

Spin Blockades to Relaxation of Hot Multiexcitons in Nanocrystals

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Supporting Information

ABSTRACT: The conjecture that, as in bulk semiconductors, hot multiexcitons in nanocrystals cool rapidly to the lowest available energy levels is tested here by recording the effects of a single cold "spectator" exciton on the relaxation dynamics of a subsequently deposited hot counterpart. Results in CdSe/CdS nanodots show that a preexisting cold "spectator exciton" allows only half of the photoexcited electrons to relax directly to the band-edge. The rest are blocked in an excited quantum state due to conflicts in spin orientation. The latter fully relax in this sample only after ~ 25 ps as the blocked electrons spins flip, prolonging the temporal window of opportunity for harvesting the retained energy more than 100 fold! Common to all quantum-confined nanocrystals, this process will delay cooling and impact the spectroscopic signatures of hot multiexcitons in all envisioned generation scenarios. How the spin-flipping rate scales with particle size and temperature remains to be determined.

Inderstanding how excess photon energy is dissipated after nanocrystal (NC) photoexcitation is essential for utilizing this energy in nanodot-based solar cells or photodetectors.¹⁻⁶ Decades of ultrafast investigation show that interband photoexcitation of quantum dots is followed by rapid relaxation of hot carriers to the quantized band-edge (BE) states within 1 or 2 ps.⁷⁻¹⁸ Due to the large oscillator strength and low degeneracy of the BE exciton transition, evolution in its intensity and spectrum have played a pivotal part in probing quantum dot exciton cooling. These allegedly start with biexciton spectral shifts while carriers are hot, changing to a photoinduced bleach (PIB) due to state filling once the exciton relaxes. Accordingly, kinetics of this PIB buildup has served to characterize the final stages of carrier cooling,¹⁰ and its amplitude per cold exciton provides a measure of underlying state degeneracy.^{19,20}

Hot *multi*excitons (MXs), generated for instance through sequential multiphoton absorption of femtosecond pulses,^{21,22} add a new relaxation process to this scenario.²³ Auger recombination (AR) reduces an N exciton state to N - 1plus heat, initially deposited in the remaining carriers and later transferred to the lattice. Depending on N, this shortens the lifetime of MXs relative to a single exciton by 2-3 orders of magnitude. Again, investigation of AR dynamics is based on the amplitude and decay kinetics of the BE bleach with interpretation based on the following assumptions: (1) that ultrafast cooling of hot excitons leads directly to occupation of the lowest electron and hole states (in accordance with the lattice temperature and the state degeneracy) and (2) that,



aside from mild spectral shifts induced in the remaining BE transitions, after carrier cooling is over the BE PIB increases linearly with N until the BE states are full (again dictated by state degeneracy).

To test these assumptions, three-pulse saturate-pumpprobe experiments were conducted in our lab, measuring fs transient absorption (TA) of PbSe NCs in the presence and absence of single cold spectator excitons.²⁴ This method hinges on the separation of time scales between AR and radiative recombination, the latter being much slower. Given the vast absorption cross sections of NCs,²⁵⁻²⁷ it is easy to excite nearly all particles in a sample with at least one photon even with ultrashort pulses. The rapid ensuing AR leads to a uniform population of NCs, all populated with a single cold exciton, within a fraction of 1 ns. One can then probe the effect of a second exciton by comparing equivalent ultrafast pumpprobe experiments in the samples with or without spectator excitons. Surprisingly, the BE bleach induced by a single relaxed exciton was found to be significantly larger than that induced by a second exciton that was added by above BE photoexcitation and left to cool down for 1-2 ps.²⁴ This finding was also shown to be consistent with the fluencedependent BE PIB saturation when exciting well above the optical band gap (BG) via comparison with simulations.

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Figure 1. Design of the saturate-pump-probe experiment: (a) Timing sequence for the three pulses. The probe is always a chirped supercontinuum generated in a BaF_2 crystal. (b) Absorption spectrum of CdSe/CdS NCs dispersed in hexane, along with the spectra of the excitation pulses (400 and 570 nm). See the text for details. (c) Overlays of TA spectra at the designated pump-probe delays. (d) Spectral cuts at the peaks of the 1S-1S bleach (at 570 nm) in black and those of the low-energy-induced absorption (at 600 nm) in red.

To unveil the cause of this discrepancy, the same approach is applied here to MXs in CdSe NCs. This serves to test the generality of the results in lead salt. Due to the reduced BE electron state degeneracy, each exciton has a much larger effect on the BE PIB in CdSe NCs, which simplifies analysis and assignment. Numerous investigations of CdSe NC photophysics have established (1) that the BE exciton absorption is practically insensitive to hole state occupancy, allegedly due to the high density of valence bands in this material;^{10,12} (2) that the BE transition in CdSe NCs reflects only a 2-fold spinrelated degeneracy in the electron states;²⁸ accordingly, one relaxed exciton should bleach one-half of the initial BE absorption band and the second erase it entirely; (3) that the much higher effective heavy hole mass in CdSe and involvement in spin-orbit coupling lead to much faster cooling of holes (<ps) relative to electrons.¹⁰ Furthermore, the rapid electron relaxation measured in CdSe NCs is assigned to Auger cooling where excess electron energy transfers to the hole and is then degraded to phonons.^{10,14}

Contrary to the assumptions outlined above, our results show that adding a hot exciton to a relaxed singly occupied CdSe NC bleaches only half of the remaining BE absorption once the initial carrier cooling is over. It is further demonstrated that incomplete bleaching by the second exciton is due to hitherto unrecognized random spin orientation conflicts between the two sequentially excited conduction electrons in part of the crystallites. The presence of this effect both in lead salts and in CdSe NCs demonstrates its generality. This discovery imposes restrictions on the utility of the BE exciton transition as a universal "exciton counter" in experiments on all kinds of semiconductor NCs.

As shown in Figure 1a, cold monoexciton saturation is performed by an intense 400 nm pulse followed by a delay of 200 ps to allow completion of AR. Figure 1b presents the absorption spectrum of the CdSe/CdS NCs along with the pulse spectra used for saturation and/or pump pulses in our experiments. Core/shells were chosen to eliminate the substantial effects of surface trapping characteristic of bare CdSe cores.^{30,31} Figure 1c presents an overlay of TA spectra covering the first 1.2 ps of pump-probe delay. Similar to earlier studies by Kambhampati and co-workers,¹³ buildup of the 1S–1S PIB is very rapid, increasing marginally during the subsequent cooling, as depicted in the right panel. The photoinduced absorption band (PIA) to the red rises at least as rapidly and decays gradually for ~2 ps. These trends are demonstrated by temporal cuts in panel (d), taken at wavelengths designated by the color-coded vertical lines in panel (c) of Figure 1.

Figure 2 demonstrates how the presence of a spectator exciton changes the transient transmission spectra following a femtosecond 400 nm excitation. We stress that in both



Figure 2. Comparison of two- and three-pulse TA measurements after weak 400 nm pumping at a series of designated pump–probe delays (a–d). Saturation pulses, like the pump, are derived by the second harmonic generation of the laser fundamental.

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experiments pump fluence has been controlled to ensure that the probability of absorbing more than one photon is negligible. Conversely, in the three-pulse experiment, the saturation pulse is much more intense and ensures that 95% of the crystallites absorb at least one photon. The four panels present transient spectra recorded in both experiments at selected delays between 100 fs and 50 ps. Three-pulse experiments have been cleaned of a minor residual contribution from crystals in which the saturation pulse has not deposited a spectator exciton or which have undergone radiative decay during the saturation process. Significant differences are apparent early on, a reduced bleach at the BE peak being the most obvious. The PIB band in three-pulse experiments is also broader and red-shifted by 6 nm (~20 meV). Another difference is that the PIA feature at 520 nm, apparent at all delays in two-pulse data, is absent once spectator excitons are present. At 1.2 ps with carrier cooling over, the remaining PIB associated with state filling is precisely half as intense in the presence of spectators. These results are in qualitative agreement with our earlier study on PbSe,²⁴ but spectator effects in CdSe are larger. At the 50 ps delay, the amplitude of the BE PIB with spectators has diminished by \sim 70% due to the presence of AR, which does not affect twopulse pump-probe, which involves long-lived single excitons.

A glance at the first three delays in Figure 2 shows that twoand three-pulse experiments differ consistently throughout carrier cooling. Notice that while spectral evolution from delay to delay is pronounced in both experiments, the difference between two- and three-pulse transient spectra at the same pump—probe delay remains nearly constant. This similarity is demonstrated in panel (a) of Figure 3 as an overlay of the subtraction of the pairs presented in Figure 2. Implications of this are first that carrier cooling dynamics is unaffected by the presence of a BE spectator exciton in this range of delays. This is further demonstrated by band integrals producing difference dipole strength over the full spectral range probed in the



Figure 3. Comparison of spectral evolution in two- and three-pulse experiments after pumping at 400 nm. (a) Subtraction of the two data sets at a series of pump-probe delays from 0.05 to 1.2 ps. (b) Band integrals of the full probed range in the two experiments, demonstrating the identical cooling kinetics. (c) Finite difference spectra obtained from the two-pulse data isolating spectral changes taking place during sequential short intervals of carrier cooling. (d) As in panel (c) for three-pulse experiments. Notice that these spectra are essentially identical in both experiments for intervals starting after 50 fs.

experiment, $\Delta D \equiv \int_{c/670}^{c/450} \frac{\Delta OD}{\nu} d\nu$, and plotted in panel (b) of Figure 3. Panels (c) and (d) display finite difference spectra extracted from two- and three-pulse data, defined as follows

$$\Delta \Delta OD(\lambda, t, \Delta t) \equiv \Delta OD\left(\lambda, t + \frac{\Delta t}{2}\right) - \Delta OD\left(\lambda, t - \frac{\Delta t}{2}\right)$$

and serve to isolate spectral changes taking place over a specific interval of time. These spectra demonstrate essentially identical spectral evolution taking place in both experiments at delays of >50 fs. They also show negligible alterations to the amplitude of PIB after this point, with spectral changes consisting primarily of the decay of a broad and structureless absorption band covering most of the probed spectra range. A second implication is that dynamic processes leading to the conserved difference in spectra shown in Figure 3a must be established considerably before the earliest 50 fs delay.

These consequences will be the subject of a separate report dealing with carrier cooling dynamics. Here we concentrate on spectra established after cooling is complete. Clearly, one of the two assumptions discussed concerning the bleach amplitude introduced by the second exciton is wrong. Either the PIB is not linear in the number of excitons³² or else not all excitons directly populate the lowest available conduction band states. In deciphering this riddle, the factor of 2 in the BE PIB between samples with or without resident excitons is a significant clue. Assume that the PIB is linear in N; what could block excitons from taking their place aside the existing spectator in the 1S^e level? In order to fill that gap, the pair of 1S^e electrons must be spin-paired, and any disparity in correct orientation could delay the final step of relaxation. A random distribution of $|\uparrow\rangle$ and $|\downarrow\rangle$ spin orientations of relaxing electrons would prohibit half of the cooling electrons from the BE until one of the electron spins flip.

Fortunately, these assumptions can be tested experimentally. In both two- and three-pulse experiments described in Figure 2, pumping was conducted high in the interband continuum²⁴ because there the cross section for absorption is nearly unaffected by the existence of other excitons.^{18,33} This provides a trivial method for ensuring an equal dose of additional excitons deposited in samples with or without spectators. However, a second exciton can also be introduced to spectatorcontaining samples by exciting directly at the BE. Quantitative comparison of the second exciton contribution to the PIB then requires accounting for the changed absorption cross section of the pump due to the spectator excitons. The benefit is that pumping at the BE guarantees that all absorbed photons populate the 1S^h-1S^e state with or without pre-existing spectator. The results of this experiment are shown in Figure 4. Panel (c) presents TA spectra just after cooling for three different experiments, two-pulse pump-probe and two cases of saturate-pump-probe, the first pumping at 400 nm and second exciting at 570 nm. Clearly, the bleach introduced by BE pumping in the presence of spectator excitons is on par with that apparent in two-pulse pump-probe. The spectra are shifted due to the additional biexciton interaction involved and the absence of residual absorption into the $1S^{h}-1S^{e}$ state when completely filled. Nonetheless, a band integral demonstrates that, despite these anticipated discrepancies, the notion that



Figure 4. Spectral and temporal evolutions from two-pulse and threepulse TA measurements. (a) Comparison of BE bleach kinetics for three-pulse experiments for different pump excitation conditions: 570 nm (solid line-circle, black) or 400 nm (solid red line). (b) Expansion of the x-axis of panel (a) up to 5 ps. (c) Comparison of TA spectra at 1.2 ps for 570 nm pump excitation in the absence (black) and presence (red) of saturation pulses; (d) TA spectra of the second exciton generated by pumping either at 570 nm (black) or at 400 nm (red) at a pump-probe delay of 35 ps. Notice how the initially very different TA spectra of the two experiments are essentially identical as AR proceeds (see the text). (e) BE bleach kinetics from 0 to 125 ps, on a split time scale. The first 1.5 ps is plotted on a linear time axis, and thereafter, data are plotted on a logarithmic scale. Pump fluences are presented in dimensionless units of η_0 , the average number of absorbed photons per NC at the front surface of the sample. (f) Comparison of the measured 1S-1S bleach saturation as a function of η_0 compared with a simulated one assuming fast decay of all excitons to the lowest available states and state filling of 1/2 of the BE band per exciton.

BE PIB varies linearly with the population of the first cold excitons in the conduction band is upheld.

The alternative is that hot MXs do not all relax to the lowest-energy states. Due to spin orientation conflicts, relaxation to $1S^e$ is partially blocked. This leads to the following predictions: (1) An electron blocked from the BE by virtue of conflicting spin orientation will be stranded above in the $1P^e$ level and induce a partial PIB of the absorptions into this band and (2) AR kinetics in spin-blocked biexcitons will appear to be slower at first because the decay of BE PIB will be partially canceled by gradual population of $1S^e$ following spin-flips of the electron (assuming flips take place on a time scale of ~20 ps). Accordingly, the difference spectrum in three-pulse experiments pumped at 400 nm should approach that obtained by directly exciting into 570 nm pumping once the frustrated biexcitons have annealed to the BE.

Our data confirm all of these predictions. In panel (c) of Figure 4, not only is the PIB by 400 nm pumping 2 times smaller than that induced at 570, there is a missing PIA feature at 520 nm, consistent with partial state-filling of 1Pe due to stranded electrons. Panels (a) and (b) show PIB decay kinetics for the same two experiments. As predicted, the AR dominated decay starts off much more rapidly for 570 nm pumping. As the delay increases, both curves merge and decay similarly to zero as ultimately all biexcitons return to single occupancy. Assuming spin-frustrated biexcitons undergo AR at the same rate as a relaxed one, comparison of these two AR kinetics leads to an exponential spin-flipping time of 25 ps (see discussion of the spin-flip mechanism below and fits in the Supporting Information Figure S1). Finally, as shown in Figure 4d, the very different TA spectra at 1 ps asymptotically converge once the remaining biexcitons have relaxed to the BE, completing the consistency test with the spin conflict hypothesis.

This selection rule for hot MX relaxation must hold in any matching scenario. As an example, panel (e) of Figure 4 brings an overlay of pump-probe PIB kinetics for a broad range of 400 nm excitation fluences. After determining the absorption cross section from the bleach amplitude at low pump fluence, as detailed in the Supporting Information (Figure S2), each fluence is designated by $\eta_0 \equiv \sigma_A \times \rho_{h\nu}$ the average number of absorbed photons per NC at the front surface of the sample. As η_0 increases, the PIB grows monotonically, increasing the portion of bleach that decays during AR. As expected, at the highest pump intensities, this decay accounts for nearly 1/2 of the bleach maximum at 1.5 ps. Knowing that absorption of the sample at 400 nm is unchanged by absorbing even a number of photons, Poisson statistics integrated throughout the depth of the sample can be used to calculate the number density of NCs that have absorbed N photons. Panel (f) brings the predicted fractional bleach amplitude assuming that all excitons relax directly to the lowest available energy states and that each 1S electron bleaches 1/2 of the 1S-1S exciton band (see details in the Supporting Information).

As η_0 is increased, the actual bleach amplitude falls short of this prediction. We assign this to the same partially frustrated relaxation demonstrated in the spectator experiments. As photons are absorbed, excitons will rapidly relax to the lowest quantized states. After the first is in place, another will only be able to relax beside it if it has a correct spin orientation. This situation is worsened with increased pump fluence as the number of biexcitons grows. Eventually, as more and more excitons are generated, at least one of the additional electrons will have a matching spin state to fill the gap and complete BE bleaching. This explains the ultimate approach of the fraction to 1 when $\eta_0 \gg 1$. Thus, this limitation concerning cooling of MXs is obvious even in very fundamental pump-probe experiments once analyzed quantitatively. It must accordingly be considered whenever the intense BE exciton bleach is utilized to quantify exciton occupation numbers when MXs are involved.

To test the plausibility of this interpretation, we developed a Lindblad master equation approach³⁴ for the spin-flip dynamics based on a quasi-particle-level structure taken from ab initio density functional calculations on a small CdSe NC (see below). These levels do not include spin-orbit interaction, which is treated as a perturbation in the ab initio model. For the purpose of discussing the spin-orbit interaction in the CdSe NCs, we use the Luttinger–Kohn



Figure 5. (a) Schematic depiction of the lowest states at the conduction BE, used for modeling the decay rate of an excited-blocked electron. See the text for explanation. (b) Temporal Lindblad master equation populations for the three adiabatic states of the model, showing the fast and slow decay transients. (c) Sensitivity of the long-lifetime τ to the spin–orbit and level displacement parameters (s and Δ , respectively) of the model.

effective mass theory^{28,35} where the molecular orbitals have the approximate form of a product between an envelope function and a lattice-periodic wave function. For the unperturbed hole states in CdSe NCs, the envelop wave function has a S^h angular momentum character while the periodic wave functions exhibit a distinctive atomic p-orbital character, which when coupled with spin gives a total angular momentum of either a low-lying doublet $J = \frac{1}{2}$ or a quartet $J = \frac{3}{2}$, denoted $1S_{3/2}^{h}$, at the BE.³⁶ Because our system is not an idealized spherical NC, we do not expect the envelop angular momentum quantum numbers to be exact constants of motion, and therefore, some spherically induced degeneracies might slightly split. The lattice periodic part of the electron eigenstates have s orbital character and therefore do not exhibit as strong spin-orbit splittings as the holes in this system. Hence, for the electron states, we take a perturbation theory approach by which they are considered eigenstates of the angular momentum operator, and spin-orbit effects will be considered later in the dynamical calculation shown below. The lowest electron levels are thus orbitalangular-momentum eigenstates, and the lowest energy doublet is $1S_{\sigma}^{e}$ where $\sigma = \uparrow,\downarrow$ are the two spin projections, followed by the $1P_{m,\sigma}^{e} m = -1$, 0, 1 closely spaced sextet. While the holes dominate the fine structure of the spin-flip dynamics in CdSe QDs,³⁷⁻³⁹ they do not play a significant role in the present phenomenon, which involves trapped, spin-orbit-induced excited-state electron spin-flips. The holes can only affect this phenomenon through a spin-exchange mechanism but do so at a much slower (nanosecond) rate and therefore are neglected here.37,39,40

In the experiment, the lowest S^e state, well-separated by an energy gap of ε_s from the $P^e_{m\sigma}$ excited state, is populated by (say) a spin-up spectator electron (S^e_{\uparrow}) , while a second hot electron, promoted by the pump pulse, is stranded in state $P^e_{-1\uparrow}$, unable to populate S^e_{\uparrow} due to Pauli blocking and therefore requiring a spin-flip before any decay can happen. The ab initio calculations showed zero spin—orbit-induced spin-flip of the spectator electron in $S^e_{\uparrow} \rightarrow S^e_{\downarrow}$ (this is to be expected when both the Bloch orbitals are s-type and the envelop angular momentum is zero). As discussed in the previous paragraph, a spin-flip due to spin-exchange with the holes has a negligible rate. Thus, further relaxation can be achieved only by a spin-flip in the P^e manifold. The ab initio calculations show that

such a flip involves change of the P^e state, e.g., $P_{-1\uparrow}^e \rightarrow P_{0\downarrow}^e$ facilitated by spin–orbit interaction, after which the decay $P_{0\downarrow}^e \rightarrow S_{\downarrow}^e$ takes place rapidly through, e.g., Auger cooling and/or phonon scattering.

The phonon modes serve as a heat-bath for absorbing the energy mismatches. Setting the energy origin at P_0^e , the total Hamiltonian of the system and bath is

$$\begin{split} H &= 2\Delta |\mathbf{P}_{-1\uparrow}^{\mathrm{e}}\rangle \langle \mathbf{P}_{-1\uparrow}^{\mathrm{e}}| - \varepsilon_{\mathrm{S}} |\mathbf{S}_{\downarrow}^{\mathrm{e}}\rangle \langle \mathbf{S}_{\downarrow}^{\mathrm{e}}| \\ &+ s(|\mathbf{P}_{-1\uparrow}^{\mathrm{e}}\rangle \langle \mathbf{P}_{0\downarrow}^{\mathrm{e}}| + |\mathbf{P}_{0\downarrow}^{\mathrm{e}}\rangle \langle \mathbf{P}_{-1\uparrow}^{\mathrm{e}}|) \\ &+ \sum_{j} \left(A_{01}^{j} |\mathbf{P}_{0\downarrow}^{\mathrm{e}}\rangle \langle \mathbf{S}_{\uparrow}^{\mathrm{e}}| + \mathrm{c.c.} \right) \frac{p_{j}}{m_{j}} \\ &+ \sum_{j} \left(\frac{p_{j}^{2}}{2m_{j}} + \frac{1}{2}m_{j}\omega_{j}^{2}x_{j}^{2} \right) \end{split}$$

where $-\varepsilon_S$ (2 Δ) are the energy differences between the S^e (P^e₋₁) and the P^e₀ levels, respectively, and *s* is the spin-flip matrix element. For weak electron–nuclear interactions, we neglect all but the linear coupling to the nuclear velocity p_i/m_i .

As a concrete system, we considered a $Cd_{36}Se_{36}$ cluster with the structure taken from ref 41 and relaxed using the Q-CHEM density functional (DFT) code $^{\rm 42}$ at the PBE/6-31G level. This gave the following parameter values, $\varepsilon_{\rm S}$ = 890 cm⁻¹ and 2 Δ = 2000 cm⁻¹, while the spin-orbit coupling s was dependent sharply on the identity of the hole states correlated with the electrons and varied in the range of 0-200 cm⁻¹. Lindblad master equations were set up in accordance with the Hamiltonian for T = 300 K. A_{01} was determined by requiring that the $P_{0\downarrow}^e \rightarrow S_{\downarrow}^e$ decay time be 0.5 ps.⁹⁻¹⁴ With these parameter values, we obtained the temporal populations of the adiabatic states shown in Figure 5b. State 2 is of $P_{-1\uparrow}^e$ character and at t = 0 has close to 0.85 population, which decays through spin-flips, at a rate of about 10 ps, to State 1, which is of $P_{0\downarrow}^e$ character. This latter state stays slightly populated at later times as it continuously feeds the S state, which is of S_{\perp}^{e} character. The rate of S state population through spin-flipping is much longer than the Auger cooling alone and takes place on a 10 ps time scale. The sensitivity of these conclusions to the parameters of the model is rather small, and the fastest rate that can be reached is \sim 4 ps. These calculations show that a

realistic model of the material under study predicts rates for spin-flip-limited cooling in the presence of a BE spectator that are consistent with that measured experimentally. This is bolstered by a demonstration of the moderate dependence of this rate on the material parameters.

Relaxation of optically polarized spin states in NCs has been investigated extensively, in part to test if semiconductor quantum dots can provide a platform for spintronic applications.⁴³ In the case of colloidal NCs, studies have concentrated on electronic states limited to the lowest $1S_{3/2}1S^{e}$ exciton manifold.^{37–39} With spin relaxation components spanning ps to hundreds of ns time scales, results of those experiments are not directly comparable to our findings for a number of reasons. First, the fine structure levels of the exciton ground state are only defined in terms of correlated hole and electron microstates, while the observable described here should involve the electron alone.^{10,12} Furthermore, analysis of polarization-dependent pump-probe experiments conducted in a grating geometry clarifies that none of the separable phases of spin polarization decay are dominated by electron spin-flips alone.44 Finally, while spin-orbit coupling defining the ground exciton sublevels stems from the "p" orbital basis of the valence band, in our case, its origin is in nonzero orbital angular momentum related to the envelope 1Pe function. Our measurements thus cover a very different process. All that can be said in comparison is that the observed time scale of a few tens of ps lies within the broad range characterizing the multiexponential decay of optically induced spin polarization in the 1S_{3/2}1S^e exciton manifold. Only future investigations of how the electron spin-flip rate measured here is effected by temperature, particle size, and crystal morphology will teach more about its relation to other magnetic relaxation processes in NCs.

The chief consequence of the described spin blockade is that a heavily relied upon measure of exciton population in NCs is inherently inaccurate whenever the sample contains MXs. As shown in our particular example, there is no delay at which the 1S PIB correctly reflects the total exciton content of our sample because the AR and spin-flips take place on similar time scales. Furthermore, this is not specific to NCs of a particular material because its effects were observed in one other system,²⁴ and the suggested mechanisms is universal. The failure to recognize this process earlier could stem from an expectation that perturbations that lead to rapid energy transfer to phonons would facilitate rapid continuous spin reorientation. It might also have been influenced by measurement of rapid components to the fine structure decay of the first exciton state, even though, as discussed above, this has been assigned to hole reorientation.

Foreseeing the impact of this previously unnoticed fundamental and universal relaxation restriction is premature. MX states are central to the concept of NC-based lasers,^{21,22} and most scenarios suggested for obtaining stimulated emission gain are based on saturating the population of the BE exciton states. Clearly, a process that puts off such conditions and allows AR to prey on the excited carriers before they contribute to population inversion is of paramount importance to that field. Furthermore, even the modest amount of energy preserved due to this spin blockade, while it lasts, may make a big difference in the yields of fast light detectors because it can significantly hasten charge transfer.⁴⁵

The spontaneous generation of MXs (MEG) following absorption of a single high-energy photon, contested by some,

continues to be reported in the literature. Efficiency of this process, expected to boost efficiency of photovoltaic devices, has been determined mostly by following the kinetics of the BE exciton PIB,²¹ and this measure could be affected by the spin blockade mechanism reported here. Finally, by moving from observation to manipulation, methods could be devised to partly fill the lowest electron state, allowing even a single excited electron to retain extra energy equal to the gap between its 1S and 1P levels for tens of ps. These few examples demonstrate that the spin conflict barrier to relaxation of biexcitons may prove to have far-reaching consequences, and therefore, its inclusion in the conceptual scheme of carrier cooling in multiply excited NCs is essential.

Results of three-pulse saturate-pump-probe experiments on CdSe/CdS QDs, along with a corroborating theoretical model, prove the following: (1) Ultrafast cooling of an electron from the interband continuum to the discrete BE levels does not facilitate rapid spin reorientation, allowing it to dynamically pair with a relaxed electron in the $1S^{e}$ state; (2) accordingly, the presence of a spectator electron at the BE poses a long-lived spin-blockage of the same spin hot electrons from decaying to 1S^e; and (3) electrons stranded in the 1P^e level due to such a blockage experience stochastic spin-flips every ~ 25 ps in the tested sample, opening the way to complete relaxation to the BE. This process will delay cooling and impact the spectroscopic signatures of hot MXs in all envisioned generation scenarios. It must therefore be considered whenever hot MXs are generated, and the interpretation of numerous earlier studies involving such scenarios may require significant revision.

MATERIALS AND METHODS

Synthesis of CdSe QDs Core. A mixture of cadmium oxide (CdO) and oleic acid (OA) in a molar ratio of 1:4 and 7.5 mL of 1-octadecene (ODE) were put in a 25 mL three-neck flask. The reaction mixture was degassed for 1 h at 100 °C under vacuum. Under nitrogen, the temperature was then raised to 300 °C until the solution turned clear, indicating the formation of cadmium oleate. Then the solution was cooled, and the octadecylamine (ODA) was added in a molar ratio of 1:8 (Cd/ ODA). Afterward, the solution was heated to 280 °C, and 8 mL of 0.25 M trioctylphosphine selenide (TOPSe) was injected under vigorous stirring. The growth was terminated after 16 min by rapid injection of 10 mL of ODE, and the reaction mixture was further cooled down by a water bath. Asprepared core CdSe QDs were precipitated twice with a 2propanol/ethanol mixture (1:1-1:2), separated by centrifugation, and redissolved in hexane.

Synthesis of CdSe QDs Coated with 1 Monolayer (ML) of CdS. The 0.1 M Cd precursor was prepared by dissolving 0.1 mmol of cadmium acetate $(Cd(Ac)_2)$ and 0.2 mmol of hexadecylamine (HAD) in 10 mL of ODE at 100 °C inside of a nitrogen-filled glovebox. The 0.1 M S precursor was prepared by dissolving 0.1 mmol of sulfur in 10 mL of ODE at 100 °C.

The coating procedure was adapted from a previous report.⁴⁶ Initially, 14.8 mL of ODE was degassed under vacuum for 1 h at 100 °C. The ODE was cooled to 65 °C, and a solution of 7.4 \times 10⁻⁴ mmol CdSe QDs in hexane was injected. Then, the Cd precursor solution was added at 65 °C. After degassing for 10 min under vacuum at 65 °C, the S precursor was added. The reaction mixture was quickly heated to 100 °C and allowed to remain for 2 h at this temperature. Then the nanoparticles were precipitated with a mixture of 2-

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propanol and ethanol (1:1-1:2), separated by centrifugation, and redissolved in hexane.

Femtosecond Pump-Probe Measurements. The CdSe/CdS core/shell QDs were prepared under an inert atmosphere inside of a nitrogen-filled glovebox. The sample was placed in an airtight 0.25 mm quartz cell for the pump-probe measurements. A home-built multipass amplified Ti-Sapphire laser producing 30 fs pulses at 790 nm with 1 mJ of energy at a 1 kHz repetition rate was used to generate the fundamental. The laser fundamental was split into different paths for generation of probe and pump pulses. The pump pulses at 400 nm were produced by frequency doubling of the fundamental 800 nm pulses, whereas the pump pulses at 570 nm were generated by second harmonic generation of signal (at 1140 nm) from an optical parametric amplifier (TOPAS 800, Light Conversion). The pump pulses at 570 nm were compressed using a grating-mirror compressor setup. Spectra of both are shown in Figure 1b. The supercontinuum probe pulses were generated by focusing 1200 nm output pulses of another optical parametric amplifier (TOPAS Prime, Light Conversion) on a 2 mm BaF₂ crystal. The pump and probe beams were directed to the sample using all reflective optics. The spot size of the pump on the sample was at least two times larger compared to that of the probe beam.

Conventional two-pulse pump-probe experiments were carried out with white light ranging from 420 to 700 nm as the probe and 400 or 570 nm pulses as the pump, with low fluence such that the average number of excitons per NCs was $\eta \approx$ 0.2. In the case of three-pulse measurements, the same two-pulse pump-probe experiments were repeated in the presence of another saturation pulse at 400 nm, which arrived \sim 200 ps earlier than the pump pulses. Raw data from threepulse measurements show a constant bleach signal (~10% of that of the initial single-exciton bleach) even a long time after completion of AR, suggesting that $\sim 10\%$ of the total number of NCs was not saturated by the strong saturation pulses. Thus, first raw data from three-pulse measurements was subtracted by 10% of the two-pulse data, and then, the subtracted data set was divided by 0.9 so that the final three-pulse data represented the fully saturated sample.

Theoretical Model. See the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jp-clett.9b00992.

Experimental determination of the absorption cross section, simulation of pump fluence-dependent bandedge bleach, and details of the theoretical modeling and calculations (PDF)

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Notes

The authors declare no competing financial interest.

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