Direct observation of the structure of band-edge biexcitons in colloidal semiconductor CdSe quantum dots

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We report on the electronic structure of the band-edge biexciton in colloidal CdSe quantum dots using femtosecond spectroscopy and atomistic many-body pseudopotential calculations. Time-resolved spectroscopy shows that optical transitions between excitonic and biexcitonic states are distinct for absorptive and emissive transitions, leading to a larger Stokes shift for the biexciton than for the single exciton. The calculations explain the experimental results by showing that there is a previously unobserved electronic substructure to the band-edge biexciton which yields two distinct families of transitions.

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Physical confinement of electrons and holes in semiconductor quantum dots yields the well-known quantization of excitonic states.1 The energy spectrum of the single exciton (X) is characterized by a coarse as well as a fine structure.1–6 While the coarse structure arises primarily from quantum confinement and spin-orbit interactions and is manifested in higher absorption bands above the band edge, the fine structure originates from electron-hole exchange interactions and lattice asymmetries, and results in an energy shift between absorbing transitions and emitting transitions.

In addition to single excitons, quantum dots are known to support quantum-confined excitonic complexes.1 The simplest excitonic complex is the neutral biexciton (XX), consisting of two electrons and two holes. Current efforts to investigate excitonic complexes1,7–15 are motivated by a desire to understand the fundamental physics of carrier interactions in nanostructures, as well as by potential applications based on optical gain1,7,16,17 and multiple exciton generation.18–20

The structure of excitonic complexes is relatively well explored in self-assembled epitaxial dots and dots grown on prepatterned substrates.11,15,18–22 However, there is still little understanding of the electronic structure of biexciton complexes in the complementary case of colloidal quantum dots—systems characterized by significantly different electronic structure, selection rules, relaxation time scales and pathways, and interaction energies. The electronic structure of the biexciton plays a central role in the physics underpinning optical gain1,7,16 and multiple exciton generation18–20 phenomena.

Here, we show that the band-edge biexciton in colloidal quantum dots does indeed possess a unique previously unobserved electronic structure. We demonstrate the existence of such structure using femtosecond spectroscopy and assign the physical origin of the observed optical transitions using atomistic pseudopotential calculations. We find that the substructure of the band-edge biexciton is fundamentally distinct in origin from the substructure of the single exciton. As a result, the transitions between excitonic and biexcitonic states are distinct for absorptive and emissive spectroscopies, yielding an observation of a biexciton Stokes shift.

In this work, we will focus on the substructure of the band-edge biexciton (1S0,1 1S0,1) in CdSe colloidal nanocrystals. Figure 1 shows schematically the single-particle energy levels (part a), the multiparticle XX energy levels and related optical transitions (part b), as well as the main measurable quantities (part c). We will use this figure throughout the Rapid Communication to define all of the quantities discussed both experimentally and theoretically. The S-like hole states at the top of the valence band [h1 and h2 in Fig. 1(a)] originate from the bulk Γ9, and Γ7, band states and are split by the crystal field due to the hexagonal wurtzite lattice structure and by deviations from the spherical shape. They are followed by the P-like hole states h3 and h4. The S-like electron state at the bottom of the conduction band [e1 in Fig. 1(a)] originates from the bulk Γ7, band state and is followed by three nearly degenerate P-like electron states (e2–e4).

The way in which the single-exciton fine structure evolves from these single-particle orbitals has been explained previously1–5 and is shown schematically in Fig. 1(b). The XX fine structure consist of two manifolds of four states each, originating from the (h1,e1) and (h2,e1) exciton configurations, respectively. The lowest exciton level of each manifold is dark, leaving three dipole-allowed optical transitions [denoted A1, A2, and A3 in Fig. 1(c)].

This energy-level structure manifests itself in experiment via Stokes shifts. The resonant X Stokes shift is caused by absorption into the bright state (A1 transition) and emission from the dark state below it. The global X Stokes shift δX = EX,abs − EX emi, where EX,abs denotes the energy of the lowest X absorption peak and EX emi the energy of the X emission peak, see Fig. 1(c)] originates from contributions of higher-energy transitions (A2 and A3) to the absorption peak and from phonon-progression contributions to the absorption and emission peaks.1–3

The lowest-energy manifold of biexciton states originates
Extrinsic biexciton binding energy, i.e., the difference between twice the X ground-state energy $E_X^0$ and the XX ground-state energy $E_{XX}^0$. This quantity can be calculated but requires high-energy resolution (at the expense of time resolution) to measure. Instead, experiments typically detect the apparent biexciton binding energy, i.e., the difference between the XX and X peaks, measured either in absorption ($\Delta_{XX}^A = E_{XX}^{abs} - E_{XX}^{em}$) or emission ($\Delta_{XX}^E = E_{XX}^{em} - E_{XX}^{em}$), as shown schematically in Fig. 1(c). These apparent binding energies are naturally different from the intrinsic binding energies.

Transient absorption (TA) experiments can detect bound biexcitons by the presence of induced absorptions in the transient spectrum. The pump pulse produces a single exciton, and the probe pulse follows the system into the biexciton. The biexciton interactions shift the level structure yielding new absorptive features in the TA spectrum. The state-resolved spectroscopic measurements were made in the pump/probe configuration with 10 fs precision, the details of which were previously described. The sample consisted of CdSe quantum dots dispersed in toluene and flowed at 300 K.

Figure 2 shows TA experiments in strongly confined CdSe quantum dots upon pumping into two different initial excitonic states ($R = 2.8$ nm, band-edge exciton at 2.00 eV). Upon excitation into the 1P exciton, the primary single-particle configuration from which the exciton originates is shown on the right-hand side. In the case of X, solid horizontal lines indicate spin-allowed states, dashed lines indicate spin-forbidden states. In the case of XX, dotted horizontal lines indicate states originating from the P-like hole states $h_1$ and $h_2$, which do not contribute to the low-energy optically allowed transitions. Vertical arrows denote dipole-allowed absorption transitions and room-temperature emission transitions. The X → XX transitions can be further classified (see text) as strong (solid-line arrows) or weak (dashed-line arrows).
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band-edge exciton. Since the pump is resonant with the band-edge exciton, there can only be two excitons populated by the pump pulse.\cite{1,16,17} The stimulated emission (SE) spectrum (at 1 ps) corresponds to the negative portion of the nonlinear absorption spectrum (OD_{NL}+\Delta OD+OD_{0}).\cite{7,16,17} \Delta_{XX}^{m} is the energy difference between the maximum of the SE spectrum and the maximum of the photoluminescence (PL) spectrum represents the same ground-state biexciton obtained in the emissive experiments.\cite{1,8-10} Our value of \Delta_{XX}^{m}=36 meV is consistent with prior emissive measurements of biexcitons.

The significant energy difference between the absorptive and emissive apparent binding energies \Delta_{XX}^{A} and \Delta_{XX}^{E} implies that the magnitude of the global XX Stokes shift (\delta_{XX}) is different from that of the global X Stokes shift (\delta_{X}). The XX Stokes shift is nontrivial in that it does not arise from the same electronic substructure that produces the single-exciton Stokes shift. The experimental values of \Delta_{XX}^{A}, \Delta_{XX}^{E}, \delta_{X}, and \delta_{XX} can be extracted from the data in Fig. 3(a).\cite{26} For three quantum-dot sizes, R=\{1.5, 2.1, 2.8\} nm, we obtain \Delta_{XX}^{A}=\{18,12,9\} meV, \Delta_{XX}^{E}=\{50,44,37\} meV, \delta_{X}=\{40,25,16\} meV, and \delta_{XX}=\{73,57,45\} meV. Our emissive experiments reproduce the results of prior emissive experiments, but our absorptive experiments yield markedly different apparent binding energies. These experiments reveal a biexciton Stokes shift which is not the same as the single exciton Stokes shift.

Calculations of the X and XX energy levels and transitions were performed using the semiempirical pseudopotential approach described in Ref. 5. We considered nearly spherical CdSe nanocrystals of radius R=1.9 and 2.3 nm, whose surfaces were passivated using ligand potentials.\cite{5} Figure 3(b) shows the calculated individual GS→X and X→XX transition energies and their oscillator strengths (GS denotes the electronic ground state) for a R=1.9 nm CdSe nanocrystal. As shown in Fig. 1(b), there are three GS→X transitions and eight main X→XX transitions, all of which are labeled in Fig. 3(b). These individual X and XX absorption and emission lines are currently not observed experimentally because of limited energy resolution (line broadening of spectra and the laser bandwidth required to maintain fs time resolution). Thus, to mimic the experimental situation, we calculated the absorption and emission spectra using a Gaussian line broadening of 100 meV, similar to the inhomogeneous broadening of an ensemble of the highest quality CdSe quantum dots at 300 K. We further note that the broadenings do not prevent insight into the electronic structure since the level shiftings are very large (10–70 meV).

The calculations were performed at T=0 K and T=300 K. The temperature affects the population of the X and XX sublevels, but the energies of the single-particle levels are assumed to be temperature independent (except for the change in the band gap with temperature). In the case of the X→XX absorption spectrum, the initial X states were populated in two different ways: (i) according to the Boltzmann distribution, starting from the lowest-energy X state and (ii) according to their normalized oscillator strengths. These two choices correspond to long and short pump/probe delay times, respectively. From the calculated absorption and emiss-

![Figure 3](https://example.com/figure3.png)

FIG. 3. (Color online) Biexcitonic signatures in absorptive and emissive experiments. (a) Comparison of absorptive and emissive experiments at the single exciton and biexciton level. The biexciton binding energies are not the same in absorptive (\Delta_{XX}^{A}) and emissive (\Delta_{XX}^{E}) experiments. The Stokes shift structure for the biexciton (\delta_{XX}) is not the same as for the single exciton (\delta_{X}). (b) Calculated energies and intensities of the GS→X (A_{1}-A_{3}) and X→XX (B_{1}-B_{3}) low-energy optical transitions for a 1.9 nm CdSe nanocrystal. In the case of X→XX absorption, solid lines indicate transitions originating from dipole-allowed (bright) X states, while dashed lines indicate transitions from dipole-forbidden (dark) X states. (c) Time evolution in absorptive experiments, revealing the shifting apparent binding energy.
In contrast, the “indirect” transitions we discussed in our prior work. The second time scale is due to carrier trapping at the interface as $T$ decreases, $\delta_X$ increases to 22 meV (18 meV) for $R =1.9$ nm (2.3 nm). This is due to the change in the position of the emission peak as higher-energy $X$ states become depopulated. At low temperature, $\delta_{XX}$ depends very sensitively on the delay time $\Delta t$. For short pump/probe delay times $\delta_{XX}$ is 12–14 meV, whereas for long pump/probe delay times $\delta_{XX}=33–35$ meV. This behavior can be rationalized by observing that at $T\sim 0$ and $\Delta t\approx 1$ ps the system is in the X “dark” state. Transition from this state to the XX ground state ($h\h_1,e\epsilon_1$) are spin forbidden. Only transitions to the XX excited state ($h\h_2,e\epsilon_1$) are dipole allowed [B$_2$ in Figs. 1(b) and 3(b)]. This selection rule shifts the center of the absorption peak to higher energy and therefore increases $\delta_{XX}$. Thus, the calculations predict that the global XX Stokes shift and the apparent XX binding energy (but not the actual binding energy) should be time-dependent quantities. The time dependence arises as the optically coupled bright states relax to their Boltzmann distributions. Experiments on the smallest dot confirm these predictions [see Fig. 3(c)]. These dynamics are due to relaxation from the optically coupled exciton states to the relaxed thermally populated exciton states. The relaxation takes place on the 80 fs time scale, consistent with recent measurements by Scholes. The increase in the picosecond time scale is due to carrier trapping at the interface as we discussed in our prior work.

Interestingly, we find that the “direct” transitions $X(h\h_1,e\epsilon_1)\rightarrow XX(h\h_1,e\epsilon_1)$ [line $B_1$ in Fig. 3(b)] and $X(h\h_2,e\epsilon_1)\rightarrow XX(h\h_2,e\epsilon_1)$ (lines $B_4$ and $B_5$) are rather strong. In contrast, the “indirect” transitions $X(h\h_1,e\epsilon_1)$ $\rightarrow XX(h\h_2,e\epsilon_1)$ and $X(h\h_2,e\epsilon_1)\rightarrow XX(h\h_1,e\epsilon_1)$ (lines $B_2$, $B_3$, $B_6$, $B_7$, and $B_8$) are generally weak. Furthermore, the indirect transitions can be lower in energy than the direct transitions, i.e., $B_5$ is lower in energy than $B_1$ and $B_2$ is lower than $B_6$. This suggests the possibility of a unique contribution to the global XX Stokes shift: the $X\rightarrow XX$ absorption is weighted more heavily toward the higher-energy direct transitions, whereas the $XX\rightarrow X$ emission is weighted more heavily toward the lower-energy indirect transitions, provided that the $h\h_2,e\epsilon_1$ emissive states are thermally populated. For a $R=1.9$ nm CdSe nanocrystal, we find that the magnitude of such shift is $\sim 4$ meV [Fig. 3(b)].

While calculated global Stokes shifts $\delta_X$ and $\delta_{XX}$ are smaller than the experimental ones, all the trends of size dependence and time dependence are reproduced. One possibility for deviation is that the calculations consider only electronic effects, whereas the measured absorption and emission spectra may have contributions from phonon-progression effects. Early calculations have shown that the inclusion of LO phonon replicas increases the X global Stokes shift.

In summary, we report on the experimental observation of a biexciton global Stokes shift, which is significantly larger than the single-exciton global Stokes shift. We also find that the apparent biexciton binding energies measured in absorptive and emissive experiments fundamentally differ because of the different states being probed. Atomistic pseudopotential calculations show that the electronic contribution to the global XX Stokes shift is almost twice as large as the global $X$ Stokes shift. Observation of the $XX$ substructure and Stokes shift is important to advance our understanding of the electronic structure of multie excitons in quantum dots and ultimately to determine how many-body interactions control optical gain and multiple exciton generation in quantum dots.

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26 See EPAPS Document No. E-PRBMDO-80-R29932 for additional experimental and theoretical details. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.