# Local-field effects on the spontaneous emission rate of CdTe and CdSe quantum dots in dielectric media

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The refractive index dependence of the spontaneous emission rate is determined using organically capped CdSe and CdTe quantum dots as probes. The radiative lifetime of the exciton emission is measured in a variety of apolar solvents with refractive indices n between 1.37 and 1.50. It is demonstrated that quantum dots provide a model system for testing theories on the influence of local-field effects on the spontaneous emission rate. The experimentally observed influence of n on the radiative lifetime is smaller than predicted by well-known models for local-field corrections but is in good agreement with a recently developed fully microscopic model for the local-field enhancement of the spontaneous emission rate. © 2004 American Institute of Physics.

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## I. INTRODUCTION

The influence of local-field effects on the spontaneous emission rate of a two level system has been the topic of both theoretical and experimental work since long.  $^{1-4}$  In the absence of local-field effects the radiative lifetime of a two level system decreases with increasing refractive index n of the surrounding medium as  $^5$ 

$$\tau_{\rm rad}(n) = \frac{\tau_{\rm vac}}{n},\tag{1}$$

where  $\tau_{\rm rad}(n)$  is the radiative lifetime of the emission in a medium with refractive index n and  $au_{\mathrm{vac}}$  is the radiative lifetime in vacuum. This simple relation between the radiative lifetime and the refractive index follows from solving the macroscopic Maxwell equations assuming a homogeneous dielectric constant over space. In reality, the two level system interacts with all surrounding microscopic dipoles of the medium in which it is embedded. This complicates the analysis. To incorporate the influence of local interactions, local-field corrections have to be introduced.<sup>6</sup> Already since the 1940s local-field effects were included in a quantitative description of the absorption and emission of light. 1-3 In the past 15 years theoretical work has resulted in the development of models in which the two-level system is placed in a cavity to account for microscopic interactions with local dipoles. The exact dependence of the radiative lifetime  $\tau_{\rm rad}(n)$  on the refractive index n is very sensitive to the choice of the cavity. Two limiting cases have been analyzed in detail: in the empty-cavity model, the oscillator is situated in an empty spherical cavity and the dependence of the radiative lifetime on the refractive index follows:<sup>7</sup>

$$\tau_{\rm rad}(n) = \left(\frac{3n^2}{2n^2 + 1}\right)^{-2} \frac{\tau_{\rm vac}}{n}.$$
(2)

In the other limit, the full- or virtual-cavity model, the two-level system is placed in a cavity with the same refractive index as the surrounding medium but the dipoles inside the cavity do not contribute to the local electric field. In this situation the radiative lifetime is described by<sup>8,9</sup>

$$\tau_{\rm rad}(n) = \left(\frac{n^2 + 2}{3}\right)^{-2} \frac{\tau_{\rm vac}}{n}.$$
(3)

The two models described above still rely on a macroscopic description of the dielectric. More recently, a fully microscopic model for local-field effects was presented using a quantum-electrodynamical, many-body derivation of Langevin-Bloch operator equations for two-level atoms embedded in a dielectric host. In the limit of no interaction between the two-level systems (a single system in a dielectric host) the radiative lifetime shows a dependence on the refractive index of the (nonabsorbing) dielectric host that is much weaker than predicted with the empty-cavity and full-cavity models and is given by 10

$$\tau_{\rm rad}(n) = \left(\frac{n^2 + 2}{3}\right)^{-1} \tau_{\rm vac}.$$
(4)

In order to test the validity of the different models, experimental work has been done in which the luminescence lifetime is measured as a function of the refractive index of the surrounding medium. In contrast to the large number of papers discussing theoretical models for local-field effects, the number of experimental studies to verify the theoretical work is very limited. The reason is that these experiments are not as trivial as they may seem.  $^{11}$  One of the complications is that the surrounding medium may influence both radiative and nonradiative decay rates through mechanisms other than a variation in the refractive index. This complicates a quantitative analysis of the influence of local-field effects on  $\tau_{\rm rad}$  and only a few experimental studies have been reported in which the theoretical models could be compared with experiment. Most insightful experiments have been done using

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 $\mathrm{Eu}^{3+}$ . The intraconfigurational  $4f^6$  transitions of the  $\mathrm{Eu}^{3+}$ ion are characterized by a long luminescence lifetime. Rikken and Kessner studied the luminescence lifetime of the Eu<sup>3+</sup> emission for complexes (Eu<sup>3+</sup>-hfa-topo,Eu<sup>3+</sup>-dpa) dissolved in hydrocarbons and fluorocarbons with different refractive indices.<sup>12</sup> They found that for the electric dipole transition the dependence of  $\tau_{\rm rad}$  on n is best described by the empty-cavity model [Eq. (2)]. Schuurmans et al. did experiments on a Eu<sup>3+</sup>-fod complex in supercritical CO<sub>2</sub>. <sup>13</sup> The refractive index of the surrounding medium was varied between 1 and 1.3 by changing the pressure between 1 and 1000 bar. These experiments confirmed the applicability of the empty-cavity model for Eu<sup>3+</sup> complexes. Luminescence lifetime measurements by Meltzer et al. for Eu<sup>3+</sup> in Y<sub>2</sub>O<sub>3</sub> nanocrystals embedded in media of different refractive index indicated that the full- or virtual-cavity model [Eq. (3)] gives a better agreement with the experimentally observed relation between n and  $\tau_{\rm rad}$ . 14

In all experiments involving Eu<sup>3+</sup> a complicating factor is the sensitivity of radiative and nonradiative relaxation rates to small changes in the immediate surroundings of the  $Eu^{3+}$  ion (in spite of the shielding of the  $4f^6$  shell of  $Eu^{3+}$ by the outer  $5s^2$  and  $5p^6$  shells). Subtle changes in the local symmetry strongly affect the radiative decay rate of the forced electric dipole transitions within the  $4f^6$  configuration, as is, for example, clear from the strong variation of the lifetime of the Eu<sup>3+</sup> emission within the inhomogeneously broadened emission line for Eu<sup>3+</sup> in the yttrium oxide nanocrystals. 14 In addition, the local dielectric surroundings will be different for Eu<sup>3+</sup> located in the middle of the nanoparticles in comparison to Eu<sup>3+</sup> ions close to the surface. As a result, the local-field effects are expected to vary between different ions in the system. This complicates the analysis of their influence on the radiative lifetime. For the Eu<sup>3+</sup> complexes corrections need to be made for nonradiative (multiphonon) relaxation to derive the radiative decay rate from luminescence lifetime measurements. The nonradiative relaxation rates may vary as the solvent is changed. 13 For the Eu<sup>3+</sup> complexes in supercritical CO<sub>2</sub> the change in pressure could affect the distance between the central Eu<sup>3+</sup> ion and the coordinating atoms from the ligand molecules or the complex geometry. Even a small change in distance can influence the radiative decay rates. In spite of the complications arising from the sensitivity of the intraconfigurational  $4f^6$  transition rates to the local surroundings, the experiments on Eu<sup>3+</sup> to establish the relation between  $\tau_{\rm rad}$  and n have until now been the most insightful ones demonstrating the influence of n on  $\tau_{\rm rad}$ .

In this paper nanocrystalline organically capped CdSe and CdTe quantum dots (QDs) are used to probe the influence of the refractive index on the radiative decay rate. Due to quantum confinement effects, discrete levels arise at the band edges and as a result semiconductor QDs are also known as artificial atoms. <sup>15–17</sup> By placing these artificial atoms in media with different refractive indices, an ideal test case is obtained to determine the relation between  $\tau_{\rm rad}$  and n if the QD luminescence is dominated by radiative decay (i.e.,  $\tau_{\rm exp} = \tau_{\rm rad}$ ). An important advantage of QDs over Eu<sup>3+</sup> is the insensitivity of the radiative decay rate of the exciton emis-

sion to changes in the local symmetry since the exciton emission of QDs is a fully allowed electric dipole transition. It is the aim of the present work to measure the influence of refractive index of the medium surrounding QDs on the radiative decay rate of the excitonic emission and to compare the results with theoretical models described above.

#### **II. EXPERIMENT**

## A. Choice of the system

The synthesis of efficiently luminescing quantum dots is crucial for the experiment. Highly efficient II-VI semiconductor nanocrystals like CdSe and CdTe can be grown in a hot solvent of organic molecules that coordinate to ions at the surface of the growing nanocrystal. 18 Typical coordinating molecules are TOPO (tri-octylphosphineoxide), HDA (hexadecylamine), DDA (dodecylamine), and TOP (trioctylphosphine). After synthesis, the surface of the semiconductor nanocrystals is well-passivated with these molecules and nonradiative recombination at surface sites is suppressed. Various groups have shown that it is possible to grow CdSe and CdTe QDs which are characterized by a high luminescence quantum yield (up to 80%) and a single exponential (radiative) decay. 19-22 It is for these QDs that the influence of the refractive index on the radiative decay rate can be studied. To this effect, the highly luminescent QDs are dissolved in various organic solvents. The refractive index of the surrounding solvent can be changed without influencing the capping of the QD. Caution should be taken to only use "inert" organic solvents, i.e., solvents that cannot bind to surface atoms of the semiconductor core and replace the capping molecules. High refractive index organic solvents like pyridine and carbon disulfide are not useful since capping exchange with these solvent molecules can take place. The solvents used in this experiment are commonly used for the dispersion of QDs and no capping exchange with the solvent molecules is expected.

# B. Synthesis of highly luminescent QDs

Two types of semiconductor QDs have been prepared to investigate refractive index dependence of the spontaneous emission rate. All syntheses were carried out in a glovebox under argon employing standard oxygen and moisture free conditions (less than 2 ppm O<sub>2</sub> and H<sub>2</sub>O).

CdTe QDs are synthesized at  $165\,^{\circ}\mathrm{C}$  in a mixture of TOP/DDA by a modified version of the method reported by Talapin *et al.*<sup>23,24</sup> In a three necked flask 10 g of dry DDA and 7 mL of TOP were heated to  $50\,^{\circ}\mathrm{C}$ . To this solution 0.22 g (1.54 mmol) Cd(Me)<sub>2</sub> in 7 mL of TOP and 0.16 g (1.25 mmol) Te powder were added. The reaction mixture was heated to  $165\,^{\circ}\mathrm{C}$  for 3 h. The final product is a viscous liquid.

To obtain a stable colloidal solution of the CdTe QDs in a variety of organic solvents, the TOP/DDA capping is exchanged by a hexanethiol capping. Capping exchange is achieved by adding 100  $\mu$ l of hexanethiol to 50  $\mu$ l of the crude solution of the CdTe QDs in TOP/DDA. After one day 5 ml of an organic solvent (hexane, octane, cyclohexane, toluene, or chloroform) is added and a stable and transparent

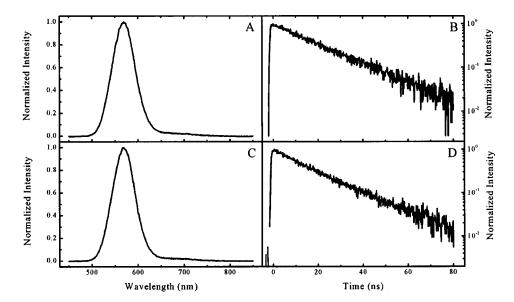


FIG. 1. Emission spectra of hexanethiol-capped CdTe quantum dots dissolved in hexane (a) and toluene (c) and luminescence decay curves of the exciton emission at 570 nm for the same solutions of QDs in hexane (b) and toluene (d). The measurements are done for 406 nm excitation at 295 K.

colloidal suspension of QDs is obtained for all solvents. The quantum efficiency of the CdTe suspensions is around 40%.

CdSe QDs are synthesized in a mixture of TOP/TOPO/HDA<sup>23,19</sup> A total of 20 g of TOPO, 10 g of HDA, and 2 mL of triethylorthoformate were placed into a 250 mL three necked, round-bottom flask, and heated slowly to 330 °C. A portion of 0.79 g (10 mmol) of Se was dissolved at room temperature in 10 mL TOP. To this solution 0.28 g (2 mmol) of Cd(Me)<sub>2</sub> was added. The temperature of the TOPO/HDA mixture was allowed to fall (the heating mantle was removed) to 300 °C at which point the TOP Se/Cd(Me)<sub>2</sub> solution was quickly injected into the mixture using a syringe. After the injection, the temperature was allowed to drop further to 180 °C. The reaction temperature was then stabilized at a growth temperature of 240 °C for two hours which results in QDs with the highest quantum efficiency in the presently used synthesis method.<sup>19</sup> CdSe QDs were dispersed in the same five organic solvents as used for CdTe for luminescence and lifetime measurements. The quantum efficiency of the CdSe QDs prepared in this way for the present experiments is around 55%.

### C. Apparatus

Luminescence spectra and luminescence lifetimes were measured using a Pico Quant diode laser ( $\lambda_{ex}$ =406 nm, 2.5 MHz repetition rate, 55 ps pulse width) as an excitation source. Emission spectra were recorded with a 0.25 m Acton Research monochromator fitted with a Princeton Instruments liquid nitrogen cooled charge-coupled device camera. To determine the lifetime of the luminescence a monochromator (0.1 m focal length, 1350 lines mm<sup>-1</sup> grating, blazed at 500 nm) was used for wavelength selection and a fast Hamamatsu H5738P-01 photomultiplier tube PMT was used for light detection. With the monochromator an emission band around the emission maximum was selected for recording the luminescence decay curves. Since the luminescence lifetime is expected to depend on the particle size (and thus emission wavelength) the decay curves were recorded at the same emission wavelength for the QDs in the different solvents. The spectral width of the detection is however not expected to give a large variation in lifetimes since there is only a weak dependence of the luminescence lifetime of the QD emission on the particle size. Luminescence decay curves were obtained using time-correlated single-photon counting via time-to-amplitude conversion (TAC) with a Time Harp 100 computer card. The laser power used for excitation was low (less than 1 mW/cm<sup>2</sup>) for two reasons: First, the ratio of stop to start pulses needs to be small (below 0.05) to assure good statistics. In addition, by using a low excitation power the formation of biexcitons (with a different decay rate) is prevented. Measurements were done on very dilute solutions (OD below 0.1 in the visible) to prevent an influence of reabsorption. The time resolution of the measurements is better than 0.5 ns and is mainly limited by the spread in transit times for the PMT. Luminescence quantum efficiencies (QE) were determined using a SPEX Fluorolog spectrofluorometer and Rhodamine B (QE=90%) as a standard. Further experimental details can be found in Refs. 24 and 19.

# **III. RESULTS**

#### A. CdTe

In Fig. 1 room temperature emission spectra are shown of CdTe quantum dots after capping exchange with hexanethiol and transfer into hexane [Fig. 1(a)] and toluene [Fig. 1(c)]. The quantum dots show a bright yellow emission with a maximum at 570 nm. The position of the emission maximum is the same in all five solvents. From the position of the exciton emission band the particle diameter can be estimated to be 3.0 nm. <sup>23,24</sup> On the right-hand side of Fig. 1 luminescence decay curves are depicted for the emission of CdTe dots in two of the solvents (hexane and toluene). The luminescence lifetime is around 18 ns in both cases. This is in agreement with the radiative decay time reported for CdTe exciton emission and indicates that the experimentally observed luminescence lifetime is indeed determined by radiative decay. Also the single exponential character of the

decay curves provides strong evidence that the luminescence is dominated by radiative decay. Exciton emission is characterized by a weak electron-phonon coupling [also in QDs (Ref. 21)]. As a result, nonradiative relaxation of the exciton by phonon relaxation processes can be neglected. The lifetime of the QD exciton emission is thus dominated by radiative decay unless energy transfer occurs to quenching centers in or close to the QD. In case of quenching by energy transfer, nonradiative decay rates will vary between QDs (due to differences in quenching rates between QDs) and nonexponential decay curves are expected. Indeed, for CdSe and CdTe QDs prepared via a different synthesis method nonexponential decay curves are observed and the faster initial decay is attributed to quenching centers. 19,22,25,26 The present observation of a purely exponential luminescence decay in Fig. 1 shows that the emission from the CdTe QDs is dominated by radiative decay. Further support for the fact that the presently observed decay curves reflect only radiative decay is obtained by measuring the wavelength dependence of the luminescence lifetime. The luminescence lifetime decreases for shorter wavelength according to the well-known  $\lambda^3$  dependence, which is valid for radiative decay only. 27,28

In spite of the strong evidence showing that the luminescence decay curves are determined by radiative decay only, the luminescence quantum efficiency of the QD solutions is around 40% and not 100%. The lower quantum yield indicates that there is partial quenching of the luminescence. This is ascribed to the presence of two types of CdTe quantum dots: bright dots, showing radiative exciton recombination and "dark" (i.e., nonluminescent) dots for which the luminescence is almost completely quenched. The luminescence decay curves for the emission from the ensemble of QDs are dominated by the radiative decay time of the bright QDs that have quantum efficiencies close to 100% and reflect the radiative exciton lifetime. Convincing evidence for the coexistence of bright dots with a purely radiative decay and dark dots in the same ensemble is presented in Refs. 26 and 29. Luminescence measurements on single QDs show the presence of bright QDs with quantum efficiencies near unity and dark QDs with a very low quantum efficiency.<sup>26</sup>

To measure the influence of the refractive index on the radiative lifetime the hexanethiolcapped CdTe QDs were dissolved in five apolar solvents spanning a range of refractive indices as wide as possible, viz. hexane (n = 1.375), octane (n=1.397), cyclohexane (n=1.427), chloroform (n=1.427)= 1.446), and toluene (n = 1.496). In all these solvents the QDs dissolve readily and form a stable and clear colloidal suspension. The luminescence decay curves were measured for the CdTe QDs in the five solutions under identical circumstances (same optical density of the QD suspension, optical density (O.D.)  $\sim$ 0.1 at 406 nm, and same laser excitation power) and the measurements were repeated ten times in order to reduce the experimental error. For the QDs in all five solvents single exponential luminescence decay curves, similar to those shown in Fig. 1, are measured. The radiative luminescence lifetimes ( $\tau_{1/e}$ ) are plotted as a function of the refractive index in Fig. 2. The radiative lifetime decreases from 18.2 ns for CdTe QDs in hexane to 17.0 ns in toluene. The error bars in Fig. 2 represent the experimental error as

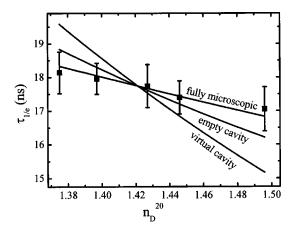


FIG. 2. Radiative lifetime of the exciton emission at 570 nm for hexanethiol-capped CdTe QDs as a function of the solvent refractive index for QDs is apolar solvents. The filled squares represent the experimental results and drawn lines are fits to the theoretical models described by Eq. (2) (empty cavity), Eq. (3) (virtual cavity), and Eq. (4) (fully microscopic).

determined from analysis of the ten measurements. It is evident that the variation in refractive index gives only a small variation in the luminescence lifetime which will be discussed below.

## B. CdSe

The exciton luminescence of CdSe QDs has been studied more extensively in the literature than the luminescence of CdTe QDs. The efficient luminescence from TOP/TOPO capped CdSe QDs is well-known and in various studies the luminescence lifetimes of this type of capped CdSe QDs have been reported. 15,19,26,29,31 The presently studied TOP/ TOPO HDA capped CdSe QDs show a bright yellow emission peaking at 572 nm. From the position of the emission maximum the particle diameter is determined to be 3.4 nm. The capped CdSe QDs readily dissolve in the same five solvents as used for the CdTe QDs. The quantum efficiency is not strongly influenced by dissolving the QDs in the various solvents and is around 55%. Just as for CdTe the exciton emission for the CdSe QDs shows single exponential decay curves in the maximum of the emission band. As an example, the decay curves measured for CdSe QDs in the solvents with the highest (toluene, n = 1.496) and the lowest refractive index (hexane, n = 1.375) are shown in Fig. 3. The luminescence decay curves are single exponential which indicates that the decay times reflect the radiative decay rate of the excitonic emission (see also the section above). The luminescence lifetime is around 26 ns, in good agreement with the radiative decay times reported for the exciton emission from CdSe QDs. 19,26,29,31,32 In a recent study on the fluorescence lifetime of the emission from single quantum dots it was demonstrated that the nonradiative decay rate can vary for a single dot.<sup>33</sup> Analysis of the luminescence decay behavior of a large number of dots during different time intervals showed that the lifetime measured during the period of maximum brightness are around 27 ns and can be considered as the radiative lifetime. This observation provides strong support for the observation that the single exponential decay

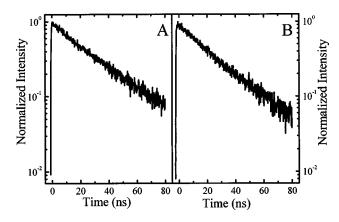


FIG. 3. Luminescence decay curves of the exciton emission at 570 nm for TOP/TOPO/HDA capped CdSe quantum dots dispersed in hexane (A) and toluene (B). The measurements are done at 295 K under 406 nm excitation.

curves measured for the QD emission reflect the radiative decay rate and that the radiative lifetime for CdSe QDs is of the order of 26 ns.

The luminescence lifetimes for the exciton emission from CdSe QDs in the five solvents are plotted in Fig. 4. The luminescence lifetime decreases from 27.7 to 25.2 ns as the refractive index of the solvent increases from 1.38 to 1.50. Just as observed for CdTe the influence of the refractive index on the luminescence lifetime is small. This observation is consistent with the reported insensitivity of the absorption cross section of CdSe QDs on the solvent refractive index reported by Leatherdale *et al.*<sup>34</sup>

## **IV. DISCUSSION**

The results described above show that both the CdTe and the CdSe QDs are ideal probes for monitoring the influence of the refractive index on the radiative decay rate. The quantum dots are small (much smaller than the wavelength of light) luminescent species that are shielded from direct con-

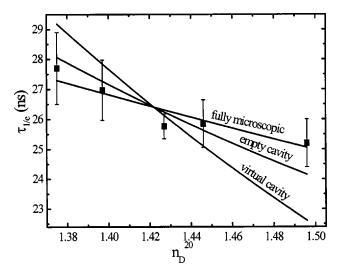


FIG. 4. Radiative lifetime of the exciton emission from TOP/TOPO/HDA capped CdSe quantum dots as function of the solvent refractive index for quantum dots in apolar solvents. The filled squares represent the experimental results and drawn lines are fits to the theoretical models described by Eq. (2) (empty cavity), Eq. (3) (virtual cavity), and Eq. (4) (fully microscopic).

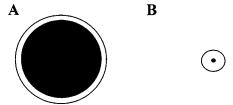


FIG. 5. Schematic picture of a quantum dot with organic capping (A) and of a Eu(fod)<sub>3</sub> complex (B). The black part indicates the luminescing core and the white part the organic capping. The two pictures have the same scale.

tact with the surrounding medium of variable refractive index by a thin ( $\sim$ 0.4-0.9 nm) capping layer. For this two-level like system the radiative decay rate will be influenced by the solvent only through a variation of the refractive index of the surrounding medium assuming that the surrounding medium does not affect the thickness or interaction with the capping layer. In view of the similar apolar character of the solvents used to dissolve the capped QDs no influence of the solvent on the capping layer is expected. As a result, the measurements of the variation of the lifetime of the quantum dot emission in media with different refractive indices will provide insight into which of the theoretical models discussed in the Introduction can explain the observed relation between  $\tau_{\rm rad}$  and n.

In order to determine which of the various models can account for the experimental results, the data in Figs. 2 and 4 were fitted to the empty-cavity model [Eq. (2)], the fullcavity model [Eq. (3)], and the fully microscopic model [Eq. (4)]. The resulting fits are plotted in Figs. 2 and 4. For both types of QD the empty cavity and the full-cavity models strongly overestimate the influence of the refractive index on the radiative lifetime and cannot explain our experimental results. The recently published fully microscopic model [Eq. (4)], however, can explain the observed (small) decrease in radiative lifetime with increasing refractive index. This shows that neither the empty-cavity nor the full-cavity model can describe the dependence of the spontaneous emission rate on the refractive index for the QDs studied. It is encouraging to see that the fully microscopic model does reproduce the measured influence of the refractive index on the radiative decay rate. More in general, the present results provide reliable experimental data on the relation between radiative decay rates and the refractive index of the medium in which a two-level system is embedded. As such, the results are important in the further development of theories that account for the influence of local-field effects on the spontaneous emission rate. It should be noted that typically ODs are not completely spherical but are slightly prolate with an aspect ratio of about 1.1. Orientation of the dipole may influence the coupling with the dielectric medium and complicate the theoretical analysis.

The difference between the present results, which show a relatively small influence of n on  $\tau_{\rm rad}$ , and the results for Eu<sup>3+</sup> complexes, for which a much stronger influence has been reported, may also be related to the different nature of the systems. In Fig. 5(A) schematic drawing showing the difference for the Eu<sup>3+</sup> complexes and the semiconductor QDs is depicted. In the case of the Eu<sup>3+</sup> complexes the

optical transition is localized within the  $4f^6$  configuration of the Eu<sup>3+</sup> ion and the transition dipole moment of the transition involved is small. The Eu<sup>3+</sup> ion is placed in a relatively large cavity (the organic complex) with a low polarizability. The interaction with the surrounding dielectric occurs through this region of low polarizability and the boundary conditions for the empty-cavity model form a good description for the Eu<sup>3+</sup> complex in a dielectric. The presently studied system is different. The optical transitions in the QDs have large transition dipole moments and the QDs have a high polarizability. The interaction with the surrounding dipoles occurs through a relatively thin capping layer of capping ligands. This situation resembles the boundary conditions for the fully microscopic model presented in Ref. 10, where Eq. (4) was obtained by considering the interaction of an embedded atom with the nearby polarizable particles of the host via the electromagnetic field. The origin of the localfield renormalization of the spontaneous emission rate is the microscopic near-dipole-dipole interaction in which the influence of the atom on each nearby oscillator is fed back to the atom. In the presently studied system an artificial atom (the CdTe or CdSe QD) is embedded in a dielectric and near-dipole-dipole interaction between the large excitonic electric dipole and dipoles of the surrounding dielectric can occur through the thin capping layer. The good agreement between the experimentally observed dependence of the spontaneous emission rate on the refractive index with Eq. (4) provides experimental support for the applicability of the fully microscopic model for the local-field enhancement of the spontaneous emission rate. It will be interesting to extend the experiments in the future to QDs in polar solvents and to widen the range of refractive indices over which the relation between n and  $\tau_{\rm rad}$  is measured. It may also be interesting to vary the thickness of a capping layer with low polarizability around the QD to investigate how the relation between n and  $\tau_{\rm rad}$  changes beyond a certain width of the capping layer when the boundary conditions change to those of the empty or full-cavity models.

# V. CONCLUSIONS

The radiative lifetime of the excitonic luminescence of CdTe and CdSe QDs has been measured as a function of the refractive index of the surrounding dielectric by dissolving capped QDs in a variety of solvents with n varying between 1.37 and 1.50. The radiative lifetime of the exciton emission is observed to decrease from 18.2 to 17.0 ns for CdTe and from 27.2 and 25.2 ns for CdSe. This dependence of  $\tau_{\rm rad}$  on n is weaker than in previously reported experiments for Eu<sup>3+</sup> complexes and the dependence predicted by theoretical models for an oscillator in an empty or full cavity. The results are well explained by a recently reported fully microscopic model based on near-dipole-dipole interactions of an embedded atom with dipoles in the surrounding medium. The results show that capped semiconductor QDs are ideal probes

for studying the influence of the refractive index on the spontaneous emission rate and provide reliable experimental data which can serve as input in the further development of theoretical models describing the influence of local-field effects on the radiative decay rate for electric dipole transitions.

### **ACKNOWLEDGMENT**

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