On the Theory of Intermittent Fluorescence of Quantum Dots

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A theory of the fluorescence intermittency of quantum dots, such as CdSe, should be consistent with a variety of experimental data,[1] including (1) an approximately $t^{-3/2}$ power law for the distribution of dark lifetimes, with no exponential "cutoff" in single molecule experiments, (2) a t^{-n} power law, with $n \geq 3/2$, for the fluorescence lifetimes that decays into an exponential at longer times; the merging of the two functional forms may be partly responsible for $n > 3/2$, (3) a spectral diffusion for the fluorescent state whose spectral second moment scales as an energy density It, the product of the incident light intensity I and the illumination time t,[2] (4) a similarly scaled behavior[3] of the fluorescence lifetime distribution, (5) a spectral diffusion second moment versus It plot that approaches saturation and whose limit varies with temperature T in accordance with a harmonic quantum model that has a nearly classical T-behavior, even at fairly low T (Fig 5, ref 3), (6) a correlation between spectral diffusion and fluorescence intermittency,[4] (7) time scales for traps[5] that appear to be in the 5 ns,[6] μs[7] and longer time regimes, for example, 1000 s[10] and (8) a ns time behavior of fluorescence in a "twilight" region, where the QD is not quite dark[6] and so where another process competes significantly with the fluorescence.

Spectral diffusion is attributed to light pulse-induced small structural displacements of ionic charges.[4] It can be described in terms of fluctuations in vertical differences of initial and final parabolic free energy curves.[3] Dark periods are attributed to Auger transitions[8] competing with fluorescence, occurring when a trap is "occupied", i.e., in which there has been an electron transfer. In a mechanism[3] for the fluorescent on-off behavior, the transition between light and dark periods occurs at an intersection (more precisely an avoided crossing) of two free energy parabolas. For one of the free energy curves, an electron (or hole) is in a surface band-edge trap and the other particle is in the bulk of the QD. A variant of this mechanism uses a deep hole trap instead of a band edge one, plus a $1S_e$ to $1P_e$ transition in the conduction band, and the previous[3] mathematical formalism.

In the immediate vicinity of the crossing there is a "twilight zone" with a probability of being in a "dark" state or in a "light" state, rather than 0 or 1. In the wide range of trap times in QDs, the very short ones do not distinguish light from dark periods, when the periods are measured on longer time-binned scales. They can contribute to a reduction of fluorescence light intensity during that period, as in an interpretation of some data in ref. 6.

In a different mechanism[9] a dark period ("off" period) corresponds to an Auger-assisted recycling of a $1S_e$ to $1P_e$ transition in the "conduction band" when it is in resonance with the transition of a hole from the valence band to a trap. In this recycling the return to the ground state is phonon-assisted. In this second mechanism the quantum dot (QD) is bright ("on" period) when these two transitions are out of resonance.

Among the predictions of the analysis in refs 3 and 11 is a $t^{-1/2}$ power law up to some time ~ t_c, followed by approximately $t^{-3/2}$ (or t^{-n}) lifetime distribution for times longer than t_c.[2] In this model in which the transition between on and off states occurs at the intersection of two parabolas, t_c is the time for the probability immediately near the intersection to fall to approximately zero. The $t^{-3/2}$ behavior then results from the usual steady-state diffusion into a "sink" at the intersection. At still longer "on" times the lifetime distribution in the model decreases exponentially, because of the effect of a forced diffusion, namely the effect of the free energy gradient on diffusion near the intersection.[3] Depending upon the model for detrapping, for example a resonance with a light-induced $1P_e$ to $1S_e$ transition, the excitation of the quantum dot below the $1P_e$ threshold could affect the off-on behavior.

Results will be described of a study[11] on a different system, interpreting the lifetimes of traps in thiocresol-capped[7] QDs in terms of the two different time regimes described above, $t < t_c$ and $t > t_c$. For this system the estimated t_c is of the order of a μs. The interpretation is limited by the small range of lifetimes in each regime.

One hurdle for theory, I believe, is the absence of an exponential "cut off" for "off" times in the single molecule experiments. That a cut-off time exists at much longer times than was reached in such studies, because of signal/noise ratio, is evident from ensemble measurements.[10] The complimentary nature of single molecule and ensemble measurements is clear.

1. Extensive references to the experimental data in the literature are cited in refs. 2 - 10. In some cases, such as datum (4) above, the data are few.
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