Untangling the ultrafast charge dynamics in colloidal quantum dots – charge trapping, charge transfer, and multiple exciton generation

A thesis submitted to The University of Manchester for the degree of Doctor of Philosophy in the Faculty of Science and Engineering

2017

Charles T Smith

The Photon Science Institute
School of Physics and Astronomy
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<tr>
<td>ADC</td>
<td>Analogue to digital converter</td>
</tr>
<tr>
<td>AMT</td>
<td>Auger mediated trapping</td>
</tr>
<tr>
<td>AOM</td>
<td>Acousto-optic modulator</td>
</tr>
<tr>
<td>BE</td>
<td>Binding energy</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>CBM</td>
<td>Conduction band minimum</td>
</tr>
<tr>
<td>CFD</td>
<td>Constant fraction discriminator</td>
</tr>
<tr>
<td>CPS</td>
<td>Counts per second</td>
</tr>
<tr>
<td>CQD</td>
<td>Colloidal quantum dot</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous wave</td>
</tr>
<tr>
<td>EHP</td>
<td>Electron-hole pair</td>
</tr>
<tr>
<td>EHPM</td>
<td>Electron-hole pair multiplication</td>
</tr>
<tr>
<td>FRET</td>
<td>Förster resonance energy transfer</td>
</tr>
<tr>
<td>EVET</td>
<td>Electronic-to-vibrational energy transfer</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
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<tr>
<td>GTI</td>
<td>Gires-Tournois interferometer</td>
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<td>GVD</td>
<td>Group velocity dispersion</td>
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<tr>
<td>HAADF</td>
<td>High angle annular dark field</td>
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<tr>
<td>IRF</td>
<td>Instrument response function</td>
</tr>
<tr>
<td>LEAM</td>
<td>Lowest energy absorption maximum</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MCP</td>
<td>Micro-channel plate</td>
</tr>
<tr>
<td>MEG</td>
<td>Multiple exciton generation</td>
</tr>
<tr>
<td>MPA</td>
<td>3-mercaptopropionic acid</td>
</tr>
<tr>
<td>ND</td>
<td>Neutral density</td>
</tr>
<tr>
<td>OD</td>
<td>Optical density</td>
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<tr>
<td>ODE</td>
<td>Ordinary differential equation</td>
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<tr>
<td>OPA</td>
<td>Optical parametric amplifier</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<td>--------------</td>
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<tr>
<td>PA</td>
<td>Photo-induced absorption</td>
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<tr>
<td>PL</td>
<td>Photoluminescence</td>
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<tr>
<td>PLE</td>
<td>Photoluminescence excitation</td>
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<tr>
<td>PLQY</td>
<td>Photoluminescence quantum yield</td>
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<tr>
<td>PMT</td>
<td>Photomultiplier tube</td>
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<tr>
<td>Q</td>
<td>Quinone (in Chapter 5)</td>
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<tr>
<td>QD</td>
<td>Quantum Dot</td>
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<tr>
<td>QY</td>
<td>Quantum yield (of MEG)</td>
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<tr>
<td>SDG</td>
<td>Synchronization and Delay Generator</td>
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<td>SHG</td>
<td>Second harmonic generation</td>
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<tr>
<td>SPM</td>
<td>Self-phase modulation</td>
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<tr>
<td>SRA</td>
<td>Stimulated Raman amplification</td>
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<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
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<td>TA</td>
<td>Transient Absorption</td>
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<tr>
<td>TAC</td>
<td>Time to amplitude converter</td>
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<tr>
<td>TCSPC</td>
<td>Time correlated single photon counting</td>
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<td>TDPA</td>
<td>Tetradecylphosphonic acid</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<td>THG</td>
<td>Third harmonic generation</td>
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<td>TOP</td>
<td>Triocetylphosphine</td>
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<tr>
<td>TPA</td>
<td>Two-photon absorption</td>
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<tr>
<td>UTA</td>
<td>Ultrafast transient absorption</td>
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<tr>
<td>UV</td>
<td>Ultra violet</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
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<tr>
<td>VBM</td>
<td>Valence band minimum</td>
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<td>WLC</td>
<td>White light continuum</td>
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<td>XPM</td>
<td>Cross phase modulation</td>
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<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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Abstract

In this thesis the charge dynamics in novel colloidal quantum dots (QDs) are investigated using ultrafast transient absorption spectroscopy, and other complementary spectroscopic techniques, to examine the mechanisms and rates of charge carrier relaxation on sub-nanosecond timescales. A deeper understanding of specific charge relaxation processes in various QD systems is achieved, with implications for the optimisation and understanding of quantum dot applications, particularly for the enhancement of QD sensitised photovoltaics.

Surface mediated charge trapping is a process which reduces the efficiency of QD based devices and complicates the analysis of QD charge dynamics. We compare the dynamics in CdTe QDs before and after surface treatment with chloride ions which we show to be capable of completely eliminating trapping, evidenced by attaining near unity photoluminescence quantum yields. This unique comparison enabled isolation of the effects of traps which has not been achieved by any other studies. Both hot and cold electron trapping processes are identified, which if unrecognised in other QD studies could lead to significant misinterpretation of results.

Charge transfer in quinone conjugated CdTe/CdS QDs is investigated for a range of average acceptor to quantum dot ratios. The charge transfer process competes with radiative recombination, resulting in efficient quenching of the PL intensity with promising applications in bio-sensors. A complex behaviour in the charge dynamics is discovered which suggests a relationship between charge transfer and surface mediated charge trapping.

We report the first measurement of multiple exciton generation (MEG) in quasi-Type II core/shell InP/CdS QDs. The quantum yield of MEG is found to be $1.22 \pm 0.01$ for an excitation photon energy equivalent to three times the band gap. This is comparable to Type I InP core/shell QDs, but the quasi-Type II structure brings several effects which have the potential to enhance device performance. The enhancement to solar cell efficiency expected from such effects are demonstrated using the Detailed Balance model.
Lay abstract

In a conventional solar cell, electrons in a semiconducting material absorb sunlight. The electrons then rapidly lose energy in the form of waste heat, by falling to the semiconductor’s band gap. This is one of the main reasons that the theoretical efficiency of a solar cell is limited to ~33%. However, an alternative process, multiple exciton generation (MEG), can occur in quantum dots (QDs). Here, some or all of the wasted energy is instead used to excite additional electrons, potentially increasing the electrical current of a solar cell and thereby its output efficiency.

QDs are microscopic semiconductor spheres of a few dozen atoms across. They have significantly different optical and electronic properties compared to large semiconductors. In addition to the process of MEG being more likely, the colour and energy of light which is efficiently absorbed and emitted can be controlled by growing different sizes of QD. This tuning of their optical properties makes QDs useful for a large range of applications in nanotechnology, which include light emitting diodes (LEDs), displays, and most promisingly, as the absorbing species in solar cells. If MEG can be optimised, the efficiency limit of a solar cell increases to 44%.

Currently, the efficiency of many QD based devices falls significantly short of the theoretical limit, primarily due to the effects of surface related charge trapping. This is a process which is not yet fully understood, but limits the potential of any QD based device. In this thesis, the interaction of charges and light in several different types of QD are measured using ultra-short laser pulses. These include: i) a surface treatment for CdTe QDs which can completely eliminate charge trapping, enabling the first ever isolation of the effects of trapping; ii) investigation of electron transfer between CdTe/CdS QDs and molecules attached to their surface; and iii) the first ever measurement of the efficiency of MEG in InP/CdS QDs. In each case, several new insights and models are developed which enhance the understanding of ultrafast charge interactions for the scientific community.
Declaration

Some of this work was carried out as part of a wider collaborative project. Data obtained by other PhD students, and used in their PhD theses, has been included to support the interpretation of the data obtained by the candidate, and this has been clearly indicated throughout this thesis. In particular, Figure 4-2 was used in the theses of Daniel Espinobarro-Velazquez, Robert Page and Hanna Radtke, a portion of the data from Figure 4-6 was used in the thesis of Daniel Espinobarro-Velazquez, and Figure 4-8 was used in the thesis of Daniel Espinobarro-Velazquez, all submitted to The University of Manchester. Data from Figure 7-2 was used in the thesis of Edward Tyrrell submitted to the University of Salford. These results were also used for the following jointly authored publications:


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List of publications and presentations


Conference posters


Book contribution

Acknowledgements

I would like to thank my supervisor, Dr David Binks, for his unwavering support and guidance throughout the course of this project. I am grateful for all of the advice and time you have given me, particularly for the help in preparing this thesis and our published works. You are a credit to the University and are unsurpassable as a PhD supervisor.

Secondly I wish to thank my postdoc, Dr Marina Leontiadou, for your support, not only with the equipment throughout this project but in so many other aspects of our work, including proof reading of this thesis. I wish to thank all the researchers we have collaborated with over the past three years, particularly those who worked with David Binks under the Enhanced MEG project, and those who established, maintained, and educated me on the experimental setups which I have used- Marina Leontiadou, Daniel Espinobarro-Velazquez, Ali Al-Otaify, Musa Cadirci, Stuart Stubbs, Samantha Hardman, Ben Spencer and Darren Graham. This work would not have been possible without the chemists who synthesised the samples, Robert Page, Claire Lydon, and Andrew Harvie. I thank you not only for your work but for your patience with my chemistry knowledge.

I would like to thank my wife Jill for her care, love and encouragement not only over this PhD, but throughout my studies at The University of Manchester. Finally, I thank Oliver, for countless discussions and problem solving sessions; our friendship which has grown over the last three years has been an invaluable contribution to the enjoyment of this degree.

I acknowledge funding for my studentship from the Engineering and Physical Sciences Research Council (EPSRC) in the form of a Doctoral Training Award.

The work in this thesis was also funded by the EPSRC under grant EP/K008544/1.
Chapter 1. Introduction

1.1. Introduction – Quantum dots and their applications

Quantum dots (QDs) are nano-scale semiconductor crystals where confinement of excited charges within the QD volume leads to significant modifications of their optoelectronic properties compared to bulk materials. The emergent properties can be exploited for many scientific and technological applications, and has led to the development of an exciting new area of semiconductor research over the last two decades focused on the engineering of charge carrier interactions on the nano-scale.

The unique properties of QDs arise from confinement of charges in three spatial dimensions; this restricts the allowed energy-momentum states to atomic-like orbitals delocalised through the QD volume. Careful chemical synthesis allows control of the crystal size, enabling tuning of these energy states, and causes alterations in the probability of different interactions between charges, light, and the environment. The control of such properties means that QDs are often considered artificial atoms, which can be tailored to specific applications.

Some processes become significantly more efficient in QDs compared to bulk materials due to quantum confinement [1-2], and can be controlled not only through the QD size but also their structure. For instance, growing a second semiconducting material around a QD to form core/shell structures can enable confinement of charges to specific regions of the structure, sometimes referred to as wavefunction engineering [3]. This enables a degree of control over carrier interactions which is not possible in bulk materials.

Restriction of charge carriers to atomic-like orbitals results in narrow optical absorption and emission bands; combined with confinement effects, this can lead to highly efficient photoluminescence (PL). The tunability of these bands makes QDs useful for tailoring to a large number of applications which are still areas of active research. These include light emitting diodes (LEDs) [4], displays [4], photodetectors [5], bioanalysis [6-7], and the gain medium in lasers [8]. Figure 1-1
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illustrates this tuning of the emission properties by control of the diameter of CdSe QDs.

Figure 1-1. Illustration of the tunability of the photoluminescence (PL) emission from CdSe QDs through control of the nanocrystal diameter (Dia.). The central image is a photograph taken under 365 nm excitation. Reprinted with permission from [7]. Copyright 2017 American Chemical Society.

A process which is expected to be significantly enhanced in QDs relative to bulk materials is multiple exciton generation (MEG), which has the potential to considerably enhance the efficiency of photovoltaic devices [9-10]. In a conventional solar cell, the maximum theoretical efficiency is limited to ~33% [11]; one of the primary reasons for this is that the energy of an absorbed photon in excess of the semiconductor band gap is rapidly lost as heat within the first few picoseconds after excitation. However, under MEG, some or all of the excess energy is instead used to excite one or more additional electrons, potentially increasing the photocurrent of a solar cell and thereby its output efficiency [12]. This process is significantly enhanced in QDs due to the confinement of charges within the QD volume. MEG makes photovoltaics one of the most promising applications for QDs, and has motivated much of the research into QDs over the last decade [9]. Synthesising a QD which has both efficient MEG and a band gap suitable to absorb a significant
fraction of solar radiation is an achievement which is highly sought after in QD research.

Many of the charge relaxation processes in QDs, such as MEG, the dissipation of energy as heat, and charge extraction, occur on sub-nanosecond timescales. These processes can be studied through the use of ultrafast lasers, which are ideally suited for both the excitation and the measurement of excited carriers in the narrow optical transitions of QDs. The primary technique used in this work is ultrafast transient absorption (TA) spectroscopy, a pump-probe technique which utilises hundred femtosecond laser pulses. These are sufficiently short to observe the rapid relaxation of charge carriers. However, the high intensity of the pulses can produce a series of experimental artefacts which must be carefully considered. This technique enables the determination of the rates of the different charge cooling and recombination pathways within QDs, which are of primary concern throughout this study.

A full understanding and control of the many physical interactions in QDs is yet to be achieved; perhaps the most challenging aspect is the presence of surface mediated charge trapping. Charge trapping can occur on picosecond to nanosecond timescales to compete with MEG, PL, and other processes, to reduce the efficiency of QD based devices. The elimination of trapping is key to unlocking the full potential of QDs, but has only been partially achieved in a select few structures. Historically, trapping has been particularly challenging for the community because it is strongly dependent on the properties of the surface of the QDs, which can vary significantly with the conditions of their preparation and handling [13-14]. The prevalence of trapping can even vary significantly between identical synthetic routines, and it can mimic the signatures of many other charge relaxation processes in spectroscopic studies. The identification of trapping and its competition with other charge relaxation mechanism is one of the central focuses of this thesis.

1.2. Thesis outline

This thesis begins with an overview of the physics necessary to understand the origin of QD’s optoelectronic properties. Particularly, how confinement of charges within a semiconducting sphere of a few nm in diameter leads to behaviour which is distinct from the properties of bulk semiconductors, and how these properties can be tuned
by the size and composition of the QD. Following this, a review of the charge relaxation processes which can occur in QDs is presented along with their relative rates and dependence on the QD’s properties. A review of the most studied QD materials is then presented, with a focus on their motivation for study and their applicability in nanotechnology.

Chapter 3 describes the experimental techniques used in this study for investigation of the optoelectronic properties of QDs. They can be broadly split into steady-state and time-resolved spectroscopic techniques, with the latter being used to investigate the sub-ns charge dynamics in QDs. The primary technique used is TA spectroscopy, for which a thorough description of the analysis techniques required for correctly interpreting the dynamics is given.

In Chapter 4, PL and ultrafast carrier relaxation are investigated in CdTe QDs before and after treatment with chloride ions. The chloride treatment is shown to be capable of completely eliminating non-radiative charge recombination in these QDs by the achievement of near-unity photoluminescence quantum yield (PLQY) [15]. This enables isolation of the effects of surface trapping on QD carrier dynamics by the comparison of trapping and trap-free QDs, which has not been achieved by any other studies [16]. The excitation dependence of the trapping dynamics are explored, where the presence of both hot and cold electron trapping are identified and characterised with significant implications for future QD studies.

In Chapter 5, charge transfer from CdTe/CdS QDs to quinone ligands bound to their surface is investigated. The charge transfer process competes with radiative recombination, resulting in significant quenching of the PL intensity. The transfer process is sensitive to the redox state of the system, such that the QDs have the potential for use as redox sensors in biological systems [17-18]. Steady-state and time-resolved spectroscopic results are presented for a range of different quantities of quinone molecule attached to the surface of the QDs to alter the efficiency of the quenching process.

In Chapter 6, we describe the first reported measurement of MEG in quasi-Type II core/shell InP/CdS QDs [19]. The efficiency of MEG is found to be comparable to Type I InP core/shell QDs [20]. However the quasi-Type II band alignment of the
core/shell structure contributes several effects which have the potential to enhance device performance. These effects include enhanced electron extraction [3], extended charge carrier lifetimes [19, 21] and additional band edge tuning through controlling the shell diameter [19]. Measurement of MEG in these QDs was particularly challenging due to high sample absorbance at photon energies above the MEG threshold, combined with the requirement to use low fluences to prevent two-photon absorption, resulting in a significantly reduced signal quality. These circumstances led to the development of a new analysis technique for determining the MEG yield for highly absorbing samples with poor signal to noise levels.

Chapter 7 describes work which was undertaken on theoretical models which explore the interaction between the various charge relaxation processes studied experimentally. In particular, their dependence on structure is demonstrated by modelling the enhancement a core/shell structure can bring to the performance of QD-sensitised solar cells exploiting MEG [19, 22]. Cd-based QDs were chosen as the model system for this work because they are the most studied, and hence best characterised, type of QD, and were also studied experimentally throughout this project.

1.3. References

Chapter 1  

Introduction


Chapter 2. Quantum dots – background and theory

2.1. Introduction

Quantum dots (QDs) are nano-scale semiconductor crystals, where confinement of excited charges within the QD volume leads to modifications of the allowed energy levels and the efficiency of different interactions between charges, light, and the environment. There is much expectation that QDs have the potential to significantly enhance the performance of many optoelectronic devices, primarily due to their size-tuneable properties for tailoring to specific applications. However, a full understanding of the many physical interactions is yet to be achieved by the scientific community. This has attracted the attention of a large number of research groups across the globe, and led to a rapidly developing area of research.

Due to a dramatic variation of QD properties with structure, composition and handling, a large number of often conflicting reports on the properties of ostensibly similar QDs have been published, often requiring new theoretical models to explain observed phenomena. This variation can be particularly large in colloidal quantum dots (CQDs), which are the focus of this thesis. In this chapter the QD theory presented will focus on the physics common to all QDs, with a focus on the properties most relevant to the systems studied in this work and reported in Chapters 4 – 7. A brief review of the most studied QD systems is also given, focusing on the motivation for their study in each case.

2.2. Energy levels and charge confinement

We begin with an overview of the atomic and solid state theory which is essential to understand the origin of the charge confinement, energy level formation and strong size-dependant properties which arise in quantum dots, and are the key to their applicability in nanotechnology. The physical models described here are fundamental to the field of solid state physics, however it should be noted that some of these models are simplified pictures for general cases, aiming only to qualitatively explain the origin of QD properties. A more rigorous approach is beyond the scope of this discussion, and in some cases involves theories still under development and in
need of experimental backing. Several excellent books have been written which explore the problems in more depth [1-2].

The possible states of an electron in an atom can be described by quantum mechanics through the four-fold scheme of quantum numbers, \( n, l, m_l, \) and \( m_s \). These refer to solutions to the Schrödinger equation, which describes the probability distribution over space for the electron in a given state in terms of a wavefunction, \( \Psi(\vec{r}) \). A single electron is limited to each state (solution) by the Pauli exclusion principle. \( n \) is the principal quantum number with values \( (1,2,3...) \), which correspond to successively higher energy solutions to the radial part of spherical solutions to the Schrödinger equation [3]. Each of these levels is split according to the remaining quantum numbers, which is known as atomic fine structure: Orbital splitting, which depends on the intrinsic orbital angular momentum of the state, governed by the orbital quantum number, \( l = (0,1,2...n-1) \), typically labelled (s, p, d...). Spin splitting, which depends on the alignment of the spins of multiple electrons given by their spin quantum number, \( m_s = \pm 1/2 \). Spin-orbit splitting according to the total angular momentum, \( l \pm s \), where \( s \) is the electron intrinsic angular momentum with value 1/2. And finally, splitting due to external interactions such as a magnetic field, where the levels are further split according to the \( z \)-component of the angular momentum, or magnetic quantum number, \( m_l = (-l \rightarrow l) \) called the Zeeman effect, alternatively splitting due to an electric field is called the Stark effect [3].

In bulk crystals the proximity of the many atomic orbitals leads to the formation of wide dense energy bands, a continuum of energy levels which can have gaps according to the original atomic level spacing and the degree of overlap. The density of levels in these bands is sufficiently high that the fine structure of atomic orbitals is lost, however the concepts will be analogous to the discussions to follow. The bands can overlap such that electrons are free to move through the crystal in unoccupied states given a small amount of energy provided either thermally or by an electric field, such materials are metals, which readily conduct electricity. Alternatively a band gap between the highest filled band, known as the valence band (VB) and the first empty band, the conduction band (CB), can form; a large band gap results in the material acting as an insulator. Crystals with a small gap, such that the occupation of the empty band is easily altered by changes in temperature or an electric field, are
semiconductors, where this variable conductivity is the property which makes them invaluable in many electronic components.

The occupation of the energy bands is best described by Fermi-Dirac statistics, which govern the thermodynamics of a distribution of identical particles which obey the Pauli exclusion principle: for a thermal distribution of identical particles with half integer spin (fermions) at temperature $T$, the probability that a state with energy $E$ is occupied is given by

$$F(E,T) = \frac{1}{e^{(E-E_F)/k_BT} + 1}$$

where $k_B$ is Boltzmann’s constant and $E_F$ is the Fermi level. If there is a state at the Fermi level, it will have a 50% chance of being occupied. The Fermi function is illustrated in Figure 2-1 at high temperature and at 0K. The Fermi level is on the order of electron volts, whereas the thermal energy $kT$ is only 0.026 eV at 300K, which is the average kinetic energy of the particles in the distribution. At 0K, the function equals 1 below the Fermi level and 0 above, which is called the Fermi energy.

For conductors the Fermi level lies within an energy band, whereas for insulators and semiconductors it lies within the band gap, such that a semiconductor at 0K will have no electrons in the conduction band, and at higher temperature a small fraction of electrons will have enough thermal energy to cross into the conduction band, this is also illustrated in Figure 2-1. Although the Fermi function has a value for energies inside the band gap, there are no states, and thus no electron population at those energies. For a description of the electron population (rather than the probability of occupation at a given level), the Fermi function must be multiplied by the density of states, a concept which will be discussed later in this chapter.
Figure 2-1. Illustration of the Fermi function and its effect on the occupation of the conduction and valence bands in a semiconductor at 0K, left, and at high temperature, right. The population of thermally excited electrons is represented in the conduction band in red.

The absence of electrons in the valence band allows the movement of the remaining valence band electrons into the vacancies. Rather than considering the motion of the many valence band electrons, the movement of the vacancy left by an excited electron can be considered as a quasi-particle which we call a **hole**, sometimes called an electron-hole, with positive charge. Just as electrons cool to occupy the lowest available energy states, we can equally consider a hole to move to occupy the highest energy electron states, i.e. the lowest energy state for the system has the valence band holes at the top of the valence band. It can also be appropriate to consider the valence band to contain empty hole levels when the system is in the ground state. It is the creation of electron-hole pairs (EHPs) by light with energy corresponding to excited electron and hole states which makes optical spectroscopy a powerful tool for determining the electronic properties of semiconductors.

The electron and hole created by the absorption of light can have a significant interaction energy associated with them as a result of their charge, a Coulomb...
interaction. This interaction becomes noticeable in quantum confined systems where
the electron and hole wavefunctions have significant overlap; the combined electron
and hole are then known as an exciton, and have an associated exciton binding
energy. This binding energy is strongly size dependent, and can result in a sub-band
below the band edge absorption \[4\]; this is used to create quantum-well lasers. There
is an additional binding energy associated with multi-excitons, which will be shown
to be an important interaction in quantum dots when considering the efficiency of
multiple exciton generation, and observing spectral features in transient absorption
spectroscopy.

The excited electrons or holes are free to move through the crystal (to conduct),
where they have an associated linear momentum, given by quantum mechanics as
\[ p = \hbar k \], where \( \hbar \) is the reduced Plank’s constant and \( k \) is the wave vector. The
possible combinations of kinetic energy and potential energy from the energy bands
is known as the band structure. From the classical expression for the kinetic energy
of a particle, \[ E_k = \frac{p^2}{2m} \], we can write

\[
E_k = \frac{\hbar^2 k^2}{2m}
\]  

(2-2)

This relationship is known as the dispersion relationship, or dispersion curve, in the
free electron model, or Somerfield model \[4\]. However, this model is completely
isotropic and predicts the same band structure for any material.

The energy band is significantly modified as a result of the periodicity of the lattice,
where the charges experience a periodic potential due to the atomic nuclei in the
crystal, which will vary depending on the direction of travel. The full, repeating band
structure can be derived using the nearly free electron model \[4\], which assumes
non-interacting electrons. It relies on Bloch’s theorem \[3\], which provides solutions
to the Schrödinger equation for a charge in a periodic potential. These solutions are
the product of two functions, one with the periodicity of the lattice, \( u_{nk}(\vec{r}) \), and a
plane wave:

\[
\Psi_{nk}(\vec{r}) = u_{nk}(\vec{r})e^{i\vec{k} \cdot \vec{r}}
\]  

(2-3)
where the index $n$ labels the different energy bands, and $k$ is an index corresponding to the wave vector of the particle, which fixes the particle momentum; the result is the quantisation of the particles’ possible momenta due to the periodic lattice. This is known as the crystal momentum. Each component of $k$ is limited to any linear combination of reciprocal lattice vectors, which for a crystal unit cell with sides of length, $L$, are given by

$$k_x = \frac{2\pi n_x}{L}; \quad k_y = \frac{2\pi n_y}{L}; \quad k_z = \frac{2\pi n_z}{L},$$  \hspace{1cm} (2-4)

where $n_x$, $n_y$ and $n_z$ are integers (0,1,2…) and the complete set of vectors $k$ is called the reciprocal lattice, or $k$-space. This model changes the dispersion curve, such that the total energy for a charge in the valence band relative to the conduction band minimum (CBM) close to $k = 0$ is

$$E_T = \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m^*} + E_g$$  \hspace{1cm} (2-5)

where $E_g$ is the band gap energy, and $m^*$ is the effective mass of the particle; both electron and hole in the crystal structure respond to forces very differently to a charge in free space, primarily due to interaction with the periodic potential of the lattice. In the nearly free electron model, this complicated response can be incorporated by the effective mass. $m^*$ is expressed in terms of the electron rest mass, $m_0$, where typical values of $m^*$ are $(0.01 – 10)m_0$, depending on the material [2, 4-5]. This mass affects the curvature of the dispersion relationship, and has important implications for the transfer of momentum between particles, and will later be shown to be critically important to the efficiency of solar devices. A complete description of the nearly free electron model finds that the band structure remains very similar to the parabolic dispersion relationship near $k = 0$. However, additional band gaps open up at unit cell boundaries in $k$-space where the parabolic bands cross, a qualitative example is shown in Figure 2-2. Significant deviation from this model arises due to the periodicity and structure of the crystal lattice, and degeneracy of the bands involved, where additional bands can overlap, each with different effective masses, and thus different dispersion relations.
Figure 2-2. Illustration of the periodic band structure resulting from the *nearly free electron* model, showing the underlying parabolic bands which remain good approximations close to \( k = 0 \).

From the quantisation of \( k \)-space emerges a very important limitation on the distribution of possible energies for the excited charges, which leads to some particularly interesting results for crystals with physically small dimensions. Just as in the atomic case, the Pauli exclusion principle limits the number of fermions which can occupy each state; we can say that only two electrons (spin up and spin down) can exist with momentum \( k(n_x, n_y, n_z) \), and that each unit cell in \( k \)-space has a volume \((2\pi/L)^3\) for each state. Combining this with the dispersion relationship, it is possible to determine the density of states at a given energy, \( \rho(E) \). For bulk materials, this gives \( \rho(E) \propto \sqrt{E} \). This result is, perhaps surprisingly, independent of \( L \). Multiplication of \( \rho(E) \) and the Fermi function (Equation (2-1)), gives the relative number of charges with energy \( E \).

Charge carriers are spatially confined within the crystal surface, an effect which this discussion has ignored until now. The surface places a rigid boundary condition on the extent of the electron and hole wavefunctions. If one of the dimensions of the crystal is comparable to the natural length scale of the electron or hole, quantum confinement effects come into play. This is known as the *quantum size effect* [6-7] and limits the possible values of \( k \) in the corresponding dimension, and thereby has a dramatic effect on \( \rho(E) \). A convenient length scale to consider utilizes the Bohr radius, \( a_B \), for an arbitrary charge carrier, given by [6-7]:

\[
\frac{2\pi}{a_B} = \frac{\hbar^2}{m^* e^2} \]
\[ a_B = \epsilon \frac{m_0}{m^*} a_0 \]  

(2-6)

where \( \epsilon \) is the dielectric constant of the material, and \( a_0 \) is the Bohr radius of the hydrogen atom. We can define three confinement regimes [8] which consider the Bohr radii of the electron, \( a_e \), hole \( a_h \) and the electron-hole pair, or exciton, \( a_{exc} \), relative to the relevant crystal dimension, \( a \):

- **Strong confinement regime:** \( a < a_e, a_h, a_{exc} \)
- **Intermediate confinement regime:** \( a_h < a < a_e, a_{exc} \)
- **Weak confinement regime:** \( a_e, a_h < a < a_{exc} \)

The confinement regime will influence the electronic structure of the valence and conduction band and the interaction of the electrons and holes therein. \( a_{exc} \) is a hydrogen-like bound state resulting from Coulomb interaction across the band gap of the electron and hole, where \( m^{-1}_{exc} = m^{-1}_e + m^{-1}_h \), and defines the length scale at which the charges begin to “feel” the boundaries of the crystal [7].

Confinement in one dimension, limiting k-space to a 2D system, results in the formation of a quantum well, where we can fix one of \( n_x, n_y, n_z \) to zero. Confinement to two dimensions, a 1D system, to fix two of \( n_x, n_y, n_z \) to zero, forms a quantum wire. Re-calculating the density of states for these systems results in a significantly different relationship to that of bulk materials, where it scales with dimensionality, \( d \), as

\[ \rho(E) \propto E^{(d-2)/2}, \quad d = 1,2,3 \]  

(2-7)

Finally confinement in all three dimensions forms a quantum dot, often referred to as a zero-dimensional system, where the density of states becomes a series of delta functions, closely resembling that of an atom or small molecule. The density of states for each of these systems is illustrated in Figure 2-3. For quantum dots, the typical crystal diameters are a few nm, but can extend to 10s of nm for materials with large \( a_B \) for one carrier or the other.
2.2.1. Particle in a sphere model

The description of the confinement regimes and the effect on the density of states is useful, but does not provide a description of the size dependant properties of quantum dots. Such a description can be achieved using the simple model of a “particle in a sphere” [8-10], which holds many similarities to the atomic confinement described earlier and is analogous to the classic physics problem of a particle in an infinite square well [6-7].

Following the works of Norris [6], and Krauss and Peterson [7], under strong confinement (\( a < a_e, a_h, a_{exc} \)), we can consider the electron and hole separately, and each to be confined in a symmetric potential, \( V \), defined by

\[
V(r) = \begin{cases} 
0 & r \leq a, \\
\infty & r \geq a, 
\end{cases}
\]  

(2-8)

where \( a \) is the sphere radius. For this potential, the solutions to the Schrödinger
equation are given by the product of radial and angular eigenfunctions:

$$\Psi_{n,l,m}(r, \theta, \phi) = C j_l(k_{n,l}r)Y_l^m(\theta, \phi), \quad (2-9)$$

where $C$ is a normalisation constant, $Y_l^m(\theta, \phi)$ are spherical harmonics, and $j_l(k_{n,l}r)$ is an $l^{th}$ order spherical Bessel function, which mandates that the wavefunction must be zero at the sphere boundary by requiring that the wave vector is $k_{n,l} = \alpha_{n,l}/a$, where $\alpha_{n,l}$ is the $n^{th}$ zero of the $l^{th}$ order spherical Bessel function. The energy of the particle (charge carrier) is given by

$$E_{n,l} = \frac{\hbar^2 \alpha_{n,l}^2}{2m^*a^2} \quad (2-10)$$

This expression is identical to that of a free particle (Equation (2-2)), except the wavevector is quantised by the boundary conditions imposed by the sphere. The expression is proportional to $1/a^2$, and is therefore strongly dependant on the size of the sphere and can be used to explain the strongly size dependant properties of quantum dots. The quantum numbers $n(1, 2, 3\ldots), l(s, p, d\ldots)$ and $m$ are analogous to those of atomic orbitals described at the start of Section 2.2.

These key attributes of the particle-in-a-sphere model are preserved if we consider a more realistic model, where rather than the charges occupying an empty sphere, we consider the periodic lattice of the crystal and the resulting potential. As in the bulk case described in the previous section, Bloch’s theorem, Equation (2-3), can be modified for the QD system using the envelope function approximation [11-12]: We assume that $u_{nk}(\vec{r})$, which accounts for the periodicity of the atomic potential, is the same in a QD as in bulk materials for $k = 0$, but not elsewhere (in $k$-space) due to the loss of translational symmetry. The remainder of the equation consists of a linear combination of plane waves which form an envelope function, $f$, which satisfies the spherical boundary conditions. The wavefunction is then given by:

$$\Psi_n(\vec{r}) = u_{n0}(\vec{r}) \sum_k C_{nk} e^{i\vec{k} \cdot \vec{r}} = u_{n0}(\vec{r})f(\vec{r}) \quad (2-11)$$
where $C_{nk}$ are expansion coefficients. The solutions to the envelope function are the same as those of Equation (2-9), such that the resulting wavefunction of the particle becomes the product of three terms, relating to the unit cell of the crystal, $u$, a spherical Bessel function that satisfies the boundary conditions of the crystal surface, $j$, and spherical harmonics, $Y$. The total wavefunction for an excited electron-hole pair in a QD can thus be written as

$$
\Psi_{ehp}(\vec{r}_e, \vec{r}_h) = \Psi_e(\vec{r}_e)\Psi_h(\vec{r}_h)
= C \left[ u_{cL_e}(k_{n_e,L_e}r_e)L^m_e \right] \left[ u_{vL_h}(k_{n_h,L_h}r_h)L^m_h \right]
$$

(2-12)

where the subscripts $c$ and $v$ refer to the conduction and valence bands respectively, and each state is defined by the electron and hole quantum numbers $n_e, L_e$ and $n_h, L_h$ respectively.

The energy of the corresponding levels for each solution to Equation (2-12) can be described by Equation (2-10), where we make the approximation that the carrier effective masses are the same as those in bulk materials. While the energy of each state scales as $1/a^2$, the electric potential between the electron and hole scale as $1/a$. This confinement energy can be expected to provide a significant contribution to the total energy. Under strong confinement the quadratic term dominates, and the electron and hole can each be treated independently as a particle-in-a-sphere, with the Coulomb term added as a first-order energy correction, $E_c$. The total energy of an electron-hole pair, $E_{ehp}$, can now be written as:

$$
E_{ehp}(n_e, L_e, n_h, L_h) = E_g + \frac{\hbar^2}{2a^2} \left( \frac{\alpha_{n_e,L_e}^2}{m_{e eff}^e} + \frac{\alpha_{n_h,L_h}^2}{m_{eff}^h} \right) - E_c
$$

(2-13)

where $E_g$ is the band gap of the equivalent bulk material, and $m_{eff}^{e,h}$ are the effective masses of the electron in the conduction band and hole in the valence band respectively [2]. Equations (2-12) and (2-13) are usually referred to as the particle in a sphere solutions to the QD spectrum. Figure 2-4 compares the resulting band structure to bulk materials. $E_c$ can be calculated from perturbation theory and is equal to $1.8e^2/4\pi\varepsilon a$, where $\varepsilon$ is the dielectric permittivity [13].
Figure 2-4. Dispersion curves for the conduction and valence bands in a bulk semiconductor, a), and in a quantum dot, b), where optical transitions, \( E = \hbar \nu \), are discrete due to the quantization of the bulk bands, according to the particle in a sphere model [6].

Thus, quantum dots function as large artificial atoms, with atomic like states with Bohr radii and energy level spacing larger than that of individual atoms. The tuning of these states can be achieved by size control of the particles during synthesis, which will be discussed in the next chapter. As in the atomic model, energy levels can be predicted which adhere to the same four quantum numbers described at the start of this section. However, due to the complex structure of quantum dots and additional charge carrier interactions, significant deviations from this model occur, the brief, qualitative results of which are discussed in the next section.

### 2.2.2. Realistic band structures in quantum dots

The single band model described so far is suitable to understand the conduction band structure in many QD systems. However additional considerations are required to explain phenomena related to holes in the valence band which are important to this work. The valence band in many bulk III-V and II-VI semiconductors arises from atomic orbitals with high degeneracy, such as for CdSe, where the conduction and valence bands arise from two-fold degenerate Cd 5s orbitals and six-fold degenerate Se 4p orbitals respectively. As a result, a multiband model is typically used to
describe the valence band [6], where the single band is replaced with 3 sub-bands termed the “heavy hole”, “light hole” and “split off” bands. These arise due to spin-orbit coupling, such that the light and heavy hole bands, which only diverge away from $k = 0$, have a total angular momentum $J = l + s = 3/2$, and the split off band with $J = 1/2$ lies deeper in the valence band. In a QD, each of these sub-bands can be considered to accommodate charges in the same manner as the single band in the particle in a sphere model, such that the resulting valence band structure in the QD is much denser than it is in the conduction band. This model is illustrated for different semiconductors in Figure 2-5.

![Figure 2-5](image)

Figure 2-5. Illustration of typical valance and conduction band dispersion curves (left) for typical III-V and II-VI semiconductors (top) and in IV-VI semiconductors (bottom), and the resulting quantum dot energy structures (right). In II-V and II-VI semiconductors, high valence band degeneracy results in splitting of the band into heavy hole (hh), light hole (lh) and split-off (so) bands. Reprinted with permission from Reference [7].

More advanced quantum mechanical treatments of the QD band structure can be performed which expand on the substructures of the two bands by considering effects such as differing orbital degeneracies, crystal structure (where the symmetry can have a significant effect), quantum dot shape, edge effects, and impurities. The primary methods are $k \cdot p$ theory which accounts for the coupling between individual
bands to analytically calculate a complete band structure [6-7, 14], and atomistic models, which builds up the band structure from a linear combination of atomic orbitals [6-7, 15]. Both approaches have been used to effectively calculate band structures and simulate electronic transitions and their competing effects in quantum dots [16-18]. Data from $k \cdot p$ calculations is used in Chapter 7 for the modelling of QD-sensitised solar cell efficiencies. Current theoretical studies using these advanced techniques have shifted their focus from the calculation of higher energy levels and band structures, to the effect of the QD surface on the charge dynamics and its interaction with the environment, with charge trapping and non-radiative recombination at the forefront. For the majority of this work however, it is sufficient to understand the band gap transition and its tunability, the thinning of the band structure from a continuum to discrete energy levels (particularly in the conduction band) and the resulting limitations on transitions due to momentum conservation and state filling.

### 2.3. Interaction with light – absorption and optical transitions

Spectroscopic techniques for measuring the electronic properties of quantum dots rely on the absorption and emission of photons between electron-hole pairs in the band structure described in Section 2.2. It can be convenient to consider transitions between excitonic states (electron-hole pairs) or to consider the electron and holes separately, as intra-band transitions can also be useful experimentally.

Following Norris [6], the probability to make an optical transition from the ground state, $|0\rangle$, to a particular electron-hole pair state, $|\Psi_{ehp}\rangle$, is given by the dipole matrix element

$$P = \left| \langle \Psi_{ehp} | \vec{e} \cdot \hat{p} | 0 \rangle \right|^2$$  \hspace{1cm} (2-14)

where $\vec{e}$ is the polarisation vector of the light, and $\hat{p}$ is the momentum operator. The carriers can be treated independently under the strong confinement regime, such that this can be written in terms of the single particle states:

$$P = \left| \langle \Psi_e | \vec{e} \cdot \hat{p} | \Psi_h \rangle \right|^2$$  \hspace{1cm} (2-15)
After inserting the wavefunctions described by the particle in a sphere model, Equation (2-12), this expression can be simplified due to the orthogonality of the envelope functions, giving

\[ P = |\langle u_e | \hat{e} \cdot \hat{p} | \Psi_{u_h} \rangle|^2 \delta_{n_e, n_h} \delta_{L_e L_h} \]  

(2-16)

where \( \delta_{n_e, n_h} \) are delta functions, which yield the simple dipole allowed optical transition selection rules \( \Delta n = 0 \) and \( \Delta L = 0 \). Thus, only optical transitions between matching \( nL \) states of the electron and hole can occur, Figure 2-6 illustrates the first three such transitions predicted by the particle-in-a-sphere model. These selection rules effectively enforce the conservation of momentum between the charge carriers.

![Figure 2-6. Illustration of the lowest energy (hν) optical transitions for a quantum dot (QD) in its ground state from the particle-in-a-sphere model, and the effect of changing the QD diameter. The energy levels are labelled according to the quantum numbers \( n = 1 \) and \( l = 1,2,3 \) (S,P,D) in Equation (2-13). Reprinted with permission from Reference [7].](image)

In the previous section, the splitting of the valence band into several sub-bands, each with atomic like quantised energy levels was described. However, this model fails to describe experimental absorption structures accurately, where additional splitting and unexpected size dependence of transitions occurs for deeper valence band states [6, 19]. The observed behaviour has been explained by mixing between the bulk valence bands, and mixing between the QD envelope functions (f) and unit cell functions (u), an effect termed S-D mixing [6-7]. The key result, is that the total QD
angular momentum has contributions from the bulk valence bands \((J = n + l)\) and its envelope function \((L)\), such that it is the total angular momentum, \(F = J + L\), which is conserved, resulting in a relaxation of the \(\Delta n = 0\) and \(\Delta L = 0\) selection rules. The valence band transitions are therefore labelled \(nLF\). For example, the lowest hole state with \(n = 1, L = S\) and \(F = 3/2\) is labelled \(1S_{3/2}\), whilst the lowest electron state (in the conduction band) remains \(1S\). Together they form the transition labelled \(1S(e)\!-\!1S_{3/2}(h)\), often lower case letters are used to distinguish electron states, becoming \(1s1S_{3/2}\). Another notable prediction of S-D mixing is the presence of a “dark exciton” in Wurtzite (hexagonal structure) CdSe QDs [20]. In these QDs, elongation of the unit cell results in prolate shaped QDs, which enhances the fine structure splitting of the valence band maximum to 10-15 meV, where the ground state to first excited state excitonic transition is optically forbidden due to requiring a net angular momentum change of 2. This was used to explain a large Stokes shift in such samples and an anomalously long photoluminescence lifetime [21-22].

Each optically allowed transition contributes a peak to the absorption spectrum of the sample. Each peak is inhomogeneously broadened, typically to 10s of meV for a colloidal quantum dot sample, such that after the first peak they overlap significantly. The origin of this width is lifetime broadening, thermal broadening, and size dispersion of the dots in the sample, where a typical CQD sample has a size dispersion of \(\sim10\%\) [23]. It is also typical that higher transitions are broader, which may be a result of more complex fine structure splitting due to the higher angular momentum of the energy levels [19]. At high energy, the absorption spectrum becomes featureless and rapidly rises monotonically. It is often modelled as a cubic background [19], where the absorption resembles that of bulk materials due to the high spectral density of transitions [24]. Figure 2-7 shows an example absorbance spectrum for CdTe QDs, and shows how the spectrum can be fit to a series of peaks with a cubic background. The experimental technique for measurement of QD absorption spectra will be described in Chapter 3, and a demonstration of the assignment of these peaks to optical transitions will arise in Chapter 4.
The absorption of light by a single quantum dot is difficult to isolate experimentally, and can be equally difficult to calculate theoretically due to the environment of the QD and contributions from surface ligands or shells, although the relative intensity of absorption peaks and their energies can see excellent agreement with predictions based on calculated band structures [16, 25]. The absolute absorption of a dot can vary dramatically based on the dielectric environment (of the solvent or polymer in which the QD is located), and also on the species of ligand and anchoring moiety used [26].

2.4. Core/shell QD structures

The formation of core/shell QD heterostructures is one of the most studied methods of controlling the interaction of excited charges both with each other and with their environment, where a nominally spherical QD of one material is surrounded by one or more layers of different semiconductor materials. The ease of synthesising core/shell particles of different combinations of semiconductor depends on the similarity of their crystal structures. It is important to match both the structure of the unit cell (cubic, tetragonal, hexagonal, etc.) and the lattice constant (size of the unit cell). A mismatch can lead to the formation of crystal defects and dislocations, which can act as centres for non-radiative charge cooling or trapping (to be discussed in Section 2.5.4), or can lead to lattice strain and the establishment of a crystal field.
which influences the electronic potential, and can result in band structure shifts [27]. The structure of the shell typically follows the template of the core, but can change to its natural bulk structure in the case of thick shells [28].

There are three main types of core/shell QD which can be formed depending on the relative band gaps and band alignments of the materials, each of which are illustrated in Figure 2-8. The first is known at a Type I QD, where the band gap of the shelling material(s) is significantly larger than that of the core, and overlaps both in the valence band and conduction band. As a result, both electron and hole are confined to the core material in their first excited state, and sometimes a number of the subsequent states. The purpose of the shell layer(s) is to act as a barrier between the photo-generated charges and the QD surface, which reduces surface-mediated relaxation and recombination, to be discussed in Section 2.5.4. Common choices of shelling semiconductor are ZnS and ZnSe [29-36] for their particularly large band gap [37].

A Type II heterostructure is formed when the band offset results in one of the carriers being confined to the core and the other to the shell when in their first excited state (at the band edge), see Figure 2-8. This dramatically reduces the wavefunction overlap between the two carriers, significantly reducing any
interaction between them, and also isolates one of the two carriers from the surface, while enhancing the interaction of the other carrier with the surface (unless a second, high band gap shell is also present). An intermediate case exists, known as a quasi-Type II structure, where one of the carriers is delocalised across both core and shell, while the other is confined to only the core or shell. This allows isolation or exposure of only one of the carriers from the surface, while maintaining electron and hole interaction. Each of the possible carrier interactions along with how different structures influence them will be discussed over the next few sections. Quasi Type II CQDs are investigated in Chapters 5 and 6.

For all types of core/shell QD, changing the diameter of the core and/or the thickness of the shell(s) will have an effect on the energy levels in both the core and the shell simultaneously [16]. This is because the carrier wavefunctions will penetrate into any barrier which is not of infinite potential, and result in a reduction in the confinement effects which lead to the enhanced energy level separation. This penetration is illustrated qualitatively in Figure 2-8, and is crucial for the interaction of carriers isolated in different parts of the structure. This size dependence and its potential effects on solar cell efficiency are modelled in Chapter 7.

### 2.5. Charge relaxation and recombination

An excited charge inside a QD will relax and dissipate its energy as it would in bulk materials, returning the system to its energetic ground state, for which there are many relaxation pathways available. This dissipation occurs through interaction with other charge carriers – both excited and in their ground states, interaction with the quantum dot crystal lattice, interaction with external fields and species, or escape from the QD. It is the competition between these pathways and the manipulation of their efficiencies which is of primary interest throughout this work. It is often convenient to consider each possible pathway individually with a characteristic rate (or lifetime), which can span several orders of magnitude. Some of the processes are dramatically enhanced by the quantum confinement effects in QDs, while being unnoticeable in bulk materials, and nearly all of the effects can exhibit strong size dependence, primarily due to the change in QD energy levels, but also due to changes in exciton binding energies [38] and surface geometries [18].
In this section the key relaxation pathways are discussed in terms of their mechanism, typical lifetimes, manipulation and utility. The relaxation process is typically referred to as *cooling*; many of the relaxation processes to be discussed only act on charges which have not yet cooled to the band edge, often referred to as *hot* charges, whilst band edge charges are referred to as *cooled* charges, which are yet to completely relax to the ground state – an unexcited QD.

### 2.5.1. Phonon cooling

In a periodic, elastic, arrangement of atoms, such as the crystal lattice of a semiconducting material, vibrations can form with a characteristic energy and are considered as a quasi-particle known as a phonon. In bulk semiconductors phonon emission, often referred to as phonon cooling, provides a fast intra-band relaxation pathway for excited charges as phonon energies can span multiple level separations. This is the primary mechanism for intra-band charge cooling down to the band edge in bulk materials, with cooling typically taking less than a ps. This is also an important cooling mechanism in QDs, however, the enhanced energy level separation dramatically reduces the rate of phonon cooling [39-40]; the process is typically limited to adjacent levels by emission of higher energy phonons, or the requirement of multi-phonon interactions, which have a significantly reduced probability. The large energy level spacing in the case of strong confinement in QDs led to the prediction of the formation of phonon-bottlenecks [40-41], spaces large enough to significantly reduce the phonon cooling rate in QDs, making other potentially beneficial processes such as multiple exciton generation (MEG) more likely. This competition can be fine-tuned by adjusting the energy level spacings through size control of the QDs, and the shell thickness in core/shell structures [16].

Phonon energies are of the order of 26 meV in bulk materials [42-43]. Theoretical models predict the existence of multiple energy level spacings larger than this energy in QDs [16], which could function as phonon bottlenecks to significantly slow cooling. Early theoretical work assumed that coupling to lattice phonons was the only important mechanism for intra-band charge cooling [40]. However, experimental studies found there to be an absence of any evidence of a phonon bottleneck, with cooling to the band edge typically taking only a few ps. This was
resolved by considering the possibility of other ultrafast cooling mechanisms which can circumvent the phonon bottleneck, principally Auger cooling mechanisms (discussed in detail in Section 2.5.3). A hot electron in the conduction band can transfer its excess energy to a hole in the valence band [44], known as Auger cooling, where due to the typically denser electronic structure (especially if in the intermediate confinement regime) the hole can more readily dissipate the energy through phonon interactions. This interaction is one motivation for the separation of electron and hole in a Type II core/shell QD as discussed in Section 2.4. Other mechanisms for bypassing the phonon-bottleneck also exist, such as relaxing via a defect induced trap state or energy transfer (to be discussed in Sections 2.5.4 and 2.5.5). These mechanisms for electron and hole phonon cooling are illustrated in Figure 2-9a.

In a crystal at non-zero temperature, there will be a distribution of phonons due to thermal excitations. It is this distribution that is responsible for the temperature of the crystal, and can be thought of as a gas of phonons, where they can be created and destroyed by random fluctuations. When in thermal equilibrium, the energy and distribution of excited phonon states scales with temperature according to Bose-Einstein statistics, where the number of phonons with a given energy increases with $k_B T$, the details of which can be found elsewhere [4]. This thermal distribution of phonons can interact with the charges in semiconductors, where they can assist in higher energy cooling mechanisms by accounting for any energy mismatch between the initial and final states, for which they are highly suited due to the broad distribution of comparatively low energy phonon states. Studies of QDs with temperature variation can reveal this behaviour; it has been shown that the absorption and photoluminescence of QDs can be strongly dependent on temperature [43], where in PbS QDs excitation by phonons is required to escape the dark exciton state described in Section 2.2.2. However, even at very low temperatures, electrons still cool to the band edge, because spontaneous phonon emission is independent of temperature [42]. It has also been suggested that a phonon participates in Auger interactions between excited charges in CdTe QDs [45]; it was suspected that MEG could be phonon assisted in order to compensate for energy mismatches, although this has been ruled out in PbSe QDs [42].
Figure 2-9. Illustrations of the key charge relaxation processes which can occur in quantum dots, see main text for detailed descriptions of each process. a) Phonon cooling, where typically multiple phonon interactions are required for electron cooling. b) Photoluminescence, the slightly higher energy first absorption peak is also shown. c) Auger recombination (left), and Auger cooling (right) where a hole can easily cool by phonon emission after accepting the electron’s energy. Blue arrows represent Auger mediated processes which occur simultaneously. d) Charge trapping. e) Charge transfer to external structures. f) Energy transfer by FRET or EVET. Processes d) e) and f) can occur for both hot and cold electrons or holes. Processes d) and e) leave a geminate charge in the quantum dot.
2.5.2. Photoluminescence

Perhaps the most intuitive mechanism for relaxation of a photo-excited electron-hole pair is radiative recombination. When preceded by photo-excitation this is termed photoluminescence (PL), and is the reverse of the absorption process, see Figure 2-9b. The electron relaxes to the valence band, “filling” the hole, and emitting a photon. The occurrence of this process from the conduction band minimum (CBM) to the valence band maximum (VBM) is responsible for the PL peak of the QD, although the process is optically allowed for any absorbing excitonic energy level. It is a slow process compared to intra-band non-radiative charge cooling, so only the band edge emission is typically observed, where the band gap is too large for further phonon cooling. Typical PL lifetimes for QDs range from a few ns to 100s of ns, although lifetimes as long as a $\mu$s have been reported for phonon-assisted emission involving dark excitons [20] (see Section 2.3). The central energy of the PL peak is typically shifted to the red from the first absorption peak, this is known as Stokes shift. This shift is typically a result of the fine structure of the band edge hole states [46], where absorption occurs from several closely packed hole states, forming a broad absorption peak at their centre, but emission occurs after relaxation to the lowest energy hole state by phonon cooling. This is indicated in Figure 2-9b.

The spectral shape of a PL emission peak closely resembles that of the first absorption peak for excitation significantly above the band gap, but is typically narrower, due to relaxation of excited charges to the bottom of the band edge fine structure. The width can also change if excited on the edges of absorption peaks, known as fluorescence line narrowing, where experiments excite samples on the edge of the first absorption peak in order to selectively observe quantum dots on the extremes of the size distribution. The result is a significantly narrowed emission spectrum, so such experiments attain a more accurate measure of the Stokes shift than comparison of typical PL and absorption spectra [47].

There are alternate relaxation processes which compete with cooling to the band edge followed by PL, and are often collectively referred to as non-radiative recombination. The competition between these two possibilities can be quantified by the photoluminescence quantum yield (PLQY), which is the ratio of photons emitted from a sample to photons absorbed by the sample. PLQY is usually expressed as a
percentage, such that 100% PLQY implies there is no non-radiative recombination occurring. Early QD samples were found to exhibit very poor PLQY, often <1%, although advances in understanding and control of the QD surface has led to PLQYs of 10s of percent in many different compositions, and approaching 100% for surface passivated QDs (to be discussed in Section 2.8). A high PLQY is desirable for QD applications which rely on the photoemission process, such as LEDs and biomarkers [48-50]. The competitiveness of PL over non-radiative processes can be significantly enhanced by Type I core/shell QD, which increase the electron and hole wavefunction overlap in the core while limiting interaction with the QD surface which can mediate non-radiative processes [32, 51-55]. Alternatively, PL can be suppressed in the interest of prolonging the time window over which charges can be extracted by utilising a Type II structure, where the electron and hole are localised to different regions of the QD [56] (see Section 2.4). Type II and quasi-Type II QDs have also been shown to exhibit dual emission peaks, corresponding to emission in both the core and shell [28], which could enhance the performance of light emitting devices desiring broad spectral emission.

2.5.3. Auger processes

The Auger effect is an energy transfer process where an electron cools to an inner-shell vacancy in an atom, and the potential energy lost by the electron is given to an outer shell electron in the same atom, which is then emitted from the system. This is more formally known as Auger ionisation. In semiconductors, an Auger mediated processes refers to any interaction where a direct exchange of energy occurs between two (or more) charges. Auger interactions are expected to be significantly enhanced in QDs due to the confinement of charges within the QD volume, leading to an enhanced wavefunction overlap of the many charge carrier states. These are also enhanced due to the relaxation of angular momentum conservation rules which were described in Section 2.2.2 [6], whereas in bulk materials, high energy phonons are required to conserve momentum in Auger transitions [57].

Auger effects are multi-charge carrier interactions, and the first kind which concerns this work is Auger recombination. In this process, an electron-hole pair in the presence of a third charge carrier can recombine and annihilate, transferring their
energy to the third charge carrier, exciting it higher into the band structure. This process is illustrated in Figure 2-9c. This process occurs with lifetimes of 10s to 100s of ps, and in some cases can compete with cooling to the band edge. Auger recombination can occur when a single QD absorbs more than one photon, resulting in the excitation of more than one exciton, and is often called multi-exciton recombination. The characteristic rate of Auger recombination scales with the number of created excitons, $N$, as

$$k_{\text{Auger}}(N) \propto N^2(N - 1)$$  \hspace{1cm} (2-17)$$

which is a statistical factor from the product of all possible conduction to valence band transitions (illustrated in Figure 2-9c) and the number of carriers which can accept the energy released by recombination [58]. This factor has been shown to give good agreement for excitation of QDs up to an average occupancy, $\langle N \rangle$, of 5 in PbSe QDs [58], but can break down if the carriers occupy energy levels with different angular momenta, which is likely for QDs with low degeneracy band edge states such as CdSe.

In the experimental techniques used in this work and described in the next chapter, Auger recombination is avoided by exciting samples with low enough fluences such that the probability of absorbing more than one photon in a single QD is negligible. Because Auger recombination cannot occur for a lone exciton in a QD, in experiments which monitor the band edge dynamics, it has a clear signature of a fast decay component down to a plateau, where the plateau corresponds to the comparatively very slow process of single exciton recombination [59]. This signature is the key to measurement of MEG in ultrafast spectroscopy which monitors the band edge dynamics, and will be discussed in more detail in Section 2.6. Some of the relaxation processes to be discussed can leave a single charge in a QD, and if that QD is then excited again, a trion is formed, which can also undergo fast Auger recombination. The rate of trion recombination has been shown to be approximately half as fast as biexciton decay [60] as expected from Equation (2-17). Trions however can be avoided experimentally by sample stirring; this will be discussed further in Section 2.6 and in Chapter 3.
Auger cooling is the second mechanism which is important in this work, and has already been mentioned when discussing phonon cooling of hot carriers. Auger cooling occurs between an electron and its corresponding hole, where one cools closer to the band edge by transferring its energy to the other, to excite it higher into its corresponding band structure. This process was used to explain the absence of a phonon-bottleneck in QD samples, where electrons cool to the band edge over gaps too large for phonon emission by transferring their energy to the hole [44, 61]. The hole can then more easily reach the band edge by phonon emission in its typically much denser band structure; this is also illustrated in Figure 2-9c. This process, like all Auger processes, is significantly enhanced by the confinement of the electron and hole inside the QD volume, such that a decrease in QD size can enhance the intra-band cooling rate despite the increase in energy level spacing [62]. Auger cooling of the electron via the hole can be reduced by confinement of the electron and hole into different regions of the QD, as is achieved in a Type II QD structure [29, 63-64] (see Section 2.4).

The third Auger mechanism which is important in this work is multiple exciton generation, sometimes called impact ionisation or carrier multiplication [58, 65-67]. MEG is the inverse of Auger recombination, where a highly excited charge carrier cools by excitation of another electron across the bandgap. Crucially, this process is not as significantly affected by the isolation of excited electron and hole, and its enhancement has been the objective of much QD research. This process will be discussed in detail in Section 2.6.

2.5.4. Trapping

Charge trapping is a process which removes single charges from the QD band structure, and is thought to isolate them at defects either within the QD or on the surface of the QD, referred to as trap sites, see Figure 2-9d. Trapping can reduce the efficiency and performance of QD based devices by competing with other potentially beneficial processes, such as MEG in solar devices, or PL in emitting devices. Trapping also significantly complicates the analysis and characterisation of other charge cooling mechanisms, because it can occur with similar characteristics and
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signals, and is thought to mediate the phenomenon of QD blinking, or PL intermittency [68-69].

Surface related trapping is particularly difficult to characterise because it shows significant sample to sample variation, be that in the trapping rates, the trap energies, or which carrier (electron or hole) is trapped. The reason for this behaviour is that QDs are particularly sensitive to their preparation and handling, such that each time a nominally identical synthesis is performed, the surface of the QDs can behave differently without affecting quick measurements like PL and absorption spectra. This sensitivity arises from the QDs having a large fraction of their atoms on the surface, where they can be under co-ordinated, that is, to have one or more dangling (un-passivated) bonds. These are usually passivated by long chain organic ligands, but these are often loosely bound to the surface, and can fail to passivate every site on the surface due to steric hindrance. This can leave the QD vulnerable to oxidation and reaction with their environment if not handled carefully [70-71].

Trapping mechanisms in QDs can have lifetimes from a few ps to a ns, and so can overlap with Auger recombination [72]. Trapping has been shown to produce significant artefacts in ultrafast experiments that can be mistaken for Auger recombination which occurs following MEG, including apparent MEG yields of 170% for excitation below the MEG threshold energy [73] (to be discussed in Section 2.6). It was also demonstrated that the presence and effect of surface states is significantly increased following prolonged exposure to high intensity radiation. However, the presence of these surface states produced a characteristically broad pump-induced absorption feature at energies just below the lowest energy absorption maximum (LEAM), which has been used to distinguish this effect from MEG [73]. Moreover, surface-mediated recombination can result in a non-mono-exponential form to the decay transients associated with this process, in contrast to the mono-exponential decay due to multi-exciton decay; this provides another way in which the two processes might be distinguished. The surface trapping rate has been shown to be strongly size dependent [38, 74], where a reduction in QD size dramatically increases the trapping, attributable to the increase in surface to volume ratio.

The mechanism of surface trapping remains poorly understood, that is, how is the energy of the carrier dissipated when it falls into the trap, and what happens to the
trapped charge over a long timescale. Some studies have shown that the traps form energy levels within the band gap [75], which are often termed either “deep” or “shallow” traps, which refers to the energy difference of the trap state from the band edge [18]. The abundance of the two types can vary between QDs within the same sample. One leading theory for the energy dissipation process to deep traps is Auger mediated trapping (AMT), where when a charge is trapped the geminate partner is excited further in its band structure, analogous to Auger cooling described in Section 2.5.3 [18]. Alternatively, the shallow traps could be close enough to the QD energy levels that phonon emission is sufficient to trap the charges, and it might be possible for a trapped charge to escape from a shallow trap by phonon interaction to return to the band edge, analogous to emission from dark exciton states. It has also been suggested that mid-band trap states could explain the absence of phonon bottlenecks by providing a cooling route to the band edge [76].

It has been demonstrated that QD surface passivation methods, such as surrounding a CdSe core with a ZnS shell [73] to form a Type I structure, can keep charges separate from trap states and hence reduce or eliminate this recombination pathway. It has also been found that shell growth can increase non-radiative charge trapping in PbS QDs due to the introduction of defects during shell growth [26]. Passivation methods will be discussed in more detail in Section 2.8. Many passivation methods run the risk of altering the other charge relaxation processes described over the last few sections, making it problematic to isolate the effects of surface trapping. Some experimental techniques can avoid this problem by using an electrochemical cell to “fill” mid-band gap trap states, in order to remove their contributions from the observed dynamics [77-78].

2.5.5. Charge transfer and energy transfer

One of the possible routes to a lower energy state for excited charges in QDs can be to leave the crystal altogether, transferring to another nearby structure, see Figure 2-9e. This charge accepting structure could be a surface ligand [79-81], a substrate/thin film [82], large acceptor molecules bound to the surface [83-87], or even another QD [77]. Typical charge transfer rates vary from a few ps [79, 81-82] so several ns [88], but in some complexes can be in the fs regime [85]. Efficient
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charge transfer, both from hot excitons [89] and those cooled to the band edge, is highly desirable for QD devices such as solar cells [80], photodetectors [90], and for some more niche applications such as redox-sensitive bio-sensors [49, 91] - an application which motivated the study of quinone-conjugated QDs described in Chapter 5. Charge transfer leaves the geminate charge of the transferred carrier in the QD which can have much longer lifetimes typically on the order of ns [84], but as long as 10s of s for large QDs [89]. This can have important implications for QDs which undergo repeated excitations, and will be discussed in Section 2.6. Often QDs are embedded in a conducting polymer for charge extraction from devices, and the band gap of such a polymer has been shown to affect charge transfer and the presence of mid-gap states [92].

Alternatively, structures outside of the QD crystal can accept energy from an excited charge within the QD allowing the charge to cool within its band structure. Such a process is generally known as energy transfer, and shares many of its properties with charge transfer such as typical lifetimes and its manipulation. However, it differs in that it does not leave a lone charge in the core or acceptor molecule, and thus doesn’t necessarily prevent photoluminescence from the QD. One such transfer process is Förster resonance energy transfer (FRET), where if an energy transition exists in an external structure which is resonant with an energy gap of a hot charge in the QD (often the band edge transition), it can transfer its energy through dipole-dipole coupling, resulting in an excited state in the acceptor structure [93]. FRET is often measured by quenching of the fluorescence of the QD [35, 94], and potentially the emission of fluorescence from the acceptor structure, typically at lower energy after additional cooling. A second important energy transfer process is electronic-to-vibrational energy transfer (EVET), where a hot carrier cools by exciting vibrational modes in the surface ligands of the QD. Several groups have shown strong dependence of the intra-band cooling rate on the specific ligand used on the surface of QDs [82, 93, 95]. The mechanism of EVET to surface ligands could explain fast carrier cooling in PbSe QDs [96]. Each of these energy transfer processes are illustrated in Figure 2-9f. Efficient energy transfer can be desirable for the enhancement of photoluminescence yields by reducing the cooling time for hot charges.
The efficiency and timescales for both charge transfer and energy transfer are very sensitive to the distance of the acceptor from the QD surface, and the molecule used to link the two species [94, 97]. The latter can vary the transfer rate from ps to 10s of ns [94, 98], and is also strongly dependent on the QD size [83] and structure, and the number of acceptor molecules [35]. Shelling of a QD, can both enhance or hinder these processes, where localisation of a carrier in the core material can enhance its interaction with external species whilst limiting processes such as Auger recombination or PL [81, 99], and equally, localisation of a particle in the core means that the shell acts as a barrier to charge or energy transfer [36, 51, 87, 100].

2.5.6. Competition and isolation

There is significant scope for confusion and false attribution of charge cooling to different relaxation processes when analysing QD charge dynamics, both due to the myriad of different cooling mechanisms, often with similar lifetimes, and the significant variance of their presence between seemingly identical samples. This has resulted in a significant number of conflicting reports on the mechanisms and rates for charge cooling. As a result, more recent studies tend to focus on the cooling rates measured, and limit their attribution of the mechanism behind the dynamics to speculation wherever possible, rather than concluding on a single cooling pathway. It is prudent to include a thorough description of the QD synthesis and any physical properties which can be determined for comparison to other studies.

A key aim of many QD charge dynamics studies is to isolate individual cooling mechanisms, or eliminate other competing mechanisms, and then attempt to demonstrate their manipulation without significant alteration of the competing mechanisms. For example this has been achieved by spatially separating excited electrons and holes (to restrict Auger processes) or by passivating the surface to eliminate charge trapping (which will be demonstrated in Chapter 4). It is usually desirable to observe the electron and hole dynamics separately, which can be achieved through careful choice of the transitions chosen in optical spectroscopy, and is a key feature of transient absorption spectroscopy, the primary technique for the study of QDs in this work.
The total transition rate between any two states in a QD is typically described by a sum of the relative contributions of each competing relaxation rate. Such a formalism has been demonstrated in particular by the Kambhampati group [101], who have for example measured the variation of the total intra-band cooling rates for electrons, $k_e$, and holes, $k_h$, with diameter, $R$, in CdSe QDs, and modelled the contributing mechanisms. Under their model the total electron and hole cooling rates were split into individual rates:

$$k_e(R) = k_{phonon}(R) + k_{ligand}(R) + k_{Auger}(R)$$  \hspace{1cm} (2-18)

$$k_h(R) = k_{phonon}(R) + k_{ligand}(R)$$  \hspace{1cm} (2-19)

where ligand cooling corresponds to energy transfer to vibrational modes in surface ligands, which was attributed to the absence of phonon bottlenecks in these QDs. The Auger cooling channel is assumed to be negligible for holes. The result of this model is shown in Figure 2-10, where the variation of the different relaxation rates over the same size range is demonstrated. Note that in this model, the Auger rate was assumed to be the difference between the experimental rate and sum of the modelled phonon and ligand rates, as a result additional alternative mechanisms cannot be ruled out. This methodology of rate isolation and attribution is useful to the field, primarily for the prediction of the impact of non-radiative cooling on potentially beneficial processes such as MEG and charge extraction, each of which are investigated later in this work.

Figure 2-10. The variation of intra-band cooling rates, $k$, with QD radius for holes (a) and electrons (b) performed by Kambhampati (see reference [101] and references therein). Circles are experimental measurements of the total cooling rate, with modelling of the contributing mechanisms (coloured lines) and the total rate (black lines) according to Equations (2-18) and (2-19). Reprinted with permission from [101]. Copyright 2017 American Chemical Society.
For depopulation of a given energy level in a single QD, an equation (such as Equations (2-18) and (2-19)) can be written as the sum of the competing rates, and would lead to a mono-exponential decay of the population. However, in any given QD sample for spectroscopic studies, one might expect there to be on the order of a micro-mole of quantum dots. There will not only be a distribution of different sizes, but also a distribution of different geometries, defects, surface traps, and surface ligands. This can change both the rates of each competing process (leading to deviation from an exponential), and potentially the presence of each process, such that it can be appropriate to consider subsets of QDs within the sample. For significant differences in the net rate of these subsets, a multi-exponential decay of the total population will arise. Such a system is studied in Chapter 4, where surface mediated trapping only occurs for one of two subsets. It must be remembered that this is not the only route to a multi-exponential decay, multi-exciton decay (Auger recombination) being another key example.

The key charge relaxation processes which compete in quantum dots are summarised in Table 2.5.6-1, with the typical timescales over which they occur in quantum dots, and crucially, the number of excited charges which participate in the process.

<table>
<thead>
<tr>
<th>Process</th>
<th>Typical Timescale</th>
<th>No. of charges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single exciton recombination (photoluminescence)</td>
<td>ns to μs</td>
<td>2</td>
</tr>
<tr>
<td>Surface trapping</td>
<td>ps to ns</td>
<td>1</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>ps to ns</td>
<td>1</td>
</tr>
<tr>
<td>Trion recombination</td>
<td>10s to 100s of ps</td>
<td>3</td>
</tr>
<tr>
<td>Multi-exciton recombination</td>
<td>10s or 100s of ps</td>
<td>4+</td>
</tr>
<tr>
<td>Carrier cooling</td>
<td>Few ps</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2.5.6-1. The key relaxation processes which occur in quantum dots along with their typical timescales and the number of excited charges which participate. See the main text of Section 2.5 for references and an explanation of each process.

### 2.6. Multiple exciton generation

The inverse of Auger recombination is termed impact ionisation, or carrier multiplication, where a hot carrier cools by excitation of one or more electron across the band gap to form additional electron-hole pairs (EHPs). The utilisation of this excess energy to produce additional electron-hole pairs rather than dissipating the
energy as heat has the potential to significantly improve the performance of photovoltaic devices; these two processes are compared in Figure 2-11. The process is well studied for bulk materials without the effects of confinement, but in QDs, confinement effects mean that exciton binding energies become significant. Therefore, in QDs impact ionisation is usually referred to as multiple exciton generation (MEG). Like the other Auger mediated processes described in Section 2.5.3, the efficiency of MEG is expected to be significantly enhanced in QDs due to the confinement of charges within the QD volume. MEG also occurs on a ps timescale, and exhibits strong size dependence due to the increased wavefunction overlap of hot and unexcited charges in smaller QDs [62, 102-103]. Due to the direct competition between MEG and phonon cooling in highly excited energy levels, the onset of MEG is observed within the first few ps of excitation, before significant cooling occurs.

![Diagram](image)

Figure 2-11. The process of multiple exciton generation (MEG) is enhanced in quantum dots (a) compared to bulk materials (b) due to quantum confinement effects. Excitation energy in excess of the band edge is used to excite additional charge carriers rather than being dissipated as waste heat. The Auger mediated process of MEG is represented by blue arrows, which occur simultaneously.

The process of MEG is energetically forbidden below a threshold energy, $h\nu_{th}$, usually quoted in units of $E_g$. Above this energy at least one of the charge carriers created by the absorption of a photon has sufficient excess energy to promote another electron across the band gap, creating a second exciton. The fundamental minimum for $h\nu_{th}$ is $2E_g$ (if we consider the biexciton binding energy as negligible – to be discussed below). This assumes that one of the carriers produced by the absorption of a photon receives all of the excess energy of the exciting photon.
However, to conserve momentum the energy must be divided between the electron and hole according to their effective masses, $m_e^*$ and $m_h^*$ respectively, increasing the threshold to:

$$h v_{th} = E_g \left(2 + \frac{m_e^*}{m_h^*}\right)$$

(2-20)

(N.B. for $m_e^* > m_h^*$ the quotient becomes $m_h^*/m_e^*$). This can be extended to the generation of more than one additional electron-hole pair, such that in the ideal case, where MEG is the dominant cooling process and $h v_{th} = 2E_g$, an additional pair is created each time the excitation energy increases by $E_g$. The number of EHPs created at a given $h v$ is called the quantum yield, $QY$, of MEG. Thus in the ideal case we have a step-like increase in $QY$ with $h v$, this is shown by the black line in Figure 2-12, along with plots for the non-ideal case, to be discussed below. For this reason, candidate materials for efficient MEG must be chosen carefully, with suitable $h v_{th}$ to ensure optimal performance with solar spectrum illumination, and $h v_{th}$ which is accessible experimentally.

![Figure 2-12. Plots of the percentage increase in MEG quantum yield, QY, with excitation energy normalised to the band gap, $h v/E_g$, for different levels of competition between MEG and hot carrier cooling parameterised by Equations (2-22)-(2-24) with $s = 2$. The ideal step-like behaviour is recovered for $P=10000$, where $\eta' = 1$. Reprinted with permission from [104]. Copyright 2017 American Chemical Society.](image)

Due to the presence of competing relaxation processes, described in Section 2.5, the experimentally observed $QY$ is reduced from the ideal step-like behaviour. Instead, a gradual rise in $QY$ is observed with increasing excitation energy above $h v_{th}$, which
itself typically appears higher than predicted by Equation (2-20). Thus MEG is characterized by measuring $QY$ as a function of photon energy normalized to $E_g$, which allows the determination of $h\nu_{th}$ and the rate of $QY$ increase beyond the threshold. A linear fit to this rise is typically performed, with the gradient giving the efficiency, $\eta$. This efficiency can be defined as the minimum amount of energy required to produce an EHP ($E_g$), divided by the actual amount of energy required to produce an additional EHP after the MEG threshold is passed; the latter quantity is referred to in the literature as the electron-hole pair creation energy [105].

A model which characterises the competition between MEG and the other cooling processes was developed by Beard et al. [104], who showed that the overall efficiency for the MEG process can be related phenomenologically to the threshold energy by:

$$h\nu_{th} = E_g + \frac{E_g}{\eta}$$  \hfill (2-21)

This relationship implies that reducing the threshold energy of the MEG process also increases $\eta$. In addition, Beard et al. [104] (following the work of Ridley [106]) parameterised the competition between the possible relaxation routes of a single hot exciton by:

$$k_{EHPM} = k_{cool} P \left( \frac{h\nu - h\nu_{th}}{h\nu_{th}} \right)^s$$  \hfill (2-22)

where $k_{EHPM}$ is the rate of cooling by electron-hole pair multiplication (EHPM), i.e. MEG, $k_{cool}$ is the rate of cooling by energy dissipation. The exponent $s$ can vary between 2 (the ideal case) and 5, and $P$ is the threshold parameter which determines whether the MEG onset is hard ($P >> 1$) or soft ($P < 1$). An efficiency, $\eta'$, can then be defined based on $P$:

$$\eta' = \frac{P}{1 + P}$$  \hfill (2-23)

which captures the competition between $k_{EHPM}$ and $k_{cool}$, and allows the parameterisation of an energy threshold for each additional EHPM event.
\[ h\nu_{\text{th}}^{(m)} = E_g \left(1 + \frac{m}{\eta'}\right) \] (2-24)

where \( m \) is the maximum number of EHPM events possible. Through Equations (2-20) to (2-24) the onset of MEG and the efficiency can be modelled for varying levels of competition between EHPM and carrier cooling. Beard et al. showed that in this model the onset of MEG is not as sharp as found experimentally, and that the \( QY \) increases approximately quadratically below 150\%, and linearly above. The increase in \( QY \) with \( h\nu \) predicted by this model is also shown in Figure 2-12 for different values of \( P \) with \( s = 2 \), where for \( P=10000, \eta' = 1 \) and the ideal step-like behaviour is formed.

Once the process of MEG has occurred, there are a minimum of two holes and two electrons present in the QD, and as a result Auger recombination becomes possible. As discussed in Section 2.5.3, this is a rapid process with a lifetime of order 10-100 ps, much quicker than recombination for single excitons which have lifetimes of order 10-100 ns. Consequently, the presence of sub-nanosecond decay of the population becomes the signature of MEG, and any measurement of MEG requires sub-picosecond time resolution as will be discussed in Chapter 3. This must however be performed for low excitation fluences for QD samples, to prevent the formation of multiple charges through successive absorption of two photons.

The first measurement of MEG in QDs was performed by Schaller and Klimov [107] in 2004, with a \( QY \) of 200\% for excitation at \( 3E_g \). This seminal work motivated the study of MEG in many other QD systems in the following years. There was some controversy in 2007 – 2009 when a lack of reproducibility emerged for \( QY \) measurements on QDs made by identical synthetic techniques [108], and some groups failed to reproduce their previous observations of MEG [109-110]. It was discovered in 2010 by Klimov et al. [111] that a significantly different MEG \( QY \) can be measured depending on whether or not a sample is stirred. The reason for this was the photocharging/trion formation effect described in Section 2.5.3, where following trapping to the QD surface the geminate partner of the trapped charge remains in the QD core and can participate in Auger recombination when the QD is next excited, mimicking the signature of MEG. It was shown that this affect can lead to an
apparent MEG $Q_Y$ of 170% even when exciting below the MEG threshold [73]. The variation in the apparent MEG $Q_Y$ reported in samples thought to be identical is testament to the sensitivity of the QD surface to their preparation and handling. Since this realisation, some careful studies have measured MEG while ensuring that samples are stirred or flowed sufficiently to counteract photocharging, this will be described in detail in Chapter 3.

The tunability of $h\nu_{th}$, through control of the QD diameter means that the properties of a QD sample can be optimised for exploitation of the solar spectrum. Any energy from solar photons in excess of the band gap will be wasted as heat in the absence of MEG. In 1961 Shockley and Queisser developed the *Detailed Balance* model [112] which calculates the theoretical efficiency limit for a conventional solar cell as 33% and occurs at $E_g=1.35$ eV, where all energy in excess of the band gap is wasted as heat. If MEG is included in the detailed balance model, this limit increases to 44% at the optimum $E_g$ value of 0.7 eV. This modelling is described in detail in Chapter 7, and expanded to include the potential benefits of Type II core/shell QDs.

There is an additional excitonic effect which can alter the MEG efficiency and ultrafast dynamics in QDs. Confinement of multiple excitons within the QD can lead to a significant Coulombic interaction energy between them, known as the bi-exciton interaction energy, $\Delta_{XX}$ [58]. This interaction can be attractive or repulsive depending on the wavefunction overlap of the four carriers, and is therefore strongly size, material and structure (core/shell) dependant [113-115]. This results in a shift of the absorption spectra of a second photon, which is an important phenomenon in transient absorption spectroscopy, to be described in Section 3.5.4. If $\Delta_{XX}$ is large and attractive, it reduces the total energy of the bi-exciton state, and as result reduces the MEG threshold. Inclusion of a large attractive $\Delta_{XX}$ in the Detailed Balance model increases the maximum theoretical efficiency to 50% [116]. As a result, materials with a large positive binding energy are sought for the enhancement of MEG.

### 2.7. Composition, materials and design

The preceding sections have described the electronic structure and cooling processes which apply to all quantum dots. However, all of them can vary significantly due to the properties inherited from the bulk material chosen. As mentioned in Section 2.1,
band gap tuning in QDs is achieved through control of their size due to the effects of quantum confinement. It is therefore important to carefully choose the base material as its bulk band gap and charge carrier effective masses determine both the confinement regime, and set the lower limit for absorption and $h\nu_{th}$. The energy level spacing will also vary significantly between different materials, altering the competition between different charge relaxation processes. Additionally, the choice of materials used in core/shell systems can dramatically change which processes are efficient by isolating charges from each other or the QD surface (see Section 2.4) and by changing the reactivity of the surface. A discussion of the most studied QD variants is given in this section, along with the motivation for their study and the key results; some of the comparisons made were published in a review of MEG in the journal *Nanomaterials* in 2015 as part of this project [65].

### 2.7.1. Pb chalcogenide QDs

PbS, PbSe, and PbTe are IV-VI semiconductors, collectively known as lead (Pb) chalcogenides (group 16 elements). They have been the most studied of all QDs in the interest of photovoltaics [70, 102-103, 117-121], and PbSe QDs were the first type in which MEG was demonstrated in 2004 [107]. The primary reason for this focus is due to the small $E_g$ of the bulk materials (e.g. 0.28 eV for PbSe [122]), which is low enough for optimum exploitation of the solar spectrum. This low $E_g$ can also be utilised in near-infrared emitting LEDs [123] and photodetectors [124]. $a_{exc}$ for PbS is 18–20 nm and 46 nm for PbSe [102], consequently, both are in the strong confinement regime for typical QD sizes of a few nm. Additionally, the bulk band structures of the lead chalcogenides are relatively simple, which extends to the QD band structures. The electron and hole have comparable effective masses, and the band gap occurs away from $k = 0$, at the L-edge of the Brillouin Zone (the unit cell in $k$-space), where $k = \pi/a$, here both the valence and conduction band edges consist of a single, uncongested band. The result is a relatively symmetrical electron and hole band structure both in its dispersion and energy level spacing (near the band edge) [7]. The sparsity of both electron and hole bands enables much easier decoupling of electron and hole transitions via the study of intra-band dynamics, and the comparable energy level spacings led to the expectation of similar cooling times for electrons and holes. However, much faster hole cooling is still observed, the
mechanism behind which remains unconfirmed but could be due to surface-mediated cooling [96].

For MEG investigations of Pb chalcogenide QDs, almost all studies report a $h\nu_{th}$ value in the range of $(2.6 - 3.0)E_g$ that is independent of diameter (with the exception of Reference [103] which describes $h\nu_{th}$ reducing with decreasing diameter). However, two recent works [102, 125] compared $\eta$ for PbS, PbSe and PbSe$_x$S$_{1-x}$ QDs and found a difference in the size-dependence between PbSe and the other materials. For PbSe QDs $\eta$ was approximately constant with size for the samples studied, at $\sim$0.4, whilst for PbS and alloyed QDs it was found to increase with decreasing QD diameter, for instance ranging from $\eta$-0.26 to $\eta$-0.4 as the diameter of PbS QDs were reduced from 9.4 nm to 4.2 nm [102] (these were consistent with other reported measurements [62, 103]). The authors were able to reconcile these results by showing that each material exhibited the same linear increase in $\eta$ with decreasing size when the physical radius was normalized to the radius at which the confinement energy equals the Coulomb energy [102].

The Pb chalcogenides are highly sensitive to oxidation [70-71], which contributed to the early controversies in reproducing MEG measurements. A significant volume of work has explored the effects of temperature, surface treatment and device integration on the changing dynamics in order to improve stability and reproducibility [23, 42-43, 126-130] (to be discussed in Section 2.8). As a result many core/shell Pb systems have been studied; Pb chalcogenides each form with a rock salt crystal structure, and can be successfully shelled with many different cubic materials. MEG in quasi-Type II PbSe/PbS and PbSe/PbSe$_x$S$_{1-x}$ QDs has been investigated [125], but no improvement in efficiency was noted. This was attributed to the small reduction in wavefunction overlap calculated for these QDs, despite the fact that an enhancement of photoluminescence emission has been reported in this system by others [55]. Shelling with CdS also forms a quasi-Type II system, where giant PbS/CdS(zinc blende)/CdS(Wurtzite) QDs with dual emission peaks [28] have been investigated, which could be useful for broad emission LEDs, but MEG has not yet been attempted.
2.7.2. Cd chalcogenide QDs

CdS, CdSe and CdTe are II-VI semiconductors known as the cadmium (Cd) chalcogenides. They are the most studied of all QD systems, due to being the first system for which highly mono-disperse and size-tuneable synthesis techniques were developed [6, 37, 131]. This provided easily resolvable optical transitions in a complete size series, enabling the exploration of the size-dependant physical properties which are key to their applicability. As a result there are a very large number of publications on Cd chalcogenide QDs, which have contributed significantly to understanding the underlying physical processes relevant to exciton dynamics in all QD systems. This was aided by a significantly reduced amount of charge trapping in these QDs compared to other systems, making studies of trapping via their PL emission highly accessible. All of the QDs studied in this thesis are wholly or partially composed of Cd chalcogenides.

They have a large $E_g$ (approx. 2 eV [108]) suitable for tuning across the visible emission spectrum, but as a consequence are not well suited for exploitation of the solar spectrum through MEG due to high $h\nu_{th}$ [65]. They can be in either the strong confinement or the intermediate confinement regime, depending on the size of the nanocrystal, for example $a_{exc}$ is 6 nm in CdSe. Cd chalcogenides can form in either a zinc blende (cubic) or Wurtzite (hexagonal) crystal structure, which can both aid or complicate core/shell growth depending on the other material used [37].

Type I Cd chalcogenide QDs have been studied very extensively, with CdSe/ZnS being amongst the first core/shell systems to show very good emission properties [37]. A PLQY of 92% has been achieved for CdTe/CdS core/shell QDs [132], although this can be equalled and in some cases surpassed by halide treated CdTe QDs [133], which will be discussed in Chapter 4. Cd QDs have been at the forefront of studies attempting to identify and characterise charge trapping, although a wide range of effects and timescales have been reported due to the significant sample to sample variation in the degree of trapping [18, 77-78, 133-141]. Comparison of trap free (near unity quantum yield) and surface trapping QDs was achieved for the first time by our group [134], through chloride treatment of the surface of CdTe CQDs, and is reported in Chapter 4.
MEG in CdSe QDs was first reported by Schaller et al. in 2005 [142] with a threshold of $2.5E_g$. Later studies on CdTe [143] and CdTe/CdSe core/shell [144] QDs gave conflicting reports of MEG, with Nair et al. [108] finding an absence of MEG in both CdSe and CdTe in 2007. As described in Section 2.6 the discrepancy between this and other reports contributed to the realization by the community that MEG efficiency measurements were being confused by experimental artefacts [72]. MEG in CdSe and CdTe QDs has not yet been revisited since the experimental techniques that are now used to suppress these artefacts were developed, and so it is not possible to quantify $\eta$ with confidence in these materials. Recent work has explored temperature dependence and further exciton cooling suppression [140, 145-148]. Gachet et al. investigated MEG in CdTe/CdSe/CdS/ZnS QDs, in which the inner CdTe/CdSe core/shell forms a Type-II heterostructure and the outer CdS and ZnS shells form a barrier between the photo-generated charges and the QD surface [144]. A value of $h\nu_{th} \approx 2.65E_g$ was observed, consistent with other studies of Cd-based QDs, and an upper limit of $\eta = 0.53$ estimated, the highest reported since the identification of the artefacts which occlude measurement.

2.7.3. InAs and InP QDs

InAs and InP are III-V semiconductors, and are the remaining types of QD which have been studied most extensively over the last two decades, although to a much lesser extent due to increased difficulty in their synthesis. They have significantly poorer optical properties compared to Cd chalcogenides [37], and suffer from very poor air stability and highly efficient surface trapping. However, their initial study was motivated by a significantly reduced toxicity compared to Cd or Pb containing QDs, and some interesting electronic properties [47].

MEG in InAs QDs was first studied in 2006, where interest was motivated by both a low $E_g$ of the bulk material (~0.4 eV), and $m^*_e < m^*_h$ and thus $h\nu_{th} \approx 2E_g$. $a_{exc}$ is 36 nm, much larger than typical QD sizes, and so InAs QDs are in the strong confinement regime. However, as with other QD types, initial results were unclear due to failed reproductions due to the presence of experimental artefacts [109-110, 149]. Subsequent studies concluded that MEG did not occur up to a photon energy equivalent to $3.7E_g$ [150]. In 2009, modelling by Califano [151] found that trion and
biexciton decay lifetimes, though similar, should be experimentally distinguishable in InAs QDs, suggesting that some other process was responsible for the discrepancies in reported MEG quantum yields. Very recently, a combined experimental and theoretical study [152] also found that the MEG quantum yield was negligible for photon energies up to at least $3.2E_g$ for InAs QDs with an $E_g$ close to the optimum value for solar cell efficiency. At low pump fluences, there was no difference found between the transients obtained from static and well-stirred samples, and hence the sub-nanosecond decays observed were attributed to surface-trapping. Furthermore, the results of the theoretical modelling found that, while MEG is energetically possible for photon energies similar to $2E_g$, the efficiency of MEG only becomes significant close to $h\nu_{th}$ for small QDs, the $E_g$ of which is too large to effectively exploit the solar spectrum due to the enhanced confinement.

Similar to InAs, InP was expected to have low $h\nu_{th} \approx 2E_g$, but in contrast has a high $E_g$ (1.7-2.0 eV) [153]. The first, and to date only, investigation of MEG in InP QDs was undertaken in 2009 by this group [23], at a time when the impact of trion formation had become apparent. Consequently, measurements were taken using well-stirred samples and at moderate pump fluences. The InP core of these QDs was surrounded by a ZnS inner shell and a ZnO outer shell designed to reduce the trapping of photo-generated charges. These precautions enabled values of $h\nu_{th} = 2.1E_g$ and $\eta = 0.3$ to be reported with confidence.

PLQY values are typically less than 1% for InP and InAs cores, but can be as high as 30% after shelling [51] or treatment with hydrogen fluoride [47]. For instance, as mentioned above, the InP QDs used to demonstrate the record low MEG threshold consisted of an InP core surrounded by a ZnS inner shell and a ZnO outer shell. Similarly, InAs QDs studied have had cores over-coated by layers of CdSe [149], ZnSe [152], or CdSe and ZnSe [150]. In these cases, the purpose of the shell layer(s) is the same: to act as a barrier between both photo-generated charges (electron and hole) and the QD surface, and thereby reduce or eliminate surface-mediated relaxation and recombination. Quasi-Type II InP/CdS QDs have also been synthesised, where an improvement of PLQY is observed by isolating the hole in the InP core. This has been shown to improve PLQY and reduce QD blinking [53, 81,
154]. MEG was reported in InP/CdS QDs for the first time as part of this work [155], and the results are presented in Chapter 6.

2.7.4. Other materials

There are many other materials which can form quantum dots and exhibit the size-dependent charge confining properties which fuel their interest, but have been studied to a much lesser extent, either due to their difficulty in synthesis, poor optical properties, or poor applicability in devices. A few examples of the most interesting cases are discussed here.

Silicon, as the most widely used and well understood semiconductor, is a natural candidate for QD design. However, unlike the materials described in the previous sections, silicon is an indirect band gap semiconductor. This means that the electron and hole’s energetic minima lie at different positions in k-space, and therefore PL from the band edge states requires phonon assistance or similar interactions to conserve momentum. Additionally, absorption and Auger energy exchanges are at much higher energies than the band gap, or also need additional momentum conserving interactions, this restricts transient absorption studies to intra-band transitions.

MEG has been reported in Si QDs [156] with a diameter of 9.5 nm and $E_g = 1.2$ eV, where $h\nu_{th} = 2.4E_g$ and a $QY$ of 2.6 for a pump photon energy of $3.4E_g$, which corresponds to $\eta = 1.6$. However, that study was undertaken in 2007 before the experimental artefacts that can affect MEG measurements were fully understood. Later investigations of MEG in close-packed Si QDs embedded in a silica matrix reported the step-like enhancement in the quantum yield of photo-generated charges that has been predicted for very high efficiency MEG [157-158]. Intriguingly, their experiments also indicate that the additional excitons are being generated not in the same QD that absorbs the photon but rather in neighbouring QDs. This is an exciting result not only because it suggests that the efficiency of MEG in real systems can approach the ideal case, and hence the full benefit to solar cell efficiency could potentially be realized, but also because it indicates that some hitherto unforeseen aspect of MEG is at work. However, as yet, these results await confirmation by other groups and so it is too early to judge their full impact [65].
QDs have also been synthesised from semi-metals, materials with a small negative band gap which becomes positive with the quantum size effect. Interest in such systems was fuelled by predictions that MEG would be most efficient in systems with the smallest bulk $E_g$ [159], which could also be tuned to optimal solar exploitation. The first experimental study of MEG in a semi-metal used QDs made from HgTe, which has a bulk $E_g = -0.15$ eV [160]. For 3.5 nm QDs with $E_g = 1.0$ eV, a $QY$ of 1.36 was measured for a photon energy equivalent to $2.9E_g$; this compares well with Pb chalcogenide QDs which typically exhibit a $QY$ of ~1.2 for excitation at ~$3.0E_g$. HgTe QDs are also notable for their resistance to oxidation – in this case, the QDs were prepared in water and open to the ambient atmosphere. Other Hg chalcogenides, have been shown to be efficient near-infrared emitters, with very high stability and brightness following shelling with CdS [161].

CuInSe2 is another promising material which is yet to gather significant attention, MEG has been measured for a range of sizes of stirred samples [162], where $h\nu_{th} = 2.4E_g$ and a $QY$ of ~1.4 for a pump photon energy of $3.7E_g$, which corresponds to $\eta=1.36$ for a combined range of QD sizes. Interestingly these QDs have an $E_g$ close to the optimum for exploitation of the solar spectrum, and a particularly long Auger recombination time which would aid charge extraction. Passivation of charge traps by ZnS shelling has also been demonstrated for these QDs [163].

### 2.8. Surface passivation

The primary purposes for seeking to control the surface of QDs is to ameliorate the surface mediated effects discussed in Section 2.5.4 that compete with the potentially beneficial processes which occur in QDs, such as MEG or PL. Surface effects also inhibit accurate measurement of QD charge dynamics through their strong sample to sample variation. Additionally, such treatments aim to prevent the QDs reacting with external agents, which could otherwise alter their properties. As discussed in Section 2.7, many QD types suffer from extreme air sensitivity. Sykora et al. [71] investigated the absorption spectra and $QY$ of PbSe QDs with exposure to air for varying times. They found that the QDs can lose up to 50% of their volume due to oxidation in air. This enhances quantum confinement and blue-shifts the absorption
peak, moving it further from the optimum value for exploitation of the solar spectrum.

Typical surface passivation methods result in long-chain organic ligands bonded to the QD surface. The choice of ligand has been shown to have dramatic effects on non-radiative recombination rates [95, 101, 164], optical properties [26, 165], and device performance [166]. As discussed in Section 2.5.5, the ligand choice can affect the intra-band cooling rates due to vibrational energy transfer, which can also affect the competitiveness of trapping. The ability of ligands to passivate the surface can be limited by steric hindrance, where there is insufficient room on the surface for the bulky ligands to bind to adjacent surface sites. It has been shown that sites on the surface with different geometries can have different charge trapping properties [18], and it has also been shown that ligands binding to different sites can have different charge interactions [94].

In thin-film QD solids the long-chain ligands are replaced with shorter ones to enhance carrier mobility; the shorter inter-QD distances enhance carrier tunnelling between QDs [82, 167-169]. This process was observed to reduce MEG efficiency, but this reduction could be reversed through infilling with inorganic compounds [170]. The authors investigated MEG in 1,2-ethanedithiol-linked PbSe QDs infilled with Al$_2$O$_3$ or Al$_2$O$_3$/ZnO through atomic layer deposition. Through time-resolved microwave conductivity measurements they found MEG efficiencies for infilled films approached the intrinsic efficiency for isolated PbSe QDs, whereas there was negligible MEG for non-infilled films.

Shelling QDs in order to form a barrier between the charges localised in the core and the surface has been discussed repeatedly in this chapter as a method to ameliorate surface trapping, in addition, it can improve the QDs oxidation resistance. Sykora et al. [71] showed that the effects of air exposure are partially suppressed in PbSe/CdSe core/shell structures, similar to the CdSe/ZnS structures used by Tyagi et al. [73] to ameliorate surface state formation. Similar effects of air exposure have also been reported for PbS QDs [70-71], and has been shown to improve device stability [127]. However, shelling QDs can change the charge confinement in the core, altering the energy level structure [16], and can act as a barrier to charge extraction.
Implementation of MEG exploiting QDs in practical devices requires efficient extraction of charges before their ultrafast recombination, a process which is strongly linked to the surface of the QD, the internal structure, and the surrounding material. This has led to the study of exciton dissociation by charge transfer to electron- or hole-acceptor molecules bonded to the QD surface. Surface treatment of QDs can however inhibit the MEG process with some studies reporting a strong variation in MEG efficiency [171-173]. One group, however, has shown that in PbS QD/methylene blue complexes the number of dissociated excitons is equal to the number of excitons generated in free QDs under the same excitation conditions, with MEG and multiple exciton dissociation efficiencies of 112% [174].

Treatment with halide ions has emerged recently as a particularly effective method of surface passivation in many different QD systems. First pioneered by treating InP QDs with hydrogen fluoride which resulted in significant PLQY improvements [47], although broadening and shifting of transitions was observed. Significant improvements in device performance have been demonstrated, such as a record efficiency for a QD-sensitised solar cell [130] which utilised chloride treated PbS QDs, and a more recent paper which reported similar results including the demonstration of significant improvements in PLQY [23]. More recently, our group has pioneered research into chloride passivated CdTe CQDs [133-134, 175], where the treatment is capable of completely eliminating charge trapping in this system, and dramatically improves air resistance. The charge dynamics in these QDs is the focus of Chapter 4, which enabled for the first time direct comparison of trap-free and charge trapping QDs. It is thought that the halide ions are capable of passivating trap sites which are inaccessible to the much larger organic ligands due to steric effects. The high electronegativity of some halide ions results in a highly stable QD surface leading to better oxidation resistance, and is less detrimental to charge extraction than thick shell passivation. Significantly improved air stability has also been demonstrated for PbSe QDs [176], and shown to slow carrier cooling [177]. Solar cells utilising chloride treated PbSe QDs were shown to be air-stable for more than 270 days, a significant improvement for these normally highly air sensitive QDs [178].
2.9. Comparison to MEG in bulk materials

Interest in MEG in QDs as a source of increased efficiency in photovoltaics was fuelled by the expected effects of quantum confinement, namely relaxed momentum conservation, slower phonon-mediated cooling rates, enhanced Auger processes and reduced dielectric screening of the QD surface [104, 119]. During the period of controversy following the emergence of the artefacts described in Sections 2.5.4 & 2.6, several groups argued that for a given photon energy, carrier multiplication occurs more efficiently in bulk PbS and PbSe than in QDs of the same material [67, 119]. It was suggested that surface effects in competition with impact ionization are much less prominent in bulk materials due to a greatly reduced surface area to volume ratio compared to a QD. Conversely, it was also argued that the MEG threshold in bulk materials is much higher due to parabolic energy momentum states demanding strict momentum conservation in exciton production.

In order to effectively compare the performance of bulk materials and QDs, careful consideration of the presentation of the data is required. As discussed by McGuire et al. [111], arguments can be made for superior performance of either depending on the quantities displayed; when plotting the \( QY \) versus the pump photon energy, bulk PbSe was shown to outperform PbSe QDs and this was the representation used by authors for the notion that MEG in QDs is less efficient than in bulk materials [118-119]. This representation, however, neglects the effect of the magnitude of the band gap and does not provide direct information about the energy efficiency, only the number of excitons produced per absorbed photon. Quantum confinement in QDs results in significantly higher band gaps meaning an MEG event corresponds to higher final energy state than an impact ionization event in bulk materials. A representation which takes these factors into account is to plot the energy yield, \( QY \times E_g \), versus the photon energy. In this way PbSe QDs were shown to transfer more energy to charge carriers than bulk material for a given photon energy, the more important consideration for photovoltaics. Confinement in fewer than 3 dimensions has also shown significant promise in recent years; highly efficient MEG has been demonstrated in PbS nanosheets [179], with \( \eta = 0.9 \). This indicates that nearly all excess energy is converted into additional electron-hole pairs, however with \( h\nu_{th} \) near 3 eV, far higher than the optimum for solar excitation.
PbS nanorods with comparable $E_g$ to QDs have also been investigated, and were shown to have double the MEG $QY$ of QDs [180].

2.10. Summary

The confinement of charges within the small volume of a semiconducting quantum dot has been shown to significantly change the allowed energy and momentum states, and alter the efficiency of different charge relaxation processes. The band gap transition and the energy level spacings are strongly size-dependent such that QDs can be tuned to optimise optical device performance.

The enhanced and tuneable energy level spacing in QDs significantly slows charge cooling, and alters the competition between the various cooling processes. The asymmetry of electron and hole energy structures has important implications for some of these processes. The relaxation processes can vary strongly depending on the QD size, material, its surface treatment, and crucially, its preparation and handling. Most critical of these processes is surface mediated trapping, which significantly reduces device performance and complicates studies of QD charge dynamics. The origin and mechanism of surface trapping is still poorly understood, and a deeper understanding will be key to the applicability of QDs in optoelectronic devices.

Much interest in QDs has been fuelled by the expectation of increased efficiency of multiple exciton generation, which has the potential to significantly enhance device performance by using photon energy in excess of the band gap to excite additional charge carriers. The efficiency of this process has been reported in many systems but has been hindered by experimental artefacts which have cast doubt on a number of early reports. Further understanding and enhancement of MEG is still at the forefront of QD research.

It remains to be seen whether the energy loss processes which reduce the efficiency of QD solar cells can be overcome to make QDs a viable choice over bulk semiconductors. However their unique charge confining properties are proving useful in many less obvious applications, and the enhanced understanding of charge carrier interactions will prove invaluable for the future of optoelectronics.
2.11. References


Charles Smith
PhD Thesis
Chapter 2

Quantum dots – background and theory


Chapter 2

Quantum dots – background and theory


Charles Smith
PhD Thesis


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Chapter 3. Experimental techniques

3.1. Introduction
The cooling of charges in colloidal quantum dots (CQD) occurs within the first few picoseconds after excitation, and the subsequent recombination occurs over nanoseconds to hundreds of nanoseconds. In order to measure the charge dynamics of these processes the use of ultrafast mode locked-lasers is key, such that the pulse duration of any excitation or probe beam is narrower than the timescale of the process under investigation. Two key techniques were used in this work: time correlated single photon counting (TCSPC), where the decay of photoluminescence (PL) intensity following ultrafast excitation reveals the coupled electron and hole dynamics; and transient absorption (TA) spectroscopy, a pump-probe technique which can reveal the occupation of pairs of energy levels within a sample over time.

Prior to ultrafast spectroscopy of a CQD sample, it is typically optically characterised by measurement of its absorption and PL spectra, which reveal the energies of the electronic transitions, and in some cases can provide measures of non-radiative transitions. Several other complementary measurements can also be performed such as measuring the photoluminescence quantum yield (PLQY) and numerous techniques for structural characterisation which can provide important insight into the reasons for variance of charge dynamics between samples.

Each of these techniques along with the equipment used in this work will be described in detail in this chapter, along with their limitations. The key analysis methods will be described along with any experimental artefacts which might be encountered, with focus on identifying the charge relaxation mechanisms described in Section 2.5.

3.2. Synthesis, preparation and handling
The appeal of QDs for applications in nanotechnology relies not only on their size tuneable optoelectronic properties but on the facile, scalable and reproducible methods by which they can be synthesised. Early synthetic techniques consisted of precipitation reactions at low temperature in the presence of stabilisers for
controlling growth, but suffered from poor optical properties and broad size dispersions [1]. These problems were inherent to the low temperature and slow growth and nucleation of QD cores, where poor PL intensity was attributed to poor crystallinity of the QDs leading to a high number of crystal defects to act as non-radiative centres. In 1993 Murray et al. [2] published their seminal paper on the hot-injection method, a high temperature approach which laid the foundation for the synthesis of many of the high quality QDs studied since [3]. This technique entails the rapid injection of metal-organic precursor materials, which each contain one of the crystal elements, into a high temperature solvent (~300°C) which is rapidly stirred, see Figure 3-1. At this temperature the precursors break down to release the crystal ions which begin to nucleate into QD cores. After a short time (~minutes) the temperature is dropped slightly and held to achieve gradual growth of the QDs. Injection of a passivating ligand and reducing the mixture to room temperature halts the growth process and yields highly mono-disperse QDs, where the high temperature acts to anneal any crystal defects. This is a colloidal synthesis technique, so the nanoparticles produced are often described as colloidal quantum dots (CQDs). The technique can be performed in as little as 100 ml of solvent so is highly accessible and readily scalable for industrial production.

Figure 3-1. Schematic representation of the hot-injection synthetic technique for production of colloidal quantum dots. Reprinted with permission from Reference [4].

Murray’s landmark paper described the synthesis of Cd chalcogenide QDs, but has since been adapted to form a wide range of different QDs. Injection of additional
reagents can produce core/shell QDs, alloyed QDs, or can coat the surface with charge accepting or trap passivating species. Such techniques can be sensitive to the timings, temperature, concentration and purity of reagents, and quality of the atmosphere, which must be clean and often anaerobic \([2, 5]\). Improvements in purity, uniformity and reproducibility of such techniques over the last decade have been a key driving force in the accelerating volume of works published on the electronic properties of CQDs.

As discussed in Section 2.8, some QDs can be highly sensitive to air exposure due to oxidation of their surface diminishing their optoelectronic performance through trap formation or changes in charge confinement. This means that even for well-established and practiced synthesis techniques the handling and preparation of the QDs for optical studies must be carefully controlled and replicated to avoid sample-to-sample variation of results.

For the spectroscopic studies carried out in this work, samples were kept in high quality glass cuvettes, sealed under nitrogen and transferred in a nitrogen environment (unless stated otherwise). Thorough cleaning of the cuvettes between samples was found to be an important factor to prevent contamination from impacting the optical properties. The cuvettes used were 10 mm path length quartz cuvettes, which have near unity transmission across the ultra violet (UV) and visible spectrum, ideally suited for investigating QDs with potential in solar or lighting applications. The 10 mm cuvette can accommodate an 8 mm stirring bar comfortably for the prevention of photocharging (to be discussed in Section 3.5.2.4). This length is also convenient for achieving acceptable optical densities for the spectroscopic studies performed after dilution by factors of 1-10 for the synthesis procedures in this work. The chosen solvent must have high transmission across the spectral range of interest, must have good solubility for the QDs, and must not introduce excessive artefacts in pump-probe spectroscopy (to be discussed in Section 3.5.3). Some optical and structural characterisation experiments (to be discussed in Section 3.6) require the deposition of QDs onto a surface to form a thin film, and may need to be performed under vacuum. In these cases there is a further risk of sample degradation due to exposure and contamination.
Chapter 3 Experimental techniques

The QDs studied in this work were synthesised by collaborating researchers; in the case of Chapters 4 and 6 by researchers in the D.J. Binks group at the School of Chemistry, at The University of Manchester, and in the case of Chapter 5 by Andrew Harvie at the University of Leeds. At the start of each chapter a brief overview of the specific synthesis technique and sample preparation is given.

3.3. Continuous wave spectroscopic techniques

3.3.1. Absorption spectroscopy

The absorption spectrum of a QD sample corresponds to optically allowed transitions from the ground state to excited states, and the consequent formation of electron-hole pairs. The spectrum typically reveals the first optically allowed transition and can show higher transitions for highly mono-disperse samples. The allowed optical transitions in a QD were described in Section 2.3, where the overlap of many broad transitions high above the band edge results in an approximately cubic rise in absorption with increasing photon energy. Since the band edge transition energy shows strong size dependence, many studies have provided empirical fitting curves for determining the QD size from $E_g$ for a given material [6-9]. Re-measuring absorption spectra and checking for changes in the band edge transition energy is a quick and simple method of checking for sample changes over time or after a different experiment. For example gradual air exposure over time can result in an etching of the QD surface and a blue shift of the band edge due to the size reduction [10]. Absorption values at the pump and probe wavelengths are of particular importance in the analysis of ultrafast spectroscopy in this work: they are used for the determination of absolute absorbance changes in transient absorption studies, for estimating whether two-photon absorption is likely at a given excitation fluence, and for compensating for solvent induced artefacts.

The absorption of light is determined by measuring the transmission, $T = I/I_0$, through the sample, where $I$ is the intensity of light transmitted through the sample for an initial intensity $I_0$. For CQD samples in suspension, there are several experimental measures for the absorption of light, the usefulness of which can vary between scientific fields. Generally, the absorption of light is characterised by its absorbance which is a measure of how the sample attenuates light. Although it is not
only absorption which contributes to attenuation of light, but also reflection and scattering. In chemistry, the absorbance, $A'$, is given by the Beer-Lambert law as

$$A' = -\log\left(\frac{I}{I_0}\right) = \varepsilon Cl$$

(3-1)

where $I$ is the intensity of light transmitted through the sample given an initial intensity $I_0$, $l$ is the optical path length (sample thickness), $\varepsilon$ is the extinction coefficient of the sample (usually measured in cm$^{-1}$ mol$^{-1}$) and $C$ (in mol) is the concentration of the sample. $A'$ is often called the optical density. In physics, it is more convenient to use an alternative measure which uses the natural logarithm:

$$A = -\ln\left(\frac{I}{I_0}\right) = n\sigma l$$

(3-2)

where $n$ [cm$^{-3}$] is the number of particles per unit volume with an absorption cross section $\sigma$ [cm$^2$]. This absorbance, $A$, is often called optical depth, (and given symbol $\tau$) and so is easily confused with $A'$ in published works, they are both unitless and linearly proportional, with $A' = \ln(10)A \approx 2.3A$. Another useful conversion between the two conventions is $\sigma = 1000 \ln(10) \varepsilon / N_A$, where $N_A$ is Avogadro’s constant. Throughout this work, absorbance will refer to the natural logarithm version, $A$. At this point it is also convenient to define the absorbance length for a sample as

$$l_A = \frac{1}{n\sigma}$$

(3-3)

Absorption spectra were acquired for QD samples using a Perkin-Elmer Lambda 1050 UV/Vis/IR Spectrometer [11]. This device is capable of measuring differences in absorption between a sample and reference sample (pure solvent) with absorption precision of <0.5% achievable around the absorption edge for the samples studied in this work. The spectrometer has two light sources which cover a spectral range of 175 to 3300 nm produced by a tungsten halogen lamp, which covers the near-infrared (NIR) and visible range (Vis), and a deuterium lamp, covering the UV range. The lamp output is passed through a filter wheel, which automatically rotates to filter parts of the lamp spectra, and then through two synchronised
monochromators, which rotate together to select the wavelength of the beam; each use one of two holographic gratings for either the NIR or UV/Vis ranges. The beams make multiple passes through a slit assembly, which can be set to automatically or manually attenuate and narrow the spectral range of the beams, and then through a common beam mask which can alter the height of the beam [12].

The beam is then passed through an optical chopper, which alternately reflects the beam towards the sample or transmits the beam towards the reference sample, a schematic representation of this system is shown in Figure 3-2. The beams then enter the sample compartment and pass through the sample and reference cuvette holders and then into the detector compartment. The intensity of each beam is detected by a three detector module [13] consisting of a PMT (for detection over 175 – 860 nm), an InGaAs photo-detector (860 – 2500 nm), and a PbS photo-detector (860 – 3300 nm), where mirrors on a translation unit alter the beam path between the three detectors.

Figure 3-2. Schematic representation of the Perkin-Elmer Lambda 1050 UV/Vis/IR Spectrometer. See main text for details. A mirrored mechanical chopper, C, alternates the excitation beam between the reference and sample [11].

Operation of the Lambda 1050 is done through UV WinLab software [14]. All lamp, monochromator and detector changes are automatically performed by the software. After selection of the excitation range the system performs a calibration scan of the excitation and reference beams (with no samples), to determine the detected beam intensity for each path over the specified range, \( I_0(\lambda) \). Each sample is then scanned.
with an optional reference sample, and the system measures the transmitted intensity, \( I(\lambda) \), over the specified wavelength range, and automatically subtracts any contribution from the reference sample. The reference beam has the added benefit of reducing the impact of any fluctuation in lamp intensity. The default output from the software is absorbance in base 10 logarithm, \( A' \), (see Equations (3-1) – (3-2)) with all corrections (due to calibration or use of beam attenuators etc.) and reference subtraction performed. Some QD samples can contain a significant amount of sediment and can appear slightly opaque. This can result in scattering of the light beam, and appear as a background rising with photon energy across the entire spectrum, which must be considered carefully if the absolute values of absorbance are critical to the study.

Due to the overlap of many excitation peaks and the approximately cubic background at high energy, the peaks can become asymmetric and their central positions difficult to determine. This problem can be alleviated by calculating the second derivative of the absorbance curve, where the centre of each peak will form a minimum (negative peak), for easier identification. An example absorption spectrum and its second derivative for CdTe CQD in toluene are shown in Figure 3-3. A scan of the reference sample (in this case, pure toluene) is also shown, which includes any contribution from the sample cuvette.

![Figure 3-3. Example of an absorbance spectrum for a CdTe QD sample, black line. Also shown is the reference scan taken of the sample solvent, Toluene, in an identical quartz cuvette, red dashed line, which has been subtracted from the sample scan. The 2nd derivative of the sample scan is shown, blue dotted line, where each minimum aids in the identification of optical transitions (re-scaled and shifted in the y-axis for clarity).](image-url)
3.3.2. Photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy measures the light produced by the recombination of electron-hole pairs, and typically is only observable for the band edge transition, or first excited state, in quantum dots. The process was described in detail in Section 2.5.2. The position of the PL peak can be a more useful indication of the QD band gap if a large Stokes shift is present, especially when estimating the threshold for MEG. The intensity of PL from a QD sample is an important indication of the amount of non-radiative recombination and charge trapping occurring. A typical PL spectrometer consists of a continuous light source for excitation of samples, a monochromator for selecting the excitation energy, a second monochromator for selecting the emission energy from the sample, and a detector. Photoluminescence excitation (PLE) spectroscopy is another important technique, where emission is only detected at the PL peak, and the excitation energy is varied. This process can also indicate the position of absorption peaks revealed by an increase in photoluminescence intensity, and can be used for accurate determination of the Stokes shift in PL line-narrowing experiments [15-16].

Steady state photoluminescence experiments were performed using a Horiba Jobin Yvon FluoroLog-3 model FL3-22iHR spectrofluorometer [17], a schematic representation for which is shown in Figure 3-4. The system uses a 450 W xenon lamp as a continuous light source which has high intensity between 240 nm and 600 nm. A double grating monochromator and optical slit select the excitation wavelength and adjust the spectral width. The resulting excitation beam is directed into the sample chamber. Any photo-emission from the sample can be collected either at 90 degrees to the excitation beam, or back through the excitation port (front face emission), with a rotating mirror selecting which is reflected to a second double grating monochromator and optical slit. Collecting emission from the front face is more efficient for highly absorbing samples, where the excitation beam can’t penetrate the whole sample. The emission beam is directed into a R928P photomultiplier tube (PMT) from Hamamatsu Corp, which has high sensitivity from 240 nm to 850 nm. The emission slits are, in part, used to prevent over-exposure of the PMT. Before the sample chamber, there is a beam-splitter which samples some
of the excitation beam onto a photo-diode. The signal from this detector is used to compensate for wavelength dependence of the excitation intensity.

Figure 3-4. Schematic representation of the optical path in the Horiba Jobin Yvon Fluorolog-3 model FL3-22iHR spectrofluorometer [17]. The T-shaped sample compartment allows the installation of a second detector module. Re-printed with permission from Reference [17].

All adjustments are computer controlled through the system’s accompanying software, FluorEssence™ 3.0, this can automatically scan over both emission and excitation wavelengths, and outputs the intensity at the PMT in photon counts per second (CPS). The system comes with a correction file for emission spectra, which scales the signal at a given wavelength to account for differences in detection efficiency of the system. For wavelengths longer than 700 nm the efficiency drops rapidly, limiting the signal quality in this region. The software can be set to scan across a defined emission and excitation range for a complete emission and excitation spectrum, which will be known as a PL map in this work.

3.3.3. Photoluminescence quantum yield

Although direct observation of any time varying process is not possible with CW excitation, some measurements can reveal information about the relative rates of competing ultrafast processes, one such measurement is the photoluminescence
quantum yield (PLQY). PLQY is a measurement of the efficiency of the photoluminescence process, and is defined as the ratio of photons absorbed by a sample to photons emitted. This is equivalent to the probability of a single absorbed photon resulting in relaxation to the ground state by radiative recombination. The PLQY can be highly excitation energy dependent (although typically a single PLQY value is quoted for samples, and the excitation wavelength is often omitted) so we can write the PLQY, $\phi$, at a given excitation wavelength, $\lambda_{ex}$, as [18]

$$\phi(\lambda_{ex}) = \frac{No. \ photons \ emitted}{No. \ photons \ absorbed} \quad (3-4)$$

PLQY is effectively a measure of the amount of non-radiative recombination, charge trapping, and charge transfer which occurs for excited charges, which interrupt the process of cooling to the band edge and radiatively recombining. For homogeneous samples, it can be also be written in terms of the relative total rates of radiative, $k_r$, and non-radiative, $k_{nr}$, pathways:

$$\phi(\lambda_{ex}) = \frac{k_r}{k_r + k_{nr}} \quad (3-5)$$

Typically, exciting higher into the band structure (hotter charges) reduces the PLQY. This could be explained by the activation of more cooling processes which aren’t available for lower levels, or by an increased cooling time (due to having more energy to dissipate) resulting in a longer window of opportunity for non-radiative processes.

For QD samples, PLQY typically shows significant variation between samples, due to being strongly related to the quality of surface passivation, something which absorption and photoluminescence spectra alone cannot reveal. As a result, it is a common measurement for QD samples before any ultrafast studies of the charge dynamics. PLQY measurements have also been used to deduce the existence of a novel variant on the MEG process in close-packed arrays of Si QDs [19], where the additional excitons are generated not in the same QD that absorbed the photon, but rather in a neighbouring QD. This separation enables the extra excitons to survive long enough to make a significant contribution to PL emission.
Measurement of PLQY can be challenging, where in order to achieve accurate and reproducible results careful elimination of systematic errors and measurement of reference samples is required for a given technique. Common sources of systematic error are: excitation source stability, wavelength dependent detection efficiency, accounting for scattering of light and anisotropy of emission direction, and reference subtraction. Additionally, sample preparation can have a significant effect on PLQY, with sensitivity to solvent purity, cleanliness of cuvettes, sample concentration, and temperature [20]. Therefore, significant discrepancies can exist in reported PLQY values between different works, which can be difficult to reconcile due to the absence of details on the experimental procedures [21].

Common methods for measuring PLQY are comparative methods [22], where the PLQY of the sample is determined by comparing to the known PLQY of a dye which is also measured. By this method a correction factor which handles all systematic errors is determined from the measured dye PLQY. However, another technique houses the sample in an integrating sphere. This is a spherical compartment lined with a highly reflective coating which diffusely scatters all emitted radiation multiple times, which eventually escapes through a single small exit port, resulting in spatially integrating the emission. The sphere negates the effect of scattering and anisotropy of absorption and emission in the sample. After scattering excitation and emission photons may be re-absorbed by the sample. This is known as an absolute method [23], which is used throughout this work.

In this work, PLQY measurements were performed using the Fluorolog-3 spectrofluorometer with its associated F-3018 integrating sphere accessory which can be mounted in the sample compartment. This integrating sphere is coated with Spectralon, which has a reflectance of over 95% from 250nm to 2.5μm. An illustration of the integrating sphere is shown in Figure 3-5; it contains a swivelling sample mount at its centre, capable of holding an 8 mm diameter, 40 mm tall cylindrical cuvette [24]. The sample holder can position the sample in the excitation beam or rotate it out of the beam such that it is excited by light scattered from the sphere surface. The sphere also contains a Spectralon baffle in front of the exit port, which ensures that all collected light has been diffused.
Figure 3-5. Illustration of the F-3018 integrating sphere for the Fluorolog-3 spectrofluorometer. The sample holder can be rotated to move the sample in and out of the beam path. Reprinted with permission from Reference [25].

By measuring the difference between the time-integrated intensity for the sample in and out of the beam, the effect of a single pass through the sample on the excitation beam can be extracted, and the PLQY determined. The procedure requires the sample cuvette and a second cuvette filled with the sample solvent as a reference, and measurement of both the scattered excitation light – the region around the excitation peak, and of the emitted light – over the emission region of interest.

This technique is based on reference [26], and the procedures used in our laboratory were developed by D. Espinobarro-Velazquez [23] also under the supervision of D.J. Binks. Significant effort was made to maximise the reproducibility of PLQY measurements. Through the repeat measurement of dye standards it was concluded that uncertainty values of ±2.5% are reasonable for this procedure. In contrast, typical literature uncertainties are ±5-10%. The results were found to be the most accurate for dilution of samples to an absorbance of 0.1 or lower. In this work, this uncertainty will be combined with any statistical uncertainty from repeat measurements wherever possible.

Details of the calculation procedure will now be given for completeness, but will not be required for understanding of the results in this work. For a single PLQY measurement, the measurement of the following six PL spectra is required, where the notation for referring to each spectrum is given:
The scattered light from the reference cuvette inside the beam path, $R_{Sc}$.

- The emitted light from the reference cuvette inside the beam path, $R_{Em}$.

- The scattered light from the sample cuvette inside the beam path, $IN_{Sc}$.

- The emitted light from the sample cuvette inside the beam path, $IN_{Em}$.

- The scattered light from the sample cuvette outside the beam path – rotated 90 degrees, $OUT_{Sc}$.

- The emitted light from the sample cuvette outside the beam path – rotated 90 degrees, $OUT_{Em}$.

The use of a neutral density (ND) filter (0.5%) was required on the emission port of the integrating sphere for measurement of the scattered excitation light to prevent overexposure of the PMT. The calculation of PLQY is performed using the Horiba Scientific Quantum Yield and Colour Calculator [27], which given the six spectra, corrects them using in-built wavelength dependent correction factors accounting for the efficiency of detection of radiation, and for the efficiency of collection of radiation by the integrating sphere. An example set of the six spectra is shown in Figure 3-6, where these corrections, including correcting for the ND filter, have been performed.

![Figure 3-6. Example of the six spectra required for measurement of the PLQY of a QD sample. The sample was CdTe CQDs diluted in toluene, and the reference (R) was pure toluene. Left – scattered (subscript Sc) excitation light centred on 420 nm. Right – emitted (subscript Em) light, the large sharp peak is the PL from the QDs, the broad small peak is emission from toluene. IN and OUT refer to the sample cuvette placed directly in the beam path or out of it.](image)

The calculation of PLQY is performed by comparison of the total emission within each spectrum. Firstly, the fractional absorption, $A_f$ which occurs due to the excitation beam hitting the sample once (i.e. excluding absorption after scattering on
the sphere surface), is determined using the difference between the scattered intensity with the sample in and out of the beam:

\[ A_f = \frac{\int OUT_{sc} - \int IN_{sc}}{\int OUT_{sc}} \]  (3-6)

where integration is performed numerically by summing each element of the spectrum. The number of photons absorbed by the sample in this single pass is then given by

\[ A = A_f \int R_{sc} \]  (3-7)

this can be considered the denominator of Equation (3-4) (note a constant of proportionality is omitted which relates to the total detection efficiency of the system, but would cancel out later in this analysis).

The number of photons emitted by the sample due to a single pass of the beam through the sample, the numerator of Equation (3-4), is more difficult to calculate. The number of photons emitted by the sample in total when in the beam is given by

\[ B = \int IN_{Em} - \int R_{Em} \frac{\int IN_{sc}}{\int R_{sc}} \]  (3-8)

where the second term is the total emission from the reference cuvette, corrected by the fraction of light absorbed by the sample when in the beam. The importance of this correction is clear in Figure 3-6, where the reference contribution is larger than the sample for wavelengths far from the QD emission. From this we need to subtract the total emission caused only by absorption of diffuse (transmitted and scattered) light. This is given by

\[ C = (1 - A_f) \left( \int OUT_{Em} - \int R_{Em} \frac{\int OUT_{sc}}{\int R_{sc}} \right) \]  (3-9)

This is equivalent to Equation (3-8) for the sample out of the beam, with the factor \((1 - A_f)\) being the transmission (and scattering) of the excitation beam by the
sample before scattering from the back of the sphere. This factor makes $C$ in fact the total emission from the sample when outside of the beam, if the excitation intensity had been reduced by a pass through the sample. The PLQY is then given by

$$\phi = \frac{B - C}{A}$$

(3-10)

### 3.4. Photoluminescence decay

Following excitation of a photoluminescent sample with an excitation pulse rather than a continuous source, the PL intensity will peak and decay back to zero. Observing the timescales of decay can reveal the rate of relaxation of the population of the band edge state, which relate to the radiative lifetime and the lifetimes of other non-radiative decay processes.

In an energy level structure where hot charges can only dissipate energy, that is, to only get closer to the band edge with any transition, the population dynamics at the band edge can only appear mono-exponential for a QD sample of identical dots, regardless of the number of possible decay paths from the band edge state. Figure 3-7 illustrates this scenario, where from the band edge with a time dependent excited population $n(t)$ there is a radiative decay route with rate $k_r$, and any number of non-radiative processes, $k_{nr1}, k_{nr2}, \ldots$.

![Figure 3-7. Illustration of the radiative, $k_r$, and non-radiative, $k_{nr1}, k_{nr2}, \ldots$, decay routes (solid lines) from the Conduction Band Minimum (CBM) with time dependent population $n(t)$, to the Valence Band Maximum (VBM).](image-url)
We can write the ordinary differential equation (ODE):

\[ \dot{n} = -k_r n - k_{nr1} n - k_{nr2} n \ldots \] (3-11)

This assumes that cooling to the band edge from the pump level is fast enough to be considered instantaneous. Equation (3-11) has the solution

\[ n(t) = n(0) e^{-(k_r+k_{nr1}+k_{nr2}+\ldots)t} \]

\[ = n(0) e^{-k_T t} \] (3-12)

where \( k_T \) is the total decay rate which will be observed as a mono-exponential decay with a lifetime \( \tau_T = 1/k_T \). The PL intensity at any given time is given by, \( I(t) = k_r n(t) \), giving

\[ I(t) = I_0 e^{-k_T t} \] (3-13)

where \( I_0 = I(0) \).

However, a mono-exponential decay is typically only observed for well passivated QD samples with high PLQY, and thus little non-radiative decay from the band edge, and little variation in the quality of QDs in the sample. In practice, a multi-exponential decay is usually observed, formed up of multiple components, \( i \), and the decay transient is fit to:

\[ I(t) = \sum_i A_i e^{-k_{i}t} \] (3-14)

where \( A_i \) are the amplitudes of each decay component.

A multi-exponential decay can be explained by two possible scenarios. Firstly the presence of multiple populations of QDs within the sample, each with different decay processes from the band edge contributing a different \( k_T \) for each population. As discussed in Section 2.5.4, such a scenario can be likely for surface related trapping, where a distribution of different amounts of passivation within a sample can lead to some dots exhibiting surface trapping while others are fully passivated. Furthermore, it has been shown that the particular location of un-passivated sites on the surface can give different trapping lifetimes, and would decay with different total
rates [28]. Secondly, a multi-exponential decay can arise when charges can be re-excited to the band edge state, for example by a de-trapping process [29-30], associated with quantum dot blinking [31]. The resulting PL decay dynamics form a tri-exponential where each rate is a function of the trapping and de-trapping rates.

A more complete picture of the PL decay of the entire QD population would be to consider that each decay process will in fact have a distribution of decay rates. It was described in Section 2.5 that practically every decay process shows dependence on QD size, and there is always an inherent distribution of sizes within a sample. Considering a distribution of rates is not usually necessary and isn’t practical experimentally due to the number of free parameters that arise. Some systems however do not fit well to a reasonable number of exponential components (more than 3 components are rarely fitted unless they occur on very different timescales). Some works fit a stretched exponential of the form \( I(t) \propto e^{-t^\beta} \) to the decay, where \( \beta \) is a free parameter of the fit. Such a procedure usually achieves a good fit, but does not provide significant insight into the underlying processes beyond comparison to other stretched exponential fits.

Since PL corresponds to the recombination of an electron-hole pair, the observed PL decay corresponds to the coupled electron and hole dynamics, which as described in Chapter 2, can have different transitions available to each of them. Particularly, electrons and holes can have very different cooling times to the band edge, which makes analysis of early-time PL decay signals particularly problematic, where both must cool in a single QD before recombination occurs. Furthermore, cooling dynamics are typically too rapid to observe using common PL decay techniques such as those described in this section. Hence the focus is usually on the decay away from the initial rise, where in order to determine which carrier is responsible for any non-radiative components, a theoretical prediction is needed, or a complementary experiment which can separate the electron and hole dynamics, such as transient absorption spectroscopy, to be described in Section 3.5.

### 3.4.1. Principle of TCSPC

A widely used technique for observing the PL decay of semiconductors is time correlated single photon counting (TCSPC) [32], and is one of the two time-resolved
techniques used to measure charge dynamics in this work. TCSPC systems benefit from the time-resolution and sensitivity of the micro-channel plates (MCPs) used for light detection. They allow biexciton decay and other ultrafast processes to be resolved, and the weak signals resulting from low excitation fluences to be readily detected, which are required to prevent photo-charging and multiple-photon absorption. Modern TCSPC systems utilise high repetition rate fs pulsed lasers as their light source, which typically achieve pulse widths of 10s to 100s of fs.

TCSPC has been used to characterise many of the non-radiative processes described in Section 2.5, including determining MEG $QY$ by measuring the components of the PL decay transient associated with single and multi-exciton recombination [33]. However, the spectral range of MCPs limits their use to QDs with band gaps larger than ~1.5 eV, greater than the ideal value for the exploitation of the solar spectrum. Similarly, MEG has also been measured by detecting the PL decay with a streak camera [34].

The principle of TCSPC is the detection of single photons emitted from a fluorescing sample and measurement of their arrival time relative to a reference signal, usually provided by the excitation source. This principle is illustrated in Figure 3-8. The technique utilises low-light, high-repetition-rate light sources, such that the probability of detecting more than one emission photon in one signal period is negligible [32]. The TCSPC electronics can be compared to a fast stopwatch with two inputs, the reference pulse and the single photon detection. The timer is started when the reference pulse arrives, and stops when the PL emission photon is detected [35]. The process is repeated at a high repetition rate and a histogram is built up of the delay times, which forms the PL decay curve.

The TCSPC electronics are key to achieving the necessary time resolution at a high repetition rate, while eliminating noise in the system through rejection of false pulses, which is complicated by the instability of both the reference and detector pulses. A schematic of the typical components is shown in Figure 3-9. The start and stop pulses can each show significant amplitude jitter [32]. Therefore, using a fixed amplitude trigger for the detection of pulses can introduce timing inaccuracy. Thus, each pulse is detected instead by a constant fraction discriminator (CFD), which triggers detection at a constant fraction difference of the pulse amplitude, achieved
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Experimental techniques

by delaying one component of the signal relative to another (effectively looking at the gradient of the pulse). When the difference between these signals crosses the baseline, detection is triggered. This crossing point can be tuned manually away from the baseline, known as the zero crossing level (ZC). Altering this parameter can eliminate artefacts in the signal caused by unusually shaped input pulses. The CFD also has a tuneable amplitude threshold for the detection of input pulses, used to eliminate electronic noise, including thermal dynode pulses from the MCP and other experimental artefacts (to be discussed).

Figure 3-8. The principle of TCSPC. The time delay between sample excitation and photoluminescence is recorded by the system, and repeated many times to produce a histogram which forms the PL decay dynamics. Reprinted with permission from Reference [35]

Figure 3-9. Overview of the electronic components in a typical TCSPC setup, see main text for a description of each component. Reprinted with permission from Reference [36].

The start and stop pulses from the CFDs are passed to a time to amplitude converter (TAC). This device outputs a single pulse with an amplitude proportional to the time delay between the start and stop pulses, achieved by the charging of a capacitor at the start pulse and its discharge at the stop pulse. The TAC has a user defined time
range for scaling of the output signal, which determines the time window of the observed PL decay. The TAC signal is passed to an analogue to digital converter (ADC) with a pre-amplifier. The ADC has a fixed number of channels which correspond to bins on the histogram of time delays forming the PL decay trace. The ADC sorts the amplitude of the TAC signal to one of the channels which is then stored in the system memory, and the system is then ready for the next start-stop event.

### 3.4.2. Experimental setup

The TCSPC experimental set up used in this project was built by S. Stubbs [37] and D. Espinabarbo-Velazquez [23], previous students in the D.J. Binks group. A schematic of the system is shown in Figure 3-10. The excitation source is a Spectra-Physics Mai Tai High Performance (HP) mode-locked Ti:Sapphire femtosecond laser, which outputs ~100 fs pulses tuneable from 720 – 850 nm at 80 MHz repetition rate with high stability [38], and a typical pulse energy of a few nJ. The MaiTai consists of a diode pumped continuous wave (CW) laser and a mode-locked Ti:Sapphire pulsed laser compressed into a single sealed unit, each of which are modelled after standalone units also manufactured by Spectra-Physics, the Millennia CW laser, and Tsunami Ti:Sapphire oscillator. Both of these systems are also used in the transient absorption laser system described in Section 3.5, where the underlying physics of both lasers is described in Section 3.5.2.2.

The high repetition rate of the Mai Tai laser could cause optical “pile-up” at the PL detector, where more than one photon is detected in one pulse period. Since the TAC will only accept one stop pulse, this will significantly change the shape of the PL decay curve by ignoring the later of any two photons. As a result the repetition rate is reduced using an APE pulseSelect [39]. This device uses an acousto-optic modulator (AOM, also known as a Bragg-cell), to selectively reject pulses from the Mai Tai. The AOM consists of a transparent crystal with an attached piezo-electric transducer which creates acoustic waves in the crystal. A signal generator powering the transducer produces wide pulses, several times the Mai-Tai pulse width, at a repetition rate which is a sub-harmonic of the Mai Tai repetition. These pulses act to gate the Mai-Tai pulses, where the Bragg-effect results in the crystal acting as an
optical grating, such that the first order refracted light is diverted out of the device, while the 0\textsuperscript{th} order light, and all light while the AOM is turned off, are blocked. The pulse selector is synchronised to a reference signal from the Mai Tai, and the phase and pulse width of the acoustic generator must be tuned for optimal pulse rejection. For this work one in every 40 pulses were selected, resulting in an output pulse train with a repetition rate of 2 MHz.

![Schematic of the TCSPC system](image)

Figure 3-10. Schematic of the TCSPC system, see main text for details. The wavelengths and repetition rates are tuneable. N.B. a wavelength of 420 nm at 2 MHz at the sample was used throughout this work.

A small fraction of the output from the pulse selector is directed to a silicon photodiode by a beam splitter. The diode signal is connected to the reference CFD, and has a sufficiently fast response time to limit pulse spreading and the introduction of excessive zero crossing inaccuracy (which limited the time resolution of early TCSPC systems [32]). Some signal from the rejected pulses adjacent to the selected pulses can sometimes remain in the beam, albeit at much lower amplitude. Careful alignment and adjustment of the pulse selector can limit these pulses, but they can also be rejected by the reference CFD by setting the CFD threshold above their amplitude. These pulses can however still excite the sample and cause fluorescence,
and as a result a small increase in amplitude is sometimes observed in the PL decay (at precisely 1/80 MHz = 12.5 ns after the main peak).

The majority of the pulse picker output is passed through an APE Harmonic Generator [40], which can double or triple the frequency of light by second harmonic generation (SHG) or third harmonic generation (THG). In this work the generator was used to double the frequency of the Mai Tai output to achieve a tuning range of 360 – 425 nm. The process of SHG will be described in Section 3.5.2 along with optical parametric amplification. In brief, as the light passes through a non-linear crystal with birefringent properties, a non-linear polarization wave is generated which radiates an electromagnetic field of double the frequency of the incident light. Phase tuning of this process is required by manually rotating the optic axis of the crystal. The SHG light is not collinear with the fundamental beam, enabling blocking of the fundamental inside the generator. The efficiency of SHG is non-linear with respect to the incident intensity of light, and so any remnants of rejected pulses from the pulse picker are significantly reduced in amplitude relative to the selected pulses.

The output from the harmonic generator is directed to a sample holder for the 10 mm quartz cuvettes by a pair of mirrors and a periscope, where at the sample the beam diameter was 2.8 mm [23], with a typical average power of 3 mW, corresponding to ~0.4 nJ per pulse.

The emission from the sample is collected at 90 degrees to the excitation beam by a focussing lens, which directs the emission into a Spex 1871 monochromator. The monochromator can be tuned across the UV-Vis spectrum and is typically set to the peak of the PL emission spectrum, determined from the steady state PL spectrum measured on the Fluorolog spectrofluorometer (see Section 3.3.2).

A Hamamatsu R3809U-5 micro-channel plate photo-multiplier tube [41] is fixed directly to the output port of the monochromator. This highly sensitive detector has a detection range of 160 – 850 nm. Any incident photons result in a cascade of photoelectrons within the device which are collected to form an output pulse for the detector CFD.

The two CFDs and all subsequent electronics are contained within an Edinburgh Instruments TCC900 computer module [35]. This module’s accompanying software
can adjust all of the manual control elements illustrated in Figure 3-9 to set the time window of detection and optimisation of the signal. The ADC has 4096 channels which each form a bin in the histogram of delay times.

The time resolution of the system is determined by the instrument response function (IRF). Any PL decay traces measured by the system will be a convolution of the PL dynamics (according to Equations (3-11) – (3-13)) and the IRF, which is typically approximated as a Gaussian peak and can be calculated from the contributions of each of the system components. The detector and light source electronic jitter is typically <25ps, and the pulse width from the Mai Tai is <100 fs [38]. The IRF of the MCP-PMT was measured upon installation by Hamamatsu Photonics with a full width at half maximum (FWHM) of 38.6 ps [41]. The width of the IRF can be calculated by the sum of the squares of these contributions which yields 46 ps [23, 37].
3.5. Transient absorption spectroscopy

Transient absorption spectroscopy (TA) is a time-resolved optical spectroscopy technique which is capable of monitoring the energy level occupation in semiconductors with high accuracy and excellent sensitivity. It is the primary technique used for the investigation of the ultrafast charge relaxation processes described in Chapter 2, and is the main technique used in this work. TA is a pump-probe technique which utilises ultrafast pulsed lasers, thus it is often called ultrafast transient absorption (UTA).

TA has several advantages over TCSPC, primarily the ability to separate electron and hole dynamics both at the band edge and in higher energy levels, and a significantly smaller time resolution which can resolve the ultrafast processes of charge relaxation, multi-exciton recombination, and charge trapping. The time resolution of a TA system is determined solely by the temporal width of the laser pulses incident on the sample, which for modern systems can be <100 fs.

TA is the primary technique for measurement of the MEG $Q_Y$, and was first used to measure MEG in 2004 [42]. As discussed in Chapter 2, the first challenge in the measurement of $Q_Y$ lies in the timescale of the MEG process. Single excitons in QDs have lifetimes of the order 10-100 ns, whilst a multi-exciton can undergo rapid Auger recombination and consequently have a lifetime of the order 10-100 ps. $Q_Y$ must thus be measured before the MEG-created excitons can undergo this rapid recombination, necessitating the use of ultrafast techniques. The second challenge lies in the requirement to use low excitation fluences. Multi-excitons can also form when a single QD is successively excited by two or more photons within the lifetime of a single exciton. In order to prevent multi-excitons forming in this way, very low excitation fluences must be used such that the average number of photons absorbed per QD per excitation pulse is much less than unity. The signature of MEG is thus the observation of multi-exciton recombination at low pump fluence. Sensitive detection techniques are consequently required to detect the weak signals resulting from such low excitation. TA is ideally suited for such measurements, where the narrow pulse widths and high stability of mode-locked Ti:Sapphire lasers are utilised. The low fluence and the high time resolution are also vital for the measurement of other ultrafast processes such as charge cooling and trapping.
without multi-exciton formation, which are of particular interest in the study reported in Chapter 4.

TA can individually measure electron and hole dynamics, and so is a complementary technique to TCSPC, described in Section 3.4, particularly when comparing the dynamics of late time TA signals, typically limited to a few ns by the use of an optical delay stage, and the early time PL dynamics, which are approaching the limits of the system IRF.

### 3.5.1. Principle of TA

TA is a pump-probe experiment which requires the use of sub-picosecond, low fluence laser beams. A high energy pump pulse creates initially hot single exciton states in the QD sample. These excitons gradually cool to the band edge primarily by phonon emission, but also crucially by Auger cooling and MEG, see Section 2.5. After a time delay, $\Delta t$, a probe pulse tuned to one of the optical transitions in the QDs is passed through the sample, and its transmitted intensity measured. Due to the finite degeneracy of the QD energy levels, band-edge excitons result in filling of the available states, resulting in either a bleaching of absorption (a reduction) or a photo-induced increase in absorption depending on the transition probed. For example, charges cooled to the band edge transition will result in a bleaching in the absorption of a probe beam tuned to the band edge transition energy. This principle is illustrated in Figure 3-11. Varying the delay between the arrival of the pump and probe pulses, enables the growth and decay of this band-edge exciton population to be measured.

Several variants of TA have been developed based on the different electronic transitions probed. Inter-band TA is the most common technique. Here the probe beam is usually tuned to the lowest energy absorption maximum (LEAM), which corresponds to a transition from a state just below the valance band maximum (VBM) to the conduction band minimum (CBM). As described in Section 2.2.2, the VBM to CBM transition is typically optically very weak in QDs and thus not well suited to TA measurements. Since holes will cool to the VBM, probing at the LEAM corresponds to an empty hole state just below the VBM, and can therefore monitor exclusively the electron population at the CBM.
A similar technique is intra-band TA, where the probe photons are tuned to a transition from the CBM to a higher state; in this case the presence of additional electrons in the CBM results in an absorption increase [43], usually called photo-induced absorption (PA). Intra-band TA is mostly used for indirect bandgap semiconductors [44], or for isolation of electron and hole dynamics in specific transitions [45-46].

Thirdly, THz-TA can be used to probe the frequency-dependent complex conductivity of a sample, from which the exciton populations can be determined through the Drude model of free carriers [47].

The time averaged reduction in intensity of the probe beam at a given pump probe delay is all that need be detected. As a result there is no requirement for ultrafast electronics as are needed in a TCSPC system, and the time resolution is determined entirely by the temporal widths of the pump and probe pulses.

3.5.2. Experimental setup

The TA system used in this work is an inter-band TA system with tuneable pump and probe energy. It was originally built by D. Graham and S. Hardman, and later modified by S. Stubbs [37], A. Al-Otaify [48], M. Cadirci [49], and M. Leontiadou, all previous researchers in the D.J. Binks group.
A schematic representation of the TA experiment is shown in Figure 3-12, excluding a breakdown of the laser system, which will be described in Section 3.5.2.2. In brief, a Ti:Sapphire regenerative amplifier, Spectra-Physics Spitfire-Pro, produces a pulsed beam at 800 nm, with 100 fs pulse width, ~1 mJ pulse energy and 1 kHz repetition rate. Using a beam splitter, 95% of this beam is passed to an optical parametric amplifier (OPA, Light Conversion Ltd. TOPAS-C) with harmonic generating (HG) crystals to produce a pump beam that is tuneable from the infra-red to the ultra-violet (blue line). The remaining 5% is used to produce the probe beam.

The pump beam is passed through a mechanical chopper synchronised to half the pulse repetition rate. This enables isolation of pump-induced signals using a lock-in amplifier, to be discussed below. A neutral density (ND) filter is used to reduce the average pump power at the sample, which is typically 1 – 3 mW.

The weaker beam from the amplifier is directed along a Newport ILS series 200 mm delay stage with a broadband hollow retroreflector; this delay stage is used to vary
the arrival time difference between pump and probe pulses at the sample. This beam is reduced to approximately 1 mW using a ND filter, then focussed onto a sapphire plate to produce a white light continuum, which is re-collimated by a second lens. A 500 mm focal length lens focusses the beam, with the sample placed at the focal point. This focussing enables easy overlap of the pump and probe beams inside the sample, and increases the uniformity of pump intensity sampled by the probe. Beam measurement and overlap will be discussed in more detail in Section 3.5.8.

Before the sample, the white light beam is split to form the probe and reference beams. After the sample, the probe and reference beams are balanced using a ND filter and re-collimated by 250 mm focal length lenses (placed a total of 750 mm from the previous lens). This lens also reduces the diameter of the beam for easier alignment. A half mirror (D-shaped) is used to align the probe and reference beams one above the other, which then enter a Princeton Instruments Acton SpectraPro 2500i imaging spectrometer, used to select the desired probe wavelength from the white light continuum. The monochromated light is directed onto a pair of Vishay Si PIN high speed photodiodes; small differences in probe and reference signals are detected using a Stanford Research Systems SR830 digital lock-in amplifier synchronised to the pump repetition after the chopper, 500 Hz (this will be explained in more detail in Section 3.5.2.3).

The beam path through the laser system (to be discussed in Section 3.5.2.2) is long, at approximately 12 m. Therefore, small changes in temperature or vibrations can alter the beam positioning in the TA setup over long periods of operation. In order to achieve and maintain a strong and consistent signal from the TA system, variation of the beam positions and powers must be checked and corrected through mirror and filter adjustment whenever possible. The beam approaching the delay stage must be aligned carefully to prevent the beam wandering when the stage is adjusted. This is made significantly easier by the retroreflector which ensures the incoming and outgoing beams are parallel. After the delay stage the beam must be carefully focussed on the sapphire plate for stable white light generation, which is mounted on a translation stage to aid its positioning. Additionally, special care must be taken to ensure the probe intersects the centre of the pump beam inside the sample.
Collectively these adjustments can limit the time over which an individual measurement can be taken if the system is performing poorly.

A computer system running a LabView [50] script capable of controlling the delay stage records the signal from the lock-in amplifier, written by B. Spencer. It can be programmed to take multiple scans across the delay stage for an individual sample by specifying the scan range, step size and number of scans. Throughout this work, the transients presented are typically averages of 10 scans. The computer also runs Princeton Instruments Spectra Sense control software [51] capable of adjusting the spectrometer to tune the probe wavelength. Additionally, it can be set to scan across the range 400-1200 nm to obtain differential absorption spectra at a chosen delay after the pump beam (set by the delay stage). The use of a white light continuum enables easy tuning to the band edge transition and the recording of absorption change spectra, a significant advantage over early TA systems which used monochromatic probe beams.

3.5.2.1. White light continuum generation

The generation of a white light continuum (WLC), sometimes called a supercontinuum, is a process where high intensity laser light is converted to light with a very broad spectral bandwidth. The process can occur in any transparent medium, but is significantly enhanced in media with high non-linear optical properties, such as photonic crystals, in the case of the TA system, a sapphire plate. Femtosecond pulses with energy of a few mJ are sufficient to generate a stable WLC in this medium, where the peak power approaches 10s of MW [52]. The use of temporally broader pulses can result in higher beam divergence.

WLC generation is a process which is well known and is used widely in scientific research [53], but the underlying physics are not yet fully understood. The broadened emission generally appears as a central white spot, used as the supercontinuum, surrounded by a diverging ring with varying colour around its perimeter. In the TA system a WLC is used as the probe beam, and another is used inside the OPA for the tuning of the pump beam, to be discussed in the next section. Various mechanisms have been suggested for the continuum generation [52], including self-focussing, self-phase modulation (SPM), ionization-enhanced SPM, and four-wave mixing.
Self-focussing is believed to play the most important role in WLC generation for femtosecond pulses, which arises from the Kerr-effect, a change in the refractive index of a medium in response to an applied electric field. For the strong fields in the centre of a high intensity laser pulse this results in the formation of a Kerr-lens, and convergence of the beam towards its high intensity centre [52]. With significant self-focussing the beam collapses towards a singularity with a high probability of multi-photon interactions, leading to the formation of a plasma of free electrons with a broad emission spectrum. Pressure in the plasma is thought to limit the self-focusing and the emission becomes collimated through the rest of the medium [53].

The threshold power for continuum generation has been shown to be coincident with the power threshold for self-focussing which is given by [52]

\[
P_{\text{crit}} = \frac{3.77\lambda^2}{8\pi n_0 n_2}
\]

(3-15)

where \(n_0\) and \(n_2\) are the linear and non-linear refractive indices of the material respectively, and \(\lambda\) is the wavelength of the incident beam. This threshold is independent of the initial beam area, however a larger beam requires a longer propagation distance in the medium before it converges sufficiently for WLC generation.

In addition to self-focussing, it is useful to understand the effects of SPM on the WLC, which results in additional spectral broadening and significant group velocity dispersion (GVD), less formally known as chirp. GVD describes the separation of different frequency components due to a frequency dependent refractive index in the material, resulting in spatial (or equivalently, temporal) spreading of the components along the beam path. SPM arises from the temporal distribution of nonlinear phase in a laser pulse, in much the same way that self-focusing arises from the spatial distribution of nonlinear phase in a laser beam [52]. The result is a change in the non-linear phase of the laser beam proportional to the rate of change of intensity over time. This manifests as a Stokes shift (red-shift) of the radiation at the leading edge of the pulse, and an anti-Stokes shift (blue shift) at the trailing edge. This broadening is inversely proportional to the pulse’s rise time, and is particularly significant for femtosecond pulses. In an ultrafast TA system, a temporal shift of several ps can
exist across the visible region of the WLC [53]. As a result the time of pump-probe overlap becomes probe wavelength dependent. Accounting for this shift will be described in Section 3.5.3.

An example spectrum of the white light continuum used for the probe beam in the TA system is shown in Figure 3-13. The probe chirp has no effect on this spectrum; it was recorded by synchronising the lock-in amplifier to the probe repetition rate (1 kHz), and as a result is independent of the pump beam, and pump-probe delay. A peak and several sub-peaks are visible around 800 nm, the wavelength of the incident beam on the sapphire plate. The spectrum is wide and relatively flat (no significant dips of low intensity) through the visible region of 500 – 700 nm, ideal for the tuning of the probe beam and measurement of absorption change spectra for the QDs studied in this work. The variation in amplitude is accounted for in the analysis process, described in Section 3.5.5. The white light spectrum can vary significantly depending on the incident power, and on the position of the sapphire plate relative to the beam focal point. It is possible to optimise the white light at a given wavelength (or wavelength range), although care must be taken not to damage the sapphire plate with excessive power near the focal point.

![Figure 3-13](image.png)

Figure 3-13. Spectrum of a white light continuum generated in the sapphire plate in the transient absorption system with an incident beam of 1 mW centred on 800 nm. The spectral sensitivities of the spectrometer and silicon photodiode have not been accounted for.

### 3.5.2.2. Femtosecond pulse generation, amplification and conversion

The laser system which provides the pump and probe pulses for the TA system determines many of the characteristics of the experiment and is almost solely
responsible for any experimental noise. For accurate measurement of absorption change transients highly stable and uniform pulses are required. The system is composed of multiple standalone modules which each play an important role in the production of ultrafast tuneable pulses with three distinct stages: pulse generation, pulse amplification and frequency conversion. A schematic for the system is shown in Figure 3-14. In this section the main optical components of each module and the underlying physics will be described in brief, but are not crucial to the understanding of the results in this work. Further details such as full optical beam paths including beam shaping, system alignment and safety procedures can be found in their operating manuals.

![Figure 3-14. Overview of the laser system which produces the pump and probe beams for the TA experiment.](image)

The first stage of the system is the generation of ultrafast pulses, which comprises of a Spectra-Physics Tsunami Ti:Sapphire oscillator [54], pumped by a continuous wave (CW) Spectra-Physics Millennia Pro. The Mai Tai laser system used in the TCSPC system described in Section 3.4.2 is a combined unit of these two systems. The Millennia [55] is a sealed cavity vanadate (Nd:YVO₄) laser which emits at 1064 nm, and is pumped by a pair of 40 W fibre coupled diode lasers, with high power transfer efficiency. The diode lasers are contained in a separate power supply unit to remove thermal load from the vanadate laser head and are air cooled. The vanadate laser head itself is temperature controlled through a water cooler for high stability. The laser cavity contains a lithium triborate (LBO) frequency-doubling
crystal, which is non-critically phase-matched to enable collinear fundamental and second harmonic oscillation in the laser cavity. This results in an output wavelength of 532 nm with typical powers of 10 – 15 W, which is extracted from the cavity by a dichroic output coupler which reflects the 1064 nm light. A portion of the output is sampled for a control loop which adjusts the diode laser power for increased stability.

The Spectra-Physics Tsunami [54] utilises Titanium-doped sapphire (Ti:Sapphire) as its laser medium which can deliver tuneable output from 690 – 1080 nm, and can be efficiently pumped by green-blue laser radiation. The output from the pump laser is focused into a narrow beam along the length of a Ti:Sapphire rod. Mode-locking of the laser is achieved by an AOM (the function of which was described in Section 3.4.2 in the TCSPS system) driven by a regeneratively-derived rf signal with a period matching the round trip time of the laser cavity, corresponding to a frequency of approximately 80 MHz. This process is tuned by changing the cavity length with a mirror on a motorized stage, which also tunes the cavity mode. The Millennia and Tsunami systems share a water cooling system for their gain media to maintain stable operation.

A set of four prisms are mounted in the beam path within the cavity, forming a Gires-Tournois interferometer (GTI), the position of two of which are adjusted by micrometers, illustrated in Figure 3-15. The prisms form a region in the cavity where the wavelengths are spatially spread, and a variable slit can select the bandwidth of lasing. The prisms also introduce negative GVD into the beam. GVD describes the temporal spreading of different frequency components in a laser pulse. Transmission through the Ti:Sapphire rod introduces positive GVD in the beam (red components lead blue components) due to SPM (as described in the previous section), which is counteracted by the prism system to achieve much narrower temporal pulse widths. In the TA system the Tsunami is operated at 800 nm and achieves pulse widths of approximately 100 fs with little chirp, and a time averaged power in excess of 500 mW.
The second stage of the TA laser system is the amplification of pulses. The Tsunami pulses have an energy of a few nJ and require amplification to approximately a mJ for use in the TA experiment for sufficient excitation of the sample and efficient wavelength tuning. The amplification stage of the TA laser system comprises of a Spectra-Physics Spitfire-Pro Ti:Sapphire regenerative amplifier [56], pumped by a Spectra-Physics Empower pulsed laser [57], and seeded by the Tsunami output pulses. Before the Spitfire-Pro the Tsunami beam is reduced in power to approximately 500 mW using a Glan-laser prism, which consists of a half-wave plate and polariser cube, where rotating the wave plate reduces the fraction of light which passes through the cube.

The Empower pump laser [57] is an intracavity-doubled, Q-switched, diode-pumped neodymium-doped lithium yttrium fluoride (Nd:YLF) laser, with a pulsed 527 nm output at high pulse energy of 10s of mJ. An Nd:YLF rod is excited by an array of photodiodes which results in emission at 1053 nm. As in the Millennia system, a LBO crystal inside the cavity frequency-doubles the output to 527 nm. Pulsing is achieved by Q-switching with an AOM to prevent oscillation of light in the cavity; these are synchronised at 1 kHz. A long upper state lifetime of the Nd:YLF crystal enables a build-up of gain in the crystal when in the low-Q state. Switching to high-Q then results in a high energy pulse output and highly efficient frequency doubling in the LBO crystal, the output from which can escape from the cavity through a
dichroic mirror. The two crystals and AOMs are cooled by a water chiller for stable operation.

The Spectra-Physics Spitfire-Pro [56] is a regenerative amplifier with three key stages: the temporal stretching of the seed pulses, amplification using the pump laser pulses, and the compression of the amplified pulses. This process is illustrated by Figure 3-16.

![Figure 3-16. Illustration of the chirped (stretched) amplification process in the Spitfire-Pro laser. Taken from Reference [56], permission to use granted by Newport Corporation, all rights reserved.](image)

The purpose of the stretching phase is to introduce significant GVD into the femtosecond pulses, to reduce the peak power before amplification. This has the combined effect of avoiding damage to the laser components due to high peak power and avoiding catastrophic self-focussing of the beam inside the gain medium. Stretching is achieved using a diffraction grating, such that longer wavelengths are sent along a shorter path length than shorter wavelengths to introduce positive GVD. A retroreflector is used to cause a second diffraction of the beam on the grating, which re-aligns the spectral components onto the same path, and reduces the need for accurate grating alignment. The same principle is used in the compressor after amplification to remove the GVD and re-attain \(~100\) fs pulse widths. In the compressor the retroreflector is mounted horizontally (rather than vertically) relative to the grating, which swaps the long and short wavelength components and reverses the GVD change.

The amplification stage utilises the polarisation of the beam to trap single pulses from the 80 MHz pulse train inside an amplification cavity containing a Ti:Sapphire rod pumped by the Empower laser. Only a small amount of gain depletion occurs for a single pass through the Ti:Sapphire rod, and so the Spitfire repeatedly passes a
single pulse through the rod until gain saturation occurs, taking approximately 20 passes, and then the pulse is ejected to the compressor.

Pulse trapping inside the optical cavity is achieved by the use of two Pockels cells; these are electronically driven devices which rotate the polarisation of transmitted light by $45^\circ$ when turned on, but are passive when turned off. The components of the amplification cavity are shown in Figure 3-17. Horizontally polarised seed laser pulses enter the amplification stage through a polarisation rotating periscope, PS$_1$, to become vertically polarised. The pulses are reflected onto the face of the Ti:Sapphire rod which is cut at Brewster’s angle for horizontally polarised light, such that the pulses are directed onto the cavity mirror CM$_1$, and are now “inside the cavity”. Before the next cavity mirror, CM$_2$, are the input Pockels cell and a quarter-waveplate. When the input Pockels cell is on, combined with the waveplate it rotates the polarisation of the beam by $90^\circ$. As a result, one of three scenarios can occur depending on the relative timing of the pulse and the Pockels cell driver [56]:

Case (a) - the input Pockels cell is on when the pulse arrives: the pulse is not selected and is rejected without passing through the Ti:Sapphire rod. In this case, the beam is rotated $45^\circ$ four times in its two passes through the Pockels cell and waveplate. As a result, it still has vertical polarisation at the rod, and is reflected back through the stretcher cavity due to the rod being cut at Brewster’s angle for horizontally polarised light. A Faraday isolator at the entrance to the stretcher stage prevents the pulse returning to the seed laser.

![Figure 3-17. Pulse selection and regenerative amplification components in the Spitfire Pro, see main text for description. Modified from Reference [56], permission to use granted by Newport Corporation, all rights reserved.](image-url)
Case (b) - the input Pockels cell is off when the pulse arrives, and is still off when
the pulse returns from cavity mirror CM₄: the pulse is now rejected after one round
trip through the amplifier. In this case, the pulse is rotated 45° twice by the
waveplate, but not by the inactive Pockels cell, to become horizontally polarised.
The pulse now passes through the rod, and is amplified. After the rod, the pulse
reflects off the next cavity mirror, CM₃, and through a horizontal polariser and
inactive output Pockels cell, onto cavity mirror CM₄. The pulse now returns along its
path (amplified again by the rod) to the still inactive input Pockels cell. The pulse
then gets a further 90° rotation by the waveplate becoming vertically polarised and is
then rejected at the rod.

Case (c) - the input Pockels cell is off for the first two passes of the laser pulse, but is
turned on before the pulse returns from CM₄: The pulse is now selected. In this case,
when the pulse returns from CM₄ and is horizontally polarised as in case (b), since
the input Pockels cell has been turned on, the pulse receives a 180° rotation as in
case (a). The pulse now remains horizontally polarised, and makes about 20 round
trips in the cavity, each time rotating by 180° and gaining in amplitude with each
round trip. The pulse is released into the compressor by activation of the output
Pockels cell, which rotates the light 90° (after two passes via CM₄) and is now
reflected off of the horizontal polariser and directed into the compressor.

The synchronization and delay generator (SDG) provides the timing for the Pockels
cells, synchronisation of the seed and pump pulses inside the amplification stage,
and provides a reference signal for synchronisation of the optical chopper and lock-
in amplifier in the TA experiment. The timing for the pump pulses and Pockels cells
must be optimised for amplification of the selected seed pulse, which is achieved by
observing the output of a fast photodiode sampling some of the intensity inside the
amplification cavity. The output of this diode is the selected pulse growing in
amplitude with each trip around the cavity, until it is ejected once the gain in the rod
is depleted. The Spitfire shares the Empower chiller for cooling of the Ti:Sapphire
rod.

5% of the Spitfire output is used to produce the probe beam, with approximately
75 mW average power. The remaining 95% is directed into the final stage of the TA
laser system, which is the tuning of pump light. A Light Conversion Ltd. TOPAS-C
optical parametric amplifier (OPA) [58] with harmonic generating (HG) crystals is used to produce the pump beam for the TA system, tuneable across the UV/Vis/IR spectrum. There are many computer controlled mechanical parts inside the OPA for optimal wavelength tuning, all of which are pre-set by the accompanying software given a user-defined output wavelength.

Inside the OPA the Spitfire output forms a pump beam, which is split such that ~80% is used for amplification, and the rest is used for generation of a White Light Continuum (WLC) in a sapphire plate (see the previous section for a description of this process). Computer controlled rotation of Brewster’s angle plates tunes the delay of the pump beam relative to the white light. A portion of the input light used for WLC generation is split off and used for pre-amplification of the white light inside a beta barium borate (BBO) non-linear crystal. A computer controlled delay stage delays the WLC before the nonlinear crystal in order to optimise amplification of 1100-1600 nm light inside the WLC. The non-linear crystal is also rotated by computer control for optimal phase matching, and a compensator is rotated to correct the beam path. The pre-amplified WLC and the pump beam are then overlapped in a second BBO crystal both spatially and temporally, which is also rotated by computer control.

In each of the non-linear crystals the process of optical parametric amplification occurs, where the overlap of a pump and signal beam results in the amplification of the signal and the emission of an idler beam with a frequency (and photon energy) which is the difference between the pump and signal. In order to achieve a high efficiency for this process the pump and signal must be phase matched, which is achieved by rotating the non-linear crystal. This has the effect of rotating the optic axis of the crystal and changing the direction of polarisation vectors of the three beams. In the TOPAS-C, rotating of the BBO crystals allows selection of the signal beam wavelength from the WLC. The computer has pre-programmed positions for the user-defined wavelength which is produced after the second BBO crystal as either the amplified signal (1200 –1600 nm) or the idler beam (1600 – 2400 nm).

After the OPA the tuning range of the TOPAS-C system is extended by two turret mounted BBO crystals also with computer controlled rotation. The first crystal can produce a fourth beam at the second harmonic of one of the three output beams, or at
the sum frequency of two of the three beams. The second crystal can then produce a fifth beam at the second harmonic of one of the four beams. After the crystals, one of a range of possible dichroic beam splitters is used to aid isolation of the desired beam which acts as the pump beam for the TA experiment.

3.5.2.3. Detection with a lock-in amplifier

A Stanford Research Systems SR830 lock-in amplifier is used to process the signals from the pair of fast photodetectors. Each detector produces a time dependent voltage due to the intensity of the probe and reference beams at the wavelength isolated by the spectrometer, $V_a$ and $V_b$ respectively. Each of these signals will also contain a significant amount of noise, primarily due to stray light and electronic noise. The lock-in amplifier outputs a time-independent voltage which is a Fourier transform on either $V_a$, or the difference between the two signals, $V_a - V_b$, at a frequency synchronised to the pump repetition rate, 500 Hz after the chopper, or the probe repetition rate, 1000 Hz, denoted $f_{500}$ and $f_{1000}$ respectively.

The Fourier transform is functionally equivalent to multiplication of the signal by a sine wave with a frequency of the reference signal, and numerical integration of the result. The output is a single voltage which is proportional to the component of the original signal which is varying at a frequency matching the reference signal. The relative phase of the sine wave and input signal is optimised by the amplifier for maximum output signal. The process is performed for many pulse periods at once to average the result of multiple sample excitations; in this work it was done over 300 ms, referred to as the time constant of the lock-in.

The Fourier transform process has two key benefits, firstly the elimination of noise in the signal which has negligible contribution at the frequency of the reference signal for stray light and electronic noise. Secondly, the process enables detection of small changes in probe intensity which are unmatched by other TA systems which use either a CCD or streak-camera for detection.

Measuring the Fourier transform of $V_a - V_b$ at 500 Hz, denoted $f_{500}(V_a - V_b)$, results in an output which is directly proportional to the change in $V_a$ induced by the pump beam in the sample. This change occurs at the frequency of the pump, 500 Hz.
Although the reference signal, $V_b$, does not have any signals varying at 500 Hz, taking the difference between the two signals (before Fourier transform) when they are balanced by an ND filter (see Section 3.5.2) reduces the impact of pulse to pulse variation on the signal. This concept is illustrated by Figure 3-18 for a photo-bleach of the probe induced by the pump.

![Figure 3-18](image)

Figure 3-18. Illustration of the signals present in the TA experiment, pulse widths are exaggerated for clarity, and neglect the response of the silicon photodiodes. After a pump pulse the transmission of the probe tuned to the quantum dot band edge is increased due to state filling. The difference between the probe and reference beams, $V_a - V_b$, is a 500 Hz signal proportional to this transmission change. The lock-in signal with frequency synchronised to the pump is used to perform a Fourier transform and is phase matched to $V_a - V_b$.

Converting from the lock-in output to fractional transmittance changes in the sample requires measurement of the initial transmittance of the probe beam. This is proportional to $f_{500}(V_a)$ in the absence of the pump beam, where the probe would need to be reduced to 500 Hz. It is more convenient to measure $f_{1000}(V_a)$ in the absence of the pump; however, a small difference between these two measurements is expected due to the change in width of the lock-in reference sine wave around the signal. This difference was found to be negligible for this TA experiment attributable to the narrow pulse widths and photo-diode response in comparison to the sine wave at either 500 Hz or 1000 Hz. As a result, the fractional transmittance change is given by:

$$\frac{\Delta T}{T} = \frac{f_{500 \text{pump}}(V_a - V_b)}{f_{500 \text{probe}}(V_a)} = \frac{f_{500 \text{pump}}(V_a - V_b)}{f_{1000 \text{probe}}(V_a)}$$

The bleach change over time is measured by changing the delay of the pump and probe beams, such a measurement is referred to as a transmission change transient in this work. A transient is recorded by scanning the delay stage and measuring
$f_{500}^{\text{pump}}(V_a - V_b)$ at each position. Before and after the scan $f_{500}^{\text{no pump}}(V_a)$ is measured, which is independent of pump-probe delay. Imperfect alignment of the delay stage, beam drifting, or a gradual reduction in WLC quality can result in small deviations in $f_{500}^{\text{no pump}}(V_a)$ during a scan, so the two values are averaged and used to calculate $\Delta T(t)/T$ at each delay position. An example transient is shown in Figure 3-19a. The change in pump-probe delay, $\Delta t$, is determined from the delay stage position, $x$, where it must be remembered that a change of 1 mm, corresponds to a 2 mm increase in path length of the probe beam. Thus

$$\Delta t = 2 \frac{\Delta x}{c} \quad (3-17)$$

where $c$ is the speed of light. A 1 mm change thus corresponds to 6.67 ps. The range of the delay stage was 200 mm, with a resolution of 0.001 mm, which is a negligible contribution to the system time resolution compared to the pulse widths.

In order to record a transmission change spectrum, referred to as a differential spectrum in this work, the delay stage position is fixed to a given pump probe delay, and the spectrometer wavelength is scanned. Due to the variation in absorbance of the sample with wavelength, it is not possible to balance the probe and reference beams using an ND filter at all wavelengths simultaneously. Consequently, the fractional transmittance change is given by

$$\frac{\Delta T}{T} = \frac{f_{500}^{\text{pump} & \text{probe}}(V_a)}{f_{1000}^{\text{probe}}(V_a)} \quad (3-18)$$

at the cost of increased noise. $f_{500}^{\text{pump}}(V_a)$ and $f_{1000}^{\text{no pump}}(V_a)$ are each measured across the wavelength range, one after the other, and their ratio taken at each wavelength to give $\Delta T(\lambda)/T$.

When measuring the probe beam at 500 Hz there are two additional signals which can be detected. These are scattered pump light, and photoluminescence induced by the pump. Each of these signals can appear as a peak in the differential spectrum (although the PL may be weak in low PLQY samples). As a result, if a spectrum is
measured in the region of the PL or excitation peaks, their contribution can be measured in the absence of the probe beam and used to correct the spectrum:

$$\frac{\Delta T}{T} = \frac{f^{pump \& probe}_{500}(V_a) - f^{pump}_{500}(V_a)}{f^{probe}_{1000}(V_a)}$$ \hspace{1cm} (3-19)

In transmission change transients these contributions appear as a constant background (due to their independence of pump-probe delay), therefore a portion of transient is measured before the pump arrives at the sample \( (t < 0) \), to determine the baseline which is subtracted from the transient. An example differential spectrum is shown in Figure 3-19b, which shows each of these components.

Figure 3-19. a) Example fractional transmittance change transient, \( \Delta T(t)/T \), for bleaching of the band edge transition in a QD sample. Only every 5th error bar is drawn for clarity. b) Raw output from the lock-in amplifier for the scans which form the numerator of Equation (3-19) for calculating a fractional transmittance change spectrum, \( \Delta T(\lambda)/T \). The two peaks in the pump only scan are from scattered pump light, centred on 525 nm, and from sample photoluminescence, centred on 570 nm. The region around the pump beam remains distorted even after subtraction from the spectrum. This was recorded with a pump-probe delay of a few ps.

Transients were collected using a LabView [50] script written by B Spencer, which can scan a defined range of delay stage positions with a given step size and take readings from the lock-in amplifier. The script can take multiple scans which are averaged to for a single transient. Throughout this work 5 – 10 scans are typically taken, and an error for each data point of the average is determined from the standard error on the mean.
3.5.2.4. Stirring and flowing samples

The TA system is equipped with a magnetic stirring system (Thermo Scientific Variomag Mini) capable of stirring the contents of a cuvette at up to 1000 rpm using a glass coated 8 mm stirring bar inside the cuvette. As discussed in Section 2.5.3, the purpose of stirring is to refresh the sample volume intersected by the pump beam to counteract any artefacts caused by photocharging of the QDs.

There was concern, however, that in stirring, QDs which have been photo-charged can return to the pump beam before any photocharging effects wear off, and a distribution of photo-charged states could build up in the cuvette. To counteract this, a flow system was developed where a large volume of sample (~600 ml) can be flowed through a cuvette, at variable and approximately constant flow rate. similar flow systems have been shown by other groups to eliminate photocharging [59].

The system used a Stenner SVP1H7 peristaltic pump, consisting of only a single wetted part (a pump tube which is “squeezed” to push fluid through the system), capable of pumping above 250 ml/min. The mechanical nature of a peristaltic pump leads to a pulsing effect in the flow of fluid around the system, undesirable for constant refreshing of the pump beam volume. To dampen the pulsing, two sample reservoirs were used: one at the inlet of the pump and one at the outlet. The result is that the pressure driving flow through the cuvette must be transferred through two nitrogen filled cavities reducing the impact of the pulsing. The wetted components of the system were carefully chosen to prevent chemical reaction with the sample, particularly the sample solvent. The pump tube was manufactured from Tygothane, and the connecting tubes from PTFE and passed tightly through rubber stoppers into glass reservoir flasks. The cuvette was a Starna quartz flow cell with 2 mm path length in order to reduce turbulence (as opposed to the 10 mm path length in the stirred cuvettes).

3.5.3. Artefacts

In transient absorption experiments there are several signals which can arise that are not due to the charge dynamics under investigation, but rather to non-linear phenomena from interaction of the high intensity pump and probe beams, or due to the (relatively) high repetition rate of excitation [60-61]. These experimental
artefacts can significantly obscure measurements, limit the time resolution of the system, or even result in false measurements of charge dynamics.

As discussed in Section 2.6, the signature of MEG is, at low pump fluences, a rapid signal decay on the sub-nanosecond time-scale corresponding to fast Auger recombination of multi-excitons. However, Auger recombination can also occur when a trion is formed within a QD. Trions can form when a hole or electron is trapped on the QD surface for a time longer than the period between excitation pulses. Its geminate charge is thus already present within the QD when an exciton is formed following photon absorption during a subsequent pump pulse. The unpaired electron or hole residing within the QD is able to receive the energy liberated in recombination, enabling fast Auger recombination of the remaining electron–hole pair, see Figure 3-20. This process can produce a sub-nanosecond decay in the signal even at low pump fluences and thus can resemble the signature of MEG.

Several careful studies [59, 62-63] have shown that sufficient stirring or flowing of the sample can refresh the QDs within the excitation volume in between pump pulses, preventing the formation of trions and thus of this misleading component to the signal. McGuire et al. [64] emphasize that the existence of long-lived charges in QDs does not seem to suppress MEG, but does complicate accurate determination of its efficiency. As described in the previous section, the TA experiment in this work can stir or flow samples to eliminate this artefact.

Figure 3-20. After charge trapping, re-excitation of a QD results in trion formation, which provides a charge capable of receiving the energy liberated in the recombination of an exciton by Auger recombination, resulting in an enhanced apparent single-exciton recombination rate. This can occur for a positive trion if an electron is trapped, a), or a negative trion if the hole is trapped, b). Blue arrows show Auger mediated processes which occur simultaneously.
Additionally there are artefacts which arise from interaction between the pump and probe beams inside the sample cuvette or solvent, each of which are well described by Lorenc et al. [61], and produce limitations on the resolution of the system in excess of the pump and probe temporal widths.

The first such artefact is two photon absorption (TPA), where the highly focussed pump and probe beam’s high photon fluxes result in a significant probability of the simultaneous absorption of one photon from each when coincident in the sample. This phenomenon can occur in the QD, its solvent and potentially in the sample cell itself. It corresponds to absorption at the sum frequency of the pump and probe, and can appear as an increase in probe absorption with a temporal width corresponding to the correlation of the pump and probe. This artefact is strongly dependent on the time dispersion of wavelengths within the probe (chirp) and velocity dispersion of pump and probe within the cell and sample [65].

Stimulated Raman amplification (SRA) is the second potential phenomenon. This occurs if the pump and probe wavelengths are spectrally very close. If so, when they coincide in space and time within the sample they can experience coupling by molecular oscillations with energy corresponding to the difference between pump and probe photon energy. The coupling is seeded by another component of the white light continuum, and can result in both increase and decrease of the TA signal depending on the relative energies of the three components.

Thirdly, the pump beam can cause cross-phase modulation (XPM) of the probe beam, analogous to SPM described in Section 3.5.2.1. In this case, the high photon density of the pump beam induces refractive index changes in the cuvette or solvent which then modify the spectrally broad probe pulse by introducing time dependent chirp. As in SPM, XPM has a dependence on the rate of intensity change of the pump beam and the sign of the change, meaning that the direction of the shift changes on each edge of the pulse. The result is a derivative-shaped artefact (positive and negative peaks) both in time and in wavelength.

These artefacts which arise due to interaction of the overlapping pump and probe beams, can generally be avoided by modifying the time increment of the delay scan between pump and probe, and avoiding too small an increment in delay. If
measurement of a weak signal around the time of pump-probe coincidence is required, the artefacts can be suppressed by reducing chirp in the white light continuum, using thin sample windows with low dispersion, and careful solvent choice (if possible) [61].

As mentioned above, these phenomena can obscure the underlying dynamics and place limitations on resolution, but can also be used to acquire knowledge of the optical properties of the system such as the pulse widths and chirp and the time of pump probe overlap, as they each occur only for coincidence of the pump and probe in space and time. As discussed in Section 3.5.2.1, significant chirp can exist in the WLC, which would appear as a shift in the time of pump-probe overlap when comparing transients at different probe wavelengths. In this work, measurement of artefacts in reference samples (solvent and cuvette only) at high fluence are used when necessary to determine the time of pump-probe overlap, \( t = 0 \). Due to the symmetry in time of many of the artefacts, their centre point is taken as an indication of \( t = 0 \), and their width can be used to estimate the system’s IRF.

If elimination of these artefacts is not possible experimentally, a post-processing technique has been formalised by Lorenc et al. [61] for subtraction of the artefact contributions from TA signals. It was found that all unwanted signals had a linear dependence on pump fluence, which allows the calculation of the artefact-free (corrected) signal, \( S_c \), as

\[
S_c = S - S_r \frac{E_s}{E_r} f
\]

where \( S \) denotes uncorrected signal measured for excitation energy \( E_s \) and \( S_r \) is the signal pertaining to the solvent measured for pump pulse energy \( E_r \). The factor \( f \) describes a decrease of mean energy in the sample due to stationary absorption (OD) by the molecules investigated, calculated by averaging the fractional absorption across the sample (see Equation (3-2) in Chapter 3.3.1):

\[
f = \frac{1}{L} \int_0^L e^{-\alpha x} \, dx = \frac{1}{L} \int_0^L e^{-Ax/L} \, dx = \frac{1 - e^{-A}}{A}
\]
where $x$ is the distance through the sample, and $A = n\sigma L$ is the absorbance of the whole sample. This method will be used to remove artefacts from transient absorption signals in Chapter 4. However, its effectiveness was found to be highly sensitive to the experimental conditions such that laser system instability can cause poor results, and the cuvette positioning and orientations of the sample and solvent must be identical relative to the beams.

### 3.5.4. Bi-exciton shift

In Chapter 2 the coulombic interaction of excited electrons and holes was described in terms of an exciton binding energy. In particular, the bi-exciton binding energy, $\Delta_{XX}$, can have important implications for the efficiency of MEG and has an interesting effect on TA spectra. The bi-exciton binding energy can be positive or negative, often called attractive or repulsive, such that the net energy of the bi-exciton is different to double the energy of a single exciton state. After the pump beam has excited an exciton in a QD, a probe photon can be absorbed to create a bi-exciton. The absorption spectrum experienced by the probe beam is shifted in energy by $\Delta_{XX}$ (corresponding to excitation directly into the bi-exciton state), this carrier-induced Stark shift is known as the bi-exciton effect or bi-exciton shift \[66\].

The effect of the bi-exciton shift on TA spectra is dependent on whether the initially hot exciton created by the pump beam has cooled to the band edge, and has been studied extensively by Klimov \[66\]. At early times after excitation, before any cooling of the pump-induced exciton, there will be no contribution from state filling to the TA spectrum at the band edge transition, however, a shift in the absorption spectrum results in an absorption change around the peak. For a single band edge transition, labelled $1S$, with energy $E_{1S}$ and linewidth $\Gamma_{1S}$, the change in band edge absorption is

$$
\Delta \alpha = A_0 \frac{\delta_{XX} (2x - \delta_{XX})}{[(x - \delta_{XX})^2 + 1](x^2 + 1)} \tag{3.22}
$$

where $A_0$ is the $1S$ absorption amplitude, $x = (h\omega - E_{1S})/\Gamma_{1S}$ is the normalised detuning from the $1S$ transition, and $\delta_{XX} = \Delta_{XX}/\Gamma_{1S}$ is the normalised bi-exciton interaction energy. This equation surmounts to the difference between two Lorentzian absorption peaks, illustrated in Figure 3-21a \[66\], where one is shifted by
Δ_{XX}. This results in the differential shape to the absorption change (a positive and negative peak) also shown in Figure 3-21a, with both a bleach feature and PA.

After carrier cooling has occurred, in addition to the shift in absorption, the state-filling effect leads to a bleaching of the 1S transition, and the resulting net absorption change can be described by
\[\Delta \alpha = \frac{A_0}{2} \frac{x^2 - 1 - 2(x - \delta_{xx})^2}{[(x - \delta_{xx})^2 + 1](x^2 + 1)} \]  \hspace{1cm} (3-23)

The corresponding absorption peaks and net change in absorption for this case are shown in Figure 3-21b.

### 3.5.5. Analysis

The time dynamics of the excited states probed in TA are readily determined from TA transients by fitting to the observed decays in signal in the same manner as was described for the TCSPC experiment in Section 3.4. However, the amplitude of fractional transmittance change is an important measurement for understanding TA data in terms of the average occupancy of the QDs, \(\langle N \rangle\), which is critical when considering multi-exciton decay.

In Section 3.5.2.3, determining the fractional change in transmittance, \(\Delta T/T\), of a sample from the TA system was described. A more useful measure which directly relates to state filling and \(\langle N \rangle\) is the fractional change in absorbance, \(\Delta A/A\). The relationship between the two can be derived by first defining the transmittance after excitation, \(T^*\), with a corresponding absorbance, \(A^*\), and using Equation (3-2) we can write \(T = I_0 e^{-A}\). Then

\[\frac{\Delta T}{T} = \frac{T^* - T}{T} = \frac{e^{-A^*} - e^{-A}}{e^{-A}} = e^{A-A^*} - 1 = e^{-\Delta A} - 1 \]  \hspace{1cm} (3-24)

where \(\Delta A\) is the change in absorbance. Rearranging for \(\Delta A\) we get

\[\Delta A = -\ln \left(1 + \frac{\Delta T}{T}\right) \]  \hspace{1cm} (3-25)

Dividing by \(A\) and approximating for \(\Delta T/T \ll 1\) yields

\[\frac{\Delta A}{A} = -\frac{1}{A} \frac{\Delta T}{T} \]  \hspace{1cm} (3-26)

The fractional change in absorbance is more suitable for comparing the amplitude of TA signals from different samples.
Immediately after excitation by the pump beam, the average occupancy of QDs, \( \langle N \rangle \), or equivalently, the number of photons absorbed, depends on their absorption cross section at the pump wavelength, \( \sigma \), and the pump fluence per excitation pulse, \( J \):

\[
\langle N \rangle = \sigma J
\]  

(3-27)

The changes in absorbance observed are due to state filling of the probe transition due to the limited degeneracy of the electron and hole states. As described in Chapter 2, and in Section 3.5.1, the band edge hole states are typically split into several close highly degenerate states, where the holes relax to the uppermost level. In TA experiments the probe beam is tuned to the lowest energy absorption maximum, corresponding to a hole state just below the band edge, where relaxed holes have negligible contribution to the state filling. We can therefore write [67-68]:

\[
\frac{\langle N \rangle}{g} = \frac{-\Delta A}{A} = \frac{1}{A} \frac{\Delta T}{T}
\]  

(3-28)

where \( g \) is the degeneracy of the electron band edge state. This equation states that the filling of the band edge is directly proportional to the reduction in absorption, or increase in transmission. Complete filling of the band edge state, \( N = g \), in every QD in the sample results in complete bleaching of the band edge transition. Throughout this work, the band edge transition corresponds to a 1S orbital with \( g = 2 \). The expression requires that both \( \langle N \rangle \) and \( \Delta T/T \) are small, and makes several other crucial assumptions which will be discussed later in this section. For comparison of \( \langle N \rangle \) in Equations (3-27) and (3-28), the peak value of \( \Delta T/T \) must be used, where it is assumed that all excited charges have cooled to the band edge, but have not yet started to relax any further. This important assumption will be challenged in Chapter 4. \( \Delta A/A \) is suitable for comparison of different TA transients because it is directly proportional to \( \langle N \rangle \), and therefore to \( J \). Some studies simply plot \( \langle N \rangle \) vs time, but this is misleading when it is suspected that all excited charges do not necessarily reach the band edge and contribute to the early time bleach. A fairer comparison which is to be used in this work is to plot \( (\Delta A/A)/(JA_{\text{pump}}) \), where \( A_{\text{pump}} \) is the absorbance at the pump wavelength, \( JA_{\text{pump}} \) is proportional to \( \sigma J \), and therefore normalisation by this factor accounts for differences in the number
of excitons created for slightly different pump conditions for a given sample, either deliberate or due to laser system instability.

As discussed in Section 2.6, the formation of multi-excitons by the pump beam is possible either by MEG or the absorption of more than one photon by a single QD from the pump pulse. The probability of a QD absorbing $N$ photons per pump pulse, $P(N)$, is determined by Poisson statistics:

$$P(N) = \frac{\langle N \rangle^N \exp(-\langle N \rangle)}{N!}$$  \hspace{1cm} (3-29)

The ratio of the probabilities of absorbing two or one photon per QD is then given by $P(2)/P(1) = \langle N \rangle/2$. This is an important concept for TA studies, where the absorption of more than one photon is to be avoided. The observation of multi-exciton decay in transient absorption or PL studies can only be taken as evidence of MEG if the pump fluence can be confirmed to be sufficiently low as to make the chance of a QD absorbing two or more photons per pump pulse negligible.

Estimating $\langle N \rangle$ is therefore an important task for any TA study, typically done through Equation (3-27). However, $\sigma$ is difficult to determine accurately [6-7, 9, 69-71], and a suspected underestimation of $\sigma$, and thus of $\langle N \rangle$, was one explanation suggested for the discrepancy in the early MEG results reported by different groups for nominally similar QDs [72]. Other explanations suggested at that time included spatial variation in $\langle N \rangle$ due to pump beam inhomogeneities and variation in the surface chemistry between samples [73]. Consequently, an analysis method for MEG was developed which does not require knowing $\sigma$. A typical pump-induced transmittance transient is shown in Figure 3-22a. $R$ is the ratio of the signal maximum, which is proportional to the average number of excitons created per QD, and the signal at a time significantly greater than the biexciton lifetime but significantly less than the single exciton lifetime, often referred to as the plateau. This latter time corresponds to when all multi-excitons created by the pump pulse have decayed to single excitons, but the resulting single exciton population has largely yet to decay. In the limit of low fluence, each excited QD has absorbed only one photon and so the population of single excitons at this latter time is equivalent to the number of absorbed photons. Any multi-exciton decay therefore corresponds to
charges excited through MEG. Thus, in this limit, $R$ corresponds to the average number of excitons created per absorbed photon, the $QY$. The low fluence limit of $R$ can be found experimentally by measuring $R$ for a range of pump fluences and fitting the following equation to the resulting data [44]:

$$R(J) = \frac{QY\sigma J}{1 - e^{-\sigma J}}$$  \hspace{1cm} (3-30)

Figure 3-22. a) A typical signal obtained from a TA experiment showing the fractional transmittance change, $\Delta T/T$, as a function of time delay between the pump and probe beams. $R$ is the ratio between the peak amplitude, $A$, and the plateau amplitude, $B$, where enough time has passed that all bi-excitons have decayed, but before any significant decay of single-excitons. b) $R$ as a function of fractional transmittance change, $\Delta T/T$, for InP QDs excited at 2.6 times $E_g$. The line is a fit to eqn (2), data from Reference [74]. c) Additional excitons produced, $(QY - 1)$, as a function of $h\nu/E_g$ for InAs QDs of different $E_g$. $h\nu_{th}$ corresponds to the point where the rise in additional excitons begins, where the gradient of the rise is the efficiency, $\eta$ [75] [76]. Reprinted with permission from Reference [76].

Figure 3-22b shows an example of this analytical procedure for MEG in InP QDs. In this case, $R$ has been plotted against the maximum value of the fractional transmittance change transient, $\Delta T/T|_{max}$, which is proportional to $\langle N \rangle$ [77].
Repeating this process for different pump wavelengths enables the number of additional excitons per absorbed photon, \((QY - 1)\), to be found as a function of photon energy normalized to \(E_g\), as shown in Figure 3-22c. From this, the values of \(h\nu_{th}\) and \(\eta\) can be determined by finding the intercept and gradient of a linear fit to the data for which \(QY > 1\), as described in Section 2.6, and shown theoretically in Figure 2-12.

There are a few notable shortcomings when analysing TA data using Equation (3-30). If the single-exciton recombination rate is comparable to the multi-exciton recombination rate, decay of the plateau can occur and result in an over-estimation of \(R\) and \(QY\). This has been corrected in some works by the introduction of a factor on the right-hand side of Equation (3-30) to account for this decay using the single exciton decay lifetime, \(\tau_x\), which might be measured on a TCSPC system. The factor is typically labelled \(\delta\) and given by \(\exp(-t/\tau_x)\), where \(t\) is the time window over which \(R\) is measured. Some works have found that an additional factor is needed for fitting of Equation (3-30). This factor is typically placed in front of both occurrences of \(\sigma J\), acting to scale the \(x\)-axis in Figure 3-22b. This can be interpreted as correcting for poor estimation of \(\sigma\), or as accounting for hot charges which do not reach the band edge.

### 3.5.6. Derivation of MEG QY for highly absorbing samples

Equation (3-30) is only valid for samples with an absorbance length, \(l_A\), at the pump wavelength which is long compared to the beam path through the sample, \(l_S\) [73]. Moreover, as discussed previously for \(l_A \ll l_S\) the value of \(\Delta T/T\) observed will be significantly reduced [77], since the volume of excited sample through which the probe beam passes is decreased as the pump beam is completely absorbed close to the front facet of the cuvette. A dilemma arises because the magnitude of \(\Delta T/T\) is also proportional to the absorbance at the probe wavelength, \(A\): reducing the sample concentration so that \(l_A\) is long compared to \(l_S\) results in a weak fractional change in transmittance. Such a scenario was encountered in this work when measuring MEG in InP/CdS QDs, the results for which are described in Chapter 6. As a result, a new expression for relating the fractional transmittance change to \(QY\) was developed, and is described in this section.
We derive an expression for $\Delta T/T$ taking into account the change in pump beam fluence along the path through the sample, following the work of Al-Otaify et al. [77], with the addition of the time dynamics of single and multi-excitons and without mathematical approximations which rely on small pump absorption.

We start our derivation with the Beer-Lambert law in the following form

$$J(z) = J_0 e^{-\alpha z} = J_0 e^{-\sigma n z}$$  \hspace{1cm} (3-31)

where $J(z)$ is the fluence of the probe beam at a distance $z$ through the sample, $J_0$ is the initial fluence of the probe beam, $\alpha$ and $\sigma$ are the absorption coefficient and cross section at the probe wavelength, respectively, and $n$ is the number of QDs per unit volume. Hence, for unexcited samples we can write

$$\frac{df}{dz} = -\sigma n J$$  \hspace{1cm} (3-32)

However for an excited sample of QDs, after cooling, state-filling reduces the absorption of the band edge state. The state filling will depend on the time delay, $t$, between the pump and probe beams, as the QDs relax to their ground state. For a band edge state with degeneracy $g$

$$\frac{df(t)}{dz} = -\sigma J \sum_{i=0}^{g} \frac{(g - i)}{g} n_i(t)$$  \hspace{1cm} (3-33)

where $n_i(t)$ are the numbers of QDs per unit volume containing $i$ excitons ($i = 0, 1, 2, \ldots$), and the sum represents the contributions to state filling for each population of QDs with sequentially more band edge excitons. This sum is limited to the case of a filled band edge, where the addition of more excitons cannot increase the band edge bleach. For a QD with band edge degeneracy $g = 2$, this becomes

$$\frac{df(t)}{dz} = -\sigma J \left( n_0(t) + \frac{(g - 1)}{g} n_1(t) + \frac{(g - 2)}{g} n_2(t) \right)$$  \hspace{1cm} (3-34)

In this case $n_2$ actually represents the number of QDs with 2 or more excitons.
The initial values of each $n_i$ (immediately after excitation by the pump beam) will be dependent on both the probability, $P_i$, of a QD absorbing $i$ photons, and by the probability of MEG occurring. The former is given by Poisson statistics,

$$P_i = \langle N \rangle^i e^{-\langle N \rangle} / i!$$

(3-35)

where $\langle N \rangle$ is the average number of photons absorbed per QD. The latter can be characterised by the MEG slope efficiency, $\eta$, which is equal to $QY-1$, the average number of additional excitons created following excitation of a single hot exciton. The occurrence of MEG will reduce the number of singly excited QDs, $n_1$, which can contribute to absorption, and increase $n_2$. Thus

$$n_0(0) = nP_0 = ne^{-\langle N \rangle}$$

(3-36)

$$n_1(0) = nP_1(1 - \eta) = n\langle N \rangle e^{-\langle N \rangle}(1 - \eta)$$

(3-37)

QDs which contain two or more excitons will have a completely filled band edge state, and $P_2 + P_3 + P_4 \ldots = (1 - P_0 - P_1)$; $n_2$ is thus given by the sum of all QDs which absorb more than one photon, plus the number of QDs which absorb a single photon and undergo MEG:

$$n_2(0) = n(1 - P_0 - P_1) + nP_1 \eta$$

$$= n(1 - e^{-\langle N \rangle} - \langle N \rangle e^{-\langle N \rangle}) + n\langle N \rangle e^{-\langle N \rangle} \eta$$

(3-38)

Substituting Equations (3-36) – (3-38) into Equation (3-34) would yield an expression for the change in probe fluence with $z$ before any recombination has occurred, as is formulated by Al-Otaify et al. [77]. However terms can be included at this stage which represent the relaxation between the multi-exciton, single-exciton and relaxed QD states.

We assume here that the pump fluence used is sufficiently low so that the probability of generating more than two excitons per QD is negligible. A biexciton may decay to a single exciton by an Auger process in which one of the constituent excitons recombines by transferring energy to one or other of the carriers of the other exciton, which then subsequently cools back to the band edge; this process is efficient and
characterised by a rate constant $k_{XX} = 1/\tau_{XX}$, where $\tau_{XX}$ is typically 10s of ps [66]. One of the constituent excitons can also in principle decay by a single exciton recombination process, such as radiative recombination, with a lifetime $\tau_X = 1/k_X$, but this is slow in comparison with $\tau_{XX}$, being typically several ns or longer [66]. After biexciton decay is complete, the remaining single excitons decay with lifetime $\tau_X$, leaving an unexcited QD, as illustrated in Figure 3-23.

\[ n_0(t) = C_1 \frac{k_X}{k_{XX}} e^{-(k_{XX}+k_X)t} - C_2 e^{-k_X t} + C_3 \quad (3-42) \]

\[ n_1(t) = -C_1 \frac{k_{XX} + k_X}{k_{XX}} e^{-(k_{XX}+k_X)t} + C_2 e^{-k_X t} \quad (3-43) \]

\[ n_2(t) = C_1 e^{-(k_{XX}+k_X)t} \quad (3-44) \]

where $C_1$-$3$ are constants. By setting $t = 0$ and using the initial conditions given by Equations (3-36) to (3-38), it can be shown that
\[ C_1 = n_2(0) \]  
\[ C_2 = n_1(0) + \frac{k_{XX} + k_X}{k_{XX}} n_2(0) \]  
\[ C_3 = n_0(0) + n_1(0) + n_2(0) \]

Combining Equations (3-36) through (3-47) allows the re-writing of Equation (3-34) in terms of only \( \langle N \rangle \), \( k_{XX} \) and \( k_X \). But first, we consider the variation of \( \langle N \rangle \) along the path of the pump beam:

\[ \langle N \rangle = \sigma_p J_p = \sigma_p J_p^0 e^{-\alpha_p z} \]  

where \( J_p^0 \) is the initial fluence of the pump beam, and \( \sigma_p \) and \( \alpha_p \) are the absorption cross section and coefficient at the pump wavelength, respectively. From this, or directly from the Beer-Lambert law we can write

\[ \frac{d\langle N \rangle}{dz} = -\alpha_p \langle N \rangle \]  

Thus the fluence change with \( \langle N \rangle \) is

\[ \frac{dj}{d\langle N \rangle} = \frac{dj}{dz} \frac{dz}{d\langle N \rangle} \]  

Substituting Equation (3-49) and (3-34) into (3-50) gives

\[ \frac{-\alpha_p dj(t)}{-\sigma j \ d\langle N \rangle} = \left( n_0(t) + \frac{(g - 1)}{g} n_1(t) + \frac{(g - 2)}{g} n_2(t) \right) \frac{1}{\langle N \rangle} \]  

Combining Equations (3-36) to (3-47) to substitute the three \( n_i(t) \) in terms of \( \langle N \rangle \), collecting like terms and remembering that \( \sigma_n = \alpha \), and \( g = 2 \) yields

\[ \frac{\alpha_p}{\alpha} dj(t) = \left( \frac{e^{-\langle N \rangle}}{\langle N \rangle} D(t) + e^{-\langle N \rangle} E(t) + \frac{1}{\langle N \rangle} (1 - D(t)) \right) d\langle N \rangle \]  

where
\[
D(t) = \frac{k_{XX} + k_X}{2k_{XX}} e^{-k_xt} - \frac{k_X - k_{XX}}{2k_{XX}} e^{-(k_{XX} + k_X)t} \tag{3-53}
\]

and

\[
E(t) = (2 - QY) \left( \frac{k_X}{2k_{XX}} e^{-k_xt} - \frac{k_X - k_{XX}}{2k_{XX}} e^{-(k_{XX} + k_X)t} \right) \tag{3-54}
\]

Integration of both sides of Equation (3-52) between the boundary conditions at the front face of the sample where \( J(t) = J_{in} \) and \( \langle N \rangle = \langle N \rangle_0 \) and rear face of the sample where \( J = J_{out} \) and \( \langle N \rangle = \langle N \rangle_f \):

\[
\frac{\alpha_p}{\alpha} \int_{J_{in}}^{J_{out}(t)} \frac{1}{J(t)} \, dJ =
\int_{\langle N \rangle_0}^{\langle N \rangle_f} \left( e^{-\langle N \rangle} D(t) + e^{-\langle N \rangle} E(t) + \frac{1}{\langle N \rangle} (1 - D(t)) \right) \, d\langle N \rangle \tag{3-55}
\]

The integration of \( e^{-\langle N \rangle}/\langle N \rangle \) is known as the exponential integral, and is equal to \( \ln \langle N \rangle \) plus an infinite geometric series in \( \langle N \rangle \), giving

\[
\frac{\alpha_p}{\alpha} \ln \left( \frac{J_{out}(t)}{J_{in}} \right) = D(t) \left( \ln \left( \frac{\langle N \rangle_f}{\langle N \rangle_0} \right) + \sum_{j=1}^{\infty} \frac{(-\langle N \rangle)^j}{j \cdot j!} \right)_{\langle N \rangle_0}^{\langle N \rangle_f} \tag{3-56}
\]

\[
-E(t) \left( e^{-\langle N \rangle_f} - e^{-\langle N \rangle_0} \right) + (1 - D(t)) \ln \left( \frac{\langle N \rangle_f}{\langle N \rangle_0} \right)
\]

\( \frac{J_{out}(t)}{J_{in}} \) is equal to the transmittance through the excited sample, \( T^*(t) \). For the unexcited sample we can write

\[
\frac{\alpha_p}{\alpha} \ln(T) = -\alpha_p l = -A_p = \ln \left( \frac{\langle N \rangle_f}{\langle N \rangle_0} \right) \tag{3-57}
\]
where $l$ is the sample thickness and $A_p$ is the sample absorbance at the pump wavelength. Subtraction of Equation (3-57) from both sides of Equation (3-56), and substituting $\langle N \rangle_f = \langle N \rangle_0 e^{-A_p}$ and $T' = 1 + \frac{\Delta T(t)}{T}$ where $\Delta T(t) = T'(t) - T$, gives

$$
\frac{A_p}{A} \ln \left(1 + \frac{\Delta T(t)}{T}\right) = 
$$

$$
D(t) \sum_{j=1}^{\infty} \frac{(-\langle N \rangle_0)^j}{j \cdot j!} \left(e^{-jA_p} - 1\right) - E(t) \left(e^{-\langle N \rangle_0} e^{-A_p} - e^{-(\langle N \rangle_0)}\right)
$$

This equation enables fitting of the time varying fractional change in transmission of the sample induced by the pump beam, where absorption of multiple photons per QD, production of multiple excitons by a single photon through MEG (via the $\eta$ term in $E(t)$), and change in pump fluence through the sample, are all taken into account. It can be thought of as a more complete version of Equation (3-28), which is typically used for analysing TA data.

### 3.5.7. Optimising sample absorption

In Section 3.5.6 it is clear that the sample dilution, which will scale the absorbance at both the pump and probe wavelengths, will have an important impact on the signal magnitude. Increasing the absorbance at the pump wavelength results in an increased fractional transmission change, $\Delta T/T$, due to more excitation of the sample, however, it will result in a reduction in net transmission, $T$, of the probe beam, which will reduce the signal to noise ratio at the detectors. We can determine the optimum sample absorbance to achieve the best signal for a given sample.

Taking Equation (3-58) for $t = 0$, neglecting terms in the sum higher than $j = 1$, and making the approximation that for small signal $\ln \left(1 + \frac{\Delta T}{T}\right) \approx \frac{\Delta T}{T}$ we can see that

$$
\frac{\Delta T}{T} \propto \frac{A}{A_p} \left(1 - e^{-A_p}\right)
$$

This was also shown in the work of Al-Otaify et al. [77]. $A$ and $A_p$ will both increase linearly with concentration, so we only need to consider maximising $(1 - e^{-A_p})$ to...
maximise $\Delta T/T$. This tells us to make the sample as concentrated as possible which results in very low probe transmission, such that little light arrives at the detectors and results in a poor signal to noise ratio. To account for this we need to multiply by the transmission at the probe wavelength, $T = e^{-A}$, so we can say

$$
signal \propto T \frac{\Delta T}{T} \propto \Delta T \propto \frac{Ae^{-A}}{A_p}(1 - e^{-A_p})
$$

(3-60)

These two equations are plotted in Figure 3-24, where it can be seen that an optimum concentration exists for overall signal. For any given sample this optimum will depend on the relative absorbances at the pump and probe wavelengths. In this work, samples were usually diluted to an absorbance of 0.1 – 0.3 at the band edge transition, which was typically very close to the optimum for excitation at 1.3 to 2 times $E_g$.

Figure 3-24. Illustration of the change in amplitude of $\Delta T/T$ and $\Delta T$ due to sample concentration. Maximising $\Delta T$ results in the highest signal to noise ratio from the system, see Equation (3-60).

### 3.5.8. Beam measurement and overlap

The knife-edge method [78-79] was applied to measure the pump and probe beam diameters at the sample position. These are important experimental parameters for calculating the pump fluence in the sample volume sampled by the probe beam, which is needed to determine the average number of photons absorbed per QD (see Equation (3-27)). It is also an important consideration in order to avoid photodegradation of QDs due to high pump fluence [80-81]. As described in Section 3.5.2, the probe beam is focussed to a spot size significantly smaller than the pump in order
to probe the region of highest pump fluence and ensure highest uniformity of pump fluence within the probed volume.

It was described by Marshall [79] that as a knife edge is moved perpendicularly across a Gaussian beam the total power detected behind the knife is given by

\[
\varphi(x) = \varphi_0 \left[ 0.5 + 0.5 \text{erf}\left(\frac{\sqrt{2}x}{\omega}\right) \right]
\]  

(3-61)

where \(x\) is the position of the knife edge relative the beam centre, \(\varphi_0\) is the total power in the beam, \(\text{erf}\) is the error function and \(\omega\) is the beam radius at 1/e² irradiance. This arises from calculating the convolution of a Gaussian peak and a step function (representing the knife-edge). Two other frequently used metrics for beam width are the 1/e beam diameter given by

\[
D_e = \sqrt{2}\omega
\]  

(3-62)

and the full width at half maximum, given by

\[
FWHM = \sqrt{2\ln(2)\omega}
\]  

(3-63)

A knife blade was securely mounted to a translation stage with adjustment accurate to 0.01 mm. This was placed at the sample position (the focal point of the focussing lens before the beam splitter, see Figure 3-12). A power meter was placed in the beam path approximately 10 cm behind the blade.

The power measurements were background corrected by subtracting the average power from measurements where the beam was fully obstructed, and normalised through division by the average of the peak power when the beam is entirely unobstructed (which was also background corrected). Example results and fits to Equation (3-61) are shown in Figure 3-25 for the probe beam and for the pump beam at 420 nm, a wavelength used frequently in this work. Also overlaid is the corresponding Gaussian beam profile in each case. The FWHM for the pump and probe beams are 1.87 ± 0.06 mm and 0.41 ± 0.02 mm respectively.
Figure 3-25. Measurements of the beam diameters of the pump at 420 nm, a), and probe, b), beams in the TA system using the knife-edge method. Red lines are fits to Equation (3-61), and blue dashed lines are the corresponding Gaussian beam profile.

It was shown in Section 3.5.5 that the absorbance change signals measured in the TA system are proportional to $\langle N \rangle = \sigma J$, but since the pump fluence falls with penetration into the sample, so will $\langle N \rangle$. For the analysis of MEG signals described in Section 3.5.6, an approach which accounts for this reduction required consideration of only the values at the front face of the sample, $\langle N \rangle_0$ and $J_0$. However an alternative approach will also be used later in this work which determines the average fluence experienced by the probe throughout the sample.

Equation (3-59) showed that the reduction in pump fluence along the pump's beam path can be accounted for by the factor $A_p^{-1}(1 - e^{-A_p})$, but two other factors also result in a change in fluence experienced by the probe relative to $J_0$. Firstly, the angle between the pump and probe beams will result in lower fluences away from the point of overlap. Secondly, the relative sizes of the pump and probe beams are an important factor, where a smaller probe beam can pick out the higher intensity centre of the pump beam. A computational approach which numerically determined the sum of these three effects was developed to determine the average fluence sampled by the probe beam.

The cuvette volume (modelled as a 1 cm$^3$ cube) was equally divided into a 3-dimensional mesh of equally spaced sampling points. The resolution of this mesh determines the accuracy and speed of the calculation, with 100 points along each axis found to be sufficient for $<0.1\%$ accuracy. At each point in the mesh the pump fluence is calculated. This is achieved by translating the coordinates to a reference frame co-linear with the pump, which is incident at $11^\circ$ to the cuvette (and probe beam).
beam). A Gaussian beam shape is assumed with total energy normalised to equal the average power of the beam. At each point in the mesh the calculated fluence is reduced by the absorbance of the sample due to the distance from the front face of the cuvette. This fluence is then weighted by the probe intensity at this point in the mesh, also assumed to be a Gaussian beam. The sum of the probe-weighted fluences at all points in the mesh is calculated. Dividing by the number of points in the mesh and by the sum of the probe weights then yields the effective fluence experienced by the probe.

For the beam diameters shown in Figure 3-25, a 1 mW average power pump beam, and a pump absorbance of 0.4, this yields an effective fluence of $1.71 \times 10^{14}$ photons cm\(^{-2}\) per pulse. This can be compared to a simpler approach of averaging the pump fluence within its FWHM, which yields $1.54 \times 10^{14}$ photons cm\(^{-2}\) per pulse, or the peak fluence at the centre of the pump beam of $4.27 \times 10^{14}$ photons cm\(^{-2}\) per pulse. The difference between these calculated values will prove to be important when calculating $\langle N \rangle$ in Section 4.4.2.

### 3.6. Structural characterisation

It is invaluable for an ultrafast study of QDs to be preceded by thorough structural characterisation of the sample. Often the aim is to validate the success of the potentially sensitive synthesis technique, and to inform on the quality and purity of the QDs produced. This includes measuring the elemental composition, size, shape, crystal structure, and any surface coating of the CQDs, each of which can play vital roles in the interpretation of studies of their ultrafast charge dynamics and other optical properties. Structural characterisation can also be important when considering the reproducibility of results, by providing important clues as to the cause of differences in charge dynamics of samples produced by identical recipes. A few of the most commonly used techniques will be described in brief in this section. In this project, these studies were undertaken by collaborators, but the corresponding results are included where appropriate in order to support the interpretation of the spectroscopic studies that comprise this thesis. Where such results are included, they are clearly indicated as being the work of collaborators.
Imaging of individual QDs is a useful achievement for determining their size, shape and size distribution. QDs are too small for conventional optical microscopy, and require the use of transmission electron microscopy (TEM), or high resolution TEM (HR-TEM) when imaging of single atoms is required. For either, QDs are deposited on a fine mesh, which can require solvent exchange for easy deposition.

X-ray diffraction (XRD) is an experiment which can determine the crystal structure of QDs by observing the diffraction patterns which emerge from interaction of X-rays with the atomic lattice. This is an important measurement on QDs composed of semiconductors which can form in more than one crystal structure, which can result in different electronic properties.

X-ray photoelectron spectroscopy (XPS) is a technique which can measure the relative abundances of different elements within the sample and can sometimes determine which atoms they are bound to. This is achieved by excitation of the sample with X-rays which result in the emission of photoelectrons with energies which can be cross-referenced with known atomic orbitals. Depth dependant XPS can be achieved by using a tuneable X-ray source which varies the mean free path and therefore the sampling depth. This is particularly useful for validating the structure of core-shell QDs. An estimate of the QD size can also be achieved which is useful for comparison to TEM images. Samples must be deposited onto a substrate, which can be problematic for air-sensitive QDs. XPS can detect surface species on the dots, so any reaction with the environment can change the surface relative to the original sample.

### 3.7. Summary

The spectroscopic techniques described in this chapter can be split into two key classes; firstly, steady-state spectroscopy of QDs, where measurement of their photoluminescence (PL) and absorption spectra reveals the optical transitions which were described in Section 2.3. The steady-state method of measuring PL quantum yield (PLQY) was also described, which reveals the degree of non-radiative recombination occurring in QDs. Secondly, time-resolved spectroscopic techniques which are time correlated single photon counting (TCSPC) and transient absorption (TA). Each of these techniques utilise ultrafast fs lasers in order to resolve the charge
relaxation processes described in Section 2.5. TCSPC is limited to observing relaxation of the band edge states through the decay of photoluminescence, whereas TA is capable of directly measuring the occupation of pairs of energy levels, but requires careful consideration of the excitation conditions and is prone to several experimental artefacts.

3.8. References

[12]. Other than in Figure 3-2, CBM refers to the Conduction Band minimum of a semiconductor.


[27]. Provided by Horiba Jobin Yvon Inc with the F-3018 integrating sphere.


[46]. SpectraSense, 9; Princeton Instruments.

Chapter 3

Experimental techniques

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Chapter 4. CdTe(Cl) CQDs – Trapping and surface passivation

4.1. Introduction
In this chapter the effects of trapping on ultrafast carrier dynamics and photoluminescence (PL) are investigated in CdTe colloidal quantum dots (CQDs) before and after treatment with chloride ions. The chloride treatment is shown to be capable of eliminating non-radiative charge recombination in these CQDs by the achievement of near-unity photoluminescence quantum yield (PLQY), enabling isolation of the effects of surface trapping on the carrier dynamics. The excitation dependence of the trapping dynamics is explored through both transient absorption spectroscopy and photoluminescence spectroscopy, where the presence of both hot and cold electron trapping are identified and characterised.

Some of the early transient absorption results presented in this chapter were published in the journal Advanced Science [1]. Two preceding publications by the D.J. Binks group reported on the synthesis, structural characterisation, steady state optical properties, and PL decay of the CdTe CQDs before and after chloride treatment [2-3], the key results from which will be discussed in this chapter due to their importance for interpretation of the ultrafast charge dynamics.

4.1.1. Charge trapping in CdTe CQDs
The performance of CQDs in many applications can be significantly limited by surface-mediated non-radiative carrier recombination. This involves the capture of carriers into states formed on the CQD surface due to unsaturated bonds, and is often referred to as surface trapping. Trapping typically occurs on sub-nanosecond timescales, and can therefore be competitive with carrier cooling and the potentially beneficial processes of multiple exciton generation (MEG), and PL, see Figure 2-9 in Section 2.5. This results in reductions in PLQY, charge extraction efficiency, and the lifetime of photo-generated charges [4]. The understanding and elimination of trapping has been the focus of many investigations and is critical to fully utilising CQDs in future devices.
Surface effects in CQDs are particularly difficult to characterise because they vary significantly not just between dots made of different materials, but also for ostensibly identical CQD samples. This significant variation between samples can be in the trapping efficiency, the trap energies or even which charge carrier is trapped. This behaviour arises due to sensitivity of CQDs to their preparation and handling, with the key factors being changes in synthesis conditions, reagent concentrations and purity, and air exposure [5-7]. The reason for this complex and sensitive behaviour is that a large fraction of a CQDs constituent atoms lie on the surface, where they can be under-coordinated, that is to have one or more dangling bonds. These bonds can be passivated by long chain organic ligands added to the surface during synthesis. However, these are often bulky, branching molecules, such that steric hindrance prevents them from passivating every surface site, leaving the surface vulnerable to its environment.

CdTe is a II-VI semiconductor, and is one of the Cd chalcogenides (CdTe, CdS and CdSe), the most studied of all QD systems. They were the first system for which highly mono-disperse and size tuneable synthesis techniques were developed [6, 8-9]. They were also the first system to achieve high PLQY, typically through shelling with a high band gap semiconductor to isolate the carriers from the surface (see Section 2.4). Cd chalcogenides have a large band gap, \( E_g \), of approx. 2 eV [10]. This is too large for efficient absorption of the solar spectrum which peaks in the near infra-red. However, they are well suited for devices which require efficient tuneable emission across the visible spectrum, and the highly-developed synthesis methods by which they can be produced, combined with their extensively studied physical and electronic structure, means that Cd chalcogenide CQDs are a very suitable model system for trapping studies.

Determining the physical origin of surface traps in Cd chalcogenides has been an aim of many investigations into understanding and eliminating non-radiative recombination. This is complicated from a chemical perspective by not knowing whether it is the electron or hole (or both) which are trapped, since the trapping of either carrier will prevent photoluminescence occurring. As mentioned above, surface atoms can be under-saturated, that is, to have one or more dangling bonds. This causes a change in the local electronic structure, resulting in the formation of
new states. If these states occur at an energy that would otherwise lie in the bandgap, they can capture carriers that have cooled to the band edge, known as ‘cold trapping’. If the new states lie above the band edges they may only be able to capture hot carriers, known as ‘hot trapping’. Califano [11] investigated this concept for CdTe using an atomistic semiempirical pseudopotential method to calculate trap times to unsaturated surface Te atoms. His model considered different geometrically unique sites on the surface of different sized QDs, shown in Figure 4-1. He predicted that the unsaturated Te atoms act as hole traps, and the position on the surface resulted in different trap rates ranging from 0.1 ps – 1 ns. The rates were shown to be strongly dependent on the dielectric environment of the QD; by considering the dielectric constants of sample solvents or oxidised QD surfaces, it was shown in a collaboration with this group that the trap rates are consistent with experimentally measured rates in the CdTe QDs used in this study [3] (to be discussed in Section 4.3.2). Califano identified two mid-bandgap trap states corresponding to singly or doubly under-saturated surface Te: one shallow trap, close to the valence band maximum (VBM), where thermal de-trapping might be possible, and the other deeper into the bandgap. The trapping of electrons was not modelled in the work of Califano, but was not ruled out, and has been demonstrated experimentally in Cd chalcogenides by a number of groups with ps trapping rates [12-13].

Within a CQD sample there is usually a dispersion of differently sized dots, typically on the order of 5-10 % [14]. This dispersion is typically limited by attempting rapid mixing of the reagents and uniform temperatures during the synthesis. These differences in size can change the properties of the CQDs, and are largely responsible for the observed linewidth of absorption and emission peaks [15-16]. The small size differences also have the potential to change the surface effects of each individual dot as the number of unique surface sites varies geometrically with size as shown in Figure 4-1, which has an effect on the trap rates [11].
Surface trapping of carriers has been shown to occur both for ‘hot’ and ‘cooled’ carriers [17-18]. Hot carrier trapping is a process which would directly compete with MEG, which has the potential to dramatically enhance solar cell efficiency. This type of trapping is critical to the interpretation of transient absorption data, and could lead, if unrecognised, to significant underestimation of CQD absorption cross sections, and in turn an underestimation of the average number of photons absorbed per CQD, \( \langle N \rangle \). The importance of \( \langle N \rangle \) was described in detail in Section 3.5.5; its underestimation could result in bi-excitonic decay being misinterpreted as being due to MEG rather than by the absorption of multiple photons, this will be discussed in detail later in this chapter. Cool trapping occurs on a timescale similar to biexciton recombination but can occur at fluences too low for a significant probability of two or more photons being absorbed by a CQD during a pump pulse, this can mimic the signature of MEG [19]. Classifying the signatures of both hot and cold trapping are therefore an important step in fully understanding any quantum dot system, particularly if overlapping spectrally or temporally with the signatures of other competing processes, see Section 2.5 for examples.

Treatment with halide ions has emerged as a particularly effective method of surface passivation, resulting in significant improvements in QDs optoelectronic properties [20] and device performance [21]. For this work CdTe CQDs were treated with chloride ions, where the chloride ions are thought to etch and replace under-saturated surface tellurium which is responsible for charge trapping. Evidence for
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this hypothesis will be presented in the first few sections, where it will be shown that the treatment can completely eliminate surface traps in these CQDs [1-2], evidenced by the attainment of near unity PLQY. Throughout this chapter the untreated and chloride treated CQDs may be referred to as CdTe and CdTe(Cl) CQDs respectively.

Nearly complete elimination of trapping presents a unique opportunity to directly observe its effects on charge dynamics by comparing CQDs before and after treatment with chloride ions. In particular, in this study ultrafast transient absorption spectroscopy is used to study sub-nanosecond charge dynamics in the CdTe CQDs before and after passivation. Such a comparison has not been possible for any other published QD systems without a passivation process which can significantly impact the charge dynamics. For example shelling of a QD with a high band gap semiconductor to form a Type I structure (see Section 2.4) has also achieved near-unity PLQY [22]. However, the change in confinement potential due to penetration of the charge carrier wavefunctions into the shell leads to a modification of the QD energy levels and bandgap [23] and can introduce defects at the core/shell interface. These changes can modify the dynamics of many of the possible cooling processes, including charge trapping.

4.2. Sample preparation and structural characterisation

4.2.1. Synthesis, chloride treatment and preparation

The CdTe QDs investigated in this chapter were synthesised at The University of Manchester, and only a brief description of the synthesis process from the precursors and subsequent chloride treatment is given here. The majority of the samples were provided by R. Page [7] who also developed the synthesis technique based on the method reported by Wang [22]. C. Lydon provided samples by the same technique later in the study; both were researchers in the D.J. Binks group.

The Cd precursor was cadmium oxide and tetradecylphosphonic acid (TDPA) in octadecane, and the Te precursor was telluride in triocetylphosphine (TOP). These were mixed at 290°C for between 30 s and 6 minutes. This produced spherical CdTe nanocrystals ranging from 3.2 nm to 4.9 nm in diameter. Chloride treatment of the QDs to passivate the surface was achieved by injection of cadmium chloride
dissolved in oleylamine and mixing at 60°C for 15 minutes. The resulting mixture is filtered and purified to isolate the QDs. Both processes were performed anaerobically (under nitrogen).

Once synthesised, the QD samples are transferred to 10 mm path length fused quartz cuvettes under nitrogen to prevent oxidation. The cuvettes have low reflectance and high transmittance, >80% for wavelengths in the range 200-2500 nm [24]. During transfer, the samples are diluted to ensure the absorption of the sample is in a suitable range to achieve a strong UTA signal (ideally 0.1-0.3 OD, see Section 3.5.7). The solvent used for dilution was toluene (also known as methylbenzene- C7H8). The concentrations of different samples do not necessarily match, directly scaling the amplitude of any PL, absorption and UTA signals (see Section 3.5.5).

The effects of air exposure on both the untreated and chloride treated samples have been investigated previously through observation of their PL [2-3]. Both were found to suffer a significant reduction in PL intensity over a few hours of being open to the atmosphere. The PL of the treated sample was shown to fall at a slower rate, as has been shown for other halide treated QDs [25]. The treated sample also exhibited a small blue shift of the emission spectrum consistent with the reversal of the filling of states at the valence band edge which will be described in the next section. For all the QDs in this investigation, if a sample was studied over a number of weeks after its synthesis, the PLQY was periodically re-measured for any signs of degradation.

4.2.2. Structural characterisation

A series of structural characterisation experiments were performed on pairs of the untreated and chloride treated CdTe CQDs by collaborating researchers and published in the Wiley journal *Small*, which included the first report of their synthesis and optical characterisation [2]. A summary of the results are shown in Figure 4-2 and will be described in this section.

High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images of a pair of untreated and chloride treated CdTe QDs were acquired by collaborators at The University of Manchester, School of Materials [2]. The
images are shown in Figure 4-2a and b; they show that the particles are roughly spherical in shape with little variation in size. From the images, average diameters of 4.6 ± 0.7 nm and 4.5 ± 0.8 nm were determined for the untreated and chloride treated samples respectively. The unchanged diameter combined with the increase in PL efficiency (to be discussed in Section 4.3) is consistent with passivation by eliminating surface traps rather than formation of a passivating shell.

X-ray powder diffraction (XRD) patterns for a pair of untreated and chloride treated CdTe QDs were also acquired by collaborators at The University of Manchester, School of Materials [2]. The observed angular diffraction peaks, shown in Figure 4-2c, are consistent with the formation of a zinc blende crystal structure. No significant change was observed for chloride treated samples indicating that the treatment did not alter the core structure.

X-ray photoelectron spectroscopy (XPS) was performed on a pair of untreated and chloride treated CdTe QDs by collaborators at the University of Manchester, School of Physics and Astronomy [2]. The aim of the investigation was to confirm that the chloride ions lie on the surface of the treated QDs. The principle of XPS is to use high energy X-rays to produce photoelectrons from the sample. The energy of the photoelectrons is then used to infer the constituent atoms by comparing to known atomic orbital energies. Figure 4-2d compares the region of the Cl 2p photoelectron peak for each sample, where no signal is observed for the untreated sample, but a clear peak indicates that chlorine is present in the treated sample. Increasing the energy of the incident X-rays increases the energy of the emitted photoelectrons, this changes their mean free path on the way out of the QD. This concept is illustrated by Figure 4-2e which shows the attenuation of different kinetic energies of photoelectron with depth in the QD and its organic ligands, where it can be seen that higher energy X-rays are attenuated less. Tuning of the X-ray energy therefore allows alteration of the average depth of origin of the emitted photoelectrons. By comparing the relative intensities of different photoelectron peaks with incident X-ray energy, the depth dependent composition of the samples were determined. Figure 4-2f shows the calculated Cl:Cd and N:Cd ratio in the treated CQD for different photoelectron energies. Nitrogen in the sample originates from the amine ligands used to passivate both untreated and chloride treated QDs. Both signals are shown to
Figure 4.2. a) and b) HAADF STEM images of CdTe QDs before and after chloride treatment respectively. c) XRD patterns of the untreated (black line) and treated (red line) CdTe samples indexed to zinc blende CdTe. d) Cl 2p XPS signal of CdTe QDs before chloride treatment (black line) and after chloride treatment (red line). e) Schematic diagram illustrating the regions of a spherical CQD (green) surrounded by an organic layer (grey) sampled by photoelectrons at normal emission for different X-ray photon energies. f) Variation of Cl/Cd and N/Cd ratios measured by XPS as a function of photoelectron kinetic energy and hence sampling depth. All data was collected and analysed by collaborating researchers and taken from Reference [2], reprinted under Creative Commons license.
fall with increasing energy indicating that both the chloride and nitrogen atoms lie on the surface of the QDs. During this study it was also noted that upon chloride treatment an increase in the number of filled band edge states near the VBM, resulting in a slight red-shift of the band gap. This is consistent with the passivation of surface traps by the donation of an electron from the chloride ions, and explains the blue-shift of the treated samples upon air exposure.

4.3. Absorption and photoluminescence

Absorption spectra of QDs are used to determine the band edge transition and can reveal higher transitions for highly monodisperse samples. Additionally the magnitude of the absorbance is an important value for correctly interpreting ultrafast studies of the charge dynamics, as will be shown later in this chapter. PL spectra reveal the band edge transition and the intensity of PL indicates the degree of non-radiative recombination. Absorption spectra were recorded using the Perkin Elmer Lambda spectrometer, and PL spectra were recorded using the Fluorolog-3 spectrometer, each of which were described in Section 3.3

Absorption and PL spectra for a CdTe and CdTe(Cl) pair of samples are shown in Figure 4-3. Toluene, the sample solvent, provided no significant contribution to the absorption for wavelengths >300 nm, and exhibited a weak broad PL emission around 500 nm which has been subtracted from the spectra shown here. For both samples the first absorption peak is well defined, and several smaller peaks can be seen at higher energies.
Before passivation, the spectral position of the first absorption peak varied from 540 to 600 nm between samples. The shapes of both the absorption and PL spectra are largely unchanged after passivation, except for a 10 – 30 nm red-shift. A previous study of the effect of the chloride treatment on CdTe QDs has shown that it typically results in a spectral change, which can either be a small blue- or red-shift depending on the net effect of several factors. The etch of surface Te reduces the size of the QD slightly and also changes the confinement which produce a blue-shift, see Section 2.2. Meanwhile the passivation of trap states near the valence band edge narrows the band gap, producing a red-shift [26]. The balance of these factors was found to be sensitive to the details of the passivation process, particular the treatment time [26].

As described in Section 3.3.1, minima in the second derivative of the absorption spectrum can be used to identify absorption peaks corresponding to energy level
transitions. The spectra for a CdTe sample are shown in Figure 4-4, where the second derivative of the absorption spectrum is also shown and used to identify the first four transitions. These transitions will be referred to as X1 – X4 in this work, where X1 is the band edge transition; these are illustrated on the right in Figure 4-4. Labelling of the transitions complies with the selection rules described in Section 2.3, and have been identified in CdTe QDs in other works [27-28]. An additional transition is expected to lie close to X3, the 1s1S\(_{1/2}\) transition [28-29]. However, as has been shown for CdSe CQDs, this transition is significantly weaker than the others [9, 30], and even went unnoticed in early spectroscopic studies due to significant overlap with the stronger transitions [31].

![Figure 4-4](image)

Figure 4-4. Absorption (solid black line) and photoluminescence (dotted red line) spectra for a CdTe CQD sample. Also shown is the second derivative of the absorption spectrum (black dashed line) where minima are used to identify the labelled transitions in the absorption spectrum. The electron and hole levels involved in the transitions are illustrated on the right, and the transitions are labelled X1-X4 (in order of increasing energy) for reference in the main text.

The features in these spectra are not significantly different prior to chloride treatment, as has been described in previous publications [1-3]. For both samples a Stokes shift between the absorption maximum and PL maximum of approximately 20 nm is observed. This is typical for Cd chalcogenide QDs [32], and arises from splitting of the state responsible for the VBM, 1S\(_{3/2}\), into several closely spaced levels with a high density of states. The state responsible for the PL is at the top, while the state responsible for the X1 peak is deeper in the valence band. This shift is an important consideration for the transient absorption results to be described in Section 4.4, where contributions from hole dynamics are negligible.
From the first absorption peak an estimate of the average diameter of the QDs can be acquired using fitting curves from published studies on a large range CdTe QDs of different sizes. A study by Yu et al. [33-34] is most frequently used in the literature, which provides an empirical fitting of CdTe QDs with absorption peaks ranging from 550 to 750 nm and diameters of 3.5 to 9 nm determined through TEM. This study was used to determine the sizes of the QDs presented in the publications discussed in Section 4.1 [2-3]. However a more recent study by Kamal et al. [35] performed an equivalent investigation with increased accuracy and validation by comparison to bulk materials, and found significant deviation from the curves of Yu et al. for QD diameters similar to those studied in this chapter. These curves were compared by Kamal et al. and are shown in Figure 4-5 along with an intermediate work by Donegà et al. [36]. The curve determined by Kamal et al. will be used for sizing QD samples in this chapter, which gives the band gap determined from the first absorption peak, $E_g$, in eV:

$$E_g = 1.51 + \frac{1}{0.048d^2 + 0.29d - 0.09}$$  \hspace{1cm} (4-1)

where $d$ is the diameter of QD in nm.

Figure 4-5. Empirical fitting of CdTe QD band gap determined from the first absorption peak, $E_g$, against diameter, $d_{QD}$, performed by Kamal et al. [35], and compared to the works of Yu et al. [33-34] and Donegà et al. [36]. Reprinted with permission from Reference [35], copyright 2017 American Chemical Society.
For the CdTe QDs studied in this chapter, the spectral position of the first absorption peak ranged from 540 to 600 nm, this indicates that the average CQD diameters ranged from 3.1 to 3.4 nm. The validity of this fitting curve is unconfirmed for chloride passivated QDs. However since TEM images showed no significant size change upon chloride treatment, the band gap of the samples before treatment will be used to estimate the size of the treated samples.

After chloride treatment of the QDs a dramatic increase in photoluminescence intensity occurs, with no significant change in the shape of the emission spectrum or the Stokes shift. The intensity increase can be quantified by PLQY measurements, which were performed using the Fluorolog-3 spectrometer with an integrating sphere, as described in Section 3.3.3. Before treatment PLQY is typically <10% which increases to approximately 90% after treatment, but in the best cases reaches unity to within experimental uncertainty. A record value of $97.2 \pm 2.5\%$ was measured [2]. This near-unity quantum yield indicates that chloride treatment can almost completely eliminate non-radiative recombination in these QDs. The XPS study on these dots [2], which was described in the previous section, concluded that the chloride resides on the surface of the QDs; this allows us to attribute the non-radiative recombination pathways in the untreated dots to surface mediated trapping processes, and to conclude that the chloride ions passivate these surface traps.

Figure 4-6 shows a histogram of the PLQY values of each separate synthesis of CdTe QDs before and after chloride treatment. The data shown includes all samples synthesised for the purposes of this study into ultrafast charge dynamics, and also the samples from the previous publication which focussed on their steady state optical properties [2]. These previous measurements were performed by D. Espinabarro-Valesquez [37]. PLQY measurements were performed on every sample studied in this work in order to confirm that thorough passivation of the surface was achieved in every synthesis.
These PLQY measurements were performed with excitation wavelengths of 450 or 420 nm, which is approximately 1.3 times the band gap, typically higher than the X4 transition. However, PLQY can be expected to vary with excitation energy if charges are not guaranteed to cool to the band edge. For PLQY measurements in the integrating sphere, sample concentration is adjusted beforehand such that the absorbance at the excitation wavelength is approximately 0.1 for accurate measurements when comparing samples [37]. This can be time consuming and give inconsistent results when attempting to measure PLQY at a range of excitation wavelengths, primarily due to the sample sensitivity to the preparation and handling such as variation in air exposure. However, for a given sample a PL map can be measured to investigate the variation of the emission spectrum and intensity with excitation energy.

4.3.1. Excitation dependent photoluminescence

PL maps were recorded using the Fluorolog-3 spectrometer, which entails recording emission spectra for a range of excitation wavelengths. The output signal is divided by a reference signal from the excitation beam to account for changes in excitation intensity with wavelength. PL maps for an untreated and chloride treated CdTe pair are shown in Figure 4-7a and Figure 4-7b respectively. The PL intensity has been divided by the fractional absorption at each excitation wavelength across the x-axis, together with the correction for excitation intensity. This ensures that each emission spectrum has been normalised to the number of photons absorbed by the sample. For each map both the intensity and peak width of the emission varies with excitation energy.

Figure 4-6. Histogram of the PLQY measurements of CdTe samples before and after chloride treatment. Includes data from Reference [2].
energy. The transitions X1-X4 identified in the absorption spectrum of Figure 4-4 appear as an increase in PL intensity, with the first and largest peak corresponding to the band edge transition, X1. Some diagonal spreading of the peaks can also be seen for this transition, where the emission peak position varies with excitation wavelength. This can be attributed to selective excitation of different sized QDs within the sample (this is the basis for fluorescence line narrowing experiments which aim to excite only the largest dots which absorb and emit on the red edge of the emission spectrum [38]). This spreading is not as evident for higher transitions due to their less pronounced peak in the absorption spectra and their increased overlap with other peaks.

Figure 4-7. Photoluminescence maps for an untreated, (a), and chloride treated, (b), CdTe CQD pair of samples. The intensity has been divided by the fractional absorption, $F_a$, at the corresponding excitation wavelength. Integration across the emission wavelength for each map is shown for the untreated and chloride treated CQDs in (c) and (d) respectively (solid lines). Also shown is the fractional absorption for each sample (dashed lines) See main text for discussion.

Figure 4-7c and d show, for the same two samples as in Figure 4-7a and b, the fractional absorption spectrum and the spectrally integrated PL emission normalised by the fractional absorption, which is proportional to the PLQY spectrum. Both
before and after treatment, the PLQY is highest at a wavelength corresponding to the centre of the PL spectra taken for excitation at 420 nm. A gradual fall in PLQY is observed as the excitation energy increases above the band gap. This observation is indicative of a hot trapping process occurring in these dots, whereby electrons or holes are more likely to be trapped if they are initially excited with higher energy, and thus have further to cool to the band edge. For cooling predominantly by phonon emission (see Section 2.5.1), where the charges cool through adjacent energy levels, the cooling time can be expected to correlate with the excess energy above the band gap. A change in gradient is apparent around 540 nm for the untreated sample, Figure 4-7c. This is likely a trapping pathway for holes because this energy lies between the 1s1S\textsubscript{3/2} and 1s2S\textsubscript{3/2} transitions (see Figure 4-4), which involve excitation to the conduction band minimum (CBM) from two different hole sates.

### 4.3.2. Photoluminescence decay

The photoluminescence decay kinetics were explored in detail by D. Espinobarro-Velazquez [37] and the results presented in two publications [2-3]. The data was collected primarily using the TCSPC system described in Section 3.4.2 with an excitation wavelength of 450 nm, the key results are described in this section for comparison and understanding of the results in the rest of the chapter.

PL decay traces for an untreated and chloride treated CdTe CQD pair are shown in Figure 4-8a. Each trace was recorded at peak wavelength of emission recorded on the Fluorolog-3 spectrometer also with excitation at 450 nm, and both have been recorded for long enough to achieve a peak count rate of 10\textsuperscript{4}. It was determined that excitation was in the low fluence regime where absorption of two photons by a single QD, and thus the possibility of bi-exciton formation, was negligible [37].

For all untreated samples studied the PL decay exhibited a number of components with differing decay times, including a rapid initial decay over the first few ns with a large relative amplitude. The overall decay required a bi-exponential or higher order fit (see Section 3.4 for a description of fitting and interpreting multi-exponential decays), with lifetimes and amplitudes varying between samples. After chloride treatment the decay becomes mono-exponential over 3 decades of decay, with a significantly lengthened PL lifetime on the order of 20 ns [2]. Similar significant
increases in carrier lifetimes have previously been shown to correlate with performance improvements in inorganic based solar cells [39].

The presence of the additional fast decay components combined with the significantly lower PLQY for the untreated sample is consistent with the presence of non-radiative charge traps acting on a number of the QDs within the sample. As discussed in Section 2.5.6, a distribution of dots with different recombination pathways will exhibit a non-monoexponential decay. This could be explained by the work of Califano [11] (see Figure 4-1), where a distribution of trap rates will exist depending on the position of un-passivated Te atoms on the QD surface, and whether they have one or two unsaturated bonds. The PL decay observed for the treated samples is consistent with the chloride ions passivating these trap sites leaving only a monoexponential decay. In a collaborating study with Califano [3] the atomistic model for predicting trap times (described in Section 4.1.1) was applied to these CQDs. It was shown that agreement between the observed PL decay times and those predicted by the model is achieved if the CQDs are modelled in a dielectric environment consistent with the presence of CdO on the surface. This highlights the importance of passivation of under-coordinated surface sites by the chloride treatment.

The effects of direct air exposure on the PL of these QDs were investigated by D. Espinobarro-Velazquez [2]. It was shown that the PLQY of both samples dropped within a few hours of a cuvette being open to the atmosphere, with a ~85% PLQY.
treated sample dropping to ~40% over 10 hours, shown in Figure 4-8b. A blue-shift of the PL peak also occurred, scaling with the drop in PLQY. This was attributed to the formation of an oxide layer, corresponding to smaller CdTe cores where the greater confinement increases the band gap. The effects of oxidation were also apparent on the PL decay, where additional fast decay components appeared for an untreated sample within an hour of exposure.

### 4.4. Transient absorption spectroscopy

Transient absorption (TA) spectroscopy was used to measure the ultrafast charge dynamics and absorption change spectra in the CdTe QDs with and without chloride treatment. The aim of the investigation was to achieve a deeper understanding of the mechanisms and signatures of non-radiative charge trapping in the sub-ns dynamics. The capability of the chloride treatment to almost completely eliminate traps in these QDs, evidenced by the attainment of near unity PLQY, presented a unique opportunity to compare the dynamics with and without trapping. Such a comparison has not been possible for any other published QD systems without a passivation process which can also significantly impact the charge dynamics by changing the energy level structure.

The temporal resolution of the TA system is limited by the laser pulse width, of ~100 fs, which is sufficiently short to observe the decay of multi-excitons created by MEG or two photon absorption, with lifetimes on the order of a few ps [27]. It is also ideally suited for observing ultrafast trapping from the band edge which is expected to occur over 10s of ps to a ns. The system resolution can also be sufficient to observe the cooling of charges to the band edge which would compete with hot trapping processes, although the timescales approach the response time of the system. The experimental setup and technique were described in detail in Section 3.5, but in brief, the pump beam, a high photon energy laser pulse with ~100 fs pulse width, excites the sample creating hot excitons which then cool to the band edge. After some time delay, a white light probe beam, also 100 fs pulse width, is passed through the sample. The probe beam will experience a reduction in absorption (i.e. an increase in transmission) at wavelengths corresponding to states which are partially filled due to excitation by the pump beam. By varying the time delay and
selected probe wavelength, the time-dependent occupation of specific energy levels can be measured.

This section will begin by focussing on the time dynamics of the electron population at the CBM, where the effects of surface traps are identified and used to isolate the processes of hot and cold charge trapping. Complementary signatures of trapping will then be presented in TA spectra. Approximately 20 independent syntheses of CdTe CQDs were investigated over the course of this study, each with a chloride treated counterpart. The study began by establishing that the same behaviour is exhibited for CQDs from independent syntheses, although with small deviations in the rates of charge relaxation. Afterwards a large amount of data was collected for a single untreated and chloride treated CdTe pair.

4.4.1. Dynamics of the conduction band minimum

For the initial investigation of the CBM dynamics in the CdTe QDs, samples were excited at 420 nm (3 eV, or \( \sim 1.3E_g \)), which is at higher energy than the X4 transition shown in Figure 4-4. At this energy a range of excited states are expected for the CQD ensemble due to the overlap of many optical transitions this high above the band gap. The samples were probed at their respective X1 transition, the first absorption maximum. As discussed in Section 4.3, the X1 transition corresponds to an electron fully relaxed to the CBM and a hole state which is just below the VBM. The high degeneracy of this hole state relative to the CBM and the rapid cooling to the VBM means that the contribution from holes is negligible [40]. The bleach transients are thus determined by the occupancy of the CBM, i.e. the 1s electron state. Figure 4-9 compares the dynamics of the CBM bleach for an untreated and chloride treated CdTe pair. A long time window which is the limit of the TA system’s optical delay stage is shown, and a short window with smaller time step. The samples were excited with a pulse beam power of 1mW with a beam diameter of 2.2 mm; which is equivalent to a fluence of \( 1.30 \times 10^{14} \) photons cm\(^{-2} \) per pulse experienced by the probe beam (see Section 3.5.8). This fluence will be shown to correspond to a negligible probability of two photon absorption in the next section.
There are three important differences between the untreated and chloride treated dynamics shown above; the observations were consistent for all of the samples studied, with only small changes to the amplitudes and timescales: i) the untreated sample shows a fast decay to a plateau with a decay constant of 10s of ps, whereas the treated sample showed no significant decay over a ns; ii) the peak amplitude of the bleach for the treated sample is significantly larger than for the untreated sample, typically by a factor of 2 to 5; iii) the signal rise time is significantly faster for the untreated sample.

The change in rise time can be quantified by measuring the time for the signal to rise from 10% to 90% of its maximum value; this is illustrated for the signal rises shown in Figure 4-9a. For four independently synthesised pairs of untreated and chloride treated QDs, the average rise times were $1.5 \pm 0.1$ ps and $2.2 \pm 0.1$ ps respectively. The corresponding average rates of energy loss of the carriers, calculated using the energy of the exciting photon in excess of the band gap, are $0.50 \pm 0.03$ eV/ps and $0.36 \pm 0.03$ eV/ps, respectively. This is a 28% decrease in the cooling rate to the
CBM following identical excitation by the pump beam. This decrease is attributable to the elimination of cooling pathways from the pump level, resulting in a slower net depletion of the pump level population.

As discussed in Section 2.5.3 and 3.5.3, a sub-ns decay to a plateau of the conduction band population in QDs can occur due to Auger recombination; a process which must be prevented in these samples for isolation of any signatures of charge trapping. In an Auger recombination event, an electron-hole pair recombine and their energy is transferred to a third charge carrier, exciting it higher into the band structure. This process typically occurs with a lifetime of 10s of ps. There are three processes which can lead to the presence of more than two carriers, each of which can be expected to behave identically in the treated and untreated samples, yet only the untreated sample shows the fast decay to a plateau. We can however explicitly show that each process is not occurring in the untreated samples in order to discount Auger recombination as the underlying mechanism.

The first process is multiple exciton generation (MEG), where a charge cools to the band edge by exciting a second electron-hole pair across the bandgap. As described in Section 2.6, MEG can only occur above a threshold energy for the exciting photon, the theoretical minimum for which is $2E_g$; excitation at 420 nm corresponds to $\sim 1.3E_g$ for all the samples studied, firmly below the threshold.

The second process is trion formation, discussed in Section 2.5.3 and 3.5.3. When a charge is trapped on the surface of a QD, its geminate charge can remain in the QD core for a long period of time, potentially longer than the pulse repetition period. If this QD is excited by the next pump pulse, a trion is formed which can rapidly decay by Auger recombination. This process was found to be responsible for early controversy in MEG measurements [41]. Trion formation is avoided by stirring or flowing samples such that the sample volume in the excitation beam is refreshed in-between successive pump pulses [42]. Figure 4-10 shows absorption change transients for untreated QDs under the same experimental conditions as Figure 4-9 for stirred, static and flowed samples. The time window of this data is comparable to typical multi-exciton recombination times of 10s of ps. No discernible difference is
observed indicating that trion formation provides no significant contribution to the band edge dynamics in these QDs.

Figure 4-10. Absorbance change transients for the band edge bleach for untreated CdTe CQD under different experimental conditions intended to prevent photo-charging. a) The same sample under static conditions (red dashed line) or stirred at 1000 rpm (black line). b) The same sample under static conditions (red dashed line) and flowed at 250 ml/min (black line). All other experimental conditions matched Figure 4-9.

The third route to Auger recombination is the absorption of more than one photon by a single QD from the pump pulse. As described in Section 3.5.5 the probability of this process is governed by Poisson statistics, and is limited by the average number of photons absorbed per quantum dot, denoted \( \langle N \rangle_{abs} \) in this chapter. The probability of two-photon absorption is made negligibly small by using sufficiently low fluences, such that on average each QD absorbs much less than one photon per pump pulse. Figure 4-11 shows absorption change transients for an untreated sample for a range of pump fluences, where each transient is normalised to its plateau. The invariance with pump fluence indicates that the fast decay component is not caused by two photon absorption. The probability of absorption of more than one photon, and the expected amplitude of the band edge bleach are related to \( \langle N \rangle_{abs} \), and are each calculated for several treated and untreated samples in the next section.
4.4.2. Estimating the numbers of hot and cold charge carriers

In addition to the contrasting time dynamics for untreated and chloride treated samples discussed in the previous section, the peak of the bleach amplitude is also significantly higher after chloride treatment. Many CQD studies assume that when an absorbed photon creates a hot exciton that it then cools to the band edge and contributes to the bleach signal. In this section we calculate the number of absorbed photons, \( \langle N \rangle_{abs} \), for several samples and compare this to the band edge occupancy, \( \langle N \rangle_{CBM} \), determined from the amplitude of the bleach signal.

The calculations are performed for four untreated and chloride treated pairs of CdTe CQD samples. For the transients which were shown in Figure 4-9, the maximum bleach amplitude for the CQDs without chloride treatment is approximately half of
Chapter 4  CdTe(Cl) CQDs – Trapping and surface passivation

the value seen after passivation, even though the pump fluence is the same in both cases and the pump absorbances are comparable. A similar difference in maximum bleach was also observed for all other samples studied following passivation with chloride treatment, typically by a factor of 2 to 5. The calculations provide significant evidence that fewer charges reach the band edge in the untreated samples due to hot trapping, and are also important for providing additional evidence (beyond that of Figure 4-11) that two-photon absorption is negligible under the excitation conditions used. \( \langle N \rangle_{abs} \) will also be used to calculate a predicted peak to plateau ratio, \( R_{pre} \), due the decay of multi-excitons to single excitons, and compared to the peak to plateau ratio observed in the transients, \( R_{obs} \).

As described in Section 3.5.5, the observed pump-induced absorption change, denoted \( (\Delta A/A)_{obs} \) in this section, is calculated from the transmission change, and is directly proportional to the occupation of the CBM, \( \langle N \rangle_{CBM} \) [27]:

\[
\frac{1}{A} \frac{\Delta T}{T} = - \frac{\Delta A}{A_{obs}} = \frac{\langle N \rangle_{CBM}}{g}
\]  

(4-2)

where \( g \) is the degeneracy of the CBM, which is 2 for CdTe QDs [9].

Independent from the bleach signal, \( \langle N \rangle_{abs} \) is given by the product of the pump fluence, \( J \), and the absorption cross section of the QDs (at the pump wavelength), \( \sigma \):

\[
\langle N \rangle_{abs} = \sigma J
\]  

(4-3)

from which we can calculate a predicted maximum bleach amplitude:

\[
- \frac{\Delta A}{A_{pre}} = \frac{\langle N \rangle_{abs}}{g} = \frac{\sigma J}{g}
\]  

(4-4)

\( \sigma \) was estimated for the CdTe CQDs from the work of Kamal et al. [35], who performed an empirical fitting of the extinction coefficient \( \varepsilon \) (L cm\(^{-1}\) mol\(^{-1}\)) at 410 nm against the CQD diameter, \( d \) (nm):

\[
\varepsilon_{410} = 10600(d)^{3}
\]  

(4-5)
Determining the diameter of each CQD sample from their absorption spectra was described in Section 4.3, using fits from the same study by Kamal et al. [35]. The extinction coefficients in that study were calculated using the Beer-Lambert law (see Section 3.3.1) with QD samples of known molar concentration [35]. After determining $\varepsilon$, we can calculate $\sigma$ ($\text{cm}^2$) using:

$$\sigma = 1000 \ln(10) \varepsilon / N_A$$

(4-6)

where $N_A$ is Avogado’s constant. In order to determine $\sigma$ at the pump wavelength as required for Equation (4-3), we multiply by the ratio $A_{\text{Pump}}/A_{410}$, since $\sigma$ scales with sample absorption.

Calculated values of $(N)_{\text{abs}}$ can be used to calculate a predicted peak to plateau ratio caused by Auger recombination following multi-photon absorption [45]. This can be derived from the Poisson distribution of absorbed photons per QD: the probability of a QD absorbing $N$ photons is given by

$$P(N) = \frac{\langle N \rangle_{\text{abs}}^N \exp(-\langle N \rangle_{\text{abs}})}{N!}$$

(4-7)

The peak of the bleach signal corresponds to the total number of photons absorbed, given by $n(N)_{\text{abs}}$, where $n$ is the total number of QDs. The plateau arises from the total number of QDs excited, $n(1 - P(0))$, where any multi-excitons have decayed to the longer lived single exciton state. Therefore

$$R_{\text{pre}} = \frac{n(N)_{\text{abs}}}{n(1 - P(0))} = \frac{\langle N \rangle_{\text{abs}}}{1 - e^{-\langle N \rangle_{\text{abs}}}}$$

(4-8)

There are several important assumptions in this expression; firstly, it assumes that an insignificant number of QDs absorb more than two photons, since a third exciton cannot contribute to the photo-bleach due to the degeneracy of the CBM ($g = 2$). This is a safe assumption in this work where the aim is to have negligible probability of more than one photon absorbed. This expression also neglects any reduction in pump fluence through the sample (including this effect was described in Section 3.5.6), which is justified due to the relatively low absorbance at the pump.
wavelengths used. Most importantly, this expression and Equation (4-4) for calculating $(\Delta A/A)_{pre}$, assume that every excited electron cools to the CBM and contributes to the bleach signal. This can be assessed by comparing to the experimentally observed bleach amplitude.

Comparing $(\Delta A/A)_{obs}$ for untreated and chloride treated (well passivated) samples under identical excitation conditions therefore allows the fraction of initially hot electrons that are trapped before they cool to the CBM to be determined. Alternatively, we can compare $(\Delta A/A)_{obs}$ and $(\Delta A/A)_{pre}$ for a single sample, which requires accurate determination of $\sigma$ and $J$. We assume that $\sigma$ is the same before and after treatment, which is supported by the negligible changes of both the amplitudes and features of absorption spectra before and after treatment and will be discussed in more detail below.

For comparison of transients under different excitation conditions (changes in either the pump fluence or wavelength) additional corrections must be applied before amplitude comparison. $\sigma$ will vary with wavelength but is difficult to determine experimentally; it is however directly proportional to the sample absorbance, $A_{pump}$, as stated above. Division of the fractional absorbance change for two different pump conditions by $JA_{pump}$ therefore provides a comparison which accounts for excitation fluence and variation of $\sigma$ for different pump wavelengths. This will be used repeatedly in the next section.

Table 4-1 shows the results of the calculations discussed above for different excitation fluences of four independently synthesised untreated and chloride treated CdTe pairs. Using Equation (4-3), $\langle N \rangle_{abs}$ is calculated, and a corresponding predicted peak bleach amplitude, $(\Delta A_{max}/A)_{pre}$ which assumes all absorbed photons result in an electron reaching the CBM. For this calculation the effective fluence experienced by the probe beam was used, calculated by the method described in Section 3.5.8 which accounts for the reduction in pump fluence along the beam path, the angle between the two beams, and the relative sizes of the beams. These expected values are compared to the observed peak bleach amplitude, $(\Delta A_{max}/A)_{obs}$, and the corresponding occupancy of the band edge, $\langle N \rangle_{CBM}$, calculated using Equation (4-2).
Table 4.1. Comparison of calculated and experimental parameters for four pairs of untreated (1U – 4U, shaded in grey) and chloride treated (1T – 4T) CdTe CQDs samples for excitation at different fluences, $J$. $(N)_{obs}$, is the calculated number of photons absorbed which is used to calculate predicted values of the band edge fractional absorbance change, $(\Delta A_{max}/A)_{pre}$, and peak to plateau ratio, $R_{pre}$. From the experimentally observed absorbance change maximum, $(\Delta A_{max}/A)_{obs}$, the occupancy of the band edge is calculated, $(N)_{CBM}$. The peak to plateau ratio observed for each sample, $R_{obs}$, is also given. For cases where only a short time window transient was measured only a lower limit of $R_{obs}$ is given. Also given is the noise on the signal for each scan for comparison to the expected and observed peak ratios.

Significant systematic discrepancies are observed for both the untreated and chloride treated samples, however the treated samples show consistently closer agreement than the untreated samples by approximately an order of magnitude. For the passivated samples, $(N)_{CBM}$ and $(\Delta A_{max}/A)_{obs}$ are typically 20 – 50% below the predicted values. The possible sources of this deviation will be discussed below.

Meanwhile, for the untreated samples (highlighted in grey in Table 4-1), the
observed and predicted values show much larger discrepancy with significant variation, where the observed values are smaller by factors of 2 – 10. This strongly suggests that for the untreated samples not every absorbed photon results in an electron at the CBM, i.e. some of the hot electrons created by pump absorption are cooling directly into a trap state, and thus not contributing to the CBM state-filling responsible for the bleach signal.

There are several possible sources of the discrepancies for the treated samples which can contribute both statistical and systematic error in the calculations:

(i) Inaccurate calculation of $J$: the calculation of $J$ (described in Section 3.5.8) considers several important aspects which reduce the fluence relative to the peak fluence in the centre of a Gaussian beam incident on the sample. These include the reduction in fluence along the beam path due to absorbance by both the sample and solvent, the angle between the pump and probe beams, and the relative sizes of the pump and probe beams. Important sources of systematic error in this calculation are the assumptions that both beams have a Gaussian profile and are accurately aligned with the centre of the sample, and the measurement of beam power using a thermal power meter which is susceptible to background variation when measuring low powers. Sources of statistical error include power measurement, beam diameters, beam angle, and sample absorbances; these together result in an estimated error of 6%.

(ii) Inaccurate estimation of $\sigma$ due to deviation from Equation (4-5): the fit is estimated as accurate to 10% by the authors [35] for their CQDs. However, as was stressed in Chapter 2, CQD properties are well known for varying between different synthesis procedures, even for different groups attempting to follow the same routine. The validity of the equation is also unconfirmed for chloride treated samples. For some sample pairs a large red-shift of the first absorption peak was observed after chloride treatment; following the sizing and cross section curves of Kamal et al., this would predict a significantly larger diameter and absorption cross section for the treated samples. However the TEM study on these dots noted no appreciable size difference upon treatment, and attributed any
spectral shifts to the filling of band edge states, and the etching of surface Te and its replacement with a CdCl layer. A significant change in absorption cross section is not expected from these changes, as a result the cross sections of the treated samples are assumed to be the same as they were before treatment which yielded better agreement for the $\langle N \rangle$ and $\Delta A_{max}/A$ calculations.

(iii) Non-unity PLQY for the treated samples means a small fraction of the excited charges may not reach the band edge. As shown in Figure 4-6 the typical PLQY for a treated sample is 80 – 90%, the PLQY was measured for each sample individually but was not found to correlate with the discrepancy in observed and predicted $\langle N \rangle$ and $\Delta A_{max}/A$. For example sample 2T in Table 4-1 had a PLQY of 99 ± 2.5 %.

(iv) Experimental error in the TA data must also be considered, which is given in Table 4-1 for each transient, determined from combining the error on repeat measurement of multiple scans and the error on the probe signal without pump excitation (see Equation (3-16) in Section 3.5.2.3).

The contributions discussed above can explain the statistical variation of the expected and observed values of $\langle N \rangle$ and $\Delta A_{max}/A$ for both the untreated and chloride treated samples, and might explain the systematic deviation of 20-50% for the treated samples. However the fact that the untreated samples show much larger discrepancy can be taken as a firm indication of the contribution of hot electron trapping related to the CQD surface.

From $\langle N \rangle_{pre}$ the predicted peak to plateau ratio for the decay, $R_{pre}$, has been calculated using Equation (4-1). This is compared to the observed ratio, $R_{obs}$, measured directly from the transients, in Table 4-1. Short time window transients were taken for each sample in order to ensure that the peak is observed (as in Figure 4-9a). In these cases the plateau is not reached so only an upper limit on $R_{obs}$ is given. For the treated samples there is no noticeable decay, even for large time windows, giving $R_{obs} = 1$. This is consistent with the predicted value of only a small peak ($R_{pre} \approx 1.1$) given the noise on the signal, which is also presented in Table 4-1. For the untreated samples, a small peak is also expected, however it is much too small to account for the significant fast decay components observed, which
yield $R_{obs} \sim 2 - 4$. This provides further evidence (see Figure 4-11), that two-photon absorption is not responsible for the fast decay components observed. The absence of any bi-exciton recombination in the treated samples might suggest that the fluence used to calculate $\langle N \rangle_{abs}$, $(\Delta A_{max}/A)_{pre}$, and $R_{pre}$ might be overestimated, and could be the principal source of the systematic discrepancy between the expected and observed $\langle N \rangle$ and $\Delta A_{max}/A$ values for the treated samples.

### 4.4.3. Hot and cold trapping

The decay in the CBM bleach signal was concluded to originate from trapping of electrons from the CBM by comparison to the surface passivated sample, and the ruling out of Auger recombination mechanisms. This decay can be referred to as a cold trapping process, since it acts on electrons which have cooled to the CBM. So far in this chapter, three important indications of a hot trapping process have also been discussed, where charges are trapped before cooling to the CBM. Firstly, the fall in PL efficiency with increasing excitation photon energy (see Figure 4-7); secondly, the increased rise time of the bleach signal after passivation (see Figure 4-9a); and thirdly, the significantly reduced bleach response for untreated CQDs demonstrated in the previous section by comparing expected and observed $\langle N \rangle$ values.

The surface trapping of hot carriers in CQDs has been discussed at length by Kambhampati [18], primarily in CdSe CQDs. The effects of hot trapping and the competition with hot carrier cooling to the band edge are discussed along with the significant impacts on device performance. The effects are distinct from those of cold carrier trapping, for example hot trapping is used to explain one form of PL intermittency in QDs, known as ‘blinking’ [46-47]. Since most TA studies on QDs only observe the decay of the band edge signal, the presence of hot trapping is rarely identified with significant certainty.

Hot and cold trapping processes need to be considered independently in this work even though they could have identical mechanisms and the destiny of the trapped charge might be the same location and energy for each process. Their individual consideration is important when looking at CBM dynamics, since hot trapping
competes with cooling to the CBM to reduce the amplitude, while cold trapping enhances the rate of relaxation from the CBM. This concept is particularly important when considering the likely energy of the trap relative to the CBM.

The origin of the differences between the band edge dynamics of the passivated and un-passivated CdTe QDs can be quantitatively understood using a simple rate equation model incorporating both hot and cold trapping, illustrated schematically in Figure 4-12. In this model, the pump beam excites electrons from the valence band to an initial ‘pump level’ with population $n_1$. From this pump level the hot electrons can cool to the CBM with a rate $k_{10}$. The CBM has an electron population $n_0$, which is measured in the TA experiment. Alternatively, the electrons in the pump level can undergo hot trapping directly to a surface state, with a rate $k_h$. Electrons can also undergo cold trapping from the CBM, with a rate $k_c$.

![Figure 4-12. Illustration of the energy levels and relaxation rates between them for the model of charge cooling to the band edge with hot and cold trapping.](image)

From this model a pair of linear ODEs can be written for the populations of the pump and CBM levels:

$$\dot{n}_1 = -(k_{10} + k_h) n_1$$  \hspace{1cm} (4-9)

$$\dot{n}_0 = k_{10} n_1 - k_c n_0$$  \hspace{1cm} (4-10)

These can be solved to give the time dependent electron population of the CBM:

$$n_0(t) = \frac{k_{10} n_1(0)}{k_{10} + k_h - k_c} \left[ e^{-k_c t} - e^{-(k_{10} + k_h) t} \right]$$  \hspace{1cm} (4-11)

The hot trapping rate constant, $k_h$, appears in both the second exponential term of Equation (4-11), which enhances the bleach rise-time, and in the denominator of the
pre-factor, reducing the bleach amplitude. Thus increasing the value of $k_h$ simultaneously decreases the rise-time and reduces the bleach amplitude. This trend is observed when comparing the treated and untreated CdTe samples in Figure 4-9a, and is demonstrated for a range of $k_h$ values in Figure 4-13. Equation (4-11) predicts that the CBM of CQDs would completely depopulate on a sub-nanosecond timescale with a lifetime given by $k_c^{-1}$. In contrast, a significant fraction of the bleach remains after ~1 ns for the untreated samples (see Figure 4-9), referred to as the plateau in the previous sections. In this model, the plateau can be attributed to a subset of the CQD population which is free of the cold trapping process at sub-nanosecond timescales. Whether this subset is also free of the hot trapping process is not yet evident but will be investigated later in this section.

![Figure 4-13. Change in the form of Equation (4-11) with increasing $k_h$, with a subset of the QDs free from the cold trapping process to form a late-time plateau.](image)

The presence of different populations of QDs within the ensemble with different trapping properties is consistent with the work of Califano [11] discussed in Section 4.1.1, where different trapping rates can be assigned to specific surface sites which are un-passivated. In any sample with surface-mediated trapping there will exist a distribution of different surface conditions, where some dots may be well-passivated by organic ligands whilst others may have one or more un-passivated surface sites. Califano showed that trapping rates of a few ps and 10s of ps can form for trapping of holes to un-passivated surface Te. Similar rates are observed here for electron trapping over both short and long time windows in Figure 4-9. The connection between the hole trapping predicted by Califano and the depopulation of electrons in the CBM observed here will be discussed later. The absence of these trapping pathways in a subset of dots with better passivation can explain the plateau observed.
Each subset of differently trapping CQDs within a sample will contribute an instance of Equation (4-11) to the overall dynamics, where the individual rates and proportions of each subset might vary significantly between different samples. Due to the large number of free parameters introduced, attempts to fit Equation (4-11) to individual transients can yield a range of acceptable fit parameters depending on the starting conditions and on the choice of instrument response function (IRF), to be discussed in more detail below. The quality of such a fit can be significantly improved by simultaneous fitting to several transients from the same sample pair, where several of the parameters can be shared between the transients. In an attempt to establish whether hot and cold trapping are independent processes, TA data was collected for samples excited directly into the CBM, and for a range of other transitions higher into the energy level structure.

In Figure 4-14a absorbance change transients for an untreated CdTe sample are shown for the pump wavelength tuned to the transitions, X4, X3, and slightly above X2 [48] (see Figure 4-4). Each transient has been normalised by its corresponding pump fluence and absorbance at the pump wavelength, $J_{A_{pump}}$, enabling direct comparison of signal amplitude. Pumping higher into the band structure can be expected to result in a decrease in the cooling rate to the CBM, $k_{10}$, as the charges have more energy to dissipate. This is evident when comparing the 3 normalised transients, shown in Figure 4-14b, where pumping at higher photon energies results in successively slower rises in the bleach signal. This trend is highlighted by the 10% - 90% rise times. Additionally, pumping at higher photon energy also results in a decrease in the peak bleach amplitude. Both of these observations are predicted by Equation (4-11), where due to the competition with the hot trapping rate, $k_{h}$, a decrease in $k_{10}$ results in both a slower signal rise and a lower amplitude. This can be interpreted as the hot trapping process having a longer window of opportunity to occur if electrons have further to cool to the CBM. Such a reduction in cooling time with excitation energy has been observed in TA studies of other CQD systems [49]. The reduced amplitude with excitation energy observed here is consistent with the PL map shown in Figure 4-7, where PL efficiency from the band edge was also shown to gradually decrease with increasing photon energy. It is also clear in Figure 4-14 that the rate of decay from the signal peak, which is determined solely by $k_{c}$,
remains approximately unchanged, however each transient is decaying to successively lower plateau amplitudes.

Figure 4-14. a) Fractional absorbance change, $\Delta A/A$, transients for an untreated CdTe CQD sample, for pump wavelength tuned to different excitation levels, X2, X3 and X4 (see Figure 4-4). The sample was probed at the X1 transition, corresponding to bleach of the CBM. Each transient has been normalised by its absorbance at the pump wavelength, $A_{\text{pump}}$, and pump fluence, $J$, to enable comparison of signal amplitude. b) data from a) normalised to the peak bleach. The 10% - 90% rise times for each transient are given in the legend.

It is not evident from comparing the transients in Figure 4-14 whether the hot trapping process is occurring in all three transients, and fitting of Equation (4-11) still leaves some ambiguity about the relative rates of cooling and trapping. It is here that the ability of the chloride treatment to eliminate all trapping can be utilised. The model described above for hot and cold trapping can be used to explain the differences between the three transients shown in Figure 4-14, and also show that the trapping processes account for the differences between the untreated and chloride treated sample shown in Figure 4-9. Table 4-2 illustrates the modifications to the model for the two subsets within an untreated sample, and for a treated sample. In each case the equation of the transient is given, along with a plot illustrating the shape of the resulting curve. In the case of the treated sample, the hot and cold trapping processes are removed ($k_c = k_h = 0$). This modifies Equation (4-11) to a simple sigmoidal rise to a plateau, with a peak population matching that of the pump level, $n_1(0)$. The untreated sample is split into two subsets with different dynamics; the first is described by Equation (4-11), where both hot and cold trapping are present. This produces a transient with a rise to a peak and then an exponential
<table>
<thead>
<tr>
<th>Sample</th>
<th>Subsets</th>
<th>Transitions</th>
<th>Subsets transients</th>
<th>Full transient</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe CQDs</td>
<td>Hot &amp; cold trapping*</td>
<td>$n_i$</td>
<td>$n_i(t) = \frac{k_{10} n_{hc}(0)}{k_{10} + k_h - k_c} \left[ e^{-k_c t} - e^{-(k_{10}+k_h)t} \right]$</td>
<td>$n_0(t) = \frac{k_{10} n_{hc}(0)}{k_{10} + k_h - k_c} \left[ e^{-k_c t} - e^{-(k_{10}+k_h)t} \right]$ + \frac{k_{10} n_h(0)}{k_{10} + k_h} \left[ 1 - e^{-(k_{10}+k_h)t} \right]$ $n_{hc}(0) + n_h(0) = n_1(0)$</td>
</tr>
<tr>
<td></td>
<td>Hot trapping only*</td>
<td>$n_0$</td>
<td>$n_0(t) = \frac{k_{10} n_h(0)}{k_{10} + k_h} \left[ 1 - e^{-(k_{10}+k_h)t} \right]$</td>
<td>$n_0(t)$</td>
</tr>
<tr>
<td></td>
<td>No trapping, no subsets</td>
<td>$n_i$</td>
<td>$n_i(t) = n_i(0) \left[ 1 - e^{-k_{10}t} \right]$</td>
<td>$n_0(t)$</td>
</tr>
</tbody>
</table>

Table 4-2. Modifications to the hot and cold trapping model for untreated (CdTe) and chloride treated (CdTe(Cl)) samples. See main text for a detailed description.

*For excitation at X2 (directly to the CBM) the hot trapping process is removed from both subsets.
decay. The peak is significantly smaller than \( n_1(0) \) due to the pre-factor of the equation, \( k_{10}/(k_{10} + k_h - k_c) \). In the second subset, the cold trapping process is removed \((k_c = 0)\). This produces a transient which is a simple rise to a plateau, however the rise time is shortened compared to the untreated case, and the amplitude reduced due to the pre-factor \( k_{10}/(k_{10} + k_h) \). The sum of the two subsets gives the transient for the entire untreated sample, a rise and then decay to a plateau. The relative fractions of each subset are quantified by the initial population in the pump level, denoted \( n_{hc}(0) \) and \( n_h(0) \) for the hot and cold trapping subset, and the hot trapping subset respectively. When comparing untreated and treated samples, \( n_{hc}(0) + n_h(0) = n_1(0) \). This equation requires that any transients are normalised relative to the number of pump photons absorbed. As was shown in Section 4.4.2, calculating the exact number absorbed can be complicated, but dividing by the pump fluence, \( J \), and the absorbance at the pump wavelength, \( A_{pump} \), is sufficient for comparison using a shared total amplitude for the decays, \( n_1(0) \).

Figure 4-15 shows the result of fitting the model described above to the three transients shown in Figure 4-14, and to a transient for the chloride treated version of the same sample which was excited at its X3 transition, labelled X3T. Each transient and its respective fit are offset in time in increments of 2 ps for clarity. A global least-squares fit was performed which included convolution with a Gaussian pulse with a width corresponding to the IRF of the system, to be discussed below. All of the fit parameters were shared between some of the transients to be consistent with the model described by Table 4-2:

- \( n_{hc}(0), n_h(0), \) and \( n_1(0) \) were shared between all transients, with \( n_{hc}(0) + n_h(0) = n_1(0) \), representing that (after normalisation by \( JA_{pump} \)) every scan represents equivalent excitation of the sample, and that for the untreated sample the relative size of the two subsets (see Table 4-2) does not vary.
- \( k_{10} \) was shared between the two transients excited at X3, representing that the rate of cooling to the band edge does not vary before and after chloride treatment, but does vary with excitation energy. This is particularly justified for this particular treated sample where the Stokes shift upon chloride treatment was small, at approximately 3 nm.
- $k_h$ and $k_c$ were shared between the three untreated transients, representing that the trapping efficiency does not significantly vary with excitation energy, but with one important exception: for excitation at X2, the hot trapping process is removed ($k_h = 0$) because this corresponds to excitation directly to the cooled band edge state for electrons (see Figure 4-4).

Figure 4-15. Data from Figure 4-14 with the addition of a transient for excitation of the chloride treated counterpart at the X3 transition (data points). The model described by Table 4-2 has been fit to each transient with parameters shared according to the description in the main text (solid lines). Each scan is offset by an additional 2ps for clarity. The fitting parameters are given in Table 4-3.

Due to sharing $n_{hc}(0)$, $n_h(0)$, and $n_1(0)$, differences in rise time and amplitude are all solely a result of the competition between intra-band cooling and hot charge trapping. The fitting parameters are given in Table 4-3, along with some useful conversions. The cold trapping rate corresponds to a lifetime of 3.4 ps, this falls within the range of values simulated by Califano [11] for hole traps to the surface (the fact that the Califano model calculates hole trapping times while we observe electron trapping will be discussed later). It is also comparable to fast decay of the CBM noted in other Cd chalcogenide systems and attributed to charge trapping [4, 50-56]. In contrast, the hot trapping rate, $k_h$, is significantly faster, with a lifetime of 0.42 ps. These significantly different rates provide strong evidence that the processes correspond to different trap sites and/or to different mechanisms of charge trapping. Lenngren et al. [17] proposed the presence of an electron trap state with energy between the CBM and the first excited electron state in CdSe CQDs. It was
identified by comparable measurements of the relaxation from different excitation levels. Such a trap state in these QDs could explain the dramatic difference in trapping rate before and after cooling to the CBM, where after cooling only slower trapping to a different trap state is possible, or, energy must be gained to enter the trap which might significantly reduce the transition rate.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Transient</th>
<th>Value</th>
<th>Useful conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_h )</td>
<td>X3,X4</td>
<td>((2.39 \pm 0.09) \text{ ps}^{-1})</td>
<td>(1/k_h = 0.42 \text{ ps})</td>
</tr>
<tr>
<td></td>
<td>X2,X3T</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( k_c )</td>
<td>X4,X3,X2</td>
<td>((0.296 \pm 0.005) \text{ ps}^{-1})</td>
<td>(1/k_c = 3.4 \text{ ps})</td>
</tr>
<tr>
<td></td>
<td>X3T</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( k_{10} )</td>
<td>X4</td>
<td>((1.50 \pm 0.05) \text{ ps}^{-1})</td>
<td>(1/k_{10} = 0.67 \text{ ps})</td>
</tr>
<tr>
<td></td>
<td>X3, X3T</td>
<td>((6.18 \pm 0.22) \text{ ps}^{-1})</td>
<td>(1/k_{10} = 0.16 \text{ ps})</td>
</tr>
<tr>
<td></td>
<td>X2</td>
<td>(\infty^\dagger)</td>
<td>(1/k_{10} = 0^\dagger)</td>
</tr>
<tr>
<td>( n_h(0) )</td>
<td>X3,X4,X2,X3T</td>
<td>((-4.62 \pm 0.01) \times 10^{-16})</td>
<td>(= 0.69 n_1(0))</td>
</tr>
<tr>
<td>( n_{hc}(0) )</td>
<td>X3,X4,X2,X3T</td>
<td>((-2.03 \pm 0.01) \times 10^{-16})</td>
<td>(= 0.31 n_1(0))</td>
</tr>
<tr>
<td>( w )</td>
<td>X3,X4,X2,X3T</td>
<td>((0.163 \pm 0.003) \text{ ps})</td>
<td>(\text{FWHM} = 0.172 \text{ ps})</td>
</tr>
</tbody>
</table>

Table 4-3. Fitting parameters from fitting the model described by Table 4-2 to the data shown in Figure 4-14 for hot and cold trapping in untreated and chloride treated samples. Some parameters were shared between various transients, given by the second column, see the main text for justification. The parameter \( w \) is the width of the Gaussian IRF convolved with the model in the fitting routine. Quoted errors are determined by the Levenberg-Marquardt algorithm utilised by OriginPro [57]. *The parameter \( k_c \) was fixed to zero for a subset of the QDs in the model (see Table 4-2). † Excitation at X2 corresponds to directly populating the CBM, equivalent to instant cooling.

The fast hot trapping rate enables competition with the intra-band charge cooling process, with rate \( k_{10} \). For each transient \( k_{10} \) varies with excitation level as expected, additionally, which process is dominant with excitation energy also varies, and the hot trapping is expected to become significantly more dominant over the cooling process for excitation even higher than X4. Excitation at X2 corresponds to directly populating the CBM, equivalent to instant cooling. Leaving this as a free fitting...
parameter results in $k_{10} > 50 \text{ ps}^{-1}$ with a large error, meaning that the rise time of the signal is limited only by the IRF of the system. The relative values of $n_{he}(0)$ and $n_h(0)$ indicate that almost a third of the CQDs within this sample experience the cold trapping process on this timescale, whilst the other two thirds contribute to the plateau. These parameters can be expected to vary significantly between independent synthesis of these CQDs, and even more so for separate synthetic recipes as they are a direct measure of the quality of the surface passivation achieved.

The X3 and X4 transitions correspond to excitation to the same electron state, the first above the CBM, as was shown in Figure 4-4. It is therefore unintuitive that there is a large difference in amplitude for these transients and of the rate $k_{10}$. As was noted in Section 4.3 an optically weak $1S_{1/2}1s$ transition is expected to lie close to X3, this corresponds to excitation directly to the CBM as in the X2 transition. This could explain the enhancement in the number of charges reaching the CBM. It should also be remembered that there is size dispersion in each sample causing a spread of the optical transitions with significant overlap, especially for transitions higher than X1. It should also be noted that the pump beam has a spectral width of approximately 10 nm. The combination of these two factors means that for any transient in this work a distribution of states will be excited. The decline in PLQY between X3 and X4 shown in Figure 4-7 also suggests that a reduction in bleach amplitude can be expected.

A 160 fs width Gaussian pulse was used as the IRF of the system in the fit shown in Figure 4-15. As was discussed in Section 3.5.3, several experimental artefacts can arise in TA, which are isolated and subtracted from the bleach signal by measuring them in the sample solvent. The width of these artefacts are often used to estimate the IRF [58]. The artefacts subtracted from the X3 and X4 excited untreated sample are shown in Figure 4-16, where 270 fs and 560 fs width Gaussian peaks are fit to each signal respectively. The fit shown in Figure 4-15 was attempted with wider IRFs ranging from 200 to 500 fs, but this resulted in a significantly smoothed rise to the signal, which was clearly inconsistent with the sharp rise of the bleach around $t = 0$. This suggests that the IRF is overestimated when extracted from the solvent artefacts. The IRF width used does have an impact on the fitted rate constants which determine the rise of the TA signals, $k_h$ and $k_{10}$. However including the IRF width
as a fitting parameter resulted in widths ranging over 100 – 160 fs depending on the starting parameters. The pulse width of the laser system is expected to range from 80 – 120 fs based on the manufacturer’s specifications and historical measurements of the system, although this can vary depending on the alignment of the amplifier (see Section 3.5.2.2). This IRF will be extended relative to this pulse width due to cross-correlation of the pump and probe beams in the sample. Cross correlation of a Gaussian pulse extends its width by a factor of approximately 1.4, consistent with the range tended to by the fitting routine. If the IRF is fixed to any of the values discussed above, the conclusions from the fit remain the same: hot trapping accounts for the differences in amplitude and rise time, and that hot trapping is only present for excitation of electrons above the CBM.

Figure 4-16. Artefacts measured in the sample solvent and subtracted from the transients shown in Figure 4-15 for excitation at X3, a), and at X4, b). A Gaussian peak is fit to the each signal and the width, \( w \), and FWHM given. The noisy tail to the right of the peak in a) was excluded from the fit.

The fit is poorest around the peak region (\( t \sim 0.2 \)) of the transient, which is the region for each sample where the contribution of artefacts have been subtracted. The necessity of removing the artefacts is clear as they often appear in the middle of a signal rise, forming transients which do not correspond to charge relaxation. However the method for artefact subtraction is prone to error: small variation in the placement of the sample cuvette can change the timing and amplitude of the artefact, and the exaggerated IRFs determined from the artefacts suggest they may not be consistent with the work of Lorenc et al. [58] which established the artefact subtraction procedure. The discrepancies in the fit around the peaks might also arise due to over-simplification of the conduction band, some effects can lead to additional splitting of conduction band levels, for example due to S-D mixing [9, 59].
as was discussed for the valence band in Section 2.3, or splitting seen in non-spherical crystals [60]. In a series of finely split energy levels, cooling can occur between adjacent levels by phonon emission, and can even jump several levels at once. It was also discussed above that excitation of a range of levels by the pump is expected. Such a ladder of transitions cannot be characterised by a single cooling rate constant, and the hot trapping rate might vary from each level. Additionally, although two subsets of QDs have been suggested in this model (QDs with and without the trapping processes), a greater variety of QDs are likely to exist with different rate constants, providing further deviation from the model.

In order to verify the assumptions made in the model, several alternative models were tested but found to yield significantly poorer fits. For example, removing the hot trapping process by fixing $k_h$ to zero. Changes in amplitude must then be achieved by significant differences in the cooling rate, $k_{10}$, for each transient. An attempt at fitting such a model is shown in Figure 4-17a, where most notably the low amplitude when pumping at X4 is unachievable. Another example is inclusion of the hot trapping process in the treated transient. Exclusion of the cold trapping process is easily justified by the absence of decay from the peak, but the presence of hot trapping might account for the slightly below unity PLQY observed in most treated samples. The result is shown in Figure 4-17b, where once again the fit is significantly poorer as the hot trapping can no longer account for the differences in amplitude between treated and untreated samples, a broader range of cooling rates and faster cold trapping is instead required.

![Figure 4-17. Failed alternative models for fitting to the bleach decays fitted in Figure 4-15. See the main text for details.](image-url)
The data presented in this chapter allows insight into charge trapping and cooling, specifically their rates, competition, abundance in an ensemble of CQDs and the likely energy of the hot electron trap. However, little insight into the mechanism of either hot or cold trapping is achieved; comparison to observations in the literature enables us to propose a model which includes the possible mechanism and destiny of the trapped charges. The mechanism for trapping of holes modelled by Califano [11] was Auger mediated trapping, where the energy dissipated by the hole by falling into the trap is transferred to the electron, exciting it higher into the band structure. The trap times modelled ranged from a few ps to a ns depending on the position of the trap on the surface, size of the QD, and number of dangling bonds at the surface site. This range overlaps with the cold trapping rate fitted in this section for electrons, of 3.4 ps. Califano suggested that the sub-ns decays of electron population from the CBM which are consistently observed in many CQD studies might be the electrons being excited out of the CBM due to Auger trapping of the holes, rather than direct trapping of the electron. This assertion could be consistent with the model fitted to the CQDs in this Section, where trapping of holes at a rate $k_c$ in a subset of the untreated QDs, Auger-excites CBM electrons either higher into the conduction band, or potentially directly into the electron trap. If the electron were excited into a higher conduction band state, it could have a second opportunity to undergo hot trapping, and its cooling to the CBM might be significantly slowed now that the hole is in the trap state, and cannot enable Auger cooling of the electron. This proposed chain of possible events is illustrated in Figure 4-18.

In Section 4.4.1 the effects of both hot and cold trapping of electrons were shown to occur regardless of whether the sample was stirred or flowed, which has been shown to eliminate the effects of carrier trapping in some types of CQD [42, 61-62]. The importance of the reduction in bleach, which we have shown can be quantitatively related to the hot-trapping rate, has not been widely recognised previously. It is key to the interpretation of transient absorption data, including that used to determine the absorption cross-section and infer MEG, where saturation of the bleach for high pump fluences as the CBM becomes fully occupied, can be used to determine $\sigma$ in ultrafast studies including those of MEG [53, 63-65]. However, if a significant fraction of hot electrons cool directly to a trap state and hence do not contribute to
the bleach then this will increase the fluence required for saturation of the band edge absorption, leading, if unrecognised, to an underestimation of $\sigma$. This will lead in turn to an underestimation of $\langle N \rangle_{\text{abs}}$ for the subset of the CQD population that is trap-free and may result in biexcitonic decay being mis-interpreted as being due to MEG rather than being caused by the absorption of more than one photon. Moreover, some studies of MEG [66] explicitly make use of the assumption that all absorbed photons cool to the band-edge in their analysis, making it even more important to determine the extent of hot-carrier trapping in the samples under study.

<table>
<thead>
<tr>
<th>$t = 0$</th>
<th>$t \approx 1/k_h$</th>
<th>$t \approx 1/k_{10}$</th>
<th>$t \approx 1/k_c$</th>
<th>$t \approx 1/k_{\text{rad}}$</th>
</tr>
</thead>
</table>

![Diagram](image.png)

Figure 4-18. Possible relaxation routes for an excited electron-hole pair in a CQD with a mid-bandgap hole trap and an electron trap above the CBM. Blue arrows represent Auger mediated processes where the electron and hole exchange energy. The mechanism of hole trapping is Auger-mediated trapping (AMT), where the electron receives the energy lost by the hole.
4.4.4. Transient absorption spectra

Significant evidence has been presented for the presence of hot and cold charge trapping in the previous section. The effects were shown to be excitation energy dependent and required a carefully thought-out model to understand the underlying processes. Similar picosecond-scale trapping has been reported previously for a number of CQD types, but is typically limited to the attribution of various decay components to charge trapping without the complementary ability to passivate the process, and without investigation of the excitation dependence.

One frequently cited signature of charge trapping in ultrafast studies of charge dynamics appears in TA spectra. The pump-probe delay time is fixed and the probe wavelength is scanned to observe spectral changes in the absorbance of the sample (See Section 3.5.2.3). Tyagi and Kambhampati [19] noted that a significant photo-induced absorption (PA) feature developed at the same time as a sub-nanosecond bleach decay component when surface traps were created on CdSe CQDs by high beam exposure. This feature appeared to the red side of the band-edge and similar PA features in this region have been observed for other CQDs [13, 43, 67-68]. It is often referred to as a “PA shelf” due to being broad, featureless, and low amplitude relative to the band edge bleach. This PA was tentatively attributed to excited state absorption from the CBM to a continuum of biexciton states, where these transitions receive oscillator strength from the presence of the surface trapped charge [12]. Tyagi and Kambhampati attributed the reduced bleach amplitude and sub-ns decay observed in the CBM dynamics of their CQDs to the overlap of the CBM bleach with this spectrally broad PA. In this section we will show that this PA feature is not responsible for the observed bleach decay despite the presence of surface traps, evidenced by the comparatively low PLQY of the untreated samples. Instead, the absorbance change observed at the X1 transition corresponds only to state filling of the CBM.

Another important feature observed in TA spectra is the shifting of transitions due to the biexciton binding energy [27]; this was described in detail in Section 3.5.4. In brief, the binding energy results in a shift in the absorbance spectrum experienced by the probe beam, resulting in a derivative-shaped absorbance change for the first absorption peak. As the charges cool to the band edge, bleaching of the X1 transition
dominates, resulting in a net negative signal. Thus, PA caused by this shift is only observed in the presence of a hot exciton, at early pump-probe delay times.

Figure 4-19a shows absorbance change spectra for a CdTe CQD sample with and without chloride treatment with the same excitation conditions described in Section 4.4.1 – pumping at 420 nm. The spectra were collected at a pump probe delay corresponding to maximum bleach of the CBM, approximately 0.7 ps. At this time, both samples share the same features albeit with different amplitudes. The large negative feature corresponds to bleaching of the X1 transition; this lowest energy bleach peak is typically labelled B1, and has been the focus of the TA studies thus far in this chapter. The positive peak to the red of the B1 bleach is a PA feature usually labelled A1, the first photo-induced absorption peak; this peak is caused by the biexciton shift, and evidence for this attribution will be given below. The A1 feature appears to extend far into the red, and rapidly drops in amplitude, in what appears to be a very weak PA shelf, barely discernible over the noise level for this system. This is consistent with a previous study [4] which only reports trapping related PA for CdTe CQDs with PLQY ~0%, whilst for ~10% PLQY, none was observed. This observation is particularly pertinent now that the synthesis techniques for many different compositions of CQDs have matured to the stage that low PLQY CQDs are less common compared to a decade earlier. To the blue of the B1 peak are additional bleach and PA features, B2 and A2 respectively; these features were not studied in this work, particularly since they are obscured by scattered pump light when exciting transitions in the range X2-X4. B2 is attributed to bleaching of the X2 transition, whilst A2 could be shifting of the X3 peak (bi-exciton shifting of transitions higher than the band edge has been observed in other CQDs [69]).

The origin of the A1 signal is confirmed by observing its presence for excitation at different pump wavelengths. In Figure 4-19b, TA spectra taken at the same pump probe delay time are shown for the pump wavelength tuned to excitation levels, X2, X3, and X4 (see Figure 4-4). These spectra have been normalised to the B1 peak. The time dynamics of the A1 feature for each case are shown in Figure 4-19c. Each transient has been normalised to the late time amplitude. It can be seen that the PA feature is only present for excitation at X3 and X4 transitions, and for less than 2 ps, rapidly becoming a negative bleach signal. Figure 4-19d compares the X3 excited...
spectrum to the same spectrum taken at a pump probe delay of 2 ps, showing that the late time bleach signal corresponds to the shoulder of the B1 peak shown in Figure 4-19a. The PA is completely absent for excitation at X2, leaving only the rise of the shoulder of the B1 bleach. The positive signal is absent for X2 pumping because this corresponds to excitation of an electron directly into the CBM (see Figure 4-4), confirming that the signal is due to the biexciton shift in the presence of hot excitons.

As described above, the A1 signal is a result of a shift in the band edge absorption peak due to the bi-exciton induced stark effect. The shape and amplitude of the peak has been shown to be directly related to the magnitude and sign of the biexciton binding energy, $\Delta_{XX}$, by Klimov [32]. It was shown that it is possible to extract a
value for $\Delta_{XX}$ from the ratio of the maximum amplitudes of the A1 and B1 signals given the linewidth of the transition (in this case approximated from the half width at half maximum of the 1S absorption peak). This gives a $\Delta_{XX}$ value of $-6.4 \text{ meV}$ for the chloride passivated sample. For the untreated sample, the same calculation yields a value of $-12.7 \text{ meV}$, however a significant overcalculation of $\Delta_{XX}$ can be expected if the B1 bleach has been significantly reduced by hot charge trapping as has been shown in Section 4.4.2. Previously reported values for CdSe CQDs were $-12 \text{ meV}$ for QD radii from 1 to 4 nm [32]. This indicates that the previously unrecognised effects of trapping could have led to an overestimation of $\Delta_{XX}$ by a factor of two.

Figure 4-20 compares the A1 and B1 bleach signals for a chloride treated and untreated pair for excitation at X3. It was shown above that the late time A1 signal corresponds to the shoulder of the B1 bleach peak. However, Figure 4-20 shows that for the untreated sample the late time A1 signal does not share the fast decay component that is observed at the centre of the B1 bleach (the centre of the $X_1$ transition). Instead, the A1 bleach remains steady as it does for the trap-free sample at both A1 and the peak of the B1 bleach. This lack of bleach decay on the shoulder of the B1 peak for untreated samples indicates that a sub set of CQDs within the untreated sample are trap free, and that they have a systematically smaller band gap than the CQDs with traps. This behaviour is also seen subtly in the integrated PL maps shown in Figure 4-7c, where the intensity (an effective measure of the PLQY) continues to increase when exciting just below the average band gap of the untreated sample. This subset could be the same subset of CQDs responsible for the plateau in the CBM bleach decay which was explored in the previous section, and attributed to a portion of CQDs which are free of the cold trapping process.

This conclusion that trap free dots have systematically smaller band gaps is consistent with a previous study performed by our group using X-ray photoelectron spectroscopy [2], which was discussed in Section 4.2.2. It was found that chloride treatment fills empty states at the valence band edge resulting in a slight narrowing (red-shift) of the band gap. Boehme et al. [12] found that unsaturated surface tellurium atoms become both electron traps as well as hole traps once oxidised. The trap-free CQDs within our untreated samples could have more un-oxidised surface Tellurium, the amounts of which will vary between individual CQDs in any given
sample due to the stochastic nature of air exposure and passivation by long chain organic ligands. This is also consistent with findings for Cl-treated CdTe thin films, where Cl at grain boundaries causes the film to become n-type [70].

![Fractional absorbance change, \( \Delta A/A \), transients for a CdTe CQD sample without (top) and with (bottom) chloride passivation. The samples were pumped at their X3 transitions under identical excitation fluences, and were probed at the peak of the B1 feature (black lines) and A1 features (red lines) from their absorbance change spectra (see Figure 4-19a).](image)

**Figure 4-20.**

**4.5. Summary**

Surface effects in CQDs remain challenging both in their elimination and characterisation due to significant variation between ostensibly similar samples. We have shown that chloride treatment of CdTe CQDs can completely eliminate surface traps without significant alteration to their other properties which affect the carrier dynamics. By comparison of the samples before and after treatment, we have shown that un-passivated surface sites mediate both hot and cold electron trapping, and formalised a model which concludes that only a fraction of CdTe CQDs within a
sample contain the cold trapping process. The absence of signatures of surface traps in transient absorption spectra was noted, however it was found that the fraction of CQDs free of cold trapping have systematically redder band gaps attributed to the filling of hole traps near the valence band maximum. These observations will be key to the interpretation of measurements of charge dynamics in CQDs where surface effects may be present.

The hot trapping process was shown to significantly reduce the number of electrons which cool to the band edge, and would compete directly with MEG. The suppression of hot traps therefore promises to increase the MEG yield, although the effectiveness of passivation with chloride ions will be material dependent, and may be incompatible with some devices. A fundamental limit on the efficiency of a solar cell with idealised MEG can be calculated using the Shockley-Queissar model [71-72], where it is assumed that all of the excess energy of solar photons above the bandgap is used to excite further additional excitons. To date, synthesised devices are still significantly below this target and adaptations of the model have been attempted to consider the contribution of charge trapping [73], which will be shown in Chapter 7. Confirmation in this work that cooling and recombination of hot charges can be excitation energy dependent, shown by the fall in the number of electrons reaching the band edge and reduced photoluminescence, provides further insight into why both MEG QY measurements and device efficiencies fall significantly short of the idealised case.

4.6. References


[48]. Excitation directly at X2 was not possible due to limitations imposed by protective eyewear used. In the case of the untreated sample in Figure 4-15, X2 was 540 nm, but the sample was excited on the shoulder of this peak at 530 nm.


Chapter 4  CdTe(Cl) CQDs – Trapping and surface passivation


[57]. OriginPro 2015 Sr2, OriginLab Corporation.


Charles Smith  PhD Thesis


Chapter 5. Quinone functionalised CdTe/CdS CQDs – Charge transfer and photoluminescence quenching

5.1. Introduction

In this chapter, charge transfer from CdTe/CdS colloidal quantum dots (CQDs) to quinone ligands bound to their surface is investigated. The charge transfer process competes with intra-band cooling and radiative recombination, resulting in a significant quenching of photoluminescence (PL) intensity, similar to surface mediated trapping. Steady-state and time-resolved spectroscopy is presented for a range of different quantities of quinone molecule attached to the surface of the CQDs to alter the efficiency of the charge transfer process. The samples were provided under collaboration with the School of Physics and Astronomy, the University of Leeds, by A. Harvie, who also performed several characterisation experiments, which will be discussed in brief.

5.1.1. Charge transfer and fluorescent sensors

One of the possible relaxation mechanisms for an excited charge carrier in a quantum dot (QD) can be to leave the crystal structure altogether, transferring to another nearby system of similar or lower potential energy. This process was described along with the competing cooling processes in Section 2.5.5, where it was noted that transfer can occur on ns to ps timescales to compete with the recombination of cooled charges [1], and compete with hot carrier intra-band cooling in some cases [2-3]. The transfer efficiency is particularly sensitive to the separation of the QD and charge acceptor, the QD size, and the QD structure [4]. Throughout this work the consideration of electron vacancies in the valence band as holes with positive charge is an important concept, particularly when the carriers have highly asymmetric band structures, as is the case in Cd chalcogenides [5]. This concept can be particularly useful in the case of charge transfer, where the injection of an electron into a QD is equivalent to the extraction of a hole.

The importance of the charge transfer process and its optimisation is intuitive for the case of photovoltaics [6-7], where charges which have absorbed solar energy must
be extracted out of the cell and replaced with cooled carriers, or in light emitting devices [8], where the converse is required – the input of high energy carriers and extraction of cooled ones after photoemission. Perhaps a less intuitive utility of this process is the development of QD-acceptor complexes as bio-sensors [9]; the efficiency of transfer to some charge accepting moieties can be dependent on their chemical environment. This enables the concept of monitoring the environment of the QDs by observation of the processes which compete with transfer, altering the QDs optical properties, in this case their PL efficiency.

It was stressed in Chapter 2 and demonstrated in Chapter 4 that the PL intensity of CQDs is highly dependent on the surface and its passivation [1]. It is this sensitivity which makes the PL intensity an effective indicator for sensing the environment of the CQDs. PL quenching can occur for individual QDs within a sample, such that net change in PL intensity indicates the concentration of the chemical species which is interacting with the QD-acceptor system. For example in the seminal paper by Medintz et al. [10], dopamine conjugated CdSe/ZnS CQDs are demonstrated as effective cellular sensors. Due to the biochemical nature of dopamine these CQDs become pH sensors, as the reduction potential of dopamine is particularly sensitive to pH, leading to alteration of the efficiency of electron transfer and PL quenching. A curve fit to the drop in PL with increasing pH was proposed for calibration of the CQDs use as bio-sensors. The large range of potential ligands which can be conjugated to the surface of CQDs [9] can be further extended by the addition of thin shells for the purpose of binding. This opens up a wide avenue of research for future CQD systems [4, 9], with tunability in addition to that provided by control of the size, structure, and composition of the CQD core.

Many of the functions of biological cells are carried out by molecules which can be considered as “nano-machines” [11]. The roles of these molecules can be dedicated to the collection and dissipation of free radicals within the cell, where they act as mobile charge carriers [12]. By this process they undergo oxidation (the donation of electrons) or redox (the acceptance of electrons). Injecting biological cells with a redox-active fluorophore can therefore provide real time indication of the prevalence of free radicals within the cell- the ‘redox environment’, and enable monitoring and a deeper understanding of the cell’s function. This concept also has potential for the
identification of disease states [4, 13-14]. For instance, the Warburg effect [15] dictates that the redox balance of cancerous cells tends to be more reduced due to a heightened dependence on glycolysis for energy production. Questions remain about the bio-compatibility of quantum dots, particularly for those composed of highly toxic heavy metals; However, redox-sensitive QDs have been applied for the sensing of particular enzymes and chemicals ex-vivo [4, 9, 14, 16-17], these include applications with significant merit outside of research, such as the detection of explosives [18].

Redox-sensitive bio-sensors have been demonstrated through the conjugation of quinones to the surface of CQDs [10-11, 13, 19-23]. A quinone is a class of organic molecule containing a benzene-like carbon ring with an even number of carbonyl (–C(=O)–) groups on the ring. They can act as efficient electron acceptors in their oxidised form due to the electronic potential of the lowest unoccupied molecular orbital (LUMO) of the molecule. In this chapter the optical properties of quinone conjugated CdTe/CdS CQDs are investigated. Significant quenching of the PL of the QDs occurs due to electron transfer to the quinones when in their oxidised, electron accepting, state, see Figure 5-1. The aim was to investigate the transfer efficiency relative to other relaxation processes, and observe the dependence on the number of quinones on the surface.

The quenching of CQD’s PL by electron transfer to acceptor molecules has been demonstrated by several groups, using a large range of different types of CQD. These include CdS [24], CdS:Mn/ZnS (Mn doped CdS cores) [25], CdSe [10, 17, 26], CdSe/CdS [27], CdSe/ZnS [13, 18, 28-30] CdTe [16, 31] CdTe/ZnS [11], PbS [32-33], and InP/ZnS [14]. However, it is rare that the mechanism and timescales of the quenching are fully quantified in terms of the transfer process to a single acceptor. In steady-state spectroscopic studies a calibration curve of intensity drop with the change in chemical environment is often presented. But such a curve is only useful if the number of acceptors on the QDs are carefully quantified. Meanwhile, time-resolved studies are often limited to the fitting of multi-exponentials to the band edge dynamics and their change in the presence of charge acceptors [3, 27, 34-35].

In the work presented in this chapter, the aim was to achieve a deeper understanding of the transfer process from CdTe/CdS CQDs to quinones by quantitatively relating
the drop in PL intensity to any changes in charge dynamics while varying the number of acceptor molecules on the surface.

![Illustration of the quinone conjugated CdTe/CdS CQDs and their redox sensitive fluorescence.](image)

Figure 5-1. Illustration of the quinone conjugated CdTe/CdS CQDs and their redox sensitive fluorescence. In their oxidised form, a), the quinone acts as an efficient electron acceptor from the CQD conduction band, resulting in a quenching of the photoluminescence (PL). In their reduced form, b), the quinones no longer accept electrons from the QD, restoring the PL efficiency. Image provided by A. Harvie, ligand not to scale.

5.2. Sample preparation and characterisation

Synthesis of the quinone conjugated CdTe/CdS CQDs was performed by A. Harvie at the University of Leeds, School of Physics and Astronomy. CdTe/CdS core/shell quantum dots were synthesised via a modified literature method [36]. In brief, cadmium chlorate hexahydrate was dissolved in ultra-pure water and thioglycolic acid. The pH was then adjusted to 11.3 by dropwise addition of NaOH. The solution was then bubbled with nitrogen for 1 hour to remove oxygen. HTe gas, created by the addition of H₂SO₄ to AlTe₂, was then bubbled through the solution while heated under reflux and stirring for 1 hour, resulting in the CdTe "core" solution. While the reaction vessel was still hot, thiourea (SC(NH₂)₂) dissolved in ultra-pure water was added. The solution was further refluxed for 1 hour resulting in the growth of a thin CdS shell of 2-4 monolayers [36]. The reaction was stopped by cooling the solution in a room-temperature water bath. The resulting particles were cleaned 3 times by centrifugation after precipitation in excess isopropanol, and resuspended in HEPES.
buffer (an organic chemical which is effective at maintaining the pH of a solution) at pH 7.2.

Quinone ligands were synthesised according to a modified literature procedure [13]. There is not yet agreed-upon nomenclature for this quinone molecule (although it is functionally similar to ubiquinone, also known as coenzyme Q10). The chemical structure once conjugated to the CQDs is shown in Figure 5-1. In this work it will be referred to simply as the quinone or abbreviated to Q. Conjugation of the quinone ligand onto the QD surface was performed at room temperature. In brief, aliquots of Q were dissolved in a small amount of DMSO. The CdTe/CdS QD solution was degassed by sonication under vacuum, filtered, and stored in an oxygen-free glove box in 4 ml aliquots. A small amount of the DMSO and Q solution was added to each aliquot, and the solutions were left stirring in the dark under nitrogen overnight. The resultant conjugates were then cleaned twice via centrifugation after dilution with excess isopropanol, and resuspended in degassed HEPES buffer at pH 7.4.

The Q:QD ratio for each aliquot was controlled by weighing of the ligand before addition to the CQDs. The estimated error on the number of molecules is 1%. The conjugation of all of the quinones to the QDs is verified by measurement of the absorbance of the supernatant after centrifugation of the QDs, where no detectable trace of the quinones was found within the sensitivity of the absorption spectrometer.

The quinones are synthesised in pairs connected by a short organic chain to a thiolate (S-S) bond. Because the thiolate bond in the quinone molecule is very strong and the concentration of both quinones and quantum dots are low, the quinones are assumed to bind to the CQDs in pairs. This results in a distribution of even numbers of quinones on the CQDs throughout the sample. This distribution will prove important when analysing the charge transfer process in the next section. The purpose of the CdS shell is to enable binding of the quinones via the sulphur atoms after breaking of the thiolate bond. The shell also protects against oxidation from the environment [37-38]: in contrast to the CdTe CQDs investigated in Chapter 4, which were highly air sensitive, these CdTe/CdS CQD are stable for several months in air.

The organic chain remaining between the quinone and the QD surface is referred to as the linker molecule, to which there are two important aspects. Firstly, since they
are bound to a single site on the acceptor molecule and the CQD, each acceptor is responsible for transfer from only one quantum dot. Secondly, the structure of the linker has a direct impact on the transfer efficiency, both due to its length and due to insulation of the acceptor from the QD core. The linker in this system is short compared to those used by Medintz et al. [10], so we can expect more efficient transfer. This has been demonstrated by Qin et al. [11], who reported significant reductions in quenching efficiency for successively longer linkers between CdTe/ZnS CQDs and a conjugated quinone which acted as an electron acceptor.

CdTe/CdS CQDs form a Type II band alignment [20] (see Section 2.4), where the hole is confined to the core and the electron is confined to the shell when in their ground state. However, the conduction band offset is small such that the confinement will be a weak effect for very thin CdS shells, as is the case for the CQDs studied here. In this case a quasi-Type II structure can form, where the electron is delocalised over both the core and shell [39]. In either case the shell can be expected to enhance rather than hinder electron transfer to the conjugates on the surface. The transition from a quasi-Type II to a Type II system is demonstrated in Chapter 7 in theoretical data for varying shell thicknesses on a Type II system. It should be considered that the Cd precursor in the synthesis includes thioglycolic acid which itself contains sulphur. It can be expected that some of this acid will degrade leading to sulphur content within the CQD core, and a degree of alloying between the core and shell. This will lead to a softening of the interface and a further reduction in separation of electron and hole wavefunctions. Preliminary results from X-ray photoelectron spectroscopy (see Section 3.6) performed by A. Harvie at the University of Leeds, and separate studies by R. Ahumada Lazo at the University of Manchester, support this notion by observation of a higher than expected sulphur content [40].

The synthesis of a single CdTe/CdS core followed by the addition of six different concentrations of quinone were prepared by A. Harvie for optical studies at The University of Manchester and are the focus of this chapter. The Q:QD ratios were 0, 2, 5, 10, 20, and 40; throughout this chapter they will be referred to by this ratio as 0Q – 40Q. Prior to this study, characterisation experiments were performed on samples for a finer increment of Q:QD ratios by A. Harvie, the key results from
which will be discussed in this section. He has also performed steady state optical spectroscopy on these samples, which will be discussed in the next section beside the results for the 0Q – 40Q samples.

For the optical studies performed at The University of Manchester, samples 0Q – 40Q were transferred to 10 mm path length fused quartz cuvettes. The cuvettes have low reflectance and high transmittance, >80% for wavelengths in the range 200-2500 nm [41]. The samples were diluted with degassed HEPES buffer to reduce the absorbance (ideally 0.1 – 0.3 OD, see Section 3.5.7) and achieve a strong TA signal. Degassing of the HEPES buffer was introduced after significant sample damage was observed by the high pump fluences of the transient absorption experiment on a previous set of quinone-conjugated samples. The damage manifested as an accumulation of opaque coagulate in the samples, which significantly changed the optical properties and resulted in very poor signal to noise ratios. The damage was found to be more severe for high Q:QD ratios, and was attributed to photo-oxidation of the ligands due to oxygen dissolved in the buffer. After degassing, signs of sample damage were no longer observed during the TA experiment, although comparison of PL measurements before and after beam exposure revealed some changes, to be discussed later in this chapter.

5.3. Steady-state spectroscopy

Absorption spectra of samples 0Q – 40Q are shown in Figure 5-2a, where the central peak corresponds to the band edge transition. The spectra were recorded using the Perkin Elmer Lambda spectrometer, described in Section 3.3.1. The first absorption peak is 525 nm (2.36 eV) for the 0Q sample, and slightly blue shifts with the addition of quinones, reaching 512 nm (2.42 eV) for sample 40Q. This shift is illustrated by the second derivatives of the absorption curves, shown in Figure 5-2b. The minimum of the second derivative gives the first absorption peak, without any distortion from the gradual rise in absorbance at shorter wavelength. Assuming a purely CdTe CQD, this band gap corresponds to a CQD diameter of approximately 2.9 nm [42] (see Section 4.3).
Figure 5-2. a) Absorbance spectra for the 0Q – 40Q samples. Spectra are offset in their y-axes for clarity; the dotted line indicates absorbance = 0 for the 40Q spectrum to highlight the shoulder which appears around 600 nm. b) Second derivatives of the spectra shown in a) for the region around the first absorption peak, where minima correspond to the average band edge transition wavelength.

A tail to the red of the band gap appears on the addition of quinones, with an amplitude which rises with $Q:QD$ ratio. This is made clear for the 40Q sample in Figure 5-2a by the inclusion of the dotted line. The origin of this feature is unclear, but is compared to an absorbance spectrum for isolated quinones in Figure 5-3. The quinones have an absorbance peak which is coincident with the tail in the samples. However, after scaling the quinone spectrum to match the concentration of quinone in the 40Q sample, the feature is approximately 200 times too small to account for the tail. The overlap of the feature with the first absorption peak of the QDs suggests that Förster resonance energy transfer may be possible to the quinones [10]. However, as discussed in Section 5.1.1, the quenching mechanism for quinone conjugated QDs has previously been reported as an electron transfer process [10-11, 13].

Figure 5-3. Absorbance spectra for the 40Q sample (black line) and isolated quinones (red dashed line). The quinone spectrum has been scaled to match the concentration of quinone in the 40Q sample, and then multiplied by 200 for clarity.
Chapter 5 Quinone functionalised CdTe/CdS CQDs

The lack of significant change to the band edge transition with the addition of quinones supports the notion that quenching of PL occurs through electron transfer from the QD to the quinone, rather than the quinone donating an electron to the QD upon conjugation. If this were the case the quenching of fluorescence would be a result of Auger recombination via the donated electron (see Section 2.5.3), but other works have shown that in this scenario a significant steady-state bleach of the first and second absorption peaks occurs due to the donated electron [30], which is not observed in our case.

Photoluminescence spectra for samples 0Q – 40Q are shown in Figure 5-4a for excitation at 420 nm (2.95 eV, ~1.25$E_g$). The spectra were recorded using the Fluorolog-3 spectrometer, described in Section 3.3.2. Each spectrum has been normalised by the sample’s fractional absorption at 420 nm to account for variation in sample concentration, although this is a small contribution. The PL intensity falls with Q:QD ratio consistent with quenching of the emission by the quinones conjugated to the surface, with more efficient quenching in the presence of more quinones. A Stokes shift of approximately 20 nm exists for all samples; this is comparable to the shifts typically observed for the CdTe CQDs investigated in Chapter 4, and arises from splitting of the state responsible for the valence band maximum (VBM), into several closely spaced levels with a high density of states. The state responsible for the PL is at the top – the VBM, while the state responsible for the first absorption peak is deeper in the valence band. This shift is an important consideration for the transient absorption results to be described in Section 5.4, where contributions from hole dynamics are negligible. The difference in intensity between the 2Q and 5Q samples is small relative to the spacing of the other drops, suggesting that either the target Q:QD ratio is inaccurate for these samples, or that a more complex behaviour exists than expected for intermediate numbers of quinone. This behaviour will be observed in several other measurements throughout this chapter. For the high Q:QD ratios the drop in PL proceeds as expected, and is shown more clearly in Figure 5-4b.
The quenching of PL intensity with increased Q:QD ratio is more accurately quantified by photoluminescence quantum yield (PLQY) measurements. PLQY was measured for the six samples using the Fluorolog-3 spectrometer and it’s integrating sphere accessory according to the method described in Section 3.3.3. The results are shown in Figure 5-5a. The PLQY of the CQDs without quinones was $28.8 \pm 2.5 \%$. This dropped with increasing Q:QD ratio as expected from the spectra shown in Figure 5-4, reaching $2.1 \pm 2.5 \%$ for the 40Q sample. As in the PL spectra intensity, the difference in PLQY between the 2Q and 5Q samples is small.

Fluorescence quenching is typically characterised through the Stern-Volmer relationship [43], where the probability of quenching is directly proportional to the
concentration of the quencher, and the process is quantified by calculation of a quenching coefficient. This treatment assumes the probability of quenching each fluorophore is equal, in other words, assumes the sample in homogeneous. However, in the quinone conjugated CQD samples studied here, the quinones are bound to the surface of individual QDs, and only contribute to the quenching of that QD. Therefore, it is important to consider the distribution of quinones and the resulting distribution of quenching probabilities. This is particularly important for low Q:QD ratios where a number of QDs will have zero quinones on their surface, and experience no quenching.

The drop in PL intensity can be quantitatively related to the charge transfer probability through the Q:QD ratio. We start with the assumption that the probability of quenching of the PL for a given QD, $P_Q$, is proportional to the number of quinones conjugated to its surface, denoted by $n$. Defining the probability of transfer to a single quinone as $P_T$, we can write

$$P_Q(n) = 1 - (1 - P_T)^n$$ (5-1)

The PL intensity, $I$, will be reduced relative to a QD with no quinones due to the chance of charge transfer:

$$I(n) = I(0) \left(1 - P_Q(n)\right)$$ (5-2)

All quinones are conjugated to the surface in pairs, where the number of pairs on each QD in the sample will follow a Poisson distribution. For an average number of quinones pairs per QD (half of the Q:QD ratio), $N$, the probability of having $k$ pairs on the surface is

$$P(k, N) = \frac{N^k e^{-N}}{k!}$$ (5-3)

and we can say that $n = 2k$. Combining Equations (5-1) – (5-3) we can calculate the reduction in PL intensity due to the distribution of different numbers of pairs in the sample. This requires averaging of the quenching probability over possible values of $k$, weighted by the probability of the QD having $k$ pairs on its surface.
\[ I(N) = I(0) \left( 1 - \sum_{k=1}^{\infty} P(k, N) P_Q(n) \right) \]

\[ = I(0) \left( 1 - \sum_{k=1}^{\infty} \frac{N^k e^{-N}}{k!} (1 - (1 - P_T)^{2k}) \right) \]

This sum has the solution

\[ I(N) = I(0)e^{N(P_T-2)P_T} \]

This expression can be used to extract the probability of charge transfer from the conduction band minimum (CBM) by comparing the steady state intensities for samples with a range of Q:QD ratios. This assumes that other forms of non-radiative charge relaxation from the CBM remain unchanged in their efficiency with the addition of quinones, an assumption which will be discussed in more detail later in this chapter. For \( P_T = 1 \), the expression reduces to \( I(0)P(0) \), which is equivalent to “static quenching” where a fluorophore is deactivated by the quencher.

Equation (5-5) has been fit to the data in Figure 5-5a, where a \( P_T \) value of 0.09 ± 0.03 was determined for samples 0Q – 40Q. The quenching of PL by the quinones was investigated more thoroughly by A. Harvie through measurement of the PL intensity for finer increments of Q:QD ratio. The data is shown in Figure 5-5b, where the intensity corresponds to the peak count rate in recorded emission spectra. The concentration of each aliquot was kept constant by the addition of weak solutions of quinone in DMSO, where in each case the total volume added was kept constant (even for the zero quinone sample an equal volume of DMSO was added). This measure of PL efficiency is not expected to be as accurate as measurement of the PLQY, but the number of data points better demonstrates the quenching predicted by Equation (5-5), where a \( P_T \) value of 0.16 ± 0.01 has been fit to the data.

The CQDs synthesised for Figure 5-5b were larger in size with average diameters of 3.1 nm determined from Reference [42], and confirmed via TEM, compared to the 0Q - 40Q core diameter of 2.9 nm [42]. Changes in quenching efficiency with QD size has been reported by other groups, although typically with an increase in efficiency with reduction in size [32]. This is usually attributed to greater average
separation of the electron from the acceptor, and therefore a reduced wavefunction overlap of the two states, and a change in the difference between the acceptor potential and the CBM. The opposite trend observed here could be attributed to the CdTe/CdS structure, which could form a Type II alignment for a thick enough shell.

The redox sensitivity of the PL quenching was demonstrated by A. Harvie by measurement of PL spectra before and after reduction of the quinones by the addition of a 20× excess of sodium dithionite. The results are shown in Figure 5-6 for a Q:QD ratio of 40:1, and compared to the same QD sample without quinones. Complete recovery of the PL intensity upon reduction is observed. A slight increase in intensity is actually observed for reduced quinones compared to the original QD. This is consistent with a study by Qin et al [11], which attributed the enhancement to passivation of the QD surface when the Quinone is in a reduced state. Note that the central wavelength of emission in Figure 5-6 is red-shifted relative to samples 0Q – 40Q, this is because larger QD cores were used in the study by A. Harvie.

![Figure 5-6](image)

Figure 5-6. Demonstration of the quenching of photoluminescence (PL) with the addition of 30 quinones per quantum dot. Upon reduction of the conjugated quinones, the PL intensity is fully recovered. Data collected by A. Harvie.

### 5.4. Transient absorption spectroscopy

Transient absorption (TA) spectroscopy was used to measure the charge dynamics in the 0Q – 40Q samples. The aim of the investigation was to observe the charge transfer process depleting the CBM of electrons on a sub-ns timescale. The experimental setup and technique were described in detail in Section 3.5, but in brief, the pump beam, a high photon energy laser pulse, with ~100 fs pulse width, excites the sample creating hot excitons which gradually cool to the band edge. After some
time delay, a white light probe beam, also 100 fs pulse width, is passed through the sample. The probe beam will experience a reduction in absorption (increase in transmission) at wavelengths corresponding to transitions which are partially filled due to excitation by the pump beam. By varying the time delay and selected probe wavelength, the time dependent occupation of specific energy levels can be measured. In this section the bleach of the band edge transition is observed which results in a signal directly proportional to the occupation of the CBM.

Figure 5-7 shows the fractional change in absorption at the band edge transition (525 – 514 nm depending on the sample) of samples 0Q – 40Q following excitation at 420 nm (~ 1.25 $E_g$) over timescales of 40, 200, and 1000 ps. As discussed in Sections 3.5.1 and 5.3, when probing this transition the measured bleach signal is proportional to the occupation of electrons at the CBM, it has been established that contribution to the signal by hole states is negligible in such samples due to their high density of states and band edge degeneracy, and their relaxation to the very top of the valence band [44-45].

For all six samples the CBM dynamics have the form of an initial peak, followed by a rapid decay to a plateau over 10s to 100s of ps. This behaviour has been observed in many CQD systems and particularly for CdTe CQDs, which were investigated in Chapter 4. There it was shown that the decay corresponded to surface mediated charge trapping from the band edge, and the plateau corresponded to CQDs in the sample which are free of this non-radiative decay process [46], and thus recombine radiatively with a time constant typically of a few ns. It was also shown that hot trapping occurs from states above the CBM, which results in a significantly reduced bleach signal at the CBM. For the 0Q sample, the experimental conditions were identical to those used for the CdTe CQDs in Chapter 4: the samples were stirred to prevent any photocharging effects [47], and were excited at sufficiently low fluences such that the probability of two photon absorption is negligible, for a detailed discussion on this point see Sections 3.5.5 and 4.4.2. Therefore, this decay is also attributed to surface mediated charge trapping. However, the form of the decay changes significantly with increased Q:QD ratio, as discussed below.
Figure 5-7. Fractional absorbance change, $\Delta A/A$, transients for samples 0Q – 40Q following excitation at 420 nm over time ranges of a) 1000 ps, c) 200 ps, and e) 40 ps. A bi-exponential fit (see Equation (5-6)) to each decay is shown (red lines) with time constants shared between the six samples. The fit parameters are shown in b) 1000 ps, d) 200ps, and f) 40 ps.

There are two notable trends with increasing quinone concentration. Firstly, a reduction in the amplitude of both the peak bleach response and the plateau, indicating that the quinones reduce the number of excited electrons which cool to the
CBM. Secondly, the overall rate of decay to the plateau increases. In order to illustrate the change in decay rate, a bi-exponential decay is fit to each transient in Figure 5-7a:

\[ A(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + y_0 \]  

(5-6)

where \( A(t) \) is the time dependent amplitude of the bleach, \( A_1 \) and \( A_2 \) are the amplitudes of two decay components with decay rates \( k_1 = 1/\tau_1 \) and \( k_2 = 1/\tau_2 \) respectively, and \( y_0 \) is the amplitude of the plateau. Bi-exponential decays have been fit to the CBM dynamics of a large number of CQD-acceptor complexes [3, 27, 32-35, 48-49], where frequently the initial amplitude of the decay is neglected, and usually the magnitude of the decay for the acceptor-free CQD is small.

It was found that performing a global fit to the transients with shared \( \tau_1 \) and \( \tau_2 \) resulted in excellent fitting. The fitting parameters are shown in Figure 5-7b, d and f. The reduction in plateau amplitude, \( y_0 \), is the primary contributor to the reduction in peak amplitude, and it can be seen that generally the faster decay component, \( A_1 \), grows and becomes dominant over the slower component, \( A_2 \). The justification for fitting a bi-exponential decay is that it was the lowest number of components required for a suitable fit on these timescales. Sharing the decay rates between each transient, enables the drawing of Figure 5-7b, from which we can easily show that a faster average decay rate occurs with increasing Q:QD ratio. However letting individual rates be fit to each transient resulted in little deviation from the shared rates.

The decay constants fit in Figure 5-7a correspond to lifetimes of 32 ps and 420 ps. However these shared parameters were found to be sensitive to the temporal range of the data. Figure 5-7c to f show the equivalent measurements and bi-exponential fits for shorter ranges of 200 and 40 ps. The observed trends are similar for all three transients, with the dominant change being the reduction in plateau amplitude. The similarity between the 2Q and 5Q samples persists, and for the short time range transients they appear out of trend. This inconsistency could be due to the realignment of the pump and probe beams for each transient.
Figure 5-8a compares the fall in fitted plateau amplitude, $y_0$, in Figure 5-7a to photoluminescence quantum yield (PLQY) measurements from Figure 5-5 and the fit to Equation (5-5). PLQY corresponds to the fraction of electron-hole pairs which undergo radiative recombination. Since only electron dynamics contribute to these TA signals, the similarity between the fall of both measurements with quinone number suggests that the fall in PL intensity can be largely attributed to the quinones providing additional non-radiative cooling for electrons from the conduction band. Fitting Equation (5-5) to the drop in plateau amplitude also gives the same $P_T$ value of 0.09 given by the PLQY.

A non-mono-exponential decay can be attributed either to the presence of different populations of CQDs in a sample with different decay dynamics (subsets), or, by a de-trapping mechanism [50], or both, as described in Section 3.4. In Chapter 4 it was concluded that different decay behaviour arises due to a distribution of dots with and without trapping, and this was supported by a theoretical work [51] which showed different trapping rates depending on the position of un-passivated sites on a QD’s surface.

With the addition of quinones, if the quenching mechanism is added to all of the QDs, and is independent of the existing decay routes, the effect on the overall dynamics would be to add an additional decay path to each subset corresponding to electron transfer. This would increase the decay rates:

$$\Delta A/A_{\text{y}}$$
\[ k_1 \rightarrow k_1 + nk_q \]  
\[ k_2 \rightarrow k_2 + nk_q \]  

(5-7)

where \( n \) is the number of quinones conjugated to the QD, and \( k_q \) is the transfer rate to a single quinone. This is analogous to the steady state model described by Equation (5-5). The additional decay route would also affect the plateau of the transient, changing the bi-exponential decay from Equation (5-6) to a tri-exponential:

\[ A(t,n) = A_1 e^{-t(k_1+nk_q)} + A_2 e^{-t(k_2+nk_q)} + y_0 e^{-tnk_q} \]  

(5-8)

As in Section 5.3, there will be a Poisson distribution in the number of quinones attached to the individual CQDs in each sample. This will lead to a range of decay rates within each subset. In each sample there will remain a fraction of CQDs with zero quinones on them, given by \( P(0) \) (see Equation (5-3)). This fraction would maintain the same decay behaviour as the 0Q sample. Considering such a distribution has been shown to be necessary for acceptor conjugated CdSe/ZnS CQD where a simple bi-exponential fit did not work [52].

Attempting to fit the model described above to the TA data over any time scale reveals two inconsistencies. Firstly, this model does not predict the significant drop in initial amplitude of the transients (the transients were normalised in Reference [52], and typically are in most charge transfer studies [3, 27, 32-34, 48]). Secondly, a value of \( k_q \) cannot be fit which accounts for the large difference in relative amplitude of the peak and plateau for each transient simultaneously. As was shown in Figure 5-7, shared decay constants fit well to the six transients, therefore increasing the decay rate by \( nk_q \) (Equation (5-7)), requires either a very small \( k_q \), such that the overall rate doesn’t change significantly, or a very large \( k_q \), such that the signal from dots with quinones decays rapidly, leaving only contributions from dots with little or no quinones. A very fast transfer rate has been reported from CdSe to methylviologen, and was shown to be competitive with Auger recombination of multi-excitons, where a transfer time of 70 fs was reported [26]. An alternative explanation which is consistent with our data and can explain the drop in decay
amplitude would be a hot charge transfer process, such that even at early decay times the high-quinone samples do not contribute to the bleach at all.

A much finer time step was used to view the early time signal for each sample, the results of which are shown in Figure 5-8b. Significant artefacts are present during the rise of each signal, which could not be removed through the methods described in Section 3.5.3 using a reference sample. This artefact is likely due to the presence of DMSO in the samples (added during the conjugation of quinones and as a control to the 0Q sample). However, it can be concluded that the decay behaviour on this timescale remains largely the same for each sample, with only a difference in initial amplitude. This amplitude is compared to the fitted amplitude ($y_0 + A_1 + A_2$) from the 1000 ps transients in Figure 5-8a, where it can be seen that the peak amplitude does not match the quenching of the PLQY and plateau amplitude. In Chapter 4, a reduced peak TA amplitude was attributed to hot trapping occurring in the conduction band, and resulted in a reduced rise time due to the enhanced overall decay rate from the pumped transition. The successively reduced amplitudes for the 0Q – 40Q samples suggests that in these samples sub-ps hot electron transfer is occurring to the quinones from these QDs. Hot transfer has been observed in other CQD-acceptor systems [2-3], where successively faster rise times were observed as the number of charge acceptors was increased. However observation of this trend is prevented for our data by the artefacts present in Figure 5-8b.

The relative amplitudes of the decay components, $A_1$, $A_2$, and $y_0$, vary significantly for each sample. This suggests there may be a relationship between the non-radiative decay mechanisms from the CBM and the quinone transfer mechanism. It has been established that the decay from the CBM for the 0Q sample can be attributed to surface mediated trapping, and also that such trapping is sensitive to the surface passivation, both in the extent of passivation and the position of traps on the surface [51]. It is therefore possible that binding quinones to specific sites on the surface could significantly change the trapping process. Binding to a site that was formerly un-passivated might simultaneously decrease the probability of charge trapping to a surface state while increasing the probability of charge transfer to the quinone. Furthermore, the particular binding site of the quinone on the surface is likely to change the transfer rate. Several works have attributed multi-exponential decays to
different couplings of acceptor molecules [32-33, 48-49]. Such stochastic behaviour could be the explanation for the trends observed here which are inconsistent with the addition of one more relaxation mechanism (Equation (5-7)) with a single relaxation rate to each quinone. An alternative explanation for this behaviour, which would be difficult to test, is deviation from a Poisson distribution of quinones on the CQDs. For example if a large number of Quinones cannot fit on the surface due to steric hindrance, this would simultaneously lower the number of QDs with either small or large numbers of quinones.

5.5. Photoluminescence decay

Photoluminescence decay kinetics were measured for the 0Q – 40Q samples using the time correlated single photon counting (TCSPC) system described in detail in Section 3.4. In brief, the sample is excited with a femtosecond pulsed laser, the time varying PL is then measured at the central wavelength of the emission peak using a multi-channel plate. The resulting dynamics reveal the coupled populations of the CBM and VBM in the CQDs. The aim of these measurements was to relate the dynamics to those measured at the CBM using the TA experiment described in the previous section, and to investigate the effects of quinones on the charge dynamics over much longer timescales.

The PL dynamics are more difficult to interpret than the TA measurements. Firstly because both the electron and hole are known to have different non-radiative decay pathways from the band edge transition, with variation of their presence and efficiency between CQDs. Observing their coupled dynamics therefore leads to a large range of net decay rates. Secondly, PL decays are typically normalised to their peak, such that the amplitude no longer indicates the relative number of charges at the band edge. This is due to the more complicated collection optics in this experiment (see Section 3.4).

De-gassing of the sample diluent was introduced to prevent sample damage from the high fluence TA pump beam, and was effective in eliminating the visible signs of damage and all their effects on the TA signal. However, investigation of the PL dynamics before and after TA revealed that minor changes to the samples were still occurring. The effect of beam exposure was a slight increase in PLQY (shown in
Figure 5-5a) and a decrease in the PL decay rate, suggesting that the charge accepting capability of the quinones was reduced. This is shown in Figure 5-9.

![Figure 5-9. Comparison of the photoluminescence (PL) decay dynamics for sample 0Q with and without prior measurement in the transient absorption (TA) experiment. The samples were excited at 420 nm.](image)

PL decay transients for the 0Q – 40Q samples are shown in Figure 5-10a following excitation at 420 nm (2.95 eV or ~1.25 $E_g$), this data was collected for samples unexposed to the TA system, but approximately 1 month after synthesis. An increase in quinone concentration results in a faster decay of PL. However, the zero quinone sample lies out of trend, with a faster decay than samples with a small Q:QD ratio. Samples lying out of trend with increased acceptor:QD ratio was also seen in the work of Medintz et al. [10].

![Figure 5-10. a) Normalised photoluminescence (PL) decay transients for samples 0Q – 40Q for excitation at 420 nm. A tri-exponential decay, $A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2} + A_3e^{-t/\tau_3}$, is fit to each transient (red lines) with shared decay constants. b) Fit parameters for the tri-exponential decays in a).](image)

In order to illustrate the differences between the decays, a tri-exponential fit was performed for each transient with the time constants of decay shared between the
three samples. The resulting fit parameters are illustrated in Figure 5-10b, where it is shown that the highest contributor to the difference between the samples is an increase in the amplitude of the fast decay component.

The zero quinone sample lying out of trend could be attributed to a small number of quinones having a mild passivating effect on the CQD surface. As discussed earlier in the chapter, un-passivated sites on the surface (surface atoms with one or more dangling bonds) can act as centres for non-radiative hole trapping \[51\]. Quinones binding to such un-passivated sites could result in a decrease in non-radiative relaxation which is not fully offset by charge transfer to the small number of quinones on the surface. This passivation of hole traps rather than electron traps is consistent with the TA results shown in Figure 5-7, where the zero quinone sample does not lie out of trend, but a significant difference is seen in the decay, due to the experiment revealing only electron dynamics at the CBM.

As in the TA experiment, the decay constants fit to PL decay transients can often be used to determine the rates of different relaxation routes for charges at the band edge. A fitted decay constant represents the contribution from all the individual decay rates acting on each subset of the CQDs in the sample. However, more complicated dynamics such as de-trapping, or back-transfer of charges can also lead to this behaviour, where a single ensemble of quantum dots can have a tri-exponential decay where the fitted rates are all linked to the different decay processes and vary un-intuitively with the rate of each process \[50\].

The observation that a zero-quinone sample can have lower PLQY and faster PL decay rate than samples with a few quinones provides further evidence that a relationship may exist between the quinones and surface traps already present in these CQDs. It has been discussed previously that surface traps can be attributed to distinct sites on the surface where a surface atom has one or more dangling bonds. A quinone binding to such a site could thus reduce the total impact of surface charge trapping, without resulting in an overall reduction in PL until a significant number of quinones are bound to the surface. The quinones may even preferentially bind to such under-coordinated sites due to the absence of surface ligands.
5.6. Summary

Electron transfer from CdTe/CdS CQDs to quinone molecules conjugated to their surface has been demonstrated for a range of average quinone to quantum dot ratios. The first measurements of the ultrafast dynamics were presented, and a complex behaviour was described which is inconsistent with a model for photoluminescence (PL) quenching which is effective at describing the steady state quenching behaviour. In particular, a significant drop in transient absorption (TA) signal amplitude with increased quinone concentration was noted. This amplitude is typically neglected in many transfer studies and suggests a hot electron transfer process is occurring in light of the results presented in Chapter 4, where the TA amplitude is linked to hot electron trapping. The change in relative amplitude of decay components in both TA and PL decay studies suggests that a dynamic relationship may exist between charge trapping and electron transfer which is more complex than other QD-acceptor systems studied in the literature.

5.7. References


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[40]. Private communication


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Chapter 6. MEG in InP/CdS CQDs

6.1. Introduction

In this chapter, we describe the first reported measurement of multiple exciton generation (MEG) in quasi-Type II core/shell InP/CdS colloidal quantum dots (CQDs). The efficiency of MEG is found to be comparable to MEG in Type I InP core/shell CQDs [1], however the quasi-Type II band alignment contributes several effects which have the potential to enhance device performance. These effects include enhanced electron extraction [2], extended charge carrier lifetimes [3-4] and additional band edge tuning through controlling the shell diameter [3]. Measurement of MEG in these CQDs was particularly challenging due to high sample absorbance at photon energies above the MEG threshold, combined with the requirement to use low fluences to prevent two-photon absorption, resulting in a significantly reduced signal quality. These circumstances led to the development of a new analysis technique for determining the MEG yield for highly absorbing samples with poor signal to noise levels. The results described in this chapter were published in The Journal of Physical Chemistry C [5] along with the synthesis and structural characterisation of the CQDs which were also performed at The University of Manchester by researchers in the D.J. Binks group.

6.1.1. Multiple exciton generation

MEG is a process which has the potential to significantly enhance the efficiency of next generation photovoltaics by harvesting energy usually wasted as heat [6-7]. In a conventional solar cell, the energy of an absorbed photon in excess of the band gap is rapidly lost as heat through the process of phonon scattering [8]. However, in a quantum dot, quantum confinement leads to increased energy level spacing and an increase in the wavefunction overlap of charge carriers. Under these circumstances the process of MEG is expected to become more efficient. The process, its characterisation, and a review of reported MEG efficiencies were described in Sections 2.6 and 2.7. In brief, a photo-excited carrier with excess energy greater than the band gap, $E_g$, can cool to the band edge by Auger-exciting an additional electron-
hole pair, resulting in additional charge carriers at the band gap, and the potential for more photo-current from a solar cell. This was illustrated in Figure 2-11.

MEG has an energy threshold, above which photo-generated carriers have enough energy for MEG to occur, $h\nu_{th}$. The theoretical minimum for $h\nu_{th}$ is $2E_g$, where all of the photon energy in excess of the band gap must be given to a single charge carrier. However, the excess energy is actually divided between the electron and hole according to their effective masses in order to conserve momentum, leading to a threshold somewhat higher than $2E_g$ (see Equation (2-20) in Section 2.6). The efficiency of MEG at a given excitation photon energy is characterised by the MEG quantum yield, $QY$, which is the average number of photo-generated carriers generated at the band edge per absorbed photon. In this work we report the first observation of MEG in InP/CdS CQDs by measurement of $QY$ following excitation at $3E_g$.

6.1.2. InP and InP/CdS CQDs

InP is a III-V semiconductor with a comparatively low bulk $E_g$ of 1.35 eV [9], and typically forms CQDs with $E_g$ of ~1.7 – 2.0 eV [10]. There have been many techniques published for the synthesis of InP CQDs, however one critical problem for InP cores are their chemical instability, such that most techniques require lengthy degassing processes and carefully controlled experimental conditions [11]. The resulting dots typically suffer from poor emission properties and are particularly sensitive to oxidation and degradation [12]. Consequently, InP CQDs typically undergo a surface treatment which attempts to passivate the core to reduce non-radiative recombination of charges. This is often achieved by treatment with passivating ions, or by shelling of the core with another semiconductor [12-18].

Studies of InP CQDs were motivated by the expectation of a low MEG threshold, $h\nu_{th} \approx 2E_g$, due to the carrier effective masses, $m_e^* \ll m_h^*$ [6], and the low toxicity of the material compared to Cd and Pb based QDs. MEG was first measured for InP/ZnS/ZnO (core/shell/shell) Type I CQDs by Stubbs et al. [1] in 2009, the same group conducting this work. The study reported a MEG efficiency of 0.3 [1], defined as the rate of increase in $QY$ with photon energy (in units of $E_g$).
The ZnS/ZnO shells, utilised by Stubbs et al. [1], passivate the InP core from non-radiative surface mediated recombination [12-13, 18-21], and can enhance the wavefunction overlap of the confined charges, for more detail see Section 2.4. However, a later study of CQD-sensitized solar cells [22] showed that the addition of such a wide band gap outer shell to CQDs can result in a significant reduction in photovoltaic efficiency, an effect attributed to the outer shell acting as a barrier to charge extraction from the QD core [23-25]. In contrast, in a Type II or quasi-Type II CQD design, one or both of the photo-generated charges are confined to the shell or delocalised across the whole CQD, eliminating the barrier to extraction for at least one charge [2, 18]. Furthermore, a reduction in wavefunction overlap of the electron and hole can result in an elevated radiative lifetime, affording more time for extraction of photogenerated charges. The impact of these effects on the efficiency of a solar cell will be modelled in Section 7.2 for a Type II structure.

A Type II design can also enhance the efficiency, $\eta$, of the MEG process itself (see Section 2.7). An upper limit to $\eta$ of 0.5 was estimated for Type II CdTe/CdSe CQD dispersions [26]. This high efficiency was attributed to a reduction in the wave function overlap between carriers resulting in a decreased rate of Auger cooling, a process that competes with MEG (see Section 2.5.3). A quasi-Type II PbSe/CdSe CQD design was used to achieve a $\eta$ of 0.3, by suppressing hole cooling which also competes with MEG in this system [27].

In this work, we study MEG in dispersions of quasi-Type II CQDs formed by the growth of a CdS shell around an InP core. Due to the relative band gap and band offsets in these materials, the electron is delocalised over the core and shell whilst the hole is confined to the InP core [15], as illustrated in Figure 6-1. These CQDs are of particular interest for MEG-enhanced solar cells for several reasons. As mentioned above, Type I CQDs based on InP cores exhibit good MEG efficiency [1], with a threshold close to the optimum of $2E_g$. The addition of a CdS shell can redshift the absorption edge significantly [15], so that it is closer to the ideal value for optimal exploitation of the solar spectrum [28]. A CdS shell has also been shown to be an effective means of passivating surface traps, evidenced by an increase in photoluminescence (PL) and reduction in PL intermittency (also known as ‘blinking’) following the addition of such a shell to InP [15]. Moreover, this surface
passivation does not come at the cost of extraction efficiency from the CQD. Wu et al. [14] showed that the characteristic electron transfer time from an InP CQD to a methylviologen acceptor molecule was just 11 ps, and was little changed after the addition of a CdS shell at 15 ps. Importantly, both of these values are much less than the biexciton lifetime in InP/CdS CQDs, which can be as long as 7 ns [15], indicating that the additional excitons produced by MEG can be extracted with high efficiency from the CQD rather than being lost to recombination.

![Schematic representation of the InP/CdS (core/shell) CQD structure and the resulting quasi-Type II band alignment [14]. Also shown is the lowest electron energy level in the conduction band and the hole energy levels corresponding to transitions labelled B1 and B2, with indicative energies corresponding to the samples studied (this labelling corresponds to bleach peaks observed in previous transient absorption studies [14]).](image)

Figure 6-1. Schematic representation of the InP/CdS (core/shell) CQD structure and the resulting quasi-Type II band alignment [14]. Also shown is the lowest electron energy level in the conduction band and the hole energy levels corresponding to transitions labelled B1 and B2, with indicative energies corresponding to the samples studied (this labelling corresponds to bleach peaks observed in previous transient absorption studies [14]).

The single exciton recombination lifetime is also extended to several hundred nanoseconds in InP/CdS CQDs, for both isolated CQDs [15] and CQD-acceptor complexes [15]; calculations for similar CdSe/CdTe CQDs indicate that the increase in recombination lifetime produced by a quasi-Type II structure can significantly increase solar cell efficiency [29]. However, it is still unclear how MEG efficiency itself will be affected by the addition of a CdS shell to an InP CQD, which will depend on the interplay of several competing processes, each of which is affected by the change in structure. The reduced wave function overlap between carriers may simultaneously reduce the rate of MEG and of the Auger relaxation with which it competes, but by different amounts. The reduced confinement resulting from the addition of the CdS shell will reduce the separation of energy levels for the electron, which may increase the rate of phonon-mediated cooling [3].
6.2. Sample preparation and characterisation

The synthesis and structural characterisation of the InP/CdS CQDs were performed at The University of Manchester by collaborating researchers, and will be described in brief in this section. It was emphasised in Chapter 2 that the optical properties and charge dynamics in CQDs are particularly sensitive to their preparation and handling; a thorough structural characterisation is therefore an important addition to the measurement of MEG to aid in the identification of differences between our samples and those in other studies. More detailed descriptions can be found published alongside the results from this chapter [5].

6.2.1. Synthesis and preparation

The InP/CdS CQDs were synthesised according to literature procedures [14-15] with slight modifications [5]. The amount of CdS precursor solution added was calculated based on the InP core size, itself calculated from the absorption spectrum, described in the literature [30].

A mixture of indium acetate (InAc₃), myristic acid and dry 1-octadecene (ODE) were degassed and kept under vacuum for 60 minutes. The mixture was then heated to 285 °C under argon, and tristrimethylsilyl phosphine was injected and the temperature dropped to 270 °C for the growth period. The reaction was stopped after 4 minutes by removing the heat source to cool to room temperature. The InP QDs were precipitated out of solution by the addition of ethanol. This was repeated several times and the washed QDs were re-dispersed in dry toluene for analysis, or in hexane for the shelling procedure.

A cadmium oleate precursor solution was prepared by dissolving CdO in oleic acid and dry ODE at 300 °C to obtain a colourless solution, which was kept above 100 °C. A sulphur precursor solution was prepared by dissolving sulphur in ODE at 100 °C. Washed InP cores in hexane were added to a mixture of degassed oleylamine and ODE. The hexane was then removed with the temperature gradually raised to 100°C under vacuum. The flask was refilled with Ar and the temperature was raised to 150 °C for the first cation addition. The cadmium precursor solution was added dropwise to the solution, followed by 10 minutes' annealing and the first injection of the sulphur solution. The temperature was then raised to 240 °C for all
subsequent precursor additions. The first shell was annealed for 30 minutes at this elevated temperature. All subsequent additions were annealed at this temperature for 45 minutes. Three layers of CdS shell were formed in the course of this reaction. After the shelling was complete, the solution was cooled to room temperature and washed by precipitating in ethanol.

For the optical studies in this chapter, the CQDs were washed and re-dispersed in dry hexane or toluene and diluted to an absorbance of 0.1 – 0.3 at the band edge transition wavelength (see Section 3.5.7). Toluene was used for some of the early experiments for excitation at 420 nm, however toluene is highly absorbing for wavelengths less than ~300 nm, and so hexane was used due to its high transmission for wavelengths as low as 200 nm. In both cases the samples were kept under nitrogen and kept in 10 mm path length quartz cuvettes.

6.2.2. Optical characterisation

Steady-state absorption and PL spectra for the InP/CdS CQDs are shown in Figure 6-2, recorded using the Lambda UV/Vis/IR and Fluorolog-3 spectrometers described in Section 3.3. For the PL measurement the sample was excited at 420 nm (2.96 eV, or $1.7 E_g$). The absorption spectrum of the InP cores before the addition of the CdS shell is also shown for comparison, where an absorption edge at 550 nm is visible. An estimate for the average InP CQD diameter can be made from this band edge using the empirical fitting curve given by Reiss et al. [30], which yields an average diameter of 3.9 nm.

On the addition of the CdS shell, the absorption edge is red-shifted to 600 nm and weakens significantly, as shown in the inset of Figure 6-2; this transition is shown in Figure 6-1, labelled as B2, which involves a hole spatially confined to the InP core and an electron delocalised over both the core and shell. The red-shift and weakening of the absorption edge are consistent with the formation of a quasi-Type II CQD, and are attributable to a decreased confinement of the electron as its wavefunction spreads into the shell. This results in a reduction of wavefunction overlap between the carriers, which reduces the absorption strength of the band edge transition [18]. The absorbance of the InP/CdS CQDs increases sharply for wavelengths less than ~500 nm; this corresponds to transitions involving a higher energy de-localised hole
as well as de-localised electron states with consequently increased wave function overlap and thus absorption strength. The lowest energy transition of this type appears at 600 nm, and is labelled as B1 in Figure 6-2, (this labelling corresponds to bleach peaks observed in previous transient absorption studies [14]). The high absorbance at wavelengths shorter than 300 nm will prove to be problematic when exciting the samples above the MEG threshold in Section 6.4.

Figure 6-2. Absorbance (black line) and photoluminescence (red line) spectra for the InP/CdS CQD sample, and absorbance (black dashes line) for the InP sample. Inset: an expanded view of the absorption edge region. The labelled absorption features, B1 and B2, correspond to the transitions illustrated in Figure 6-1.

No significant PL was obtained from the InP cores, consistent with the literature where significant emission from InP CQDs is typically only achieved after some form of surface treatment [12, 17, 31]. After the addition of the CdS shell emission increased and the photoluminescence quantum yield (PLQY) was measured to be 10 ± 2 %, measured on the Fluorolog-3 spectrometer with its integrating sphere by the method described in Section 3.3.3. This increase can be attributed to the CdS shell acting as a barrier that reduces the interaction of holes with the CQD surface, which has been shown to mediate non-radiative recombination [18, 32-33]. The PL spectrum has a peak at 700 nm and a half-width at half-maximum on the short wavelength side of 50 nm. The spectral range of the instrument used limited the measurement to wavelengths shorter than ~780 nm. These observations are consistent with previous results for InP/CdS CQDs [14-15] and other quasi-Type II CQDs [2].
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The large Stokes shift observed here is typical for InP CQDs, and has been attributed to splitting of the band edge by the electron-hole exchange interaction [17, 34]. It was also shown that the shift can be significantly size-dependant which could explain why the PL peak is significantly broader than the absorption peaks; a similarly broad PL peak was observed by another group and found to be largely attributable to size dispersion in the sample of only ~10% [17]. Typically, the first absorption peak is assigned as the band gap of a CQD sample, however due to the large Stokes shift and very broad PL peak for these CQDs, a better estimate of the lowest lying state can be made from the PL peak at 700 nm, and has been used throughout this chapter. This will be important when considering the threshold for MEG in these CQDs.

6.2.3. Structural characterisation

Powder X-ray diffraction (XRD) experiments were performed on the InP and InP/CdS CQDs [5] in order to determine their crystal structures. The measured diffraction patterns are shown in Figure 6-3, recorded by C. Lydon, and are compared to reference peaks. The diffraction peaks observed for the InP CQDs agree well with the expected peak positions and relative intensities for the cubic phase of InP. Dennis et al. [15] reported that for ‘giant’ InP/CdS CQDs with CdS shells that were up to 4 nm thick, the CdS forms in its more thermodynamically stable hexagonal phase. However, here the diffraction peaks are little changed on the addition of the shell, and are consistent with the formation of CdS in its cubic phase (zinc blende/Hawleyite). This indicates that for thin shells the cubic template provided by the InP is a more important factor than thermodynamic stability in determining the lattice structure of the shell.

The average diameter of 20 InP/CdS CQDs measured from a transmission electron microscopy (TEM) image, shown in Figure 6-3, was found to be 5.2 ± 0.1 nm, with a standard deviation of 0.6 nm [5]. The image was recorded by C. Lydon and N. Savjani. The InP core diameter was determined as 3.9 nm from the absorption spectrum (shown in Figure 6-2) [30], indicating that the shell thickness is approximately 0.7 nm. This is approximately equal to three monolayers of CdS,
based on a bond length of 0.2527 nm for CdS in its cubic (zincblende) structure [35], and is consistent with the number of layers expected from the synthesis technique.

Figure 6-3. Left: X-ray diffraction patterns for the InP (red) and InP/CdS (black) CQDs. Reference peaks for InP (red) and cubic phase (zincblende/Hawleyite) CdS (black) are also shown (Powder Diffraction Files 01-073-1983 and 00-042-1411, respectively). Right: TEM image of the InP/CdS CQDs [5]. Data from both figures was collected and analysed by C. Lydon and N Savjani.

X-ray photoelectron spectroscopy (XPS) was used to investigate the composition of the InP and InP/CdS CQDs [5] by P. Clark. The ligands on the as-synthesised CQDs were exchanged for 3-mercaptopropionic acid (3-MPA) in order to prevent charging during exposure to the X-ray beam. The normalised In 3d, P 2p, Cd 3d, and S 2p core peaks are presented in Figure 6-4 for both the InP core and the InP/CdS CQDs. Figure 6-4a and b were used to determine that the core has a P:In ratio of 0.4 ± 0.1, and this ratio was not significantly different after the addition of the CdS shell at 0.5 ± 0.1, indicating that the core composition is not appreciably changed by the shelling process. The low value of the P:In ratio determined by XPS measurements has been reported previously [36-37] for InP CQDs synthesised by the same method, and was attributed to the presence of an In rich surface. In Figure 6-4b the lower binding energy (BE) P 2p doublet (P 2p$_{3/2}$ at 128.9 eV) is characteristic of InP. The second, higher BE doublet (P 2p$_{3/2}$ at 133.3 eV), is attributed to InPO$_x$, and indicates oxidation of the InP cores. The same degree of oxidation can be seen both before and after the addition of the shell, implying that no further oxidation of the core occurs during the shelling procedure. Similar observations have been reported previously for InP CQDs and were attributed to the conversion of the top layer of InP into InPO$_x$ (where $x = 3,4$) [36]. However, the authors noted further oxidation on the
addition of a ZnS shell, which is not observed here for the case of a CdS shell [36-37].

![Figure 6-4](image)

Figure 6-4. Comparison of X-ray photoelectron spectra for an InP (red) and InP/CdS (black) CQDs in the region of peaks corresponding to: a) In 3d, b) P 2p, c) Cd 3d, d) S 2p. The spectra are normalised to the In 3d signal for each sample. This data was collected and analysed by P. Clark.

Observation of the Cd 3d and S 2p signals, shown in Figure 6-4c and d, revealed that Cd and S are present in broadly equal amounts, with Cd:In and S(CdS):In ratios of 2.6 ± 0.3 and 3.2 ± 0.5 respectively, consistent with the addition of a CdS shell to the InP core. Two S 2p doublets were observed in the InP/CdS sample, one characteristic of CdS at 161.7 eV BE [38], and a second at 162.9 eV BE attributed to the 3-MPA ligand bound to the CQD surface. The latter was also observed in the InP sample, which was also capped with 3-MPA. No S 2p doublets were observed at higher binding energies (centred around 168 eV BE), where sulphur oxidation products such as SO$_4^{2-}$ and SO$_3^{2-}$ would be present [39], indicating that the shell did not oxidize.
The Cd 3d:In 3d XPS ratio was used to calculate the shell thickness of the CdS shell with an analytical model developed by Shard [40]. This method also requires the core size, determined as 3.9 nm from the absorption spectrum, and the inelastic mean free paths of electrons in the core and shell material, calculated with the TPP-2M formula [41-43]. This calculation revealed a thickness of 0.7 ± 0.1 nm, approximately equal to three monolayers of CdS [35], and thus gave total diameter of 5.2 ± 0.2 nm, consistent with the size extracted from TEM imaging of the core/shell CQD.

6.3. Photoluminescence decay

Measurement of photoluminescence decay curves was undertaken for the InP/CdS CQDs using the time correlated single photon counting (TCSPC) system described in detail in Section 3.4. In brief, the sample is excited with a 100 femtosecond pulsed laser, and the time varying photoluminescence is then measured at the central wavelength of the emission peak using a highly sensitive multi-channel plate. The aim of these measurements was to determine the single exciton recombination lifetime, which can be a useful parameter for the extraction of the MEG QY from the transient absorption data.

Figure 6-5a shows a PL decay curve for the InP/CdS CQDs following excitation at 420 nm (2.96 eV, or 1.7 $E_g$). A bi-exponential fit to the decay curves is shown, with fitted decay constants of 14 ± 0.5 ns and 160 ± 1 ns, with a half lifetime of 59 ns. This half lifetime is comparable to the work of Wu et al. [14] who reported a half lifetime of 60 ns for InP/CdS CQDs; they also reported a half lifetime for InP CQDs of 4 ns and a decay which appeared to contain fast and slow components comparable to those fitted in Figure 6-5a. The fast decay was attributed to non-radiative decay of single excitons, and the slow component is comparable to PL decay lifetimes of ~100 ns reported elsewhere [12, 17, 31] for highly emissive InP CQDs which had undergone surface treatments.

The single exciton recombination lifetime is useful for the analysis of TA data in order to attempt separation of single exciton decay and multi-exciton decay during analysis [6], where multi-excitons are created either by MEG or by the absorption of multiple photons from the pump beam. This separation is usually achieved by the
inclusion of a term in the fitting function which reflects the fraction of excitons which will decay by single-exciton recombination over the temporal range of the TA experiment – typically 0.1 – 2 ns, such a term was described beside Equation (3-30).

Figure 6-5. Photoluminescence (PL) decay transients for InP/CdS CQDs (black line). a) Transient measured over 400 ns with a bi-exponential fit to the decay (red line), which yielded time constants of 14 ± 0.5 and 160 ± 1 ns. b) Transients measured over 10 ns with a mono-exponential fit to the decay (red line), which yielded a time constants of 3.6 ± 0.5 ns (note the line appears curved on this logarithmic scale due to an offset corresponding to slower components), the same decay is observed for a transient at 3 times the excitation fluence (blue line).

Fits to PL decay curves for a given CQD sample can vary significantly depending on the time window used for measurement and fitting [44], in both the number of components required for satisfactory fitting and the values of the fitted parameters. The decay can have many components with lifetimes spanning several orders of magnitude due to the competition between non-radiative and radiative decay. As described in Section 3.4, each component of a multi-exponential decay corresponds to a subset of quantum dots with different trapping mechanisms (or the same mechanisms acting with different rates). A theoretical work by Califano [45] is cited repeatedly in this thesis, which showed that the position of an un-passivated site on the surface of a QD can change the trapping rate to the surface. Furthermore, due to the distribution of different sized CQDs and the stochastic nature of the severity of non-radiative decay between nominally identical CQDs, there will exist a distribution of lifetimes for each decay process, resulting in deviation from an exponential decay.

In order to more accurately determine the rate of decay on a timescale comparable to the multi-exciton decay measured in a TA experiment, shorter time window PL decay data is shown in Figure 6-5b, where a mono-exponential fit yielded a decay
constant of \(3.6 \pm 0.5\) ns. Two decay curves are shown for excitation at two different pump powers in order to show that multi-photon absorption is not contributing to the fast decay component observed (see Section 2.5.3).

6.4. Measuring MEG with transient absorption spectroscopy

Transient absorption (TA) spectroscopy was used to measure the ultrafast charge dynamics in the InP/CdS CQDs, with the aim of measuring the MEG quantum yield, \(QY\). The temporal resolution of the TA system is limited by the laser pulse width, of \(\sim 100\) fs, which is sufficiently short to observe the decay of multi-excitons created by MEG, with lifetimes on the order of a few ps to 10s of ps [46]. The experimental setup and technique were described in detail in Section 3.5, but in brief, the pump beam, a high energy laser pulse with \(\sim 100\) fs pulse width, excites the sample creating hot excitons which then cool to the band edge. After an adjustable time delay, a white light probe beam, also 100 fs pulse width, is passed through the sample. The probe beam will experience a reduction in absorption (an increase in transmission) at wavelengths corresponding to transitions to states filled as a result of the pump beam excitation. By varying the time delay and probe wavelength, the time dependent occupation of specific energy levels can be measured. In this section the focus is on the electron population at the CBM.

The signature of MEG is a fast decay component of the order of a few ps for the band edge bleach, due to Auger recombination of multi-excitons [6, 8]. However, multi-excitons can also be created by the absorption of more than one pump photon by a single CQD. The probability of such an event is governed by Poisson statistics where the average number of photons absorbed per CQD, \(\langle N \rangle\), is directly proportional to the pump fluence. As a result, the probability of two-photon absorption becomes negligible for sufficiently low fluence, whereas the probability of MEG occurring remains constant. The MEG \(QY\) is thus given by the relative magnitude of the multi-exciton component to the single-exciton component in a decay transient in the limit of low fluence [8]. Further details can be found in Section 2.5. This is typically determined by measuring the ratio of the bleach magnitude before and after multi-exciton decay, \(R\), for a range of fluences, and extrapolating to the value corresponding to negligible fluence [8]. However, the expression typically
used for this extrapolation is only valid for samples with an absorbance length, \( l_A \), for the pump wavelength which is long compared to the beam path through the sample, \( l_s \) \([8, 47]\). In Section 3.5.6, a new expression was derived, Equation (3-58), which can be used to determine \( QY \) even in cases where \( l_A \ll l_s \), and was published beside the results in this chapter \([5]\).

The InP/CdS CQD samples studied here are just such a case for which \( l_A \ll l_s \); as shown in Figure 6-2, the pump absorbance, \( A_p \), at the shortest possible pump wavelength for the TA system of 232 nm is 7 OD, ~40 times greater than at the probe wavelength of 470 nm. This corresponds to an \( l_A \) of 1.4 mm, with an effective \( l_s \) of 10 mm (the cuvette path length).This means that 63 % of the pump beam is absorbed in the first 14 % of the beam path. This was the motivation for the derivation of Equation (3-58), which is repeated here for convenience;

The time dependent, pump-induced, fractional transmittance change, \( \Delta T(t)/T \), is described by

\[
\frac{\Delta T(t)}{T} = \frac{A}{A_p} \left[ D(t) \sum_{n=1}^{\infty} \frac{(-\langle N \rangle_0)^n}{n \cdot n!} (e^{-n A_p} - 1) - E(t) \left( e^{-(\langle N \rangle_0 e^{-A_p} - e^{-\langle N \rangle_0}} \right) \right] \tag{6-1}
\]

where \( \langle N \rangle_0 \) is the average number of photons absorbed per CQD as the pump beam enters the sample, \( A \) and \( A_p \) are the absorbance at the probe and pump wavelengths respectively, and

\[
D(t) = \frac{k_{XX} + k_X}{2k_{XX}} e^{-k_{X}t} - \frac{k_X - k_{XX}}{2k_{XX}} e^{-(k_{XX}+k_X)t} \tag{6-2}
\]

\[
E(t) = (2 - QY) \left( \frac{k_X}{2k_{XX}} e^{-k_{X}t} - \frac{k_X - k_{XX}}{2k_{XX}} e^{-(k_{XX}+k_X)t} \right) \tag{6-3}
\]

where \( k_{XX} \) and \( k_X \) are the rate constants for decay of biexcitons and single excitons respectively. The expression takes into account the MEG \( QY \), both single and multi-exciton decay, multi-photon absorption by single QDs, and reduction in pump fluence through the sample due to small \( l_A \) \([5]\).
6.4.1. Results and discussion

Initially the ultrafast response of the InP/CdS CQDs was assessed for excitation below the MEG threshold, using a pump wavelength of 420 nm (2.96 eV, or 1.7 $E_g$). The pump beam had 1mW average power and a diameter of 2.2 mm, which is equivalent to a fluence of $1.3 \times 10^{14}$ photons cm$^{-2}$ per pulse (see Section 3.5.8). Figure 6-6a shows the fractional transmittance change spectrum acquired at a pump-probe time delay of 3 ps, corresponding to the time of maximum bleach signal. Two distinct bleach peaks are observed, corresponding to the B1 and B2 transitions observed in the linear absorption spectrum (Figure 6-2), and are both attributed to state-filling of the conduction band edge due to electrons. Figure 6-6b compares the normalised decay dynamics of each feature, which were found to occur with identical rates, as has been observed previously for InP/CdS CQDs [14] and in other quasi-Type II CQDs [2], supporting the attribution that both features correspond to the same electron energy level. Each transition involves a different hole state, confined to different regions of the CQD (see Figure 6-1), but the same band edge electron level. As in many CQD systems, contributions from holes to the bleach signal are negligible due to the high degeneracy and density of states of the valence band levels involved [48]. Both of these bleach features thus allow the transient population of photogenerated band-edge electrons to be monitored; for the remainder of this study the B1 bleach was used, due to its larger response and thus better signal-to-noise ratio.

![Figure 6-6](image-url)

Figure 6-6. Fractional transmittance change, $\Delta T/T$, spectrum for the InP/CdS CQD sample collected at a pump-probe delay of ~3 ps. The sample was pumped at a wavelength of 420 nm with an effective fluence of $1.3 \times 10^{14}$ photons cm$^{-2}$ per pulse. The large feature for wavelengths less than ~430 nm is due to scattered pump light.
Figure 6-7 compares the decay dynamics of the B1 bleach for the same sample under stirred and static conditions. As described in Section 3.5.2.4, charges can become trapped on the surface of some CQD types for a time longer than the duration between pump pulses. This can result in the formation of a trion when an exciton created by the absorption of a subsequent pump photon combines with the geminate partner of the trapped charge. These trions decay on a similar time-scale to biexcitons, and their presence can lead to an over-estimation of the MEG $Q_Y$ if not identified [49]. However, it has also been shown [50-51] that sufficient stirring or flowing of the sample can prevent trion formation by refreshing the pumped sample volume. The similarity of the amplitude and decay of the bleach signal confirms that photo-charging is not of concern for these CQDs under the experimental conditions used here. All other TA data in this chapter was collected with stirred samples.

We proceed to measure the decay dynamics for a range of pump fluences above and below the expected MEG threshold. The MEG threshold in core/shell CQDs can be difficult to estimate due to the different electronic properties of the two materials, specifically their band gaps and carrier effective masses [52-53]. The threshold for a quasi-Type II system can however be expected to lie between the predicted thresholds for the composite materials, which are 2.1 $E_g$ and 2.2 $E_g$ for InP and CdS respectively based on the carrier effective masses [6, 54]. In this work we pump the InP/CdS CQDs at wavelengths of 420 nm and 232 nm, corresponding to excitation photon energies of 2.96 eV and 5.35 eV, respectively. Taking the peak of the PL as a measure of $E_g$, these photon energies are equivalent to 1.7$E_g$ and 3.0$E_g$ and thus

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correspond to pumping below and above the threshold for MEG, respectively. If we take the first absorption peak (B2) as the band gap as is more typically done in CQD studies, these photon energies correspond to $1.4E_g$ and $2.6E_g$.

Figure 6-8. Fractional transmittance change, $\Delta T/T$, transients for the peak of the B1 bleach for the InP/CdS CQD sample below and above the MEG threshold. a) The sample was pumped at a wavelength of 420 nm with incident fluences of $(0.5 – 3) \times 10^{14}$ photons cm$^{-2}$ per pulse. b) Sample pumped at 232 nm with incident fluences of $(0.4 – 4.8) \times 10^{14}$ photons cm$^{-2}$. Red lines are fits using Equation (6-1).

The evolution of the B1 bleach for a range of pump fluences, $J$, is shown in Figure 6-8 for pump wavelengths of 420 nm (2.96 eV, or $1.7E_g$) and 232 nm (5.35 eV, or $3E_g$). The pump fluences were adjusted by varying the average pump power using an ND filter. At 420 nm the range was 0.5 – 3.0 mW corresponding to a fluence range of $0.7 – 3.9 \times 10^{14}$ photons cm$^{-2}$ per pulse, and at 232 nm was 0.05 – 0.8 mW,
estimated as an effective fluence of $0.4 - 4.8 \times 10^{14}$ photons cm$^{-2}$ per pulse (see Section 3.5.8). When operating the TA system at 232 nm, the average power attainable is lower than at 420 nm, and in addition the beam diameter is smaller. Due to the high absorbance at 232 nm, the pump and probe beams were overlapped closer to the front face of the sample cuvette in order to maximise the detected transmission change.

High fluence UV light has the potential to damage CQD samples; the mechanism for this sample damage is unclear but has been attributed to photo-oxidation of surface ligands, or photo-activated reaction of CQD surface atoms with the environment [55]. Signs of sample damage were observed for some InP/CdS CQD samples early on in this investigation, where for high fluence excitation at 232 nm an opaque suspension would form in as little as half an hour. This suspension would reduce the transmission of the sample, and due to sample stirring result in a significant increase in signal noise. In order to prevent sample damage, the 232 nm pump beam was widened with a lens to match the 420 nm beam. The transients were measured in order of increasing power, and a sample was then discarded and replaced if any suspension was formed. Additionally, the data was carefully scrutinized; each transient is an average of 10 or more scans, and if the amplitude of these scans were found to vary systematically (due to gradual sample damage), or if the probe transmission was significantly different before and after the scans (given by $f_{1000}^{\text{probe}}(V_a)$, see Section 3.5.2.3), the data was not used.

The combination of lower peak power and higher pump absorbance, resulted in the significantly reduced signal to noise ratio for 232 nm pumping compared to 420 nm pumping as shown in Figure 6-8. One of the major advantages of the new fitting expression, is that $R$ is fixed to monotonically increase with plateau amplitude and pump fluence (when the fitting parameters, $QY$, $k_x$, $k_{XX}$, and the input parameters $A$ and $A_p$, are shared between the individual transients). This means that a positive (or negative) spike in noise in the first few ps after the signal rise cannot result in fitting of a multi-exciton component which is out of trend with the other transients – an occurrence which prevented satisfactory fitting by the conventional analysis technique.
Each of the transients in Figure 6-8 exhibit a very rapid initial rise of a few ps duration followed by a decay to a plateau. This behaviour is typical for CQDs [48], where the rise corresponds to increasing state-filling as photo-excited electrons cool to the band edge after excitation by the pump beam. The decay corresponds to the recombination of multi-excitons, formed either by MEG or by the absorption of more than one photon per CQD per excitation pulse. The reduction in magnitude of this fast decay component as the pump fluence is decreased is due to the fall in probability of a single CQD absorbing more than one photon. The plateau is associated with state-filling by single excitons which recombine with a lifetime that is long compared to the duration of the experiment. From the PL decay transients shown in Section 6.3, we know this to be \(3.6 \pm 0.5\) ns, so we can expect 8% loss in amplitude over the time window of this TA data.

A global fit of Equation (6-1) to the transients shown in Figure 6-8 was undertaken for both pump wavelengths simultaneously. The values of \(A_p\) and \(A\) were determined from the steady-state absorbance spectrum. \(k_X\) and \(k_{XX}\) were shared fitting parameters between all of the transients, both above and below the MEG threshold. The value of \(QY\) was fixed to unity for transients corresponding to excitation below the MEG threshold, whilst a \(QY\) value for pumping at a photon energy of \(3E_g\), common to the corresponding transients, was determined from the fit. A different value for \(\langle N \rangle_0\) was fit to each individual transient, which should be proportional to the pump fluence, \(J\). This is the parameter which determines the amplitude of the peak and plateau of each scan, and ensures that the amplitudes correlate with the observed ratio of multi-exciton to single-exciton recombination. The sum over \(n\) in Equation (6-1) was calculated to \(n = 6\), which was determined to be high enough that the change in peak \(\Delta T(t)/T\) fitted was <1% if more terms were included.

This process yielded an MEG \(QY\) of \(1.22 \pm 0.01\), for pumping at a photon energy equivalent to \(3E_g\). For InP/ZnS/ZnO Type I CQDs with a similar \(E_g\), an MEG \(QY\) of \(1.18 \pm 0.03\) for a photon energy equivalent to \(2.6E_g\) has been previously reported [1]. However, that work used the position of the absorption edge as a measure of \(E_g\), rather than the PL peak as in this study; using instead the PL peak, yields a photon energy equivalent to \(2.7E_g\). For its reported efficiency of 0.3 (the rate of increase of
Chapter 6

MEG in InP/CdS CQDs

With excitation energy, the Type I InP/ZnS/ZnO CQDs would thus be expected to have a MEG $QY$ of $1.27 \pm 0.04$ for a pump photon energy equal to $3E_g$. The efficiency of the MEG process in CQDs with an InP core thus seems to be not greatly affected by the change from a Type I to a quasi-Type II core/shell heterostructure, with the difference in MEG $QY$ at $3.0E_g$ reported for the two types being similar to the experimental accuracy.

This process yielded bi-exciton and single-exciton lifetimes of $\tau_{XX} = k_{XX}^{-1} = 50 \pm 2$ ps and $\tau_X = k_X^{-1} = 3.05 \pm 0.06$ ns respectively. This biexciton lifetime is consistent with the value of $58 \pm 12$ ps reported for similar InP/CdS CQDs excited below the MEG threshold [15]. It is also somewhat larger than the $41 \pm 3$ ps biexciton lifetime reported for the InP/ZnS/ZnO (core/shell/shell) Type I CQDs with a similar $E_g$, consistent with the reduced wave function overlap in a quasi-Type II CQD. Moreover, at 50 ps this lifetime is significantly longer than the characteristic time for electron transfer to an acceptor molecule reported by Wu et al. [14], suggesting that extraction of the additional charge carriers generated by MEG should be possible with good efficiency in this system. The importance of charge extraction in the theoretical efficiency of photovoltaics utilising Type II core/shell CQDs is modelled in Section 7.2. The single exciton lifetime measured is also consistent with the lifetime, determined by PL decay transients in Section 6.3, of $3.6 \pm 0.5$ ns.

### 6.5. Summary

The multi-exciton dynamics in InP/CdS quasi-Type II CQDs have been investigated on a sub-nanosecond time-scale using ultrafast transient absorption spectroscopy, and the MEG quantum yield measured for the first time in this system. A new analysis technique for determining the MEG $QY$ from TA data in cases of high pump absorbance has been demonstrated with its merits over the established methods. The MEG $QY$ was determined to be $1.22 \pm 0.01$ for excitation at 3 times the band gap, a value not adversely different to previous measurements of Type I InP CQDs [1]. However, with the quasi-Type II structure come the advantages of extended carrier lifetimes, with consequent potential for improved charge extraction, and additional band gap tuning, which will enhance the effective exploitation of multiple exciton generation in photovoltaic devices.
6.6. References


[20]. Lim, K., Jang, H. S., Woo, K., Synthesis of blue emitting InP/ZnS quantum dots through control of competition between etching and growth. *Nanotechnology* 2012, 23.


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Chapter 7. Modelling

7.1. Introduction

This chapter describes work which was undertaken on theoretical models during this project. This modelling enabled a better understanding of the interaction between the various dynamical processes studied experimentally, their dependence on structure, and how they affect the performance of CQD-sensitised solar cells. Cd-based CQDs were chosen as the model system for this work because they are the most studied, and hence best characterised, type of CQD, and were also studied experimentally as the subject of this thesis. The results from the model which describes solar cell efficiency were published as part of two works in the journal Solar Energy Materials & Solar Cells [1-2].

7.2. Type II CQD sensitised solar cell efficiency in the Detailed Balance model

7.2.1. The Detailed Balance model with MEG

Theoretical efficiency limits for conventional solar cells can be explored using the ‘Detailed Balance’ model, first described by Shockley and Queisser [3]. The model considers the electrical current generated in a cell under solar illumination at thermal equilibrium, where four unavoidable losses [3-4] are considered: (1) photons with energy, \( h\nu \), below the band gap, \( E_g \), are not absorbed; (2) carrier energy in excess of the band gap is lost as heat; (3) thermodynamic loss: the available energy (Gibbs free energy, or chemical potential) of the thermalized excited states is always less than the internal energy, with the consequence that the photovoltage (or, output chemical potential) must be less than \( E_g \); and (4) radiative recombination: a small fraction of the excited states radiatively recombine with the ground states at maximum power output.

The Detailed Balance model was later modified to include the process of multiple exciton generation (MEG) [5-7], where some of the photon energy in excess of \( E_g \) can be used to generate additional electron-hole pairs in the cell, as illustrated in Figure 7-1a and b. This process was described in detail in Section 2.6. In the ideal
case, it is assumed that all photons with an energy greater than \( E_g \) are absorbed and produce a number of excitons dependent on \( h\nu \) and \( E_g \), described by the quantum yield of MEG, \( QY(h\nu, E_g) \). The photogenerated current density, \( j_{pg} \), is thus given by:

\[
j_{pg} = e \int_{E_g}^{\infty} QY(h\nu, E_g)\phi(h\nu)\,d(h\nu)
\]  

(7-1)

where \( e \) is the electronic charge and \( \phi(h\nu) \) is the spectral photon flux density. This is offset by a loss of photogenerated current due to recombination. The recombination current density, \( j_r \), is given by [5]:

\[
j_r = \frac{2\pi e}{h^3 c^2} \int_{E_g}^{\infty} QY(h\nu, E_g)(h\nu)^2 \left( \exp\left(\frac{h\nu - eVQY}{kT}\right) - 1 \right)^{-1} \,d(h\nu)
\]  

(7-2)

where \( h \) is Planck’s constant, \( c \) is the speed of light, \( V \) is the operating voltage of the cell, \( k \) is Boltzmann’s constant and \( T \) is the temperature (set to 300 K for this work). \( V \) is assumed equal to a constant quasi-Fermi level separation and is determined by finding the value which maximizes the photo-voltaic efficiency, \( \eta_{pv} \), of the cell:

\[
\eta_{pv} = \frac{jV}{I}
\]  

(7-3)

where \( j = j_{pg} - j_r \) is the total current density, and \( I \) is the total solar irradiance, in this work taken as the AM1.5 solar spectrum [8] with a total irradiance of 1 kW m\(^{-2}\). An assumption must be made on the exact form of \( QY(h\nu, E_g) \): for idealised MEG a photon produces an additional exciton for each increase in energy of \( E_g \), thus:

\[
QY(h\nu, E_g) = \sum_{m=1}^{\infty} \theta(h\nu, mE_g)
\]  

(7-4)

where \( \theta(h\nu, mE_g) \) is the Heaviside step function (equal to 1 for \( h\nu > mE_g \), 0 otherwise). This is the ideal step-like increase shown in Figure 2-12. Note that limiting \( m \) to 1 limits \( QY \) to 1 for excitation energy above \( E_g \), i.e. no MEG.

Figure 7-1c illustrates how, for the case of ideal MEG and for a range of \( E_g \) values, the incident solar energy is divided between extraction from the cell (absorption
followed by MEG if above threshold, and then not recombination), radiative recombination, and waste heat generation, with the balance being accounted for by photons with energy too low to be absorbed \((h\nu < E_g)\). As the bandgap increases a larger fraction of solar photons do not have enough energy to be absorbed, indicated by the blue section, and for lower bandgap the threshold for MEG is lower. At the optimum \(E_g\) value of 0.7 eV, the cell efficiency is 44%; in comparison, without MEG the optimum efficiency is 33%, and occurs at \(E_g = 1.35\) eV. Figure 7-1d compares the current density-voltage characteristics of a cell benefiting from ideal MEG to one for which MEG is negligible: MEG increases the short-circuit current density by a factor of \(~3\) whilst decreasing the open-circuit voltage by a factor of \(~2\). The efficiencies shown in Figure 7-1c correspond to the optimised voltage according to Equation (7-3).

![Diagram](image)

Figure 7-1. a) Without the process of MEG a large amount of solar photon energy in excess of the band gap is wasted as heat, with MEG, b), this energy is used to excite additional electron-hole pairs. c) Energy division in a QD sample exhibiting ideal MEG modelled using Equation (7-4) if illuminated by the AM1.5 solar spectrum. d) Comparison of current density, \(j\), as a function of operating voltage for QD solar cells of optimum \(E_g\) with and without ideal MEG. e) Comparison of solar cell efficiency versus \(E_g\), simulated using Equation (7-5), for PbSe QDs with experimentally derived \(\eta\) and \(h\nu_{th}\) [9], to the ideal case from c) and the case with no MEG.
As described in Section 2.6, a significant biexciton binding energy can exist in some materials, which can result in a reduction of the MEG threshold in the case of large positive binding. It has been shown that including this effect increases the maximum attainable efficiency to 50\% [10], where a binding energy of -0.1 eV was used, the maximum value reported for a QD at that time [11].

The ideal step-like increase in MEG has not been observed experimentally, instead a linear increase in $QY$ above the MEG threshold, $h\nu_{th}$, is typically observed, as described in Section 2.6. Such a linear rise can be described by:

$$QY(h\nu, E_g) = \theta(h\nu, E_g) + \eta \theta(h\nu, h\nu_{th})(h\nu - h\nu_{th})/E_g$$ (7-5)

where $\eta$ is the efficiency of MEG (the gradient of the rise in $QY$ with energy in units of $E_g$). Using Equation (7-5), Figure 7-1e shows how the photovoltaic efficiency varies with $E_g$ for PbSe QDs with experimentally reported $\eta$ and $h\nu_{th}$ values of 0.4 and 2.6 $E_g$ respectively [9], as described in Section 2.7.1. Also included for comparison are the efficiencies for ideal MEG from Figure 7-1c, and no MEG. It is evident that only a marginal increase in cell efficiency is attainable for low $E_g$ using PbSe QDs. In order to realize significantly enhanced solar cell efficiency, QDs with $E_g = 0.7 – 1.3$ eV and a MEG threshold close to the minimum required by energy conservation, $2E_g$, are required.

### 7.2.2. Modifications based on Type II QD band structure calculations

In Chapter 2 the competing relaxation mechanisms available to excited charges were discussed at length, the efficiency of which vary depending on the energy level structure of the QDs, tuneable through their size and composition. The competition between the mechanisms directly affects the efficiency of any devices aiming to utilise QDs. For example QD-sensitised solar cells would benefit from enhancement of the efficiency of MEG and charge extraction whilst slowing intra-band charge cooling and radiative recombination. Band structures and radiative lifetimes of CdSe/CdTe Type II QDs were calculated by collaborators, J. Miloszewski, T. Walsh, and S. Tomić, at the University of Salford. The calculations were performed for a range of core sizes and shell thicknesses using a combination of single particle (2,6)-
band $k \cdot p$ and many-electron configuration interaction Hamiltonians. These calculations were used to model the impact of processes which compete with MEG in the Detailed Balance model, and were published beside the band structure calculations in *Solar Energy Materials & Solar Cells* [1-2].

Figure 7-2a shows the variation in wavelength of the first absorption peak, $1S_{1/2}1S_{3/2}$, for variation in shell thickness, $a_s$, for different core radii, $a_c$. Also shown are experimental data from References [12-13], for a core radius of 1.7 nm with different shell thicknesses determined by TEM. For thin shells the change in transition wavelength is approximately linear and attributable to enhanced confinement within the core, in this region they function as quasi-Type II CQDs, as expected for the thin shelled CdTe/CdS CQDs investigated in Chapter 5. For shells greater than 0.5 nm, a more significant increase in transition wavelength occurs (a reduction in $E_g$), due to the formation of a Type II QD structure (see Section 2.4) [2].

![Graph showing variation of transition wavelength and radiative lifetime](image)

Radiative lifetimes, $\tau_{rad}$ of the $1S_{1/2}1S_{3/2}$ state were calculated from the excitonic wavefunctions, see Reference [2] for details. The lifetimes are plotted in Figure 7-2b for a range of core and shell thicknesses. A significant increase in the radiative lifetime is observed when the structure transitions to a Type II confinement regime around $a_s = 0.5$ nm, due to separation of the electron and hole.

The effect of an elevated radiative lifetime is to extend the amount of time charges spend at the band edge, increasing the probability that the charge can be extracted and contribute to the electrical current from the cell. Thus, we consider a fifth loss
mechanism in the Detailed Balance model, which utilises the probability of escape, \( P_{\text{esc}} \), of a cooled charge in the QD. This can be expressed in terms of the characteristic lifetime of the escape process, \( \tau_{\text{esc}} \), and the radiative lifetime, \( \tau_{\text{rad}} \):

\[
P_{\text{esc}} = \frac{\tau_{\text{esc}}^{-1}}{\tau_{\text{esc}}^{-1} + \tau_{\text{rad}}^{-1}}
\]  

(7-6)

Figure 7-3 shows the variation in efficiency with shell thickness predicted by including this factor in the Detailed Balance model for solar cells utilizing CdSe/CdTe QDs as the absorbing species for \( a_c \) of 1.5 nm and 2 nm. \( E_g \) and \( \tau_{\text{rad}} \) were taken from the data in Figure 7-2, and MEG was excluded (\( QY(h\nu, E_g) = 1 \) for \( h\nu > E_g \)). \( \tau_{\text{esc}} \) is varied from 0.1 ns, indicating fast charge transfer as reported by some authors [14-16], to 100 ns. The predicted efficiency of the device increases significantly with the thickness of the CdTe shell for both core sizes, primarily attributable to the change in radiative lifetime. As expected, a long carrier escape lifetime can significantly reduce the efficiency. This will be a crucial element to the effectiveness of any devices hoping to utilise thick shells, and poses a particular challenge to the preparation and environment of the QDs. Effective passivation methods such as bulky ligands, surface treatment or additional shells, which can dramatically increase the quantum yield of CQDs [17-19], have been shown to sometimes hinder charge extraction [20]. This can reduce the yield of photovoltaic devices where carriers are Coulombically bound to CQD-surface molecule interface unless operated with an external field [21-22].

![Figure 7-3. Solar cell efficiency given by the modified Detailed Balance model for cells sensitised with CdSe/CdTe Type II QDs for core radii, \( a_c \), of 1.5 nm (left) and 2.5 nm (right) and varying shell thicknesses and lifetime of charge carrier escape, \( \tau_{\text{esc}} \).](image-url)
Figure 7-3 demonstrates that competition with charge extraction at the band edge has an important impact on cell efficiency in the absence of MEG. However, from band structure calculations we can also predict the impact of processes which compete with MEG during intra-band charge cooling. As described in Section 2.5, the two key competing processes are phonon cooling, and Auger cooling. Phonon cooling entails the emission of thermal vibrations in the QD, which have an energy of approximately 30 meV at room temperature [23]. The enhanced energy level separation in QDs compared to bulk semiconductors led to the prediction of phonon bottlenecks – energy level spacings too large for cooling via phonons [24-26]. However, the impact of any phonon bottlenecks is circumvented by the contributions of Auger cooling [25, 27], where charges cool by transferring their energy to another excited charge carrier. Auger cooling is expected to be significantly slowed in Type II QDs by separation of the electron and hole, and the presence of phonon bottlenecks might change significantly with the addition of shells due to reduced confinement of high energy levels delocalised over both core and shell.

The full excitonic band structure for a range of core and shell sizes of CdSe/CdTe QDs are shown in Figure 7-4. As in Figure 7-2a, the first transition energy falls with increasing shell thickness, as do all the subsequent transitions, and a reduction in the level spacing and increase in splitting due to spin-orbit coupling occurs. However,

![Figure 7-4](image-url)

Figure 7-4. Conduction band energy levels in CdSe/CdTe Type II QDs for four different core radii, $a_c$ and varying shell thicknesses. Also shown, as a grey line, is an electron energy above the band edge equal to $E_p$. Below this energy (shaded grey), the electron has insufficient energy for MEG to occur. Calculated by J. Miloszewski, T. Walsh, and S. Tomić, at the University of Salford [1].

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even for thick shells a number of gaps in excess of 30 meV persist (see Reference [1] for details of these gaps in both the conduction and valence band). These gaps persist above the energetic threshold for MEG, illustrated in Figure 7-4 by the grey shaded region below energies of $2E_g$. This means that the suppression of Auger cooling possible in a Type II system would not be significantly offset by the elimination of phonon bottlenecks in the conduction band in the case of thick shells.

These results were incorporated into the Detailed Balance model by considering the competition between phonon cooling, Auger cooling, and MEG. The energetic minimum for MEG is $2E_g$ assuming that all the excess energy is given to a single charge carrier. More accurately, the energy is shared between the electron and hole according to their respective effective masses, $m_h^*$ and $m_e^*$, such that the threshold is given by [14]:

$$E_{th} = 2 + \frac{m_e^*}{m_h^*} \quad (7-7)$$

The heavy hole and electron effective masses in CdTe are $0.8m_0$ and $0.09m_0$ respectively [28] and the electron effective mass in zinc blend CdSe is $0.11m_0$ [29] (where $m_0$ is the electron rest mass); taking the average electron effective mass for the two materials yields $E_{th} = 2.1E_g$. A modification to the ideal step-like behaviour for a threshold of $2E_g$, Equation (7-4), is required, such that each time the energy increases by a further $E_{th} - E_g$, $QY$ increases by 1:

$$QY(h\nu, E_g) = \sum_{m=1}^{\infty} \theta \left( h\nu, E_g + m(E_{th} - E_g) \right) \quad (7-8)$$

It has been shown that the rate of Auger cooling in CdSe/CdTe QDs has a strong dependence on the shell thickness due to the separation of electrons and holes in the Type II structure [30]. In particular, the Auger cooling lifetime grows abruptly by two orders of magnitude for $a_s > 1$ nm. Combined with the results indicating the persistence of phonon bottlenecks with the addition of thick shells shown in Figure 7-4, we assume that MEG is dominant for $a_s > 1$ nm, where it is well described by the step-like $QY$ of Equation (7-8), but for thinner shells MEG is considered negligible [1]. Figure 7-5a shows the resultant cell efficiency for a range
of core and shell diameters with and without the inclusion of MEG. It shows that an increase in efficiency can be expected for larger cores, primarily due to the reduction in band gap closer to the optimum value shown in Figure 7-1c. Efficiency also increases with increasing shell thickness due to MEG becoming dominant over Auger cooling. Figure 7-5b shows how the short-circuit current density, $J_{SC}$, and open-circuit voltage, $V_{oc}$, vary for the case where MEG is included. The increase in efficiency with either $a_c$ or $a_s$ is accompanied by a decrease in $V_{oc}$ and an increase in $J_{SC}$, as was observed in Figure 7-1b (given by the points where the curves cross the x and y axis).

Figure 7-5. a) Solar cell efficiency given by the Detailed Balance model for cells sensitised with CdSe/CdTe Type II QDs for different core radii, $a_c$, and for varying shell thicknesses with (dashed lines) and without (solid lines) the inclusion of MEG. b) Short-circuit current density, $J_{SC}$, and open-circuit voltage, $V_{oc}$, in the case of included MEG.

7.2.3. Conclusion

The results in this section show that MEG has the potential to significantly enhance the efficiency of solar cells by utilising energy typically wasted as heat to produce additional photocurrent, with a peak efficiency of 44% attainable for a band gap of 0.7 eV. Calculations of the band structure in Type II CdSe/CdTe QDs have been used to show how the competition between different carrier relaxation mechanisms affords several efficiency enhancements due to the separation of electrons and holes in Type II core/shell structures. These observations should apply to any QD system utilising a Type II or quasi-Type II structure.
7.3. Monte-Carlo modelling of carrier relaxation

7.3.1. Introduction and motivation

In Section 2.5, the many different relaxation routes available for an excited charge in a QD were described in detail along with their conditions, relevant energy states, typical transition rates, and their effects on the observed charge dynamics. Many of the processes involve energy states significantly above the band edge, with populations which are difficult to measure experimentally. This is due to a combination of spectral overlap, high degeneracy, broad linewidths within an ensemble of QDs, and, most significantly, short-lived occupancy compared to the temporal resolution of current experiments.

In the preceding chapters the carrier dynamics of the band edge in QDs are analysed in terms of the underlying relaxation mechanisms from a single pumped energy level. For example in Section 4.4.3 the relaxation of hot electrons to the band edge whilst competing with both hot and cold trapping is modelled. An analytical solution for the band edge population over time is derived by finding solutions to systems of linear ordinary differential equations (ODEs). However, the complexity of the rate equations formed and their solving escalates rapidly if additional energy levels or cooling processes are included. It becomes particularly difficult with the addition of intermediate relaxation levels, back-transfer of charges (de-trapping), or consideration of a distribution of rates, energy levels, or types of QD (e.g. trapping or non-trapping).

A computational model was created which can calculate the time dependent carrier dynamics for large systems of energy levels which uses the principle of Monte-Carlo modelling. This model serves as a useful tool for the investigation of charge relaxation processes in a complex energy structure. The model has significantly more flexibility than the analytical solutions derived in Sections 4.4.3 and 3.5.6, although with the downside of longer computation time and a larger number of input parameters.
7.3.2. Monte-Carlo sampling scheme

Monte-Carlo methods track the evolution of a system with a large range of possible interactions by using pseudo-random numbers to statistically sample from a distribution of all the possible interactions given their relative probability (or rate). In this case, a one-dimensional, many-particle Monte-Carlo model is constructed, where the transitions of an arbitrary number of electrons and holes in a QD gradually cool through the band structure, by many possible relaxation paths. Averaging the time dependent population of each level over a large number of simulations yields a numerical solution for the population dynamics of every energy level in the system.

The sampling is achieved by inverse distribution sampling [31]. As an example, consider two energy levels, with an electron in the upper level. The electron can relax to the lower level with a rate $k_r$, or can be trapped to an unknown location, with a rate $k_t$. The total decay rate from the upper level is $k = k_r + k_t$. The probability that a transition will occur after a time, $t$, is then given by Equation (7-9), and is known as the probability density function, $pdf$, and shown in Figure 7-6a.

The cumulative distribution function, $cdf$, is given by integrating the $pdf$, given by Equation (7-10) and shown in Figure 7-6b. This is then inverted to form the inverse $cdf$, denoted $cdf^{-1}$, given by Equation (7-11) and shown in Figure 7-6c. The inverse $cdf$ can convert a uniformly distributed variable to a distribution which matches the original $pdf$, i.e. a random number, $u_i$, on the interval 0 to 1, can be used to generate the time the electron stayed in the upper level, $s_i$, given by Equation (7-12), which is distributed to match the $pdf$.

Once a decay time, $s_i$, has been sampled, a decay mechanism is selected based on sampling of their relative rates. This is also performed with a uniformly distributed random number: in our example, if $u_i < k_r/k$, then recombination occurs, otherwise, trapping occurs. This principle can be extended to include an arbitrary number of decay processes between any number of levels in the system, and multiple carriers relaxing simultaneously.
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\[ P(t) = \text{pdf}(t) = \frac{e^{-tk}}{k} \] (7-9)

\[ cdf(u) = \int_0^u \text{pdf}(t) = 1 - e^{-uk} \] (7-10)

\[ cdf^{-1}(u) = -\frac{\ln(1-u)}{k} \] (7-11)

\[ s_i = -\frac{\ln(u_i)}{k} \] (7-12)

Figure 7-6. a) Illustration of the probability density function, pdf, given by Equation (7-9). b) Illustration of the cumulative distribution function, cdf, given by Equation (7-10). c) Illustration of the inverse cumulative distribution function, cdf⁻¹, given by Equation (7-11). cdf⁻¹ can be used to sample the pdf - using uniformly distributed random numbers, uᵢ, to produce decay times, sᵢ, an example is drawn for uᵢ = 0.9. In each of these example plots k is set to 1.

7.3.3. Charge carrier relaxation in quantum dots

Simulation of the relaxation of an electron-hole pair in a quantum dot was constructed based on the sampling method described above with a large number of energy levels with several possible relaxation mechanisms. Energy levels were calculated using the particle in a sphere model [32], described in Section 2.2.1, where a typically heavier hole effective mass compared to the electron leads to smaller energy level spacing in the valence band. Although this model does not accurately reproduce a quantum dot’s energy levels, as discussed in Section 2.2, it is used to demonstrate the capability of the simulation to model relaxation through a series of levels. Each iteration of the simulation begins with the electron and hole in an excited state, and continues until both have either been trapped or radiatively...
recombine. The model was constructed with a large range of possible decay processes in order to demonstrate its flexibility.

As discussed in Section 2.5, the primary relaxation pathways available for a hot exciton are phonon cooling, Auger cooling, surface trapping, radiative recombination, and MEG with rates denoted by $k_{ph}$, $k_{Aug}$, $k_{Surf}$, $k_{rad}$, and $k_{MEG}$ respectively. Each of these processes were included in the model to illustrate their effects on the dynamics. However, as discussed in Section 2.5, the rates of each of these processes in each part of the energy level structure are not well known, and so a number of simplifying assumptions are made:

- If MEG occurs, the charge relaxes directly to the band edge, and a new electron-hole pair is excited directly to the band edge.
- The rate of phonon cooling between two levels is reduced according to the energy difference between the levels, such that it is only efficient over gaps less than the typical phonon energy of 30 meV [23].
- The energy dissipated from Auger cooling is lost from the system, rather than being transferred to another charge.

Although not necessary, a differential equation analogous to the construction of the analytical models in Sections 4.4.3 and 3.5.6 can be written for each level to illustrate these processes. If each energy level in the conduction band is identified by the index $i$ (where $i = 1$ corresponds to the conduction band minimum (CBM) with orbital quantum numbers $n = 1$ and $l = s$), the electron population at that level, $n_i$, can be represented by the differential equation:

\[
\dot{n}_i = -k_{MEG}^i n_i - k_{Surf}^i n_i - k_{rad}^i n_i - \sum_{j=1}^{i-1} k_{ph}^{ij} n_i + \sum_{j=i+1}^{N} k_{ph}^{ji} n_j - \sum_{j=1}^{i-1} k_{Aug}^{ij} n_i + \sum_{j=i+1}^{N} k_{Aug}^{ji} n_j
\]

(7-13)

where $k^i$ are rates which depopulate level $i$, $k^{ij}$ is a rate from level $i$ to level $j$, and $i = N$ corresponds to the highest energy level which is initially populated. Positive
(negative) terms represent charges arriving at (leaving) level $n_i$. The equation for the CBM, $n_1$, has the modification that all negative terms except for radiative recombination are removed, and an additional term for MEG is included:

$$+2 \sum_{j=2}^{N} k_{MEG}^j n_j$$  (7-14)

Figure 7-7 shows an example of relaxation through the conduction band of a CdTe QD based on this model. The QD properties and all constants in Equations (7-13) and (7-14) were estimated based on typical values for QDs as discussed in Chapter 2. The resulting population growth and decay behave as expected, with a sigmoidal rise at the CBM level before a long lived decay, and a cascade of electrons cooling between the intermediate levels. The inset shows the calculated energy levels and their labels according to the particle in a sphere model.

![Figure 7-7](image-url)

Figure 7-7. The population dynamics of the conduction band levels in an ensemble of QDs excited in the highest energy level. Bold lines show the highest (red) and lowest (blue) level populations, the populations are normalised by the initial population of the highest level. Inset: the energy levels of the conduction band (in units of $E_g$), where the orbital labels (n,l) are given on the right, calculated by the particle in a sphere model based on CdTe QDs.

The model was extended to consider a number of additional physical features of QDs, and experimental features which arise in optical spectroscopy. Some of which
can be difficult to include in analytical treatments such as those used in Sections 4.4.3 and 3.5.6:

- Multiple excitations of a single QD and the introduction of Auger recombination.
- The degeneracy of each energy level can be included, such that filling of the band edge transitions could occur. This is important if simulating MEG for high energy excitation. Additionally all transition rates are reduced according to the number of vacancies in the carrier-accepting level.
- Positioning of a trap state within the energy bands such that trapping can only occur from specific levels.
- Auger cooling of one charge results in excitation of another charge into higher energy levels.
- De-trapping from a shallow trap state.
- Convolution with an instrument response function to compare to experimental data.

Since each iteration of the relaxation of an electron-hole pair is constructed and simulated separately, it is easy to simulate a distribution of starting conditions, most of which are considerably more difficult to include in an analytical solution. Examples include:

- A size distribution of quantum dots, changing the energy levels or any of the other properties.
- A distribution of excitation energies due to the spectral width of an excitation pulse, and a distribution of excitation times, due to the temporal width of the pulse.
- A distribution of the starting levels of the electron and hole (due to the overlap of peaks in the absorption spectrum).
- A distribution of relaxation rates or the presence of the mechanism, such as dots with and without surface traps.
- A distribution in the number of photons absorbed by each quantum dot.

Some examples of the band edge populations simulated using the model whilst including all of the above modifications are included below, where the plots are
intended to be similar to the experimental data presented throughout this thesis, but are not direct attempts at reproducing the dynamics.

Figure 7-8 compares the rise of the band edge population with and without a single intermediate level between the excited level and the conduction band. The time of excitation is distributed over a 100 fs Gaussian pulse, and the population is convoluted with a 100 fs Gaussian pulse, this is analogous to the measurements performed in Section 4.4 on CdTe QDs using the transient absorption system with pump and probe beams of approximately 100 fs pulse width. This figure shows the effect of the intermediate level on the 10%-90% rise times, a metric used to compare data in Chapter 4.

![Figure 7-8](image-url)

**Figure 7-8.** Comparison of the simulated population dynamics in the conduction band minimum (CBM) with, a), and without, b), an intermediate level between the CBM and the pumped energy level. Both plots are normalised to the number of QDs excited.

Figure 7-9a compares the band edge population for a range of efficiencies of the MEG process, showing both the enhanced yield of electrons and the rapid decay down to a plateau which is the experimentally observed signature of MEG in quantum dots. Figure 7-9b shows a comparable scenario, however the peak is caused by the absorption of more than one photon by a single QD, where for each transient the fraction of QDs which undergo two photon absorption, $F_{TPA}$, is changed, which is proportional to the excitation fluence in an experimental system. In these two plots, the peak to plateau ratios (which are determined for experimental data repeatedly in this thesis) look similar in both cases. However, only in the case of MEG is the rise time of the signal decreased, and could be a useful way of telling the two processes apart. To our knowledge, this has not yet been exploited experimentally, primarily due to the rise time of the band edge bleach in CQDs.
approaching the temporal resolution of most transient absorption laser systems. This is just one example of the insights possible from this model which could be utilised in experimental studies in the future.

![Figure 7-9. Simulated population dynamics of the conduction band minimum for a) increasing rate constants for the multiple exciton generation, \( k_{MEG} \), and b) increasing fraction of quantum dots which start with two excitons at the pump level due to two photon absorption, \( F_{TPA} \). Both plots are normalised to the number of QDs excited.](image)

### 7.3.4. Conclusion

A simulation of carrier relaxation in CQDs using the principles of Monte-Carlo modelling has been constructed and demonstrated for the variance of several relaxation mechanisms. The model has significant potential for the simulation of complex systems of energy levels with many relaxation mechanisms which cannot be easily simulated by analytical solutions to ODEs which are typically used. A large number of free parameters were introduced in the model whilst demonstrating the ability to model many competing mechanisms and a number of experimental features, including distributions of different quantum dots and experimental excitation profiles.

### 7.4. References


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Chapter 8. Summary, conclusion, and outlook

Quantum dots (QDs) are nano-scale semiconductor crystals where quantum confinement of charge carriers results in size-dependant energy level structures, and significant modifications to the possible carrier relaxation mechanisms and their rates. These unique properties can be exploited to enhance the efficiency of many optoelectronic devices, and have scope for many new novel scientific applications. However, a full understanding and control of the possible charge carrier interactions is yet to be achieved by the scientific community, such that quantum dots present an exciting and rapidly developing area of research which is the focus of many groups across the globe.

The key to unlocking the full potential of quantum dots is to enhance the efficiency of charge relaxation mechanisms which are critical to device performance, whilst eliminating or inhibiting processes which reduce device performance, which have largely prevented QDs from effectively competing with established technologies outside of scientific research. For example, a QD-sensitised solar cell would benefit from the enhancement of multiple exciton generation (MEG) and charge extraction, whilst carrier thermalisation, recombination, and trapping need to be slowed or eliminated. Many of these interactions occur within the first few picoseconds following the absorption of a photon, and are challenging to isolate and characterise in any QD system. The focus of this study was to enhance the understanding of the competition between carrier relaxation processes in different QD systems.

QDs have spectrally distinct optical absorption and emission features, and low degeneracies for excited states at the band edge. This makes optical spectroscopy an effective tool for measuring their electronic properties, particularly the carrier dynamics. To measure the carrier dynamics on picosecond to nanosecond timescales, two ultrafast time-resolved spectroscopic techniques were used in this work: time correlated single photon counting (TCSPC) and transient absorption (TA), each of which utilise femtosecond pulsed lasers to resolve charge relaxation in QDs. In TCSPC, the decay of photoluminescence (PL) intensity from a sample after excitation with a laser pulse is measured using a highly sensitive multi-channel plate. This enables determination of the radiative lifetime, and assessment of non-radiative...
decay paths from the band edge which act on nanosecond timescales. TA is a technique with greater time resolution achieving sub-picosecond time-scales, and was the main technique used throughout this work. This resolution is sufficient to observe multi-exciton interactions, charge trapping and even intra-band cooling. It is a pump-probe experiment which measures the change in absorption of a broadband probe pulse following excitation by a pump pulse. Bleaching of absorption features in a QD sample then correspond to state-filling of energy levels in the QD structure. By varying the time delay between pump and probe, the time-dependant occupation of energy levels can be determined. The technique requires careful consideration of the excitation conditions and is prone to several experimental artefacts which have been carefully evaluated in this work.

These time-resolved techniques were supported by steady-state spectroscopic experiments. Absorption and emission spectroscopy were used to characterise the band structure of the QDs, revealing the optical transitions and photoluminescence peak. The photoluminescence quantum yield (PLQY) was also determined, a measurement which directly quantifies the degree of non-radiative carrier recombination occurring in a QD sample. QDs are notorious for their potential to show variation in their properties between separate syntheses, particularly if done by different synthetic methods. As a result, each of these steady-state spectroscopic techniques are valuable contributions to any charge dynamics study, along with structural characterisation such as transmission electron microscopy, X-ray photoelectron spectroscopy and X-ray diffraction, which have all been shown and analysed in this work where available.

Perhaps the most significant obstacle to utilising QDs in many devices are the effects of surface mediated charge trapping. This process has been shown to occur to both hot and cooled charge carriers, and directly competes with MEG, radiative recombination and charge extraction. Trapping is among the least understood process which can occur in QDs, primarily because its presence and effects can vary significantly between different QD systems, and even between ostensibly similar samples. In this work, a unique investigation into charge trapping was achieved; surface treatment of CdTe QDs using chloride ions was shown to be capable of completely eliminating trapping without significantly altering its other optoelectronic
properties [1]. This enabled the isolation and characterisation of the effects of trapping.

By comparison of the CdTe QDs before and after chloride treatment, we showed that un-passivated surface sites mediate both hot and cold electron trapping, and formalised a model which concludes that only a fraction of CdTe QDs within a sample contain the cold trapping process. Cold trapping caused a rapid depopulation of the band edge population, consistent with the observations of many other QD studies [2-5]. This was accompanied by a significant reduction in the peak amplitude of the band edge bleach due to hot trapping, which is recovered upon surface passivation. The absence of signatures of surface traps in transient absorption spectra was noted, however it was found that the portion of QDs free of cold trapping have systematically redder band gaps attributed to the filling of hole traps near the valence band maximum. These observations will be valuable to the interpretation of charge dynamics in QDs where surface effects may have significant contributions, particularly for studies which rely on the amplitude of the band edge bleach for determination of the excitation density of the QDs. The initial results of this study were published in the journal Advanced Science [6].

The excitation photon energy dependence of the trapping processes were observed in both TA and steady-state PL spectroscopy. The efficiency of the hot trapping process was shown to increase with excess energy above the bandgap by simultaneously fitting the hot and cold trapping model to data from several transients. This has implications for studies of MEG where direct comparison of the carrier dynamics for excitation at different energies is required. The increased efficiency of a hot trapping process might result in an underestimation of the excitation density, which could enable multi-exciton recombination to be falsely attributed to MEG rather than two-photon absorption. Since hot trapping competes with MEG, its suppression by surface treatment promises to increase the MEG yield, although the effectiveness of passivation with chloride ions will be material dependent, and may be incompatible with some devices. To date, synthesised devices are still significantly below the maximum attainable thermodynamic efficiency [7]. Confirmation in this work that cooling and recombination of hot charges can be excitation energy dependent, shown by the fall in the number of electrons reaching the band edge and reduced
photoluminescence, provides further insight into why both MEG quantum yield ($QY$) measurements and device efficiencies fall significantly short of the idealised case.

The construction of core/shell quantum dots, where a QD is coated in a second semiconducting material, present opportunities for additional modification to QD’s properties beyond those afforded by tuning of their diameter. Core/shell QDs have been investigated in many studies and are categorised according to the relative offsets of the band edges of the composite materials, which allow confinement of electrons and holes into different regions of the QD. In this work, two quasi-Type II core/shell QD systems are investigated but with different motivations. In these systems an excited electron is delocalised over both the core and shell of the QD, whilst the hole is confined to the core in its first excited state.

The charge dynamics in quinone conjugated CdTe/CdS QDs were investigated, where electron transfer to the quinone molecules was demonstrated for a range of average quinone to quantum dot ratios. These QDs have the potential to act as redox-sensitive bio-sensors; it was shown that the electron transfer process quenches the PL intensity when the quinones are oxidised, and that the PL recovers as the redox environment of the system is changed. Measurements of the ultrafast dynamics were presented, where the competition between charge transfer and cooling was observed using TA and TCSPC. A complex behaviour was discovered which is inconsistent with a model for the PL quenching which is effective at describing the steady state quenching behaviour. In particular, a significant drop in TA amplitude with increased quinone concentration was noted. This amplitude is typically neglected in many charge transfer studies, and suggests a hot electron transfer process is occurring, analogous to the hot trapping observed in the chloride treated CdTe QDs. The change in relative amplitude of decay components in both TA and PL decay studies suggests that a relationship may exist between charge trapping and electron transfer which is more complex than other QD-acceptor systems studied in the literature. This system requires additional investigation to fully understand the origin of the signals observed; measuring of the carrier dynamics of a quinone conjugated QD sample before and after reduction may allow isolation of the charge transfer dynamics, and investigation of additional samples with different core diameters will
be required to fully examine the mechanism and resulting efficiency of the charge transfer process.

The second core/shell QD system investigated in this work was InP/CdS QDs, where the aim of the study was to measure MEG in this system for the first time. MEG has the potential to significantly enhance the efficiency of solar cells by using energy typically wasted as heat to excite additional electron-hole pairs, and thereby increase the photocurrent. This can be observed as an increased amplitude of TA signals with a fast multi-exciton recombination component, but must be carefully separated from multi-photon absorption. The search for a QD material which exhibits both efficient MEG, a bandgap suitable for exploitation of the solar spectrum, and the potential for efficient charge extraction, is an achievement which is highly sought after by the scientific community.

Using TA spectroscopy, the MEG QY was measured for the first time in InP/CdS QDs. A new analysis technique for determining the QY from TA data in cases of high pump absorbance was demonstrated with merits over the established methods. The MEG QY was determined to be $1.22 \pm 0.01$ for excitation at 3 times the band gap, a value similar to previous measurements in Type I InP core/shell QDs [8]. However, with the quasi-Type II structure come advantages which could enhance device performance: additional tuning of the optical band gap is achievable by control of the shell thickness, which provides additional scope for optimising the absorption of the solar spectrum; and extended carrier lifetimes, with consequent potential for improved charge extraction. These results were published in *The Journal of Physical Chemistry C* [9].

The three primary results chapters in this thesis investigated different materials of QDs, each of which demonstrate properties which are invaluable to the exploitation of quantum dots as the absorbing species in photovoltaics, and indeed in many other applications: i) a well passivated surface which does not exhibit significant surface trapping, such as the chloride treated CdTe QDs; ii) an efficient route for charge extraction, explored in the quinone conjugated CdTe/CdS QDs, and iii) a structure which can exhibit efficient MEG and charge extraction, potentially enhanced by a core/shell structure such as the InP/CdS QDs. A deeper understanding of each of the charge relaxation processes and their analysis has been achieved. Some of their
potential merits were modelled by calculating their effect on solar cell efficiency. The Detailed Balance model [10-11] for the efficiency of a solar cell was modified to illustrate the benefits of a Type II structure based on band structure and radiative lifetime calculations of CdSe/CdTe QDs. Several efficiency enhancements were demonstrated due to the separation of electrons and holes in Type II core/shell structures, observations which apply to any QD system utilising a Type II or quasi-Type II structure. These results were published in the journal *Solar Energy Materials & Solar Cells* [12-13].

There is still significant scope for the development of new quantum dot materials, particularly as the understanding and control of synthetic routines for current systems increases, such as semi-metals, alloyed QDs, perovskites, and different crystal structures. But, there is also significant potential for the combination of different synthetic processes, such as the shelling of QD’s, surface treatments and the conjugation of charge extraction moieties demonstrated in this work. Finding systems where such combinations can function harmoniously for the optimal benefit to devices will be a significant challenge, both in the synthetic approach and for their analysis. As has been demonstrated repeatedly in this work, when multiple charge relaxation processes are occurring simultaneously the charge dynamics can become difficult to interpret. In Chapter 7, a Monte-Carlo model was demonstrated which might have significant appeal in such systems due to its ability to model an arbitrary number of complex interactions in a QD, particularly with its capacity to include experimental artefacts which are unavoidable in the experimental techniques currently available.

In conclusion, quantum dots provide an exciting and highly active area of research, broadly focussed on either their demonstration in new technological and scientific applications, or developing a deeper understanding of their chemical, optical, and electronic properties. The results presented in this thesis provide unique contributions to the field pertaining to the measurement and analysis of charge carrier relaxation in novel colloidal quantum dots on ultrafast timescales, each of which are important steps to the optimisation and application of quantum dot technologies.
8.1. References


