State Filling and Stimulated Emission by Colloidal

InP/ZnSe Core/Shell Quantum Dots

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Abstract

Colloidal InP-based quantum dots (QDs) have been widely studied for luminescent color conversion or electroluminescence, yet the nature of the emitting state remains a matter of debate and reports on stimulated emission by these materials are nearly absent. Here, we investigate the properties of photo-excited InP/ZnSe QDs using femtosecond transient absorption spectroscopy. We show that the evolution of the band-edge bleach with increasing exciton number can be interpreted as state filling of the conduction- and valence-band edge states by delocalized electrons and holes. In line with this interpretation, net stimulated emission is observed once the average exciton number exceeds 1. We account for this lower-than-expected gain threshold and for the spectral properties of the gain band by reckoning that the Stokes shift between band-edge absorption and emission is the dominant spectral shift. The underlying exciton-phonon coupling leads to a stimulated emission mechanism, where also single excitons could lead to net optical gain. To fully profit from this advantageous stimulated emission scheme, we argue that InP/ZnSe QDs with more narrow
emission lines are needed and spurious trapping of electron-hole pairs at high exciton numbers must be suppressed, for example by better controlling the composition of the core/shell interface.

**Keywords**

opto-electronics, III-V semiconductors, nanocrystals, quantum confinement, light-matter interaction

After the first demonstration of net optical gain and amplified spontaneous emission across the band-gap transition in colloidal CdSe quantum dots (QDs),\(^1\) research into QDs as a printable, active material for optical amplifiers, super luminescent diodes or lasers proliferated.\(^2\)–\(^5\) Optical gain by QDs is typically assigned to the filling of the quantized band-edge states by electrons and holes, which block light absorption and create pathways for stimulated emission across the band-edge transition.\(^2\) As demonstrated using CdSe-based QDs, progressive state filling results in a saturated gain spectrum that is the mirror image of the absorbance spectrum,\(^6\) and that is characterized by a high material gain of several 1000 cm\(^{-1}\) and nearly temperature-independent gain characteristics.\(^7\)–\(^9\) Using such CdSe-based QDs, various types of lasers were demonstrated, including engineered devices such as vertical-cavity surface-emitting lasers,\(^10\) distributed feedback lasers,\(^11,12\) or integrated microdisk lasers.\(^13\) While these QD lasers initially operated under femtosecond, and later under nanosecond pulsed or quasi-continuous optical pumping,\(^14\) recent work showed the first steps towards electrically pumped devices.\(^15\) This progress was made possible by the introduction of innovative QD heterostructures, which were mostly aimed at reducing the Auger recombination rate of multi-excitons and thus prolong the lifetime of the inverted state.\(^16\)–\(^18\) Here, in particular CdSe/CdS core/shell QDs proved highly suited, for which an optimal balance between material gain and inverted-state lifetime can be found by adapting the core and shell sizes.\(^8,9\)

Following the restrictions on the use of cadmium in electronic appliances, InP-based QDs are emerging as the most viable substitutes for CdSe-based QDs as printable, spectrally narrow and
fast emitters.\textsuperscript{19,20} Economic synthesis methods for InP and InP-based core/shell QDs have been developed,\textsuperscript{21} and the use of these QDs for lighting and display applications, either as luminescent color convertors or electroluminescent emitters, is widely studied.\textsuperscript{22,23} On the other hand, reports on optical gain or stimulated emission by InP-based QDs are rare and lack follow-up research,\textsuperscript{24} a situation that may be related to the limited understanding of the opto-electronic properties of excitons and multi-excitons in these QDs. The few studies that address multi-exciton dynamics by femtosecond spectroscopy focus on Auger recombination of biexcitons or surface trapping of single excitons,\textsuperscript{23,25–27} but do not provide a quantitative analysis of state filling, the reference model for CdSe-based QDs. In fact, even the mechanism of radiative recombination in InP-based QDs remains a matter of debate. Ensemble-level and single-dot photoluminescence studies showed fine-structure properties and radiative lifetimes characteristic of strongly confined excitons.\textsuperscript{25,28,29} Nevertheless, the presence of substitutional zinc that acts as a shallow hole trap was linked to the relatively broad, presumably trap-related, emission line of InP-based QDs.\textsuperscript{30} While synthesis-dependent variations of zinc incorporation may account for these differences,\textsuperscript{31} this unclarity mostly calls for more insight in the opto-electronic properties of photo-excited InP-based QDs.

Here, we present a comprehensive study on the relation between state filling, charge-carrier dynamics, and stimulated emission in photo-excited InP/ZnSe and InP/ZnSe/ZnS QDs by means of femtosecond transient absorption (TA) spectroscopy. We first use probe delay/photon energy transient absorbance maps to identify the main electronic transitions and outline the alignment of the band-edge states in the InP core and the ZnSe shell. Focusing on the band-edge transition, we demonstrate that increasing the average number of electron-hole pairs after optical pumping, i.e., the exciton number \(<N>\), raises the contribution of biexciton recombination to the decay of the band-edge bleach and we report sample-dependent Auger recombination rates of 0.010 – 0.015 ps\(^{-1}\). Moreover, we show that for exciton numbers up to 1.5–2.0, a state-filling model can consistently describe all aspects of the band-edge bleach and the radiative exciton recombination, given a sample-dependent effective degeneracy of the valence-band edge in the range 5–9.
Further increasing \( \langle N \rangle \), on the other hand, leads to a nearly instantaneous loss of electron-hole pairs. Nevertheless, we observe net stimulated emission at exciton numbers \( \langle N \rangle > 1.0 \), which develops into a broader gain band at higher \( \langle N \rangle \) that overlaps with the photoluminescence spectrum. Arguing that the Stokes shift of 80–90 meV between exciton absorption and emission is the dominant spectral shift, we describe the development of stimulated emission through a combination of state filling and a fixed shift between absorbing and emitting transitions. After correcting for the initial electron-hole pairs loss, this approach leads to a quantitative match with experimental data, where the Stokes shift accounts for the unexpectedly low gain threshold. Hence, next to confirming that state filling provides an apt description of photo-excited InP-based QDs, these results highlight that InP/ZnSe QDs can benefit from strong exciton-phonon coupling to attain a low gain threshold and a high material gain. To fully exploit this advantage, further progress is needed to narrow the emission line, suppress the initial loss of electron-hole pairs, and slow down Auger recombination.

**Results**

**Material Properties**

For this study, we made a comprehensive characterization of 4 different InP/ZnSe and InP/ZnSe/ZnS core/shell QDs. Each sample was synthesized using a specific implementation of the hot-injection method published by Tessier et al.\(^{21}\) In brief, we first formed InP core QDs by reacting \( \text{InCl}_3 \) with tri-oleylaminophosphine in oleylamine in the presence of \( \text{ZnCl}_2 \). As shown in Supporting Information S1, these InP core QDs have an average diameter of 3.1 nm and a size dispersion of 10\%. In the same reaction mixture, ZnSe and ZnS shells were subsequently grown by the successive addition of zinc oleate and tri-octylphosphine (TOP) selenide or TOP-sulfide, respectively. A more detailed description of the synthesis method is provided in the Methods section. Data shown in the main text pertain to the InP/ZnSe core/shell QDs labeled as sample A, unless mentioned otherwise. For simplicity, we will refer to this sample as InP/ZnSe QDs.
Figure 1: Overview of main material properties. (a) Bright-field TEM image of InP/ZnSe QDs used in this work. (b) Absorbance spectrum of InP/ZnSe QDs, highlighting the energy of the \((\epsilon_{X,a})\) InP band-edge transition, \((\epsilon_{X^*,a})\) the InP excited-state transition and \((\epsilon_{\text{gap},\text{ZnSe}})\), the ZnSe band-edge transition. See Supporting Information S1 for details on the determination of the transition energies. Inset: Detail of (red) the absorbance spectrum around the InP band-edge transition and (blue) the photoluminescence spectrum. The central energy of (2.02 eV) the emission band and (2.11 eV) the band-edge transition have been indicated. (c) Transient photoluminescence including (red line) a best fit to a delayed emission model. Inset: Cross-section spectrum, highlighting the integrated cross section of the band-edge transition used to estimate the oscillator strength of this transition.

Figure 1a shows an overview transmission electron microscopy image (TEM) of the InP/ZnSe core/shell QDs (sample A). Similar to previously published TEM images, we obtained somewhat faceted nanocrystals that can be described in essence as quasi-spheres, see Supporting Information S1 for an overview of average sizes. The absorbance spectrum of these InP/ZnSe QDs, as plotted in Figure 1b, exhibits three readily observable features. In line with previous reports, we assign the two lower energy features, labeled as \(\epsilon_{X,a}\) and \(\epsilon_{X^*,a}\), to the band-edge and the first excited-state transition in the core InP QDs. These lines are heterogeneously broadened, mostly because of the size dispersion of the InP core QDs, see Supporting Information S1. The pronounced rise in absorbance above 2.75 eV, on the other hand, is related to electronic transitions within the ZnSe shell. As outlined in Supporting Information S1, we estimated the transition energies as indicated in Figure 1b using a second derivative analysis of the absorbance spectrum and the bleach minima of the transient absorbance spectra. Moreover, as shown in the inset of Figure 1c, the transition energies \(\epsilon_{X,a}\) and \(\epsilon_{X^*,a}\) were used as constraints for deconvoluting
the absorbance spectrum and obtain the band-edge absorption band.

As can be seen in the inset of Figure 1b, the band-edge absorption feature $\varepsilon_{X,a}$ is mirrored by the band-edge photoluminescence (PL), which yields an 0.15 eV wide emission band centered at 2.02 eV. The resulting Stokes Shift – which we write as $2\Delta_S$ – of 0.09 eV is comparable to figures reported before for InP/ZnS or InP/ZnSe QDs synthesized with a similar method. In the literature, this shifted emission band has been assigned to transitions involving charge carriers trapped in shallow defects, or to a pronounced exciton-phonon coupling. After pulsed photo-excitation, we obtained a PL transient that combines a rapid initial decay with a long-lived component that cannot be described using a single time constant, see Figure 1c. Given the similarity between this PL transient and the emission transients reported in the literature for CdSe QDs, we fitted the InP/ZnSe PL decay to the delayed emission model proposed by Rabouw et al. As outlined in Supporting Information S1 and Table 1, such a fit yielded an undelayed-emitter fraction of 70% and a radiative recombination rate of 0.034 ns$^{-1}$, corresponding to a lifetime of 28 ns. This figure is comparable to previously published luminescent lifetimes for exciton recombination in InP/ZnSe QDs. The corresponding figures for all samples included in this study have been listed in Table 1.

Table 1 lists the different characteristics as discussed above for all samples included in this study. As shown in Supporting Information S1, these different samples were formed starting from highly similar InP core QDs. On the other hand, samples A and D, consist of an InP/ZnSe core/shell structure only, whereas samples B and C have a more involved InP/ZnSe/ZnS core/shell/shell composition. Clearly, this additional ZnS shell significantly enhances the photoluminescence quantum yield, an observation in line with previous literature studies. Considering the absorbance spectra of these different samples shown in Supporting Information S1, one sees that the absorbance by the ZnSe shell at photon energies above ~2.75 eV relative to the InP core absorbance is not identical for the different samples. This observation indicates
Table 1: Overview of main experimental characteristics of the 4 InP-based QD samples analyzed for this study including (d) the average diameter, \( \varepsilon_{X,a} \) the energy of the band-edge transition, \( 2\Delta S \) the Stokes shift, (PQLY) the photoluminescence quantum yield and \( k_{X,\text{rad}} \) the estimated radiative recombination rate. Diameters are given plus/minus one standard deviation of the size histogram. PLQY was measured using 2.952 eV (420 nm) excitation light.

<table>
<thead>
<tr>
<th>label</th>
<th>system</th>
<th>d (nm)</th>
<th>( \varepsilon_{X,a} ) (eV)</th>
<th>( 2\Delta S ) (eV)</th>
<th>PLQY (%)</th>
<th>( k_{X,\text{rad}} ) (ns(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>InP/ZnSe</td>
<td>7.8 ± 1.4</td>
<td>2.11 ± 0.01</td>
<td>0.09 ± 0.01</td>
<td>45</td>
<td>0.034</td>
</tr>
<tr>
<td>B</td>
<td>InP/ZnSe/ZnS</td>
<td>7.6 ± 1.4</td>
<td>2.13 ± 0.01</td>
<td>0.08 ± 0.01</td>
<td>72</td>
<td>0.029</td>
</tr>
<tr>
<td>C</td>
<td>InP/ZnSe/ZnS</td>
<td>8.4 ± 1.3</td>
<td>2.12 ± 0.01</td>
<td>0.08 ± 0.01</td>
<td>88</td>
<td>0.030</td>
</tr>
<tr>
<td>D</td>
<td>InP/ZnSe</td>
<td>6.7 ± 1.0</td>
<td>2.14 ± 0.01</td>
<td>0.09 ± 0.01</td>
<td>60</td>
<td>0.035</td>
</tr>
</tbody>
</table>

that the yield of the ZnSe shell growth is not always identical during the synthesis procedure, and the samples have been labeled from A to D according to a decreasing absorbance by ZnSe.

**Transient Absorbance and the Energy-Level Diagram of InP/ZnSe QDs**

Figures 2a-b depict probe delay/photon energy maps of the transient absorbance \( \Delta A \) of InP/ZnSe QDs recorded at room temperature following photo-excitation using a 120 fs pump pulse centered at 2.583 eV (480 nm) that generated on average \( \langle N \rangle = 0.55 \) and \( \langle N \rangle = 7.2 \) electron-hole pairs per QD, respectively. These exciton numbers were estimated using the absorption cross section \( \sigma_{480} \) as listed in Table 2, see Supporting Information S2 for details. Focusing first on the low excitation-number \( \Delta A \) map, one sees that pulsed photo-excitation results in three long-lived bleach bands. Centered at 2.11, 2.36 and 2.68 eV, respectively, these bands can be readily identified in the transient absorbance spectra at 3 and 500 ps shown in Figure 2c. Similar bleach spectra of InP/ZnSe QDs were recently published in the literature.\(^{38}\) Moreover, we retrieved the same three bleach features in \( \Delta A \) maps recorded after resonant excitation and on samples with a higher PLQY, see Supporting Information S3. Next to these bleach bands, a distinct short-lived
Figure 2: Transient absorption spectroscopy of InP/ZnSe QDs. (a-b) Transient absorbance $\Delta A$ of InP/ZnSe QDs plotted as a function of the pulse delay and the probe photon energy after photo-excitation at 2.583 eV using a 120 fs pump pulse creating $\langle N \rangle = 0.55$ or 7.2 electron-hole pairs per QD. Note the different color coding in both maps. The dashed lines highlight the main spectral features. (c,e) $\Delta A$ spectrum at a 3 and 500 ps pump-probe delay. The lines highlight the same features as in (a-b). (d,f) (markers) $\Delta A$ at a fixed photon energy of 2.11 eV and (white line, d) best fit to a double exponential decay yielding the rapid decay rate as indicated and (white line, f) best fit to a triple exponential decay keeping the two slowest components fixed to the values found in (d), yielding the indicated additional decay component. (g) Resulting alignment of energy levels in the InP core and the ZnSe shell. (h) Representation of Auger recombination and hole excitation as processes relevant at higher exciton number.

Transient bleaching feature appears in the low excitation $\Delta A$ map at $\sim 2.84$ eV. Given the correspondence with the transitions identified in the linear absorbance spectrum shown in Figure 1b, we assign the features at 2.11, 2.36 and $\sim 2.84$ eV to the bleach of the band-edge and excited-state transition of the InP core, and the band-edge transition of the ZnSe shell. These assignments are indicated in Figures 2a-b.
Opposite from the features at 2.11, 2.36 and ∼2.84 eV, the bleach band at 2.68 eV has no straightforward link to the linear absorbance spectrum. As shown previously for CdSe QDs, such a long-lived feature may result from a spectral shift of a higher-energy transition.\textsuperscript{39} However, the derivative of the absorbance spectrum, which is proportional to the absorption change caused by a spectral shift,\textsuperscript{40} does not contain any feature at this photon energy, see Supporting Information S3. Alternatively, being present in the low excitation-number $\Delta A$ map, at long delay times and after resonant excitation, the bleach band at 2.68 eV can reflect a true bleach of a transition involving either the InP valence-band or conduction-band edge state. Since we retrieved the ZnSe band-edge bleach at ∼2.84 eV, this interpretation would put the level offset between either the InP and ZnSe valence-band edge states or the InP and ZnSe conduction-band edge states at 0.16 eV at the most. Different computational studies on InP QDs agree on the fact that the energy difference between the quantized levels in the InP conduction band is considerably larger than in the valence band.\textsuperscript{41–43} Hence, the energy difference of 0.25 eV between the InP core transitions at $\varepsilon_{X, a}$ and $\varepsilon_{X^*, a}$ will mainly reflect the gap between the first (1S) and the second (1P) conduction-band level. However, if the offset of 0.16 eV were to separate the InP and ZnSe conduction-band edge states, the 1P level would fully delocalize in the ZnSe conduction-band edge. A more likely interpretation of the 2.68 eV bleach feature is therefore obtained within the energy band diagram shown in Figure 2g, which puts the valence-band offset between InP and ZnSe at 0.16 eV. In line with the observed long-term bleach features, this diagram assigns the transitions at 2.36 and 2.68 eV to electronic excitations from the valence-band edge to the excited level in the InP conduction band and to the ZnSe conduction-band edge, respectively. Note that this diagram shows the energy of the actual single-electron states in the InP/ZnSe QDs analyzed, not the alignment of the bulk energy bands.

A surprising aspect of the energy-band diagram obtained from the transient absorbance is the small offset between the InP and ZnSe valence-band states, which is different from the expected based on bulk band-offsets.\textsuperscript{44} Even so, a similar band-alignment was recently deduced for
InP/ZnSe QDs using X-ray photo-electron spectroscopy, and assigned to the interfacial dipole across an In-rich InP/ZnSe interface.\textsuperscript{45} To further support this interpretation, we highlight the variation of the differential absorbance at the InP band-edge transition $\varepsilon_{Xa}$ with increasing probe delay. As can be seen, the band-edge bleach reaches a maximum value after $\sim 2$ ps, a delay that probably reflects the cooling of electrons towards the conduction-band edge. As shown in Supporting Information S3, the 2.68 eV bleach band attains on the other hand its maximum almost instantaneously. This lack of electron-cooling fingerprint supports the assignment of this band to a transition involving the InP valence-band edge rather than the conduction-band edge.

At longer probe delays, the band-edge bleach exhibits a moderate decay characterized by a well-defined $\sim 0.01$ ps\textsuperscript{-1} component and a minor slower component that is more difficult to quantify given the 3 ns delay-time window available, see Figure 2d. As can be seen in Figure 2e-f, increasing the exciton number mostly results in a more pronounced initial bleach and a more rapid band-edge bleach decay, which now includes and additional 0.1 ps\textsuperscript{-1} component. As confirmed in the next section, both the 0.1 and the 0.01 ps\textsuperscript{-1} components can be assigned to Auger recombination of multi-excitons, a process schematically depicted in Figure 2h, where the smallest rate constant corresponds to the biexciton Auger recombination rate $k_{2X}$. Furthermore, Figure 2e indicates that the difference between the 2.68 and the 2.84 eV bleach features blurs at higher exciton numbers, such that both bands appear rather as a single feature that gradually shifts to lower energy with increasing delay time. This observation suggests that at higher pump intensity, thermal excitation of holes may result in a broader occupation of valence-band states by holes in the InP core and the ZnSe shell (see Figure 2h), which can hide the clear difference we observed at lower exciton numbers between transitions involving the InP and the ZnSe valence-band edge at 2.68 eV and $\sim 2.84$ eV, respectively.

In particular in the high exciton-number transient absorbance spectrum shown in Figure 2e, a spectrally broad photo-induced absorption (PA) is visible at photon energies below the band-edge transition. As discussed in more detail in Supporting Information S3, this PA scales proportional
to the exciton number, and exhibits the same decay dynamics as the band-edge bleach. Similar PA bands were reported for CdSe and PbSe QDs, and assigned to absorption from surface-localized defects or intraband absorption,\textsuperscript{46,47} while a recent study on InP QDs related this PA feature to transitions involving conduction-band electrons.\textsuperscript{27}

**The State Filling Model**

In the case of CdSe QDs, the band-edge bleach has been systematically assigned to state filling of electron and hole states.\textsuperscript{2,3,6,8} As depicted in Figure 3a, the occupation of band-edge levels by electron-hole pairs blocks absorbing transitions and opens up pathways for stimulated emission.

![Figure 3: The state-filling model. (a) Representation of the optical transitions used to model the band-edge bleach in the state-filling model, including (red) absorption and (blue) stimulated emission in an unexcited QD and a QD containing (X) one or (2X) two $e^/-h^+$ pairs. The QD has 2-fold degenerate conduction and valence-band edges and each transition is characterized by the same oscillator strength $f_0$. (b-d) Variation of (blue, b) the initial bleach, (green, c) the long-term bleach and (red, d) the multi-exciton ratio after photo-excitation according to the state-filling model for 3 different values of the valence-band edge degeneracy $g_h$ as indicated, and keeping $g_e$ fixed at two.](image)
At room temperature, e⁻/h⁺ pairs are quickly scattered across the different band-edge states. As outlined in Supporting Information S4, the absorbance of a photo-excited system can be calculated in that case by assigning a fixed oscillator strength to each pair of states and introducing the fraction \( P_N \) of QDs that hold \( N \) electron-hole pairs.\(^6\)\(^,\)\(^8\)\(^,\)\(^42\) Moreover, while a single electron-hole pair can have a radiative lifetime of 20-30 ns, Auger processes can induce a rapid, non-radiative recombination of multiple electron-hole pairs within 50-100 ps. In view of these markedly different lifetimes, we propose three different bleach quantities to evaluate the predictions of the state-filling model when applied to InP/ZnSe QDs, see Supporting Information S4:

1. The initial bleach IB. This is the reduction \( \Delta A(0) \) of the band-edge absorbance immediately after photo-excitation, normalized relative to the band-edge absorbance. Assuming that at this point, recombination of multiple \( e^-/h^+ \) pairs is absent, IB is modelled by assuming that the fractions \( P_N \) follow a Poisson distribution with on average \( \langle N \rangle \) excitations per QD.

2. The long-term bleach LB. This is the reduction \( \Delta A(\infty) \) of the band-edge absorbance after all multiple \( e^-/h^+ \) pairs have recombined to a single \( e^-/h^+ \) pairs, under the assumption that no single \( e^-/h^+ \) pairs are lost by trapping, normalized relative to the band-edge absorbance. LB is modelled by assuming that only \( P_0 \) and \( P_1 \) are different from zero and that \( P_0 \) is still obtained from a Poisson distribution with on average \( \langle N \rangle \) excitations per QD.

3. The multi-exciton ratio MR. This is the ratio between the initial, additional bleach \( \Delta A_{MX}(0) \) due to multiple \( e^-/h^+ \) pairs and the initial bleach \( \Delta A_X(0) \) due to single \( e^-/h^+ \) pairs. Again, this number is modelled by assuming that the fractions \( P_N \) follow a Poisson distribution with on average \( \langle N \rangle \) excitations per QD. Opposite from IB and LB, the multi-exciton ratio is internally calibrated in the sense that it is not affected by the presence of QDs that instantaneously lose photogenerated \( e^-/h^+ \) pairs.

As outlined in Supporting Information S4, the variation of the bleach quantities with \( \langle N \rangle \) depends on the degeneracy \( g_e \) and \( g_h \) of the band-edge states. Figures 3b-c therefore represent the
predicted bleach quantities for $g_e = 2$ and $g_h = 2, 4$ and 8. One sees that the initial bleach levels off at $\Delta A(0) = -2$ – a situation of complete inversion of the band-edge transition – with an initial slope that decreases with increasing $g_h$. The long term bleach, on the other hand, evolves towards $-(g_e + g_h)/(g_eg_h)$ with increasing $\langle N \rangle$, with an initial slope that scales with the same factor. Finally, the initial linear increase of the multi-exciton ratio with $\langle N \rangle$ – which reflects the $\langle N \rangle^2$ scaling of the biexciton occupation – has a fixed initial slope of 0.5, a point we confirm in Supporting Information S4. Also here, the limit at high $\langle N \rangle$ strongly depends on the actual level degeneracies and exceeds 1 for $g_h > 2$, see Supporting Information S4.

Auger Recombination and State Filling in InP/ZnSe Quantum Dots

To analyze the InP/ZnSe bleach in view of the state-filling model, Figure 4a represents the band-edge bleach transients obtained for exciton numbers $\langle N \rangle \approx 1.0$ at the most. As can be seen, the $\sim 0.01$ ps$^{-1}$ decay component becomes more prominent with increasing $\langle N \rangle$, without apparently

![Figure 4: Band-edge bleach analysis. (a) Decay of the band-edge bleach at 2.11 eV after photo-excitation pulses creating an average exciton number as indicated. The white lines represent best fits to a double exponential decay with two global rate constants interpreted as the biexciton Auger rate $k_{2X}$ and a single-electron trapping rate $k_{Xtrap}$. The fitting amplitudes $\Delta A_X$ and $\Delta A_{MX}$ describing the initial bleach due to single excitons and the additional initial bleach due to multi-excitons are indicated. (b-c) Representation of the bleach quantities as indicated, including (symbols) estimates from the global fit of the band-edge bleach and (lines) predictions by the state-filling model using $g_{e80} = 2.0 \times 10^{-15}$ cm$^2$, $g_e = 2$ and $g_h = 9$. The experimental estimates of the initial and long-term bleach have been corrected for photo-induced absorption.](image-url)
speeding up. Moreover, all traces feature an additional, slower decay component. In line with literature studies on CdSe QDs,\textsuperscript{2} and previous work on InP-based QDs,\textsuperscript{25} we tentatively assign the $\sim 0.01 \text{ ps}^{-1}$ decay component to Auger recombination of biexcitons, and the slower component to trapping of single excitons. Building on this initial assignment, we analyzed the band-edge bleach $\Delta A(t)$ at these different exciton numbers by means of a global fit to a two exponential decay with fixed rates for Auger recombination ($k_{2X}$) and exciton trapping ($k_{X, \text{trap}}$) on top of a constant bleach feature that represents longer-lived single excitons:

$$
\Delta A(t) = \Delta A_{MX} e^{-k_{2X}t} + (\Delta A_X - \Delta A_{X, \infty}) e^{-k_{X, \text{trap}}t} + \Delta A_{X, \infty}
$$

(1)

Here, the amplitudes $\Delta A_{MX}$, $\Delta A_X$ and $\Delta A_{X, \infty}$ have been defined so as to obtain a direct link with the bleach quantities:

$$
\text{IB} = \frac{\Delta A(0)}{A_0} = \frac{\Delta A_{MX} + \Delta A_X}{A_0}
$$

(2)

$$
\text{LB} = \frac{\Delta A(\infty)}{A_0} = \frac{\Delta A_{MX}}{A_0}
$$

(3)

$$
\text{MR} = \frac{\Delta A_{MX}(0)}{\Delta A_X(0)} = \frac{\Delta A_{MX}}{\Delta A_X}
$$

(4)

As can be seen in Figure 3a, Eq 1 yields a good fit to the experimental bleach transients, from which we estimate $k_{2X} = 0.0103 \pm 0.0001 \text{ ps}^{-1}$ (see Table 2) and $k_{X, \text{trap}} = 0.43 \pm 0.01 \text{ ns}^{-1}$. From the best-fit amplitudes listed in Supporting Information S5, it follows furthermore that only about 30% of the remaining excitons is lost through the additional trapping component. Moreover, a similar analysis applies to the other samples included in this study, although the resulting Auger rates $k_{2X}$ vary between 0.0103 and 0.0158 ps$^{-1}$ across the different samples, see Table 2. Since an additional decay component, faster than $k_{2X}$, develops for exciton numbers $\langle N \rangle$ larger than 1, we analyzed these transients using a three-exponential decay. Here, $k_{2X}$ and $k_{X, \text{trap}}$ were kept...
fixed at the values obtained from the global fit of the band-edge bleach transient at lower exciton
numbers, see Supporting Information S5.

The extension of Eq 2-4 to decay traces recorded at higher exciton number is straightforward,
see Supporting Information S5. Figures 3b-c therefore display the bleach quantities as deduced
from global fits to the band-edge bleach decay as a function of \( \langle N \rangle \). However, to compare these
experimental bleach quantities of InP/ZnSe QDs with the prediction of the state-filling model, a
precise determination of \( \langle N \rangle, g_e \) and \( g_h \) is needed. To obtain these numbers, we used as the sole
adjustable parameter the absorption cross section \( \sigma_{480} \) at the pump wavelength, which relates the
measured photon flux \( f_{ph} \) to the exciton number \( \langle N \rangle \):

\[
\langle N \rangle = \sigma_{480} \times f_{ph}
\]

As outlined in Supporting Information S6, we obtained best estimates for \( \sigma_{480} \) as listed in Table
2 by matching the experimental and theoretical multi-exciton ratios. Moreover, once \( \sigma_{480} \) is known,
the absorbance spectrum can be recalibrated to yield the cross-section spectrum as shown in the
inset of Figure 1c. In that case, an effective exciton degeneracy \( g^* \) can be calculated by combining
the radiative exciton recombination rate \( k_{X,rad} \) with the integrated cross section \( \sigma_{iX} \) of the band-
edge transition:\textsuperscript{7}

\[
g^* = \frac{en_S^2\omega^2}{c^2\pi^2\hbar} \frac{\sigma_{iX}}{k_{X,rad}}
\]

Here, \( e \) is the elementary charge, \( n_S \) the refractive index of the solvent, \( \omega \) the angular frequency
of the emitted light, \( c \) the speed of light and \( \hbar \) Planck’s constant. Note that \( g^* \) can be different
from the product \( g_e \times g_h \) due to thermal excitation of electrons or holes to higher conduction or
valence-band levels. Computational studies on InP QDs invariably yield the lowest conduction-
bond state as a 2-fold degenerate level that is well separated from the first excited conduction-
band state.\textsuperscript{41,42,48} Therefore, we interpret in what follows the overall exciton degeneracy obtained
from Eq 6 as \( 2g^*_h \), leaving the effective hole degeneracy \( g^*_h \) as the only unknown.
Table 2. Overview of the characteristics of the 4 InP-based QD samples analysed in this study as deduced from the transient absorption spectra, including \( (k_{X,\text{rad}}) \) the estimated radiative recombination rate (see also Table 1), \( (\sigma_{480}) \) the cross section at 480 nm, \( (g_h^*) \) the effective hole degeneracy and \( (k_{2X}) \) the biexciton Auger recombination rate.

<table>
<thead>
<tr>
<th>label</th>
<th>system</th>
<th>( k_{X,\text{rad}} ) (ns(^{-1}))</th>
<th>( \sigma_{480} ) (nm(^2))</th>
<th>( g_h^* )</th>
<th>( k_{2X} ) (ps(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>InP/ZnSe</td>
<td>0.034</td>
<td>0.20 ± 0.01</td>
<td>9 ± 2</td>
<td>0.0103</td>
</tr>
<tr>
<td>B</td>
<td>InP/ZnSe/ZnS</td>
<td>0.029</td>
<td>0.15 ± 0.01</td>
<td>9 ± 2</td>
<td>0.0121</td>
</tr>
<tr>
<td>C</td>
<td>InP/ZnSe/ZnS</td>
<td>0.030</td>
<td>0.10 ± 0.01</td>
<td>5 ± 1</td>
<td>0.0158</td>
</tr>
<tr>
<td>D</td>
<td>InP/ZnSe</td>
<td>0.035</td>
<td>0.08 ± 0.01</td>
<td>5 ± 1</td>
<td>0.0138</td>
</tr>
</tbody>
</table>

Figures 3b-c show the comparison of the experimental and estimated bleach quantities based on our best estimate of \( \sigma_{480} \) and the corresponding electron and hole degeneracies. Clearly, at low exciton numbers \( (\langle N \rangle < 2) \), the state-filling model can provide a comprehensive description of all bleach quantities of InP/ZnSe QDs for the optimal cross section of \( 2.0 \times 10^{-15} \) cm\(^2\) and \( g_h^* = 9 \), see Table 2. Similar results are obtained for all samples involved in this study, see Supporting Information S6. As shown in Table 2, the resulting cross sections fall in the range \( 0.8-2.0 \times 10^{-15} \) cm\(^2\); numbers that are comparable to previous literature estimates based on the saturation of the band-edge photoluminescence of InP/ZnSe QDs,\(^{25}\) and with theoretical estimates based on a spherical InP/ZnSe model and bulk optical constants, see Supporting Information S7. In addition, the best estimates for the effective hole degeneracy \( g_h^* \) vary from 5 to 9. These figures are somewhat larger than the degeneracy \( g_h = 4 \) that is typically assigned to the 1S\(_{3/2}\) highest valence-band level.\(^{41,42}\) As mentioned, such a larger-than-expected effective hole degeneracy can result from the thermal excitation of holes to states deeper in the valence band, as argued before for CdTe QDs.\(^{49}\) In the case of InP/ZnSe QDs, thermal excitation of holes is not unlikely given the relatively dense packing of quantized states in the valence band,\(^{27,30}\) and the small offset with the levels in the ZnSe valence band. We therefore conclude that a state-filling model can describe the band-edge bleach of InP/ZnSe at sufficiently low exciton numbers, which confirms the assignment.
of the difference between the initial and the long-term bleach to the recombination of multi-excitons.

The comparison between the estimated and predicted bleach quantities in Figures 4b-c highlights that at high exciton number, in particular the initial bleach and the multi-exciton ratio do not increase as expected. This trend was a characteristic of all samples included in this study, see Supporting Information S6. Such an evolution could be due to a lowering of the absorption cross section by state filling upon pumping. However, as can be seen in Figure 2c-e, the bleach at the pump wavelength of 480 nm – corresponding to a photon energy of 2.58 eV – is minimal, and only amounts to a small fraction of the linear absorbance at this wavelength. Therefore, the too low initial bleach at high exciton numbers may indicate that multi-excitons are lost through trapping and recombination pathways that are not operational at low exciton numbers. Interestingly, opposite from the bleach quantities, the photo-induced absorption increases linearly with \( \langle N \rangle \), also at the highest exciton numbers. Provided that the photo-induced absorption is correctly assigned to transitions involving conduction-band electrons, this observations may indicate that multi-excitons are mostly lost by rapid hole trapping.

**Stimulated Emission – Experimental Observation**

As indicated in Figure 3a, the state-filling model calculates \( \Delta A \) by adding absorption and stimulated emission for all possible band-edge transitions in a QD with a given exciton number. Since \( g_e = 2 \), this sum will result in net stimulated emission for any QD holding at least 2 electron-hole pairs,\(^1\) and optical amplification should result once \( \langle N \rangle \) is sufficiently large, a condition underscored by the white background in Figure 3b. In a transient absorbance map, net stimulated emission is identified by the non-linear absorbance \( A = A_0 + \Delta A \) turning negative, which implies that the photo-excited sample will amplify rather than reduce the probe light intensity. Figure 5a therefore represents a probe delay/photon energy map of the non-linear absorbance after a pump
Figure 5: Stimulated emission by InP/ZnSe QDs. (a) Pump delay/photon energy map of the non-linear absorbance $A$ of InP/ZnSe QDs obtained by adding the linear absorbance $A_0$ to the transient absorbance $\Delta A$ recorded after photo-excitation at 480 nm with a pump pulse creating 5.0 electron/hole pairs on average per QD. The white contour delineates the area where $A$ turns negative. Vertical dashed lines indicate the central position of (2.02 eV) the band-edge photoluminescence, (2.11 eV) the band-edge absorption and (2.36 eV) the first excited state transition. (b) Spectrum of the non-linear absorbance $A_{2\text{ps}}$ at a fixed 2 ps probe delay for excitation pulses creating $N$ as indicated. The grey background represents the band-edge photoluminescence spectrum and the vertical lines indicate that central emission wavelength and the band-edge absorption. (c) Minimum non-linear absorbance $A_{2\text{ps}}$ as a function of $N$. The vertical lines indicate the average exciton number where (1.05) net stimulated emission is first observed and (5.0) net stimulated emission is maximal. (d) Transient absorbance at 1.95 eV showing the pump-probe delay window in which net stimulated emission occurs and an indication of the relevant decay rates.

pulse creating on average $\langle N \rangle = 5.0$ electron-hole pairs per QD. These maps are obtained by adding the linear absorbance $A_0$ of the sample, as recorded prior to transient absorption spectroscopy, to the transient absorbance spectrum $\Delta A$. Through the specific color coding that highlights probe delay/photon energy combinations where $A$ turns negative, we readily discern a net stimulated emission band that is redshifted relative to the band-edge bleach at 2.11 eV, and that disappears after $\sim 40$ ps.

For a more detailed spectral analysis, Figure 5b depicts the non-linear absorbance at a fixed probe delay of 2 ps for different excitation pulses of increasing intensity. Here, three observations stand out. First, increasing $\langle N \rangle$ results in a progressive reduction of the band-edge bleach, which almost reaches full transparency in line with the estimated initial bleach plotted in Figure 3b.
Second, as discussed before, a spectrally broad photo-induced absorption develops, which is clearly visible at photon energies below the band-edge transition. Third, a stimulated emission band appears that can overcome the photo-induced absorption and yield the net amplification feature shown in Figure 5a. Interestingly, the stimulated emission spectrum rather coincides with the band-edge photoluminescence than being an inversion of the band-edge absorption, as expected for the state filling model as developed in Figure 4a.

Figure 5c represents the minimal value of $A_{2ps}$ found in the different non-linear absorbance spectra shown in Figure 5b. One sees that net stimulated emission is first obtained when $\langle N \rangle = 1.05$, and attains a maximum at $\langle N \rangle = 5.0$, a pump level we selected for the non-linear absorbance map shown in Figure 5a. Finally, Figure 5d plots the non-linear absorbance transient at 1.95 eV as obtained for the $\langle N \rangle = 5.0$ pump pulse. As shown in Figure 5d, a best fit to a triple exponential yields two rapid decay components of 0.2 and 0.02 ps$^{-1}$, figures in line with the description of multi-exciton Auger recombination for the band-edge bleach after high intensity pump pulses, see Supporting Information S4. Since the stimulated emission feature disappears in line with the multi-exciton decay, we assign the occurrence of net stimulated emission to multi-excitons formed in InP/ZnSe QDs by photo-excitation. Nevertheless, an intriguing result obtained here is the net stimulated emission threshold $\langle N \rangle$ of 1.05. This number is significantly smaller than the value of 2.26 predicted by the state-filling model for $g_h = 9$ (see Supporting Information S5), even if it applies to the non-linear absorbance without correcting for the photo-induced absorption.

**Stimulated Emission – Model Description**

When depicting the state-filling model in Figure 4a, we assumed that the band-edge transition occurs at a fixed energy, regardless of the occupation of a QD by electron-hole pairs. In reality, however, differences in attractive electron-hole and repulsive electron-electron and hole-hole Coulomb interactions can shift multi-exciton transitions to higher or lower photon energy. In the case of CdSe/CdS core/shell QDs, for example, it was argued that the redshift of the biexciton
transition by net attractive Coulomb interactions accounts for a considerable reduction of the gain threshold occupation $\langle N \rangle$ as compared to the predictions of the state-filling model.\cite{ref8} In the case of InP/ZnSe QDs, however, we found little evidence of significant spectral shifts. Figure 5b already indicated that increasing the occupation number mostly reduces rather than shifts the band-edge absorption. This conclusion is corroborated by a comparison of the non-linear absorption after long delay times, i.e., when only QDs holding one electron-hole pair remain. As shown in Supporting Information S8, no significant spectral shift appears in these biexciton absorption

![Energy level diagram](image)

**Figure 6:** The Stokes-shift model for net stimulated emission by InP/ZnSe QDs. (a) Energy level diagram showing the relation between the energy of $(\varepsilon_{X,a})$ exciton absorption, $(\varepsilon_{X,e})$ exciton emission, $(\varepsilon_{2X,a})$ biexciton absorption and $(\varepsilon_{2X,e})$ biexciton emission, and $(2\Delta_3)$ the Stokes shift and $\Delta_{2X}$ the biexciton Coulomb interaction. Arrows indicate (red) absorption and (blue) stimulated emission. (b) Non-linear absorbance according to the Stokes-shift model for exciton numbers as indicated. The band-edge absorption and emission have been described through Gaussians with a width equal to that of the band-edge photoluminescence and shifted by 0.09 eV. Band-edge degeneracies were taken as $g_e = 2$ and $g_h = \ldots$
9. (c) Energy and relative optical density of the maximum optical gain taken from (markers) experiment and (full lines) Stokes-shift model predictions. In the filled area, the predicted optical gain is smaller than the measurement noise. (d) Comparison of experimental optical gain spectra and predictions by the Stokes-shift model. The indicated numbers denote the estimated exciton number and, in brackets, the effective exciton number.

spectra. Note that this finding is in line with published emission spectra of single InP/ZnSe QDs, where the biexciton emission was observed a mere 9.5 meV to the red of the exciton line. Interestingly, as compared to the biexciton shift, the band-edge photoluminescence exhibits a Stokes shift $2\Delta_s$ of 90 meV relative to the band-edge absorbance.

As argued before in the literature, the same Stokes shift will apply to the biexciton absorption, whose transition energy in absorption $(\varepsilon_{2X,a})$ and emission $(\varepsilon_{2X,e})$ must therefore be written as (see Figure 6a):

$$\varepsilon_{2X,a} = \varepsilon_{X,e} + \Delta_{2X} = \varepsilon_{X,a} - (2\Delta_s - \Delta_{2X}) \quad (7)$$

$$\varepsilon_{2X,e} = \varepsilon_{2X,a} - 2\Delta_s = \varepsilon_{X,e} - (2\Delta_s - \Delta_{2X}) \quad (8)$$

Here, $\varepsilon_{2X,a}$ and $\varepsilon_{2X,e}$ represent the photon energy resonant with biexciton absorption and emission, and $\Delta_{2X}$ is the biexciton Coulomb interaction. According to Eq 8, the minor net biexciton shift in emission spectra can be understood as the result of a near cancellation of the Stokes shift and a repulsive biexciton Coulomb interaction. In that case, Eq. 7 shows also that the biexciton absorption will nearly coincide with the exciton absorption. Moreover, also stimulated emission from exciton or biexciton states will then overlap with the exciton emission spectrum.

If the Stokes shift between exciton absorption and emission is the dominant spectral shift, the non-linear absorbance spectrum can be described as the sum of two counteracting bands that are related to band-edge absorption and band-edge stimulated emission, respectively. For a given exciton number $\langle N \rangle$, the relative optical density related to both bands can be expressed through the state-filling model, which requires that $g_e$ and $g_h$ are known. Figure 6b represents the predictions of this Stokes-shift model, where we represented the experimental absorption and
emission bands with interpolated spectra (see Supporting Information S1) and implemented the band-edge degeneracies of InP/ZnSe QDs as $g_e = 2$ and $g_h = 9$. In particular, one can notice the considerable reduction of the band-edge absorption and the progressive appearance of net stimulated emission, overlapping with the band-edge photoluminescence spectrum, with increasing occupation number. The asymmetry between the pronounced bleach of the band-edge absorption and the more sluggish buildup of net stimulated emission is related to the different degeneracies of the conduction-band and valence-band edge. For $g_e = 2$ and $g_h = 9$, a QD that holds two or more electron-hole pairs will no longer absorb light, yet stimulated emission can only match the original absorption for QDs that hold 9 electron-hole pairs.

Since the data underlying the simulated non-linear absorption spectra shown in Figure 6b were taken from the InP/ZnSe QDs studied here, we can compare the predictions of the Stokes-shift model with the experimental data on net stimulated emission by InP/ZnSe QDs. In Figure 6c, we therefore plot the predicted and measured photon energy and the optical density – relative to the band-edge absorption – of the maximum of the stimulated emission band of InP/ZnSe QDs. Here, the gain band was corrected for photoinduced absorption, and the colored area represents exciton numbers where the predicted gain is smaller than the measurement noise. In line with the evaluation of the bleach quantities (Figures 3b-c), one sees that the Stokes-shift model captures the experimental data well at low exciton numbers, i.e., $\langle N \rangle < 2$. In fact, we observe net stimulated emission as soon as the model predicts a net gain larger than the measurement noise and the gain spectra peak close to the predicted photon energy.

On the other hand, the measured net stimulated emission lags behind the prediction of the Stokes-shift model with increasing exciton number. Since net stimulated emission requires multiple electron-hole pairs per QD, this observation probably reflects the previously discussed point that less electron-hole pairs than expected remain after high-intensity photoexcitation. To further corroborate this idea, we defined the effective exciton number as the value $\langle N \rangle$ should take to account for the measured initial bleach. In Figure 6d, we compare the measured stimulated
emission spectra after correction for photo-induced absorption with the spectra predicted by the Stokes-shift model for this effective exciton number. In that case, a more consistent description of the experimental gain spectrum is obtained, even if stimulated emission is still overestimated at higher exciton numbers. We therefore conclude that introducing a Stokes shift in the state-filling model introduced before to describe optical gain in colloidal CdSe-based QDs can provide an apt description of optical gain in InP/ZnSe QDs.

Discussion

As shown in Figure 3, a state-filling model can provide a comprehensive description of the different aspects of the band-edge bleach that involves a consistent oscillator strength for absorbing and emitting transitions, provided that the hole degeneracy $g_h$ takes a sample-dependent value between 5 and 9. The contribution of both the delocalized electron and the delocalized hole to the transient absorption is corroborated by the presence of bleach bands that involve states at the InP valence-band edge but not at the conduction-band edge, and by the development of optical gain with a net oscillator strength – after correction for the loss of electron-hole pairs – in line with the predictions of a state-filling model. We thus conclude that in the case of the InP/ZnSe and InP/ZnSe/ZnS QDs synthesized for this study, both absorbing and emitting transitions – spontaneous and stimulated – are related to the formation or recombination of band-edge excitons, not unlike the state-of-the-art understanding of these transitions in CdSe-based QDs.\textsuperscript{3–5} In line with this outcome, we do not assign the Stokes shift of 80–90 meV to emissive transitions involving shallow traps,\textsuperscript{30} but rather to intrinsic relaxation properties of the exciton in InP-based QDs, for example due to exciton-phonon coupling. Note that such a strong coupling of the exciton emission to phonons was also observed through fluorescence line narrowing experiments at cryogenic temperatures,\textsuperscript{29,33} and could be related to the small offset between the InP and ZnSe valence band levels, as argued previously for CdSe/CdS QDs with a similarly small offset between the conduction-band states.\textsuperscript{51}
As outlined already in the literature, exciton-phonon coupling can be highly beneficial for the development of net stimulated emission in colloidal QDs. Figure 7 illustrates the gist of this reasoning, where state filling is combined with a simplified description of exciton-phonon coupling along a single atomic configuration coordinate Q. The starting point is that exciton-exciton Coulomb interaction and exciton-phonon coupling both induce a cascade of shifted exciton lines with increasing exciton number. When only Coulomb shifts are operational, transitions in

![Diagram of electron and hole levels in a quantum dot](image)

**Figure 7:** Impact of exciton-exciton (Coulomb) and exciton-phonon coupling (Stokes) induced shift on QD absorption spectra. (a) Representation of the state-filling model, including the labels used for describing the relevant transitions. (b) Representation of the total energy of a QD along a coordinate axis. The different lines pertain to \( E_0(Q) \) the unexcited QD, \( E_X(Q) \) the QD holding one electron-hole pair, and \( E_{2X}(Q) \) the QD holding two electron-hole pairs. The dashed line represents the energy \( E_{2X}(Q) \) in the absence of Coulomb interaction. Shifts caused by \( \Delta_X \) exciton-phonon coupling and \( \Delta_{2X} \) exciton-exciton interaction are indicated. The lines are drawn assuming \( \Delta_{2X} = 2\Delta_S \). (c-e) Spectra showing the contributions of \( A \) red band-edge absorption and \( E \) blue stimulated emission for QDs with different exciton numbers as indicated by the first subscripted number in the case of (c) Coulomb-shifts only, (d) Stokes shifts only and (e) counteracting Coulomb and Stokes shifts. Spectra are artificially narrowed for clarity and calculated assuming \( g_h = 2 \). (f-h) The same, calculated assuming \( g_h = 9 \).
Table 3 Overview of spectral descriptors relevant for net stimulated emission for the 4 InP-based QDs samples in this study, including \( \langle G_{\text{max}} \rangle \) the maximum gain, corrected for photo-induced absorption, (PLQY) the photoluminescence quantum yield, and \( k_{2X} \) the biexciton Auger recombination rate. \( G_{\text{max}} \) is expressed relative to the exciton peak absorption. All transient absorbances are determined at 2 ps probe delay and an exciton number \( \langle N \rangle = 5.0 \).

<table>
<thead>
<tr>
<th>sample</th>
<th>( G_{\text{max}}/A_{X,\text{max}} )</th>
<th>PLQY (%)</th>
<th>( k_{2X} ) (ps(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.20</td>
<td>45</td>
<td>0.0103</td>
</tr>
<tr>
<td>B</td>
<td>0.16</td>
<td>72</td>
<td>0.0120</td>
</tr>
<tr>
<td>C</td>
<td>0.14</td>
<td>88</td>
<td>0.0158</td>
</tr>
<tr>
<td>D</td>
<td>0.08</td>
<td>60</td>
<td>0.0132</td>
</tr>
</tbody>
</table>

absorption and stimulated emission that connect the same two exciton numbers \( N \) and \( N + 1 \) have the same transition energy. Taking \( g_e = 2 \), this means that only stimulated emission from the tri-exciton \( \langle N \rangle = 3 \) will be unopposed by absorption, see Figure 7c. Through exciton-phonon coupling, on the other hand, transitions starting from a QD with a given exciton number occur at the same energy. As a result, also stimulated emission from the biexciton will not be countered by absorption, see Figure 7d. Moreover, the different relation between the exciton number and the Coulomb or exciton-phonon coupling induced shifts makes that a repulsive Coulomb interaction can systematically shift transitions in absorption to the blue of the stimulated emission band. As a result, already stimulated emission from the single exciton can be free of counteracting absorption, see Figure 7e. While this point was made for exciton/biexciton combinations in the literature,\(^{50} \) we show in Supporting Information S9 that the same reasoning applies to higher order multi-excitons, a result that underpins our use of the Stokes-shift model with two fixed bands in Figure 6.

The analysis of the transient absorbance spectra of InP/ZnSe QDs shown in Figure 6 indicates that these QDs closely follow the predictions of a state-filling model under the condition where the biexciton Coulomb repulsion almost fully counteracts the Stokes shift. Even so, the considerable effective degeneracy we found for the valence-band edge of InP/ZnSe QDs tempers the positive
impact of this interplay between Stokes and Coulomb shifts on optical gain. As shown in Figure 7f-g, stimulated emission by the exciton and the biexciton are relatively weak when $g_h = 9$, only attaining 5.5 and 22% of the band-edge absorption, respectively. Therefore, especially the single-exciton gain is easily countered by spurious photo-induced absorption processes and line broadening, which results in considerable overlap between the shifted stimulated emission spectrum and the absorbance spectrum. As a result, net stimulated emission in InP/ZnSe QDs is still related to biexcitons and only occurs for the samples analyzed here when $\langle N \rangle > 1.0$. Under such conditions, the rapid Auger recombination with rates in the range $0.01 - 0.015$ ps$^{-1}$ will be an issue for practical applications, as it was for the first generation of CdSe-based QDs.$^{52}$ Moreover, the larger the hole degeneracy, the higher the exciton number needed to reach the highest possible material gain. Here, a second issue is the difficulty of InP/ZnSe QDs to preserve multi-excitons after photo-excitation with high intensity light pulses. While the underlying loss channels are unknown, the result is a material gain spectrum that only reaches $\sim 20\%$ of the original band-edge absorption regardless of pump power for the best sample we analysed, see Table 3. Next to the maximal gain $G_{\text{max}}$ attained at a nominal exciton number $\langle N \rangle = 5$ and a probe delay of 2 ps, Table 3 lists the photoluminescence quantum yield and the biexciton Auger recombination rate for the different InP/ZnSe and InP/ZnSe/ZnS QDs prepared for this study. Note that these samples were originally ordered by a decreasing contribution of the ZnSe-shell absorbance, which we use as a measure for the volume of ZnSe in these different QDs. On the other hand, $G_{\text{max}}$ will be lower the more a QD sample suffers from instantaneous multi-exciton loss.

According to the numbers in Table 3, we find that $G_{\text{max}}$ decreases in line with the volume of ZnSe, while a clear correlation with the photoluminescence efficiency is absent. This suggests that charge-carrier trapping at the core/shell interface, rather than at the QD outer surface, limits the development of net stimulated emission in InP/ZnSe QDs. Possibly, better strain relaxation by thicker ZnSe shells partially mitigates problems of interfacial charge-carrier trapping. On the other
hand, recent theoretical work indicated that the electronic properties of InP/ZnS and InP/ZnSe core/shell QDs might be extremely sensitive to the actual interface structure, and also experimental studies showed that the selective oxidation of the InP/ZnSe core/shell interface can strongly reduce non-radiative recombination of electron-hole pairs. In addition, the data in Table 3 also indicate that within the two subsets of InP/ZnSe and InP/ZnSe/ZnS QDs, the samples showing the highest gain also have slower Auger recombination. This correlation between a better performing core/shell interface in terms of stimulated emission and slower Auger recombination suggests that not unlike the case of CdSe/CdS QDs, engineering the InP/ZnSe interface can help enhancing key characteristics for QD stimulated emission, such as the preservation of multiple electron-hole pairs and the suppression of Auger process.

**Conclusions**

We studied the properties of photo-excited InP/ZnSe and InP/ZnSe/ZnS QD samples using femtosecond transient absorption spectroscopy. From the experimental data, we deduced the alignment of the single-electron band-edge states in the InP core and the ZnSe shell and quantified biexciton Auger recombination rates at $0.01 - 0.015 \text{ ps}^{-1}$. Moreover, we found that for exciton numbers up to 1.5–2.0, all aspects of the band-edge bleach and the radiative exciton recombination can be consistently described by state filling of the band edges by photo-generated electrons and holes. Accordingly, we demonstrated that net stimulated emission occurs at exciton numbers $\langle N \rangle > 1.0$, which leads at higher exciton numbers to broad gain band that overlaps with the photoluminescence spectrum. We interpret the stimulated emission characteristics, starting from the notion that the Stokes shift between exciton absorption and emission greatly exceeds the net biexciton shift. This idea can quantitatively account for the observed behavior where the exciton absorption line gradually diminishes, while a stimulated emission band coinciding with the exciton photoluminescence gradually increases with increasing exciton number. While such a stimulated emission mechanism could give rise to single exciton gain, the relatively broad
emission line, the relatively large hole degeneracy and the occurrence of photo-induced absorption make that net stimulated emission still results from biexcitons or higher-order multi-excitons, even if the observed threshold is surprisingly low. Here, an issue of the InP/ZnSe QDs studied here is the rapid loss of multi-excitons, possibly related to nearly instantaneous hole trapping. Hence, to make InP/ZnSe QDs fully exploit strong exciton-phonon coupling and attain a low gain threshold and a high material gain, further progress is needed to narrow the emission line, suppress the initial loss of electron-hole pairs, and slow down Auger recombination. In particular the latter two aspects could be attained by a more careful engineering of the core/shell interface.

Materials and Methods

Synthetic Methods

Chemicals. Indium(III)chloride (99.999%), tris(diethylamino)phosphine (97%), dodecane-thiol (≥ 98%), triethylamine (≥ 99%) and zinc oxide (99.999%) were purchased from Sigma-Aldrich. Zinc(II)chloride (≥ 98%) was obtained from Merck. Tri-n-octylphosphine (> 97%) and sulfur powder (99.999%) were collected from Strem Chemicals. Selenium powder 200 mesh (99.999%), oleic acid (technical 90%), trifluoroacetic acid (99%), trifluoroacetic anhydride (> 99%) and octadecene (technical 90%) were acquired from Alfa Aesar. Acetonitrile (> 99.9%) and tetrabutylammonium hexafluorophosphate (98%) were purchased from VWR. Methanol was obtained from Fisher Chemicals. Oleylamine (80-90%), calcium(II)hydride (93%) and zinc acetate (99%) were purchased from Acros Organics. Acetone (99.5%), 2-propanol (99.7%) and anhydrous toluene (≥ 99.8%) were purchased from Chem-Lab Analytical. Oleylamine and octadecene were dried over calcium(II)hydride, degassed via a vacuum distillation and stored over molecular sieves in a nitrogen-filled glovebox prior to use. All other chemicals were used without further purification.

Zinc(II)Oleate Synthesis. We used a procedure proposed by Dhaene et al. for the formation of
zinc oleate. More specifically, 3.66 g (45 mmol) of zinc oxide was mixed in 20 mL (383 mmol) of acetonitrile and, while cooled, 6.36 mL (45 mmol) of trifluoroacetic anhydride and 0.69 mL (9 mmol) of trifluoroacetic acid were added. A clear and colourless solution was obtained upon reaching room temperature. This zinc trifluoroacetate solution was added to a mixture of 25.55 g (90.45 mmol) of oleic acid, 10.29 g (101.7 mmol) of triethylamine and 180 mL (2.351 mol) of 2-propanol resulting in the formation of a white precipitate. Dissolution of the product occurred at reflux temperature and a following slow cooling to -20°C leads to white crystals which were filtered off and washed with cold methanol. The synthesized powder was dried under vacuum and a chemical yield of 94% is obtained.

Colloidal synthesis of InP/ZnS QDs. The procedure is based on the method previously published by Tessier et al. To start the synthesis, 50 mg (0.23 mmol) of indium(III)chloride, as indium raw material, and 150 mg (1.10 mmol) of zinc(II)chloride, as zinc raw material, were mixed in 1.5 mL (7.58 mmol) of anhydrous oleylamine. The mixture was stirred and degassed at 120°C for an hour and then heated to 180°C under inert atmosphere. Upon reaching 180°C, 0.25 mL (0.91 mmol) of tris(diethylamino)phosphine, transaminated with 1 mL (5.05 mmol) of anhydrous oleylamine, was quickly injected in the reaction mixture described above and the InP nanocrystal synthesis proceeded. After 30 minutes, the dispersion was cooled to 120°C and 60 mg (0.16 mmol) of tetrabutylammonium hexafluorophosphate, 0.15 mL (8.33 mmol) of water and 1 g (1.58 mmol) of zinc(II)oleate mixed in 1 mL (3.03 mmol) of oleylamine and 2 mL (6.25 mmol) of 1-octadecene where added as a surface treatment prior to ZnS shell growth. Subsequently, the mixture was stirred and degassed for an hour. Afterwards, 0.8 mL of a stoichiometric TOP-S (2.24 M) solution was injected and the temperature was raised to 300°C. At this temperature, the shell growth went on for one hour. Following on the reaction, the temperature had been set at 240 C and 0.5 mL (2.09 mmol) of dodecanethiol was swiftly injected. Ten minutes later, the reaction was stopped by cooling down the mixture. InP/ZnS QDs were then precipitated once using acetone, redispersed in toluene and stored in a N₂-filled glovebox.
Colloidal Synthesis of InP/ZnSe QDs. Analogous to the InP/ZnS QD synthesis, 50 mg (0.23 mmol) of indium(III)chloride, as indium raw material, and 150 mg (1.10 mmol) of zinc(II)chloride, as zinc raw material, were mixed in 2.5 mL (7.58 mmol) of technical oleylamine. The mixture was stirred and degassed at 120°C for an hour and then heated to 180°C under inert atmosphere. Upon reaching 180°C, 0.25 mL (0.91 mmol) of tris(diethylamino)phosphine, transaminated with 1 mL (5.05 mmol) of anhydrous oleylamine, was quickly injected the reaction mixture described above and the InP nanocrystal synthesis proceeded. After 30 minutes, the dispersion was cooled to 120°C and 60 mg (0.16 mmol) of tetrabutylammonium hexafluorophosphate, 0.15 mL (8.33 mmol) of water and 1 g (1.58 mmol) of zinc(II)oleate mixed in 1 mL (3.03 mmol) of oleylamine and 2 mL (6.25 mmol) of 1-octadecene where added as a surface treatment prior to ZnSe shell growth. Subsequently, the mixture was stirred and degassed for an hour. Afterwards, 0.8 mL of a stoichiometric TOP-Se (2.24 M) solution was injected and the temperature was raised to 330°C. At this temperature, the shell growth went on for 28 minutes. Following on the reaction, the temperature had been set at 240°C and 0.5 mL (2.09 mmol) of dodecanethiol was swiftly injected when passing 300°C. Ten minutes later, the reaction was stopped by cooling down the mixture. InP/ZnSe QDs were then precipitated once using acetone, redispersed in toluene and stored in a N₂-filled glovebox.

Colloidal Synthesis of InP/ZnSe/ZnS QDs. InP/ZnSe/ZnS QDs were synthesized following the method described above for InP/ZnSe QDs, with an additional step for the ZnS outer shell formation. Subsequent to the ZnSe shell growth, the reaction mixture was cooled down to 120°C, after which 200 mg (1.1 mmol) of zinc(II)acetate was added and the mixture was stirred and degassed for one hour. Consecutively, 0.5 mL of a stoichiometric TOP-S (2.24 M) solution was injected and the temperature was raised to 300°C. After one hour of ZnS shell growth, the temperature had been set to 240°C and 0.5 mL (2.09 mmol) of dodecanethiol was injected. Ten minutes later, the reaction was stopped by cooling down the mixture to room temperature. InP/ZnSe/ZnS QDs were then precipitated once using acetone, redispersed in toluene and stored
in a N₂-filled glovebox.

**Pump-probe Spectroscopy**

Samples were excited using 120 femtosecond pump pulses at 2.583 eV (480 nm), created from the 800 nm fundamental of an amplified laser system operating at 1 kHz (Spitfire Ace, Spectra Physics) through non-linear conversion in an OPA (Light Conversion TOPAS). Probe pulses were generated in a thin calcium fluoride crystal using the 800 nm fundamental. The pulses were delayed relative to the pump using a delay stage with maximum delay of 6 ns. The probe spectrum in our experiments covers the UV-VIS window from 400 nm up to 750 nm. The pump beam is continually chopped at a frequency of 500 Hz. The different samples were dispersed in an optically transparent solvent (toluene) and continuously stirred to avoid charging or photo-degradation. The sample concentration was taken so as to obtain an optical density of ~ 100 mOD at the pump wavelength, which constitutes an optimal trade-off between signal intensity at the band-edge transitions and limited absorption at the pump wavelength as to assure a uniform pumping of the sample.

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**Supporting Information Available**

The Supporting Information provides additional material concerning (S1) characterization of the InP/ZnSe and InP/ZnSe/ZnS QDs, (S2) the determination of exciton numbers, (S3) the analysis of specific TA features, (S4) global fits of the band-edge bleach transients, (S5) the state-filling model, (S6) the analysis of the bleach quantities for all samples, (S7) theoretical estimates of the absorption cross section, (S8) the non-linear absorption at long pump-probe delays, and (S9) the determination of transition energies including Stokes shifts and Coulomb shifts.
Notes

The authors declare no competing financial interest.
References


Graphical TOC Entry