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Published in:
Physical Review Letters

Link to article, DOI:
[10.1103/PhysRevLett.95.236804](https://doi.org/10.1103/PhysRevLett.95.236804)

Publication date:
2005

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
van Driel, A. F., Allan, G., Delerue, C., Lodahl, P., Vos, W. L., & Vanmaekelbergh, D. (2005). Frequency-dependent spontaneous emission rate from CdSe and CdTe nanocrystals: Influence of dark states. *Physical Review Letters*, 95(23), 236804. DOI: 10.1103/PhysRevLett.95.236804

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Frequency-Dependent Spontaneous Emission Rate from CdSe and CdTe Nanocrystals: Influence of Dark States

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(Received 10 June 2005; published 1 December 2005)

We studied the rate of spontaneous emission from colloidal CdSe and CdTe nanocrystals at room temperature. The decay rate, obtained from luminescence decay curves, increases with the emission frequency in a supralinear way. This dependence is explained by the thermal occupation of dark exciton states at room temperature, giving rise to a strong attenuation of the rate of emission. The supralinear dependence is in agreement with the results of tight-binding calculations.

DOI: [10.1103/PhysRevLett.95.236804](https://doi.org/10.1103/PhysRevLett.95.236804)

PACS numbers: 73.21.La, 78.47.+p, 78.55.Et, 78.67.Hc

Semiconductor nanocrystals have a huge potential for application as monochromatic light sources in biological research, photonic studies, and opto-electrical devices [1–9]. The most important class of semiconductor nanocrystals are colloidal nanocrystals, in practice CdTe and CdSe. Because of quantum confinement, nanocrystals possess discrete electron and hole energy levels [7,8]. As a consequence, optical absorption occurs at discrete energies which are determined by the size and the shape of the nanocrystal host [9]. At low excitation density, light emission is due to decay of the lowest exciton state to the ground state. The possibility of tailoring the exciton emission energy by the nanocrystal size has led to a worldwide interest in light-emitting semiconductor nanocrystals. An open question is how the size and the emission frequency of a semiconductor nanocrystal control the excitons' spontaneous emission decay rate. Such a study is currently feasible due to the availability of colloidal nanocrystal suspensions with a high quality. These suspensions form a unique model system to probe the frequency dependence of Fermi's golden rule; the emission frequency can be tuned via the crystal size without changing the chemistry. Understanding of the exciton dynamics in the regime of strong confinement is important, not only for purely scientific reasons. The rate of spontaneous emission determines the statistics of the output of a single photon source [3], the light intensity of incoherent sources, consisting of nanocrystal assemblies, such as light emitting diodes [6], and the output of coherent sources such as lasers [5]. In addition, the high luminescence efficiency combined with a narrow homogeneous linewidth make nanocrystals ideal probes in photonic studies [3,4].

In this Letter, we report on the frequency-dependent decay rate of excitons in colloidal CdSe and CdTe nanocrystals at room temperature. We show that the luminescence decay curves, at a given frequency, are very close to single exponential. For both CdSe and CdTe nanocrystals, the decay rate increases with the emission frequency in a

supralinear way, in contrast to a linear relation for an ideal two-level exciton system or a cubic relation for an ideal two-level atom. From complementary calculations based on tight-binding theory, we conclude that the supralinear increase is caused by thermal population of various hole states with low transition probability (i.e., dark states) that lie close to the ground state. The frequency-dependent rate can thus be understood on basis of elementary quantum mechanics. The excellent agreement with the theoretical rates shows that measured rates are completely determined by radiative decay and highlights the importance of exciton storage in dark states.

The rate of a spontaneous transition from an excited electron-hole state $|j\rangle$ to the ground state $|0\rangle$ can be derived from Fermi's "golden rule"

$$\Gamma_j = \frac{e^2}{3\pi\epsilon_0 m^2 \hbar c^3} \omega_j |\langle 0|\mathbf{p}|j\rangle|^2, \quad (1)$$

where e is the electron charge, ϵ_0 the permittivity of free space, m the electron rest mass, \hbar Planck's constant, c the speed of light, ω_j the frequency of the emitted light, and $\langle 0|\mathbf{p}|j\rangle$ the matrix element of the momentum that is related to the dipolar matrix element by $\langle 0|\mathbf{p}|j\rangle = im\omega_j \langle 0|\mathbf{r}|j\rangle$ [9,10]. The size dependence of Γ_j will be determined by the size dependence of the matrix element $\langle 0|\mathbf{p}|j\rangle$ and emission frequency ω_j . Assuming that the electron-hole states near the band extrema can be written as a product of a Bloch function $\mu(\mathbf{r})$ and an envelope function $\phi(\mathbf{r})$, it can be shown that the matrix element of the momentum for an allowed transition is given by $\langle \mu_c|\mathbf{p}|\mu_v\rangle$ [9], where c and v denote the conduction and valence bands, respectively. Interband transitions are thus largely determined by the Bloch functions, which are defined by the crystal lattice only. As a consequence, $\langle \mu_c|\mathbf{p}|\mu_v\rangle$ does not depend on the size of the nanocrystals, and the decay rate of an ideal two-level exciton is expected to be proportional to the emission frequency; $\Gamma_j = \text{const} \cdot \omega_j$. This is in agreement with several theoretical studies [8,11,12].

Experimental data on the size-dependent strength of the optical transitions are limited. The extinction coefficient has been studied for several nanocrystal suspensions [13–17]. However, the data are not sufficient to show how the squared dipolar matrix element depends on the size of the nanocrystal. Direct determination of the radiative lifetime from luminescence decay curves has proved troublesome due to the fact that the decay curves are influenced by both nonradiative and radiative recombination. As a consequence, decay curves are often multiexponential [18]. This means that not all the nanocrystals emit light at the same rate or the decay rate varies in time [19]. Encouraged by the availability of suspensions of CdSe and CdTe nanocrystals [20] with a high photoluminescence efficiency ($\geq 50\%$) we decided to study the exciton decay rate as a function of the frequency of the emitted light. The decay curves were obtained by time-correlated single photon counting. Emission was excited with a Pico Quant pulsed laser (100 ps, 406 nm) and detected with a monochromator (0.1 m focal length, 1350 lines/mm grating, blazed at 500 nm) and a Hamamatsu photomultiplier tube. In Fig. 1 a luminescence decay curve for a CdSe suspension is shown. The data are well described by a single-exponential model, as confirmed by a goodness of fit $\chi_r^2 = 1.4$. A stretched-exponential model resulted in a stretch parameter $\beta = 0.99$, very close to the single-exponential limit of $\beta = 1$.

In Fig. 2, the decay rate is plotted versus the emission frequency for CdTe and CdSe nanocrystals, respectively. Data from two CdTe and two CdSe suspensions are plotted in each of the figures. These data unambiguously show for the first time that the rate of excitonic decay increases strongly with frequency. The decay rate was deduced with three different procedures [21]; the luminescence decay curve was fitted with a single exponential, a stretched exponential, and the average arrival time was calculated. The χ_r^2 values and the β values were deduced

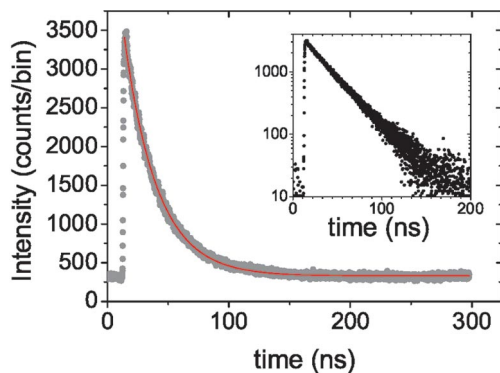


FIG. 1 (color). Luminescence decay curve of exciton emission from CdSe nanocrystals at $620 \text{ nm} \pm 5 \text{ nm}$ (filled circles). Single-exponential fit (red curve), with background as adjustable parameter, yields a rate of $0.037 \pm 0.003 \text{ ns}^{-1}$ and a χ_r^2 value of 1.4. A stretched-exponential model yields a rate of 0.036 ns^{-1} and a β value of 0.99. Inset: the background corrected decay curve in a semilogarithmic plot.

from single-exponential and from stretched-exponential fits, respectively. The χ_r^2 values are low (≤ 2) and the β value varies between 0.91 and 1.00. Most of the curves have a β value larger than 0.99. Clearly the decay curves are nearly single-exponential which means that, at a given frequency, all the nanocrystals emit light with the same rate. This forms a first indication that our decay curves are completely determined by radiative decay [19]. We can rule out the possibility of energy transfer between closely spaced nanocrystals [22]: first the concentration of nanocrystals was intentionally kept very low ($< 10^{-7} \text{ mol/l}$); second, the results for (sterically stabilized) CdTe nanocrystals were compared with charge-stabilized nanocrystals, which strongly repel each other at short distances. Thus, we conclude that the exciton emission decay rates increase with frequency.

Figure 2 reveals that the experimental decay rates increase faster with emission frequency than the linear behavior of a two-level exciton system (blue lines). Therefore, we must consider the complex valence band structure of CdTe and CdSe; several hole levels are located close to the top of the band. This leads to other exciton states close to the lowest-energy exciton. Excitons in these states have

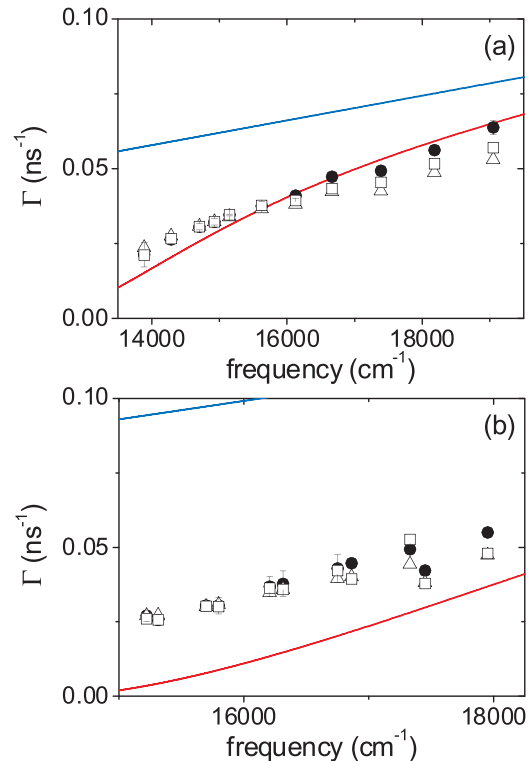


FIG. 2 (color). Decay rate of emission from CdTe (a) and CdSe (b) nanocrystals. The decay rate is deduced with single-exponential fit (filled black dots), average arrival time (open triangles), and stretched-exponential fit (open squares). The blue lines show the decay rates for a two-level system and pass through the origin [Eq. (2), $\Delta E_j > kT$]. The red curves show the rate according to Eq. (3) and take dark excitonic states into account.

a much lower probability for spontaneous decay to the ground state and a high rate of exchange with the lowest-energy exciton. Because of the thermal distribution, the population of the lowest-energy exciton will be reduced and thus the rate of radiative recombination will be lowered. If an infinite lifetime is assumed for the higher-energy excitons, it can be shown that:

$$\Gamma_{\text{rad}} = \Gamma_1 \left[1 + \sum_{j=2}^N \exp\left(\frac{-\Delta E_j}{kT}\right) \right]^{-1}, \quad (2)$$

where k is Boltzmann's constant, T the temperature, Γ_1 the decay rate for the lowest exciton state as given by Eq. (1), and ΔE_j the energy separation with respect to the ground exciton state. The sum can be approximated using the density of states of a macroscopic crystal [23] leading to

$$\Gamma_{\text{rad}} = A\omega \left[1 + \frac{R^3}{6\sqrt{\pi}} \left(\frac{2m^*kT}{\hbar^2} \right)^{3/2} \right]^{-1}, \quad (3)$$

where A is a constant, m^* is the hole effective mass, and R is the crystal radius, which determines the emission frequency. Verifying Eq. (3) by temperature dependent experiments has proved troublesome due the limited temperature window in which the quantum efficiency is constant [24]. The effect of thermal occupation of optically nonactive states as a function of crystal size is caught by the separation between the different exciton levels (ΔE_j). For nanocrystals with a larger radius the total number of states is larger and therefore the separation between the states is smaller. As a consequence, thermal population of higher exciton levels is more important in larger nanocrystals. This means that the radiative decay rate of the large crystals at low frequency is more reduced than the rate of small crystals at high frequency. Consequently, the decay rate increases supralinearly with frequency, instead of linearly for an ideal two-level exciton system. The exciton decay rate calculated with Eq. (3), with A as the only adjustable parameter, is presented in Fig. 2 (red curves) as a function of the frequency of the emitted light. The relation between R and ω was obtained from tight-binding calculations. Clearly, the red curves show agreement with our measurements in the case of CdSe and excellent agreement in the case of CdTe. The supralinear dependency of the decay rate can thus be understood on basis of Fermi's golden rule, if thermally activated dark excitonic states are accounted for.

At a given temperature, the rate of radiative exciton decay depends on the details of the band structure, determined by the crystal lattice. In the above considerations several approximations are used to obtain Eq. (3), i.e., infinite lifetimes for higher exciton states and density of states of a macroscopic crystal. While this is helpful to get physical insight, a more detailed calculation, based on tight-binding or pseudopotential models, is required to obtain quantitative decay rates. We have performed tight-binding calculations of the radiative decay rate for spheri-

cal zinc blende CdTe and CdSe nanocrystals with various sizes [25]. The calculated decay rates for CdTe are in quantitative agreement with the experimental results over the accessible frequency range (see red dots in Fig. 3). This shows that nonradiative decay has a negligible influence on our decay curves. In the case of CdSe the tight-binding results show a supralinear relation between the radiative decay rate and the emission frequency (in agreement with the experimental results), but the absolute value is 75% too low. To understand the origin of this discrepancy, we have performed calculations using several sets of tight-binding parameters. We find that the absolute values of the emission rates are sensitive to these parameters due to a subtle coupling between close-spaced hole states. A similar discussion on the splitting and ordering of levels in the effective mass approximation can be found in the literature [26–28]. Importantly, we find that the supralinear evolution with frequency remains unaffected for all parameter sets.

The agreement between the supralinear trend in experiment and in theory must mean that the experimental decay curves are almost completely determined by radiative decay. Based on this we argue that the nonradiative decay rate can be neglected. The correlation between single-exponential decay curves and a negligible nonradiative rate is confirmed by results on single nanocrystals [19,29]. Reference [19] reports that when a single nanocrystal reveals single-exponential decay, its nonradiative decay rate is negligible. For a large number of nanocrystals with the same diameter of 6.5 nm and emission frequency $\sim 1.7 \times 10^4 \text{ cm}^{-1}$, a radiative single-exponential lifetime of 25 ns was observed, in excellent agreement with our results. In Ref. [29] it is shown that a significant fraction of the nanocrystals is completely dark. This necessarily means that the efficiency of the emitting nanocrystals is much higher than the efficiency of the suspension. Therefore, our measured 50% quantum efficiency can be explained in simple terms as follows: half of the nanocrystals have a low emission efficiency, while the other half have near-unity emission efficiency. It is the

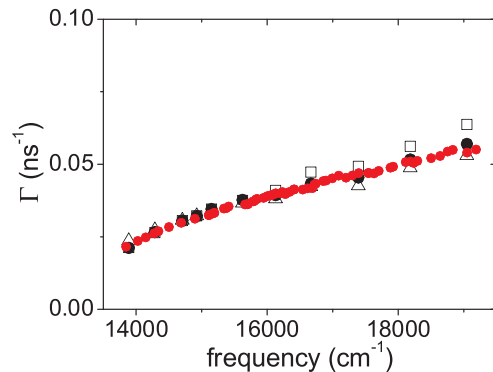


FIG. 3 (color). Radiative decay rate from tight-binding calculations (red dots) for CdTe [same experimental data as in Fig. 2(a) are plotted].

photons from these latter nanocrystals that mostly contribute to our measured signals.

We have shown for the first time how the spontaneous emission rate of semiconductor nanocrystals depends on the frequency of the emitted light. Comparison with theory shows that spontaneous emission is considerably attenuated due to occupation of dark excitonic states. These results may lead to a better understanding of a number of dynamic effects that are currently studied, such as exciton dephasing, radiative recombination of nanocrystals in photonic crystals [4], and Förster energy transfer [22,30].

We thank P. Vergeer and J.J. Kelly for fruitful discussions. This work was supported by the Stichting Fundamenteel Onderzoek der Materie (FOM) and Chemische Wetenschappen (CW) with financial aid from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

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