OPTICAL AND MATERIAL PROPERTIES OF COLLOIDAL SEMICONDUCTOR NANOCRYSTALS

by

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Graduate Department of Chemistry
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Abstract

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Doctor of Philosophy
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This thesis presents an exploration of the photophysics of colloidal semiconductor nanocrystals using both linear and non-linear optical measurement techniques. These optical methodologies are used to follow population dynamics in both singly and multiply excited nanocrystal systems as well as determine material properties of the ensemble. Topics covered in the thesis include, the identification and characterization of bulk-like nanocrystals, study of the fine structure states of the lowest energy exciton, single and multiexciton population dynamics, acoustic phonon modes, elasticity and surface stress properties of a colloidal ensemble in solution.

Through linear spectroscopy, the properties of both quantum confined and bulk-like colloidal semiconductor nanocrystals are compared. The identification of a model system of bulk-like nanocrystals with a non-standard absorption profile serves to resolve an ambiguity in literature concerning their characterization. The remainder of the thesis is focused on the size-dependent properties of quantum confined CdSe colloidal nanocrystals. The population dynamics and material properties of these systems are studied using a nonlinear optical technique called transient grating. A third order transient grating measurement with a cross-polarized configuration, which follows the relaxation within the fine structure levels of the lowest energy exciton state, is demonstrated and used to compare systems with different crystal field splittings. Transient grating experiments performed with specific polarization sequences allow for selective observation of
the dynamics amongst nearly degenerate levels at room temperature. Cross-polarized transient grating is also used to observe a quantized acoustic phonon mode in a series of nanocrystal samples. The observation of this mode allows experimental determination of the elasticity and surface stress of the nanocrystal ensemble in solution. The anisotropic origin of the acoustic phonon is discussed using a combination of theoretical analysis, modelling and experimental data. In addition, third- and fifth-order transient grating experiments are used to study exciton and multiexciton population relaxation dynamics. The work presented here spans the optical and material properties of quantum confined and ‘bulk’ nanocrystals. This thesis attempts to illustrate the broad scope of the observed behaviour of colloidal nanocrystal systems and to contribute to a greater understanding of their physical properties.
To my Aunt Alice, who showed me how to weather illness with grace

and to my family, who supported me through it all
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“While I’m still confused and uncertain, it’s on a much higher plane, d’you see, and at least I know I’m bewildered about the really fundamental and important facts of the universe.” Treatle nodded. “I hadn’t looked at it like that,” he said, “But you’re absolutely right. He’s really pushed back the boundaries of ignorance.”

Terry Pratchett, Equal Rites
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Chapter 1

Introduction and Perspective
1.1 The Optical and Material Properties of Colloidal Semiconductor Nanocrystals

Colloidal semiconductor nanocrystals are a class of materials whose properties are determined by their physical dimensions. Since their size and shape can be controlled synthetically, these systems may be used to create designed materials with specific properties. However, this goal of controlled design requires a complete knowledge of the physics of these materials, which has not yet been achieved. The research presented in this thesis aims to contribute to our understanding of both the material and optical properties of colloidal semiconductor nanocrystal systems through the study of their photophysics.

Owing to the novel optical and material properties of semiconductor nanocrystal systems, their potential applications are legion, including light emitting diodes [1, 2, 3], lasing media [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14], components for quantum computing, information and spintronics [15, 16, 17, 18, 19, 20, 21], solar cells and photovoltaics [22, 23, 24, 25, 26, 27, 28, 29, 30] and they have found some success as biological labels [31, 32, 33, 34, 35]. The attractiveness of colloidal semiconductor nanocrystals for device applications is a result of their scalable optical and material properties as well as their easy processability.

Colloidal semiconductor nanocrystals are composed of a nanoscale semiconductor core surrounded by a shell of organic ligand molecules [36, 37]. These molecules act as surfactants, suspending the nanocrystal in solution, preventing uncontrolled growth and agglomeration of the nanoparticles. They allow the nanocrystals to be chemically manipulated as if they were large molecules, with solubility and chemical reactivity determined by the ligands. In addition, they provide electronic passivation of the nanocrystals by terminating dangling bonds on the surface. The unterminated dangling bonds can affect the emission efficiency because they lead to a loss mechanism where electrons or holes (in the case of CdSe capped with trioctylphosphine oxide, it is primarily the holes that are
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trapped) are rapidly trapped at the semiconductor surface before photons can be emitted. Using colloidal chemical synthesis, it is possible prepare nanocrystals with nearly atomic precision with diameters ranging from nanometres to tens of nanometres and a size dispersion as narrow as five percent standard deviation.

1.2 Classes of Colloidal Semiconductor Nanocrystals

The optical and material properties of semiconductor nanostructures can be considered to lie in an intermediate regime between the molecular and the bulk as a result of their finite dimensions. This ‘in between’ description encompasses both main classes of colloidal semiconductor nanocrystals divided based on their optical properties: quantum confined and bulk-like. Although the majority of the existing literature is focused on quantum confined systems, which have size-tuneable optical properties, nanocrystals with optical properties similar to those of bulk semiconductors also exist. Both types of system are considered in this thesis.

In a bulk semiconductor, the dimensions of the system are essentially infinite compared to the dimensions of the carriers, electrons and holes. In this case, the wavefunctions are standing waves in the material, spread over an infinite number of unit cells. The resulting density of states is continuous except in the region of the band gap. The concept of ‘infinite’ boundary conditions of the crystal lattice, relative to the electron or hole wavefunction in a bulk system, is clear when considering a macroscopic block of semiconductor material. However, it is not immediately obvious that nanoscale materials may also display ‘bulk’ optical properties.

Confinement in one-, two- or three-dimensions based on the physical size of the material changes the boundary conditions imposed on the wavefunctions and quantizes the behaviour of the electrons and holes. Confinement of the wavefunctions in one-dimension
is associated with a quantum well system. A system confined in two-dimensions is called a quantum wire, while a system confined in all three-dimensions, which has a discrete density of states, is called a quantum dot. The quantum confined systems in this thesis correspond to three-dimensional confinement. The boundary conditions associated with the spatial confinement of the wavefunctions, in turn, modify the density of states. The resulting change in the density of states, from a continuous band in the bulk to discrete levels in a quantum dot, is analogous to the particle in a box model in quantum mechanics [38, 39]. The physical dimensions required to spatially confine the electron or hole depend on the size of the electron and hole wavefunctions, which are determined by the properties of the specific material.

Despite nanometre scale, if the semiconductor crystal in all three-dimensions is significantly larger than the electron and hole wavefunctions, it follows that it will have bulk-like optical properties. Indeed, there are semiconductor nanocrystal systems with physical dimensions of less than ten nanometres that have bulk-like optical properties. The determining factor is the degree of confinement of the wavefunctions relative to the size of the nanocrystal. Although ‘bulk’ nanocrystals exist and have many desirable properties, they have not been extensively researched. It should be noted that in addition to strongly confined and bulk-like there is an intermediate confinement regime, where the size of the wavefunctions is approximately equal to the size of the nanocrystal. However, only the properties of strongly confined and bulk-like systems are explored in this thesis.

Quantum confined semiconductor nanocrystals have been the focus of intense study over the past three decades due to their size tuneable optical properties and unique physical characteristics. This area of research was founded in the early 1980s when researchers at Bell Laboratories [40] in the United States and the Yoffe Institute [39, 41, 42, 43] in Russia, then the U.S.S.R, independently described the properties of nanometre sized quantum confined semiconductor crystals. This work was quickly followed by studies on colloidal samples [44, 45], leading to a further understanding of their optical and physical
properties. Within less than a decade, a preliminary theoretical framework to describe the observed properties had been proposed and work was underway to explore the fundamental physics of these materials.

Much of the early work on quantum confined semiconductor nanocrystals focused on semiconductor-doped glasses. These materials are characterized by broad size distributions and offer no possibility of control over the shape or interface characteristics of the particles. The limitations of these doped glasses, particularly the large static inhomogeneity caused by a broad size distribution, obscured observation of many of the fundamental physical processes. However, the study of quantum confined nanocrystals underwent a revolution in 1993 when it was discovered that nucleation and controlled growth of colloidal semiconductors could be achieved by injecting highly reactive organometallic precursors into a solvent system that coordinates to the colloid surface [36]. Although colloidal nanocrystal synthesis had been demonstrated previously [44, 45] this new methodology, which was simple and reproducible, represented a significant advance. This development in synthetic procedures opened new avenues for research, including increased processability, the possibility of mass production and chemical manipulation for tailored shape control. In particular, this reliable method of making high quality samples allowed the exploration of phenomena that had been previously unobservable due to static inhomogeneity associated with broad size-distributions.

Despite the significant progress that has been made towards controlling the synthesis of colloidal semiconductor nanocrystals, many of their optical and material properties are not fully understood. Many of the properties of quantum confined nanocrystals are size-dependent, including the band gap, fine structure level spacing, exciton binding energy, exchange interaction, melting point, elasticity, surface stress, frequency of the acoustic phonon modes, among others. Some representative properties are shown in Figure 1.1. Since these quantities are size-dependent they are directly linked to the physical dimensions of the nanocrystals. As a result, the ability to tune the size or shape of the
nanocrystals through synthetic methods translates into a means of controlling their physical properties [46, 47]. In a ‘bulk’ nanocrystal, although the optical properties are not determined by the physical dimensions of the particle, until, of course, they approach the confinement regime, some of the material parameters may differ from that of a macroscopic crystal based on the relatively small number of atoms and the large surface to volume ratio. Through studying the photophysics of both ‘bulk’ and quantum confined semiconductor nanocrystals we can elucidate the links between morphology, optical and material parameters. The next section summarizes the current status of knowledge of the photophysics of semiconductor nanocrystals.

1.3 Current Understanding of the Photophysics of Colloidal Semiconductor Nanocrystals

1.3.1 Absorption and Photoluminescence

One of the defining features of a semiconductor is the band gap, which separates the conduction and valence bands. Upon absorption of light, an electron is promoted from the valence to the conduction band. The wavelength of light absorbed and emitted from this material is determined by the width of the band gap, as shown in Figure 1.2(a) and (b). In semiconductors, when an electron moves from the valence to the conduction band, the resulting gap left in the valence band is called a hole, as shown in Figure 1.2(d). In a prototypical bulk semiconductor, the density of states of the two bands is essentially continuous.

In a semiconductor system, an exciton can be formed through an energy lowering Coulomb interaction between the negative electron and the positive hole. In analogy with the hydrogen atom, the spatial extent of the exciton wavefunction is described by
Figure 1.1: Some examples of size-dependent properties of quantum confined semiconductor nanocrystals. In a strongly confined semiconductor system, the absorption and the emission wavelengths are determined by the nanocrystal radius, \( R \). Panel (a) presents a series of absorption spectra of colloidal CdSe nanocrystal samples ranging in size from \( R = 1.18 \) nm (bottom, purple trace) to \( R = 1.99 \) nm (top, dark red trace) clearly showing the position of the lowest energy exciton state (lowest energy peak) shifting through the visible region. Panel (b) shows the size-dependence of the acoustic phonon mode in CdSe colloidal nanocrystals with the largest to smallest radius nanocrystal sample presented in order from the bottom (bright yellow trace) to the top (black trace). The last panel, (c), represents surface stress in colloidal nanocrystal samples, with an internal force (black arrows) balanced by an external pressure (blue arrows), which is also size-dependent.
a quantity called the exciton Bohr radius. Like the hydrogen atom, the lowest energy set of states is comprised of closely bound electron-hole pair configurations. These are the optically active bound exciton states that absorb and emit light. The attractive interaction between the electron and hole lowers the energy of the exciton relative to the band gap of the bulk material by an amount referred to as the binding energy. For most semiconductor nanocrystal systems, this binding energy is relatively small, on the order of tens of meV, compared to the band gap, which is usually in the eV range. The energy associated with optical absorption of the lowest energy exciton state is called the optical gap and is defined as the band gap minus the binding energy. While the formation of excitons is not favoured in most bulk semiconductors, it is significantly enhanced in quantum confined systems.

In a quantum dot, the three-dimensional confinement modifies the Hamiltonian, adding a potential that restricts how far apart the electron and the hole can be. This forced spatial overlap results in a discrete density of states. The position of these states and, therefore, the absorption spectrum, depends on the spatial confinement of the exciton, which is determined by the physical size of the nanocrystal. To a first approximation, this quantum confinement effect can be described using the particle in a box or a simple quantum box model \[38, 39\], as discussed in the previous section. The energy levels of quantum confined semiconductor nanocrystals can be represented in terms of two basic frameworks. One is modelled closer that that of a bulk system with separate electrons and holes, as shown in Figure 1.2(d), while the other is mapped onto exciton states, as shown in Figure 1.2(e). Both pictures describe aspects of the physics of the system. Photoexcitation of strongly confined semiconductor nanocrystals results in the formation of excitons. In this type of system it is usually correct to deal only with exciton states, but in certain cases it is useful to consider the electron and the hole separately. For bound excitons this separate electron and hole picture is not strictly true \[48\]. However, dissociation of the exciton can occur thermally, or by other methods, since the binding
energy is generally only on the order of tens of meV. Other processes such as charge separation and localization of the hole on a trap state or relaxation processes that affect the electron and the hole in different ways can then follow the dissociation. In these cases, the separate electron and hole picture is intuitively useful, although, it assumes a preceding step requiring dissociation of the exciton.

The absorption spectrum of a textbook bulk semiconductor, as presented in Figure 1.2(c), is continuous except for the step-function-like increase in absorption cross-section at the band gap energy. However, there are exceptions to this rule where semiconductors with bulk optical properties can have an absorption spectrum with clear peak features. For instance, the absorption spectrum of bulk EuS contains peaks that are not exciton features nor associated with quantum confinement but are due to localization of the electrons. In a strongly quantum confined semiconductor system, the confinement changes the continuous energy bands of a bulk semiconductor into discrete exciton energy levels. The exciton energy levels produce peaks in the absorption spectrum as shown in Figure 1.1(a).

The linear absorption spectrum provides a map of initially excited energy levels. In a quantum confined semiconductor nanocrystal system, absorption primarily populates exciton states. Following photoexcitation, the excited state may decay radiatively or non-radiatively. A portion of this excitation will relax through photoluminescence (a. k. a. fluorescence) processes. The amount of absorbed light that is reemitted as fluorescence in a quantum confined nanocrystal depends strongly on the nature of the surface. In nanocrystals, a large percentage of the atoms are close to the surface and, as such, it has a strong effect on the particle. These surface atoms belong to incomplete unit cells, resulting in dangling bonds. Some of these atoms are bound to the organic ligands that suspend the nanoparticles in solution, however, the rest of the surface atoms remain unterminated. It is at these unterminated atoms that an electron or a hole may become trapped following photoexcitation. In the case of CdSe capped with trioctylphosphine
Figure 1.2: Representations of the photophysics of semiconductors, both bulk and quantum confined. The top three panels (a), (b) and (c) correspond to bulk systems, while the bottom two, (d) and (e), correspond to quantum confined semiconductor nanocrystals. Panel (a) shows the delocalized orbitals and continuous levels of the conduction and valence bands separated by the band gap represented in real space. Panel (b) shows the same bands plotted in reciprocal space as energy, $E$, versus wavevector, $k$. The standard absorption spectrum for a direct band gap bulk semiconductor system is presented in (c). The step-like rise corresponds to the position of the band gap and is followed at higher energy by absorption into the continuum of states. Panel (d) presents an electron and hole picture of the energy levels of quantum confined semiconductor nanocrystals. The blue dot represents the hole left in the valence band following absorption of a photon. The green dot is the electron in the conduction band. In this picture, the electron is excited into a higher energy state and relaxes initially through radiationless internal conversion (IC) processes. Following the IC process, the electron may emit and relax back to the ground state or move into a surface trap state. Other possible processes involve the hole transferring to the trap state or the electron transferring energy to the hole and scattering it deeper into the valence band. Panel (e) presents the excited states of a quantum confined semiconductor nanocrystal in an exciton basis, where $g$, $e$, $b$ and $t$ are the ground, exciton, biexciton and triexciton states.
oxide (TOPO), the ligand binds to the cadmium atoms, leaving the selenium atoms free. As a result, it is primarily the holes that are trapped at the surface. This trapping process mainly serves to quench the fluorescence. In a bulk system, non-radiative relaxation is generally strongly favoured at room temperature due to coupling to the continuum of vibrational states, resulting in little fluorescence.

### 1.3.2 Relaxation Processes in Semiconductor Nanocrystals

Following photoexcitation in a confined semiconductor nanocrystal system, the excited states can relax through a variety of radiative and non-radiative pathways. Photoexcitation can create single or multiple excitons within an individual nanocrystal depending on nonlinearities or the incident intensity. The processes that return the system to the ground state following excitation remain the subject of intense investigation [49, 50, 51]. For instance, radiationless transitions, such as internal conversion or Auger-like processes, likely play an important role in relaxation. However, the exact nature of these processes in different semiconductor nanocrystal systems is an unresolved issue.

Following optical absorption, the exciton may be excited into a manifold of states associated with vibrations or the fine structure, which arise from exchange and crystal field effects. The exciton can relax nonradiatively through these levels before recombinining or otherwise returning to the ground state. This relaxation can be thought of in analogy to internal conversion in molecules; however, the details of the process in nanocrystals are significantly different than in molecular systems. In a molecular system, internal conversion occurs rapidly due to high frequency vibrational modes, which have energies comparable to the level spacing. In a strongly confined semiconductor nanocrystal, the energy spacing of the electronic levels is significantly larger than the available low frequency vibrational bath modes, which are optical or acoustic phonons. In the early to mid nineties it was believed that this lack of compatibility between the energy
separation of the electronic states and the vibrational modes would lead to a so-called ‘phonon-bottleneck’ characterized by slow relaxation timescales on the order of picoseconds [52, 53, 54]. However, this phonon bottleneck is not observed experimentally. For example, in CdSe nanocrystals the observed interband relaxation is very fast, occurring on sub-picosecond timescales [55, 56, 57, 58, 59, 60]. An Auger-like process, involving a transfer of energy from the electron to the hole, may partially explain this fast relaxation [61, 62, 63, 64, 65]. If the hole is more massive than the electron, which is the case in II-VI and III-V semiconductors, then it has closer spaced energy levels and the ultrafast relaxation can occur through coupling to the bath modes. The Auger-like process in quantum confined semiconductor nanocrystals involves irreversible energy transfer from an electron to a hole. To satisfy energy conservation, the additional energy required or produced by this process is given to a third body ‘spectator’ that may be either an electron or a hole. It is still unclear if this proposed Auger-like effect completely describes the ultrafast relaxation. Further complications include possible contributions of surface ligands to exciton relaxation [51, 65, 66, 67, 68].

1.3.3 Multiple Excitons in Semiconductor Nanocrystals

Unlike in molecular systems, semiconductor nanocrystal systems can easily accommodate multiple excitons [69]. These multiexcitons can be generated through excitation with high intensity light sources [70], nonlinear processes [50, 60, 71, 72, 73, 74, 75], or excitation with an incident laser pulse at energies above the multiple exciton generation threshold [25, 76, 77, 78, 79, 80, 81]. In strongly confined colloidal semiconductor nanocrystals this threshold is approximately three times the band gap [82]. It has been reported that the multiple exciton generation phenomena can be used to produce highly sensitive ultraviolet photodetectors [76] and may be used to develop novel solar cell materials [83, 84, 85, 86].
Despite the potential importance of multiple excitons, their dynamics and relaxation processes are not fully understood. Their observation is complicated since in a confined system the excitons interact \[87\], modifying the energy levels and obscuring the dynamics. Additionally, the multiple exciton states have extremely complicated fine structures \[71\].

\subsection{Vibrations in Semiconductor Nanocrystals}

A discussion of the photophysics of semiconductor nanocrystals is incomplete without considering the vibrational bath modes. In this system, these modes are quantized lattice vibrations called phonons. The phonons are generally classified based on the way they propagate through the lattice. In crystals with more than one atom per primitive cell, vibrations involving a displacement of the unit cell’s centre of mass, where the adjacent atoms oscillate in phase, are called acoustic. Out of phase oscillations, where atoms in the unit cell move opposite to each other, are called optical modes. Following solid state physics conventions; the phonons can be divided into transverse or longitudinal modes. In a transverse mode, the displacement is perpendicular to the direction of the wavevector, while the displacement in longitudinal modes is parallel. However, the transverse and longitudinal labels are less significant in finite lattices, where the modes are invariably mixed.

In optical experiments, both types of phonon may participate in the observed dynamics. The optical modes can be directly excited by the absorption of a photon since they are associated with non-propagating displacements, while the acoustic modes, which involve real mass displacements, are driven indirectly as a result of the change in electronic distribution following photoexcitation. The phonons couple to the excitation through different mechanisms. Acoustic modes in small nanocrystals are primarily coupled through the deformation potential, which is related to the strain tensor, while the optical modes couple
through the polar Fröhlich interaction. Owing to the different coupling mechanisms, the
two classes of phonons have different observed size-dependences. It is well known that the
vibrational modes contribute to the homogeneous broadening of the nanocrystal system
and participate in the relaxation processes. However, the exact role of the phonons in
the excited state dynamics is unclear.

1.3.5 Ultrafast Nonlinear Optical Experiments on Semiconductor Nanocrystals

Although linear spectroscopy is preferable due to its simplicity, it provides limited in-
formation for systems that are complicated by the distribution of sizes. When linear
optical techniques are not sufficient, more complicated nonlinear optical experiments are
performed since they have additional parameters that can be used to isolate different con-
tributions to the signal. As a result, much of the research on the photophysics of quantum
confined semiconductor nanocrystals has employed nonlinear spectroscopic techniques.

Colloidal nanocrystal samples are composed of an ensemble of sizes whose distribution
is determined by the synthetic method used to produce them. The range of nanocrystal
sizes corresponds to a distribution of energy levels and other size-dependent proper-
ties, resulting in an inherently inhomogeneously broadened system. Note that bulk-like
semiconductor nanocrystal systems are not affected in the same way by inhomogeneous
broadening since the optical properties are not size-dependent.

Some early nonlinear studies of quantum confined colloidal semiconductor nanocrystals
used the three-pulse photon echo technique since, in an ideal two level system, this
experimental methodology can selectively remove the inhomogeneous broadening. Ini-
itially, this technique was used in an attempt to isolate the homogeneous component
associated with vibrational modes [88, 89]. This experiment and the similar three-pulse
photon echo peak shift did provide insight into the origin of the disorder in these systems
[90, 91]. However, the measurements were hampered by the fact that the homogeneous and inhomogeneous broadening components could not be completely separated since the optical properties of the nanocrystals were considerably more complex than expected and do not correspond to a two level model.

Population dynamics have been studied in colloidal nanocrystal systems using pump-probe or transient absorption and transient grating techniques. Early work on multiexciton dynamics and relaxation was performed through pump-probe measurements using a 400 nm pump and a white light continuum probe [55, 57, 58, 92, 93]. Both intra and interband relaxation in colloidal semiconductors have been studied using a variety of pump-probe experiments [50, 56, 65, 94, 95, 96, 97, 98]. In addition to pump-probe, transient grating experiments have been performed to follow population dynamics in colloidal semiconductor nanocrystal systems. Although transient grating measurements are conceptually similar to pump-probe measurements, they allow additional levels of experimental control. For example, third- and fifth-order transient grating measurements have been used to selectively study exciton and biexciton dynamics [60] and polarization controlled transient grating measurements have been used to study the dynamics within the fine structure of the first exciton state of colloidal semiconductor nanocrystals [49, 99, 100, 101, 102, 103, 104, 105].

1.4 Aims and Outlook

The general goal of this thesis is to contribute to a greater understanding of the photo-physics of colloidal semiconductor nanocrystals. The topics explored include: the role of phonons, multiexcitons, dynamics within the first exciton state, bulk-like versus quantum confined systems and the interplay between the optical and the material properties. This thesis presents an exploration of some interrelated aspects of the material and optical
properties of colloidal semiconductor nanocrystals, using both linear and nonlinear optical measurement techniques. The optical methodologies presented here follow population dynamics in both singly and multiply excited nanocrystal systems and are used to determine certain material properties of the ensemble. Through the combination of theoretical descriptions and modelling with experimental data, it is possible to work towards a unified understanding of the optical and material properties of colloidal nanocrystal systems.
1.5 Organization of the Thesis

In this thesis, optical measurements are used to study aspects of the optical and material properties of colloidal semiconductor nanocrystals. The relationships between the chapters and the general organization of the thesis is presented in Figure 1.3.

**Chapter 1:** Provides background on the photophysics of semiconductor nanocrystals and discusses the current status of the field. Outlines the organization of the thesis and clarifies contributions from collaborators.

**Chapter 2:** Reports the experimental demonstration of a measurement technique that follows relaxation dynamics in the fine structure of the lowest energy exciton state of quantum confined CdSe colloidal nanocrystals.

**Chapter 3:** The experimental technique introduced in Chapter 2 is used to compare relaxation in the fine structure states of colloidal CdSe nanocrystals with wurtzite and zinc blende crystal structures; exploring the effect of the crystal structure on the fine structure states due to the crystal field splitting.

**Chapter 4:** This chapter goes beyond the lowest energy exciton state in CdSe colloidal nanocrystals, studying the relaxation processes of multiple excitons using third-and fifth-order spectroscopy.

**Chapter 5:** Not all colloidal semiconductor nanocrystals display quantum confined optical properties. Depending on the relative size of the nanocrystal compared to the spatial extent of the exciton, some nanoparticle systems behave as bulk semiconductors. The properties of bulk colloidal semiconductor nanocrystals are studied in this chapter using EuS and Ag$_2$S as model systems.
Chapter 6: This chapter employs third-order polarization control spectroscopy to observe acoustic phonon modes in colloidal CdSe nanocrystal samples. The observed acoustic phonon mode is then used to determine elasticity and surface strain of the nanocrystals in solution.

Chapter 7: Building on the results from Chapter 6, this chapter investigates the origin of the acoustic phonon mode and discusses the strain induced mixing of the fine structure states in colloidal CdSe nanocrystals.

Chapter 8: Concludes the thesis and provides an outlook on future work.

Appendix A: Presents a derivation of the Tauc equation, used in Chapter 5.

Appendix B: Discusses the links between the colloidal chemistry concept of surface tension or stress and the classical theory of elasticity. Provides background for Chapter 6.

1.6 Contributions to Published Work Included in Thesis

Much of the work presented in this thesis has been previously published and benefitted from collaborations with other researchers. In this section, I clarify the contributions by collaborators to the work presented.
Chapter 2 is primarily composed of research previously published in:

“Dynamics within the exciton fine structure of colloidal CdSe quantum dots”

*V. M. Huxter, V. Kovalevskij and G. D. Scholes*


In this article, the experiments were performed by V. Kovalevskij and myself. I performed the data analysis and made the figures jointly with Prof. Scholes. Prof. Scholes wrote the majority published article, while I contributed sections to the main text and wrote the supporting information.

Chapter 3 is being prepared for submission

“Spin Relaxation in Zinc Blende and Wurtzite CdSe Quantum Dots”

*V. M. Huxter, J. Kim, S. S. Lo, A. Lee, P. S. Nair and G. D. Scholes*

In this chapter, I conducted the experiments, characterized the samples and performed the data analysis. S. Lo assisted in some of the experiments. A. Lee and P. S. Nair synthesized and purified the CdSe nanocrystal samples. I made the figures and wrote the majority of the text with some contributions from J. Kim.

Chapter 4 was adapted from:

“Nonlinear optical approach to multiexciton relaxation dynamics in quantum dots”

*V. M. Huxter and G. D. Scholes*

Journal of Chemical Physics, Vol. 125, Article Number 144716 (2006)

I collected and analyzed the data, wrote the simulations and the paper. The interpretation and approach was developed jointly with Prof. Scholes.

Chapter 5 was adapted from:

“Demonstration of bulk semiconductor optical properties in processable Ag$_2$S and EuS
nanocrystalline systems”

*V. M. Huxter, T. Mirkovic, P. S. Nair, and G. D. Scholes*


T. Mirkovic prepared the EuS nanocrystals and obtained transmission electron microscopy images for all samples. P. S. Nair prepared the Ag$_2$S nanocrystals. I performed the experiments, analyzed the data and wrote the paper in consultation with Prof. Scholes.

Chapter 6 was adapted from:

“CdSe Nanoparticle Elasticity and Surface Energy”

*V. M. Huxter, A. Lee, S. S. Lo, and G. D. Scholes*


A. Lee synthesized and purified the CdSe nanocrystal samples and obtained the scanning transmission electron microscopy images. S. Lo assisted with some of the experiments. I collected and analyzed the data, optically characterized the nanocrystal samples, wrote and used the response function simulation of the data, performed simulations using the elastic sphere model. Prof. Scholes wrote the elastic sphere model program. I developed the interpretation and wrote the paper in consultation with Prof. Scholes.

Chapter 7 is being prepared for submission

“Acoustic Phonon Strain Induced Mixing of the Fine Structure Levels in Colloidal CdSe Quantum Dots Observed by a Polarization Grating Technique”

*V. M. Huxter and G. D. Scholes*

I collected and analyzed the data and wrote the simulations. I wrote the paper, developed the interpretation and theoretical basis in consultation with Prof. Scholes.
Chapter 2

Dynamics Within the Exciton Fine Structure of Colloidal CdSe Quantum Dots
2.1 Chapter Summary

The current chapter presents measurements performed using a crossed polarized ultrafast transient grating technique. This technique employs polarization sequences to measure relaxation timescales within the fine structure of the lowest energy exciton state of colloidal CdSe nanocrystals. The cross polarization methodology takes advantage of the complex nature of the transition dipole moments to observe fine structure dynamics in a randomly oriented colloidal system, despite the fact that the energy separation of these levels is on the order of tens of meV.

The measurements presented in this chapter represent the initial colloidal semiconductor spin flip results obtained using the cross polarized transient grating technique. Following subsequent work [49, 105, 106], our understanding of the spin flip mechanism has evolved from what was originally published in 2005. As opposed to a direct flip between the $F = +1$ and $F = +1$ fine structure states mediated by a long-range exchange interaction, our recent work has shown that the transitions are more complex, which is further addressed in Chapter 3. This present chapter provides a bit of a historical perspective on our initial experiments.


2.2 Introduction

The size-dependent optical properties of semiconductor quantum dots have been widely studied in recent years [107]. Clear optical absorption features assigned to the $1S_{3/2}1S_e$, $2S_{3/2}1S_e$, and so forth, exciton states are evident in ensemble spectra. Each of those absorption bands is split into a fine structure by crystal asymmetry effects and the exchange interaction [108, 109]. However, there is a lack of experimental studies of that manifold of states because it spans only tens of meV and is consequently hidden by the inhomogeneous broadening of the spectrum arising from the sample size-distribution. According to previously reported calculations, the fine structure of CdSe consists of eight states, five of which are optically bright [109, 110, 111, 112]. Of these, one state with total angular momentum $F = 0$ has a linearly polarized transition moment and four states, those with $F = \pm 1$, obey selection rules for absorption of circularly polarized light.

Earlier experimental studies of the exciton fine structure states in colloidal quantum dots have concentrated on the splitting between dark ($F = \pm 2$) and bright states ($F = \pm 1$), which originates from the short-range part of the electron-hole exchange interaction [113, 114, 115]. It has been predicted that for quantum dots with an anisotropic shape, an interaction arises between the $F = \pm 1$ exciton states mediated by the long-range part of the exchange interaction [116]. At low temperatures, particularly in the presence of a strong magnetic field, that asymmetry-induced exchange interaction is seen as a splitting of the bright exciton transitions [117]. Based on these observations, we initially believed that the size-dependent zero-field long-range exchange interaction promoted the transitions from one bright exciton state to the other. The discussion of the exchange in this chapter represents our initial attempts to explain the spin flip mechanism. However, recent work [49, 105, 106] has shown that the transitions in the fine structure are more complicated than initially thought. Instead of a direct $F = \pm 1$ to $F = \mp 1$ transition, the process is mediated through the $F = \pm 1^L$ to $F = \mp 2$ pathways, where the superscript $L$ indicates the lower energy $F = \pm 1$ states (see Figure 3.1(a)).
Optical pumping of excitons, using circularly polarized light can establish exciton spin polarization in oriented crystals by projecting photon angular momentum onto an exciton state [118, 119, 120]. Therefore, in oriented systems, transitions between the $F = \pm 1$ states can be monitored by circular-polarization photoluminescence anisotropy decays, as has been reported for quantum wells [121, 122, 123, 124]. However, investigations of exciton orientation and relaxation in rotationally isotropic systems, such as an ensemble of colloidal quantum dots, have been hampered because it is not evident how selection rules for optical excitation can be exploited. In order to explore the dynamics of transitions between the exciton fine structure levels, a new approach was recently proposed [125]. This method, based on measuring the decay of a transient polarization grating, is sensitive to exciton state history rather than excited state population. In other words, the signal decays proportionally to the number of quantum dots probed in a different exciton state to that prepared by the optical pump. We report here results of application of that method to measure transitions from $F = +1$ to $F = -1$ exciton fine structure states and vice versa for CdSe quantum dots.

2.3 Experimental Methods

High-quality CdSe colloidal quantum dots passivated with trioctylphosphine oxide were prepared using an organometallic route [36]. Those samples were dispersed in optical-quality polymer films, which were maintained under vacuum for the experiments at 293 K. We have ascertained that the physics we report here is independent of sample preparation, including passivating ligands and host matrix. Ultrafast laser pulses of 20–36 fs duration were generated using a setup described previously [90]. Measurements were undertaken using third-order transient grating (3-TG) spectroscopy, similar in principle to the ubiquitous pump-probe method. However, the pump pulse is split into a pair of
beams that have different wavevectors, $k_1$ and $k_2$, which arrive simultaneously to photoexcite the sample at a crossing angle of a few degrees (in the theory, they are assumed to be collinear). A probe beam with wavevector, $k_3$, monitors the evolution of ground and excited-state density as a function of time delay, $t_p$. 3-TG signals are seen in the phase-matched directions $k_s = -k_1 + k_2 + k_3$ and $k_r = k_1 - k_2 + k_3$, which facilitates spatial isolation of background-free signals. Detection of those signals on a photodiode yields the homodyne-detected 3-TG signal intensity as a function of the pump-probe time delay, $I_{HOM}(t_p)$. The bandwidth of the pulses accommodates possible inelasticity in the four-wave mixing process.

2.4 Results and Discussion

An important difference between 3-TG and ultrafast pump-probe measurements is that the polarization of each of the three laser beams as well as an analyzer in the signal path can be independently arranged. In the present work we discuss permutations of orthogonal linear polarizations, labelled vertical (V) and horizontal (H). For the majority of linear or circular polarization conditions, the 3-TG signal is expected to decay according to surface trapping and exciton recombination kinetics [125]. We find that to be the case, as shown in Figure 2.1(a). However, if the pump pulse pair are cross-polarized (e.g. vertical/horizontal = V/H), and likewise for the probe/analyzer pair, then a completely different kind of kinetics is predicted to be measured by the decay of the signal [125]. That prediction is consistent with the experimental results shown in Figure 2.1(b). Counterintuitively, that experiment records the rate of transitions among $F = \pm 1$ exciton states in quantum dots [125]. It is worth mentioning that we are not observing an optical Kerr effect in these data. Furthermore, we note that a similar experiment cannot be devised using circularly polarized pulses (see Table 2 of Reference [125]).
Figure 2.1: Plots of 3-TG data recorded using various polarization sequences for 5.0 nm diameter CdSe, 293 K in a poly(butylmethacrylate) free-standing film. Polarization sequences for pulses 1–3 and the analyzer in the signal path, if included, are indicated in the inset, where V = vertical, H = horizontal, and M = magic angle. In those tables, s and r refer to data recorded in either the $k_s$ or $k_r$ phase-matched signal directions, respectively where $k_s = -k_1 + k_2 + k_3$ and $k_r = k_1 - k_2 + k_3$. The information is listed in the same order (top to bottom) as the curves in the corresponding plot. (a) Populations gratings. (b) Polarization gratings.

The polarization grating established by the pump pulse pair in our experiment is analogous to that discussed previously, for example, to measure sodium vapour velocity distributions [126]. However, because the selection rules for optical excitation of quantum dot excitons involve complex transition moments, the readout of the polarization grating decay by the probe is important. A qualitative understanding of the experiment can be garnered by considering the polarization grating properties and decay, as discussed by Fourkas et al [127]. A cross-polarized linear excitation (e.g. VH) forms a transient population grating with a spatially varying polarization along each fringe, changing from left-hand circular to elliptical to linear to elliptical to right-hand circular, and so on.
The diffracted intensity of the probe beam decays if any process disrupts that spatial polarization modulation, for example, rotational diffusion of a transition dipole. In the present case, the modulation is diminished when the circularly polarized transition moment flips with transitions between the $F = +1$ and $F = -1$ exciton states. When the quantum dot $c$-axis is antiparallel to the $k$-vector of the incident radiation, right-handed circularly polarized light excites the states with total angular momentum $F = +1$, while left-handed circularly polarized light excites states with $F = -1$.

A general microscopic description of the phenomenon was reported previously by evaluating rotational averaging for the coherent 3-TG spectroscopy [125]. A rotational average for any third-order nonlinear spectroscopy is obtained by considering the action of a sequence of laser pulses, polarized in the laboratory frame according to the tensor $S_{abcd}$, on the internal selection rules acting in the nanocrystal frame, which respond as $T_{\alpha\beta\gamma\delta}$ [128, 129, 130].

$$\langle P^{(3)}(\tau, t_p, t) \rangle = CP^{(3)}(\tau, t_p, t)$$

(2.1)

where $C = S_{abcd}T_{m_{\alpha\beta\gamma\delta}}I^{(4)}$ and $P^{(3)}(\tau, t_p, t)$ is the third-order induced polarization radiated by the sample. The tensor $I^{(4)}$ relates space-fixed to nanocrystal-fixed frames via rotationally averaged direction cosines. The field part, $S_{abcd}$, provides the polarization sequence of the three incident laser pulses and the signal field radiated in the phase-matched direction. The susceptibility part, $T_{\alpha\beta\gamma\delta}$, is given by the response of the quantum dot according to transition moments for the relevant transitions. The superscript, $m$, labels the various pathways for generating a signal, for example, ground-state recovery or excited-state absorption. The result of such an analysis is simply a scalar that determines the signal intensity, for example $C = 1/5$ for the VVVV polarization sequence.

The principle of the cross-polarized 3-TG experiment with a VHVH polarization sequence is that the sign of this rotational averaging factor changes if the exciton fine structure state changes during the delay time, $t_p$, between pump and probe. A sign
change in $C$ is equivalent to a $\pi$ phase shift of the radiated signal field $P^{(3)}(\tau, t_p, t)$ [105].

Immediately after the pump pulse sequence, apart from nanocrystals excited to an $F = 0$ state, half the excited nanocrystals in the ensemble, $n_{+1}$, will initially be in a state with $F = +1$, while the other half, $n_{-1}$, will have been photoexcited to a state with $F = -1$. Dark states are not observed. Under those conditions the rotational averaging contributes a factor of $C = 2/15$. However, if the exciton fine structure state for some population of quantum dots changes during $t_p$, then $n_{+1}$ and $n_{-1}$ decrease with corresponding increases in $n'_{-1}$ and $n'_{+1}$, where the prime indicates the change in exciton state. The latter population is spectroscopically indistinguishable from the initially excited population except that the rotational averaging factor changes sign for the signal associated with the population of quantum dots that are in the opposite $|F| = 1$ exciton fine structure state to that initially excited by the pump pulse; $C' = -2/15$. That sign change provides a means of detecting transitions $F = +1 \leftrightarrow F = -1$, that we call exciton spin relaxation to be consistent with similar dynamics known for quantum wells [123, 124]. The intensity of the homodyne-detected 3-TG signal therefore evolves according to,

$$I_{HOM}(t_p) \propto \int_0^\infty dt \left| P^{(3)}(0, t_p, t) \times \left[ \frac{2}{15} (n_{+1} + n_{-1}) - \frac{2}{15} (n'_{-1} + n'_{+1}) \right] \right|^2$$

(2.2)

where $P^{(3)}(0, t_p, t)$ is the induced third-order polarization as a function of pulse delay time between the temporally overlapped pump sequence and the probe, $t_p$, radiated by the sample over time $t$. Because the exciton transfer dynamics are faster than other contributions to the signal decay, $I(t_p)$, decays as the $F = \pm 1$ population evolves towards the equilibrium,

$$n_{+1} + n_{-1} \leftrightarrow n'_{-1} + n'_{+1}$$

(2.3)

The rate of exciton spin relaxation can therefore be determined because the cross-polarized 3-TG ensemble polarization decays as $\exp(-2k_s t_p)$. For homodyne-detected signals, the measured intensity decays approximately as $\exp(-4k_s t_p)$, where $k_s$ is the exciton spin relaxation rate. The $F = 0$ exciton state population that follows selection
rules for linearly-polarized light, always contributes a positive-signed signal, therefore, providing a background decaying according to the exciton recombination kinetics.

In Figure 2.2(a) we compare polarized 3-TG data collected in the $k_s$ phase matching direction using ultrafast laser pulses of 23 fs duration, centred on resonance with the lowest-energy exciton transition. The sample is 5.0 nm mean diameter nanocrystalline CdSe. The VVVV (all vertical) polarization sequence reveals the relatively long exciton recombination time as well as associated surface trapping dynamics, as is well known from pump-probe studies [92]. The VHVV trace is smaller by two orders of magnitude. Theoretically, that signal should be zero, but in practice it provides a measure of the baseline signal arising from imperfect polarization conditions. The VHVH signal is initially as intense as the VVVV signal, but decays rapidly to an effective baseline determined by the signal from the population of quantum dots initially excited to the $F = 0$ state. Marked quantum beats with the frequency $\omega_{LO} = 25.8$ meV, corresponding to the LO-phonon, are evident in these data. Similar quantum beats are known, for example, from the work of Mittleman et al [89].

The decay of the VHVH 3-TG signal derives from a distinctly different mechanism than those used in many ultrafast spectroscopies, where the decay of signal intensity is proportional to exciton recombination or spectral diffusion. Such methods are insensitive to exciton spin relaxation dynamics because of the degeneracy of the states, the large inhomogeneous broadening that obscures the fine structure, and the fact that circularly-polarized selection rules do not yield a suitable anisotropy experiment for an isotropic ensemble. The VHVH 3-TG experiment relies on an interference of polarizations from an ensemble to produce the measured intensity decay, where the signal polarization changes sign after any exciton spin flip. Thus the measurement is unaffected by inhomogeneous line broadening. However, the exciton transfer rate is strongly size-dependent, so we actually measure a distribution of rates according to the overlap of the laser pulse spectrum with the absorption band. Such a distribution appears as a single exponential in a curve.
Figure 2.2: (a) Comparison of 3-TG data [5.0 nm diameter CdSe, 293 K in a poly (butylmethacrylate) free-standing film] for the VVVV, VHVH, and VHVV polarization sequences. For perfect polarization of the pulses, there would be no signal for the VHVV sequence. (b) VHVH 3-TG data in the $k_s$ phase matched signal direction (points) for CdSe nanocrystals, labelled according to their average radii. The solid lines correspond to fits using Equation 2.4.
fitting procedure [131].

Figure 2.2(b) shows the decay of the VHVH 3-TG data for CdSe quantum dots of various sizes. The VHVH 3-TG signals contain a long time decay contribution associated with exciton recombination, but the decay is dominated by $k_s$. The marked size-dependence of this exciton transfer rate, $k_s$, is evident. To analyze these data, input parameters for a nonlinear least-squares analysis were obtained using a Hankel singular value decomposition algorithm. For the VHVH 3-TG signals, the exciton recombination rate $k_\infty$ was also a fixed parameter. Analysis of the VHVH 3-TG data retrieved fits according to

$$I_{HOM}(t_p) \approx A_1 e^{-4k_s t_p} + A_{LO} e^{-2k_{LO} t_p} \cos(\omega_{LO} t + \phi) + A_3 e^{-k_\infty t_p}$$  \hspace{1cm} (2.4)

shown as the solid lines. Here, $k_{LO}$ is the damping rate for quantum beats assigned to the LO-phonon frequency and $\phi$ is the phase of the oscillations. This is the usual way to obtain an approximate fitting of the homodyne-detected transient grating data [132]. For the fastest decaying homodyne-detected signals, the first exponential in the fit actually represents a cross term between the exciton reorientation term and damping of the LO-phonon. We have verified that by reconstructing homodyne-detected data from the real and imaginary parts of heterodyne-detected data [102]. It was necessary to correct for those entangled kinetics in the results for the two smallest quantum dots. Detailed modelling of the kinetics shows their precise relationship to the measured signals, as reported elsewhere along with heterodyne-detected data [102, 104].

The rates of exciton spin relaxation versus mean diameter of the quantum dots are plotted in Figure 2.3. Examination of these data suggests that the exciton spin relaxation rate $k_s$ depends on quantum dot radius $R$ with an attenuation going as $\sim R^{-4}$ to $R^{-6}$. Considering a Fermi golden rule rate expression, $k_s = (2\pi/\hbar)|V_{LR}|^2 \rho_F$ where $V_{LR}$ is the long-range exchange interaction and $\rho_F$ is the density of final states, that result is consistent with the anticipated size-dependence of the long-range contribution to the
Figure 2.3: Plot of the exciton spin relaxation rate (symbols) vs. mean radii of the quantum dots. A point obtained from heterodyne-detected data [102] is marked with an asterisk. The dashed line is a calculation of the rate assuming a Fermi Golden rule expression for the rate (see text) and an empirical $R^{-3}$ form of the long-range exchange interaction.

exchange interaction for approximately spherical quantum dots. Tagakahara [116] estimates that size-dependence of $V_{LR}$ to follow $\sim R^{-3}$, while a dependence closer to $R^{-2}$ is predicted by the atomistic calculations reported by Franceschetti et al [110]. Note, as explained previously, that the above discussion presents our initial hypothesis for the exciton spin flip mechanism, providing a historical perspective on the experiment, and does not represent our current understanding – see Chapter 3.

2.5 Conclusion

In conclusion, we have shown that it is possible to probe the interactions between the quantum dot exciton fine structure states through measuring the dynamics of transitions
among those states. This was made possible by using an ultrafast transient polarization grating method and making use of the quantum dot selection rules for absorption of circularly polarized light. Significantly, it was demonstrated that such an experiment is possible even in a rotationally isotropic system. The results for colloidal CdSe quantum dots revealed a strong size-dependence for the exciton spin relaxation. A consequence of these observations is that internal exciton spin relaxation proceeds more rapidly than resonance energy transfer between small quantum dots, thus influencing orientation factors and hampering opportunities for using resonance energy transfer to transmit exciton spin states through space [133].

2.6 Supporting Information

In order to study carrier dynamics, the decay of a spatial population grating was monitored using an ultrafast probe pulse. The full width half maxima (FWHM) and the time bandwidth products (TBWP) of the laser pulses are reported in Table 2.1. The absorption spectra and the corresponding laser profiles are presented in Figure 2.4. The transient grating signals discussed in this chapter were collected in the phase matched direction corresponding to the wavevector \( k_s = -k_1 + k_2 + k_3 \) as shown in Figure 2.5. In addition to the signals previously discussed we also collected time integrated data for the following polarization combinations: VVVV, VVHH, HHVV, VHVH, HVHV, HVVH, VHHV, HHVH, HVVV, VHVV and VVHV in both the \( k_r \) and the \( k_s \) signal directions. These polarization combinations comprise the three classes of transient grating signals that are obtained from the various polarization dependencies: normal transient gratings, baselines and the crossed linear polarization signal.

Due to the broad spectral linewidth of the laser pulses as well as the size-distribution within the sample, it is possible for different states within the ensemble to be probed by
Table 2.1: VHVH Polarized Transient Grating Experimental Parameters for CdSe Passivated with TOPO in a Free-Standing Polymer Film

<table>
<thead>
<tr>
<th>Nanocrystal Radius (nm)</th>
<th>Centre Wavelength (nm)</th>
<th>FWHM (fs)</th>
<th>TBWP(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.55</td>
<td>515</td>
<td>36</td>
<td>0.61</td>
</tr>
<tr>
<td>1.70</td>
<td>530</td>
<td>25</td>
<td>0.56</td>
</tr>
<tr>
<td>1.95</td>
<td>550</td>
<td>24</td>
<td>0.57</td>
</tr>
<tr>
<td>2.50</td>
<td>590</td>
<td>20</td>
<td>0.62</td>
</tr>
</tbody>
</table>

\(^a\)Assuming Gaussian pulse envelopes

each of the optical interactions. For instance, both pump beams could interact with one particular state while the probe beam interacts with a different state. This situation would be observed as exciton recombination, which contributes to the long time offset. Alternatively, the pump beams could create a superposition that would provide a contribution that only appears in the coherent spike.

2.6.1 Additional Supporting Measurements

Additional measurements were performed on a model dye system (Rhodamine 6G in ethanol), CdSe quantum dot samples passivated with TOPO and dispersed in toluene as well as a CdSe quantum dot sample passivated with a different ligand (dodecylamine) and suspended in a free-standing PMMA film. The analysis of the dye solution served as a control measurement since there should be no difference in the signal observed for the all vertical, VVVV, and the crossed polarization, VHVH, configuration. This was done to ensure that the observed signal was not due to an experimental artifact. The VVVV and VHVH transient gratings in the \(k_s = -k_1 + k_2 + k_3\) signal direction for the dye are presented in Figure 2.6. The CdSe solution sample was analyzed to verify that there is no significant contribution attributable to the polymer matrix. Similarly, a CdSe
Figure 2.4: Absorption and laser spectra for various sizes of CdSe nanocrystal samples passivated with TOPO and embedded in an optically clear polymer film.

Figure 2.5: The beam arrangement for the 3TG experiment is presented schematically. (Top) The incident excitation beams have been split into three components with wavevectors $k_1$, $k_2$ and $k_3$ generating the transient grating signal which appears at $k_s = -k_1 + k_2 + k_3$ according to phase matching conditions. (Bottom) An in-plane view of the beams after the sample, perpendicular to the perspective of the top image.
quantum dot sample passivated with a different ligand (dodecylamine) and suspended in a PMMA film was analyzed to study the possible surface state contributions to the observed response. The VVVV transient gratings for a CdSe sample capped with TOPO in a polymer film, a CdSe sample capped with TOPO dispersed in a toluene solution and a CdSe sample capped with dodecylamine in a polymer film are presented in Figure 2.7(a). The comparison is complicated a little by the fact that the CdSe nanocystal cores in each of the three samples presented were not exactly the same size. The absorption maxima for the amine-capped sample corresponded to 523 nm, the absorption maxima for the sample in toluene solution corresponded to 525 nm and the absorption maxima for the sample in a polymer film was 530 nm. The VHVH transient gratings for the three CdSe samples are presented in Figure 2.7(b). The difference in surface state contributions between the CdSe samples passivated with TOPO and the one passivated with dodecylamine are visible in the VVVV trace, however, the fine structure equilibration time scales are short enough in the VHVH trace that the surface states do not significantly contribute. The time scales obtained from the samples, CdSe capped with TOPO, analyzed in solution versus the samples analyzed in polymer film do not show any significant differences.
Figure 2.6: Transient grating traces measured in the $k_s = -k_1 + k_2 + k_3$ signal direction of a Rhodamine-6G dye solution in ethanol plotted on a semi-log scale. The top trace corresponds to the VVVV polarizer configuration while the bottom trace corresponds to VHVH.
Figure 2.7: Transient grating traces plotted on a semi-log scale obtained in $k_s = -k_1 + k_2 + k_3$ signal direction for the (a) VVVV polarization combination and the (b) VH VH polarization combination. In both (a) and (b) the top trace (black) corresponds to the CdSe capped with TOPO in a polymer film (absorption peak centred at 530 nm), the middle trace (pink) corresponds to the dodecylamine capped CdSe (absorption peak at 523 nm) and the bottom trace (green) corresponds to the CdSe capped with TOPO in a toluene solution (absorption peak at 525 nm). The traces have been offset for clarity.
Chapter 3

Spin Relaxation in Zinc Blende and Wurtzite CdSe Quantum Dots
3.1 Chapter Summary

Using the experimental methodology initially demonstrated in Chapter 2, this chapter reports exciton spin relaxation dynamics in colloidal wurtzite and zinc blende CdSe quantum dots. The zinc blende (cubic base) quantum dots have a simpler fine structure as compared to wurtzite (hexagonal base) due to differences in the crystal field splitting. Comparing fine structure relaxation timescales, which are associated with changes in the total angular momentum of the occupied exciton state (an exciton ‘spin flip’), in sets of nanocrystal samples with different fine structure degenerancy provides insight into the underlying mechanism of the relaxation process. As opposed to the previous chapter, the spin flip mechanism described in this section corresponds to our current understanding of the fine structure equilibration process.
Chapter 3. Spin Relaxation in Zinc Blende and Wurtzite CdSe QDs

3.2 Introduction

Quantum confined semiconductor nanocrystals are characterized by size-dependent optical properties, arising from the spatial confinement of the electron and hole wavefunctions. In these materials, the physical size of the nanocrystal determines the degree of confinement and, therefore, changing the size of the nanocrystal shifts the energy levels [134]. For example, in quantum dots (QDs), which are spherical quantum confined semiconductor nanocrystals, the degree of confinement is determined by the diameter of the nanocrystal. This is analogous to the picture of quantum confinement described by the simple model of a particle in a box [135]. As a result, QDs have electronic states of discrete energies as in atoms and molecules. These well-defined electronic states have been considered as candidates for the applications of quantum information and spintronics [20, 21], where the spins are used as units for data processing and electronic devices.

Photoexcitation of a strongly quantum confined QD system, such as CdSe, results in the formation of excitons. Excitons are electron-hole pairs that are bound through an energy lowering Coulomb interaction. The optical spectroscopy of CdSe QDs can be described in terms of single excitation configurations associated with transitions from a four-fold degenerate conduction band to a two-fold degenerate valence band. These configurations are mixed through the exchange interaction between the electron and hole, resulting in the exciton fine structure [109, 136, 137]. Due to strong spin-orbit coupling in CdSe, the fine structure states are not eigenstates of spin. As a result, these levels of the lowest energy exciton state of CdSe QDs are labelled in terms of their total angular momentum, $F$, which is a combination of the spin and orbital angular momenta and defines the spin of an exciton. The $F = 0$ states, an upper bright and a lower dark (triplet state), have linearly polarized selection rules. The $F = \pm 2$ states are optically dark. In a nanocrystal with wurtzite structure, the upper and lower $F = \pm 1$ states are optically active and have selection rules that allow for photoexcitation of the $+1$ and the $-1$ levels by right- and left-circularly polarized light respectively. In nanocrystals with a
Figure 3.1: Schematic of the exciton fine structure associated with the lowest energy exciton state for CdSe QDs with (a) wurtzite and (b) zinc blende crystal lattices. The dashed lines indicate dark states while the solid lines represent bright states. The fine structure levels are presented with representative absorption spectra from CdSe QDs with the corresponding crystal structures.

In a CPH-3TG experiment, four ultra-short coherent laser pulses with crossed lin-
ear polarizations are employed: pump pulse pair, probe, and local oscillator. When two
cross linearly polarized light pulses interact in the medium, a periodic spatial pattern of
right- and left-circular polarization, called a ‘polarization grating’, is generated [127]. If
the crystallographic c-axis of each QD is aligned in the laboratory frame, according to
the optical selection rules of wurtzite and zinc blende semiconductors, the polarization
grating turns into a pattern of angular momentum projections between \( F = +1 \) and
\( F = -1 \) exciton states, i.e. a spin grating [139]. Despite the fact that the colloidal CdSe
QD samples are not oriented, photoselection can still occur as a consequence of their
complex transition dipole moments and the polarization sequence [125]. In the CPH-
3TG experiment, a time-delayed probe pulse is diffracted off the spin grating, inducing
the radiation of the signal in the same direction as the local oscillator pulse. This signal
decays as the transient spin grating becomes randomized by spin relaxation in the exciton
fine structure.

Some of the transitions that occur in the exciton fine structure involve a flip of the sign
of the total angular momentum, i.e. exciton spin + to − and vice versa. The transitions
accompanying the exciton spin flip are manifested as a decay of the measured CPH-3TG
signal. This signal becomes zero when the system reaches a dynamic equilibrium where
there are an equal number of excitons with flipped and conserved spins. Thus, the CPH-
3TG technique follows the history of an exciton spin by measuring whether or not the
total angular momentum of an exciton state has changed since its initial excitation [49].

Here, it should be noted that this technique measures the spin relaxation dynamics of
randomly oriented colloidal QDs since the signal decay arises from the destructive inter-
ference between rotationally averaged responses of excitons with conserved and flipped
spins [105]. This is in contrast to other techniques that have been used for studying
spin relaxation in QDs, for example, time-resolved Faraday rotation [140, 141, 142] and
time-resolved photoluminescence with circularly polarized light [143, 144, 145, 146]. In
both techniques, spin orientation is optically created by circularly polarized photoexci-
tation of suitably oriented QDs and its subsequent relaxation is manifested as the decay of the signal. However, since these techniques rely on sample alignment to maximize spin orientation, they have been mostly applied to study spin relaxation in well-aligned self-assembled QDs as opposed to the randomly oriented colloidal system studied in this work.

In the present work, we report exciton spin flip rates for a series of different sized colloidal zinc blende and wurtzite CdSe QDs measured using the CPH-3TG technique. The paper is organized as follows. The next section presents the experimental details of the ultrafast measurements as well as the sample preparation and characterization. The third section describes the results and discusses them considering the differences between the fine structure of the lowest energy exciton state in the wurtzite and zinc blende QDs. In the last section, we summarize the results and present conclusions.

3.3 Experimental

In order to study the difference between the exciton spin flip rate associated with cubic and hexagonal crystal structures, we used the CPH-3TG technique to measure two series of different sized colloidal CdSe QDs, one set with wurtzite structure and the other with zinc blende. Colloidal wurtzite CdSe QD samples capped with trioctylphosphine oxide (TOPO) ligands were prepared using an organometallic technique [36]. The zinc blende colloidal CdSe QD samples were synthesized following the method of Deng and co-workers [147]. A series of five wurtzite and six zinc blende samples with varying average radius were studied. The average radius of each of the wurtzite samples was 1.6, 1.69, 1.79, 1.96 and 2.13 nm, while the average radius of the zinc blende samples was 1.37, 1.49, 1.67, 1.77, 2.04 and 2.8 nm. All the QD samples studied were approximately spherical in shape. The samples were washed using a successive precipitation method, which used
methanol (wurtzite samples) or dry acetone (zinc blende samples) to precipitate out the QDs. They were then isolated by centrifugation and re-dispersed in toluene.

The wurtzite and the zinc blende samples were characterized using absorption measurements, scanning transmission electron microscopy (STEM), to verify the morphology, and powder X-ray diffraction (PXRD), to verify the crystal structure. The STEM images were obtained using a Hitachi HD-2000 dedicated STEM operating at 200 kV. The PXRD measurements were obtained using a Siemens D5000 diffractometer using a high-power Cu Kα source operating at 50 kV and 35 mA with a Kevex solid-state detector. A step scan mode was used for data collection with a step size of 0.02 deg and time of 2.5 s per step. Absorption measurements were taken before and after the CPH-3TG experiments to verify that no degradation had occurred.

A representative STEM image, a representative PXRD measurement for one of the zinc blende samples, and absorption traces for all the samples measured are shown in Figure 3.2. The average size of the QDs in each sample was determined using the position of the first exciton peak [148] since the absorption spectrum is a measurement of the entire ensemble. The error in the size-distribution of each sample was estimated from the full width at half maximum of a Gaussian function fit to the first exciton peak, which provides a measure of the ensemble distribution of QD sizes. Care was taken to avoid the second transition to the high-energy side of the first transition. Due to synthetic considerations, the average size-distribution of the zinc blende QDs was larger than the average size-distribution of the wurtzite samples. The error in the measured exciton spin relaxation rate was estimated from the spread of the values obtained from repeat measurements.

The heterodyned third-order transient grating (3TG) experiments were performed using a previously described experimental setup [104]. In the 3TG experiment, two non-collinear, temporally coincident beams interact with the sample, creating a transient grating. After a time delay, $t_p$, a probe pulse interacts with the sample to monitor the de-
Figure 3.2: (a) Representative scanning transmission electron microscope (STEM) image of the zinc blende CdSe QD samples studied. The QDs shown in the STEM image are from the $R = 1.37$ nm zinc blende sample (b) Representative powder X-ray diffraction (PXRD) measurement of the zinc blende CdSe QDs studied, shown with the predicted peaks for the $F - 43m$ or zinc blende point group. This particular PXRD measurement was performed on the $R = 2.04$ nm zinc blende sample. Normalized absorption spectra, offset for clarity, for the (c) wurtzite and (d) zinc blende CdSe QD samples studied.
Chapter 3. Spin Relaxation in Zinc Blende and Wurtzite CdSe QDs

cay of the grating, and the signal is radiated into the $-k_1 + k_2 + k_3$ signal direction, which is spatially overlapped with the local oscillator beam to allow for heterodyned detection.

The 3TG experiment allows for individual polarization control of both pump interactions, the probe and the signal (using an analyzer). By permuting the linear polarizations of the pumps, probe and analyzer, it is possible to cycle through the tensor elements of the third order signal [125, 149]. In the present experiment, the polarization combinations VVVV, VHVH and VHHV were measured, where V and H correspond to vertical and horizontal linear polarizations, with the two pumps, the probe and the analyzer labelled from left to right. The 3TG signals measured with the latter two polarization sequences, VHVH and VHHV, correspond to CPH-3TG signals, which are sensitive to exciton spin relaxation dynamics. The laser pulse was tuned to be resonant with the lowest energy exciton transition of each of the QD samples. Further details of the experiment have been described elsewhere [49]. All measurements were performed at 293 K using low incident laser intensity to avoid higher order, biexciton or thermal grating induced effects. The QD samples were suspended in dilute solution in toluene at an optical density of approximately 0.3 in a 1 mm path length cuvette.

3.4 Results and Discussion

The 3TG signals were collected with VVVV, VHVH, and VHHV polarization sequences for each of the wurtzite and zinc blende samples. The heterodyned 3-TG measurements allow us to measure both the real (refractive index) and imaginary (absorption) components of the signal. However, we are only interested in the absorptive part of the signal and, therefore, only the imaginary component was analyzed.

The VVVV 3TG signal monitors the relaxation dynamics of the exciton population, which is the same type of information obtained from a pump-probe experiment. The
VVVV trace consists of a relatively slow decay associated with exciton recombination and surface trapping dynamics. The VHVH and VHHV signals, that is, CPH-3TG signals, contain both the exciton spin flip corresponding to a fast exponential decay, as well as the exciton population dynamics found in the VVVV signal. However, the cross-polarized VHVH and VHHV signals are dominated by spin flip dynamics with the population dynamics comprising a small percentage of the overall signal and decaying on a much longer timescale. Although the VHVH and VHHV signals contain the same information, they are oppositely signed. This is due to the fact that the rotational averaging factors for the two polarization combinations are oppositely signed, producing a positive VHVH and a negative VHHV exciton spin flip contribution to the signal. More specifically in the CPH-3TG measurement, excitons with flipped and with conserved (the same sign of total angular momentum that they had upon initial excitation) spins radiate third order signals that are oppositely signed in a rotationally averaged ensemble [105].

The observed signal from the 3TG measurement can be written as,

$$I_{HET}(t_p) \propto \int_0^\infty dt \, Re\{E_{LO}^*(t_p, \Delta \phi)P^3(0, t_p, t)[C(n_{\uparrow}^{-1} + n_{\downarrow}^{-1}) + C'(n_{\uparrow}^{-1} + n_{\downarrow}^{-1})]\} \quad (3.1)$$

where $C$ and $C'$ are the rotational averaging factors for the conserved and flipped signs of the total angular momentum respectively and the subscript $LO$ refers to the local oscillator. For the VHVH (VHHV) signal, these factors are $C = 2/15(-2/15)$ and $C' = 2/15(2/15)$. In contrast, for the VVVV signal, $C = C' = 1/5$. As a result, the VVVV 3TG signal does not contain the same exciton spin flip dynamics that appear in the CPH-3TG signals. The details of the rotationally averaging factors have been discussed elsewhere [104, 125].

In the CPH-3TG experiment, we use linear polarization combinations. This means that excitons can also be excited to the $F = 0$ state. However, population in the $F = 0$ state does not directly contribute to the exciton spin flip rate. Instead, it contributes to the overall positive long delay time offset of the CPH-3TG signals [102].

Representative VVVV, VHVH and VHHV 3TG signals are shown in Figure 3.3(a).
Figure 3.3: (a) Third order heterodyne transient grating signals for the polarization combinations VVVV, VHVH and VHHV from top to bottom respectively for the $R = 2.8$ nm zinc blende sample. The inset shows the same VVVV, VHVH and VHHV signals plotted with the time axis on a log scale. (b) Semi-log plot of the VHVH signal for two similar sized samples, one with zinc blende ($R = 2.04$ nm) and the other with wurtzite ($R = 2.13$ nm) crystal structures showing a faster spin flip timescale for the zinc blende sample.

The traces shown were obtained for the 2.8 nm radius zinc blende QD sample. Figure 3.3(b) shows a comparison of short time delay behaviour for VHVH traces of similarly sized zinc blende (2.04 nm radius) and wurtzite (2.13 nm radius) QD samples. The fast decaying component in these traces corresponds to the exciton spin flip dynamics. It is clear that the zinc blende sample has a significantly faster spin flip rate than the similarly sized wurtzite sample. The oscillations superimposed on the decay at time delays of less than 2 picoseconds are associated with the well-known longitudinal optical phonon mode of CdSe [89]. This mode appeared in all of the data sets and corresponded to a frequency of approximately $206 \text{ cm}^{-1}$.

The data sets were analyzed to obtain the contributing timescales using an empirical
fitting function [105]. The VVVV signal was fit using three exponentials, which was the minimum number that could recover the decay. One exponential, associated with exciton recombination had a long nanosecond timescale that could not be fully resolved in our experiments, which had a maximum pump-probe time delay, $t_p$, of 850 picoseconds. The other two exponentials likely correspond to surface trapping dynamics and were on the order of picoseconds to tens of picoseconds, consistent with previous results [49, 60, 93, 99, 102]. The timescales and relative amplitudes obtained from the VVVV data were then used to analyze the VHVH and VHHV traces, allowing us to account for the exciton population relaxation dynamics in the CPH-3TG signals and to obtain the exciton spin flip rate. The VHVH and VHHV data sets were fit using the function [104, 105],

$$I_{VHVH,VHHV}(t_p) = [A_1 \exp(-2k_s t_p) + A_2] I_{VVVV}(t_p)$$  \hspace{1cm} (3.2)

where $k_s$ is the exciton spin flip rate and $I_{VVVV}$ is the VVVV signal. $A_1$ and $A_2$ account for the amplitudes of the exciton spin flip and exciton recombination contributions to the CPH-3TG signal respectively.

Our recent work has shown [49, 103] that relaxation within the fine structure in larger QDs can be complicated. In large CdSe QDs, the VHVH and VHHV CPH-3TG signals have a biexponential spin flip decay instead of the single exponential described in the fitting function, Equation 3.2. From kinetic simulation of relaxation in the exciton fine structure, it was found that the biexponential decay arises from complex interplay of various spin flip transitions involving hole spin, electron spin and exciton spin. However, since the nanocrystal QDs studied in this report were approximately spherical and of small enough dimensions, only one exponential was observed.

An average exciton spin flip rate, $k_s$, was determined by fitting the VHVH and VHHV traces using Equation 3.2 and averaging over the repeat measurements for each sample. The exciton spin flip rates determined for each sample are shown in Figure 3.4. Comparing the average spin flip rates for each sample, we observed that the rates measured for the zinc blende QDs are larger than those measured for the wurtzite samples. This
Figure 3.4: Log-log plot of the exciton spin flip rate versus the average QD radius. The diamond markers correspond to the rate determined for the zinc blende CdSe QD samples, while the squares correspond to the measured rate for wurtzite CdSe QDs. The circles are additional data points from Chapter 2 for the relaxation rate associated with wurtzite spherical QDs. The dashed line is an $R^{-4}$ power law line fit through the wurtzite QD data points. The solid line is also an $R^{-4}$ power law line to guide the eye. The error bars were obtained as described in the text.

corresponds to a faster timescale for comparably sized QDs. The difference in rate can be seen directly in Figure 3.3(b), with the VHVH trace for the zinc blende sample decaying more rapidly than that of the wurtzite sample. The exciton spin flip rates measured for the wurtzite QDs in the present experiment are consistent with those reported in Chapter 2. The spin flip timescales from the previous chapter are also presented in Figure 3.4 for comparison.

The observed exciton spin flip rates for both the wurtzite and zinc blende QD samples follow specific size-dependence with respect to the average radius. In Figure 3.4, the dashed and the solid line correspond to an $R^{-4}$ size-dependence of the rate, where $R$ is the average radius of a sample. Previous work has shown that the primary relaxation
process in wurtzite CdSe QDs is associated with the $F = +1(-1)$ to $F = -2(+2)$ (‘hole spin flip’) transition and that this process follows a $R^{-4}$ dependence [49, 102]. In our present measurements, we observe that the zinc blende CdSe QDs also follow the same $R^{-4}$ dependence, which suggests that they are undergoing the same hole spin flip process.

The $R^{-4}$ size-dependence and primary relaxation pathway involving the dark $F = \pm 2$ state is different than our preliminary hypothesis for the spin flip mechanism, which we proposed with the initial measurements as presented in Chapter 2. This first concept involved a long-range exchange mediated spin flip with an $R^{-3}$ size-dependence. However, as research progressed and many additional data points were obtained [49, 102, 103, 104, 105], it became clear that the transitions within the fine structure were more complex and that the spin flip followed an $R^{-4}$ power law. Note that this trend may break down for very small nanocrystals, approaching cluster size, where other contributions may dominate.

The observed $R^{-4}$ dependence of the exciton spin flip rate for both wurtzite and zinc blende QDs is likely associated with the large spin-orbit coupling parameter in CdSe, which is just over 400 meV for both bulk wurtzite [150] and zinc blende [151]. In addition to strong spin-orbit coupling, CdSe does not have inversion symmetry (non-centrosymmetric) and is composed of heavy atoms. In this type of system, due to the Dresselhaus effect, the spin-orbit interaction couples the $F = +1(-1)$ with the $F = -2(+2)$ exciton states. Using a Fermi Golden Rule rate expression, the spin flip rate associated with the $F = +1(-1)$ to $F = -2(+2)$ spin flip transition is described as,

$$k_s = \left(\frac{2\pi}{\hbar}\right)|M|^2\rho_f \quad (3.3)$$

where $\rho_f$ is the density of final states and $M$ is the matrix element that promotes the $F = +1(-1)$ to $F = -2(+2)$ transition. As a result of the Dresselhaus effect, $M$ scales as $1/a^2$, where $a$ is the exciton radius, and therefore, $k_s$ scales as $1/a^4$ or as $R^{-4}$ for a strongly confined system. Further details of the above discussion can be found in one of our previous papers [49].
We observed that the exciton spin flip rate is larger for zinc blende QDs compared to wurtzite QDs of a given size. Following our previously published kinetic model [102, 49], the transition between the upper $F = +1(-1)$ and the lower $F = +1(-1)$ states occurs rapidly since there is no change in the total angular momentum. The difference in energy between these levels is fairly small; on the order of $kT$ at room temperature for both crystal structures, and as such, through coupling to a bath spectral density these transitions can occur rapidly. In addition, the transition between the upper $F = +1(-1)$ and the lower $F = +1(-1)$ states does not have a direct effect on the CPH-3TG signal since $F$ does not change. It is reasonable to assume that the exciton spin relaxation dynamics start from the lower $F = +1(-1)$ state and are associated with transitions to the $F = -2(+2)$ state involving a change in the sign of the total angular momentum for both the wurtzite and the zinc blende QDs. This assumption is in agreement with previously published kinetic simulations that were used to analyze exciton spin flip data in CdSe QDs [49]. The change in the exciton spin flip rate between zinc blende and wurtzite QDs can only be understood in terms of the modification of the level structure or coupling between the fine structure states resulting from the differences in the crystal structures. This is likely due to two possible effects: (1) a change in the magnitude of the Dresselhaus effect and thus the coupling between $F = +1(-1)$ and the $F = -2(+2)$ states or (2) an energy conservation argument due to the close energy spacing of the $F = +1(-1)$ and the $F = -2(+2)$ states.

In terms of the first possibility, the Dresselhaus effect is known to depend on the symmetry of the crystal structure [152], which could account for the observed difference in the exciton spin flip rates between the wurtzite and the zinc blende QDs. The zinc blende structure consists of two interpenetrating face-centred cubic lattices whereas the wurtzite structure consists of two interpenetrating hexagonal close-packed lattices. Zinc blende has higher symmetry than wurtzite with equal lattice constants ($a = b = c$). On the other hand, wurtzite is anisotropic with lattice constants $a = b \neq c$. This difference
can modify the Dresselhaus effect and may affect the coupling factor mixing the lower $F = +1(-1)$ and the $F = -2(+2)$ states, resulting in a different factor for the zinc blende and wurtzite QDs. Greater mixing of the lower $F = +1(-1)$ and the $F = -2(+2)$ states would result in a faster exciton spin flip rate.

In terms of the second possibility, due to the larger degeneracy of the fine structure levels in the zinc blende QDs, the lower $F = \pm 1$ and the $F = \pm 2$ states are very close in energy. Note that although the lower $F = \pm 1$ and the $F = \pm 2$ states are much closer in energy in the zinc blende than in the wurtzite QDs, it is unlikely that the separation between them is exactly zero due to shape asymmetry and other perturbations. Dynamics between these states resulting in a spin flip could occur through coupling to a bath spectral density. Although the exact nature of this spectral density is unclear, the larger level spacing in the wurtzite QDs may account for the slower observed exciton spin flip rate.

The spin relaxation rates determined in this work can be compared to the results of previous studies [141, 142, 143, 144, 145]. However, the observed spin relaxation rate varies considerably depending on the temperature, the type of QDs (self-assembled or colloidal, charged or neutral), the type of carrier of interest (electron, hole, exciton), and external perturbation (external magnetic field, charging of QDs), making direct comparison between the studies difficult. In general, at low temperature and zero field, the electron spin relaxation time was determined to be on the order of hundreds of picoseconds to nanosecond timescales in self-assembled QDs [141, 142, 143, 144, 145], while it can be further extended up to millisecond timescale by laser cooling of a charged QD [153, 154]. In contrast, the hole spin relaxes faster than the electron spin with a relaxation time as short as tens of picoseconds [143, 144]. Since the spin flip rate measured by the CPH-3TG mainly originates from hole spin flip via transitions between bright $F = +1(-1)$ and dark $F = -2(+2)$ states, it should be compared to hole spin relaxation rates reported in the previous studies. In contrast to the intensely studied electron spin
relaxation time, much less is known about the hole spin relaxation dynamics. This is partly due to inaccessibility of time-resolved photoluminescence methods to study hole spin relaxation dynamics in neutral QDs. Only recently, hole spin relaxation dynamics of self-assembled QDs were measured in charged [143] and neutral QDs using an approach combining circularly and linearly polarized excitation [144], giving a hole spin relaxation time of 15 – 30 picoseconds at 77 K. Considering that our measurements were made at room temperature, using more strongly confined colloidal QDs, the hole spin flip times in the range of hundreds of femtoseconds to a few picoseconds in our work can be considered comparable to the results of the previous studies, although direct comparison between self-assembled and colloidal QDs might be inappropriate.

Spin relaxation in colloidal QDs has been studied as well using the time resolved Faraday rotation (TRFR) technique [141, 142]. The measured TRFR signal showed multi-exponential decays with components of ∼ 100 picosecond and 10 nanosecond timescales. However, the TRFR signal of colloidal QDs arises only from selected subsets that are suitably oriented at the moment of excitation. Additionally, the optical selection rules for circularly polarized light are poorly defined in majority of QDs oriented at a random angle. As a result, the origin of each decay component was not clearly assigned due to ambiguity arising from random orientation in addition to the size-distribution of colloidal QDs. This is in contrast to the CPH-3TG technique that selectively measures the spin relaxation dynamics in QD samples of random orientation. As a result, direct comparison between the timescales observed in these two techniques may not be reasonable.

The exciton spin flip rates we observed are on the order of hundreds of femtoseconds to a few picoseconds in both the wurtzite and the zinc blende QDs. Using the rotational averaging factors associated with the CPH-3TG experiments, we were able to unambiguously measure the spin relaxation dynamics in colloidal QD samples. Considering the fact that these measurements were made at room temperature on small colloidal QD systems, the observed timescales are consistent with other reported measurements of the
hole flip rate.

3.5 Conclusion

Using the CPH-3TG technique, we measured the exciton spin flip rate for a series of different sized CdSe QDs with wurtzite and zinc blende crystal structures. The exciton spin flip rate was found to follow an $R^{-4}$ size-dependence and is associated with the $F = +1(-1)$ to $F = -2(+2)$ transitions, which are coupled through the large spin-orbit interaction by the Dresselhaus effect. We observed that the zinc blende QDs have a larger spin relaxation rate than wurtzite QDs. The larger exciton spin flip rate in zinc blende can only be understood through the differences in the fine structure levels between the cubic and the hexagonal crystal structure arising from the crystal field splitting or changes in the mixing between the fine structure states.
Chapter 4

Nonlinear Optical Approach to Multiexciton Relaxation Dynamics in Quantum Dots
4.1 Chapter Summary

The previous two chapters described third-order nonlinear experiments, which studied relaxation within the fine structure of the lowest energy exciton state of colloidal CdSe spherical nanocrystals. This chapter explores a different facet of the photophysics of semiconductor nanocrystals through third- and fifth-order nonlinear ultrafast experiments that explore higher order excitation dynamics in colloidal CdSe nanocrystals.

Unlike the majority of molecular systems, quantum dots can accommodate multiple excitations, which is a particularly important attribute for potential lasing and solar cell applications. This chapter demonstrates the concept of using \( n \)th-order nonlinear spectroscopies in the transient grating configuration as a means of selectively exciting \((n - 1)/2\) excitons and probing the subsequent relaxation dynamics. Through comparison of third- and fifth-order experiments for CdSe colloidal quantum dots, this chapter reports a direct observation of multiparticle dynamics on ultra-short time scales. Time constants associated with multiexciton recombination and depopulation dynamics are reported. Deviation from a Poisson model for the distribution of photoexcited excitons, biexcitons and triexcitons is also discussed.
4.2 Introduction

Quantum confined semiconductor nanocrystals or quantum dots are materials characterized by size tuneable properties fundamentally different from those observed in the bulk [38, 41, 134, 155]. One of the interesting aspects of these systems is the way in which they differ from molecules, specifically in terms of their capacity to accommodate multiple excitations. That property has recently been the subject of investigation [24, 25] since it is of particular importance for solar energy conversion [22, 23, 24] and has provided further motivation to explore the microscopic details of exciton dynamics and relaxation in quantum dots.

Bound electron hole pairs, known as excitons, are formed upon optical excitation of bulk semiconductors. Under sufficiently intense excitation, excitons will continue to form until a point, known as the dissociation threshold, where screening interactions dominate over the Coulomb interaction and an electron-hole plasma is formed [156]. This threshold imposes a limit on the maximum number of excitons per unit volume and usually corresponds to approximately one bulk excitonic volume, as determined by the inverse cubic power of the exciton Bohr radius.

Conversely in strongly confined quantum dots, where nanocrystal radii are smaller than the exciton Bohr radius, the imposed spatial restriction leads to an enhanced Coulomb binding interaction [157, 158, 159], an increase in the exchange energy [113, 160, 161, 162, 163] and a reduction in the relative effect of screening because, in these finite structures, there is a large difference between the dielectric constants of the quantum dot and that of the surrounding material [158]. As a result, multiexciton states in which more than one exciton occupies the bulk excitonic volume can exist with an enhanced binding energy.

Notably, quantum dots display large optical nonlinear effects. These nonlinearities provide a novel direction from which to approach the issue of dynamics through spectroscopy. Using \((n + 1)\)-wave mixing techniques and the associated phase matching con-
ditions, it is possible to spatially isolate \( n \)th order contributions to the observed signal [164, 165]. The order of the spectroscopy is determined by the number of field-matter interactions, allowing effective experimental isolation of the dynamics associated with a specific number of excitons per quantum dot. This follows directly from the concept that an \( x \) photon absorption process can produce \( x \) excitons and includes, for example, the creation of a biexciton via a two photon absorption [75, 166, 167, 168, 169].

Biexcitons and other multiexcitons have been studied both theoretically and experimentally to gain insight into their fundamental physical properties. These excited electronic states are potentially relevant to schemes for quantum computing and cryptography [170, 171, 172] or as a source for entangled photon pairs [173]. Furthermore, a thorough understanding of the relaxation dynamics of these states is essential for the development and refinement of quantum devices such as single-photon emitters [174, 175, 176] and lasers [4, 177, 178].

This chapter demonstrates the concept of using \( n \)th-order transient grating spectroscopy as a direct, systematic experimental technique to explore multiexciton states and the details of the associated relaxation dynamics through selective excitation of \((n - 1)/2\) excitons. We report a direct observation of multiparticle dynamics on an ultra-short time scale through comparison of third- and fifth-order experiments for CdSe colloidal quantum dots. Specifically, the selective transient grating method enables the study of relaxation dynamics for multiexciton systems.

The technique we report here differs from the ubiquitous pump-probe technique in two important ways. A lower incident intensity is required due to the fact that the separation of the pump interaction allows for spatial isolation of the signal components based on phase matching conditions and beam geometry. In this way, it is only necessary to use the minimum intensity required to observe a third-, fifth- and so on order signal as opposed to pumping a large amount of population density out of the ground state. Furthermore, the spatial division of the signal results in the contributions from
different multiexciton states being emphasized in separate signal directions. Since the individual pump interactions can originate from different beams, this allows for control of the characteristics of each interaction including polarization, wavelength and intensity. This directly affects the nature of the grating formed in the sample and can potentially be used to explore a wide variety of dynamic behaviour. In this chapter, we focus on a one colour, single polarization, low intensity, three beam experiment to selectively probe the band edge dynamics.

4.3 Experiment

4.3.1 Sample Preparation and Experimental Procedure

Experiments were performed on colloidal CdSe quantum dot samples prepared by an organometallic synthesis route [36] and passivated with trioctylphosphine oxide (TOPO). All measurements were made at room temperature (293 K). Five of the analyzed samples with average radii of 1.38, 1.67, 1.9, 1.96 and 2.36 nm were dispersed in toluene. Two samples with average radii of 1.56 and 1.76 nm were suspended in a polymethylmethacrylate (PMMA) film. We also studied a sample with a radius of 1.64 nm capped with dodecylamine and suspended in a PMMA film to consider surface effects. The samples in solution were continuously pumped through a 200 µm path length flow cell to eliminate possible contributions from thermal effects and sample oxidation. The polymer film samples were mounted in an evacuated optical cryostat and kept under vacuum to prevent sample oxidation. To minimize the possibility of local field effects and inter-dot interactions, the optical density of each sample was \( \sim 0.2 - 0.4 \).

In order to study carrier dynamics, a pair of pump pulses resonant with the lowest exciton peak excited the sample and the decay of a spatial population grating was monitored using an ultrafast probe pulse. The general experimental setup has been previously
described [90]. We generated ultra-short laser pulses with temporal full width half maxima of 50, 36, 24, 26, 22, 25, 24 and 20 fs, centred at 2.52, 2.14, 2.37, 2.36, 2.32, 2.27, 2.25 and 2.13 eV respectively, using a noncolinear optical parametric amplifier pumped by a regeneratively amplified Ti-sapphire laser. The resulting beam was split into three parallel components, which were aligned into an equilateral triangle configuration and focused into the sample as shown schematically in Figure 4.1(a) and (b). The crossing angle between the beams was $\sim 2^\circ$. Two of the beams (1 and 2) were used as pump pulses to create a spatial population grating. A third probe pulse (3) was scattered off the grating into specific phase matched directions and its integrated intensity was collected. The arrival of the probe pulse was delayed by time, $t_p$, with respect to the first two pulses using a delay stage. Control of the relative time delays is essential for the experiment since it directly affects the contributions to the different signal directions. It is possible to construct various surfaces as shown in Figure 4.1(c) by varying the delay ($\tau_c$) between pulse 1 and 2 and the delay ($t_p$) between pulse 2 and 3. The resulting surface consists primarily of photon echoes (obtained by varying the $\tau_c$) and contains a transient grating along the axis corresponding to $t_p$. The surface presented in Figure 4.1 is experimental data obtained using the 1.38 nm radius sample, capped with TOPO and dispersed in toluene.

The third-order normal transient grating (3-TG) was measured in the phase matched direction corresponding to the wavevector $-k_1 + k_2 + k_3$. The fifth-order transient grating (5-TG) was collected in the $-2k_1 + 2k_2 + k_3$ direction. 3-TG measures excited state dynamics associated with exciton recombination, while as we show here, 5-TG contains additional contributions corresponding to biexciton relaxation. The 3-TG and 5-TG signals were measured both simultaneously and separately. The simultaneously collected signals served as a control to ensure that beam drift and other experimental conditions were not skewing the results. However, these measurements had to be made at a higher intensity in order to observe the third- and the fifth-order simultaneously with a typical
Figure 4.1: The beam arrangement for the 3-TG and 5-TG experiments is presented schematically. (a) The incident excitation beams have been split into three components with wavevectors $k_1$, $k_2$ and $k_3$ generating the 3-TG signal, which appears at $-k_1 + k_2 + k_3$ according to phase matching conditions, and the 5-TG signal that appears at $-2k_1 + 2k_2 + k_3$. (b) An in-plane view (perpendicular to the perspective in (a)) of the beams after the sample including the 3-TG and 5-TG signals. Varying the relative time delays can be used to produce surface plots as shown in (c). The surface plot in (c) was obtained experimentally using the 1.38 nm radius sample, capped with TOPO and dispersed in toluene. The z-axis of (c) (intensity) is presented on a log scale.
pulse intensity of 30 nJ. The measurements were also performed separately in order to attempt to limit the experiments to the minimum excitation energy required to obtain a signal. These experiments typically used pulse energies of approximately 10 nJ for the third-order.

### 4.3.2 Data Analysis

Population relaxation dynamics in quantum dots can be described as a sum of exponentials, dependent on the dynamics of the excitons [92]. In the third-order traces, three contributing exponential terms were identified. The third-order time constants, obtained from single exponential analysis of the linear regions on a semi-log scale, were used in a nonlinear least squares analysis to obtain relative amplitudes and produce a three exponential fit. The time constants and amplitudes obtained were further verified by performing a Hankel singular value decomposition on the data to ensure that the values obtained by this second method were equivalent to those obtained by the first, within error limits.

The 5-TG signal comprises both exciton and biexciton population gratings, therefore, it includes time constants associated with biexciton as well as exciton dynamics. The 5-TG traces were initially analyzed using a Hankel singular value decomposition methodology, which confirmed the presence of the third-order time constants as well as two additional components observed only in the fifth-order. The time constants and amplitudes for the additional components were used as initial input parameters for a nonlinear least squares analysis. The third-order time constants were input as fixed parameters (values obtained from the 3-TG analysis) in the nonlinear least squares analysis along with appropriate amplitudes. The nonlinear least squares analysis refined the fit and obtained the values reported.

Analysis of the transient grating traces requires consideration of the homodyne detec-
tion scheme. In a homodyne configuration the observed decay will be appear as square of the contributing time constant components as shown in Equation 4.6. Note that a homodyne measurement reports the modulus square of the polarization assuming that the real and the imaginary components are equal. Therefore, exponentials corresponding to the individual time constants will appear, as well as, dependent exponential contributions associated with the difference between the time constants. The effect of the cross terms arising from the differences between the time constants cannot be disregarded in this case since they are not necessarily small. A simulated decay curve containing only the individual time constant exponential terms is compared to one also including the difference exponential terms in Figure 4.2. The combination terms were expressly considered in the data analysis of the transient grating curves.

4.4 Theory

3-TG is a well-known third-order transient spectroscopy that is sensitive to population dynamics [179]. In a 3-TG experiment, the $-k_1 + k_2$ pump pulses arrive simultaneously at the sample, creating a density grating of ground ($|g\rangle\langle g|$) and exciton ($|e\rangle\langle e|$) populations. The evolution of these populations are monitored by the probe pulse, $k_3$, which arrives after a time delay, $t_p$, according to the dynamics governing bleaching, stimulated emission (SE) and excited state absorption (ESA) contributions. Transient grating can be described in analogy to traditional pump-probe since both techniques measure pump induced excited state dynamics, however, they differ in significant ways. In a transient grating experiment, the pump interaction is split into separate beams which form a population density grating in the sample. In a 3-TG experiment the pump is split into two beams while in a 5-TG experiment two or four beams may be used. If two beams are used for the fifth-order experiment, each beam interacts twice; if four beams are used
Figure 4.2: Calculated transient grating curves including (blue, broken line) and omitting (green, unbroken line) the difference exponential terms arising from the homodyne nature of the measurement. The inset is a comparison of the two calculated curves at short probe delay times. The curves were generated using equal amplitudes, a time constant of 600 fs for the damped cosine and the following exponential time constants: 100, 1000, 10000, 1000000 fs.
each one interacts individually. Also, the transient grating technique allows for the use of total excitation intensities that are considerably lower than the typical pump-probe experiments.

The separation of the pump interactions introduces another level of experimental control since all of the beams propagate in different directions. Properties of the beams such as polarization or relative phase can be independently modified. Furthermore in a transient grating experiment, different order signals scatter into specific phase matched directions corresponding to wavevector combinations, allowing spatial isolation (see Figure 4.1). Information beyond direct population decay can be obtained by modifying the polarization scheme, as discussed elsewhere [125]. In the present experiments all of the excitation beams were $S$ polarized. The current experiment further differs from many other transient absorption (pump-probe) studies in that it consists of band edge single colour excitation, increasing the selectivity for probing the first exciton transition.

In the weak field limit, justifiable in cases such as these experiments where the incident fields are significantly weaker than the internal electric fields, the electric field interactions are weak enough that a perturbative order-by-order expansion of the polarization in terms of the radiation field is valid. In this case, an $n^{th}$ order polarization arises from $n$ field-matter interactions at times $t_1, \ldots, t_n$ with wavevectors $k_1, \ldots, k_n$. Thus for the third-order, there are three component wavevectors $k_1, k_2$ and $k_3$ associated with each field-matter interaction. In the fifth-order, there are five possible component wavevectors $k_1, k_2, k_3, k_4$ and $k_5$. A 5-TG experiment may have each wavevector interacting separately as long as the pump interactions occur simultaneously. Alternatively a 5-TG experiment may have $k_1 = k_2$ and $k_3 = k_4$ resulting in two pump wavevectors, each interacting twice with the sample.

The signal arising from the induced third-order polarization is scattered according to phase matching conditions and the specific interactions into the $\pm k_1 \pm k_2 \pm k_3$ directions. Since we are concerned exclusively with the transient grating experiment, only
the $-k_1 + k_2 + k_3$ normal time ordered phase matching direction will be considered. The time ordering of the pulses is defined by the relative time delays, where the centre to centre time delay between the first and second pulse is defined as $\tau_c$ and the centre to centre time delay between the second and third pulses is defined as $t_p$. In the normal time ordered case, both $\tau_c$ and $t_p$ are greater or equal to zero so that pulse 1, 2 and 3 interact in that order sequentially (for a positive time delay) or simultaneously (for zero delay). In a transient grating experiment the time delay between the pump pulses, $\tau_c$, is set to zero and the delay between the pump interactions and the probe is scanned, $t_p$. Note that varying $\tau_c$ as shown in Figure 4.1(c) results in a photon echo experiment.

The coherent nonlinear optical response of semiconductors is characterized by many-body structures, such as excitons and biexcitons. The formation of these structures in response to optical excitation and their subsequent dynamics can be treated using a microscopic density matrix theory [180, 181]. In this situation, a hierarchy of many-point density matrices describes the dynamics of the system under the influence of a driving laser field. As a result of the Coulomb interaction, an exact calculation of the electrodynamic observables derived from single-particle density matrices requires analysis of the entire infinite hierarchy of many-body density matrices. However, the hierarchy can be truncated when the strength of optical excitation is used as a perturbation parameter. Although the full many-body theory is required for an exact treatment of the nonlinear optical response, a phenomenological few-level description can be used successfully, retaining the physics of the response in the limit where continua are not involved. In fact, the few level model can be directly linked to the many-body density matrix description of the dynamics as has been previously shown [182].

The phenomenological few level model does not originate directly from a projection of the equations of motion onto a set of eigenfunctions. Instead a set of new dynamic objects are defined in terms of definite particle number states such as: $|g\rangle$ (zero excitons), $|e\rangle$ (one exciton), $|b\rangle$ (two excitons), $|t\rangle$ (three excitons) and so on depending on
the order of the excitation. The dynamic objects of interest in this situation are diagonal elements of the density matrix. In terms of a transient grating measurement, the few level model can be used directly since we are only interested in the dynamics of exciton populations (diagonal elements of the density matrix) with the assumptions that the sample is initially a zero particle system and that all many body excitations are created through the field-matter interactions. Contributions to the transient grating signal can arise from excited state absorption, ground state recovery and stimulated emission. The observed response also contains time constants associated with surface states and may contain higher order contributions dependent on the incident pump intensity. However, the higher order contributions will appear with a reduced prefactor since they are a consequence of a power expansion in the field.

The third-order induced polarization evolves during the time, $t$, after the probe pulse and takes the form,

$$
P^{(3)}_{-k_1+k_2+k_3}(0, t_p, t) = \int_0^{\infty} dt \int_0^{\infty} dt_p [C_{GSR}^{(4)}R_{GSR}^{(3)}K_{GSR}^{(3)}(t_p, t) + C_{SE}^{(4)}R_{SE}^{(3)}K_{SE}^{(3)}(t_p, t) - C_{ESA}^{(4)}R_{ESA}^{(3)}K_{ESA}^{(3)}(t_p, t)] E_1^*(t - t_p)E_2(t - t_p)E_3(t)$$

where we have used a notation similar to that of Xu et al. [183]. $E_1(t - t_p)$ and $E_2(t - t_p)$ are the electric fields of the two pump pulses, $E_3(t)$, is the electric field of the probe pulse and $*$ indicates the complex conjugate. The terms GSR, SE and ESA refer to the ground state recovery, stimulated emission and the excited state absorption components respectively. The $C^{(4)}$ terms correspond to rotationally averaged observables and have been discussed in detail elsewhere [125], however, since the experiment was performed with all of the excitation beams set to the same linear polarization, all of these factors are equal to $\frac{1}{5}$. The $R^{(3)}$ terms are the relevant third-order nonlinear response functions, which contain all of the information necessary for the calculation of the optical response. These terms are presented in Section 4.8.

The $K^{(3)}$ factors represent the kinetic components of the third-order response de-
scribed by the evolution of the ground and excited state population. The present experiment is primarily sensitive to GSR associated kinetics, which is described by the factor,

$$K_{GSR}^{(3)}(t_p, t) = a_1 e^{-t_p/\tau_1} + c_1 e^{-t_p/\tau_{D1}} + c_2 e^{-t_p/\tau_{D2}}$$

(4.2)

$K_{GSR}^{(3)}$ corresponds to the $B_1$ dynamics identified by Klimov et al. [57, 93]. The term $\tau_1$ represents exciton recombination. The last two terms associated with $\tau_{D1}$ and $\tau_{D2}$ are time constants associated with surface defects and passivation, which have been previously studied [56, 57, 93, 184, 185, 186], although the exact nature of the surface states remains unknown. It is assumed that there are no local field effects or contributions from energy transfer between nanocrystals, which is a good approximation when the optical density of the sample is low.

In the 5-TG experiment, the pump sequence $-2k_1 + 2k_2$ produces $|g\rangle\langle g|$ and $|e\rangle\langle e|$ population gratings, as above [187], but can also provide a biexciton population ($|b\rangle\langle b|$) via a two-photon absorption pathway. Actually, there are a number of ways of generating the $|b\rangle\langle b|$ population owing to the many-body nature of the nonlinear optical response [188, 189]. We are concerned here just with the ensuing population dynamics. As discussed previously with respect to the third-order, the fifth-order response will be discussed considering only the $-2k_1 + 2k_2 + k_3$ normal time ordered phase matching direction. Again, the ordering of the pulses is defined by the relative delays, where the centre to centre time delay between the first and second pulse can be defined as $\tau$; between the second and third pulse as $\tau'$; between the third and fourth pulses as $\tau''$ and between the fourth and fifth pulses as $t_p$. In the normal time ordered case, all of the time delays are greater or equal to zero so that pulses 1, 2, 3, 4 and 5 interact in that order sequentially (for a positive time delay) or simultaneously (for zero delay). In a 5-TG experiment the first four pulses arrive simultaneously so that $\tau$, $\tau'$ and $\tau''$ are equal to zero and the time delay, $t_p$, is scanned to collect the signal. The fifth-order induced polarization evolves
during the time \( t \) after the probe pulse and takes the form,

\[
P^{(5)}_{-k_1+k_2-k_3+k_4+k_5}(0,0,0,t_p,t) = \int_0^\infty dt \int_0^\infty dt_p \left\{ 2 \text{Im}\left[C_{GSR}^{(6)} R_{GSR}^{(5)} (K_{GSR}^{(5)}(t_p,t) + K_{GSR}^{(3)}(t_p,t)) \right. \right. \\
\left. + C_{SE}^{(6)} R_{SE}^{(5)} (K_{SE}^{(5)}(t_p,t) + K_{SE}^{(3)}(t_p,t)) \right\} \\
\times E_1^*(t-t_p) E_2(t-t_p) E_3^*(t-t_p) E_4(t-t_p) E_5(t) \]

where, as above, \( E_1(t-t_p), E_2(t-t_p), E_3(t-t_p) \) and \( E_4(t-t_p) \) are the electric fields of the four pump pulses while, \( E_5(t) \), is the electric field of the probe pulse. In a 5-TG experiment, the pump interaction can occur via four individual beams with separate \( k \) vectors (as shown in Equation 4.3) or through two interactions from two beams. In the present experiment, only two independent pump beams with unique \( k \) vectors were used.

By re-labelling the interactions, the expression for the fifth-order polarization can be written as follows,

\[
P^{(5)}_{-2k_1+2k_2+k_3}(0,t_p,t) = \int_0^\infty dt \int_0^\infty dt_p \left\{ 2 \text{Im}\left[C_{GSR}^{(6)} R_{GSR}^{(5)} (K_{GSR}^{(5)}(t_p,t) + K_{GSR}^{(3)}(t_p,t)) \right. \right. \\
\left. + C_{SE}^{(6)} R_{SE}^{(5)} (K_{SE}^{(5)}(t_p,t) + K_{SE}^{(3)}(t_p,t)) \right\} \\
\times E_1^*(t-t_p) E_1(t-t_p) E_2^*(t-t_p) E_2(t-t_p) E_3(t) \]

As above, the \( C^{(6)} \) factors correspond to rotational averaging factors. For linear polarization of the beams all of the \( C^{(6)} \) terms are equal [130, 190].

Considering only the \(-2k_1+2k_2+k_3\) signal direction and making the same assumptions as for the third-order, the total number of possible independent Liouville space pathways is reduced to four (and their complex conjugates). Two of these pathways contribute to the ground state recovery and two to the stimulated emission. Again, since ESA to a fourth state, \(|t\rangle\), is possible and using all of the above restrictions, two additional pathways must be considered that contribute to the ESA term. The Liouville pathways contributing to the fifth-order signal and the relevant fifth-order response functions in the static limit are included in the Section 4.8.
The $K^{(5)}$ factors represent the kinetic components unique to the fifth-order response describing the evolution of the different contributing populations. The kinetic factor for the GSR term associated with a biexciton grating, assuming a sequential relaxation process, is,

$$K_{GSR}^{(5)}(t_p, t) = b_1 e^{-t_p/\tau_3} + b_2 e^{-t_p/\tau_4}$$ \hspace{1cm} (4.5)

The fifth-order response contains factors arising from biexciton and higher order contributions. We propose that the components corresponding to the $\tau_3$ and $\tau_4$ terms represent time constants associated with biexciton recombination and excited exciton state dynamics.

In the present work we use a homodyne detection scheme such that the signal intensity as a function of delay time, $t_p$, for an $n$-TG experiment is:

$$I^n(t_p) = \int_0^\infty dt |P_{-lk_1+lk_2+k_3}(t_p, t)|^2$$ \hspace{1cm} (4.6)

where $l = (n - 1)/2$.

In contrast to transient absorption methods, many of which are inherently heterodyned, direct fitting of the homodyne detected signals retrieves the modulus square of the polarization, resulting in observed time constants that are half of the actual time constants (see Section 4.3.2).

As a direct result of the two-fold degeneracy of the $1S$ state, band edge excitation of CdSe quantum dots as used in the present experiment, can only generate excitons and biexcitons. However, other multiexciton combinations, such as triexcitons, are possible using higher energy excitation as demonstrated in the multiple exciton generation (MEG) experiments [25] and in pump-probe measurements using a 400 nm pump and a white light continuum probe [92]. In order to put the present work into context with other multiexciton experiments, we consider two methods of determining relative populations, the Poisson distribution and equations of motion. Although these two treatments do not directly apply to the band edge of CdSe nanocrystals, they are valuable for examining
the role of multiexciton states in quantum dots in general.

The relative populations of exciton, biexciton and triexciton states for any pump intensity are usually determined according to a Poisson distribution based on the average excitation density per quantum dot \([25, 92]\). However, since the excitation events are not strictly independent, we expect possible deviations from the predicted poissonian populations. Here we estimate the significance of such deviations by simulating the response using a density matrix approach. In this method, equations of motion can be derived to describe the population densities, where \(\rho_{gg} = |g\rangle\langle g|\), \(\rho_{ee} = |e\rangle\langle e|\) and so on. Assuming the population densities can be calculated to seventh order (triexciton, biexciton, exciton and ground state populations) we can write the following coupled differential equations,

\[
\frac{\partial}{\partial t} \rho_{gg} = \frac{i}{\hbar} E \rho_{ge} + \Gamma_e \rho_{ee} \tag{4.7a}
\]

\[
\frac{\partial}{\partial t} \rho_{ge} = \frac{i}{\hbar} [E \rho_{gg} + \varepsilon_e \rho_{ge}] - \gamma_e \rho_{ge} \tag{4.7b}
\]

\[
\frac{\partial}{\partial t} \rho_{ee} = - \frac{i}{\hbar} E \rho_{ge} - \Gamma_e \rho_{ee} + \Gamma_b \rho_{bb} \tag{4.7c}
\]

\[
\frac{\partial}{\partial t} \rho_{eb} = \frac{i}{\hbar} [E \rho_{ee} + \varepsilon_b \rho_{eb}] - \gamma_b \rho_{eb} \tag{4.7d}
\]

\[
\frac{\partial}{\partial t} \rho_{bb} = - \frac{i}{\hbar} E \rho_{eb} - \Gamma_b \rho_{bb} + \Gamma_t \rho_{tt} \tag{4.7e}
\]

\[
\frac{\partial}{\partial t} \rho_{bt} = \frac{i}{\hbar} [E \rho_{bb} + \varepsilon_t \rho_{bt}] - \gamma_t \rho_{bt} \tag{4.7f}
\]

\[
\frac{\partial}{\partial t} \rho_{tt} = - \frac{i}{\hbar} E \rho_{bt} - \Gamma_t \rho_{tt} \tag{4.7g}
\]

where \(E\) is the incident field of the ultrafast laser pulses, \(\varepsilon_e, \varepsilon_b\) and \(\varepsilon_t\) are the transition energies from the ground to the first excited state, from the first excited state to the second excited state and from the second excited state to the third excited state respectively. The terms \(\gamma_e, \gamma_b\) and \(\gamma_t\) are the dephasing rates of a coherence for an exciton, biexciton and triexciton respectively. Similarly, \(\Gamma_e, \Gamma_b\) and \(\Gamma_t\) are the relaxation rates of an exciton, biexciton and triexciton population.

Predictions based on the equation of motion simulation and calculated using a Poisson distribution are shown in Figure 4.3, where \(N_{eh}\) is proportional to the intensity of
the incident beam [25]. There are two different regimes to consider: low and high excitation intensity. In the low intensity limit, when there is significantly less than one exciton per quantum dot, the Poisson distribution is a relevant description of the system. In this limit, Poisson distribution predicts a higher absolute number of biexcitons and triexcitons than the equation of motion treatment, however, we are mainly concerned with the relative predicted amounts. In the high intensity limit, approximated by an occupancy of more than one exciton on average, the difference between the Poisson distribution predictions and the equation of motion simulations is significant. In fact, the exciton population deviates at even lower occupancy, as shown in Figure 4.3. At higher intensity, the equation of motion simulation predicts a different relative biexciton and triexciton population than expected from a Poisson distribution treatment. Note that an average exciton occupancy per quantum dot between 0.5 and 2.0 is generally of interest for studies of multiexciton relaxation dynamics in quantum dot systems.

The difference between the two limits is not unexpected since the Poisson distribution is based on the assumption of rare events and should only be valid at low incident intensity. For instance, once the threshold for stimulated emission is surpassed, the excitation events are no longer completely independent. The equation of motion calculations rely on a perturbation expansion treatment and cannot be extended to the high field intensity limit, where there would be significantly more than one exciton per quantum dot. However, it is still valid within the range of interest for the present experiment. Consideration of the difference between the equation of motion treatment and the Poisson distribution may be useful in terms of multiple exciton generation [24, 25] and lasing applications [4, 178].
Figure 4.3: The lines with markers correspond to values obtained for the exciton, biexciton and triexciton population densities calculated using an equation of motion treatment. The population densities correspond to the same time after interaction with an optical field of different relative intensity. The parameters used in the equation of motion simulation correspond to an arbitrary quantum dot with a first transition of 2.33 eV with $\gamma_e$, $\gamma_b$ and $\gamma_t$ set to 100 fs and $\Gamma_e$, $\Gamma_b$ and $\Gamma_t$ set to 1 ns, 15 ps and 1.5 ps respectively. The lines without markers correspond to the predicted probability, assuming a Poisson distribution, of forming an exciton, biexciton or triexciton as shown. All of the values are plotted versus total exciton occupancy on a log-log scale.
4.5 Results

Figure 4.4 shows the low intensity 3-TG and 5-TG traces for an intermediate sized quantum dot sample with \( R = 1.67 \) nm. The samples were excited on resonance with the first exciton transition to ensure that the population time, \( t_p \), follows the decay of the transient grating. This decay is primarily due to the relaxation of the exciton populations according to the \( B_1 \) bleach identified by Klimov and co-workers [57, 93].

Measurements were also made on a dye, Rhodamine-6G (Rh6G) in ethanol, which approximates a model two level system. This was done to confirm that there is no difference between the 3-TG and 5-TG traces in that instance, since in a two level system there are no additional multiexciton contributions in either the third- or the fifth-order.

Third- and fifth-order transient grating traces for Rh6G are presented in Figure 4.5. The 3-TG and 5-TG measurements were collected simultaneously and are plotted on a log scale with separate y-axes. The oscillations are polarization beats associated with vibrational modes of the molecule.

A comparison of the two transient grating signals for the CdSe quantum dots in

\[ \text{Table 4.1: Average Parameters Obtained from 3-TG and 5-TG CdSe Traces} \]

<table>
<thead>
<tr>
<th>Radius</th>
<th>TBWP(^1)</th>
<th>Sample Matrix</th>
<th>( \tau_{D1}(\text{fs}) )</th>
<th>( \tau_{D2}(\text{ps}) )</th>
<th>Biexciton ( \tau_3(\text{ps}) )</th>
<th>Excited Exciton ( \tau_4(\text{fs}) )(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.38 nm</td>
<td>0.51</td>
<td>TOPO/toluene</td>
<td>188</td>
<td>3.8</td>
<td>9.1</td>
<td>90</td>
</tr>
<tr>
<td>1.56 nm</td>
<td>0.61</td>
<td>TOPO/PMMA</td>
<td>284</td>
<td>4.9</td>
<td>13.7</td>
<td>95</td>
</tr>
<tr>
<td>1.64 nm</td>
<td>0.58</td>
<td>dodecylamine/PMMA</td>
<td>680</td>
<td>7.8</td>
<td>15</td>
<td>100</td>
</tr>
<tr>
<td>1.67 nm</td>
<td>0.55</td>
<td>TOPO/toluene</td>
<td>541</td>
<td>5.7</td>
<td>18.2</td>
<td>112</td>
</tr>
<tr>
<td>1.76 nm</td>
<td>0.60</td>
<td>TOPO/PMMA</td>
<td>420</td>
<td>5.8</td>
<td>20.3</td>
<td>175</td>
</tr>
<tr>
<td>1.9 nm</td>
<td>0.49</td>
<td>TOPO/toluene</td>
<td>751</td>
<td>7.1</td>
<td>24</td>
<td>170</td>
</tr>
<tr>
<td>1.96 nm</td>
<td>0.62</td>
<td>TOPO/toluene</td>
<td>750</td>
<td>8.5</td>
<td>28</td>
<td>250</td>
</tr>
<tr>
<td>2.36 nm</td>
<td>0.49</td>
<td>TOPO/toluene</td>
<td>1223</td>
<td>10</td>
<td>51</td>
<td>390</td>
</tr>
</tbody>
</table>

\(^{1}\)Time-bandwidth product \( \Delta \tau \Delta \nu \) for the excitation pulses assuming Gaussian pulse envelopes.

\(^{2}\)The \( \tau_1 \) timescale, on the order of ns, was too long to be accurately measured.
Figure 4.4: Time integrated transient grating data measured for (a) 3-TG \((-k_1 + k_2 + k_3)\) (top trace, green) and the 5-TG \((-2k_1 + 2k_2 + k_3)\) (bottom trace, blue) experiments on the 1.67 nm radius colloidal CdSe quantum dot sample dispersed in toluene. The traces are plotted on a semi-log scale with separate y-axes. Panel (b) is a close up of the short time region after the coherent spike. The 3-TG data was fit over a range of 60 fs to 25000 fs to the expanded function 

\[
|a_1 e^{-x/\tau_1} + c_1 e^{-x/\tau_{D1}} + c_2 e^{-x/\tau_{D2}} + a_c e^{-x/\tau_c} \cos(\omega + \phi)|^2,
\]

where the parameters were found to be \(a_1 = 0.36, \tau_1 = 1 \text{ ns}, c_1 = 0.06, \tau_{D1} = 541 \text{ fs}, c_2 = 0.12, \tau_{D2} = 5.7 \text{ ps}, a_c = 0.01, \tau_c = 340 \text{ fs}, \omega = 208 \text{ cm}^{-1} \text{ and } \phi = 0.7 \text{ rad}.\) The 5-TG data was fit in a similar manner over the same range using the function for the third-order plus two additional exponential terms inside the modulus squared bracket \(a_2 e^{-x/\tau_2} + a_3 e^{-x/\tau_3}.\) The exponential parameters were found to be \(a_1 = 0.5, \tau_1 = 5 \text{ ns}, a_2 = 0.08, \tau_2 = 112 \text{ fs}, a_3 = 0.13, \tau_3 = 18.2 \text{ ps}, c_1 = 0.08, \tau_{D1} = 541 \text{ fs}, c_2 = 0.3 \text{ and } \tau_{D2} = 5.7 \text{ ps}.\)
Figure 4.5: Time integrated transient grating data for 3-TG \((-k_1 + k_2 + k_3)\) and the 5-TG \((-2k_1 + 2k_2 + k_3)\) experiments on a model two level dye system, Rhodamine-6G in ethanol. The inset is a close up of the traces at short probe delay times. The traces in both cases are plotted on semi-log scale with separate y-axes and have been offset for clarity.
Figure 4.4 reveals that the 5-TG data contain additional decaying components not evident in the 3-TG data, while the third- and fifth-order transient grating measurements on the dye revealed identical decay profiles. The control experiment suggests that the differences between the quantum dot TG signals arise from multiparticle interactions, as anticipated. Quantum beats are also visible in Figure 4.4, arising from coherent excitation of the longitudinal phonon mode at approximately 208 cm$^{-1}$ [89]. A summary of the averaged exciton kinetic parameters from the analysis of the CdSe quantum dot measurements as well as the averaged time bandwidth products (TBWP) are presented in Table 4.1.

The power dependencies of the signals in the $-k_1 + k_2 + k_3$ (3-TG) and $-2k_1 + 2k_2 + k_3$ (5-TG) directions for a quantum dot sample were measured simultaneously by varying the intensity of the incident light. The measured power dependencies were directly compared by plotting them against each other, as shown in Figure 4.6, on a log-log scale. This plot illustrates the difference between the two signals, providing a comparison of the differing contributions to the measured response. The slope of a straight line fit to the data on a log-log scale returns the power difference between the two signals. A slope of 2 is expected if the 3-TG signal direction contains third-order contributions (exciton dynamics) while the 5-TG signal direction contains fifth-order contributions (biexciton and exciton dynamics), since they should be separated by two orders with respect to the expansion in the field. Comparison of the third- and the fifth-order signals in Figure 4.6 revealed that the slope corresponded to a value of 1.9, which is very close to the expected value of 2. The slight variation is due to the fact that at higher incident intensities additional order signals can contribute to the observed response with a relatively larger effect on the third-order signal.

Time constants for the third-order data were assigned with reference to previous work [55, 56, 57, 92, 93] in accordance with the model detailed above. Of the three time constants, two are associated with surface traps and defects [56, 57, 93, 185], and the
third time constant corresponds to exciton recombination [191]. In Equation 4.2, \( \tau_1 \) is associated with the depopulation dynamics of exciton quantized states and corresponds to exciton recombination. The \( \tau_1 \) timescale is on the order of nanoseconds and was too long to accurately obtain from our measurements. The time constants associated with the surface defects, \( \tau_{D_1} \) and \( \tau_{D_2} \), depend on the age and the degree of surface passivation of the colloid used in the experiment. The surface states of quantum dots are of interest in terms of trapping effects and possible dynamic contributions. The internal dynamics at room temperature appear to follow the same trend regardless of the sample matrix. There seemed to be a weak dependence on nanocrystal size for the time constants and amplitudes associated with surface-trapping, possibly connected to surface to volume ratios, the different relative energies of the crystal faces or varying degrees of passivation. The surface-associated time constants for the dodecylamine passivated sample differed from those for comparably sized TOPO capped dots, however, this difference was rela-
tively small. Without a systematic study of surface modifications it is difficult to draw any definitive conclusions regarding the surface dynamics.

The main source of uncertainty in the measurements arises from the size distribution of the samples, which was approximately 10%. However, some photoselection is achieved due to the effect of the laser pulse spectrum [105]. Other possible contributions to the uncertainty include the time-range scanned (for longer time constants), which was limited based on the probe delay, possible convolution with the coherent spike (for very short timescales), sample variation, and laser spectrum and power drift. This latter effect was controlled by comparing laser spectra before and after each measurement to verify that there was no significant difference. The possible contributing uncertainties make a reliable estimate of the error very difficult. Estimation of the error based on run-to-run variation or other methods underestimates the overall uncertainties, so we do not indicate those error limits.

4.6 Discussion

Figure 4.7(a) shows the average values of the time constant, \( \tau_3 \), obtained from the 5-TG traces. We suggest that this time constant corresponds to the process of biexciton recombination since the fifth-order response probes biexciton dynamics. In support of that assignment, \( \tau_3 \), is seen to be comparable to previously reported values for CdSe quantum dot biexciton recombination times [74, 92, 93, 184, 192]. The biexciton to exciton decay becomes increasingly rapid with decreasing nanocrystal size, following a cubic dependence in the radius, \( \tau_3 \propto R^3 \), or a linear volume dependence. This result is in close agreement with previous results [92, 93].

Biexciton to exciton decay, or biexciton population relaxation, can occur through either radiative or non-radiative processes. It has been observed that the radiative con-
Figure 4.7: The nanocrystal size-dependence of (a) the time constants assigned to intra-band relaxation associated with an exciton excited state and (b) biexciton recombination. Both graphs are presented on a log-log scale with a line that corresponds to a cubic radius dependence.

tribution to the biexciton population decay occurs on a time constant comparable to that associated with exciton recombination [191], which is reasonable in the case where additional electron correlation effects are insignificant. However, biexciton recombination is observed, both in our data and in previous work [74, 92, 93, 184, 192], to occur on a time constant that is faster than exciton recombination by at least an order of magnitude. In this situation, a non-radiative process associated with a shorter time constant competes with the radiative process and dominates the observed population decay. Based on previous studies, this process is possibly the result of an Auger-type relaxation, a pathway initially proposed by Efros et al. [61] where energy is dissipated through coupling to the quasi-continua of hole states. Other possible mechanisms have been proposed including multiphonon [193] or polaron mediated processes [194, 195], and defect interactions [196]. However, various studies [55, 57, 58, 74, 192, 197] have shown that these explanations do not account for all of the experimental data.

The average value for the time constant, $\tau_4$, obtained from the 5-TG data is shown
in Figure 4.7(b) as a function of nanocrystal size. This fast timescale is most likely due to the radiationless relaxation of an excited exciton state [64, 198, 199, 200, 201]. This assignment is supported by consideration of the power dependence results, Figure 4.6, which indicate that signal in the $-2k_1 + 2k_2 + k_3$ is comprised of fifth-order contributions from excitons and biexcitons. Also, the average exciton occupancy was calculated for the third- and the fifth-order based on the laser intensity and the absorption cross section of the sample [202]. On the basis of experimentally obtained parameters, such as the incident laser intensity, we determined that the average occupancy was 0.2 and 0.9 excitons per quantum dot for the third- and fifth-order experiments respectively. For a generalized sample with an average occurrence of 0.9 we expect 20 % biexciton and 1.6 % triexciton, based on the equation of motion simulation, which indicates that even for the higher intensity experiments, the expected triexciton population is very low. In fact, both the Poisson distribution and the equation of motion predictions support the selectivity of the experiment since they indicate that there would potentially be very little triexciton and a significant contribution from excitons and biexcitons in the fifth-order signal. However, note that band edge excitation for a CdSe spherical nanocrystal is limited to exciton and biexciton contributions.

In the fifth-order experiment, there are two main possibilities resulting from the two-photon excitation: the formation of a biexciton or an excited state exciton. The biexciton is populated through the sequential formation of two excitons that interact via an attractive Coulomb interaction, typically lowering the total energy by tens of meVs. A two-photon absorption can also populate a higher, totally symmetric electronic state of an exciton [203, 204]. The excited exciton can then relax rapidly though a radiationless transition process to the lowest exciton state. These two, two-photon absorption processes are distinct from each other and could potentially be separated using a two colour experiment or through polarization conditions, however, in our one colour experiment they are distinguished by their different associated timescales.
The $\tau_4$ constant follows the same cubic radius, or linear volume, dependence as $\tau_3$ as shown in Figure 4.7. An Auger type relaxation process has been proposed as a potential explanation for the previously observed cubic radius dependence of the relaxation of the biexciton. In the Auger description, recombination occurs via a three particle process where the electrons and the holes are considered separately. The energy from the recombination of an exciton is transferred to a third particle, which can be an electron or a hole. This third particle, which may form part of another exciton, is excited to a higher energy state. If we consider the Auger mechanism in terms of the electronic state representation the kinetic process can be written as, $\text{Biexciton} \rightarrow \text{Excited Exciton State} \rightarrow \text{Exciton}$. The first step from biexciton to excited exciton state would be rate limiting since the biexciton relaxation is much slower than the nonradiative relaxation of the excited exciton state to the lowest energy exciton state. The Auger process as described implies a specific mechanism for the deactivation of the multiple excitation, however, this type of process can be more generally described simply as exciton-exciton annihilation. In this case the relaxation is considered in terms of an excitonic picture providing a general description of the process. This does not assert a particular mechanism, but simply implies disappearance and includes the possibility of an Auger type relaxation process. This annihilation picture lends itself particularly to the type of case where we are considering spectroscopic levels of a delocalized exciton [47] with the assumption of a strong Coulomb interaction.

Exciton-exciton annihilation is generally described in molecular systems in terms of a two step process where two excitations in the first excited exciton state interact, raising one of the excitons to a higher excited state and transferring the other exciton into the ground state, while satisfying energy conservation. The exciton in the higher excited state then relaxes back to the first excited state by internal conversion [205]. This is traditionally a molecular description that has been studied extensively [198, 199, 200, 201, 206, 207, 208, 209] and generally refers to an interaction between
localized excitons at a distance. However, it can also apply to a delocalized exciton system, such as quantum dots, since in the exact limit the delocalized and localized exciton pictures become equivalent [210].

In our experiment the relaxation process associated with $\tau_4$ occurs directly as a result of a two photon absorption from the pump interaction and from the relaxation of the biexciton. However, the excited exciton state associated with the timescale, $\tau_4$, may be the state that mediates biexciton relaxation, since it satisfies the conditions that it is near resonant in energy with the biexciton state and it decays rapidly to a lower electronic state. The present experiment is not suited for revealing a connection between the states via kinetics because at this point we have not attempted to photoexcite just one of those states. Nonetheless, the observation of the existence of this pair of states, and measurement of their decay dynamics is an important first step.

4.7 Conclusion

In conclusion, we have demonstrated in this work the concept of using $n$th-order nonlinear transient spectroscopies in the transient grating configuration as a means of selectively exciting $(n - 1)/2$ excitons in a semiconductor and probing the subsequent relaxation dynamics. Through the order dependence of the number of field-matter interactions, fifth-order measurements enabled direct observation of time constants associated with biexciton dynamics. This method is general and can be used to examine multiexciton dynamics in a wide range of systems. In fact, the method is applicable to any system where the generation and decay of multiple excitations is of interest. One of the primary benefits of the $n - TG$ method arises from the minimal intensities required and the systematic aspects of the technique. The spatial separation of the signal allows for a systematic manner in which to study multiexciton dynamics, selecting excitons in the
third-order signal and exciton and biexciton dynamics in the fifth-order.

We identified two decay processes, with the time constants $\tau_3$ and $\tau_4$, associated with excitation of CdSe colloidal nanocrystals in the fifth-order experiment. Careful consideration of the average excitation density per nanocrystal and power-dependence of the signals led us to conclude that the states associated with $\tau_3$ and $\tau_4$ both result from two-photon excitation. Deviations between populations predicted by an equation of motion simulation and a Poisson distribution treatment were discussed. Both of these time constants followed a cubic dependence on the nanocrystal radius, and $\tau_3$ was clearly assigned to biexciton recombination. We assigned $\tau_4$ to relaxation from an excited exciton state. Interestingly, that time constant was significantly faster than decay of the biexciton. We suggested that the excited exciton state might provide a deactivation pathway for radiationless biexciton decay via exciton-exciton annihilation, possibly via an Auger-type mechanism.

4.8 Supporting Information

Nonlinear response functions are determined by summing over the different possible pathways in Liouville space. These pathways are graphically represented as double-sided Feynman diagrams describing the evolution of the density matrix and are presented in Figure 4.8(b) for the third-order, and in Figure 4.8(c) for the fifth-order.

Considering the third-order response of a two level system, there are 48 possible contributing Liouville space pathways. This is reduced to 24 possibilities for degenerate frequency pulses, and then further reduced to 8 if the incident fields are resonant with the $|g\rangle \rightarrow |e\rangle$ transition.\footnote{i.e. $2^n$ pathways are independent where $n$ is the order of the spectroscopy} If the impulsive limit and normal time ordering are assumed, then there are only two contributing pathways (and their complex conjugates). In these
experiments, ESA to a third electronic state, \( |b \rangle \), is also possible. Using the above restrictions only one additional pathway (and its complex conjugate) must be considered to account for the ESA contribution. The contributing pathways for the third-order response are shown in Figure 4.8. The negative sign associated with the ESA term in Equation 4.2 is due to the odd number of interactions on the bra, the right side of the Feynman diagram. Using the well-known Green’s function formalism [132, 187, 211, 212], the third-order response functions are

\[
R^{(3)}_{GSR}(0, t_p, t) = \mu_{ge}^{(4)} e^{-i\omega_e t} [G_{eg}(t)G_{gg}(t_p)G_{ge}(0)]
\]

(4.8)

\[
R^{(3)}_{SE}(0, t_p, t) = \mu_{ge}^{(4)} e^{-i\omega_e t} [G_{eg}(t)G_{ee}(t_p)G_{ge}(0)]
\]

(4.9)

\[
R^{(3)}_{ESA}(0, t_p, t) = \mu_{ge}^{(2)} \mu_{eb}^{(2)} e^{-i\omega_e t} [G_{be}(t)G_{ee}(t_p)G_{ge}(0)]
\]

(4.10)

where \( G_{eg} \simeq e^{-\Gamma t} \), which corresponds to the inhomogeneous line broadening or static limit. The term, \( \mu_{ge} \), corresponds to the transition dipole moment operator linking the ground and first exciton state and \( \mu_{eb} \) corresponds to the transition dipole moment operator between the first and second exciton states.

The contributing fifth-order response functions are

\[
R^{(5)}_{GSR}(0, 0, t_p, t) = \mu_{ge}^{(6)} e^{-i\omega_e t} [G_{eg}(t)G_{gg}(t_p)G_{eg}(0)G_{gg}(0)G_{ge}(0)]
\]

\[+ [G_{eg}(t)G_{gg}(t_p)G_{ge}(0)G_{ee}(0)G_{ge}(0)] \]

(4.11)

\[
R^{(5)}_{SE}(0, 0, t_p, t) = \mu_{ge}^{(6)} e^{-i\omega_e t} [G_{eg}(t)G_{ee}(t_p)G_{eg}(0)G_{gg}(0)G_{ge}(0)]
\]

\[+ [G_{eg}(t)G_{ee}(t_p)G_{ge}(0)G_{ee}(0)G_{ge}(0)] \]

(4.12)

\[
R^{(5)}_{ESA}(0, 0, t_p, t) = \mu_{ge}^{(2)} \mu_{eb}^{(2)} \mu_{bt}^{(2)} e^{-i\omega_e t} [G_{tb}(t)G_{bb}(t_p)G_{eb}(0)G_{gb}(0)G_{ge}(0)]
\]

\[+ [G_{tb}(t)G_{bb}(t_p)G_{eb}(0)G_{ee}(0)G_{ge}(0)] \]

(4.13)

The terms \( \mu_{ge} \), \( \mu_{eb} \) and \( \mu_{bt} \) correspond to the transition dipole moments linking the ground and first exciton states, the first and second exciton states and the second and third exciton states respectively.
Figure 4.8: (a) A simplified state level representation of the few level model. (b) Double-sided Feynman diagrams for the third-order signal that appears in the normal time ordered $-k_1 + k_2 + k_3$ direction. Each diagram corresponds to a response function associated with ground state recovery (GSR), stimulated emission (SE) and excited state absorption (ESA). (c) The double sided Feynman diagrams for the fifth-order signal in the $-2k_1 + 2k_2 + k_3$ normal time ordered signal direction. For the fifth-order, a pair of diagrams contribute to each of the response functions associated with GSR, SE and ESA.
Chapter 5

Demonstration of Bulk Semiconductor Optical Properties in Processible Ag$_2$S and EuS Nanocrystalline Systems
Chapter 5. Optical Properties of Bulk Semiconductor NCs

5.1 Chapter Summary

The preceding chapters have explored the nonlinear optical properties of quantum confined semiconductor nanocrystals. However, not all semiconductor nanocrystals display the distinct photophysics of quantum confined systems. This chapter examines another class of semiconductor nanocrystals, which have fundamentally different optical properties characteristic of the corresponding bulk materials. These nanocrystals combine the desirable processing properties of colloidal particles with bulk semiconductor optical properties. As a result, these materials are likely to play a complementary role to quantum confined structures as another building block for the development of new technologies.

Two model bulk colloidal semiconductor nanocrystal systems, EuS and Ag$_2$S, are studied in this chapter using linear optical spectroscopy. The Ag$_2$S nanocrystals represent a straightforward, textbook example of bulk semiconductor optical properties. However, the EuS nanocrystal system is more complicated since it has linear optical properties that may be mistaken for quantum confined.
5.2 Introduction

Semiconductor nanocrystals (NCs) are colloidal single crystals that have been widely examined in recent years to elucidate the origins and applications of size-tuneable properties. Size-tuneable optical properties are particularly desirable for applications in light-emitting devices, lasers, and biological labelling [6, 13, 32, 33, 213]. Strong confinement effects, characteristic of many NCs (‘quantum dots’), give them an electronic structure more like molecules than semiconductors and this is of special interest in areas such as quantum information [214]. However, while all colloidal quantum dots are NCs, not all NCs are colloidal quantum dots. This distinction between bulk and confined nanocrystals is not always obvious depending on the characteristics of the bulk band structure. In this chapter we show that the optical spectra of bulk semiconductor NCs can exhibit surprising features that may be confused with quantum confinement effects by comparing the optical properties of two bulk nanocrystal systems, Ag$_2$S and EuS.

Bulk semiconductors have revolutionized a breadth of technologies as a consequence of the way electronic levels form delocalized bands. Although the development of new quantum dot systems have dominated semiconductor nanocrystal research, we suggest that the field of bulk NC synthesis and characterization is complementary to the well-established field of quantum confined NCs, and offers great potential for the discovery of materials that exploit the desirable electronic and magnetic attributes of bulk semiconductors on the nanoscale. A key advantage foreseen for these NCs is that they are easily processed and they can potentially be programmed for intelligent self-assembly [215].

The realization of the scope and potential of nanoscience has stimulated the discovery of many routes for semiconductor quantum dot synthesis. Many of these reports seek to demonstrate quantum confinement effects; that is, size-tuneable absorption features as demonstrated in compelling pioneering work [36, 216]. Compared to the extensive amount of research directed towards creating novel quantum dot systems, little work has been directed towards thinking about the potential of colloidal synthesis for the minia-
turization of semiconductors while retaining the essential attributes of the bulk material. There are some notable exceptions to this including nanocrystalline TiO$_2$, which has been extensively studied for use in photovoltaics [217]. Bulk semiconductors have been, and continue to be, essential components in almost all aspects of technology. They differ from quantum confined semiconductors in that carriers are located in bands rather than discrete energy levels, thus producing the well known electronic properties. Nanocrystals that have these same properties could potentially find wide application in micro- and nano-electronics because they may facilitate processing of devices on small length scales without introducing complicating quantum effects. These materials would exploit the advantages of nanocrystals, such as enhanced processability and the possibility of tailoring specific shapes through chemical synthesis, while retaining the desirable properties of bulk semiconductors.

5.3 Nanocrystal Sample Characterization

In this chapter we report the characterization of two model colloidal NCs, Ag$_2$S and EuS, and show that they have optical properties similar to the corresponding bulk materials. Ag$_2$S nanoparticles were synthesized by a novel solvent free method (see experimental section 5.6.1) and the EuS nanoparticles were synthesized by thermal decomposition of a single-source precursor [218]. After purification, both the EuS and the Ag$_2$S nanoparticles were dispersed in toluene. The particle size-distribution of both the Ag$_2$S and the EuS samples were characterized using transmission electron microscopy (TEM). Representative TEM images are shown in Figure 5.1. Powder X-ray diffraction (PXRD), Figure 5.1(b), found that the Ag$_2$S NCs were in the monoclinic crystal form. Previous work [218] confirmed that EuS NCs were prepared in the rock salt structure.
Figure 5.1: TEM image (a) and PXRD data (b) for the Ag$_2$S colloidal nanocrystal sample as well as TEM images for the four EuS colloidal nanocrystal samples with average diameters of (c) 9 nm (d) 10 nm (e) 15 nm and (f) 23 nm.
5.4 Results and Discussion

Ag$_2$S is one of the oldest known semiconducting materials. It is most commonly found as silver tarnish and is widely used in photography, IR detectors, thermo power cells and luminescent devices. The absorption spectrum of colloidal Ag$_2$S nanocrystals, as shown in Figure 5.2(a), represents a textbook example of a bulk semiconductor. The monotonic increase in the absorption cross-section follows the increasing density of electronic states above the band gap. Unlike in quantum dot NCs, excitons are not a distinctive feature of bulk materials, owing to their small binding energy ($\sim$5–10 meV) [47]. Excitons can play an important role in the optical properties of bulk materials at very low temperatures, however, all measurements were done at room temperature, hence we do not find evidence for Ag$_2$S excitons in the NCs.

The optical absorption edge of an idealized parabolic band bulk semiconductor with allowed direct transitions can be fit using the Bardeen or Tauc equation where the absorption coefficient is described by,

$$\alpha h\nu = A(h\nu - E_g)^n$$

where $\alpha$ is the absorption coefficient measured as a function of photon energy $h\nu$, $A$ is a constant factor determined by the transition probability, $E_g$ is the energy gap and $n$ is a number that depends on the type of transition process where $n = 1/2$, 2, 3/2 or 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect electronic transition respectively. A derivation of Equation 5.1 is given in Appendix A. Since the transitions in EuS and Ag$_2$S are allowed direct, the Tauc equation requires $n = 1/2$ for each material. Therefore, a straight line fit to a plot of $(\alpha h\nu)^2$ versus $h\nu$ gives a linear version of the Tauc equation as shown in Figure 5.2(b). The x-intercept of the line fit to the data corresponds the optical band gap. For Ag$_2$S we find that $E_g = 1.06 \pm 0.2$ eV, in good agreement with literature values for the corresponding bulk material [219, 220]. Note that close to the band gap, a model independent linear extrapolation derived using
Figure 5.2: Absorption spectrum of (a) Ag$_2$S colloidal nanocrystals plotted as absorption versus photon energy, representing typical bulk semiconductor behaviour, and (b) a close-up of the band gap region plotted as $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ with a linear fit to the rising edge associated with the Tauc equation (dashed line) indicating the position of the band gap. (c) Normalized absorption spectra plotted on an energy scale for four different diameter EuS nanocrystal samples with average diameters from top to bottom of 9 nm, 23 nm, 15 nm, and 10 nm. An absence of a size-dependent peak shift is evident.
a Taylor expansion of Equation 5.1 can also be used to obtain an approximate value for $E_g$.

Even more compelling is to consider examples from an enormous variety of semiconductors whose quirks can provide a signature of bulk properties in a colloidal material. Such a semiconductor material is EuS, which should exhibit bulk behaviour on the nanoscale according to the estimated electron and the hole Bohr radii, which are less than 1 nm [221]. EuS has been the subject of ongoing experimental and theoretical investigation because of its interesting magnetic properties. EuS exhibits ferromagnetic behaviour with a Curie temperature of 16 K and is a candidate model system for demonstrating spintronic or optoelectronic phenomena. It has been predicted to possess the ideal properties of a Heisenberg ferromagnet and to be a model for local-moment magnetism [222, 223]. It is also an example of a bulk semiconductor material with a strikingly anomalous absorption spectrum. Consistent with reported bulk characteristics, we find a distinctive peak at approximately 2.35 eV in the absorption spectra of the nanocrystalline EuS samples. This feature could be (and has previously been) mistaken for an exciton band in EuS NCs.

The lack of quantum confinement in the EuS nanocrystals studied is clearly demonstrated in Figure 5.2(c), where a significant change in the average radius of the nanocrystal sample has no observable effect on the absorption band positions. However, if EuS nanocrystals have optical properties like the bulk material, then why is a peak evident in the absorption spectrum? In fact, the EuS nanocrystal absorption spectrum corresponds closely with that of the bulk material, and the peaks can be assigned based on previous studies using soft X-ray spectroscopy, reflectivity measurements, and photoemission measurements. A direct comparison between the 23 nm diameter EuS nanoparticle sample with a bulk reference spectrum [224] is shown in Figure 5.3. It is clear that the two spectra correspond closely, especially at low energies. Deviation at the higher energy side of the spectrum, in particular the peak at approximately 4.9 eV, has been assigned
to ligand absorption in the nanocrystal sample [218]. The peak in the reference bulk spectrum at 4.45 eV appears as a shoulder in the nanocrystal spectrum on the side of the strong ligand absorption.

The onset of the absorption on the low energy side of the spectrum corresponds to transitions from the localized $4f^7$ valence states into the $5d$ conduction sub bands. Analysis of the rising edge of the absorption spectrum using Equation 5.1 estimates the band gap to be $1.69 \pm 0.23$ eV, which is in reasonable agreement with the band gap of the bulk material, 1.65 eV [225, 226, 227]. The $5d$ level is divided by a crystal field splitting of approximately 2.1 eV [225] at room temperature into lower $t_{2g}$ and upper $e_g$ levels. The identity of the upper peak in the EuS bulk nanocrystal (BNC) samples is somewhat obscured by absorption features previously ascribed to the surface ligands [218]. Careful ligand exchange experiments reveal the $e_g$ band (visible as a shoulder) to lie at approximately 4.45 eV in the BNC samples. The crystal field splitting thus determined from the EuS BNC absorption spectra (2.1 eV) is indicated in Figure 5.3. The values determined from our absorption measurements agree closely with the bulk EuS measurements.

Other transitions contribute to the absorption spectrum, since the level structure of EuS is relatively complicated. The main bands are further broadened by complex, multiple particle excitations corresponding to $4f^7 \rightarrow 4f^6(7F_J)5dt_{2g}, 5de_g$ transitions. Also, the width of the $f-d$ transition is at least 0.6 to 0.7 eV, primarily due to the energetic width of the final state [224, 225]. The asymmetry to the high-energy side of the 2.35 eV and 4.45 eV bands can be attributed to transitions from $3p^6$ to the $5d$ states. Other relatively weak transitions originating from the $3p^6$ states also contribute to the total absorption spectrum. These assignments are indicated in Figure 5.3.

Within the scope of bulk semiconductor properties, there is a wide variation in optical properties and behaviour. Thus, we speculate that nanocrystals that could be potentially mistaken for quantum confined structures on the basis of anomalous absorption spectra
Figure 5.3: Absorption spectrum of colloidal EuS nanocrystals (solid line) plotted on an energy scale with a reference bulk spectrum (dashed line) obtained from Reference [224]. The horizontal bars across the top indicate the identity of the components contributing to the spectrum. Note that in addition to the primary components indicated there are also contributions from multiparticle $4f^7 \rightarrow 4f^6(^7F_J)5dt_{2g}, 5d{e_g}$ transitions (see text).
does not only apply to EuS. For example, TlSe, Mg$_2$Sn, Mg$_2$Ge, MnO, and even Fe$_3$O$_4$
[228, 229] all have distinctive features in their absorption spectra. One of the most attrac-
tive attributes of semiconductor nanocrystals is their versatility in terms of shape control
and processability. This adaptability has been one of the driving forces behind many of
the recent reports of nanocrystal synthesis. In the same manner as other nanoscale mate-
rials, bulk nanoparticles can self assemble into arrays or superstructures [230, 231]. They
can be functionalized with polymers [232] and can be blended into mechanical mixtures
to form composite materials such as nanocrystal-polymer films [26]. We envision that
bulk nanoparticles can occupy a complementary role to quantum confined structures as
another building block for the development of new technologies.

Even though EuS and Ag$_2$S nanocrystals have nanometre scale diameters, and as such
are finite materials, our results suggest that they have optical properties characteristic of
the corresponding bulk materials. Therefore, for the lower energy states observed here,
the band structure is relatively unchanged as compared to the bulk and the nanocrystals
behave as bulk analogs. Although deviations from the bulk band structure are possible
at higher energies, if the band structure is preserved in these nanocrystal systems then
other properties such as the dielectric constant and the effective masses of the carriers
may also retain their bulk values. In fact, these systems may be potential models for
establishing the scaling or non-scaling of parameters that depend on the full band struc-
ture. This is of particular importance in terms of examining the size scaling of dielectric
properties [233] and for calibrating infinite lattice models, such as $k \cdot p$ theory, where
bulk parameters are often applied in the calculations for nanoscale systems.
5.5 Conclusion

This chapter demonstrated that EuS and Ag$_2$S nanocrystals exhibit optical absorption spectra similar to the corresponding bulk materials. EuS shows interesting features in its optical absorption spectrum, yet these bands were shown not to shift with large changes in average nanocrystal diameter and were assigned to features characteristic of the bulk spectrum. In each material, band gaps were estimated from the absorption spectra using Equation 5.1 and were found to correspond closely to literature values. Bulk colloidal nanoparticles represent easily processible materials with attractive physical properties. As a result, the development of bulk nanoparticles is forseen to complement progress in quantum dot synthesis with a view toward future device innovations.

5.6 Supporting Information

5.6.1 Experimental Methods

Ag$_2$S nanoparticles were synthesized via a solvent free method. Silver nitrate and dithiooxamide were used as silver and sulphur precursors respectively. The precursors were mixed with hexadecylamine (HDA), the capping agent, using a mortar and pestle and compressed into a pellet in a pellet-making machine. The pellet consisted of the following layers. Layer 1: 0.05 mmol HDA; Layer 2: 0.1 mmol HDA and 0.1 mmol AgNO$_3$; Layer 3: 0.1 mmol HDA; Layer 4: 0.1 mmol HDA and 0.1 mmol dithiooxamide; Layer 5: 0.05 mmol HDA. The pellet was placed in a vial, purged with nitrogen gas and slowly heated in an air oven to 50–60 °C, just above the melting point of HDA, for about 20 minutes. The pellet melted slowly, producing a black solid. The Ag$_2$S nanocrystals were isolated from the melt by dispersing in acetone. The precipitate formed was separated by centrifugation, washed with acetone, and re-dispersed in toluene.
The single-source precursor route employed for the preparation of EuS nanocrystals was similar to the previously reported synthetic procedure [218]. The heteroligand lanthanide diethyldithiocarbamate complex \( \text{Eu(Ddtc)}_3(\text{Bipy}) \) was prepared as described in Reference [218]. Four EuS colloidal nanoparticle samples were prepared with average diameters of 9 nm, 10 nm, 15 nm and 23 nm. The 10 nm diameter sample was prepared by adding the precursor, \( \text{Eu(Ddtc)}_3(\text{Bipy}) \) (0.5 g), to the growth solution containing octadecene (2.5 mL) and oleylamine (2.5 mL) at room temperature. The resulting mixture was heated to 280 °C under argon, followed by a 25 minute long growth period at that temperature. The 15 nm and 23 nm diameter samples were prepared using the same methodology as described above but using different amounts of the bipyridine (bipy) precursor (1 g and 1.25 g respectively). The 9 nm diameter sample was prepared by heating oleylamine (2.5 mL) to 280 °C under argon. A slurry containing the precursor (0.5 g) in octadecene (2.5 mL) was injected into the hot oleylamine and the nanocrystals were grown for 25 minutes. Following each synthesis, the nanocrystals were purified by precipitation with anhydrous methanol and ethyl acetate. The precipitate was collected by centrifugation and subsequently dispersed in toluene.

The diameter of the EuS and Ag$_2$S samples was determined using transmission electron microscopy (TEM) measurements. The TEM images were recorded using a TEI Technai 20 instrument equipped with a Gatan camera and the powder X-ray diffraction (PXRD) measurements were carried out on a Siemens D5000 diffractometer using a high-power Cu Kα source operating at 50 kV and 35 mA with a Kevex solid-state detector. A step scan mode was used for data collection with a step size of 0.02 deg and time of 2.0 s per step. The PXRD data for Ag$_2$S and representative TEM images for each sample are shown in Figure 5.1.

Absorption spectra of the EuS and Ag$_2$S colloidal nanocrystals suspended in toluene were measured using Cary 100 and Cary 5000 UV/Visible NIR spectrometers. The samples were measured against a toluene reference in 1mm quartz cuvettes. The Ag$_2$S sample
was measured with an original maximum optical density (O.D.) of 1.1 on a wavelength scale. The four EuS samples were measured with a maximum O.D. of 0.9, 0.8, 0.83, 0.2 for the 9 nm, 10 nm, 15 nm and 23 nm samples respectively on a wavelength scale. All of the measurements collected on a wavelength scale were then converted to an energy scale with the appropriate coordinate transformation of abscissae and ordinates.
Chapter 6

CdSe Nanoparticle Elasticity and Surface Energy
6.1 Chapter Summary

This chapter returns to the polarization control method used in Chapters 2 and 3. In those previous chapters, the cross polarized heterodyne third-order transient grating (CPH-3TG) technique was used to study the dynamics within the fine structure of the lowest energy exciton state of CdSe nanocrystals. In the present chapter, the CPH-3TG methodology is used to observe a coherent acoustic phonon mode, which probes the size-dependent deviation of the elastic material properties from those of the bulk. The size-dependence of the elastic modulus is then used to ascertain information about the relative surface energies of the nanocrystals and suggests the extent and depth of surface reconstruction. In terms of colloidal systems, the surface stress is of particular interest since it is related to the chemical potential and determines the growth kinetics and stability of the particles.
6.2 Introduction

Surface energy becomes increasingly important as particles (colloids, nanoparticles) become smaller. In fact, many of the physical properties of colloids are entirely dictated by surface energy, which is the energy associated with the interface between two phases. Nanoparticles are typically spherical to minimize their surface-to-volume ratio and physical manifestations of surface energy include significant melting point depression compared to bulk materials. More fundamentally, surface energy decides whether an interface is stable, or if one phase will expand and disperse into the other. Interplay of these processes is central to the kinetic growth of colloids in solution. The surface energy of nanoparticles can be related to elastic constants [234], which up to now are generally assumed to be similar to those of the corresponding bulk material. Here we show that the elastic properties of prototypical CdSe semiconductor nanoparticles differ substantially from those of bulk CdSe. We find that the resistance of these nanoparticles to deformation (the elastic modulus) is merely 40% of that of the bulk at a radius of 2.0 nm and diminishes inversely with size until a critical point is reached at an approximate radius of 1.4 nm. A nanocrystal’s energy is therefore not simply a sum of surface and interior bulk terms, and thus it does not scale directly with the surface to volume ratio [235]. Instead, energy-minimizing structural relaxation, intrinsic to the solid phase, plays a significant role in lowering surface energy.

The elastic properties of a material are microscopically related to bond lengths and interatomic potentials, therefore, they determine the vibrational modes. Thus, while macroscopic probes of elastic properties at the nanoscale are difficult or impossible, elastic properties of nanoparticles can be quantified passively by measuring the vibrational frequency of acoustic phonon modes. Using this approach, detailed below, we determined elastic moduli of colloidal CdSe nanoparticles capped with trioctylphosphine oxide (TOPO) ligands and dispersed in toluene solvent at 293 K.

The elastic parameters of a system characterize the linear, totally reversible regime
of physical deformation. This elastic response is described using the ratio of stress to strain. Since stress and strain can be quantified in different ways in a three-dimensional solid, there is a set of interdependent elastic moduli. Although the results are applicable to all of the moduli, we will focus on the ‘bulk’ modulus. The bulk modulus, which we will call simply the elastic modulus to avoid confusion with multiple uses of the word ‘bulk’, measures a substance’s resistance to uniform compression at a fixed temperature and is a convenient way to describe the elastic response of three-dimensional materials.

6.3 Results and Discussion

The elastic moduli, determined as a function of the mean size of the colloidal CdSe samples examined in the present study, are plotted in Figure 6.1 together with the one available literature data point [236]. The elastic modulus of bulk wurtzite CdSe is reported [237] to be 53 GPa. We find that the elastic moduli of the colloidal wurtzite CdSe nanoparticles are significantly lower than the bulk value and show a marked size-dependence down to a radius of \( \sim 1.4 \) nm. Samples with average radii 1.4 nm and below have an elastic modulus that is approximately constant, with a mean value of 12 GPa. In other words, these small nanoparticles are 4 times more compressible than bulk CdSe. These data may be fitted to a sigmoidal function that extrapolates from the size-independent small nanoparticle regime to the bulk regime of size-independent elasticity, predicting the latter onset at a radius of approximately 4 nm. This observed size-dependent softening of the nanoparticles is supported by physical measurements on other nanoparticle systems [238, 239, 240, 241].

The first step in obtaining these results was to measure the frequency of an acoustic phonon (vibrational) mode for each sample. In bulk materials acoustic phonons are propagating compression waves, but, in elastic bodies with spherical shape, they are
Figure 6.1: The elastic modulus plotted as a function of the average radius of colloidal CdSe nanoparticles capped with TOPO and suspended in toluene (293 K). Two regimes are apparent, with little size-dependence for small particles and rapidly changing elastic properties for larger particles. The inset shows the experimental points (circles) with a literature point [236] (triangle) and a fit to a sigmoid curve with an upper limit that approaches the bulk value of the elastic modulus.
quantized modes that describe the set of three-dimensional standing waves in the body. The mathematical treatment of this problem was first developed by Lamb in 1882 [242] and has since been successfully applied to systems ranging from metal nanoparticles [243] to geophysics [244]. This theory allows us to find elastic constants for each CdSe nanoparticle sample with known mean size from measured acoustic mode frequencies.

These acoustic phonon frequencies are $\sim 10 \text{ cm}^{-1}$, so rather than using a frequency domain technique, such as Raman spectroscopy, where the band is obscured by the Rayleigh scatter, we employed a time domain technique. Specifically, we used a background free pump-probe method known as transient grating together with phase-sensitive heterodyne detection [245]. We found that the quantum beats exposing the acoustic phonon frequency were detected with the optimum contrast to the background decay of the signal by using a crossed polarization sequence of laser pulses for excitation and probing. This method, known as cross-polarized heterodyned third-order transient grating (CPH-3TG) spectroscopy [104, 127], is sensitive to transition moment depolarization of the nanoparticle excitons. When the unit cell is at equilibrium, the transition dipole is circularly polarized. The action of the phonon mode distorts the unit cell, lowering its symmetry. This deformation, described through the strain tensor $\varepsilon_{ij}$, mixes the fine structure levels in the first exciton transition, combining states with linearly and circularly polarized selection rules [104]. Further explanation is given in the supporting information see Section 6.5.3 and Chapter 7.

The experimental CPH-3TG signals, a representative of which is shown in Figure 6.2(a), were fitted to sums of exponentials. The residuals, plotted in Figure 6.2(b), show clear oscillations assigned to the $l = 2, m = 0$ spheroidal acoustic mode that couples to the nanoparticle exciton via the deformation potential coupling and satisfies the Raman selection rules [246, 247]. Fourier transformation of the residual trace, Figure 6.2(c), yields the mode frequencies.

The acoustic phonon oscillations were modelled using Lamb’s elastic sphere model.
Figure 6.2: (a) A representative CPH-3TG signal trace as a function of pump-probe delay, $t_p$, for a nanoparticle sample with $R = 1.69$ nm (points) fitted to a sum of exponentials (solid line). (b) The residual from this fit. (c) Fourier transform of the residual revealing the longitudinal optical phonon at 208 cm$^{-1}$ and the acoustic phonon at 13 cm$^{-1}$.
(ESM), which relates the frequency, $\nu$, of each eigenmode of a uniform elastic sphere to its radius $R$, density $\rho$, and the elastic Lamé's constants, $\lambda$ and $\mu$, by solving an equation for the displacement vectors $u$ of each mode [248]:

$$\rho \frac{\partial^2 u}{\partial t^2} = (\lambda + \mu) \text{grad div } u + \mu \nabla^2 u$$

Solutions of Equation 6.1 for the displacement vector of the spheroidal eigenmodes gives the relation to the eigenfrequency $\nu$, as shown in Equation 6.2,

$$\rho \nu^2 = (\lambda + 2\mu) h^2 = \mu k^2$$

where $h$ and $k$ are described elsewhere [249]. Solutions of Equation 6.1 under the boundary condition that there is a stress-free interface with the surroundings allows us to calculate the frequency of the $l = 2, m = 0$ spheroidal acoustic mode as a function of $R$.

The resulting inverse $R$ dependence of $\nu$ is shown in Figure 6.3(a) for bulk CdSe elastic parameters. It is apparent that the experimental frequencies are significantly lower than those predicted using bulk values. Additionally, the apparent lack of size-dependence of the measured frequency for $R > 1.4$ nm does not match the size-dependence predicted using bulk values. This size-independent regime suggests interplay of competing effects. Our observation that the measured frequencies differ by a factor of $\sim 2$ from those predicted using the ESM and bulk parameters suggests that the intrinsic elastic properties of the nanoparticles depend on size. Thus, the experimental data were modelled by using the ESM together with size-dependent elastic parameters. The following relation was used to relate the Lamé's constants to elastic ('bulk') modulus, $K$:

$$K = \lambda + \frac{2\mu}{3}$$

The values of $K$, obtained by fitting the measured frequency for each nanoparticle by adjusting $\lambda$ and $\mu$, are plotted in Figure 6.1. To calculate the elastic parameters of each sample, $\lambda$ and $\mu$ were adjusted until the ESM yielded the measured frequency. The crystal structures of these samples are all wurtzite, so there are not serious structural
changes as a function of nanocrystal size, and we assume that the system can be modelled in the elastic regime. Hence we assume that there is a uniform, small, change in the bond force constants as a function of nanocrystal size and that anisotropy in the elastic response is similar in form, but not magnitude, to that of the bulk material. This ensures a linear relationship between $\lambda$ and $\mu$. These assumptions allow us to scale $K$, and thus according to Equation 6.3, restrict the ratio between $\lambda$ and $\mu$ to be that of bulk CdSe.

In our analysis we have also assumed that the nanocrystals of each size have approximately the same density. More precisely, this means that we have assumed that the changes in elastic properties as a function of nanocrystal size influence the acoustic phonon frequencies much more significantly than the density changes. For instance, to recover the observed frequency for the 1.3 nm sample by changing density alone would require almost a 5-fold increase in density, which is unphysical. The surface structural relaxation can have a strong effect on the total energy, but we assume it causes a negligible change in the nanocrystal volume.

Molecules or atoms at a surface have a different energy than in the bulk phase, and that energy difference is described by surface tension or stress. Although surface tension relates to liquid systems and surface stress to solids, the surface stress of a spherical isotropic solid particle in solution can be related to the concept of surface tension. An equation that has proven useful in the past to determine the surface stress of a solid spherical particle with cubic crystal symmetry is,

$$g = -\frac{3}{2} \frac{\Delta a}{a} KR$$  \hspace{1cm} (6.4)

where $g$ is the isotropic surface stress, $K$ is the elastic modulus, $R$ is the radius of the particle and $\Delta a/a$ is the relative change in the lattice constant, $a$. This equation states that the surface stress of the particle can be determined by measuring the relative change in lattice constant. Equation 6.4 is well suited for determining the surface stress of systems where it can be attributed to changes in lattice parameters, but where the bulk modulus is unchanged. An example of this involves explaining phase transitions as a
function of applied pressure. However, since our data suggests that the elastic parameters depend on the nanocrystal size, we interpreted our results using a theory that connects the bulk modulus to surface stress within the framework of the ESM.

Here we relate the strain to the surface tension at equilibrium for a quantum dot of radius $R$ that behaves as an isotropic elastic body. Further background is given in Appendix B. We equate a small thermodynamically reversible relative change in volume, $\Delta V/V = \varepsilon_{ii}$, otherwise known as the cubic dilation to an internal pressure $p$ as shown in Equation 6.5. In other words, at equilibrium $p$ balances $K$ [250],

$$\varepsilon_{ii} = -p/K$$  \hspace{1cm} (6.5)

where $\varepsilon_{ik}$ is the strain tensor, $K$ is the elastic modulus or compressibility defined in terms of the Lamé constants as shown in Equation 6.3. Although $K$ is shown without indices it is technically also a tensor since the modulus is defined as the ratio of stress (a tensor) to strain (also a tensor). However, for crystals with cubic symmetry or higher, $K$ is an isotropic quantity. The internal pressure in Equation 6.5 is defined in terms of the stress tensor. The relative change in the volume depends only on the diagonal components of the stress tensor, $\sigma_{ik}$ [250].

At equilibrium the nanocrystal maintains constant volume because the internal pressure $p$ (implicitly defined relative to the external pressure) is opposed by an external compression$^1$. This force, associated with the work necessary to form a new unit of area by stretching, is defined differently for liquids and solids because the long-range order in solids creates a distinction between elastic and plastic strains. For a liquid, this force is referred to as the surface tension $\gamma$, and is a scalar. For a solid it is described by the surface stress tensor, $g_{ik}$. For an isotropic solid sphere we have [251],

$$2g_{ik}/R - p = 0$$  \hspace{1cm} (6.6)

$^1$The sign of the pressure refers to a force exerted by the solid on the surface balancing the opposite signed compression force exerted by the surroundings on the solid.
Now, combining Equations 6.5 and 6.6 under equilibrium conditions gives,

\[ g_{ik} = \varepsilon_{ii}KR/2 \]  \hspace{1cm} (6.7)

In our experiment we measure \( K \) for a nanocrystal of known radius \( R \). Quantifying Equation 6.7 is important because changes in the surface stress determine other properties of the system such as the chemical potential, the melting temperature, and heat capacity [252]. From Figure 6.1, we can see that \( K \) is a function of \( R \), which was not previously known. Therefore, the surface stress as well as other related properties depends on \( K \) as much as on the surface to volume ratio. We determine the scalar surface stress \( g \) by substituting the mean scalar strain \( \varepsilon_{ii} \rightarrow \frac{1}{3}Tr(\varepsilon_{ik}) \) into Equation 6.7. The resulting scalar surface stress, \( g \), normalized per unit surface area, is presented in Figure 6.3(b).

Owing to the large surface to volume ratios characteristic of colloidal nanoparticle systems, the surface is known to have a significant effect on physical properties. For example, it is known that the phase diagram of nanocrystals is dependent on size, including solid-solid phase transitions [253, 254, 255] and there is significant depression of nanoparticle melting points relative to the bulk material. In the case of bulk CdS, the melting point is 1678 K compared to approximately 575 K for a CdS nanoparticle with radius about 1.3 nm [256]. Understanding the observed behaviour of colloidal systems has relied on arguments based on the surface to volume ratio, and therefore, the relative importance of the surface as the key parameter. Understanding shape control during colloidal growth has been achieved by expanding upon this model to specify individual crystal faces [257, 258]. The CPH-3TG experiment measures the average properties of the system; therefore, the results we report here correspond to a zeroth order picture, measuring an average crystal face, average surface stress and average material parameters at equilibrium.

Previous studies on the surface tension of colloidal nanocrystals considered lattice contraction and pressure change while assuming a constant elastic modulus [236, 259]. This implicitly assumes that the surface to volume ratio is the main contributing factor
Figure 6.3: (a) Note that the plot is on a log-log scale. The broken line is the prediction of the elastic sphere model using bulk CdSe elastic parameters ($\nu \propto 1/R$). The solid circles are the experimentally measured acoustic phonon frequencies. Model CdSe nanoparticle structures for selected sizes are shown (not drawn to scale). (b) The scalar surface stress, $g$, calculated using Equation 6.7 from the experimentally obtained radius dependent elastic modulus and normalized per unit area.
to the change in the observed properties [235]. By reporting the change of the elastic modulus with size, we are suggesting that the thermodynamics of these nanoscale colloids are determined by the interplay between the surface energy and the compensating effect of changing material parameters. In Figure 6.3(b), the surface stress per unit area passes through an obvious minimum following the approximate functional dependence of the elastic modulus. While all the nanocrystals are stable, because the surface stress is negative, the minimum in the plot Figure 6.3(b) corresponds to the nanocrystal size that we observe to be the easiest to synthesize for this particular set of experimental parameters. As an additional test, we calculated surface stress using the lattice contraction values and formula in Reference [236]. If the elastic modulus determined from the present measurement is used, we obtain a curve similar to the one in Figure 6.3(b). However, using a fixed bulk value for the elastic modulus produces a significantly different curve.

The significant observed modification of the elastic parameters in nanocrystals is surprising, especially when considering the system from a bulk perspective. For instance, a similar factor of four change in the speed of sound, which can be used in certain systems to evaluate elastic parameters, would be enormous even when comparing completely different bulk materials. As a result, if the nanocrystals are modelled simply as the sum of a bulk sphere and a surface term, the observed change in the elastic parameters is unexpected. However, this gets at the very definition of nanoscience, where the materials occupy a middle ground between bulk and molecular descriptions. These semiconductor nanocrystals are fundamentally different ‘nanoscale’ systems and do not correspond to a bulk description with modified surface-associated boundary conditions. Here, the surface is not a separate perturbation but a critical aspect of the system as a whole. An example of this can be found by considering the significant decrease in the melting point temperatures in nanocrystals [256], which is associated with the changing material properties.

The relationship between the surface stress and the elastic modulus gives us information about the physical manifestations of strain through the changing elastic parameters.
In turn, these elastic parameters describe the changing material properties caused by energy minimization driven surface reconstruction. Figure 6.3(a) highlights a change in the size-dependence of the frequency of the acoustic phonon mode between the \(<1.42\) and \(>1.57\) nm radius samples. To get a feel for the structural differences between CdSe nanoparticles smaller and larger than 1.4 nm, we modelled nanocrystals using bulk lattice spacing and counted the number of atoms close to the surface as a percentage of total atoms. For the sample at 1.42 nm radius, just over 50% of all the atoms are within two lattice spacings of the surface. It has been shown that this is the region of the nanocrystal that is most strongly affected by the surface [260, 261]. While for the sample at 1.57 nm, only approximately 30% of the atoms are this close to the surface. Thus \(R = 1.4\) nm is a transitional region. At smaller radii, the surface dominates over contributions from the interior and at larger radii the surface becomes less significant. This transitional region coincides with the point where more than half of the atoms are within two lattice spacings of the surface, therefore, the overall structure is strongly effected by surface reconstruction, which drives the change in the material parameters.

Surface reconstruction involves a geometry reorganization of the layer of atoms on a surface to mitigate the higher surface energy. It has been well studied because it directly impacts surface physiochemical properties, for example adsorption isotherms. In a colloidal nanocrystal system, reconstruction at the surface is linked to the interaction between the organic ligands and the inorganic surface. The nature of the ligand/surface interface of colloidal semiconductor nanocrystals is complex. The surface is composed of different crystal faces, each having a different energy. This energy difference has previously been exploited to control the growth and morphology of colloidal nanocrystals [257, 258]. These colloidal systems are stabilized by the presence of ligands on the surface, which lower the energies of the surface crystal faces, thus acting as a surfactant. Our observations further emphasize the interplay of ligand binding and the role of surface reconstruction in these systems, contributing towards a further understanding of the
size-dependent aspects of the ligand-surface interaction.

6.4 Conclusion

The size-dependence of the nanoparticle elastic modulus yields a measure of how deeply surface reconstruction propagates into a crystal because the loss of stiffness we observe is tied to weakening of the bonds in the CdSe wurtzite crystal lattice. This result may clarify the issue of lattice spacing and distortion [36, 262, 263]. We found that the point at which the elastic modulus ceases to depend on size is when half the atoms are within two lattice spacings of the surface, which is consistent with studies quantifying the propagation of surface reconstruction effects into the nanocrystal [260, 261]. That implies that the wurtzite lattice is fully relaxed at $R = 1.4$ nm and smaller. At this point, surface reconstruction corresponds to geometry relaxation of the entire nanoparticle, where the properties of the nanoparticle do not arise from a sum of surface and bulk components. The changing material parameters of the nanoparticles as a function of size ameliorate surface stress, as shown in Figure 6.3(b). In other words, we show that in addition to the surface to volume ratio, the size-dependent modification of the fundamental elastic properties (i.e. structure) governs the nanoparticle thermodynamics and reactivity. This is evidence for a modification of the paradigm for how the energy of colloids scales as a function of size, and indicates the relationships between surface energy and surface reconstruction in nanoparticles. The implications of this finding are not confined to explaining size- and temperature-dependent physical properties of nanocrystals, but have ramifications also for surface chemistry as well as the structure and energy of interfaces in colloidal heterostructures.
6.5 Supporting Information

6.5.1 Experimental Methods

Heterodyne-detected transient grating experiments were performed using different polarization combinations (CPH-3TG) as described elsewhere [104]. Acoustic phonon frequencies were determined using the VHVH and VHHV (V = vertical and H = horizontal) polarization sequences. The transient grating experiment is similar to pump-probe, however, the two pump interactions are separated spatially but not temporally. This spatial separation allows for individual control of the polarization of each pump interaction, the probe and the signal using an analyzer. All measurements were performed at 293 K using low incident intensity of < 6 nJ/pulse. CdSe nanoparticles were prepared and isolated using literature procedures [36, 37]. For CPH-3TG measurements, the nanocrystal samples were suspended in toluene at an optical density of approximately 0.3 in a 1 mm path length cuvette. In order to verify the size distribution and shape of the nanocrystals, scanning transmission electron microscopy (STEM) images were recorded using a Hitachi HD-2000 dedicated STEM operating at 200 kV. STEM images for the samples measured are presented in Figure 6.6.

The error in the size distribution of each nanocrystal sample was estimated by fitting the lowest exciton peak in the absorption spectrum to a Gaussian function. Care was taken to avoid the second transition to the high-energy side of the first transition. The full width half maxima of the Gaussian provides a measure of the distribution of nanocrystal sizes over the whole ensemble, which is an advantage compared to size estimations from STEM that only examine a restricted sub-ensemble. Although the transformation from frequency to nanocrystal size is not completely linear, this approximation is acceptable over the small ranges concerned here. Absorption spectra for all samples can be found in Figure 6.5. The error in the experimentally observed frequency was estimated as the standard deviation of repeated measurements.
6.5.2 Selection Rules

The identification of the particular mode was based on previous work. In a perfectly spherical nanocrystal, both the $l = 0$ and the $l = 2$ modes are active based on group theory arguments [246]. However, for a dipolar Raman scattering mechanism, the $l = 0$ mode has a much lower activity than the $l = 2$ mode [264]. It has also been shown that only the lower frequency modes are active [247], making the lower energy $l = 2$ mode more favoured than the $l = 0$. Additionally, the colloidal nanocrystals, while close, are not perfectly spherical. The slight ellipticity of the particles lifts the degeneracy of the valence band allowing more favourable coupling to the $l = 2$ mode [91]. The higher frequency longitudinal optical mode is also visible in all of the traces and does not change frequency significantly, within error, over the range of the samples [89, 265].

6.5.3 Further Discussion on Origin of Anisotropy Signal

The anisotropy dependence of the CPH-3TG measurements arises from transition dipole moment depolarization due to symmetry lowering of the unit cell as the nanocrystal vibrates, as is further discussed in Chapter 7. The net wavefunction, shown below in Equation 6.8, is a combination of circularly and linearly polarized states.

$$\Psi = \Psi_{\pm 1} + \lambda \Psi_0$$  \hspace{1cm} (6.8)

where $\Psi$ is the net wavefunction, $\Psi_{\pm 1}$ is the wavefunction of the circularly polarized $F = \pm 1$ states, $\Psi_0$ is the wavefunction of the linearly polarized $F = 0$ state, where $F$ is the total angular momentum and $\lambda$ is a small time-dependent mixing parameter that is proportional to the strain tensor $\varepsilon_{ij}$. The relation in Equation 6.8 holds as long as we as-
assume that the effect of the strain is linear and can therefore be treated as a perturbation [266]. This linear assumption is implicit in describing elastic behaviour and is justified since the system is experiencing small changes during the vibration. The effect of the dipole moment depolarization on the observed signal is shown in Figure 6.4.

The CPH-3TG technique is sensitive to the changing polarization of the dipole transition moment, and therefore, it is essentially an anisotropy-type measurement. By permutation of the polarization of the pump, probe and analyzer, the standard anisotropy signal can be calculated using the all parallel polarized and the crossed pump and probe-analyzer signals. The resulting calculated anisotropy shows the same acoustic phonon mode observed in the cross polarized signals, as shown in Chapter 7. In addition to the standard anisotropy, the results were verified by comparing the experimental traces recorded using various polarization sequences to simulated signals.

6.5.4 Absorption Spectra and Scanning Transmission Electron Microscopy Images

Absorption spectra of the CdSe colloidal nanocrystals suspended in toluene were measured using a Cary 100 UV/Visible spectrometer. The samples were measured against a toluene reference in 1 mm quartz cuvettes at room temperature with an optical density for the first exciton peak of approximately 0.3. The absorption spectra for all samples are shown in Figure 6.5. Scanning transmission electron microscopy (STEM) images for all of the samples were recorded using a Hitachi HD-2000 dedicated STEM operating at 200 kV. Images for each sample are shown in Figure 6.6.
Figure 6.4: The acoustic phonon mode induces strain in the nanocrystal, resulting in a time varying value of the strain tensor $\varepsilon_{ij}$. The change in the average value of the strain tensor is proportional to a weighting factor $\lambda$ that describes the degree of mixing between the $F = \pm 1$ and $F = 0$ states in the exciton fine structure. This is due to symmetry lowering of the unit cell by the acoustic phonon. Since the $F = \pm 1$ have circularly polarized transition dipole selection rules and the $F = 0$ has a linearly polarized selection rule, the varying mixing between the states induces a time dependent change in the net transition dipole from circular to elliptical as depicted in the bottom panel. This creates a time dependent anisotropy oscillation in the observed signal.
Figure 6.5: Absorption spectra for samples with radii from left to right of 1.18 nm, 1.21 nm, 1.30 nm, 1.35 nm, 1.42 nm, 1.57 nm, 1.69 nm, 1.82 nm and 1.99 nm. The traces have been offset for clarity.
Figure 6.6: Scanning transmission electron microscopy images of all measured samples. The mean radii of the samples are (a) 1.18 nm (b) 1.21 nm (c) 1.30 nm (d) 1.35 nm (e) 1.42 nm (f) 1.57 nm (g) 1.69 nm (h) 1.82 nm and (i) 1.99 nm.
Chapter 7

Acoustic Phonon Strain Induced Mixing of the Fine Structure Levels in Colloidal CdSe Quantum Dots Observed by a Polarization Grating Technique
7.1 Chapter Summary

This chapter expands on the results presented in Chapter 6, exploring the origin of the observed quantum beat in the cross polarized heterodyne detected ultrafast transient grating (CPH-3TG) signal. Further experiments are presented that show that the observed quantum beat, which arises from a coherent acoustic phonon mode in the nanocrystals, appears in anisotropy-type signals. The action of this mode induces a periodic strain in the nanocrystal that lowers the symmetry of the unit cell, mixing the fine structure states and their transition dipole moments. This mixing is manifested in anisotropy signals as a depolarization, which periodically modifies the rotational averaging factors.

This chapter returns to the study of the fine structure levels of the lowest energy exciton state that began in Chapters 2 and 3. It incorporates the concept of using optical techniques to study the material properties of a randomly oriented ensemble system in situ from Chapter 6. Observation of the acoustic phonon mode leads to an understanding of the interplay between the macro/microscopic and the material/optical properties of quantum confined colloidal nanocrystal systems.
7.2 Introduction

Semiconductor quantum dot systems are characterized by size-tuneable optical properties. In the strong confinement regime, where the diameter of the nanocrystal is small compared to the exciton Bohr radius, the nanocrystals have discrete electronic energy levels associated with bound electron-hole pairs called excitons. In this regime, the physical size and shape of the nanocrystal determines its optical properties. As a result, these materials have been extensively studied for their potential use in a range of applications including photovoltaics [26, 27], fluorescent biological tags [32, 33], lasers [4, 5, 6, 7, 8, 9, 10, 11, 12] and as a multiple exciton generating material for solar cells [24, 25]. However, the nanoscale dimensions of these systems have implications beyond the optical properties, resulting in material characteristics that differ from the corresponding bulk materials, leading to modified solid-solid phase transitions [253, 254, 255], melting point depression [256] and changes in elasticity [267].

Chapter 6 used nonlinear optical measurements to determine the material properties of a semiconductor nanocrystal system. Observation of a quantized acoustic phonon mode, using an optical polarization grating technique, allowed us to report the size-dependent modification of the elastic parameters and surface stress in small colloidal CdSe nanocrystals. This chapter derives the origin of the acoustic mode in the signals, explaining the mechanism behind its observation and exploring its physical effects in the nanocrystal lattice. We show that the polarization grating technique is sensitive to phonon induced strain that mixes the fine structure states of the first exciton transition.

This chapter is organized in the following way. The next section, 7.3, provides a general description of the optical and acoustic phonon modes in semiconductor nanocrystal systems. Section 7.4 qualitatively describes the polarization control methodology, as well as the fine structure optical properties of the first exciton state of CdSe nanocrystals. This leads into the fifth section, 7.5, which describes the specifics of the rotational averaging that makes polarization control possible in a colloidal semiconductor. In section
7.6, the experimental methods are presented, including a brief description of the laser setup and sample characteristics. Following the description of the experimental techniques, section 7.7 presents the results of the transient grating measurements obtained using different polarization combinations and comparison with literature results. Section 7.8 discusses the results, including the origin of the acoustic phonon mode in different polarization signals. The elastic sphere model and the assignment of the acoustic phonon mode are explained as well as the strain induced mixing of the fine structure levels. Response function simulations are also presented. Finally, in section 7.9 we summarize and draw conclusions.

7.3 Phonon Modes in Semiconductor Nanocrystals

Phonons, which are quantized lattice vibrations, are generally categorized as either acoustic or optical. Acoustic modes, which tend to be low frequency, involve a displacement of the centre of mass of the unit cell, where the movement of the atoms has the same amplitude, direction and phase. Optical modes, which are generally higher in energy, only involve an internal degree of freedom, where atoms in the unit cell move opposite to each other. The two types of phonon couple to the electronic bands through different mechanisms and have separate size-dependences in nanocrystals.

The acoustic phonon modes of a small nanocrystal can be described in terms of the elastic deformation of a homogeneous particle using the elastic sphere model [242, 268]. These modes are strongly size-dependent and couple to the electronic states through the deformation potential. In polar semiconductors, the acoustic phonons may also be coupled to the electronic states through a piezoelectric term, which depends on lattice polarization. However, in the small size limit, the deformation potential coupling dominates the piezoelectric component [248, 269, 270, 271, 272].
In CdSe nanocrystals, the longitudinal optical (LO) mode at approximately 208 cm\(^{-1}\) is well characterized as it is commonly observed in resonant optical ultrafast nonlinear measurements [49, 60, 89, 91, 99, 265, 270, 271, 273, 274]. It is only weakly dependent on the particle radius and is \( \propto 1/\sqrt{R} \) where \( R \) is the radius of the nanocrystal [249]. In the small nanocrystal limit, little size-dependence has been observed experimentally [89, 265, 270, 271, 273, 274]. The LO mode couples to the electronic states through the polar Fröhlich interaction [91, 265, 274] and is easily observed in time dependent ultrafast measurements. As a result, this mode has been extensively studied. Since the behaviour of the optical phonon is fairly well understood, it can provide a comparison to aid in our understanding of the acoustic mode.

As opposed to the LO phonon, the acoustic modes have historically been more elusive and, as a result, are less studied. The first observation of a coherent acoustic phonon in a colloidally synthesized semiconductor nanocrystal (PbS) was reported by Krauss and Wise in 1997 [271]. More recently, acoustic phonon modes have been observed experimentally in colloidal CdSe nanocrystals [97, 270, 275, 276, 277, 278]. Previous experimental efforts have focused on the acoustic phonons due to their role as important bath modes for relaxation and decoherence [91, 97, 275, 277, 276, 278] and as the main component of pure dephasing in the homogeneous line width [248, 279, 280]. However, as shown in recent work, the acoustic phonon modes can also be used as a probe to study the material characteristics of colloidal nanocrystals, such as elastic parameters and surface strain [267] – see Chapter 6. Since the acoustic phonon is coupled through the deformation potential, it can be used to report on the size-dependence of structural details of the nanocrystals. As it acts on the nanocrystal lattice, it induces a periodic strain that oscillates with the period of the mode. This induced strain modifies the optical spectrum of the nanocrystals by mixing the fine structure states of the first exciton transition. While it is possible to observe the acoustic phonon in other ultrafast experiments, such as pump-probe or three pulse photon echo, by using a polarization grating method that
is sensitive to the mixing of the fine structure we are able to clearly and consistently resolve the mode.

### 7.4 Cross Polarization Measurements and the Fine Structure of the First Exciton State of CdSe Nanocrystals

The first exciton state of CdSe spherical nanocrystals with wurtzite crystal structure is split into eight fine structure states as a result of the exchange interaction and the crystal field effect [109, 137]. These levels are labelled by the projection of their total angular momentum \( F \) onto the \( c \)-axis, which is distinguishable from the \( a \)- and \( b \)-axes in a hexagonal base system (in other words, in terms of the basis vectors, \( a = b \neq c \)). The total angular momentum is used to distinguish the fine structure levels since, due to valence band mixing, only the parity and total angular momentum are good quantum numbers [108]. The eight sub-states of the lowest energy exciton transition \((1S_{3/2} - 1S_e)\) are comprised of four with \( F = \pm 1 \), two with \( F = \pm 2 \) and two with \( F = 0 \), as shown in Figure 3.1(a). The \( F = 2 \) states are optically passive or ‘dark’ in the dipole approximation since photons cannot have an angular momentum projection of \( \pm 2 \), and as such, these states are not associated with optical selection rules. The states with \( F = \pm 1 \) and \( F = 0 \) are divided into upper and lower states according to their relative energy. All four of the \( F = \pm 1 \) states are bright and have circularly polarized selection rules, with right hand circularly polarized light exciting the +1 states and left hand circularly polarized light exciting the −1 states. The lower \( F = 0 \) is dark (a triplet state) while the upper \( F = 0 \) state is bright with a linearly polarized optical selection rule. Owing to these specific selection rules, polarization control in a transient grating experiment has
been successfully used to study relaxation in the fine structure despite the fact that these levels are separated by a small energy gap on the order of approximately 10–40 meV depending on the diameter of the nanocrystal. However, these selection rules can also be used to observe acoustic phonon modes based on the way that the levels mix when the nanocrystal experiences a strain.

The fine structure in CdSe nanocrystals with different morphologies [49, 99, 102, 103, 104, 105] has been studied using a crossed polarization heterodyne transient grating (CPH-3TG) methodology. In the CPH-3TG experiment, transient grating signals are measured using crossed linear polarization combinations VHVH and VHHV for the two pumps, the probe, and an analyzer placed after the sample respectively, where $V =$ vertical linear polarized light and $H =$ horizontal linearly polarized light. In a standard transient grating experiment with all linear polarized beams (i.e. VVVV), the two pump beams create a grating of chromophores in the ground or excited state. This population grating, and therefore the signal, decays as the excited states return to the ground state. In a CPH-3TG experiment, the crossed linearly polarized pump pulses create a polarization grating in the sample, producing a periodic spatial pattern of right and left circular polarization [127, 281, 282]. As a result of the selection rules associated with the fine structure states, the polarization grating produces a periodic grating of angular momentum projections. This projection depends on the orientation of the nanocrystals relative to the laboratory frame of reference. For example, if the nanocrystals were all aligned relative to their $c$-axes in the laboratory frame, the cross polarized pump pulses would create a grating of $+1$ and $-1$ states, which is analogous to a spin grating. In a colloidal system, the nanocrystals are randomly oriented, however, the CPH-3TG signal does not vanish as a consequence of rotational averaging. By taking advantage of interference between oppositely signed signal contributions in a rotationally averaged system [125], the CPH-3TG experiment allows us to measure changes in the total angular momentum of the exciton. While a transient grating experiment with all parallel linear polarizations
measures population decay, a CPH-3TG experiment measures depolarization.

7.5 Rotational Averaging in a Colloidal Semiconductor Nanocrystal System

The signal generated from an optical polarization experiment such as CPH-3TG performed on a randomly oriented sample entirely depends on the rotational averaging. The effect of polarization control is not immediately obvious. It is well known that polarized pulses interacting with a randomly oriented sample can selectively excite the subset of that system which happens to be properly aligned relative to the incident beams. For example, this type of photoselection is exploited for fluorescence anisotropy measurements. In the CPH-3TG experiment, the pump pulses photoselect a subset of the ensemble with appropriately aligned \(c\)-axes. The evolution of this subset is subsequently followed using the polarized probe and analyzer. It is these two interactions that allow for observation of the dynamics within the fine structure states. This result is not intuitively obvious and is determined by working out the rotational averaging factors based on the polarization sequence used and the transition dipole moments of the system. In the special case of wurtzite or zinc blende semiconductors, the complex nature of the transition dipole moments contributes a sign to the rotational averaging factors that allows us to follow the evolution of the exciton states initially photoselected by the pump interactions.

In systems with complex transition dipole moments such as CdSe semiconductor nanocrystals, crossed linear polarization sequences create an interference effect between signal contributions with oppositely signed rotational averaging factors [102, 105, 125]. The CPH-3TG signals are essentially difference measurements that allow for indirect measurement of equilibration within the fine structure states of the first exciton transition. This is despite the fact that these are rotationally averaged systems excited with
laser pulses whose bandwidth vastly exceeds the energy separation of the near degenerate states, as previously shown [49, 99, 102, 103, 104, 105]. The rotational averaging factors allow us to understand the effect of polarized interactions on a randomly oriented sample.

The rotation averaging factors relate the nanocrystal frame of reference to the laboratory frame of reference. In this way, they allow us to understand how the action of pulses polarized in the laboratory frame affect the rotationally averaged colloidal nanocrystal sample. Additional details of the rotational averaging procedure can be found in References [104, 125] and the references therein. The rotationally averaged observable, $C$, which represents the material response to incident radiation can be written as,

$$C = \langle S_{i_1 \cdots i_n} T_{i_1 \cdots i_n} \rangle$$  \hspace{1cm} (7.1)$$

where $S_{i_1 \cdots i_n}$ and $T_{i_1 \cdots i_n}$ are tensors of generalized rank $n$ associated with a nonlinear spectroscopy of $(n-1)$th order. $S_{i_1 \cdots i_n}$ is the polarization tensor describing the action of the incident light in the laboratory frame on the nanocrystal. $T_{i_1 \cdots i_n}$ represents the nanocrystal response to the action of the incident light. However, the transition dipole moments that describe the response of the nanocrystal to the light are in a nanocrystal fixed frame. Therefore, in order to determine the rotational averaging factors, the laboratory and the nanocrystal frames must be related to each other. This can be done using a Euler transform, where the components of $T_{i_1 \cdots i_n}$ are referred to a nanocrystal frame where they are rotationally invariant by the direction cosine, $\ell_{i_n \lambda_n}$, describing the angle between the laboratory, $i_n$, and nanocrystal fixed, $\lambda_n$, frames. The observable, $C$, can now be written as,

$$C^{(n)} = S_{i_1 \cdots i_n} T_{\lambda_1 \cdots \lambda_n} I_{i_1 \cdots i_n;\lambda_1 \cdots \lambda_n}^{(n)}$$  \hspace{1cm} (7.2)$$

where $I_{i_1 \cdots i_n;\lambda_1 \cdots \lambda_n}^{(n)}$ is the rotation average of the direction cosine product $[130, 283]$.

For any third-order nonlinear spectroscopy, the rotationally averaged expressions can
be determined using [130],

\[
I^{(4)}_{abcd;\alpha\beta\gamma\delta} = \frac{1}{30} \begin{pmatrix}
\delta_{ab}\delta_{cd} \\
\delta_{ac}\delta_{bd} \\
\delta_{ad}\delta_{bc}
\end{pmatrix}^T \begin{pmatrix}
4 & -1 & -1 \\
-1 & 4 & -1 \\
-1 & -1 & 4
\end{pmatrix} \begin{pmatrix}
\delta_{\alpha\beta}\delta_{\gamma\delta} \\
\delta_{\alpha\gamma}\delta_{\beta\delta} \\
\delta_{\alpha\delta}\delta_{\beta\gamma}
\end{pmatrix}
\tag{7.3}
\]

where \(a, b, c, d\) are the laboratory frame indices and \(\alpha\beta\gamma\delta\) are the nanocrystal frame indices.

Defining, \(\hat{e}_a, \hat{e}_b, \hat{e}_c, \hat{e}_d\) as the polarization associated with pump one, pump two, the probe and the analyzer, respectively, the tensor \(S\) can be written as

\[
S_{abcd} = \hat{e}^*_a\hat{e}_b\hat{e}^*_c\hat{e}_d.
\]

The tensor \(T\) is written in terms of the transition dipole moments, \(\mu\), so that

\[
T_{\alpha\beta\gamma\delta} = \mu^*_\alpha\mu_\beta\mu^*_\gamma\mu_\delta.
\]

Since the signal is collected in the \(-k_1 + k_2 + k_3 - k_{\text{Signal}} = 0\) phase matching direction, the tensors \(S\) and \(T\) become

\[
S_{abcd} = \hat{e}^*_a\hat{e}_b\hat{e}^*_c\hat{e}_d\text{ and } T_{\alpha\beta\gamma\delta} = \mu^*_\alpha\mu_\beta\mu^*_\gamma\mu_\delta\text{ where } * \text{ indicates complex conjugate.}
\]

Using the dipole approximation and the above equations, \(C^{(4)}\) for a resonant experiment can be written as,

\[
C^{(4)} = \frac{1}{30} \begin{pmatrix}
(\hat{e}^*_a\hat{e}_b)(\hat{e}_c\hat{e}^*_d) \\
(\hat{e}^*_a\hat{e}_c)(\hat{e}_b\hat{e}^*_d) \\
(\hat{e}^*_a\hat{e}^*_c)(\hat{e}_b\hat{e}_c)
\end{pmatrix}^T \begin{pmatrix}
4 & -1 & -1 \\
-1 & 4 & -1 \\
-1 & -1 & 4
\end{pmatrix} \begin{pmatrix}
(\hat{\mu}^*_\alpha\hat{\mu}_\beta)(\hat{\mu}^*_\gamma\hat{\mu}_\delta) \\
(\hat{\mu}^*_\alpha\hat{\mu}_\gamma)(\hat{\mu}^*_\beta\hat{\mu}_\delta) \\
(\hat{\mu}^*_\alpha\hat{\mu}_\delta)(\hat{\mu}^*_\beta\hat{\mu}_\gamma)
\end{pmatrix}
\tag{7.4}
\]

This expression allows us to determine the rotational averaging weighting factors for the experiment. It is clear from Equation 7.4 that the combination of the transition dipole momenta and pulse polarization sequence determines the rotational averaging factors. The rotational averaging factors, \(C^{(4)}\), for an unstrained CdSe nanocrystal with circularly polarized selection rules associated with the fine structure \(F = \pm 1\) states have been reported previously [125]. In this case, the transition dipole moments are \(\bar{\mu}_+ = (X, iY, 0)\) and \(\bar{\mu}_- = (X, -iY, 0)\) for the \(F = +1\) and \(F = -1\) states respectively [109]. The corresponding polarization vectors for right and left circular polarization are written as \(\hat{e}_R = (\hat{e}_x - i\hat{e}_y)/\sqrt{2}\) and \(\hat{e}_L = (\hat{e}_x + i\hat{e}_y)/\sqrt{2}\) [125]. These definitions will be revisited
when the action of the phonon on the transition dipole moments is discussed.

### 7.6 Experimental Methods

A series of nine colloidal wurtzite CdSe nanocrystal samples capped with trioctylphosphine oxide (TOPO) with average radii ranging from 1.18 nm to 1.99 nm were prepared and isolated using literature procedures [36, 37]. In order to verify the size distribution and shape of the nanocrystals, scanning transmission electron microscopy (STEM) images were recorded using a Hitachi HD-2000 dedicated STEM operating at 200 kV. The STEM images for all samples are presented in Figure 6.6. Absorption spectra for all samples were measured using a Cary 100 UV/Vis spectrometer before and after the experiments to set the optical density and monitor that no sample degradation occurred. Absorption spectra for all samples are presented in Figure 6.5. For the ultrafast nonlinear measurements, the nanocrystal samples were suspended in toluene at an optical density of approximately 0.3 in a 1 mm path length cuvette. All measurements were performed at 293 K using low incident intensity (< 6 nJ/pulse).

The laser setup has been described previously [104]. Briefly, in this experiment, laser pulses from a Ti:sapphire amplified laser with a 1KHz repetition rate are converted into pulses in the visible wavelength range using a non-collinear optical parametric amplifier (NOPA). The wavelength of the laser was tuned to approximately 5 nm to the red of the lowest exciton peak of each CdSe colloidal nanocrystal sample studied. These pulses were compressed using a quartz prism pair to compensate for the dispersion. The compression allowed us to obtain pulses with full width half maximums of 20 to 30 fs. Optical Kerr effect measurements were performed on carbon tetrachloride in a 1 mm pathlength cell placed at the sample position to provide a non-resonant autocorrelation. After the compression, the beam was divided using a beamsplitter into a strong pump and a weak
probe, and a time delay between the two pulses was introduced using a motorized translation stage. To ensure low incident power, the intensity of the pump and the probe beams were controlled individually using a half-waveplate polarizer pair. The polarization of the probe was set at 45° relative to the pump beam. This was done so that the VVVV and VVHH or the VHVH and VHHV signals could be measured simultaneously. The intensity controlled and temporally separated beams were then used as inputs to a third-order optical heterodyne transient grating experimental setup.

Following the methodology of the Fleming [284] and Miller [245] groups, a diffractive optic was used to generate four passively phase stabilized beams, with two each from the pump and the probe input beams. The specific details of this experimental setup have been described elsewhere [102, 104]. After the diffractive optic, the beams were collimated and focused into the sample. The polarization of each beam was independently controlled using half-waveplates inserted in the collimated region. Using a box geometry, the signal radiated in the \(-k_1 + k_2 + k_3\) phase matching direction is overlapped with the local oscillator (the fourth beam from the diffractive optic). Overlapping the signal with the local oscillator allows for heterodyne detection, which linearizes the signal and permits separation of the diffractive (real) and absorptive (imaginary) components.

In a transient grating experiment, two spatially separate, time-coincident pump beams, \(k_1\) and \(k_2\), are focused into the sample with a small crossing angle, creating a population grating. After a time delay \(t_p\) (population time) a probe pulse \(k_3\) interacts with the sample and a signal is generated in the phase matched direction \(-k_1 + k_2 + k_3\). The transient grating measurement is similar to a pump-probe type of experiment. However, in transient grating, the two pump interactions are separated spatially. This spatial separation allows for individual control of the polarization of each pump interaction, the probe and the signal, using an analyzer. Polarization control in a transient grating experiment can obtain additional information beyond simple population dynamics. Using specific polarization combinations, this technique can be used to study relaxation in the fine structure
states of the first exciton transition of CdSe quantum dots as shown in Chapters 2 and 3. Additionally, as we show below, polarization control can also allow for the study of nanocrystal strain, which causes mixing of the fine structure states.

Heterodyne detected ultrafast transient grating measurements using polarization combinations VVVV, VVHH, VHVH and VHHV (note that the VHVH and VHHV are ‘CPH-3TG’ measurements) were performed on the colloidal CdSe nanocrystal samples. The VHVH and VHHV pair were recorded simultaneously, as were the VVVV and VVHH signals. All measurements were repeated at least five times. The imaginary (absorptive) component of the signal was recorded.

7.7 Results

In a transient grating experiment, the permutations of pump, probe and analyzer linear polarizations that produce non-zero signal, VVVV, VVHH, VHVH and VHHV can be divided into two pairs that contain similar information. Broadly, the VVVV and VVHH pair measure population decay while the crossed polarized pair, VHVH and VHHV, measure depolarization. Note that population decay also appears in the cross-polarized signals but as a long time offset relative to the fast equilibration dynamics, with the same components as in the normal transient grating signal but with a small prefactor [102]. Essentially, the VHVH and VHHV signals consist of both an anisotropy-like response and a standard transient intensity decay. If the action of the acoustic mode on the nanocrystal is an anisotropy effect, both sets of signal pairs can be used to observe the phonon quantum beat.
Figure 7.1: CPH-3TG measurements performed on a colloidal CdSe nanocrystal sample with an average radius of 1.69 nm. Panel (a) shows the imaginary component of the heterodyne detected VHVH (top, green trace) and the VHHV (bottom, blue trace) polarization combination signals in the third-order transient grating configuration. (b) presents the same data on a semi-log scale to emphasize the short time behaviour of the traces, both the acoustic and the optical phonon modes are visible. A close up of the short population time profiles of the VHVH (top, green) and the VHHV (bottom, blue) signals in panels (c) and (d) clearly show the optical (c) and the acoustic (d) phonon modes. The optical and the acoustic modes display a different phase relationship between the VHVH and the VHHV signals. Panel (e) presents the residuals obtained by fitting the signal traces to a series of exponentials for the VHVH (green) and VHHV (blue) signals. The Fourier transform of the VHVH residual (green trace in panel (e)) is presented in panel (d). Both the optical and the acoustic mode are visible in the Fourier transform.
7.7.1 CPH-3TG Experiments

Figure 7.1 presents representative CPH-3TG traces for a colloidal CdSe nanocrystal sample. Panel (a) shows the imaginary component of the CPH-3TG signal for both the VHVH (initially positively signed, green trace) signal and the VHHV signal (initially negatively signed, blue trace). Panel (b) presents the same traces shown in 7.1(a) but with the population time (probe delay time), $t_p$, axis on a log scale. The semi-log plot clearly shows both the acoustic phonon and the LO phonon modes. The linear regions in (b), which correspond to single exponential decays, show the short time delay region with the fine structure equilibration and the longer time region comprising exciton population dynamics associated with surface trapping and decay.

Figure 7.1(c) and (d) are close ups of the short time delay region of the VHVH and the VHHV CPH-3TG signal. The LO phonon mode, with a frequency approximately $208 \text{ cm}^{-1}$, most clearly seen at time delays less than $5 \text{ ps}$, is superimposed on the lower frequency acoustic phonon mode. Both the LO and the acoustic phonon modes are visible in the VHVH and the VHHV signals. Additionally, each mode has a specific phase relationship between the two cross polarized signals. The oscillations of the optical mode, shown in Figure 7.1(c), are mirror images of each other. For the optical mode, an increase in the VHVH signal associated with the quantum beat corresponds to an increase in the VHHV signal. Note that an increase for the VHHV signal is defined as ‘negative’ relative to the VHVH signal due to the rotational averaging factors. The acoustic mode has a different phase relationship between the crossed polarized signals, as shown in panel (d). For the acoustic mode, the oscillations move together. This means that when the amplitude increases in the VHVH signal, it decreases for the VHHV signal. The phase relationship between the VHVH and VHHV signals for the acoustic mode is opposite of that for the optical mode. These phase relationships for the optical and the acoustic modes, which are discussed further in Section 7.8.3, were constant for all CdSe samples measured. The acoustic phonon mode persists past the fast exponential decay,
which indicates that the origin of the acoustic phonon mode is separate from processes associated solely with the fine structure equilibration.

In order to determine the frequency of the observed modes, the VHVH and the VHHV traces were fit to a series of exponentials to deconvolute the population and fine structure relaxation dynamics from the phonon modes. The residuals of those fits were then Fourier transformed to obtain the frequencies of the phonon modes. The residuals from the VHVH and VHHV data are shown in Figure 7.1(e) and the Fourier transform of the VHVH residual is shown in Figure 7.1(f). Both of these plots are representative of those obtained for all samples. We observed that the frequency of the LO mode did not shift with size, within experimental uncertainty. This result is consistent with theoretical predictions and other ultrafast experiments as described in Section 7.3. However, the acoustic phonon mode was observed to be size-dependent as we have reported previously [267] (see Chapter 6). Figure 7.2 presents the residuals from the VHVH CPH-3TG traces for all samples measured. Both the optical and the acoustic modes are visible in all of the residual traces.

### 7.7.2 VVVV, VVHH Experiments and Calculated Anisotropy

Representative VVVV and VVHH polarization combination third-order heterodyne transient grating signals are presented in Figure 7.3. The signals in Figure 7.3 were measured for a sample with an average radius of 1.35 nm. Both the VVVV and the VVHH signals follow population dynamics, including surface trapping and population decay. These components have exponential decay profiles with relatively long timescales ranging from picoseconds (for surface trapping) to nanoseconds (for relaxation of the exciton) [60, 102]. Although both polarization combinations have the same decay profile, the VVHH signal has a lower intensity and a smaller coherent spike than the VVVV signal. In the VVHH signal, the different polarization of the probe and analyzer compared to the pump inter-
Figure 7.2: The size-dependence of the acoustic phonon modes. Residuals (points) and two damped cosine fit to the residuals (lines) obtained from the VHVH traces for all samples measured are presented in order of size. The residual from the VHVH trace measured for the sample with the smallest average nanocrystal radius ($R = 1.18$ nm) is at the top and the residual for the sample with the largest average nanocrystal radius ($R = 1.99$ nm) is at the bottom. A clear size-dependence is observed for the low frequency acoustic phonon mode. The traces have been offset for clarity.
actions removes some scatter components. Also, the interaction between the grating and the probe is slightly different. Only the optical phonon mode is visible in the VVVV and VVHH traces. The optical mode can be more clearly seen in the inset, which shows a close up of the short time delay behaviour of both traces. The acoustic phonon mode is not visible in either the VVVV or VVHH signals.

Although the acoustic phonon mode is not visible in either the VVVV or the VVHH trace, information from the mode is contained in those experiments. These traces can be used to calculate an anisotropy signal, which reveals the acoustic phonon. The acoustic phonon mode is observable in the VHVH and VHHV signals, which both access the anisotropy, as well as the calculated anisotropy since it is indirectly observed in these traces by generating a depolarization. Representative anisotropic and isotropic responses calculated from the VVVV and VVHH traces are shown in Figure 7.4. The trace in panel (a) is the uncorrected anisotropy calculated by subtracting the VVHH signal intensity, $I_{VVHH}$, from the VVVV signal intensity, $I_{VVVV}$. The calculated uncorrected anisotropy resembles the measured VHVH signal. Both the optical and the acoustic modes are evident in this trace and are more clearly seen in the inset, which is a close up at short time delays. The isotropic component is calculated as $I_{VVVV} + 2 * I_{VVHH}$ and is presented in Figure 7.4(b). The acoustic phonon mode does not appear in this trace, however, the optical mode does and can be clearly seen in the inset, which is a close up of the short time delay behaviour. The anisotropy, as calculated in panel (a), must be corrected to remove components from the third-order polarization. The corrected anisotropy, $r$, is determined from $I_{VVVV}$ and $I_{VVHH}$ using the following equation,

$$r(t) = \frac{I_{VVVV}(t) - I_{VVHH}(t)}{I_{VVVV}(t) + 2 * I_{VVHH}(t)} \quad (7.5)$$

The trace calculated from Equation 7.5 has a small exponential component. The residual obtained when the calculated, corrected anisotropy, $r(t)$, is fit to an exponential function is shown in Figure 7.4(c).

Both the acoustic and the optical phonon modes appear in the corrected anisotropy
Figure 7.3: Imaginary component of the heterodyned detected third-order transient grating signal measured for a CdSe colloidal nanocrystal sample with an average radius of $R = 1.35$ nm using the VVVV (top, blue) and VVHH (bottom, green) polarization combinations. The decay profile in these signals is dominated by long-timescale exponential decays. The optical phonon mode is clearly visible at short time delays (population times) as shown in the inset. The acoustic phonon mode is not observed.
signal calculated from the VVVV and VVHH transient grating data. The Fourier transform of the residual of the corrected anisotropy, presented in Figure 7.4(d), shows the frequency of both the optical and the acoustic modes. The optical mode appears in both the anisotropic and the isotropic response, while the acoustic mode only appears in the anisotropic traces. This is due to the specific origin of both of the phonon modes. In an optical vibration in CdSe, the Cd and the Se ions move opposite to each other, creating a time varying dipole moment. This oscillating dipole moment can easily couple to the excitation through the Fröhlich interaction. An acoustic phonon mode, as we explain in the next section, distorts the unit cell and mixes the transition dipole moments of the fine structure states. This mixing modifies the rotational averaging factors and appears as a depolarization, resulting in an oscillation of the observed anisotropic trace. For each colloidal CdSe sample, the frequency of the acoustic mode measured using the cross polarized VHVH and VHHV signals was the same as that obtained from the calculated anisotropy.

The acoustic phonon mode is damped in all measured samples after two or three periods, while the optical mode persists for an average of 20 cycles. There are several processes that contribute to the damping of the acoustic mode. The acoustic phonon is a low frequency process on the order of \(10 \text{ cm}^{-1}\) in a material with small dimensions, which is easily dissipated. The period of this mode is on the order of picoseconds, and therefore, over the timescale of a single oscillation there are many dissipative interactions that contribute to the damping. Because of the importance of the surface in nanocrystals, dissipative interactions with the surroundings contribute to the damping of the mode after one to two periods. Additionally, the colloidal CdSe sample being studied here is an ensemble system that contains a distribution of nanocrystal sizes. In order to observe the acoustic phonon it is necessary to have high quality samples with very narrow size distributions. However, even in a colloidal sample with a narrow size distribution there is a range of nanocrystals with different diameters as a consequence of the synthetic method.
Figure 7.4: The isotropic and anisotropic traces calculated from VVVV and VVHH heterodyne detected third-order transient grating signals intensities ($I_{VVVV}$ and $I_{VVHH}$) measured for a colloidal CdSe nanocystal sample with an average radius of $R = 1.35$ nm. Panel (a) presents the uncorrected anisotropy calculated as $I_{VVVV} - I_{VVHH}$. Both the optical and the acoustic phonon are clearly observable, especially at short population times as shown in the inset. Panel (b) shows the isotropic response calculated as $I_{VVVV} + 2 \times I_{VVHH}$. Only the optical mode is observable at short population times as shown in the inset. The corrected anisotropy is calculated using Equation 7.5. The residual of the corrected anisotropy is presented in panel (c). Panel (d) presents the Fourier transform of the residual in panel (c). Both acoustic and optical modes are visible in the Fourier transform.
For larger nanocrystals, the effect of the distribution is less significant since the frequency of the acoustic mode is relatively insensitive to size, as shown in Chapter 6. However, for the smaller samples, the frequency of the mode is more strongly size-dependent and the varying frequencies from a continuum of differently sized nanocrystals will destructively interfere, contributing to a more pronounced damping. The optical modes are much higher frequency and as such are not as profoundly affected by interaction with the surroundings. Additionally, since the frequency of the optical phonon is not strongly size-dependent, it has less dependence on the size-distribution of the sample.

### 7.7.3 Comparison to Literature Results

The frequencies of the acoustic phonon modes observed in the nanocrystal samples measured are presented in Table 7.1. These values were obtained by averaging the frequency obtained from all of the Fourier transforms of the VHVH, VHHV and the calculated anisotropy residuals for a particular sample. The observed frequencies ranged from $\sim 13 \text{ cm}^{-1}$ to $\sim 17 \text{ cm}^{-1}$. Although this may seem like a small change, this represents an increase of 30% for a change in radius of $\sim 0.8 \text{ nm}$, as well as a significant modification of the elastic properties as shown in Chapter 6.

The acoustic phonon mode frequencies obtained in our measurements compare closely with the few other experimental observations. However, comparison is complicated since there are relatively few direct observations of the acoustic phonon modes, and most of the previous work has been performed on larger nanocrystals than those measured here or on core-shell CdSe semiconductor nanocrystals. These core-shell nanocrystals have a CdSe ‘core’ which is overcoated with a larger band gap material, typically CdS or ZnS. This is done to reduce the number of surface traps, producing nanocrystals with higher quantum yields. However, it is not necessarily reasonable to directly compare the acoustic phonon modes of core-shell and standard quantum dots. Usually the size
Table 7.1: Frequency and Energy of the Measured Acoustic Phonon Mode

<table>
<thead>
<tr>
<th>Average Nanocrystal Radius (nm)</th>
<th>Frequency of Acoustic Phonon Mode (cm(^{-1}))</th>
<th>Energy of Acoustic Phonon Mode (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.18</td>
<td>16.7</td>
<td>2.07</td>
</tr>
<tr>
<td>1.21</td>
<td>15.9</td>
<td>1.97</td>
</tr>
<tr>
<td>1.30</td>
<td>14.5</td>
<td>1.8</td>
</tr>
<tr>
<td>1.35</td>
<td>14.1</td>
<td>1.75</td>
</tr>
<tr>
<td>1.42</td>
<td>13.6</td>
<td>1.69</td>
</tr>
<tr>
<td>1.57</td>
<td>13.1</td>
<td>1.62</td>
</tr>
<tr>
<td>1.69</td>
<td>13.0</td>
<td>1.61</td>
</tr>
<tr>
<td>1.82</td>
<td>12.9</td>
<td>1.6</td>
</tr>
<tr>
<td>1.99</td>
<td>12.9</td>
<td>1.6</td>
</tr>
</tbody>
</table>

of the core is given based on the calibration curves associated with the linear absorption spectrum and not the total diameter of the particle. The addition of a shell must be considered if we are modelling the particles as isotropic elastic spheres (see Chapter 6 or Section 7.8.1), in which case the shell would contribute in addition to the core. The interface between the shell and the core may affect the modes and the shell material may be considered as a rigid matrix, which is known to modify the phonon modes [285, 286].

The closest comparison comes from indirect temperature resolved photoluminescence lifetime measurements [287]. The energies obtained in Reference [287] from \(\sim 1.7\) meV to \(\sim 0.8\) meV are from seven nanocrystal samples spanning a range of sizes from \(R = 1.35\) nm to \(R = 3.15\) nm respectively. Both the size-dependence and magnitude of these values are similar to our results, which span in energy from 2.1 meV to 1.6 meV for nine samples with sizes from \(R = 1.18\) nm to \(R = 1.99\) nm respectively. Reference [278] provides a comparison of acoustic phonon energies associated with the \(l = 2, m = 0\) mode obtained from transient absorption [288] and photoluminescence lifetime measurements [287, 289] all of which are consistent with our results.

Direct measurements of the acoustic phonon mode in CdSe nanocrystals also compare favourably with our results, although, as mentioned above, the nanocrystals studied
are mostly core-shell and of larger size. Modelling this system as an elastic sphere (see Chapter 6 or Section 7.8.1), we expect that, for a given mode, the energy or frequency decreases as the radius increases. The reported energies for the acoustic phonon mode obtained from emission lines [276] of 1.3 and 1.8 meV for larger core-shell particles with core radii of 3 and 5 nm, which does not include the shell, is comparable to our measurements. Photoluminescent studies of core-shell-shell CdSe-CdS-ZnS nanocrystals [277] report an energy of 1.2 meV for a core radius of 1.65 nm, which again does not include the shells. This value is lower than our measured results, however, it is still close especially considering the effect of the two shells. In Reference [275], oscillations in high intensity pump-probe measurements attributed to acoustic phonon modes were reported with energies of 3 meV and 1.6 meV for nanocrystals with radii of 1.95 nm and 3.5 nm respectively. These results are slightly higher in energy than expected from our measurements, which may be associated with the high intensity measurement. However, these values are still close to the values observed in the present experiment. Recent time domain pump-probe measurements report [97, 270] an energy of 2.3 meV for a nanocrystals with $R = 2.7$ nm. This result is relatively high energy as compared with our data and literature results. This measurement may be accessing a higher energy mode than the current experiment, however, this result is still within a reasonable energy range.

7.8 Discussion and Theory

7.8.1 Acoustic Phonon and the Elastic Sphere Model

In order to understand the action of the phonon modes we consider the elastic properties of the nanocrystals to be similar to those of isotropic elastic spheres. The acoustic phonon modes of a free (stress-free interface) spherical nanocrystal can be described in terms of the discrete vibrations of a homogeneous particle using an elastic continuum
model. This model, first described by Lamb in 1882 [242], is known as the elastic sphere model and has been used successfully to describe acoustic modes in nanoscale spherical particles [91, 241, 247, 249, 265, 271, 290, 291, 292, 293, 294, 295, 296]. Using a stress-free boundary condition, assuming that the nanocrystal is spherical and the vibrations are within the linear elastic regime, the phonon modes can be described by,

\[
\rho \frac{\partial^2}{\partial t^2} u = (\lambda + \mu) \text{grad div } u + \mu \nabla^2 u
\]  

(7.6)

where \(\rho\) is the density of the nanocrystal, \(u\) is the displacement vector and \(\lambda\) and \(\mu\) are the Lamé parameters. Solving this equation gives two kinds of eigenmodes, spheroidal and torsional. These two sets of modes are differentiated by the change in the material density during the vibration. A spheroidal mode is generally characterized by a varying overall change in the material density, while a torsional mode involves only shear motions that do not change the overall density of the material. Owing to the spherical symmetry, these modes are classified by angular momentum number. The Lamé parameters, \(\lambda\) and \(\mu\), can be used to calculate the elastic modulus of the material as shown in Equation 6.3.

As described in Chapter 6, the experimentally observed phonon frequency can be used to determine the Lamé parameters using Equation 7.6, which can then be used to calculate the elastic modulus.

The acoustic phonon modes in CdSe nanocrystals couple to the excitation mainly through the deformation potential. When the deformation potential is the dominant interaction, only spheroidal modes can contribute. Of those modes, the \(l = 0, m = 0\) and the \(l = 2, m = 0\) modes are potentially active based on group theory arguments in a perfectly spherical nanocrystal [246]. Both of these modes are primarily surface modes, the internal modes are essentially inactive [297]. The \(l = 0\) is purely radial and symmetric and is often referred to as a ‘breathing’ mode. The \(l = 2\) mode is a quadrupolar, ‘football’ mode, with mixed longitudinal and transverse components. However, for a dipolar Raman scattering mechanism, the \(l = 0\) mode has a much lower Raman activity than the \(l = 2\) mode [264]. In fact, in a cubic crystal the \(l = 0\) is inactive [297]. It has also been
shown that only the lowest frequency modes are active [247], making the lower energy $l = 2$ mode [298] more favoured than the $l = 0$. Additionally, the colloidal nanocrystals are not perfectly spherical. The slight ellipticity of the particles lifts the degeneracy of the valence band allowing more favourable coupling to the $l = 2$ mode [91].

The assignment of the acoustic phonon to the $l = 2, m = 0$ mode is further supported by the observed anisotropy behaviour. The $l = 0$ and the $l = 2$ modes distort the crystal in different ways due to the symmetry of the vibration. As a result, they have different polarization characteristics [285, 299] as a function of the incident light. The $l = 0$ mode does not change the symmetry of the unit cell and does not change the polarization, while the $l = 2$ depolarizes the signal [297]. As a result, cross polarized measurement such as CPH-3TG or an anisotropy measurement would be more sensitive to the $l = 2$ mode.

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The elastic sphere model describes the acoustic modes of the spherical colloidal nanocrystals based on their elastic properties. The elastic behaviour of a solid material can be described using the elastic modulus, which is defined as the ratio of stress to strain. Stress is defined as the applied force per unit area, while strain is defined as the deformation of the solid in response to the applied stress. Strain induced deformation of the crystal lattice changes the electronic energy structure. In the linear, elastic regime, this change is proportional to the strain tensor, which can be written as [266],

$$\epsilon_{\alpha\beta} = \frac{1}{2} \left( \frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) $$ (7.7)

where $u(x)$ is a vector describing the displacement of a point in the lattice due to strain.

The action of the acoustic phonon mode in the nanocrystal creates a time varying strain in the crystal lattice. The strain tensor, Equation 7.7, describing the acoustic mode is directly dependent on the displacement. In the elastic sphere model, in order to describe the strain and, therefore, the action of the phonon, the displacements must be evaluated. The phonon displacement vector, $u(r)$, in this model is associated with a component of the angular momentum ($l$) and its z-component ($m$). $u(r)$ is written as
where $R$ is the radius, $L_{lm}(hr)$ and $N_{lm}(kr)$ are vector spherical harmonics, $p_{lm}$ and $q_{lm}$ are coefficients of a set of linear equations [249]. In spheroidal modes the radius is included explicitly because, the spherical harmonics $L$ and $N$, are dimensionless. For a spheroidal mode, the eigenfrequency $\omega$ is related to the values $h$ and $k$ (see Chapter 6) through the expression $\rho \omega^2 = (\lambda + 2\mu)h^2 = \mu k^2$

Once the displacement is determined, in principal it should now be possible to quantify the strain and determine its effect on the lattice. However, the elastic sphere model treats the nanocrystal as an isotropic particle, which is acceptable for macroscopic (meaning averaged over the whole nanocrystal) properties such as elasticity in which the individual movement of the atoms are lost. Since the strain induced mixing of transition dipole moments is determined by relative distortions of the unit cell, the vector displacements of the atoms within the unit cell must be considered. This is an atomic level problem. In this case, the displacement determined using the elastic sphere model cannot be used to describe the unit cell level distortion.

### 7.8.2 Group Theory and Strain Induced Mixing of the Fine Structure States

The motion of atoms in the unit cells of a crystal lattice correspond to normal modes and can be described by group theory transformations. The application of a strain to a crystal lattice, lowers its symmetry, changing its associated point group. For a hexagonal crystal lattice, such as wurtzite, an arbitrary strain acting in a plane perpendicular to the six-fold axis (screw axis) transforms point group class as $C_{6v} \rightarrow C_2$ [266]. The effect of a small strain, limited to terms linear in the strain tensor, can be treated as a
perturbation to the total Hamiltonian of the system $H_{total} = H_0 + H_\epsilon + H_{exch}$, where $H_0$ is the unperturbed Hamiltonian, $H_\epsilon$ is the strain Hamiltonian and $H_{exch}$ is the exchange contribution. Incorporating spin, the basic form of the strain Hamiltonian in the electron-hole representation can be written as,

$$H_\epsilon = \langle \psi_i | \hat{H}_\epsilon | \psi_j \rangle = \begin{pmatrix} H_1 & 0 \\ 0 & H_1 \end{pmatrix}$$  \hfill (7.9)

The specific form of the $\psi$ functions can be found in Reference [49]. The Hamiltonian in 7.9 has been split into the two spin components $\alpha$ (spin up) and $\beta$ (spin down). Using group theory to describe the transformation of the unit cell in response to an applied strain the Hamiltonian, $H_1$, is [266],

$$H_1 = \begin{pmatrix} f & h & j & 0 \\ h^* & g & 0 & j \\ j^* & 0 & g & -h \\ 0 & j^* & -h^* & f \end{pmatrix}$$  \hfill (7.10)

where,

$$f = \frac{l + m}{2} (\epsilon_{xx} + \epsilon_{yy}) + m \epsilon_{zz}$$ \hfill (7.11)

$$g = \frac{1}{3} \{ f + 2[ m (\epsilon_{xx} + \epsilon_{yy}) + l \epsilon_{zz} ] \}$$ \hfill (7.12)

$$h = -\frac{1}{\sqrt{3}} n (i \epsilon_{xz} + \epsilon_{yz})$$ \hfill (7.13)

$$j = \frac{1}{\sqrt{3}} \left[ \frac{1}{2} (l - m) (\epsilon_{xx} - \epsilon_{yy}) - in \epsilon_{xy} \right]$$ \hfill (7.14)

The $f, g, h,$ and $j$ functions are written in terms of the strain tensor $\epsilon_{mn}$ and the nonzero, independent components of the deformation potential operator $l = D^{XX}_{xx}$, $m = D^{XX}_{yy}$ and $n = 2D^{XY}_{xy}$.

To understand how the strain mixes the fine structure levels, we write the Hamiltonian
in the exciton fine structure basis,

\[
H = \begin{pmatrix}
E_{-1} + f & h & j & 0 & \chi \\
\chi & E_0 + g & 0 & j & \chi \\
j^* & 0 & E_{+1} + g & -h & \chi \\
0 & j^* & -h^* & E_{+2} + f & \chi \\
\chi & \chi & j^* & 0 & E_0 + g & -h \\
\chi & \chi & 0 & j^* & -h^* & E_{+1} + f
\end{pmatrix}
\] (7.15)

The diagonal terms are labelled by the total angular momentum of the fine structure states and \( \chi \) represents the exchange factors. In this basis, the mixing of the levels based on the strain induced distortion of the unit cell can be read directly. From Equation 7.15, the \( F = \pm 1 \) states mix with the \( F = 0 \) states through the \( h \) factor. Theoretically, it should be possible to calculate all the level mixings by evaluating the \( h \) and \( j \) factors, which would require the strain tensor, the deformation potential operator, and the displacement vectors. For a specific applied strain this could be done using the Bloch functions, however, this assumes that the crystal lattice is infinite, which is an extremely poor approximation in a nanocrystal. In a nanocrystal undergoing a periodic strain, the Bloch functions do not transform as desired by group theory. As the nanocrystal experiences a strain due to the action of the acoustic phonon, each unit cell deforms slightly differently, which obscures a symmetry argument. The acoustic phonon mode creates a complex standing wave in the nanocrystal distorting individual unit cells in different ways. As a result, the strict property of translational symmetry is lost. A proper description of the strain and the deformation would require accounting for all of the unit cells. In other words, correct evaluation of the mixing would require an atomistic model. However, Equation 7.15 can be used to determine generally how the fine structure levels mix.
7.8.3 Phonon Induced Origin of the Anisotropy

From the Hamiltonian in Equation 7.15 it can be seen that the strain induced in the nanocrystal by the acoustic phonon mixes the fine structure levels $F = 0$ and $F = \pm 1$. The $F = 0$ state has a linearly polarized transition dipole moment and the $F = \pm 1$ states have circularly polarized selection rules. The action of the phonon periodically strains the nanocrystal, mixing these transition dipole moments. The net result is that the transition dipole moment of the $F = \pm 1$ states oscillates between pure circular (unstrained) and elliptical (strained), which is a combination of the circular and linear transition dipole moments of the mixed states. Note that most of the transition strength is in the $F = \pm 1$ states, so it is reasonable to consider the modification of the $F = \pm 1$ transition dipole moment. This modification appears in the measured anisotropy and CPH-3TG signals as a depolarization. Since the dynamics in the VVVV, VVHH and calculated isotropy are not directly affected by this small depolarization it would not appear in those signals. As expected, the acoustic phonon mode appears in the calculated anisotropy and the CPH-3TG experiments as shown in Figures 7.1 and 7.4 and does not appear directly in the VVVV, VVHH or isotropic response as shown in Figures 7.3 and 7.4(b).

Depolarization through mixing of the transition dipole moments enters into the CPH-3TG traces as a modification of the rotational averaging factors. Even if the mixing is small, the combination of linearly and circularly polarized transitions produces an elliptically polarized transition dipole moment. Using the Jones vector formalism, which represents polarization as a complex vector, the different polarizations can be described in terms of $x$ and $y$ components for a wave propagating in the $z$-direction. The Jones
vector for linearly polarized light is $[300, 301, 302]$.

$$E_{\text{Horizontal}} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$ \hspace{1cm} (7.16)

$$E_{\text{Vertical}} = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$ \hspace{1cm} (7.17)

For circularly polarized light the Jones vector is,

$$E_{\text{CP}} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ \pm i \end{bmatrix}$$ \hspace{1cm} (7.18)

where $-i$ corresponds to right and $+i$ to left circularly polarized light. The general form of elliptical polarized light with non-vanishing $x$ and $y$ components for an arbitrary phase is,

$$E_{\text{EP}} = \frac{1}{\sqrt{1 + \left| \kappa \right|^2}} \begin{bmatrix} 1 \\ \kappa \end{bmatrix}$$ \hspace{1cm} (7.19)

where $\kappa$ is a complex number of the form $a \pm bi$. The expression in Equation 7.19 represents left elliptical light if $\text{Im} \ kappa$ is positive and right elliptical light if $\text{Im} \ k$ is negative. It is straightforward to show in this representation that elliptical light is a linear combination of linear and circularly polarized components. Ignoring normalization, the elliptical light can be written as,

$$E_{\text{EP}} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} + \begin{bmatrix} 1 \\ \pm i \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \pm i \end{bmatrix} = \begin{bmatrix} 1 \\ \kappa \end{bmatrix}$$ \hspace{1cm} (7.20)

where the sign of $i$ depends on whether the light is right or left polarized.

The acoustic phonon generated strain modifies the transition dipole moments from linear and circular to elliptical as the fine structure levels are periodically mixed. The oscillating modified transition dipole moments are observed in the anisotropy-type measurements as a depolarization. These changing transition dipole moments modify the
rotational averaging factors. Using the method outlined in Section 7.5, the general form of the modified rotational averaging factors can be determined. The exact value of $\kappa$ in the modified transition dipole moment depends on the amount of mixing, which is likely small since the crystal is in the linear elastic regime but cannot be exactly determined without an atomistic model. However, an exact quantitative value is not necessarily needed since the qualitative behaviour of the rotational averaging factors in response to a change in the transition dipole moments is of interest. Using Equation 7.4, the rotationally averaged factors for elliptically polarized transition dipole moments in CdSe nanocrystals can be determined for the contributing components of the third-order signals such as ground state recovery, excited state absorption and stimulated emission.

Rotational averaging factors for the unstrained crystal with circularly polarized selection rules have been previously determined [125]. For the CPH-3TG experiments (VHVH and VHHV polarization combinations) these terms are $C^{(4)} = \pm 2/15$, where the sign depends on the signal direction, the specific process (i.e. excited state absorption, ground state recovery or stimulated emission) and whether or not the exciton has changed its total angular momentum. For a strained nanocrystal, the elliptically polarized transition dipole moments have both real and imaginary components with $\kappa = a \pm bi$ where $a$ and $b \neq 0$. The rotational averaging factors, evaluated using Equation 7.4, for a strained nanocrystal with a transition dipole moment written as shown in Equation 7.19 have the form,

$$C_{EP}^{(4)} = \pm \frac{2}{15} \kappa^2$$

If $\kappa = a + bi$, then

$$C_{EP}^{(4)} = \pm \frac{2}{15} [(a^2 - b^2) + 2abi]$$

As shown in Equation 7.22 the rotational averaging factors for the strained crystal are complex numbers. This is in contrast to the rotational averaging factors for the unstrained crystal, which are real numbers. For instance, this means that in a particular
experiment, the rotational averaging factors oscillate from $\pm 2/15$ to $\pm (2/15)\kappa^2$ and between real and complex numbers during the acoustic phonon quantum beat.

The complex value of the rotational averaging factor indicates that the system behaves in a similar manner to that of a chiral system. In a CPH-3TG experiment, the equilibration in the fine structure states associated with the fast exponential decay in these signals, on the order of hundreds of femtoseconds, is the result of a destructive interference effect between contributing signals [105]. This interference decays the signal, providing a measure of the timescales of transitions within the fine structure. The acoustic phonon has a period on the order of picoseconds, which is longer than the equilibration timescale as shown in Figure 7.1. The observation of the acoustic phonon is due to the strain induced mixing of the transition dipole moments of the $F = \pm 1$ and $F = 0$ states, which can occur during and after equilibration of the population in the fine structure states. The mixing of these levels due to the phonon induced strain is a different effect than the ‘spin flip’-type dynamics of the fine structure equilibration.

The strain induced mixing mechanism is supported by the observed phase relationship between the VHVH and VHHV signals as shown in Figure 7.1(d). In the CPH-3TG measurements, transitions to the linear polarized $F = 0$ state appear as a positive offset in the VHVH and VHHV signals [49]. The action of the acoustic phonon periodically strains the crystal, resulting in mixing of the $F = \pm 1$ and $F = 0$ states. This mixing, which changes the rotational averaging factors as described above, modifies both signals towards more ‘positive’ signal (positive defined relative to the y-axis in Figure 7.1(d)) associated with a linearly polarized state at the same time delay. This means that when the phonon increases the VHVH signal intensity, with an increase defined as positive on the axis in Figure 7.1(d), it decreases the VHHV signal intensity, with an increase defined as negative on the axis in Figure 7.1(d), due to the sign of the rotational averaging factor. This occurs since the linearly polarized state appears as a positive offset regardless of the polarization combination measured. This can be clearly observed by re-plotting the
Figure 7.5: The absolute value of the imaginary component of the heterodyned detected third-order transient grating signal measured for a CdSe colloidal nanocrystal sample with an average radius of \( R = 1.69 \) nm for the VHVH (top, green) and VHHV (bottom, pink) polarization combinations. The data in this figure is the same as that presented in Figure 7.1(c) and (d), however, the VHHV data has been multiplied by \(-1\) to obtain the absolute value of the trace in order to obtain a direct comparison between the signals. The traces have been offset for easier comparison. Panel (a) shows a close up of the acoustic phonon, while panel (b) shows a close up of the optical phonon mode.

VHVH and VHHV signals using the absolute value of the intensity on the y-axis as shown in Figure 7.5(a).

In comparison to the acoustic mode, the LO phonon has a different phase dependence between the VHVH and VHHV signals as shown in Figure 7.1(c). The LO mode has eigenfunctions similar to that of a spheroidal \( l = 0 \) mode \([299]\) and does not have a depolarizing effect on the signal. As a result, the optical mode appears in both the calculated anisotropic and isotropic traces as shown in Figure 7.4 and it affects the VHVH and VHHV signals in the same way, as shown in Figure 7.5(b), where the two traces are re-plotted using the absolute value of the signal. The difference in the anisotropic behaviour of the optical and the acoustic modes is characteristic of the symmetry origins
of both modes. In addition, it is demonstrates the fundamentally different way in which the acoustic and optical mode affect the nanocrystal. Observation of the two modes in the VHVH and VHHV measurements is due to the fact that these signals are the product of an anisotropy-type response and a normal intensity decay. In the cross polarized transient grating experiments (VHVH and VHHV), the acoustic modes are clearly resolved with the specific phase relationship between the two signals as a result of the anisotropic character of the experiment. On the other hand, the LO modes, which have the opposite phase relationship between the VHVH and VHHV signals, are not associated with the strain-induced mixing of the fine structure states but appear as a component of the standard transient intensity decay.

7.8.4 Response Function Simulations

The depolarizing origin of the acoustic phonon and its periodic modulation of the rotational averaging factors were modelled using response function simulations. Transient grating signals were calculated following the methods in References [132, 211, 303]. The total response function, \( R(t,t_p) \), can be used to calculate the signal, \( S(t_p) \),

\[
S(t_p) = \int_0^\infty dt |R(t,t_p)| \quad (7.23)
\]

where \( t_p \) is the population or probe delay time, and \( t \) is the polarization time over which the integration is performed. Using the rotating wave approximation and only considering contributions to the \( k_{\text{Signal}} = -k_1 + k_2 + k_3 \) phase matching signal direction, the response function can be broken into two components, describing the evolution of the ground state population \( R_{gg} \) and the excited state population \( R_{ee} \) and written as [303],

\[
R_{gg}(t,t_p) = R_{ee}^r(t,t_p) \exp[iQ_{gg}(t,t_p)] \quad (7.24)
\]

\[
R_{ee}(t,t_p) = R_{ee}^r(t,t_p) \exp[iQ_{ee}(t,t_p)] \quad (7.25)
\]
Figure 7.6: Response function simulations of the VHVH (top, purple) and the VHHV (bottom, blue) third-order transient grating signals. The phonon mode was included by modifying the rotational averaging factors to include a small oscillatory component associated with the periodic strain induced mixing of the fine structure levels.

where $R^e$ contains the real part and $Q$ contains the imaginary part of the line broadening function, $g(t)$ [211]. In this treatment, the pulse durations are finite [303] but are assumed to be short, with the first and second pulses overlapping exactly at time zero.

$$g(t) = \frac{2\lambda k_b T}{\hbar \Lambda^2} \left[ \exp(-\Lambda t) + \Lambda t - 1 \right] - i \left( \frac{\Lambda}{\Lambda} \right) \left[ \exp(-\Lambda t) + \Lambda t - 1 \right]$$

(7.26)

where $T$ is the temperature, $k_b$ is the Boltzmann constant, $\lambda$ is the coupling parameter (reorganization energy) and $\Lambda^{-1}$ is the timescale of the nuclear dynamics. Values of $\lambda = 200 \text{ cm}^{-1}$, $\Lambda = 0.01 \text{ fs}^{-1}$ and $T = 298K$. Equation 7.26 is valid in the high temperature limit where $k_b T \gg \hbar \Lambda$.

Calculations were performed for the VVVV, VHVH and VHHV transient grating signal polarization combinations. The response functions for different signal contributions were multiplied by the appropriate rotational averaging factor depending on the signal polarization combination. A simplified model of the fine structure equilibration involving two states was included in the response functions using a simple kinetic model. In order
to model the depolarization due to the periodic strain induced fine structure level mixing caused by the acoustic phonon mode, the rotational averaging factors were modified as,

$$C^{(4)} = (1 - \xi)C^{(4)}_{\pm 1} + \xi C^{(4)}_0$$  \hspace{1cm} (7.27)

where $C^{(4)}_{\pm 1}$ and $C^{(4)}_0$ are the rotational averaging factors for the $F = \pm 1$ and $F = 0$ states respectively. $\xi$ is a small factor that describes the mixing of the fine structure states and included a time dependent sinusoidal component.

The simulated VHVH and VHHV traces are presented in Figure 7.6. The oscillating value of the rotational averaging factor, as a result of the level mixing and changing transition dipole moments, recovers the experimentally observed phonon phase relationship. Note that the traces presented in Figure 7.6 are meant to be compared to the data as obtained experimentally, shown in Figure 7.1(d). Comparison with Figure 7.5(a) would require taking the absolute value of both signals, which corresponds to multiplying the VHHV trace by $-1$ due to the sign of the rotational averaging factor.

### 7.9 Conclusion

In this chapter, we used polarization control methodologies in a transient grating configuration to observe the $l = 2, m = 0$ acoustic phonon quantum beat for nine different sized colloidal CdSe nanocrystal samples. CPH-3TG signals were obtained for the VHVH and VHHV signals, and the isotropic and anisotropic response was calculated from the VVVV and VVHH polarization combination transient grating signals. Response function simulations were also performed to model the effect of the acoustic phonon on the polarization control signals.

The CPH-3TG experiment is sensitive to depolarization and can be used to study phenomena that affect the transition dipole moments of the fine structure states. When the nanocrystal experiences a strain as a result of the action of an acoustic phonon, the
symmetry of the crystal lattice is lowered, mixing the fine structure states and their transition dipole moments. Depending on the states mixed, this modification is manifested as a depolarization of the polarization grating. The oscillating induced strain mixes the transition dipole moments changing them from left and right circular to left and right elliptical with the period of the phonon mode. This appears in the measured time domain data as a quantum beat. Since the strain affects the dipole moments, the observation of this mode is an anisotropy effect. As a result, this oscillation also appears in the anisotropy calculated from transient grating traces measured with VVVV and VVHH polarization combinations.

The action of the $l = 2$, $m = 0$ acoustic phonon mode on the CdSe nanocrystal modifies its material properties, inducing a periodic strain which mixes the $F = 0$ and $F = \pm 1$ fine structure states. This mixing changes the rotational averaging factors that describe the interaction between polarized laser pulse sequences and the transition dipole moments of the semiconductor nanocrystals. The acoustic phonon quantum beat periodically induces a strain in the nanocrystal. As the nanocrystal goes from strained to unstrained to strained, the rotational averaging factors change from complex numbers to real numbers to complex numbers, respectively. The complex rotational averaging factors of the strained nanocrystals can be compared to the response of a chiral system. The oscillating nature of the rotational averaging factor in response to the action of the acoustic phonon mode was modelled using response function simulations, which reproduced the experimental results.

By using different polarization combination tensors to selectively excite an acoustic phonon mode, it is possible to use nonlinear optical properties to simultaneously study the material and optical properties of randomly oriented colloidal nanocrystals as an ensemble in solution. The strain induced mixing of fine structure states allows us to understand the microscopic effects of stress on the atomic level distortion of the unit cell of the crystal. This nanocrystal system provides an example of the interplay between
macroscopic and microscopic properties involved in understanding the physics and chemistry of a material. Macroscopic properties, such as elasticity and surface stress, which is linked to the chemical potential, can be determined by considering the nanocrystal as a whole (i.e. as an isotropic elastic sphere). However, many of the details of the physics of a material occur at a microscopic level. In this case, the strain induced mixing of the fine structure states must be understood by considering the atomic-level distortion within the unit cell. This interplay between the macro and the microscopic determines the properties of materials and is a critical component towards a complete understanding of current systems, as well as towards the rational design of new materials.
Chapter 8

Summary and Conclusions
This thesis explored some aspects of the photophysics of colloidal semiconductor nanocrystals, focusing particularly on relaxation dynamics following optical excitation. For colloidal semiconductor nanocrystal systems, we showed that optical spectroscopy can be used as a tool to elucidate not only the optical and dynamic processes but also their material characteristics. Drawing together the interrelated threads of optical and material properties, the size-dependences and relaxation behaviour, allowed some interesting insights into the physics and chemistry of colloidal nanocrystal systems. Each of the chapters contributed another piece of the puzzle towards a more complete understanding of the photophysics of these materials. The contributions from each chapter are outlined in the following paragraphs.

Chapter 2 demonstrated a polarization controlled ultrafast transient grating experiment that permits measurement of the dynamics within the fine structure of the lowest energy exciton state of a rotationally averaged CdSe colloidal system. This measurement is possible despite the small energy separation of the fine structure levels and the random orientation of the nanocrystals. Measuring the dynamics within these states gives us a greater understanding of the physics of these materials including radiationless transitions and exciton spin flip rates.

In Chapter 3, the experimental technique demonstrated in Chapter 2 was used to study the crystal structure dependent differences in the fine structure relaxation rates between colloidal CdSe nanocrystals with hexagonal wurtzite and cubic zinc blende structures. The physical difference in the lattices corresponds to a difference in the crystal field effect, which affects the degeneracy of the levels. This chapter contributes to a further understanding of the photophysics of quantum confined colloidal semiconductor nanocrystals, specifically towards elucidating the physical mechanisms driving the relaxation within the fine structure.

Chapter 4 took the thesis in a slightly different but related direction, presenting research concerning third- and fifth-order nonlinear spectroscopy as well as multiexciton
Chapter 8. Summary and Conclusions

This chapter explored both inter and intraband size-dependent relaxation dynamics in a quantum confined colloidal semiconductor nanocrystal system using a transient grating experimental technique, which took advantage of phase matching conditions to selectively observe exciton and biexciton dynamics. Since the discovery of multiple exciton generation, there has been a strong impetus towards understanding these multiexciton dynamics particularly in terms of potential solar cell applications. The technique demonstrated in this chapter is a general method that could potentially be used to study multiexciton dynamics in any system that can accommodate them. The major advantages of the demonstrated technique are its selectivity, potential experimental flexibility concerning the colour and polarization of the interacting laser pulses and low incident intensity requirements.

Chapter 5 explored the optical properties of bulk-like semiconductor nanocrystals using Ag$_2$S and EuS as model systems. These materials represent an overlooked class of nanocrystal that combines the desirable chemical synthetic aspects and easy processability of colloidal systems with the useful properties of bulk semiconductors. Through linear optical spectroscopy, this chapter clarified the bulk-like nature of the optical properties of EuS nanocrystals, which had been a significant source of confusion in the literature.

Chapter 6 employed the polarization controlled experimental technique, initially demonstrated in Chapters 2 and 3, to observed the acoustic phonon modes in rotationally isotropic colloidal CdSe nanocrystals. The observation of the acoustic phonon mode related the optical properties to the material properties of colloidal nanocrystals in solution. Specifically, the size-dependence of the acoustic phonon mode provided insight into the changing elastic properties of the nanocrystals. This was novel since previously it had been largely assumed that the elastic properties of semiconductor nanocrystals were similar to that of the bulk material, which was based largely on lattice spacings observed in high resolution transmission electron microscope images. The changing elastic properties emphasized the importance of the surface and surface reconstruction in small nanocrys-
tals. Based on the measured size-dependence of the elastic properties, it was possible to calculate the size-dependence of the surface stress. This has important consequences for synthetic work since the surface stress in colloidal nanocrystals is related to the chemical potential, which determines the rate of growth or dissolution of the particles.

Chapter 7 builds on the observation of the acoustic phonon mode presented in Chapter 6, further exploring the origin of the mode in the polarization controlled signals. The appearance of the acoustic phonon in anisotropy-type experiments that measure depolarization occurs as a result of strain induced symmetry lowering, which mixes the fine structure states. The work in this chapter demonstrates the interplay between micro and macroscopic processes as well as the assumptions involved in the models associated with either of those processes. For instance, the elastic sphere model assumes that the sphere is composed of an isotropic material but, in order to understand the observed anisotropy behaviour it is necessary to consider the distortion at an atomic (microscopic) level. In this case, the isotropic assumption means that the elastic sphere model is not very useful. However, the elastic sphere model is perfectly suited to describing a macroscopic, meaning that it is averaged over the whole nanocrystal, property such as elasticity. Elucidating the nature of the acoustic phonon mode is also important in terms of the homogeneous broadening and the relaxation dynamics of the system since it is a major component of the bath.

The research presented in this thesis encompasses several different but related aspects of the photophysics of colloidal semiconductor nanocrystals. Spanning optical and material properties, quantum confined and ‘bulk’, this thesis has attempted to illustrate the broad scope of the observed behaviour of these systems. It is hoped that studies outlined in this thesis will provide a basis for future work towards a further understanding of the photophysics of colloidal semiconductor nanocrystals.
Appendix A

Derivation of the Absorption Coefficient for Generalized Direct Bandgap Semiconductors - a.k.a. the Tauc Equation
A.1 Absorption Coefficient

Start with a general expression for the absorption coefficient $\alpha$

\[
\alpha = \frac{(\hbar \omega) \text{(transition probability/volume time)}}{\text{total incident intensity (energy/unit time/area)}}
\] (A.1)

or

\[
\alpha = \frac{\text{total energy absorbed per unit time}}{\text{total incident intensity (energy/unit time/area)}}
\] (A.2)

Which means that

\[
\alpha = \frac{(\hbar \omega) (W_{i\rightarrow f})}{I}
\] (A.3)

To solve the above equation we need to get an expression for $W_{i\rightarrow f}$ and $I$

A.2 Expression for $I$

The rate depends on the strength of the field which can be measured as intensity, $I$, which is the energy flux per unit area.

$I$ is the time average of the Poynting vector $\vec{S}$ which is defined as,

\[
\vec{S} = \frac{c}{4\pi} \vec{E} \times \vec{B}
\] (A.4)

Where $\vec{E}$ is the magnetic field and $\vec{B}$ is the magnetic field.

Note that the Poynting vector (units of Watts per meter squared) indicates the magnitude of the energy flux density but also the direction of energy flow. For simple electromagnetic waves the Poynting vector is in the same direction as the wavevector $k$. (n.b.
Maxwell’s equations)

We will use the Coulomb gauge for simplicity and in part so that later we can get a unique solution for the vector potential $\vec{A}$. The Coulomb gauge is defined as $\nabla \cdot \vec{A}$ (assuming steady fields).

In the Coulomb gauge $\vec{H} = \vec{B}$, where $\vec{H} =$magnetic field strength.

\[ \vec{S} = \frac{c}{4\pi} \vec{E} \times \vec{H} \quad (A.5) \]

Since $\bar{I}$ is equal to the time average of $\bar{S}$ so,

\[ \bar{I} = \langle \bar{S} \rangle \quad (A.6) \]

using the vector identity, from the vector triple product,

\[ \Re \langle A \rangle \times \Re \langle B \rangle = \frac{1}{2} \Re (AB^*) \quad (A.7) \]

\[ \bar{I} = \langle \bar{S} \rangle = \frac{c}{4\pi} [\Re \langle \vec{E} \rangle \times \Re \langle \vec{B} \rangle] \quad (A.8) \]

\[ \bar{I} = \frac{c}{8\pi} \Re (\vec{E} \times \vec{B}) \quad (A.9) \]

In a vacuum, the electric and the magnetic field amplitudes are zero so $\vec{E} = \vec{B}$

\[ \bar{I} = \frac{c}{8\pi} |\vec{E}^2| \quad (A.10) \]

Now define $\vec{E}$

\[ \vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t} \quad (A.11) \]
Appendix A. Tauc Equation

For a particular vector potential of the radiation field $\vec{A}$

\begin{equation}
\vec{A} = A_o \cos(\vec{k} \cdot \vec{r} - \omega t) \pm i A_o \sin(\vec{k} \cdot \vec{r} - \omega t) \tag{A.12}
\end{equation}

\begin{equation}
\vec{A} = A_o \exp[i(\vec{k} \cdot \vec{r} - \omega t)] \tag{A.13}
\end{equation}

\begin{equation}
\vec{A} = A_o \exp[i(\vec{k} \cdot \vec{r} - \omega t)] + c.c. \tag{A.14}
\end{equation}

Which is a transverse plane wave
and therefore,

\begin{equation}
\vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t} = \frac{i \omega}{c} \vec{A} \tag{A.15}
\end{equation}

$\vec{A}$ doesn’t necessarily have a unique value but it does in this case since we are using the Coulomb gauge.

Now getting back to $I$

\begin{equation}
I = -\frac{c}{8\pi} |\vec{E}|^2 = \frac{c}{8\pi} \frac{w^2}{c^2} |\vec{A}|^2 = \frac{w^2}{8\pi c} |\vec{A}|^2 \tag{A.16}
\end{equation}

### A.3 Fermi’s Golden Rule

$W_{i \rightarrow f}$ in the $\alpha$ expression is the Fermi golden rule and is used to calculate the rate of a transition from $|i\rangle$ (initial state) to $|f\rangle$, where $|f\rangle$ is a single state in the continuum:

\begin{equation}
W_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | H^' | i \rangle|^2 \rho(h\omega) \tag{A.17}
\end{equation}

Where $\rho(h\omega)$ is the density of final states, distribution sharply centered at $E_f = E_i$ (this can be rewritten as a delta function depending on the system etc. i.e. $\delta(E_f - E_i - h\omega)$)

From first order perturbation theory

\begin{equation}
H^' = \frac{e}{m_o} \vec{A} \cdot \vec{p} \tag{A.18}
\end{equation}

Where $m_o$ is the free electron mass and $\vec{p}$ is defined as $\vec{p} = i\hbar \nabla$. This is a well known result (so I won’t derive it here)
So,

$$|\langle f | H' | i \rangle|^2 = (\frac{\epsilon}{m_o})^2|\bar{A}|^2|\langle f | p | i \rangle|^2$$  \hspace{1cm} (A.19)

Let’s leave the matrix element for now (this is the momentum matrix element) and go to the expression for $\rho(\hbar \omega)$

### A.4 Density of States

To get an expression for $\rho(\hbar \omega)$ we need to calculate the joint density of states, which is defined as the number of electronic states in the conduction and valence bands that are separated by a given photon energy $\hbar \omega$.

Assume that the semiconductor system has simple parabolic bands and that the effective masses determine the dispersion.

In momentum space the energy-k expressions for the valence and the conduction bands can be written as,

$$E_v(k_v) = \frac{-\hbar^2 k_v^2}{2m_v^*}$$  \hspace{1cm} (A.20)

$$E_c(k_c) = E_g + \frac{\hbar^2 k_c^2}{2m_c^*}$$  \hspace{1cm} (A.21)

By conservation of momentum,

$$\hbar \bar{k}_v + \hbar \tilde{q} = \hbar \tilde{k}_c$$  \hspace{1cm} (A.22)

Where $\bar{k}_v$ and $\tilde{k}_c$ are the initial and final wavevectors respectively of the electron and $\tilde{q}$ is the wavevector of the photon. $\tilde{q}$ is usually very small compared to $e^-$ wavevectors so that term can usually be ignored. So, $\tilde{k}_c = \bar{k}_v = \tilde{k}$

Now, by conservation of energy

$$E_v + \hbar \omega = E_c$$  \hspace{1cm} (A.23)
Appendix A. Tauc Equation

So,

\[ E_c - E_v - \hbar \omega = 0 \quad (A.24) \]

Using the energy-k expressions

\[ E_g + \frac{\hbar^2 k^2}{2m_c} + \frac{\hbar^2 k^2}{2m_v} - \hbar \omega = 0 \quad (A.25) \]

\[ E_g + \frac{\hbar^2 k^2}{2} \left( \frac{1}{m_c} + \frac{1}{m_v} \right) - \hbar \omega = 0 \quad (A.26) \]

Let \( m^* \) be the reduced mass

\[ \frac{1}{m^*} = \frac{1}{m_c} + \frac{1}{m_v} \quad (A.27) \]

So,

\[ E_g + \frac{\hbar^2 k^2}{2m^*} = \hbar \omega \quad (A.28) \]

It is now necessary to determine the density of states. For an ideal parabolic band direct gap semiconductor with the bandgap at the Γ point in \( k \) space, it can be assumed (this is a rough approximation) that electronic transitions only occur at \( \hbar \omega \geq E_g \).

The density of states in momentum space (this is a well known result) is,

\[ \rho(k) = \frac{k^2}{2\pi^2} \quad (A.29) \]

And the density of states per unit energy range is,

\[ \rho(E) = \frac{2\rho(k)}{\frac{dE}{dk}} \quad (A.30) \]

Note that the derivation of the above two equations can be found in most solid state textbooks.

\( E \equiv \hbar \omega \) so \( \frac{dE}{dk} \) is the derivative with respect to \( k \) of \( E_g + \frac{\hbar^2 k^2}{2m^*} \).

\[ \frac{dE}{dk} = \frac{\hbar^2 k}{m^*} \quad (A.31) \]
Appendix A. Tauc Equation

Now substituting back into the expression for $\rho(E)$

$$\rho(E) = 2\frac{\rho(k)}{\hbar k} = 2\left(\frac{k^2}{2\pi^2}\right)\left(\frac{m^*}{\hbar^2 k}\right) = \frac{km^*}{\pi^2 \hbar^2}$$  \hspace{1cm} (A.32)

where $k$ comes from,

$$\hbar \omega = E_g + \frac{k^2 k^2}{2m^2}$$  \hspace{1cm} (A.33)

$$k = \left[\frac{2m^*}{\hbar^2} (\hbar \omega - E_g)\right]^{\frac{1}{2}}$$  \hspace{1cm} (A.34)

So,

$$\rho(E) = \frac{m^*}{\pi^2 \hbar^2} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} (\hbar \omega - E_g)^{\frac{1}{2}}$$  \hspace{1cm} (A.35)

So the joint density of states is (simplifying the prefactor),

$$\rho(E) = \rho(\hbar \omega) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} (\hbar \omega - E_g)^{\frac{1}{2}}$$  \hspace{1cm} (A.36)

Only one unknown is left before we can calculate $\alpha$

A.5 Momentum Matrix Element

Note that determining this factor can be quite complicated

$|\langle f|p|i\rangle|^2$ is the average of the squared matrix elements for transitions between Bloch states in the valence and conduction bands

This matrix element can be obtained from $\vec{k} \cdot \vec{p}$ theory (effective mass approximation theory)

$$p_{if} = \langle f | \exp \left[ (i\vec{k} \cdot \vec{r})\epsilon \cdot \vec{p} \right] | i \rangle$$  \hspace{1cm} (A.37)

For a Bloch function

$$\varphi = [c_f U_{j0} + \Sigma_{a} U_{a0}] \exp (i\vec{k} \cdot \vec{r})$$  \hspace{1cm} (A.38)
Using second order perturbation theory (I won’t show all the steps here since this is fairly well known) you get:

\[ E_f(k) = E_f(0) + \frac{\hbar^2 k^2}{2m_o} + \frac{\hbar}{m_o} \vec{k} \cdot \vec{p}_{ff} + \sum_{i \neq f} \frac{\hbar^2}{2m_o^2} |\vec{k} \cdot \vec{p}_{fi}|^2 \frac{E_f(0) - E_i(0)}{E_f(0) - E_i(0)} \]  
(A.39)

Where \( E_f(0) - E_i(0) \) is equal to \( E_g \) and where the extrema are at \( \vec{k} = 0 \) and \( \vec{p}_{ff} = 0 \)

So,

\[ \frac{m_o}{m^*} = 1 + \frac{2}{m_o} \sum_i |\vec{i} \cdot \vec{p}_{fi}|^2 \]  
(A.40)

\[ \frac{m_o}{m^*} = 1 + \frac{2}{m_o} |\langle f|p|i \rangle|^2 \frac{E_g}{E_g} \]  
(A.41)

\[ \frac{1}{m^*} = \frac{1}{m_o} + \frac{2|\langle f|p|i \rangle|^2}{m_o^2 E_g} \]  
(A.42)

So we’re a bit stuck now... so make an approximation: let \( m^* \ll m_o \) (usually valid in direct bandgap semiconductor systems) and we get,

\[ \frac{1}{m^*} = \frac{2}{m_o^2 E_g} |\langle f|p|i \rangle|^2 \]  
(A.43)

\[ \frac{m_o^2 E_g}{2m^*} = |\langle f|p|i \rangle|^2 \]  
(A.44)

So the momentum matrix element is just equal to a constant defined by \( \frac{m_o^2 E_g}{2m^*} \)

Now sub back into the expression for \( W_{i \rightarrow f} \)

\[ W_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f|H'|i \rangle|^2 \rho(\hbar\omega) \]  
(A.45)

\[ W_{i \rightarrow f} = \frac{2\pi}{\hbar} \left( \frac{e}{m_o} \right)^2 |\vec{A}|^2 \left( \frac{m_o^2 E_g}{2m^*} \right) \left( \frac{1}{2\pi^2} \right) \left( \frac{2m^*}{\hbar^2} \right)^{\frac{3}{2}} (\hbar\omega - E_g)^{\frac{1}{2}} \]  
(A.46)

### A.6 Putting the Whole Thing Together and Solving for \( \alpha \)

So sub back into \( \alpha \)

\[ \alpha = \frac{(\hbar\omega)(W_{i \rightarrow f})}{I} \]  
(A.47)
Appendix A. Tauc Equation

\[ \alpha = \frac{(\hbar \omega)^{\frac{2\pi}{\hbar}} (\frac{e}{m_0})^2 |\tilde{A}|^2 \frac{m^2_e E_g (\frac{1}{2m^*}) (\frac{2m^*}{\hbar^2})^{\frac{1}{2}} (\hbar \omega - E_g)^{\frac{1}{2}}}{\frac{\mu^2}{8\pi e |\tilde{A}|^2}}}{(A.48)} \]

Simplifying

\[ \alpha = \frac{8ceE_g}{\hbar} \left( \frac{2m^*}{\hbar^2} \right)^{\frac{1}{2}} \frac{(\hbar \omega - E_g)^{\frac{1}{2}}}{\hbar \omega} \] (A.49)

Putting the constants into a single factor \( C \)

\[ \alpha = C \left( \frac{\hbar \omega - E_g}{\hbar \omega} \right)^{\frac{1}{2}} \] (A.50)

Or

\[ (\alpha \hbar \omega)^2 = C^2 (\hbar \omega - E_g) \] (A.51)

Where \( C \) is just a scaling factor

So,

\[ (\alpha \hbar \omega)^2 = (\hbar \omega - E_g) \] (A.52)

We get a linear function in a plot of \((\alpha \hbar \omega)^2\) versus \(\hbar \omega\)

A.7 A Short Appendix Concerning Finite Temperature

Consider the Fermi function

\[ f(E) = \frac{1}{\exp\left[ \frac{E - \mu}{k_B T} \right] + 1} \] (A.53)

In a continuous system with Fermi-Dirac statistics this gives us the occupation for states above absolute zero.

At finite temperature these factors become multiplication factors. This comes in from the following equation

\[ \rho(\omega)d\omega = \frac{\hbar \omega^3 \eta^3}{\pi^2 c^3} \frac{d\omega}{\exp\left[ \frac{\hbar \omega}{k_B T} \right] - 1} \] (A.54)
For absorption

\[ f(E_i) = [1 - f(E_f)] \] \hspace{1cm} \text{(A.55)}

and for emission

\[ f(E_f) = [1 - f(E_i)] \] \hspace{1cm} \text{(A.56)}

Absorption minus emission gives us

\[ f(E_i) - f(E_f) \] \hspace{1cm} \text{(A.57)}

At low temperatures only the bottom state is occupied and \( f(E_i) = 1 \) and \( f(E_f) = 0 \)...so at low enough temperatures the multiplication factor is just 1.
Appendix B

Development of the Relationship Between the Young-Laplace Equation and the General Theory of Elasticity for Solids
B.1 Thermodynamic Derivation of the Young-Laplace Equation

Infinitessimal reversible changes in a two phase system produce corresponding infinitesimal reversible changes in the thermodynamic parameters so for example $A \rightarrow A + dA$ etc.

The basic equation for the internal energy of a one phase system with many components is

$$dU = TdS - pdV + \sum_i \mu_i dn_i$$

(B.1)

Where $\mu_i$ is the chemical potential of $i$. The first term is the heat flow, the second term is the mechanical work, and the last term is the so called chemical work. (Note that this is a generic thermodynamic equation).

Now define $U'$ and $U''$ for infinitessimal changes

$$dU' = TdS' - p'dV' + \sum_i \mu'_i dn'_i$$

(B.2)

$$dU'' = TdS'' - p''dV'' + \sum_i \mu''_i dn''_i$$

(B.3)

Backtracking a bit now, for a system with two phases (regions etc.) with a surface between them (i.e. solid, solution and interface) any extensive thermodynamic property such as $U$ can be distributed among the three parts

$$U^\sigma = U - u'V' - u''V''$$

(B.4)

Where $U$ is the total internal energy, $u'V'$ and $u''V''$ are the contributions from the different phases and $U^\sigma$ is the energy of the surface.

So, using the above equations the internal energy of the Gibbs surface is

$$dU^\sigma = TdS^\sigma + \gamma dA + \sum_i \mu^\sigma_i dn^\sigma_i$$

(B.5)
Noting that $U^\sigma = U - U' - U''$ and $S^\sigma = S - S' - S''$ we get

$$dU = TdS - p'dV' - p''dV'' + \gamma dA + \sum_i (\mu'_i dn'_i + \mu''_i dn''_i + \mu'_i \sigma_i)$$  \hfill (B.6)

For an infinitessimal process occurring in a constant volume at constant temperature the change in the Helmholtz free energy is (constant $V$, constant $T$)

$$dF = d(U - TS) = dU - TdS$$  \hfill (B.7)

$$dF = -p'dV' - p''dV'' + \gamma dA + \sum_i (\mu'_i dn'_i + \mu''_i dn''_i + \mu'_i \sigma_i)$$  \hfill (B.8)

At constant volume the system does no mechanical work so $-p'dV' - p''dV'' + \gamma dA = 0$ and $dV' = -dV''$ so,

$$-p'dV' - p''dV'' + \gamma dA = 0 = (p' - p'')dV'' + \gamma dA$$  \hfill (B.9)

$$\Delta pdV'' = \gamma dA$$  \hfill (B.10)

Since the change in area for a generic curved surface is

$$dA = \left(\frac{1}{R_1} + \frac{1}{R_2}\right) dV$$  \hfill (B.11)

We now have

$$\Delta pdV'' = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) dV''$$  \hfill (B.12)

And therefore for a sphere

$$\Delta p = \frac{2\gamma}{r}$$  \hfill (B.13)

Which is the Young-Laplace Equation

As an additional note, if we start from

$$dF = -p'dV' - p''dV'' + \gamma dA + \sum_i (\mu'_i dn'_i + \mu''_i dn''_i + \mu'_i \sigma_i)$$  \hfill (B.14)
At constant T, V, and for a rigid system with no chemical reactions etc. we get an expression for the surface tension

$$\gamma = \left( \frac{\partial F}{\partial A} \right)_{T,V}$$  \hspace{1cm} (B.15)

Note that the surface tension is a simplified (averaged, scalar) version of the surface stress tensor. The tensorial treatment should really be used when dealing with a solid particle that has an associated directionality bias.

### B.2 Thermodynamics of Deformation of Elastic Solids

Consider a deformed body where the deformation changes such that the displacement vector $u_i$ changes by a small amount $\delta u_i$. We'll determine the work by internal stresses as a result of this change by multiplying the force

$$F_i = \frac{\partial \sigma_{ik}}{\partial x_k}$$  \hspace{1cm} (B.16)

(where $\sigma_{ik}$ is the stress tensor and $x_k$ is the coordinate) by the displacement $\delta u_i$ and integrating over the volume of the body. Which gives us,

$$\int \delta R dV = \int \frac{\partial \sigma_{ik}}{\partial x_k} \delta u_i dV$$  \hspace{1cm} (B.17)

Where $\delta R$ is the work done by the internal stresses per unit volume. By integrating and using the fact that the strain tensor, $u_{ik}$ (note that $u_{ik}$ is defined as $u_{ik} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right)$, is symmetric, we get

$$\delta R = \sigma_{ik} \delta u_{ik}$$  \hspace{1cm} (B.18)

So, the work associated with deformation $\Delta R$ is equal to $\sigma \Delta u$. The above is true for an elastic deformation.

Assume that the deformation process is infinitesimally changing at constant temperature so that thermodynamic equilibrium is established and the process is reversible.
Change in the internal energy, $U$, corresponds to the difference between the change in heat per unit volume and the work, $dR$, done by the internal stresses. For a reversible process, the heat is $TdS$ where $T$ is the temperature and $S$ is the entropy. So,

$$dU = TdS + \sigma_{ik} du_{ik} \quad (B.19)$$

Since the Helmholtz free energy ($F$) is $F = U + TS$, therefore,

$$dF = -SdT + \sigma_{ik} du_{ik} \quad (B.20)$$

At constant temperature we get,

$$\sigma_{ik} = \left( \frac{\partial F}{\partial u_{ik}} \right)_{T,V} \quad (B.21)$$

Which is similar to the expression above for $\gamma$ in terms of the partial derivative of the Helmholtz free energy. Note that $dA$ in the expression for $\gamma$ can be redefined in terms of an arbitrary extension (as done for the general description of the elastic solids) where an increase in area $dA$ is equal to an extension of length $l$ multiplied by a direction $dx$.

Now we will develop the relationship between the Helmholtz free energy, the stress and strain tensors and elastic constants.

## B.3 The Relationship between the Helmholtz Free Energy, the Stress and Strain Tensors and the Elastic Constants

We first want to get an expression for the Helmholtz free energy in terms of the strain tensor. If the deformation is small, for isotropic materials the we can expand in powers of $u_{ik}$. With some rearrangement based on the fact that the free energy is a scalar and
on the fact that the undeformed state of the solid (isothermal, no external forces) has $\sigma_{ik}$ and $u_{ik}$ equal to zero, and therefore, no linear term in the expansion, we get,

$$F = F_0 + \frac{1}{2} \lambda u_{ii}^2 + \mu u_{ik}^2$$  \hspace{1cm} (B.22)

Where $\lambda$ and $\mu$ are the Lamé parameters.

Any deformation can be represented as a combination of shear and compression using the following identity for the strain

$$u_{ik} = (u_{ik} - \frac{1}{3} \delta_{ik} u_{ll}) + \frac{1}{3} \delta_{ik} u_{ll}$$  \hspace{1cm} (B.23)

Where the first term is shear (the sum of the diagonal terms $\delta_{ii} = 3$) and the second term is the compression.

Putting the two equations above together we get a new expression for the free energy

$$F = \mu (u_{ik} - \frac{1}{3} \delta_{ik} u_{ll})^2 + \frac{1}{2} K u_{ll}^2$$  \hspace{1cm} (B.24)

Where

$$K = \lambda + \frac{2}{3} \mu$$  \hspace{1cm} (B.25)

is the bulk modulus (modulus of compression) and $\mu$ is the shear modulus.

To determine the stress tensor we want the partial derivatives of $F$ with respect to $u_{ik}$ (as shown above). We first take the whole derivative (at constant $T$)

$$dF = K u_{ll} du_{ll} + 2\mu (u_{ik} - \frac{1}{3} u_{ll} \delta_{ik}) d(u_{ik} - \frac{1}{3} u_{ll} \delta_{ik})$$  \hspace{1cm} (B.26)

$$dF = [K u_{ll} \delta_{ik} + 2\mu (u_{ik} - \frac{1}{3} u_{ll} \delta_{ik})] du_{ik}$$  \hspace{1cm} (B.27)

Therefore the stress tensor is

$$\sigma_{ik} = K u_{ll} \delta_{ik} + 2\mu (u_{ik} - \frac{1}{3} \delta_{ik} u_{ll})$$  \hspace{1cm} (B.28)

So, this gives the stress tensor in terms of the strain tensor for an isotropic solid.

To get the strain in terms of the stress we take the sum of the diagonal terms (which is
zero for the second part of the above equation) and we get,

\[ u_{ii} = \frac{\sigma_{ii}}{3K} \]  

(B.29)

Note: from A Treatise on the Mathematical Theory of Elasticity by A. E. H. Love

The displacement \( \frac{u}{x} = \frac{v}{y} = \frac{w}{z} = \frac{-p}{3K} \) where p is pressure etc.

**B.4 A Comment on the Pressure Stress Relation**

The Young-Laplace equation gives us a relationship between the change in pressure and the surface tension

\[ \Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]  

(B.30)

Imagine a solid body undergoing deformation: stress (which is a force) can arise from a pressure (positive or negative depending on inward or outward force)

\[ \sigma_{ik} = p \delta_{ik} \]  

(B.31)

Where \( \delta_{ik} \) is the displacement.

At equilibrium, the pressure from the inside is balanced by an internal force

\[ p_i df = \sigma_{ik} df_k \]  

(B.32)

Where \( df \) is a surface element.

If we define a unit vector \( n \) normal to the surface, directed outwards, we can then write \( df_k = n_k df \) and get

\[ p_i = \sigma_{ik} n_k \]  

(B.33)

So a change in pressure induces a restoring force

\[ \Delta p_i = \Delta \sigma_{ik} n_k \]  

(B.34)
and

\[ \Delta p_i = \Delta \sigma_{ik} n_k = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]  \hspace{1cm} (B.35)

The averaged change in the stress tensor is proportional to the change in the surface ‘tension’

\[ \Delta p = \Delta \sigma_{ij} n_j = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]  \hspace{1cm} (B.36)

**B.5 Thermodynamics of Surfaces: The Relationship Between Work and the Young-Laplace Equation**

The total work done by a system with two phases expanding a volume against an external pressure is

\[ dw = -p'dV' - p''dV'' + \gamma dA \]  \hspace{1cm} (B.37)

when the total volume of the system is \( V \) and the external pressure is \( p' \), \( V \) becomes \( V = V' + V'' \) and \( dV = dV' + dV'' \). The work done by the system on the surroundings is

\[ dw = -p'dV = -pdV - p'dV'' \]  \hspace{1cm} (B.38)

This becomes

\[ dw = -p'dV = -pdV - p'dV'' = -p'dV' - p''dV'' + p''dV'' - p'dV'' \]  \hspace{1cm} (B.39)

Since \( \Delta p \) is equal to the Young-Laplace equation then,

\[ dw = -p'dV' - p''dV'' + \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) dV'' \]  \hspace{1cm} (B.40)

This relationship gives the total energy for the distortion of a body including the surface component

As an additional note, the work for a sphere is

\[ dw = -p'dV' - p''dV'' + \left( \frac{2\gamma}{r} \right) dV'' \]  \hspace{1cm} (B.41)
B.6 Surface Tension, Stress and Strain and the Relationship to the Elastic Parameters

Consider a curved closed surface - an isotropic liquid droplet in solution. The work to deform this surface is associated with the local change in area

\[ dA = ldx \]  \hspace{1cm} (B.42)

So the work done to deform the surface is

\[ dw = \gamma dA = \gamma ldx \]  \hspace{1cm} (B.43)

Where \( l\delta x \) gives the directional displacement (in one dimension as written here) and \( \gamma \) is the surface tension associated with the interface as defined by the Young-Laplace equation.

Note that in this case the total work is

\[ dw = -p'dV' - p''dV'' + \gamma dA \]  \hspace{1cm} (B.44)

Now with respect to the elasticity of a solid particle. The change in a particular unit area can be described in terms of a change in the strain tensor (describing the distortion) multiplied by the stress tensor (which describes the amount of ‘force’ in each direction). So,

\[ dw = \sigma_{ik} u_{ik} \]  \hspace{1cm} (B.45)

Note this is the same as in the earlier section on the thermodynamics of deformation of elastic solids.

From this we can see that \( \gamma \) and \( \sigma \) are analogous (with \( \gamma \) being the scalar isotropic representation of the tensor \( \sigma \)).

Since, as shown above, the elastic parameters are proportional to the stress tensor, therefore the surface tension, \( \gamma \), is also proportional to the elastic parameters.
B.7 Elasticity, Surface Stress, Final Derivation

Using our understanding of the elastic sphere system, we can now relate the elastic modulus to the surface stress of the nanoparticle. Since we are assuming that a nanocrystal with radius, $R$, behaves as an isotropic elastic sphere, we can relate a small relative volume change (also known as the cubic dilation) $\Delta V/V = \varepsilon_{ii}$ to an internal pressure $p$:

$$\varepsilon_{ii} = -p/K$$  \hspace{1cm} (B.46)

where $\varepsilon_{ik}$ is the strain tensor and the internal pressure is defined in terms of the strain tensor $\sigma_{ik} \rightarrow -p\delta_{ik}$ (B.31) and $K = \lambda + (2/3)\mu$ is the elastic modulus (B.25), or compressibility, defined in terms of the Lamé constants, $\lambda$ and $\mu$, as described above. At equilibrium the nanocrystal maintains constant volume because the internal pressure $p$ (implicitly defined relative to the external pressure) is opposed by an external compression known as surface tension, $\gamma$. For an isotropic sphere (as shown above),

$$2\gamma/R - p = 0$$  \hspace{1cm} (B.47)

Combining these equations under equilibrium conditions gives,

$$\gamma = \varepsilon_{ii}KR/2$$  \hspace{1cm} (B.48)

Note that $\gamma$, which is a scalar for liquids, becomes a tensor for a solid sphere and is usually represented by $g_{ik}$. In our experiment we measure $K$ for a nanocrystal of known radius $R$ and $\varepsilon_{ii} = Tr(\varepsilon_{ik}) = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$ (which is unitless). Hence, we can determine the surface tension (units GPa nm $\rightarrow$ Nm$^{-1}$). In order to make a comparison, this needs to be normalized by surface area of the particle, which results in units of pressure per unit area.
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