Frequency-dependent spontaneous emission rate from CdSe and CdTe nanocrystals: Influence of dark states

van Driel, A. F.; Allan, G.; Delerue, C.; Lodahl, Peter; Vos, W. L.; Vanmaekelbergh, D.

Published in:
Physical Review Letters

Link to article, DOI:
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. https://doi.org/10.1103/PhysRevLett.95.236804
Frequency-Dependent Spontaneous Emission Rate from CdSe and CdTe Nanocrystals: Influence of Dark States

A. F. van Driel,1,* G. Allan,2 C. Delerue,2 P. Lodahl,3,† W. L. Vos,3,‡ and D. Vanmaekelbergh1

1Debye Institute, Utrecht University, P.O. Box 80 000, 3508 TA Utrecht, The Netherlands
2Département ISEN, IEMN (CNRS, UMR 8520), 41 Boulevard Vauban, 59046 Lille CEDEX, France
3Complex Photonic Systems (COPS), Department of Science and Technology and MESA+ Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
(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

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 excitation 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”

$$\Gamma_j = \frac{e^2}{3\pi\epsilon_0 m c^3} \omega_j |\langle 0|p|j\rangle|^2,$$

(1)

where $e$ is the electron charge, $\epsilon_0$ the permittivity of free space, $m$ the electron rest mass, $h$ Planck’s constant, $c$ the speed of light, $\omega_j$ the frequency of the emitted light, and $|\langle 0|p|j\rangle|$ the matrix element of the momentum that is related to the dipolar matrix element by $|\langle 0|p|j\rangle| = im\omega_j |\langle 0|r|j\rangle|$ [9,10]. The size dependence of $\Gamma_j$ will be determined by the size dependence of the matrix element $|\langle 0|p|j\rangle|$ and emission frequency $\omega_j$. 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 $\langle \mu_c|p|\mu_v\rangle$ [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, $\langle \mu_c|p|\mu_v\rangle$ 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; $\Gamma_j \propto \omega_j$. 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 (>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 \( \chi^2 \approx 1.4 \). 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 \( \chi^2 \) values and the \( \beta \) values were deduced from single-exponential and from stretched-exponential fits, respectively. The \( \chi^2 \) values are low (\( \leq 2 \)) and the \( \beta \) value varies between 0.91 and 1.00. Most of the curves have a \( \beta \) 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} 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. 1 (color).** Luminescence decay curve of exciton emission from CdSe nanocrystals at 620 nm ± 5 nm (filled circles). Single-exponential fit (red curve), with background as adjustable parameter, yields a rate of 0.037 ± 0.003 ns^{-1} and a \( \chi^2 \) value of 1.4. A stretched-exponential model yields a rate of 0.036 ns^{-1} and a \( \beta \) value of 0.99. Inset: the background corrected decay curve in a semilogarithmic plot.

**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:

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

(2)

where $k$ is Boltzmann’s constant, $T$ the temperature, $\Gamma_1$ the decay rate for the lowest exciton state as given by Eq. (1), and $\Delta E_j$ 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

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

(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 ($\Delta E_j$). 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 $\omega$ 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-
photon grafted to these latter nanocrystals that mostly contrib-ute 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 attenu-ated 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 pho-tonic crystals [4], and Förster energy transfer [22,30].

We thank P. Vergeer and J. J. Kelly for fruitful discus-sions. This work was supported by the Stichting Funda-menteel Onderzoek der Materie (FOM) and Chemische Wetenschappen (CW) with financial aid from the Neder-landse Organisatie voor Wetenschappelijk Onderzoek (NWO).

*Electronic address: a.f.vandriel@phys.uu.nl
†Also at: Research Center COM, Technical University of Denmark, Dk-2800 Lyngby, Denmark.
‡Also at: FOM Institute for Atomic and Molecular Physics (AMOLF), NL-1098 SJ Amsterdam, The Netherlands.

[1] W. C. W. Chan and S. Nie, Science 281, 2016 (1998).
[2] M. Bruchez, M. Moronne, P. Gin, S. Weiss, and A. P. Alivisatos, Science 281, 2013 (1998).
[3] P. Michler, A. Kiraz, C. Becher, W. V. Schoenfeld, P. M. Petroff, L. D. Zhang, E. Hu, and A. Imamoglu, Science 290, 2282 (2000).
[4] P. Lodahl, A. F. van Driel, I. S. Nikolaev, A. Irman, K. Overgaag, D. Vanmaekelbergh, and W. L. Vos, Nature (London) 430, 654 (2004).
[5] C. J. Wang, B. L. Wehrenberg, C. Y. Woo, and P. Guyot-Sionnest, J. Phys. Chem. B 108, 9027 (2004).
[6] S. Coe, W. K. Woo, M. G. Bawendi, and V. Bulovic, Nature (London) 420, 800 (2002).
[7] A. L. Efros and A. L. Efros, Fiz. Tekh. Poluprovodn. (Sankt-Peterburg) 16, 1209 (1982) [Sov. Phys. Semicond. 16, 772 (1982)].
[8] L. E. Brus, J. Chem. Phys. 80, 4403 (1984).
[9] A. L. Efros, M. Rosen, M. Kuno, M. Nirmal, D. J. Norris, and M. G. Bawendi, Phys. Rev. B 54, 4843 (1996).
[10] C. Delerue and M. Lannoo, Nanostructures: Theory and Modeling (Springer-Verlag, Berlin, 2004).
[11] T. Takagahara, Phys. Rev. B 36, 9293 (1987).
[12] Y. Kayanuma, Phys. Rev. B 38, 7977 (1988).
[13] T. Rajh, O. I. Micic, and A. J. Nozik, J. Phys. Chem. 97, 11999 (1993).
[14] T. Vossmeier, L. Katsikas, M. Giersig, I. G. Popovic, K. Diesner, A. Chemseddine, A. Eychmuller, and H. Weller, J. Phys. Chem. 98, 7665 (1994).
[15] C. A. Leatherdale, W. K. Woo, F. V. Mikulc, and M. G. Bawendi, J. Phys. Chem. B 106, 7619 (2002).
[16] A. Striolo, J. Ward, J. M. Praunslitz, W. J. Parak, D. Zanchet, D. Gerion, D. Milliron, and A. P. Alivisatos, J. Phys. Chem. B 106, 5500 (2002).
[17] W. W. Yu, L. Qu, W. Guo, and X. G. Peng, Chem. Mater. 15, 2854 (2003).
[18] S. A. Crooker, T. Barrick, J. A. Hollingsworth, and V. I. Klimov, Appl. Phys. Lett. 82, 2793 (2003).
[19] B. R. Fisher, H. J. Eisler, N. E. Stott, and M. G. Bawendi, J. Phys. Chem. B 108, 143 (2004).
[20] We have prepared CdTe [31,32] and ZnSe/CdSe [33] nanocrystals with a luminescence quantum yield of 50% and without defect-related emission. Nanocrystal suspensions contain a collection of differently sized particles, distributed around a certain average size. The photoluminescence of such a suspension is inhomogeneously broad-ened [34]. The size-dependent decay rate can therefore be probed by measurements at varying frequency in the emission band of the suspension.
[21] The decay rate was deduced with stretched exponential [35] $f(t) = (\frac{t}{t_f})^\beta \exp(-t/t_f)^\beta$ where $\beta$ varies between zero and one. The $\beta$ value illustrates how close the decay curve is to single exponential: $\beta = 1$ means that the decay curve is single exponential. The expectation value is $\langle t \rangle = \frac{1}{\Gamma} = \int_0^{\infty} t f(t) dt = \frac{1}{\Gamma} \Gamma (\frac{1}{\beta})$ where $\Gamma (\frac{1}{\beta})$ is the gamma function. The average time between the start pulse and the stop pulse (i.e., the photon arrival time) was calculated from the experimental data. For single-exponential decay this average is equal to the decay time.
[22] S. A. Crooker, J. A. Hollingsworth, S. Tretiak, and V. I. Klimov, Phys. Rev. Lett. 89, 186802 (2002).
[23] C. Kittel, Introduction to Solid State Physics (Wiley, New York, 2004), 7th ed.
[24] S. F. Wuister, A. van Houselt, C. de Mello Donegá, D. Vannaekebergh, and A. Meijerink, Angew. Chem., Int. Ed. 43, 3029 (2004).
[25] The tight-binding Hamiltonian matrix is written in a $sp^3d^5s^* $ basis including spin-orbit coupling and with interactions restricted to first nearest neighbors. The parameters are obtained by fitting the experimental effective masses and a reference bulk band structure calculated using the ab initio pseudopotential code ABINIT in the local density approximation. These parameters are transferred without change from the bulk situation to the nano-crystals passivating the surfaces with pseudohydrogen atoms. The matrix elements of $p$ are calculated following Ref. [36].
[26] T. Richard, P. Lefebvre, H. Mathieu, and J. Allegre, Phys. Rev. B 53, 7287 (1996).
[27] A. L. Efros and M. Rosen, Appl. Phys. Lett. 73, 1155 (1998).
[28] H. X. Fu, L. W. Wang, and A. Zunger, Appl. Phys. Lett. 73, 1157 (1998).
[29] Y. Ebenstein, T. Mokari, and U. Banin, Appl. Phys. Lett. 80, 4033 (2002).
[30] C. R. Kagan, C. B. Murray, M. Nirmal, and M. G. Bawendi, Phys. Rev. Lett. 76, 1517 (1996).
[31] S. F. Wuister, I. Swart, J. A. Mews, J. Phys. Chem. B 107, 7463 (2003).
[32] D. V. Talapin, S. Haubold, A. L. Rogach, A. Kornowski, M. Haase, and H. Weller, J. Phys. Chem. B 105, 2260 (2001).
[33] P. Reiss, J. Bleuse, and A. Pron, Nano Lett. 2, 781 (2002).
[34] F. Koberling, U. Kolb, G. Philipp, I. Potapova, T. Basche, and A. Mews, J. Phys. Chem. B 107, 7463 (2003).
[35] C. P. Lindsey and G. D. Patterson, J. Chem. Phys. 73, 3348 (1980).
[36] G. Allan and C. Delerue, Phys. Rev. B 70, 245321 (2004).