How the Polaronic Nature of Perovskite Nanocrystals Determines Multiexciton Properties

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Abstract

Perovskite nanocrystals are a new class of material that have drawn much interest for their high intrinsic photoluminescence quantum yields and simple syntheses. These APbX₃ nanocrystals are able to span the visible spectrum through halide composition: chloride emit blue while bromide and iodide emit green and red respectively. The green emitting APbBr₃ in particular have been focused on due to higher stabilities relative to the chloride and iodide species. Research into the properties of CsPbBr₃ has highlighted the polaronic nature as having a large effect on the electronic properties. The highly polar lattice of CsPbBr₃ causes the polaron to have this large impact. This contrasts the traditional II-VI and III-V semiconductor nanocrystals, such as CdSe, which have covalently dominated bonding.

This thesis summarises my work on the emissive properties of CsPbBr₃ nanocrystals. The first section focuses on the temperature dependent photoluminescence and how the nanocrystals used are bulk-like and not quantum confined (>10nm in edge length). This was done through Franck-Condon modeling which showed the photoluminescence was dominated by homogeneous broadening. This was vital for future work demonstrating that the polaron that forms around the exciton contributes to confining the exciton.

The second and third sections contain time resolved photoluminescence with high time resolution (3ps). The fitting of time resolved multi-excitonic spectra is the focus of the second section. Unconfined semiconductors should show little evidence of multiexcitons in the photoluminescence spectra. Therefore, polaronic confinement of excitons was invoked

to account for the confinement effects in a spatially unconfined nanocrystal. The third section was an extension of the second project with temperature dependence. With a focus on the fast multiexciton emission, the decay rates an quantum yields were calculated. The multiexciton emission was found to slow down and increase in brightness at low temperatures. This is the first report of the temperature dependence of Auger rates in perovskite nanocrystals.

The fourth section is a combination of analysis done in the previous three sections. With high time resolution and temperature dependence, the linewidth kinetics of the exciton was shown. This time dependence revealed fine structure of the exciton. The addition of a second exciton state allows additional Frank-Condon analysis to reveal the full linewidth temperature dependence. Additionally, Auger heating is shown using high fluences at 4K. As multiexcitons nonradiatively recombine, The lattice is heated which caused linewidth broadening.

Résumé

Les nanocristaux de pérovskite constituent une nouvelle catégorie de matériaux qui ont suscité un grand intérêt en raison de leurs rendements quantiques élevés de photoluminescence intrinsèque et de leur simplicité de synthèse. L'APbBr₃, qui émet dans le vert, a fait l'objet d'une attention particulière en raison de sa plus grande stabilité par rapport aux espèces chlorure et iodure. La recherche sur les propriétés du CsPbBr₃ a mis en évidence la nature polaire qui a un effet important sur les propriétés électroniques. Le réseau hautement polaire du CsPbBr₃ permet au polaron d'avoir un impact important. Cela contraste avec les nanocristaux semi-conducteurs II-VI et III-V traditionnels, tels que le CdSe, dont la liaison est dominée par la covalence.

Cette thèse résume mon travail sur les propriétés émissives des nanocristaux de CsPbBr₃. La première section se concentre sur la photoluminescence dépendante de la température et sur la façon dont les nanocristaux que j'ai synthétisés sont en vrac et non confinés quantiquement (>10nm en longueur de bord). Cela a été fait grâce à la modélisation de Franck-Condon qui a montré que la photoluminescence était dominée par un élargissement homogène. Ce résultat était essentiel pour les futurs travaux de notre groupe, qui montrent que le polaron qui se forme autour de l'exciton contribue à confiner l'exciton.

Les deuxième et troisième sections contiennent la photoluminescence résolue en temps avec une haute résolution temporelle (4ps). L'ajustement des spectres multi-excitoniques résolus en temps est le point central de la deuxième section. Les semi-conducteurs non confinés devraient montrer peu de signes de multiexcitons dans les spectres de photoluminescence. Par conséquent, le confinement polaronique des excitons a été invoqué pour expliquer les effets de confinement dans un nanocristal spatialement non confiné. La troisième section était une extension du deuxième projet avec la dépendance de la température. En se concentrant sur l'émission rapide des multiexcitons, les taux de décroissance et les rendements quantiques ont été calculés. On a constaté que l'émission multiexciton ralentit et augmente en brillance à basse température. Il s'agit du premier rapport sur la dépendance en température de l'émission Auger dans les nanocristaux de pérovskite.

La quatrième section est une combinaison des analyses effectuées dans les trois sections précédentes. Avec une haute résolution temporelle et une dépendance à la température, la cinétique de la largeur de ligne de l'exciton a été montrée. Cette dépendance temporelle a révélé la structure fine de l'exciton. L'ajout d'un deuxième état d'exciton permet une analyse Frank-Condon supplémentaire pour révéler la dépendance de la température de la largeur de ligne complète. De plus, le chauffage Auger est montré en utilisant des fluences élevées à 4K. Comme les multiexcitons se recombinent de manière non radiative, le réseau est chauffé, ce qui entraîne un élargissement de la largeur de ligne.

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Table of Contents

	Abst	actii	i
	Rés	méiv	'
	Ackr	owledgements	i
	List	f Figures	'iii
	List	f Tables	۲
1	Intro	duction 1	
	1.1	Semiconductor Properties	,
		1.1.1 Excitons	,
		1.1.2 Colloidal Semiconductors Nanocrystals	;
		1.1.3 Multi-photon Processes	;
	1.2	Lead Halide Perovskite Nanocrystals)
		1.2.1 Lead Halide Perovskites)
		1.2.2 Polarons)
		1.2.3 Perovskite Nanocrystal Synthesis	ŀ
		1.2.4 Properties	,
		1.2.5 Applications	ŀ
	1.3	Thesis overview)
	1.4	References	;
2	Exp	srimental 53	;
	2.1	Synthesis of Colloidal CsPbBr ₃ Nanocrystals $\ldots \ldots \ldots \ldots \ldots \ldots \ldots 53$;

	2.2	Standard Characterization	54
	2.3	Streak Camera Work	55
		2.3.1 Temperature Dependent Photoluminescence	55
		2.3.2 Time Dependent Photoluminescence	56
		2.3.3 Data Processing	58
	2.4	References	60
2	The	Temperature Dependence of the Dhoteluminescence of CoDhPr	
3	Ner		61
	Nan	ocrystals Reveals Phase Transitions and Homogeneous Linewidths	01
	3.1	Abstract	62
	3.2		62
	3.3	Results and Discussion	64
	3.4	Conclusions	70
	3.5	References	71
4	The	absorbing state of a bulk perovskite nanocrystal transforms into a	
	qua	ntum confined emitting state	77
	4.1	Abstract	78
	4.2	Introduction	78
	4.3	Results and Discussion	81
	4.3 4.4	Results and Discussion References	81 92
-	4.3 4.4	Results and Discussion	81 92
5	4.3 4.4 The	Results and Discussion	81 92
5	4.3 4.4 The tem	Results and Discussion	81 92 98
5	4.3 4.4 The tem 5.1	Results and Discussion	81 92 98 99
5	4.3 4.4 The tem 5.1 5.2	Results and Discussion	81 92 98 99 99
5	4.3 4.4 The tem 5.1 5.2 5.3	Results and Discussion References bright multiexcitons of all-inorganic perovskite nanocrystals at low berature Abstract Introduction Results	81 92 98 99 99
5	4.3 4.4 The tem 5.1 5.2 5.3 5.4	Results and Discussion	81 92 98 99 99 100

	5.4.2	Optical and structural characterization	109
	5.4.3	Time-resolved photoluminescence	109
5.5	Refere	nces	111

6 Revealing fine structural dynamics within the exciton and multiexciton manifolds of CsPbBr₃ perovskite nanocrystals 115 6.1 Abstract 116 6.2 Introduction 116

6.3	Result	s
6.4	Metho	ds
	6.4.1	t-PL experimental details
	6.4.2	t-PL modeling and fitting
	6.4.3	Frank-Condon Modeling

7 Conclusion 139 7.1 Summary 139 7.2 Outlook 143 7.3 References 147

A	A Appendix			
	A.1	Supporting information for: The temperature dependence of the		
		photoluminescence of $CsPbBr_3$ nanocrystals reveals phase transitions and		
		homogeneous linewidths	. 150	
		A.1.1 Experimental	. 150	
		A.1.2 Modeling	. 151	
	A.2	Supporting information for: The absorbing state of a bulk perovskite		
		nanocrystal transforms into a quantum confined emitting state	. 153	
		A.2.1 Materials	. 153	

	A.2.2	Methods	153	
	A.2.3	Optical and structural characterization	155	
	A.2.4	Time-resolved photoluminescence	155	
	A.2.5	State-resolved pump probe experimental setup	157	
A.3	Suppo	rting information for: The bright multiexcitons of all-inorganic		
	perovs	kite nanocrystals at low temperature	162	
A.4	Suppo	rting information for: Revealing fine structural dynamics within the		
	exciton and multiexciton manifolds of CsPbBr $_3$ perovskite nanocrystals 164			
	A.4.1	t-PL experimental details	164	
	A.4.2	t-PL modeling and fitting	165	
	A.4.3	Frank-Condon Modeling	166	
A.5	Refere	nces	171	

List of Figures

- 1.1 (a) Emission from CsPbX₃ NCs (black data points) plotted on CIE chromaticity coordinates and compared to most common colour standards (LCD TV, dashed white triangle, and NTSC TV, solid white triangle). (b) Photograph (λ_{exc} = 365 nm) of highly luminescent CsPbX₃ NCs-PMMA polymer monoliths to show the variety of colours possible using perovskite nanocrystals. Reprinted with permission from Protesescu et al. Nano Lett. 2015, 15, 6, 3692–3696. Copyright 2015 American Chemical Society.
- 1.2 a), A schematic illustration of charge-carrier recombination in 3D perovskites. b),c), Related quantum yield excitation density characteristics with b) varying bimolecular recombination coefficients and c) varying non-radiative monomolecular recombination coefficients. d), A schematic illustration of charge-carrier recombination in quantum-confined perovskites.
 e), Related PLQY-excitation density plots with varying trap-assisted non-radiative recombination rate constants. Reprinted from Liu et al. Nature Materials. 20, 10–21. (2021), with permission Copyright 2021 Springer Nature.¹⁸

2

1.3 The development of perovskite emitters and LEDs. a) Material diversity of metal halide perovskite emitters. Beyond 3D structures, nanostructures (including quantum-confined structures) can be obtained by decreasing the crystal size or reducing the structural dimensionality, resulting in increased electron-hole (exciton) binding energy. b) Development of LEDs with different emitters and different light emissions; the red, green and blue symbols denote red/near-infrared, green and blue LEDs, respectively. Reprinted from Liu et al. Nature Materials. 20, 10–21. (2021), with permission Copyright 2021 Springer Nature.¹⁸

4

6

- 1.4 Example band structure of metals, semimetals and semiconductors. There is no clear band gap between conduction and valence bands in metals. Metals instead have a partially filled band allowing conduction. Semiconductors have a clear separation between valence and conduction bands. Therefore electrons must be promoted through thermal energy into the empty conduction band to allow conduction. Electrons can also be promoted to the conduction band through absorption of a photon with energy higher than the band gap. Semimetals are often said to have a band gap equal to 0. This gives them metallic and semiconductor-like properties. E_f marks the Fermi level above which no electrons will be present at 0K.
- 1.5 a) A combination of atomic orbitals leads to formation of electronic bands.
 b) Dopants are in band and lead to higher carrier densities. They are either p or n dopants which are electron acceptors or donors respectively. n-type dopants are shown leading to carrier concentrations in the conduction band.
 Traps have discrete energy levels and are either shallow (close to or in the band edge) or deep (in the middle of the band gap).

- 1.6 a) An impression of an exciton in a lattice the electron (in blue) orbits around the hole (in red) similar to a hydrogen atom. b) Example absorbance and photoluminescence of a semiconductor (CsPbBr₃ nanocrystals) 10
- 1.7 a) Examples of exciton relaxation. b) Types of transition. c) Example time dependent photoluminescence of CsPbBr₃ nanocrystals. The IRF (instrument response function) is also included. The IRF is a measure of the time resolution of the instrument and must be convolved with the exponential decay when fitting.
 12
- 1.8 a) Quantum dot schematic. The size of the nanocrystal allows control of the band gap. b) Size dependence of the band gap with Equation 1.9. c) Cartoon depicting the stages of nucleation and growth for the preparation of monodisperse NCs in the framework of the LaMer model. As NCs grow with time, a size series of NCs may be isolated by periodically removing aliquots from the reaction vessel. d) Representation of the simple synthetic apparatus employed in the preparation of monodisperse NC samples. (panels c and d are reprinting with permission from Murray et al. Annu. Rev. Mater. Sci. 2000.30, 545-610. Copyright 2000 Annual Reviews.) . . . 15

- 1.10 a) Saturation curve that follows Equation 1.10. b) Poisson distribution that follows Equation 1.11. The y-axis represents the fraction of nanocrystals with the respective number of absorbed photons.
 18
- 1.11 a) Structure of a cubic lead halide perovskite. The lead halide octahedral cage is supported by the A cation in green. b) Representative PL spectra of CsPbBr₃ nanocrystals showing band gap control through halide composition. Reprinted with permission from Protesescu et al. Nano Lett. 2015, 15, 6, 3692–3696. Copyright 2015 American Chemical Society. c) Example device layout of a lead halide perovskite solar cell. d) Left: energy levels of a defect intolerant semiconductor such as CdSe. Right: energy levels of lead and bromide with respect to the band gap. Deep trap states will lower the quantum yield of a semiconductor. Reprinted with permission from R. E. Brandt et al. Chem. Mater. 2017, 29, 11, 4667–4674. Copyright 2017 American Chemical Society. 21
- 1.13 a) Cartoon of a CsPbBr₃ nanocrystal. The nanocrystal is covered in "hairy" ligands (the entire nanocrystal is in fact covered). b) Hot-injection synthesis of perovskite nanocrystals. The Cs-oleate precursor is synthesized in a separate air-free flask. An ice bath is used to cool and quench the reaction after injection.
 25

- 1.15 a) The three common crystal structures of CsPbBr₃ which depend on the lead halide angle. Axial and equatorial halide atoms are shown in the bottom left in red and blue respectively. Cubic has 180° angles while tetragonal has a bent axial Pb-X-Pb angle. Orthorhombic has an additional bend between equatorial halide atoms. b) One crystal structure theory called nanotwins has many crystal domains in one nanocrystal with dislocations between the domains. Adapted with permission from [7]. Copyright 2017 American Chemical Society.
- 1.16 Common ligands used as capping agents of CsPbBr₃ nanocrystals.
 Oleylamine and oleic acid are a dual ligand system often used together.
 Lecithin and sulfobetaine are zwitterionic ligands that cap the nanocrystal unaided by other ligands.
 30
- 1.17 a) Experimental versus theoretical (effective mass approximation, EMA) size dependence of the band gap energy. Reprinted with permission from Protesescu et al. Nano Lett. 2015, 15, 6, 3692–3696. Copyright 2015 American Chemical Society. b) Size dependent Stokes shifts for CsPbX₃ nanocrystals. Reprinted with permission from Brennan et al. J. Phys. Chem. Lett. 2020, 11, 13, 4937–4944 Copyright 2020 American Chemical Society. 32

- 1.18 Effect of polaron formation and confinement on lineshape 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. Ref. [56] by Colin Sonnichsen, et al. is licensed under CC BY 4.0.
- 1.19 a) Three level energy system diagram including a legend. The population inversion must be between states 1 and 2. b) Four level energy system diagram. The population inversion must be between states 2 and 3. c) Pump-fluence dependence of the emission from a CsPbBr₃ NC film. d) Variable stripe-length experiment for estimation of modal net gain for the CsPbBr₃ NC film. c) and d) are reprinted from Ref. [134] by Sergii Yakunin et al. (licensed under CC BY 4.0.)

33

- 2.1 Examples spectra of CsPbBr₃ nanocrystals in toluene. a) Absorbance spectrum b) Photoluminescence excitation spectrum c) Photoluminescence spectrum.

- 2.3 Full streak trace with the pump scatter at 3.1eV and the signal at 2.4eV. The x-axis is the time dependence with the the energy (or wavelength) on the y-axis.
 58
- 3.1 Material overview. (a) Absorbance and fluorescence of CsPbBr₃. (b) Cubic perovskite structure (grey lead, blue cesium, brown halide). (c) TEM image of a CsPbBr₃ sample (the white scale bar is 20nm).
 64
- 3.2 Temperature dependent photoluminescence data. (a) Normalized temperature dependent 2D plot of PL data. (b) Temperature dependence of the PL FWHM (Γ) compared to Boltzmann constant. (c) Energy shift of the PL with temperature. The orange and green lines are linear fits and are guides for the eye only.
 66

4.2 Overview of the spectral dynamics of metal-halide perovskite bulk NC from 10 fs to 200 ps using a suite of three time-resolved spectroscopies. a) Two-Dimensional Electronic (2DE) spectroscopy of CsPbl₃ NC, at a population time, t₂, of 20 fs. b) 2DE spectroscopic lineshapes over time. Shown are the diagonal and anti-diagonal linewidths, representing the total and the homogeneous linewidths, respectively. c) Early time response for State Resolved Pump/Probe (SRPP) spectroscopy of CsPbBr₃ NC, pumping into the band edge. d) The SRPP spectroscopy reveals an optical bleach with a time dependent linewidth and peak energy. e) Early time response for energy-resolved time-resolved photoluminescence (t-PL) spectra of CsPbBr₃ NC. Pumping was performed at 3.1eV under high excitation conditions. f) The t-PL spectra show complex time dependence of the spectral linewidth and peak energy.

84

4.3 Spectrally and temporally resolving multi-excitonic bands from t-PL spectra of CsPbBr₃ NC. a) The spectra near 200 ps are well described by a single Gaussian. This peak (red) corresponds to the single exciton emission, of a 1S¹ → G emission pathway. b) The spectra near 40 ps are well described by two Gaussians. This new peak (green) corresponds to the bi-exciton emission, of a 1S² → 1S¹ emission pathway. c) The spectra near 5 ps are well described by two additional Gaussians. These new peaks (blue) correspond to the tri-exciton emission, of a lower energy 1S²1P¹ → 1S¹1P¹ emission pathway and a higher energy 1S²1P¹ → 1S² emission pathway.
d) The resulting early time (-5 – 5 ps) spectra from the Poisson model for 0.23 mJ/cm² which is a ⟨N⟩ value of 0.037. e) The resulting spectra from the Poisson model for 3.42 mJ/cm² which is a ⟨N⟩ value of 0.56. f) The resulting spectra from the Poisson model for 45.64 mJ/cm² which is a ⟨N⟩ value of 7.4.

- 4.4 Energy resolved pumping rules out hot carrier effects in CsPbBr₃ NC. a) tPL spectra at high fluence at two different photon energies reveals identical spectra at t = 4 ps. The low fluence spectrum of a single exciton emitting is shown for comparison. b) The total spectral bandwidth as a function of time for two different photon energies at the high fluence multiexciton regime. The inset shows the time dependent bandwidth for the low fluence single exciton regime. c) The peak energy as a function of time for two different photon energies at the high fluence multiexciton regime. The inset shows the high fluence multiexciton regime.

- 5.2 a) Time resolved photoluminescence (t-PL) at 300K with 100ps time resolution. b) t-PL at 4K with 100ps time resolution. c) Integrated decays produced from a) and b). d) t-PL at 300K with 3ps time resolution. e) t-PL at 4K with 3ps time resolution. f) Integrated decays produced from d) and e).102
- 5.3 a) Biexponential fits of decays from 3 temperatures. b) Extracted decay rates from biexponential fits following Equation 5.1 and Equation 5.3. The fast decay rate k_1 is in red and the slow decay rate k_2 is in blue. c) The extracted fractional f_1 from Equation 5.2. The sum of f_1 and f_2 is 1. . . . 104
- a) Example extraction of areas from MX and X decay rates. b) Temperature dependent quantum yield of X. c) Temperature dependent quantum yield of MX calculated from Equation 5.6. d) Temperature dependent radiative (in blue) and nonradiative (in grey) rates for X. e) Temperature dependent radiative (in red) and nonradiative (in grey) rates for MX. The lines in b and c are linear fits, while in d and e the lines are polynomial fits and are guides for the eye.

- Illustration of excitonic and biexcitonic levels in the transient photoluminescence 6.1 (t-PL) spectra of perovskite nanocrystals (NC). a) An illustration of the relevant ideas of polarons and quantized excitons in a perovskite NC. Shown to scale is an exciton of Bohr length 7 nm and a NC of edge length 15 nm, for CsPbBr₃ NC studied here. b) Schematic of an exciton, biexciton, and respective energy levels that arise from quantum confinement. V_{XX} denotes the interactions between holes and electrons. $\langle \Delta_{XX} \rangle$ and $\langle \Delta_{MX} \rangle$ represent the mean biexciton and multiexciton binding energies respectively. It is essential to considering a mean due to fine structure. c) and d) show the t-PL spectra at 300 and 4K, showing both the exciton and the multiexciton emission spectra. The exciton spectra are obtained from low fluence spectra whereas the MX spectra are from high fluence spectra from which the low fluence spectra are subtracted. See Appendix A for additional details and Figure 6.2 for excitation densities. The mean binding energies are defined spectroscopically above and are found to be: $\langle \Delta_X X \rangle$ goes from 44.8 meV at 300K to 20.3 meV at 4K, and the MX binding energies go from -81.1 meV at 300K to -19.0 meV at 4K. Note that the negative binding energy merely is a result of the spectroscopic designation. 120
- 6.2 t-PL spectra of CsPbBr₃ nanocrystals over two time windows, two temperatures, and two excitation densities. High excitation density corresponds to $\langle N \rangle = 3.05$ -3.34 or 25.2-27.6 μ J/cm², while low excitation density corresponds to $\langle N \rangle = 0.024$ -0.027 or 0.20-0.22 μ J/cm². High fluence reveals spectral dynamics that are only visible within the first 100 ps that has been previously unobserved. Cooling attenuates the magnitude of the early time spectral dynamics. The low fluence regime does not show the same fast dynamics as high fluence.

- 6.3 A quantitative analysis of the spectral dynamics is obtained by the spectral linewidth trajectories. Γ is the Full Width Half Maximum. Linewidth trajectories are shown for two temperatures, and two excitation densities, over two timescales. For each trajectory, an asymptote is shown where it appears for the long time low fluence data as Γ_{∞} . Energy differences at particular times are shown. The top row shows the low fluence data and the bottom row shows the high fluence data. The high fluence data schematically illustrate the decay of XX and MX populations as discussed in the text.
- 6.4 Overview of how the energetics and spectral dynamics are all connected kinetic and thermodynamic processes. a) Calculated temperature dependence of PL linewidth with inclusion of coupling to phonons. Shown are curves at two different couplings which dictate the high temperature slope and the low temperature offset. Only a model with two fine structure states dressed with these different couplings reproduces the experimental dependence. At high temperature there is thermal equilibrium between the two states and at low temperature there is relaxation to the lower state. b) Schematic illustration of Two State Model via displaced harmonic oscillators. The two states are separated by some Free energy difference, and each has its own Huang-Rhys coupling, S = $\Delta^2/2$. c) - d) The linewidth trajectories and the temperature dependence of the linewidth enables observation of temperature trajectories shown over two time windows. The schematic illustrates the decay of the XX and MX populations which form the thermal impulse via Auger heating. e) Schematic illustration of relevant

- 7.1 Temperature dependent photoluminescence data. a) Temperature dependence of the PL FWHM (Γ) compared to Boltzmann constant.
 "Equation 3" is 3.3 while "FC fitting" represents the Frank-Condon fitting done. b) Energy shift of the PL with temperature. The orange and green lines are linear fits and are guides for the eye only.
- 7.2 Spectrally and temporally resolving multi-excitonic bands from t-PL spectra of CsPbBr₃ NC. a) c) The early time spectra are well described by four Gaussians. The red and green peaks correspond to single and biexcitonic emission. The blue peaks correspond to the tri-exciton emission, of a lower energy $1S^{2}1P^{1} \rightarrow 1S^{1}1P^{1}$ emission pathway and a higher energy $1S^{2}1P^{1} \rightarrow 1S^{2}$ emission pathway. b) The time dependent fits of the 3 peaks (the areas of high and low energy MX peaks are summed).
- 7.3 Temperature dependent relaxation rates. a) Decay rates of the single exciton decomposed into radiative (blue) and nonradiative (grey) rates.
 b) Decay rates of the multiexcitons decomposed into radiative (red) and nonradiative (grey) rates.
 141

- 7.5 UED and diffuse scattering signals from photodoped SnSe. (A) Equilibrium scattering pattern of SnSe oriented along the [100] direction, with key vectors, the square BZ (b* c* plane), and high-symmetry points indicated.
 (B) Regions of interest for scattering as described in the text, shown around reflection (002) as an example; 1, Bragg intensity; 2, small-wavevector phonons; 3, larger-wavevector phonons. (C) Line cut across the horizontal line shown in (B). The Bragg peak line shape is fit with a Voigt profile (solid black line). (D) Transient (photoinduced) ultrafast electron scattering intensity changes in several regions of the BZ shown in (A) and (B). Reprinted from René de Cotret, et al. 2022 PNAS CC BY-NC-ND 4.0 [7].
- 7.6 Examples of lead-free perovskite crystal structures. a) Cs2AgBiBr₆ double perovskite crystal structure. The structure is very similar to CsPbBr₃ with the replacement of two lead atoms with one bismuth and one silver atom. b) Cs₂SnI₆ perovskite-like structure. The tin halides form a octahedral lattice similar to perovskites but offset in each layer. 145
- A.2 Instrument Response Functions and Gaussian fits of (A) 3.1eV pump and
 (B) 2.6eV pump for time resolved photoluminescence. The error is produced
 during fitting of the IRF.
- A.3 Spectral overlap between the laser spectrum and the samples. (A) CsPbl₃ nanocrystals in toluene (B) CdSe nanocrystals in toluene (C) Nile Blue in ethanol.
 158
- A.4 TG-FROG trace of the pulses employed in the 2DES experiments on CsPbl₃ shown in the main manuscript, corresponding to pulses of 13-15 femtoseconds.
 A.5 Illustration of how the anti-diagonal linewidth (and its FWHM) is extracted

A.6	The fluence dependence of multiexcitons in $CsPbBr_3$ as measured by state	
	resolved pump probe spectroscopy.	160
A.7	Summary of the parameters for the samples employed in the 2DES study.	160
A.8	Summary of biexciton binding energies in the literature for $CsPbBr_3$	
	and $CsPbI_3$. The first six experiments are emissive including t-PL (time	
	resolved photoluminescence), SPPL (single particle photoluminescence)	
	and HS (heralded spectroscopy). The second half of the table details TA	
	(transient absorbance) experiments. Temperatures are assumed to be	
	room temperature unless reported otherwise. *various fluences/absorbed	
	photons were used in these experiments.9-18	161
A.9	Instrument response functions from a) picosecond and b) nanosecond	
	experiments. Measured from the pump scatter at 3.1eV and fit with a Voigt	
	function.	162
A.10	0 a) Ratios of MX/X rates from Figure 5.4. a) Radiative rates and b)	
	nonradiative rates.	163
A.11	1 Inverse temperature vs lnk . a) Plot for the MX decay. The lnk_{Auger} is in	
	grey while the radiative rate is in red. b) lnk rates for the single exciton	
	with radiative in blue and nonradiative in grey. Note that none of the rates	
	display Arrhenius behaviour except perhaps the nonradiative rate for the	
	single exciton.	163
A.12	2 Spectra of $CsPbBr_3$ nanocrystals. a) Absorbance and photoluminescence	
	with 350nm excitation. b) Example of subtraction process as shown in	
	Figure 1. The relative intensity of the low fluence is based on normalizing the	
	spectra to the intensity at late time (see Figure S3 for fluence dependence	
	of PL decays). The XX and MX binding energies are then estimated from	
	the low fluence (single exciton) peak	164

- A.14 Fluence dependence of time resolved photoluminescence at 4K. a) PL(t) decays found through averaging the streak traces along the energy axis at various fluences. b) A/B ratio of the PL where A is defined as the maximum intensity and B is defined as the intensity at 300 ps.
- A.15 The time dependent photoluminescence energy shifts with comparisons of 300 and 4K. a) low fluence picosecond data showing a 5meV blueshift over 200ps. b) The high fluence picosecond data gives a 25 and 4 meV blueshift in 200ps. c) The low fluence dataset with a 2ns time range shows no obvious shift for either temperature. d) The high fluence nanosecond dataset gives 20 and 4 meV blueshifts for 300 and 4K respectively. 167

A.17 PL decays used to approximate the XX and MX lifetimes at 4K. a) Example streak camera image showing time dependent PL. The red and blue areas show the approximate energy range used to calculate the decays in c) and d). a) The full integrated PL decay. A triexponential fit resulted in decay constants of 23.45 +/- 0.96, 144.20 +/- 19.37, 1301 +/- 352 ps. The high error in the third lifetime is due to the short time range of the experiment. c) The decay and fit from the red area in a) (2.29 to 2.35 eV). The fit resulted in time constants of 26.28 +/- 0.88 and 113.34 +/- 4.65 ps. The time constant of 113.34ps was approximated as the XX lifetime. d) The decay and fit from the blue area in a) (2.42 to 2.45 eV). The fit resulted in time constants of 19.86 +/- 1.99 and 151.77 +/- 13.27 ps. The time constants of 19.86 and 113.34 ps were approximated as the MX and XX lifetimes respectively. Note that the energy ranges were estimated from the subtraction plot in Figure 1d in order to maximize the fraction of biexciton or multiexciton signal. . . . 170

List of Tables

1.1	Material parameters at 300 K for common semiconductors. Note that	
	values reported for CsPbBr3 are extremely variable therefore only the	
	bandgap and relative permittivity are reported. ^{1,28,33}	9
2.1	Streak text file format. The NaN (not a number) in the zero position is a	
	placeholder. Time is either in ns or ps depending on the time range while	
	wavelength is in nm. The remaining area is a 2100x2100 array of intensity	
	values. For the photoswitch mode, the final 600 pixels are often cut off	
	resulting in a 2100x1500 array. $Z_{i,j}$ represents the intensity values of the	
	array.	59
3.1	Fitting parameters for equations as well as Franck-Condon fitting	70
A.1	Coupling constants for common semiconductor NCs ^{3,5,6}	152

Chapter 1

Introduction

Perovskite nanocrystals were first synthesized in 2015.¹ This field is seen as a quickly maturing area of research. However, the properties of perovskite nanocrystals are far from solved. For example, the exciton fine structure of CsPbBr₃ was seen as solved by many in 2018.² More recent works give a different theory for the exciton fine structure.^{3,4} Many view both theories as the correct one. This can be extended to other properties such as the crystal structure^{5–7} and biexciton binding energies^{8,9} which are also unsolved. Many of these problems will be eventually resolved in the literature.

Perovskite nanocrystals are based on a material called lead halide perovskites. The bulk form has found use in technologies such as solar cells and light emitting diodes.¹⁰ Solar cells in particular have increased in importance recently due to their use in reducing reliance on carbon based energy sources. Silicon solar cells dominate the solar energy market currently. However, they require high purity (99.999%) and have high upfront energy costs. Lead halide perovskites are an emerging semiconductor material that may fix these issues without sacrificing efficiencies. Bulk lead iodide perovskite solar cells are already being commercialized.¹¹ However for LEDs, the nanocrystal form is the more interesting variety.



Figure 1.1: (a) Emission from CsPbX₃ NCs (black data points) plotted on CIE chromaticity coordinates and compared to most common colour standards (LCD TV, dashed white triangle, and NTSC TV, solid white triangle). (b) Photograph (λ_{exc} = 365 nm) of highly luminescent CsPbX₃ NCs-PMMA polymer monoliths to show the variety of colours possible using perovskite nanocrystals. Reprinted with permission from Protesescu et al. Nano Lett. 2015, 15, 6, 3692–3696. Copyright 2015 American Chemical Society.

Colloidal semiconductor nanocrystals are the focus of research in the LED field. There are two primary reasons for this: ease of manufacturing and colour tunability. The colloidal nature of the nanocrystals allows simple device manufacturing through drop- or spin-casting. In traditional semiconductor nanocrystals, the colour is tuned using the size of the nanocrystals. This material is then called a quantum dot.¹² In contrast, the colour of perovskite nanocrystals is controlled through composition. Virtually any visible colour can be made using these perovskite nanocrystals as seen in (Figure 1.1).¹ The control of colour in a device is defined with the CIE colour space (Figure 1.1a). In the LED field, the green emitting lead bromide nanocrystals are the most compelling for applications due

to their stability, narrow emission, and high intrinsic quantum yields.^{1,13,14} These specific LEDs could find use in display applications such as in televisions.

An important phenomenon to the LED is the exciton. The exciton is the bonded electron-hole pair that is created when light is absorbed and destroyed in order for light to be emitted. Therefore, it is important for the properties of this quasiparticle to be well understood. A simple way of analyzing the exciton properties is through spectroscopy of the emitted light. In traditional covalent semiconductors, such as Si, GaAs, CdSe, the exciton is well understood. However, lead halide perovskite have very unique properties due to the ionic nature of the lattice. The bond polarity leads to interesting properties such as liquid-like dynamics^{15,16} and dynamic disorder.^{7,17}



Figure 1.2: a), A schematic illustration of charge-carrier recombination in 3D perovskites. b),c), Related quantum yield excitation density characteristics with b) varying bimolecular recombination coefficients and c) varying non-radiative monomolecular recombination coefficients. d), A schematic illustration of charge-carrier recombination in quantumconfined perovskites. e), Related PLQY-excitation density plots with varying trap-assisted non-radiative recombination rate constants. Reprinted from Liu et al. Nature Materials. 20, 10–21. (2021), with permission Copyright 2021 Springer Nature.¹⁸ One open question is how these properties of perovskite nanocrystals affect the efficiencies of LED devices. At high excitation densities, the efficiency of an LED "droops" (Figure 1.2e).¹⁸ This droop is due to the interactions of two or more excitons in a single nanocrystal. In traditional semiconductor nanocrystals, there is a strong size dependence to this phenomenon: larger nanocrystals have higher efficiencies at high current densities. Perovskite nanocrystals do not have a strong size dependence in comparison (Figure 1.3).¹⁹ It is unknown exactly why perovskite nanocrystals differ from traditional quantum dots. Questions remain for the nature of multiexcitons, and single excitons, in perovskite nanocrystals. However, probing multiexcitons is a problem the Kambhampati group is well versed in.^{20–23} Photoluminescence spectroscopy is a powerful tool for probing the emitting states, including multiexcitons. Combining temperature, time and fluence dependence allows for studying the emission in a variety of conditions



Figure 1.3: The development of perovskite emitters and LEDs. a) Material diversity of metal halide perovskite emitters. Beyond 3D structures, nanostructures (including quantum-confined structures) can be obtained by decreasing the crystal size or reducing the structural dimensionality, resulting in increased electron–hole (exciton) binding energy. b) Development of LEDs with different emitters and different light emissions; the red, green and blue symbols denote red/near-infrared, green and blue LEDs, respectively. Reprinted from Liu et al. Nature Materials. 20, 10–21. (2021), with permission Copyright 2021 Springer Nature.¹⁸

which will allow a deeper understanding of the physics at play in lead halide perovskite nanocrystals. First, the underlying semiconductor physics at play must be explored.

1.1 Semiconductor Properties

Semiconductor and semiconductor derived materials are the basis of technologies that have allowed Digital Age. The transistor is the most highly produced piece of technology ever: over 10²¹ were estimated to be produced in 2019.²⁴ Other technologies that semiconductors have allowed includes solar cells, light emitting diodes (LEDs), and solid state lasers among many other technologies.²⁵ In order to design better semiconductor devices, fundamental research must be done to guide material design. For example, understanding why some compositions are unstable directs where researchers should focus to fix stability issues.¹³ In application such as lasing, materials are pushed far from equilibrium. In the case of lasing, many photons are absorbed by a single nanocrystal creating a high energy state.²⁶ It is important to understand material proprieties in these non-equilibrium conditions if CsPbBr₃, or other perovskites, are to be used. Conditions such as large temperature variations and a high number of absorbed photons are described in this thesis. To understand how these conditions affect materials, a basis of semiconductor physics must first be established.

Semiconductors are a class of material that are defined differently depending on the field. A incomplete, but useful simplification, is that any material with a band gap above 0 and below 4 eV is a semiconductor.²⁷ Figure 1.4 shows an example metal, semimetal, and semiconductor which has a clear band gap. This range will change depending on use of the semiconductor. Other definitions are based on the nature and values of electrical conductivity.²⁸ For this thesis, a semiconductor is restricted to direct band crystalline conductors that absorb IR to near UV light (i.e. with a bandgap <4).

One of the defining features of semiconductors, in comparison to molecules, is the electronic band structure. A single atom has discrete energy levels called atomic



Figure 1.4: Example band structure of metals, semimetals and semiconductors. There is no clear band gap between conduction and valence bands in metals. Metals instead have a partially filled band allowing conduction. Semiconductors have a clear separation between valence and conduction bands. Therefore electrons must be promoted through thermal energy into the empty conduction band to allow conduction. Electrons can also be promoted to the conduction band through absorption of a photon with energy higher than the band gap. Semimetals are often said to have a band gap equal to 0. This gives them metallic and semiconductor-like properties. E_f marks the Fermi level above which no electrons will be present at 0K.

orbitals. As more atoms are added, molecular orbitals are formed, and the energy spacing decreases. However, due to the Pauli exclusion principle, the orbitals can never overlap in energy.²⁹ For the micrometer size scale and above, this results in broad energy bands (Figure 1.5a). Bands are a combination of orbitals with energy spacings orders of magnitude less than k_BT at room temperature. The bands are constructed of orbitals and therefore have s, p or hybridized sp character (i.e. s-like or p-like).³⁰ The filled band below the Fermi level is called the valence band while the unfilled band above is called

the conduction band. In an intrinsic (undoped) semiconductor, conductivity is due to the conduction band being partially filled by thermal energy. Excitation of electrons into the conduction band leaves behind electron holes in the valence band. These electron holes, simply called holes, can be treated as positively charged pseudo-particles.

Charge in semiconductors can also be introduced through impurities. Traps are impurities which are, energetically, within the band gap (Figure 1.5b). Traps are named due to the ability to trap charges which has a detrimental effect on semiconductor device performance. Doping is a process where a small amount of certain atoms is added to increase hole or electron concentration. For example, in silicon, phosphorous and aluminum are added to n- and p-dope respectively. A doped semiconductor is then referred to as extrinsic rather than intrinsic. The concentration of dopants raises the conductivity. In the band structure, dopants are near the conduction or valence band edge. As carrier concentration increases, the properties of a semiconductor approach those of a metal.³¹

There is a clear separation between metals and semimetals, which have no band gap, and semiconductors which have a gap.³¹ This band gap allows for optical transitions between the valence and conduction band due to photon absorption and emission. However, optical transitions can not change the momentum of an electron. Crystal momentum is an important property of semiconductors; it is a necessary degree of freedom to describe the full band structure of a semiconductor. Direct transitions are vertical in momentum space and only require a photon while indirect transitions require a photon and a phonon to conserve momentum. Optical processes in a semiconductor often involve an electron-hole pair called an exciton.³²

1.1.1 Excitons

The primary phenomenon studied in this thesis is the exciton. An exciton is a quasiparticle formed with an excited electron and hole pair. An exciton can be treated


Figure 1.5: a) A combination of atomic orbitals leads to formation of electronic bands. b) Dopants are in band and lead to higher carrier densities. They are either p or n dopants which are electron acceptors or donors respectively. n-type dopants are shown leading to carrier concentrations in the conduction band. Traps have discrete energy levels and are either shallow (close to or in the band edge) or deep (in the middle of the band gap).

similarly to the hydrogen atom due to it being an electron orbiting a positive charge. Similar to a hydrogen atom, the electron and hole have a characteristic radius and binding energy.^{29,31,32} The radius, known as the exciton Bohr radius, is calculated using

$$r_B = \frac{m_0 \epsilon_r}{\mu^*} a_B n \tag{1.1}$$

while the exciton binding energy is calculated with

$$E_B = \frac{\mu^*}{m_0} \frac{1}{\epsilon_r^2} \frac{R}{n^2}$$
(1.2)

where r_B is the Bohr radius of the exciton, E_B is the exciton binding energy, μ^* is the reduced effective mass of the exciton, m_0 is mass of an electron, ϵ_r is the effective relative permittivity of the material, a_B is the Bohr radius of the hydrogen atom, 5.29×10^{-11} m, n is the exciton energy state, and R is the Rydberg constant of hydrogen, 13.6 eV. The Bohr radius of most crystalline semiconductors is on the order of 1-100 nm, and the binding energy is on the order of 1-100 meV. Coulombic attraction makes the energy of an exciton slightly less than the band gap for bulk semiconductors. The binding energy of a semiconductor has a exponential relationship with the band gap.²⁸ Optically, an exciton is created through absorption of a photon with an energy greater than the optical band gap.³²

Table 1.1: Material parameters at 300 K for common semiconductors. Note that values reported for CsPbBr₃ are extremely variable therefore only the bandgap and relative permittivity are reported.^{1,28,33}

Material	m_e^*	m_{hh}^*	ϵ_r	E_{eg} (eV)	E_B (meV)	<i>a</i> *(nm)
GaAs	0.063	0.50	13.2	1.42	4.4	12.5
ZnS	0.34	1.76	8.9	3.54	49.0	1.7
CdSe	0.11	0.45	10.2	1.74	11.6	6.1
ZnO	0.28	0.59	7.8	3.37	42.5	2.2
CsPbBr ₃	-	-	10-30	2.36	-	7
BN	0.752	0.38	5.1	6.08	131	1.1

Absorption of a photon with no or moderate excess energy (i.e. energy greater than the band gap) can lead to two scenarios: generation of a exciton or of free carriers. Radiative recombination of a electron-hole pair can also occur and results in the emission of a photon. Unlike generation of an exciton, recombination only involves the states closest to the band edge; this therefore results in a narrow emission (10s-100s of meV at 300K). The photon energy for this process is governed by the band gap and the exciton binding energy

$$h\nu = E_q - E_B \tag{1.3}$$

for a direct band semiconductor. This process is called spontaneous emission and is a type of photoluminescence.²⁷ Impurities and crystal dislocations complicate emission by trapping charges.³²



Figure 1.6: a) An impression of an exciton in a lattice the electron (in blue) orbits around the hole (in red) similar to a hydrogen atom. b) Example absorbance and photoluminescence of a semiconductor (CsPbBr₃ nanocrystals)

Trapping of an electron or hole of an exciton reduces the probability of radiative recombination. The competing process is aptly named nonradiative recombination. Defects and charged impurities can combine with a electron or hole to prevent photoluminescence. Traps can also slow the process of photoluminescence which increase the probability of nonradiative effects.³² There are two other main nonradiative phenomenon: multi-phonon emission and the Auger effect.

Multi-phonon emission is the process where multiple phonons are created to reduce excess energy and relax the electron it's ground state. However, most phonons are below 100 meV in energy; it would take 40 phonons to relax an exciton of 2 eV with a phonon energy of 50 meV.³⁰ There are few energy levels within the band gap of a pure semiconductor; therefore, multi-phonon emission is more likely in doped semiconductors with a small band gap. It is also possible that phonons can allow for additional nonradiative

pathways "horizontally" through momentum space. However, the majority of nonradiative effects for single excitons are trap mediated.³⁴ The Auger effect involves an intra-gap excitation of a charge carrier in unison with the exciton relaxation (Equation 1.4).³² These nonradiative phenomenon complicate the time dependence of exciton relaxation.

A common method of measuring the time dependence of exciton relaxation is time dependent photoluminescence (PL(t)). The methods of analyzing time dependent photoluminescence are not specific to semiconductors. The radiative relaxation rate is k_r ; however, this value is usually not measured directly. PL(t) can instead measure the effective relaxation rate: k_{eff} . The effective rate is equal to the sum: $k_{eff} = k_r + k_{nr}$ where k_{nr} is the nonradiative rate. Each of these rates can also be state in terms of the inverse, the lifetime, τ such that

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}}.$$
 (1.4)

The time dependence of photoluminescence intensity can then be defined as

$$I(t) = I_0 e^{-t/\tau_{eff}}$$
(1.5)

where I(t) is the time dependent intensity and I_0 is the intensity at time zero. The PL-t can be measured with techniques such as time correlated single photon counting (TCSPC, Equation 1.4). In the limit where the nonradiative rate is zero, the absorption and emission of a photon will be perfectly efficient. This value is known as the internal quantum efficiency:

$$\eta = \frac{\tau_r^{-1}}{\tau_{eff}^{-1}}$$
(1.6)

where η is the internal quantum efficiency (often known as the quantum yield). A common way of measuring the quantum yield is with a reference dye. Once the quantum yield and

total lifetime of a material are known, the radiative and nonradiative rates can be solved for. The quantum yield is an extremely important property for applications. As the total efficiency of a device is a product that includes the quantum yield, a quantum yield of 0.5 lowers the efficiency by half. Much of the above time dependant theory assumes there is linear, mono-exponential decay.³⁵



Figure 1.7: a) Examples of exciton relaxation. b) Types of transition. c) Example time dependent photoluminescence of CsPbBr₃ nanocrystals. The IRF (instrument response function) is also included. The IRF is a measure of the time resolution of the instrument and must be convolved with the exponential decay when fitting.

Multi-exponential decay can occur if there are multiple emitting species. For example, the surface and core of a semiconductor nanocrystal can have separate relaxation rates.³⁶ In this case, the time dependence of photoluminescence intensity is defined as a sum:

$$I(t) = \sum_{i} \alpha_{i} e^{-t/\tau_{i}}$$
(1.7)

where α_i and τ_i are the intensity factor and lifetime respectively for decay *i*.³⁵

The temperature dependence of exciton recombination is the combination number of factors. For instance, the band gap of a semiconductor will change with temperature. This effect is often fit to the purely empirical formula known as the Varshni equation:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}$$
(1.8)

where $E_g(0)$ is the band gap at absolute zero, and α and β are empirical constants.³⁷ Although the temperature dependence of the band gap is known to be a combination of change in lattice constants and electron-phonon interaction, there is no universal relation that can describe all semiconductors.³⁰ The emission peak width of a semiconductor will also change with temperature. The dominant effect is that at lower temperature less vibrational levels will be occupied leading the lower peak widths. This phenomenon can be modelled using the Franck-Condon principle.³⁸

1.1.2 Colloidal Semiconductors Nanocrystals

As a semiconductor particle decreases in size, the spacing between energy levels in the bands increases. Another effect is as the particle diameter approaches the Bohr diameter of the exciton, quantum confinement occurs which increases the band gap (Figure 1.8a).³⁹ Coulombic attraction of the exciton also has an effect on the band gap. The quantum confinement shift for the lowest energy state can be approximated as

$$\Delta E \simeq \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\epsilon R}$$
(1.9)

where *R* is the particle radius, m_e and m_h are the effective masses of the electron and hole respectively, ϵ is the permittivity of the material ($\epsilon = \epsilon_0 \epsilon_r$) and *e* is the elementary charge.^{29,40} The first term represents the spatial confinement of the exciton, while the second term represents the Coulombic attraction of the electron and hole. Polar semiconductors have a high permittivity; therefore, the second Coulombic term can be ignored as an additional approximation. This effect can be utilized to colloidally synthesize materials where the band gap (and emission energy) depend on the nanocrystal size. These materials are often called colloidal quantum dots.

Colloidal quantum dots were first synthesized aqueously,⁴¹ but later methods synthesized aliphatic colloids with hot injection syntheses.⁴² For II-IV semiconductors (such as CdSe), this involves injection of a solution containing the nonmetal chalcogenide into a hot solution (> 300°C) containing the metal (Figure 1.8d).⁴³ In the LaMer model, the growth of the nanoparticles during the synthesis starts with nucleation of small particles followed by a process called Ostwald ripening; this involves the growth of larger particles while smaller particles are dissolved (Figure 1.8c).⁴⁴ Another important reaction component is the ligand which plays an important role during the reaction. The ligands can help dissolved the precursors and have a large impact on the resulting nanoparticles. Nanoparticle shape and size control can be attained through careful selection of ligands.⁴⁵ Also while a bare nanoparticle has a reactive surface, and would quickly precipitate out of solution, the ligands stabilizes the surface and allows the nanoparticle to be colloidally suspended. The ligand can be altered to allow suspension in a variety of solvents from non-polar aliphatic solvents, like hexane, to water.⁴⁶ In addition to ligands, an inorganic shell can also be used to stabilize the surface. This allows a much higher photoluminescence quantum yield compared to an unshelled quantum dot. For commercial applications, InP based quantum dots are popular due to the lack of toxic



Figure 1.8: a) Quantum dot schematic. The size of the nanocrystal allows control of the band gap. b) Size dependence of the band gap with Equation 1.9. c) Cartoon depicting the stages of nucleation and growth for the preparation of monodisperse NCs in the framework of the LaMer model. As NCs grow with time, a size series of NCs may be isolated by periodically removing aliquots from the reaction vessel. d) Representation of the simple synthetic apparatus employed in the preparation of monodisperse NC samples. (panels c and d are reprinting with permission from Murray et al. Annu. Rev. Mater. Sci. 2000.30, 545-610. Copyright 2000 Annual Reviews.)

heavy metals.⁴⁷ A newly discovered class of nanocrystal called perovskite nanocrystals can reach 80% quantum yields without any post synthesis modifications.¹

1.1.3 Multi-photon Processes

The previous discussions assume strictly one photon optical processes. However, multi-photon processes are also possible at high fluences. Fluence is a measure of photons in either energy/area or photons/area. The fluence threshold for these processes is lower in small nanomaterials where excitons (or other processes) are more likely to interact. The reduced volume increases the Coulomb interactions between charge carriers. Multiexcitons are the most common multi-photon process in the field of colloidal semiconductors.^{48,49}

A biexciton is created when a semiconductor nanocrystal absorbs two photons which leads to the formation of two excitons. Similar to a single exciton, the biexciton has a binding energy due to Coulombic forces; this often lowers the biexciton energy compared to a single exciton.²⁰ As the fluence is increased, triexciton (and higher) formation is also possible. The term multiexciton is often used to refer to triexcitons and above.⁵⁰ When the analyte material is a ensemble of colloidal semiconductors, the statistics of the number of excitons per particle must be considered.

In an ensemble, the number of excitons per particle cannot be exactly calculated. Instead Poisson statistics are used to find the distribution of multiexcitons across the ensemble. It is first necessary to find the absorption cross section of the material; this can be found using a saturation curve. After the absorption cross section is found, the Poisson distributions can be found for all fluences.⁵¹ The two equations used are as follows:

$$I(f) = a(1 - e^{-f\sigma_{\lambda}}) = a(1 - e^{-\langle N \rangle})$$
(1.10)



Figure 1.9: Electronic structure of the biexciton BX. (a) Biexcitons are most often studied using PL experiments, revealing a well-defined shift interpreted as the binding energy Δ_{BX} . This simple picture disregards the electronic structure of the exciton, which is revealed by the exciton Stokes shift δ_X . (b) The electronic structure of strongly confined semiconductor NCs can be represented in the exciton basis (left) or the electron–hole basis (right). The exciton basis includes the interactions between electrons and holes (middle). The degeneracy of the electron–hole configurations is indicated on the right panel. Reprinted from S. Palato, Journal of Chemical Physics, 152, 104710, (2020), with the permission of AIP Publishing.

$$P(k) = \frac{\langle N \rangle^k e^{-\langle N \rangle}}{k!} \tag{1.11}$$

where I(f) is the PL intensity as a function of fluence, *a* is a normalization constant, *f* is the fluence in photons/area, σ_{λ} is the absorbance cross-section, $\langle N \rangle$ is the average number of absorbed photons per nanocrystal and P(k) is the fraction of nanocrystals at absorbed photons *k*. Poisson statistics state that after pulsed excitation, nanocrystals have a distribution of absorbed photons (Figure 1.10b). This distribution will change as time evolves, as multiexcitons relax faster than single excitons.⁵² It is important to note that not all materials follow Poisson statistics; a saturation curve is one piece of evidence that the material is Poissonian.



Figure 1.10: a) Saturation curve that follows **Equation 1.10**. b) Poisson distribution that follows **Equation 1.11**. The y-axis represents the fraction of nanocrystals with the respective number of absorbed photons.

Similar to single excitons, multiexcitons have radiative and nonradiative decay processes. Multiexcitons have a very different time dependence when compared to single excitons, however. The existence of multiple excited electrons allows relaxation pathways that are not available to nanocrystals with a single exciton.⁵³ The most common, and best

studied, non-radiative mechanism for multiexcitons is known as Auger recombination. In a semiconductor nanocrystal, Auger recombination involves the recombination of one exciton; and rather than emission of this energy as light, a second exciton is promoted to a higher energy state (Figure 1.7a).⁵⁴ Auger recombination of biexcitons is often a order of magnitude or more faster than spontaneous emission of biexcitons. The radiative rates of a biexciton are on the same order of magnitude as single excitons.⁵⁵

As a result of the binding energies and the additional decay pathways, multiexcitons can be observed with a variety of techniques.²⁰ Time resolved photoluminescence, such as TCSPC, can resolve the faster decay rates of multiexcitons.⁵⁴ Spectroscopic photoluminescence without time dependence can also resolve multiexcitons peaks if the binding energies are large.⁴⁸ Absorptive methods have also been used. Pump-probe spectroscopy can similarly be used to resolve both spectroscopic and kinetic signatures of multiexcitons.^{21,56} As multiexcitons are fluence dependent, these methods often depend on a pulsed laser with fluence control. More advanced techniques, such as two-dimensional electronic spectroscopy, can give more in-depth information like the inhomogeneous binding energies of biexcitons.⁵⁷

1.2 Lead Halide Perovskite Nanocrystals

1.2.1 Lead Halide Perovskites

Perovskite is a generic crystal structure with the form ABX₃. It was commonly used to describe oxides such as SrTiO₃. B cations and X anions create an octahedral framework with a large gap. This large gap is supported by the A cation. Figure 1.11a shows a high symmetry cubic perovskite; however, other low symmetry types are possible. Two common low symmetry types are tetragonal and orthorhombic. Cubic is often the high temperature phase while orthorhombic is the low temperature phase, with tetragonal as intermediate (Figure 1.15a).⁵⁸

The existence of lead halide perovskites (LHP) has been known since the 1950s.⁵⁹ However, it was not until 2009 that methylammonium lead iodide attracted attention as a possible light absorbing layer for solar cells.¹⁰ Since then, other applications of interest have been developed including lasers and scintillators.^{60,61} The main attraction of lead halide perovskite solar cells is the potential low cost while maintaining efficiencies close to silicon based technologies; a maximum efficiency of 25.5% has been reached as of 2020.⁶² Another use is in perovskite/silicon tandem solar cells where efficiencies have reached 29.3%.⁶³ Along with practical uses, lead halide perovskites have physical properties that have drawn much interest.

Lead halide perovskite materials range from the near-UV chloride variants to the near-IR iodide containing perovskites.^{1,13} This band gap flexibility is one major draw for applications (Figure 1.11c). These materials are also known to have inherent trap resistance, or defect tolerance, which assists in device efficiencies. The defect tolerance is due to the energy levels of lead and halides; the energy levels correspond to shallow traps whereas in other semiconductors, defects result in deep traps. (Figure 1.11d).⁶⁴ The bonding nature in lead halide perovskites is also of interest; the bonds are known to be much more ionic and soft than most covalent semiconductors.⁶⁵ This ionicity leads interesting properties such as the formation of polarons that are several unit cells in diameter.⁶⁶

1.2.2 Polarons

A polaron is a coherent disturbance of charge in a lattice due to charge carriers. For example, a free electron will cause polarization by attracting all positive ions and repulsing all negative ions (Figure 1.12a).⁶⁷ The polaronic nature of lead halide perovskites has been the focus of many publications.^{16,68–70} The electron-phonon interaction is the basis of the phenomenon, and the relative strength of this interaction can be found with

$$\alpha = \frac{1}{2} \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_{r}\epsilon_{0}} \right) \frac{e^{2}}{\hbar\omega_{LO}} \left(\frac{2m^{*}\omega_{LO}}{\hbar} \right)^{\frac{1}{2}}$$
(1.12)

where ω_{LO} is the frequency of the LO phonon, e and m^* are the charge and effective mass of an electron respectively, and ϵ_{∞} and $\epsilon_{r}\epsilon_{0}$ are the absolute high-frequency and static



Figure 1.11: a) Structure of a cubic lead halide perovskite. The lead halide octahedral cage is supported by the A cation in green. b) Representative PL spectra of CsPbBr₃ nanocrystals showing band gap control through halide composition. Reprinted with permission from Protesescu et al. Nano Lett. 2015, 15, 6, 3692–3696. Copyright 2015 American Chemical Society. c) Example device layout of a lead halide perovskite solar cell. d) Left: energy levels of a defect intolerant semiconductor such as CdSe. Right: energy levels of lead and bromide with respect to the band gap. Deep trap states will lower the quantum yield of a semiconductor. Reprinted with permission from R. E. Brandt et al. Chem. Mater. 2017, 29, 11, 4667–4674. Copyright 2017 American Chemical Society.

permittivities respectively.* α is called the Fröhlich coupling constant and is generally higher for more polar crystals.⁶⁷ Lead halide perovskites are a polar semiconductor and have intermediate α values of 2-5.⁶⁶ This is called the Landau-Pekar model. It should be noted that the Landau-Pekar model is an approximation that works best in the strong coupling regime and with small polarons; there are a variety of formalisms and computational methods used to describe polarons in materials.⁷¹ However, Landau-Pekar is the only method used herein.

Polarons in a crystal have a characteristic size similar to an exciton. The size can be estimated with

$$R_{pol} = \sqrt{\frac{\hbar}{2m^*\omega_{LO}}} \tag{1.13}$$

where R_{pol} is the polaron size. The mass of the polaron, m_p , and self-energy, E_{self} , can be approximated with

$$m_p \simeq m^* \left(1 + \frac{\alpha}{6} + 0.0236 \alpha^2 \right)$$
 (1.14)

$$E_{self} \simeq \hbar \omega_{LO} (-\alpha - 0.0152\alpha^2) \tag{1.15}$$

where the self-energy is a measure of self-trapping where carriers are localized by polarons (Figure 1.12b).^{67,71} For CsPbBr₃, the size has been estimated to be 2-5nm. Polarons for hybrid organic-inorganic perovskites are estimated to be larger.^{16,70} The self-trapping of charges occurs when the self-energy is large (relative to thermal energy, k_bT). This self-trapping is separate from defect based traps that can occur in many materials, including semiconductor nanocrystals. However, the self-trapping could lead to charge localization which would have drastic effects on applications such as in solar

^{*}Permittivities are often called dielectric constants. However, dielectric constants should strictly refer to the static relative permittivity of a material: ϵ_r . Values for the low (static) and high frequency limits are often quoted. Depending on the field, these definitions can vary widely.

cells. For instance, polarons can lower charge carrier mobilities.⁷² The size and selfenergy of a polaron have inverse dependencies on the LO phonon energy: $R_{pol} \propto \omega^{-1/2}$ and $E_{self} \propto \omega^{1/2}$ (Figure 1.12c). Therefore, small polarons are more likely to cause trapping when the other parameters are unchanged. The self-energy of a polaron is also dependent on the polarity of the material (i.e. $\epsilon_{\infty}^{-1} - \epsilon_r \epsilon_0^{-1}$). A more polar material can have both a larger polaron radius and a high self-energy. CsPbBr₃ is an example of this with a 2-5nm polaron and a self-energy of ~45meV.⁵⁶ It should be noted that lead halide perovskites have broad phonon modes unlike II-VI and III-V semiconductors.¹⁶



Figure 1.12: a) Artistic view of a polaron caused by an electron. The Coulombic forces between the electron and the lattice will cause coherent displacement in the lattice. b) A exciton trapped by the self energy of the polaron. This will cause polaronic confinement in the proper conditions. c) R_{pol} and E_{self} have opposite dependencies on ω_{LO} . In the intermediate polaron size regime, confinement of the charge carriers can occur.

The interaction between an exciton and a polaron is aptly named an exciton-polaron, but this quasiparticle is still poorly understood theoretically.⁷¹ If the Bohr radius of the exciton is much smaller than the polaron radius, the results would be two non-interacting polarons from the electron and hole. However, two interacting large polarons would result when the Bohr radius is similar in size to the polaron.⁷³ This is a much more complex system to calculate than a single polaron. Experimentally, exciton-polarons have been observed in C₆₀, monolayer transition metal dichalcogenides, and lead halide perovskites.^{69,74,75} Similar to a polaron from a single charge, an exciton-polaron can result in trapping of charges. It is hypothesized that that screening of charges in certain perovskite materials, along with the inherent defect tolerance, is what leads to high efficiencies in solar or LED applications.^{76,77}

1.2.3 Perovskite Nanocrystal Synthesis

The first synthesis of all-inorganic perovskite nanocrystals was published in 2015.¹ In contrast to quantum dots, the band gap was mostly controlled with composition rather than nanocrystal size. Specifically the band gap of CsPbX₃ (where X is a halide) was varied from 3 to 1.5 eV by varying the halide between chloride, bromide and iodide.¹ However, it is possible to control the size of the nanocubes to create quantum dots.⁷⁸ The chloride, bromide and mixed Cl/Br lead halide perovskites are known to be quite stable, however, the redder iodide and mixed Br/l versions are not stable.¹³ Pure CsPbl₃ tends to aggregate and form the non-perovskite "yellow phase".⁷⁹ Various methods have been used to slow this transition but ultimately the perovskite phase is thermodynamically unstable at room temperature.^{80–82} The "black phase" CsPbl₃ forms at the high temperatures of the hot injection method.⁸³ The standard ligands used are oleylamine and oleic acid (Figure 1.16). However, other methods using different ligands have been developed.^{84,85}

Hot injection is the standard method of synthesizing perovskite nanocrystals. However, a variety of other methods are possible. Ligand Assisted Reprecipitation (LARP) is a room



Figure 1.13: a) Cartoon of a CsPbBr₃ nanocrystal. The nanocrystal is covered in "hairy" ligands (the entire nanocrystal is in fact covered). b) Hot-injection synthesis of perovskite nanocrystals. The Cs-oleate precursor is synthesized in a separate air-free flask. An ice bath is used to cool and quench the reaction after injection.

temperature method that involves dissolving the the constitute ions in a polar solvent and then dropping the solution into a non-polar solvent that contains the ligands.⁸⁶ Wet ball milling has been shown as a possible low cost method of synthesizing certain lead halide perovskites. Wet balling milling could allow a much lower amount of solvents to be used.⁸⁷ Microwave synthesis is another high temperature method that involves potentially high pressures.^{88,89} This could allow other high pressure phases to be synthesized. It is also possible to create shapes other than nanocubes.

Nanocubes were the first synthesized shape, but the shape of a nanoparticle has effects properties including the exciton.⁹⁰ Applications such as lasers can be aided by shape controlled nanocrystals.⁹¹ Nanoplatlets of CsPbX₃ have been synthesized though ligand surface control.⁹² Some methods have synthesized platelets on the micrometer scale.⁹³ Further studies have extended this shape control to nanowires, including wires into the micrometer range.⁹⁴ Many different shapes have been synthesized (Figure 1.14A-F).⁹⁵ The shape anisotropy of these materials can be utilized through the emission of polarized light. This is potentially useful in lasing applications.^{96–98} Nanowires are utilized in nanophotonic applications where small feature sizes are vital.⁹⁰ These shape controlled





materials often have different electronic properties than nanocubes. When a nanoparticle is confined in different dimensions, the density of states varies (Figure 1.14G). However, they are made of the same material and share chemical properties.

1.2.4 Properties

Perovskite nanocrystals are cube shaped and range in size from 4-15nm.^{1,78} The defect tolerance and polaronic nature remain in the nanocrystal form. Indeed, the defect tolerance is vital for high quantum yields which is of interest for emission applications. Similar to bulk lead halide perovskites, the control over the band gap comes from altering the halide composition.¹ In terms of three pure halide compositions (i.e. CsPbCl₃, CsPbBr₃ and CsPbI₃), it is known that the bromide and iodide nanocrystals have high quantum yields as synthesized. However, the chloride nanocrystals need post synthesis modifications to reach the same quantum yields.⁹⁰ The stability also varies depending on composition.

In terms of stability, the green emitting bromide perovskites have been the most stable. One of the deciding factors in the stability of a perovskite material is the relative sizes of the ions. There are two equations that are used to predict if a compound will form in a perovskite structure:

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)}$$
(1.16)

$$\mu = \frac{r_B}{r_X} \tag{1.17}$$

where *t* is the Goldsmith tolerance factor, μ is the octahedral factor, and r_A , r_B and r_X are the ionic radii of the three atoms. These values are based on atomic packing geometries and both must fall within a certain range in order to form a stable perovskite

structure. The estimated stability ranges are 0.88 < t < 1.1 and $0.41 < \mu < 0.89$. The values of *t* and μ for CsPbBr₃ are 0.92 and 0.5 respectively.^{13,99} This thesis focuses on CsPbBr₃ due to the stability issues in the chloride, iodide and mixed halide perovskite nanocrystals.^{83,100,101} The size stabilization of nanocrystals is well known; the small size of the particles causes higher surface energies which can stabilize different crystal phases.^{102,103} The nanocrystals form at the high temperature of the hot injection synthesis, and the size stabilization allows the chloride and iodide species to be kinetically stable for a short period of time. It also causes the thermodynamic stability of CsPbBr₃.^{83,100,101} Understanding the crystal structure is vital to understanding the stability of a material.



Figure 1.15: a) The three common crystal structures of CsPbBr₃ which depend on the lead halide angle. Axial and equatorial halide atoms are shown in the bottom left in red and blue respectively. Cubic has 180° angles while tetragonal has a bent axial Pb-X-Pb angle. Orthorhombic has an additional bend between equatorial halide atoms. b) One crystal structure theory called nanotwins has many crystal domains in one nanocrystal with dislocations between the domains. Adapted with permission from [7]. Copyright 2017 American Chemical Society.

The crystal structure of CsPbBr₃ at room temperature was first hypothesized to be the cubic perovskite.¹ Newer studies then showed that the crystal structure was instead orthorhombic with a orthorhombic to cubic phase transition at high temperature.⁵ An additional report painted a more complicated picture involving the phenomenon called nanotwins. This involves multiple crystal domains a single nanocrystal with dislocations between the domains as shown in Figure 1.15b. This effect complicates the analysis of

crystal diffraction data.⁷ It is also theorized that multiple crystals structures can coexist. Signatures of orthorhombic and cubic species were seen in the same sample.^{6,104} It is possible that nanotwins can have separate crystal structures in the same nanocrystal. The temperature dependence of phase transitions is known to vary depending on size of nanoparticles, likely due to the variation in surface energy.^{103,105} This also could depend on the ligands used to stabilize the surface.

The ligands used in the standard hot injection synthesis of CsPbBr₃ are oleylamine and oleic acid (Figure 1.16.¹ During the synthesis, the oleylamine is protonated and coordinates to the halides while the oleic acid is deprotonated and coordinates to the lead and cesium ions. This allows the ions to dissolved into solution, and after the reaction, the ligands coordinate to the nanoparticle surface allowing for colloidal suspension. The surface properties of CsPbBr₃ nanocrystals is still controversial. Some studies suggest that the ammonium ligand headgroup substitutes for a cesium ion on the surface.^{106,107} Others suggest the ammonium ligand is binding to the halides through a hydrogen bridge (i.e. hydrogen bonding), or that an ammonium-oleate ligand complex is binding to the surface.¹⁰⁸ The acid-base nature of the dual ligand system is extremely important. For example, an acidic ligand with a higher pK_a increases the rate at which the ammonium ligand is protonated; this increases the surface coverage of the ammonium ligand.⁸⁰ The choice of ligand also affects the growth of the nanocrystals during synthesis. Shorter chain ammonium ligands tend to create nanoplatelets rather than nanocubes due to shorter chain lengths. Shorter alkyl chain lengths for the acidic ligand increases nanocube size, possibly due to steric effects.¹⁰⁹ Increasing the acidic ligand concentration has the same effect due to the increase in acidity.¹¹⁰ However due to the ionic nature of the ligand binding, the ligands are highly dynamic and easily detach from the surface.¹⁰⁸

Free ligands are in equilibrium with the surface bound state that favours the free state, when compared to a covalently bound systems.¹¹¹ This causes the nanocrystal to become bare as the colloid is purified. A bare nanocrystal is much more likely to react with other species or aggregate with other nanocrystals. This is likely the cause of instability in



Figure 1.16: Common ligands used as capping agents of CsPbBr₃ nanocrystals. Oleylamine and oleic acid are a dual ligand system often used together. Lecithin and sulfobetaine are zwitterionic ligands that cap the nanocrystal unaided by other ligands.

CsPbBr₃ nanocrystals. To combat this, some newer syntheses have utilized a single zwitterionic ligand rather than the dual acid-base system. A zwitterionic ligand has a headgroup with both a positive and negative charge; this allows bidentate ligand binding which increases the surface binding energy of the ligand.⁸⁴ A low cost natural product ligand called lecithin was also used as a ligand.⁸⁵ Lecithin has the added benefit of being a zwitterionic ligand.

In addition to the surface, the crystal lattice of CsPbX₃ is also highly dynamic. The labile nature of lead halide perovskites allows mobility of ions through the lattice. This has been utilized by exchanging the halides in the nanocrystals; for example, it is possible to completely swap the bromide ions in CsPbBr₃ nanocrystals for chloride ions, creating CsPbCl₃ nanocrystals.^{112,113} It is also possible to change the B site ion although this has more drastic effects on the nanocrystals. The shape of the nanocrystals are irreversibly altered upon B site substitution.¹¹⁴ Although the energy levels of the constituent atoms are the primary reason, it is believed that the dynamic lattice could contribute to the defect tolerance of CsPbBr₃.^{115,116}

Similar to bulk lead halide perovskites, the nanocrystal form is found to have a high defect tolerance. This is readily apparent as CsPbBr₃ nanocrystals have a high

photoluminescence quantum yield without post synthesis modifications.¹ This is largely due to the position of defect energy levels within the conduction and valence band or as shallow traps. Deep traps have a more drastic effect on the quantum yield.^{117,118} It has also been suggested that polarons in lead halide perovskite shield charge carriers from traps.^{119,120} The high quantum yields are present despite the large surface areas of the nanocrystals; this is in contrast to II-IV semiconductor nanocrystals where surface modifications are needed to reach quantum yields above 50%.¹²¹ Indeed, the photoluminescence quantum yield was shown to have little dependence on the size.⁷⁸

The size of CsPbBr₃ is known to effect various electronic properties. CsPbBr₃ quantum dots can be synthesized.⁷⁸ However, the size at which a nanocrystal becomes a quantum dot is less clear. A convenient cutoff is where the cube edge length is less than the Bohr diameter of 7 nm.¹²² A typical sizing curve for the quantum confinement effects of the band gap can be seen in Figure 1.17a. For example, the Stokes shift and biexciton binding energy are known to change with nanocrystal size.^{8,123} However, above 7 nm these size effect are minimized.

Above 7 nm edge length, it is expected that CsPbBr₃ nanocrystals would only show signs of weak confinement. However, it is apparent that nanocrystals over 10nm in size have some characteristics of quantum confinement. For example, the emitting state of CsPbBr₃ has been shown to have a manifold of states that is consistent with quantum confinement on the nanosecond scale.¹²⁴ However, the nanocrystals are too large to spatially confine the exciton. This effect has been rationalized through the polaronic confinement of the exciton rather than spatial confinement. This effect is analogous to the self-trapping of charges through polarons but over several unit cells rather than one. Similar confinement effects have been observed in ultrafast pump-probe measurements.⁵⁶ It is theorized that the self-energy of the polaron created by the exciton causes a confinement effect which results in quantized bound states (Figure 1.18a). This results in a blueshift as the polaron is formed and a redshift as the exciton thermalizes through the polaronic states (Figure 1.18d). Interestingly, the idea of intrinsic quantum



Figure 1.17: a) Experimental versus theoretical (effective mass approximation, EMA) size dependence of the band gap energy. Reprinted with permission from Protesescu et al. Nano Lett. 2015, 15, 6, 3692–3696. Copyright 2015 American Chemical Society. b) Size dependent Stokes shifts for CsPbX₃ nanocrystals. Reprinted with permission from Brennan et al. J. Phys. Chem. Lett. 2020, 11, 13, 4937–4944 Copyright 2020 American Chemical Society.

confinement has also been applied to Bulk FAPbl₃. Although polarons were not invoked, it is possible that polaronic confinement is the cause of this intrinsic confinement.¹²⁵ Emissive experiments with picosecond time resolution will offer an additional confirmation



Figure 1.18: Effect of polaron formation and confinement on lineshape 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. Ref. [56] by Colin Sonnichsen, et al. is licensed under CC BY 4.0.

of these conclusions, although rigorous calculations are needed to confirm the physics of such a unique phenomenon. This self-trapping could lead to charge localization which could have drastic effect on applications such as in solar cells and LEDs, especially in bulk perovskites that depend on charge mobility.^{72†}

[†]Note that I contributed to citations [56, 124] in the form of synthesis of perovskite nanocrystals.

1.2.5 Applications

Lead halide perovskites have a variety of proposed optoelectronic applications. In the bulk, solar cell applications are the closest to commercialization. Specifically, multijunction silicon/perovskite solar cells are being commercialized. Lead halide perovskite are a direct band semiconductor which allows a thinner layer to be used compared to an indirect band semiconductor like silicon.²⁷ The solution processing of lead halide perovskites is also a major advantage for device applications.⁹⁰ The nanocrystal form can also be used in solar cell applications. However, the organic capping ligands used in nanocrystals have a large effect on charge transport. The ligands are required to passivate and stabilize the surface currently but also reducing transport efficiency.⁹⁰

The main application of interest for lead halide nanocrystals is for light emitting diodes (LEDs). Specifically, LEDs for display applications have drawn the most interest.^{126,127} This is due to the narrow and efficient emissions of ~25nm and over 90% quantum yield respectively.¹²⁸ Display applications require 3 LEDs with RGB (red green blue) to produce almost any colour. The green emitting APbBr₃ species have been the most effective at this role due to high efficiencies and the specific wavelength of the emission. APbl₃ species are efficient but emit above 680nm while the ideal wavelength for a display led is ~650nm. This compares to APbBr₃ which emit close to the ideal green of ~520nm.¹²⁹ Mixing of halides allows blue and red emitters to reach more ideal wavelengths. However, mixed halides are often less stable, and the two halides have a phase separation in an applied electric field.^{130,131} Therefore, the green emitting perovskite nanocrystals are a potential substitution for more expensive InP based quantum dots current in use in devices.⁹⁰ In applications that require high light intensity, Auger recombination can limit the efficiency of LEDs due to the high number of excitons.¹⁸ Lasing is even more demanding in terms of the average number of photons per nanoparticle.^{132,133}

Similar to LEDs, the ability to modify the bandgap through halide composition drew much interest to lead halide perovskites for laser applications.^{133,135} Lasers require high



Figure 1.19: a) Three level energy system diagram including a legend. The population inversion must be between states 1 and 2. b) Four level energy system diagram. The population inversion must be between states 2 and 3. c) Pump-fluence dependence of the emission from a CsPbBr₃ NC film. d) Variable stripe-length experiment for estimation of modal net gain for the CsPbBr₃ NC film. c) and d) are reprinted from Ref. [134] by Sergii Yakunin et al. (licensed under CC BY 4.0.)

excitation levels that creates a population inversion between two states. The most efficient example of this is a 4 level system as seen in Figure 1.19b.^{32,133} This high excitation level creates an environment where nonradiative processes are possible. In semiconductor nanocrystals, this occurs when multiexcitons are created, and therefore, Auger recombination is a concern. Decreasing the Auger recombination rate will allow the excitons to recombine radiatively more efficiently.^{54,55} In semiconductor nanocrystals such as perovskites, the most common type of lasing discussed is amplified spontaneous

emission (ASE).¹³⁴ ASE is a method where the pump light is focused into a line of varying strip length where the strip forms an optical cavity (Figure 1.19d). The amplification depends on both the fluence and the strip length. Two major issues remain in any commercialization of lead halide perovskites: stability issues¹³⁶ and the toxicity of lead. Lead is already used in electronic devices but limits are in place for lead concentrations. These issues are present in both the nanocrystal and bulk forms.

1.3 Thesis overview

The remaining chapters describe the temperature, time and fluence dependence of the photoluminescence of cesium lead bromide perovskite nanocrystals. The combination of the three variables with high time resolution is unique in the Kambhampati Lab, and my analysis of the experiments is contained herein.

Chapter 2 is the experimental chapter describing the synthesis, characterization and data processing steps necessary to recreate the works in Chapters 3-6.

Chapter 3 is adapted with permission from *J. Phys. Chem. C.* 2021, 125, 49, 27504–27508. Copyright 2021 American Chemical Society. This chapter discusses the temperature dependence of photoluminescence from perovskite nanocrystals. It is a foundational paper that is necessary to show that the perovskites nanocrystals studied here are bulk-like nanocrystals.

Chapter 4 is adapted from Strandell, et al. which is currently under review. It explores the fluence dependence for time resolved photoluminescence of CsPbBr₃ nanocrystals. The existence of multiexcitons at higher fluences is proof that the bulk-like nanocrystals also have quantum confinement properties.

Chapter 5 is adapted from a manuscript current under preparation (Strandell, et al.). This chapter describes the temperature dependence of Auger recombination from

multiexcitons in $CsPbBr_3$ nanocrystals. The quantum yield and relaxation rates are discussed.

Chapter 6 is adapted from a manuscript current under preparation (Strandell, et al.). This chapter describes the temperature dependence of temperature dependence of CsPbBr₃ nanocrystals on the picosecond time scale. Fine structure of the exciton is revealed through analysis of time dependent linewidths at 4K. I am the sole first author of the four described manuscripts. The appendix includes supporting information from the four manuscripts.

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Chapter 2

Experimental

This chapter discusses the experimental methods employed for the contents of this thesis. This includes details of the synthesis for materials used, as well as instrumental and experimental information for the streak camera. Data processing and modelling can also be found herein. Many of these methodologies are already included in Chapters 3-5 and the appendix; however, this chapter summarizes these and includes more details.

2.1 Synthesis of Colloidal CsPbBr₃ Nanocrystals

All perovskite nanocrystals used in this thesis were synthesized using the hot injection method. There are many versions of perovskite nanocrystal hot injection syntheses, but the one followed most closely was the original 2015 Protesescu et al.¹ The reaction took place in a air-free Schlenk line, using two separate flasks. In the reaction flask, 74mg of PbBr₃ was dissolved in 10mL hexadecane* with 1mL each of oleylamine and oleic acid. The Cs-precursor was made by dissolving 108mg of Cs₂CO₃ in 5mL of hexadecane and 1mL of oleic acid. Both of these mixtures were heated to 120°C under vacuum to dissolve the solids and remove water. The solutions were then put under argon, and the

^{*}Tech grade 1-octadecene is used in the literature often. Hexadecane has a slightly lower boiling point but is often more pure. Either can be used.

temperature of the reaction flask was raised to 180°C. The temperature of the Cs-precursor flask was kept above 100°C for the synthesis. The Cs-precursor can be reused for multiple syntheses and was kept under argon when not under use. 0.8mL of the Cs-precursor was injected into the reaction flask; the reaction immediately takes place and was quenched using an ice bath after 10 seconds.

To isolate the large 10-20nm sized nanocrystals from the reaction mixture, no toluene or antisolvent was added at this point. The reaction mixture was centrifuged at high speeds (12000 rpm, 21000G) for 10 minutes. The supernatant was discarded and the precipitate suspended in toluene. The resulting colloid was centrifuged two times at low speeds (6000rpm, 5000G) for 2 minutes each to remove larger crystals (i.e. the precipitate was discarded).

2.2 Standard Characterization

Absorbance spectroscopy was performed using a Cary 4000 UV-Vis Spectrophotometer, and fluorescence spectroscopy was performed using a Cary Eclipse Fluorescence Spectrometer. Photoluminescence and photoluminescence excitation spectra were both collected. The colloidal solutions were diluted by a factor of 200, and all spectra were collected using fused quartz cuvettes. The slits of the fluorescence spectrometer were set to 2.5nm for both emission and excitation slits.



Figure 2.1: Examples spectra of CsPbBr₃ nanocrystals in toluene. a) Absorbance spectrum b) Photoluminescence excitation spectrum c) Photoluminescence spectrum.

Transmission electron microscopy was performed using a Talos F200X G2 TEM on carbon coated copper grids with a 400 mesh. The colloidal solutions should be diluted by 2-10x depending on the starting concentration and the desired nanoparticle density for the TEMs. A high density of nanoparticles allows easier particle sizing. However, the electron beam will sublimate the organics present and make obtaining a high quality picture more difficult. The diluted solutions were drop-cast directly on the TEM grids and allowed to dry under vacuum.

2.3 Streak Camera Work

The majority of the spectroscopy in this thesis was done using the Kambhampati Group's time resolved photoluminescence setup (an Axis Photonique TRS time-resolved spectrometer). The setup used is a streak camera paired with a spectrograph. For the purposes of this work the setup is referred to as a "streak camera" for simplicity. The streak camera can be operated in both non-time resolved and time resolved modes. The time ranges of the time resolved modes range from 1000ns to 700ps. There is a trade-off between time resolution and total time probed. The majority of work in this thesis involves the non-time resolved, the 10ns, or the 700ps modes. Temperature dependence was also used with this setup by installing a cryostat.

2.3.1 Temperature Dependent Photoluminescence

The sample films were created by drop casting a sample solution of 4% polystyrene in toluene onto either glass or fused quartz substrates. The temperature dependent photoluminescence experiments were performed using two experimental setups. The glass transition temperature of polystyrene is greater than 300K at this molecular weight.² The streak camera coupled to a Janis SHI-4XG-5 closed cycle cryostat collected time resolved and non-time resolved spectra from 4 to 300 K. Additionally, an Avantes AvaSpec-Mini2048CL spectrometer coupled to a Janis SuperTran-VP cryostat was used

to collect spectra down to 77 K. The samples were excited with either a 405nm Coherent OBIS laser or a frequency doubled Coherent Legend Elite Duo HE+, 1 kHz rep. rate (800nm doubled to 400nm wavelength).

2.3.2 Time Dependent Photoluminescence

The operation principle of a wavelength resolved streak camera is as follows: The light enters the streak camera's spectrograph through a slit. The slit width is changeable and is proportional to the signal intensity. Higher slit widths will broaden the signals in the wavelength axis however. The light then enters a spectrograph where the light is separated into wavelengths (Figure 2.2a). The light enters the streak tube through a photocathode. The photocathode converts the light into electrons which are accelerated with a a voltage of 15kV into the streak tube. The electrons are focused with a variety of electro-optical lenses (Figure 2.2b). To produce non-time resolved spectra, the electrons then hit the fluorescent screen converting the electrons into light which can be recorded by the CCD. To produce a time resolved image, the electrons can be swept across the CCD with the sweep plates by varying the voltage across them.

Two different time modes were used. The first is a electronically triggered mode with a time range of 10ns. This mode has an IRF (instrument response function) FWHM of approximately 100ps. The FWHM of the IRF defines the time resolution of each streak trace. Additionally, the streak tube can be optically triggered with a (usable) time range of approximately 250ps; this gives a time resolution of 3-5ps. The optical trigger is performed using a 800nm pulse which is detected by a photoswitch.³ The wavelength resolution of both modes is 0.6 nm (approximately 2.5 meV at 500nm). The trace, and its corresponding background measurement, is obtained from 10-20 averages with exposure times of 0.5-10s. The exposure times must be corrected if a intensity comparison is required between two separate traces. If multiple fluences and pump wavelengths were used, the order was randomized to reduce systematic errors.



Figure 2.2: a) The optical setup of the time resolved photoluminescence experiment. The collection optics are two 90° off-axis parabolic mirrors that collimate and then focus the sample emission. The collection optics can be operated either in backscatter (shown) or at 90° to the pump beam. b) The streak tube of the camera. The light enters at the top left and is converted into electrons. The electrons pass through the streak tube and are converted into light at the bottom right to be detected by the CCD. ©Axis Photonique Inc. http://www.axis-photon.com/streak-camera/axis-trs-ultrafast-time-resolved-spectrometer/

The final trace is obtained with some post-processing procedures. First, the background is subtracted from the trace. A 1% shear correction is applied to correct for electrode and detector alignment. The value for this is obtained from traces collected with a static bias. The intensity is then corrected for uneven time bins, followed by conversion from wavelength to energy (including the Jacobian correction).⁴ Pump scatter is used to find the IRF and time zero.

When a colloidal sample was used, the sample is flowed (vertically) in a 0.5 mm path length flow cell using a peristaltic pump (Masterflex 77390-00) to lower laser exposure and to prevent build-up of aggregates. The streak camera was used to collect time resolved spectra. The pump laser was a frequency doubled 3.1eV from a Ti:sapphire regenerative amplifier (Coherent Legend Elite Duo HE+, 1 kHz rep. rate, 800nm). Additionally, a

2.5-2.7eV pump was produced from a Coherent OPerA Solo Optical Parametric Amplifier (OPA) for use in some experiments. This is useful when testing if the excess pump energy has an effect on photoluminescence dynamics.



Figure 2.3: Full streak trace with the pump scatter at 3.1eV and the signal at 2.4eV. The x-axis is the time dependence with the the energy (or wavelength) on the y-axis.

2.3.3 Data Processing

Data processing of streak images was performed using Python. The streak camera produces 2101x2101 txt files that include the time and wavelength as seen in Table 2.1.[†] The exact size of the array can change depending on settings in the software. Various post experiment corrections have to be performed including a background subtraction and

[†]It is also possible that "fits" files (extension .FIT or .fits) types are used. Use the Python package astropy to handle these files.

a shear correction. The photoswitch mode has no built-in conversion from pixels to time and wavelength; therefore, the indexes are in CCD pixel positions. The correction pipeline includes this conversion. My pipeline then creates an hdf5 file to decrease load times of the data later. The correction pipeline and example analysis scripts can be found on GitHub here.

Table 2.1: Streak text file format. The NaN (not a number) in the zero position is a placeholder. Time is either in ns or ps depending on the time range while wavelength is in nm. The remaining area is a 2100x2100 array of intensity values. For the photoswitch mode, the final 600 pixels are often cut off resulting in a 2100x1500 array. $Z_{i,j}$ represents the intensity values of the array.

NaN	Time (ps or ns)					
<	$Z_{0,0}$	$Z_{0,1}$	$Z_{0,2}$	$Z_{0,3}$	•••	$Z_{0,j}$
Vavelength (n	$Z_{1,0}$	$Z_{1,1}$	$Z_{1,2}$	$Z_{1,3}$	• • •	$Z_{1,j}$
	$Z_{2,0}$	$Z_{1,1}$	$Z_{2,2}$	$Z_{2,3}$	• • •	$Z_{2,j}$
	$Z_{3,0}$	$Z_{0,0}$	$Z_{0,0}$	$Z_{3,3}$	• • •	$Z_{3,j}$
	:	÷	÷	÷	۰.	÷
m)	$Z_{i,0}$	$Z_{i,1}$	$Z_{i,2}$	$Z_{i,3}$	•••	$Z_{i,j}$

The time resolved photoluminescence data allows one to compare spectra at different times or compare PL decays at different wavelengths. An extensive analysis of time dependent spectra is found in Chapter 4. By fitting the time dependent spectra using multi-Gaussian analysis, the multiexcitons can be separated from the single exciton in wavelength. The addition of fluence dependence gives extra support to this analysis. At low fluence and at late times, only the single exciton should be emitting. For high fluences, multiexcitons should be present at early times. The knowledge of the processes present in the material used should guide how additional Gaussians (or other lineshapes) are added. See Chapter 4 for an example of using multi-Gaussian analysis with time resolved photoluminescence data from CsPbBr₃ nanocrystals.

It should be noted however that one must be careful during multi-Gaussian fitting. Fitting a lineshape with 3 Gaussians has 9 degrees of freedom: amplitude, width and center for each peak. This allows lineshapes to be fit "well". Therefore, there should always be fixed degrees of freedom to avoid overfitting. For example, the fitting performed in Chapter 4 never had more than 3 degrees of freedom due to fixing of the peak widths and centers. For fitting, it is recommended to use the Python package Lmfit. This package has many pre-built models such as Gaussian and Step-functions. LMFIT also automatically reports parameter fitting errors, chi-squared values, and other fitting results.

2.4 References

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Chapter 3

The Temperature Dependence of the Photoluminescence of CsPbBr₃ Nanocrystals Reveals Phase Transitions and Homogeneous Linewidths

This chapter is adapted with permission from *J. Phys. Chem. C.* 2021, 125, 49, 27504–27508. Copyright 2021 American Chemical Society. I am the sole first author with Patanjali Kambhampati as an additional author. I performed all experiments. PK and I both wrote the manuscript. This chapter discusses the temperature dependence of photoluminescence from perovskite nanocrystals. It is a supporting paper showing that the perovskites nanocrystals studied here are bulk-like nanocrystals. This is an observation that supports the hypothesis of polaronic confinement of excitons that is central to this thesis.

3.1 Abstract

Semiconductor perovskites are known to be strongly coupled to a dynamically disordered lattice. Two key phenomena to consider are phase transitions and phonon contributions to homogeneous linewidths. Each of these parameters will be highly dependent on material parameters and would benefit from a simple measure. Here we perform temperature dependent photoluminescence spectroscopy on bulk CsPbBr₃ perovskite nanocrystals. The data reveals a discontinuity in the energy gap suggesting a phase transition between orthorhombic and cubic phases. The temperature dependence of the linewidth reveals negligible coupling to the ligands but strong coupling to polar optical phonons via the Fröhlich coupling. This temperature dependence suggests homogeneous line broadening dominates the observed linewidths.

3.2 Introduction

Lead halide perovskites have been one of the most exciting materials of the energy and optical material fields. The single crystal or polycrystalline types have found uses in lasers,¹ solar cells,² and detectors.³ Following the development of films, perovskite nano- crystals (PNCs) inversions have been developed. PNCs are of interest for light emitting diodes,^{4,5} solution-processed solar cells⁶ and lasers.⁷ The interest for LED and solar cells is partially due to resistance to trap states which leads to high photoluminescence quantum yields.⁸ Colloidal PNCs can reach 90% PLQY without post-synthesis modifications.⁹ Additionally, PNCs have a narrow emission that is tunable between the near-UV and near-IR. The generic APbX₃ material is remarkably flexible in terms of nano-structuring: nanocubes, wires, sheets and quantum dots have all been synthesized.^{9–13}

For NCs, the green emitting bromides have had the most interest (Figure 3.1). Interest in applications for these materials necessitates the understanding of the underlying

physics. Two areas of interest are the exciton fine structure^{14–16} and crystal structure.^{17–21} Both are somewhat controversial in that they have had competing theories published. The room temperature crystal phase of CsPbBr₃ NCs was first reported as cubic⁹ (Pm3m̄, Figure 3.1b) but reports of tetragonal (P4/mbm)¹⁵ and orthorhombic (Pbnm or Pnma)¹⁷ followed.

The bulk CsPbBr₃ literature shows very different results than for the NC regime. In the bulk, the lowest temperature phase transition of CsPbBr₃ is at 361K (orthorhombic to tetragonal). Therefore, the room temperature form is orthorhombic.²² The high surface energy of a nanocrystal can stabilize low temperature phases.^{23,24} For the temperature dependence of CsPbBr₃ NCs, much of the confusion in the literature on the crystal structure is likely due to the dual-phase nature of the nanocrystals.

Single nanocrystal TEM shows that CsPbBr₃ nanocrystals are primarily cubic with minority of orthorhombic NCs (at room temperature).²⁰ THz results have found that between 100 and 150K the percentage of orthorhombic to tetragonal nanocrystals increases (up to 50% orthorhombic at 7K).²¹ This contrasts the bulk characteristic where CsPbBr₃ is orthorhombic below 361K.²² For CsPbI₃, it has been shown that size reduction allows the nanocrystals to form cubic lattices whereas the bulk quickly changes into the "yellow phase" orthorhombic. Similarly, MAPbBr₃ has been shown to have a size dependent phase transition between the cubic and tetragonal phases.²⁵ These results combine to show a picture where the CsPbBr₃ nanocrystal are polymorphic with both orthorhombic and cubic character. There is still confusion over the nature of individual nanocrystals, as single crystal TEM results contrast the partial orthorhombic model from ensemble measurements. It is known that the crystal phases can coexist in a single nanocrystal for traditional oxide perovskites as well (i.e. polymorphism).^{26,27} Contrasting results have shown a pure orthorhombic phase at room temperature while the lowest temperature phase change was established to be at 332K.^{19,28} Due to the complexities of establishing structure, and the plethora of structures available, one aims for a simple measure of structural transformations.



Figure 3.1: Material overview. (a) Absorbance and fluorescence of CsPbBr₃. (b) Cubic perovskite structure (grey – lead, blue – cesium, brown – halide). (c) TEM image of a CsPbBr₃ sample (the white scale bar is 20nm).

3.3 Results and Discussion

In this study, we performed temperature dependent photoluminescence (PL(T)) on CsPbBr₃ nanocrystals (Figure 3.2a) with edge lengths larger than 10 nm. Importantly, these NC are in the bulk-like regime and should not be considered as quantum dots. a point which we have recently reviewed.²⁹ The temperature was varied between 4 and 300K. CsPbBr₃ NCs were synthesized using the well-known hot injection method (see Supporting Information for additional experimental methods).⁹ The slope of the photoluminescence excitation and the absorbance are very similar. This results in a flat quantum yield spectrum for these materials. The flat quantum yield spectrum arises due to the large quantum yield with weak hot carrier trapping.^{30,31} For more detailed analysis, the spectra are Jacobian correcting into energy units.³² The energy shifts and full width half maxima (FWHM) were then extracted (Figure 3.2 b and c). The Stokes shift of CsPbBr₃ was previously reported as independent of temperature in this range (between 43-46 meV).³³ Therefore, the assumption was made that the peak emission energy and band gap shifted equally. The peak width dependence of temperature follows the standard curve (for semiconductor nanocrystals) that is flat from 4 to 50K and curve into a linear line between 50 and 300K.³⁴

However, the energy shift of lead halide perovskites is unusual when compared to most semiconductors. For instance, semiconductors typically redshift in energy as temperature increases;³⁴ in contrast, lead halide perovskites blueshift with increasing temperature. This effect has been well described in other works. The dependence of the band gap on temperature is known to be a function of electron-phonon coupling and lattice expansion. This interplay often results in a small (and negative) band gap slope at low temperatures that gradually increases with temperature. Another feature that contrasts CsPbBr₃ is the sudden change in slope for the band gap shown in Figure 3.2c. This effect is occasionally by inconsistently seen in the literature but not rationalized.^{35–37} The temperature dependence of the band gap is reduced above a certain threshold (~150K). The complexity of the crystal structure can cause challenges in observing temperature phase changes in diffraction experiments for CsPbBr₃ NCs.³⁶ However, experiments have been done which show the orthorhombic-tetragonal-cubic phase changes.¹⁹ Synchrotron experiments have provided important insight into the structure,¹⁸ but simpler experiments are needed to quickly and inexpensively provide an understanding of the crystal structure.

Some PL(T) studies of CsPbBr₃ NCs have concluded there are no phase transitions at cryogenic temperatures. However, only phase transitions with an obvious discontinuity in the peak emission slope were considered (i.e. first-order transitions). Second-order phase transitions should show no discontinuation in the emission. First-order transitions show discontinuations due to lattice reconstruction while second-order phase transitions result in displacement rather than reconstruction.³⁸ Regardless of the order, the initial task is the observe whether there are transitions and at what temperature they occur. Polymorphism is a complication to the first and second order phase transition model.

In the bulk CsPbBr₃ example, the low temperature transition at 361K is known to be first order.³⁹ However, bulk-like nanocrystals may be different than single crystal CsPbBr₃. One report using PL(T) showed no obvious discontinuity in the band gap between 100 and 500K in CsPbBr₃.⁴⁰ The inconsistency between bulk and NC is due to high surface-to-volume ratios affecting the thermodynamics of phase transitions for the NCs.²⁴ We



Figure 3.2: Temperature dependent photoluminescence data. (a) Normalized temperature dependent 2D plot of PL data. (b) Temperature dependence of the PL FWHM (Γ) compared to Boltzmann constant. (c) Energy shift of the PL with temperature. The orange and green lines are linear fits and are guides for the eye only.

propose the change in slope could therefore be a sign of a change in crystal structure. However, the lack of structural data makes it difficult to definitively assign. The main point is that a discontinuity is observed, and this phenomenon is often consistent with a phase change. We propose these temperature dependent photoluminescence studies are a simple method for an initial search for phase transitions. It is known that lattice expansion can vary with crystal phase.^{41,42} A change in thermal expansion rate could cause the band gap to have a lower temperature dependence above 150K.

Most PL(T) studies fit the peak shift to Equation 3.1 (Varshni equation).

$$E_g(T) = E_0 - \frac{(\alpha T^2)}{(T+\beta)}$$
 (3.1)

The Varshni equation, however, has little physical meaning: it is phenomenological. E_0 is the band gap at 0K while α and β are empirical fitting parameters.⁴³ The wide use of the approximation in Equation 3.1 is due to the complexity of the dependence of the band gap on temperature and the lack of a microscopic theory. Equation 3.1 fails to fit the specific PL(T) curve of CsPbBr₃ NCs (Figure 3.3b). It is impossible to create a universal equation to describe the temperature dependence of any band gap.⁴³ We have previously described the effects of temperature on PL linewidth and band gap in terms of phonon coupling.³⁴

The two main factors in the shift in band gap are thermal expansion of the lattice and electron-phonon interaction.⁴³ Some attempts have been made to approximate the lattice expansion and electron-phonon coupling. These approaches often use linear thermal expansion. Silicon, for example, has a negative expansion coefficient before rapidly increasing above and leveling off above 400K.⁴⁴ Thermal expansion for CsPbBr₃ has been shown to be nonlinear as well.³⁶ Therefore, the approach of approximating lattice expansion and electron-phonon coupling will only be valid in narrow temperature ranges. How pressure and temperature are linked results in another difficulty for these methods. A pressure and temperature dependence study of MAPbl₃ have allowed researchers to robustly describe the effect of electron-phonon coupling to polar optical phonons is given by Fröhlich.

$$\alpha_{e-ph} = \frac{e^2}{\hbar} \frac{1}{4\pi\epsilon} \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_0}\right) \sqrt{\frac{m^*}{2\hbar\omega_{LO}}}$$
(3.2)

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. The polaron for CsPbBr₃ was previously found to be from α_{e-ph} = 1 – 3 and additionally was calculated here as 2.03 using the Franck-Condon LO phonon energy in Table 3.1.⁴⁶



Figure 3.3: Modeling of the temperature dependent PL. (a) PL peak energy dependence on temperature. The orange line shows how the fitted Varshni equation fails with this curve. (b) Thermally weighed Franck-Condon factors at 4, 77 and 300K. (c) Fitting of linewidth data with FC and Equation 3.4 (Franck-Condon and LO phonon respectively).

The temperature dependence of the PL spectra reflects vibronic coupling which can then be extracted from experiment. Equation 3.3 is commonly used for fitting the PL linewidth

$$\Gamma(T) = \Gamma_0 + \gamma_{ac}T + \frac{\gamma_{LO}}{e^{E_{LO}/k_bT} - 1}$$
(3.3)

$$\Gamma(T) = \Gamma_0 + \frac{\gamma_{LO}}{e^{E_{LO}/k_b T} - 1}$$
(3.4)

where Γ is the full width half max, Γ_0 is the inhomogeneous broadening at T = 0K, γ_{ac} is the coupling strength to acoustic phonons, γ_{LO} is the coupling strength to the longitudinal optical phonon, and E_{LO} is the optical phonon energy. Reported experimental Raman modes from CsPbBr₃ are below 200cm⁻¹.⁴⁷ The acoustic broadening term was dropped from Equation 3.3 for fitting giving Equation 3.4. Both equations were used to fit the linewidth giving LO phonons of 11.06 and 14.52 meV for Equation 3.3 and Equation 3.4 respectively. These values are indeed below 200cm⁻¹ or 24.8meV.

In order to glean more microscopic insight, Franck-Condon analysis of the temperature dependent lineshapes was done (Figure 3.3 b and c). Two displaced harmonic oscillators were used to model the lineshape temperature dependence. The overlap between vibronic states were calculated with thermally weighted Franck-Condon factors. Franck-Condon (FC) factor modeling follows previously published results and more information on calculations are included in the SI. All fitting results are shown in Table 3.1. The resulting S value was consistent with previously reported coupling values, and inconsistent with II-VI semiconductor NCs (Table A.1) such as CdSe.³⁴ This is due to weak polarization in II-VI NCs and strong polarization in ionic perovskite NCs. We were able to fit the experimental data without inhomogeneous broadening. In fact, the addition of inhomogeneous broadening would reduce the quality of the fit.

Franck-Condon	
S	
1.161 ± 0.003	
$E_{LO}(meV)$	
28.75 ± 0.01	
$\omega_0(eV)$	
2.39	
-	
-	

Table 3.1: Fitting parameters for equations as well as Franck-Condon fitting.

Peak broadening is caused by both homogeneous and inhomogeneous broadening. The question is which broadening dominates. One source of homogeneous broadening is the phonon broadening as temperature increases. For confined semiconductor systems, size distributions lead to inhomogeneous broadening.²⁹ However, the samples in this study are bulk-like NCs that are weakly confined. In the absence of confinement included heterogeneous broadening, homogeneous broadening will dominate which is consistent with our modeling.

3.4 Conclusions

In conclusion, we performed temperature dependent photoluminescence of CsPbBr₃ NCs. The temperature dependence of the PL suggests the presence of a potential change in crystal structure. However, future work to further gain insight into the crystal structure of CsPbBr₃ should contain Cryo-TEM studies to observe how temperature affects the structure of single nanocrystals. XRD and PL studies with pressure dependence can also be combined with temperature to gain lattice expansion and electron-phonon interaction information as has been done for MAPbI₃. The temperature dependence of the linewidth does not show this discontinuity. It does however reveal the homogeneous linewidth is dominated by coupling to phonons and there is negligible inhomogeneous broadening consistent with bulk-like NCs.

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Chapter 4

The absorbing state of a bulk perovskite nanocrystal transforms into a quantum confined emitting state

This chapter is adapted from a manuscript currently under review. I am the sole first author with Colin Sonnichsen, Hélène Seiler, and Patanjali Kambhampati as additional authors. I performed the time resolved photoluminescence experiments. HS and CS performed the 2DE and SRPP experiments respectively. PK and I both wrote the manuscript. This chapter discusses the multiexcitonic photoluminescence from perovskite nanocrystals and how this fits with the hypothesis of polaronic confinement in bulk-like nanocrystals.

4.1 Abstract

We monitor the time evolution of excited perovskites using Two-Dimensional Electronic spectroscopy, State-Resolved Pump/Probe spectroscopy, and time-resolved photoluminescence spectroscopy. These three spectroscopies span the time regime from 10 fs to 200 ps, wherein the transformation from absorbing to emitting states takes place. The striking observation from the photoluminescence data is these bulk nanocrystals emit quantum confined multiexcitons. These multiexcitons have strong interaction energies and follow the Poisson statistics consistent with strongly confined quantum dots, and unexpected for bulk nanocrystals that are twice the Bohr length. By virtue of strong polaronic quantum confinement of excited states, emission from triexcitons is observed, in which one see both ground and excited configurations recombining. Energy resolved pumping is used to demonstrate that absorption into the band edge produces behavior identical to absorption into highly excited states, both of which are bulk-like. We observe these physically bulk perovskite nanocrystals evolve on a distribution of ultrafast timescales from a bulk electronic structure to a quantized electronic structure due to exciton polaron formation.

4.2 Introduction

Semiconductor perovskites have been under intense investigation since their tremendous performance was seen in photovoltaic applications.¹ Since then, these perovskites have seen use in lasing,² light emitting diodes,³ detectors,⁴ and an ever increasing array of applications. This soft ionic lattice is of the ABX₃ form where A is a monovalent cation (Cs⁺, CH₃NH₃⁺, CH(NH₂)₂⁺, etc.), B is Pb²⁺ and X is a halide anion (Cl⁻, Br⁻ or l⁻). These materials can be realized in various forms such as single crystals,⁵ thin films,⁶ bulk nanocrystals,⁷ and quantum confined forms (dots,⁸ rods,⁹ and sheets¹⁰). All but the spatially confined forms should yield bulk-like physics.¹¹ The charge carrier

and lattice structural dynamics seems to be dynamical disorder which may be related to polaron formation. These physical processes are enabled by their soft ionic lattice which enables these anharmonic molecular dynamics.^{12,13}

The question of dynamic disorder and polaron formation has been addressed in a number of experimental and theoretical works (12, 14, 15).^{12,14,15} What has emerged is a picture of a phonon glass / electron crystal in order to explain the defect tolerant behavior of semiconductor perovskites.¹⁶ The main idea is that the lattice modes are glassy for these ionic crystals, unlike their covalent cousins for which structural perfection is the goal.¹⁷ A number of experiments have revealed complex structural dynamics. In particular, Two-Dimensional Electronic (2DE) spectroscopy has revealed liquid-like lineshape dynamics in bulk perovskite nanocrystals (NCs).¹⁸ What other properties does this glassiness confer? What other remarkable properties do semiconductor perovskites support in light of their unique combination of lattice dynamics and electronic structure? Some studies have indirectly suggested that these liquid-like dynamics lead to confinement of excitons through formation of polarons.^{17–19}

Quantum confinement of excitons in quantum dots and related nanostructures is well known. There are a number of indicators of quantum confinement effects. Multiexciton formation is one of the defining spectroscopic processes of quantum confinement,²⁰ and the phenomenon in quantum dots is well explored both in pump-probe^{21,22} and fluorescence experiments.^{23–28} In addition, biexcitons have been explored using 2DE spectroscopy.²⁹ The combination of these techniques is powerful when probing the excited state dynamics of semiconductor nanocrystals.³⁰ The main observation in contrast to the bulk is biexciton interaction strengths of up to 40 meV²⁰ and moreover a spectrum to the biexciton.^{29–31} The combination of absorptive and emission experiments enables a more in depth analysis, and this combined method should be extended to more novel
materials. All of these techniques have been applied separately to perovskite NCs.^{17–19} This includes probing biexcitons with time resolved photoluminescence (t-PL).³² What is missing is real time observation of how the absorbing state evolves into the emitting state.

Here, we use a suite of three ultrafast spectroscopies to reveal that perovskite bulk nanocrystals evolve on an ultrafast timescale from an absorbing state which is characterized by a bulk electronic structure to an emitting state which is characterized by a quantized electronic structure, we refer to as a quantum drop due to the glassy response.^{16,18,33,34} We focus upon emission from strongly interacting quantum confined multiexcitons as indication of quantum confinement, giving rise to quantum drop formation a liquid-like quantum dot. Two-Dimensional Electronic spectroscopy, State-Resolved Pump/Probe (SRPP) spectroscopy, and t-PL spectroscopy all reveal that absorption takes place into a bulk state, consistent with the length scale of these nanocrystals. This bulk-like absorbing state evolves on a 300 fs timescale due to polaron formation. SRPP data has provided initial glimpses into the implications of polaron formation in terms of quantum confinement effects.¹⁷ Polaron formation is consistent with quantum confinement of charges into polaronic excitons. Lacking from those absorptive experiments, however, is direct spectroscopic evidence of the quantized effects one expects of a quantum The t-PL spectroscopy reveals emission from strongly confined polaronic exciton. interacting quantized multiexcitons, a hallmark signature of quantum confinement effects. The interaction strengths for perovskite NC at twice the Bohr length are consistent with conventional CdSe QD at half the Bohr length. Remarkably, the multiexcitonic emission includes emission from triexcitons, from both lower and upper recombination channels, of a lower energy $1S^21P^1 \rightarrow 1S^11P^1$ emission pathway and a higher energy $1S^21P^1 \rightarrow 1S^2$ emission pathway, respectively. These observations of confined multiexcitonic emission in bulk perovskite nanocrystals reveals a surprising electronic structural transformation from a bulk absorbing state to a quantized emitting state by virtue of the unique properties of polarons in perovskites.

4.3 **Results and Discussion**

Figure 4.1 provides an overview of the problem of electronic structural dynamics in semiconductor perovskites. The bulk NC are shown to support polaron formation with some polaron length scale. Within this spherical polaronic potential forms confined exciton polaron,^{33–36} Figure 4.1a. A number of experiments have already confirmed via simple size dependent band edge energies that these 15 nm NC are in the bulk regime.¹¹ Yet the polaron radii is 3nm with well depth of 47 meV, based upon simple material parameters.^{16,17} To what extent do such potentials support polaronic excitons, let alone quantum confined polaronic excitons?

There have been a number of recent experiments and theoretical works that have suggested that the structural dynamics of semiconductor perovskites is characterized by dynamic disorder that initially evolves the system via glassy polaron formation.^{12,37–39} 2DE experiments have shown liquid like lineshape dynamics and SRPP experiments have shown that polaron formation suggests quantum confined polaron exciton formation.^{17–19} In contrast, the steady-state single NC PL experiments reveal a complex and strongly coupled excitonic structure that is inconsistent with bulk excitons.^{26,40–43} What is missing is a real time connection between absorption and emission and thereby connecting the bulk to the guantized states, Figure 4.1b. Experiments are performed on bulk NC of CsPbBr₃ and CsPbl₃. Shown in Figure 4.1c is a transmission electron microscope (TEM) image of a 15 nm CsPbBr₃ NC. Figure 4.1d shows the linear spectroscopy and salient energetics. The absorption spectrum has a band edge at 2.38 eV, with a spontaneous PL emission at 2.43 eV. There is a Stokes Shift of 50 meV. In order to perform energy resolved pumping experiments, we exploited two pump photon energies of 2.6 eV and 3.1 eV, corresponding the excess energies of 220 meV and 730 meV respectively. The idea of changing the pump photon energy is to probe the effects of hot carriers and also density of states which increases and becomes even more bulk-like at high energy.



Figure 4.1: Overview of the transformation from the absorbing state to the emitting state for a semiconductor perovskite bulk nanocrystal due to exciton polaron formation. a) Schematic illustration to scale of a 15 nm CsPbBr₃ NC in which a polaron is formed which creates a boundary thus quantizing excitons. This quantization evolves over some timescale. b) Diagram showing absorbing and emitting states. Photon absorption is consistent with the idea of bulk NC yielding bulk electronic structure at all energies. c) Transmission Electron Microscope (TEM) image of bulk NCs (the white scale bar in 20nm across). d) Linear absorption spectrum, photoluminescence spectrum (PL), and photoluminescence excitation (PLE) spectrum. Also shown are the pump spectra used for energy resolved pumping.

These simple linear steady-state spectroscopies cannot reveal insight into the electronic dynamics and structural dynamics and the ways in which they are connected. For that we turn to a suite of three ultrafast spectroscopies: 2DE, SRPP, and t-PL, Figure 4.2. The main idea of 2DE spectroscopy here is to resolve homogeneous vs

total linewidths as a function of time for the first few hundreds of femtoseconds. Shown in Figure 4.2a is a 2DE spectrum of CsPbl₃ NC at a population time, $t_2 = 20$ fs. The excitation axis is E_1 and the emission or probe axis is E_3 . Experiments are done on CsPbl₃ to be resonant with the 2DE pulse spectrum. Figure 4.2b shows the anti-diagonal and diagonal linewidths as a function of time, t₂. The anti-diagonal linewidth which represents the homogeneous linewidth evolves on the 300 fs timescale due to spectral diffusion from polaron formation. We have previously discussed this response in terms of liquid-like lineshape dynamics. Other spectroscopies have also suggested liquid-like properties of these perovskites.^{16,32} This liquid-like behaviour is consistent with the idea of a phonon-glass electron crystal. Figure 4.2c shows the SRPP spectrum of CsPbBr₃ NC in the first two ps when pumped directly into the band edge. Shown in this 1D spectroscopy is ultrafast bleaching and excited state absorption as a function of time. There are complex spectral signatures here. Figure 4.2d shows the optical bleach bandwidth (FWHM) and center as a function of time. SRPP data has recently suggested indirectly that in the first 300 fs after polaron formation, quantum confined polaronic excitonic formation takes places. We have suggested these quantum confined polaronic excitons as quantum drops due to their quantized electronic structure and liquid-like structural dynamics. The lineshape dynamics take place on an initial 300 fs timescale of polaron formation followed by a slower ps response which corresponds to exciton thermalization in the manifold of polaronic excitonic states.¹⁷

These absorptive spectroscopies do not suggest that the initially excited state is quantum confined. As should be the case for 15 nm NC, they are bulk-like. Pumping directly into the band edge creates Auger recombination signals of triexcitons, inconsistent with QD at their band edge.¹⁷ Only after the 300 fs timescale of polaron formation, does the SRPP data show the suggestions of a rich excitonic structure that arises from quantum confinement, such as via polarons. The clearest evidence of exciton type behaviour arises from PL spectroscopy. The single NC PL spectroscopy shows excitonic



Figure 4.2: Overview of the spectral dynamics of metal-halide perovskite bulk NC from 10 fs to 200 ps using a suite of three time-resolved spectroscopies. a) Two-Dimensional Electronic (2DE) spectroscopy of CsPbI₃ NC, at a population time, t₂, of 20 fs. b) 2DE spectroscopic lineshapes over time. Shown are the diagonal and anti-diagonal linewidths, representing the total and the homogeneous linewidths, respectively. c) Early time response for State Resolved Pump/Probe (SRPP) spectroscopy of CsPbBr₃ NC, pumping into the band edge. d) The SRPP spectroscopy reveals an optical bleach with a time dependent linewidth and peak energy. e) Early time response for energy-resolved time-resolved photoluminescence (t-PL) spectra of CsPbBr₃ NC. Pumping was performed at 3.1eV under high excitation conditions. f) The t-PL spectra show complex time dependence of the spectral linewidth and peak energy.

fine structure and the t-PL spectroscopy shows multiexciton formation.^{26,40–43} We show in Figure 4.2e t-PL spectra of CsPbBr₃ NC under near band edge excitation and high fluence multi-photon absorption conditions in order to observe complex spectral dynamics of possible multiexcitons.^{23–28} Figure 4.2f shows the time-resolved bandwidth and peak energy for the t-PL data. The data reveals complex spectral dynamics on a fast 5 ps timescale and a slow 50 ps timescale. Whilst the time evolution of the 2DE and the SRPP data is now well understood, the t-PL data is less clear. These streak camera based experiments with a 3 ps time resolution provide a first glimpse into the emitting state and whether it supports multiexcitons via polaronic excitonic quantum confinement.

Figure 4.3 shows the spectral decomposition of the t-PL signals into contributions from excitons (X), biexcitons (XX), and higher multiexcitons (MX) of which the triexciton (XXX) is the lowest. When exciting into the band edge at high fluence over various times, one sees the complex spectral lineshapes in greater detail. At late time one sees a signal that is well described by a single Gaussian and corresponds to the PL from the single exciton recombining via, a $1S^1 \rightarrow G$ emission pathway. With a spherical confinement potential from the polaron, one expects a hydrogenic spectrum as seen in QD and the solvated electron and image potential states.³⁹ At intermediate time one sees a second Gaussian peak arising, see the Supplemental for details of the fitting procedure. This second peak is to the red and corresponds to PL from XX and has a represents a biexciton binding energy of 48 meV. Recombination here corresponds to a $1S^2 \rightarrow 1S^1$ emission pathway. At early time one sees sidebands arising further to the red and also to the blue. These sidebands correspond to XXX recombination.^{27,28} These new peaks correspond to the tri-exciton emission, of a lower energy $1S^{2}1P^{1} \rightarrow 1S^{1}1P^{1}$ emission pathway (180 meV redshifted with respect to X) and a higher energy $1S^21P^1 \rightarrow 1S^2$ emission pathway (83 meV blueshifted with respect to X). These fitting procedures are applied to spectra over 200ps (see the Supplemental fitting procedure details). The biexciton and multiexciton show lifetimes of 39ps and 14ps respectively. We note that the XX binding energy itself is a controversial



Figure 4.3: Spectrally and temporally resolving multi-excitonic bands from t-PL spectra of CsPbBr₃ NC. a) The spectra near 200 ps are well described by a single Gaussian. This peak (red) corresponds to the single exciton emission, of a $1S^1 \rightarrow G$ emission pathway. b) The spectra near 40 ps are well described by two Gaussians. This new peak (green) corresponds to the bi-exciton emission, of a $1S^2 \rightarrow 1S^1$ emission pathway. c) The spectra near 5 ps are well described by two additional Gaussians. These new peaks (blue) correspond to the tri-exciton emission, of a lower energy $1S^21P^1 \rightarrow 1S^11P^1$ emission pathway and a higher energy $1S^21P^1 \rightarrow 1S^2$ emission pathway. d) The resulting early time (-5 – 5 ps) spectra from the Poisson model for 0.23 mJ/cm² which is a $\langle N \rangle$ value of 0.037. e) The resulting spectra from the Poisson model for 3.42 mJ/cm² which is a $\langle N \rangle$ value of 0.56. f) The resulting spectra from the Poisson model for 45.64 mJ/cm² which is a $\langle N \rangle$ value of 7.4.

number, as recently discussed by Oron. The SI tabulates the variety of measurements and numbers reported.⁴⁴ These interaction energies and lifetimes are consistent with the behavior of strongly confined nanocrystals which are half the Bohr length rather than these bulk nanocrystals which are twice the Bohr length. The bulk interaction energies are usually 2 orders of magnitude smaller. Consistent with exciton multiplicities in a quantum confined system, a Poisson model is applied to the early time fitting results to extract the fluence dependence of each multiexciton. These results are shown in Figure 4.3d-f. These binding energies as well as the presence of triexciton emission is consistent with the behavior of multiexcitonic PL from strongly confined quantum dots.^{23–28}

In order to rule out hot carrier effects, we perform t-PL experiments with energy resolved pumping. In addition to performing near band edge excitation with 220 meV of excess electronic energy, we perform excitation at 3.1 eV with 730 meV of excess energy to thermalize. These two initial conditions might show differences based up electronic structure and the timescale of carrier relaxation. Figure 4.4 shows the t-PL data at both excitation conditions. Figure 4.4a shows the time integrated t-PL spectra at early time (-5 – 5 ps) for high fluence for both near band edge and 3.1 eV pumping as well as low fluence for 3.1 eV pumping. The high fluence spectra are identical regardless of pump photon energy. The spectra reveal no detectable presence of hot carrier emission at 3.1 eV, nor do they show different spectral response due to any differences in electronic structure as a function of excess energy. Pumping into both initial electronic state produces the identical t-PL response.

Figure 4.4b-c show the time-dependent FWHM and peak energy under four conditions (fit using a single Gaussian). Those conditions are near band edge vs 3.1 eV excitation to probe the effects of excess electronic energy and hot electronic t-PL, and also low fluence vs high fluence to probe the character of the absorbing state and the emitting



Figure 4.4: Energy resolved pumping rules out hot carrier effects in CsPbBr₃ NC. a) t-PL spectra at high fluence at two different photon energies reveals identical spectra at t = 4 ps. The low fluence spectrum of a single exciton emitting is shown for comparison. b) The total spectral bandwidth as a function of time for two different photon energies at the high fluence multiexciton regime. The inset shows the time dependent bandwidth for the low fluence single exciton regime. c) The peak energy as a function of time for two different photon energies at the high fluence multiexciton regime. The inset shows the time dependent peak energy for the low fluence single exciton regime.

state. The high fluence data reveals that there is no difference for near band edge and 3.1 eV pumping. Both excitation energies result in the same emitting state within the IRF of the instrument. In both cases, one sees complex spectral dynamics due to multiexciton formation and recombination.⁴⁵ The FWHM shows relaxation from an initially large value to a smaller value on two timescales of 20 and 200 ps. The peak position shows an initial redshift followed by a blueshift on the 10 and 200 ps timescales, respectively. The insets of the figures show the low fluence data which are also identical for both pump photon energies and they show no measurable dynamics. The complex behavior of the high fluence data is a characteristic of multiexcitonic emission. Whereas the absence of spectral dynamics in the low fluence regime is characteristic of single exciton PL. The combination of energy dependent pumping at low and high fluences reveals that the identical multiexcitonic and single excitonic states are prepared and monitored on the 3 ps time resolution of the t-PL spectrometer.

In order to better understand the complex spectral dynamics in Figure 4.4, we decompose the t-PL data into components from X to MX as shown in Figure 4.3. Figure 4.5 shows the results of this spectral decomposition analysis. We note that this method of analysis is well established for t-PL studies of MX in strongly confined QD.^{20,28,30,32} The main point from these works on MX in QD is that there are interaction strengths from 10 – 40 meV rather than the orders of magnitude smaller strengths one finds in the bulk. In addition to seeing strong interaction energies, one sees rapid MX recombination via picosecond Auger processes. Finally one sees filling of atomic shells, and biexcitonic fine structure. Figure 4.5a shows the spectrally integrated t-PL data at near band edge pumping at various excitation fluences. The t-PL transients show increasing number of fast components at higher fluence, consistent with the well-known behavior of MX in QD. Figure 4.5b shows the spectrally integrated saturation curve for near band edge pumping at early time of t = 4 ps. Notably one can absorb many photons and create many excitons with near band edge pumping, not just excitation at 3.1 eV. This observation is part of a consistent picture of similarly bulk electronic structure at all excess electronic energies. Figure 4.5c and 4.5d show the fluence dependence of the Poisson model for 3.1eV and 2.6eV pumps respectively. The time dependence of MX fitting is shown in Figure 4.5e and 4.5f. The time dependence shows the XXX emission decay with a 19ps time constant and the XX decay with a 50ps time constant. This numbers are consistent with the behavior of strongly confined nanocrystals in the quantum dot regime. Being twice the Bohr length, these NC are 4 times larger than strongly confined QD. Remarkably, these bulk NC appear like strongly confined QD for the emissive states.

In summary, a combination of three ultrafast spectroscopies was applied to bulk CsPbBr₃ nanocrystals that are twice the Bohr length. 2DE spectroscopy revealed the initial polaron and liquid-like dynamics of the perovskite NCs in early time, consistent with the idea of a phonon-glass electron crystal recently discussed. SRPP spectroscopy



Figure 4.5: Decomposing multiexciton populations in CsPbBr₃ NC. a) Spectrally integrated t-PL as a function of time and fluence. b) Spectrally integrated intensity as a function of exciton multiplicity, $\langle N \rangle$, at early time. c) Peak area of each multiexcitonic band as a function of fluence for 3.1 eV excitation integrated over -5 - 5 ps. d) Peak area of each multiexcitonic band as a function of fluence for 2.6 eV excitation integrated over -5 - 5 ps. c) and d) were modelled using a Poisson Distribution. e) Peak areas of each multiexcitonic band as a function of time, for 3.1 eV pump at 4.56 mJ/cm². f) Peak areas of each multiexcitonic band as a function of time, for 2.6 eV pump at 3.44 mJ/cm². The smooth curves represent exponential decays of 5ns, 39ps, and 14ps for X, XX, and MX decays respectively.

indirectly suggested that femtosecond polaronic confinement of this electronic crystal gives rise to quantum confinement effects and do not reveal interaction strengths. The absorptive spectroscopies consistently reveal a picture of bulk electronic structure at all energies, within the 500 femtosecond. In contrast, emissive spectroscopies on the 10s of picoseconds timescale provide evidence of quantum confinement like behavior in particles that are twice the Bohr length. The trajectory from absorption to emission reflects the process of dynamic confinement. We propose that this dynamic confinement arises from polaron formation on the sub-picosecond timescale. This dynamic confinement is in contrast to the static confinement found in NC that are half the Bohr length, but yields similar interaction strengths.

4.4 References

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Chapter 5

The bright multiexcitons of all-inorganic perovskite nanocrystals at low temperature

This chapter was in preparation as of initial submission of this thesis. Dallas Strandell will be the sole first author with Patanjali Kambhampati as an additional author. I performed all experiments. PK and DS both wrote the manuscript. This chapter discusses the observation that the multiexcitonic quantum yield increases from 300 to 25K. A phenomenon in which two excitons are repulsed due to polarons is offered as a potential explanation for the effect.

5.1 Abstract

Semiconductor perovskites have experienced great interest due to their performance in photovoltaics. More recently they have seen similar promise in light emissive devices for which the material goals are not the same. In emissive applications one aims for bright emission at a range of carrier concentrations, especially at multiexciton levels where efficiency droop may take place due to Auger recombination. Multiexciton behavior in large perovskite nanocrystals is less well understood. Multiexcitons generally do not emit brightly due to efficient nonradiative Auger processes competing with radiative decay. Surprisingly, we observe efficient light emission from multiexcitons in bulk CsPbBr₃ perovskite nanocrystals. We show that the radiative rate of multiexcitons increases at low temperature in conjunction with a decrease in the non-radiative Auger rates at low temperature. At 25K, we report a 20% quantum yield from multiexcitons, in concert with efficient single exciton emission.

5.2 Introduction

Semiconductor perovskites have attracted considerable attention recently for their performance in photovoltaics. Perovskites have achieved record power conversion efficiencies due to their remarkable properties such as having a soft, defect tolerant lattice.^{1–3} In addition to their defect tolerance, perovskites in the nanocrystal (NC) form have high photoluminescence (PL) quantum yields (QY), narrow emission linewidths, and broad spectral tunability thereby rendering them promising materials for light emissive applications as well, including lasers⁴ and light emitting diodes (LEDs).^{5,6} Moreover, the ease of synthesis and solution processability of NC form of perovskites renders them favorable for future optoelectronic devices.⁷

One of the key issues in light emissive application is the behavior of the system at high carrier concentrations which would connect to high brightness conditions in LEDs

and lasers. Under weak excitation conditions there will be approximately one exciton (X)per NC, corresponding to a carrier concentration of 3 x 10¹⁷ cm⁻³ for a bulk NC with an edge length of 15 nm, twice the Bohr length. Under these conditions, the well-known PL response of the single exciton is observed. Under higher excitation levels one can produce biexcitons (XX) or higher multiexcitons (MX). Under higher carrier concentrations of 10¹⁸ cm⁻³ one observes multiexciton physics in strongly confined semiconductor guantum dots.⁸ In bulk solids, one will not see MX formation due to the weak interaction strengths of 1 meV being much smaller than kT.9,10 It remains unclear as to whether MX physics will dominate in bulk-like perovskite nanocrystals. Moreover, the behavior of MX physics is not well understood in perovskites in general, especially in light of the competition between radiative and non-radiative decay of the MX states.^{11,12} Beyond being an experimental curiosity under exotic conditions, MX are highly important to lasers and LEDs by virtue of their Auger based non-radiative decay pathway that is very efficient in guantum dots. These Auger recombination processes can limit the optical gain lifetime in laser applications⁸ and can control the high brightness performance of LEDs due to efficiency droop.^{13,14} In order to develop semiconductor perovskite nanocrystal for future light emissive application, the factors which control the competition between MX PL and Auger decay need to be understood.

5.3 Results

Here, we perform time-resolved PL (t-PL) on bulk CsPbBr₃ NC from 300 K to 25K, with a time resolution of 3 ps, sufficient to see the MX kinetics at all temperatures. At high excitation fluences the characteristic behavior of MX PL is seen in these 15 nm bulk NC. In addition to the exciton peak (X), high fluence produces sidebands corresponding to PL from XX and higher MX. These side bands are red/blueshifted by over 30 meV, which is unexpected for a bulk NC, with at most very weak confinement. These interaction strengths are consistent with strongly confined QD, which is not the physical system of



Figure 5.1: a) Schematic of Auger recombination. One exciton will nonradiatively recombine, transferring energy to the second exciton. b) Absorption spectrum in blue. Linear and MX photoluminescence (produced from subtraction of the high fluence and the low fluence datasets). c) TEM of CsPbBr₃ nanocrystals. The white scale bar is 20nm. d) The single exciton increases in brightness and becomes quicker at lower temperatures. This property of multiexciton emission was previously unreported in CsPbBr₃ nanocrystals.

these nanocrystals. The MX signal shows a fast decay on the sub-100 ps timescale at 300 K, consistent with strongly confined QD,⁸ but unanticipated here. The temperature dependence of the PL intensity and decay rates are used to extract the radiative and nonradiative decay rates for X and MX, for the first time. The radiative decay rate of X increases at low temperature; the group of Lounis has suggested this is due to reduced spin relaxation rates at low temperatures.^{15–17} Remarkably the radiative decay rate of the MX PL also increases at low temperature suggesting that the bright states of the MX are correlated to the X. In contrast, the non-radiative Auger recombination rate is measured and shows an inverse temperature dependence compared to the radiative rates. These low temperature measurements reveal that the QY of MX can be as high as 20% by

virtue of the slower non-radiative decay. These experiments reveal insight into the MX physics which dominates at high carrier concentration and describes their functioning in high brightness optoelectronic applications.



Figure 5.2: a) Time resolved photoluminescence (t-PL) at 300K with 100ps time resolution. b) t-PL at 4K with 100ps time resolution. c) Integrated decays produced from a) and b). d) t-PL at 300K with 3ps time resolution. e) t-PL at 4K with 3ps time resolution. f) Integrated decays produced from d) and e).

The temperature dependence of photoluminescence dynamics at the nanosecond scale are well known for CsPbBr₃ nanocrystals. At lower temperatures the single exciton decay becomes faster and monoexponential.¹⁸ Higher fluences create multiexcitons which decay faster than single excitons due to Auger recombination. Auger recombination is the dominant pathway for multiexcitons due to fast relaxation rates at room temperature. Multiexciton dynamics are often IRF limited in time resolved photoluminescence measurements (Figure 5.2a-c). We performed a time resolved photoluminescence

experiment with picosecond time resolution to resolve the multiexciton dynamics (Figure 5.2d-f). The fluence used corresponded to a $\langle N \rangle$ value of 1.29. Additionally, the temperature dependence was performed for the multiexciton kinetics of CsPbBr₃ nanocrystals. At the nanosecond timescale, no variation in the multiexciton kinetics between room and cryogenic temperatures was observed. This is due to the 100ps time resolution of these measurements. In contrast, the picosecond measurements show a striking difference in the first 100 ps at cryogenic vs room temperatures (Figure 5.2f).

Fits of the temperature dependent decays were performed as shown in Figure 5.3. Biexponential fits were performed following

$$I(t) = \alpha_1 e^{-t/\tau_1} + \alpha_2 e^{-t/\tau_2}$$
(5.1)

where I(t) is the time dependent intensity, $\alpha_{1,2}$ are the amplitudes, and $\tau_{1,2}$ are the lifetimes. From the extracted values the fractional intensities, f_i , and the kinetic decay rates, k_i , are found with:

$$f_i = \frac{\alpha_i \tau_i}{\sum_x \alpha_x \tau_x} \tag{5.2}$$

$$k_i = \frac{1}{\tau_i}.\tag{5.3}$$

The fast and slow decay rates, k_1 and k_2 , are seen in Figure 5.3b. The two rates have an opposite temperature dependent trend with the single exciton decay rate increasing at lower temperatures while the multiexciton decay rates decrease. The trend of the exciton decay rate is well known and has been described elsewhere.¹⁸ However, no trend in the multiexciton decay rate in CsPbBr₃ nanocrystals with temperature has been reported. The fractional intensity of the multiexciton increases at cryogenic temperatures (Figure 5.3c). Therefore, a greater fraction of total light emitted is due to multiexcitons at low temperature.



Figure 5.3: a) Biexponential fits of decays from 3 temperatures. b) Extracted decay rates from biexponential fits following Equation 5.1 and Equation 5.3. The fast decay rate k_1 is in red and the slow decay rate k_2 is in blue. c) The extracted fractional f_1 from Equation 5.2. The sum of f_1 and f_2 is 1.

Time resolved photoluminescence measures the total relaxation rate rather than the radiative rate of the emitter. To calculate the radiative and nonradiative rates, the quantum yield of the emitter, Q, is used:

$$Q = \frac{k_{rad}}{k_{rad} + k_{nonrad}}$$
(5.4)

$$k = k_{rad} + k_{nonrad} \tag{5.5}$$

where k_{rad} and k_{nonrad} are the radiative and nonradiative rate respectively. This analysis can be performed for both single- and multi-excitons. For single excitons, the nonradiative decays will be dominated by trapping that causes blinking of an emitter. Auger recombination will dominate the nonradiative rate of multiexcitons.¹⁹

Through the fractional intensities for the single and multiexciton (Figure 5.4a), the quantum yield for the multiexciton can be estimated. The single exciton can accurately be assumed to approach a high quantum yield at absolute zero (Figure 5.4b). With the assumption that the absorbance cross-section of the nanocrystals does not change over



Figure 5.4: a) Example extraction of areas from MX and X decay rates. b) Temperature dependent quantum yield of X. c) Temperature dependent quantum yield of MX calculated from Equation 5.6. d) Temperature dependent radiative (in blue) and nonradiative (in grey) rates for X. e) Temperature dependent radiative (in red) and nonradiative (in grey) rates for MX. The lines in b and c are linear fits, while in d and e the lines are polynomial fits and are guides for the eye.

the temperature range, The relative area of the multiexciton emission can be used to calculate the MX quantum yield (Figure 5.4c):

$$Q_{MX}(T) = \frac{A_{MX}(T)}{A_X(0K)} Q_X(T)\phi$$
(5.6)

where $Q_{MX}(T)$ is the temperature dependent quantum yield of the multiexciton, $A_{MX}(T)$ is the temperature dependent area of the multiexciton, $A_X(0K)$ is the area of the single exciton at 0K, $Q_X(0K)$ is the quantum yield of the single exciton at 0K (~ 1), and ϕ is the ratio between the Poisson distribution values of $\langle N \rangle > 1$ and $\langle N \rangle = 1$. With this method, the quantum yield of the multiexcitons reaches approximately 0.2 at cryogenic temperatures.

Using the temperature dependent quantum yields and the total decay rates for both single- and multi-excitons, the radiative and nonradiative rate were calculated as shown in Figure 5.4. The two decays have similar trends where the nonradiative rates trend lower with low temperatures while the radiative rates have the opposite dependence. These rate changes cause the brighter emission seen at low temperature. The decay rates and quantum yields have a clear trend with temperature from 25-300K as seen in Figure 5.4 d and e. Plots of $ln(k_{Auger}) \propto T^{-1}$ were also calculated (see the SI: A.3). It is evident that the Auger rate does not follow an Arrhenius trend. Long lived multiexcitons are an important quality for lasing applications. For light emitting diode applications, bright multiexcitons are not as significant, but slow Auger rates allow for higher current densities. The performance "droop" effect occurs at large charge carrier concentrations at high current.^{20,21} Figure A.10 in the SI shows the ratios of relaxation rates for the radiative and nonradiative rates. The radiative rate of the multiexciton increases to twice that of the single exciton below 150K. The nonradiative rate of the multiexciton is 40x faster from 300-150K and then increases to >100 below 150K. In CdSe nanocrystals it is known that the radiative rates of a biexciton is 4 times that of the single exciton.²² This is due to statistics and spin selection rules.

The brightening of single exciton emission at low temperatures is well known. Phonon mediated trapping of charges is less likely at cryogenic temperatures which increases the quantum yield. Perovskite nanocrystals have high instrinic quantum yields, and therefore, the decay is dominated by radiative decay rates.^{23,24} However, the temperature dependence of multiexciton emission is less understood. At room temperature, Auger recombination dominates multiexciton emission in most semiconductor nanocrystal, due to fast Auger recombination rates. In contrast, the emissive pathway of a multiexciton has decay rates on the order of a single exciton radiative rates. This results in very low MX quantum yields for most materials, without post-synthesis modifications. Post synthesis modifications, such as shelling, have been used in quantum dots such as CdSe/ZnSe to decrease Auger rates.⁸

The temperature dependence of Auger rates has been studied in covalent semiconductor nanocrystals such as CdSe and CdTe. The dependence was shown to be weak or to follow $ln(k_{Auger}) \propto T^{-1}$ which leads to a small slope at high temperatures and a large dependence at cryogenic temperatures.²⁵ The broad acoustic phonon modes were said to facilitate Auger recombination, and at lower temperatures these nuclear motions are frozen out.^{26,27} Other work has shown very weak temperature dependence in CdSe nanocrystals.²⁸ Even in CdSe and similar quantum dots, which are well understood materials, the temperature dependence of Auger recombination is poorly understood. In perovskite nanocrystals, there has been no reports of temperature dependent as of yet.

In lead halide perovskites, there is screening of charges due to the formation of polarons in the highly polar lattice. This can lead to repulsion of the electron and hole. The repulsion can slow the recombination rates between the hole and electron.²⁹ It is possible that two exciton-polarons are also affected by this phenomenon. Indeed, it has been suggested that the polaronic nature of the CsPbBr₃ lattice stabilizes the biexciton; the stabilization occurs through polaron-induced Coulombic effects.³⁰ The same study suggested that polaron-induced become stronger at low temperatures. It is possible that polarons dominate at low temperatures as phonons are longer lived at lower temperatures.³¹ This effect explains the lower radiative multiexciton rate at low temperatures.

In summary, we performed time dependent photoluminescence measurements at various temperatures. Through extraction of the decay rates and quantum yields of single and multiexcitonic emission, we calculated the radiative and nonradiative rates. We found that the quantum yield of the multiexciton increased by over 5x from room temperature to 25K. Further work will involve computations to explain this phenomenon. Although most devices are not operated at cryogenic temperatures, these results provide information on material properties. Therefore, understanding this effect, through computations, could guide future material synthesis and device fabrication.

5.4 Methods

5.4.1 CsPbBr₃ nanocrystal syntheses procedure

The PNCs were synthesized using a method slightly modified from Protesescu et. al.⁷ The Cs-precursor was prepared in a three-neck flask with Cs_2CO_3 (50 mg), OIAc (0.5 mL) and ODE (2.5 mL) (or a multiple if many reactions were performed). PbBr₂ (140 mg), OIAm (1 mL), OIAc (1 mL) and ODE (10 mL) were added to the reaction three-neck flask. Both mixtures were briefly brought under vacuum, and the temperature was increased to 120 °C. The flasks were then further degassed for 30 minutes once the set point was reached. Under argon, the temperature was increased to 180 °C. 0.5 mL (0.1 mmol Cs) of the Cs-precursor was injected into the reaction flask, and the reaction was quickly quenched in an ice-water bath. 10-15 mL MeAc was added as an anti-solvent and the sample was centrifuged at 12000 rpm (21000 G) for 10 minutes. The PNCs were subsequently redispersed in 5 mL toluene. Further centrifugation was done at 5000 rpm (8750 G) for 2 minutes to remove any undissolved solids and large NCs from the sample. Films were spin coated on a quartz slide with 4% w/w polystyrene in solution. The glass transition temperature of polystyrene is greater than 300K at this molecular weight.³²

5.4.2 Optical and structural characterization

TEM measurements were performed on a Talos F200X (for CsPbBr₃) electron microscope. The samples were prepared by placing a drop of diluted nanocrystals solution on C-coated Cu TEM grids. UV-Vis and fluorescence spectroscopy were done with Cary 4000 UV-Vis and Cary Eclipse Fluorescence spectrometers respectively.

5.4.3 Time-resolved photoluminescence

Time-resolved photoluminescence (t-PL) measurements were conducted utilizing a streak camera (Axis TRS, Axis Photonique Inc.). The sample is placed in a closed-cycle helium Janus cryostat for temperature dependent measurements. The sample is excited with a 3.1eV pump, with a duration of <100 fs generated by frequency doubling of the output of a Ti:sapphire regenerative amplifier (Coherent Legend Elite Duo HE+, 1 kHz rep. rate) in a 100 μ m BBO crystal. The fluorescence is collected at 90°, collimated, and subsequently focused onto the streak camera slit using a pair of off-axis parabolic mirrors.

Two modes were used: with energy resolution and without. With energy resolution, the PL is dispersed by a spectrometer (Acton SP-2358i, 150g/mm, 500nm blaze), accelerated in a bilamellar streak tube (Photonis P820) and imaged using an air-cooled CCD (Spectral Instruments 1200 series). However, the spectrometer was bypassed for most measurements. The results from this mode are shown in Figure 5.3 and 5.4. The streak tube is optically triggered with a time range of approximately 300 ps. Overall, the average time and energy resolution of the traces are 3 ps and 2.5 meV. The trace, and its corresponding background measurement, is obtained from an average of 15 exposures lasting 10 seconds each.

The final trace is obtained with minimal post-processing procedures. Namely, a 1% shear correction is applied to correct for electrode and detector alignment. The value for this is obtained from traces collected with a static bias. The intensity is then corrected

for uneven time bins, followed by conversion from wavelength to energy (including the Jacobian correction). Pump scatter is used to estimate the IRF.

5.5 References

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Chapter 6

Revealing fine structural dynamics within the exciton and multiexciton manifolds of CsPbBr₃ perovskite nanocrystals

This chapter was in preparation as of initial submission of this thesis. Dallas Strandell will be the sole first author with Patanjali Kambhampati as an additional author. DS performed all experiments. PK and DS both wrote the manuscript. This chapter compares the exciton dynamics of CsPbBr₃ nanocrystals at 4K and 300K. The low temperature and high time resolution of the experiment reveals the fine structure of the exciton through lineshape kinetics.
6.1 Abstract

Perovskite nanocrystals are under intense investigation for their outstanding optical and electronic properties. The ability to further develop devices is contingent upon advancing understanding of the physics of light emission from these materials. The excitonic fine structural nature of the lowest emitting state is now well understood via single particle spectroscopy at 4K. However, the presence of higher fine structure states, kinetics within the fine structure, and multiexcitonic fine structure remains poorly understood due to a lack of experimental probes. Here, we use time-resolved photoluminescence spectroscopy with an improvement from 100 ps to 3 ps resolution which reveals complex spectral dynamics of both excitons and multiexcitons in CsPbBr₃ nanocrystals. These spectral dynamics were missed in all prior experiments due to lack of time resolution. Immediately revealed is a previously unobserved fine structure to the multiexcitons that dictates the multiexciton interaction energies which are currently controversial. These interaction energies give rise to linewidth trajectories for excitons and multiexcitons, observed at both 300 and 4 K. These trajectories unravel new fine structure to excitons and multiexcitons, and importantly the non-equilibrium kinetics and equilibrium thermodynamics within this fine structure. Modeling reveals that the bandwidth dynamics is largely dictated by coupling to phonons rather than electronic energy gaps. Finally, the bandwidth trajectories reveal complex patterns of decay, buildup, and ultimate decay, due to a sequence of Auger heating steps that we resolve.

6.2 Introduction

Semiconductor perovskites have been under intense investigation for their performance in photovoltaic devices which was then learned to arise from their remarkable properties such as defect tolerance.^{1,2} This defect tolerance may be related to their glassy ionic lattice which undergoes complex structural dynamics on a distribution of timescales

from femtoseconds to picoseconds.^{3,4} Since the early work on perovskite thin films, a new class of systems has emerged in the form of perovskite nanocrystals (NC).^{5,6} As in the case of NC based quantum dots (QD), these perovskite NC can be size tuned from the bulk limit of 15 nm to the QD limit of 5 nm edge lengths.^{7,8} Hence one can introduce size control as a new means of introducing functionality to these materials. The NC versions are also attractive for the reasons largely discussed in the existing NC literature such as facile synthesis, solution processability, non-classical light sources, and other emissive applications from lasers to LEDs.^{9–12}

Beyond the initial application in light absorptive devices like photovoltaics, P NC are now being explored for light emissive applications due to their favorable emissive properties such as having high quantum yields at 300K, fast radiative recombination, and support for emission from multiexcitons (MX) in addition to emission from excitons (X).^{10,11} It is the strong overlap of electron/hole pairs and strong correlations which give rise to the excitonic physics in semiconductors. The emissive states are characterized by photoluminescence (PL) spectroscopy which is generally steady-state measurements of single NC at low temperatures, or time-resolved PL (t-PL) of ensembles measured at various temperatures.^{13,14} Notably the t-PL measurements on ensembles are done with streak cameras with 100 ps time resolution, fast enough to observe the slowest population kinetics but not fast enough to observe the dynamics between manifolds of quantum states.¹⁵

The single NC PL experiments have been important to reveal the fine structure splittings present even in bulk perovskite NC that can be 1-2 meV in energy, 10x greater than such splittings in bulk semiconductors and consistent with strongly confined QD surprisingly.^{14,16–18} A recently debated point in the fine structure was whether the lowest energy state was optically bright or dark in perovskite nanocrystals.^{14,19,20} The most recent experiments have revealed that the lowest state is in fact dark, and it is more pronounced with QD sized NC due to the size dependence of the splittings.²¹ The t-PL experiments are done at a range of fluences, generally at 300K, wherein high fluence excitation reveals

the presence of PL from XX to the red of the PL from X.²² These experiments reveal the exciton-exciton interaction energies – biexciton binding energies - and decay pathways. But here there is also great controversy over as simple a measurement as the biexciton binding energy.^{23,24} Beyond a simple measure of the biexciton binding energy, one also aims to evaluate the presence of excitonic structure to biexcitons and other multiexcitonic complexes. In short, the physics of excitons gives rise to the emissive properties of perovskite nanocrystals, which remains in its early stages of investigation.

6.3 Results

Here, we apply t-PL spectroscopy with 3 ps resolution, over 30x faster than nearly all other measurements, to reveal previously unobserved excitonic structure to perovskite NC. Experiments were done at low fluence to probe excitons and high fluence to probe Experiments were done at 300K and 4K to unravel line broadening multiexcitons. processes and dynamics within this previously unobserved excitonic structure. By virtue of our 3 ps time resolution, we are able to see rich spectral dynamics in the first 50 ps that would be unresolved in prior experiments. At high fluence we observe MX PL from both XX and XXX, consistent with the literature. But the same experiments at 4K reveal a totally different set of binding energies that are different by a factor of 2-3 from the 300K experiments. This temperature dependence of the MX binding energies suggests that there is a spectrum of states and not a single state with a single binding energy. Lower temperature populates multiexcitonic states with much smaller binding energies. The presence of a spectrum of multiexcitonic states is important to verify as it reveals the interactions which give rise to these states, it sheds insight into the controversy of the biexciton binding energies, and it reveals how temperature can be a control for multiexcitonic states that was previously unconsidered. The early time dynamics at low fluence in the X regime also reveal previously unobserved excitonic structure. At 4K we observe a line narrowing of the PL by 25 meV that is not observable at 300K. This line narrowing is assigned to giant excitonic fine structure that is 10x larger than the currently observed fine structure splittings. This excitonic structure suggests that these bulk P NC support quantum confinement effects, which is unexpected given their size. The experiments at 4K at high fluence reveal a complex temperature trajectory that arises from a competition between Auger heating and lattice thermalization.

Figure 6.1 shows an overview of the problem at hand and the relevant spectroscopy. Figure 6.1a shows a schematic illustration of the perovskite lattice undergoing a polaronic structural distortion about the exciton. Due to the ionic anharmonic lattice, these perovskites undergo complex structural dynamic ranging from fs to ps. The dynamics on the 300 fs timescale are assigned to polaron formation. Moreover recent work by our group and by Silva have suggested that the polaron confines charges to give rise to stronger excitonic quantum confinement.^{25–28} Illustrated here is an example of a quantum confined state of a carrier as arises in strongly confined QD. In all semiconductors there is excitonic fine structure at the 0.1 meV energy scale that is not relevant here. In strongly confined QD this fine structure has a splitting of the lowest states of 1-2 meV and an overall bandwidth of 10 meV.¹⁷ In the case of strongly confined QD they also have a coarse excitonic structure with energy splittings of 100 – 300 meV, based upon NC size.²⁹

In the case of QD and bulk P NC, one cam also observe biexcitons (XX) which are redshifted from twice the excitonic energy by the biexciton binding energy, Δ_{XX} . But if there is a spectrum to the excitonic states, one must ask if there is a spectrum to the MX states and their relevance to the spectroscopy and device performance of these systems. The spectrum of biexcitonic states is shown in Figure 6.1b. Our group has shown that there is indeed fine structure and coarse structure to X and MX in CdSe NC that are strongly confined. Indeed we previously have shown that the biexciton Stokes shift exists and is larger than the exciton Stokes shift.³⁰ Do such effects apply to P NC, especially in this bulk like limit? The presence of fine structure in X will give rise to multiple transitions and perhaps a time dependence to the PL as shown here. The presence of fine structure to



Illustration of excitonic and biexcitonic levels in the transient Figure 6.1: photoluminescence (t-PL) spectra of perovskite nanocrystals (NC). a) An illustration of the relevant ideas of polarons and quantized excitons in a perovskite NC. Shown to scale is an exciton of Bohr length 7 nm and a NC of edge length 15 nm, for CsPbBr₃ NC studied here. b) Schematic of an exciton, biexciton, and respective energy levels that arise from quantum confinement. V_{XX} denotes the interactions between holes and electrons. $\langle \Delta_{XX} \rangle$ and $\langle \Delta_{MX} \rangle$ represent the mean biexciton and multiexciton binding energies respectively. It is essential to considering a mean due to fine structure. c) and d) show the t-PL spectra at 300 and 4K, showing both the exciton and the multiexciton emission spectra. The exciton spectra are obtained from low fluence spectra whereas the MX spectra are from high fluence spectra from which the low fluence spectra are subtracted. See Appendix A for additional details and Figure 6.2 for excitation densities. The mean binding energies are defined spectroscopically above and are found to be: $\langle \Delta_X X \rangle$ goes from 44.8 meV at 300K to 20.3 meV at 4K, and the MX binding energies go from -81.1 meV at 300K to -19.0 meV at 4K. Note that the negative binding energy merely is a result of the spectroscopic designation.

Figure 6.1c-d shows the PL spectra obtained to reveal the spectra of X and MX at 300K and 4K. The spectra of X are obtained from the t-PL data measured with low fluence excitation. There is a large narrowing of the PL bandwidth of X that is larger than $k_B T_{300K}$ which we will discuss later in more detail. The MX spectra are obtained by taking the t-PL spectra at high fluence and subtracting the PL from X (see the SI for additional details). This subtractive procedure is common for analysis of MX PL from NC as shown by Klimov and others.^{31,32} Revealed at 300K is PL from XX and MX, where we consider MX to arise from an XXX type of transition such as $1P11S2 \rightarrow 1S2$. This is the excited state recombination channel that has been seen in CdSe NC by several groups and suggests a similar atomic like filling of shells in these P NC, much to our surprise. The mean XX, and MX binding energies are 44.8 and -81.1 meV at 300K, and 20.3 and -19.0 meV at 4K. The differences in the XX binding energies suggest a fine structure to XX that is 25 meV = $k_B T_{300K}$. In the case of MX, we consider the first MX state to be the triexciton, XXX. A consistent definition of XXX binding energy would be relative to the XXX absorbing state or relative to the transition energy from $3X \rightarrow 2X$, thrice to twice the exciton energy without binding. In the absence of these numbers we use an operational definition in which the blueshift with respect to the X PL is reported. Hence the MX or XXX state is reported as having a negative binding energy but this is only due to the operational definition we use. The MX states are also bound. Using the same spectroscopic designations of mean binding energies, we previously obtained $\langle \Delta_{XX} \rangle$ = 11meV and $\langle \Delta_{MX} \rangle$ = -128 meV for CdSe quantum dots.³⁰ Not only are these binding energies in bulk-like P NC consistent with strongly quantum confined CdSe NC, they are strongly temperature dependent as spectroscopic observables. This temperature dependence should arise from excitonic fine structure, and the quantum state resolved dynamics within.



Figure 6.2: t-PL spectra of CsPbBr₃ nanocrystals over two time windows, two temperatures, and two excitation densities. High excitation density corresponds to $\langle N \rangle$ = 3.05-3.34 or 25.2-27.6 μ J/cm², while low excitation density corresponds to $\langle N \rangle$ = 0.024-0.027 or 0.20-0.22 μ J/cm². High fluence reveals spectral dynamics that are only visible within the first 100 ps that has been previously unobserved. Cooling attenuates the magnitude of the early time spectral dynamics. The low fluence regime does not show the same fast dynamics as high fluence.

Figure 6.2 gives an overview of the t-PL data at low and high fluences at 300K and 4K, in the ps and ns time regimes. Notably most t-PL measurements have a time resolution of 100 ps and only show the data in the first few ns rather than the first tens of ps as we do here. Shown are two time windows, 100 ps with 3 ps resolution, and 2 ns with 100 ps resolution in the left and right columns, respectively. The four rows show t-PL data at high fluence ($\langle N \rangle >$ 3) and low fluence ($\langle N \rangle <$ 0.03), along with high temperature (300K) and low temperature (4K). Here, $\langle N \rangle$ refers to the number of excitons per NC, where $\langle N \rangle =$ 1 corresponds to a carrier excitation density of 3x10¹⁷ cm⁻³. See the Supplement for a detailed discussion of experimental methods and analysis.

The most striking data in terms of spectral dynamics is in Figure 6.2a. These data are under conditions of high fluence and high temperature. The main observation is that the spectra are broader at early time due to MX recombination, and the spectral dynamics in the first 10 ps arises from XXX recombination processes, especially from the upper channel, $1S21P1 \rightarrow 1S2$. Then slower dynamics are seen on the 50 ps timescale. Notably all these spectral dynamics were missed in prior experiments due to lack of time resolution. The ns data remarkably show some spectral dynamics, suggesting that even on the ns timescale there is more to the emission than simple population kinetics.

Cooling the NC from 300K to 4K creates dramatic differences in the spectral dynamics, as shown in Figure 6.2c-d. On the sub 100 ps timescale the effect of cooling seems to be complex and shows dynamics on two timescales of 10 and 50 ps that are in opposite direction in amplitude to each other. In terms of energies, cooling clearly causes a marked blueshift, which is well known in perovskites, but also shows complex changes to the spectral kinetics as we reveal here. Overall, the amplitudes decay slightly more slowly on the 100 ps timescale, but far more rapidly on the 2 ns timescale for the case of high fluence excitation conditions.

Figure 6.2e-h show the same data under low fluence conditions. Here, low fluence corresponds to $\langle N \rangle < 0.03$, corresponding to 9×10^{15} cm⁻³ in terms of carrier concentration. The aim here is to isolate the exciton spectral dynamics from the multiexciton spectral

dynamics, strikingly shown above. The low fluence data is less striking on these time and energy scales. The ns data are consistent with the literature in terms of the kinetics and their temperature dependence. Their spectral dynamics are rarely revealed, even on the ns timescale. The 100 ps time window data initially look static. But closer analysis of the spectra also reveals complex spectral dynamics; they are merely smaller in amplitude in the case of cold excitons vs hot multiexcitons.

In order to perform more a quantitative analysis of the spectral dynamics the spectral bandwidths, Γ , is reported in terms of Full Width Half Maximum (FWHM). See the Supplement for details of the data analysis. Reported in Figure 6.3 are the linewidth trajectories. These linewidths are the result of temperature in that for an atomic system undergoing pure dephasing, 300K = 26 meV and 4K = 0.35 meV. The linewidths are clearly greater, as is their temperature dependence suggesting the excitonic physics is more complex. The topic of line broadening in P NC has been intensely investigated with nearly all results focusing on the low temperature response of single NC measured at steady-state. There have been 2DE measurements of line broadening dynamics in the absorbing state. But there are no measures of linewidth dynamics of excitons, let alone multiexcitons in P NC. For the emitting state, the single NC data reveal an excitonic fine structure, $\sim 1 \text{ meV}$, and a weak coupling to phonons, S ≈ 0.4 at 4K. In addition, these experiments reveal large heterogeneous broadening of \sim 40 meV, which is very dependent upon synthesis. These points were discussed in recent work on P NC linewidths by Raino and Kovalenko.³³

Figure 6.3a-b show the linewidth trajectories at low fluence, at two temperatures, at two timescales. In each trajectory, an asymptote is shown at Γ_{∞} , corresponding to the linewidth measured at late time (2 ns) and low fluence, corresponding to the fully relaxed exciton PL that would be seen in a steady-state experiment. The main two initial observations on the ps timescale are that there are no observable dynamics at 300K but there are dynamics at 4K, and the linewidth increases with temperature much faster than k_B .

We assign the linewidth narrowing observed at 4K to relaxation within the excitonic fine structure. These dynamics could not be seen in any prior experiment due to lack of time resolution, and not going to low enough temperatures. The linewidth narrowing is 25 meV over the first 100 ps. The narrowing process itself should arise from the fully relaxed absorbing state to transition into some initial distribution of final emitting states which are governed by the relevant matrix elements as a quantum process. This distribution of initial excitonic states will then undergo relaxation to thermodynamic equilibrium over some timescale. That timescale we observe 408 +/- 17 ps based of fitting of an exponential decay. The question of the amplitude of the narrowing being 25 meV suggests the possibility of giant excitonic fine structure splittings of 25 meV.

But further analysis below will show that the above described situation is too simple. It misses a key feature required in any modeling or understanding of these spectroscopic results. In the case of the 300K linewidth trajectories, the absence of dynamics could be inferred as arising from a hot thermal distribution of excitons. The disconnect once again arises in the energy levels required are close to 2 meV whereas the spectral energies and widths are 20 meV. The answer to the puzzle of reconciling the linewidths observed relative to thermal energies arises from inclusion of coupling to phonons. Our group has discussed at length the influence of coupling to phonons in the PL spectra of QD. These points were restated in the recent results on perovskite nanocrystals by Raino and Kovalenko.³³ The temperature dependence as well as the amplitude of the linewidth trajectories can be understood by a simple two excitonic fine structure state model, with inclusion of coupling to phonons. This model will be discussed below and in the Supplement.

The low fluence data on the ns timescale shows the final stages of thermalization and represents the baseline for the final system linewidths. Where the data becomes far richer is for the high fluence data on both the ps and ns timescale. Figure 6.3c-d shows the high fluence data at two temperatures at two timescales. On the 100 ps window the linewidth trajectories rich; they do not monotonically decrease, whether with a simple or a complex functional form. In the case of the 4K trajectory, it is clear that there is a fast immediate

decay on the 10 ps timescale. Remarkably there is then a linewidth increase on the 50 ps timescale. And then a linewidth decrease on the 100 ps timescale. This behavior is repeated at 300K albeit with less of a pronounced amplitude to the increase in linewidth. On the other hand the linewidth trajectory at 300K shows larger spectral amplitude to the narrowing. This spectral dynamics is consistent with relaxation within the multiexcitonic fine structure. Indeed, both transient absorption (TA) and Two-Dimensional Electronic (2DE) spectroscopy has shown an excitonic structure to XX that is larger than in X. On the ns timescale, the initial response is partially missed, and the buildup in linewidth from the initial decay is missed. The ns data do show the final stages in relaxation and how slowly the system is relaxing given the presence of enhanced linewidths even at 2 ns, for high fluence excitation.

In order to disentangle population kinetics from other effects on the spectral dynamics, also shown in Figure 6.3c-d are representations of the population decay of XXX and XX. These population decays were obtained in two ways to confirm the same number for the lifetimes. The lifetimes of XX and XXX are 113.34 and 19.86 ps respectively. See the Supplement for details of how the lifetimes are extracted by both spectrally resolved and spectrally integrated methods. Focusing on low temperature data on the 200 ps timescale, the linewidth trajectory well follows the XXX lifetimes at early time and the XX lifetime at later times. There is, however, the non-monotonic deviation to the trajectory wherein there is an increase in the linewidth, peaking again at 100 ps. The linewidth trajectories clearly deviate from the XX lifetime on this timescale. On the 2 ns timescale, this deviation from the linewidth trajectory and the XX lifetime remains. These additional contributions to the linewidths and their trajectories do not arise from multiexciton emission but arise from other effects. The same qualitative behavior is seen at 300K, albeit less pronounced due to thermal effects. In each trajectory, the amplitude of the early time offset is smaller for the 2 ns window than for the 200 ps window due to time resolution being less at the slower time window. See the Supplement for details.



Figure 6.3: A quantitative analysis of the spectral dynamics is obtained by the spectral linewidth trajectories. Γ is the Full Width Half Maximum. Linewidth trajectories are shown for two temperatures, and two excitation densities, over two timescales. For each trajectory, an asymptote is shown where it appears for the long time low fluence data as Γ_{∞} . Energy differences at particular times are shown. The top row shows the low fluence data and the bottom row shows the high fluence data. The high fluence data schematically illustrate the decay of XX and MX populations as discussed in the text.

In order to rationalize these observations of linewidth trajectories at low fluence in the single exciton regime and at high fluence in the multiexciton regime, we create a simple model as show in Figure 6.4. Figure 6.4a illustrates the main problem to resolve for the linewidth trajectories and their temperature dependence in the single exciton regime. The temperature dependence of the PL lifetimes of P NC are well studied both at the ensemble and the single NC level. In all cases there is a standard "hockey stick" functional form, wherein there is a high temperature slope and a low temperature offset. Coupling to phonons increases the high temperature slope and also increases the low temperature offset, as discussed in the Supplement and in other works. The problem is that the experimental temperature dependence of linewidth at 300K and linewidth at 4K cannot be reproduced by a single excitonic state. One can reproduce the slope or the offset, but not both. We then invoke a two-state model to represent the temperature dependence.

This model is shown in Figure 6.4b and was previously invoked by us to describe the temperature dependence of the PL linewidth from surface and core excitons in CdSe NC. In the two-state model, it is now assumed that a minimal model requires two excited excitonic states. These states are separated by some free energy difference that dictates their thermodynamics at equilibrium. These states are separated in phonon coordinate by having dissimilar displacements (coupling). The Huang-Rhys coupling $S = \Delta^2/2$, where Δ is the dimensionless displacement along some phonon coordinate. In this minimal model we assume only one phonon coordinate, but it can easily be generalized to more coordinates.

This model predicts the observed temperature dependence to the linewidth at all temperatures via a combination of kinetics and thermodynamics. At low temperature there is unidirectional kinetics from upper to lower states. At high temperatures there is reversible equilibrium between these states that must be separated by energies smaller than k_BT . In order to reproduce the experimental temperature dependence of the exciton PL, we have two exciton states separated by a free energy difference of X meV, smaller than k_BT_{300} as required to maintain equilibrium. The main reason for the strong spectral

dynamics of 10 – 20 meV is not the energy difference but arises due to differences in coupling to the phonons. As discussed in the Supplement, we predict the S for the lower state to be 0.4, from single NC experiments, and S for the upper state is fitted to the experimental data to obtain its value of 1.5. At low temperature the linewidth narrowing monitors the decay from the upper to the lower excitonic state(s). At high temperature there is thermodynamic equilibrium between the two excitonic emitting states. The two-state model well describes the temperature dependence and time dependence of the linewidths at the single exciton level.

The two-state model also describes the complex non-monotonic linewidth trajectories seen in the high fluence data. The key observation to focus upon is that the linewidth trajectories can peak at later times and decay much slower than the XXX or XX lifetimes. These increases to the linewidth can be understood as the result of Auger recombination of multiexcitons creating an Auger heating process. The process of Auger recombination in NC and QD has been well described.^{34–38} The main idea is that quantum confinement causes fast Auger recombination in which a multiexciton that is cold rapidly recombines to produce an exciton that is electronically hot. This hot exciton then thermalized by heating the lattice. So we consider each process of XXX \rightarrow XX and then XX \rightarrow X as providing a heat pulse on the timescale of the Auger lifetime of a given state. This transient temperature rise from Auger heating then dissipates as the system ultimately relaxes to thermodynamic equilibrium. From the temperature dependence of the linewidth, we can then obtain a transient temperature trajectory that reveals the Auger heating and thermal equilibration processes. Figure 6.4c-d show these temperature trajectories on the 200 ps and the 2 ns timescale due to recombination of XXX and XX, respectively. Figure 6.4e schematically illustrates this Auger heating process in which one sequentially evolves from $\mathsf{XXX}_{\mathsf{cold}} \to \mathsf{XX}_{\mathsf{hot}} \to \mathsf{XX}_{\mathsf{cold}} \to \mathsf{XXX}_{\mathsf{hot}} \to \mathsf{X}_{\mathsf{cold}}.$

In summary, we performed time resolved photoluminescence measurements on CsPbBr₃ nanocrystals at 300 and 4K. The observations of the linewidth evolution through time and temperature required a two state model to fit with Frank-Condon progressions.



Figure 6.4: Overview of how the energetics and spectral dynamics are all connected kinetic and thermodynamic processes. a) Calculated temperature dependence of PL linewidth with inclusion of coupling to phonons. Shown are curves at two different couplings which dictate the high temperature slope and the low temperature offset. Only a model with two fine structure states dressed with these different couplings reproduces the experimental dependence. At high temperature there is thermal equilibrium between the two states and at low temperature there is relaxation to the lower state. b) Schematic illustration of Two State Model via displaced harmonic oscillators. The two states are separated by some Free energy difference, and each has its own Huang-Rhys coupling, S = $\Delta^2/2$. c) - d) The linewidth trajectories and the temperature dependence of the linewidth enables observation of temperature trajectories shown over two time windows. The schematic illustrates the decay of the XX and MX populations which form the thermal impulse via Auger heating. e) Schematic illustration of relevant recombination and heating steps.

At 4K, the early time photoluminescence is produced from both states while the low energy model with lower phonon coupling describes the late time photoluminescence. At room temperature, the state with high phonon coupling dominates the photoluminescence at all times. Additionally, the high fluence regime shows evidence of time dependent heating due to multiexciton Auger recombination at 4K. The additional heat due to Auger recombination could cause detrimental heating in application such as LEDs or coherent emitters. Therefore, understanding the magnitude of this effect is vital for applications.

6.4 Methods

6.4.1 t-PL experimental details

Time-resolved photoluminescence (t-PL) measurements were conducted utilizing a streak camera (Axis TRS, Axis Photonique Inc.). The sample, dispersed in toluene, is flowed in a 0.5 mm path length flow cell using a peristaltic pump (Masterflex 77390-00). The sample is excited with a range of pulse, at 3.1eV, with a duration under 100 fs generated by frequency doubling of the output of a Ti:sapphire regenerative amplifier (Coherent Legend Elite Duo HE+, 1 kHz rep. rate) in a 100 µm BBO crystal. Additionally, a 2.6eV produced from a Coherent OPerA Solo Optical Parametric Amplifier (OPA) was used for CsPbBr3 measurements. The fluorescence is collected at 90o, collimated, and subsequently focused onto the streak camera slit using a pair of off-axis parabolic mirrors. The PL is dispersed by a spectrometer (Acton SP-2358i, 150g/mm, 600nm blaze), accelerated in a bilamellar streak tube (Photonis P820) and imaged using an air-cooled CCD (Spectral Instruments 1200 series). The streak tube is optically triggered with a time range of approximately 250 ps. Overall, the average time and energy resolution of the traces are 3 ps and 2.5 meV. The trace, and its corresponding background measurement. is obtained from an average of 10 exposures lasting 1 seconds each. Fluences were randomized to reduce systematic errors. The cryostat used was a Janis SHI-4XG-5 closed cycle helium cryostat. The final trace is obtained with minimal post-processing procedures. Namely, a 1% shear correction is applied to correct for electrode and detector alignment. The value for this is obtained from traces collected with a static bias. The intensity is then corrected for uneven time bins, followed by conversion from wavelength to energy (including the Jacobian correction). Pump scatter is used to find the IRF.

6.4.2 t-PL modeling and fitting

Time dependent spectra were produced by slicing the data along time in 5ps (or 50ps for nanosecond data) slices (e.g. a 10ps time point was produced by averaging the spectra between 7.5 and 12.5ps). The peak widths in Figure 3 were produced through fitting the time dependent spectra with a Voigt lineshape. The peak centers were also approximated with this method and are shown in Figure A.15. The FWHM and peak center errors in Figure 3 and Figure A.15 are both produced from the fits while the time error was set to a static 5.7ps based on error propagation of the slice width and IRF.

6.4.3 Frank-Condon Modeling

Detailed description of Franck-Condon modeling can be found in prior publications.^{29,39} Briefly, Equation A.1 is used to calculate the thermally weighted Franck-Condon factors:

$$\sigma(\omega) = |\mu_{eq}|e^{-S(2\overline{n}+1)}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}(2\overline{n}+1)^n\overline{n}^m\delta(\omega-\omega_{eq}-(n-m)\omega_0)$$
(6.1)

where *n* and *m* are the vibration levels, ω is the energy, *S* is the Huang-Rhys factor, ω_0 is the vibrational mode of the harmonic oscillator, ω_{eg} is the excitation frequency (i.e., the center energy of the spectra), and \overline{n} is the phonon occupation number: $\overline{n} = (e^{(\hbar\omega_{k_bT} - 1)})^{-1}$. The transition probabilities were calculated from m=0 to m=10. However, the probabilities above m=4 can likely be approximately as 0. Each transition probability delta function was then broadened with a Voigt profile of 30 meV. The envelope of peak maximum was fit to

a Voigt profile. The process was repeated with an additional peak separated by ΔG . The sum of the two resulting states was used for the two-state model:

$$\sigma(\omega) = \sigma(S = 0.4) + f\sigma(S = 1.5)$$
 (6.2)

where σ represents the FWHM. Additional experimental details can be found in section A.4.

6.5 References

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Chapter 7

Conclusion

7.1 Summary

This thesis explores experimental evidence of polaronic effects in the photoluminescence spectroscopy of CsPbBr₃ nanocrystals. Chapter 3 offered a foundational exploration of large bulk-like nanocrystals. The temperature dependent photoluminescence was measured. From Franck-Condon fitting of the photoluminescence linewidth (Figure 7.1a), it was concluded that the broadening could be described with homogeneous broadening alone. This supports the observation that the CsPbBr₃ nanocrystals were bulk-like as quantum confined nanocrystals would have large inhomogeneous broadening. This result is consistent with more recent observations of single CsPbBr₃ nanocrystals.¹ Also discussed was a slope change in the in the photoluminescence energy shift as seen in Figure 7.1b. This slope change is consistent with a phase change at 150K.

The fluence dependence of time resolved photoluminescence was discussed in Chapter 4 (Figure 7.2). At high fluences, clear signals of multiexciton emission were observed. Bulk semiconductors have very small multiexciton binding energies compared to quantum confined nanocrystals.² Since the CsPbBr₃ nanocrystals used in this work are twice the Bohr diameter in size, there should be little spectral evidence of multiexcitons.

Multiexciton emissions with strong binding energies (i.e. shifted in energy compared to the single exciton peak) were hypothesized to be evidence of polaronic confinement of the exciton. This is consistent with previous work showing evidence of confinement in pump-probe spectroscopy.³



Figure 7.1: Temperature dependent photoluminescence data. a) Temperature dependence of the PL FWHM (Γ) compared to Boltzmann constant. "Equation 3" is 3.3 while "FC fitting" represents the Frank-Condon fitting done. b) Energy shift of the PL with temperature. The orange and green lines are linear fits and are guides for the eye only.

The temperature dependence of multiexciton kinetics was reported in Chapter 5 (Figure 7.3). This represents the first report on the multiexcitonic temperature dependence in perovskite nanocrystals. Through analysis of these kinetics, the emissions of the single exciton and multiexcitons were separated in time. The photoluminescence quantum yields of the single and multiexciton were estimated through the assumptions that the quantum yield of the single exciton approaches unity at 0K. With the quantum yields and kinetics, the rates were separated into radiative and nonradiative rates. The radiative rates for the single and multiexcitons were found to have similar dependence on temperature. The nonradiative rate for the multiexciton (i.e. the Auger recombination rate) was found to have a strong dependence on temperature. This observation is quite unique, and we invoked a theory that local polaronic effects start to dominate at lower temperatures. Auger recombination may depend on higher energy phonons which are frozen at low



Figure 7.2: Spectrally and temporally resolving multi-excitonic bands from t-PL spectra of CsPbBr₃ NC. a) c) The early time spectra are well described by four Gaussians. The red and green peaks correspond to single and biexcitonic emission. The blue peaks correspond to the tri-exciton emission, of a lower energy $1S^{2}1P^{1} \rightarrow 1S^{1}1P^{1}$ emission pathway and a higher energy $1S^{2}1P^{1} \rightarrow 1S^{2}$ emission pathway. b) The time dependent fits of the 3 peaks (the areas of high and low energy MX peaks are summed).

temperature. The polarons were said to stabilize the biexcitons through polaronic influence on hole-hole and electron-electron interaction.⁴



Figure 7.3: Temperature dependent relaxation rates. a) Decay rates of the single exciton decomposed into radiative (blue) and nonradiative (grey) rates. b) Decay rates of the multiexcitons decomposed into radiative (red) and nonradiative (grey) rates.

In addition to the analysis performed on multiexciton kinetics, time dependent linewidth analysis at 4 and 300K is reported in Chapter 6 (Figure 7.4). The analysis showed unexpected linewidth narrowing on the picosecond time scale at 4K and low fluence. This observation, along with Franck-Condon modeling, revealed a second higher energy state in the fine structure of the exciton. This higher energy state has a large electron-phonon coupling according to Frank-Condon modeling with a Huang-Rhys parameter, S, of 1.5 compared to S=0.4 of the lower energy state. This two state model was also used to model the temperature dependence of the steady state linewidth. Additionally, experiments with higher fluence at 4K revealed the phenomenon Auger heating. This occurs as the lattice is heated during nonradiative multiexciton recombination.



Figure 7.4: A quantitative analysis of the spectral dynamics is obtained by the spectral linewidth trajectories. Γ is the Full Width Half Maximum. Linewidth trajectories are shown for two temperatures, and two excitation densities, over two timescales. For each trajectory, an asymptote is shown where it appears for the long time low fluence data as Γ_{∞} . a) The decrease in linewidth over 200ps at 4K shows decay of a previously populated, higher energy state. b) The Auger heating is seen during the rise of the linewidth from 10-100ps during biexciton recombination. The orange and green areas show the estimated multiexciton and biexciton decay lifetimes.

These separate studies combine to show a bulk-like nanocrystal that is strongly affected by the polar bonding of the lattice. CsPbBr₃ has large, strong polarons that interact with the exciton to form an exciton-polaron. This exciton-polaron results in spectroscopic signals consistent with quantum confinement in a bulk-like system. As most of the potential applications of perovskite nanocrystals are optoelectronic, the exciton-polaron should be a major focus of future research.

7.2 Outlook

The most vital step for future work should be to construct a rigorous theoretical framework to describe polarons in lead halide perovskites. Much of the work done in the field so far as been semi-empirical or experimental. For a review of how polarons in materials are treated computationally see Ref[5].* However, this is not a trivial problem to solve from first-principles. Lead halide perovskites nanocrystals are a difficult system to compute, and the additional complexity of larger nanocrystals increases the difficulty. It is still a solvable problem, but one that will likely require an entire thesis by itself. As of yet, only simple empirical models have been applied to polarons in lead halide perovskites.⁶ The temperature dependence of the Auger rates may be the simplest problem in this thesis that can be computationally solved. Although if the rates depend on polaronic effects this may not be the case. Work has already begun on attempting to compute this phenomenon.

From an experimental view, there is more to be done that could give a clearer picture to the exciton-polaron problem. Time resolved structural dynamics would be a useful tool to search for signatures of polarons in the structure. For example, time dependent X-ray and electron diffraction have been used to probe polarons in materials (Figure 7.5).^{7,8} These methods probe structural dynamics and therefore can more directly measure the effects of

^{*}This review covers how polarons have been treated in many materials, including metal halide perovskites. The treatments are incredibly varied even in just the lead halide perovskite field.

polaron formation. Indeed, evidence of polaron formation has been seen in time resolved X-ray diffraction data.⁸ Time and angle resolved photoelectron spectroscopy is another technique that has been used to view polaron dynamics.^{6,9} Polaron formation in CsPbX₃ is said to occur within a picosecond.^{10,11} Therefore, time resolution can be a concern for these methods although X-ray diffraction⁸ and electron diffraction^{12†} can have sub 100fs time resolution.



Figure 7.5: UED and diffuse scattering signals from photodoped SnSe. (A) Equilibrium scattering pattern of SnSe oriented along the [100] direction, with key vectors, the square BZ ($b^* - c^*$ plane), and high-symmetry points indicated. (B) Regions of interest for scattering as described in the text, shown around reflection (002) as an example; 1, Bragg intensity; 2, small-wavevector phonons; 3, larger-wavevector phonons. (C) Line cut across the horizontal line shown in (B). The Bragg peak line shape is fit with a Voigt profile (solid black line). (D) Transient (photoinduced) ultrafast electron scattering intensity changes in several regions of the BZ shown in (A) and (B). Reprinted from René de Cotret, et al. 2022 PNAS CC BY-NC-ND 4.0 [7].

In the Kambhampati lab, there are a variety of projects still left for perovskite nanocrystals. Two-dimensional electronic spectroscopy is difficult to perform at the green wavelengths of lead bromide nanocrystals. However, progress is being made in this

[†]pre-print

regard and experiments should help confirm the polaronic nature of these nanocrystals. Additionally, anomalous behaviour was observed under 25K in the temperature dependent Auger rates. A project focusing on Auger rates at temperatures below 50K might shed light on this phenomenon. The experiments discussed in this thesis can also be repeated with hybrid organic/inorganic perovskite nanocrystals, such as formamidinium lead bromide (FAPbBr₃), to understand how the organic cation changes the properties. FAPbBr₃ has been less studied compared to CsPbBr₃.

In terms of the commercialization of perovskite nanocrystals, the two main obstacles are material stability and high lead content. While work has been done to extend the stability of perovskite nanocrystals, shelling will be necessary to extend the life in order



Figure 7.6: Examples of lead-free perovskite crystal structures. a) Cs2AgBiBr₆ double perovskite crystal structure. The structure is very similar to CsPbBr₃ with the replacement of two lead atoms with one bismuth and one silver atom. b) Cs₂Snl₆ perovskite-like structure. The tin halides form a octahedral lattice similar to perovskites but offset in each layer.

for commercialization to happen. Much of the stability issues in the green lead bromide nanocrystals comes from the extremely labile surface. This dynamic surface causes nanocrystals to agglomerate and form micron size particles.¹³ Shelling can also help prevent oxygen, water and other impurities from interacting with the perovskite. Only through shelling with a stable material will these issues be solved. Although some progress has been made in this regard,¹⁴ shelled nanocrystals are not yet widely used outside of synthetic based literature.

For lead content, it is unlikely displays containing lead will be commercialized. Lead in soldering has been banned in the EU since 2006. A similar fate could happen to lead in displays. Current lead limits are based on mass fraction in the total device. This allows for some applications such as in tandem solar cells where the total perovskite mass will be reduced. However in the early 2000s, some companies were attempting the commercialize displays containing CdSe nanocrystals. The EU then proceeded to ban cadmium in electronics above 0.01% in reaction. It is unlikely that companies will risk attempting to commercialize a product with similar risks. There have been many attempts at producing lead free halide perovskites. These materials are often of the double perovskite structure^{15–18} or a perovskite-like structure as seen in Figure 7.6a and 7.6b respectively.^{19,20} Many of these materials have indirect band gaps and/or lack the defect tolerance that the lead provides; none have reached the quantum yields of lead halide perovskites. However, other materials that do not have high defect tolerance have been commercialized such as InP based quantum dots and silicon. These materials still have a long way until they reach a useful state.

7.3 References

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Appendix A

Appendix

This appendix contains the supporting information for Chapter 3, 4 and 5.

A.1 Supporting information for: The temperature dependence of the photoluminescence of CsPbBr₃ nanocrystals reveals phase transitions and homogeneous linewidths

A.1.1 Experimental

Lead(II) bromide (PbBr₂, \geq 98%), oleic acid (OIAc, \geq 70%), cesium carbonate (Cs₂CO₃, \geq 99.9%), 1-octadecene (ODE, \geq 70%), oleylamine (OIAm, \geq 70%), methyl acetate (MeAc, 99%) and polystyrene (192000 MW) were purchased from Sigma-Aldrich.

The PNCs were synthesized using a method slightly modified from Protesescu et. al.¹ The Cs-precursor was prepared in a three-neck flask with Cs_2CO_3 (50 mg), OIAc (0.5 mL) and ODE (2.5 mL) (or a multiple if many reactions were performed). PbBr₂ (140 mg), OIAm (1 mL), OIAc (1 mL) and ODE (10 mL) were added to the reaction three-neck flask. Both

mixtures were briefly brought under vacuum, and the temperature was increased to 120 °C. The flasks were then further degassed for 30 minutes once the set point was reached. Under argon, the temperature was increased to 180 °C. 0.5 mL (0.1 mmol Cs) of the Cs-precursor was injected into the reaction flask, and the reaction was quickly quenched in an ice-water bath. 10-15 mL MeAc was added as an anti-solvent and the sample was centrifuged at 12000 rpm (21000 G) for 10 minutes. The PNCs were subsequently redispersed in 5 mL toluene. Further centrifugation was done at 5000 rpm (8750 G) for 2 minutes to remove any undissolved solids and large NCs from the sample. Films were spin coated on a quartz slide with 4% w/w polystyrene in solution. The glass transition temperature of polystyrene is greater than 300K at this molecular weight.²

Transmission electron microscopy was performed with a Thermo Scientific Talos F200X TEM. Absorption spectroscopy was performed on a Cary UV/Vis, and photoluminescence spectroscopy was performed on a Cary fluorescence spectrometer. Temperature and time dependent photoluminescence spectroscopy (4-300K) was performed with a Closed-cycle helium Janus cryostat and an Axis TRS streak camera. The pump laser was 400nm from a frequency doubled Legend Elite Duo. 1 nJ/pulse was used for the excitation. These values appear in Figure 3.2 and 3.3 with an instrument resolution of 0.6nm (3meV at 500nm) Additional temperature dependent PL was done with a Horiba Fluoromax-2 spectrometer coupled with a liquid nitrogen cryostat (77 – 300K).

A.1.2 Modeling

Detailed description of Franck-Condon modeling can be found in prior publications.^{3,4} Briefly, Equation A.1 is used to calculate the thermally weighted Franck-Condon factors:

$$\sigma(\omega) = |\mu_{eg}|e^{-S(2\overline{n}+1)}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}(2\overline{n}+1)^n\overline{n}^m\delta(\omega-\omega_{eg}-(n-m)\omega_0)$$
(A.1)
where *n* and *m* are the vibration levels, ω is the energy, *S* is the Huang-Rhys factor, ω_0 is the vibrational mode of the harmonic oscillator, ω_{eg} is the excitation frequency (i.e., the center energy of the spectra), and \overline{n} is the phonon occupation number: $\overline{n} = (e^{(\hbar\omega_{k_bT} - 1)})^{-1}$. The transition probabilities were calculated from m=0 to m=8. However, the probabilities above m=4 can likely be approximately as 0 (Figure A.1). Each transition probability delta function was then broadened with a Voigt profile if inhomogeneous broadening was added. If no broadening was added, the envelope of peak maximum was fit to a Voigt profile to extract the FWHM.



Figure A.1: Example plot of transition probabilities vs n with S=1 and T=300K. Only $m \le 5$ were calculated here. Calculated using Equation A.1

Table A.1: Coupling constants for common semiconductor NCs^{3,5,6}

Material	S
CdSe	0.025
PbS	0.33
PbTe	0.15
$CsPbBr_3$ calc.	2.03
CsPbBr ₃	1.57

A.2 Supporting information for: The absorbing state of a bulk perovskite nanocrystal transforms into a quantum confined emitting state

A.2.1 Materials

Lead(II) bromide (PbBr₂, \geq 98%), lead(II) iodide (PbI₂, \geq 98%), cesium carbonate (Cs₂CO₃, \geq 99.9%), 1-octadecene (ODE, \geq 70%), oleic acid (OIAc, \geq 70%), oleylamine (OIAm, \geq 70%), Diisooctylphosphinic acid (DOPA 70%), and methyl acetate (MeAc, 99%) were purchased from Sigma-Aldrich.

A.2.2 Methods

CsPbl₃ - 2DES synthesis procedure

The synthesis of these perovskite nanocrystals (NCs) followed previously reported hotinjection methods with some modifications.^{1,7}

In a three-neck flask, Cs_2CO_3 (0.60 mol) and Diisooctylphosphinic acid (DOPA) (0.20 mol) were injected into octadecene (ODE, 10 mL), which was preheated at 100 °C. The solution was dried for 1 hour at 120 °C under vacuum. The temperature was increased to 150 °C under an argon atmosphere, ensuring that all of the DOPA and Cs_2CO_3 reacted to form a Cs-phosphinate solution. The solution was then kept at 100 °C for future injection.

At the same time, PbX₂ (0.38 mmol) was dissolved in ODE (10 mL) in a three-neck flask and the solution was dried for 1 hour at 120 °C under vacuum. After complete solubilization, dried oleylamine (OLA, 1 mL) and dried DOPA (1 mL) were injected under an argon atmosphere. The temperature was then increased to 140-200 °C and the hot Cs-oleate solution (0.8 mL) was subsequently injected. After 5 seconds, the flask was

cooled down to room temperature by an ice-water bath. Depending on the temperature of injection, a strong light red (140 °C) to dark red (200°C) emission was observed.

The product was then centrifuged for 5 min at 12000 rpm and the excess lead iodide was discarded. The supernatant was mixed with tert-butanol (t-BuOH) (volume ratio of 2:1 with ODE) and centrifuged for 25 min at 12000 rpm. The supernatant was then discarded in order to remove the excess of ligands and the NCs were re-dispersed in toluene under an ambient atmosphere and stored, in the absence of light, at 2 °C for characterization.

Prior to the 2DES experiments, the sample was bubbled with argon for at least 30 minutes. This was observed to prevent degradation over the timescale of the experiments (2-4 hours for a complete set). During the experiments, the sample was flowed in a 0.2 mm thick cell (Starna) with a peristaltic pump to ensure that the laser hits fresh sample.

CsPbBr₃ – SRPP and PL(t) syntheses procedure

The PNCs were synthesized using a method slightly modified from Protesescu et. al.¹ The Cs-precursor was prepared in a three-neck flask with Cs₂CO₃ (50 mg), OIAc (0.5 mL) and ODE (2.5 mL) (or a multiple if many reactions were performed). PbBr₂ (140 mg), OIAm (1 mL), OIAc (1 mL) and ODE (10 mL) were added to the reaction three-neck flask. Both mixtures were briefly brought under vacuum, and the temperature was increased to 120 °C. The flasks were then further degassed for 30 minutes once the set point was reached. Under argon, the temperature was increased to 180 °C. 0.5 mL (0.1 mmol Cs) of the Csprecursor was injected into the reaction flask, and the reaction was quickly quenched in an ice-water bath. 10-15 mL MeAc was added as an anti-solvent and the sample was centrifuged at 12000 rpm (21000 G) for 10 minutes. The PNCs were subsequently redispersed in 5 mL toluene. Further centrifugation was done at 5000 rpm (8750 G) for 2 minutes to remove any undissolved solids and large NCs from the sample. Films were spin coated on a quartz slide with 4% w/w polystyrene in solution. The glass transition temperature of polystyrene is greater than 300K at this molecular weight.²

A.2.3 Optical and structural characterization

Transmission Electron Microscope (TEM)

TEM measurements were performed on a Jeol JEM-2100F (for CsPbl₃) or Talos F200X (for CsPbBr₃) electron microscopes equipped with energy-selective X-ray spectrometer for chemical analysis. The samples were prepared by placing a drop of diluted nanocrystals solution on coated Cu TEM grids.

Linear Spectroscopy

UV-Vis and fluorescence spectroscopy were done with Cary 4000 UV-Vis and Cary Eclipse Fluorescence spectrometers respectively.

A.2.4 Time-resolved photoluminescence

t-PL experimental details

Time-resolved photoluminescence (t-PL) measurements were conducted utilizing a streak camera (Axis TRS, Axis Photonique Inc.). The sample, dispersed in toluene, is flowed in a 0.5 mm path length flow cell using a peristaltic pump (Masterflex 77390-00). The sample is excited with a range of pulse, at 3.1eV, with a duration of <100 fs generated by frequency doubling of the output of a Ti:sapphire regenerative amplifier (Coherent Legend Elite Duo HE+, 1 kHz rep. rate) in a 100 µm BBO crystal. Additionally, a 2.6eV produced from a Coherent OPerA Solo Optical Parametric Amplifier (OPA) was used for CsPbBr3 measurements. The fluorescence is collected at 900, collimated, and subsequently focused onto the streak camera slit using a pair of off-axis parabolic mirrors. The PL is dispersed by a spectrometer (Acton SP-2358i, 150g/mm, 500nm blaze), accelerated in a bilamellar streak tube (Photonis P820) and imaged using an air-cooled CCD (Spectral Instruments 1200 series). The streak tube is optically triggered with a time range of approximately 250 ps. Overall, the average time and energy resolution of the

traces are 3 ps and 2.5 meV. The trace, and its corresponding background measurement, is obtained from an average of 10 exposures lasting 1 seconds each. Fluences and pump wavelengths were randomized to reduce systematic errors.

The final trace is obtained with minimal post-processing procedures. Namely, a 1% shear correction is applied to correct for electrode and detector alignment. The value for this is obtained from traces collected with a static bias. The intensity is then corrected for uneven time bins, followed by conversion from wavelength to energy (including the Jacobian correction). Pump scatter is used to find the IRF.

t-PL modeling and fitting

t-PL spectra were produced by integrating along the time axis. For example, time ranges of 4 ps were integrated in Figure 5e and 5f. The single exciton peak was found by fitting the later time spectra with a single Gaussian peak. This sigma and center of this peak were then locked. A second Gaussian was added at intermediate time to find the XX peak center (the sigma value was locked to the same value as for the X peak). It was then found that at high fluence, 2 additional Gaussians had to be used to fit the dynamics at early time. The width of theses peaks was also locked to the width of the X Gaussian. Using these 4 energy values, the full 200ps decay was fit resulting in Figure 5e and 5f. This method was used for all fluences and both pump energies. The amplitudes for the X emission were fixed to below 110% of the 200ps amplitude. The single exciton decay is known to be well over 1 ns at room temperature (3).

Conversely, a single Gaussian was used to fit the entire time dependent spectrum (shown in Figure 4). The FWHM and peak centers were extracted over the 200ps decay. This was performed for both 3.1 and 2.6 eV pumps for all fluences.

Poisson modeling was then done using the initial values from the multi-Gaussian fitting at early time. These values were fit to a Poisson distribution for all fluences. The results are shown in Figure 3 d-f for 3 fluences and Figure 4c and 4d for both pumps and all fluences. To increase model simplicity, only $\langle N \rangle < 4$ were permitted to be emissive.⁸

A.2.5 State-resolved pump probe experimental setup

The experiments performed were detailed in Sonnichsen et al.⁹ Relevant details are discussed herein.

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 beamsplitter 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.^{9–18}



Figure A.2: Instrument Response Functions and Gaussian fits of (A) 3.1eV pump and (B) 2.6eV pump for time resolved photoluminescence. The error is produced during fitting of the IRF.



Figure A.3: Spectral overlap between the laser spectrum and the samples. (A) CsPbl₃ nanocrystals in toluene (B) CdSe nanocrystals in toluene (C) Nile Blue in ethanol.



Figure A.4: TG-FROG trace of the pulses employed in the 2DES experiments on CsPbI₃ shown in the main manuscript, corresponding to pulses of 13-15 femtoseconds.



Figure A.5: Illustration of how the anti-diagonal linewidth (and its FWHM) is extracted from the 2D spectra.



Figure A.6: The fluence dependence of multiexcitons in CsPbBr₃ as measured by state resolved pump probe spectroscopy.

Sample	Pulse energy	Laser spot size in sample	OD in 200 μm cuvette	Synthesis
CsPbl ₃	5 nJ	100 μm	0.3	See sect. 1.1
CdSe	10 nJ	100 μm	0.3	NNIabs
Nile Blue	20 nJ	100 μm	0.3	Sigma Aldrich

Figure A.7: Summary of the parameters for the samples employed in the 2DES study.

Reference	Method	Material	Size (nm)	٨٧	Binding Energy (meV)
This work	t-PL	CsPbBr₃	12	*	48
Wang et al.	t-PL (10K)	CsPbBr₃	9	*	50
Castaneda et al.	t-PL		11.5		40
		CsPbBr₃	7.4	2	100
		CsPbl₃	12.8		25
			7.4		90
Yin et al.	SP PL (4K)	CsPbl₃	9	0.05	14
Lubin et al.	HS	CsPbBr₃	5.9	0.1	10
		CsPbl₃	7.2	0.3	1
Makarov et al.	TA	CsPbl₃	11.2	0.1	11
Aneesh et al.	TA	CsPbBr ₃	11	0.04	30
Yumoto et al.	TA	CsPbl₃	6	0.1	35
Ashner et al.	TA	CsPbBr ₃	6, 8, 10	0.3	-10 – -2
Shen at al.	TA	CsPbBr ₃	16	12.8	21.7
Sonnichsen et al.	TA	CsPbBr₃	12	*	3.2

Figure A.8: Summary of biexciton binding energies in the literature for CsPbBr₃ and CsPbI₃. The first six experiments are emissive including t-PL (time resolved photoluminescence), SPPL (single particle photoluminescence) and HS (heralded spectroscopy). The second half of the table details TA (transient absorbance) experiments. Temperatures are assumed to be room temperature unless reported otherwise. *various fluences/absorbed photons were used in these experiments.^{9–18}

A.3 Supporting information for: The bright multiexcitons of all-inorganic perovskite nanocrystals at low temperature



Figure A.9: Instrument response functions from a) picosecond and b) nanosecond experiments. Measured from the pump scatter at 3.1eV and fit with a Voigt function.



Figure A.10: a) Ratios of MX/X rates from Figure 5.4. a) Radiative rates and b) nonradiative rates.



Figure A.11: Inverse temperature vs lnk. a) Plot for the MX decay. The lnk_{Auger} is in grey while the radiative rate is in red. b) lnk rates for the single exciton with radiative in blue and nonradiative in grey. Note that none of the rates display Arrhenius behaviour except perhaps the nonradiative rate for the single exciton.

A.4 Supporting information for: Revealing fine structural dynamics within the exciton and multiexciton manifolds of CsPbBr₃ perovskite nanocrystals





Figure A.12: Spectra of CsPbBr₃ nanocrystals. a) Absorbance and photoluminescence with 350nm excitation. b) Example of subtraction process as shown in Figure 1. The relative intensity of the low fluence is based on normalizing the spectra to the intensity at late time (see Figure S3 for fluence dependence of PL decays). The XX and MX binding energies are then estimated from the low fluence (single exciton) peak.

The average excitons per particle $\langle N \rangle$, is calculated from the PL fluence dependence with the equation:

$$I_{PL} = a(1 - e^{-\langle N \rangle}) = a(1 - e^{-F_{ph}\sigma_{400}}$$
(A.2)

where I_{PL} is the PL intensity, a is a normalization constant, $\langle N \rangle$ is the average number of absorbed excitons per particle, F_{ph} is the fluence in photons/cm2, and σ_{400} is the absorption cross section at 400nm. The intensity dependence on F_{ph} was fit producing an absorption cross section of 5.9864x10⁻¹⁴ cm² which was used to calculate $\langle N \rangle$.



Figure A.13: Gaussian fit of the 3.1eV pump for time resolved photoluminescence resulting in the instrument response function (IRF). The error is produced during fitting.

A.4.2 t-PL modeling and fitting

Time dependent spectra were produced by slicing the data along time in 5ps (or 50ps for nanosecond data) slices (e.g. a 10ps time point was produced by averaging the spectra between 7.5 and 12.5ps). The peak widths in Figure 3 were produced through fitting the time dependent spectra with a Voigt lineshape. The peak centers were also approximated with this method and are shown in Figure A.15. The FWHM and peak center errors in Figure 3 and Figure A.15 are both produced from the fits while the time error was set to a static 5.7ps based on error propagation of the slice width and IRF.



Figure A.14: Fluence dependence of time resolved photoluminescence at 4K. a) PL(t) decays found through averaging the streak traces along the energy axis at various fluences. b) A/B ratio of the PL where A is defined as the maximum intensity and B is defined as the intensity at 300 ps.

A.4.3 Frank-Condon Modeling

Detailed description of Franck-Condon modeling can be found in prior publications.^{3,4} Briefly, Equation A.1 is used to calculate the thermally weighted Franck-Condon factors:

$$\sigma(\omega) = |\mu_{eg}|e^{-S(2\overline{n}+1)}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}(2\overline{n}+1)^n\overline{n}^m\delta(\omega-\omega_{eg}-(n-m)\omega_0)$$
(A.3)

where *n* and *m* are the vibration levels, ω is the energy, *S* is the Huang-Rhys factor, ω_0 is the vibrational mode of the harmonic oscillator, ω_{eg} is the excitation frequency (i.e., the center energy of the spectra), and \overline{n} is the phonon occupation number: $\overline{n} = (e^{(\hbar \omega_{k_b T} - 1)})^{-1}$. The transition probabilities were calculated from m=0 to m=10. However, the probabilities above m=4 can likely be approximately as 0. Each transition probability delta function was then broadened with a Voigt profile of 30 meV. The envelope of peak maximum was fit to a Voigt profile. The process was repeated with an additional peak separated by ΔG



Figure A.15: The time dependent photoluminescence energy shifts with comparisons of 300 and 4K. a) low fluence picosecond data showing a 5meV blueshift over 200ps. b) The high fluence picosecond data gives a 25 and 4 meV blueshift in 200ps. c) The low fluence dataset with a 2ns time range shows no obvious shift for either temperature. d) The high fluence nanosecond dataset gives 20 and 4 meV blueshifts for 300 and 4K respectively.

$$\sigma(\omega) = \sigma(S = 0.4) + f\sigma(S = 1.5)$$
 (A.4)

To extract the peak width, the FWHM was calculated for the sum of the two peaks following Equation A.4. The resulting model had two Frank-Condon progressions with Huang-Rhys parameters of 0.4 and 1.5 and a ΔG of 5 meV. Additionally, the higher energy state with S=1.5 was multiplied by the thermal population factor, f, considering the energy splitting of 5 meV. At high temperature the higher energy peak as a higher impact on the total peak width. The full temperature dependence of peak widths was then calculated resulting in the two peak model seen in Figure 6.4a. The typical curve of the peak width temperature dependence has a small dependence at low temperature and a large dependence at high temperatures. This dependence results from the phonon occupation, \bar{n} ; at low temperatures phonons have little impact on the peak width, and linear dependence once phonons can thermally occupy higher states.

The lifetimes for XX and MX were extracted from fitting PL decays as shown in Figure A.17. The full integrated decay was fit with a triexponential approximating MX, XX and X decay lifetimes. However for a more accurate approximation, decays were calculated for specific energy ranges to increase relative XX and MX intensities. This method resulted in lifetimes of 19.86 +/- 1.99 and 113.34 +/- 4.65 ps for MX and XX respectively at 4K.



Figure A.16: Overview of Franck-Condon modeling. a) Plots of peaks produced from Franck-Condon progressions. Note that energy shifts are not modeled here. b) The temperature dependence of peak widths depends on the Huang-Rhys parameter, S. Higher S values result in larger slopes at high temperatures but also higher widths at low temperatures.



Figure A.17: PL decays used to approximate the XX and MX lifetimes at 4K. a) Example streak camera image showing time dependent PL. The red and blue areas show the approximate energy range used to calculate the decays in c) and d). a) The full integrated PL decay. A triexponential fit resulted in decay constants of 23.45 +/- 0.96, 144.20 +/- 19.37, 1301 +/- 352 ps. The high error in the third lifetime is due to the short time range of the experiment. c) The decay and fit from the red area in a) (2.29 to 2.35 eV). The fit resulted in time constants of 26.28 +/- 0.88 and 113.34 +/- 4.65 ps. The time constant of 113.34ps was approximated as the XX lifetime. d) The decay and fit from the blue area in a) (2.42 to 2.45 eV). The fit resulted in time constants of 19.86 and 113.34 ps were approximated as the MX and XX lifetimes respectively. Note that the energy ranges were estimated from the subtraction plot in Figure 1d in order to maximize the fraction of biexciton or multiexciton signal.

A.5 References

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