Polaronic quantum confinement in bulk CsPbBr₃ perovskite crystals revealed by state-resolved pump/probe spectroscopy

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Disorder is intrinsic to weakly bound ionic systems and gives rise to specific electronic processes. In recently developed perovskite ionic crystals, this dynamic lattice disorder is inferred to give rise to properties of interest, such as defect tolerance. Here, the elementary excitation of interest is the polaron, a localized lattice distortion. We employ state-resolved pump/probe spectroscopy to monitor electron and lattice dynamics in bulk CsPbBr₃ perovskite crystals. The data report surprising line-shape dynamics. Rather than causing redshifting of the band edge exciton, polaron formation gives rise to confinement induced dynamical processes leading to a blueshift in the band edge bleach feature. In these ionic nanocrystals, the formation of quantum confined excitons arises from the polaronic potential, as opposed to physical confinement in conventional covalent quantum dots, resulting in an excitation of a quantum confined exciton polaron. This state may represent an alternative quasiparticle.

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I. INTRODUCTION

Semiconductor perovskites have remarkable optical properties that have generated much interest. What is interesting is their defect tolerance made possible by a soft lattice that supports polaron formation. While polarons are known to impact their properties, what is missing is their impact upon the initial excitonic properties of absorption and relaxation. We present pump/probe spectroscopy with sufficient time resolution to observe how polarons couple to excitons and control the manner in which excitons relax and recombine. These experiments reveal that perovskites support an alternative state of quantum confined excitonic polarons. This state may represent a unique quasiparticle.

Recent interest has arisen in ionic semiconductors, as illustrated by semiconducting perovskites, due to their attractive electro-optical properties [1–4]. In the case of perovskites a key feature is their defect tolerance. This defect tolerance is inferred to be related to the glassy quality of an ionic lattice [5–8]. In this phonon glass electronic crystal, the elementary excitation of interest is the polaron [9–15]. The polaron is a localized lattice distortion associated with an electronic excitation. Ionic systems form polarons due to their glassy lattices. The electronic signature of polaron formation has been directly observed in two-dimensional electronic spectroscopy (2DES) of CsPbI₃ nanocrystals [16]. Other evidence for polaron formation comes from computational studies [10], transport measurements [9,17], time-resolved

x-ray scattering [18], and direct band mapping through angle-resolved photoemission spectroscopy [19]. Low-frequency, overdamped acoustic modes are responsible for the lattice reorganization, and these have been found in low-frequency, temperature dependent Raman spectroscopy across all crystal phases of CsPbBr₃ and CH₃NH₃PbBr₃ [20]. In contrast, covalent systems couple to the lattice via delocalized phonons [21–23] that dissipate heat to acoustic phonons and eventually the nanocrystal surface ligands [24]. Exactly how the dynamic disorder of ionic semiconductors confers optical and electronic properties is of great contemporary interest. One desires direct spectroscopic probing of how the energies are derived from the polaron dynamics. The salient ideas of electron-lattice coupling spanning covalent to ionic lattices are illustrated in Fig. 1. CdSe nanocrystal QDs present the covalent limit. Their relatively narrow size dispersion and good electronic properties make them an ideal sample for comparison. Their response is shown in Figs. 1(a)–1(f). One observes coherent lattice dynamics and the response of a stiff covalent crystal. Figure 1(a) shows the linear spectroscopy of absorption and emission. With QDs one has pronounced quantum confinement effects apparent in the simple linear spectroscopy, due to physical confinement of the exciton. In covalent QDs, the electronic excitations couple to lattice modes via coherent phonons [Fig. 1(b)]. Illustrated is a polar optical phonon. Figure 1(c) is a schematic showing wave-packet dynamics on the electronic excited state potential energy surface (PES), shown in blue, after photoexcitation from the ground state PES (red). The response is described by normal modes: delocalized and coherent. These can be detected in 2DES as a coherent beating of the signal along the diagonal and antidiagonal linewidths [Fig. 1(d)]. This can also be detected in state-resolved pump/probe (SRPP) spectroscopy as in Fig. 1(e). These lattice modes undergo coherent motion which in the frequency domain corresponds to well-resolved Lorentzian peaks [Fig. 1(f)].

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FIG. 1. Schematic overview of electron-lattice dynamics in covalent and ionic systems. (a) Linear absorption and emission from CdSe nanocrystal quantum dots (QDs). (b) Schematic illustration of a polar optical phonon: a normal mode of the lattice. (c) Real-space representation of electron-lattice dynamics. Shown are displaced harmonic oscillators which can represent two electronic states with two different lattice modes. Ultrafast excitation creates a wave packet in the excited state which can undergo coherent motion (covalent). (d) In two-dimensional electronic spectroscopy (2DES), the line shape expands and contracts along diagonal axes as the wave packet moves along the upper state in (c). (e) Schematic illustration of time-domain observation of wave-packet motion. Inset: Cartoon of a ligand-passivated quantum dot. (f) Frequency-domain analog of the above. (g) Linear absorption and emission for CsPbBr₃ nanocrystals (NCs). Inset: TEM image of a single CsPbBr₃ NC. Scale bar is 5 nm. (h) Schematic illustration of a polaron: A local mode of the lattice. (i) Real-space representation of electron-lattice dynamics. Ultrafast excitation creates a wave packet in the excited state which can undergo diffusive motion (ionic). (j) In 2DES the line shape undergoes spectral diffusion as the wave packet incoherently relaxes to the energy minimum in (i). (k) Schematic illustration of time-domain observations of wave-packet motion. Inset: CsPbBr₃ crystal structure. (l) Frequency-domain analog of the above.

In contrast to CdSe, the response of ionically bound soft lattices, such as CsPbBr₃ perovskite nanocrystals (NCs), was recently shown to have isomorphisms [16] with liquid phase solvation dynamics [25,26]. Figure 1(g) shows the linear absorption and emission of these CsPbBr₃ NCs. The size of these crystals puts them in a bulk size regime, their edge length of 20 nm [inset of Fig. 1(g)] is significantly greater than the exciton Bohr diameter of 7 nm [27]; hence these can be

considered bulk systems. No quantum confinement is evident in the linear spectroscopy.

Bulk NCs were chosen to circumvent effects from physical confinement. Other studies have shown the important effect of strong quantum confinement on the linear and excited state spectroscopy of these perovskite NCs [28–31]. Another reason to work with bulk NCs, as opposed to thin films, is that one has better control over the number of excitations within some space—defined by the NC volume. Figure 1(h) shows the lattice reorganization after photoexcitation; instead of delocalized coherent motion, there is a local overdamped reorganization around the excited carrier. Wave-packet movement along the excited state PES is diffusive and incoherent [Fig. 1(i)]. This results in a response as shown in Figs. 1(j) and 1(k). In 2DES it is spectral diffusion, as the wave packet incoherently explores the energy landscape [Fig. 1(j)]. In SRPP it is a highly damped signal that quickly approaches the pure electronic response [Fig. 1(k)]. In an overdamped system with dynamic disorder, the local modes result in a broad spectral density as in Fig. 1(l).

Figure 2 shows an overview of the SRPP data in both systems. Figures 2(a)–2(d) show the response of CsPbBr₃ NCs, while CdSe QDs are shown in Figs. 2(e) and 2(f). Figure 2(a) shows the response after resonant band edge excitation for CsPbBr₃ NCs. There is a rapid shifting in the main bleach feature that is not apparent for CdSe nanocrystal QDs [Fig. 2(e)]. This rapid shift is completely hidden when pumping the sample at energies greater than the band gap, i.e., 3.1 eV [Fig. 2(b)]. With a higher-energy pump pulse, other signals are apparent, such as a broad, short-lived photoinduced absorption (PIA) to the red of the band edge, as seen in Figs. 2(b) and 2(e).

By monitoring the main bleach feature through time, it is possible to detect wave-packet motion along the excited state through modulations of the pump/probe signal. These are shown in Figs. 2(c) and 2(g), for CsPbBr₃ NCs and CdSe nanocrystal QDs, respectively. The electronic response [red line in Figs. 2(c) and 2(g)] is subtracted from the data (blue markers) to yield the lattice response (green line, right axis). The frequency space analog of the lattice response is shown in Figs. 2(d) and 2(f) for CsPbBr₃ NCs and CdSe nanocrystal QDs, respectively. In ionic CsPbBr₃ NCs the response is incoherent and diffusive. Such a response is shown by the overdamped response in Fig. 2(c) and the broad low-frequency response in frequency space. This response is akin to a spectral density of local phonon modes, rather than discrete vibrations. One sees such spectral densities commonly in liquids and glasses [25,32,33]. For covalent CdSe, the lattice response is coherent, as shown by the clear oscillations in Fig. 2(g), and well-resolved Lorentzian peaks in Fig. 2(h). Both systems can be modeled by a multimode Brownian oscillator [red lines in Figs. 2(d) and 2(h)]. Model details are presented in the Appendix.

II. RESULTS

The line-shape dynamics for both CsPbBr₃ and CdSe are quantified in Fig. 3. Details of the fitting procedure and example fits can be found in the Appendix. Figure 3(a) shows the evolution of the 2.42 eV bleach linewidth in CsPbBr₃. Initially

FIG. 2. Overview of state-resolved pump/probe (SRPP) data. Top row: CsPbBr₃ NCs. Bottom row: CdSe nanocrystal QDs. (a) SRPP data for CsPbBr₃ perovskite NCs with band edge excitation and (b) 3.1 eV excitation. (c) Band edge bleach dynamics (blue) and electronic response (red) following band edge excitation. Remaining dynamics are due to lattice reorganization (green). (d) Frequency-domain response of lattice (blue) and multimode Brownian oscillator model (red). (e) SRPP data for CdSe with 2.0 eV excitation and (f) 3.1 eV excitation. (g) Band edge bleach dynamics (blue) and electronic response (red) following band edge excitation. Remaining dynamics are due to lattice reorganization (green). (h) Frequency-domain response of lattice (blue) and multimode Brownian oscillator model (red).

the linewidth is limited by the pump pulse bandwidth of 24 meV. The peak subsequently broadens in the first picosecond, then continuously narrows over the next 200 ps. Figure 3(b) shows the relative movement of the bleach in CsPbBr₃. The peak rapidly blueshifts in the first picosecond,

redshifts very slightly over the next 20 ps, then remains static. This fast blueshift is entirely inconsistent with what one would expect from polaronic stabilization.

In CdSe QDs, the linewidth of the main bleach feature at 2.0 eV undergoes a very slight narrowing of ~ 1.5 meV over 200 ps [Fig. 3(c)] while the position of the bleach feature [Fig. 3(d), inset] blueshifts by ~ 2 meV over 200 ps. Both the line narrowing and blueshifting in CdSe can be attributed to the recombination of biexcitons. The biexciton signal appears as an additional bleach on the red side of the main bleach feature, determined by the biexciton binding energy and oscillator strength [34–36]. As biexcitons recombine in CdSe QDs with a timescale of ~ 2050 ps, this additional bleach disappears, leading to the observed narrowing and blueshift of the main bleach feature. For CsPbBr₃, the fast process in both the line broadening and blueshifting can be assigned to polaron formation [12,16]. The slow process of line narrowing in CsPbBr₃ NCs is an interesting observation that cannot be assigned to hot carriers because of the pump energy. We assign the observed line narrowing process in CsPbBr₃ to thermalization within an exciton fine structure. This invocation of fine structure is supported by bulklike [37,38] and quantum confined [39] single crystal photoluminescence (PL) measurements and well established semiconductor theory [40].

One might expect from polaron formation to observe a redshift of the principal bleach feature, as opposed to the observed blueshift. The blueshift occurs because the effect of polaronic confinement will shift the ground state exciton to higher energies, yielding a blueshift in the transition energy, while polaron formation shifts the state to lower energies. The competing nature of these processes is depicted in Fig. 4. Figure 4(a) shows the difference between a polaron and a confined polaron-exciton: A typical polaron will have a small binding energy and produce a single bound state. Due to confinement, the polaron-exciton has a deeper potential well, and

FIG. 3. Spectral line-shape dynamics from SRPP spectroscopy. Top row: CsPbBr₃ perovskite NCs. Bottom row: CdSe QDs. (a) Change in linewidth and (b) spectral mean energy of the band edge bleach in CsPbBr₃. Cartoon: CsPbBr₃ unit cell. (c) Change in linewidth and (d) spectral mean energy of the band edge bleach in CdSe NCs. Cartoon: Ligand-coated CdSe QD. Insets in (a)–(d) Long time dynamics of respective features.

FIG. 4. Effect of polaron formation and confinement on line-shape dynamics. (a) A typical polaron is weakly bound with only one bound state. A quantum drop will have a spectrum of bound states, and possibly a richer fine structure within those states. (b) Confinement shifts the ground exciton state to higher energy. (c) Polaron formation decreases exciton energy through lattice coupling, described through the frequency-frequency correlation function. (d) The total effect is an initial fast blueshift followed by a slow relaxation among fine structure states.

produces multiple bound states with a richer fine structure. Figure 4(b) depicts the effect of confinement; a narrowing potential well will shift quantum levels to higher energies. Polaron formation will reduce the potential energy of the exciton, transferring that energy to the lattice, as in Fig. 4(c). Polaron formation can be described through the frequency-frequency correlation function, which relates a transition frequency at time zero to that transition frequency at a later time t . The sum of these effects is shown in Fig. 4(d), a rapid blueshift followed by a slow thermalization.

Further evidence for polaronic quantum confinement effects can be observed in hot carrier relaxation dynamics and multicarrier recombination kinetics [41–44]. These two processes are vastly different in bulk and confined systems, as different relaxation channels gain or lose importance [45,46]. In quantum confined structures excitons relax through unimolecular Auger enhanced paths [47] as opposed to bimolecular [48] or trimolecular paths [41]. This makes Auger processes a sensitive probe of quantum confinement effects.

Figures 5(a) and 5(b) show the relaxation of excited charge carriers. To observe relaxation of single carriers, the evolution of the pump/probe signal is monitored for both 2.4 and 3.1 eV pump energies simultaneously. A state-resolved approach controls for relaxed state dynamics by subtracting the pump/probe signal with resonant band edge excitation from the pump/probe signal from a more energetic pump [46].

FIG. 5. Evidence for quantum confined carrier dynamics in CsPbBr₃ perovskite NCs. (a) The time dependent survival probability revealed by SRPP. Signal measured corresponds to electron population. Model discussed in text. (b) Evidence of electron to hole energy transfer following dynamic confinement. Cartoons: An initially hot electron population cools through energy transfer to hot holes (left). After electron relaxation, holes relax through phonon coupling to the lattice (right). (c) Multiexciton recombination dynamics (red markers). Shown are fits to a model assuming a maximum multiplicity of 3 (black lines). (d) Amplitudes for the model presented in (c).

This yields a $\Delta\Delta OD$ trace that directly tracks the difference between highly excited carriers and band edge carriers to yield state specific relaxation rates [49].

The pump/probe spectral signatures depend on the state of the exciton. It has been previously shown in II-VI NCs that the band edge bleach reflects electron population [50]. The subband edge PIA is due to absorption from a ground state exciton to a biexciton. Thus dynamics in the PIA reflect exciton dynamics [43,44]. These spectral signatures allow for the disentangling of relaxation channels. Here, the bleach at 2.44 eV is used to follow electron relaxation [Fig. 5(a)]. With a 3.10 eV pump energy electrons are pumped relatively high in the conduction band, and relax through a complicated pathway described by quantum kinetics. A simple model is proposed here, where the electrons initially relax rapidly through a dense manifold of states. Other models can be found in the literature [51,52]. As the electrons approach the band edge, the density of accessible states decreases, causing relaxation to slow down. Model details can be found in the Appendix. The fit returns the expected result; an initially fast rate of $\sim 9 \text{ ps}^{-1}$ slows down over 300 fs to a final rate of $\sim 4 \text{ ps}^{-1}$. This nonexponential relaxation is a sign of bulklike decay becoming quantum confined, as the polaronic confinement dynamically creates sparse energy levels.

The dynamics of the subband gap PIA reveals observations on excitons in these perovskites. Figure 5(b) shows the $\Delta\Delta OD$ signal at 2.36 eV. Here both a growth and a decay are apparent. In analogy to previous work in CdSe QDs, the growth is a sign of electron to hole energy transfer through two-particle intraband Auger relaxation [46]. A growth in this signal is not possible without energy transfer from hot electrons to holes. The growth is well resolved; as can be seen

in Fig. 5(b), the fit is performed only after 100 fs. The fast rise is followed by a slower decay through phonon coupling, as is observed in physically confined II-VI nanocrystal QDs [45].

Multiexciton recombination kinetics can further reveal the presence of quantum confinement effects [41,42,53,54]. Figures 5(c) and 5(d) show the presence of multiexcitons through the decay of the bleach at 2.42 eV after resonant band edge pumping. Figure 5(c) shows the bleach signal under increasing pump fluence. At low fluence the ΔOD signal is mostly due to single excitons (X). As fluence increases biexcitons and triexcitons become sequentially more populated and contribute to the signal. These each have their own decay constant, allowing for a fairly simple fitting procedure to extract relative populations of each excitonic species. Model details and fit results can be found in the Appendix. Figure 5(d) shows the amplitudes of each component as a function of fluence. There is a clear saturation behavior for both excitons and biexcitons, direct evidence of the existence of confined excitons. Recent results from time-resolved PL have also shown evidence for quantum effects in bulk sized perovskite NCs [55].

III. CONCLUSIONS

Given that the physical size of these NCs is ~ 20 nm, and the exciton Bohr diameter is ~ 7 nm, the question naturally arises as to the origin of the observed confinement effects. In short, the polaronic potential causes confinement. Basic polaron properties can be derived from the static and optical dielectric constants, phonon energies, and effective mass of the bare carriers [56]. The electron-phonon coupling constant α describes how well a charge is screened by the lattice. This is given by Eq. (1):

$$\alpha = \frac{e^2}{\hbar} \frac{1}{4\pi\epsilon} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \sqrt{\frac{m^*}{2\hbar\omega_{LO}}}, \quad (1)$$

where ϵ is the vacuum dielectric constant, ϵ_∞ and ϵ_0 are the optical and static dielectric constants, m^* is the carriers' reduced mass, and ω_{LO} is the LO phonon frequency. This coupling constant determines the polaron binding energy, according to Eq. (2):

$$\frac{\Delta E}{\hbar\omega_{LO}} \approx -\alpha - 0.0159\alpha^2. \quad (2)$$

Such an analysis yields polarons with a binding energy of ~ 47 meV [9] for CsPbBr₃, in agreement with experimental results [16]. The polaron diameter is further found to be on the order of 5 nm [10], yielding weak confinement for carriers. This value is in line with computational work on MaPbX₃ [57].

These SRPP data reveal that excitation of band edge carriers in bulk perovskite NCs promptly leads to polaron formation on the ~ 300 fs timescale, consistent with many prior reports [10,12,16]. What is unique is the observation that polaron formation gives rise to confinement of these charges. The polaron's binding energy of ~ 47 meV and the diameter of ~ 5 nm create polaronic confinement. This polaronic confinement leads to quantum confined polaron-excitons, in analogy with physical confinement yielding quantum dots.

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APPENDIX

1. Synthesis of CsPbBr₃ NCs

Lead(II) bromide (PbBr₂, $\geq 98\%$), cesium carbonate (Cs₂CO₃, $\geq 99.9\%$), 1-octadecene (ODE, $\geq 70\%$), diisooctylphosphonic acid (DIOPA, $\geq 70\%$), oleylamine (OAm, $\geq 70\%$), and methyl acetate (MeAc, 99%) were purchased from Sigma-Aldrich.

The perovskite NCs were synthesized using a method modified from Protesescu *et al.* [27] and Wang *et al.* [58]. The Cs precursor was prepared in a three-neck flask with Cs₂CO₃ (50 mg), DIOPA (0.5 ml), and ODE (2.5 ml). PbBr₂ (140 mg), OAm (1 ml), DIOPA (1 ml), and 1-octadecene (10 ml) were added to the reaction three-neck flask. Both mixtures were briefly brought under vacuum at room temperature. The temperature was increased to 150 °C under argon until all solids were dissolved. The temperature was then decreased to 120 °C. The flasks were then further degassed for 20 min under vacuum. Under argon, the temperature was increased to 140 °C. Then 0.5 ml (0.1 mmol Cs) of the Cs precursor was injected into the reaction flask, and the reaction

FIG. 6. Further linear characterization of CsPbBr₃ NCs. (a) Linear absorption (black), emission (blue), excitation (red), and X1 pump (filled gray curve) spectra. (b) TCSPC of sample emission (black). Data modeled with a biexponential decay (red) convolved with the instrument response function (blue).

FIG. 7. Additional TEM images of the IPNCs studied here. Scale bars are 20 nm (a) and 10 nm (b).

was quickly quenched in an ice-water bath. Next 10–15 ml MeAc was added as an antisolvent and the sample was centrifuged at 12 000 rpm (21 000 G) for 10 min. The perovskite nanocrystals (Perovskite NCs) were subsequently redispersed in 5 ml toluene. Further centrifugation was done at 5000 rpm (8750 G) for 60 s to remove large NCs and precursors from the sample.

2. Linear characterization

The absorption, PL, and photoluminescence excitation (PLE) spectra were collected in 1 cm quartz cuvettes. The NC samples were dissolved in toluene and the solution was diluted ($OD \sim 0.05$) to minimize self-absorption. Steady state absorption measurements were performed on a Varian Cary 300 UV/Visible spectrophotometer. The PL and PLE spectra were measured on an Agilent Cary Eclipse spectrofluorometer. Transmission electron microscope (TEM) images were acquired on a Philips CM200 transmission electron microscope (TEM) (200 keV). Linear optical properties are shown in Fig. 6. TEMs are shown in Fig. 7.

3. State-resolved pump/probe spectroscopy

Ultrafast pulses are produced from a Coherent Legend Ti:sapphire regenerative amplifier system (1 kHz, 800 nm, 70 fs, 2.4 mJ). Eighty percent of the pulse energy is used to pump two OPAs, only one of which is used here. The remaining 20% is split at a 90/10 beam splitter to create a 3.1 eV pump (90% arm) and a white-light continuum (10% arm). The 3.1 eV pump is created in a BBO crystal cut for second-harmonic generation of 800 nm. The white light probe arm is created in a 1 mm sapphire plate, which passes through a prism compressor to correct for chirp. Each pump arm (2.4 and 3.1 eV) passes through a chopper and delay stage. The choppers operate at 333 Hz and are phased such that over three shots the sample is excited by pump 1, then the next shot by pump 2, and then not excited at all. By comparing the transmission of the unexcited sample to the transmission of the excited sample with the two independent pump beams, two pump/probe experiments can be performed in parallel. Dechirping of the pump/probe spectra is performed by detecting one wavelength at a time, and moving the delay stage

at each wavelength to compensate for residual chirp of the white light continuum. All experiments were carried out at room temperature.

State-resolved pump/probe spectroscopy (SRPP) enables clean unraveling of excited state processes in perovskites, and is compared to what has been done in CdSe NCs [59,35,21,60,61]. By spectrally tuning the pump pulse into resonance with specific states, one is better able to discriminate among excitonic processes [35,21,49,62]. Focusing on CsPbBr₃ NCs as opposed to CsPbBr₃ films enables benchmark comparison to well studied CdSe NCs, and it also enables working in a single excitation per particle regime.

4. Multimode Brownian oscillator

Due to the liquidlike properties of quantum drops [9] the interaction between the exciton and lattice in CsPbBr₃ NCs may be modeled using the well known theory of solute-solvent interactions [33,63]. The multimode Brownian oscillator model provides an analytical expression for the

FIG. 8. Model of linear absorption. (a) Linear absorption of CdSe nanocrystal quantum dots and fit to a sum of Gaussian peaks. (b) Fit residuals.

TABLE I. Fit parameters for linear absorption.

Parameter	A_{X1}	σ_{X1} (meV)	E_{0X1} (eV)	A_{X2}	σ_{X2} (meV)	E_{0X2} (eV)	A_{X3}	σ_{X3} (meV)	E_{0X3} (eV)	a	b	c
Value	0.68	34.2	1.9926	0.47	53.3	2.066	0.82	104	2.327	2.5	-8.9	8.0
Std. Err.	0.02	0.3	3×10^{-4}	0.01	1.2	2×10^{-3}	0.07	4.2	4×10^{-3}	0.3	1.1	1.0
Rel. Err. (%)	3	0.9	0.1	2	2.2	0.9	9	4	1.6	12	12	12

spectral density of a bath comprised of a series of vibrational modes. The spectral density $C(\omega)$ is given by the sum in Eq. (A1),

$$C(\omega) = \sum_j C_j(\omega) \propto \sum_j \frac{\lambda_j \omega_j^2 \omega \gamma_j}{(\omega_j^2 - \omega^2)^2 + \omega^2 \gamma_j^2}, \quad (\text{A1})$$

where ω_j , λ_j , and γ_j are, respectively, the frequency, coupling strength, and damping of the j th bath vibrational mode [64]. Raman spectra of bulk CsPbBr₃ reveal a series of vibrational modes at low frequency [20]. The bath may then be approximated as a continuous spectral density by using a series of underdamped ($\gamma_j = 0$) vibrational modes separated by a small frequency difference $d\omega$. If the coupling strength λ_j of these modes follows a Gaussian distribution, the sum simplifies to the form in Eq. (A2),

$$C(\omega) \propto \frac{\lambda}{\omega_0} \exp\left(-\frac{\omega^2}{\omega_0^2}\right), \quad (\text{A2})$$

where ω_0 is the central frequency of the distribution [64]. This spectral density is plotted in Fig. 2(d) in the main text and gives a tentative spectral density for liquidlike polaron formation in CsPbBr₃.

In contrast, the spectrum in Fig. 2(h) (main text) reveals two well defined peaks corresponding to the LO and LA phonons of CdSe. The spectral density of the bath in CdSe therefore does not call for a continuous solvationlike spectral density. The LO and LA phonons may be modeled with two underdamped Brownian oscillators following Eq. (A1), giving Lorentzian line shapes for the respective peaks with broadening defined by the damping parameters γ_j .

FIG. 9. The ΔOD spectrum of CdSe modeled by Eq. (A2). (a) Fit results. (b) Fit residuals.

5. Extracting line-shape dynamics in CdSe

To fit the pump/probe spectrum of CdSe NCs, one must first fit the linear absorption spectrum to extract the positions, widths, and relative amplitudes of excitonic peaks. The results of this fit are shown in Fig. 8. The model used is given in Eq. (A3). All parameters are allowed to vary at this stage. See Table I.

$$\Delta\text{OD}(E) = \sum_{i=1}^3 A_{Xi} \exp\left[\frac{-(E - E_{0Xi})^2}{2\sigma_{Xi}^2}\right] + a + bE + cE^2. \quad (\text{A3})$$

Using the best fit parameters from the fit to the linear absorption, the pump/probe spectrum can be fit to a model proposed previously [65]. This model is given by Eq. (A4):

$$\begin{aligned} \Delta\text{OD}(E) \propto & \sum_{i=1}^3 A_i \exp\left[\frac{-(E - E_{0i})^2}{2\sigma_i^2}\right] \\ & - A_1 \exp\left[\frac{-(E - E_{01})^2}{2\sigma_1^2}\right] \\ & + \alpha_1 \exp\left(\frac{-(E - (E_{01} - \Delta_1))^2}{2\sigma_1^2}\right) \\ & + \alpha_2 \exp\left(\frac{-(E - (E_{02} - \Delta_2))^2}{2\sigma_2^2}\right) \\ & + \alpha_3 \exp\left(\frac{-(E - (E_{03} - \Delta_3))^2}{2\sigma_3^2}\right). \quad (\text{A4}) \end{aligned}$$

The negative sum corresponds to ground state bleach, due to a depopulated ground state after excitation. The second negative term corresponds to stimulated emission from the first excited state to the ground state. The following three positive terms correspond to excited state absorption to a

FIG. 10. Fit results after allowing the $X1$ linewidth and peak position to vary as a function of time.

TABLE II. Binding energies and excited state absorption strengths from a fit of Eq. (A4).

Parameter	α_1/A_{X1}	Δ_1 (meV)	α_2/A_{X2}	Δ_2 (meV)	α_3/A_{X3}	Δ_3 (meV)
Value	0.69	3.2	0.732	7.7	0.94	18
Std. error	0.02	0.5	0.015	1.9	0.08	4
Rel. error (%)	3	14	2	25	9	22

manifold of biexciton states, with binding energies given by Δ_i and absorption α_i . These are the only values allowed to vary; the other parameters are fixed by the linear absorption. The result of this fit is shown in Fig. 9. The entire $\Delta OD(E, t)$ data set is used in a global fit to Eq. (A2). The returned values and their errors are reported in Table II.

These results are in line with those reported by Zhang *et al.* [65], who found binding energies of 3.4, 9.7, and 28.3 meV for the X_1X_1 , X_1X_2 , and X_1X_3 biexcitons, respectively. However, the CdSe nanocrystal quantum dots used in that study were slightly larger, with a band edge exciton energy of 1.96 eV.

At this stage the ΔOD spectrum is well described. Now the position and width of the $X1$ exciton is allowed to vary. This is translated to the stimulated emission and excited state absorption contributions as well. The only parameters allowed to vary in Eq. (A3) are E_{01} and σ_1 . The amplitude is fixed by normalizing each pump/probe spectrum. The fitting results at several pump/probe delays are shown in Fig. 10.

6. Fitting the B1 line shape in CsPbBr₃ NCs

The B1 line shape was taken to be due to single excitons only, due to the low excitation fluence and the resonant pump energy. As a simple model a Gaussian peak shape was assumed, and only energies between 2.3 and 2.5 eV were used in the fit. A few example fits are shown in Fig. 11.

As is shown in Fig. 12, the fast dynamics is completely hidden for a 3.1 eV pump. Hot carriers are created and obfuscate the polaron signal, due to the broad thermal distribution at energies above the band edge. See Table III.

FIG. 11. Fitting the B1 line shape after band edge pump of CsPbBr₃ NCs. B1 line shape (circles) and Gaussian peak fits (solid lines) for the B1 feature for three pump/probe delays.

7. Electron relaxation

The relaxation of initially hot electrons is nonexponential; instead there is a time varying rate of relaxation. Such an approach is more general than a simple mono- or biexponential decay. This is modeled according to Eq. (A5).

$$\frac{dn_e}{dt} = -k(t)n_e. \quad (\text{A5})$$

Integrating Eq. (A5) yields the time dependent excited electron population, which is reflected in the ΔOD signal.

$$n_e(t) = n_{e0} \exp \left[- \int_0^t k(t') dt' \right]. \quad (\text{A6})$$

A model for $k(t)$ must now be proposed. For the sake of simplicity, we used a linearly varying model, that begins at some value k_{start} at $t = 0$, and ends at some value k_{final} at $t = t_{\text{stop}}$, i.e.,

$$\begin{aligned} &= k_{\text{start}}, \quad t \leq 0, \\ k(t) &= \frac{k_{\text{stop}} - k_{\text{start}}}{t_{\text{stop}}} t + k_{\text{start}}, \quad 0 \leq t \leq t_{\text{stop}}, \\ &= k_{\text{stop}}, \quad t \geq t_{\text{stop}}. \end{aligned} \quad (\text{A7})$$

FIG. 12. Pumping CsPbBr₃ NCs at 3.1 eV. (a) Gaussian fits to the B1 feature. (b) Gaussian center and linewidth over time.

TABLE III. Fitting parameters for multiexponential curves in Fig 3.

	A_1	τ_1	A_2	τ_2	A_3	τ_3	Offset
Position	-7.05 ± 0.16 meV	532 ± 17 fs	0.708 ± 0.047 meV	37 ± 9 ps	—	—	2.428 eV
Linewidth	-2.5 ± 0.8 meV	540 ± 150 fs	2.4 ± 0.9 meV	1.7 ± 0.4 ps	5.89 ± 0.11 meV	101 ± 5 ps	19.13 ± 0.13 meV

The three parameters used to fit the trace in Fig. 4(a) were k_{start} , k_{stop} , and t_{stop} . There was no bias in initial parameters or limits to return a decelerating rate of relaxation.

8. Auger fitting

The auger recombination data were modeled to a three-step cascade, namely, triexcitons recombining to form biexcitons, which then recombine to form single excitons. Single excitons decay with a lifetime of 7 ns, based on time-correlated single photon counting measurements [Fig. 6(b)]. The model used is given by Eq. (A8):

$$\Delta\text{OD}(t) = A_{Xi} \exp\left(-\frac{t}{\tau_X}\right) + A_{XXi} \exp\left(-\frac{t}{\tau_{XX}}\right) + A_{XXXi} \exp\left(-\frac{t}{\tau_{XXX}}\right). \quad (\text{A8})$$

Each transient has an independent set of initial conditions, i.e., A_{Xi} , A_{XXi} , A_{XXXi} , and all of them share the three time constants τ_X , τ_{XX} , and τ_{XXX} .

9. Polaron model

The polaron parameters described in the text are found through a Fröhlich coupling of charges to optical phonons. The dimensionless parameter α is a measure of the strength of electron-phonon coupling, given by Eq. (A9),

$$\alpha = \frac{e^2}{\hbar} \frac{1}{4\pi\epsilon} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \sqrt{\frac{m^*}{2\hbar\omega_{\text{LO}}}}, \quad (\text{A9})$$

where ϵ is the vacuum dielectric constant, ϵ_∞ and ϵ_0 are the optical and static dielectric constants, m^* is the carriers' reduced mass, and ω_{LO} is the LO phonon frequency. Using this approach, perovskites have been found to have intermediate to large electron phonon coupling values in the range of 1.5–2.7 [10,66].

The value of α further determines the mass of the polaron. Due to the lattice dressing, polarons are always heavier than bare carriers or bare excitons. Their mass is given by Eq. (A10), in the limit of small α :

$$m_p \approx m^* \left(1 + \frac{\alpha}{6} \right). \quad (\text{A10})$$

Polaron radii are determined by carrier mass and phonon frequency alone, as given by Eq. (A11):

$$l_p = \sqrt{\frac{\hbar}{2cm^*\omega_{\text{LO}}}}. \quad (\text{A11})$$

Previous work puts this in the range of 2–5 nm [10,66].

The polaron binding energy was estimated according to Eq. (A12), taken from [67]. Using the optical phonon frequency of 4.07 THz and coupling constant α of 2.7 from [10], one finds a binding energy of 47 meV.

$$\frac{\Delta E}{\hbar\omega_{\text{LO}}} \approx -\alpha - 0.0159\alpha^2. \quad (\text{A12})$$

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