript{7F1} MD over the total (ED+MD) emission intensity ratio. Within the experimental accuracy (largely determined by significant uncertainties in quantum yield QY), a good agreement was obtained assuming an \( n^3 \) dependence of MD transition rate. In spite of these two insightful studies, a systematic and accurate investigation using model systems to study the relation between \( k_{\text{MD}} \) and \( n \) is still lacking. As shown previously, doped NCs serve as ideal probes for photonic effects\textsuperscript{11,12,17−21}. The size of NCs is well below the hundreds of nanometers over which photonic effects influence transitions for emitters inside NCs. The local coordination of emitters is fixed in the nanocrystalline host and is the same as in bulk material. Because the local coordination is unaffected by the solvent surrounding NCs, an ideal model system is realized in which only the variation in solvent refractive index in fluences radiative decay rates of emitters inside NCs. In the present work, we report two NC model systems (NaYF\textsubscript{4}:Eu\textsuperscript{3+} and NaYF\textsubscript{4}:Gd\textsuperscript{3+}) to accurately determine the dependence of MD transition rates on \( n \). The photonic effects in the present study involve a homogeneous dielectric medium with a limited range of \( n \) (1.35 to 1.53). In the past decades, a much wider variation

![Figure 1](image1.png)

**Figure 1.** TEM images of (a) NaY\textsubscript{0.9}Eu\textsubscript{0.1}F\textsubscript{4} core and (b) NaY\textsubscript{0.9}Eu\textsubscript{0.1}F\textsubscript{4}@NaYF\textsubscript{4} core−shell NCs (scale bar = 50 nm). (c) Emission spectra of core and core−shell NCs dispersed in chlorobenzene for 465 nm \textsuperscript{5F0}−\textsuperscript{5D2} excitation. (d) Energy level diagram of Eu\textsuperscript{3+}. Emission in the orange/red spectral region includes forced ED (\textsuperscript{5D0}−\textsuperscript{5F2}, \textsuperscript{5D0}−\textsuperscript{5F4}) and MD (\textsuperscript{5D0}−\textsuperscript{7F1}) transitions.

![Figure 2](image2.png)

**Figure 2.** Decay curves of Eu\textsuperscript{3+} emission at 615 nm after pulsed 465 nm excitation for (a) NaY\textsubscript{0.9}Eu\textsubscript{0.1}F\textsubscript{4}@NaYF\textsubscript{4} NCs in solvents with different \( n \) and for (b) core and core−shell NCs in diethyl ether with single exponential fits. Fit residuals are shown below. (c) Average lifetimes for NaY\textsubscript{0.9}Eu\textsubscript{0.1}F\textsubscript{4} (blue) and NaY\textsubscript{0.9}Eu\textsubscript{0.1}F\textsubscript{4}@NaYF\textsubscript{4} (red) NCs. The black dots give lifetimes determined from a single exponential tail (\( t > 1 \) ms) fit for core−shell NCs. The green dashed line marks the radiative lifetime based on the bulk radiative lifetime and solvent refractive index. Drawn lines are fits to eq 6.
in refractive index has been demonstrated in complex photonic and plasmonic structures, which give rise to much stronger variations in the luminescence properties.22–26 NaYF₄:Eu³⁺ and NaYF₄:Gd³⁺ NCs were synthesized using known colloidal synthesis techniques (see Supporting Information (SI) for details). Transmission electron microscopy (TEM) images show monodisperse and nearly spherical ∼22 nm NaY₅.₆Eu₅.₄F₄ core NCs (Figure 1a) and slightly prolate ∼28 × 25 nm NaY₅.₆Eu₅.₄F₄@NaYF₄ core–shell NCs (Figure 1b). Oleate ligands on the surface allow the NCs to colloidally stabilize in apolar solvents with different n to investigate the influence of the photonic environment.11,12 Six commonly used solvents are diethyl ether (n = 1.35), hexane (n = 1.38), octane (n = 1.40), chloroform (n = 1.45), toluene (n = 1.50), and chlorobenzene (n = 1.53). Figure 1c presents emission spectra resulting in identical emission spectra except for slight changes in relative intensities due to photonic effects (vide infra).

To investigate the relation between k_MD and n, we first consider the total 5D₀ decay rate. Figure 2a shows the decay curves of 5D₀ emission for core–shell NCs in different solvents (see also Figure S1). Ideally, the decay curves are single-exponential, but as a result of quenching, e.g., through coupling with high energy ligand vibrations, there is a contribution from nonradiative multiphonon relaxation (MPR), especially for Eu³⁺ ions close to the surface. The highest energy vibrational modes contributing are C–H stretching vibrations (∼3000 cm⁻¹) from oleate ligands on the NC surface and solvent molecules. For core–shell NCs, MPR is reduced. It affects only the initial decay and is similar for the different solvents. Two fitting procedures were used, based on the average lifetime τ_avg (see SI for details) and single exponential fitting. For core NCs, τ_avg of the 5D₀ state decreases from 6.1 to 4.8 ms upon increasing n from 1.35 to 1.53. A similar trend is observed for the core–shell NCs with longer luminescence lifetimes (7.0 ms vs 6.1 ms in core NCs in diethyl ether, Figure 2b) as the inert shell suppresses quenching by MPR.27,28 Also, there is a stronger deviation from single exponential decay for Eu³⁺ in the core-only NCs. This deviation can be appreciated by comparing the fit residuals that show a systematic deviation for the initial part of the core-only decay curves.

The radiative rates kᵣ for individual 5D₀→Fj transitions can be determined from the total radiative decay rate and relative emission intensities (branching ratio) derived from emission spectra. The nonradiative decay rate k_nr can be determined from the total decay rate and reduces QY. If the 5D₀ lifetime of Eu³⁺ in bulk NaYF₄ is known, the upper limit of the QY of Eu³⁺-doped NCs can be quantitatively determined using eq 6.

\[
\tau_{avg} = QY_{bulk} \left( \frac{I_{ED}}{I_{tot}} \frac{n^2_{NC}}{n_{NC}} + \frac{I_{MD}}{I_{tot}} \frac{n^3}{n_{NC}} \right)
\]  

I_ED/I_MD and I_MD/I_tot denote the fractions of ED and MD emission in the total integrated emission intensity for 5D₀→Fj transitions in bulk material. The NC-cavity local field factor \(f_{NC} \) is used and \( \tau_{bulk} \) is the 5D₀ lifetime of Eu³⁺ in bulk NaYF₄ (6.2 ms from measurements on bulk NaY₅.₆Eu₅.₄F₄ in excellent agreement with 6.2 ms reported by Tanner and co-workers).30 With \( \tau_{bulk} \), the observed branching ratios and n of NaYF₄ (1.5),10 we find for k_MD 14.3 s⁻¹ (very close to the theoretical value of 14.4 s⁻¹) and for k_ED 75.3 s⁻¹. To investigate the measured variation in radiative lifetime with n, Figure 2c plots \( \tau_{avg} \) as a function of n. Fitting the data with eq 6 gives a good agreement using QYs of 77% and 87% for core and core–shell NCs, respectively. The slightly longer decay times derived from single exponential tail fits for core–shell NCs give an even higher QY of 93%. Note that actual QYs will be lower as the lifetimes reflect only emissive dopants in the ensemble.12,31 Instead of QY, k_MD can be quantitatively determined to give a better agreement with experiment (Figure S2).

The analysis shows that the combination of an n³ dependence for k_MD and the NC-cavity model for k_ED can quantitatively explain the observed variation of radiative decay rates. The good agreement between experiment and theory indicates that MD transition rates follow the theoretically predicted n³ dependence. An alternative method to test the validity of the n³ dependence is based on intensity ratios of ED and MD emission lines. Since nonradiative decay quenches both types of emission equally, the variation in ED/MD intensity ratio is a reliable method to test the n dependence of k_MD relative to k_ED without QY as additional fitting parameter. The difference in n dependence for k_ED and k_MD shows that
relative intensities of MD and ED transitions will change with $n$. The stronger $n^3$ dependence predicts an increase in relative intensity for MD emission lines with $n$. From the emission spectra the relative intensities of MD ($^5D_0^−^7F_1$) and ED ($^5D_0^−^7F_2$ and $^5D_0^−^7F_4$) transitions were determined. Very weak emission lines corresponding to $^5D_0^−^7F_0$ transitions are neglected in the present analysis. In Figure 3a, measured branching ratios for the MD and ED transitions are plotted together with the expected variation assuming an $n^3$ dependence for MD transitions (eq 5) and the NC-cavity model (eq 4) for ED transitions. The agreement is good and values for $k_{MD}$ (14.4 s$^{-1}$) and $k_{ED}$ (78.2 s$^{-1}$) are determined, which are consistent with theory and the results from bulk NaYF$_4$. To further verify the $n$ dependence, Figure 3b shows the experimentally observed ratio $I_{ED}/I_{MD}$ (red dots) and the red line shows the calculated ratio with $k_{MD}$ proportional to $n^3$ with $k_{MD} = 14.4$ s$^{-1}$ and $k_{ED}$ following the NC-cavity model with $k_{ED}$ (78.2 s$^{-1}$). Clearly, the $n^3$ dependence for $k_{MD}$ is in excellent agreement with the experimentally observed ratios. The blue and green lines show fits for a fixed $n^3$ dependence for $k_{MD}$ and different $n$ dependencies for $k_{ED}$, viz., the virtual cavity model (eq 2, blue line) and the real cavity model (eq 3, green line). Only the NC-cavity model can explain the experimentally observed variation in $I_{ED}/I_{MD}$ assuming an $n^3$ dependence for $k_{MD}$. The variation in $I_{ED}/I_{MD}$ in the narrow refractive index range investigated here is limited (see Figure 3). However, intensity ratio changes over an order of magnitude can be realized by making use of high refractive index materials based on metal or semiconductor nanomaterials.

This will allow a complete reversal of ED to MD intensities for emitters showing both types of emission.

To provide further evidence for the $n^3$ dependence of $k_{MD}$, we also investigated the decay times of MD emission from Gd$^{3+}$ in NaYF$_4$. Gd$^{3+}$ has the 4f$^7$ configuration and the first excited state ($^8S_{7/2}$) for this stable half-filled shell configuration is in the UV. The $^8P_{7/2}^−^8S_{7/2}$ emission around 311 nm and has a large MD transition probability (high value for the MD matrix element (L +2S) of $-0.52$). Using this value, the MD transition rate for the $^8P_{7/2}^−^8S_{7/2}$ transition in bulk NaYF$_4$ is $k_{MD} = 102$ s$^{-1}$ ($\tau = 9.8$ ms, see SI for details). This value is very close to the observed bulk decay rate ($k = 108$ s$^{-1}$ for $\tau = 9.3$ ms). This confirms that the $^8P_{7/2}^−^8S_{7/2}$ transition of Gd$^{3+}$ in NaYF$_4$ has 95% MD character, which makes the Gd$^{3+}$P$_{7/2}^−^8S_{7/2}$ emission ideal for investigating the influence of $n$ on MD transition probabilities. The emission spectrum of Gd$^{3+}$-doped NCs is shown in Figure 4a. For the narrow $^6P_{7/2}^−^8S_{7/2}$ emission around 311 nm the decay dynamics are shown in Figure 4b in solvents with different $n$ (see also Figure S3). Upon increasing $n$ from 1.35 to 1.53 the $^6P_{7/2}$ lifetime decreases from 9.6 to 6.9 ms (Figure 4c). The results are fitted to an $n^3$ dependence (eq 5). An excellent agreement is observed, confirming that the MD transition probability increases with $n^3$ as expected theoretically. Alternatively, this $n^3$ dependence of $k_{MD}$ is confirmed by $n^3$ fits in Figure S4. This $n^3$ dependence is stronger than the $n$ dependence for ED transitions. As a result, the branching ratio in an emission spectrum consisting of mixed
MD and ED transitions will change and the relative intensity of MD transitions will increase with $n$ (see also Figure 3a). From the radiative lifetime of Gd$^{3+}$ emission in bulk NaYF$_4$ we can calculate radiative lifetimes for emission in different solvents (vide supra). The calculated lifetimes are longer than the observed lifetimes, indicating that there is some quenching of the luminescence, probably by trace amounts of UV-absorbing organic chromophores in the solvents.\(^{38,39}\) The QY of Gd$^{3+}$ emission in core–shell NCs is determined by fitting the experimentally observed lifetimes to

$$\tau_{\text{avg}} = \frac{QY}{\tau_{\text{bulk}} n_{\text{NC}}^3 / n^3} \quad (7)$$

In Figure 4d the results are shown. A good agreement between experiment and theory is obtained for a QY of 77% for $\tau_{\text{avg}}$ and 82% for the tail fitting results.

In conclusion, the influence of the photonic environment on MD transition probabilities has been systematically investigated using Eu$^{3+}$- and Gd$^{3+}$-doped NaYF$_4$ NCs as model systems. Varying the refractive index of the solvent in which NCs are dispersed reveals a strong increase of the MD transition probability with $n$. For Eu$^{3+}$-doped NCs, all experimental results (ED/MD intensity ratios and decay rates) are in excellent agreement with the theoretically predicted $n^3$ dependence for MD transition probabilities if the variation in $n$ dependence is assumed to obey the NC-cavity dependence (see also Figure 3a). From $\tau_{\text{avg}}$ and $\tau_{\text{shell}}$, the influence of the local environment on radiative transitions are important for understanding and controlling optical properties through variations in the photonic environment.

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