EXCITED STATE PROPERTIES OF NOVEL SOLUTION PROCESSED
INORGANIC AND HYBRID PHOTOVOLTAIC MATERIALS

BY

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A storm is here, blue sky above
The storm I see, blue sky I don't
The storms all pass, blue sky remains.

Abstract

Novel solution processed inorganic and hybrid photovoltaic materials have shown great promise in low-cost energy market and advanced optoelectronic device applications. Materials like colloidal nanocrystals could potentially transform device manufacturing with printing or spraying based processing, however often the excited state properties of these emerging materials are not well understood. The lack of fundamental knowledge of charge carrier formation, trapping and relaxation processes obstructs the development of the materials and devices. Therefore we employ time-resolved femtosecond spectroscopy methods such as differential reflectance, diffusion, interferometry and primarily transient absorption spectroscopy to study the characteristics of a range of novel photovoltaic materials. Different materials and their aspects are analysed in the six data chapters of this thesis with first three chapters concerning inorganic colloidal nanocrystals and final three concentrating on the analysis of metal halide perovskite family in bulk and nanocrystal forms.

Iron pyrite nanocrystals, which tend to show poor performance in devices due to active surface states, are examined. In particular, the effects of novel surface passivation approach of coating iron pyrite nanoparticles with shells is analysed using transient absorption and long wavelength range steady state absorption spectroscopy techniques. The coated nanocrystals were found to display significant modulation of the surface state behaviour which was governed by the shell properties while the iron pyrite core remained photoactive. The analysis revealed the effectiveness of the new iron pyrite nanocrystal surface defect modulation approach which could potentially solve the issues associated with iron pyrite performance in devices.

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is another novel semiconductor which suffers from trapping effects due to its tendency to form defects. We investigated CZTS nanocrystal properties using transient absorption along with standard steady state and integrating sphere absorption measurements. Rapid relaxation of band edge carriers to a broad defect distribution was found which limited CZTS carrier lifetimes. In addition, plasmon influence induced by CZTS nanocrystal defects was also resolved. The prominent sub-state state influence on

the CZTS excited state dynamics revealed that the defects must be efficiently passivated or their formation must be suppressed for effective material performance.

Transient absorption spectroscopy along with steady state property analysis was also used to help characterize the properties of a range of silicon nanocrystals doped with different transition metals. Doping of nanoparticles can open new ways to control their properties but the field is relatively new and doped silicon nanoparticles have not been widely explored. By comparing undoped particle excited state dynamics to doped nanocrystals we discovered rapid exciton transfer to new dopant introduced states which must be taken into account for the consideration of doped silicon nanocrystal applications.

Recently metal halide perovskites emerged as the leading novel photovoltaic material family and while a lot of research efforts have been put into bulk material, perovskite nanocrystals have been less widely researched. We analysed a range of CsPbBr₃ nanocrystals spanning different quantum confinement regimes in relation to the bulk material using transient absorption spectroscopy. Comprehensive analysis of different aspects of quantum confinement influence was carried out considering state focusing, bandgap renormalization, degeneracy and carrier cooling. The results highlighted that quantum confinement effects were mostly significant for the smallest CsPbBr₃ nanocrystals that are currently available (~4 nm) while the larger nanocrystal photophysics was better described as a small perturbation on the free carrier photophysics established for the bulk material.

The final two chapters concentrated on the photorefractive metal halide perovskite effects. Transient absorption and a range of differential reflectance measurements were employed to study anomalous metal halide perovskite TA response which obstructed the excited state resolution in previous literature. Here the anomalous features were isolated and attributed to the photorefractive effect and were further analysed using frequency domain interferometry. Photoinduced changes in the refractive index of the metal halide perovskite films and nanocrystals were measured with a femtosecond time resolution. The findings allowed for better understanding of metal halide perovskite excited state dynamics and accurate hot carrier temperature and effective mass determination as well as photoinduced refractive index characterization which is crucial for the design of such

applications as optical switching, modulating and recording devices, probing techniques, lasers, single photon emitters and hot carrier solar cells.

Collectively, this thesis provides an insight into fundamental properties of a range of novel solution processed inorganic and hybrid photovoltaic materials.

Publications

Work carried out in this thesis has contributed to the following publications:

Chapter 3

McGrath, A. J.; Yu, C.; Fiedler, H.; **Butkus, J.**; Hodgkiss, J. M.; Halpert, J. E., *Dual-Functional Optoelectronic and Magnetic Pyrite/Iron Selenide Core/Shell Nanocrystals. The Journal of Physical Chemistry C* 2017, 121 (14), 8220-8226.

Contribution: Transient absorption measurements and analysis along with NIR steady state absorption measurements and writing of related parts of the publication.

Chapter 4

McVey, B. F. P.; **Butkus, J.**; Halpert, J. E.; Hodgkiss, J. M.; Tilley, R. D., *Solution Synthesis and Optical Properties of Transition-Metal-Doped Silicon Nanocrystals. The Journal of Physical Chemistry Letters* 2015, 6 (9), 1573-1576.

Contribution: Transient absorption measurements, analysis and writing of related parts of the publication.

Chapter 6

Butkus, J.; Vashishtha, P.; Chen, K.; Gallaher, J. K.; Prasad, S. K. K.; Metin, D. Z.; Laufersky, G.; Gaston, N.; Halpert, J. E.; Hodgkiss, J. M., *The Evolution of Quantum Confinement in CsPbBr₃ Perovskite Nanocrystals. Chemistry of Materials* 2017, 29 (8), 3644-3652.

Contribution: Transient absorption measurements, a part of steady state spectroscopy measurements along with a majority of data analysis and publication writing.

Chapter 7

Price, M. B.; **Butkus, J.**; Jellicoe, T. C.; Sadhanala, A.; Briane, A.; Halpert, J. E.; Broch, K.; Hodgkiss, J. M.; Friend, R. H.; Deschler, F., *Hot-carrier cooling and photoinduced refractive index changes in organic-inorganic lead halide perovskites. Nature Communications* 2015, 6, 8420.

Contribution: Simultaneous transmission-reflection measurements and intrinsic absorption extraction.

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List of Abbreviations

BBO	Beta barium borate
BG	Bandgap
BGR	Bandgap renormalization
BS	Beam splitter
C.B.	Conduction band
CW	Continuous wave
CZTS	Copper zinc tin sulfide
CZTSe	Copper zinc tin selenide
DFT	Discrete Fourier transform
DOS	Density of states
FDI	Frequency domain interferometer
FFT	Fast Fourier transform
GSB	Ground state bleaching
KK	Kramers-Kronig
LED	Light-emitting diode
LOESS	Local regression
LSPR	Localized surface plasmon resonance
MA	Magic angle
NC	Nanocrystal
NIR	Near-infrared
PCE	Power conversion efficiency

PDA	Photodiode array
PIA	Photoinduced absorption
PL	Photoluminescence
PV	Photovoltaic
SS	Steady state
TA	Transient absorption
TEM	Transmission electron microscope
UV	Ultraviolet
V.B.	Valence band
VASP	Vienna Ab initio Simulation Package
Vis	Visible
XRD	X-ray diffraction
YAG	Yttrium aluminium garnet

Chapter 1

Introduction

1.1 Motivation

Optoelectronics have emerged over the 20th century as one of the sciences that now defines the information age. It paved way for fiber-optic communications that supported the development of the internet which is an integral part of the global society and became the basis for the modern technology with display screen integration. Optoelectronics are also quickly becoming a significant part of the energy market which is one of the major global markets promising to overthrow the dominant fossil fuel sector with the evolution of solar cells.¹⁻² From photodiodes, to lasers, to solar cells, material research and development has been one of the driving forces in pushing the boundaries of the optoelectronic device limitations. Materials like GaAs, CdTe, $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ and silicon have been steadily researched and have achieved success in multiple device fields such as the solar cell market with current silicon and thin-film devices standing at a competitive level with fossil fuel energy production technologies.³⁻⁴ However, these materials are considered technologically mature and there are limited paths for their future development and potential for revolutionary advances which opens a big market for new optoelectronic materials.⁵

As an example of the importance of material research we consider the energy market. Currently pollution and global warming have become some of the most prominent social issues, and while the use of conventional solar cell technologies offers a way to alleviate these problems with competitive costs to the fossil fuels, their integration is low.⁶ It is partly due to the already established standing, convenience and low initial integration costs of the 'unclean' energy.⁷ In order to support solar cell integration, political approaches have been taken, however this can often be a slow and unreliable means

leading to prolonged irreversible environmental damage.⁸⁻¹⁰ Research of new materials suitable for new photovoltaic device applications and current device improvement could result in drastic solar cell device and integration price drop.¹¹ This would jump start their usage in the energy market due to the driving force of economical considerations of significantly lower prices than any of the competing energy technologies. As a result the environmental damage would be reduced and other problems associated with conventional fuels such as limited quantity, dangerous exploitation and political manipulation would be prevented.¹²⁻¹⁴

Semiconductor materials are at the heart of optoelectronics as they provide the basis for photon coupling to charges. A significant part of the optoelectronic material development is not just limited to solar cell devices, but extends to applications such as photodiodes, light emitting diodes and semiconductor lasers.¹⁵⁻¹⁶ It relies heavily on the understanding of the fundamental properties of the materials. A range of these properties can be accessed through spectroscopic analysis which can reveal material potential in different device types, functionality improvement pathways and could suggest new optoelectronic applications.¹⁷⁻¹⁸ This chapter provides an introduction to semiconductor basics and describes the main semiconductor excitation processes, carrier types involved and their effects on the material along with the possible recombination mechanisms.

1.2 Semiconductor basics

Semiconductors are materials that belong between conductors and insulators in terms of their electrical conductivity characteristics. Typically semiconductors are composed of atoms which form an ordered structure called the crystal lattice. The ordered crystals are composed of so called unit cells which are repeating segments of the crystal with a particular combination of atoms associated with them. The structure allows for the formation of a periodic potential across the material which governs its electrical conductivity. We note that different levels of crystal order are possible allowing for the existence of poly-crystalline and amorphous materials.¹⁹

Semiconductors display an energy threshold of photon absorption, defined as the bandgap of the semiconductor which plays an important role in the unique properties of these

materials. This leads us to the discussion of semiconductor energy bands. In a crystalline material there is a large number of closely spaced energy levels which form energy bands. The bands are a collection of individual energy levels of electrons around each atom. The wavefunctions of the neighbouring atoms overlap, however Pauli exclusion principle does not allow for the electron energy levels to be the same which results in closely spaced energy levels forming energy bands.²⁰ The band formation model from atomic orbitals of a periodic lattice arrangement is represented in Figure 1.1. The initial electron energies occupying two atomic orbitals split into bands of closely spaced energy levels as the electron wavefunctions overlap with reducing lattice constant of the crystal. The band model is crucial for the understanding of semiconductor behaviour in devices as it defines their energy transitions, electrical conductivity and other properties. One example of the governed characteristics is the concept of the effective carrier mass. It arises from the periodic atom potential effect on carriers described by Bloch functions and helps simplify carrier movement in the lattice by approximating its behaviour to a free particle with a material-dependent mass which helps understand carrier mobility in semiconductors. Bloch functions can be used to describe the periodic potentials of a semiconductor resulting in grouping energy levels to bands separated by energy bandgaps.²¹

Figure 1.1. Schematic of carbon energy bands versus lattice constant, where a_0 is the lattice constant of a diamond crystal and E_v and E_c are the valence and conduction band energies respectively.

Kronig-Penney model is a simplified model for an electron motion in a one dimensional periodic potential.²² In the model the potential $V(x)$ is represented by a periodic square

function as shown in Figure 1.2. It relies on the solution of Schrödinger equation (Eq. 1.1) to determine the electronic state occupation, where E is energy, V is the potential, x is the position, Ψ is the wavefunction and m is mass of a particle with the general solution represented by Equation 1.2, where P and B are defined in Equations 1.3.²² The model allows for the analytical determination of dispersion relation expression and electron density of states. The graphical representation of the general solution is shown in Figure 1.3, where the left hand side of the equation imposes limits from -1 to 1 which limits the allowed values of k inducing gaps in the dispersion relation. A schematic of a dispersion relation of particle energy versus wavenumber is shown in Figure 1.4 where the forbidden ranges of energies are regions without valid solutions to Schrödinger's equation. Although the Kronig-Penney model is an oversimplification of a three dimensional band structure and semiconductor crystal it can be used to show how the band structure can be calculated from a periodic potential of a crystal.²⁰

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + V(x)\Psi = E\Psi \quad (1.1)$$

$$\cos(ka) = P \frac{\sin(Ba)}{Ba} + \cos(Ba) \quad (1.2)$$

$$B = \frac{\sqrt{2mE}}{\hbar} \quad P = \frac{mV_0ba}{\hbar^2} \quad (1.3)$$

Figure 1.2. Schematic of Kronig-Penney periodic potential model, where b is the potential barrier spacing and a is the period.

Figure 1.3. Graphical representation of solutions of Equation 1.2.

Figure 1.4. A schematic of a reduced-zone $E(k)$ diagram.

Full energy band diagram of a semiconductor can be a highly complex system with multiple partially filled and completely filled as well as empty bands over multiple crystal directions.²³ However, it can be simplified to reflect the highest partially empty and the lowest partially filled bands which often dominate the semiconductor properties of interest.²⁰ An example of a simplified energy band diagram is shown in Figure 1.5, where C.B. is the conduction band, V.B. is the valence band and E_g is the bandgap.

The bandgap can decrease with rising temperature due to the increase of interatomic spacing from temperature induced atomic vibrations which results in the decrease of the average potential experienced by the carriers. Such modulation of semiconductor

properties through material lattice expansion/contraction can also be modified by other means such as application of tensile stress or by the introduction of material impurities (doping) which can have a range of other effects on the material properties and its excited state behaviour.²⁰

Figure 1.5. Energy band diagram schematic of half-filled and overlapping metal bands, full insulator band separated by a large bandgap and almost full semiconductor band separated from an almost empty band by a smaller bandgap. The grey colour fill reflects band filling.

System temperature also affects the carrier distribution which is largely responsible for the opposite semiconductor electrical conductivity dependence on temperature to metals. Carrier distributions can be described by probability density functions which define the energy level occupation in a given system. Fermi-Dirac distribution is one of such distribution functions used to describe the occupancy of energy levels by fermions (half-integer spin particles which obey Pauli exclusion principle).²⁴⁻²⁵ A Fermi function describing a system is shown in Equation 1.4, where E is the energy, k_b is the Boltzmann constant, T is the temperature and E_f is the Fermi energy. Fermions tend to fill the energy states with the lowest energy levels first followed by higher lying states, with each energy level filled by no more than two electrons of opposite spin. At $T = 0$ K the energy levels are filled up to the Fermi energy level, while at higher temperatures the distribution transitions gradually from completely filled towards empty states as shown in Figure 1.6.²⁰

$$f(E) = \frac{1}{1 + e^{(E-E_f)/k_b T}} \quad (1.4)$$

Figure 1.6. Fermi function examples at different temperatures.

Normally the bands that are not filled do not contribute to the electrical conductivity of the material, however the partially filled bands which contain both electrons and empty energy levels at higher energies do. These unoccupied levels allow for the carriers to gain energy when moving in an applied electric field therefore they can contribute to the electrical conductivity of the material. We note that the almost full valence band also contributes to the electrical conductivity of the material which is described by the movement of holes, a concept that defines an absence of an electron in terms of a particle that behaves in a similar way to an electron but with a positive charge.¹⁹

One of the important characteristics of a semiconductor is not shown in the simplified energy band diagram (Fig. 1.5). A semiconductor may have a direct or an indirect bandgap depending on what wavenumber do the conduction band minimum and valence band maximum occur at.²⁰ If the two occur at the same wavenumber, the semiconductor is said to have a direct bandgap, otherwise when they occur at different wavenumbers the semiconductor is said to have an indirect bandgap as shown in Figure 1.7. The main differences in properties between the two cases comes from the conduction band and valence band transitions. For a transition to occur, the conservation of energy and crystal momentum must be satisfied. In direct bandgap materials the transitions, for example, from conduction to valence band can simply occur through photon emission. The electron annihilates with a hole releasing the excess energy as a photon since the two carriers share the same momentum. However, in the case of the indirect bandgap semiconductor, the electron must recombine with a hole through an emission of an additional quasiparticle

called a phonon. Phonons are quantized lattice vibrations which can carry the momentum difference between the recombining indirect bandgap electrons and holes, as photons alone cannot carry crystal momentum.²⁶ Phonon involvement in transitions makes such processes less likely to occur leading to significant optical property differences between direct and indirect bandgap materials. For example, silicon is an indirect bandgap semiconductor and solar cells made out of this material typically need to be very thick in comparison to direct bandgap materials such as CdTe as the light absorption coefficients of the former are substantially lower.²⁷ Light emitting diodes are typically based on direct bandgap semiconductors due to the same reason of different transition probabilities.^{20, 26}

Figure 1.7. Schematic of direct and indirect bandgap semiconductors compared in energy versus crystal momentum band plots.

1.3 Excited states

Excited state properties of semiconductors govern the mechanisms that define the optoelectronic device performance.²⁰ Semiconductors can be excited by photons which provide electrons with above bandgap energy generating holes. The excited semiconductor is out of equilibrium and the subsequent carrier evolution through a range of different mechanisms that return the system to its equilibrium state govern a range of semiconductor characteristics. Excited state properties and dynamics in semiconductors

have fuelled countless theoretical and experimental studies due to their complexity and importance in device functionality.²⁸⁻³¹

1.3.1 General mechanisms

Figure 1.8 shows a schematic example of excitation and recombination processes, considering dominant electron dynamics for simplicity. Photons with energies equal or above the bandgap energy can be absorbed by the valence band electrons promoting them to the conduction band. If the absorbed photon energy is greater than the bandgap energy, the carriers possess excess energy which appears as kinetic energy. Such carriers are far from equilibrium and cannot be described by Boltzmann statistics.³² Just after the excitation these initial carrier distributions rapidly interact with each other through carrier-carrier collisions and intervalley scattering forming a quasi-equilibrium with a Boltzmann-like distribution with their temperature reflecting the kinetic energy distribution. These carrier distributions with excess kinetic energies above the conduction band display temperatures above that of the lattice temperature and therefore are termed hot carriers. This initial carrier interaction process is called carrier thermalization (Fig. 1.8.2)) and typically occurs very rapidly (<100 fs).³²

Figure 1.8. Schematic band diagram example of semiconductor excitation and non-equilibrium carrier dynamics, where processes depicted are 1) photon absorption, 2) thermalization, 3) cooling, 4.a) charge separation, 4.b) charge recombination.

After the excited carriers form an equilibrium among themselves they need to equilibrate with the semiconductor lattice. The second step is the hot carrier equilibration with the lattice through carrier-phonon interactions in which the excess energy of carriers is transferred to phonons. Phonons acting in this process are typically the longitudinal optical vibration modes of the material.³² A carrier can lose its excess energy to phonons through multiple separate interactions or an Auger process involving another carrier type which then relaxes through its phonon interaction. The process is called carrier cooling and it takes place until the carriers heat the lattice forming an equal temperature between each other (Fig. 1.8.3)). The final relaxation stage brings the system to its initial equilibrium state. The electrons can recombine through multiple different recombination mechanisms producing the final electron and hole populations equal to the ones prior to the photoexcitation or they can undergo separation and can be used to produce photocurrent in photovoltaic devices. We note that this example considers pulsed excitation while under steady illumination the carriers would establish a steady non-equilibrium carrier population with continuous excitation and various relaxation processes.^{20, 26}

1.3.2 Carrier types

1.3.2.1 Free carriers and excitons

In a simple case of a single photon semiconductor excitation a free electron hole pair is formed.²⁶ The two carriers formed are independent quasi-particles which carry electric charge and upon exertion of electric field can move through the medium forming electric current in devices such as solar cells. However, the particle pair has opposite charges, therefore the two carrier types can exert attractive Coulomb forces on each other leading to a formation of an exciton. Such bound electron-hole pair no longer represents two independent quasi-particles but an individual quasi-particle with a net neutral charge. The Coulombically bound electron-hole pair has internal energy lower than the unbound electron and hole (lower than the bandgap energy) with its binding energy on the order of meV in typical inorganic semiconductors. In order for the excitons to be used in devices as photocurrent, the exciton needs to dissociate into free charge carriers which can be a significant performance limitation in such materials as organic semiconductors where exciton binding energies can reach as high as ~ 1 eV.³³ However, excitons can typically recombine with characteristic types of radiative recombination which can be useful for luminescent device applications or probing techniques. We note that three main types of excitons can be defined according to the size of their radius: Frenkel excitons, charge transfer excitons and Wannier excitons.²⁶

1.3.2.2 Hot carriers

In the previous section we defined hot carriers with excess energy which is dissipated through phonon emission. Hot carrier research has been fuelled by the promise of hot carrier devices which could drastically increase efficiencies of devices such as solar cells allowing to break the $\sim 33\%$ Shockley-Queisser limit if exploited efficiently.³⁴⁻³⁵ However, it is often very difficult to examine hot carrier characteristics due to their typically short lifetimes and unclear manifestation in measurements.^{18, 36}

1.3.2.3 Polarons

An interesting consideration that arises from semiconductor phonons is the formation of a special quasi-particle. The movement of electrons and holes can be typically approximated as a movement through a semiconductor lattice in which the atoms are frozen in space in covalently-bonded crystals.³⁷ However, in ionic or highly polar crystals

this approach is challenged as the conduction electron and lattice ion interaction through Coulombic forces can result in strong electron-phonon coupling. In such a case the electron can be surrounded by a cloud of virtual phonons which corresponds to electron pulling or pushing the surrounding lattice ions depending on their charge. The electron and its virtual phonons can be treated as a composite particle called a polaron which is represented in Figure 1.9.³⁷ We note that a similar mechanism can also apply to holes. Conventional polarons based on LO phonons can be categorized into multicarrier polarons as well as large and small polarons depending on their size in relation to the crystal lattice. Polarons can have a strong influence on charge transport, effective carrier mass and can affect carrier-carrier interactions, however the many-body nature of polarons meant that even the basic polaron theory is still being refined to this day.³⁷

Figure 1.9. Simplified representation of a polaron in ionic lattice.

1.3.2.4 Trapped carriers

Some of the most important types of charge carriers are trapped carriers. Charge carrier trapping arises when carriers excited to the conduction band are transferred to a set of electronic states with energies lying between the highest occupied and the lowest unoccupied material states. Such new states can be introduced by impurities, sub-phases or lattice disorder. Although disordered lattice states can be present in bulk materials, surface states where the lattice is terminated can be a significant source of disorder.³⁸ This concept is especially important in nanocrystals as the particles have large surface to volume ratios with a large potential for disorder. Carrier trapping can result in a range of negative effects on the performance of a material in devices through photoluminescence quenching, provision of rapid carrier relaxation pathways and prevention of charge

extraction.³⁸ Figure 1.10 shows an example of trapping mechanism effects. After photoexcitation carriers can relax to lower energy traps where they cannot be extracted leading to poor device performance. Carrier trapping effects can vary greatly among different materials and their variations, it is therefore important to investigate and understand trapping in particular systems which would help to determine material suitability for device applications and their future development directions.³⁸⁻⁴¹

Figure 1.10. Schematic of trapping effects in relation to charge extraction mechanism.

1.3.3 Excited state effects

Some substantial effects can act in an excited semiconductor which can strongly affect its fundamental properties. Some of the phenomena related to this work will be discussed here with any further details described in the relevant results and discussion chapters.

The presence of excited carriers can affect the bandgap energy of a semiconductor. Electron-hole pairs or excitons in a crystal lattice can lower semiconductor bandgap due to Coulomb correlation and exchange effects. This effect is called the bandgap renormalization and typically is most prominent at high carrier densities. The effect can have a significant impact on the laser design as the many-body effects present in such devices can modulate the bandgap energy by as much as $\sim 2\%$.⁴²

At increasing carrier densities the charge carriers can also undergo changes in their states. One of such states is called electron-hole plasma which arises through Mott transition. At increasing excitation intensities the excitation density increases leading to an increase of free electron-hole pairs even if excitons dominate the system as some of them tend to

ionize even at low temperatures. At a certain carrier density the attractive Coulomb effect is destabilized and any excitons cease to exist as bound electron-hole pairs. This phenomenon arises from the effective screening of the Coulomb interaction between electrons and holes due to surrounding free carriers. When the screening length approaches the free exciton radius, excitons become unstable and electron-hole plasma of a metallic character driven by Fermi statistics is generated. The carrier density at which this happens is called Mott density. This effect is gradual and can reduce exciton binding energy as well as modulate carrier behaviour and is important to understand for the design of high carrier density device applications.²⁶

Another form of charge carrier screening can arise from lattice screening. The charges may become localized to spatially distinct locations through the interaction with ionic crystal lattice which can inhibit carrier recombination, modulate transport or form charged domains.⁴³ The effect is closely related to the polaron theory discussed in the previous section.

High carrier densities may also result in substantial effects on hot carrier dynamics. With increasing excitation densities hot carrier cooling may be slowed down as the probability of carriers to re-absorb phonons increases leading to prolonged hot carrier lifetimes.³² The effect is called the hot phonon bottleneck and is highly desirable for hot carrier device applications which can be highly limited by the typically short hot carrier lifespans.^{18, 35} The positive effects of this phenomenon may be combined with quantum confinement influence which was also considered to play a role in prolonging hot carrier cooling times. The increased energy spacing induced by the quantum confinement can result in a condition for the electrons to cool through multiple phonon processes which greatly reduces the probability of such process. However, the effect has not been commonly observed in standard quantum dot systems and is subject to discussion with suggestions of Auger-like thermalization mechanism which limits the quantum confinement effects on hot carrier lifetimes. In the mechanism, the hot electron transfers the energy to the hole which is typically heavier and proceeds to cool through rapid phonon emission over its more densely spaced energy levels.³²

Excitation pulse modulates the extinction coefficient of the semiconductor which essentially results in the change of its absorption characteristics, however the excitation

can also result in strong changes in the real part of the refractive index of the material. There are multiple photo-induced mechanisms which can modulate the refractive index of the material. Virtual electronic processes such as Kerr or Stark effects caused by below bandgap excitation can rapidly change the refractive index of the material, however they are typically not strong. Thermal effects such as those induced by hot carrier cooling is the second refractive index modulation mechanism which can be strong but disappears with heat diffusion. The presence of free carriers can typically result in strong changes in the refractive index of the medium through electric field effects and intraband or interband absorption effects. The effect disappears with carrier diffusion or recombination which could be used as a control mechanism in photoinduced refractive index change based devices.⁴⁴⁻⁴⁶ In fact, the effect has been established as one of the highest sensitivity nonlinear optical effects and is crucial for the development of optical communication technologies and lasers. This effect is continued to be investigated in many materials for the applications in optical manipulation devices such as optical switches or modulators.

A special case of semiconductor excited state effects is carrier relation to plasmonic effects. Localized surface plasmon resonances (LSPRs) are resonant oscillations of the conduction band electrons at the interface of the material initiated by incident light.⁴⁷ The LSPR mechanism is depicted in Figure 1.11. Nanoparticles of different metals such as Cu, Ag or Au display LSPRs and this effect has been shown to be useful in multiple different applications such as sensors, nanomedicine, catalysis and energy conversion.⁴⁸⁻⁵⁰ The effect can also occur in semiconductor nanocrystals of materials like Cu_{2-x}S , Cu_{2-x}Se or ZnO and can manifest itself through different mechanisms in the spectroscopic techniques used in this work.⁵¹⁻⁵² It can promote excited material absorption properties therefore it is important to consider for better understanding of material characteristics and potential uses of the effect.

Figure 1.11. Schematic representation of electron delocalization due to electromagnetic field effects (LSPR mechanism).

1.3.4 Recombination mechanisms

Recombination of an excited electron and a hole is a process in which the two carriers annihilate each other through electron occupation of the empty space associated with the hole. The release of the energy difference between the initial and the final states of the process and the types of particles involved lead to a number of different possible types of recombination mechanisms. Carrier recombination can be a limiting factor or a functionality principle of devices such as solar cells or light emitting diodes depending on their purpose. In this section we outline the main carrier recombination mechanisms which can take place after semiconductor excitation.

Geminate recombination is the recombination of the generated electron-hole pair which is typically bound through Coulombic interaction (exciton). As discussed in the previous section their separation is required for charge extraction in photovoltaic devices, however their recombination is often accompanied by photon emission which can be employed in luminescence applications.²⁶ The process is shown in Figure 1.12.

Figure 1.12. Schematic of carrier recombination mechanisms.

Non-geminate recombination is a process in which free electron and hole recombine either radiatively or non-radiatively. Its rate is related to the densities of electrons and holes according to Equation 1.5 below which can rely on the equal carrier density approximation, where n and p are the densities of electrons and holes respectively and k is the non-geminate recombination coefficient.⁵³

$$R \approx knp \approx kn^2 \quad (1.5)$$

Trap assisted recombination is a process in which an electron relaxes through an energy state within the bandgap formed by an impurity or a structural defect. The trapped electron often cannot participate in device functionality designed for the material conduction and valence energy bands therefore it is often an undesirable mechanism. The trapped electron then can often only recombine with a hole from its trap state completing the recombination process.²⁰

Stimulated emission is a special case of radiative electron-hole recombination, which can be used for light amplification under a certain set of conditions of thermodynamic equilibrium and population inversion. In brief, an incoming photon interacts with an electron in its excited state causing it to recombine with a hole and emit a photon with the same phase, frequency, polarization and direction of travel as the incident photon.

This phenomenon is treated in the context of quantum mechanics and has been widely exploited in different laser systems.²⁶ Its mechanism is depicted in Figure 1.12.

Auger processes can permeate non-radiative carrier recombination as shown in the bottom middle section of Figure 1.12.^{20, 54} The process requires a presence of three quasi-particles whether two electrons and one hole or two holes and one electron. The energy released during electron-hole recombination is transferred to a third quasi-particle promoting it to a higher energy level. In the subsequent processes the excess kinetic energy of the third particle is typically rapidly transferred to the lattice by phonon emission permitted by the quasi-continuous character of the band. Auger recombination can play an important role in highly excited materials or in localized volumes such as nanocrystals. Different Auger recombination mechanisms can be classified depending on excitonic or free carrier nature and different trap interaction.

In the other cases where carriers recombine non-radiatively, the energy is dissipated through a range of pathways other than photon emission. The non-radiative recombination can follow a mechanism or a mixture of mechanisms such as multiphonon emission, where carriers provide energy to the lattice over bandgap relaxation with the energy equal to a multiple of phonons as shown in Equation 1.6. We note that this process can become highly improbable depending on its order governed by the number of phonons involved if no intermediate energy levels are present. The non-radiative recombination can also result in creation of lattice defects through a localized excitation transferring its energy to an atom as a whole and putting it into an interstitial position called a Frenkel defect (interstitial atom and vacancy). The process can either be transient or permanent and can play a significant role in photolysis. Another form of non-radiative energy dissipation alters the material through photochemical changes which, as an example, can lead to such processes as the growth of silver clusters in silver halide materials. Such non-radiative energy relaxation pathways which substantially alter the compositional form of the material can be utilized in applications like the formation of latent photographic images.²⁶

$$E_g = n\hbar\omega \quad (1.6)$$

Where n is the phonon number and $\hbar\omega$ is the energy of a given phonon.

We note that the processes described here represent the basic recombination mechanisms which can be sub-divided into multiple other types depending on their interaction with phonon number, type and interaction character, excitation intensity, material components, trap types and carrier properties.^{20, 26}

1.4 Nanocrystals

Semiconductor nanocrystals are nanometer sized crystalline particles composed of semiconductor lattices. Nanocrystals typically range between 1 and 100 nm in size and display size-dependent optical and electronic properties.⁵⁵ Early nanocrystal research made use of particles embedded in glass matrices, however today the nanocrystals are typically synthesized as solution suspended colloids coated with a monolayer of surfactants or as epitaxial structures grown on solid substrates. Their size, shape, crystallographic structure and surface conditions allow for a broad tunability of their properties which make them suitable for a large range of applications such as light emitting diodes, photodetectors, solar cells, memory devices, photocharge generators, medical applications, etc.⁵⁶ Figure 1.13 shows an example picture of varying composition tuned nanocrystal suspension luminescence. The promising utilization prospects of nanocrystals catalyzed their research which broadened the understanding of size-dependent material properties. Besides the high control of nanocrystal properties, one of the biggest appeals of semiconductor nanocrystals is their potential in simple and cheap device manufacturing techniques. A range of easy to synthesize and well-controlled materials composed of inexpensive elements could be suitable for solution processed nanocrystal device applications.⁵⁷⁻⁵⁹ Solution processed nanocrystals promise low-temperature device fabrication through printing, in which optoelectronic devices can be applied to large areas of flexible or rigid surfaces from nanocrystal inks. Nanocrystal device application by spraying is another example of their potential in simple manufacturing techniques. Such fabrication methods offer extremely low production costs and are highly suitable for large scale manufacturing which could revolutionize areas such as transistor, light emitting diode and solar cell markets.⁶⁰

Figure 1.13. Perovskite nanocrystals with different composition excited with UV light.

One of the most significant phenomena acting in nanocrystals is the quantum confinement effect. In nanocrystals charge carrier motion is restricted due to the highly limited dimensions of the lattice, and although the bulk crystalline structure is retained the properties of the material can change drastically. This deviation is closely related to the so called exciton Bohr diameter, a distance in an electron-hole pair. As the nanocrystal dimensions approach the exciton Bohr diameter, the quantum confinement effects increase altering the original bulk material properties. The nature of the effect lies in the quantization of kinetic energy of the quasi-particle and can be explained by a standard particle in a box model, where particle trapped in a quantum well has its motion restricted to a region comparable to its de Broglie wavelength so that it can only occupy discrete energy levels which depend on the dimensions of the potential well.²⁶ Where de Broglie wavelength describes the quantum-mechanical wave-particle nature in terms of the system momentum. We note that the degree of quantum confinement effects can vary along different dimensions of the materials as shown in Figure 1.14, which is why quantum confined nanocrystal shape can have a large impact on its properties.^{26, 61}

Figure 1.14. Schematic of density of states of different semiconductor structures.

One of the most commonly observed quantum confinement manifestations in semiconductor nanocrystals is the blue shift of the band edge absorption and emission energies. It arises from the increase of the spacing between the energy levels and hence the bandgap energy as the discrete energy levels develop departing from the continuous bulk material bands. However, such a strong change in the nature of the material can induce a range of other alterations in its properties with potentially strong effects in its device performance. While models have been proposed which help predict confined carrier behaviour their accuracy and validity is limited.^{32, 62} Fortunately the quantum confined material properties can be examined experimentally with a wide range of its properties important for the understanding of device functionality accessible spectroscopically.²⁰

Chapter 2

Methodology

2.1 Steady state absorption spectroscopy

Steady state absorption spectroscopy was carried out using different absorption spectrometer setups with specific details described in relevant results and discussion chapters. This section describes the general principles of the measurements.

Light emitted from Xe lamp (example source) is transmitted through a diffraction grating or prism based monochromator in order to select a specific wavelength of light. The light is then directed to a sample chamber where it is transmitted through a sample. The transmitted light intensity is then recorded on a detector such as silicon diode detector. The same process is repeated scanning across different wavelengths which provides the experiment with spectral resolution. The absorption data recorded is commonly presented in optical density form calculated from the Equation 2.1.⁶³

$$OD = -\log\left(\frac{I}{I_0}\right) \quad (2.1)$$

Where I is the intensity of light transmitted through the sample and I_0 is the reference light intensity without the sample. We note that the steady state absorbance data presented in this thesis has the relevant blank sample defined in related results and discussion chapters subtracted. This is done in order to account for the absorbance effects which are not coming from the sample material of interest. A baseline absorption spectrum is collected in the same way as the sample spectrum and is subtracted from the sample absorption reading giving the optical density of the investigated material as shown in Equation 2.2.

$$OD_s = -\log\left(\frac{I}{I_0}\right) + \log\left(\frac{I_{blank}}{I_0}\right) \quad (2.2)$$

Where I_{blank} is the intensity of light transmitted through the blank sample. An example of absorption spectra of the sample, blank and blank subtracted sample absorption is shown in Figure 2.1.

Figure 2.1. Steady state absorption spectra of solvent (hexane) in 1 mm cuvette labelled ‘blank’ and metal halide nanocrystal suspension with and without the blank absorption measurement subtraction.

2.2 Femtosecond laser system

All ultrafast measurements carried out in this work used Spectra-Physics laser system where near-infrared mode-locked Ti:sapphire Spectra-Physics MaiTai laser pulses were amplified by Spectra-Physics Spitfire Pro Ti:sapphire amplifier pumped with Spectra-Physics Nd:YLF Empower 527 nm laser pulses (Fig. 2.2). This section provides the general description and working principles of the laser system used with more details described in Spectra-Physics system manuals available online on the Spectra-Physics website.

Mode-locked MaiTai Ti:sapphire laser output was used to seed the ultrafast amplifier. The laser comprises of two lasers, a continuous wave (CW) diode-pumped laser and a mode-locked Ti:sapphire pulse laser. The CW laser produces 532 nm output which is used to pump the Ti:sapphire laser. The pumped Ti:sapphire cavity laser provides 84

MHz near-infrared output centred at around 800 nm with <100 fs pulse width which is sent to the Spitfire amplifier.

The high repetition rate and low energy pulses from MaiTai laser are first stretched in time when received in the amplifier using group velocity dispersion (chirp) in order to prevent damage to the optics during the amplification process due to intense beam self-focusing arising from the refractive index modulation of the propagation medium. The chirp is introduced using a diffraction grating system which can be used to tune relative wavelength component travel times, in the case of pulse stretcher, increasing the length of the pulse and hence reducing its peak power.

The second amplifier step amplifies the stretched pulse. The 527 nm Empower pump laser excites Ti:sapphire amplifier crystal with a synchronous energy pulse just before the arrival of the stretched seed pulse. The seed pulse then passes through the excited medium causing stimulated emission, which amplifies the pulse in the same direction and at the same wavelength. The pulse is amplified multiple times before it is released from the cavity. Pulse trapping (and ejection) in the regenerative amplifier cavity is achieved by polarization control, the cavity is designed to trap light of a selected polarization which can be modulated electronically by electro-optic crystalline material which acts as a $\frac{1}{4}$ waveplate when selected voltage is applied to it (Pockels cell system).

The amplified and stretched pulse then enters the third step of the amplifier: pulse compression. The pulse wavelength components are chirped by a diffraction grating system in a similar principle to the pulse stretching mechanism. The spatially spread beam is flipped in the compressor changing the relative wavelength component travel times which allows for the previously delayed frequencies to catch up. This recompresses the stretched pulse giving an amplified output with close to its original duration.

The output pulses are centred at around 800 nm with a pulse width of about 100 fs and 3 kHz repetition rate. We note that the repetition rate is reduced in comparison to the MaiTai seed laser rate due to selective pulse amplification in the regenerative amplifier.

Figure 2.2. Schematic of the femtosecond laser system and propagating pulses.

2.3 Pump-probe experiments

Amplifier output is split for it to be used as pump and probe pulses which are needed for the time-resolved spectroscopy measurements carried out in this work. This section discusses the general pump and probe light experimental setup, generation mechanisms and properties with any specific measurement setup characteristics described in the relevant results and discussion chapters.

2.3.1 Probe

A fraction of the 800 nm fundamental output was used to generate a white light supercontinuum required for broadband spectral resolution of the pump-probe experiments. The intense 800 nm amplifier output light was guided and focused on a thin CaF_2 or $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) crystal window which generates spectrally broad white light continuum. The spectral broadening of the intense monochromatic light is a complex interplay of nonlinear effects acting during the beam propagation through the medium. The accumulation of nonlinear effects arise from the self-focusing of the focused high intensity beam which further increases its intensity in the medium. The high intensity beam generates plasma (through multi-photon ionization) which defocuses the beam and

when defocusing compensates for the self-focusing of the beam a filament is created where the supercontinuum is generated. Other nonlinear effects also contribute to the light broadening such as self-steepening which broadens the pulse towards shorter wavelengths.⁶⁴ The unamplified white light generation is a highly sensitive process and careful tuning for stable output over the required wavelength range is carried out by adjusting the intensity and spot size of the fundamental light as well as the focal point position in relation to the crystal and the crystal angle. In addition, the crystal can be mechanically translated in order to avoid rapid degradation depending on the type of the crystal used. The generated white light supercontinuum is then collimated and guided to the pump-probe measurement setup employed. We note that the residual fundamental light is physically blocked in the white light beam after the generation in order to avoid excitation, degradation or any nonlinear effects when the sample is probed. The acquirable probing spectral range in our system ranges between 300 - 1600 nm, however the light stability and intensity varies across different wavelengths depending on the setup which can affect the quality of the measured wavelength ranges. We also note that before the sample the probe travels through reflective optics only in order to avoid spectral chirp. An example of a probe light spectrum generated is shown in Figure 2.3.

Figure 2.3. Example white light probe spectrum generated using YAG crystal (800 nm region filtered).

A small amount of spectral chirp with up to ~300 fs depending on the wavelength range is, however, normally present in the measurements resulting from different refractive indices experienced by the different wavelengths of light which leads to varying light speeds in a transparent medium such as the walls of a quartz cuvette.⁶⁵ In the measurements the chirp manifests itself as a different temporal onset of time zero across

the wavelength spectrum measured. The chirp profile is fitted using Matlab software which was used for the time zero correction setting it to the same relative time point across all wavelengths. We note that besides chirp other experimental artefacts may be present at time zero position. These include two photon absorption, instrument response function, stimulated Raman amplification and cross phase modulation. These artefacts typically only last on the femtosecond timescales around the time zero position and can have complex mechanisms which have been described in the literature.⁶⁶⁻⁷¹

We note that the calibration of the probe wavelengths was carried out by measuring the white light spectra with a range of bandpass filters with known wavelength transmission values. The measured wavelength positions were then fitted to a prism equation for the particular material used for a prism such as BK7 optical glass which allowed for the wavelength calibration of the spectrometer.

2.3.2 Pump

The 800 nm amplifier output can be used as a pump to excite some materials, however for different materials with different energy bandgaps 800 nm pump can be too low in energy for direct single photon bandgap excitation, in addition different excitation energies may also be required to investigate different aspects of the material. Therefore pump radiation wavelength tuning is required. The pump characteristics and wavelength tuning methods are discussed in this chapter.

One pump wavelength modulation approach is to use frequency doubling (second harmonic generation).⁷² Intense 800 nm light is guided to a nonlinear crystal where two 800 nm photons are annihilated to generate shorter wavelength (higher energy) photon of 400 nm propagating in a similar direction. The mechanism behind frequency doubling is briefly discussed here. The optical response of the non-linear material is described by induced polarization, with a non-linear polarization component that radiates twice the frequency of the input light becoming significant at high light intensities. In order to obtain a second harmonic output at the end of the crystal the dipoles induced by light propagating across the material must radiate in phase for their coherent contribution which is obtained through phase-matching conditions.⁷² The nonlinear crystal often used for this purpose is beta barium borate (BBO) and in this work the phase-matching

condition is tuned by the adjustment of the crystal angle in relation to the incident beam for efficient frequency doubling. The output beam is then filtered with a shortpass filter to remove the fundamental light and obtain a monochromatic pump. We note that in this work frequency doubling was also carried out on different seed wavelengths as described in relevant results and discussion chapters.

Figure 2.4. Picture of metal halide perovskite nanocrystal suspension sample excited with 400 nm pump.

Frequency doubling allows only for a limited selection of excitation light wavelengths. For a wider wavelength tuning of the fundamental 800 nm light a two-stage parametric amplifier of white light continuum with frequency mixers (Light Conversion TOPAS-C) was used. Amplified monochromatic light across UV-visible-NIR wavelengths can be obtained using the system through nonlinear white light generation, separation and amplification processes.⁷³⁻⁷⁴ In brief, a fraction of the 800 nm fundamental light is used to generate a white light continuum in a sapphire plate. The continuum is then stretched and a wavelength is selected through pulse delay and crystal angle adjustment, which is amplified by another fraction of the fundamental pulse in a pre-amplifier crystal. The amplified beam is then separated and collimated. A large fraction of the fundamental input beam is then used to amplify the selected wavelength in a second nonlinear crystal in a collinear arrangement. A typical functioning mechanism of optical parametric amplifier is shown in Figure 2.5.⁷⁵ The output light can then be used in TOPAS-C mixers for an extended tuning range employing frequency doubling, sum frequency generation and difference frequency generation. Sum frequency generation is a non-linear process based on generation of higher frequency radiation from two different lower frequency photons according to energy conservation Equation 2.3.⁷⁶ While difference frequency

generation is the annihilation of two different frequency input photons generating light with a frequency that is the difference between them as described by Equation 2.4.⁷⁶

$$\hbar\omega_3 = \hbar\omega_1 + \hbar\omega_2 \quad (2.3)$$

$$\hbar\omega_3 = \hbar\omega_1 - \hbar\omega_2 \quad (2.4)$$

Where, ω_1 and ω_2 are the input photon angular frequencies and ω_3 is the angular frequency of the output photon. Frequency mixing is carried out in BBO crystals and the output light is filtered using wavelength separators and bandpass filters to separate the required wavelengths. We note that manual crystal angle and beam delay adjustment of TOPAS-C was carried out in order to obtain better stability of the selected wavelength light which improves the quality of the measurement giving more uniform TA signal intensities across measurements. More detailed description of the parametric amplifier system used is available in the Light Conversion TOPAS-C user manual.

Figure 2.5. Schematic of optical parametric amplification process, where solid arrows denote virtual energy level transitions and dashed lines represent photons.

After wavelength tuning the pump beam was then guided and aligned on a linear mechanically controlled delay stage with a mounted retroreflector. Changing the position of the retroreflector on the delay stage allowed for the control of the path length of the pump which changed the relative pump pulse timing in relation to the probe pulse needed for the time-resolved measurements. The length of the delay stage was the limiting factor of the temporal femtosecond measurement range (~ 3 ns depending on the measurement setup). The pump pulse was then guided to the pump-probe measurement setup employed.

The intensity of the pump was tuned with a variable ND filter which allowed to obtain measurements at different excitation densities. We note that measurements were carried out at different excitation intensities in order to check if the measurement range is not affected by excitation density effects which can change carrier recombination dynamics through multiparticle effects.²⁶ However, in some cases the intensity was tuned to collect a range of excitation density dependent TA measurements which allow for the examination of these high excitation density effects. The pump fluence was calculated according to Equation 2.5.

$$f = \frac{P}{A * R} \quad (2.5)$$

Where P is the pump power measured with a Thorlabs photodiode power sensor, A is the pump beam area measured using a Microsoft webcam with a known pixel size and R is the pump repetition frequency (1.5 kHz chopped).

2.4 Transient absorption spectroscopy

Transient absorption spectroscopy has found a widespread implementation in studying the excited state dynamics of a wide range of materials.^{69, 77-79} It provides a direct access to track absorbing states which can be unresolvable in other spectroscopic methods such as time-resolved photoluminescence spectroscopy. Aspects like charge carrier nature, recombination pathways and lifetimes, carrier interaction with lattice, environment and other carriers, material state distribution, quantum confinement, state filling and phonon effects can be probed using transient absorption spectroscopy. By allowing for the examination of these sample aspects the measurements help understand the fundamental material's properties and potential which are crucial for unravelling the underlying photophysics governing its performance in devices.^{18, 69, 80} This section describes the general principles and the setup of the transient absorption spectroscopy measurements which was extensively used in this work to study the excited state dynamics of a range of materials with any particular setup details described in the individual results and discussion chapters.

Transient absorption spectroscopy is a time-resolved pump-probe spectroscopy technique used to monitor the excited state absorption of a measured sample.⁸¹⁻⁸² It relies on two laser beams used to excite and probe the material. Figure 2.6 shows the schematic of the setup employed. A broadband white light continuum (probe) is transmitted through a sample which absorbs part of the light with a minor change in its state population and is guided to a spectrometer where it is dispersed by a dispersive optics, in this example, a prism. The dispersed spectrum is then recorded on a linear photodiode array.

Figure 2.6. Schematic of time-resolved transient absorption spectroscopy system. Figure accredited to Alex J. Barker and Shyamal K. K. Prasad.

The second monochromatic laser pulse (pump) is used to excite the probed sample area at half the repetition rate (1.5 kHz) of the probe pulse (3 kHz). The repetition rate of the pump is halved by physically blocking every second pulse with a synchronized rotating chopper blade. The pump pulse changes the state population of the sample which modulates its absorption. The probe pulses transmitted through the sample at its excited state when the pump is present (pump on) and its steady state when the pump is not present (pump off) then display different spectral intensities due to the absorption changes in the material between its different states. We note that the pump and probe polarization was set to the so called magic angle of $\sim 54.7^\circ$ to each other, in order to eliminate polarization and photoselection effects (unless stated otherwise in specific chapters).⁸³ We also note that the pump energy and intensity can be changed to examine different aspects of the sample which is expected to recover to its initial steady state within about 333 μs after the excitation due to the measurement repetition rate employed.

The transient absorption measurement signals obtained are typically presented in a form of normalized differential transmission calculated as shown in Equation 2.6. Where T_{on} and T_{off} are the recorded transmitted probe light intensities in the pump on and pump off measurement cases respectively.

$$\frac{\Delta T}{T} = \frac{T_{on} - T_{off}}{T_{off}} \quad (2.6)$$

In addition to the spectral resolution, transient absorption measurements also offer temporal resolution. This is achieved by collecting the differential transmission spectra at different relative probe and pump pulse positions in time which are varied by a delay stage. The path length of the pump is changed with different delay stage positions which alters its pulse arrival time in relation to the fixed probe pulse. The temporal resolution of the experiment is limited by the laser pulse width which in this work is ~100 fs.

We note that transient absorption measurement data presented in this work are typically averaged over several measurement repetitions as noted in the experimental chapter sections in order to improve signal-to-noise ratios. The individual repetition signals were compared to each other in order to avoid any sample evolution effects within the measurement timeframe. We also note that the spectroscopic measurements were carried out under room temperature.

The recorded transient absorption measurement can be typically presented as a surface composed of multiple spectral recordings at different delay times, individual spectral traces at selected time integrals or kinetic traces across selected spectral regions as shown in Figure 2.7.

Figure 2.7. Example transient absorption measurement of metal halide perovskite film a) TA surface map, b) TA spectral trace integrated over 2 to 4 ps as shown by the red transparent rectangle in the TA surface map, c) TA kinetic trace integrated over 740 to 750 nm as shown by the blue transparent rectangle in the surface map.

As shown in Figure 2.7, transient absorption data can display both positive and negative features which can arise from different effects. A schematic of possible TA feature mechanisms is shown in Figure 2.8. The positive (bleaching) signatures shown as red TA surface features may arise from the reduced absorption of the material in its excited state in comparison to its steady state as displayed by rows 2 and 1 of Figure 2.8 respectively. While the negative (blue) photoinduced absorption signatures may arise from the absorption of the excited carriers to states which were previously unavailable or were absorbing at different wavelengths in the steady state as shown in row 3 (Fig. 2.8). We note that the signals may arise from multiple other effects such as stimulated emission, trap state absorption, photorefractive effects, plasmon absorbances, etc. The analysis of these signals is often supported by different fitting techniques described in relevant

results and discussion chapters of this work, which were carried out using either OriginLab OriginPro or MathWorks Matlab data analysis software.

Figure 2.8. Schematic representation of the possible nature of transient absorption features.

Chapter 3

Iron pyrite nanocrystals: charge carrier dynamics and surface effects

Parts of this chapter have been published in the following article:

McGrath, A. J.; Yu, C.; Fiedler, H.; Butkus, J.; Hodgkiss, J. M.; Halpert, J. E., Dual-Functional Optoelectronic and Magnetic Pyrite/Iron Selenide Core/Shell Nanocrystals. The Journal of Physical Chemistry C 2017, 121 (14), 8220-8226.

3.1 Introduction

Pyrite-phase iron sulphide (FeS_2) is one of the most common sulphide materials which was first explored in 1980's as a potential photovoltaic (PV) semiconductor. It soon lost interest as the device efficiencies did not reach 1 % at the time.⁸⁴ However, recently the interest in iron pyrite has been revived after other thin film technologies such as CdTe and CIGS have gained commercial success.⁸⁵ Iron pyrite benefits from easy synthesis control as it has a low complexity cubic lattice shown in Figure 3.1, which allows for fewer material sub-phases to develop. The material displays a bandgap of about 1 eV and a number of characteristics that make pyrite attractive for large scale solar cell absorber layer applications including low toxicity, good carrier mobility and high optical absorption coefficients of about 10^5 cm^{-1} .⁸⁶⁻⁸⁸ The estimated pyrite layer thickness needed to absorb enough light for an efficient PV performance can be up to 1,000 times thinner than the conventional silicon active layer solar cells.⁸⁹ In addition, the material is composed of highly earth-abundant elements which allow for very low material and processing costs. In fact FeS_2 ranks highest in regards to material availability among a

wide range of existing semiconductors with potential for substantially lower cost solar cells, promising an estimated material extraction cost of ~ 0.000003 cents/W.⁵⁹

Figure 3.1. Iron pyrite face-centred cubic lattice structure schematic.

More recent pyrite studies reported power conversion efficiencies (PCEs) of up to $\sim 3\%$ with a large amount of the recent work focusing on pyrite NCs as light absorbers in photovoltaic devices.⁹⁰⁻⁹³ The NC approach offers solution processing of devices along with material property tunability which for example may be used to increase the small iron pyrite bandgap of ~ 1 eV to more favourable energies for solar cell applications of around 1.4-1.5 eV. However, pyrite nanocrystal performance is primarily limited by the material's tendency to form defects at the surface. The defects are commonly associated with sulphur vacancies which tend to form FeS phases creating electronic states within the bandgap and reducing device photovoltage.⁸⁶ While other studies also suggest the negative influence of the low material bandgap which can promote metallic-like behaviour in semiconductor materials, small quantum confined NCs could solve the low energy bandgap associated issues but would result in even stronger surface defect contribution due to large strongly quantum confined NC surface to volume ratios.⁸⁵ It is therefore important to establish and characterize a way to modulate the detrimental iron pyrite surface effect influence.

In this study we employ transient absorption (TA) spectroscopy in order to analyse the excited state behaviour of iron pyrite NCs which have very limited studies on the ultrafast timescales.⁹⁴⁻⁹⁵ We consider plasmon influence on the TA response which may be important in the material performance and unravel the nature of iron pyrite NC transient

absorption spectra. We then analyse a range of iron pyrite family sample variations in order to examine the effects on FeS₂ NC surface induced by a new pyrite surface passivation technique and find a significant modulation of the surface state behaviour in iron pyrite NCs coated with a thin FeSe_x shell.

3.2 Experimental

3.2.1 Samples

Iron pyrite nanocrystals were synthesised according to procedures described in the literature.⁸⁸ Four different samples based on iron pyrite family were synthesized: ~60 nm pyrite nanocrystals, ~15 nm pyrite nanocrystals, FeSe_x nanocrystals and a core-shell nanocrystal sample with 60 nm iron pyrite core coated with 2.5 ± 1.5 nm FeSe_x shell. The samples were characterized using XRD and high resolution electron micrographs (Fig. 3.2). The TEM images reveal that the morphology and size of FeS₂ nanocrystals coated with FeSe_x shell were largely unchanged in relation to the uncoated FeS₂ nanocrystals. The FeSe_x coating layer was shown to be thin in relation to the FeS₂ nanocrystal core via energy dispersive X-ray spectroscopic analysis. Further sample characterization is provided in the literature.⁸⁸ The synthesis and sample characterization was carried out by Chenlong Yu under the supervision of Jonathan E. Halpert.

Figure 3.2. TEM images of A) as-synthesized pyrite nanocubes and B) pyrite/selenide core/shell nanocubes. C) XRD patterns taken from the pyrite seeds and the core/shell product, with reflections indexed to pyrite (FeS_2) and FeSe. D–F) Scanning TEM energy dispersive X-ray analysis of $\text{FeS}_2/\text{FeSe}_x$ nanocubes. G) High-resolution TEM analysis of the core (top) and shell (bottom) of a $\text{FeS}_2/\text{FeSe}_x$ core/shell NC, with FFT spectra indicated. Reprinted with permission from⁸⁸. Copyright 2017 American Chemical Society.

3.2.2 Steady state absorption spectroscopy

Ultraviolet to visible (UV-Vis) range absorption spectra were taken with a Varian Cary 50 Bio UV-Visible Spectrophotometer. The absorption spectra extended to the near-infrared (NIR) wavelength range were taken with a Varian Cary 5000 UV-Vis-NIR Spectrophotometer. In both cases the absorption spectrum of solvent in 1 mm quartz cuvette was taken and was subtracted from the absorption spectra obtained measuring the solution suspended sample in the 1 mm quartz cuvette.

3.2.3 Transient absorption spectroscopy measurements

Excited state dynamics were studied using ultrafast transient absorption spectroscopy, in which 400 nm excitation (pump) pulses were generated from the second harmonic of an amplified Ti-sapphire 800 nm laser and were chopped at half of the amplifier rep-rate. A portion of the 800 nm output was focused in to 3 mm YAG crystal for near-infrared and linearly translated 3 mm CaF₂ crystal window for visible measurements; the generated white light supercontinua were used to probe the samples. After transmission through a sample the probe was spatially dispersed using an optical glass prism and read out at 3 kHz using a linear CMOS photodiode array (Imaging Solutions Group) for visible and linear-IR photodiode array (Entwicklungsbuero Stresing) for near-infrared measurements. Temporal experimental resolution was limited by ~200 fs total instrument response function. Approximately 2000 shots were averaged at each time point and repeated for 2 times. Sample dispersions for room temperature spectroscopic measurements were contained in a 1 mm path length fused quartz cuvette.

3.2.4 Derivative spectroscopy analysis

Second order derivatives were calculated from second polynomial order Savitzky-Golay smoothed spectral data using OriginLab OriginPro graphing software. The derivative analysis technique allows for clearer distinction of bands, in particular distinguishing small bands in broad features with the derivative minima denoting band turning points. The method is also beneficial as it reduces the errors caused by scattering or size distribution effects and corrects for baseline inaccuracies arising from such contributions as instrument instabilities or sample mispositioning by reducing any constants to zero.

3.3 Results and Discussion

3.3.1 Iron pyrite steady state absorption analysis

We examine steady state absorption spectra of 60 nm iron pyrite NCs using a standard UV-Vis absorption spectrometer and compare the findings to an extended spectral measurement to near-infrared absorption region. We further analyse the expected

transitions and effects important for later excited state analysis by employing a derivative spectroscopy approach.

We carried out steady state absorbance measurements on 60 nm iron pyrite NC solution suspension using a standard (Cary 50 Bio) UV-Vis absorption spectrometer covering ~250 to 1100 nm spectral range (Fig. 3.3a). In order to obtain a bandgap estimate of the material Tauc plot method was applied to the absorption spectra. Tauc plot approach is a technique used to investigate optical bandgaps in semiconductors initially proposed by Tauc *et al.* and later developed by Davis and Mott.⁹⁶⁻⁹⁸ The steady state absorption spectrum is converted to Tauc response according to the expression below (Eq. 3.1).⁹⁹

$$T_r = (\alpha h\nu)^{1/r} \quad (3.1)$$

Where h is the Plank's constant, ν is the photon frequency, r is a constant which denotes the nature of the electronic transition, namely $r = 1/2$ for direct allowed and $r = 2$ for indirect allowed transitions and α is the absorption coefficient defined in Equation 3.2.

$$\alpha = 2.303 \frac{OD}{l} \quad (3.2)$$

Where OD is the optical density and l is the thickness of the medium. Plotting the obtained Tauc response against energy (in eV) converted from the wavelength according to Equation 3.3 gives the Tauc plot (Fig. 3.3b).

$$E = h \frac{c}{\lambda e} \quad (3.3)$$

Where E is the energy [eV], c is the speed of light, λ is the wavelength and e is the electronvolt energy. The intersection position of the extrapolated linear Tauc plot regime with $Y = 0$ is the estimated bandgap energy. Figure 3.3b shows the Tauc plot of iron pyrite NCs with the estimated bandgap energy of about 1.23 eV. The value obtained is somewhat higher than the expected direct material bandgap of approx. 1 eV.⁸⁵

Although the absorption analysis gives comparable results to the literature, the measurements carried out with the standard UV-Vis absorption spectrometer only reach up to 1100 nm (~1.1eV) which is on the edge of the bandgap region. This can result in an error of the bandgap energy estimate as lower energy linear Tauc plot regimes may be

present in the absorption spectrum outside the measurement range. The limitation also results in a loss of important spectral information related to such effects as sample disorder or scattering which is often positioned around the bandgap region and is crucial for the accurate sample characterization.

Figure 3.3. a) 60 nm iron pyrite nanocrystal steady state UV-Vis absorption spectrum, b) corresponding direct bandgap Tauc plot with the linear regime (red line) extrapolated to x-axis positioned at $Y = 0$.

In order to improve the steady state sample characterization we carried out absorbance measurements extending into the near-infrared (NIR) wavelengths. We used a long range UV-Vis-NIR absorption spectrometer (Cary 5000) allowing for a wide wavelength range coverage of up to 3300 nm. The extended range absorption spectrum of 60 nm FeS_2 sample is shown in Figure 3.4a.

Figure 3.4. a) Long wavelength range 60 nm iron pyrite nanocrystal steady state UV-Vis-NIR absorption spectrum and baseline profile of 1 mm cuvette with chloroform, b) corresponding direct bandgap Tauc plot.

We apply the Tauc plot analysis to the long range absorption spectrum and find the bandgap of about 1.25 eV (Fig. 3.4b). The bandgap value is close to the one extracted from the standard shorter range spectrum. However, it is clear from the NIR data that the absorption spectrum of the material does not have a well-defined band edge absorption onset around the expected bandgap region of about 1200-1400 nm. Instead, a broad absorption tail extending to low energies is observed which may be the cause of the small deviation between the extracted and expected bandgap values. The broad NIR absorption tails can be indicative of sample disorder or scattering influence. We note that the contributions could be resolved by using an integrating sphere.

In the long range absorption spectrum we observe some low energy absorbance features appearing at 1685, 2365, and a region of 2690-2980 nm, which could be related to such effects as plasmon absorption bands. However, the actual material absorption spectrum at such low energy wavelengths can be affected by strong solvent absorption signatures. The transparent grey trace shown in Figure 3.4a represents the baseline measurement taken with the sample solvent only. It is clear that the long wavelength features are not real iron pyrite absorption signatures but rather baseline artefacts most likely corresponding to the strong infrared solvent vibronic absorption bands which affect the background subtraction.¹⁰⁰

In order to clearly define any spectral absorption features which may be diluted by the broad absorption profile second order derivative of the long range absorption spectrum was taken (Fig. 3.5). We find four strong spectral signatures indicated by the absorption derivative spectrum. A broad feature spanning 730-775 nm and two sharp features peaking at 505 and 810 nm were observed above bandgap which will later be discussed in relation to the excited state TA measurement transition resolution. A well-defined sub bandgap derivative minimum is also observed at around 1420 nm (~0.9 eV) which is in good agreement with an indirect transition energy expected for the material.⁸⁷ There also appears to be an indication of a derivative feature at around 1.1 - 1.05 eV which is close to the expected direct bandgap transition energy and is probably indicative of the absorption edge, however it is relatively poorly defined.

Figure 3.5. Second order derivative of long wavelength range steady state absorption spectrum of 60 nm FeS₂ NCs. Grey dotted lines indicate the minima of the strongest derivative features.

3.3.2 TA response analysis of iron pyrite

Transient absorption spectroscopy measurements were carried out on 60 nm iron pyrite nanocrystal suspensions probing over Visible to NIR wavelengths. The TA response was analysed and the features were attributed to the specific excited state behavior in the material.

Transient absorption spectral slices of 60 nm FeS₂ NCs taken at different times after pump excitation are shown in Figure 3.6. We observe a positive photobleaching signature peaking at around 720-750 nm with an indication of another bleaching feature at higher energies spanning towards 500 nm (the edge of the spectral range measured). The two ground state bleaching signatures observed here correspond well to the positions of the steady state absorption transitions indicated via the differential analysis method in the previous section. The strongest GSB feature around the 720-750 nm (1.72 eV) likely represents the bleaching of $3d\ t_{2g} \rightarrow e_g^*$ iron pyrite transition which has a predicted energy of about 1.7 eV.¹⁰¹⁻¹⁰²

Figure 3.6. Normalized transient absorption spectra of 60 nm FeS₂ NCs at various times after above bandgap photoexcitation with 400 nm pump pulses.

While we observe optical transition bleaching in the high energy end of the spectrum, the low energy range TA is dominated by a broad photoinduced absorption (PIA) feature. The PIA spans from about 800 to 1400 nm and displays short time spectral evolution dynamics with a peak shift from around 1020 to 920 nm. It is not clear what causes the PIA signal and we will in turn consider the possible plasmon and trapping effect influence on the observed signature. Plasmonic effects, expected to manifest in the NIR region, have been previously suggested in pyrite materials, we therefore consider the plasmon influence in our spectroscopic analysis.¹⁰³⁻¹⁰⁴ Surface plasmon resonance is a collective oscillation of the surface conduction electrons driven by the incident light which typically induces pronounced absorption bands.¹⁰⁵ Plasmons are often expected to be generated from the thermal concentration of free carriers in noble metal nanoparticles such as gold and silver. Some semiconductor NCs with high conduction band carrier concentrations can also display plasmonic behaviour with absorption bands in the NIR region.^{52, 106-107} Since pyrite is expected to display a high conduction band carrier concentration due to its small bandgap and as the typical lattice irregularities such as sulphur vacancies can also introduce defects of metallic nature, iron pyrite nanocrystals may indeed permeate surface plasmon effects.^{52, 59, 105}

We now discuss the possibility of intrinsic carrier population induced plasmonic behaviour manifesting in the iron pyrite TA spectra as the dominant PIA feature. Typically plasmonic bands arising from the intrinsic carrier population would be

observed as pronounced low energy material dependent absorption peaks in the steady state absorption spectrum.¹⁰⁷⁻¹⁰⁸ As seen in the long wavelength range absorption spectrum (Fig. 3.4a), such peaks were not present apart from the baseline artefacts discussed earlier. This indicates negligible intrinsic carrier density plasmon influence. In addition to the steady state analysis argument, a typical case of transient absorption response of the material arising from intrinsic carrier density plasmonic effects would manifest as a strong low energy bleaching feature rather than PIA.¹⁰⁷⁻¹⁰⁸ It would arise due to the modulation of the intrinsic carrier density which permeated surface plasmons before the excitation with the pump pulses. In our case we do not see such effect and instead of bleaching our spectrum is dominated by the PIA, indicating no resolvable intrinsic conduction carrier population permeated plasmonic behaviour in our measurements.⁴⁷

We also discuss the possibility of plasmonic behaviour manifesting in the TA spectrum as the PIA signature in relation to the photoexcited carriers permeating plasmonic effects. Photoinduced plasmonic absorption could arise if it was driven by the carriers promoted to the conduction band, in such case the plasmonic features would be highly sensitive to the photoinduced carrier concentration. The spectral position of the plasmon TA features would be expected to shift with photoinduced carrier density as it modulates the plasmon frequency.^{107, 109} Different nanocrystal environment could also heavily affect the plasmonic features due to high plasmon sensitivity to the nanocrystal surface-medium interface. We examine TA spectral evolution of a FeS₂ NC sample with varying carrier density as shown in Figure 3.7a. No pronounced PIA feature dependence was observed suggesting limited plasmon influence on the TA data. In addition the FeS₂ NCs were measured in two different solvent suspensions which would affect any plasmonic interaction, however no resolvable differences were observed in the broad PIA transient absorption feature suggesting it is not a signature induced by surface plasmon resonance.

Figure 3.7. Normalized transient absorption spectral slices of a FeS₂ NC sample low energy PIA feature a) over varying excitation fluences, b) of nanocrystals suspended in different solvents integrated over 2-100 ps time (due to low signal-to-noise ratio of CHCl₃ NC suspension measurement) after excitation with 400 nm pump.

Rather than an absorption signature of surface plasmons, the low energy PIA feature is likely arising from intraband or trapped state absorption. Pyrite displays a large defect and p-type vacancy distribution which is largely localized at the surface of pyrite nanocrystals.¹¹⁰ Given the prevalence of low energy defect distribution in iron pyrite nanocrystals the PIA is most likely a signature of surface state absorption.

We further investigate the dynamics of the low energy PIA feature in order to clarify its nature. The signature appears to display short time spectral dynamics as shown in Figure 3.6 with a peak shift to higher energies within a few picoseconds after the excitation. We carry out global fitting analysis in order to decompose the TA response into the exponentially decaying species and isolate their kinetics. The fitting separates the constituent TA spectral components which share the same dynamics allowing to investigate their relative evolution which can result in TA spectral shifts arising from their overlapping contributions. Best data fit was obtained by fitting 3 components which resolved excited state dynamics with lifetimes of 1.3 ps, 256 ps and 14.4 ns. The longest component extracted here is about an order of magnitude outside the measurement time scope hence it mostly serves as a constant fit offset while the shorter components shown in Figure 3.8 isolate physical material processes evolving within the 1 ns. The fast 1.3 ps component reflects the time scale of the rapid TA spectral evolution indicated in the PIA spectral shift and represents the influence of band to trap transitions or rapid carrier

intraband relaxation.⁹⁴⁻⁹⁵ The intermediate fitting component isolates the broad PIA response as shown in Figure 3.8. In previous research of FeS₂ positron lifetime measurements were used to investigate pyrite trap dynamics and trap lifetimes of 235-286 ps were reported. The intermediate TA component extracted here isolates the PIA signature with a lifetime of 256 ps which confirms the defect nature of the PIA feature observed in the 60 nm pyrite nanocrystal TA measurements.¹¹¹

Figure 3.8. Globally fitted exponential TA decomposition of 60 nm FeS₂ NCs showing two component decay associated spectra.

3.3.3 Surface effect modulation

Pyrite has been identified as one of the cheapest potential photovoltaic materials and employing nanocrystals could make it even more cost effective for device development.⁸⁵ However, pyrite performance in devices has been hindered by strong trapping characteristic amplified by the large NC surface area. Surface disorder has been identified as the major contributor to the trapping issues associated with the primary device loss mechanisms, therefore it must be understood and addressed.^{85-86, 112} Here we examine a range of different iron pyrite nanocrystal sample variations in order to identify the FeS₂ NC surface defect behaviour and examine the effects of surface passivation approach of coating the FeS₂ nanoparticles with FeSe_x shell.

We carry out transient absorption measurements on large surface to volume ratio iron pyrite nanocrystals with dimensions on the order of ~15 nm as well as 60 nm FeS₂ NCs coated with $\sim 2.5 \pm 1.5$ nm FeSe_x shell (Core-shell) and compare their spectral response

to the excited state behaviour of 60 nm FeS₂ NCs. Iron selenide has a close crystal lattice match to iron pyrite and displays a direct bandgap of approx. 1.2 eV, close to that of pyrite.⁸⁸ Combined with its low toxicity and wide abundance iron selenide makes a good candidate to be used for the FeS₂ nanocrystal defect modulation in particular for reducing the effects of sulphur vacancies on iron pyrite nanocrystal surface which have profound effect on the optoelectronic NC behaviour.^{85, 112} The 15 nm iron pyrite NC sample has surface to volume ratio roughly 4 times larger than the 60 nm pyrite nanocrystals and may serve as a reference point of a system with larger surface defect influence. The transient absorption spectral slices of the three iron pyrite sample variations are shown in Figure 3.9a. The data displays a noisy region around the 800 nm wavelength range therefore we use a local regression (LOESS) smoothing in order to smooth the data for a clearer representation (Fig. 3.9b). The regression used is a common data analysis technique which is particularly good for presenting data trends. All three samples display a broad photoinduced absorption signature with lifetimes on the order of a few hundred picoseconds, which was earlier attributed to the surface trapping response in the 60 nm Pyrite NCs. In spite of the similarities, some pronounced differences in the PIA feature are observed between the three samples. The PIA feature peaks at around 890 nm in the 60 nm Pyrite NCs, but the peak blue-shifts to 760 nm in 15 nm NC sample and red-shifts to 1030 nm in the core-shell nanocrystals. The 735 nm GSB signature seen in FeS₂ NCs also develops across the different samples. The core-shell TA response displays stronger state bleaching while it appears to vanish in the 15 nm NC spectrum.

Figure 3.9. a) Transient absorption spectra of 60 and 15 nm FeS₂ and FeS₂-FeSe_x core-shell NCs probed at 10 ps. b) The corresponding spectra smoothed using LOESS smoothing.

The blue-shifting of the PIA peak seen in the smaller 15 nm FeS₂ NCs could be argued to be a signature of quantum confinement induced state shift to higher energies which could also explain the disappearance of the GSB feature in terms of its energy shift. However, the estimated iron pyrite Bohr diameter is around 2.6 nm, which is significantly lower than the 15 nm NC size.¹¹³ This suggests negligible quantum confinement effects, unlikely to explain the disappearance of GSB as a large quantum confinement induced energy shift. Unlike quantum confinement, the surface states are expected to have a much more pronounced effect on carrier dynamics in comparison to the 60 nm NCs due to the significantly larger surface to volume ratio. In this model stronger surface defect effects could result in a stronger PIA response which would overwhelm the overlapping intrinsic iron pyrite material transition bleach represented by the ~735 nm GSB feature and in turn appear to shift to higher energies. While the opposite effect is observed in the core-shell nanoparticles it could also be explained by the same model. In core-shell NCs the GSB becomes more pronounced in relation to the PIA and the PIA feature shifts to lower energies. In a similar fashion to the influences discussed for the 15 nm NCs, the observations may indicate a reduction of surface trapping influence. We carry out global fitting analysis on the range of samples in order to isolate the PIA signature and assess the suggested surface defect behaviour (Fig. 3.10).

Figure 3.10. PIA component decay associated spectra of globally fitted exponential TA decomposition of 60 and 15 nm FeS₂ and core-shell (FeS₂-FeSe_x) NCs.

The samples were globally fitted according to a model discussed earlier in the 60 nm FeS₂ sample TA analysis section to isolate the surface defect contribution. The broad PIA component lifetimes extracted were 124, 256 and 455 ps for 15 nm, 60 nm and core-shell

NC samples respectively. The lifetimes may indicate more rapid carrier recombination in the system with stronger iron pyrite surface defect state influence, however the values are on a similar order and may have limited significance. Figure 3.10 shows the extracted intermediate lifetime spectral components which isolate the PIA feature in the three samples. The spectral PIA component profile of the 15 nm pyrite NCs matches the profile of the 60 nm NCs well. The finding confirms that the same surface effect mechanism is present between the two samples and the peak shift observed in the TA spectra is most likely a result of stronger 15 nm surface effect response in the TA spectrum in relation to the GSB feature. The core-shell nanoparticles, however, behave differently. The same defect state behaviour response in TA spectral profile attributed to the sulphur surface vacancies in the 15 and 60 nm iron pyrite NCs is not observed when the FeSe_x shell is applied to the nanocrystal surface. Instead, the PIA displays a different spectrum shifted to lower energies. This finding indicates that the iron pyrite surface state behaviour was effectively modulated by the FeSe_x coating.

We now compare the 60 nm iron pyrite and the core-shell sample TA spectral response to the FeSe_x NCs. As expected the FeSe_x NC spectrum shown in Figure 3.11 reveals high energy range behaviour which does not indicate the presence of the bleaching signature unique to the iron pyrite NCs. While the core-shell NCs display the GSB feature related to the 60 nm FeS_2 NCs at short wavelengths, the spectral similarities depart in the PIA dominated long wavelength end. Instead of following the FeS_2 spectral response, the core-shell sample appears to match the FeSe_x NC profile. The findings indicate that the coated particles retain the intrinsic excited state behaviour of the FeS_2 core while the iron pyrite surface state behaviour is modulated by the FeSe_x coating layer.

Figure 3.11. Transient absorption spectra of 60 nm FeS_2 , FeS_2 - FeSe_x Core-Shell and FeSe_x NCs probed at 10 ps. Spectral break added around 800 nm region for clarity.

3.4 Conclusion

We used broadband transient absorption and UV-Vis-NIR steady state absorption measurements to examine the excited state dynamics and effects of material surface modulation approach in a range of different iron pyrite family NC samples. 60 nm iron pyrite NCs were found to display strong surface state absorption response dominating the low energy TA measurement range. The excited and steady state responses were also analysed in terms of surface plasmon resonances both from intrinsic and photoexcited carrier population, however no resolvable plasmonic effects were observed. Global fitting analysis method was used to isolate the surface effect response with an estimated lifetime in a few hundred picosecond range. We find an apparent surface state absorption shift in smaller 15 nm nanocrystals arising from stronger surface state influence in relation to the pyrite energy transition bleaching signature. In contrast, FeS_2 nanocrystals coated with a thin FeSe_x shell displayed an apparent surface state absorption shift to lower energies. Global fitting revealed that the defect absorption mechanism between the small 15 nm and large 60 nm iron pyrite NCs is essentially the same with differences in TA spectra explained by the relative feature magnitude change, while the core-shell nanoparticles revealed a significant surface defect behaviour modulation introduced by the FeSe_x coating. Further comparison with FeSe_x NC response revealed that the iron pyrite core is still photoactive in core-shell nanoparticles with the surface behaviour dominated by the

FeSe_x response. The findings help characterize iron pyrite excited state behaviour and support the potential of the new iron pyrite NC surface defect modulation approach.

Chapter 4

Doping effects on silicon nanocrystals

Parts of this chapter have been published in the following article:

McVey, B. F. P.; **Butkus, J.**; Halpert, J. E.; Hodgkiss, J. M.; Tilley, R. D., *Solution Synthesis and Optical Properties of Transition-Metal-Doped Silicon Nanocrystals. The Journal of Physical Chemistry Letters* 2015, 6 (9), 1573-1576.

4.1 Introduction

Silicon has been widely used in the semiconductor industry for decades and is one of the best researched semiconductor materials in the world. It dominates the large scale photovoltaics market partially because it has favourable optoelectronic properties. Silicon is also one of the most abundant elements in the Earth's crust, it is nontoxic and currently is relatively cheap to process.¹¹⁴ Despite its good characteristics which have been broadly researched and already established commercial success the improvement of the material was more recently approached in terms of nanoscale development. The use of silicon in nanocrystal form may allow for improved current device functionalities and extend its applications beyond the limits of the bulk material. Its size and surface tuned properties along with large scale manufacturability offer great potential in LEDs, solar cells, biological applications, etc.¹¹⁴⁻¹²²

Although silicon NC research has taken many directions since the first reported visible photoluminescence observation in silicon nanostructures in 1990s, doping of silicon NCs with metal dopants has been relatively unexplored.¹²³⁻¹²⁵ The doping approach allows for a greater material property tunability such as emission control, electrical transport and magnetism which could make the NCs suitable for such applications as contrast agents.¹²⁴⁻¹²⁶ Previous studies on doping of Cd and Zn based NCs showed promise for

the field of doped nanocrystals which may play an important role in the future of silicon NC applications.¹²⁷⁻¹³²

In this study we examine the excited state dynamics of ~2.5 nm silicon NCs using ultrafast TA spectroscopy and compare them to the same size silicon NCs doped with a small amount of Ni, Mn or Cu atoms. We discuss the excitonic and trapping influence on the undoped silicon nanocrystal TA response and analyse its evolution with doping. We find strong doping effects on the silicon NC dynamics and propose a model explaining the changes in relation to the excited and steady state sample properties.

4.2 Experimental

4.2.1 Samples

Undoped and doped silicon nanocrystals were synthesised according to procedures described in the literature.¹²³ Four ~2.5 nm NC samples were synthesised of undoped silicon and silicon doped with Ni, Mn or Cu. The samples were characterized using energy dispersive X-ray spectroscopy and transmission electron microscopy measurements. Nanocrystals synthesised were shown to be spherical and monodisperse with comparable sizes between doped and undoped NCs (Fig 4.1). Atomic composition was determined via energy dispersive X-ray spectroscopy showing doped nanocrystal stoichiometries of $\text{Mn}_{0.006}\text{Si}$, $\text{Ni}_{0.006}\text{Si}$ and $\text{Cu}_{0.007}\text{Si}$. Further details of sample characterization are provided in the literature.¹²³ The synthesis and sample characterization were carried out by Benjamin F. P. McVey under the supervision of Richard D. Tilley.

Figure 4.1. a-d) TEM images of undoped and doped Si nanocrystals (Scale bar = 10 nm). Reprinted with permission from¹²³. Copyright 2015 American Chemical Society.

4.2.2 Steady state measurements

Photoluminescence measurements were recorded using Shimadzu RF-5301PC spectrofluorometer. Absorbance measurements were recorded using Agilent diode array spectrometer. Steady state absorption measurements were taken by Benjamin F. P. McVey under supervision of Richard D. Tilley.

4.2.3 Transient absorption spectroscopy measurements

Excited state dynamics were monitored using ultrafast transient absorption spectroscopy setup described in more detail in Chapter 2. NC dispersions for spectroscopic measurements were contained in a 1 mm path length fused quartz cuvette. Samples were excited with 280 nm pump (frequency doubled 560 nm output from TOPAS-C optical parametric amplifier, which was chopped at half of the 3 kHz amplifier rep-rate). The doubling was carried out close to the sample in order to minimize the losses of the 280 nm pump intensity induced by the propagation through the optical setup. Broadband

supercontinuum probe pulses were generated in a CaF_2 plate (UV-Vis range) or a YAG crystal (NIR range). The spectra were recorded using a linear UV-Vis photodiode (Entwicklungsbuero Stresing) array and a linear IR photodiode array (Entwicklungsbuero Stresing) for UV-Vis and NIR measurements respectively.

4.3 Results and Discussion

4.3.1 Steady state characterization

Steady state analysis provides an important insight into undoped and doped silicon nanocrystal sample properties which are discussed here in order to help understand the system and its excited state response analysed via TA spectroscopy in the later sections. Nanocrystal sizes and dopant material concentration is considered along with the absorbance and emission spectra suggesting strong dopant effects in comparison to undoped silicon NCs. The steady state characterization measurements and synthesis were carried out by Benjamin F. P. McVey under supervision of Richard D. Tilley.

The undoped silicon nanoparticles analysed were spherical with an average diameter of $\sim 2.1 \pm 0.3$ nm as determined from the TEM images, while the Si NCs doped with Mn, Ni and Cu displayed diameters of 2.4 ± 0.4 , 2.5 ± 0.4 and 2.5 ± 0.4 nm respectively. Closely matching particle sizes allowed for the comparison of the doping properties without the influence of different size effects.

The doped Si NCs displayed the following stoichiometries: $\text{Mn}_{0.006}\text{Si}$, $\text{Ni}_{0.006}\text{Si}$ and $\text{Cu}_{0.007}\text{Si}$. An average NC had an estimated 360 atoms with an average of 2-3 dopant atoms per NC. The small dopant ratio confirms the dominant presence of Si meaning any differences induced in the particle properties should arise from the Si interaction with the dopant rather than the dynamics of the dopant alone.

The steady state absorption and emission spectra are considered (Fig. 4.2) in order to analyse the differences between a series of doped and undoped silicon nanoparticles. While the silicon NC absorption spectra suggest similar sample bandgaps in the region of ~ 4.3 eV the spectral shapes appear to change with doping, in particular the relative magnitude of the low energy absorption shoulder increases in the doped samples. In

addition the higher energy spectral profile departs the undoped Si absorbance with similar signatures between the Ni and Mn doped NCs, while the Cu doping induces a different spectral evolution with sharper absorption peaks. The different Cu spectral profile in relation to other dopants may be related to the different doping characteristics. The Mn and Ni are expected to physically dope the Si NC surface while the Cu atoms better penetrate the Si NC core as indicated by photostability measurements due to the high diffusion coefficient of Cu and its higher solubility in Si.¹²³ Photoluminescence spectra also indicate a pronounced modulation of the Si NC properties with doping. All doped samples display PL red shifts of up to 40 nm in relation to the undoped particles due to introduction of dopant states lying within the bandgap.¹³³ In addition, the PL emission wavelengths appear to be dependent on the excitation light energy in the undoped NCs while interestingly this dependence disappears in the doped NCs.¹²³ The steady state absorption and PL measurements indicate a strong modulation of the Si NC properties by the introduction of dopant metals, however to better understand the doping influence on silicon NCs excited state dynamics need to be considered.

Figure 4.2. Normalized absorption and emission ($\lambda_{\text{exc}} = 360$ nm) spectra of undoped and doped silicon NCs. The black dotted line is added to emphasize the emission shift between undoped and doped silicon NCs. The inset of each contains colour photographs of doped and undoped NCs dispersed in hexane under illumination by a 360 nm UV light. Reprinted with permission from¹²³. Copyright 2015 American Chemical Society.

4.3.2 Silicon nanocrystal excited state analysis

We carried out transient absorption measurements on undoped silicon nanocrystal solution suspensions and examined the excited state response over the visible and near-infrared wavelength ranges. We discuss the influence of excitons and trap states on the observed dynamics.

Undoped silicon nanocrystal TA spectra were analysed in the visible range. Figure 4.3 shows the TA surface and spectra of the undoped silicon NCs excited with UV pump. We observe two distinct photoinduced absorption bands. A sharp high energy feature peaking at around 345 nm and a broad PIA signature spanning the long wavelength end of the spectrum with a peak at around 475 nm. The sharp absorption feature close to the bandgap is a typical band edge exciton absorption signature expected in such strongly confined ~ 2 nm silicon NCs, with physical dimensions significantly lower than the bulk Bohr radius of about 8-9 nm.¹³⁴⁻¹³⁶ We note that if shorter wavelengths were monitored

the exciton feature would appear as a derivative profile around the bandgap energies with sharp shorter wavelength bleaching and sharp longer wavelength PIA. However, only the longer wavelength side of the derivative feature is probed in this case with the band edge exciton bleaching falling outside the attainable measurement spectral range limited by the low intensity deep UV light generated by the CaF_2 crystal and large high energy radiation losses in the optical setup. The broad below bandgap absorption features are often associated with defect states in other inorganic NCs and in the case of silicon NCs have also been previously attributed to photoinduced absorption from the population of surface trap states.¹³⁷

Figure 4.3. Transient absorption measurement of undoped silicon NCs excited with 100 fs pump pulses centred at 280 nm probed in the visible range a) surface map, b) spectral slices at different times past the excitation.

The infrared absorption signatures of the undoped NCs are shown in Figure 4.4a. The IR range is dominated by PIA signatures which share the same dynamics in the low and high IR energy ends as shown in Figure 4.4b indicating a single mechanism probed here. We carry out exponential kinetics fitting in order to resolve the nature of the IR signature. The kinetics were fitted from 500 fs in order to avoid any short time measurement artefact influence. The IR signature could not be fitted to a single exponential indicating multiple effects on its dynamics with best fitting exponential lifetimes of 1.1 and 52.6 ps. The lifetimes were compared to the ones extracted from the visible spectral features with excitonic absorption fitting a single monoexponential with 1.4 ps lifetime and trapping signature fitting double exponential with 1.0 and 33.5 ps lifetimes. The similar behaviour observed between the visible trapping feature and the IR signature suggests that the two signatures are likely different absorption features probed belonging to the same system

with global fitting supporting this conclusion showing good fits with shared 1.0 and 48.4 ps lifetimes. While the short time trapping component relates well to the exciton lifetime indicating its correlation to the trapping dynamics. The observations suggest a mechanism where the photogenerated excitons are rapidly transferred to traps in about 1 ps with trapped carriers then recombining on the 50 ps timescales.

Figure 4.4. Transient absorption measurement of undoped silicon NCs excited with 100 fs pump pulses centred at 280 nm probed in the near-infrared range a) spectral slices at different times past excitation, b) normalized kinetic traces probed at long and short wavelengths.

4.3.3 Doping effects

Transient absorption measurements were carried out on the doped silicon NC samples. The doped NC excited state dynamics were compared to the undoped silicon NC response over the UV-visible and NIR spectral ranges. The doping was found to have a pronounced effect on the excited state response of the silicon NCs due to introduction of the sub-bandgap states.

Visible wavelength range transient absorption spectral responses of the undoped silicon and the NCs with the three different dopants analysed are shown in Figure 4.5. We observe dramatic changes induced by the doping. The 345 nm exciton absorption peak seen in the undoped silicon NCs diminishes in the TA spectra 1 ps past the excitation when doping is introduced. The relative effect appears to be similar across all three dopant metals with minor differences in the quenched peak region profile. The second obvious trend is the evolution of the surface trap absorption feature. The PIA peak shifts from ~475 nm for undoped NCs to longer wavelengths (589, 590 and 600 nm) in the

doped NCs. In all three doped NCs the trapping feature displays a shift of ~ 100 nm which correlates well with the similar steady state photoluminescence peak red-shifting behaviour across all three doped samples. The TA trapping signature displays small spectral differences between the different transition metal dopants, however in general the doping effects appear to be similar with strong quenching of the exciton absorption signature and a shift of the trapping absorption profile likely due to the new states introduced within the bandgap.

Figure 4.5. Low energy peak normalized spectral slices at 1 ps of transient absorption measurements of doped and undoped silicon NCs excited with 100 fs pump pulses centred at 280 nm, probed in the visible range.

We examine the doping effects in relation to the excited state kinetics shown in Figure 4.6. In line with the spectral analysis the temporal exciton dynamics display exciton quenching in the doped NCs with the reduction of the short picosecond feature evolution seen in the undoped NCs. We carry out a reference TA measurement on a sample with NC solvent only and find that the exciton dynamics of the doped NCs is obstructed by the temporal range limitation of the experiment response suggesting any significant excitonic absorption is evolving within a few hundred femtoseconds. In contrast, the low energy trapping absorption signature dynamics appear to display prolonged relaxation times with substantial intensity remaining past 10 ps in the doped NCs while the undoped sample relaxation appears to be more rapid. Some small differences are observed between the different dopant element dynamics in this case with Cu signal lasting longer than the other two dopant samples possibly relating to its more intrinsic doping characteristic,

however in general the different dopant trapping effects are similar when contrasted to the undoped NCs. The observations suggest more rapid charge carrier relaxation to the trap states with slower trap state dynamics further distinguishing the doped NCs from the undoped.

Figure 4.6. Normalized temporal dynamics comparison of exciton (340-350 nm integral) and trap (500-600 nm integral) visible range transient absorption measurement features of doped and undoped silicon NCs excited with 100 fs pump pulses centred at 280 nm.

We consider the sample doping effects on the near-infrared transient absorption response. Figure 4.7a shows the near-infrared TA spectra of the range of nanocrystal samples measured. The doped NC spectra display broad photoinduced absorption signatures comparable to the undoped NCs, but with marginally more uniform profile. Namely, there is an absence of the weak absorption dip in the doped NCs seen around 1000-1200 nm in the undoped silicon sample, which may indicate a wider doped NC defect distribution. However, it is difficult to accurately attribute the broad infrared PIA signatures with little spectral turning points as the NIR features are not fully resolved due to the experimental spectral range limitation. While only the edge of the infrared PIA feature is monitored its dynamics can still provide an accurate excited state evolution representation. Figure 4.7b shows the infrared feature kinetics probed at ~ 1500 nm over the four NC samples analysed. Similar to the visible range trapping feature dynamics, the

NIR kinetics reveal slower PIA evolution induced by the doping. The doping induced dynamics are also similar among different dopants with even less pronounced deviations than in the UV-visible range. The near-infrared TA analysis supports the modulation of the excited state dynamics with NC doping indicated in the visible range.

Figure 4.7. Transient absorption measurements of doped and undoped silicon NCs excited with 100 fs pump pulses centred at 280 nm probed in the near-infrared range a) 1 ps spectral slices normalized to the shortest wavelength range magnitude, b) normalized kinetic traces over 1400-1600 nm integral.

We propose a model which helps explain the analysed system in relation to the different optical responses observed between the doped and undoped silicon NCs. The left side of Figure 4.8 represents the undoped nanocrystal energy level schematic with the corresponding optical transitions. Upon photoexcitation the carriers are excited to the band edge and when probed with broadband white light supercontinuum, typical band edge exciton absorption is observed through exciton self-renormalization interaction with estimated renormalization energy of about 0.5 eV and lower energy photoinduced absorption to a wide distribution of higher lying states.¹³⁸ The exciton responses live for around 1 ps until the charges populate silicon trap states with longer lifetimes. When probed, the trapped carriers absorb the light promoting them to higher lying states which appear as photoinduced visible and NIR absorption signatures in the TA measurements with similar dynamics determined by the same trap states. The range of mid-gap trap states are emissive and carriers trapped at different energy trap states, in the case of sub-bandgap excitation, governed by the excitation energy, emit at different energies. This explains the sub-bandgap excitation energy dependent emission wavelengths observed in the undoped silicon NC photoluminescence measurements. The right side of Figure 4.8

represents the doped silicon NC energy level schematic, where the dopants modulate silicon trap states or introduce a dominating trapping mechanism. In this case the carriers are more rapidly trapped in the states distributed closer to the conduction band energies resulting in the faster reduction of exciton response in the TA spectra. We note that the 1 ps lifetime TA dynamics components seen in the undoped NCs, diminish to under 500 fs lifetimes in the doped NCs in accordance to this explanation. When probed, the trapped carriers display lower energy photoinduced absorption TA responses due to the smaller energy differences between the higher lying states and the new mid-gap trap states. The steady state photoluminescence measurements of the doped NCs reveal emission energy invariance with different sub-bandgap excitation energy along with the red-shifts in the PL excitation spectra shown in Figure 4.2.¹²³ The observed PL behaviour suggests the new dopant traps emit through a fixed energy state with an energy loss mechanism such as phonon emission. The simple model explains the differences between the doped and undoped silicon NC systems in relation to the steady and excited state measurement observations.

Figure 4.8. Simplified energy level schematic proposed for the optical transitions observed in doped and undoped silicon NCs, where arrows denote photon transitions combined with any phonon assisted transitions for simplicity, ϵ denotes emissive states, C. B. and V. B. are the conduction and valence bands respectively, $h\nu$ denotes a photon and grey numbers are the approximate estimated state and transition energies (energies not to scale).

4.4 Conclusion

We carried out broadband transient absorption measurements on ~ 2.5 nm silicon NCs along with different transition metal doped NC samples and characterized the systems and doping induced differences in relation to their excited and steady state responses. Undoped silicon NCs displayed band edge excitonic absorption along with longer lived trap state absorption signatures in the visible range. Trap state mediated absorption dominated the NIR wavelength range as suggested by the dynamics matching the visible trap absorption signature. Doping the NCs with less than 1 dopant atom per 100 silicon atoms resulted in strong changes in the steady state sample properties along with excited state behaviour. The excitonic absorption seen in the undoped NCs was quenched by the doping with dynamics evolving within the limit of the instrument response function. In contrast, the visible trapping absorption dynamics were prolonged with doping and the trapping spectral profile developed red shifting by around 100 nm in each of the doped samples. The analysis of infrared TA was limited by the attainable experimental wavelength range, however the temporal dynamics suggested similar doping effects seen in the visible range. The observations suggested more rapid exciton transfer to dopant trap states. Despite the small differences between the sample dynamics of different transition metal dopants their general effects on the steady and excited state properties appear to be comparable when contrasted to the undoped silicon NCs. Finally, we proposed a model that explains the dopant induced changes in silicon NC properties through a modulation of sub-bandgap states according to the steady and excited state behaviour observations.

Chapter 5

Excited state dynamics of CZTS nanocrystals

5.1 Introduction

Quaternary semiconductor $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has recently emerged as a potential photovoltaic material with a favourable bandgap of around 1.4-1.5 eV.¹³⁹⁻¹⁴⁰ It is composed of four different earth abundant elements which have significantly lower raw material costs than the current market photovoltaic thin-film absorbers. Its properties are similar to CIGS which has already been successfully used in thin film technologies, but unlike current thin-film technologies CZTS is non-toxic and has a significantly lower material price making it an excellent absorber material alternative for solar cell applications.¹⁴¹⁻¹⁴² It also displays high absorption coefficients of over 10^4 cm^{-1} and is expected to have exciton binding energies close to the room temperature which is favourable for the formation of free carriers.¹⁴³⁻¹⁴⁴ However, the multicomponent nature of CZTS means that during its synthesis the elements could potentially form different phases like kesterite, stannite and wurtzite. In addition coexisting secondary compounds can form with most of the relevant ones being ZnS, CuS, Cu_2S , SnS, SnS_2 and Cu_2SnS_3 . Although kesterite CZTS phase is the most thermodynamically stable, the free energy differences are predicted to be only ~3 and 5 kJmol^{-1} in comparison to stannite and wurtzite phases respectively making them nearly as energetically favourable to form as the kesterite phase (a schematic of wurtzite crystal structure is show in Figure 5.1).¹⁴⁵ It is therefore often challenging to synthesise phase pure CZTS for device applications. Currently the best performing CZTS based photovoltaic devices are composed of CZTS type thin films with partial sulphur replacement with selenium and display power conversion efficiencies of up to 12.6 %.¹⁴⁶⁻¹⁴⁷

Figure 5.1. Crystal structure schematic of wurtzite phase CZTS.

Sulphur element replacement with selenium improves CZTS device performance through more stable pure phase formation and although its properties can be altered by the crystal composition control, the use of CZTS nanocrystals could further improve the material performance in devices through enhanced tunability of material properties.¹⁴⁸ In addition, the nanocrystals offer solution based processing and the possibility of printed device manufacturing which is highly appealing for low cost and large scale device market applications. However, to date CZTS nanocrystal based devices produce over ~30% lower power conversion efficiencies than the bulk materials.^{146, 149-150} The complex quaternary crystal structure of CZTS was found to contribute to a formation of a range of secondary phases which can permeate detrimental effects to the devices.¹⁵¹⁻¹⁵² Nanocrystals are particularly prone to disorder due to the large density of surface boundaries in comparison to the bulk material. The pronounced formation of the defect states may be the reason for the poorer nanocrystal performance in devices. The defect influence on the performance of the material can be analysed via ultrafast spectroscopy techniques. Although CZTS nanocrystals have been first synthesised in 2009, their excited state dynamics, in particular transient absorption responses, have not been broadly researched.¹⁵³⁻¹⁵⁵ A single transient absorption study of colloidal CZTS NCs has focused on quantum confinement effect resolution in two different sized NC samples over a narrow 300 nm visible spectral range and found a shift of a visible photoinduced absorption band with quantum confinement and its short lifetime of up to 20 ps.¹⁵⁴ Longer lifetimes of up to ~100 ps were resolved in another study, however it analysed large CZTS single crystals which can have limited appeal in device applications.¹⁵⁵ The

limited understanding of the fundamental charge formation processes and their relaxation in NCs along with the CZTS sub-phase state importance and their influence on their dynamics can obstruct the development in the field.

In this study we analyse the excited state dynamics of ~12 nm CZTS and CZTSe nanocrystals using transient absorption spectroscopy. We characterize the observed UV-visible TA signatures in relation to CZTS band transitions and defect states. Anomalous near-infrared absorption features are also observed and characterized via varying nanocrystal environment measurements. We also compare the excited state behaviour in CZTS nanocrystals to $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) nanocrystal response and propose a simple model describing the observed excited state dynamics.

5.2 Experimental

5.2.1 Samples

CZTS nanocrystals were synthesized using one-pot hot injection synthesis method described in more detail in the literature.¹⁵⁶ Monodisperse CZTS nanocrystals with ~11-13 nm sizes were indicated by TEM measurements (Fig. 5.2a, b). For TEM measurements of CZTS nanocrystals a small drop of a dilute solution (2-4 mg/mL) was drop cast onto carbon coated gold grids. The TEM used was a JEOL 2100F operated at 200 KV. Image analysis involved determination of nanocrystal size. This was carried out using ImageJ software. The XRD patterns with major diffraction lines indexed (Fig. 5.2c) matched the wurtzite phase of CZTS. Sample preparation for XRD involved drop casting a concentrated solution of nanocrystals (50 mg/mL) dispersed in a volatile solvent (n-hexane) onto a low background silicon holder. The X-ray machine used was the PANalytical X'Pert Pro Multi-purpose diffractometer using a copper emission source. Material synthesis and characterization were carried out by Benjamin F. P. McVey under the supervision of Richard D. Tilley and Jonathan E. Halpert.

Figure 5.2. a) Low resolution transmission electron microscope image of CZTS NCs. b) Histogram showing the range of CZTS NC sizes produced. c) XRD pattern of CZTS NCs, the major diffraction lines are indexed. Courtesy of Benjamin F. P. McVey.

5.2.2 Steady state absorption

UV-visible-near-infrared absorption spectra were recorded using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. The integrating sphere absorption measurements were carried out using a modified Ocean Optics ISP-80 integrating sphere with 200-1100 nm detection range spectrometer setup coupled with fibers. The samples were measured in cylindrical glass tubes with more details described in the literature.¹⁵⁷ The integrating sphere measurements were carried out with the help from Matthias Meyer under the supervision of Eric Le Ru.

5.2.3 Transient absorption

Excited state dynamics were studied using ultrafast transient absorption spectroscopy setup described in more detail in Chapter 2. NC dispersions for spectroscopic measurements were contained in a 1 mm path length fused quartz cuvette. Samples were excited with either 400 or 532 nm pump (TOPAS-C optical parametric amplifier).

Broadband supercontinuum probe pulses were generated in a CaF_2 plate (UV-Vis range) or a YAG crystal (NIR range). The spectra were recorded using a linear UV-Vis photodiode (Entwicklungsbuero Stresing) array and a linear IR photodiode array (Entwicklungsbuero Stresing) for UV-Vis and NIR measurements respectively.

5.3 Results and Discussion

5.3.1 Transient absorption of CZTSe nanocrystals

CZTS material performance can be improved by the modification of crystal composition, in particular exchanging sulphur with selenium which leads to the formation of $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe). CZTS type photovoltaic devices made with selenium have been shown to perform better than pure CZTS devices.¹⁴⁸ The exchange is expected to reduce the trapping mechanism formation in CZTS nanocrystals in particular reducing sulphur and sulphur vacancy mediated trapping states which may be responsible for the losses in devices.^{58, 148} Defect state effects can result in complex excited state dynamics therefore we first examine CZTSe nanocrystal samples using transient absorption spectroscopy measurements which to our knowledge has not been done before and discuss the findings which will help understand more complex CZTS nanocrystal behaviour examined in the later sections.

Transient absorption measurements were carried out on CZTSe nanocrystal suspensions (Fig. 5.3) along with steady state absorption measurements discussed in the following section. Two distinct PIA features were observed over the visible and near-infrared spectra. The visible PIA feature observed displays gradual relaxation with the spectral band profile retained while it relaxes with two lifetime components of 490 fs and 60 ps (globally fitted exponentials with a calculated average lifetime of approximately 6.4 ps). This suggests a representation of a simple excited state mechanism. We consider the theoretical literature estimates of CZTSe density of states in order to resolve the nature of the feature. The second (conduction) energy band lies 2 eV above the bandgap, which closely matches the energy of the visible PIA transition peak.¹⁵⁸ This leads us to suggest

the visible PIA feature represents the band edge carrier absorption to this band therefore its dynamics directly relate to the CZTSe band edge carrier population.

Figure 5.3. Visible and IR range peak trace normalized transient absorption spectra of CZTSe nanocrystals at various times past above bandgap excitation with 400 nm pump pulses.

We also observe a PIA signature in the near-infrared region which may indicate another band edge carrier transition or such effects as trapped carrier absorption or a presence of plasmonic absorption. The NIR absorption onset is immediate and the relative dynamics match the band edge carrier dynamics as shown in Figure 5.4a well. We note that the global fitting also links the two features suggesting they both represent band edge carrier absorption. This leads us to suggest that no spectroscopic trapping response is observed in CZTSe nanocrystal measurements which would typically appear as spectral profile development and/or features with different dynamics. We also note that no excitation intensity dependent development of kinetics were observed meaning single nanocrystal excitation regime is being monitored (Fig. 5.4b). The plasmonic nature of the near-infrared PIA is also unlikely as the feature relaxes with little spectral development over time (no carrier density dependence), in a similar way to the visible range signature. Although the near-infrared band likely represents band edge carrier absorption, it peaks at around 1.2 eV where no bands for direct interband transitions of either electrons or holes are available from the theoretical band structure estimates.¹⁵⁸ This low energy absorption may be representative of intraband absorption or indirect transitions which may be responsible for the signature as similar energies are available for the estimated indirect energy band transitions.

Figure 5.4. a) Kinetic traces of visible and near-infrared CZTSe PIA peak integrals normalized at 1 ps past excitation with 400 nm pump pulses. b) Normalized kinetic traces of near-infrared CZTSe PIA peak of 7.5 times different excitation fluence measurements.

The analysis of the CZTSe samples reveals a presence of two PIA features in the excited state response which represent band edge carrier absorption. The carriers on average live for 6.4 ps with a minority population of carriers with lifetimes as long as 60 ps. The data suggests no resolvable trapping response in the transient absorption measurements with only the band edge carrier dominated signals which is consistent with the tendency of phase pure CZTSe formation.

5.3.2 Steady state analysis

We carry out a range of steady state absorption measurements on CZTS and CZTSe nanocrystal suspensions in order to help characterize CZTS sample behaviour. Broad spectral signatures with an unexpected long wavelength range absorption band were observed in the long range absorption experiments. The absorption spectra were further analysed by employing integrating sphere absorption measurements which suggested disordered system character with possible plasmonic behaviour.

Long wavelength range steady state absorption measurements were carried out on solution suspended CZTS and CZTSe nanocrystals with UV-Vis-NIR absorption spectrometer. Figure 5.5 shows the obtained absorption spectrum along with the relative baseline profile which accounts for the sharp perturbations in the absorption spectrum of the sample arising from such effects as strong solvent absorption signatures. Bulk CZTS bandgap ranges around 1.4-1.5 eV (~850 nm) which is expected to be similar to the ~12

nm CZTS nanocrystal bandgap as the nanocrystals are significantly above the $\sim 5\text{-}6$ nm Bohr diameter.^{139-140, 159} However, no typical bandgap signatures are observed around the region, instead the region appears to overlap with an onset of an unexpected absorption feature in the long wavelength region. The anomalous absorption feature appears as a broad and well defined band spanning from around 1000 to 2000 nm with a peak at around 1500 nm. The feature is positioned significantly below the expected CZTS bandgap and is likely not a feature of a direct CZTS band transition. Neither does it display typical absorption behaviour of sub-gap state disorder. Similar low energy features are often associated with plasmon absorbance bands. Sub-phases like $\text{Cu}_{1.94}\text{S}$ can form in CZTS materials contributing to sample disorder and have been previously shown to display plasmonic absorption bands with very similar profile and spectral position to the absorption observed here leading us to suggest the presence of the same mechanism.¹⁶⁰ Steady state absorption spectrum of CZTSe nanocrystal suspension stretching to near-infrared wavelengths is also shown in Figure 5.5. We do not observe the broad near-infrared plasmonic absorption bands seen in CZTS nanocrystals, only the sharp NIR features attributed to baseline artefacts. The observation supports the sulphur sub-phase based nature of the plasmonic band observed in CZTS nanocrystals.

Figure 5.5. Long wavelength range steady state absorption spectrum of CZTS nanocrystal suspension plotted against scaled absorption spectrum of CZTSe nanocrystal suspension and relative baseline profile (offset and scaled for clarity).

In order to clarify the bandgap and confirm that the anomalous increase in the steady state absorption at long wavelengths is a real absorption signature we carry out integrating sphere absorption measurements. The black trace in Figure 5.6 represents the obtained

standard absorbance spectrum using a different setup. We observe a similar absorption spectrum with the broad rise in the longest wavelength absorption with little spectral signatures across the rest of the spectrum except a marginal dip which is observed at around 880 nm, the expected bandgap region, however it is likely an experimental artefact given its magnitude and no apparent effects on the adjacent spectral profiles leading us to confirm we do not observe a clear band edge absorption onset in the measured spectrum. Typically there are two main phenomena which can strongly dilute the band edge absorption signatures: disorder and scattering. Integrating sphere measurements account for sample scattering which helps distinguish between the two effects and determine if the long wavelength feature is a real rise in sample absorbance.

The steady state absorption spectrum of CZTS nanocrystal suspensions obtained using an integrating sphere setup is represented by the brown trace in Figure 5.6. The integrating sphere allows for the collection of the probe transmitted through, reflected and scattered by the sample which is contained inside the sphere through multiple diffuse reflections off its walls. The measurement provides an absorption spectrum which is arising from the absorption of the sample alone unlike in the standard free space absorption measurements which display effects like scattering as absorption. Figure 5.6 shows the comparison between the absorption spectra obtained using standard and integrating sphere steady state absorption setups. The differences between the spectra reveal scattering contribution to the absorption magnitude of up to 0.1 OD across the wavelength range measured, however the scattering does not appear to strongly influence the general absorption profile suggesting a prominent sample disorder which obstructs the CZTS bandgap. The finding is in agreement with the CZTS nanocrystal tendency to form a range of sub-phases. Furthermore, the long wavelength range rise in absorption appears to be a real absorption effect since it is present in the integrating sphere measurements as underlined by the grey dashed line (Fig. 5.6).

Figure 5.6. Steady state absorption spectra of CZTS nanocrystal solution suspension measured using standard steady state absorption setup and integrating sphere setup. Dashed grey lines mark the magnitudes of the longest wavelength signatures.

The steady state analysis of CZTS nanocrystals revealed a strong presence of sample disorder common for the material. The disorder obstructed the optical CZTS bandgap and is likely the cause of the observed plasmonic absorption band in the long wavelength regime. The CZTSe nanocrystals did not display the near-infrared plasmon absorption band, however it is still not clear how the excited state features would relate to the plasmon effect. Further time-resolved transient absorption measurements need to be considered in order to help characterize the nature of CZTS nanocrystal properties.

5.3.3 Transient absorption of CZTS nanocrystals

CZTS nanocrystals are expected to display a more prominent trapping behaviour than CZTSe based materials. It is important to understand how do CZTS defects affect the excited state dynamics as they govern the device performance. Transient absorption spectroscopy measurements were carried out on CZTS nanocrystal suspensions probing over UV-visible and near-infrared wavelengths. The obtained TA responses were analysed and the nature of the observed signatures was proposed.

Transient absorption measurement spectral slices of CZTS nanocrystal suspension in chloroform are shown in Figure 5.7. The spectral range extended to UV region is dominated by photoinduced absorption signatures. At 300 fs past the excitation we observe 3 distinct PIA bands: a narrow UV band peaking at 350 nm, a visible range

signature with a peak at 560 nm and a broad NIR photoinduced absorption extending to wavelengths longer than our experimental range with a peak at around 1250 nm. The well-defined UV and visible range peaks correspond to about 3.5 and 2.2 eV energy values respectively. Theoretical electronic band structure calculations in the literature suggest the presence of two CZTS bands lying at ~ 2 and ~ 3 eV above the bandgap in similar CZTS structures which agree with the observation of the two PIA bands in our TA measurements with comparable energy values.^{158, 161-163} We note that weak bleaching is also observed between the two bands in excitation intensity dependent measurements which corresponds well to the high energy band bleach. The 350 and 560 nm TA bands observed share the same dynamics as determined by the global dynamics fitting (discussed later). This leads us to suggest that the two UV-visible range PIA signatures seen in early times past the excitation represent CZTS band transitions from the band edge carrier population which is not initially affected by CZTS disorder states.

Figure 5.7. Visible and IR range peak trace normalized transient absorption spectra of CZTS nanocrystals at various times past above bandgap excitation with 400 nm pump pulses.

Temporal dependence of the CZTS photoinduced band transition features reveals strong spectral development. The two PIA bands decay within 1 ps leaving a longer lived broad PIA response spanning the UV-visible range. Global fitting resolves lifetimes of 220 fs and 25 ps for the double peak and the broad PIA responses respectively with an average lifetime of ~ 8 ps. We note that no excitation intensity dependent kinetics were observed (Fig. 5.8a). Previous study of CZTS single crystals employing photoluminescence and

reflectivity spectroscopy methods found photoexcited carriers rapidly localizing to a broad range of shallow CZTS tail states formed by impurities and defects with time constants between several to a few tens of picoseconds.¹⁶⁴ The UV-visible TA dynamics observed in the colloidal nanocrystals here could be explained with a similar model. Upon photoexcitation the carriers occupy CZTS band edge from which they display well-defined absorption bands to higher lying CZTS energy levels. The well-defined absorption bands disappear as the band edge carriers quickly relax to a wide distribution of sub-states from which broad PIA response arises. The mechanism is in agreement with the prominent system disorder indicated by the steady state absorption measurements and contrasts to CZTSe as expected where the excited state dynamics are dominated by the band edge carriers which retain their absorption profile over the relaxation time of the system without any sub-state induced spectral development.

The observation agrees well with the visible range excited state behaviour seen in CZTSe nanocrystals. We note that the CZTS measurement spectral range extends to UV wavelengths where a PIA band is observed while in the CZTSe measurements the measurements extended to the visible wavelengths due to different experimental setup used. Visible band seen here resembles the 645 nm transition band of CZTSe nanocrystals with a peak shift of about 90 nm or 0.3 eV to higher energies. It likely represents the redistribution of the band energies with sulphur replacement which increases the bandgap energy by ~0.4-0.5 eV.¹⁶⁵⁻¹⁶⁶ While the CZTS spectra rapidly develops due charge transfer to sub-states, the less defective CZTSe system retains the band edge carrier absorption band over the system relaxation time. In addition, the kinetics observed in CZTSe system differ from the CZTS nanocrystals with around 3-4 times relatively more significant long lifetime component contribution to the dynamics in the latter which is likely a trapping contribution.

Figure 5.8. a) Normalized kinetic traces of visible CZTS PIA peak of 5 times different excitation fluence measurements (the low fluence measurement was limited to 30 ps temporal range). b) Kinetic traces of visible and near-infrared CZTS PIA peak integrals normalized at peak and 1 ps past excitation with 400 nm pump pulses.

In contrast to the UV-visible range, the near-infrared CZTS photoinduced absorption feature does not display the same spectral evolution. In fact, the dynamics of the near-infrared feature are significantly shorter than the higher energy features as shown in Figure 5.8b. The near-infrared signature relaxes on the short time scale which corresponds to the two UV-visible range CZTS band transition peak dynamics (as determined by the global fitting), without the significant subsequent spectral profile development. The link suggests the phenomenon represented in the NIR is only active before the carriers are trapped. Although the feature may be related to the signature seen in CZTSe near-infrared range, it also displays different spectral profile and temporal dependence along with different spectral position relation to the visible transition bands. Therefore its nature and relation to CZTSe near-infrared absorption is not clear and needs to be further analysed.

5.3.4 Near-infrared PIA analysis

We analyse the influence of nanocrystal environment on the near-infrared photoinduced absorption signatures in order to determine any plasmonic effect influence. TA responses are compared between the nanocrystals suspended in different solutions and nanocrystals deposited on films.

The steady state absorption measurements revealed the presence of plasmon absorption band peaking at 1500 nm in CZTS nanocrystals. Upon photoexcitation the bleaching of the plasmonic band is expected, however we observed a photoinduced absorption signature with a peak at around 1250 nm and a complex non-Gaussian profile in the TA measurements. This behaviour could be influenced by multiple overlapping signatures of 1500 nm plasmon absorption band bleaching seen as the lower PIA magnitude at longer wavelengths, plasmon-driven absorption permeated by the photoinduced carriers (as described in more detail in Chapter 3) and intrinsic state absorption.

Localized surface plasmon resonances can have a strong dependence on the nanocrystal surface properties and a modulation of the plasmonic effect may be achieved by changing the surrounding nanocrystal medium. Figure 5.9 shows the spectral TA comparison between nanocrystals suspended in chloroform and dichloromethane. We observe a signature peak shift of up to ~100 nm and a weak spectral shape development. The long wavelength PIA response flattens in the dichloromethane suspension and tends towards positive values in the short wavelength range. Although some differences are present between the two different solvent suspensions suggesting the plasmonic influence in the near-infrared region, further analysis is needed to confirm the feature dependence on the medium.

Figure 5.9. Near-infrared range normalized PIA feature comparison between CZTS nanocrystals suspended in chloroform and dichloromethane excited with 532 nm pump pulses a) 300 fs past excitation, b) 1 ps past excitation.

Nanocrystals were deposited on quartz films and their TA response was compared to the TA measurements of nanocrystal suspensions in chloroform (Fig. 5.10). We observe a

strong spectral response development with apparent PIA feature shift to longer wavelengths in films and an emergence of ground state bleaching at wavelengths close to the bandgap region. The expected CZTS bandgap lies in the 1.4-1.5 eV range and the bleaching feature is observed at around 1.3 eV (950 nm) suggesting the band edge bleach with either lower than expected bandgap value, strong feature overlap or some influence of bleaching from tailing states. The strong TA spectral differences observed between the films and solutions suggest the presence of plasmonic effects in the near-infrared spectrum. The isolated nanostructures are expected to display stronger plasmonic effects than the films with bulk-like outer nanocrystal environment, which can result in different overlap with TA features such as positive band edge bleaching. We note that the significant spectral differences were only present in the near-infrared range while the UV-vis range was mostly unaffected by the varying nanocrystal environment.

Figure 5.10. Near-infrared range normalized PIA feature comparison between CZTS nanocrystals suspended in chloroform and deposited on films excited with excitation density matched 400 nm pump pulses a) 300 fs past excitation, b) 1 ps past excitation.

The varying nanocrystal medium analysis suggests that the near-infrared excited state region of CZTS nanocrystals may be affected by plasmonic effects indicated in the steady state absorption analysis. In addition, the temporal spectral development of the near-infrared PIA feature which displays blue shifting (Fig. 5.7) not seen in the non-plasmonic CZTSe further supports the attribution. The near-infrared TA signals show signs of possible influence of band edge bleaching, along with plasmonic band bleaching and potential absorption. We note that the region may also contribute from the similar indirect transition or intraband absorption effects seen in CZTSe. The near-infrared TA response

relates directly only to the untrapped carriers, however the overlapping features of the CZTS measurements complicate the exact resolution of the nature of the spectral signatures in the region.

5.3.5 Model

In this section we describe a simple model explaining the observed UV-visible transient absorption features in CZTS nanocrystals and their evolution with defect state transitions.

Figure 5.11 shows the schematic of CZTS energy level and transition diagram. The samples are excited with above bandgap excitation pulses and before the carriers relax to a distribution of below bandgap defect states, CZTS band transition features are observed. The UV and visible PIA bands seen in the early time TA spectra arise from the band edge population of carriers absorbing to two higher lying energy levels. The overlapping UV-Visible regime and bandgap region bleaching signatures arise from the transitions denoted by the red dashed arrows. After the carriers are transferred to the defect states, the broad photoinduced absorption represented by the blue transparent arrows dominates the spectra due to the wide distribution of the absorbing states. We note that some trap states may be inaccessible by TA spectroscopy which can result in carrier lifetime differences from other literature estimates for example longer lifetimes estimated from time-resolved measurements of photoluminescence arising from a particular defect state emission.¹⁶⁷⁻¹⁶⁸ Here we find that upon photoexcitation the CZTS band edge carriers transfer to the trap states in under 1 ps and remain in defect states with lifetimes on the order of a few tens of picoseconds which shows how CZTS nanocrystal device performance can be degraded if the defect states are not efficiently passivated or their formation is suppressed. The system contrasts to CZTSe excited state dynamics as expected, in which the carriers are not transferred to trap states but remain at the band edge until they recombine. We also note that although the NIR region can display complex behaviour it is related only to the carriers that are not trapped in both the CZTS and CZTSe samples meaning it could be used as a system probe.

Figure 5.11. Energy level schematic for the optical transitions observed in CZTS nanocrystals, where the arrows denote excitation, carrier and TA transitions.

5.4 Conclusion

We investigated the steady state properties and excited state dynamics of CZTS nanocrystals by employing broadband transient absorption spectroscopy along with integrating sphere and infrared steady state absorption measurements. The nanocrystals were found to display pronounced disorder and defect-induced plasmonic absorption band in the steady state measurements. The defects strongly influenced the excited state behaviour with initial population of CZTS band edge charges rapidly relaxing to a broad defect distribution. PIA signatures were observed in the near-infrared regime and were found to be influenced by plasmonic effects via analysis of their behaviour in relation to the nanocrystal environment. Before carrier relaxation to the defect states, distinct UV-visible absorption bands were observed and attributed to CZTS band transitions. The CZTSe nanocrystal properties were also examined in relation to CZTS and reduced defect influence along with prolonged lifetimes and spectral feature shifts were observed. We did not observe plasmon influence in CZTSe nanocrystals which supported the attribution of their sulphur governed sub-state nature. Finally, we proposed a band model which

explained the observed UV-visible transient absorption response of the CZTS nanocrystals with prominent trapping influence which was not observed in CZTSe nanocrystal measurements.

Chapter 6

Evolution of quantum confinement in metal halide perovskite nanocrystals

Parts of this chapter have been published in the following article:

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6.1 Introduction

Metal halide perovskites have emerged in the past five years as some of the most promising materials for photovoltaic applications.¹⁶⁹⁻¹⁷¹ The properties for which perovskites were initially synthesized in the late 90s have come back into focus recently, namely, their ability to exhibit bright, stable light emission with wavelength tunability, ideal for such photo- and electroluminescence applications as light emitting diodes and electrically pumped lasers.^{18, 172} After the recent intensive research efforts on the material class, perovskites were also found to display great potential in other applications like NOR flash memory and solar cells.^{18, 173-174} The general formula of perovskites is ABX₃ with the structure presented in Figure 6.1, where A is methyl ammonium or Cs, B is Pb/Sn and X is I/Br or a coexistence of several halogens, variation of which allows for relatively simple optical and electrical property tunability.¹⁷⁵ In order to improve the perovskite material viability for the device applications their optical and electrical properties can be fine tuned with one of the most broadly researched approaches of exchanging and mixing the halide components. It allows for gradual tuning of material parameters, however such problems as ion migration and material instability emerge which are detrimental to the

device performance.¹⁷⁶⁻¹⁷⁷ In addition to the thin film and bulk perovskites, nanosized perovskite materials have also shown great promise with their quantum confinement tunable properties ideal for such applications as electrically pumped lasers.^{57, 178} Recently, Protesescu et al. reported a synthetic route to composition and size-tuned perovskite nanocrystals (NCs) made from CsPbX_3 , ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).⁵⁷ This material family retains the lead-halide motif at the heart of the semiconducting band structure of organometal halide perovskites, but with the organic cation replaced by cesium. While efforts have been made to synthesize CH_3NH_3 based NCs, they have displayed poor stability and difficult synthesis control unlike the cesium based nanocrystals.^{57, 179} CsPbBr_3 particles with edge lengths ranging from ~ 4 – 12 nm were synthesized with tunable bandgaps of up to ~ 0.4 eV ($\sim 15\%$) higher than the bulk which should put the smallest available particles in the range of the strong quantum confinement regime.

Figure 6.1. Simplified perovskite lattice structure schematic.

Quantum confinement is a phenomenon that affects optical and electronic properties of the material which is subject to physical size constraints on the order of nanometers. It arises due to constraints on the carrier wave functions, perturbing the bulk material energy levels. The phenomenon has been widely examined because of the appeal of fine tuning material characteristics and exploited in a range of colloidal inorganic quantum dots over the past 20 years.¹⁸⁰ One of the best studied quantum dot materials is CdSe, its bandgap tunability throughout the visible spectrum was exploited for such applications as LEDs, PVs, lasers, biological labelling, optical filters, and sensors.¹⁸¹⁻¹⁸⁷ Extensive research done on CdSe resulted in quantum dots that can be synthesized in relatively small sizes with respect to their Bohr diameters, which allows to achieve material bandgaps larger by ~ 2 eV than that of the bulk material.

A material's Bohr diameter is the diameter of the exciton quasiparticle unique to the material, which is an important parameter that helps define the quantum confinement regime estimates in relation to the nanocrystal size. Figure 6.2 shows the quantum confinement region definition schematic. NCs with dimensions larger than the Bohr diameter are considered to be in the weak quantum confinement regime, while particles smaller than the Bohr diameter belong to the strong quantum confinement regime. Sometimes an intermediate quantum confinement regime is also defined around the Bohr diameter region if the effective masses between electrons and holes are significantly different.²⁶ We note that particles that are not significantly larger than their crystal lattice constant must be treated as clusters because they cannot be assumed to be periodic.

Figure 6.2. Schematic of quantum confinement regions and wavefunctions in relation to Bohr diameter.

Given that bulk samples of related organometal halide perovskites are characterized by charge carriers filling a continuum of states, and that relatively modest optical absorption and emission shifts are seen in the CsPbX_3 NCs, it remains to be seen how quantum confinement manifests in the photophysics of perovskite NCs as a function of size.^{57, 188-189} Do discrete excitonic and biexcitonic states emerge producing strong changes in excited state dynamics, or does confinement in perovskite NCs merely induce a small perturbation of the free carrier photophysics established for the bulk materials?

In this study, we use transient absorption spectroscopy along with steady state spectroscopy for extensive analysis of bulk CsPbBr_3 and a size-tuned series of CsPbBr_3 NC (spanning the weak to strong quantum confinement regimes) properties in relation to the quantum confinement effects. We consider quantum confinement influence in the steady state absorption and photoluminescence spectra and compare the Tauc plot

extracted bandgaps to the theoretical bandgap estimates based on the effective mass approximation. We examine the excited state behaviour evolution across the samples with varying dimensions in order to resolve the quantum confinement influence on such effects as state-filling dynamics, bandgap renormalization, carrier cooling, and hot-phonon bottleneck. We also consider perovskite cation influence to the charge carrier dynamics, which has been previously suggested to heavily affect the excited states due to such effects as charge carrier screening speculated to arise from methylammonium cation dipole.⁴³

6.2 Experimental

6.2.1 Samples

CsPbBr₃ nanocrystal synthesis was carried out using procedures adapted from those reported by Protesescu *et al.*⁵⁷ Three separate monodisperse populations of cubic nanoparticles of CsPbBr₃ were synthesized with average nanocube edge size of 8.6, 7.3 and 4.1 nanometres with the size tuning achieved through reaction time and temperature control. The average nanocrystal sizes were determined from high resolution electron micrographs (Fig. 6.3). The micrographs of the NCs show them to be primarily composed of monodisperse single crystals with fast-Fourier transform and XRD patterns matching the cubic phase of CsPbBr₃ (Fig. 6.4). Further synthesis and sample characterization details are provided in the literature.¹⁹⁰ The synthesis and size characterization were carried out by Parth Vashishtha under the supervision of Jonathan E. Halpert.

Figure 6.3. a,d,e) TEM images of different sized CsPbBr₃ NCs, including b) imaging of lattice planes of CsPbBr₃ nanocrystal and c) a fast Fourier transform (FFT) image from b) showing the crystallinity of the nanocrystals. Courtesy of Parth Vashishtha.

Figure 6.4 a) XRD Spectra of CsPbBr₃ Nanocrystals, b) XRD Spectra of CsPbBr₃ Microcrystalline Film. Standard CsPbBr₃, PbBr₂, and CsBr graphs were taken from Panalytical X'Pert Highscore Plus with the respective reference codes: 04-017-4526, 01-085-1089, and 00-004-0586. Reprinted with permission from¹⁹⁰. Copyright 2017 American Chemical Society.

6.2.2 Steady state spectroscopy

Steady state absorption spectra were taken with a Varian Cary 50 Bio UV-Visible Spectrophotometer. The absorption spectra of quartz substrate and hexane in 1 mm cuvette were taken and were subtracted from the absorption spectra obtained measuring CsPbBr₃ bulk film deposited on quartz substrate and NC suspensions in hexane in 1 mm cuvette respectively.

Steady state photoluminescence measurements of bulk films and NC solution suspensions in polished 10 mm quartz cuvette were carried out using Horiba Fluorolog-3 Spectrofluorometer. The nanocrystal suspension PL was taken by Parth Vashishtha. The samples were excited with 400 nm excitation beam and the emission was monitored with a 420 nm longpass filter blocking the excitation wavelength. The measurements were compared against blank emission measurement runs of quartz substrate and hexane solvent and no artefacts influencing sample emission spectra were observed.

6.2.3 Transient absorption spectroscopy

Transient absorption spectroscopy measurements were carried out in a similar transient absorption setup described in more detail in Chapter 2. The 400 nm excitation beam was used to excite linearly translated NC solution suspension samples in 1 mm quartz cuvettes sealed in inert N₂ environment. The bulk films were measured in a mounted spectroscopic vacuum chamber run under dynamic vacuum. Approximately 6000 shots were averaged at each measurement time point and repeated for at least of four scans.

6.3 Results and Discussion

6.3.1 Quantum confinement

Currently metal halide perovskite nanocrystals can be synthesised in sizes close to the Bohr diameter, while CdSe nanocrystals can be typically synthesized with dimensions below their Bohr diameter which put them well in the strong quantum confinement regime and result in photophysics dominated by discrete hydrogen-like excitonic states.

These states contribute to bandgap shifts of up to ~115% with respect to the bulk value and result in phenomena like well-defined excitonic peaks in the ensemble absorption spectra of monodisperse samples, molecular-like intraband and multi-excitonic transitions, including strong photobleaching effects in the latter case, strong polarization effects, faster radiative recombination lifetimes, and increased Auger recombination than is observed in bulk materials.¹⁹⁰ Inorganic metal halide perovskite CsPbBr₃ nanocrystals have been recently synthesized by Protesescu *et al.* although currently the material cannot form monodisperse NCs in sizes as small as CdSe quantum dots with respect to the Bohr diameter.⁵⁷ The smallest monodisperse CsPbBr₃ NCs used in this study still fall under the predicted strong quantum confinement regime, with sizes modestly smaller than the CsPbBr₃ Bohr diameter of ~7 nm.¹⁹¹ Figure 6.5 shows a representation of one of the ranges of CsPbBr₃ NCs studied here with respect to their bulk Bohr diameters. The large NCs with average edge length of 8.6 nm (NC-8.6) are predicted to be in the weak quantum confinement regime, where the confinement effects are not expected to produce discrete energy states but rather redistribute the bulk density of states (DOS) into semidiscretized band of states, an intermediate between single band and molecular-like states.^{190, 192} The 7.3 nm edge length of the NC-7.3 sample closely matches the 7 nm Bohr diameter putting the NCs between the strong and weak quantum confinement regimes, while the smallest 4.1 nm edge length NC-4.1 sample particles display most of their dimensions below the Bohr diameter with only their longest, the diagonal length, extending towards the Bohr diameter. It is not clear, however, if the strong quantum confinement behaviour seen in strongly confined CdSe NCs will still manifest in the smallest CsPbBr₃ NCs predicted to be in the strong quantum confinement regime. We note that the degree of quantum confinement can also vary along different dimensions of anisotropically structured particles allowing for the existence of 1-D and 2-D excitonic materials, although NC-4.1 samples mostly fall in the strong quantum confinement regime estimate.¹⁹⁰

Figure 6.5. Relative size schematic comparison between Bohr diameter and 3 different size NC samples used in this study.

6.3.2 Steady state analysis

Steady state spectroscopy measurements can give an insight into material's properties and help characterize quantum confinement effects. We carry out steady state absorption and photoluminescence (PL) measurements on the CsPbBr₃ bulk films and three different size nanocrystal solution suspensions (NC-8.6, NC-7.3 and NC-4.1). We observe a pronounced evolution of the steady state responses with decreasing dimensions of the material from bulk to the smallest 4.1 nm NCs (Fig. 6.6). The photoluminescence peaks gradually blue-shift with decreasing sample size from 522 to 495 nm. The shifting emission is in agreement with the blue shifting bandgap estimates obtained from the Tauc plots given in Figure 6.7. The estimated bulk film bandgap of 2.37 eV increases to 2.5 eV (Table 6.1) in the smallest NCs due to quantum confinement which is a shift of about 6% of the bulk value, small change in comparison to the modulation energies obtainable in more developed quantum dot systems.¹⁹³⁻¹⁹⁴

Figure 6.6. Steady state absorption and photoluminescence spectra of four CsPbBr₃ samples showing emission peaks at 522, 516, 512 and 495 nm for Bulk, NC-8.6, NC-7.3 and NC-4.1 samples respectively.

Figure 6.7. Direct bandgap Tauc plots of the four CsPbBr₃ samples with the linear regime extrapolated to x-axis.

Table 6.1. NC size estimates, steady state measurement data and derived values.

	Film	NC-8.6	NC-7.3	NC-4.1
Edge length (nm)	-	$8.59 \pm 1.0\%$	$7.32 \pm 0.74\%$	$4.14 \pm 0.57\%$
PL peak (nm)	522	516	512	495
PL FWHM (nm)	20	22	21	32
BG (eV)	2.37	2.38	2.40	2.50
BG/BG_{bulk}	1.00	1.00	1.01	1.06

While the material bandgaps appear to correlate with the blue shifting emission of the samples in agreement with quantum confinement the band edge absorption features which can give better insight into sample behavior are difficult to resolve. We calculate the second order derivative of steady state sample absorption spectra which allows to quantify the positions of the lowest energy absorbing transitions more accurately and plot them against the emission peaks as shown in Figure 6.8. By taking the difference between the absorption peak and the first minima of the absorption derivative we define the Stokes shift (Δ_s). Bulk films display a Stokes shift of about 68 meV, which is larger than the shifts observed in the largest NCs, an unexpected finding given larger disorder expected in NCs. However, as NC sizes decrease the Stokes shift appears to increase reaching 88 meV in the smallest NC-4.1 sample. Stokes shifts are normally derived from the steady state absorption measurements in the literature and in this case may indicate an increasing disorder in smaller NCs with increasing surface to volume ratio. While the large Stokes shift value observed in bulk films does not agree with this explanation it may relate to the thermalization effects of the material.

Figure 6.8. Second order derivative of steady state absorption spectra of a set of CsPbBr₃ perovskite samples plotted against the corresponding PL. Dotted red lines indicate the peak positions of first derivative minima and PL peaks. Top right corner is the value of the Stokes shift.

Spectroscopic excited state analysis related to the steady state PL may offer a more accurate way to analyse Stokes shift due to more clearly defined lowest band transitions. We carry out the derivative Stokes shift analysis on the TA data, analogous to the steady state absorption method, with the long time GSB feature indicating the lowest transition energy. Figure 6.9 shows the second order derivative of 10 ps transient absorption spectra measured at low fluences over the range of CsPbBr₃ samples plotted against the respective PL emission data. We obtain lower Stokes shift estimates via TA due to reduced scattering influence and more clearly defined lowest energy transition, rather than a convolution of transitions monitored by standard steady state absorption technique. Closer matching Stokes shift values are extracted between the bulk and two largest NC samples, while smallest NCs display relatively large Stokes shift potentially indicating stronger surface or thermalization effects. We note that the transitions, especially in the smallest NCs, where the medium does not consist of continuous perovskite material, may

also be influenced by refractive index changes discussed in Chapter 8 and photoinduced refractive index change could be used to define the band transitions more accurately and applied in a wide variety of systems.

Figure 6.9. Second order derivative of 10 ps TA spectra of a set of CsPbBr₃ perovskite samples plotted against the corresponding PL. Dotted red lines indicate the peak positions of first derivative minima and PL peaks. Top right corner is the value of the Stokes shift.

Steady state absorption profiles provide an additional insight into CsPbBr₃ sample properties. We observe a strong band edge absorption peak in the bulk film steady state absorption spectra which diminishes in NC spectra, indicating lower exciton influence in the NCs in comparison to the bulk material. The effect counters the expected excitonic behaviour in NCs, however it was also observed and analysed in other literature and was attributed to diminishing exciton binding energy due to the influence of surface effects, which will be discussed in more detail in Chapter 8.¹⁹⁵⁻¹⁹⁶ We also observe new, higher energy, absorption peaks developing in the smallest 4.1 nm edge length NCs as the NC bandgap energy increases to 2.5 eV. These new signatures may be a manifestation of the

quantum confinement induced energy level splitting, which relates to the confinement regimes defined by the nanocrystal dimensions relative to the exciton Bohr diameter.²⁶

We use effective mass approximation to model the theoretical bandgap values (Eq. 6.1) and compare them to the experimental estimates.

$$\Delta E = \frac{\hbar^2 \pi^2}{2m^* r^2} \quad (6.1)$$

Where ΔE is the bandgap modulation, m^* is the exciton reduced mass and r is the particle radius.⁵⁷ Figure 6.10 shows the experimental and theoretical bandgaps plotted against the predicted quantum confinement regimes.⁵⁷ The experimentally obtained bandgaps are in a good agreement with the theoretical estimates with a small deviation in the largest NCs possibly due to either size or bandgap estimate inaccuracy. Both the experimental and theoretical bandgap estimates of the NC-4.1 sample still fall under strong quantum confinement regime estimate which supports the formation of discrete states suggested by the steady state absorption spectral profile evolution. While the NC-8.6 is in the weak and NC-7.1 sample stands around the region of intermediate quantum confinement regime.⁵⁷ We note that although excitonic influence may affect the accuracy of the estimates, the deviation is assumed to be small.

Figure 6.10. Experimental versus theoretical (effective mass approximation) size dependence of the bandgap energy with quantum confinement regimes noted in relation to the Bohr diameter.

We examine bulk CsPbBr_3 films and a range of different size NC samples using steady state spectroscopy techniques and observe a gradual increase in bandgap absorption and emission energies with decreasing material dimensions. An indication of discrete energy

level development is observed in the smallest 4.1 nm edge length NCs which agrees with the strong quantum confinement regime predicted for this sample. We also examine the Stokes shifts and find limited steady state measurement based estimate accuracy even with differential spectroscopy analysis technique used, however transient absorption spectroscopy appears to provide a more accurate picture of the analysed system due to well defined state transition signatures.

6.3.3 Assignment of TA features

The photoexcited state behaviour of the CsPbBr₃ bulk films and a range of different size NC samples were studied via transient absorption measurements. Bulk films displayed similar TA effects to the response seen in CH₃NH₃PbI₃ thin films, while NCs departed the bulk-like mechanism with decreasing dimensions.

We compare the spectral CsPbBr₃ bulk film TA response to the effects displayed in CH₃NH₃PbI₃ perovskites. Low fluence measurement spectral series of different times past the excitation are given in Figure 6.11. We observe three distinct spectral features displayed by the CsPbBr₃ bulk films also seen in thin films of other lead halide perovskites such as CH₃NH₃PbI₃ leading us to suggest the same spectra assignment here. A dominant long lived ground state bleaching feature peaking at around 516 nm, close to the bandgap energy of the sample, reflects the bleaching of band-to-band transitions by photocarriers filling states at the edges of valence and conduction bands.^{18, 188, 197} The monomodal shape of the CsPbBr₃ film GSB signature is characteristic of the Burstein-Moss effect observed in the polycrystalline CH₃NH₃PbI₃ films, where the effective density of electron and hole states follow parabolic semiconductor bands according to the Equation 6.2.

$$N_{c,v} = 2 \left(\frac{m_{e,h} k_b T}{2\pi\hbar} \right)^{\frac{3}{2}} \quad (6.2)$$

Where N_c and N_v are the effective density of states in the valence and conduction bands respectively, m_e and m_h are the effective masses of electrons and holes respectively, k_b is the Boltzmann constant and T is the temperature. The short-lived sub-bandgap feature, once thought to originate from bound excitons, instead most likely derives from a

bandgap renormalization leading to a momentary increase in unoccupied states at energies slightly below the ground state bandgap.^{18, 197-199} These states are quickly reoccupied by relaxation of hot carriers, observed via the high energy broadening of the bleaching feature at early times.¹⁸ Finally, the broad negative differential transmission feature above the bandgap is likely to correspond to photoinduced reflection as shown in $\text{CH}_3\text{NH}_3\text{PbI}_3$ film analysis in Chapter 7.

Figure 6.11. Normalized transient absorption spectra of four CsPbBr_3 samples measured at various times after above bandgap photoexcitation with low fluence 100 fs pulses centred at 400 nm.

The largest NCs display similar TA spectra to the bulk films while the smaller NCs show a development of more complex features. We observe the high energy PIA feature, also seen in the bulk films, in the NC samples which likely corresponds to increased scattering in the NC suspensions from the same photorefractive effect discussed in more detail in Chapters 7 and 8.¹⁸ In general the TA spectra of the NC-8.6 sample (Fig. 6.11b) closely mirrors the typical bulk perovskite behavior described in the previous paragraph, suggesting that the weak quantum confinement has little effect on the bulk band-filling effect. While smaller NC samples exhibit several similarities with the bulk and largest NC-8.6 sample spectral profiles, they exhibit some pronounced differences that reflect

the quantum confinement influence. Each spectral series in Figure 6.11 is dominated by the GSB feature, but as expected from the linear absorption spectra (Fig. 6.6), the GSB peak blue-shifts with decreasing NC size. The second obvious trend is that the GSB feature develops a multimodal structure which is most pronounced for the smallest (NC-4.1) particles, but is also seen emerging for the NC-7.3 particles that are near the strong quantum confinement regime. The evolution of GSB structure in the strong confinement regime will later be explored in more detail.

Finally, each of the TA spectra include the signature subgap PIA peak at early times from bandgap renormalization. This peak has previously been described as arising from exciton–exciton interaction, where the presence of an exciton reduces the energy of subsequent exciton absorption.^{18, 200} While conceptually similar to bandgap renormalization, we keep the bandgap renormalization description because the peak is present in bulk films and, like in organometal halide perovskites, it rapidly disappears on the subpicosecond time scale of carrier cooling.^{18, 82} By comparing the energy of the bandgap renormalization PIA peak with the main GSB position, we are able to quantify the bandgap renormalization energy as a function of NC size. As shown in Table 6.2, we find that the bandgap renormalization energy increases with decreasing sample size from 0.048 eV in the bulk sample to as high as 0.115 eV in the NC-4.1 sample, a signature of quantum confinement.²⁰¹⁻²⁰² The bandgap renormalization enhancement reveals potentially stronger excitonic behavior of smaller NCs and may be due to a combination of increased Coulomb interactions with decreasing particle size, easier crystal lattice deformation, or reduced screening from ionic nuclei effect in smaller NCs.^{26, 202-203}

Table 6.2. Low fluence measurement values of bandgap renormalization and short time cooling monoexponential lifetimes.

	Film	NC-8.6	NC-7.3	NC-4.1
BGR (eV)	0.048	0.068	0.070	0.115
τ_{cool} (fs)	651 ± 97	319 ± 54	325 ± 31	363 ± 20

6.3.4 TA bleach peaks and the focused density of states

Some of the new TA bleach peaks of the NC-4.1 sample observed over the 430–480 nm region (Fig. 6.11d) correspond to new peaks emerging in the linear absorption spectrum (Fig. 6.6). However, it is not immediately clear if the 450 nm TA peak corresponds to the linear absorption profile. We take the second order derivative of the linear absorption spectrum which allows for much clearer discrimination of bands, with the derivative minima clearly representing the TA peak positions. It is clear from Figure 6.12 that all of the linear absorption band positions determined through the second order derivative correspond precisely to the GSB peaks observed in the TA spectrum, with a minor energy difference seen in the lowest energy peak possibly due to broader linear absorption edge.

Figure 6.12. TA spectrum of NC-4.1 sample at low excitation fluence plotted together with the second order derivative of the corresponding UV–visible absorption spectrum with the grey dotted lines representing the positions of the energy levels predicted in the steady state measurement.

Figure 6.11c also reveals a weak shoulder on the high-energy side of the NC-7.3 GSB peak, which is barely perceptible in the linear absorption spectrum. The reason that TA spectroscopy resolves the emergence of new GSB peaks more clearly than linear spectroscopy is that TA spectroscopy is a differential technique that only shows transitions involving a small population of photocarriers near the band edge, rather a convolution of the full range of vertical band-to-band transitions.

In the TA spectra shown in Figure 6.11c and d, the presence of bleaching peaks well above the band edge in the NC-7.3 and particularly NC-4.1 samples is associated with a focusing of the DOS due to quantum confinement. The multiple distinct GSB peaks

observed for NC-4.1 in Figure 6.11d indicate emergence of molecular-like states instead of continuous bands, as predicted from the NC dimensions being smaller than the Bohr diameter.¹⁹² The lack of distinct higher lying transitions in the largest particles confirms our expectation that the NC-8.6 sample does not experience strong quantum confinement effects, but closely resembles the TA spectra of the bulk material. The quantum confinement induced state focusing effects in the 8.6 nm and 4.1 nm CsPbBr₃ NCs studied here are depicted in Figure 6.13.

Figure 6.13. Transient absorption spectral traces of large (NC-8.6) and small (NC-4.1) NC samples and corresponding schematic of molecular energy state development from continuous bulk-like bands.

6.3.5 TA relaxation dynamics

The time series of TA spectra recorded at low excitation density can be used to resolve relaxation dynamics of excitations in the CsPbBr₃ samples. In all cases, relative bleaching intensity is transferred from higher energy toward the lower energy band edge feature over time. For the bulk film and largest NC-8.6 sample, the spectral relaxation is resolved as a simple spectral narrowing toward the band edge. This behavior mirrors bulk organometal halide samples, for which the spectral relaxation is related to the Boltzmann distribution of carriers cooling in an approximately constant DOS (Eq. 6.3).¹⁸ This suggests similar cooling mechanisms present and fitting the high energy GSB shoulder of NC-8.6 sample to the hot carrier model produces carrier temperatures as high as 570

K in the low fluence and 2400 K in the high fluence measurements. However, the presence of photorefractive effect contribution in CsPbBr₃ bulk film and NC-8.6 sample means that the temperature magnitudes obtained from the direct application of Boltzmann model to the $\Delta T/T$ spectra will be perturbed as described in more detail in Chapter 7. Moreover, the presence of additional bleaching peaks in the NC-7.3 and NC-4.1 samples means that the simple Boltzmann model cannot be used to parametrize their spectral shapes directly. However, if carrier cooling was still bulk-like in the samples measured, the statistical occupation of states would still mean that TA bleaching spectra recorded during cooling were linked via a Boltzmann function superimposed on their nonuniform DOS. The effect of nonuniform DOS on bleaching spectral shapes can be cancelled out by taking ratios of spectra at different times to reveal the underlying Boltzmann contribution to the spectral shapes. Figure 6.14 (left panel) shows the ratio of pairs of TA spectra for each of the bulk, NC-8.6, NC-7.3, and NC-4.1 samples. These TA ratios for bulk and NC-8.6 samples fit well to the Boltzmann distribution as expected, and the NC-7.3 sample also deviates minimally from the Boltzmann distribution (Fig. 6.14a–c). In contrast, only the smallest NCs are not well described by a Boltzmann function, with distinct peaks remaining in the spectral ratio in Figure 6.14d. The observed deviation from bulk-like cooling dynamics for only the strongly confined NC-4.1 sample points to the influence of discrete state-to-state transitions rather than a continuous band relaxation.

$$\Delta T/T \propto e^{\frac{E_g - E}{k_b T_c}} \quad (6.3)$$

In order to analyse the temporal hot carrier dynamics, we extract relative carrier cooling kinetics from the spectral relaxation of the samples based on the time-dependence of TA intensity ratios. Carrier cooling dynamics were equated to the spectral evolution of the high energy shoulder of band edge GSB as this perovskite TA feature has been previously shown to originate from hot carriers by Price *et al.*¹⁸ The TA spectra at each time point measured was normalized to the band edge bleach peak and temporal kinetics were extracted as the integral over the high energy spectral evolution region for each of the samples. We note that the relative cooling dynamics profile extracted via this method is the same as the Boltzmann fitting extracted carrier cooling kinetics profiles in bulk samples and is not affected by the photorefractive effect described in more detail in Chapter 7. The results of this analysis are shown in the right panel of Figure 6.14. The

bulk film exhibits rapid carrier cooling on a sub-ps time scale, similar to previously studied organometal halide perovskite films.¹⁸ The nanocrystal samples also exhibit sub-ps carrier cooling, with lifetimes about twice as short as that of the bulk material (see Table 6.2). The parametrization of spectral relaxation suggests that the carrier cooling mechanism in large 8.6 nm NCs is similar to that of the bulk material while the smallest NCs depart the bulk-like cooling due to discrete state-to-state carrier transitions. In spite of a different cooling mechanisms observed, the hot carrier cooling time scale of the smallest NCs is similar to the largest NCs with only a marginal indication of prolonged hot carrier lifetimes with decreasing NC size at the low excitation densities used here ($\ll 1$ exc./NC), although some thermalization differences may occur within the 200 fs temporal response of our experiment.

Figure 6.14. Left column: ratio of normalized 400 fs and 1 ps spectral slices with corresponding best Boltzmann profile fits (dashed line). Energy scale offset for clarity by 0.19, 0.055, 0.04 eV for film, NC-8.6, and NC-7.3 samples, respectively. Right column: carrier cooling dynamics extracted from spectral evolution of the same data on the early picosecond time scale.

6.3.6 Excitation density estimates

Sample excitation density is a significant parameter in pump-probe spectroscopy, which governs the monitored photoexcited carrier dynamics, especially affecting confined systems where a few excitations per particle could change the nature of available states and relaxation pathways. It is therefore important to determine the average number of excitations per NC present in a system examined via TA measurements.

We estimate the excitation densities in NCs experimentally considering individual sample particle concentration and their absorption cross section. Particle concentration was calculated considering the Equation 6.4.

$$c_N = c * N_A \quad (6.4)$$

Where N_A is the Avogadro constant and sample molar concentration is defined in Equation 6.5.

$$c = \frac{n}{V} \quad (6.5)$$

Where V is the volume of the sample and sample moles were obtained from Equation 6.6.

$$n = \frac{N}{N_A} \quad (6.6)$$

The particle number in sample N was calculated from Equation 6.7.

$$N = \frac{m}{m_p} \quad (6.7)$$

Where m is the mass of sample and m_p is the particle mass defined in Equation 6.8.

$$m_p = \frac{c_M}{m_M} \quad (6.8)$$

Where m_M is the mass per molecule obtained considering the atomic masses of the Cs, Pb, and three Br atoms in the CsPbBr_3 perovskite molecule and c_M is the molecule count per particle obtained from Equation 6.9.

$$C_M = \frac{V_{NC}}{V_{molecule}} \quad (6.9)$$

Where nanocrystal volume V_{NC} was obtained from the TEM estimates of the average nanocrystal edge length and molecule volume $V_{molecule}$ was calculated from the literature value of the CsPbBr_3 lattice constant of 5.874 Å.²⁰⁴ The samples were weighted by Parth Vashishtha. The obtained particle concentration was then used in the absorption cross section based estimates of the excitation densities.

We determine the NC sample frequency dependent absorption cross sections experimentally using Equation 6.10.²⁰⁵

$$\sigma_a(\omega) = \frac{2.303(OD)}{c_N l} \quad (6.10)$$

Where OD is the optical density of the sample at excitation wavelength obtained from steady state absorption measurements, l is the path length of 1 mm of the quartz cuvette used in the spectroscopic measurements.²⁰⁵ The excitation density per particle was then obtained via Equation 6.11, where the excitation fluence was calculated considering the excitation pulse power and area as described earlier in Chapter 2.

$$N_{ex} = \sigma_a(\omega) * f \quad (6.11)$$

Where f is the excitation fluence. An example of the excitation densities estimated for NC-8.6 sample is show in the second column of Table 6.3.

We check the experimentally obtained excitation densities against the theoretical estimates of the sample excitation densities. Theoretical estimates were calculated considering complex refractive index relation to the sample absorption cross section given in Equation 6.12.

$$\sigma_a(\omega) = V * \frac{n_r}{K} |C(\omega)|^2 \sigma_b(\omega) \quad (6.12)$$

Where V is the volume of the nanocrystal, n_r and K are the real and imaginary parts of the refractive index respectively obtained from literature estimates, C is the local field correction factor (complex number) given in Equation 6.13 and σ_b is the theoretical bulk absorption coefficient estimate defined in Equation 6.14.²⁰⁵⁻²⁰⁶

$$C(\omega) = \frac{3m_2^2}{m_1^2 + 2m_2^2} \quad (6.13)$$

$$\sigma_b(\omega) = \frac{4\pi K(\omega)}{\lambda} \quad (6.14)$$

Where m_1 and m_2 are the complex refractive indices of the material and solvent respectively, λ is the wavelength. The theoretical nanocrystal absorption cross section model assumes the sample absorption as if the film was dissolved in a solvent but accounts for the solvent effects via the local field correction factor based on complex refractive index relation between the material and the solvent.

The comparison between the excitation density estimates calculated through theoretical and experimental approaches for different excitation fluences of NC-8.6 sample is shown in Table 6.3 (columns 2 and 3). The estimated experimental excitation densities match the theoretical estimates well with up to ~18% deviation (NC-7.3 and NC-4.1 sample deviation is lower) which support the goodness of the experimental excitation density estimate. We note that the application of this theoretical calculation method with known experimentally obtained absorption cross section values and sample sizes introduces system parameter constraints which could help the characterization of the refractive indices of the solution suspended particle system.

Table 6.3. Excitation density comparison between experimental and theoretical estimates and corrected values.

Fluence (photon/cm²)	Experimental exc. dens. Exc./NC	Theoretical exc. dens. Exc./NC	Corrected exc. dens Exc./NC
6.3*10 ¹²	0.11	0.13	0.11
5.2*10 ¹³	0.92	1.08	0.77
5.2*10 ¹⁴	9.15	10.82	3.67
3.5*10 ¹⁵	61.06	72.20	6.33

Next we account for the absorption saturation behaviour in order to extract the actual sample excitation densities. The small excitation beam size used in this experiment

allowed to reach high excitation fluences which as shown above can result in measurement excitation density estimates of tens of excitations per nanocrystal. However, it is unlikely that a single nanocrystal will absorb such energy and sustain 60 excitations. Instead, the NCs are expected to absorb less light with a few excitations present resulting in an absorption saturation.²⁰⁷ In order to correct for the high fluence excitation induced absorption saturation we compare the band edge transient absorption GSB amplitude 1 ps past the excitation (to avoid any short time artefacts without any significant recombination effects) with the experimentally estimated excitation densities. Figure 6.15 shows this comparison and as expected we observe a nonlinear behaviour with the excitation density estimates at the highest fluence measurements. In order to correct for the absorption saturation induced excitation density estimate deviation we use the linear behaviour present in the lowest fluence excitation density estimates to correct for the highest fluence estimate deviation. The correction assumes the linear TA-excitation density condition holds in the high fluence measurements. The corrected values are given in column 4 of Table 6.3. The correction retains similar low fluence excitation density values but has a high impact in the highest excitation fluence region reducing the initial estimate from 61 excitations/NC to ~6 excitations, a physically reasonable value.

Figure 6.15. CsPbBr₃ TA magnitude versus the estimated uncorrected excitation density and high fluence excitation density correction.

We estimate the excitation density values experimentally and find them closely matching to the theoretical model estimates. At highest excitation densities we observe an absorption saturation behaviour which departs the linear relation to the TA and correct the excitation density values using a linear model.

6.3.7 High fluence dependent TA spectroscopy

High fluence dependent TA spectroscopy is a powerful way to probe state filling and recombination dynamics in semiconductors. In bulk organometal halide perovskite films, the Burstein–Moss effect is manifest as a broadening of the main GSB peak to higher energy as more photocarriers fill the continuum of states in the valence and conduction bands.^{18, 188, 197} In NCs, on the other hand, the statistical distribution of occupied states is localized to each individual particle that can be considered as independent of other NCs in dilute solution. In these confined systems, a multiple excitations per particle could change the nature of available states and rapid relaxation pathways.

The TA spectra measured in CsPbBr₃ bulk films and 8.6, 7.3 and 4.1 nm nanocrystals evolve heavily with increasing excitation fluence. Figure 6.16 shows intensity dependent TA spectra recorded at 100 fs for each of the samples as a function of excitation fluence (converted to excitation densities and normalized). The TA spectra of the bulk CsPbBr₃ in Figure 6.16a exhibits the signature Burstein–Moss effect that is also resolved in bulk organometal halide perovskite films;^{188, 197} higher excitation density results in the GSB signature broadening to higher energies. The NC-8.6 sample represents a similar, but more pronounced behavior, while the NC-7.3 sample shows evidence of the same effect, albeit convoluted with the perturbed GSB peak shape arising from state focusing. The complex set of quantum confinement induced GSB peaks is even more obvious for the NC-4.1 sample under high fluence excitation.

Figure 6.16. Normalized ultrafast TA spectra of Film, NC-8.6, NC-7.3, and NC-4.1 samples probed at 100 fs after 400 nm excitation measured at different sample excitation densities specified in the legends (excitation/cm³), where number in brackets denotes average number of excitations per NC.

The temporal strongly quantum confined NC sample dynamics analysis reveals a fast TA lifetime component developing with increasing excitation densities (Fig. 6.17a). In line with previous studies of CsPbBr₃ NCs, the relative amplitude of the fast component scales

according to the probability of more than one excitation occupying each particle, as per the Poisson distribution (Fig. 6.17b).^{200, 208} The lifetime of the fast component was isolated by subtracting the intensity-independent component from NCs occupied by one excitation, as shown in Figure 6.18. Similar to previous reports, this analysis yields fast component lifetimes of ~ 20 , 40, and 45 ps for NC-4.1, NC-7.3, and NC-8.6 samples, respectively.^{200, 208} Although Makarov et al. attributed the fast component to biexcitons and Auger recombination, we note that statistical occupation of NCs with two excitations will also result in a fast component, regardless of whether the bound biexciton quasiparticle is formed; bimolecular recombination of free unbound charges confined to the same discrete volume will also produce a fast decay component with a discrete lifetime.²⁰⁰ Indeed, Castañeda et al. found that only NCs $< \sim 7$ nm obey the linear scaling of lifetime with volume expected for bound biexcitons, whereas larger NCs exhibited a weaker $V^{0.38}$ scaling.²⁰⁸ Consistent with our view that a fast lifetime component does not necessarily reflect bound biexciton quasiparticles, Castañeda et al. only resolve a red-shifted biexciton emission signature for the smallest NCs. It is also apparent in our broadband TA data that this kinetics analysis for multiply excited particles depends on which probe wavelength is selected because population decay is convoluted with spectral relaxation, which is prolonged at high fluence.

Figure 6.17. a) NC-4.1 sample band edge GSB temporal dynamics over varying excitation density. b) Probability ratio of more than one excitation per NC and probability of 1 or more excitations per nanocrystal vs TA component ratio of multiple excitations and single excitation per NC. The close to 1:1 linear dependence plotted as red line is in agreement with excitation density estimates and their relation to the TA component nature.

Figure 6.18. NC-4.1 sample excitation density dependent biexciton dynamics obtained by subtracting the single exciton GSB kinetics contribution, monitored over a wavelength integral over the GSB peak. We note that smaller integrals around the peak region can produce shorter lifetimes.

6.3.8 Degeneracy

Discrete states formed in the smallest NCs allow for their degeneracy determination via the TA signal dependence analysis on the excitation density. By considering excitation density proportionality to the TA signal magnitude and applying Poisson statistics, as well as analyzing the TA signal saturation as a function of particle occupancy, we estimate degeneracy of 2 for the band edge state of the NC-4.1 sample. Figure 6.19 shows statistical excitation density contributions of possible degeneracies versus TA signal. The corresponding state degeneracy is expected to have a $\sim x^1$ dependence, where x is the TA magnitude. We use Poisson's statistics to obtain an estimate of nanocrystal occupancies at given average excitation densities. We define 'Non-deg' as the case where the band edge state is non-degenerate and depends on probability of >0 excitation/NC; 'Deg = 2', as the case where the band edge state has degeneracy of 2 and depends on nanocrystals with excitations of 1 and ($>1*2$), where $*2$ factor corresponds to double contribution to the TA signal; 'Deg = 3', as the case where the band edge state has degeneracy of 3 and depends on nanocrystals with excitations of 1 and ($2*2$), where $*2$ factor corresponds to double contribution to the TA and $>2*3$, where $*3$ corresponds to triple contribution to TA. The poor linearity of Non-deg case shows that the band edge state is degenerate and the best fitting case with $\sim x^{0.98}$ dependence suggests the degeneracy is 2. However, the case where degeneracy is 3 is relatively close to linear dependence with $\sim x^{1.12}$ and Poisson's statistics may be limited at higher excitation densities due to the assumption of

independent events, we therefore support this analysis with an additional approach. Figure 6.20 shows the estimate of band edge TA saturation in relation to the excitation densities in NC-4.1 sample. The plotted fit suggests the band edge state of NC-4.1 has a degeneracy of 2. This conclusion agrees with occupancy theory for Fermions in a molecular-like energy state and supports the formation of discrete energy levels in a strongly confined 0-D structure of 4.1 nm CsPbBr₃ NCs. The same analysis for larger NCs shown in Figure 6.21 suggests that they can accommodate much higher occupancies showing a broad saturation with an onset at ~ 4 and stretching towards ~ 10 excitations/NC, as expected for a bulk-like system.²⁶

Figure 6.19. NC-4.1 sample Poisson state contribution estimates vs early time TA estimated over varying excitation fluences. Linearity estimates are plotted as fits with power coefficient given in the legend.

Figure 6.20. NC-4.1 sample early time TA magnitude vs corresponding average excitation density with free parameter sigmoid fit for saturation estimate.

Figure 6.21. a) NC-8.6 and b) NC-7.3 sample early time TA magnitude vs corresponding average excitation density with free parameter sigmoid fit for saturation estimate.

6.3.9 High fluence hot carrier cooling dynamics

Finally, we report the dependence of hot carrier cooling dynamics on sample excitation density, shown in Figure 6.22. Short subpicosecond cooling is observed in all of the samples at low excitation fluences. However, at excitation densities above approximately 10^{19} cm^{-3} , slow hot carrier lifetime feature develops prolonging relaxation time dramatically for bulk and NC samples, with dynamics on the order of 10 ps. The extension of carrier cooling time scales at high fluence may indicate the presence of a hot phonon bottleneck due to phonon reabsorption, where the probability of carriers reabsorbing lattice phonons increases with higher excitation densities, which then result in longer hot carrier lifetimes.¹⁸ A recent study on $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs observed a similar hot carrier behavior and attributed it to Auger-heating effect.²⁰⁹ The hot carrier decay time scales and behavior observed for low and high carrier densities in nanocrystals appear surprisingly similar between the CsPbBr_3 and $\text{CH}_3\text{NH}_3\text{PbBr}_3$, suggesting the MA cation has a limited effect on the hot carrier relaxation in NCs. It is an important finding given the literature speculations on the importance of the complex CH_3NH_3 cation influence on charge dynamics in perovskites, also indicating that the intrinsic CH_3NH_3 phonon modes do not play a significant role in carrier cooling.⁴³ In the case of CsPbBr_3 , similar fluence dependent dynamics are also observed when comparing bulk and nanocrystal samples. Moreover, the lifetimes appear to scale with excitation density rather than excitations per NC. The low sensitivity to NC size suggests that these high

fluence cooling dynamics are intrinsic to the material and are not strongly affected by quantum confinement.

We also consider the charge carrier screening effect on the carrier dynamics. Charge carrier screening is a mechanism that governs carrier behavior at high excitation densities. It disrupts the excitonic interaction via the presence of Coulombic forces from surrounding carriers, impeding electron energy transfer to holes which can reduce available phonon transitions and promote phonon bottleneck effect. When an increasing excitation concentration in a material reaches Mott density, exciton interaction is minimized due to charge screening and carriers behave like electron-hole plasma. By considering electron-hole system described by classical Boltzmann statistics we calculate the Mott density for bulk CsPbBr₃ via Eq. 6.15.²¹⁰

$$N_M = (1.19)^2 \frac{k_B T}{2a_x^3 E_x} \quad (6.15)$$

Where a_x is the Bohr radius of 3.5 nm and E_x is the exciton binding energy of 40 meV. At room temperature the CsPbBr₃ Mott density is $\sim 1 \times 10^{19}$ excitations/cm³. This value coincides with the excitation densities where the long hot carrier lifetime component appears; perhaps suggesting that charge screening may suppress cooling, for example by reducing electron–hole coupling with phonons.

Figure 6.22. Hot carrier cooling dynamics dependence on excitation density. Excitation densities are specified in the legends [$\text{excitation}/\text{cm}^3$], where number in brackets denotes average number of excitations per NC.

6.4 Conclusion

We have used broadband ultrafast TA spectroscopy along with steady state absorption and PL spectroscopy techniques to examine the development of quantum confinement in size-tuned cubic CsPbBr_3 NCs in comparison to the bulk material. Different size particle samples used in this study were estimated to span weak to strong quantum confinement regimes and the steady state absorption along with PL spectra indicated the presence of quantum confinement influence through the blue shifting development of the spectra. We estimated Stokes shifts using differential steady state absorption and transient absorption spectroscopy approaches and found that standard steady state absorption measurements produced inaccurate Stokes shift estimates. Transient absorption measurements also revealed similar bulk CsPbBr_3 perovskite photoresponse to the methylammonium based metal halide perovskites. Examining the excited state dynamics we found that larger NCs with edge lengths >7 nm (which are in the range of most previous studies) exhibit similar

spectral dynamics to the bulk material; TA bleaching spectra reflect carriers filling uniform density of states, and accelerated decay of multiply excited particles can be understood as bimolecular recombination of uncorrelated charges simply confined to the same volume. Only the smallest NCs revealed TA spectral features consistent with strong quantum confinement; focusing toward discrete energy states, high bandgap renormalization energy, and departure from a Boltzmann statistical carrier cooling. Subpicosecond carrier cooling appeared to be rather insensitive to the NC size. Carrier cooling dynamics on the order of 10 ps were observed at high excitation fluences due to hot phonon bottleneck or Auger effects. However, across all NC samples and the bulk material, hot carrier lifetimes were found to scale with volumetric excitation density rather than particle occupation number, suggesting that the hot carrier dynamics were not strongly affected by the quantum confinement in this case. Finally, we resolved a band edge state degeneracy of 2 for the strongly confined 4.1 nm NCs, in agreement with models of discrete state formation for strongly confined NCs. Our results highlight that quantum confinement effects are only important for the smallest CsPbBr₃ NCs that are currently available (~4 nm edge length). For the larger NCs (>7 nm) - in the weak confinement regime - photophysics is better described as a small perturbation on the free carrier photophysics established for the bulk material.

Chapter 7

Anomalous TA spectral response of metal halide perovskites

Parts of this chapter have been published in the following article:

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7.1 Introduction

Bulk metal halide perovskites have experienced an explosive development in the photovoltaic field over the past five years with current solar cell devices reaching efficiencies of over 20%. Combined with easy device fabrication and element abundance perovskites pose as strong candidates for large scale photovoltaic market integration.²¹¹⁻²¹² Most commonly studied $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite is a direct ~ 1.6 eV bandgap semiconductor with long carrier diffusion lengths and lifetimes as well as exceptionally weak exciton binding energies of about 30 meV which are favourable traits for solar cell and other applications.^{18, 172, 175} In order to successfully integrate perovskites in devices via comprehensive functionality development, a good understanding of their excited state properties is required.

Semiconductor properties such as carrier scattering times, hot carrier temperatures, effective masses of electrons and holes are some of the main parameters governing the optoelectronic performance of the material and can be accessible spectroscopically. A number of transient absorption studies resolving some of the main $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite spectral features have been previously reported.¹⁹⁷⁻¹⁹⁸ Figure 7.1 shows an

example spectral slice of a typical TA measurement of metal halide perovskite bulk film. Features such as ground state bleaching at band edge energies have been related to the band edge carriers filling the lowest conduction and valence band energy states, however the understanding of the perovskite excited state behaviour has been hindered by anomalous TA spectral features. In particular, a broad photoinduced absorption feature dominating the high energy end of the spectra down to the band edge energies has not been well understood and has been subject to multiple studies proposing different models of charge carrier behaviour.^{197-198, 213-214} A very large perovskite bandgap state renormalization red-shifting perovskite absorption band due to a buildup of directed local electric field effects or lattice heating influence and a dual perovskite excited state nature with regenerating charge transfer state models explaining the photoinduced absorption feature have been proposed.²¹³⁻²¹⁴ Such models may have important implications in understanding the exceptional optoelectronic properties of perovskites and fine tuning material performance in devices. However, extensive research with definite confirmation of the nature of the anomalous TA response is still lacking which leaves the excited state behaviour of perovskites subject to speculations. Here, we propose the influence of the photoinduced reflectivity changes of perovskite materials which can affect the transient absorption measurements resulting in anomalous spectral features.

Figure 7.1. Transient absorption measurement of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite excited with 100 fs pump pulses centred at 600 nm spectral trace at 1 ps past excitation.

Photoexcited states are expected to induce changes in the real and imaginary parts of the dielectric function in all semiconducting materials. These changes lead to modulation of absorption and reflectivity of the sample. In standard TA spectroscopy of materials with

small refractive indices such as organic semiconductors, the change in sample reflectivity is expected to be negligible. Metal halide perovskites, however, display large refractive index values of around 2.5 (for $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the visible range), therefore a relative change of the real part of the refractive index can result in a strong modulation of sample reflectivity.²¹⁵ Most current transient absorption studies discuss the changes in the transmitted probe signals assuming they arise only from the changes in the sample absorption, however these changes may in fact be probing sample reflectivity changes in high refractive index materials such as metal halide perovskites. It is therefore important to consider both the photoinduced changes in the absorption and reflectance of the perovskites to fully understand their spectroscopic excited state response.

In this study we consider standard transient absorption response of bulk perovskites in relation to the anomalous high energy PIA signature. We analyse differential perovskite reflectance signal behaviour through different experiments and relate the findings to the standard TA measurements. By using a synchronized transmittance-reflectance setup we obtain the intrinsic absorption signal of bulk perovskites which explains their anomalous behaviour in standard transient absorption measurements. We also attempt to clarify the excited state dynamics of perovskite nanocrystals using a scattering experiment setup.

7.2 Experimental

7.2.1 Samples

$\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite bulk films deposited on Al_2O_3 scaffold were prepared by Anouk Briane and suspensions of CsPbBr_3 perovskite nanocrystals with ~9 nm diameter were synthesised by Parth Vashishtha under the supervision of Jonathan E. Halpert. Material synthesis and characterization details are given in Chapter 6 and in the literature.^{18, 190}

7.2.2 Transient absorption spectroscopy measurements

Excited state dynamics were monitored using an ultrafast transient absorption spectroscopy setup described in more detail in Chapter 2. Perovskite films were measured in an inert N_2 environment sealed with a silicon ring between two quartz substrates. The

samples were excited with 600 nm pump (TOPAS-C optical parametric amplifier output, chopped at half the 3 kHz amplifier rep-rate). Broadband supercontinuum probe pulses were generated in a CaF₂ plate and polarized at the magic angle with respect to the pump. The spectra were recorded using a linear UV-Vis photodiode (Entwicklungsbuero Stresing) array.

7.2.3 Transmission-reflection spectroscopy measurements

Transmission-reflection spectroscopy measurements were carried out in a modified transient absorption spectroscopy setup described in section 7.2.2. The sample was mounted on a manual rotational stage and set to the required measurement angle in relation to the incident probe. Either the transmitted or reflected probe light was guided to and diffracted by 150 g/mm diffraction grating in Princeton Instruments Acton SP2150 spectrograph and read out with a photodiode (Entwicklungsbuero Stresing) array. In the case of simultaneous transmission-reflection measurements the transmitted and reflected probe light was coupled to optical fibers making sure the same type of optics were used for both beam paths and the two probes were read out simultaneously on a separate dual photodiode array channels (Entwicklungsbuero Stresing).

7.2.4 Transmission-scattering spectroscopy measurements

Transient-scattering spectroscopy measurements were carried out using the laser system described in Chapter 2. The perovskite nanocrystal suspensions were measured in 1 mm quartz cuvettes sealed in inert N₂ environment. The samples were excited with 400 nm pump and probed with a broadband white light supercontinuum generated in a CaF₂ plate. The transmitted light was guided to and dispersed in a spectrometer (Acton SP2300 by Princeton Instruments) and read out with an intensified CCD camera (PI-MAX3 by Princeton instruments) that was synchronized to the laser. In the case of scattered light measurements the scattered light was collected with a 90° parabolic mirror set to close proximity to the sample with the main probe light physically blocked and recorded in the same way described for the transmitted light. The differential spectra were calculated from separate pump on and pump off measurements. The transient scattering experiment setup was built and measurements were carried out with the help from Kai Chen.

7.3 Results and Discussion

7.3.1 Transient absorption response of perovskites

Transient absorption measurements on $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films were carried out in a standard TA setup and the typical spectral features observed in the organometal perovskite family were discussed. Spectroscopic features were considered in relation to band edge transition bleaching and hot carrier state filling along with the anomalous high energy PIA signal.

Transient absorption responses of $\text{CH}_3\text{NH}_3\text{PbI}_3$ bulk films shown in Figure 7.2 are discussed. We observe a strong bleaching signature peaking at ~ 745 nm. The bleaching is peaking around the expected bandgap region of the material with a long lifetime stretching out to nanosecond range indicating no recombination before 100 ps as shown in the temporal dynamics in Figure 7.3. The signature has been previously attributed to photocarriers filling the valence and conduction band edge states and indicates some of the reasons for the good photovoltaic performance of perovskite devices, namely the presence of long lived free carriers.

The bleaching also displays short time spectral profile evolution shown in Figure 7.2b. Hot carrier dynamics may manifest in TA measurements and in this case may be related to the evolution of the short wavelength edge shoulder of the bleaching signal narrowing towards the band edge energies on a rapid below 1 ps timescale which is comparable to the hot carrier lifetimes in other NCs.²¹⁶⁻²¹⁷ Although this rapid spectral narrowing may reflect cooling of hot carrier population via filling of lower energy states, the uncertainty over the TA signatures has limited the data interpretation.^{197-198, 213-214} In particular, the influence of the photoinduced absorption spanning the high energy end of the TA spectra has been subject to many speculations and given its proximity to the bleaching feature it may be the cause for short time evolution and general profile of the bleach. The comparison of temporal dynamics between the GSB and the high energy PIA signals are shown in Figure 7.3. The kinetics of the photoinduced absorption signature appear to mirror the bleaching signal of the band edge carriers with the exception of the short time kinetics where the short time evolution of TA spectral profile takes place.

Figure 7.2. Transient absorption measurement of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite excited with 100 fs pump pulses centred at 600 nm a) surface map, b) normalized spectral slices at different times past excitation.

Figure 7.3. Temporal excited state dynamics probed at 675 nm and 745 nm of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite transient absorption measurement excited with 100 fs pump pulses centred at 600 nm normalized at 100 ps.

Another photoinduced absorption feature is also observed in the transient absorption measurements. The signature lies on the long wavelength side of the bleaching signature and appears to evolve on the same time scales as the rapid spectral profile evolution discussed earlier as indicated in Figure 7.2b. The signal may be related to the high energy PIA signature given its temporal similarities to the shorter wavelength profile evolution indicating for example, a rapid shift of the anomalous PIA feature profile to higher energies while overlapping with the bleaching features or it may be of an unrelated nature.

It is clear that the cause and effects of the dominant PIA feature, must be fully understood before any definite information about the excited state properties of metal halide perovskites can be extracted from the TA measurements.

7.3.2 Transmission-reflectance measurements

We carried out transient absorption and transient reflection measurements on $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films and investigated the obtained signals and their evolution in relation between the two measurement modes in order to help understand the excited state signatures of perovskites in standard TA measurements.

Pump-probe measurements were carried out on $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite bulk films with an incident probe set to 45 degree angle to the sample as shown in Figure 7.4. The transmitted probe was monitored giving differential transmission signal according to Equation 7.1.

$$\Delta T/T = \frac{I_T^* - I_T}{I_T} \quad (7.1)$$

Where I_T and I_T^* are the measured probe intensities transmitted through the sample with pump off and pump on cases respectively. Measurements under the same experimental conditions were also carried out on the perovskite films using the part of the probe reflected off the sample as show in Figure 7.4. The differential reflection signal was obtained according to Equation 7.2, where I_R and I_R^* are the measured probe intensities reflected off the sample with pump off and pump on cases respectively.

$$\Delta R/R = \frac{I_R^* - I_R}{I_R} \quad (7.2)$$

Figure 7.4. Pump-probe measurement schematic with 45° probe incidence angle to the sample.

We compare the obtained transient absorption and reflection signatures. Figure 7.5a shows the transient absorption perovskite profile obtained with the 45 degree probe pulse

incidence angle. The general spectral TA profile obtained here matches the TA spectral signatures obtained in the standard TA setup (Fig. 7.2b) well.

The differential reflection measurement spectra displayed in Figure 7.5b show a very different response. The spectra develop complex multimodal features which do not appear to mirror the TA signals. The reflection mode signatures display turning points at around 680, 725, 755 and 785 nm while TA signatures mainly turn at 650-685, 745 and 775 nm. However, the differential reflection signals display temporal spectral evolution dynamics with timescales very similar to the transmission mode measurements suggesting the two modes may be linked.

Figure 7.5. $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite excited with $8 \mu\text{J}/\text{cm}^2$ fluence 100 fs pump pulses centred at 600 nm with white light probe incidence angle of 45° normalized spectral slices at different times past pump excitation of a) transmitted probe, b) reflected probe differential measurements.

In order to check for any possible pump induced differences between the two measurement modes and standard TA, different pump fluences were measured. Figure 7.6 shows the normalized 10 ps spectral profiles of the reflection and transmission modes. No late time spectral profile dependence on the pump fluence was observed in the differential reflection and transmission measurements. The observation also agrees with the standard TA measurement spectral behaviour with fluence where the probe arrives at 90° to the sample.

Figure 7.6. $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite excited with 100 fs pump pulses centred at 600 nm with white light probe incidence angle of 45° normalized spectral slices at 10 ps differential measurements over different excitation fluences of a) transmitted probe, b) reflected probe modes.

7.3.3 Angle dependence

We further analyse the transient absorption and reflection measurement mode signal relation by considering the probe angle dependent effects on the recorded spectra. The similarities observed suggest close relation between the absorption and transmission spectra.

We carried out transient absorption and reflection measurements over different incident probe angles and analysed the signals in relation to each of the measurement modes. The incident probe angle was varied from 20° to 50° with the attainable angle range limited by the physical experimental setup limitations, namely size of probe pick up optics in the setup used and nitrogen capsule dimensions in which the sample was sealed. Figure 7.7a shows the differential reflection of perovskite film spectra at different probe incidence angles. We observe a clear evolution of the differential reflection spectral profile. The longest wavelength positive spectral signature appears to broaden to longer wavelengths with sharper probe incidence angles, along with similar trend on its shorter wavelength shoulder. The most pronounced evolution, however, appears around the 675-740 nm region with strong signature shifts to longer wavelengths with smaller incidence angles and relative growth of the short wavelength positive feature peak. An interesting observation is that more pronounced evolutions are observed at angles of 30° and lower while larger angles display a less pronounced variation. This effect will be discussed in later sections.

Figure 7.7. $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite excited with $8 \mu\text{J}/\text{cm}^2$ fluence 100 fs pump pulses centred at 600 nm 10 ps normalized spectral slices over varying white light probe incidence angles differential measurements of a) reflected probe, b) transmitted probe. Inset in b) is the smaller scale TA short energy shoulder of the bleaching signature.

Figure 7.7b shows the dependence of the TA signal on the probe angle of incidence. It is clear that the differences between the varying angle measurements observed in the differential reflectance spectra are not as pronounced in the transmission mode. The long wavelength range along with the GSB peak appear to show minor variation while the shorter wavelength range displays more pronounced dependence on the angle of incidence. The transmission mode bleaching shoulder appears to red shift or lower as the positive reflectivity feature around the 700 nm region red shifts with decreasing angle of incidence.

The angle dependant spectra recorded in the reflectance mode show strong reflectivity signal dependence on the incidence angle, while the transmission mode displays the dependence which is less pronounced. The measurements suggest the positive differential reflectivity spectral features may induce negative signals in the transmission mode meaning the observed photoinduced absorption may in fact be photoinduced increase in sample reflectivity recorded in the standard TA measurements. The reflectivity influence, however, does not necessarily appear to be dominant across the entire TA spectra. For the probe incidence angle range investigated here, there is typically less reflected than transmitted light which supports the lower angle dependence influence observed in the transmission mode. We note that no influence of excitation fluence on the late time different probe incidence angle spectral profiles was observed.

7.3.4 Synchronized transmission-reflection measurements

The initial transmission and reflectivity measurements suggested the influence of photoinduced reflectivity changes on the transient absorption perovskite response. We therefore set up a simultaneous transmission-reflection experiment and obtain the intrinsic differential absorption response by correcting the TA measurements for the reflectivity changes.

We carried out simultaneous transmission and reflection measurements on $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite bulk films with 45° probe angle of incidence using a dual photodiode array camera as described in the experimental section of this chapter. The setup used allowed to obtain TA and reflectivity signatures under identical measurement conditions. The measurement must be carried out simultaneously as the exact light intensity values are needed for direct transmission and reflection mode comparison, otherwise such effects as white light evolution and instability will have major influence on the analysis. Figure 7.8a shows the simultaneously measured differential spectra of the transmission and reflection modes. The increased sample reflectivity may correspond to the increase in the perceived sample absorption in the transmission mode. We note that the two differential spectra are calculated according to their corresponding spectral intensities therefore adding them together directly will not result in the actual intrinsic absorption spectrum due to their distorted relative proportions as shown in Figure 7.8b.

Figure 7.8. a) Simultaneously measured transient absorption and reflection spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite bulk films measured with 45 degree probe incidence 10 ps past $8 \mu\text{J}/\text{cm}^2$ fluence 600 nm pump excitation, b) direct sum of corresponding spectra.

Instead, in order to account for the reflectivity change induced light intensity differences in the transmission mode, the differential intrinsic absorption spectrum must be calculated using common intensities obtained through simultaneous transmission-reflection measurements according to Equation 7.3 below and not by the individually weighted addition of the two responses as noted by the inequality.

$$\frac{\Delta T_A}{T_A} = \frac{(I_T^* + I_R^*) - (I_T + I_R)}{I_T + I_R} \neq \frac{I_T^* - I_T}{I_T} + \frac{I_R^* - I_R}{I_R} \quad (7.3)$$

Where T_A is the transmitted intrinsic absorption probe intensity. The obtained intrinsic absorption spectra are given in Figure 7.10a. We observe a complete disappearance of the anomalous photoinduced absorption feature in the blue spectral end which is prominent in standard TA measurements. The intrinsic absorption spectra also reveal that the early time development of the GSB spectral profile on the short wavelength range shoulder is not arising from the influence of the anomalous PIA signature but is a part of the bleaching signal overlapping with the PIA. The intrinsic absorption spectra also reveal that the rapidly evolving long wavelength range PIA feature is an absorption induced signature and does not relate to the reflectance induced PIA.

The findings are significant as for the first time the TA signals of metal halide perovskites can be fully and accurately characterized. In relation to these measurements Michael Price has developed a model that fully describes the perovskite TA features attributing the rapid PIA feature to bandgap renormalization and carrier filling model along with relating hot carrier cooling to the evolution of the GSB short wavelength shoulder feature.¹⁸ By fully understanding the perovskite TA response and accounting for the high energy PIA the intrinsic absorption bleach profile can be modelled allowing for the characterization of such parameters as effective carrier masses and hot carrier temperatures and their cooling dynamics.¹⁸ The examples of such analyses carried out by Michael Price are shown in Figure 7.9.

Figure 7.9. a) An example of carrier cooling curves at stated carrier densities obtained through hot carrier fitting. b) An example of different models of change in absorption coefficient due to the presence of photo-excited states. The model best fitting the obtained intrinsic absorption response of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite estimates effective carrier masses of about $0.14 m_0$ and effective mass asymmetry of ~ 3 .¹⁸

We note that despite fully understanding the standard TA spectral features, the intrinsic absorption measurements carried out here must be used in order to obtain the fitted effective mass and carrier temperatures as they are governed by the GSB spectral shape which is perturbed by the broad reflectance PIA signature. Figure 7.11 shows an illustration of a metal halide perovskite TA region which is typically fitted according to Boltzmann distribution given by Equation 7.4 in order to extract hot carrier temperatures.¹⁸

$$\frac{\Delta T}{T} \propto e^{\frac{E_f - E}{k_b T_c}} \quad (7.4)$$

Where E_f is the fermi energy, k_b is the Boltzmann constant and T_c is the carrier temperature. The approach has become popular among the perovskite TA spectroscopist community with a number of papers using it to characterize hot carrier temperatures.^{18, 209, 218-219} Since accurate hot carrier characterization is highly important in understanding semiconductor materials and can lead to such applications as highly efficient hot carrier solar cells we stress that the fitting must be carried out on intrinsic absorption profile as the fitting temperatures extracted are dependent on the spectral shape of the hot carrier absorption signature which is located on the high energy end of the TA spectrum, the region where the reflectivity induced spectral perturbation is most prominent. We also note that the TA band edge bleaching peak kinetics remain unaffected with reflectivity

changes and follow the same trend as the intrinsic absorption dynamics as shown in Figure 7.10b.

Figure 7.10. a) Normalized intrinsic differential absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite bulk film measured with 45 degree probe incidence at different times past 600 nm pump excitation. b) Normalized kinetics of 10 nm integral over bleaching peaks of TA and intrinsic absorption measurements.

Figure 7.11. Normalized early time TA spectra of CsPbBr_3 metal halide perovskite NC sample measured in a wide spectral range configuration. Early time above bandgap spectral broadening indicates the presence of hot carrier distributions. Inset: above bandgap GSB shoulder region, where carrier temperatures are obtained by global fit to a Boltzmann distribution.

7.3.5 Reflectance-TA contribution analysis

Here, we consider the influence of the transient signal in the differential reflectivity measurements of bulk perovskite films and account for it by subtracting the expected transient signal in relation to the estimate of the reflected transient light intensity.

We estimate the TA signal contribution to the reflectivity spectra by considering two main sample reflections monitored in the reflectivity mode. Figure 7.12a shows the schematic of the probe interaction with the sample which absorbs transmitted light in the steady state according to its experimentally measured steady state absorption spectrum (governed by absorption A). The incident probe I_o is transmitted through the sample where the light spectrum I_T is monitored in the experimental transmission mode. The probe also experiences two main reflections contributing to the I_r spectra monitored in the experiment consisting of IR (the probe only experiencing sample reflectivity) and $IR2$ (the probe affected by sample absorption). In order to obtain the true photoinduced reflectivity spectra, IR needs to be isolated since the experimentally monitored I_r will be affected by the photoinduced absorption signatures. We note that this analysis accounts for the monitored light intensity changes induced by the air/substrate and substrate/air reflections represented with brown arrows in Figure 7.12b through consideration of the angle geometry, refractive indices and Fresnel equations. Measurement with p polarized probe is analysed here for simplicity. According to the Figure 7.12a monitored variables are defined in Equation set 7.5 and are used to derive the variables given in Equation set 7.6 through geometric considerations.

$$\begin{aligned} I_o &= I_T + I_r + A * x + A * y \\ I_r &= z + y - A * y \\ I_o &= x + z \end{aligned} \tag{7.5}$$

$$\begin{aligned} x &= I_o - z \\ y &= \frac{I_r - z}{1 - A} \\ z &= \frac{\left(\frac{I_o - I_T - I_r - A * I_o}{A} * (1 - A) \right) - I_r}{A - 2} \end{aligned} \tag{7.6}$$

Figure 7.12. a) Simplified sample probe light reflection schematic with transmitted and reflected light notations b) simplified sample-substrate-environment probe light reflection schematic.

According to Equation 7.6 set, IR component of I_r is equated to z and IR2 component is equated to y affected by sample absorption after transmission (noted y_A). The estimated IR and IR2 component spectra contributing to the recorded I_r spectra are then defined, with an example of the spectra given in Figure 7.13. We observe a strong reflectance only (IR) component influence to the recorded spectrum in the shorter wavelength range, however the sample absorption affected contribution to the reflectivity spectrum (IR2) increases with longer wavelengths with significant intensity contribution at the long wavelength range of the measurement. The findings suggest dominant photoinduced reflectance signal effects in the shorter wavelength range with stronger photoinduced absorption influence at the red end of the spectra.

Figure 7.13. Example of p polarized probe reflectance spectrum of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite bulk film and corresponding estimates of IR and IR2 component contributions.

We now estimate the differential reflectivity spectra corrected for the contribution of photoinduced absorption change signal. Transient absorption change can be defined as $A = -\log(I_T^*/I_T)$ with “*” denoting pump on measurement. By assuming the IR2 component has identical excited state absorption features to the transmission mode measurements, with relative magnitude only affected by the extra path length through the sample in comparison to the TA mode, we define the reflectance mode TA absorption as $CA = -\log(IR2^*/IR2)$, where C is a constant equal to two (double the sample path length) and the pump on spectra IR2* is defined as $IR2^* = IR(10^{-2A})$. The reflected probe signals of the substrate/sample interface only (IR) were then derived by subtracting the photoinduced absorption change affected probe i.e. $IR = I_r - IR2$; $IR^* = I_r^* - IR2^*$.

Figure 7.14b shows the measured differential reflectance and the corrected reflectance spectra. The blue end of the spectrum appears to remain unchanged while at the red end it is affected by the TA signal correction. Interestingly, the positive feature peaking at around 765 nm appears to diminish with the correction reducing the complexity of the reflectance spectrum. The correction makes the reflectance spectra resemble a derivative feature closer, which is similar to the photoinduced refractive index change profile of other semiconductor materials.⁴⁴

By using the isolated photoinduced reflectance estimate, the corrected intrinsic absorption signal was defined in Equation 7.7.

$$\Delta T_{Ac}/T_{Ac} = \frac{(I_T^* + IR^*) - (I_T + IR)}{I_T + IR} \quad (7.7)$$

The intrinsic absorption spectrum of perovskite films is compared to the corresponding corrected spectrum shown in Figure 7.14a. We observe similar spectral profiles between the corrected and uncorrected spectra, with the blue end PIA feature fully accounted by the commonly weighted reflectance in both of the cases. However, some differences are present in the relative profiles with a small blue shift of the long wavelength range shoulder of the GSB feature as well as some development of the short wavelength range shoulder in the corrected signal. Although the correction induced differences in the spectral profile of intrinsic absorption are relatively small they can contribute to inaccuracies in modelling of the perovskite system. For example the blue end shoulder of the GSB feature can be fitted to a Boltzmann distribution which allows for the extraction

of hot carrier temperatures, in this case resulting in ~ 40 K difference between the uncorrected and corrected spectra estimates. Since accurate hot carrier characterization is highly important for such application as solar cells this effect must be understood and accounted for.

Figure 7.14. Pump-probe measurement of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite bulk films excited with 600 nm pump pulses a) normalized intrinsic absorption and corresponding corrected spectra 10 ps past excitation, b) reflectance mode spectrum and corresponding corrected spectrum 1 ns past excitation, selected for clearer display of spectral profile behaviour with applied correction.

The correction analysis reveals that the uncorrected simultaneous transmission-reflection measurements provide a good estimate of the intrinsic differential absorption response of the system but suggests a correction for reflected TA signal contribution can be used for more accurate system analysis and modelling. However, we note that the correction discussed here is a simplified model which relies on the dominant reflection/transmission interaction, low secondary reflection influence, complete light collection, no scattering effect influence, excitation beam profile and density uniformity, temporal invariance between transmission and reflection mode and limited influence of AlO_3 scaffold assumptions. In order to analyse photorefractive sample effects without the need to rely on a simplified model correction and allow for more accurate fitting of system properties along with a broader applicability, an additional experimental approach could be developed. The different reflectivity effect analysis approach discussed later in Chapter 8 could support in-depth system modelling with more parameter constraints provided by the photoinduced refractive index change resolution.

7.3.6 Reflectance spectral analysis

We now explain the observed reflectivity measurement spectral behaviour in relation to Fresnel equations and polarization dependence measurements in order to clarify the nature of the differential reflectivity signals.

Figure 7.15 shows the differential reflection spectral dependence on the probe polarization, the spectra were taken at the magic angle (in relation to the pump), s and p probe polarizations. The signals develop strongly with different probe polarizations, namely the blue end of the spectrum grows with polarization turning from s to p and diminishes in the red end.

Figure 7.15. Differential reflection spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite bulk film measured with 45 degree probe angle of incidence with different polarizations at 10 ps past 600 nm pump excitation. Inset: corresponding spectra normalized to minimum signal values.

Figure 7.16 shows the probe reflectance estimates calculated from Fresnel equations (Eq. 7.8 and 7.9) for the investigated system, where the angle of incidence on the x-axis refers to the previously defined probe incidence to the substrate side of the sample (the angles for Fresnel equations were calculated through Snell's law).²²⁰

$$R_s = \left(\frac{n_1 \cos \theta - n_2 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta\right)^2}}{n_1 \cos \theta + n_2 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta\right)^2}} \right)^2 \quad (7.8)$$

$$R_p = \left(\frac{n_1 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta\right)^2} - n_2 \cos \theta}{n_1 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta\right)^2} + n_2 \cos \theta} \right)^2 \quad (7.9)$$

Where s and p denote polarization, n_1 and n_2 are the refractive indices of the 1st and 2nd media and θ is the angle of incidence. As previously revealed in the intrinsic absorption measurements and the reflected TA signal analysis, the positive feature in the blue end of the reflectance spectra is expected to mostly arise from the photoinduced reflectivity change. The p-polarization displays higher photoinduced reflectance intensity (Fig. 7.15) in line with the stronger p-polarization reflectance estimate from the Fresnel equations. While the s-polarization also shows the expected lower reflectivity behaviour with the magic angle response between the s- and p-polarizations. However, the red end of the reflectance spectra shows behaviour which differs from the simple reflectance behaviour with the spectral intensity decreasing with polarization turning from s to p. This observation agrees with the reflected TA signal analysis discussed in the previous section and supports the reflectance measurements having TA signals mixed in the red end of the reflectance spectrum which become proportionately lower as the reflectance off the glass-perovskite interface increases. This effect also explains the complex reflectance spectral signatures observed along with the transmission mode spectral angle dependence.

Figure 7.16. Sample reflectance estimates derived from Fresnel equations for s and p probe polarizations with x-axis converted to the angle of incidence to the sample from the angle of incidence between the substrate and perovskite through Snell's law.

In addition, the reflectance estimates also help explain the reflectance spectral dependence on the angle of incidence observed in Figure 7.7a, where the large angles show less pronounced spectral magnitude variation in comparison to the 20-30 degree angles. We note that the Fresnel equations used here describe a simplified system with assumptions of low magnetic perovskite response and little scaffold influence, while the estimates may not represent the behaviour exactly they provide good insights to the trends of the system.

7.3.7 Nanocrystal scattering effects

Metal halide perovskite nanocrystal transient absorption signals were investigated in relation to the photoinduced refractive index changes. The measurements were carried out using high sensitivity intensified CCD camera with large collection angle setup for improved collection of light scattered by the nanocrystal suspension. The measurements were likely limited by the TA signal presence in the scattered light.

We carried out transient absorption measurements on CsPbBr₃ perovskite nanocrystal solution suspensions using an intensified CCD camera setup described in more detail in the experimental section of this chapter. We note that the experiment was carried out in forwards scattering mode with transmitted probe light physically blocked as the backwards scattering mode with parabolic mirror set to the front side of the sample could not collect enough light for a measurement. Figure 7.18a shows the obtained transient absorption spectra. We note that the data quality is lower than in the previous sections due to the different measurement setup used without the shot-by-shot pump on and off shot detection. The spectral features observed closely resemble the spectra seen in the bulk perovskite films with strong GSB component and the photoinduced absorption present in the blue wavelength end of the spectra, attributed to the photoinduced reflectivity changes in the bulk perovskites as discussed in the previous section. Here the photoinduced absorption of NCs may arise from the same photorefractive effect observed in the bulk material, appearing as photoinduced change in nanocrystal scattering rather than film interface reflectivity (Fig. 7.17b, c). The NCs measured here are around 10 nm in diameter which is lower than the light wavelengths used allowing their scattering to be approximated close to a point source scattering. In this case the reflectivity measurement

setup used in the previous sections cannot be used due to the low levels of light and large light collection losses due to multidirectional NC scattering. Instead, a more sensitive setup with intensified CCD camera with large light collection angle is used in order to obtain a differential scattering spectrum of the nanocrystal suspensions. We note that here the rapidly evolving long wavelength PIA feature is outside the measurement spectral window, however it is typically present in the TA spectra of CsPbBr₃ perovskite nanocrystals as shown in the previous chapter.

Figure 7.17. a) ICCD large angle light collection scattering setup schematic. Probe interaction schematic with b) film, c) nanocrystal.

Figure 7.18. ICCD large angle light collection setup pump-probe measurement of CsPbBr₃ perovskite NC suspension at different times past 100 fs pump excitation centred at 400 nm a) normalized transmission mode spectra, b) normalized scattering mode spectra.

Differential scattering spectra of perovskite NC suspensions obtained are shown in Figure 7.18b. We observe a strong positive feature at around 480 nm and a negative signal in the range of 400-450 nm. Unlike in the bulk film perovskite measurements, these features do

not appear to correspond to the bulk reflectivity spectral features. Instead, the scattering spectra appears to mirror the transient mode spectrum well with some spectral broadening. The broadening may indicate some photoinduced refractive index change influence, but the dominant contributor to the scattering mode measurement appears to arise from the TA response. This effect is likely caused by the multiple scattered light interactions with NCs (transmission and reflection), with more significant transmitted light proportion and generally stronger TA response.²²¹

The complex nanocrystal scattering interaction and low levels of light do not allow for the photorefractive effect resolution or correction using the reflectivity approach and underline the problem of the reflectivity spectral contamination with TA signals. We note that similar high energy PIA signatures are typically present in a wide range of different metal halide perovskite TA spectra, however the experiment underlines the limitation of the samples that can be used when examining photoinduced reflectivity changes through the transmittance-reflectivity measurement method.^{190, 197, 199} All of the transmitted and reflected light needs to be collected for an accurate simultaneous transmittance-reflectivity measurement, which means films that display scattering or NC suspensions cannot be used for the determination of the real photoinduced intrinsic absorption change. We note that in a theoretical case an integrating sphere could be used to collect all of the transmitted, reflected and scattered light allowing to monitor the real absorption change in scattering samples, however such a setup is not desirable in ultrafast spectroscopy because it would greatly diminish the temporal resolution of the experiment due to the multiple reflections taking place within the integrating sphere. However, the photoinduced reflectivity changes of the samples can be examined by using an experimental frequency domain interferometry approach which will be discussed in the following chapter (Chapter 8).

7.4 Conclusion

We carried out standard transient absorption measurements on $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite bulk films and showed that the understanding of the excited state behaviour in perovskites is obstructed by anomalous photoinduced absorption response dominating the high

energy end of the TA spectra. By setting up reflectance experiment and carrying out differential reflectance measurements on the perovskite films we revealed complex reflectance signal profile which appeared to be related to the TA signatures through similar rapid spectral profile evolution dynamics. Further analysis on probe incidence angle dependence suggested that the anomalous PIA signal seen in standard TA measurements is influenced by the positive (increased) reflectance features in the differential reflectivity spectra.

In order to account for the photoinduced reflectance changes in the transient absorption measurements we built a synchronized transmission-reflectance setup and carried out the measurements on perovskite bulk films. Using common weightings of the measured transmittance and reflectance mode light intensities we calculated the differential intrinsic absorption response of the metal halide perovskites. The obtained intrinsic absorption spectra revealed that the anomalous PIA feature is not actual photoinduced absorption but rather photoinduced increase in sample reflectivity which shows up as PIA in standard TA measurements and is fully accounted for by the reflectance spectra. Further analysis of the reflectance spectra using polarization dependence measurements and Fresnel equations helped understand the reflectance spectral features and suggested that the blue end of the spectra is governed by the photoinduced reflectivity while the red end is influenced by TA signals.

Anomalous photoinduced absorption features have also been observed in TA measurements of metal halide perovskite nanocrystals. In order to prove that these signatures arise from the same photorefractive effect shown for the bulk films we carried out large collection angle scattering experiments on CsPbBr₃ perovskite nanocrystal suspensions. The obtained NC scattering signals mostly resembled the corresponding TA signals with some spectral broadening. The observations suggested the multiple NC light scattering effects also involve a significant light transmission interaction which results in a TA profile dominated scattering signal. The measurements underlined the significance of TA influence in the scattering/reflectance measurements and revealed the limitations of the experimental approach.

Finally, we estimated the transient signal influence in the bulk film reflectance measurements and corrected for it by considering the beam propagation model through

the sample. The correction produced generally similar intrinsic absorption profiles to the uncorrected spectra but revealed small influence on some spectral parts. If unaccounted for, the small differences were shown to result in inaccuracies in system modelling based on the intrinsic absorption profile of the sample.

The findings revealed that the anomalous photoinduced absorption signal seen in standard perovskite TA analysis is in fact a signature of increased sample reflectivity arising from the photoinduced change in large perovskite refractive index which for the first time allowed for full characterization of perovskite TA response. The intrinsic absorption obtained via simultaneous transmission-reflectance measurements allowed for system modelling isolating such parameters as effective carrier masses and hot carrier temperatures. However, to directly access the fundamental parameter changes responsible for the photorefractive effect and extend measurement applicability a different experimental approach needs to be considered.

Chapter 8

Interferometry measurements of refractive index changes in perovskites

8.1 Introduction

Extensive studies of metal halide perovskites have been published ever since high photovoltaic efficiencies of these materials have first been reported in 2012.²²²⁻²²³ A significant part of the studies have focused on the dynamics of photoinduced charge carriers examined via ultrafast time-resolved transient absorption spectroscopy which helped to characterize the photoexcited state properties and established spectroscopic perovskite analysis methods.^{18, 79, 190, 195, 197} However, standard TA spectroscopy only monitors the imaginary part of the nonlinear susceptibility, while photoexcitation induces multiple other effects such as band filling, plasma intraband transitions, bandgap shrinkage and Coulombic interactions that affect both the real and imaginary parts of the material's response function. Complex refractive index of the material is modified upon photoexcitation, which can display substantial changes in semiconductors that have large unperturbed refractive index values around the bandgap such as perovskites ($n \geq 2$) as suggested by the previous chapter. This effect can strongly influence material's interaction with light, therefore its accurate resolution can have important implications in the development of nonlinear optical applications.

In laser applications the change in the refractive index can be used to characterize the gain and material parameters at high excitation densities which are crucial for the device design. This research is also important for designing optical switching devices where the optical gate pulse can be used to modulate the refractive index of the material which then can alter either the direction of propagation, phase or transmission of another optical

pulse. In a similar fashion the knowledge of optical absorption coefficient and refractive index changes are also important for optical modulating and recording devices, single photon emitters, transition characterization and probing techniques.^{44, 46}

As discussed in Chapter 7 upon exciting $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskites we observe anomalous perturbations in the TA spectra which suggest strong changes in the real part of the refractive index. The synchronized transmittance-reflectivity measurement allowed to measure the convolution of the light changes from reflected and transmitted spectra uncovering the intrinsic TA signal. The method was effective in resolving the reflectivity based anomalous TA signature, however it suffered from limitations such as sample scattering (discussed later in the results and discussion section) and could not directly measure the change in real part of the complex refractive index coefficient, which could allow for more accurate and in depth analysis of the photoexcited system, needed for engineering of laser gain media and other devices.

We employ a frequency domain interferometer (FDI) technique which allows to directly access the photoinduced changes in the refractive index of a material on the ultrafast timescale and apply it to investigate CsPbBr_3 perovskite bulk films and nanocrystals. The interferometry method used was built by modifying the standard TA setup which allowed it to be used to obtain standard TA measurements by simply blocking one of the interferometer arms. This allowed to obtain the TA signal under the identical conditions used for the refractive index measurements. The interferometry setup used produced good spectral interference fringe visibility because the two interfered white light pulses followed the same path set before they were transmitted through the same sample. It was also stable and had little sensitivity to beam deflection due to the same white light pulse path and short Michelson interferometer component arm length, allowing to accurately measure the small changes in the refractive index of the samples.

This interferometry method had first been used in 1992 by Kobayashi *et al.*²²⁴ It allowed to extract the small refractive index differences induced by the pump from the interference fringe shifts in the recorded probe spectra. Although effective, this method has not been adapted in standard semiconductor spectroscopic analysis. For the first time we apply this interferometry technique to analyse metal halide perovskites and show its analytical capabilities in modern semiconductor spectroscopy.

In this chapter we describe the frequency domain interferometry technique and its application to CsPbBr₃ perovskite analysis. We resolve the photoinduced changes in the real part of the refractive index and transmission coefficients and use them to explain the free carrier and exciton dynamics in relation to standard TA measurements.

8.2 Experimental

8.2.1 Samples

The samples were synthesised and characterized by Parth Vashishtha as described in more detail in Chapter 6 and in the literature.¹⁹⁰ CsPbBr₃ bulk film samples deposited on Z&Z quartz substrates were mounted in a spectroscopic vacuum chamber and measured under a dynamic vacuum. The 8.6 nm CsPbBr₃ NCs were suspended in hexane and the spectroscopic measurements were carried out in 1 mm quartz cuvette sealed in inert N₂ environment.

8.2.2 Steady state absorption spectroscopy

Steady state absorption spectra were collected using a Varian Cary 50 Bio UV-Visible Spectrophotometer. The absorption spectra of quartz substrate and hexane in 1 mm cuvette were taken and were subtracted from the absorption spectra obtained measuring CsPbBr₃ bulk film deposited on quartz substrate and NC suspension in hexane in 1 mm cuvette respectively.

8.2.3 Pump-probe frequency domain interferometry

We built a frequency domain interferometry setup by modifying an ultrafast transient absorption spectroscopy setup described in Chapter 2 in order to monitor photoinduced refractive index change dynamics on an ultrafast time scale in relation to the transient absorption response.

In the FDI setup 400 nm excitation (pump) pulses were generated from the second harmonic of an amplified Ti-sapphire 800 nm laser and were chopped at half of the amplifier rep-rate. The pump was filtered with a variable ND filter to the required

excitation intensities. A portion of the 800 nm output was focused in to a linearly translated 3 mm CaF_2 crystal window and the generated white light supercontinuum was polarized at the magic angle with respect to the pump. The white light was then split with a 50:50 broadband beam splitter aligned 45° to the incoming pulse and sent to 2 interferometer arms reflecting off a fixed mirror (M1) and a mirror mounted on a manual linear delay stage with an accuracy of $\sim 5 \mu\text{m}$ (M2) as shown in Figure 8.1. The two white light pulses were then reflected and transmitted through the beam splitter (BS) towards the sample with a time delay between them set by the difference in the Michelson interferometer arm length. After transmission through the sample the pulses were then diffracted by 1200 g/mm diffraction grating in Princeton Instruments Acton SP2150 spectrograph and read out at 3 kHz using a linear CMOS photodiode array (Imaging Solutions Group). The camera was mounted on a x-y-z manual translation stage allowing for an accurate spectral alignment. The pump-probe delay was varied using a retroreflector mounted on a computer controlled mechanical delay stage. Temporal experimental resolution was limited by the ~ 200 fs total instrument response function. Approximately 6000 shots were averaged at each time point and repeated for an average of four scans.

Figure 8.1. Frequency domain interferometer setup schematic.

8.3 Results and Discussion

8.3.1 Frequency domain interferometer

Here we describe the main working principles of the frequency domain interferometer experiment used to analyse the photoinduced refractive index changes in metal halide perovskites on the ultrafast timescale.

Frequency domain interferometry is based on the interference of two delayed white light beams on the multichannel detector after a temporal broadening induced by a diffraction grating. After the white light is split and sent out from Michelson interferometer the beams travel along the same optical path with a time delay between them as represented on the left side of Figure 8.2. However, after passing the diffraction grating the beams broaden resulting in a temporal overlap induced interference fringes recorded on the photodiode array (Fig. 8.2 right side). It is important to have an estimate of the induced beam broadening because if the initial temporal displacement of the two beams is too large, the interference will not be observed. On the other hand, if the beam displacement is very small while beam broadening condition is large, the obtained temporal range of the experiment will be unnecessarily lower than the attainable range which can also impact spectral resolution as discussed later.

Figure 8.2. Temporally displaced white light pulse schematic before (left) and after (right) diffraction grating induced broadening.

The angular diffraction grating geometry which causes beams to broaden is represented in Figure 8.3. The path difference is induced between light rays reflected from the

opposite ends of the grating leading to a temporal broadening of the beam. Temporal beam broadening is estimated via Equation 8.1.²²⁵

$$\Delta t = \frac{GLM\lambda_0}{c} \quad (8.1)$$

Where G is the groove density, L is the illumination width, M is the diffraction order, λ_0 is the wavelength and c is the speed of light.²²⁵ For an incident beam of about 2 mm in the region of 500-540 nm and grating of 1200 g/mm, the beam broadening is estimated to be ~5-6 ps.

Figure 8.3. Diffraction grating beam geometry schematic.

Figure 8.4 shows the spectral interference patterns observed when two white light pulses interfere after the diffraction grating. In one instance the pulses are delayed by 800 fs, which results in wide, high amplitude interference fringes, because of the good pulse overlap after the diffraction grating induced broadening of the pulses by about 5-6 ps. In the other case, the pulses are delayed by 2 ps, which results in less intense and narrower interference fringes as a result of reduced pulse overlap as defined by the cosine term in the wave Equation 8.2. A scaled spectrum with one Michelson interferometer arm blocked is shown to not produce any interference signatures, seen in two beam FDI mode.

The 800 fs displacement offers better spectral resolution of the interference features, however it limits the time range of the experiment to only about 800 fs which is expected to be too short to cover hot carrier evolution dynamics in perovskites, therefore the FDI measurements were carried out with 2 ps delay between the reference and probe pulses which gives intense enough interference fringes and required experimental time range. We note that the time delays longer than about 2 ps produced interference fringes that

were too weak to be clearly resolved because of the reduced pulse overlap. If even longer time range is required for the resolution of photoinduced refractive index changes that could cover effects lasting longer than about 2 ps, it can be achieved by using a different interferometry technique such as a space domain Sagnac interferometer.²²⁶ However, the setup cannot be implemented as a modification to the TA setup and it is highly sensitive to such effects as beam drift and given the sufficient time range offered by FDI is outside the scope of the current study.

Figure 8.4. Interference patterns measured in FDI mode with 2 ps and 800 fs delays between two white light pulses plotted against scaled spectrum obtained with probe beam only (reference Michelson interferometer arm blocked).

The FDI is used to extract the phase difference between the spectral interference patterns observed in pump on and pump off cases. Figure 8.5 shows an FDI measurement pulse diagram, where the chopped pump position in time can be changed by a variable delay stage. In the case where excitation pulse arrives between the two white light pulses, only one pulse experiences photoinduced refractive index change, while the other does not. This results in a phase shift of the observed interference fringes between pump on and pump off spectra which can be related to the refractive index change considering the electromagnetic wave equations describing the system. The interference spectrum without the excitation is defined in the Equation 8.2.²²⁷

$$|E_1(\omega) + E_2(\omega)|^2 = |E_1(\omega)|^2(2 + 2 \cos \omega T) \quad (8.2)$$

Where ω is the angular frequency, E_1 and E_2 is the electromagnetic field of probe and reference pulses respectively, T is the delay between the two white light pulses. While the interference spectrum with excitation is expressed in Equation 8.3.

$$|E_1(\omega, \tau) + E_2(\omega)|^2 = |E_1(\omega)|^2(1 + e^{-2\Delta K(\omega, \tau)} + 2e^{-\Delta K(\omega, \tau)} \cos[\omega T - \Delta\phi(\omega, \tau)]) \quad (8.3)$$

Where ΔK is the amplitude change and τ is the excitation pulse delay time. It is clear from the two equations that the phase difference between pump on and pump off interference spectra cases is governed only by the $\Delta\phi$ term which is defined in Equation 8.4.

$$\Delta\phi = \frac{-\Delta n \omega l}{c} \quad (8.4)$$

Rearranging Equation 8.4 gives the photoinduced change in the refractive index, which can be extracted by considering the phase difference of the interference fringes and thickness of the medium (Eq. 8.5).

$$\Delta n = \frac{-\Delta\phi c}{\omega l} \quad (8.5)$$

Where c is the speed of light and l is the thickness of the medium. In the other two experiment cases (Fig. 8.5a and c) where the pump arrives before and after both of the white light pulses pass the sample, phase results in the difference between the excitation modulated probe ($\Delta\phi(\omega, \tau - T)$) and reference ($\Delta\phi(\omega, \tau)$) pulses and no phase modulation respectively, these cases are not relevant to the current study. The different interferometer white light setup cases and temporal pump setup cases with the expected measurement signals are noted in Table 8.1 with the strong FDI phase difference response expected with the pump between the onsets of the two probe pulses.

Figure 8.5. Pulse diagram of FDI showing 2 ps temporal delay between the broadband light pulses and a variable time monochromatic pump pulse.

Table 8.1. Table diagram of setup signals expected to be observed with different white light configurations in interferometer and three excitation pump temporal position cases shown in Figure 8.5.

Setup	a)	b)	c)
Probe only	$\Delta T/T$ ($\tau=1$)	$\Delta T/T = 0$	$\Delta T/T = 0$
Reference only	$\Delta T/T$ ($\tau=3$)	$\Delta T/T$ ($\tau=1$)	$\Delta T/T = 0$
Probe + Reference	$\Delta\phi$ ($\tau=3$) - $\Delta\phi$ ($\tau=1$)	$\Delta\phi$ ($\tau=1$)	$\Delta\phi = 0$

One of the advantages of the frequency domain interferometer setup is that it allows to carry out standard transient absorption measurements by simply blocking one of the Michelson interferometer arms i.e. blocking M1 or M2 represented in Figure 8.1. We note that a possible improvement of the setup is an introduction of a mechanical chopper to the reference beam arm of the Michelson interferometer, which would then allow the FDI and standard TA dataset collection in a single measurement. Figure 8.6a and b shows the $\Delta T/T$ maps of probe only and reference only TA measurements obtained by blocking reference and probe Michelson interferometer arms respectively. Each of the measurements display closely matching TA spectra typical to the metal halide perovskite material family.^{190, 197, 199} The only significant difference between the two spectra is the onset of the TA signal. The probe only measurement signal arises at about 0 s and reference at about 2 ps. This is the temporal difference between the two white light pulses set in the interferometer, which was aligned by fixing the probe mirror (M1 in Fig. 8.1) to an arbitrary $t = 0$ s position and shifting the reference mirror (M2) using a manual

translation stage, while monitoring the onset of reference TA signal in relation to the $t = 0$ s time.

Figure 8.7a shows the $\Delta T/T$ surface obtained with both of the interferometer arms unblocked. We observe the cumulative-like contribution to the $\Delta T/T$ signal from both of the white light pulses with an appearance of fringe pattern in the spectrum. The GSB peak dynamics of the reference and probe TA as well as FDI in $\Delta T/T$ mode are presented in Figure 8.7b. We observe closely matching temporal feature onsets. The differences in early time signal magnitudes observed are induced by the different relative intensity change in the cumulative white light spectra. The $\Delta T/T$ mode representation of FDI measurement supports a conceptual explanation of the system, however the phase difference between the pump on and pump off spectra is the main parameter of interest in this case which allows for the extraction of photoinduced refractive index change.

Figure 8.6. CsPbBr₃ bulk film $\Delta T/T$ surface measured in the frequency domain interferometer setup with a) the probe beam only, b) the reference beam only.

Figure 8.7. a) CsPbBr₃ bulk film $\Delta T/T$ surface measured in the frequency domain interferometer setup with both probe and reference beams. b) 6 nm integral over the GSB peak feature peaking at 525 nm in $\Delta T/T$ measurements with probe only, reference only, probe and reference modes.

8.3.2 Phase difference extraction

In order to extract the phase difference values between the pump on and off interference spectra two methods were tested. Figure 8.8 shows a schematic of the pump induced spectral phase shift and the phase resolution methods.

The first method labelled ‘peak analysis’ sets a phase space by defining two adjacent pump off peaks as 2π , then the difference between the first pump off interference fringe peak and the corresponding pump on peak is taken as the phase shift in the defined phase space. The following pump off peak is then taken as the first peak and the phase space is redefined, repeating the method across the entire interference spectrum produces a phase difference spectrum. This method assumes low peak to peak phase space variation.

The second method is based on the discrete Fourier transform (DFT) and is computed using a fast Fourier transform (FFT) algorithm implemented with the help from Shyamal K. K. Prasad. A spectral range window covering at least one full interference oscillation signature in a pump on spectrum is created and FFT is carried out in the region which decomposes the interference signatures into constituent frequency components according to Equation 8.6 below.²²⁸

$$X_k = \sum_{n_s=0}^{N_s-1} x_n e^{-\frac{i2\pi kn_s}{N_s}} \quad (8.6)$$

Where X_k is a complex number and denotes amplitude and phase of frequency k , N_s is the number of samples, n_s is the considered sample. The most prominent extracted component is selected and its phase value is subtracted from the pump off shot phase value obtained from the corresponding window FFT analysis carried out on the pump off spectrum. The FFT window is then shifted by an increment spectral value and the same analysis is carried out on the new spectral window until the phase difference values are extracted over the whole interference spectral range.

Figure 8.8. Schematic of interference pattern phase shift between pump on and pump off shots with represented phase shift analysis methods.

Figure 8.9 shows a comparison between the phase difference spectra extracted using the two phase extraction methods. The two methods produce closely matching phase difference values, however the peak analysis provides a lower spectral resolution governed by the density of the interference fringes, while FFT allows for better spectral resolution set by the incremental FFT window shift. We will therefore use FFT analysis as the preferred phase difference extraction method. The high spectral resolution provided by the method appears unnecessarily noisy therefore we apply a LOESS smoothing which gives a clearer spectral representation of the data shown in Figure 8.9 (cyan trace). The upcoming figures of the phase difference and its derivative spectra will be presented using this smoothing method.

Figure 8.9. Phase difference spectra of CsPbBr₃ bulk film at 1.8 ps extracted via peak analysis and FFT methods displaying matching data profiles.

8.3.3 Change in refractive index coefficient of bulk metal halide perovskite

We investigate the obtained changes in the real part of the refractive index in CsPbBr₃ bulk films in relation to their temporal and excitation intensity dependence. We also use Kramers-Kronig relations to extract and analyse the photoinduced changes in the transmission coefficient.

FDI measurement was carried out on CsPbBr₃ bulk film over -1 ps to 200 ps time range and the FFT processing was applied to the interference spectra with and without excitation at each measured time point which allows to build a phase difference surface presented in Figure 8.10. We observe a zero phase change at times earlier than 0 s and a relatively strong signal until just after about 2 ps which quickly diminishes in later times, corresponding to the difference signal between the two phase changes of the reference and probe pulses. As expected the most pronounced region of phase change map lies between 0 s and 2 ps (Fig. 8.7a and b) which is when only the probe pulse interacts with the photoexcited medium and the reference does not. This strong photoinduced phase change region is directly related to the refractive index change as shown in Equation 8.4 allowing for a simple conversion to Δn .

Figure 8.10. Phase difference map of CsPbBr₃ bulk film extracted via FFT processing method.

Average sample thickness, which was used in the refractive index conversion was estimated to be 101.3 nm from Dektak thickness profile measurements taken by Parth Vashishtha. Figure 8.11a shows examples of the photoinduced refractive index change spectral profiles extracted from the FDI phase change measurements at varying excitation

fluences. Figure 8.11b shows an example of the temporal change in the refractive index evolution at low excitation fluence plotted against the blank film measurement of Δn . We observe the derivative-like spectra around the bandgap region expected for the refractive index change profiles in semiconductor materials.^{44, 229} The refractive index changes at different times with varying excitation densities for the high and low energy derivative profile peaks are shown in Figure 8.12. The refractive index behaviour differs at different times past photoexcitation and different energies. This complex behaviour is difficult to model accurately and measuring it directly is invaluable in such applications as laser design where the carrier density dependent refractive index change governs the cavity mode frequencies.²³⁰

Figure 8.11. a) Photoinduced refractive index change spectra of CsPbBr₃ bulk film at 1.8 ps over varying excitation fluences. b) Photoinduced refractive index change spectra of low fluence CsPbBr₃ bulk film measurement over different times plotted against 400 fs refractive index change spectra of a blank film measurement.

Figure 8.12. Refractive index change magnitude dependence on the fluence measured at 400 fs and 1.8 ps Δn spectra at high and low energy peaks.

We successfully use the FDI technique to directly probe the photoinduced refractive index changes in metal halide perovskite bulk films observing coefficient differences ranging from ~0.1 down to an order of 10^{-3} . These findings are vital in the design of nonlinear devices such as lasers, as any changes of material interaction with light can have a significant impact on the device functionality. However, to further explore this material analysis approach photoinduced changes in the transmission coefficient were extracted as well.

Kramers-Kronig (KK) relation is a mathematical method used to connect the real and imaginary parts of linear susceptibility, where susceptibility quantifies a change of an extensive property under the variation of an intensive property. The relations were first derived in 1920's and apply within a theory of analytic complex functions connecting the real part of an analytic function to an integral containing its imaginary part and vice versa. The KK relations have been widely used in linear optics in helping to characterize such system parameters as dielectric functions, refractive indices, absorption and gain.²³¹⁻²³² The KK relations are also applicable to nonlinear susceptibility change given the causality condition is satisfied for the response function, namely Equation 8.7.

$$Y(t_0) \propto x(t), \quad t \leq t_0 \quad (8.7)$$

Where Y is the system output, x is the system input, t_0 and t are the corresponding times, meaning the output of the system cannot depend on the future inputs.²³¹⁻²³²

Standard time-resolved transient absorption spectroscopy offers a way to monitor a change in the imaginary part of the nonlinear susceptibility, but its response can arise from a mixture of other different physical effects which complicates its relation to the real part of the refractive index. More importantly, KK relations cannot be applied to standard time-resolved TA spectroscopy methods because they break the causality condition as the excitation pulse causes a time-dependent change in the material state before it is probed with another pulse. This makes it impossible to resolve the real part of the linear susceptibility through standard KK relations using TA spectroscopy.

In the case of FDI method, however, the excitation pulse arrives between two white light pulses causing the phase modulation of the interference patterns. Under this system condition, it has been proven that the KK relations are valid allowing for the extraction

of the time-resolved change in the transmission coefficient.²³³ We apply the KK transformation method on the change of the refractive index data by implementing an inverse Hilbert transform algorithm in Matlab and extract the photoinduced changes in the transmission coefficient shown in Figure 8.13.

We note that the mathematical transformation can result in a loss of a function constant, potentially present in Δn surface. At low energies the transmission coefficient is expected to be zero and if it is the case in our KK transformed data that would prove the initial Δn function is not offset by a constant which would be lost after the KK transformation and result in an offset spectrum with a non-zero low energy transmission coefficient. Therefore, an extended spectral range measurement at $3.7 \mu\text{J}/\text{cm}^2$ fluence was carried out by measuring the FDI and TA signatures at three overlapping spectral windows. The CMOS camera was shifted in a dimension along the spectrum dispersed after the diffraction grating using a linear translation stage and measurements were carried out without changing any other parameters or setup. The obtained spectra were calibrated by fitting the TA profiles to $3.7 \mu\text{J}/\text{cm}^2$ TA measurement carried out with $150 \text{ g}/\text{mm}$ diffraction grating. The white light dispersed by $150 \text{ g}/\text{mm}$ diffraction grating allows to measure around 465 to 820 nm wavelength range which was calibrated using a set of notch filters. The narrow wavelength range provided by the $1200 \text{ g}/\text{mm}$ diffraction grating had to be used instead of $150 \text{ g}/\text{mm}$ in the FDI measurements due to small beam broadening induced ($\sim 700 \text{ fs}$) by the less dense grating. The long range measurement allows to check for any ambiguity which may be induced by the KK transformation as it can result in an offset, however as seen in Figure 8.13, no such effect appears to be present in the measurement as the ΔK reduces to 0 in the low energy range as expected. We also note that the KK transformations were carried out with the Δn profile outside the spectral measurement range fitted to another high energy range measurement profile and linear functions in order to minimize any boundary condition distortions.

Figure 8.13. Spectra of photoinduced changes in the refractive index and transmission coefficient extracted from the long spectral range $3.7 \mu\text{J}/\text{cm}^2$ CsPbBr₃ film FDI measurements at 1.5 ps overlaid with steady state absorbance spectrum on a relative scale.

8.3.4 Transmission coefficient TA signal

We use the change in the transmission coefficient to model a transient absorption response and compare it to the experimentally obtained TA response.

The obtained change in the transmission coefficient data can be converted to the apparent change in the absorption coefficient according to Equation 8.8.

$$\Delta\alpha = \frac{4\pi\Delta T_R}{\lambda} \quad (8.8)$$

Where λ is the wavelength. In turn, the change in the apparent absorption coefficient can be used to estimate the TA signal according to the following relationship (Eq. 8.9).¹⁸

$$\frac{\Delta T(\alpha)}{T} = -l * \Delta\alpha \quad (8.9)$$

Where l is the thickness of the medium.¹⁸ Figure 8.14 shows the estimated transmission coefficient based TA signal estimates plotted against TA and refractive index coefficient change spectra at two different time points. The estimate of the transmission coefficient profiles contributing to TA signal are in good agreement with the standard TA measurement spectra. The magnitudes are also closely matching, with a small deviation of ~15% between the TA estimate and experimental profile magnitudes at the spectral region where $\Delta n = 0$.

We discuss the small differences in magnitudes observed between the estimated and experimental TA profiles. In the range where the change in real part of refractive index is zero, the TA spectra would be expected to only contribute from ΔT_R and therefore the magnitudes between the experimental TA and apparent absorption coefficient TA contribution should be the same. The difference observed may mean that the GSB peak of the experimental TA is also contributing from effects like stimulated emission or it may arise as a scaling error from the sample thickness estimate, which in this case is likely the cause given similar scaling mismatch in below bandgap spectral profiles, where Δn is also close to zero (Fig. 8.14a) and limited accuracy of Dektak thickness measurements. The ΔT_R TA contribution profile scaled to match the TA magnitude at $\Delta n=0$ region is plotted against the experimental TA spectrum in Figure 8.15. Close spectral profile matches are observed supporting the accuracy of the FDI measurements. We note that in the nonlinear measurement case the transmission coefficient obtained through KK transformation includes contributions from changes in the absorption, reflection and sample scattering.²³²

Figure 8.14. Transient absorption spectrum and corresponding photoinduced changes in refractive index and transmission coefficients with estimated transmission coefficient change contribution to TA spectrum of CsPbBr₃ bulk film measured at a) 400 fs and b) 1.5 ps.

Figure 8.15. Experimental transient absorption spectrum plotted against the scaled ΔT_R contribution to the TA profile at 400 fs.

8.3.5 Nanocrystal FDI

Metal halide perovskite nanocrystals have become one of the most broadly researched perovskite fields due to their potential in property tunability and simple solution processing, perfect for cost-efficient device applications.^{18, 190, 234} However, the spectroscopic research of nanocrystals has been lagging behind the perovskite films. Unlike in bulk films, nanocrystal photorefractive response has not been well characterized as the NCs do not display a direct light reflection but rather scattering. This makes it impossible to examine the photoinduced reflectivity effect of nanocrystals in the simultaneous transmittance-reflection measurements, even with the large collection angle setup described in Chapter 7. We employ FDI in order to measure the ultrafast time-resolved changes in the refractive index response of CsPbBr₃ NCs.

We carried out FDI measurements on 8.6 nm CsPbBr₃ NC solution suspension. Figure 8.16 shows the experimental TA and the extracted relative Δn change. The coefficients are noted as relative values because the nanocrystal solution medium thickness is not clearly defined and in this case is taken as an arbitrary value approximately corresponding to the film layer thickness with a similar absorbance magnitude also limited by the cuvette thickness ($0 < l < 1$ mm). The thickness value only governs the magnitude scaling of the extracted refractive index coefficient change spectra, while the relative profiles remain unaffected. We observe CsPbBr₃ nanocrystal TA spectra similar to the spectra seen in CsPbBr₃ films in the standard TA measurement mode. We also observe a derivative-like

refractive index change profile which agrees well with the behaviour seen in the bulk films along with similar approximate magnitudes suggesting similar photorefractive effect influence on the sample properties and TA signals. Although the measurement accuracy can be limited by the assumptions on the medium thickness the setup allows for the extraction of broadband time-resolved photoinduced refractive index changes on an ultrafast timescale in NC suspensions underlining the versatility of the FDI method in measuring photorefractive effects in different systems. The data obtained can be used in device design or more accurate modelling of the measured materials.

Figure 8.16. Transient absorption spectrum and corresponding relative photoinduced changes in refractive index of CsPbBr₃ NC solution suspension measured at 1.5 ps after 15 $\mu\text{J}/\text{cm}^2$ 400 nm pump excitation.

8.3.6 Free carrier refractive index contribution

In this section we estimate the free carrier contribution to the change in the refractive index of perovskite films and find its dominant influence in the low energy end of the spectra. We then analyse perovskite film and nanocrystal behaviour differences in the steady and excited state spectroscopic measurements in relation to the excitonic and free carrier behaviour and show how the free carrier induced refractive index change at low energies can be used to isolate and monitor the free carrier dynamics in semiconductors. The analysis is important in deconvoluting exciton and free carrier semiconductor responses which govern device functionality. The approach also allows for the excited state analysis of highly absorbing materials such as large perovskite single crystals where standard TA measurements cannot be carried out around the strongly absorbing bandgap region.

We consider the free carrier contribution to the change in the refractive index. In Drude model, the plasma effect induced change in the refractive index is given by Equation 8.10.⁴⁴

$$\Delta n_{free\ carrier} = -\left(\frac{e^2 \lambda^2}{8\pi^2 c^2 \epsilon_0 n}\right) \left(\frac{N}{m_e} + \frac{P}{m_h}\right) \quad (8.10)$$

Where e is the elementary charge, λ is the wavelength, ϵ_0 is the vacuum permittivity, n is the unperturbed refractive index of the material averaging around 2 for CsPbBr₃ in the considered spectral region, m_e and m_h are the effective electron and hole masses respectively.^{44, 206} We plot the estimated free carrier contribution to Δn against the measured change in the refractive index in Figure 8.17. The free carrier contribution at high energies appears to be minimal in relation to the total change in the refractive index. However, as energies become lower the contribution from other effects such as band filling or bandgap renormalization decreases while free carrier effect increases as $\Delta n_{plasma} \propto \lambda^2$. At the lowest energies measured we see that free carrier induced change in the refractive index becomes the dominant contributor to the measured change in the refractive index as shown in the inset of Figure 8.17. This is a significant finding because it suggests that the free carrier dynamics can be isolated and monitored using the FDI method by measuring below bandgap Δn signal.

Figure 8.17. Experimental change in the refractive index spectrum at 1.8 ps of CsPbBr₃ 3.7 $\mu\text{J}/\text{cm}^2$ bulk film measurement and free carrier model contribution to the change in the refractive index. Inset: low energy end of the figure showing dominant free carrier contribution.

In the case of a typical bulk $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite material free carriers are expected to be generated almost immediately after the photoexcitation, with little exciton influence due to the low exciton binding energy considered to be lower than the room temperature energy ≤ 25 meV.^{197, 235} However, in CsPbBr_3 perovskites the binding energies are higher and estimated to be larger than the room thermal energy with 35 meV.²³⁶ Figure 8.18 shows normalized steady state absorption spectra of CsPbBr_3 bulk film and 8.6 nm NC sample. We observe a strong excitonic absorption peak at the band edge of CsPbBr_3 bulk film, which diminishes in the NC spectrum. This observation suggests stronger excitonic behaviour in films than in the 8.6 nm NCs. The effect is counter-intuitive because one would expect stronger exciton interaction in NCs due to the influence of quantum confinement. A similar counter-intuitive effect has also been previously observed in other perovskites. $\text{CH}_3\text{NH}_3\text{PbI}_3$ films which had larger grain sizes displayed stronger excitonic behaviour at low temperatures than films with smaller grain sizes.¹⁹⁵ A similar effect, observed here was also seen in other CsPbBr_3 studies.¹⁹⁶ The disappearance of the exciton induced absorption band in the steady state absorption spectra of NCs and films with smaller grain sizes was attributed to the reduction of exciton binding energy due to stronger surface effects in smaller bulk grains and NCs.¹⁹⁵ The effect counters the quantum confinement and therefore bulk films show stronger exciton behavior than NCs.

Figure 8.18. Normalized steady state absorption spectra of CsPbBr_3 bulk films and 8.6 nm NCs.

We also observe unexplained differences in the short time ultrafast charge carrier dynamics between the bulk films and NCs which may be related to the differences in exciton and free carrier behaviour. Figure 8.19 shows the band edge GSB dynamics

comparison between the excitation density matched CsPbBr₃ bulk film and nanocrystal TA measurements. We observe a rapid short time decay in bulk films which is not present in the NC dynamics. After about 2 ps rapid excited state evolution in bulk films the dynamics between the bulk films and NCs equalize and both of the samples appear to follow the same relaxation mechanism. Given the strong exciton influence in bulk films and the fact that excitons typically display lifetimes orders of magnitude shorter than free carrier lifetimes, the rapid evolution may be indicative of a presence of exciton population which rapidly recombines while the free carrier population remains present in the long times.¹⁹⁵

Figure 8.19. Normalized transient absorption kinetic traces integrated over 10 nm GSB peak of excitation density matched CsPbBr₃ bulk film and 8.6 nm NC solution.

We test this hypothesis by considering the intensity dependent TA dynamics. Figure 8.20 shows normalized intensity dependence of TA bulk film GSB kinetics and a trace of nanocrystal TA kinetics. At the lowest fluences we observe the strong short time decay signature in bulk films but as the excitation fluences increase, the feature gradually diminishes. At highest excitation fluence the bulk film dynamics match the dynamics profile of the free carrier NC system kinetics. This observation is in agreement with the suggested excitonic nature of the short time kinetics component seen in bulk CsPbBr₃ at low fluences. As the excitation fluence increases, the amount of charge carriers present in the material increases leading to multiple carrier Coulombic interactions which reduce exciton binding energies favouring free carrier formation. The mechanism is a typical carrier screening effect present in semiconductors.²⁶ The observations are consistent with the explanation of the short time TA kinetics feature seen arising from a presence of

exciton population in CsPbBr₃ perovskite bulk films, which appears to decay within 2 ps leaving the system with long lived free carriers.

Figure 8.20. Normalized transient absorption kinetics integrated 10 nm over GSB peak of CsPbBr₃ bulk film at different intensities plotted against nanocrystal TA kinetics.

We now compare the TA dynamics of CsPbBr₃ system with the evolution of Δn of bulk films in the low energy region where the free carriers are expected to dominate the signal according to the plasma model discussed earlier (Fig. 8.21). Free carrier dominated Δn region kinetics of the bulk film do not display the rapid exciton decay feature seen in the bulk film TA. Instead the Δn dynamics follow the excited state profile seen in the free carrier dominated NCs and high fluence bulk measurements rather than the excitonic low fluence bulk film signature. This supports the FDI as a method to isolate the free carrier dynamics, in this case showing that the rapid short time charge carrier evolution seen in bulk films at low fluences is not a signature of free carriers.

Figure 8.21. Normalized transient absorption kinetic traces integrated over 10 nm GSB peak of excitation density matched CsPbBr₃ bulk film and 8.6 nm NC solution plotted against normalized kinetics trace of free carrier dominated change in refractive index region (2.117 – 2.135 eV) of CsPbBr₃ bulk films.

We compare the Δn dynamics at different energies. At the band edge, the Δn dynamics show a pronounced short lived decay (Fig. 8.22), similar to the exciton dynamics seen in TA measurements. At this energy the free carrier contribution to the total Δn signal is small therefore the dynamics are not restricted to the free carrier evolution profile. The short time signature diminishes in Δn dynamics when monitored at high energies, where the hot carrier effects are most prominent. Hot carriers are expected to be less excitonic due to higher energies possessed in comparison to the carriers at the lowest energy band edge state and will not follow the same exciton influenced mechanism. Although the exciton signature is not present in lowest energy region Δn dynamics, it does not perfectly match the hot carrier Δn profile due to different effect contributions to Δn at higher energies in comparison to the lowest energy Δn where it is mainly dominated by the single free carrier contribution.

Figure 8.22. Normalized Δn kinetic traces taken at three different regions: low energy 2.34 eV region of the band edge, high energy 2.43 eV region where the hot carrier influence is well pronounced and at the lowest spectral range measured at 2.12 eV.

We model the free carrier contribution to the change in the refractive index and show relatively low plasma influence to the total refractive index change at the band edge and higher energies. The free carrier contribution, however, becomes dominant in the low energy region below the bandgap. We reveal that a rapidly decaying kinetics feature seen in the low fluence TA measurements of CsPbBr₃ is a signature of exciton population and use the low energy refractive index change dynamics to prove that FDI can be used to isolate the free charge carrier evolution. We show a significant presence of exciton population recombining within 2 ps in the low fluence CsPbBr₃ bulk film measurements, which may contribute to the reasons why CH₃NH₃ perovskite based photovoltaic devices typically perform better than the Cs based devices with over twice as high solar cell efficiencies, as CH₃NH₃ perovskites are expected to have lower exciton influence due to lower binding energies.^{234, 237} We note that similar strong short lived (~3 ps) exciton decays were also observed in orthorhombic CH₃NH₃PbI₃ perovskite phase at 77 K with significantly higher exciton binding energy than the room temperature crystal phase, while we observe it in CsPbBr₃ bulk films at room temperature which can have a significant impact on the device performance if the exciton influence is not taken into account or reduced by employing surface effects on the binding energy or other means.¹⁹⁵ We note that at lower energies the free carrier Δn signatures become stronger and the low energy Δn spectra could be used not only to obtain more accurate free carrier dynamics but could also be fitted according to the Drude plasma model in order to obtain such

parameters as unperturbed refractive index, carrier density or an estimate of effective carrier masses.

8.4 Conclusion

In summary, we have built a frequency domain interferometer and successfully used it to extract the photoinduced phase changes in CsPbBr_3 bulk films and nanocrystal suspensions. The time-resolved spectral changes in the real part of the refractive index were obtained and changes in the transmission coefficient were extracted via Kramers-Kronig relations. The transmission coefficient was used to model the transient absorption signals which agreed with the standard experimental TA measurements. Similar refractive index change profiles were measured between CsPbBr_3 bulk films and NC suspensions revealing comparable photorefractive effect responses and broad FDI method applicability. The direct measurement of the refractive index change also allowed for the estimate of the dominant region of free carrier contribution to the change in the refractive index which was used to isolate the free carrier dynamics. By analysing CsPbBr_3 perovskite spectroscopic data we showed that FDI could be used as a free carrier probe which could help deconvolute exciton and free carrier dynamics in various systems.

Conclusions and future directions

Research of new photovoltaic materials has become increasingly important with a rapid growth of photovoltaic device markets and advanced optoelectronic device development. A number of novel solution processed inorganic and hybrid photovoltaic materials have shown great potential in the field, however often their excited state properties are not well understood.

Materials like colloidal nanocrystals are highly appealing for large scale and low cost device applications. Simple printing and spraying manufacturing processes offered by them could transform industries such as the solar cell market. In addition, hybrid materials particularly metal halide perovskites have shown promise for advanced optoelectronic device applications like hot carrier or tandem photovoltaics, electrically pumped lasers and NOR flash memory. While attempts have been made to produce devices with these emerging materials, the lack of fundamental knowledge of charge carrier formation, trapping and relaxation processes does not allow for their comprehensive development and clear understanding of material limitations and true potential. Time-resolved femtosecond spectroscopy solves this problem as it allows to track charge carrier evolution processes. We use a range of spectroscopy methods such as differential reflectance, diffusion, interferometry, steady state and differential transient absorption spectroscopy to study a range of novel photovoltaic materials with a potential to revolutionize optoelectronic markets. Different colloidal nanocrystals were analysed in this work followed by an extensive examination of one the most widely researched emerging photovoltaic material classes: metal halide perovskites.

One of the studied photovoltaic materials, iron pyrite nanocrystals, offers the lowest material costs among the emerging photovoltaic technologies, however its application in devices has been hindered by poor performance due to active surface defect states. We analysed the effects of a novel iron pyrite nanocrystal surface passivation approach on the excited state dynamics. A range of nanocrystals were examined via transient absorption spectroscopy and the passivation technique was shown to have a significant effect on the nanoparticle properties. Iron pyrite nanocrystals passivated with a thin

coating layer of another semiconductor were shown to retain the excited state characteristics of the iron pyrite core while the surface state dynamics were governed by the shell material. The study revealed the effectiveness of the new iron pyrite surface defect passivation approach and supported its potential in solving the issues associated with poor material's performance in devices.

Another class of colloidal semiconductors, quaternary CZTS, provides a possibility of more extensive material property tunability and has displayed good performance in devices, although its potential has also been limited by prominent tendency to form sub-states. Transient absorption along with long range steady state and integrating sphere absorption spectroscopy techniques were used to investigate the sub-state effects on the characteristics of the material. CZTS nanocrystal behaviour was compared to CZTSe nanocrystals which tend to form with better phase purity and rapid band edge carrier relaxation to a broad defect distribution was discovered in CZTS samples. The defects limited the band edge carrier lifetimes and resulted in the appearance of plasmonic effects. The measurements revealed prominent defect state influence on the excited state dynamics of CZTS nanocrystals and underlined the need for efficient defect passivation or formation suppression for effective material performance in devices.

Established photovoltaic materials such as silicon have also been subject to new development approaches which could open up new application possibilities. The characteristics of silicon nanocrystals doped with transition metals have been investigated using transient absorption spectroscopy and steady state techniques. A range of silicon nanocrystals doped with three different elements were analysed and their behaviour was compared to the undoped silicon nanoparticles. Rapid exciton transfer to new dopant induced states which also influenced other material properties was discovered. Nanocrystal doping allows for enhanced tunability of material's characteristics, however our research suggests the dopant state effects must be taken into account in the consideration of doped silicon NC applications.

Extended work on the colloidal nanocrystals could involve their excited state analysis in functioning devices under varying bias conditions. Models of charge carrier transfer could be developed for the nanocrystal systems which would further help understand their functionality in devices. In addition, low temperature measurements could be carried out

which could help investigate material's fine band structure splitting and carrier coupling to phonons. Comparative or simultaneous measurements with time-resolved photoluminescence measurements could also be carried out giving better insight into system properties and more accurate analysis by isolating emissive state characteristics. Directions for future nanocrystal development for particular devices such as LEDs could be outlined taking carrier recombination mechanisms into account.

Metal halide perovskites have recently emerged as the leading novel photovoltaic material family. The materials displayed exceptional optoelectronic properties and a few years of their development in the solar cell field resulted in power conversion efficiencies well above any emerging photovoltaic materials. Despite extensive research efforts put into metal halide perovskites some fields like perovskite nanocrystals lacked characterization of their excited state dynamics. We analysed a range of CsPbBr₃ perovskite nanocrystals with varying sizes spanning different quantum confinement regimes using transient absorption spectroscopy and compared the findings to the bulk material properties. Comprehensive analysis of different quantum confinement effects was carried out considering state focusing, bandgap renormalization, degeneracy and carrier cooling dynamics. The results revealed that quantum confinement influence was most prominent for the smallest CsPbBr₃ nanocrystals which are currently available (~4 nm) while the more commonly examined larger nanocrystal photophysics was better described as a small perturbation on the free carrier photophysics established for the bulk material. Extension of this work could involve development of a defined-contribution carrier cooling model and examination of it and quantum confinement effects in even more strongly quantum confined NCs if methods for smaller particle synthesis were to be developed.

Transient absorption measurements of metal halide perovskites were found to display some anomalous features which were also observed across different perovskite literature. The features were previously attributed to a range of different mechanisms with no common agreement among the literature. We employed transient absorption and a range of differential reflectance measurements to study the anomalous excited state response of metal halide perovskites and contrary to the previous attributions proved it is a signature of a photorefractive effect. The effect was then further analysed using a frequency domain

interferometry technique. Photoinduced changes in the refractive index of metal halide perovskite films and NCs were resolved with a femtosecond time resolution. The broadband refractive index characterization is crucial for the design of such applications as optical switching, modulating and recording devices, probing techniques, lasers, single photon emitters and hot carrier solar cells. Further directions of this work could involve building of a longer temporal range interferometry setup for extended analysis of free carrier deconvolution method for TA measurements and analysis of excited state dynamics of highly absorbing materials such as large single crystals. In addition, a standardized setup could be built to simultaneously measure TA and photorefractive effects and used to re-address and accurately characterize the excited state dynamics of other high refractive index semiconductors.

Appendix 1 – Some metal halide perovskite ideas

Screening

Screening phenomenon occurs when carriers surrounding an exciton interfere with Coulombic electron-hole attraction reducing their excitonic behaviour and favouring free carrier system instead. With increasing excitation density of the sample the number of free surrounding carriers increases and their screening results in a system of free electrons. Due to this high excitation density the bandgap of the semiconductor reduces and in fact we directly observe this behaviour in our TA data: for highest excitation of ~9 nm perovskite NC sample the sub bandgap PIA which reflects band gap renormalization shifts to lower energies. We do not see this effect in smaller NC samples because of the lower excitation densities achieved. When it comes to time-resolved photoluminescence we do not see any fluence dependence in sample kinetics, this in fact is a signature of electron hole plasma (EHP) as this kind of system would not display recombination enhancement factor. Another signature of EHP is the broadening of the emission band (due to plasma density increase) and we observe this in our time-resolved photoluminescence spectra. This suggests charge screening in perovskites and supports free charge generation in perovskites rather than excitons.

The screening reduces the exciton binding energy but this effect can be compensated by the BG reduction. -> Mott insulator-metal transition, metallic character of perovskites possible through e-h plasma at high excitation densities.

Polaron perovskite cation relationship

This paper speculates polaron existence in $\text{CH}_3\text{NH}_3\text{PbX}_3$ perovskites.⁴³

Polaron- electron or hole that polarizes and locally deforms an ionic lattice.

CsPbBr_3 materials are highly ionic and thus well stoichiometric and ordered which in itself favours fewer defect states.⁵⁷ However, even in nanocrystals with significant

proportion of surface dangling bonds which could introduce midgap trap states we do not observe strong trapping influence. Although, it is estimated that CsPbBr_3 effective carrier masses stand around $0.15m_{e/h}$ which are similar to the $\text{CH}_3\text{NH}_3\text{PbX}_3$ perovskite effective mass values. Carriers with such low masses would in fact be heavily affected by scattering via LO phonons and defect states which would result in short carrier lifetimes, meaning that they must be protected from scattering. The small effective mass estimates are of electron before it's dressed in nuclear polarization and the paper puts polaron mass in $\text{CH}_3\text{NH}_3\text{PbX}$ between 10 to $300m_e$. It is because a polaron propagating through a lattice is strongly mass-enhanced, because of the lattice distortion it has to coherently carry along.

The formation of polaron is also favoured by the fact that carrier mobility in perovskites is rather slow given such small effective mass estimates. In prototypical semiconductors with similar effective carrier mass carrier mobilities are 1-2 orders of magnitude higher. This difference can be explained by a presence of high mass polarons. With electron-phonon interactions (Frohlich mechanism) occurring in polar semiconductors and ionic crystals such as lead halide perovskites.

The polarons are relatively common but in this paper⁴³ it's speculated in $\text{CH}_3\text{NH}_3\text{PbX}_3$ they may be quite unique due to two interpenetrating lattices of PbX^- for carrier transport and CH_3NH_3^+ which is more susceptible to geometric deformation including motion of the permanent dipole of CH_3NH_3^+ in each organic cage. The authors have signified that the organic CH_3NH_3 sublattice with its dipole moment reorientation plays a unique role in stabilizing and localizing charge carriers, however in our case where the complex CH_3NH_3 cation is replaced by plain Cs atoms we still observe similar polaronic trends in charge behaviour as in $\text{CH}_3\text{NH}_3\text{PBX}_3$ perovskites suggesting a common mechanism. In support to this the cooling timescales of the hot carriers observed in $\text{CH}_3\text{NH}_3\text{PbX}_3$ perovskites are comparable to those of CsPbX_3 perovskites which could be both consistent with the formation of a large polaron. In this paper the formation was speculated to be due to reorientation/wobbling of the CH_3NH_3^+ cations but clearly if present the polaron formation is there when CH_3NH_3^+ is also replaced with Cs atoms.

Extra note from the paper:

Such spatially distinct polaron with e/h in PbX^- sublattice and polarization cloud in CH_3NH_3^+ sublattice can be seen as interfacial Frohlich polaron which is formed at an interface between e.g. semiconductor and a polarizable dielectric material. Similarly, polarons can form at the internal “interfaces” of the two sublattices in hybrid perovskites, giving rise to the charge carrier properties attractive for solar cells or other optoelectronics.

Charge induced lattice deformation

In insulators and semiconductors, both organic and inorganic, where the crystal constituents are electronically closed shells, the interionic repulsion does not allow ions to move closer than the distance of a lattice constant during crystallization. However, if the crystal is excited, the excitation of individual constituents relaxes the strong repulsive character between sites in the neighbourhood of an excitation. This allows ions to move closer and a localised lattice deformation gets automatically formed at the excited lattice site. Considering we observe this as a long range effect (as the polaron considered in perovskites is large) it changes the lattice binding parameters over a long range resulting in a change in dielectric constant of the material hence the photoinduced reflectivity increase observed as PIA in TA. Higher relative polaron influence can result in increasing above bandgap PIA with decreasing crystal size.

Smaller crystal lattice may be physically easier to deform and injected charges strain a larger proportion of the lattice. Hence the crystal gets more deformed when a carrier is present leading to the change of its fundamental parameters such as dielectric constant. We could potentially monitor this deformation by observing the above bandgap PIA which directly follows the charge kinetics and concentration as it would be expected for this case. This effect results in larger above bandgap PIA observed with decreasing crystal size as the deformation potential increases. ‘It is predicted than in QDs polar carrier coupling to LO phonons should be strongly reduced comparing to bulk systems, however coupling via deformation potential is predicted to be enhanced by a factor proportional to R^{-2} (r-dot radius).’

Hysteresis

Snaith *et. al.*²³⁸ describes the anomalous perovskite hysteresis as combined effect of ion migration through the perovskite and trapping of charge carriers at the perovskite interfaces. The mechanisms of the two in perovskites are not well known, especially the ion migration.

Under applied bias carriers are forced towards the perovskite-electron transport material interfaces where the long range polaron loses its effective mass with reducing coupling to the perovskite lattice. This in turn increases its susceptibility to trapping which is well present at the interface states, hence the trapping effects observed which would normally be minimal with large polarons present.

In some systems non-radiative carrier recombination can be permeated by creation of defects which could be the mechanism responsible for the ion transport based hysteresis in perovskites. Given an electronic excitation is localized at some atom (as per our polaron system) occupying a regular lattice position (in perovskites it's probably PbX section), relaxation of such an excited atom into ground state can proceed in the following way: the released excitation energy is transferred to the relevant atom as a whole, which is thus 'kicked off' into an interstitial lattice position, creating a so-called Frenkel defect (a vacancy plus interstitial atom). This defect can be either transient or permanent depending on whether the interstitial atom does or does not return into its original lattice site once the excitation is terminated. From literature the diffusion (required for hysteresis) of such vacancies or interstitial atoms comes from the thermal energy of atomic vibrations. The binding to other atoms of these interstitials is usually relatively weak and they can diffuse through easily. This hysteresis mechanism could essentially be polaron permeated/generated. In order for this non radiative recombination to make possible the following criteria must be fulfilled:

1. Localization of electronic excitation must occur. Happens when the photoexcited electrons and holes move through the lattice slowly. Polarons are perfect candidates for this, i.e. perovskites.
2. Energy of self-trapped exciton must be higher than the energy of defect formation. The energy required for an atom to jump to interstitial position is around 1.5-3.5 eV, i.e. which means that the creation of such defect is mainly a feature of wide-

bandgap semiconductors with a high fraction of ionic bonding. Perovskites are good candidates for this.

3. Protection against heat. The phonon mode concerned should belong to local modes resulting from an increase of spring constant around the localized excitation. (Limits spread of the heat via LO phonons over entire crystal, from Michael Price's *et. al.* paper suggestion LO phonon interaction is weak (after possible polaron formation) and may also be permeated by low E phonons (acoustic)).
4. Orientation criterion. The localized excitation should have a suitable symmetry in the crystal lattice so that creation of interstitial atom is energetically favourable.

This gives good ground to the existence of ionic hysteresis mechanism and supports the idea of polarons.

In addition to this the kinetics mismatch between TA and PL is discussed, in the other measurements we established PL fluence is independent in the EHP, however we did observe fluence dependence in the TA which is permeated through the interacting non-radiative recombination mechanisms such as the defect-ion transport mechanism described above. And in general the high electron phonon coupling favours the non-radiative (phonon permeated) recombination. 'Non-radiative recombination of a localized centre via local phonon emission becomes very efficient, provided the centre is in strong enough interaction with the lattice.' Relatively low quantum yield as well as strong TA-PL kinetics mismatch indicates that this may be the case.

Points:

In support that the screening may be present within the perovskite lattice (due to dipole polarization or other), we observed faster PL with decreasing NC size. That means when the crystal becomes smaller the Coulombic coupling between e- and h+ can be increasing which is normally screened in the lattice. This results in much higher radiative recombination efficiency observed in TRPL kinetics in smaller crystals. The same effect may play a combined (via phonon) role in the higher deformation of the lattice seen as increasing above bandgap PIA in smaller crystals. This may also contribute to the higher band gap renormalization in smaller crystals as the Coulombic interaction is strengthened.

Effective polaron mass within a smaller lattice (less long-range electron-phonon coupling) may be smaller therefore the shorter lifetimes seen in TA (/combination of shorter PL).

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