Ultrafast charge carrier and coherent phonon dynamics study of semiconductor nanostructures using femtosecond transient absorption spectroscopy

Dong, Shuo

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**Ultrafast Charge Carrier and Coherent Phonon Dynamics
Study of Semiconductor Nanostructures using Femtosecond
Transient Absorption Spectroscopy**

A thesis submitted to the Nanyang Technological University in
fulfilment of the requirement for the degree of

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by

Dong Shuo

School of Physical and Mathematical Sciences
Division of Physics and Applied Physics
Nanyang Technological University

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Abstract

Semiconductor nanomaterials are poised to revolutionize the field of electronics. Their low-cost synthesis and unique optoelectronic properties are aligned to the needs of modern industry. The miniaturization of semiconductor electronic components can achieve higher performance in a smaller volume, and the easily tailored electronic structure as a consequence of quantum confinement effect gives life to a myriad of semiconductor devices. Accompanying the emergence of a large number of promising applications is the challenge to monitor, understand and eventually manipulate the physical properties of these semiconductor nanostructures. Beyond the extensive research on the quantum confinement effect of semiconductor nanostructures, another striking quantum mechanical phenomenon in nanoscale systems that has attracted intense attention is that of electronic coherence. To investigate coherent electronic motion in low-dimensional semiconductors, we employ transient absorption spectroscopy with few-cycle laser pulses. The broadband spectra overlap with the two lowest-lying excitonic states of colloidal CdSe quantum dots (QDs), thus preparing a superposition of $1S_e 1S_h$ and $1S_e 2S_h$ states. The excitonic coherence, with a 15-fs dephasing time, is clearly discerned from our optical pump-probe data at 77 K. An ultrafast charge migration over a 1-nm-length scale with rates that can potentially exceed 1 Å/fs is reconstructed. The temperature-dependent dephasing time established that the electronic decoherence is partially induced by acoustic phonon scattering, with the dominant contribution arising from either exciton-defect scattering and/or exciton-exciton scattering. The inherent size distribution of the ensemble QDs contributes to inhomogeneous dephasing of electronic coherence. Fortunately, quasi-two-dimensional colloidal nanoplatelets (NPLs) have recently emerged as a new class of materials with monodisperse thicknesses of atomic precision, leading to relatively narrower absorption and emission bands compared with QDs. After photoexcitation at the bandgap of CdSe/CdS

core/shell NPLs, band selective probing is used to separate the electron and hole dynamics. Pump fluence-dependent measurements reveal a sub-picosecond Auger-mediated hole trapping process with an effective second-order rate constant of $3.5 \pm 1.0 \text{ cm}^2/\text{s}$. At high excitation intensity, where the initial exciton number $N_0 > 1$, the spectral blue shift in the first-moment time traces indicates a concomitant Auger hole heating process, along with electron cooling dynamics, which is especially evident as a time-dependent red-shift when $N_0 < 1$. In addition to the Auger-like charge carrier dynamics, the oscillatory signals resolved in the first-moment time trace are the fingerprints of coherent phonons. Four types of coherent phonons are observed, including the well-known longitudinal optical (LO) and surface optical (SO) phonon modes of CdSe. At the same time, two newly resolved frequencies of $\sim 5 - 10 \text{ cm}^{-1}$ and $\sim 20 \text{ cm}^{-1}$ are assigned to the in-plane and out-of-plane breathing-mode acoustic phonons, respectively. The increase in the frequency of the in-plane phonon mode and the variation of the initial oscillation phase with exciton density both suggest that the in-plane coherent acoustic phonon is impulsively generated by displacive excitation when $N_0 < 1$ and by sub-picosecond Auger hole trapping process when $N_0 > 1$. This observation is consistent with the absence of carrier quantum confinement in the lateral plane of NPLs. Analysis of the experimental data within a classical mechanical framework for wave packet propagation on the excited and trap state potentials yields the relative dimensionless displacement of the two states. On the other hand, the initial phase of $\sim \pi$ rad observed for the out-of-plane coherent phonon, independent of N_0 , suggests displacive excitation as the mechanism for generation of the out-of-plane coherent acoustic phonon. The coherent and incoherent dynamics of carriers and phonons described in this thesis provide further insight into the photophysical behavior of nanostructured CdSe QDs and NPLs.

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Chapter 1

Introduction

One of the biggest surprises of the twenty-first century comes from the small scale, nanoscience. People are more and more used to this interesting new field of science and technology intertwined with our daily lives by means of nanoscale materials in electronic devices, energy conversion, medicine field and even consumer products. Among the material with reduced size to nanometer scale, semiconductor nanostructures have been under intense attention for the last few decades.¹⁻⁵ As the cornerstone of modern electronic industry, the miniaturization of semiconductor favors a variety of applications. The most straightforward example is the capability improvement of electronic devices, reducing the weight and power consumption. The large surface-to-volume ratio in nanoparticles exposed the material more to the surroundings which can be beneficial in photocatalysis.⁶ As an important optical application, semiconductor nanoparticle based light emitters deliver higher performance in terms of brightness, efficacy and color accuracy.⁷ Meanwhile, considering the low-cost synthesis and absorption extended to near-infrared (NIR) range, these nanoscale semiconductor materials stand out as a promising candidate of next generation solar cells.⁸⁻⁹

Among the abundant advantages of semiconductor nanostructure, one of the most attractive characteristics is the tunability of band structure. The strong size-, shape- and composition-dependence of physical properties have received considerable experimental and theoretical attention motivated by both fundamental science and the potential applications.¹⁰⁻¹² To understand the behaviors of semiconductor nanostructures, it is

necessary to explore the ultrafast electronic dynamics in such low dimensional systems, which plays a vital role in the optoelectronic performances. For example, intra- and inter-band relaxations of charge carriers largely determine the efficiency of photovoltaic devices and coherent light emitters.¹³⁻¹⁴ The effect of concomitant electron-phonon coupling on energy and electron transport properties in nanoelectromechanical system has been theoretical studied and experimental demonstrated.¹⁵⁻¹⁷ Moreover, the strong Coulomb carrier-carrier interaction due to the spatial confinement within nanoscale particles leads to certain interesting phenomena which are typical absent in bulk material, like Auger processes,¹⁸⁻¹⁹ electronic coherence²⁰⁻²² and multiple exciton generation (MEG).²³⁻²⁴ As a part of interdisciplinary study of semiconductor nanomaterial, this thesis focuses on the investigation of ultrafast dynamics of charge carriers and coherent motions of valence electrons and phonons within CdSe based nanostructures, specifically in picosecond-to-femtosecond time scale, by virtue of profound understanding and further design.

Before the discussions of time-dependent works involved in this thesis, some basic concepts of semiconductor nanostructure will introduce in Chapter 1, followed by the band structure characterization via UV/vis absorption and photoluminescence (PL) spectroscopy. Additionally, few selected aspects regarding the ultrafast dynamics within semiconductor nanostructures are briefly reviewed. Femtosecond transient absorption (TA) spectroscopy along with the experimental setup will be described in Chapter 2. The representative pump-probe measurement of CdSe quantum dots (QDs) was illustrated as an instrumental example. Chapter 3 focuses on the observation of electronic coherence in CdSe QDs at cryogenic temperatures and the discussion of rapid dephasing mechanisms. In Chapter 4, we investigate the sub-picosecond Auger-mediated hole trapping process in quasi-two-dimensional CdSe/CdS core/shell nanoplatelets (NPLs). The coherent phonon dynamics of NPLs, especially acoustic phonon modes, are further monitored and analyzed in Chapter 5.

The in-plane breathing phonon is proposed to be triggered by the ultrafast charge carrier migration in the planar dimensions. The last Chapter summaries this thesis and outlines the future plan.

1.1 Band structure of semiconductor nanostructure

Semiconductor nanostructures possess an intermediate phase between bulk and atom. The electronic structure is discrete near bandgap and becomes continuous at high energy levels.²⁵⁻²⁶ The appearance of quantized energy states in a nanoscale semiconductor is due to the quantum confinement effect which was first proposed by Efros.²⁷ Another consequence of quantum confinement effect is the increment of the band gap. The wave function of semiconductor nanostructure $\Psi(r)$ is the product of Bloch wave function $\psi_{bloch}(r)$ representing the bulk property, and envelope function $\varphi_{env}(r)$ which describes the confinement effect. Noted the confinement in x-, y- and z-direction can be different. Here, we use the simple case that three dimensional confinements are the same. The envelope function is the solution of Schrödinger equation for ‘particle-in-box’ problem. Resemble the orbitals in a hydrogen atom, a series of eigenvalues can be solved when the dimensions reduced to or smaller than the corresponding exciton Bohr radius. In linear absorption, it predicts the discrete energy levels. At the same time, the band gap of semiconductor nanoparticle becomes the sum of the fundamental bulk band gap and the confinement energy, $E(r) = E_g^0 + E_{conf}(r)$, which is inversely proportional to size.

The usual categorization of semiconductor nanostructures according to confined dimensionality can be as follows. (i) Zero-dimension nanostructure: Spherical nanoscale particle also named quantum dot and nanocrystal (NC).^{3,14,28-29} The tight charge carrier confinement in three dimensions attracted increasing effort to investigate the optoelectronic properties of these ‘artificial atoms’ aimed at a large number of potential applications.³⁰⁻³²

In Chapter 3, we will elaborate the electronic coherence in colloidal CdSe quantum dots.

(ii) One-dimension nanostructure: Cylinder-like particle, for instance, quantum wire and rod with the nanometer scale cross section and a typical micrometer length.³³⁻³⁴ The confinement effect appears in the transverse direction and electrons are free along the longitudinal dimension. (iii) Two-dimension nanostructure: Thin film geometry with the one dimensional confinement of electrons perpendicular to the planar surface, like quantum well.³⁵⁻³⁷ The ultrafast charge carrier and coherent phonon dynamics of recently emerged quasi-two-dimensional CdSe/CdS core/shell nanoplatelets (NPLs) will discuss more in Chapter 4 and 5, respectively.

1.1.1 Excitons

Instead of moving independently, the photoexcited electron in conduction band (CB) and the leave-behind positively charged carrier (hole) in valence band (VB) form a stable quasi-particle, which is the so-called exciton.³⁸ As the elementary response of coherent light-matter interaction in semiconductor nanostructure, the generation and decay of excitons are tightly related to the optoelectronic properties. Excitonic signatures appear in absorption and PL spectra as the well-resolved peaks near band gap (Figure 1.2 & 1.3), which represent the optically allowed transitions. To describe the motion of exciton, people use center-of-mass, $m^* = m_e m_h / (m_e + m_h)$ in the weak confinement regime, where $m_{e(h)}$ is the effective mass of electron (hole). Therefore, atomic-like energy diagram of semiconductor nanostructure comprising eigenstates in CB and VB is labeled with excitonic states. As a consequence of Coulomb interaction, the formation of exciton lowers the resonant energy of excitonic states, described with exciton binding energy E_{EBE} . The exciton binding energy can be calculated from the energy difference between optical absorption and the corresponding luminescence energy, i.e., $E_{EBE} = E_{abs} - E_{PL}$, which

shows size dependence.³⁹ The decreased dimensionality in semiconductor increases the exciton binding energy which means the excitons are more stable in low-dimensional structures than bulk systems.⁴⁰ Together with confinement effect, the total band gap can be expressed as $E(r) = E_g^0 + E_{conf}(r) - E_{EBE}(r)$.

Another consequential phenomenon of strong Coulomb interaction is the appearance of biexciton state (bound two electron-hole pairs) which is typically absent in bulk semiconductor.⁴¹⁻⁴² Due to the transitions from excitonic to biexcitonic ground and excited states, additional absorptions lying at the low- and high-energy side of exciton resonance were theoretical predicted.⁴³ The induced absorption features near the bleaching of single excitonic state were observed in semiconductor QDs using optical pump-probe spectroscopy.⁴⁴ The small energy shifts arise from biexciton binding energy defined as, $\delta E = 2E_X - E_{XX}$, where E_X and E_{XX} are the energies of single exciton and biexciton ground states, respectively.⁴⁵⁻⁴⁶ Theoretical studies show a significant increase of the biexciton binding energy with decreasing size.^{43,47} Current effort to investigate the biexcitonic structure is motivated by the central role of excitonic complexes plays in the physics underpinning optical gain⁴⁸⁻⁴⁹ and multiple exciton generation processes.⁵⁰⁻⁵²

1.1.2 Phonons

The quanta of lattice vibration called phonon which in general can be divided into optical and acoustic modes. The optical phonon mode refers to the out-of-phase vibration of atoms within a unit cell which commonly oscillate with high frequency. Whereas, the acoustic phonon describes the vibration of the whole lattice whose frequency is relatively low. From phonon propagating direction perspective, atoms displaced from their equilibrium positions as longitudinal and transverse running waves. In a bulk crystal, wave vector selection rule for first-order Raman scattering requires $q \approx 0$, in which way

determines the phonon energy from dispersion curve. The miniaturization of semiconductor introduces not only the concept of the spatial confinement of charge carriers but also the quantized vibration of the lattice. The finite phonon modes relax the selection rules thus affect the phonons behaviour. Particularly, confined acoustic phonon can be calculated as the vibration of homogenous free-standing elastic particle based on Lamb's theory.⁵³ Thus, the mechanical property of nanostructures would dramatically modify the acoustic phonon mode.

Using femtosecond laser pulses with pulse duration shorter than the vibrational oscillation period, it is possible to initiate the coherent phonons. In time-resolved spectroscopy, the photogenerated coherent phonons manifest themselves as oscillatory signals shown in both real and imaginary parts of the refractive index, periodical modulating the transient spectrum. There are two kind of generation mechanisms most commonly used to exploit the coherent phonons, impulsive stimulated Raman scattering (ISRS)⁵⁴ and displacive excitation of coherent phonon (DECP).⁵⁵ The field-driving nonresonant ISRS creates a wave packet motion in the ground state, resulting sinusoidal-like oscillation. The coherent vibrational motion in an excited state may occur when the pump photon energy detuned to the absorption resonances. In DECP scheme, after photoexcitation the displaced coordinate of potential energy surface (PES) triggers the relaxation-driving wave packet in the excited system, displaying as a cosine oscillation. It is worthwhile to mention that resonant ISRS can also lead to wave packet dynamics in the excited state corresponding to all Raman-active phonon modes.⁵⁴ However, DECP mechanism only induces the breathing mode (A_1) with no change in lattice symmetry.

1.1.3 Heterostructure

Semiconductor heterostructure with the band gap engineered by stacking layers of different chemical compositions, is the essential element for customized and high-performance electronic maneuvers. With the well-developed synthetic procedures, like molecule beam epitaxy and chemical vapor deposition, the fabrication of heterostructure can be delicately controlled including the chemical components, dimensions and layer arrangement. By modifying the staggered energy band alignment, it is possible to investigate, understand and eventually control the optoelectronic property of nanostructure based devices which concept motivated comprehensive research efforts since the 1970s.

Figure 1.1. (a) Band alignment of type I semiconductor heterostructure composited with two different band offsets ΔE_{CB} and ΔE_{VB} in conduction and valence band, respectively. The generated exciton in semiconductor 1 transfer to the region of semiconductor 2. (b) Band alignment of type II semiconductor heterostructure prompts the generated electron to transfer to semiconductor 2 with hole localized in the original site. Type II band structure can be staggered in another direction in which way distributing the hole wave function over two regimes and trapping the electron within semiconductor 1.

As shown in Figure 1.1, the semiconductor heterostructure can be classified as (i) “Type I”, in which case the minimum of CB and the maximum of VB lie in the same layer; (ii) “Type II”, if the band extrema can be found in different components. With the small band offset in CB (VB) heterojunction, “quasi Type II” heterostructure localizes the hole (electron) within one layer and redistributes another type of charge carrier along the hybrid structure. An extreme case may also happen when the bandgaps of two species overlap with each other, which is known as a broken gap. Both band alignments in CB and VB redistribute the wave function of excited carrier over the spatial extent, facilitated the charge extraction and transport in photovoltaics devices.

1.2 Characterization in steady-state optical spectrum

Before the investigation of ultrafast dynamics within a low-dimensional system, we need to know some basic information of a semiconductor nanostructure sample, such as the band structure, lattice crystalline, and surface characteristics accordingly. The local mechanical properties of nanoscale materials can be obtained by diversified microscopy techniques. For example, the surface topography of 2D material is commonly retrieved from atomic force microscopy (AFM). Transmission electron microscopy (TEM) can capture the high-resolution image of sample and the even higher resolution surface image can be approached by scanning tunneling microscopy (STM) to atomic level. Compared with numerous microscopies which require strict sample preparation, optical spectroscopy provides an easy and fast way to explore the fundamental optical properties of the sample. In this section, we introduce two frequently used steady-state optical spectroscopies, linear absorption and photoluminescence.

1.2.1 Temperature dependent linear absorption spectrum

Linear absorption is a simple and commonly used coherent spectroscopy, which describes

one input field coherently acts on the dipoles of the sample generating a macroscopic polarization.⁵⁶ The linear light-matter response propagates in the transmitted direction of incident light meeting the energy and moment conservation. The incident light would be absorbed when the photon energy matched the energy gap between two quantized electronic levels, providing useful information of band structure. Following the Beer-Lambert law, an absorption spectrum is obtained by measuring the frequency-resolved transmittance of input and output light $A = -\log I_{out}/I_{in}$.⁵⁷ In our experiment, a stabilized tungsten halogen light source from Thorlabs combined with Oxford OptistatDry cryostat prepares the linear absorption spectrum with 4 to 300 K temperature range, as shown in Figure 1.2. The temperature dependence of energy gaps follows Varshni relation which defines the variation of the energy gap (E_g) with temperature (T) in semiconductor as the following,

$$E_g = E_0 - \alpha T^2 / (T + \beta) \quad (1.1)$$

where E_0 is the energy gap at 0 K, α and β are constants. The temperature dependent energy gap shifts predicted by Varshni equation are agreed with the experimental data of several kinds of semiconductors, like Si, Ge, GaAs, InP and InAs.⁵⁸ The input spectrum was collected from the transmission of the reference sample to avoid the environmental influence and extract the pure sample signal.

It should be mentioned although the energy structure can be resolved from absorbance spectrum, what is missing is the information about the origin of this energy gap. For example, in a semiconductor heterostructure (Figure 1.1), the peaks resolved from the absorption spectrum cannot be distinguished between the absorbance features of two types of semiconductors. The ambiguity appears more in condensed phase, considering the homogeneous (intrinsic lifetime) and inhomogeneous (multiple static frequencies)

linewidth broadening. At the same time, there is limited information about the kinetic dynamics in linear absorption spectrum which requires nonlinear time-resolved spectroscopy.⁵⁹ In the next chapter, we will introduce pump-probe spectroscopy, which uses two laser pulses to monitor the light-matter interaction in time domain.

Figure 1.2. Temperature dependent absorption spectra of CdSe QDs from 4 to 300 K. The two well-resolved absorbance peaks shown at all applied temperatures represent the two lowest excitonic energy levels. The red shift of absorption spectrum with increasing temperature basically arises from the band gap shrinkage at high temperature following Varshni relation.

1.2.2 Photoluminescence spectrum of CdSe quantum dots

Complementary to absorption spectroscopy, photoluminescence (PL) spectroscopy records the light emission as a result of relaxation from high-lying to lower energy state.⁶⁰ In semiconductor nanostructures, PL spectrum typically reflects the excitonic recombination processes occurring near the band gap and trap states.

Figure 1.3. PL spectrum (black) upon 530 nm excitation and absorbance (blue) of CdSe QDs at ambient temperature. The energy difference between band gap features shown in these two spectrum reflects the exciton binding energy. This PL spectrum is collected by our collaborator, Sabyasachi Chakraborty from Prof. Yinthai Chan's group.

A representative PL spectrum of CdSe QDs at the room temperature is plotted in Figure 1.3, together with the absorption spectrum. The energy gap between the dominant PL feature at 1.96 eV and band edge peak at 2.00 eV in absorption spectrum is the Stark shift arising from exciton binding energy. A relevant technique, photoluminescence excitation (PLE) spectroscopy measuring the PL signal with continuous frequency detuned incident light, is sensitive to the electronic structure and often used to detect low absorbance samples.⁶¹ Incorporating with a streak camera, the time resolved photoluminescence (TR-

PL) measurement is a commonly used tool to explore the exciton lifetime of semiconductor materials.⁶²⁻⁶³

1.3 Ultrafast dynamics of semiconductor nanomaterials

By using linear spectroscopy, we get a glance at the optical properties and electronic structure of nanomaterials. In this section, the ultrafast dynamics of charge carriers and phonons which determined the optoelectronic and thermal performances of quantum-confined objects would be discussed.⁵⁹ As mentioned before, the electronic dynamics of semiconductor nanostructures are significantly different from bulk materials due to the discrete energy levels and large surface-to-volume ratio. Here, we provide a short survey of some important topics regarding excitonic dynamics, including the intra- and inter-band charge carriers relaxations and electron-phonon interactions. There is also a brief introduction of electronic coherence which plays a vital role in energy transfer process.

1.3.1 Intra-and inter-band charge carrier relaxations

In nanoscale materials, a non-equilibrium carriers distribution can be generated immediately following the photoexcitation with an intense laser pulse, which would reach the thermal equilibrium via carrier-carrier and carrier-phonon scattering. The charge carrier thermalization occurs typically within a few hundred femtoseconds which could be excitation density and temperature dependent.⁶⁴⁻⁶⁵ One of the following nonradiative processes, intraband relaxation, describes the carrier depopulation of higher energy state and a complementary growth of the low-lying excitonic state.^{37,66} In bulk semiconductors, the hot electron intraband relaxation was dominated by coupling to longitudinal optical (LO) phonons via Fröhlich interaction.⁶⁷⁻⁶⁹

The phonon-assisted carrier relaxation process was predicted to be dramatically hindered in spatially confined nanostructures due to the restriction of energy conservation, known as “phonon bottleneck” phenomena.⁷⁰ However, the subpicosecond-to-picosecond electron intraband relaxation dynamics in II-VI QDs were reported using femtosecond TA spectroscopy, comparable with the timescale of hot electron cooling in bulk semiconductors.⁷¹⁻⁷⁵ Moreover, the size dependent measurements revealed an enhancement of the energy loss rate by decreasing the radius of materials which is opposite to the expected slowdown of intraband energy relaxation. The similar phenomena were also observed in other 0D⁷⁶⁻⁷⁷ and 1D⁷⁸ semiconductors. The absence of phonon bottleneck clearly indicates the non-phonon-assisted intraband relaxation pathway in the low-dimensional semiconductors. For now, the most widely adopted mechanism is Auger-type electron-hole scattering that was suggested by Klimov & McBranch.⁷² As shown in Figure 1.4, the excess energy of electron relaxation is transferred to a hole exciting it to a higher energy state or directly ionizing it. Later on, Guyot-Sionnet’s experiments supported this Auger-type mechanism, demonstrating a significant reduction of electron relaxation rate in the absence of spectator hole using different hole capping molecules.^{75,79-80} To further verify the Auger-like process, it is necessary to investigate the intraband hole dynamics directly which supposed to be faster than that of the electron. By using detuned pump energy, the state-to-state transition rates of electron and hole near the band edge of CdSe QDs were revealed by Kambhampati *et al.*, exhibiting a multichannel picture of exciton relaxation dynamics.^{14,81-82} With the separation of electron and hole dynamics, the size confinement independence and the sensitivity to the surface passivation of hole decay rate rationalized an alternative nonadiabatic transition pathway mediated by surface trapping.⁸³ Furthermore, the two-photon photoemission (2PPE) measurements evidenced the competitive hot carriers relaxation channels of Auger-type electron-hole energy transfer

and fast hole trapping process in different ligands coverage CdSe QDs,⁸⁴ which demonstrated the important role of ligands in determining the intraband and interband relaxation dynamics.¹²

Figure 1.4. Schematic diagrams from left to right represent the photogeneration of exciton in excited state (black), phonon assisted relaxation (red), Auger-type relaxation of electron (green) and nonradiative transition to trapping states (orange).

Unlike predominant nonradiative intraband relaxation channels, the charge carrier interband relaxation in semiconductors has alternative radiative and nonradiative recombination pathways. Radiative recombination produces a photon accompanied by spontaneous emission near the band edge with a typical nanosecond radiative lifetime in QDs.⁸⁵⁻⁸⁶ On the other hand, nonradiative recombination mainly occurs via charge carrier trapping and Auger-like processes. The high fluorescence quantum yield of semiconductor nanostructures (core/shell colloidal QDs up to $\sim 85\%$) is one the most favorable optical properties, leading to a large range of potential applications, such as light emitting diodes

(LED),⁸⁷ photodetectors⁸⁸ and biosensing.⁸⁹ The efficiency of these fluorescence-based devices is dependent on the competitive channels of radiative and nonradiative recombination, which highlight the importance of understanding the interband relaxation dynamics. It has been reported that nonradiative Auger recombination could accelerate the PL decay to picosecond scale.⁹⁰ The annihilation energy of an exciton is not emitted as a photon but instead is transferred to a third charge carrier (Figure 1.5).

Figure 1.5. Interband radiative recombination diagram is showed in the left side column. The other three columns illustrate the nonradiative recombination pathways including phonon-assisted, direct trapping and Auger recombination process, from left to right.

This nonradiative recombination can be effectively suppressed by spatial separation of the electron and hole wave functions in the form of type II heterostructure.⁹¹ Opposite to shortening the radiative lifetime by Auger recombination, dark exciton, parallel spin electron hole pair, possesses a long-lived radiative lifetime. The corresponding dynamics

can be established by the persistent fluorescence at low temperature ($T < 10$ K) in which case the bright exciton thermal population can be neglected.⁹²

A universal phenomenon observed in light emitters, including molecules, semiconductor nanoparticles and macroscopic systems is fluorescence intermittency or blinking. The random appearance of high fluorescence (on-state) and low fluorescence (off-state) periods span from microseconds to seconds timescale. In semiconductor quantum confined systems, this effect in single CdSe QD was first reported by Nirmal⁹³ and then observed in other types of nanostructures.⁹⁴⁻⁹⁶ It is generally agreed that charge carrier trapping process is the origin of fluorescence blinking, but the detailed understanding is in debate. Two distinct types of blinking scenarios were proposed. Charging model (A type) assumes the on and off periods corresponding to neutral and charged nanostructure system, respectively. Auger quenching is an efficient non-radiative recombination pathway for the charged nanocrystal (Figure 1.5). Another sort of blinking (B type) suggests the fluctuation of trapped chargers, mostly in surface sites, can nonradiatively recombine with its counterpart determines the photoluminescence lifetime.⁹⁷⁻⁹⁹

1.3.2 Phonon dynamics

The fundamental processes in semiconductor nanoparticles such as exciton confinement and relaxation dynamics have attracted extensive research effort as introduced above. Another important component of physical properties is electron-phonon coupling which plays a major role in the optoelectronic and thermal performance. First of all, the temperature dependence of the energy gaps of semiconductors is due to electron-phonon interaction.¹⁰⁰⁻¹⁰¹ The band gap shifting can be described in a Bose model with exciton-phonon coupling constant,

$$E(T) = E(0) + 2a n(T). \quad (1.2)$$

Here, $E(0)$ accounts for the exciton energy at $T = 0$ K, a represents electron-phonon coupling constant and the average phonon number $n(T) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ follows Bose-Einstein distribution. In addition, phonon scattering also leads to temperature dependent linewidth broadening which contribution can be evaluated as

$$\Gamma(T) = \Gamma_0 + \Gamma_A T + \Gamma_O n(T), \quad (1.3)$$

where the first term is the homogenous linewidth broadening component, the second is the acoustic phonon contribution with electron-acoustic-phonon coupling strength Γ_A , and the last term is due to optical phonon scattering with electron-optical-phonon coupling strength Γ_O . In the case of II-VI semiconductor like CdSe, the electron-phonon coupling mechanisms can be roughly summarized as the optical phonon modes coupled via Fröhlich interaction while acoustic phonon by means of deformation and piezoelectric potential.¹⁰²⁻¹⁰⁵ To qualify the electron-phonon coupling strengths, Huang-Rhys factor S is often used and can be extracted from the first moment oscillation amplitude A by the relation $2\hbar\omega S = A$.¹⁰⁶

Generally, phonon dynamics in semiconductor nanostructures accompany with relaxation and dephasing processes of charge carriers. The former one leads to the energy dissipation limited the thermodynamic efficiency of bulk photovoltaic devices since a large amount of solar power lost to heat.¹⁰⁷ As a reduction in the dimensionality, the discrete energy level of semiconductor nanostructure is expected to suppress the phonon dynamics due to the mismatch of energy gap, hence enhances the energy conservation.^{71,108-109} On the other hand, electronic dephasing process via electron phonon scattering preserves the

energy conservation but destroys the coherence between excitonic states.¹¹⁰⁻¹¹¹ To harness and exploit the quantum coherent motion in nanoscale materials, a striking phenomenon for quantum information applications, it is essential to understand and control phonon behaviors.

1.3.3 Electronic coherence

Quantum coherence describes the superposition of quantum states driven the wave-like motion. In a simple two levels system, eigenstate $|1\rangle$ and $|2\rangle$, the statistical properties can be described in terms of density matrix operator:

$$\rho = \sum_j P_j |\psi_j\rangle\langle\psi_j|, \quad (1.5)$$

where P_j is the fraction factor of state ψ_j with $j = 1, 2$. The density matrix obeys the Liouville equation and can be written as

$$\rho = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}. \quad (1.6)$$

The diagonal elements represent the probability of finding the system in state $|1\rangle$ and $|2\rangle$, i.e., the population in these two eigenstates. The off-diagonal elements represent the coherence and are determined by the phase correlation between these two eigenstates. If the relative phase of two wave functions is randomly distributed, then the off-diagonal term vanishes and system shows no coherence. On the contrary, with well-defined phase relationship, the system possesses electronic coherence. Considering the practical optical transitions from ground state $|0\rangle$ to two excited states $|1\rangle$ and $|2\rangle$, the broad spectral bandwidth of a ultrashort laser pulse impulsive excites the two transitions simultaneously

with well-defined phase generating the electronic coherent motion whose period given by $\hbar/\Delta E$, where ΔE is the energy difference between $|1\rangle$ and $|2\rangle$.

Compared with the vibrational coherence which mostly occurs on femtosecond-to-picosecond timescale, the detection of electronic coherence challenges the time-resolved measurements, requiring the better time resolution to sub-femtosecond or even attosecond scale. By virtue of high-order harmonic generation and attosecond science, the sub-femtosecond coherent valence electrons motion in krypton ions was observed in real time using isolated attosecond extreme ultraviolet (EUV) probe pulses.¹¹² The coherent superposition of transitions from spin-orbit splitting of $4p^{-1}$ subshells ($4p_{3/2}^{-1}$ and $4p_{1/2}^{-1}$) to $3d^{-1}$ within Kr^+ present the long-lived characteristic modulation with a period of 6.3 fs in transient EUV absorption spectra. Another technique, two-dimensional electronic spectroscopy (2DES), has the potential to identify electronic coherences by their cross peak and oscillation frequency. 2DES has been used to scrutiny some light-harvesting systems such as Fenna-Matthews-Olson (FMO) complex¹¹³ and the PC645 complex.¹¹⁴ Photosynthetic complexes absorb solar light and then transmit the energy through molecules to reaction centres by antenna proteins. Investigated by 2DES, the quantum coherence was implied to play the wire role along distant molecules rather than the semiclassical hopping among excited states. Inspired by the extremely high-efficiency energy transfer in the photosynthetic systems, considerable attention has been paid to exploit this quantum-mechanical effect in nanoscale materials, such as low-dimensional semiconductor nanostructures.^{20-22,111} The excitonic coherent motion with 15-fs dephasing time in CdSe nanocrystals was firstly reported by Scholes using 2DES technique.²⁰ The broadband laser pulse spectrally overlaps with the two lowest-energy excitonic states, preparing the excitonic superposition of heavy hole (HH) and light hole (LH) in VB. Later, ‘persistent’ lifetime (~ 80 fs) quantum coherence between $1S_e$ and $1P_e$ state in CB of CdSe

QDs was reported by Engel.²² Recently, colloidal semiconductor NPLs, a system decreased the inhomogeneous broadening due to the well-defined thickness, unraveled a long-lived excitonic coherence lasting up to ~20-30 fs in few monolayers and core/shell structure.²² In Chapter 3, we investigated the temperature-dependent excitonic coherence of CdSe QDs using femtosecond TA spectroscopy. The interexcitonic quantum coherence within nanostructures is influenced by the charge carrier relaxation, inhomogeneous broadening and electron-phonon coupling which will be discussed more in detail.

Chapter 2

Femtosecond Transient Absorption Spectroscopy

To observe the ultrafast dynamics ($<10^{-12}$ s) of chemical and atomic processes which exceed the speed of detector (classical electronic equipment, like a fast streak camera, could realize only picosecond temporal resolution), time-resolved spectroscopies with ultrashort laser pulses were used to monitor light-matter interaction. Several ultrafast interrogation techniques have been developed and commonly applied. For example, the most widely used pump-probe technique is able to investigate the time-dependent population dynamics via temporally delayed two laser pulses;¹¹⁵ up-conversion spectroscopy improves the sensitivity by focusing the luminescence of sample and gating pulse at a nonlinear crystal. With more than two laser pulses, four-wave-mixing (FWM) method allows the sensitive and background free detection; 2DES technique has the potential to distinguish the electronic correlation as introduced above; the recently developed femtosecond stimulated Raman spectroscopy (FSRS) provides the vibrational information with high temporal and spatial resolution. Moreover, the spatial-resolved photoemission electron microscopy (PEEM) as well as angle-resolved photoemission spectroscopy (ARPES) which can directly observe electron distribution in reciprocal space, can be upgraded with a typical pump-probe framework and hence enable to explore the transient dynamics. Regarding the diversified time-resolved spectroscopies, most of them are based on pump-probe configuration. Here, we focus on femtosecond transient absorption spectroscopy, a combination of ultrashort laser pulse and pump-probe technique.

2.1 Ultrashort laser pulse generation

The investigation of ultrafast physical and chemical phenomena is accompanied with the advance of ultrashort laser pulses. Since the first demonstration of mode-locking laser which is the basis for modern femtosecond laser pulse over fifty years ago, the development and improvement of these ultrashort lasers have been through few generations, from dye laser to solid-state bulk laser based on ion doped crystals, together with fiber optics advancement from 1970s, later developed toward the current most popular self-mode-locked Ti:sapphire lasers. For now, an extensive ultrashort laser portfolio (i.e. <40 fs) over a different spectral range and with high pulse energy (typical *mJ*/pulse) can be commercially achieved.

The further spectral broadening of laser pulse based on the nonlinear effect self-phase modulation (SPM) may happen when an intense laser is propagating through a nonlinear media which could be a drop of water, a piece of glass or photonic crystal fiber. Corresponding to optical Kerr effect, SPM leads to the spectral broadening of laser pulse via inducing different phase shift to different frequency components and generating new frequency. The quality of the output white light depends on the input pulse energy, third-order nonlinear coefficient and dispersion relation of media. The well-established pulse compression technique based on SPM in a single-mode optical fiber followed by the chirp compensation can generate ~5 fs laser pulse, but limited the pulse energy to nanojoules range.¹¹⁶⁻¹¹⁷ In our experiment, 25-fs laser pulses from an amplified Ti:sapphire laser system (800 nm, 1 kHz; Coherent) focused into a hollow core fiber placed in a high-pressure chamber filled with noble gas. The wavelength of output frequency-broadening pulses spans from ~500-950 nm with overall > 50% fiber transmission (Figure 2.1). This

gas-based pulse compression scheme is the currently favored technique to obtain the few-cycle high power laser pulses.¹¹⁸⁻¹¹⁹

Figure 2.1. Spectral broadening in helium gas at $p = 2.0$ bars. The input pulses with ~ 50 nm full width half maximum (FWHM) (black) enter the hollow core fiber and produce the frequency-broadened laser pulses which spectral bandwidth spanning from 500 to 950 nm.

2.1.1 Chirped pulse optimization

A subsequent aspect of spectral broadening by SPM is the spectral phase distortions which are inevitably introduced by propagating through optics and reflecting from dielectric surfaces. It is critical to characterize and control the phase profile of ultrashort laser pulse, not only due to its vital role in determining the pulse duration but also it may modify the photochemical dynamics. For example, after impulsive photoexcitation of a molecule system, the nuclear wave packet would evolve in the excited state. However, the relative arrival timing of different frequency components in a single pulse could change the wave packet dynamics to another potential energy surface. Phase information of femtosecond pulse can be obtained from simple autocorrelation measurement. Other

established phase measurement methods include frequency-resolved optical gating (FROG) which provides retrieved phase profiles, and spectral phase interferometry for direct electric-field reconstruction (SPIDER) which is suitable to characterize the single ultrashort pulse.

In general, group-velocity dispersion (GVD), $\varphi''(\omega) = \frac{\lambda^3}{2\pi c_0^2} \frac{d^2 n(\lambda)}{d\lambda^2}$, is a characteristic of wavelength λ dependent group velocity of light (first derivative of refraction index $n(\lambda)$). Positive GVD or chirp describes the red-shift of leading edge of an ultrashort pulse which occurs in the most cases. On the other hand, the negative chirp means high-frequency side possesses the larger group velocity. In order to obtain the transform-limited (TL) laser pulse, several methods can be used to introduce the negative chirp compensating the positive chirp, like a pair of prisms and chirped mirrors. In our experimental setup, the broadband laser pulses (truncated from 550-750 nm for experimental requirement) are pre-compressed with pairs of chirped mirrors to within $\sim 1.5\times$ of the transform-limited duration. Subsequently, multiphoton intrapulse interference phase scan (MIIPS) combined with high-order dispersion compensation by means of a spatial light modulator-based pulse shaper (FemtoJock, Biophotonic) yields transform limited 6-fs pulses.

MIIPS is a single beam pulse shaping method to characterize phase profile of an ultrashort laser pulse and compensate the unwanted phase distortions. To modulate the spectral phase chirp, a reference function $f(\omega)$ can be introduced by liquid crystal dual-mask spatial light modulator (LC-SLM) is added into local phase profile $\phi(\omega)$. Then, the second harmonic generation (SHG) spectrum of modulated pulse with the sum of two phase profiles $\varphi(\omega) = \phi(\omega) + f(\omega)$ is detected from which would retrieve the $\phi(\omega)$. The TL pulse, $\varphi(\omega) = 0$, generates the maximum SHG signal. Moreover, the pulse shaper is able

to impose arbitrary phase mask $f(\omega)$ that provides the flexibility to control the phase profile and achieve designed chirped pulse.

Figure 2.2. (a) Spectrum (black line) and spectral phase (blue line) of the transform-limited broadband laser pulse. (b) The reconstructed temporal profile yields a pulse duration of 6-fs FWHM.

Figure 2.2a shows the measured phase of TF pulse after MIIPS. In the practical setup, the incident femtosecond laser pulse is decomposed by a grating (spectral disperser) and a curved mirror (focusing element). The spectral patented mask programmed by liquid crystal modulator array modifies the phases of individual frequency components. Implemented with a reflection geometry, the modulated beam is direct back through the same grating and a second curve mirror, This so-called folded 4f system is ideally free of temporal dispersion, which means the output pulse would be identical to the input without

the SLM. The output light from pulse shaper is focused to a second harmonic crystal (usually BBO crystal).

2.2 Ultrafast transient absorption spectroscopy

Femtosecond transient absorption spectroscopy can be used to investigate the time-dependent population relaxation, chemical kinetics and wavepacket dynamics in the pump-probe configuration with ultrashort laser pulses.¹¹⁵

Figure 2.3. Schematic illustration of transient absorption spectroscopy setup.

In this technique, an ultrashort laser pulse is split into two fractions, the intense beam ‘pump’ prompt the sample to a non-equilibrium state, the other beam arm ‘probe’ monitors the properties change in reflectance and transmittance. The two incident laser pulses are adjusted to be spatial overlapped with each other in the sample where the beam size of the pump is larger than the probe, in order to guarantee the detection of a uniformly photoexcited region. The time evolved optoelectronic properties are investigated by varying the time delay (Δt) between the arrival of pump and probe pulses. The transmitted probe beam is spectrally dispersed in a 300 mm spectrograph and detected on a 1024-element linear array detector, which allows a range of wavelengths to be detected simultaneously. The detector has a read-out rate of 1 kHz and is synchronized to the 500 Hz optical chopper positioned in the path of the pump beam. Dependent on the type of experiment and inspected sample system, the frequency of two laser pulses can be identical or selective altered as a two-color pump-probe spectroscopy.

Transient absorption spectroscopy reflects the nonlinear third-order polarization $P^{(3)}(t) = \epsilon_0 \chi^{(3)} E(t)^3$ with permittivity ϵ_0 and third-order linear electric susceptibility $\chi^{(3)}$. The signal is radiated collinear with the transmitted probe, thus matching the wave vector conservation $k_{sig} = +k_{pump} - k_{pump} - k_{probe} = k_{probe}$. The detector (CCD, photodiode and etc.) identifies the intensity of the transmitted probe (light field E_{pr}) together with the nonlinear signal

$$\begin{aligned}
 I(t, \tau) &= \frac{nc}{4\pi} |E_{pr}(t) + E_{signal}(t, \tau)|^2 \\
 &= \frac{nc}{4\pi} |E_{pr}(t)|^2 + \frac{nc}{2\pi} \text{Im}\{E_{pr}(t)E_{signal}^*(t, \tau)\} + \frac{nc}{4\pi} |E_{signal}|^2
 \end{aligned} \tag{2.1}$$

Thus, the differential intensity in probe vector direction with and without the pump laser excitation can be expressed as

$$\Delta I(t, \tau) = \frac{nc}{4\pi} (|E_{pr}(t) + E_{signal}(t, \tau)|^2 - |E_{pr}(t)|^2). \quad (2.2)$$

Given $|E_{signal}|^2$ will be a relative small contribution, so can be neglected, and subtraction the constant component from the incident field $|E_{pr}(t)|^2$, we get the differential intensity

$$\Delta I(t, \tau) \propto \text{Im}\{E_{pr}(t)E_{signal}^*(t, \tau)\}. \quad (2.3)$$

We can also choose to evaluate the Fourier transform of equation (2.3) to get the spectral resolved differential intensity

$$\Delta I(\omega, \tau) \propto \text{Im}\{E_{pr}(\omega)E_{signal}^*(\omega, \tau)\}. \quad (2.4)$$

2.3 Transient absorption measurement of CdSe quantum dots

TA spectroscopy records the differential absorption spectrum $\Delta A(\omega, t)$, i.e. the excited absorption spectrum minus ground state absorption spectrum, as a response of light-matter interaction. In our TA spectroscopy, differential transmission $\Delta T/T(t) = \frac{T_{pump\ on}(t) - T_{pump\ off}(t)}{T_{pump\ off}(t)}$ spectrum was collected as a function of time delay. Based on Beer-Lambert law, differential absorption can be calculated as the expression $\Delta A = -\log(\Delta T/T + 1)$. The negative TA signal (ΔA) arises from ground state bleaching as a consequence of population in the ground state being promoted to the excited state decreased the ground state resonant absorption. Another contribution of the negative signal is stimulated emission corresponding to the transitions from excited state to ground state. On the other hand, the positive signal is provided by excited state absorption which term explain itself as the charge carrier population in the excited state reexcited to a higher

energy level. Noted that probe beam induced emission and absorption are typical debilitated considering the weak intensity of probe pulse.

Figure 2.4. (a) Time-resolved TA spectrum of CdSe QDs upon excitation with narrowband pulses resonant to the lowest excitonic energy state at 77K. The oscillatory features come from coherent phonon. (b) TA spectra at 1-ps time delay contains the features of induced absorptions (A_i) and bleaching signals (B_i). The labels for the transient spectral features follow the notation of Klimov *et al.*¹⁻²

To elaborate how to read TA spectra, a representative contour plot of CdSe QDs is shown in Figure 2.4 as an example, upon narrowband pump resonant to the lowest excitonic states $1S_e 1S_{3/2}$. The dominant features in TA spectra result from state filling and Coulomb multiparticle interaction like carrier-induced Stark effect. The negative signal ($\Delta A < 0$)

was mainly attributed to ground state bleaching features B_1 and B_2 , corresponding to the transition from $1S_{3/2}$ and $2S_{3/2}$ states in VB to $1S_e$ state in CB, respectively. This effect only affects the transitions with occupied states and intrinsic sensitive to the sum of electron and hole occupation numbers.¹²⁰ In addition to state filling, the carrier-induced Stark effect is interpreted as the transition from single excitonic state to biexcitonic state transitions leading to a modification of the dipole selection rules and shift of the energy levels.¹²¹

In Figure 2.4b, one can unambiguously observe the positive signal ($\Delta A > 0$) A_2 as a sign of transition $|1S_e 1S_{3/2}\rangle \rightarrow |1S_e 1S_{3/2}; 1P_e 1P_{3/2}\rangle$. The red-shift with respect to the third lowest excitonic energy state $1P_e 1P_{3/2}$ results from the biexciton binding energy, $\delta E_{13} = E_1 + E_3 - E_{13}$. Subscripts represent the excitonic state and E_{13} is the biexcitonic state energy. The absent of photon induced absorption A_1 which corresponds to the transition $|1S_e 1S_{3/2}\rangle \rightarrow |1S_e 1S_{3/2}; 1S_e 1S_{3/2}\rangle$ stems from the spectral overlap with bleaching signal B_1 . The dominant negative ground state bleaching spectrally covers the positive signal A_1 , making it hard to be resolved. The oscillatory signature with the frequency of 210 cm^{-1} predominantly arises from LO phonon of CdSe.

Chapter 3

Electronic Coherence in CdSe Quantum Dots

A large portion of the content and figures of this chapter are reprinted or adapted from Shuo Dong, Dhara Trivedi, Sabyasachi Chakraborty, Takayoshi Kobayashi, Yinthai Chan, Oleg V. Prezhdo, and Zhi-Heng Loh, “Observation of an Excitonic Quantum Coherence in CdSe Nanocrystals”, *Nano Lett.* 2015 **15** (10), 6875-6882. Reproduced by the permission of American Chemical Society.

3.1 Introduction

Recent observations of electronic and/or vibronic coherences^{113,122-124} in biological light harvesting complexes by ultrafast multidimensional spectroscopy have led to speculation that such phenomena are exploited to boost energy transfer efficiencies in photosynthesis.¹²⁵ Quantum coherences between electronic states manifest themselves as periodic oscillations of the electronic density with time, in which the modulation frequencies scale with the energy differences between the participating eigenstates.¹²⁶ Motivated by fundamental scientific interest and potential applications, studies of electronic coherences have also been extended to a variety of nanoscale artificial light harvesting systems.^{22,127-130} Indeed, theoretical studies have put forth the possibility of harnessing electronic quantum coherences to enhance the photocurrent and photovoltage output of solar cells.¹³¹

Among the multitude of artificial light harvesting systems, semiconductor nanocrystals,¹³²⁻¹³³ also known as quantum dots (QDs), stand out due to their desirable

optical properties²⁹ and relatively well-established synthetic procedures.¹³⁴ The latter allows exquisite control over the size and shape, and hence, the photophysical properties of these nanocrystals. High incident-photon-to-current conversion efficiencies of 8.55% have been demonstrated¹³⁵ by solar cells that incorporate QDs as the photosensitizer.¹³⁶ While the excited-state dynamics¹⁴ and the coherent phonon phenomena¹³⁷⁻¹³⁸ of semiconductor nanocrystals have been actively investigated, it is only in recent years that excitonic quantum coherence has been studied in CdSe QDs.²⁰⁻²¹ Two-dimensional electronic spectroscopy (2DES) performed on zinc-blende CdSe QDs at ambient temperature reveals a coherent superposition between $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ excitonic states, for which a dephasing time of 15 fs is found.²⁰ More recent 2DES measurements elucidate multi-level quantum coherences with dephasing times that extend to ~ 100 fs.²¹ These studies did not address the excitonic decoherence mechanism, for which physical insight is all the more critical given the disparate dephasing time scales reported. In addition, the possibility of steering coherent phonon wave packet dynamics by the excitonic coherence remains unexplored.

Here, femtosecond optical pump-probe spectroscopy is employed to investigate coherent excitonic motion associated with the $1S_e1S_{3/2}$ – $1S_e2S_{3/2}$ excitonic superposition in wurtzite CdSe QDs. In contrast with zinc blende CdSe QDs, it is noteworthy that excitonic coherences in the thermodynamically more stable wurtzite form of CdSe have so far eluded detection.¹³⁹ Spectral signatures of excitonic coherence are clearly discerned from our low-temperature optical pump-probe data, from which an ultrafast charge migration that is mediated by excitonic quantum coherence is reconstructed. Results from temperature-dependent measurements are suggestive of decoherence induced by exciton-acoustic phonon scattering, although the dominant contribution to decoherence is found to be temperature-independent. Finally, the presence of excitonic coherence is found to

suppress exciton-LO-phonon coupling while the exciton-LA-phonon coupling is enhanced. These observations are supported by semiclassical *ab initio* molecular dynamics (AIMD) simulations.

3.2 Sample preparation and characterization

Colloidal wurtzite-type CdSe QDs are synthesized by our collaborator, Prof. Yinthai Chan from National University of Singapore, and measured in our lab as received.

Figure 3.1. (a) TEM micrograph of the CdSe QD sample, which is provided by Prof. Yinthai Chan’s group. The histogram of the QD dot sizes is shown in inset. The CdSe QDs have an average diameter of 6.1 nm and 6% size-dispersity. (b) Variable-temperature UV/visible absorption spectra of CdSe quantum dots collected within the 77–140-K temperature range. The spectra are offset by 0.01 absorbance unit for clarity. The dashed line shows the absorption spectrum collected at 295 K for a toluene solution of the CdSe QD sample.

The synthesis method follows literature procedure¹³⁴ before they are dispersed in a poly(methyl methacrylate) (PMMA) matrix and spin-coated onto a 1.5-mm-thick fused silica window. The average diameter of the QDs is 6.1 nm with 6% rms dispersity, as determined by transmission electron microscopy (TEM). The narrow size dispersity, further evidenced by the well-resolved features in the absorption spectrum (Figure 3.1b), is critical in allowing the observation of spectral signatures of excitonic quantum coherence. The optical absorption spectrum of the CdSe QDs in toluene solution at 295 K reveals a band edge of 1.99 eV (Figure 3.1b), which suggests a mean diameter of 6.4 nm for the CdSe QDs.¹⁴⁰ The mean diameter inferred from the band-edge absorption energy is in good agreement with that obtained from transmission electron microscopy, from which an average diameter of 6.1 ± 0.4 nm is measured (Figure 3.1a).

3.3 Experimental and simulation methods

Femtosecond transient absorption spectroscopy with broadband pump and probe laser pulses is employed to investigate the excitonic coherence in our lab. *Ab initio* molecular dynamics simulations were performed by Prof. Oleg V. Prezhdo's group from University of Southern California, theoretically supported what we measured.

3.3.1 Femtosecond transient absorption spectroscopy

The optical pump-probe setup employs few-cycle pulses in the visible and pulse-to-pulse measurements of the differential transmission spectra. The details of the apparatus can be found in Chapter 2. For the study reported herein, MIIPS is incorporated to characterize and compensate for the residual high-order dispersion of the broadband laser pulses,⁶⁶ thereby furnishing transform-limited ~6-fs pulses in the 550 – 750-nm spectral range for experiments.

Figure 3.2. (a) Raw $\Delta T/T$ spectra of the CdSe QD thin-film sample as a function of time delay. (b) $\Delta T/T$ spectra of a PMMA thin-film sample. (c) Processed $\Delta T/T$ spectra obtained after subtraction of the PMMA response (Figure 3.2b) from the raw data (Figure 3.2a).

The typical excitation fluence is 0.4 mJ cm^{-2} and the corresponding average number of excitons per QD is $\langle N \rangle \sim 0.3$. Pump and probe pulses are orthogonally polarized to

suppress contributions from scattering and coherent artifacts, which could otherwise obfuscate the short-lived excitonic coherence signal. In addition, coherent artifacts from the PMMA matrix are eliminated by subtracting the measured response of a pure PMMA sample (Figure 3.2b) from the signal of the QD sample (Figure 3.2a).

3.3.2 *Ab initio* molecular dynamics simulations.

The $\text{Cd}_{33}\text{Se}_{33}$ cluster with a diameter of 1.3 nm was constructed using bulk wurtzite lattice. Recent experiments¹⁴¹ have shown that such “magic” size cluster is one of the smallest stable CdSe QDs that support a crystalline-like core.¹⁴²⁻¹⁴³ These properties make $\text{Cd}_{33}\text{Se}_{33}$ an excellent model for studying electronic and vibrational properties of semiconductor QDs. The cluster geometry was optimized using *ab initio* density functional theory with a plane wave basis, as incorporated in the Vienna *ab initio* simulation package (VASP).¹⁴⁴ The PBE functional¹⁴⁵ with projector-augmented-wave (PAW) pseudopotentials¹⁴⁶ was employed in a converged plane wave basis. The simulations were performed in a periodically replicated cubic cell with at least 8 Å of vacuum between QD replicas. The fully optimized structure was then heated to the desired temperatures with repeated velocity rescaling. 3-ps-long microcanonical MD trajectories were generated using the Verlet algorithm with the 1-fs time step and Hellmann-Feynman forces. The decoherence time was obtained with the semiclassical optical response formalism,¹¹⁵ which allows one to use the MD simulation. The pure-dephasing time is associated with fluctuations of the energy levels due to coupling of the electronic degrees of freedom to phonons. The fluctuations in the energy levels are best characterized in terms of correlation functions. The pure-dephasing function is defined as,

$$D(t) = \exp(i\omega t) \langle \exp\left(-\frac{i}{\hbar} \int_0^t \Delta E(\tau) d\tau\right) \rangle, \quad (3.1)$$

where the angular brackets denote thermal averaging. The dephasing function can be approximated using the second-order cumulant expansion as,

$$D(t) = \exp(-g(t)), \quad (3.2)$$

where

$$g(t) = \frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} \langle \Delta E(\tau) \Delta E(0) \rangle d\tau_2. \quad (3.3)$$

The method based on the cumulant expansion shows better numerical convergence than the direct expression equation (3.3), which involves averaging of an oscillating function. Both direct and cumulant methods have shown excellent agreement with experiment for several systems.¹⁴⁷⁻¹⁴⁹ The data reported below are based on the cumulant expansion.

3.4 Results and discussions

The optical absorption spectrum of the CdSe QD thin-film sample collected at 77 K is shown in Figure 3.3. The spectrum reveals well-resolved peaks at 2.04, 2.14, and 2.32 eV, which correspond to transitions to the $1S_e1S_{3/2}$, $1S_e2S_{3/2}$, and $1P_e1P_{3/2}$ excitonic states, respectively; note that the background rising towards the high-energy side of the spectrum is due to Rayleigh scattering by the thin-film sample. Photoexcitation of the sample by transform-limited, broadband laser pulses of 6-fs duration and spectral range of 550 – 750 nm results in the formation of a coherent superposition of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ excitonic states. The normalized differential transmission $\Delta T/T$ spectra obtained at 77 K show positive features, which correspond to ground-state bleaching and stimulated emission from the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ excitonic states, as well as negative features, which can be assigned to excited-state absorption to the biexciton manifold. Temporal oscillations in the time-resolved $\Delta T/T$ spectra can be assigned to coherent longitudinal-optical (LO) and longitudinal-acoustic (LA) phonons, with frequencies of 208 and 18 cm^{-1}

¹, respectively. Inspection of the $\Delta T/T$ signal at short time delays ($t < 100$ fs) reveals an additional high-frequency, albeit short-lived oscillatory component (Figure 3.4a), which is suggestive of excitonic quantum coherence.

Figure 3.3. Linear absorption spectrum of the CdSe QD thin-film sample (black line) and the spectra of the broadband (blue line) and narrowband (red line) laser pulses. The absorption spectrum can be fit to a sum optical transitions to the three lowest excitonic states (dashed lines), in addition to Rayleigh scattering (dotted line). The spectrum of the broadband laser pulse excites predominantly the transitions to the two lowest-energy excitonic states. The inset shows the excitonic level diagram denoted with the optical transitions observed in the absorption spectrum.

Further analysis of the early-time oscillatory signal is performed on a time trace obtained at a probe wavelength in the band-edge transition region where the amplitude of the coherent LO phonon is a minimum. In this way, the contribution of the coherent LO phonon to the signal can be neglected. The resultant time traces obtained at 77, 100, 120, and 140 K show that the early-time oscillation becomes more rapidly damped with temperature (Figure 3.4b).

Figure 3.4. (a) Differential transmission spectrum collected as a function of time delay following excitation of 6.1-nm-diameter wurtzite-type CdSe QDs at 77 K, revealing strongly damped, high-frequency oscillations that are due to excitonic quantum coherence. (b) Time-resolved differential transmission signal collected in the region of the band-edge transition for temperatures of 77, 100, 120, and 140 K (top to bottom). The solid lines are fits to equation (3.4).

To extract the damping times, the time traces are fit to the function

$$S(t) = \sqrt{\frac{4 \ln 2}{\pi \Delta_{IRF}^2}} \exp\left(-\frac{4 \ln 2 t^2}{\Delta_{IRF}^2}\right) * \Theta(t) \quad (3.4)$$

$$\times [A_1 + A_2 \cos(\omega t + \varphi) \exp(-t/\tau)],$$

which is a convolution of a damped oscillation atop a step function with a normalized Gaussian instrument response function of FWHM Δ_{IRF} . In the expression, $\Theta(t)$ is the Heaviside function with amplitude A_1 , and A_2 , ω , φ , and τ are the amplitude, frequency, phase, and damping time of the oscillation, respectively. The fits to the time traces are shown in Figure 3.4b and the fit parameters ω , φ , and τ are summarized in Table 3.1.

Table 3.1. Parameters obtained from the fit of the early-time periodic oscillation to equation (3.4).

Temperature / K	Frequency ω / cm^{-1}	Phase φ / π rad	Damping time τ / fs	Dephasing time T_{12}^* / fs
77	851 ± 17	0.14 ± 0.02	14.7 ± 1.2	15.8 ± 1.5
100	756 ± 21	0.07 ± 0.02	14.1 ± 1.0	15.1 ± 1.2
120	753 ± 63	0.18 ± 0.05	13.8 ± 3.8	14.7 ± 4.2
140	750*	0.13 ± 0.04	11.4 ± 2.4	11.9 ± 2.6

(* The oscillation frequency at 140 K was fixed to allow the fit to converge.)

The frequencies of the oscillations observed at $t < 100$ fs are $\sim 750 - 850 \text{ cm}^{-1}$ for the range of temperatures employed in the experiments. In the absence of phonon modes with such high frequencies, the origin of the short-lived oscillatory component can be attributed to coherent excitonic dynamics. This assignment is bolstered by the following observations. First, the measured oscillation frequency coincides with the $\Delta E \approx 0.091 - 0.093 \text{ eV}^{-1}$ energy separation between the $1S_e 1S_{3/2}$ and $1S_e 2S_{3/2}$ excitonic states determined for the CdSe QD sample over the same temperature range (Table 3.2). The good agreement between ΔE and ω strongly suggests that the observed oscillations originate from excitonic quantum beats. Second, the retrieved oscillation phases for all temperatures are ~ 0 rad, which implies that the exciton density distribution starts its oscillation from an extremum, as one would expect for the excitation of a coherent superposition by transform-limited laser pulses.^{112,150}

Table 3.2. Absorption maxima of the optical transitions to the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ excitonic states of the CdSe QDs studied here. The $1S_e1S_{3/2}$ – $1S_e2S_{3/2}$ energy gap and the corresponding coherence period are also calculated.

Temperature (K)	E_{1s} (eV)	E_{2s} (eV)	ΔE (eV)	T_p (fs)
77	2.056	2.147	0.091	45
100	2.051	2.143	0.092	45
120	2.046	2.139	0.093	44
140	2.041	2.133	0.092	45

A coherent superposition of excitonic states encodes the motion of exciton density. In the present work, a superposition of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ excitonic states yields a hole radial wave packet, described by the time-dependent wave function

$$\Psi(r, t) = c_{1s}(t)\psi_{1s}(r) \exp(-iE_{1s}t/\hbar) + c_{2s}(t)\psi_{2s}(r) \exp(-iE_{2s}t/\hbar), \quad (3.5)$$

where $\psi_{1s}(r)$ and $\psi_{2s}(r)$ are the $1S_{3/2}$ and $2S_{3/2}$ hole radial wave functions with coefficients $c_{1s}(t)$ and $c_{2s}(t)$, respectively, and E_{1s} and E_{2s} are the associated eigenenergies. The coefficients are, in principle, time-dependent due to the decay of the $1S_e2S_{3/2}$ excited state to the $1S_e1S_{3/2}$ band-edge state with a time constant of 245 fs,¹⁴ as well as the further relaxation of the $1S_e1S_{3/2}$ state to the ground state and/or to trap

states.¹⁵¹ The hole wave functions are obtained from solving the Luttinger Hamiltonian that includes an additional spherical confinement potential.¹⁵² The corresponding motion of the radial hole density is given by the expression

$$|\Psi(r, t)|^2 = c_{1s}^2(t)|\psi_{1s}(r)|^2 + c_{2s}^2(t)|\psi_{2s}(r)|^2 + 2c_{1s}(t)c_{2s}(t)\psi_{1s}(r)\psi_{2s}(r)\cos[(E_{2s} - E_{1s})t/\hbar]\exp(-t/T_{12}), \quad (3.6)$$

where a phenomenological damping term with time constant T_{12} has been introduced to account for the decoherence between the $1S_{3/2}$ and $2S_{3/2}$ hole states. In the limit that the population dynamics are slow compared to the decoherence time, i.e., $T_{12} \ll T_{1s}, T_{2s}$, where T_{1s} and T_{2s} are the population decay time constants of the $1S_{3/2}$ and $2S_{3/2}$ hole states, respectively, $c_{1s}(t)$ and $c_{2s}(t)$ can be assumed to be time-independent. That is, $c_{1s}(t) = c_{1s}(0)$ and $c_{2s}(t) = c_{2s}(0)$, where $c_{1s}(0) = 0.849$ and $c_{2s}(0) = 0.528$ are determined by the initial excitation conditions. In this limit, the experimentally measured damping time τ corresponds to T_{12} .

It is important to note that observations of coherent dynamics by ensemble-averaged pump-probe measurements are complicated by inhomogeneous dephasing.¹⁵³ In the present work, inhomogeneity of the optical response arises primarily from the finite size dispersity of the CdSe QD sample. In a recent 2DES study, the influence of size dispersion was effectively eliminated by analyzing the dephasing of the zero-quantum coherence at a specific coherence energy, thereby yielding the decoherence time for only a narrow subset of QD sizes.²¹ Here, we account for inhomogeneous dephasing by considering the normal distribution of oscillation frequency $\omega = (E_{2s} - E_{1s})/\hbar$ that arises from the size-dependence of E_{2s} and E_{1s} .¹⁵⁴ Due to the size-dependence of the $1S_e 1S_{3/2} - 1S_e 2S_{3/2}$

energy gap ΔE , and hence the coherent oscillation period T_p , the damping time τ obtained from our ensemble measurements reflects the inhomogeneous dephasing time T_{12} .¹⁵³ Fortunately, the well-characterized size dispersity of our sample and the established dependence¹⁵⁴ of ΔE on the QD radius R allow us to retrieve the homogeneous dephasing time T_{12}^* in the following way. First, with knowledge of the size-dependence of ΔE , the normal distribution of sizes $S(R)$ can be converted to a normal distribution of oscillation frequencies $F(\omega)$, where $\omega = (E_{2s} - E_{1s})/\hbar$. The measured temporal response $S(t)$ is therefore given by the sum of damped oscillations, with each oscillation component weighted by $F(\omega)$. That is,

$$S(t) = \int_0^\infty d\omega F(\omega) \cos(\omega t + \varphi) \exp(-t/T_{12}^*), \quad (3.7)$$

where φ is the oscillation phase and T_{12}^* is the homogeneous dephasing time. Evaluation of the above integral for a normal distribution $F(\omega) = \exp[-(\omega - \bar{\omega})^2/2\sigma^2]$, where $\bar{\omega}$ is the mean frequency and σ is the standard deviation, yields

$$S(t) \sim \cos(\bar{\omega}t + \varphi) \exp\left[-\left(\frac{t}{T_{12}^*} + \frac{\sigma^2 t^2}{2}\right)\right]. \quad (3.8)$$

In the experiments, the damping of the coherence is modeled by an exponential function. Hence, substituting $t = \tau$ into equation (3.8) and setting the value of the exponent to be -1 yields the following expression for T_{12}^* :

$$T_{12}^* = \tau \left(1 - \frac{\sigma^2 \tau^2}{2}\right)^{-1}. \quad (3.9)$$

Our size distribution corresponds to a standard deviation σ of $0.0258 \text{ rad fs}^{-1}$ for the angular frequency of the $1S_e 1S_{3/2} - 1S_e 2S_{3/2}$ energy gap. From the above analysis, it can be deduced that the size dispersity of the sample results in an insignificant ($<10\%$) reduction

in the homogeneous dephasing time (see Table 3.2). It should be noticed that equate two decay functions at one point is not exact accurate. However, in order to obtain the analytic solution of homogeneous dephasing time T_{12}^* , we equaled these two functions at the characteristic $1/e$ time constant of exponential decay as an approximation.

According to our estimates, the experimentally measured $T_{12} = 14.7 \pm 1.2$ fs at 77 K corresponds to a homogeneous dephasing time of $T_{12}^* = 15.8 \pm 1.5$ fs (see Table 3.2). This result is supported by AIMD simulations performed on a 1.3-nm-diameter $\text{Cd}_{33}\text{Se}_{33}$ model cluster, which yield a decoherence time of 17 fs at 77 K for the $1S_e1S_{3/2}-1S_e2S_{3/2}$ excitonic superposition. While the use of a QD with smaller radius R in the simulations constitutes an approximation, given that higher acoustic phonon frequencies¹³⁷ ($\omega_a \sim R^{-1}$) and stronger electron-phonon coupling via the deformation potential¹⁵⁵ ($S \sim R^{-2}$) would predict shorter decoherence times, we note that the computed $1S_e1S_{3/2}-1S_e2S_{3/2}$ energy gap of the model QD (0.08 eV) is similar to the experimental value of 0.09 eV. As a result, the amplitude of the phonon-induced fluctuations for the model QD is expected to be commensurate with that of the experimental system.¹⁵⁶ According to linear response theory,¹¹⁵ the computed dephasing time should therefore be directly comparable to the experimental results.

The experimental data can be used to reconstruct the time-evolution of the hole radial distribution function (Figure 3.5). The radial distribution function that is initially peaked at a radius of 1.04 nm moves to 1.76 nm in 22 fs. The corresponding charge migration rate of 0.33 Å/fs is comparable to some of the fastest electron transfer rates inferred for strongly coupled electron donor-acceptor systems.¹⁵⁷⁻¹⁵⁹ In the present work, *the observed ultrafast charge migration is driven solely by excitonic quantum coherence without the involvement of nuclear motion.* We note that the charge migration distance can

be increased by spectral shaping of the excitation laser pulse to achieve equal population of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ excitonic states, which would extend the inner and outer turning points of the radial wave packet to 0.97 nm and 1.98 nm, respectively. Furthermore, because the radial distribution function at the moment of coherent photoexcitation is governed by the relative phases of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ excitonic states, and as phase coherence is lost, this initial radial distribution function asymptotically evolves into that given by the relative populations of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ states, the rate of charge migration can be increased simply by reducing the decoherence time. In the present system, for example, the initial and asymptotic hole densities are peaked at 1.04 nm and 1.67 nm, respectively. Hence, a shortened decoherence time of 1 fs would yield a charge migration rate of 2 Å/fs. A corollary to this point is that coherent charge migration can be expected as long as the initial and asymptotic charge density distributions are different, even when the decoherence time is ultrashort.

Figure 3.5. Radial distribution functions $r^2|\Psi(r, t)|^2$ of the hole density reconstructed from the experimental data collected at 77 K for the time delays **(a)** 0 fs, **(b)** $T_p/4$, **(c)** $T_p/2$, **(d)** $3T_p/4$, **(e)** T_p and **(f)** 100 fs, where $T_p = h/(E_{2s} - E_{1s})$ is the classical orbital period. For the CdSe QD studied here, T_p corresponds to 44 fs. The plot at 100 fs is representative of the asymptotic hole density. The radius of the QD a_0 is 3.05 nm in the present work.

Examining the temperature-dependence of the excitonic decoherence provides insight into the decoherence mechanism. In bulk semiconductors, carrier decoherence occurs via carrier-carrier and carrier-phonon scattering.^{5,160} In the case of semiconductor QDs, three-pulse photon-echo measurements reveal optical dephasing rates that scale linearly with sample temperature T .¹⁶¹⁻¹⁶² In the limit $k_B T \gg \hbar\omega_a$, where k_B is the Boltzmann constant and ω_a is the frequency that characterizes the quasi-continuum of acoustic phonons, the linear temperature dependence suggests exciton-phonon scattering involving low-frequency, incoherent acoustic phonons as the dominant dephasing

mechanism. Such linear scaling has also been observed, for example, in the case of GaAs quantum wells,¹⁶³ carbon nanotubes,¹⁶⁴ and dye molecules in the condensed phase.¹⁶⁵ Within experimental error, our temperature-dependent T_{12}^* values follow the linear relation $1/T_{12}^*(T) = \Gamma_{12}(T) = \Gamma_{12}(0) + aT$, where $\Gamma_{12}(0) = 45 \pm 8 \text{ ps}^{-1}$ is the temperature-independent offset and $a = 0.22 \pm 0.09 \text{ ps}^{-1}\text{K}^{-1}$ is the slope (Figure 3.6). It is evident that $\Gamma_{12}(0)$ dominates the decoherence rates that are obtained in the 77 – 140-K range, with the temperature-dependent term aT accounting for only ~30% of the measured decoherence rate.

Figure 3.6. The measured excitonic decoherence rates (black squares) exhibits a linear dependence on temperature with an offset. The decoherence rate computed by AIMD simulations at 77 K is also shown (red circle), which calculation is completed by Dhara Trivedi from Prof. Oleg V. Prezhdo’s group.

This result suggests that decoherence of the $1S_e1S_{3/2} - 1S_e2S_{3/2}$ excitonic superposition in the 77 – 140-K temperature range is only partially induced by acoustic phonons. Possible origins of $\Gamma_{12}(0)$ include exciton-exciton scattering between the two excitonic states that comprise the superposition,¹⁶⁶ as well as scattering that involve surface defects.¹⁶² The former could be enhanced by the complex exciton fine structure of the

wurtzite CdSe QDs,¹⁶⁷ whereas the latter is conceivable for the ligand-capped QDs examined here. Finally, while we caution against the direct comparison between optical dephasing rates and intraband dephasing rates, which is not meaningful,¹⁶⁸ we note that the slope a obtained from our experiments is $\sim 4\times$ larger than the value of $a \sim 0.06 \text{ ps}^{-1}\text{K}^{-1}$ obtained for the optical dephasing rates of similar-sized CdSe QDs.¹⁶² The origin of this discrepancy is unknown and requires a systematic study over a wider temperature range.

While *incoherent* acoustic phonons are found to participate in the decoherence of the $1S_e1S_{3/2}-1S_e2S_{3/2}$ excitonic superposition, the experimental data also reveals the influence of the excitonic superposition on the behavior of the *coherent* phonons of CdSe QDs. Two types of coherent phonon modes are known to exist in CdSe quantum dots:¹³⁸ the coherent LO phonon (208 cm^{-1}) and the coherent LA phonon (18 cm^{-1}). In the present work, both modes are apparent in the first-moment time trace $\langle \Omega^{(1)}(t) \rangle$ computed about the band-edge transition (Figure 3.7). The first moment $\langle \Omega^{(1)} \rangle$ of a differential transmission spectrum is related to the energy gap between the bands which are optically coupled by the probe pulse.¹⁶⁹ Considering the contributions from both LO and LA phonons, $\langle \Omega^{(1)}(t) \rangle$ can be fit to the expression

$$\begin{aligned} \langle \Omega^{(1)}(t) \rangle = & A_{\text{LO}} \cos(\omega_{\text{LO}}t + \varphi_{\text{LO}}) \exp(-t/\tau_{\text{LO}}) \\ & + A_{\text{LA}} \cos(\omega_{\text{LA}}t + \varphi_{\text{LA}}) \exp(-t/\tau_{\text{LA}}), \end{aligned} \quad (3.10)$$

where A_{LO} , ω_{LO} , φ_{LO} , and τ_{LO} (A_{LA} , ω_{LA} , φ_{LA} , and τ_{LA}) correspond to the amplitude, frequency, phase, and damping time of the LO (LA) phonon, respectively.

Figure 3.7. (a) $\Delta T/T$ signal as a function of time delay for a probe photon energy of 1.98 eV, obtained following the phase-coherent excitation of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ states. The inset shows the FFT power spectrum, which reveals oscillation frequencies that can be assigned to the LA and LO phonons of the CdSe QD. (b) $\Delta T/T$ signal as a function of time delay for a probe photon energy of 2.01 eV, obtained following the selective excitation of the $1S_e1S_{3/2}$ state. The inset shows the FFT power spectrum, which reveals oscillation frequencies that can be assigned to the LA and LO phonons of the CdSe QD. (c) The spectral first moment computed about the band-edge transition for both broadband coherent excitation (top panel) and narrowband state-selective excitation (bottom panel) of the CdSe QD sample at 77 K. Note the different

span of the vertical scales. **(d)** Huang-Rhys factor S_{LO} obtained at different temperature for the LO phonon. **(e)** Huang-Rhys factor S_{LA} obtained at different temperatures for the LA phonon. The increase in S_{LA} with temperature, observed with narrowband excitation, is described by a linear fit (dashed line). **(f)** AIMD trajectories of the phonon-induced fluctuations of the E_{1s} (black) and E_{2s} (red) energy gaps, as well as the difference $E_{2s} - E_{1s}$ (blue). The inset shows the FFT amplitudes of the energy gaps. The peaks at 60, 120, 170, and 230 cm^{-1} can be assigned to the TA, LA, TO, and LO phonon, respectively.

To clarify the influence of coherent excitonic motion on coherent phonon dynamics, the first-moment time traces obtained with narrowband, state-selective excitation to the $1S_e 1S_{3/2}$ state are also recorded (Figure 3.7b). The $\langle \Omega^{(1)}(t) \rangle$ traces obtained under the two different excitation conditions reveal qualitative differences (the detail fitting parameters are tabulated in Table 3.3 & 3.4.): excitation of the $1S_e 1S_{3/2} - 1S_e 2S_{3/2}$ superposition drives predominantly the coherent LA phonon whereas state-selective excitation mostly yields the coherent LO phonon. The observed suppression of the coherent LO phonon and the enhancement of the coherent LA phonon can be further quantified by computing their corresponding Huang-Rhys factors S_i ($i = LO, LA$).¹⁷⁰ As mentioned in Chapter 1, the Huang-Rhys factor characterizes the exciton-phonon coupling strengths and can be extracted from the $\langle \Omega^{(1)}(t) \rangle$ oscillation amplitude by the relation¹⁰⁶ $A_i = 2\omega_i S_i$.

Table 3.3. Summary of parameters obtained from the fit of the oscillatory spectral first moment to equation (3.10), obtained after broadband excitation of the $1S_e1S_{3/2}-1S_e2S_{3/2}$ coherent superposition.

Temperature (K)	A_{LA} (meV)	ω_{LA} (cm ⁻¹)	τ_{LA} (ps)
77	0.073±0.010	17.4±0.4	4.2±0.9
100	0.082±0.007	17.7±0.2	5.1±0.9
150	0.091±0.009	18.0±0.3	4.1±1.7
200	0.092±0.002	18.6±0.2	4.0±0.7
250	0.089±0.004	18.2±0.2	2.5±0.3
295	0.088±0.015	18.0±0.3	—

Temperature (K)	A_{LO} (meV)	ω_{LO} (cm ⁻¹)	τ_{LO} (ps)
77	0.14±0.02	208.7±0.4	5.0±1.8
100	0.11±0.01	209.5±0.3	3.6±0.6
150	0.12±0.02	208.0±0.3	3.0±0.5
200	0.11±0.01	207.5±0.3	2.5±0.4
250	0.11±0.01	209.6±2.0	0.7±0.2
295	0.08±0.01	207.5±1.1	—

(Note that the damping times τ_{LO} and τ_{LA} were omitted from equation (3.10) in the fitting of the data collected at 295 K because they could not be reliably extracted from the data.)

Table 3.4. Summary of parameters obtained from the fit of the oscillatory spectral first moment to equation (3.10), obtained after selective excitation of the $1S_e1S_{3/2}$ state.

Temperature (K)	A_{LA} (meV)	ω_{LA} (cm ⁻¹)	τ_{LA} (ps)
77	0.063±0.010	18.2±0.7	—
100	0.065±0.023	18.8±0.6	—
150	0.18±0.057	18.7±0.6	5.7±4.0
200	0.19±0.019	17.5±0.7	—
250	0.37±0.071	18.0±0.6	3.5±1.3
295	0.34±0.130	18.7±0.4	—

Temperature (K)	A_{LO} (meV)	ω_{LO} (cm ⁻¹)	τ_{LO} (ps)
77	0.91±0.03	210.8±0.1	3.7±0.2
100	0.65±0.02	210.5±0.1	3.2±0.2
150	0.89±0.04	210.0±0.1	3.0±0.3
200	0.57±0.06	209.8±0.4	2.2±0.4
250	0.45±0.04	209.2±0.5	2.5±0.6
295	0.54±0.07	208.5±0.3	2.6±0.4

Several observations can be made about the S_{LO} and S_{LA} values measured over the temperature range of 77 – 295 K (Figures 3.7d & e). First, it is evident that simultaneous excitation of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ states as compared to state-selective excitation of only the $1S_e1S_{3/2}$ state leads to a one order-of-magnitude suppression of S_{LO} over the entire temperature range of 77 – 295 K. Second, broadband excitation of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ states yields relatively temperature-invariant S_{LA} values, whereas a linear increase in S_{LA} with temperature is observed for excitation of only the $1S_e1S_{3/2}$ state. The latter observation can be rationalized in terms of a linearly increasing phonon occupation number in the electronic ground state with temperature, which in turn launches an excited-state vibrational wave packet with a larger nuclear displacement amplitude upon photoexcitation.¹⁷¹ From the experimental data, it can be deduced that the intrinsic Huang-Rhys factor for the LA phonon, accessed in the low-temperature limit and therefore independent of the phonon occupation number, is larger for coherent excitation of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ states than for selective excitation of the $1S_e1S_{3/2}$ state.

AIMD simulations reveal that the LO-phonon-induced modulation of the E_{1s} and E_{2s} gaps occur in phase, signifying similarly signed electron-LO phonon coupling matrix elements for the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ states (Figure 3.7f). In this case, the energy difference $\Delta E = E_{2s} - E_{1s}$, which encodes the coherent excitonic superposition, exhibits suppressed LO phonon oscillations (Figure 3.7f inset). In agreement with experiment, the simulation results show that phase-coherent excitation of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ states leads to a ~10-fold suppression of the LO phonon mode. These results mirror qualitatively the previously observed suppression of the radial breathing mode (RBM) coherent phonon following the simultaneous excitation of the E_{11} and E_{22} transitions of single-walled carbon nanotubes by broadband, few-cycle laser pulses.¹⁷² On the other hand, the AIMD

simulations predict the suppression of the coherent LA phonon with simultaneous excitation of the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ states, even though the experimental results point to an enhancement. This contradiction between experiment and theory suggests the direct involvement of excitonic motion in driving the LA phonon, an effect that is not considered in the AIMD simulations. Intuitively, the ultrafast radial charge migration that is associated with the $1S_e1S_{3/2}-1S_e2S_{3/2}$ excitonic superposition impulsively alters the electronic potential along the radial direction, which in turn triggers atomic motion along the radial coordinate, i.e., the coherent LA phonon is launched. The observed temperature-independence of S_{LA} can be attributed to the persistence of coherent charge migration even at elevated temperatures. Similar launching of coherent phonons by ultrafast charge transfer has been observed.¹⁷³⁻¹⁷⁴ In the resonant coupling regime, Bloch oscillations in semiconductor quantum wells have been shown to drive coherent LO phonons adiabatically.¹⁷⁵

3.5 Conclusion

The direct observation of coherent valence electron motion represents one of the holy grails in femtochemistry and attosecond physics.^{112,176} Compared to coherent exciton migration in photosynthetic light harvesting complexes,^{113,122-124} or to charge migration that has been predicted for ionized molecules,¹⁷⁷⁻¹⁷⁹ the relative simplicity of the electronic structure of QDs makes them an attractive platform for visualizing coherent electron motion. Pioneering investigations of excitonic coherences in zinc blende-type CdSe QDs by 2DES spectroscopy, however, yielded largely disparate compositions of the excitonic superpositions and decoherence times despite similar experimental conditions.²⁰⁻²¹ In the present work, optical pump-probe spectroscopy performed on a highly monodisperse sample of wurtzite-type CdSe QDs reveals unambiguous spectral signatures of quantum

coherence between the $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$ exciton states. The high signal-to-noise ratio afforded by our experimental data allows the first reconstruction of ultrafast charge migration in a nanoscale system that is driven solely by excitonic quantum coherence.

The valence radial wave packet that is observed in this work is reminiscent of atomic Rydberg radial wave packets that were previously generated with picosecond pulses.¹⁸⁰ Unlike the numerous revivals exhibited by Rydberg wave packets,¹⁸¹ however, the QD excitonic superposition is found to decohere within a fraction of the classical orbit period. Variable temperature measurements reveal that the decoherence originates predominantly from electronic factors – exciton-exciton scattering, exciton fine structure, and defect scattering – rather than the presence of the phonon bath. This observation suggests that efforts to achieve extended decoherence times should focus on engineering the excitonic structure of QDs and minimizing the number of defect sites. Another possible avenue for further exploration is to investigate how the decoherence of the excitonic superposition is affected by the presence of *coherent* phonons that are simultaneously generated by the excitation pulse.

Through the observation of coherent LO and LA phonons in the present work, we have elucidated the effect of excitonic coherence and the associated ultrafast charge migration on the behavior of the phonons. This result paves way for the coherent control of atomic motion¹⁸²⁻¹⁸³ via the optical manipulation of valence electron densities.¹⁸⁴ In addition, when applied to donor-acceptor motifs in which the CdSe QD serves as either the hole donor or acceptor,¹⁸⁵⁻¹⁸⁶ the ultrafast charge migration that occurs within the CdSe nanocrystal can potentially be harnessed to gate charge transfer on ultrashort time scales.

Chapter 4

Sub-Picosecond Auger-Mediated Hole Trapping Process in CdSe/CdS Core/Shell Nanoplatelets

The intrinsic size inhomogeneity limits the investigation of electronic coherence in QDs. Recently emerged quasi-two-dimensional colloidal nanoplatelets (NPLs) as a new class of semiconductor nanomaterials is a promising system to study the long-lived interexcitonic coherent motion. Compared with QDs, thin film structure NPLs possess the narrower absorption and emission spectra due to the monodisperse thicknesses of atomic precision. However, the sub-picosecond carrier dynamics of NPLs at the band edge remain largely unknown, despite their importance in determining the optoelectronic properties of these materials. In this chapter, we use a combination of femtosecond transient absorption spectroscopy and nonadiabatic molecular dynamics simulations to investigate the early-time carrier dynamics of CdSe/CdS core/shell NPLs.

4.1 Introduction

The optoelectronic properties of semiconductor nanoparticles can be tuned by precise control over their size, shape and chemical composition.^{133,187-188} Quasi-two-dimensional colloidal nanoplatelets (NPLs) with atomically precise thicknesses of only a few layers has recently been added to the family of nanomaterials that already includes quantum dots and nanowires.¹⁸⁹⁻¹⁹⁰ In this emergent class of semiconductor nanomaterials, the existence of one-dimensional quantum confinement is evidenced by the red shift of the

absorption spectra with increasing thickness.¹⁹¹ This size-dependent optical property of NPLs is analogous to that observed for quantum dots.¹⁵⁴ However, unlike the finite size dispersion that accompanies the synthesis of quantum dots, which yields optical linewidths limited by inhomogeneous broadening,¹⁹² the ability to control the thicknesses of colloidal NPLs with atomic precision leads to relatively narrower absorption and emission bands for NPLs.^{189,193} Moreover, the suppressed fluorescence intermittency of NPLs¹⁹⁴ relative to quantum dots^{97,99} has been explained in terms of the spatial delocalization of excitons along the lateral dimensions of the NPL leading to the reduced Auger-mediated trapping of carriers. These desirable characteristics of NPLs facilitate their application as efficient light emitters and lasing media.¹⁹⁵⁻¹⁹⁶

The optoelectronic properties of semiconductor materials, including NPLs, are determined to a large extent by the carrier dynamics near the band gap.⁵ Competing carrier relaxation channels, such as radiative recombination, exciton-exciton annihilation, and carrier trapping followed by non-radiative recombination dramatically affect the optoelectronic performance characteristics of these materials. In highly excited semiconductor nanomaterials, strong Coulombic interaction between carriers leads to the emergence of nonradiative Auger decay as an additional relaxation channel, in which the relaxation of one carrier is accompanied by the concomitant excitation of another.^{65,197} To date, investigations of the carrier dynamics and energy transfer of NPLs have focused primarily on elucidating processes that occur on the picosecond to nanosecond time scales following above-band-gap photoexcitation.¹⁹⁸⁻²⁰² Time-resolved photoluminescence spectroscopy furnishes exciton lifetimes in the range of 0.3 – 20 ns at cryogenic temperatures¹⁹⁹ and in addition, elucidates Auger-mediated trapping and recombination rates of $\sim 0.1 - 5 \text{ ns}^{-1}$;^{199,201} these carrier trapping kinetics are consistent with the results of optical-pump terahertz-probe measurements.¹⁹⁹ Electron cooling following above-band-

gap photoexcitation is found by two-photon photoemission spectroscopy to occur with a time constant of 2 ps.²⁰² On the sub-picosecond time scale, optical pump-probe spectroscopy reveals ultrafast interfacial charge transfer in quasi-Type-II CdSe/CdTe core/crown NPLs²⁰³ and competing in-plane exciton diffusion and hole trapping process in CdSe/CdS core/crown NPLs.²⁰⁴ Finally, two-dimensional electronic spectroscopy unravels a long-lived excitonic coherence in NPLs.²²

Here, we present a femtosecond transient absorption spectroscopy study of the early-time carrier dynamics that accompanies the band-edge photoexcitation of CdSe/CdS core/shell NPLs. An observed sub-picosecond decay component in the hole population is assigned, with the aid of fluence dependence measurements, to Auger-mediated hole trapping. At the same time, analysis of spectral shifts uncovers concomitant Auger hole heating and electron cooling dynamics. Simulations based on a combination of tight-binding density functional theory and nonadiabatic molecular dynamics reveals the sub-picosecond dynamics of Auger hole trapping by a shallow trap state and the concomitant Auger hole heating process.

4.2 Sample preparation and characterization

CdSe/CdS core/shell NPLs are synthesized by our collaborator, Lian Jie from Prof. Yinthai Chan's group, according to the protocol of ref. 188. CdSe NPLs were synthesized based on a previously reported method with slight modifications.¹⁸⁹ A cadmium myristate stock solution was first synthesized by heating 3.5 mmol of cadmium oxide (CdO, $\geq 99.99\%$) with 7 mmol of myristic acid (MA, 98%) in 10 ml 1-octadecene (ODE, 90%) at 250 °C until the solution turned clear and colorless. For the synthesis of the CdSe NPLs, 24 mg of Se powder, 1 mL of the cadmium myristate stock solution and 15 ml of ODE were degassed under vacuum at 80 °C for 30 min in a 3-neck round bottom flask

(RBF). After degassing, the temperature was ramped up to 240 °C. As the temperature reached 195 °C, 80 mg of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ was introduced to the RBF, resulting in a color change from pale yellow to orange. This indicated the successful nucleation and growth of small CdSe particles. Upon reaching a temperature of 240 °C, the reaction was allowed to stir for ~8 min. Subsequently, 2 mL of oleic acid (OA, 90%) was added to the reaction flask, and the overall mixture was allowed to cool down to room temperature. To process the NPLs from growth solution, about 10 mL of hexane and 20 mL of ethanol were added to the reaction flask and centrifuged. The supernatant was discarded, leaving a light orange NPL precipitate. The precipitate is then re-dispersed in 15 mL of hexane and allowed to undergo centrifugation, whereupon the precipitate is discarded. This allows for 3 ML NPLs with large lateral sizes to be selectively removed. Excess ethanol is then added to the retained supernatant, resulting in precipitation of the 4 ML NPLs. The mixture is then centrifuged and the supernatant discarded, allowing for the NPLs to be recovered as a powder.

The procedure for the synthesis of core/shell CdSe/CdS NPLs was adapted from the atomic layer deposition approach reported by She *et al.*, where alternating layers of Cd and S are successively deposited onto a CdSe NPL.¹⁹⁵ Prior to shell growth, CdSe NPLs (as described above) were dissolved in 4 mL of hexane. The first S layer was deposited by introducing 50 μL ammonium sulfide in 5 mL *N*-Methylformamide (NMF, 99%) to the solution of CdSe NPLs in hexane. Upon successful deposition of the S layer, phase transfer of the CdSe NPLs from hexane to NMF occurs. The S-coated CdSe NPLs were precipitated from NMF by adding a mixture of acetonitrile and toluene. The suspension was then centrifuged and the supernatant was discarded. The precipitation was then re-dispersed in 5 mL of NMF. The first Cd layer was then deposited by adding 1.5 mL of 0.25 M Cd-NMF solution (333 mg of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ dispersed in 5 mL of NMF). The solution was allowed

to stir for 1 min, after which the NPLs were precipitated by the addition of acetonitrile and toluene. After centrifuging and discarding the supernatant, the NPLs were re-dispersed in NMF. The above procedure yields CdSe NPLs sandwiched by a 1 ML CdS shell. To grow a 2 ML thick CdS shell, the deposition steps described above were repeated. For our experiments, CdSe NPLs sandwiched by 2ML of CdS were dispersed in a solution of 5-amino-1-pentanol (AP) and diluted with ethanol to a desired concentration.

Figure 4.1. (a), (b) HRTEM micrograph of the CdSe core-only and CdSe/CdS core/shell NPLs with 1.75 ± 0.37 nm and 2.52 ± 0.28 nm thickness, respectively. The right bottom inset figures are from [100] direction. Absorption spectrum of (c) CdSe core-only NPLs and (d) CdSe/CdS core/shell NPLs. Noted the HRTEM figures are measured in Prof. Yinthai Chan's group.

Unless stated otherwise, all the reactions were conducted in oven-dried glassware under nitrogen atmosphere using standard Schlenk line techniques. All the chemicals were used as received without further purification. All solvents were used as received.

Both core and shell are known to adopt the zinc blende lattice in these NPLs. High-resolution transmission electron microscopy (HRTEM) reveals the dimensions of the NPLs to be $(28.8 \pm 3.1) \times (7.1 \pm 1.1) \times (2.5 \pm 0.3)$ nm (Figure. 4.1b). By comparison of the optical transition energies with those reported by Talapin *et al.*,¹⁹⁵ the NPLs are found to comprise 4.5 monolayers of CdSe, in agreement with the thickness of the core-only NPL as determined by TEM (Figure. 4.1a). Combining this CdSe core with 2 monolayers of CdS shell on each of the two large facets gives an overall thickness of 2.4 nm,²⁰⁵ in good agreement with the thickness found by transmission electron microscopy.

4.3 Experimental method and nonadiabatic molecule dynamics simulation

Optical transient absorption spectroscopy is performed with narrowband pump pulses centered at 2.03 eV and broadband probe pulses that span 1.66 – 2.29 eV, sufficient to encompass the HH-CB and LH-CB transitions. The broadband pulses are produced by spectral broadening of the 25-fs output from an amplified Ti:sapphire laser system (800 nm, 1 kHz; Coherent) in a helium-filled hollow-core fiber followed by chirped mirror compression. The output pulses of 10 fs duration centered at 650 nm with a spectral bandwidth of ~ 200 nm enter the optical pump-probe apparatus. The narrowband pump pulse is generated by inserting a 10-nm bandpass filter into the original broadband pulse. A piezo-driven translation stage incorporated into the probe beam generates a computer controlled time delay between pump and probe pulses. A second-order intensity cross-correlation between pump and probe pulses, performed in a 10 μ m thick BBO crystal

located at the position of the sample target, reveals a time resolution of 81 fs FWHM (Figure 4.2). The beam diameters ($1/e^2$) of the pump and probe beams at the sample are 100 and 81 μm , respectively.

Figure 4.2. The pump probe cross-correlation profile yields an instrument response of 81 fs FWHM.

The room-temperature linear absorption spectrum exhibits two well-resolved peaks centered at 2.03 and 2.19 eV (Figure 4.3a), which correspond to excitonic transitions from the CdSe valence band (VB) heavy-hole (HH) and light-hole (LH) states to the conduction band (CB), respectively (Figure 4.3b). The narrowband, ~ 80 -fs pump pulse centered at 2.03 eV is resonant with the HH-CB transition, whereas the broadband, sub-10-fs probe pulse spans the HH-CB and LH-CB transitions. As opposed to above band-gap photoexcitation employed in previous studies,¹⁹⁸⁻²⁰⁴ selective photoexcitation of the lowest-energy HH-CB excitonic transition eliminates interband relaxation within the conduction and valence bands, thus simplifying the analysis of the experimental data. Moreover, because the excitation pulse creates carriers only in the HH and CB bands, probing of the LH-CB transition furnishes only the electron dynamics, whereas probing of the HH-CB transition reports on both the electron and hole dynamics.^{66,83,206-207} Performing a global analysis of

the traces simultaneously collected about the HH-CB and LH-CB probe transitions therefore yields the separate electron and hole dynamics of the NPL.

Figure 4.3. (a) Room-temperature linear absorption spectrum of CdSe/CdS core/shell NPLs (black line) and the spectra of narrowband pump (red) and broadband probe (blue) laser pulses. The absorption peaks at 2.03 and 2.19 eV correspond to the HH-CB and LH-CB excitonic transitions, respectively. The narrowband pump pulse is resonant with the HH-CB excitonic transition, whereas the spectral range of the 1.68 – 2.25-eV broadband probe pulse spans both HH-CB and LH-CB transitions. (b) Schematic illustration of the band alignment showing the HH-CB and LH-CB transitions centered at the CdSe core.

The Auger-assisted hole trapping dynamics in the CdSe/CdS core/shell nanoplatelet was modelled using the recently developed methodology²⁰⁸ combining non-adiabatic (NA) molecular dynamics (MD) with self-consistent charge (SCC) tight-binding density functional theory (DFTB) by Prof. Oleg Prezhdo.²⁰⁹⁻²¹⁶ The simulations were performed in the adiabatic representation, in which an electronic structure calculation method produces both the energy levels and NA coupling as functions of nuclear positions. All quantum-mechanical calculations, including geometry optimization, electronic

structure, and adiabatic MD, were carried out using the SCC-DFTB method²⁰⁹⁻²¹⁶ as implemented in DFTB+ code.^{212,214} Parameter set (Slater-Koster files) used in these calculations were extensively tested for a variety of Cd-chalcogenide systems.²¹⁷ Motivated by the experiment, the Cd-terminated (001) polar surfaces of the CdSe/CdS core/shell platelet was constructed using zinc-blende lattices. The CdSe core contained 5 layers of Cd atoms and 4 layers of Se atoms. Two additional layers of CdS were added on each side of the core to represent the shell. Both Cd surface layers of the shell were stabilized by passivation with organic acetate ligands. The resulting system was periodically replicated in three dimensions. 30 Å of vacuum were added between the replicas in the direction perpendicular to the passivated (001) surface, representing a two-dimensional nano-platelet. The simulation cell contained 2×2 unit cells with the optimized cell constant of 8.5418 Å.

After fully optimizing the structure at 0 K, the system was heated to 300 K using velocity rescaling. Then, a 3 ps micro-canonical trajectory was generated using the Verlet algorithm²¹⁸ with the 1 fs time step and Hellman-Feynman forces. At each snapshot, the energy of the Kohn-Sham molecular orbitals and the NA coupling constants were calculated, and this time dependent information was used to perform NA-MD using the global flux surface hopping (GFSH) method,²¹⁹ developed recently to handle Auger-type phenomena²¹⁹⁻²²⁰ and implemented within the PYthoneXtension for Ab Initio Dynamics (PYXAID) program.^{156,221}

4.4 Results and discussions

A representative contour plot of the time-resolved transient absorption spectrum $\Delta A(E, t)$ as a function of probe photon energy E and time delay t is shown in Figure 4.4a.

Figure 4.4. (a) Time-resolved differential absorption spectra collected at an excitation fluence of 0.28 mJ/cm^2 , which generates 6.7 excitons per NPL. (b) A representative ΔA spectrum collected at 1-ps time delay shows negative ΔA signal peaks at the HH-CB and LH-CB transitions. The shaded areas represent the range of energies used to compute the zeroth and first moments for the HH-CB and LH-CB probe transitions. (c) Zeroth moment time traces calculated about the HH-CB (black) and LH-CB (red) transitions. The initial fast decay component in HH-CB time trace is assigned to hole dynamics while the slow decay present in both time traces is attributed to electron dynamics.

The negative ΔA signal, peaked about the HH-CB and LH-CB transitions (Figure 4.4b), originates from the ground-state bleaching of the HH-CB and LH-CB transitions, as well as the stimulated emission from the HH-CB excited state, in agreement with previous works.¹⁹⁸ The electron and hole population dynamics can be extracted from the spectral zeroth moments $\langle E_m^{(0)}(t) \rangle$ ($m = \text{HH}$ or LH) computed about the HH-CB and LH-CB transitions, where

$$\langle E_m^{(0)}(t) \rangle = \frac{\int_{E_{m,i}}^{E_{m,f}} \Delta A(E, t) dE}{E_{m,f} - E_{m,i}}. \quad (4.1)$$

In the above expression, $E_{m,i}$ and $E_{m,f}$ define the spectral range that is used to compute the zeroth moment. Here, the spectral range corresponds to the FWHM of the ΔA bands, hence minimizing interference from possible spectral overlap between the HH-CB and LH-CB transitions. Because the pump pulse is resonant with the HH-CB transition, $\langle E_{HH}^{(0)}(t) \rangle \propto -[n_h(t) + n_e(t)]$ yields the combined time-evolution of the hole and electron populations, whereas $\langle E_{LH}^{(0)}(t) \rangle \propto -n_e(t)$ reflects only the electron population dynamics. The fast decay component present only in the $\langle E_{HH}^{(0)}(t) \rangle$ trace points to a rapid depopulation of holes, whereas the residual slow decay, identical to that observed for the $\langle E_{LH}^{(0)}(t) \rangle$ trace, suggests a >10 -ps lifetime for the electron in the conduction band (Figure 4.4c).

Excitation fluence-dependence measurements shed light on the origin of the sub-picosecond decay of hole population inferred from the $\langle E_{HH}^{(0)}(t) \rangle$ trace. The number of excitons per NPL is determined according to the procedure outlined by Pelton *et al.*²⁰¹ First, the saturation fluence F_s is obtained by measuring the magnitude of the normalized differential absorption signal $|\Delta A/A|$ at the band edge as a function of excitation fluence F

(note that $\Delta A/A$ is negative because of the dominant contribution by bleaching to the transient signal). The resultant data (Figure 4.5) can be fit to the expression

$$\left| \frac{\Delta A}{A} \right| = \frac{\alpha F}{1 + F/F_s} \quad (4.2)$$

where α is a constant. The fit shown in Figure 4.4 gives $F_s = 0.19 \pm 0.02 \text{ mJ/cm}^2$. With this value for F_s , the average initial exciton number per NPL is given by

$$N_0 = \frac{F \sigma_{abs}}{h\nu} \frac{1}{1 + F/F_s} \quad (4.3)$$

$h\nu$ is the photon energy of the pump pulse and $\sigma_{abs} = 9.34 \times 10^{-14} \text{ cm}^2$ is the absorption cross-section at the pump photon energy of 2.03 eV.¹⁹⁵

Figure 4.5. Pump fluence dependence of the magnitude of the normalized differential absorption signal $|\Delta A/A|$ at the band edge. The solid line shows the fit to equation (4.2), which yields a saturation fluence F_s of $0.19 \pm 0.02 \text{ mJ/cm}^2$.

Based on these conditions, within the range of pump fluences used in the experiment, which yield $N_0 = 2 - 12$, the $1/e$ time constant that characterizes the fast decay of $\langle E_{HH-CB}^{(0)}(t) \rangle$ decreases from 250 fs to 100 fs with increasing N_0 . The observed exciton density-dependent dynamics is suggestive of a hole depopulation process that involves two or more excitons.

Figure 4.6. Global fitting of fluence-dependent early-time zeroth moment time traces based on second-order kinetics convolved with a Gaussian instrument response. The initial average exciton numbers N_0 are 2.7, 4.5, 6.7, and 7.8.

Analysis of the $\langle E_{HH}^{(0)}(t) \rangle$ traces collected over the range of pump fluences shows that the temporal evolution of the hole density $n_h(t)$ follows second-order kinetics:

$$\frac{dn_h(t)}{dt} = -kn_h^2(t), \quad (4.4)$$

where k is the effective second-order rate constant. The solution to the above differential equation is

$$n_h(t) = \frac{n_h(0)}{1 + kn_h(0)t}, \quad (4.5)$$

where $n_h(0) = N_0/A$ is the initial hole density and A is the area of the NPL ($28.8 \times 7.1 \text{ nm}^2$). Global fitting of 5 fluence-dependence datasets, each comprising 6 – 7 different fluences, yields $k = 3.5 \pm 1.0 \text{ cm}^2/\text{s}$ (Figure 4.6).

The observation of second-order kinetics suggests Auger-mediated hole trapping as the dominant pathway for the sub-picosecond decay of the hole population, whereby the energy released by hole capture goes to excite another carrier, which can be either another hole (Figure 4.7a) or an electron (Figure 4.7b). In this process, the participation of a second carrier for the purposes of energy and momentum conservation accounts for the emergence of second-order kinetics. Note that a more commonly observed origin of second-order kinetics, exciton-exciton annihilation,²²²⁻²²³ can be ruled out based on the absence of a correspondingly fast decay in the electron population, as deduced from the $\langle E_{LH}^{(0)}(t) \rangle$ trace remaining constant for $>10 \text{ ps}$.

Figure 4.7. (a) Schematic illustration of intraband and (b) interband Auger-mediated hole trapping, in which the energy released by hole capture (solid arrow) is transferred either to another heavy hole in the VB or to an electron in the CB (dashed arrow), respectively. Note that the trap states are assumed to be located within the band gap.

Further evidence for Auger-mediated hole trapping comes from the spectral first moments $\langle E_m^{(1)}(t) \rangle$ ($m = \text{HH}$ or LH), defined as

$$\langle E_m^{(1)}(t) \rangle = \frac{\int_{E_{m,i}}^{E_{m,f}} E \Delta A(E, t) dE}{\int_{E_{m,i}}^{E_{m,f}} \Delta A(E, t) dE}. \quad (4.6)$$

Intuitively, $\langle E_m^{(1)}(t) \rangle$ furnishes the time-dependent energy gap between bands that are optically coupled by the probe pulse.^{169,224} Mathematically speaking, the calculation of spectral first moment characterizes center of mass within a specific probe energy range as defined in Eq.4.6. The time trace of first moment records the energy evolution of optical transition which is suitable to analyze the wave packet motion.²²⁵ Analogous to the interpretation of the zeroth moment traces, $\langle E_{LH}^{(1)}(t) \rangle$ reflects the time-dependent energy distribution of electrons, whereas $\langle E_{HH}^{(1)}(t) \rangle$ yields the time-dependent joint energy distributions of electrons and holes. Beyond the oscillatory features that are associated with the coherent LO phonon of CdSe (Figure 4.8), a decrease in $\langle E_{HH}^{(1)}(t) \rangle$ is observed with time at low exciton densities (Figure 4.8a), similar to that observed across all excitation fluences for $\langle E_{LH}^{(1)}(t) \rangle$ (Figure 4.8b). This time-dependent red shift is attributed to carrier cooling and follows exponential dynamics. Under excitation fluences that yield $N_0 < 1$, where Auger-mediated trapping is inoperative, the red shifts observed for $\langle E_{HH}^{(1)}(t) \rangle$ and $\langle E_{LH}^{(1)}(t) \rangle$ traces both yield a time constant of 0.84 ± 0.09 ps (Figures 4.8a & b). The common time constant suggests that the major contribution to the observed time-dependent red shift is electron cooling. This timescale is consistent with the sub-picosecond electron cooling dynamics inferred from time-resolved two-photon photoemission (TPPE) spectroscopy, which identified phonon emission as the dominant electronic relaxation pathway.²⁰² The

limited involvement of an Auger-type relaxation mechanism inferred from the TPPE study implies that the ultrafast trapping of holes elucidated in the present work is unlikely to impede electron cooling in NPLs, contrary to what is found for nanocrystals.⁸⁴

Figure 4.8. (a) Spectral first moment time traces $\langle E_{HH}^{(1)}(t) \rangle$ obtained at different initial exciton numbers N_0 . The experimental condition $N_0 < 1$ excludes the possibility of Auger process. For clarity, all time traces are vertically shifted to yield a zero offset at 3 ps. Solid lines show the fit to a combination of blue shifting via second-order kinetics

kinetics and exponential red shifting kinetics. The residual oscillatory signal originates from the coherent longitudinal optical (LO) phonon of CdSe. **(b)** $\langle E_{LH}^{(1)}(t) \rangle$ traces computed about the LH-CB transition. A red shift with time delay is observed for all values of N_0 and is fit to exponential decays (solid lines). **(c)** $\langle E_{HH}^{(1)}(t) \rangle$ (top) and $\langle E_{LH}^{(1)}(t) \rangle$ (bottom) traces obtained with 2.00-eV photoexcitation, detuned to the red of the HH-CB transition at 2.03 eV.

With increasing exciton number N_0 , the spectral shift direction for $\langle E_{LH}^{(1)}(t) \rangle$ remains independent of N_0 (Figure 4.8b). On the other hand, a blue shift emerges in the $\langle E_{HH}^{(1)}(t) \rangle$ time trace, eventually becoming the dominant feature at the highest exciton densities employed in our experiments (Figure 4.8a). The blue shift observed exclusively in $\langle E_{HH}^{(1)}(t) \rangle$ is therefore indicative of carrier heating in the VB that accompanies Auger-mediated hole trapping (Figure 4.7a).⁷⁸ The $\langle E_{HH}^{(1)}(t) \rangle$ traces follow a combination of blue shifting via second-order kinetics and exponential red shifting kinetics. Interestingly, the observed spectral blue shift is well described by the second-order rate constant k extracted from analysis of the $\langle E_{HH}^{(0)}(t) \rangle$ traces. This agreement further supports Auger heating as the mechanism behind the blue shift. Additional evidence for Auger heating in the VB comes from measurements that employ excitation pulses tuned to 2.00 eV (Figure 4.8c), below the nominal 2.03-eV band gap of the CdSe/CdS core/shell NPL. The generation of cold excitons under such conditions obviates carrier cooling, thereby allowing the identification of any observed spectral shifts with Auger heating. The first moment traces reveal a sub-picosecond blue-shifting of $\langle E_{HH}^{(1)}(t) \rangle$, absent in the case of $\langle E_{LH}^{(1)}(t) \rangle$. Taken together, these results point to the ultrafast Auger heating of holes. The residual slow blue-shift dynamics

observed for $\langle E_{LH}^{(1)}(t) \rangle$ is consistent with previous observations of Auger recombination on the ~ 100 -ps timescale.²⁰⁰⁻²⁰¹

It is important to note that Auger-mediated hole trapping is rigorously a three-body process, whose instantaneous rate depends linearly on the hole trap density n_{tr} and quadratically on the hole density n_h . Hence, the effective second-order rate constant k is related to n_{tr} and the Auger decay rate constant k_{Auger} by $k = \frac{1}{2}k_{\text{Auger}}n_{tr}$. The factor of $1/2$ accounts for the fact that only one of the two holes that are involved in the Auger process is trapped. In addition, the above expression for k assumes that n_{tr} is time-independent, i.e., $n_{tr}(0) \gg n_h(0)$, thereby allowing the analysis of the time traces within the framework of pseudo-second-order kinetics; the validity of this approximation is supported by the good agreement between the experimental decay and the fit to second-order kinetics.

The hole trapping kinetics uncovered in the present work is more than three orders of magnitude faster than that previously determined by time-resolved photoluminescence spectroscopy.¹⁹⁹ At an exciton density of $9.8 \times 10^{11} \text{ cm}^{-2}$ ($N_0 = 2$), for example, the effective trapping rate of $k_{eff} = kn_h(0) = 3.4 \text{ ps}^{-1}$ is $\sim 2,800\times$ larger than the earlier reported trapping rate of 1.22 ns^{-1} . The large hole-trapping rate obtained herein could originate from a large k_{Auger} rate constant and/or a high density of trap states n_{tr} . As in the case of quantum dots, the relaxation of constraints imposed by energy and momentum conservation as a result of quantum confinement, albeit only in one-dimension in the case of NPLs, facilitates many-body Auger processes. In fact, the effective trapping time constant of $\tau = k_{eff}^{-1} = 0.29 \text{ ps}$ for $N_0 = 2$ is similar to the < 0.5 -ps hole trapping time constants measured for CdSe quantum dots bearing thiol⁸⁴ and pyridine²²⁶ capping ligands.

In the limit that the Auger-mediated hole trapping dynamics is regulated by the diffusion of excitons, i.e., hole trapping occurs in the presence of excess trap states and is exciton-diffusion limited, the in-plane exciton diffusion coefficient D can be estimated by employing the following assumptions. First, the N_0 excitons initially created by photoexcitation are uniformly distributed about a NPL of area A , such that the maximum two-dimensional spatial extent of an individual exciton is $\pi\langle r_{max}^2 \rangle = A/N_0$, where $\langle r_{max}^2 \rangle$ is the maximum mean square displacement of the exciton due to diffusion. Second, Auger trapping occurs instantaneously between adjacent excitons once their mean square displacement reaches the maximum spatial extent, i.e., $\langle r(t)^2 \rangle = \langle r_{max}^2 \rangle$. Third, the time taken for an exciton to reach its maximum spatial extent and hence, undergo Auger trapping, is $\tau = 1/kn_h(0) = A/kN_0$. Finally, by applying the Einstein relation for diffusive motion in two dimensions, $\langle r_{max}^2 \rangle = 4D\tau = 4DA/kN_0$, we obtain the relation $k = 4\pi D$. Hence, the exciton diffusion coefficient along the plane of the NPL is $D = 0.28 \pm 0.08 \text{ cm}^2/\text{s}$, comparable to the hole diffusion coefficient of $0.52 \text{ cm}^2/\text{s}$ determined at 300 K,²²⁷ but two orders of magnitude smaller than the previously reported exciton diffusion coefficient of $26 \text{ cm}^2/\text{s}$ at 40 K.²²⁸ This decrease in D with temperature results from the dominant role played by exciton-phonon scattering in governing the size of the diffusion coefficient.

In order to elucidate the mechanism of the Auger-assisted hole trapping process, it is simulated using the recently developed state-of-the-art methodology²⁰⁸ which combines nonadiabatic molecular dynamics with self-consistent tight-binding density functional theory.²⁰⁹⁻²¹⁶ The simulated system consists of a CdSe core and a CdS shell with thicknesses in line with those determined experimentally. Despite partial ligand-exchange with 5-amino-1-pentanol, the shell is primarily passivated with acetate ligands, in accord with the synthesis procedure employed in experiments. Incomplete surface passivation arises from

the steric crowding of ligands on the CdS shell, resulting in trap states that are associated with the unsaturated bonds on the polar surface.²²⁹

Figure 4.9. Projected density of states of CdSe/CdS core/shell NPLs. Black, red and blue curves represent the CdSe core, CdS shell and acetate ligands, respectively. Labels (1) and (2) denote the shallow and deep trap states, respectively.

The calculated partial density of states (PDOS) of the CdSe/CdS/acetate core/shell/ligand NPL by Sougata Pal from Prof. Oleg V. Prezhdo's group is shown in Figure 4.9. The band alignment CdSe/CdS heterostructures depends on the relative thicknesses of the core and shell.²³⁰ In the present work, the VB maximum (VBM) localizes primarily on the CdSe core, with minor contributions from the CdS shell. The CB minimum (CBM) arises from the shell, with strong contributions from the passivating ligands. The system exhibits two types of hole trap states, located 0.2 eV (TS_{shallow}) and 0.7 eV (TS_{deep}) above the VBM. Both trap states localize predominantly in the shell, with a minor component on the ligands.

The simulated charge density distributions of the VBM, CBM and trap states reveal localizations that match the assignments based on the PDOS. Thermal-induced structural fluctuations result in all states exhibiting preferential localization towards either the top or

bottom surface of the NPL. In particular, the VBM (Figure 4.10a) is shifted towards the bottom of the core, while the CBM (Figure 4.10b) is localized primarily within the top shell layer.

Figure 4.10. Computed charge density distributions of (a) VBM, (b) CBM, (c) TS_{shallow}, and (d) TS_{deep}.

The difference in the preferential localization of the hole and electron decreases the electron-hole coupling and provides a possible explanation for the absence of an electron-assisted Auger hole trapping pathway in the experiments. The charge densities also rationalize the major difference in the roles of the two trap states. TS_{shallow} (Figure 4.10c) localizes on the same side of the system as the VBM, while TS_{deep} (Figure 4.10d) localizes on the opposite side. Consequently, the computed canonically averaged coupling to the VBM is two orders of magnitude higher for TS_{shallow} (24.42 meV) than TS_{deep} (0.22 meV). The difference in the coupling magnitudes, combined with the factor of 4 difference in depths of the two trap states, strongly suggest that the sub-picosecond hole trapping dynamics observed in the experiment is induced entirely by the shallow trap.

The simulations reveal that the majority of the hole transfer from the VBM to TS_{shallow} occurs within 0.3 ps, with a slower component extending to 1 ps (Figure 4.11). This biphasic behavior is typical of most quantum dynamical processes: the initial fast, Gaussian-like quantum dynamics arises from the strong coupling of a few states to the initial state at short times, whereas slower exponential dynamics, indicative of statistical behavior, emerge only after the quantum system has explored a broad range of states that are weakly coupled to the initial state. The simulated timescale of the fast hole trapping process is consistent with the experimentally observed sub-picosecond Auger-mediated hole trapping. It is noteworthy that TS_{deep} , which is localized deep within the band gap, remains essentially unpopulated on the 1 ps timescale. This is in stark contrast to the hole trapping efficacy exhibited by the shallow trap state.

The simulations reveal an increase in energy of the second hole that is excited by the Auger mechanism during trapping of the first hole, in support of the experimentally observed Auger heating of the valence band. The Auger heating of the second hole is eventually negated by phonon-induced relaxation, as can be seen from the decrease of the

energy of the hole starting at ~ 0.8 ps (Figure 4.11). The phonon frequencies that mediate hole relaxation (Figure 4.11 inset) can be identified from Fourier transforms of the energy gap fluctuations between the VBM and states within the VB. The calculated frequencies suggest that relaxation of the second hole is facilitated by both optical phonons^{1,231} at $180 - 200 \text{ cm}^{-1}$ and low frequency acoustic modes below 50 cm^{-1} . Holes that are excited deep into the VB by Auger heating dissipate their energy almost exclusively to the optical modes. Following their cooling to the vicinity of the VBM, the holes lose smaller amounts of energy via both optical and acoustic modes.

Figure 4.11. Simulated Auger-mediated hole trapping dynamics in a CdSe/CdS core/shell NPL. Shown are the population of $\text{TS}_{\text{shallow}}$ (red line) and the energy of the second hole excited by the Auger mechanism during trapping of the first hole (blue line). The inset presents the influence spectra of phonon modes that are responsible for relaxation of the second hole located at 1.3 eV (dashed line) and 0.02 eV (solid line) away from the VBM.

4.5 Conclusion

In summary, we have employed femtosecond transient absorption spectroscopy to investigate the early-time carrier dynamics of CdSe/CdS core/shell NPLs near the band gap. The use of a narrowband pump pulse that is resonant with the HH-CB transition and a broadband probe that monitors the HH-CB and LH-CB transitions simultaneously allows electron and hole dynamics to be disentangled. The experiments unravel a sub-picosecond Auger-mediated trapping of a hole and the concomitant excitation of another hole in the HH valence band, in good agreement with results obtained from nonadiabatic molecular dynamics simulations based on tight-binding density functional theory. The Auger trapping process is characterized by an effective second-order rate constant of $k = 3.5 \pm 1.0 \text{ cm}^2/\text{s}$. Such an ultrafast hole trapping, hitherto unobserved, bears important implications. For example, stimulated emission processes under conditions of multiexcitonic optical gain can be affected,^{195,232} and charge localization hinders efficient carrier extraction from photovoltaic materials.^{200,233}

Chapter 5

Frequency-Tunable Coherent Acoustic Phonons in Colloidal CdSe/CdS Core/Shell Nanoplatelets Driven by Auger Trapping

On top of the hot carrier dynamics of CdSe/CdS core/shell nanoplatelets, the oscillatory modulation were ambiguously resolved in the first moment time traces, as the signature of coherence phonons. In this chapter, we focus on the observation of four types of coherent phonons including two high-frequency oscillations attributed to longitudinal optical (LO) and surface optical (SO) phonon modes of CdSe, and hitherto unobserved two acoustic modes using femtosecond transient absorption spectroscopy. With increasing pump fluences, the frequency of the in-plane acoustic mode increases from 5 to 11 cm^{-1} , whereas the frequency of the out-of-plane mode remains at $\sim 20 \text{ cm}^{-1}$. Analysis of the oscillation phases suggests that the coherent acoustic phonon generation mechanism transitions from displacive excitation to sub-picosecond Auger hole trapping with increasing pump fluence.

5.1 Introduction

Acoustic phonons play a dominant role in heat transport and in determining the thermoelectric properties of low-dimensional semiconductor nanostructures.⁵ In addition, the properties of acoustic phonons are also intrinsically related to the mechanical properties of nanomaterials.^{53,155} Manipulation of acoustic phonon modes in spatially confined nanoscale materials can be effected by controlling their characteristic geometry, surface

termination, and, in the case of alloys, chemical composition.^{173,234-235} These various approaches to tuning the properties of acoustic phonons have been applied to the engineering of piezoelectric devices.²³⁶

As a result of their low frequencies, the investigation of acoustic phonons by frequency-domain Raman spectroscopy can be challenging. An alternative approach is to employ time-domain optical pump-probe spectroscopy. In this technique, vibrational wave packet motion induced by a pump pulse leads to amplitude and/or spectral modulations of the probe pulse as a function of pump-probe time delay. Fourier transformation of the probe signal along the time axis yields the frequency of the coherent phonon. The specific implementation of pump-probe spectroscopy to investigate the behavior of phonons, known as coherent phonon spectroscopy,⁵⁴⁻⁵⁵ has been applied to a multitude of nanostructures, such as carbon nanotubes,²³⁷⁻²³⁹ semiconductor nanocrystals,^{138,162} and two-dimensional transition metal dichalcogenides.²⁴⁰ Low-frequency acoustic phonon modes have also been elucidated in semiconductor quantum wells²⁴¹⁻²⁴² and nanocrystals,^{104,137} as well as metallic nanoparticles.²⁴³⁻²⁴⁴ Compared to frequency-domain measurements, coherent phonon spectroscopy directly furnishes the electron-phonon coupling strengths^{106,245} and provides insight into the mechanism by which the coherent phonons are generated.^{173-174,246}

Here, we employ optical pump-probe spectroscopy to resolve the coherent optical and acoustic phonons of CdSe/CdS core/shell semiconductor nanoplatelets (NPLs). NPLs have recently emerged as a new class of II-VI nanomaterials that have so far comprised of nanocrystals¹⁵⁴ and nanowires.²⁴⁷ Analogous to semiconductor quantum wells, colloidal semiconductor NPLs exhibit one-dimensional carrier quantum confinement due to their nanometer-scale thicknesses.¹⁹¹ The ability to control the thicknesses of NPLs with atomic precision leads to samples with unprecedented monodispersity.¹⁸⁹⁻¹⁹⁰ The narrow

absorption and photoluminescence spectra,¹⁹³ along with their suppressed fluorescence intermittency,¹⁹⁴ favor the application of NPLs as efficient light emitters and lasing media.^{195,248} Previous time-resolved studies have focused on the carrier dynamics of NPLs,^{22,199,201,203-204} while little is known about the phonon dynamics and the exciton-phonon coupling strengths. Steady-state photoluminescence and Raman measurements have unraveled the in-plane LO phonon,^{101,249-251} in addition to the out-of-plane LO phonon²⁵¹ and SO phonons.²⁵⁰ Beyond the previously observed LO and SO phonons, our femtosecond optical pump-probe measurements reveal the existence of in-plane and out-of-plane coherent acoustic phonons. The former exhibits an excitation fluence-dependent frequency. Analysis of the oscillation phases provides insight into the coherent phonon generation mechanisms. The measurements furnish Huang-Rhys factors that characterize the exciton-acoustic phonon coupling strengths.

5.2 Experimental results and discussions

It has been experimental proved that the initial photoexcited state plays an indispensable role in coherent phonon generation and dephasing processes¹⁷³ via well-established exciton-phonon couplings mechanisms.¹⁵⁵ To eliminate the contribution from highly excited charge carriers and simplify the analysis, narrowband pump laser was selective resonant to the lowest excitonic state which corresponds to HH-CB transition of CdSe, centered at 2.03 eV. With the transform-limited broadband probe pulse which spectral span from 1.65 to 2.30 eV, a time resolution of 81 fs FWHM was achieved which facilitate the observation of coherent phonon mode up to 411 cm^{-1} wave number.

Figure 5.1. Spectral first moment time traces $\langle E^{(1)}(t) \rangle$ of HH-CB transition obtained at different initial exciton numbers N_0 . Solid lines represent the fit as a combination of blue shifting via second-order kinetics and exponential red shifting kinetics. The inset figure shows the room temperature linear absorption spectrum of CdSe/CdS core/shell NPLs as well as the narrowband pump laser (grey area) resonant to the bandgap.

As described in Chapter 4, photoexcitation of the HH-CB transition of the CdSe/CdS core/shell NPL sample leads to a combination of ultrafast carrier dynamics and coherent phonon dynamics. The mixture of carrier and phonon dynamics is evident from the time-dependent spectral first moment $\langle E^{(1)}(t) \rangle = \int_{E_i}^{E_f} E \Delta A(E, t) dE / \int_{E_i}^{E_f} \Delta A(E, t) dE$, where E is the probe photon energy, t is the pump-probe time delay, ΔA is the differential absorbance signal, and E_f and E_i define the limits of the HH-CB transition over which the first moment is computed (Figure 5.1). Because the carrier dynamics define the baseline on top of which signatures of coherent phonons are found, accurate knowledge of the carrier dynamics is essential to reliably extract information on coherent phonons from the data. This is especially critical for the low-frequency acoustic phonon modes observed in this work. Previous fluence dependent measurements (Chapter 4) performed on the same sample with identical 2.03-eV photoexcitation established that the observed sub-

picosecond dynamics originates from Auger mediated hole trapping, which is characterized by an effective second-order rate constant of $3.5 \pm 1.0 \text{ cm}^2/\text{s}$. In the $\langle E^{(1)}(t) \rangle$ traces, Auger trapping manifests itself as a blue shift due to concomitant Auger heating. In addition, a spectral red shift rising from the hot electron cooling is apparent at low pump intensities.

The residual time traces $\langle E_{\text{res}}^{(1)}(t) \rangle$ obtained following the removal of the carrier dynamics baseline encodes coherent phonon dynamics. The observable $\langle E_{\text{res}}^{(1)}(t) \rangle$ is particularly well-suited for investigating vibrational wave packet dynamics because wave packet motion results in modulations of the probe transition energy. The $\langle E_{\text{res}}^{(1)}(t) \rangle$ time trace obtained for $N_0 = 0.8$ is shown in Figure 5.2a. It is evident that multiple frequency components are present. Quantitative analysis of $\langle E_{\text{res}}^{(1)}(t) \rangle$ is performed by fitting it to a sum of damped cosine functions

$$\langle E_{\text{res}}^{(1)}(t) \rangle = \sum_i A_i \cos(\omega_i t + \varphi_i) \exp(-t/\tau_i), \quad (5.1)$$

where, A_i , ω_i , φ_i and τ_i correspond to amplitude, frequency, initial phase, and damping time of oscillation component i , respectively. The best fit requires four components, whose parameters are summarized in Table 5.1.

Figure 5.2. (a) Semi-log plot of residual oscillations in the first moment time trace of HH-CB transition obtained from the subtraction of energy shifting features with initial exciton number $N_0 = 0.8$. The best fitting result (black) reveals four oscillatory components exist in the raw data (grey dashed line). (b) Reconstructed vibrations from fitting result include two acoustic phonon modes with frequency 5.2 (blue) and 20.1 cm^{-1} (red); two optical phonon modes at 191.4 (orange) and 209.3 cm^{-1} (green) which can be assigned to SO and LO phonons, respectively.

Figure 5.2b shows the contributions of the individual components, reconstructed from the fit parameters. The high-frequency mode at 209 cm^{-1} corresponds to the in-plane LO phonon, in good agreement with the bulk CdSe LO phonon frequency of $\sim 210 \text{ cm}^{-1}$, as well as the frequencies for the LO phonon in CdSe NPLs obtained previously from frequency-domain measurements.^{105,162} A second high-frequency mode at 191 cm^{-1} is

assigned to the SO phonon mode, given its proximity to the previously reported SO phonon frequency of 188 cm^{-1} for CdSe NPLs.²⁵⁰ Beyond the two optical phonon modes, two low-frequency components at 5.2 ± 0.2 and $20.1 \pm 0.4 \text{ cm}^{-1}$, hitherto unobserved, can be assigned to coherent acoustic phonons. The first-moment modulations of both acoustic modes exhibit initial phases ϕ_i that closely approach π rad: $(0.89 \pm 0.06)\pi$ and $(0.95 \pm 0.03)\pi$ rad for the 5.2 and 20.1 cm^{-1} modes, respectively, indicative of wave packet motion in the excited state triggered by displacive excitation (Figures 5.3a and 5.3b).

Table 5.1. Fitting parameters according to equation (5.1), for the residual oscillation signal shown in Figure 5.2.

Oscillation i	$\nu_i (\text{cm}^{-1})$	$A_i (\text{meV})$	$\phi_i (\pi)$	$\tau_i (\text{ps})$
1	5.2 ± 0.2	0.013 ± 0.002	0.90 ± 0.07	--
2	20.2 ± 0.4	0.082 ± 0.009	0.95 ± 0.03	1.66 ± 0.22
3	191.4 ± 1.1	0.183 ± 0.030	0.40 ± 0.05	0.60 ± 0.07
4	209.3 ± 0.3	0.153 ± 0.020	0.70 ± 0.02	1.60 ± 0.15

Note: oscillation 1 is undamped in our experiments, i.e., the damping time is much longer than the scan time delay 12 ps.

In this process, vibrational wave packet motion along the electronically excited-state potential energy curve starts from one extremum of the lattice displacement coordinate, hence giving rise to an initial oscillation phase of either 0 or π rad. The initial blue shift of the differential absorption peak with time delay rules out the encoding of the wave packet

motion in the stimulated emission signal, which should exhibit an initial red shift with time delay to give an initial oscillation phase of 0 rad.

Figure 5.3. Schematic illustrations of vibrational wave packet propagation for the (a) in-plane and (b) out-of-plane coherent acoustic phonons. Photoexcitation from the GS launches a vibrational wave packet on the ES potential by displacive excitation. The vertical and horizontal axes denote the potential energy $V(Q_i)$ and the acoustic phonon displacement coordinate Q_i , respectively. The probe pulse interrogates the absorption of ES by coupling the ES and ES* states. For $N_0 \gtrsim 3$, Auger hole trapping occurs and transfers the vibrational wave packet on timescales of τ_{tr} from ES to TS, where it is subsequently coupled to TS* by the probe pulse. The dimensionless displacements between ES and ES* and between TS and TS* are denoted by Δ_{ES} and Δ_{TS} , respectively.

Furthermore, because ground-state bleaching and excited-state absorption produce out-of-phase spectral shifts, i.e., $\phi_i^{ESA} = \phi_i + \pi$, the retrieved phase of the excited-state absorption is ~ 0 rad, implying that the excited-state absorption exhibits an initial red shift. This red shift in turn suggests that the excited-state absorption probe transition accesses a

final state (ES*) that is displaced further away from the ground state (GS) than the excited state (ES), as shown in Figure 5.3. This trend is consistent with ES* having formally $N_0 + 1$ excitons for an ES with N_0 excitons. In order to simplify the interpretation of the experimental data, we refer to ϕ_i^{ESA} in the remainder of this thesis. The anti-correlation of excited-state absorption in first moment time trace is explained as follow.

The differential absorbance $\Delta A(E)$ spectrum comprises ground-state bleaching (GSB), stimulated emission (SE) corresponding to the negative ΔA signal and excited-state absorption (ESA) corresponding to the positive ΔA signal. In semiconductor nanostructures, the primary contribution of $\Delta A(E)$ spectrum near the bandedge arises from GSB and ESA components.² The probe beam induced emission is typical debilitated considering the weak intensity of probe pulse. Here, our transient absorption spectrum is the spectral overlapping of predominant GSB signal and minor ESA contributor. The oscillation of first moment time trace $\langle E_{\Delta A}^{(1)}(t) \rangle$ with initial phase ϕ reflects the energy fluctuation induced by the vibrational wave packets. The wave packet motion $\langle E_{\text{wp}}^{(1)}(t) \rangle$ in GSB signal is correlated with oscillation of $\langle E_{\Delta A}^{(1)}(t) \rangle$ such that the initial phase $\phi^{\text{GSB}} = \phi$. On the other hand, The ESA spectrum $A_{\text{WP}}(E, t)$ moves along the opposite direction of the $\Delta A(E, t)$ spectrum shown in Figure 5.4a, considering the contrary spectral sign. The anti-correlated motion of two spectra yields an out-of-phase spectral shift between $\langle E_{\Delta A}^{(1)}(t) \rangle$ and $\langle E_{\text{wp}}^{(1)}(t) \rangle$ time traces, i.e., $\phi^{\text{ESA}} = \phi + \pi$ (Figure 5.4b and 5.4c).

Figure 5.4. (a) Schematic diagram of differential absorbance $\Delta A(E, t)$ spectrum (blue) and wave packet $A_{wp}(E, t)$ (red) shown in ESA signal. The corresponding first moment time traces are shown in (b) and (c), respectively. The initial phase of $\langle E_{\Delta A}^{(1)}(t) \rangle$ and $\langle E_{wp}^{(1)}(t) \rangle$ is π rad shifted.

Coherent phonons are detected in optical spectroscopy due to exciton-phonon coupling: coherent phonons modulate the energy levels of the excitonic states, which in turn give rise to the observed oscillations of the probe transition energy $\langle E_{res}^{(1)}(t) \rangle$. Coupling of optical phonons to excitons involve the Fröhlich interaction, whereas acoustic phonons are coupled via the deformation and piezoelectric potentials. Theoretical studies on II-VI semiconductor nanocrystals¹⁵⁵ and quantum wells²⁵² suggest that the deformation potential interaction dominates exciton-acoustic phonon coupling. It is important to note that displacive excitation launches only coherent phonons that involve the totally symmetric breathing modes of the lattice.⁵⁵ This constraint suggests that the 5.2- and 20.1-cm⁻¹ vibrations can be assigned to in-plane and out-of-plane acoustic modes, respectively.

At higher pump fluences, the frequency of the in-plane mode (ω_{in}) exhibits a pronounced fluence dependence, increasing from 5.2 – 11 cm⁻¹ over the range of $N_0 \sim 1 -$

9 (Figure 5.5a), whereas that of the out-of-plane mode (ω_{out}) fluctuates in the range of $\sim 19 - 25 \text{ cm}^{-1}$ without any discernible fluence dependence (Figure 5.5b). The initial phase of the in-plane component ($\phi_{\text{in}}^{\text{ESA}}$) undergoes a π -phase jump at $N_0 \gtrsim 3$ (Figure 5.5c), whereas that of the out-of-plane component ($\phi_{\text{out}}^{\text{ESA}}$) deviates from ~ 0 rad at $N_0 \gtrsim 3$ (Figure 5.5d). Finally, the oscillation amplitudes of both in-plane (A_{in}) and out-of-plane (A_{out}) components decrease with N_0 (Figures 5.5e and 5.5f).

The increase of the in-plane acoustic phonon frequency ω_{in} with N_0 rules out the electronic softening of phonon modes²⁵³⁻²⁵⁴ as its origin. Electronic softening occurs when an increasing fraction of bonding electrons that is photoexcited into anti-bonding states weakens the lattice, hence reducing the phonon frequency. Instead, the observed increase in ω_{in} with N_0 can be intuitively rationalized in terms of a carrier density distribution with a larger number of nodes coupling more favorably to higher-frequency phonons. With increasing fluence, more excitons N_0 are delocalized along the lateral dimension of the NPL,²² resulting in an exciton density distribution with a higher spatial frequency. Note that a similar scaling of coherent LA phonon frequencies with the inverse-periodicity of carrier distributions has previously been observed in semiconductor quantum wells.^{241,255} On the other hand, the out-of-plane frequency ω_{out} is relatively independent of N_0 because the addition of excitons to NPLs occurs preferentially along the lateral dimension than the thickness direction, where the energy penalty is higher as a result of quantum confinement.²⁵⁶

Figure 5.5. Oscillation frequencies (a) ω_{in} and (b) ω_{out} , oscillation phases (c) $\phi_{\text{in}}^{\text{ESA}}$ and (d) $\phi_{\text{out}}^{\text{ESA}}$, the corresponding corrected trap state phase $\phi_{\text{in}}^{\text{TSA}}$, $\phi_{\text{out}}^{\text{TSA}}$ and oscillation amplitudes (e) A_{in} and (f) A_{out} as a function of initial exciton number N_0 .

The abrupt π -phase jump in $\phi_{\text{in}}^{\text{ESA}}$ and the pronounced deviation of $\phi_{\text{out}}^{\text{ESA}}$ from ~ 0 rad appear for initial exciton numbers $N_0 \gtrsim 3$. Both observations suggest that a mechanism other than displacive excitation is responsible for the generation of coherent acoustic phonons at high N_0 values. We consider the possibility that the sub-picosecond Auger-mediated trapping of holes in NPLs,²⁵⁷ which becomes operative nominally at $N_0 > 2$, could provide the impulse for driving coherent phonons in NPLs. Given the previously

measured Auger trapping rate constant and our experimental conditions, the time constant for Auger trapping τ_{tr} is expected to decrease from ~ 0.3 ps to ~ 0.1 ps with increasing N_0 . The sub-picosecond trapping times, being shorter than the acoustic phonon oscillation periods $T_i = 2\pi/\omega_i$, satisfy the condition for the impulsive excitation of coherent acoustic phonons by Auger-mediated trapping; in the present work, T_{out} fluctuates in the range of 1.4 – 1.7 ps and T_{in} decreases from 6.4 ps to 3.0 ps with increasing N_0 . Auger hole trapping transfers the ES population and its associated vibrational coherence to the hole TS on a timescale of τ_{tr} . Immediately following Auger trapping, the first-moment of the trap-state absorption oscillates with an initial phase $\phi_i^{\text{TSA}} = \omega_i \tau_{\text{tr}} + \phi_i^{\text{ESA}}$ ($i = \text{in, out}$). In the case of the in-plane acoustic phonon, the vanishingly small $\omega_{\text{in}} \tau_{\text{tr}}$ term compared to $\phi_{\text{in}}^{\text{ESA}}$ implies $\phi_{\text{in}}^{\text{TSA}} \approx \phi_{\text{in}}^{\text{ESA}}$ (Figure 5.5c). For the out-of-plane phonon, however, $\omega_{\text{out}} \tau_{\text{tr}}$ is smaller than, but not negligible compared to $\phi_{\text{out}}^{\text{ESA}}$. Correction for the finite Auger trapping time at $N_0 \gtrsim 3$, and hence, the time needed for the out-of-plane vibrational wave packet to appear on TS, recovers $\phi_{\text{out}}^{\text{TSA}} \sim 0$ rad, similar to the $\phi_{\text{out}}^{\text{TSA}}$ values obtained at $N_0 < 3$ (Figure 5.5d); the observed deviations at higher N_0 values warrant further investigations. Note that the π -phase jump in $\phi_{\text{in}}^{\text{TSA}}$ upon Auger trapping ($N_0 \gtrsim 3$) points to initial wave packet motion along opposite directions on the ES and TS potential energy curves for the in-plane acoustic phonon mode (Figure 5.4a). On the other hand, the similar out-of-plane phases measured before ($\phi_{\text{out}}^{\text{ESA}}$ for $N_0 < 3$) and after Auger trapping ($\phi_{\text{out}}^{\text{TSA}}$ for $N_0 \gtrsim 3$) suggests that the initial motions of the out-of-plane wave packet on both ES and TS occur in the same direction (Figure 5.4b).

The manner in which Auger-mediated hole trapping initiates coherent acoustic phonons in NPLs is analogous to the previously reported mechanism of coherent LA phonon generation in CdSe nanocrystals by surface trapping.⁷ The exciton wave function, initially delocalized along the lateral plane of the NPL, becomes localized upon trapping.

The emission of transient electric fields that accompanies hole trapping sets off coherent acoustic waves in the NPLs via piezoelectric coupling to the CdSe lattice. The creation of in-plane coherent acoustic phonons by this mechanism is particularly favorable because the lateral plane of the NPLs contains the [110] direction, along which the piezoelectric coupling coefficient for the zinc-blende lattice is the largest.²⁰⁵ Similar launching of the coherent LO phonon in CdSe nanocrystals by ultrafast charge transfer to an electron acceptor has also been observed.¹⁷³⁻¹⁷⁴ In these systems, coupling of the acoustic and optical phonons to the charge migration event occurs via the piezoelectric⁷ and Fröhlich interactions,¹⁷³⁻¹⁷⁴ respectively. Another well-established mechanism for coherent phonon generation, impulsive lattice heating induced by ultrafast carrier cooling,²⁵⁸ is expected to contribute negligibly in this case. The ultrashort laser pulse generates hot electron which rapidly thermalizes and impulsively heats the lattice. The increasing temperature of lattice can be estimated using specific heat capacity formula,

$$\Delta T = \frac{Q}{m \times s} \quad (5.2)$$

where Q is the dissipated heat from hot carrier cooling, m is the mass and s is the specific heat capacity. From a Tauc analysis of optical absorption spectrum, the band gap of CdSe/CdS NPLs is 1.93 ± 0.11 eV.²⁵⁷ Upon narrowband pump at 2.03 eV, the heat distributed from a hot electron is 0.1 eV. With the dimensions of CdSe core layer ($28.8 \times 7.1 \times 1.75$ nm³), crystal density $\rho = 5.664$ g/cm³,²⁰⁵ and specific heat capacity of CdSe, $s = 0.49$ J g⁻¹ K⁻¹,²⁵⁹ the lattice temperature of NPL increases 0.016 K per exciton. Given our experimental condition, the maximum temperature increase is 0.14 K with initial exciton number $N_0 = 9$. In comparison, the generation of coherent acoustic phonons in metal nanoparticles by this mechanism is accompanied by a typical lattice temperature increase of $\sim 10^1 - 10^2$ K.²⁶⁰ Finally, due to the relatively long τ_{tr} compared to the optical

phonon period, we note that Auger trapping is unlikely to be responsible for the coherent LO and SO phonons observed herein. The coherent optical phonons behaviors are plotted in Figure 5.6 against the initial exciton number. The Huang-Rhys factor of LO phonon is $S = 0.0030 \pm 0.0002$ at $N_0 = 0.9$, one order magnitude smaller than CdSe quantum dots.²⁶¹

Figure 5.6. Oscillation frequencies (a) ω_{LO} and (b) ω_{SO} , oscillation phases (c) ϕ_{LO} and (d) ϕ_{SO} , and oscillation amplitudes (e) A_{LO} and (f) A_{SO} as a function of initial exciton number N_0 .

The amplitudes A_{in} and A_{out} report on the dimensionless displacements between states that are coupled by the probe transition, i.e., between ES (TS) and ES* (TS*). The dimensionless displacement Δ_i is obtained from the amplitude A_i and frequency ω_i of the phonon mode by employing the relation $\Delta_i = \sqrt{A_i / \hbar \omega_i}$ ($i = \text{in, out}$). Both Δ_{in} and Δ_{out} exhibit a general decrease with increasing N_0 (Figure 5.7), reflecting a decrease in the fractional change of the equilibrium geometries of the ES and TS states with increasing N_0 . This trend follows the decrease in the fractional exciton population change between ES (TS) and ES* (TS*) as N_0 increases. At the lowest exciton number employed in this study ($N_0 = 0.9$), the dimensionless displacements furnish Huang-Rhys factors of $S_{\text{in}} = 0.011 \pm 0.002$ and $S_{\text{out}} = 0.016 \pm 0.002$, where Δ_i is related to S_i by $S_i = \Delta_i^2 / 2$. The small S_{in} and S_{out} values indicate that electron-acoustic phonon coupling in NPLs is weak, consistent with the results of temperature-dependent spectral linewidth measurements, which reveal a small, but non-negligible contribution of acoustic phonons to the linewidth.¹⁰¹ Interestingly, the Huang-Rhys factors for the in-plane and out-of-plane acoustic modes are comparable, despite the disparate spatial extents of the exciton along the in-plane and out-of-plane directions. It is also instructive to compare the Huang-Rhys factors for NPLs to those obtained for CdSe nanocrystals of comparable quantum-confined dimensions. Optical pump-probe spectroscopy performed on 3.1-nm-diameter CdSe nanocrystals furnishes $S = 0.13 \pm 0.03$ for the LA phonon mode,¹³⁸ one order-of-magnitude larger than the S_{in} and S_{out} of NPLs. The stronger exciton-acoustic phonon coupling for nanocrystals can be attributed to the spatial confinement of the carrier wave functions in all three dimensions compared to NPLs, which exhibit only one-dimensional quantum confinement.

Figure 5.7. Dimensionless displacements for the (a) in-plane Δ_{in} and (b) out-of-plane Δ_{out} acoustic phonon modes as a function of initial exciton number N_0 .

5.3 Conclusion

In conclusion, coherent phonon spectroscopy elucidates the in-plane and out-of-plane acoustic phonon modes of CdSe/CdS core/shell NPLs generated by band-gap photoexcitation. These acoustic phonon modes appear alongside the previously observed LO and SO phonon modes of these materials. At low pump fluences, the coherent phonons are launched by displacive excitation. At high fluences, the coherent acoustic phonons are likely triggered by the piezoelectric coupling of the NPL lattice to an Auger-mediated hole trapping process. The in-plane acoustic phonon frequency exhibits a pronounced fluence dependence, which suggests the possible application of these NPLs as nanoscale, frequency-tunable piezoelectric electromechanical resonators operating at $\sim 10^2$ GHz frequencies. The Huang-Rhys factors of $\sim 10^{-2}$ for both acoustic modes are one order of magnitude smaller than that for the LA phonon of CdSe nanocrystals. These electron-phonon coupling strengths can be used to benchmark large-scale ab initio simulations of

nanoscale materials.²⁰⁸ In addition, the weak exciton-acoustic phonon coupling suppresses electronic energy dissipation via phonons and supports long-lived quantum coherences and potentially high carrier mobilities. These desirable properties, together with their tunable optical transition energies, make NPLs an attractive material for optoelectronics.

Chapter 6

Summary and future work

The tunable discrete energy levels of semiconductor nanostructures facilitate the design of high-performance electronic devices. The flexible optoelectronic properties based on quantum confinement effect make low dimensional semiconductors stand out as a promising candidate in a remarkable extensive fields, such as solar cells, nanoscale electronic devices, light-emitting nanodevices, laser technology, waveguide, chemicals and biosensors. The early time electron and phonon dynamics which determined the physical properties have attracted intensive research efforts owing to the fundamental phenomenal study and applied devices design.

In this thesis, coherent and incoherent electron and phonon dynamics are discussed in CdSe based QDs and NPLs. The electronic coherence is a quantum mechanical phenomenon prepared by the superposition of two discrete energy states. The high efficient energy transport induced by coherent electronic motion in nature light harvesting systems inspires the study of this striking quantum effect in nanoscale semiconductors. In Chapter 3, excitonic quantum coherence was investigated in colloidal CdSe QDs using femtosecond transient absorption spectroscopy at cryogenic temperatures. As the fingerprint of electronic coherent motion, the oscillatory signal lasting for 15-fs was observed at 77 K. The short-lived excitonic coherence between valence electrons partially results from the temperature dependent factor, electron-acoustic-phonon coupling. The dominant temperature independent contributions include the exciton-exciton and exciton-defect scatterings. The complex fine excitonic structure and inherent size dispersion accelerate the

electronic decoherence in QDs. Recently emerged semiconductor NPL structure dramatically decreases the inhomogeneous linewidth broadening, due to the precise thickness control to atomic level. The investigation of CdSe/CdS core/shell NPLs comprises two parts: (i) the ultrafast charge carrier dynamics near the band gap; (ii) coherent phonons dynamics especially acoustic phonon modes. The first work was introduced in Chapter 4, demonstrating a sub-picosecond Auger hole trapping processes. After resonant photoexcitation at the band edge, an Auger-type HH dynamic was observed with an effective second-order rate constant of $k = 3.5 \pm 1.0 \text{ cm}^2/\text{s}$. Pump fluence dependent energy blue-shift shown in the first moment time traces indicated the consequent Auger hole heating process. The total kinetic scenario can be described as a HH was captured by the shallow trap site and transferred the excess energy to another HH. Besides the ultrafast Auger mediated hole trap dynamics, coherent phonon signatures were also unambiguously detected on top of hot carrier dynamics which was discussed in Chapter 5. The observed four types of coherent phonon modes include two new resolved acoustic phonon which assigned to in-plane and out-of-plane breathing modes, as well as two well-established optical phonons (LO and SO). The fluence dependence of vibrational frequency and initial phase of in-plane phonon indicates the impulsive coherent phonon generation via Auger-like charge carrier migration. Furthermore, dimensionless displacements for the relevant potential energy curves are also obtained.

The investigation of ultrafast charge carrier and coherent phonon dynamics provide the further understanding of NPL nanostructure. However, the initial motivation of interrogating the coherent excitonic motion within these quasi-2D nanoparticles is expected to process in future. The long-lived electronic coherence in NPLs benefits the investigation of multiple dephasing mechanisms even at ambient temperature. At the same time, temperature dependent quantum coherence measurement down to 4 K would be performed

in QDs in order to explore the intrinsic decoherent mechanism. With gradually sophisticated pulse shaping techniques, it would be intriguing to study the contributions of phase profile and exciton population to quantum coherence via rigorous controlling the laser pulse chirp.

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