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INVESTIGATION OF EXCITONIC PROPERTIES AND HOT-CARRIER COOLING IN LEAD SULFIDE QUANTUM DOTS

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by

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ABSTRACT

Hot-carrier cooling, which has been predicted to be slowed in semiconductor quantum dots (QDs) due to the anticipated hot-phonon bottleneck, has not been readily observed, with carrier cooling rates of QDs approaching bulk cooling rates. PbS QDs are excellent potential candidates to exhibit extended hot-carrier lifetimes since confinement of both electrons and holes are nearly identical, thus circumventing an efficient Auger mechanism which has been found to increase cooling rates in other materials. Despite, the advantages of PbS QDs for enhanced hotcarrier lifetimes, rapid thermalization of hot-carriers persist in these materials and the mechanism which directs this fast cooling is not well understood. Using a combination of steady-state and time-resolve, electronic optical spectroscopy, this work has provided new insights into the behavior of excited electronic states in PbS QDs. This work identified the spectroscopic signature of the formally forbidden $1S_{e(h)}$ - $1D_{e(h)}$ intraband transition, allowing vibronic coupling to be investigated for this high energy state, along with the 1P_{e(h)} and band edge states. It was determined that significant homogenous broadening of these states occurs as a result of a highly size-dependent exciton-phonon coupling mechanism. It is this vibronic coupling that results in resonant energy relaxation pathways between the intraband states of the QDs that are amplified for smaller diameter nanocrystals, leading to rapid bulk-like cooling in these materials. Additionally, steady-state and time-resolved vibrational spectroscopy were used to identify possible sources of the vibronic coupling in PbS QDs. Through this work, vibrational coupling in PbS QDs, was found to be independent of the types of ligands at the crystalline surface and was in fact mediated by the surface phonons. Strong nonadiabatic coupling is occurs at the QD surface because of the broad phonon spectrum associated with the strained crystalline lattice, dangling bonds, and exposed crystal facets. This work suggests that surface modification techniques that reduce the coupling of electronic states to surface phonons may enable quantum confined structures with slower carrier cooling rates. Such surface modifications may include the use of thin inorganic shells or controlled composition gradients to reduce dangling bonds and tune the lattice strain at QD surfaces.

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LIST OF ABBREVIATIONS

ICC	intermolecular coordinate coupled
PDI	perylene dimmide
СТ	charge transfer
ET	energy transfer
OPV	organic photovoltaic
D/A	donor/acceptor
Mid-IR	mid-wavelength infrared
ITO	indium tin oxide
МСТ	mercury cadmium telluride
OPA	optical parametric amplifier
OPO	optical parametric oscillator
Nd:YAG	neodymium doped yttrium aluminum garnet
Ti:Sapphire	titanium sapphire
PL	photoluminescence
ТА	transient absorption (spectroscopy)
ns-TA	nanosecond transient absorption (spectroscopy)
CQD	colloidal quantum dot
QD	quantum dot
HPLC	high performance liquid chromatography
UV/Vis	ultraviolet/visible
Vis/NIR	visible/near-wavelength infrared
NIR	near-wavelength infrared
Mid-IR	mid-wavelength infrared
FTIR	Fourier transform infrared
ESA	excited state absorption
GSB	ground state bleach

GIXRD	grazing incidence X-ray diffraction
EA	electro-absorption
HCE	hot carrier extraction
MEG	multiple exciton generation
eV	electron-volts
kТ	room temperature (~298 K)
LO	longitudinal optical
IR	infrared
FWHM	full width at half maximum
SAS	species associated spectrum
P-P-PC	pump-push-photocurrent probe
ns-TA	nanosecond transient absorption
PV	photovoltaic
PC	photocurrent
РЗНТ	poly(3-hexylthiophene)
РСВМ	phenyl-C61-butyric acid methyl ester
PFTBT	poly((9,9-dialkylfluorene)-2,7-diyl-alt-[4,7-bis(alkylthiophen-5-yl)-2,1,3-benzothiadiazole]- 2,2-diyl
S/N	signal-to-noise ratio
TWh	terawatt hour
IPV	inorganic photovoltaic
V _{oc}	open circuit voltage
J _{sc}	short circuit current
SF	singlet fission
II	impact ionization
S ₀	ground state energy level
S_1	first excited singlet energy level
T ₁	first excite triplet energy level

СМ	carrier multiplication
EMI	electromagnetic interference
ITO	indium tin oxide
FTO	fluorine-doped tin oxide
TiO ₂	titanium dioxide
ns-ms	nanosecond-to-millisecond
O.D.	optical density
ΔPC/PC	change in photocurrent
ΔΑ	change in absorbance
SDL	standard detection limit
IRAV	infrared active vibrational mode

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CHAPTER 1

BACKGROUND AND MOTIVATION

1.1 Introduction

Driven by a robust global economy and stronger heating and cooling needs, global energy demand grew by 2.3% in 2018 to more than 146,000 TWh, its fastest pace in over a decade.¹ While natural gas was responsible for nearly half of the rise in energy consumption, electricity continues to position itself as the fuel of the future, with global electrical demand increasing by 4% to more than 23,000 TWh.² This growth is pushing electricity toward a 20% share in the final consumption of energy.² Furthermore, the growth of electricity over the next two decades is forecast to outpace the growth of total energy demand, with a projected 62% increase through the year 2040.³ Natural gas is expected to remain the leading source of electricity production over the next 20 to 30 years which will cause global CO₂ levels to continue to rise at alarming rates.⁴ It is because of the detrimental global effect of increasing CO₂ levels and the depletion of nonrenewable energy sources that alternative, sustainable sources of electricity production are needed.

In 2016 in the U.S., renewable sources made up approximately 15% of the net electricity generation, with the bulk coming from hydropower and wind power at 6.5% and 5.6%, respectively.⁵ Solar energy, on the other hand, accounted for only 1.6% of the total U.S. electricity generation,⁵ but has the potential to overcome many of the limitations of current energy sources. In one hour, enough energy from the sun reaches the earth to fulfill all of the world's electricity demands for an entire year. Based on the average solar panel electrical efficiency across the U.S., it would take 21,250 square miles of solar panels to meet the country's electrical needs, which is approximately 0.5% of American land, or about half of the

land currently leased by oil and gas. In general, 40% of the total U.S. electrical demand could be supplied by the installation of solar panels on rooftops alone.⁶ With such a huge potential, solar energy has positioned itself as a viable energy source to supply the U.S.'s and the rest of the world's electricity needs.

The current global market for solar cells is dominated by silicon, with Si-based solar cells comprising more than 90% of the total market.⁷ The driving forces behind the dominance of Sibased solar cells in the marketplace has been the high efficiency and long stabilities of these types of cells, along with the fact that Si solar cells are relatively inexpensive at ~\$0.30/W.⁸⁻⁹ Unfortunately at a cost of \$0.30/W, Si solar cells are roughly 3-4 times the cost of carbon based fuels.¹⁰ Additionally, the production of Si solar cells cannot be scaled to meet global energy demands, due to the large time and energy investment needed to purify and manufacture solar cells of this material.¹¹ Moreover, even high purity single crystalline Si-based devices, which exhibit the highest efficiencies, have only reached 26.1% efficiency, while amorphous Si solar cells have only achieved maximum efficiencies of 14%.¹² Due to thermodynamic limitations of single junction solar cells, Si-based devices have a maximum theoretical efficiency limit of only 33%.¹³⁻¹⁴ In order for the world's economy to completely convert to electricity generated through solar photovoltaics, the issues of scalability and limited maximum efficiency need to be overcome. For this reason, new classes of materials are being studied which are able to circumvent the issues with Si, and potentially unlock the potential to power the world.

1.2 Next Generation Solar Cells

Over the last few decades, there has been a major push to develop new types of solar cell materials which can be processed from solution as thin films using inexpensive precursors materials.¹¹ Materials that are targeted for use in solution processable solar cells have higher

extinction coefficients than Si, allowing them to be made much thinner than typical Si based devices, resulting in less material being used in the manufacturing process.¹¹ The possibility of solution processing, opens up the opportunity for photovoltaic devices to be manufactured on very large scales by scalable casting methods such as blade coating, inkjet printing, and roll-to-roll processing. These types of processing methods boast the potential to construct solar cells at a rate that is capable of meeting the world's energy demands, as well as the possibility of lowering the cost per Watt to levels which are comparable to carbon based energy sources.¹¹ An additional advantage of this class of material is that they may be printed onto flexible substrates, permitting solar cell devices to be lighter, more portable, and adopt unique shapes. Shape portability opens a larger number of applications in which solar can be applied as well as making solar cells more aesthetically pleasing than the traditional large, flat solar panels that have been commercialized.¹⁵

To date, there have been many different solution processable materials that have been created for potential applications as future photovoltaic materials and can be broadly grouped into three main classes: organic photovoltaics (OPVs),¹⁶ nanomaterials,¹⁷ and inorganic photovoltaics (IPVs).¹⁸⁻²² Despite their potential for affordable, scalable energy, photovoltaic devices of these materials have failed to be successfully commercialized. One of the main reasons that these materials have been unsuccessful as solar cells thus far has been the low power conversion efficiencies achieved for even the highest efficiency cells of each material. One type of IPV material that has shown significant promise in recent years is perovskites, especially lead halide perovskites. Within the last five years, the maximum efficiency of perovskite single junction devices has shot up from ~14% to ~24.2%, rapidly converging on the maximum efficiency of single crystal Si-based devices.¹² Owing to their performance and ease of synthesis,

the popularity of these materials has sky-rocketed in the literature in recent years with many researchers "jumping onto the perovskite bandwagon". Despite their high performance and ease synthesis however, perovskites do suffer from a few key downfalls that make them less suitable than other alternative materials. Perovskites have been plagued with stability issues ranging from photo-degradation to water and air instabilities which have hindered their application outside of the laboratory.²³⁻²⁴ Though there are ongoing research efforts to curb the downsides of perovskites, these single junction devices also suffer from the same thermodynamic maximum efficiency as Si solar cells and therefore their power conversion efficiencies are capped at a theoretical 33%.¹³⁻¹⁴ With power conversion efficiencies limited to below 33%, a greater number of PV devices will be needed to supply the world electrical demands, requiring an increased investment of energy, time, and money into manufacturing devices and necessitating larger areas of land to be consumed by solar panels.

1.3 Overcoming the Shockley-Queisser Limit

The calculation of the thermodynamic maximum efficiency of a solar cell takes into account many different energy loss mechanisms, and includes consideration of the bandgap of a material, radiative and non radiative losses, and thermalization losses.¹⁴ Of the loss mechanisms which hinder the efficiency of a PV device, thermalization losses play the largest role.²⁵ Thermalization losses arise when photons with energy greater than the bandgap of the material are absorbed. The excess energy from these photons is lost in the device by radiating heat to the environment as the electron cools rapidly to the bandedge. This cooling process is typically mediated by the excitation of optical and acoustic phonon modes within the crystalline lattice of the material.²⁶ The energy lost to heat is unable to be harvested to produce electricity and the overall efficiency suffers. **Figure 1-1** highlights the regions of the solar spectrum which are

available to be harvested by Si-based solar cell devices and shows the large percentage of high energy photons that result in large thermalization losses.²⁷ In order to overcome the Shockley-Queisser limit and increase the efficiency of solar cells, the amount of energy which is lost by the absorption of ultraviolet and blue photons must be recovered in some way.



Figure 1-1. Losses in ideal silicon solar cells which give rise to the Shockley-Queisser limit. Reproduced with permission from reference 27.

The ability to overcome the maximum theoretical efficiency of single junction solar cells represents a critical challenge to implement solar energy as a major source of electricity and the utilization of high energy photons is a critical strategy to increase overall efficiencies. Devices comprised of materials which are suitable for overcoming the Shockley-Queisser limit have been branded third generation solar cells, and consist of two major classes of materials. The first type of material that has the potential for higher than 33% maximum conversion efficiency is a select group of organic chromophores which can undergo a process known as singlet fission.²⁸ The process of singlet fission is a physical process involving at minimum two molecules that converts a single high energy photon into two excited triplet excitons. Because this process is able to take

advantage of high energy photons by mitigating thermal losses, this mechanism alone increases the maximum theoretical efficiency of a singlet fission PV device to 44%.²⁹ In singlet fission a photon initially creates an excited singlet state in one chromophore, which then interacts with a second chromophore in the ground state, sharing its energy and converting the singlet energy into two triplet states with half the energy (**Figure 1-2**).²⁸ Singlet fission therefore has the potential to increase the internal quantum efficiency of a device to up to 200%, resulting in the potential to double the short circuit current (J_{sc}).³⁰ In order for this process to be efficient, the energy of the triplet state (T₁) must be less than half of the energy of the singlet state (S₁).



Figure 1-2. Singlet fission diagram involving two chromophores. (1) The chromophore on the left undergoes initial excitation to S_1 . (2) The excited chromophore shares its energy with the chromophore on the right, creating a T_1 state on each. Reproduced with permission from reference 28.

Furthermore, because the relaxation mechanism of a triplet exciton to the ground state involves a spin flip, the process is slow, extending the lifetime of triplets well beyond that of singlet lifetimes. Typically a longer lived excited state, increases the probability that created carriers will be extracted.¹⁹

The gain in J_{sc} that singlet fission affords comes at a cost however. Since the triplet energy levels are less than half of the singlet energy levels in chromophores targets for singlet fission, the open circuit voltage (V_{oc}) of these types of PV devices is cut in half, limiting their maximum overall performance. Moreover, triplet excitons are more difficult to harvest compared

to singlet excitons because they are spin forbidden from emitting light and have higher binding energies which hinder charge separation.³¹ Further difficulties arise when considering complex processes involving the dynamic competition of singlet fission with radiative and nonradiative recombination channels, intersystem crossing and energy or charge transfer from the singlet state.³² To overcome the limitations with singlet fission, researchers have looked to use singlet fission chromophores in conjunction with other materials which are able extract the energy from the triplet excitons and shuttle that energy to an acceptor molecule/material.³² Another route to overcome the downfalls of singlet fission chromophores that is garnering a lot of attention in recent years is the use of singlet fission materials as a selective absorber in conjunction with Sibased solar cells.³³ In this application, the singlet fission materials are placed on top of a Si solar cell and absorb the high energy blue photons of light that would otherwise be converted to heat in a Si solar cell. The singlet fission chromophore then downconverts the absorbed high energy photon into two low energy excitations which can be transferred to the the Si device through either charge or energy transfer (CT or ET). While this method offers a lot of promise to decreases thermalization losses in Si-based solar cells, significant technical challenges remain in transferring the energy between the singlet fission chromophores and the Si layer. Furthermore, the need to utilize Si-based devices also falls victim to the issues described earlier with large scale manufacturing.

Another class of material that boasts the potential to overcome the Shockley-Queisser limit is nanomaterials, and more specifically, colloidal quantum dots (CQDs).³⁴⁻³⁵ Owing to the effects of quantum confinement, the bandgap of QDs can be controlled by simply changing the size of the nanocrystals, rather than changing the material composition. This creates the potential for QD materials to have their bandgaps tuned across nearly the entire solar spectrum. An

example of this ability is presented in **Figure 1-3** for PbS QDs in particular, in which all but a small portion of the near-infrared (NIR) region of the solar spectrum can be absorbed by the indicated particle diameters.³⁶ In the simplest case, the ease with which the bandgap can be tuned in QDs allows a researcher to match the absorbance of the material with a desired wavelength to maximize efficiency. For a single junction solar cell, the ideal bandgap is ~1.1 eV.¹⁴ Expanding upon this property further, different sized particles of the same material may be used in a single device to absorb a higher percentage of the solar spectrum. The method can be implemented by building up layers of different size in the appropriate order, without the need for a multijunction device.³⁷ By absorbing a larger portion of the solar spectrum, device efficiencies can be increased to a maximum of 66% in QD materials by using an infinite stack of bandgaps.^{36, 38} Another advantage of CQDs is the ability to exchange the native ligands used to synthesize the particles for a wide variety of ligands suitable for many applications. Through ligand exchange interdot interactions and surface properties can be tuned.³⁹ Furthermore ligands have been found to control the energy levels of the conduction and valence bands of ODs without effecting the



Figure 1-3. Absorption spectrum of PbS quantum dots of various sizes overlapping with the solar irradiance spectrum. Reproduced with permission from reference 36.

bandgap (**Figure 1-4**).⁴⁰ This ability to continually tune the bandedges relative to vacuum provides a synthetic route to appropriately match the QD active layers energy levels to the work functions of the contacts, increasing charge collection efficiency.



Figure 1-4. The measured conduction and valence band energies of PbS QDs with various ligands, highlighting the ability to tune the energy levels of QDs through ligand exchange. Reproduced with permission from reference 40.

In addition to the capability to control the bandgap and band energies of CQDs, these materials are also ideal candidates to undergo the processes of multiple exciton generation (MEG) and hot carrier extraction (HCE). MEG is similar to singlet fission in that multiple bandedge excitons are created in the QD from the absorption of a photon that has >2x the bandgap energy. Mulitple exciton generation occurs through an impact ionization (II) mechanism and it has been determined that by using higher energy photons, a greater number of excitons can be created (**Figure 1-5**).⁴¹ For instance, one study found that using soft X-ray photons with an energy of >7x the bandgap, a PbSe QD was able to produce 7 excitons for every photon absorbed.⁴² The ability to multiply carriers using MEG in QDs increases the potential J_{sc} of the device, yet the theoretical maximum efficiencies for MEG are the same as for singlet fission at ~44%.³⁸



Figure 1-5. Diagram showing the process of MEG for a QD. Reproduced with permission from reference 41.

In QDs, the efficiency of II and therefore MEG is enhanced due to the confinement of electrons and holes which causes them to interact strongly with one another. Likewise, because the energy levels which comprise the valence and conduction bands are no longer bulk-like and are instead discrete (atomic-like), hot-carrier cooling is expected to be slow in QD materials. The energy separation between states is significantly larger than the energy of an optical phonon in the materials and therefore cooling via phonons is expected to occur via a low probability multiphonon scattering event. The prediction of slow-carrier cooling in QDs, due to the large energy separation of the band states has been termed the hot-phonon bottleneck, and results in the prediction that hot carriers can have extended lifetimes, onto the nanosecond and longer timescales. Because the rate of carrier cooling in QDs is predicted to be similar or slower than the rate of MEG, carrier multiplication (CM) should occur in these materials with high

efficiency. This implies that when a photon with high energies is absorbed by a QD, instead of rapidly relaxing to the band edge as it does in bulk materials, the energy is stored until II can occur forming a biexciton in the QD.⁴³

Another and potentially more exciting opportunity that arises from the prediction of slowed carrier cooling rates in QD materials is the potential to extract hot charges directly from a device known as hot carrier extraction. By employing HCE in a QD device, the V_{oc} is increased above what it would normally be for excitons at the band edge. This increase in V_{oc} results in a maximum theoretical efficiency for single junction device of 66%,⁴⁴ a significant improvement over SF and MEG mechanisms SF and MEG and nearly double the theoretical efficiency limit of first generation single junction devices.

Despite this potential application of MEG and HCE to overcome the Schockley-Queisser limit in QD solar cell devices, there have been few reports to date that have made working devices employing these processes. The major challenge of with both MEG and HCE is the absence of a phonon bottleneck in QD materials. Despite the prediction of slowed carrier cooling, observation of this phenomenon has proven to be difficult with few experimental reports measuring slow thermalization.⁴⁵⁻⁴⁶ In fact, carrier cooling rates in QD materials have been found to be as fast as or faster than themalization rates measuring in the bulk materials.⁴⁷⁻⁴⁹ The absence of a phonon-bottleneck implies that another cooling mechanism is activated in QDs which is able to facilitate rapid thermalization to the band edge. To create solar cells which are able to take advantage of HCE and MEG, the cooling mechanism in QDs must be identified so that the process may be eliminated from the material, either through new synthetic routes or post processing treatments. It is the main goal of this dissertation to identify and understand the key mechanisms which give rise to rapid-carrier cooling in PbS QDs, and to better understand their excitonic properties, in order to develop design rules which can be used to produce QD materials that exhibit slowed carrier cooling.

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CHAPTER 2

INSTRUMENTATION/TECHNNIQUE DEVELOPMENT

ABSTRACT: In order for scientific and technological advances to be made and reach the end users on relevant timescales, it is necessary that the appropriate research tools are made available to as many researchers as possible and which are capable of performing experiments under relevant *in situ* conditions. Failure to do so will result in slowed development of technologies that can solve many of society's greatest current challenges, along with potentially increasing the development costs of the technology. In order to facilitate in situ measurements in the field of solar energy conversion, a promising new technique known as electro-optical, pump-pushphotocurrent probe (P-P-PC) spectroscopy was developed and tested. This technique was specifically developed to be sensitive to minority species in samples and to determine the source of conducting states in PbS QD photovoltaic devices. Despite its application to monitor PV device characteristics, especially dark states, it was found to suffer greatly from experimental artifacts and complications which made the technique unsuitable for accurate scientific experiments. From the lessons learned through developing P-P-PC spectroscopy, it was determined that the laser intensities traditionally employed in transient absorption (TA) spectroscopy quickly degraded solar cell performance. Such high laser intensities have been used to determine much of what scientists believe is occurring in a solar cell materials under working conditions; actualities that may well not be true. These and other lessons learned from the development of P-P-PC spectroscopy resulted in the development of new technologies that improve the performance of nanosecond-to-millisecond, broadband transient absorption (ns-ms TA) spectroscopy by orders of magnitude. With these improvements to ns-ms TA spectroscopy, measurements are now possible without the need of high intensity laser pulses. In fact, taking

advantage of these technologies, TA measurements can now be readily conducted on PV materials under less than one sun equivalent average power and approaching less than 10x sun peak intensity. The low excitation energy densities needed for these new TA measurements may allow TA spectroscopy to be performed on working devices, without degrading device performance and allowing real *in situ* measurements of solar cell operation. Moreover, the methods used to improve the performance of ns-ms TA spectroscopy can be incorporated into commercially available instrumentation, enabling the production of high-sensitivity, low-cost, high-throughput ns-ms TA spectrometers. These spectrometers have the ability to increase the accuracy and efficiency of scientific measurement while increasing the availability of such an important analytical technique to a greater number of researchers across many disciplines. It is this increased access to state-of-the-art instrumentation by scientists that pushes the boundaries of scientific discovery and efficiency.

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2.1 Introduction

Many scientific and technology challenges face our evolving society, ranging from the treatment of diseases¹⁻³ to the development of sustainable sources for energy production.⁴⁻⁶ In order for researchers to tackle the challenges on the forefront of science and technology, they need to have access to the necessary tools and equipment capable of performing measurements under conditions which, as nearly as possible, reproduce *in situ* conditions. Without accessibility to the high-performance tools they require, researchers tend to find alternative methods to conduct experiments and obtain results, such as constructing 'home-built' instruments.⁷⁻⁹ Though the use of home-built instruments and finding alternative methods to conduct measurements may be beneficial to the academic development of young researchers, it typically results in slowed scientific progress, increased overall cost, and an increased likelihood of measuring experimental artifacts or false-positives/negatives.

The circumstances outlined above are especially true in the case of developing and improving solar energy conversion devices. Optimization of new photovoltaic and photocatalytic materials and devices requires the understanding and control of physical and chemical properties that occur under the influence of one sun's worth of energy. Large deviations from these *in situ* conditions can likely result in the monitoring of low probability characteristics or behaviors in the sample, which then lead to false interpretations of the events which occur under solar conditions. Incorrect interpretation of such artifacts even by a single scientist can have detrimental effects on the entire field, delaying progress and increasing costs. It is therefore imperative that new experimental methods be developed and high-performance instrumentation be made available to as many scientists as possible to help expedite scientific and technological discovery while keeping costs low. Furthermore, experimental artifacts that exist due to certain

techniques or practices must be identified and defined precisely, in order to educate researchers to their existence and help to avoid incorrect assignments.¹⁰



Figure 2-1. Two different predicted models for electron conduction in PbS QD devices. In the band-toband model, electrons are transported between band states, with wavefunctions localized on the core of the QDs. Trap-to-trap model predicts that localized trap electron density located at the QD surfaces mediate charge transport, possibly due to increased electronic wavefunction overlap between trap states on adjacent dots.

2.2 Ultrafast Pump-Push-Photocurrent Probe Spectroscopy

Ultrafast electro-optical P-P-PC spectroscopy was targeted as a new analytical technique that would be capable of measuring the behavior of electrons in working PV devices to identify the conducting species in a variety of solar cell materials.¹¹⁻¹² The specific aim of this technique's

development was to determine whether bright band states were the conducting species in PbS QDs, or if transport was mediated by dark states. This hypothesis was based on previous work, in which trap-to-band transitions were identified in PbS QDs in the mid-IR TA spectroscopy, and could therefore be selectively perturbed.¹³⁻¹⁴ Furthermore, trap states are localized at the surfaces of QDs and therefore predicted to have increased electronic overlap with neighboring QD states compared to confined core states (Figure 2-1).^{13, 15, 16} It was believed that this increased electronic wavefunction overlap could mean that trap states were actually mediating charge transport in PbS QD devices. Distinguishing whether band or trap states are responsible for conduction in PbS QD devices is not possible with existing TA spectroscopy and therefore a new technique needed to be developed. Using the P-P-PC, transitions in the QD could be selectively excited using a combination of pump and push ultrafast laser pulses and their effect on the photocurrent extracted from the device could be measured. Consequently, this technique would be sensitive to both bright and dark states in the QD devices. In addition to PbS CQD devices, this technique could have additional applications for many different types of PV materials, to determine the roles that various states play in charge transport in working devices.

Pump-push-photocurrent probe spectroscopy is analogous to traditional pump-push-probe spectroscopy,¹⁷⁻¹⁸ however instead of using a pulse of light to probe the materials properties, the photocurrent generated from the PV device is used as a probe. First, an ultrafast pump laser pulse impinges on the sample device, creating excitons. Because the sample is a working device, the excitons are able to dissociate into free electron and holes, which are transported to their respective contacts, and extracted from the device as photocurrent. The photocurrent generated from the pump pulse (PC_{pump}) is then amplified and converted to a photovoltage using a transimpedance amplifier, the output of which is fed into a digital oscilloscope, measuring the

photovoltage (V_{pump}) over time. The signal from the oscilloscope is then integrated to yield a single voltage value and recorded.

At some delay time (τ) after the pump laser pulse hits the sample, a second push laser pulse strikes the sample and is specifically tuned to the absorbing wavelength of a particular excited state species. In the case of PbS QDs, the push pulse could be tuned to the trap-to-band transitions, pushing electrons out of the trap states, and back into band states. The changes in the excited state properties of the material imposed by the push pulse, create either an increase or decrease in the measured photocurrent (PC_{push}) that is generated. This PC_{push} is recorded the same way that PC_{pump} is, and the values of PC_{pump} and PC_{push} are then used to calculate the change in photocurrent induced by the push pulse according to **Equation 2-1**.

$$\frac{\Delta PC}{PC} = \frac{PC_{pump+push} - PC_{pump}}{PC_{pump}} = \frac{\int V_{pump+push}dt - \int V_{pump}dt}{\int V_{pump}dt}$$
(2-1)

By varying the delay between pump and probe pulses (τ) in an analogous manner to ultrafast pump-probe spectroscopy, the time-dependent behavior of the species interrogated by the push



Figure 2-2. Simplified Jablonski diagram for the various transitions that can be analyzed for their effect on photocurrent in a PbS QD device using P-P-PC. The pump and push pulses can be selectively tuned to either the trap-to-band or intraband transitions. The change in photocurrent is measured as a change in voltage across a known resistor.

2-2 shows simplified Jablonski diagrams for P-P-PC on QD devices. The push pulse can be tuned to either the intraband absorption or to the trap-to-band transitions, allowing for distinct depopulation of either the trap states or of the band edge to determine the conducting species.

When performing P-P-PC spectroscopy, understanding the sign of the signals is extremely important. For example, if trap states mediate charge transport in PbS QD devices, then by tuning the push pulse to the trap-to-band transition will act to decrease the concentration of trap states which are the conducting states. This reduction in the concentration of conducting states should them cause a negative change in photocurrent. Alternatively, if traps do not conduct current and instead band states are responsible for photocurrent, then by pushing trap states into the band with the push pulse, there is an increase in the concentration of electrons in conducting states and an increase in photocurrent should be observed in the measurement (positive change in photocurrent). Without the ability to resolve the sign of the photocurrent, the technique is unable to distinguish the states which contribute to photocurrent. Accordingly, the P-P-PC technique that was developed utilized a specially designed, transimpedance amplifier to amplify the minuscule (pA) electrical current that was created from the test devices, and allowed for the sign of the signals to be determined. Furthermore, the amplifier that was designed for this specific minimized noise caused by electromagnetic interference (EMI) as much as possible, to enable the even smaller changes in photocurrent (0.01%) to be resolved.

Though in principle the technique is relatively straightforward, there were significant challenges to be overcome in order to create a functioning technique. The first problem that was encountered dealt with the stability of the PV device compared to thin film samples which are normally used in TA spectroscopy.¹⁹ In a working device there is, at minimum, a front

transparent contact, a back metallic contact, and the absorbing material. Oftentimes, there are other additional layers that are utilized in order to increase the device efficiency by adjusting contact work functions and controlling the direction of electron and hole migration. In TA, only the actively layer of the device is studied, and the remaining layers are not present in the sample. It was found that at the typical pump energy densities (>10s-100s µJ/cm²) utilized for TA spectroscopy, the lifetime of working devices was only a few laser shots.^{19, 20, 21} Rapid damage was found to occur in photovoltaic devices of PbS QDs, poly(3-hexylthiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM), and P3HT:poly((9,9-dialkylfluorene)-2,7-diyl-alt-[4,7-bis(alkylthiophen-5-yl)-2,1,3-benzothiadiazole]- 2,2-diyl (P3HT:PFTBT). As the samples were degraded, the measured photocurrent produced by shining the laser on the sample was reduced until it was no longer observable on the oscilloscope, using the P-P-PC detection apparatus. The



Figure 2-3. Transient absorption traces of the polaron in a P3HT:PCBM device at 1-10 and 51-60 hours of continuous pump and probe beam exposure. The absence of a significant change in the intensity or the decay rate implies that the active layer is unchanged over the course of the measurement.

damage that occurred to the devices was not just local damage due to burning the sample with the laser beam, but the entire device was degraded. Simply moving the laser to a new spot on the sample did not improve the measured photocurrent. Further analysis using a home-built solar simulator that illuminated the entire device, showed that, once degraded, the device lost all diode characteristics.

To determine the cause of the sample device degradation, TA spectroscopy was performed on a P3HT:PCBM device in reflective probe beam geometry and the kinetic signature was monitored over a period of sixty hours. Sixty hours was the longest exposure time measured, since the laser system used to conduct the ultrafast pump-probe measurements became unstable.



Figure 2-4. P-P-PC signals measured using progressively lower pump energy densities on P3HT:PFTBT devices, and the resulting device lifetimes at the various laser intensities.

The integrity of the TA signal is therefore predicted to be maintained for more than 60 hours. The data from the earliest and longest TA scans are presented in **Figure 2-3**, and demonstrate that the kinetic traces of the earliest and longest sample exposure times are identical. This data suggests that the degradation in the samples is not a result of damage to the active layer in the device but due to deterioration of one of the other layers. The deterioration in device performance was likely a result of damage to the metallic back contact of the device or to the interface between the different contacts and the active layer. It is possible that the front contact was damaged by the laser pulses as well, however because the front contact is transparent, both laser pulses were expected to very weak absorbance in the conductive oxide contact material.

The degradation of the device functionality on a much faster timescale than deterioration of the active layer highlights one of the key challenges of this technique. **Figure 2-4a** showcases the significance of this degradation in the measured P-P-PC signal on a P3HT:PFTBT device. Each scan was approximately 5 minutes in duration with the signal intensity in **Figure 2-4a** being reduced by ~66% within that period. For the data shown in **Figure 2-4**, the pump pulses were set to 400 nm by frequency doubling the output of a Ti:Sapphire laser with a repetition rate at 1 kHz and a 100 fs pulse duration. The push pulses were tuned to 2,000 nm by using the idler output of an OPA pumped by the same Ti:Sapphire laser used for the pump. Pushing the sample at 2,000 nm delocalizes the polarons which form in P3HT:PFTBT, providing sufficient energy to depopulate electrons which are bound by the polaron, thus increasing photoconductivity.

In order to extend the lifetime of a device, long enough to collect a sufficient number of scans to average a signal, the pump laser energy density needed to be lowered. **Figure 2-4** demonstrates the iterative progression of lowering pump laser fluences on the sample, and measuring P-P-PC signals for as long as possible. By decreasing the lifetime of the pump laser

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by four orders of magnitude, the lifetime of a device could be extended by more than three orders of magnitude. In addition to lengthening the degradation time of the sample however, lowering the pump pulse energy density during P-P-PC also reduces the signal size, requiring longer sample averaging to resolve a signal. In order to build up sufficient signal-to-noise (S/N) for the P-P-PC signals shown in **Figures 2-4b** through **2-4d**, a significantly greater number of scans were averaged together. The need to increase the total number of scans to produce a signal resulted in a significant increase in the amount of time required to measure one kinetics trace at a single wavelength from minutes to more than 15 hours. The need to measure samples for such long lengths of time greatly complicates this technique and reduces its overall applicability to solve a wide range of problems for PV devices.

The complications which arise from sample device degradation and long scan times can, however, be overcome through meticulous experimental setup and monitoring of the scan over time. This increased time and effort is justifiable if the signals to be measured provide intriguing, new insights into materials behavior that could not be obtained using any other, simpler methods.



Figure 2-5. Comparison of TA and P-P-PC signals of the decay kinetics of polarons in a P3HT:PCBM device.

It was found however that the majority of the experiments that P-P-PC can perform are not unique. It turns out that P-P-PC spectroscopy does not provide significant insight into device properties that cannot be garnered using simpler, proven analytical techniques such as TA spectroscopy and pump-push-probe (optical) spectroscopy. This fact is supported by data shown in Figure 2-5 where a TA signature of a P3HT:PCBM devices is shown along with the P-P-PC trace. Using two different probe methods, both of the traces in Figure 2-5 report on the lifetime of the polaron in P3HT:PCBM. Moreover, the P-P-PC data reveals that upon destabilizing the polaron in P3HT:PCBM, photocurrent is increased as a result of increased electron mobility. This conclusion is a straightforward conclusion that does not provide any new insights into the mechanism of charge separation, transport, or extraction in the OPV devices, and has been understood as fact for decades. Furthermore, the TA signature measured required only a few hours of averaging to collect, whereas the P-P-PC decay trace required more than 20 hours to acquire, and still has very poor S/N. Therefore, this technique is only suitable to answer a few niche questions which remain on certain materials, such as the specificity of the conducting states in PbS QD devices. This lack of new material understanding in all but a few niche examples again hampers the widespread application of this technology.

In order to examine PbS QDs using the P-P-PC methods and determine the conducting states, all of the aforementioned issues had to be dealt with. After suitable changes were made to improve the device stability, along with the substantial learning curve to set up and conduct the experiments correctly, P-P-PC measurements were able to be successfully made on PbS QD devices. A transient signal of PbS QDs measured using P-P-PC is shown in **Figure 2-6** with 532 nm pump and 2,200 nm probe wavelengths. At time zero, there is a sharp decrease in the change in conduction of the sample, which is then followed by a Δ PC/PC signal that continues to



Figure 2-6. P-P-PC signal of PbS QD device capped with I/MPA ligands. The pump and push wavelengths were 532 nm and 2,200 nm, respectively.

decrease over the entire time-axis of the measurement (6 ns). Since preliminary experiments suggested that the push pulse was tuned to trap-to-band transitions, it was originally believed that this negative signal was caused by trap-to-trap transport in PbS QD devices. In this case, when the push pulse exited trapped electrons and pushed them back into the band states, the photocurrent was reduced due to a reduction in the concentration of electrons in conductive states. Moreover, it suggested that carrier trapping in PbS QDs occurred on both ultrafast and nanosecond timescales. Owing to the fact that these results were conducted to ensure that the results measured in the P-P-PC experiments were real.

In order for this technique to function properly, there are a series of theoretical assumptions that were made and needed to hold true. One of these assumptions is that only the pump laser should create photocurrent in the device. This is an assumption that was found to not hold true for the PbS devices measured, along with the OPV devices. In all of the devices, the push laser pulse created a significant photocurrent in the devices. The magnitude of the push

induced photocurrent was always larger the photocurrent measured with only the pump laser present. Such a large induced photocurrent by the push pulse was likely a result of the significantly higher energy densities necessary to measure a change in the photocurrent. Such high peak powers created by the ultrafast laser pulses could have easily driven nonlinear absorption processes in the sample or could have excited the active layer directly through a very weak absorption tail into the near-IR. It is also possible that, due to the high push laser intensity, that heat was generated in the device, resulting in an increased Fermi level and increase in the transient dark current of the devices.²² The final possibility is that a small fraction of the intense push laser pulse could be absorbed by the back contact of the device (Au, Ag, or Al) creating photocurrent directly in the metal.²³ It is important to note, that although measured photocurrent signatures were large due to the extreme sensitivity of the detection apparatus, the actual photocurrent generated in the device was extremely small, typically less than 1 pA. Therefore, any of the listed possibilities could have easily been responsible for the generation of photocurrent created by the push pulse. In order to conduct this measurement correctly, the pushinduced photocurrent needed to be subtracted from the data, resulting in a double difference experiment instead of a single difference experiment, further decreasing signal to noise and adding additional complications. Because this issue was identified early on, a subtraction protocol was incorporated into the P-P-PC technique and this artifact was subtracted from the PbS data in Figure 2-6.

Besides the issues outlined above, there was another challenge of the P-P-PC technique that was discovered. Owing to its high sensitivity and low photocurrent values, the measured signatures in P-P-PC spectroscopy are extremely susceptible to absorbed energy density of the pump laser in the active layer. Any slight deviations in the pump beam size, energy density, or pointing affect the P-P-PC signature immensely. **Figure 2-7** compares the measured signals from a poorly collimated pump beam with that of a well collimated pump laser. The energy density of



Figure 2-7. P-P-PC decay traces for a P3HT:PCBM device with a well collimated and poorly collimated pump laser

the pump laser pulse changes at the sample with the poorly collimated beam, which affects the number of absorbed photons in the overlap region of the pump and push pulses. With this slight change in absorbed photons, the number of electrons that are created is altered, thus affecting the measured change in photocurrent. From the example shown in **Figure 2-7** it is apparent that these slight changes in collimation can dominate the measured signals. Pointing and shot-to-shot instabilities of the pump and push lasers are also a major concern and have similar effects on the acquired data.

Analyzing the PbS QD, Δ PC/PC signal in **Figure 2-6**, it appears that there could be pointing or collimation artifacts which give rise to the constant decrease in the single intensity on the nanosecond timescale. Though possibly still present, all efforts were made to eliminate the chances of pointing and collimation artifacts being present in the data. Experiments were

conducted numerous times on the same and different PbS devices on multiple different days and all showed identical P-P-PC signals. For this reason, it was believed that these types of artifacts were not present in the measured change in photocurrent on the nanosecond timescale.

In addition to pointing and size stability issues of the pump laser, the technique is also extremely susceptible to changes in the refractive index of the various layers within the device. When the pump or push laser is absorbed by the material, the refractive index is affected due to



Figure 2-8. Diffuse transient reflection and transient reflection measurements of (a) ITO and FTO glass compared with neat glass substrates and (b) a PbS QD device stack. Measurements were conducted with 532 nm pump and 2,200 nm probe laser wavelengths.

the rearrangement of the electronic structure in the excited state. ²⁴ Furthermore, even very slight changes in temperature of the device can impact the refractive index, which has already been identified as a potential issue. The pronounced changes in refractive index are the principles underpinning photothermal deflection spectroscopy. ^{25, 26} A slight change in the refractive index of the device can modify the absorption and quality of overlap of the laser pulses by the sample affecting the number of carriers created and the amount of photocurrent measured. For instance, a reduction in the absorption of the push pulse that is modulated by a change in the refractive index of the pump pulse would appear in the P-P-PC experiments a change in photocurrent. This measured $\Delta PC/PC$ signal does not report on the change in photocurrent of the state under investigation, and is instead an artifact that cannot easily be subtracted from the data.

In order to identify this type of artifact in the data, transient reflectance and diffuse transient reflectance measurements of the push/probe pulses were performed on various of the devices using 532 nm pump and 2,200 nm push wavelengths, identical to the P-P-PC experiments on PbS QDs (**Figure 2-6**). Diffuse transient reflectance measurements for glass, blank fluorine-doped tin oxide (FTO), and indium tin oxide (ITO) substrates are shown in **Figure 2-8a**. From these data, it is apparent, that both FTO and ITO glass slides produce appreciable changes in the amount of scattered light, whereas glass does not have a measurable signal. These changes in reflectance resemble the longer timescale signals of the P-P-PC signals measured on PbS QD devices which utilized ITO as the transparent contact.²⁷ Further experiments on PbS QD devices revealed additional artifacts which may be present in the P-P-PC signal (**Figure 2-8b**). The change in the diffuse reflectance of the QD device was measured in between the contacts of the device and therefore eliminated the FTO and Al layers from the measurement. The signals created for this case are a result of either the PbS active layer itself or

from a thin layer of TiO_2 that was added to the devices to increase electron extraction. By performing transient reflectance measurements directly on the device itself, a different signal could be measured that represented another artifact that was present in the measurements.

While these changes in refractive index must be present in TA spectroscopy, they are



Figure 2-9. Transient reflectance measurement and transient photocurrent traces of a working PbS QD devices. The P-P-PC signal needed to be scaled to compare with the change in reflection due to the inability to measure transient reflectance kinetics at similar pump energy densities used for the electro-optical measurements.

likely minimized due the large optical signals that are measured on thin film samples without additional layers that are present in a device stack. Due to the large changes in refractive indices of the various layers in the device, it was found that P-P-PC spectroscopy was particularly susceptible to these types of artifacts and dominated the measured signals. This is made very apparent by **Figure 2-9** in which the change in reflectance of the device stack is shown along with a scaled Δ PC/PC signal. The two signals are remarkably similar, but with opposite signs. The change in photocurrent has an opposite sign than the change in reflectance because the pump pulse decreases the absorbance of the push/probe pulse by increasing the amount of reflected

light. This reduction in the number of photons absorbed results in a decrease in photocurrent measured from the device. Thus, the P-P-PC signals that were measured for PbS QDs were determined to be not caused by trap-to-trap transport, but by an artifact inherent to the technique, which could not be eliminated without further complicating the technique and introducing greater error.

Additional support for the assignment of the P-P-PC signal in PbS QD devices to not be caused by trap-to-trap transport came when it was determined that the push pulse used was not tuned to trap-to-band transitions, but resulted in intraband transitions. Later work done on these PbS materials identified the 2,200 nm push pulse to be resonant with a higher energy intraband transitions. Details on the assignment of these transitions can be found in **Chapter 3** of this thesis. QD synthesis and passivation techniques have been improved since the preliminary work was conducted on PbS in the lab, and these new techniques yield high quality QDs which minimize the concentration of trap states. ^{27, 28, 29} Because the materials that we studied have been used to produce some of the highest performing QD devices, these materials were expected to have very low trap concentrations. In fact, upon further analysis these PbS QDs did not exhibit any trap-to-band transitions in the NIR or mid-IR. Without the ability to push trap-to-band transitions the P-P-PC method became an answer looking for a question. With the loss of the niche experiments that P-P-PC spectroscopy was targeted for, along with the artifacts and challenges associated with the technique, it was decided that electro-optical spectroscopy was no longer worth pursuing. Instead TA spectroscopy would be used to study PbS QD materials for solar cell applications. Despite the failures of P-P-PC spectroscopy, lessons learned throughout the development of the technique would be utilized to revolutionize TA spectroscopy, unlocking

the possibility to target new problems on the forefront of science and technology with high sensitivity, accuracy and speed.

2.3 Broadband Nanosecond-to-Millisecond Flash Photolysis Spectroscopy

In order to better understand the electronic properties of PbS QDs in their excited state, ns-ms TA measurements were performed. Ns-ms time-resolved spectroscopy is an instrumental technique that enables the measurement of dynamics occurring in a plethora of chemical, biochemical, and materials chemistry systems. ^{19, 8, 7} Such dynamics lead to unique, significant insights into the molecular-level qualities that lead to their ultimate physical and chemical properties, which cannot be directly assessed by alternate experimental means. For example, numerous physical and chemical processes occurring on the nanosecond-to-millisecond timescale, such as charge trapping, charge recombination, and charge/energy transfer in solar cells, can be monitored.^{11, 30, 31, 32} Routine TA techniques include ultrafast pump-probe spectroscopy and time-dependent steady-state spectroscopy, ^{33, 34} which can only access physical and chemical changes occurring on femtosecond to early nanosecond or hundreds of milliseconds-and-later timescales, respectively. These technologies have been extensively developed with widespread commercial products available. Nanosecond-to-millisecond TA on the other hand has not been a widespread technique, with no commercial instruments having the capabilities needed to measure the PbS signals. Therefore, there was a need to develop a homebuilt spectrometer that met the necessary requirements.

The kernel of all the limitations that scientists have faced when implementing nanosecond-to-millisecond TA spectroscopy is the miniscule signal sizes provided by measuring subpopulations within the sample. The small signal sizes arise from the requirement to investigate samples using the lowest excitation laser fluences possible in order to avoid sample degradation and to follow physical and chemical processes within a linear signal response regime. The need to use significantly lower pump energy densities for TA was one of the main takeaways from the development of P-P-PC. Having to lower pump energies creates the requirement of a high-sensitivity instrument, whose detection system increases the absorption S/N ratio to unprecedented levels. Because the signal size is limited by the sample and the experimental conditions,³⁵ the primary criterion for this technology was the development of noise suppression techniques.

Thus far, using available technologies, scientists have succeeded in implementing sensitive time-resolved spectroscopy using unique noise-suppression strategies in ultrafast pumpprobe (femtosecond-to-early-nanosecond) and time-dependent steady-state spectroscopy (hundreds of microseconds-and-later) instrumentations. These noise suppression strategies are either not available or are severely limited to implementation in nanosecond-to-millisecond instrumentation. In particular, ultrafast pump-probe spectroscopy generally employs a gatedintegrator or lock-in amplifier detection scheme that suppresses noise using electronic bandwidth limiters and boost signals by enabling isolation and integration of detected signals over specific time periods. Such detection schemes have been successfully employed in the past for nanosecond-to-millisecond time-resolved spectroscopy, however, the number of scans needed to improve S/N is severely limited because the acquisition of the signal across the entire nanosecond-to-millisecond time window ("time-sampling") takes an impractical amount of realtime. This, in turn, leads to poor detection sensitivity. In addition, ultrafast pump-probe spectroscopy further increases S/N by increasing the signal level (S) through the use of high peak power lasers. High peak power lasers employed for this type of spectroscopy are quite large, complex, and expensive and thus limit their application almost exclusively to large academic

institutions throughout the world. On the other hand, time-dependent, steady-state spectroscopy has overcome the S/N problem through a variety of alternative methods. An example of such a strategy is the incorporation of a Michelson interferometer into the detection system, leading to the so-called "Fourier-transform infrared" (FTIR) spectroscopy instrument. Superior S/N strength is achievable through the measurement of the signal in the time-domain, which takes advantage of the interference characteristics of light waves used in the experiment. This measurement requires an oscillating translation motion of one of its optical components in order to generate interference patterns needed to collect signals. Because of this, the implementation of FTIR methods into the detection of signals with ns-ms time-sampling ability, while possible, is incredibly time-consuming and complex. Thus, the acquisition of an adequate number of scans to achieve sufficient S/N again requires impractical amounts of real-time sampling, leading to poor detection sensitivity.

A superior method for acquiring ns-ms, TA signals is flash-photolysis spectroscopy.^{36, 37} This method is advantageous because the detected signal is electronically time-resolved, allowing the sampling of time points across the ns-ms to be collected for a single laser pulse. Consequently, the acquisition time for a scan (containing all the time-samples needed) is very short by comparison to the ultrafast pump-probe and steady state techniques. However, the primary challenge for the flash photolysis method, fundamentally arising from the process of electronically time-resolving the signal, is the effective suppression of noise. Because it is electronically time-resolved, the signal cannot be integrated over time using gated integrators, electronic bandpass filters, or lock-in amplifiers, since these severely relinquish time-sampling and time-resolution. Thus, other methods for suppressing noise (not just improving S/N by increasing the number of signals averaged) are needed. To date, previous technology has

achieved mediocre sensitivities of >10⁻⁵ O.D.^{7, 35} Because of this, the application of nanosecondto-millisecond TA spectroscopy has been limited either to sample systems producing the highest signals, or to experiments in which extremely high energy laser-excitation conditions are employable. Limited experimental studies have merely avoided the noise suppression issues at the forefront of nanosecond-to-millisecond, TA spectroscopy by increasing the signal, often times at the cost of accurate/realistic data and damage to samples.

Drawing from the knowledge garnered during the development of P-P-PC in diagnosing



Figure 2-10. Venn diagram of the three major components/technological advancements which have been combined for high sensitivity TA spectroscopy. Outside of the Venn diagram are boxes which identify where the technologies were first developed, along with sample data collected when only two particular components are used. The center plot demonstrates the significant improvement in S/N when all three technologies are merged in the correct manner. (Note: all the collected data are transient absorption decays of PbS QDs and were collected under identical conditions other than eliminating the specified component from the instrument.)

and managing electrical noise, a major source of noise in flash photolysis measurements, new technology was developed for nanosecond-to-millisecond TA spectroscopy.³⁸ The technology was developed iteratively over the course of 5 years. The technology developed, incorporates three different noise suppression technologies in a unique manner to improve S/N by more than 100-fold compared to ultrafast pump-probe methods and more than 3 orders of magnitude improvement over to existing ns-ms TA spectrometers. The three technologies that were combined to produce the highest S/N ratio were the utilization of short-pulse width Nd:YAG lasers developed for laser engraving and micromachining, DC-coupled detectors along with high flux probe light sources extensively developed for steady state spectroscopy, and new digitizers with rapid rearm times originally established for the automotive industry. It is the collection of these three techniques in a novel manner that provides the excellent S/N ratio of the TA instruments. Figure 2-10 is a Venn diagram highlighting the intersection of the three technologies. In the center of Figure 2-10 is a TA decay trace of a PbS QD that was measured using all three technologies in concert with a pump energy density of 100 nJ/cm². The probe had a frequency of 2500 cm⁻¹ for this measurement which was tuned to the intraband transition in the QD and monitored the lifetime of the QD's band edge. This center decay trace is well resolved and took less than five minutes to collect. Around the outside of the of the figure are data that were collected on the same PbS QD sample under identical conditions and the same number of averaged scans, however having one of the noise suppression technologies removed. For the data displayed in the top center plot of **Figure 2-10**, digitizers with rapid rearm capabilities were removed and resulted in the measurement of noise only. There is no resolvable signal from this dataset. In the bottom left hand plot of Figure 2-10, the measurement was conducted with the use of short pulsewidth, high-repetition rate lasers. This data does exhibit a poorly resolved

decay signal of the QD, albeit with significant noise fluctuations superimposed on the signal of interest and the data took over two hours to collect. The final plot on the bottom right of **Figure 2-10** demonstrates a signal that eliminated the use of high flux probe light sources and DC-coupled detectors. While this signal does have lower intensity noise compared to the data collected without rapid rearm digitizer, the plot does not display and resolvable signal. These results highlight the fact that it is only the assembly of the three different noise suppression strategies that produce such high S/N ratios for TA spectroscopy. Furthermore, the improvements in S/N that occur by adding the different techniques is not an iterative process with linear improvements made with the addition of each method. Instead the methods work together in a cooperative manner to exponentially increase S/N.

After the discovery of the correct noise suppression technology was made, it was necessary to both qualitatively and quantitatively determine the improvements of the current technology of existing TA instruments. To determine the level of sensitivity of the instrument, pump power-dependent measurements were conducted on a PbS QD film, again probing the



Figure 2-11. Excitation energy-dependent mid-IR transient absorption measurements for a 3.2 nm diameter PbS QD film capped with oleic acid. The lowest energy measured was 38 nJ/cm² and the highest energy measured was 940 nJ/cm². All scan times were less than 1 hour. The blue curve corresponding to 38 nJ/cm² excitation energy density yielded a resolvable ~1 μ O.D. signal.

intraband transition in the mid-IR. As the energy of the pump laser is reduced, the corresponding concentration of excited state is also reduced, reducing the overall intensity of the TA signal measured. The power-dependent data is displayed in **Figure 2-11**, with the highest energy density measurements at 940 nJ/cm² and the lowest being 38 nJ/cm². The inset of **Figure 2-11** highlights that all of the energies measured produced signal intensities which were highly linear with energy density, indicating that nonlinear processes were not occurring during the measurements, as expected for such low pump energy densities. From this data, the standard detection limit (*SDL*) of the instrument was calculated using **Equation 2-2**, with intensity of signal at zero concentration (S₀) and the standard deviation of the blank (σ_{blank}).

$$SDL = S_0 + 3\sigma_{blank} \tag{2-2}$$

The detection limit for the instrument was found to be 100 nanoO.D. which is more than 100x smaller compared to most pump-probe instruments sensitivities as well as more than 1,000x better than commercially available TA instruments.

To further analyze the improvements made to the ns-ms TA method, the instrument utilizing the noise suppression strategy was compared to a previously built instrument in the literature. ^{7, 39} In order to conduct these comparisons, the instrument from literature was emulated using the instrumentation that was available. The results of these comparisons can be found in **Figure 2-12. Figure 2-12a** represents a polaron kinetic signal a film of P3HT:PCBM with a pump wavelength of 532 nm and probe wavelength of 2,200 cm⁻¹, measured using the emulated instrument from the literature, This kinetics traces was collected over a period of 8 hours and 350,000 laser shots were averaged together with no measurable signal, only a large amount of noise. This plot is in stark contrast to the data presented in **Figure 2-12b** in which the TA instrumentation using the three noise suppression technologies was used to measure the same

sample under identical conditions. This plot shows the ~20 μ O.D. change in absorbance that was measured, which is approximately two orders of magnitude smaller than the noise floor that was determined in **Figure 2-12a**. Furthermore, the same number of laser shots as the previously reported instrument were collected, however the new instrumentation was able to collect this data under 3.5 minutes.



Figure 2-12. Comparison of the signals measured on a P3HT:PCBM thin film sample using (a) and (c) an instrument which emulated prior state-of-the-art technology and (b) and (d) the technology developed using the combination of three distinct noise suppression technologies. The number of laser shots averaged were held constant at 350,000 for the kinetics traces in (a) and (b), whereas the scan time was held constant at 30 minutes for the spectra in (c) and (d).

In addition to analyzing kinetics traces on the same sample setting the number of scans equal to one another, the measured spectra of the two instruments were also compared, this time however the time of the scan was equal. These data are shown in **Figures 2-13c** and **2-12d**. What is very apparent between the two different 30-minute scans is that the technology that incorporates the three different noise suppression techniques in the proper manner has a much superior performance. Almost no signal can be resolved in the 30-minute spectrum of the prior instrument, whereas with the improved TA spectrometer, detailed analysis of the broad electronic signatures, as well as the infrared active vibrational modes (IRAVs) is possible.

The improvement which have been made to ns-ms TA spectrometers represent significant technological advances over existing technologies. With these technological achievements, the sensitivity of broadband nanosecond TA spectroscopy have been improved by orders of magnitude. With such high sensitivities, it becomes possible for pump laser intensities to be reduced to measure PV devices under significantly less extreme conditions than previously thought possible. It has been demonstrated that at energy densities needed for TA spectrometers implementing this new technology can be below one sun average power and approaching 10 sun peak powers at the sample and still measure appreciable signals. The lowest pump laser fluence TA measurements conducted used similar energy densities that were found to not degrade PV device performance in P-P-PC spectroscopy. The ability to measure appreciable signals at such low energies implies that TA can be performed on working devices without degrading performance or damaging the cell in any way. Moreover, the reduction of the pump laser fluence allows for new material systems to be studied, such a delicate biological samples which otherwise could not withstand the intense laser field needed for TA. Finally, because the sensitivity has been improved to such great extents, new signals can be resolved in many

different materials that have been buried beneath the noise floor of the experiments. Measuring these signals can have profound effects on our understanding of these material systems. The technology that was developed can be applied to commercial TA enabling high sensitivity, high throughput, low cost, robust TA spectrometers. With such potential, TA can become a much more widespread technique, driving scientific and technological achievements on the cutting edge of chemistry, biology, physics and materials science.

2.4 Conclusion

A novel approach to measure P-P-PC spectroscopy of trap states in PbS QD devices was initially developed using a specifically designed transimpedance amplifier. While this technique was successfully implemented on OPV and QD devices, the occurrence of experimental artifacts which could not be subtracted from the data, resulted in the absence of any significant conclusions that could be made from the measurements. It was these experimental artifacts and additional challenges that led to the abandonment of the technique. The time spent developing P-P-PC spectroscopy was not wasted however, and the insights gather while developing the technique were able to be applied to ns-ms, broadband TA spectroscopy. Using such knowledge, significant advances were made in the sensitivity and throughput of flash-photolysis spectroscopy resulting from the specific combination of three different noise suppression techniques. The development of this technology enables TA spectroscopy to measure new types of samples which have been previously immeasurable due to photo-degradation. Moreover, with such high sensitivity and throughput, TA spectroscopy can provide new insights in old materials through the ability to resolve signals that have been concealed beneath the noise floor of existing technologies. Finally, the techniques were developed can be incorporated in commercially available TA spectrometers to produce, high sensitivity, high throughput, robust, affordable instruments with the ability to grow access to this type of spectroscopy to a greater number of

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researchers. With the proper tools available to a large percentage of scientists, scientific and technological advances can be expedited reaching the end users of the technologies sooner, with the potential for long lasting societal impacts.

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CHAPTER 3

RESONANT RELAXATION IN LEAD SULFIDE QUANTUMS DOTS

ABSTRACT: Observations of the hot-phonon bottleneck, which is predicted to slow the rate of hot carrier cooling in quantum confined nanocrystals, have been limited to date for reasons that are not fully understood. Time-resolved infrared spectroscopy was used to directly measure and identify high energy intraband transitions in PbS colloidal quantum dots (CQDs). Direct measurements of these intraband states permitted detailed analysis of the electronic overlap of the quantum confined states that may influence their relaxation processes. In smaller PbS nanocrystals, where the hot-phonon bottleneck is expected to be most pronounced, relaxation of parity selection rules combined with stronger exciton-vibrational coupling leads to greater spectral overlap of transitions among the quantum confined states. This creates pathways for fast energy transfer and relaxation that bypass the predicted hot-phonon bottleneck. In contrast, larger, but still quantum confined nanocrystals, do not exhibit such relaxation of the parity selection rules and possessed narrower electronic states. These results are consistent of slower relaxation dynamics that have been measured in larger quantum confined systems. These findings indicate that, at small radii, electron-phonon interactions overcome the advantageous increase in energetic separation of the electronic states for PbS quantum dots. Selection of appropriately sized quantum dots, which minimize spectral broadening due to exciton-vibrational interactions while maximizing electronic state separation, is necessary to observe the hot-phonon bottleneck. Such optimization may provide a framework for achieving efficient hot carrier extraction and multiple exciton generation in CQD photovoltaic devices.

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3.1 Introduction

Lead chalcogenide colloidal QDs have been targeted as potential hot-carrier extraction or multiple exciton generation photovoltaic materials in particular because of their small bulk bandgaps and large exciton Bohr radius. These features lead to strong quantum confinement¹⁻² with large energy separations between the atomic-like states that are significantly larger than the energy of a single optical phonon in the nanocrystals.²⁻³ Such an energetic mismatch between the low frequency phonon spectrum and higher energy spacing between quantum confined energy states led to the prediction of a "hot-phonon bottleneck"⁴ for these materials.⁵ The corresponding reduction in carrier-phonon interactions was predicted to lead to the ability to overcome traditional thermodynamic limits to solar energy conversion by the direct utilization of hot carriers in hot carrier extraction devices⁶⁻⁹ or through multi-exciton generation (MEG) processes.¹⁰

The hot-phonon bottleneck has been predicted to be most clearly observed in smaller, more strongly quantum confined nanocrystals because the energy spacing between electronic states depends inversely on size. However, with the exception of a few notable examples,¹¹ most measured rates of hot carrier cooling from high energy states in quantum confined systems to the band edge are often comparable to, or faster than, the rates of thermalization in the corresponding bulk materials.^{4, 12-13} For the case of CdS/CdSe QDs, rapid carrier cooling has been shown to be strongly dependent on size, with faster relaxation rates occurring for nanoparticles with decreasing radius.^{12, 14} Although this observation is counter-intuitive, it has been explained in II-VI systems using an Auger mechanism in which energy from an electron in a higher energy state is transferred to a hole, which has a larger effective mass and therefore more closely spaced energy levels.¹⁴⁻¹⁷ The spacing of these hole energy levels is much closer to

the energy of bulk phonon modes and therefore the hole is able to efficiently cool to the band edge in a similar manner to thermalization in the bulk material, facilitating rapid cooling in these materials.

In contrast to CdSe and related II-VI systems, IV-VI nanocrystalline systems such as PbS and PbSe have nearly equal electron and hole effective masses, which should prevent the Auger cooling mechanism from causing rapid carrier cooling in these systems.^{2, 18} Yet, despite identical effective masses, rapid carrier cooling has also been observed in lead chalcogenide colloidal QDs¹⁸⁻²² for reasons that are not fully understood. Transient absorption (TA) spectroscopy has been used to probe hot-carrier cooling in colloidal QD systems by creating highly excited excitons and then following the growth of the intraband $1S_{e(h)}$ - $1P_{e(h)}$ transition in the mid-infrared (mid-IR)^{7, 10, 13, 23} that appears as charge carriers cool to the band edges. However, these studies did not directly probe the high energy states through which carriers cooled prior to reaching the thermalized band edges and thus identification of the carrier cooling process has been elusive. Because the underlying mechanism of carrying cooling in IV-VI quantum confined systems has not been identified, it has been difficult to develop design rules for how to control and limit these cooling processes.

Directly probing the higher energy quantum confined levels, such as $1D_{e(h)}$ states in PbS and PbSe systems has remained difficult because they exhibit symmetry forbidden electronic transitions from the $1S_{e(h)}$ excitonic band states.²⁴⁻²⁵ However, using high sensitivity TA spectroscopy²⁶⁻²⁸ it is possible to directly examine such higher energy in the mid-IR to near-IR on nanosecond timescales. This capability enables the observation of the formally forbidden $1S_{e(h)}$ -1D_{e(h)} intraband transitions. The absorption strength of the $1S_{e(h)}$ -1D_{e(h)} intraband transition

was found to be strongly dependent on the confinement energy of the electronic wavefunctions due to breakdown in symmetry of the QD lattice, consistent with previous reports.^{19, 20, 24, 29, 30}

The ability to directly measure the formally forbidden $1S_{e(h)}-1D_{e(h)}$ intraband transitions in quantum confined PbS nanocrystals enabled the investigation of the spectral linewidths and therefore the energetic overlap of higher energy electronic states in the strong confinement regime. The spectral linewidths of the quantum confined states were found to be dominated by homogeneous line broadening, which results primarily from vibronic coupling, especially on the nanosecond timescale of the experiments.^{2, 31-35} Through TA spectroscopy, it was found that the spectral density of intraband transitions in the smaller PbS colloidal QDs are significantly broader in comparison to larger diameter QDs. The spectral widths of the intraband transitions increase in width with a power-law dependence as the diameters of the nanocrystals decrease, with higher energy states being more strongly affected by decreasing nanoparticle size. These broad electronic transitions were determined to have significant overlap with one another, with smaller dots having a greater degree of overlap.

It is the combination of broken symmetry due to size-effects and enhanced excitonvibrational coupling that lead to resonant electronic relaxation pathways in the smallest, most strongly quantum confined PbS nanocrystals. These relaxation channels are suppressed in larger, but still quantum confined nanocrystals, because of their decreased vibronic coupling. These findings suggest that the fast carrier cooling dynamics observed in the most strongly quantum confined PbS and PbSe systems may be a result of resonant energy relaxation pathways.¹⁸⁻²⁰ The investigation outlined in this chapter indicates that there exists a balance between carriervibrational interactions and electronic energy level separation for QDs. It may be necessary to strike the optimal balance of these competing processes in order to reduce carrier cooling rates to maximize the potential for direct use of hot carriers⁶⁻⁹ or MEG.¹⁰ The study also reports new methodology to help identify new quantum confined systems that may exhibit lower vibronic coupling such as Type I and Type II core/shell architectures. These more complex nanostructures may be capable of more efficient charge carrier multiplication for device applications through reduction of disorder at their surfaces and therefore minimizing exciton-vibrational coupling in semiconducting nanocrystals.³⁶⁻³⁹

3.2 Elucidating Excited State Electronic Transitions

Colloidal QD films of PbS nanocrystals, capped with oleate were prepared by spin-casting from concentrated solutions onto CaF_2 substrates with a thin mesoporous alumina adhering layer and were characterized using visible to near-IR absorption, TA, and photoluminescence (PL) spectroscopies. Films of PbS colloidal QDs capped with the native oleate ligands were studied since the long insulating ligands inhibit charge transport and electronic coupling among the nanocrystals.⁴⁰⁻⁴¹ In addition to films, colloidal solutions of PbS in carbon tetrachloride at ~ 2 mg/mL concentration were examined to assess the potential influence of nanocrystal aggregation on the electronic states measured in the films and to clearly identify intrinsic electronic transitions in the QDs. Represented in **Figure 3-1** are nanosecond broadband transient absorption spectra measured in films of PbS colloidal QDs of varying sizes/bandgaps. The spectra are represented on an energy scale in electron-volts (eV) and reflect the transient electronic states in the oleate capped PbS QD film following optical excitation at 532 nm and 15 μ J/cm² absorbed energy density per pulse. Figure 3-2 depicts the broadband TA spectra of colloidal solutions of PbS QDs measured under identical conditions as the films, and demonstrates the striking similarity of the solution data to the film data.

Steady state near-IR (NIR) absorption spectra of colloidal solutions of the PbS quantum dots used in the deposition of each film are included below each transient absorption spectrum for reference in **Figure 3-1**. The first excitonic transitions in the steady state NIR absorption spectra



Figure 3-1. Nanosecond broadband transient absorption spectra of four films of different size PbS QDs capped with oleate: (a) 2.9 nm, (b) 3.1 nm, (c) 3.7 nm, and (d) 4.9 nm. The red line shows the fit to the data using the sum of three log-normal functions representing the low frequency (violet) and high frequency (cyan) induced absorption features, along with the GSB (green). Vis-NIR absorption spectra are shown beneath the transient absorption spectra with log-normal fits (grey).Orange spheres represent the diameter of the QDs.

of the PbS colloidal solutions were fit using log-normal distributions and the central frequency of the fits represent an approximate optical bandgap and were utilized to calculate the diameters of the QDs examined. Log-normal distributions are common in the colloidal sciences due to a growth process that is size-independent and can be explained using Gibrat's law.⁴²⁻⁴⁴ The



Figure 3-2. Transient absorption spectra of colloidal solutions of PbS QDs capped with oleate ligands at 20 ns for **(a)** 2.9 nm, **(b)** 3.1 nm, **(c)** 3.7 nm, and **(d)** 4.9 nm diameter dots. Red lines show the fit to the data using the sum of three log-normal functions representing the $1S_{e(h)}$ - $1P_{e(h)}$ (violet) and $1S_{e(h)}$ - $1D_{e(h)}$ (cyan) transitions, along with the bleach (green). Orange spheres represent the diameter of the QDs.

diameters obtained from fitting the solution absorption spectra in **Figure 3-1** to PbS QD sizing curves established in the literature were 2.9 nm, 3.1 nm, 3.7 nm, and 4.9 nm.⁴⁵ Uncertainty in the optical bandgaps for the QDs led to an uncertainty in the sizes of \pm 0.1 nm. The diameters obtained from the absorption spectra were in agreement with high resolution TEM images collected from QDs deposited from the same stock solutions (**Figure 3-3**). The different size QDs will be identified according to their diameters in the remaining discussion.

The TA spectra in **Figures 3-1** and **3-2** span the entire near-IR to mid-IR spectral ranges and cover multiple electronic transitions in addition to the first excitonic transition of the PbS films. The spectra are shown at a time delay of 20 ns following pulsed excitation of the films. Excitation energies for all TA measurements were sufficiently low (< 0.1 photons/QD) to avoid nonlinear effects from the formation of biexcitons and trions, to eliminate excessive thermal loads on the samples, and to protect the samples from degradation throughout the experiments. The TA data are represented as open circles that are overlaid with fit functions composed of three log-normal line shapes that were used to describe the electronic transitions appearing in the spectra. The negative-going ground state bleaches (GSB) in the transient absorption spectra were very similar to the energies of the excitonic transitions of the corresponding absorption spectra of the colloidal solutions, indicating that assembly of the nanocrystals into the dense film had negligible influence on their electronic properties.

The functions used to model the TA spectra are of extremely high fidelity compared to the data. Only slight deviations between the data and fit functions occur on the lower energy side of the GSB peaks, which can be assigned to an induced absorption caused by the linear Stark effect.⁴⁶⁻⁴⁸ The second derivative-like shape of these absorption features in the transient absorption spectra were found to be not caused by thermal effects on the GSB that have been

identified in other systems.²⁶ Because of the low absorbed energy densities used in the measurements, sample temperatures were not expected to exceed a few degrees above kT, and therefore thermal signatures in the data were unlikely. In order to positively rule out thermal effects as the cause of the ESA feature on the low energy side of the GSB, temperature-dependent NIR absorption measurements were performed on the 2.9 nm QD film and the data is presented in **Figure 3-4**. The data shows that the optical bandgap shifts to higher energies when the temperature is increased, opposite to the trend observed in the TA data. This result indicates that sample heating during the experiment would result in an induced absorption on the high energy side of the bleach which is not present in the measurements.



Figure 3-3.TEM images for (a) 2.9 ± 0.3 nm, (b) 3.1 ± 3 nm, (c) 3.7 ± 0.4 nm, and (d) 4.9 ± 0.4 nm PbS QDs.

Similar positive signatures have been measured in the TA spectra of PbS QDs near the GSB. These signatures have been attributed to biexciton, trions or a linear Stark effect. Biexcitons and Trions rapidly recombine rapidly on picoseconds or faster timescales.^{17, 49-50} Since the TA data is measured at a pump-probe delay time of 20 ns, the spectral features on the low energy side of



Figure 3-4. (a) Temperature dependent Vis-NIR absorption spectra of a colloidal 2.9 nm PbS QD film capped with native oleate ligands and (b) difference spectra from kT.

the GSB must be a result of the linear Stark effect, which occurs as a result of the variation in the QD electric field when excited. The assignment of this positive feature on the low energy side of the GSB to a slight shift in the bandgap due to the linear Stark effect is consistent with previous reports.^{46, 48}

The broad positive-going features appearing in the mid-IR range of the transient absorption spectra of the PbS films in **Figures 3-1** and **3-2** exhibit a marked size-dependence of their transition energies, spectral widths, and asymmetries. The peak transition energies shift to lower values as the diameter of the QDs increases, which is expected for the size-dependent intraband transitions. Additionally, the widths of the transient absorption features narrow significantly with increasing QD diameter in accord with the changes in spectral widths of the first excitonic transitions measured in the absorption spectrum for each sample. Finally, the transient absorption features of the smallest quantum dots exhibit the greatest asymmetry, which decreases monotonically with increasing size (decreasing excitonic bandgap).

The broad ESA features of the quantum dot films and solutions cannot be adequately described by a single symmetric or asymmetric lineshape function within the experimental precision of the measurements. Evidence for the need for multiple functions to fit the data is presented in **Figures 3-5a-g. Figures 3-5a, 3-5c**, and **3-5e** correspond to attempts to model the data using a single log-normal, skew-Gaussian, and Gaussian function, respectively. These functions very clearly do not match the curvature of the data, and can be readily eliminated as appropriate models. **Figure 3-5b** shows the sum of two log-normal functions, which was chosen as the most appropriate model to fit the data and is included in **Figure 3-5** for comparison of the quality of the fit that this model has to the dataset. In addition to very high fidelity to the data, the sum of two log-normal functions also upholds physical relevance which will be described in detail shortly. In **Figure 3-5d**, the best fit for the sum of two skew-Gaussian distributions is shown. The quality of the fit is fairly good, although this model is not as strongly correlated with the data as the sum of two log-normal distributions. In addition to having a slightly different curvature than the data, skew-Gaussian distributions are not know to have any physical relevance

to colloidal systems, whereas log-normal functions are used to describe a size-independent growth processes as in the case for the QDs. For this reason the sum of two skew-Gaussians was not chosen as the correct fit to the data. Next, an attempt was made model the data with the sum of two Gaussian functions (Figure 3-5f) but was found to have very poor correlation with the data. In addition, the higher energy Gaussian function used to model the data extended below 0 eV in order to fit the broad linewidth of the high energy transition. A negative difference in energy between initial and final states is irrelevant, and from this observation, it was concluded that two Gaussians were not a suitable model. Finally, Figure 3-5g shows the sum of three Gaussian functions used to represent the data. Three Gaussian functions are able to reproduce the spectra quite accurately; however the quality of the fit is not any greater than that for the sum of two log-normal distributions. Since fitting the data with three Gaussians is a more complex model than fitting with the sum of two log-normal distributions, without improving the fit quality, the sum of two log-normal functions was chosen as the most suitable model to the data. Furthermore, no physical relevance was able to be determined from the relative energies of the three Gaussians used to model the data, again confirming that the model was insufficient to represent the data. In addition to requiring the fewest number of functions to accurately represent the data, log-normal distributions are known have significant physical relevance in colloidal sciences, and are consistent with size-independent growth processes.

Further support for the use of two functions to reproduce the TA spectra measured can be found through careful analysis of the curvature of the data. There is a change in curvature that is most pronounced in the 3.7 nm PbS film, which exhibits two concave-down regions around 0.25 eV and 0.65 eV (indicated by arrows in **Figure 3-1c**). These concave down regions are indicative of two separate, but overlapping transitions in the mid-IR region. The broad widths of the two



transitions observed for smaller diameter QD samples obscure these two concave-down regions,

Figure 3-5. Possible models and their fits to the experimental data of a 2.9 nm PbS QD film capped with oleate ligands with (a) 1 log-normal distribution, (b) sum of 2 log-normal distributions, (c) 1 skewnormal distribution, (d) sum of 2 skew-normal distributions, (e) 1 Gaussian function, (f) sum of 2 Gaussian functions, and (g) sum of 3 Gaussian functions.

but their asymmetric lineshapes indicate that a self-consistent model with two distinct transitions is needed to describe the transient absorption spectra of all QDs. Likewise, the largest diameter QD samples measured had very week higher energy ESA signatures, which hindered the observation of the two distinct concave down regions. The shaded functions appearing under the TA spectra in **Figures 3-1** and **3-2** represent the individual log-normal functions whose sum resulted in the best fit curves which are overlaid on the experimental data (red traces). The functions used to fit film and solution data were nearly identical with only slight deviations in the central frequency, width, and intensity. The similarity between the solutions and film data highlights the robust nature of the fitting parameters used.

The low energy ESA in the TA spectra of the oleate capped PbS QD samples was readily assigned to the $1S_e$ - $1P_e$ and $1S_h$ - $1P_h$ intraband transitions from comparison of similar electronic signatures from literature.^{13, 51} On the timescales of these measurements, all carriers are expected to have thermalized to the band edge of the QD and any multiexcitonic or highly excited electronic states present should have annihilated or relaxed well before the 20 ns time-delay.^{7, 12-13} Furthermore, intraband transitions from the $1S_{e(h)}$ - $1P_{e(h)}$ states⁵¹⁻⁵² of the PbS QDs of various sizes are predicted to occur at similar energies to that of the lower energy transitions in the TA spectra. To highlight this prediction, a plot of the central frequency of the functions used to model the low energy transitions *versus* the optical bandgaps of the QD samples is shown in **Figure 3-6a**, and reveals a linear correlation as expected from prior assignments.^{25, 53-54} The energy of these this intraband transition can be predicted by the K+P four-band envelope function model which describes the size-dependent changes of the electronic states within the quantum confined nanoparticles, as has been developed elsewhere.^{1, 55} Comparison of the predicted and observed $1S_{e(h)}$ - $1P_{e(h)}$ transition energies in **Figure 3-6a** (circles) demonstrates quantitative

agreement between the model and experimental values, confirming the assignment of the $1S_{e(h)}$ - $1P_{e(h)}$ transitions in the QD films. Due to the similarity of the functions used to model the solution data, the same assignment of the low energy ESA to the $1S_{e(h)}$ - $1P_{e(h)}$ transition can be made, and does not necessitate a separate plot. Because the effective masses of electrons and holes are nearly identical in PbS QDs, the $1S_e$ - $1P_e$ and $1S_h$ - $1P_h$ transitions predicted by the model are too similar to permit the assignment of the specific transition which best agrees with the measured values reported here. Higher spectral resolution or additional experiments would be needed to make an assignment of hole and electron specific transitions.

The need to fit the positive-going features in the transient absorption spectra with two lineshape functions indicates that the spectra contain contributions from another excited electronic process in addition to the $1S_{e(h)}$ - $1P_{e(h)}$ transition. The possibility that this higher energy transition arises from the absorption of trap states, as has been suggested from measurements of PbS QD films capped with various different ligands.⁵⁶ To test this hypothesis, the time-evolution of the various transitions present in the TA data of the 2.9 nm PbS colloidal quantum dot film were investigated as shown **Figure 3-6b**. A qualitative comparison of the TA spectra at different time delays revealed that there is no significant spectral evolution in the data, a trend that was consistent for all QD diameters studied as films and in colloidal suspensions (Appendix).

In addition to the qualitative analysis of the spectral changes over time, decay kinetics were also compared for the peak of the $1S_{e(h)}-1P_{e(h)}$ transition and higher energy ESA feature with the inverse recovery of the GSB peak of the 2.9 nm PbS film in **Figure 3-6c**. Overlaid on these decays is a photoluminescence (PL) trace measured on the same QD film capped with oleate ligands. The decay traces of the ESA and GSB signatures were found to be identical and precisely match the PL lifetime within experimental uncertainty. Moreover, the decay traces of

both the $1S_{e(h)}$ - $1P_{e(h)}$ transition and high energy ESA in the TA spectra match the bleach recovery and PL decays in solution and film samples for all size QDs investigated (Appendix). From these observations, the possibility of higher energy TA features arising from trapped-carrier absorption was effectively ruled out. If there were an appreciable concentration of trapped carriers within the samples then it is likely that the recovery of the GSB would occur more slowly than the radiative lifetime indicated by the PL decay. This is because the GSB peak is sensitive to both emissive and non-emissive trap states while the PL decay reports the kinetics of only the emissive excitons; trapped electrons or holes would recombine nonradiatively.²⁸ Furthermore, if



Figure 3-6. Characterization of ESAs for oleate capped PbS QD films. (a) Calculated $1S_{e(h)}-1P_{e(h)}$, and $1S_{e(h)}-1D_{e(h)}$ transitions as a function of optical bandgap with experimental data points obtained from fitting the low and high energy ESAs. (b) Transient absorption spectra collected at select time slices with specific wavelengths used for (c) kinetic decay comparison of the bleach, photoluminescence, $1S_{e(h)}-1P_{e(h)}$, and $1S_{e(h)}-1D_{e(h)}$ transitions. The various transitions are shown in (d).

the high energy transition centered at 0.88 eV in the 2.9 nm PbS film arose from trap state absorption, then it would be predicted to have a time-dependence that is markedly different from both the $1S_{e(h)}$ - $1P_{e(h)}$ transition at ~0.44 eV and the PL decay trace. Since all of the kinetic traces measured are in strong agreement, trap state absorption was ruled out as causing the observed excited state transitions. Moreover, it was predicted that significant trap concentrations would not be present for the oleate capped samples studied, due to the completeness of passivation of the native QD ligands.

Having eliminated the possibility of trap states giving way to the signals measured in TA spectra, it was hypothesized that the high energy transition spanning the mid-IR to NIR arose from the formally forbidden $1S_{e(h)}$ - $1D_{(h)}$ transition (Figure 3-6d). Reasoning suggests that the systematic variation of the intensities of these transitions in the quantum dot films may indicate some type of size-dependent symmetry breaking mechanism that caused these transitions to become weakly allowed. To test this hypothesis, the size-dependent, intraband $1S_{e(h)}$ - $1D_{e(h)}$ transition energies of QDs were calculated using the K•P model and were plotted versus the corresponding optical bandgaps in **Figure 3-6a** (blue data).^{1, 55} The calculated $1S_{e(h)}$ - $1D_{e(h)}$ transitions (dotted and dashed lines) are compared with the energies of the higher energy excited state transitions (circles) obtained from the log-normal fits of the TA data. The comparison reveals that the higher energy ESAs correlate quantitatively with the calculated $1S_{e(h)}$ - $1d_{e(h)}$ transitions of the PbS QDs. From this analysis it was also noted that the energy splitting between electron and hole specific transitions predicted from the K•P model for both the $1S_{e(h)}$ - $1P_{e(h)}$ and $1S_{e(h)}$ - $1d_{e(h)}$ transition is well below the energy separation between the lower and higher energy transitions in the data. This indicates that the appearance of the two distinct ESA features in the NIR to mid-IR region cannot be explained by separate hole and electron hole transitions. Instead,

the higher energy ESA feature is assigned to a completely different electronic process, namely the formally dipole forbidden $1S_e-1D_e$ and $1S_h-1D_h$ intraband transitions.^{18, 25, 51}

The low and high energy ESA features in the TA spectra of **Figures 3-1** and **3-2** will be referred to as the $1S_{e(h)}$ - $1P_{e(h)}$ and $1S_{e(h)}$ - $1D_{e(h)}$ transitions, respectively here and in the following discussion. Due to the breadth of the TA features and the similarity between the predicted electron and hole absorption energies, the splitting of the electronic transitions that may be due to electron *versus* hole specific intraband transitions were indistinguishable. Therefore, generic nomenclature of the transitions is upheld.

3.3 Relaxation of Parity Selection Rules

It was surprising that the $1S_{e(h)}$ - $1D_{(h)}$ transition was observed in the TA data, as this transition should be forbidden by the Laporte selection rule since the $S_{e(h)}$ and $D_{e(h)}$ states have the same parity.^{1, 24, 57} The observation of this absorption feature therefore suggests that a mechanism must exist which relaxes the dipole selection rules in nanocrystals, especially for the smallest diameter QDs studied. Though relaxation of parity selection rules has been identified previously in the ground state absorption spectra of PbS QDs, these measurements were unable to characterize the breakdown of selection rules for the excited state transitions in QDs and more specifically, the higher energy $1D_{e(h)}$ state.³⁰

Fortunately, the ability to directly measure the $1S_{e(h)}-1P_{e(h)}$ and $1S_{e(h)}-1D_{e(h)}$ intraband transitions in the mid-IR and NIR TA spectra permitted a systematic investigation of the sizedependence of the oscillator strengths of these transitions to help identify the underlying origin for the relaxation of the Laporte selection rule. **Figure 3-7a** represents a plot of the area of the line shapes used to fit the $1S_{e(h)}-1P_{e(h)}$ and $1S_{e(h)}-1D_{e(h)}$ transitions of QD films capped with oleaic acid films *versus* the volumes of the PbS QDs determined from their calculated radii. Similar analysis can be found in **Figure 3-7b** for colloidal PbS solutions. The area of the log-normal functions was used as an estimate for the relative oscillator strength of the different transitions. The areas of these line shapes have been scaled by the corresponding area of the GSB for each



Figure 3-7. Area of log-normal fits to the transient absorption spectra at 20 ns normalized to the area of the bleach for (a) oleate capped films and (b) oleate capped solutions in carbon tetrachloride. Solid lines represent the line of best fit for the data points to emphasize the linear relationships the trends.

size QD film in order to account for subtle differences in densities of absorbed photons or sizedependent extinction coefficients for the nanocrystals. Because the oscillator strengths of quantum confined excitonic transitions are known to vary with the volumes of the quantum dots,⁵⁸ this normalization scheme allowed for the isolation of the size-dependent changes to the oscillator strengths of the excited state transitions, and how these changes deviated from this expected volumetric scaling. Note that the areas of the GSB peaks in each quantum dot film were automatically scaled to unity because of this normalization scheme and were included in **Figure** **3-7** as a guide to the eye. Both film and solution analysis resulted in nearly identical results, confirming that the measured trend is strictly a result of QD size and is not caused by interdot interactions.

The variation of the areas of the intraband transitions in **Figure 3-7** attempts to quantify the size dependence of the oscillator strengths observed in the transient absorption spectra represented in **Figures 3-1** and **3-2**. It was found that the $1S_{e(h)}$ - $1D_{e(h)}$ transition has the greatest relative oscillator strength in the smallest PbS QDs examined herein, leading to the most asymmetric lineshape in excited state absorption spectra. As the sizes of the quantum dots increased, the oscillator strengths of the $1S_{e(h)}$ - $1D_{e(h)}$ transitions decreased with a corresponding increase of the oscillator strength of the $1S_{e(h)}$ - $1P_{e(h)}$ transitions. This variation is characteristic of 'oscillator strength borrowing' that can arise from coupled, nearly degenerate transitions that form a Fermi resonance⁵⁹ or from systems in which a break of symmetry allows a formally forbidden transition to become allowed. In the latter case, the break of symmetry can also suppress the oscillator strength of the normally symmetry allowed transitions. A break in symmetry would thus exhibit behavior that is consistent with the data.

Relaxation of selection rules has been predicted to occur in lead-salt QDs due to asymmetric wavefunctions that are amplified as the nanocrystal size decreases due to a shift of the center of the crystalline lattice away from the QD center of symmetry.^{19-20, 24, 29, 60-61} Relaxation of parity selection rules has been measured in PbS QDs using a combination of one- and two-photon absorption measurements in which asymmetric absorption features were characterized.³⁰ These studies investigated selection rules for the $1S_{e(h)}$ and $1P_{e(h)}$ energy levels of the QDs and showed that relaxation of parity selection rules present in PbS QDs, with small diameter nanocrystals exhibiting the most pronounced breakdown of parity. The relaxation of parity selection rules was

attributed to a breakdown in the wavefunction inversion symmetry, consistent with previous predictions.^{19-20, 24, 29, 60} Inversion symmetry breaking was demonstrated to be more pronounced for smaller QDs with smaller radii.³⁰ Such a size-dependent effect on the relaxation of selection rules is consistent with the experimental data in this study. Therefore the increase in absorption probability of the $1S_{e(h)}$ - $1D_{e(h)}$ transition is assigned to the relaxation of parity selection rules due to increased breaking of inversion symmetry of the electronic wavefunction with shrinking QD radii.

3.4 Size-Dependent Exciton-Vibrational Coupling

In addition to the size-dependent oscillator strength changes discussed above, the mid-IR TA measurements permitted the linewidths of the intraband transitions to be directly measured. The spectral widths of the intraband transitions include contributions from both homogeneous and inhomogeneous broadening. Inhomogenous broadening in the samples is largely mediated by the size-distribution of the nanocrystals.^{32-34, 62} This size-inhomogeneity has been alleviated somewhat in the experiments by synthesizing the QDs following procedures that result in a narrow size-distribution. While contributions from homogenous and inhomogeneous line broadening are present in the data, they can be discretely separated without the use of multidimensional spectroscopy. The widths of the GSB features in the TA spectra of the samples however, could be taken as upper limits on the contribution of inhomogeneous broadening to the lineshapes of the PbS films. If only inhomogenous broadening were occurring in the samples, and both intraband transitions are subject to identical QD size distributions, then the ESAs should have similar linewidths as the GSB feature. It was found that GSB peaks, however were significantly narrower than the both the $1S_{e(h)}-1P_{e(h)}$ and $1S_{e(h)}-1D_{e(h)}$ transitions, indicating that

homogeneous is playing a role in the linewidth of the ESAs. In fact, it was determined that homogenous broadening dominates the linewidths of these features.

Homogenous linewidths of electronic transitions in PbS quantum dots have been previously shown to be dominated by vibronic coupling, especially on the ~20 ns timescale on which the data was collected.^{2, 31-35, 63} Because this time scale is sufficient for the electronic states to relax to the lowest energy vibrational level of the QD band edge, the homogenous linewidth of the transitions is expected to be largely effected by vibronic coupling of the $1P_{e(h)}$ and $1D_{e(h)}$ states. On these long timescales, the influence of vibronic coupling on the $1S_{e(h)}$ states should be



Figure 3-8. Variances of the $1S_{e(h)}-1P_{e(h)}$, $1S_{e(h)}-1D_{e(h)}$ and bleach features from the fits to the TA data for different size oleate capped PbS QD (a) films and (b) solutions. Solid lines represent power law fits to the data points.

negated. **Figure 3-8** represents the variance (width parameter) of the log-normal functions used to fit the GSB peak and the $1S_{e(h)}$ - $1P_{e(h)}$ and the $1S_{e(h)}$ - $1D_{e(h)}$ transitions in the TA spectra of the PbS films and solutions *versus* the volume of the nanocrystals. Stronger exciton-vibrational coupling is expected in smaller nanocrystals because the confinement may increase the coupling of electronic and nuclear degrees of freedom.^{33-34, 62} Furthermore, stronger vibronic coupling may exist in smaller diameter QDs, due to an increased proportion of surface area relative to the volume of the QD. The surface of the QD is a likely candidate for strong vibronic coupling since many vibrational degrees of freedom exist from ligands and the deviation of the crystalline lattice away from the bulk. Stronger exciton-vibrational interactions are consistent with the sizedependent variance parameters observed in the data.

The size-dependence of the variance parameters of all three transitions for the solution and film data were fit using power law functions, similar to previous measurements of the homogenous line broadening in CdSe QDs with the form $\Gamma(V) = bV^{-n}$, where V is the volume of the QD, the y-intercept, b, accounts for size independent factors contributing to the linewidth, and the exponent, n, controls the size-dependent scaling of the linewidth.³³ The y-intercepts of the transitions in **Figure 3-8** were quantitatively higher for higher energy transitions and revealed that higher energy states are more strongly coupled to vibrational modes in PbS QDs than lower energy states. Size-independent sources of the vastly larger variances measured for higher lying states can be eliminated since the widths of the three separate transitions were measured in each QD. For every diameter QD measured, higher energy states consistently displayed greater exciton-vibrational coupling. As the diameter of the QD is reduced, stronger vibronic coupling is detected and most pronounced for the highest energy intraband transition measured. For the oleate capped QDs analyzed, the size-dependent variable (n) of the 15_{e(h)}-

 $1P_{e(h)}$ and $1S_{e(h)}$ - $1D_{e(h)}$ transitions was found to be double that of the GSB ($1S_{h}$ - $1S_{e}$). The larger value of n for these higher energy transitions indicates that vibronic coupling of these states is more dependent on diameter of the QD.

Previous work has suggested that longitudinal optical (LO) phonon modes in QDs interact strongly with electronic states. This type of coupling was identified through size-dependent



Figure 3-9. Calculated variances of the $1S_{e(h)}$ - $1P_{e(h)}$, $1S_{e(h)}$ - $1D_{e(h)}$ and bleach transitions measured in TA spectra highlighting the linear dependence on $1/R^3$ for oleate capped (a) films and (b) solutions. linewidth measurements of the ground state that scaled as R^{-3} .³³ A linear dependence on R^{-3} is consistent with the phonon coupling magnitude given by the Huang-Rhys factor proportional to the square of the Fröhlich interaction.⁶⁴⁻⁶⁵ When the calculated variances of the data were plotted against R^{-3} a linear trend consistent with the prediction of LO vibronic coupling was observed (**Figure 3-9**). Due to experimental uncertainty however, a positive assignment of vibronic coupling to LO modes cannot be made.

3.5 Resonant Energy Relaxation Circumvents the Phonon Bottleneck

Because the IR transient absorption spectra in **Figures 3-1** and **3-2** were measured at 20 ns time delay following optical excitation of the PbS QD films, the transient absorption features represent transitions originating from the same states, the $1S_{h}-1S_{e}$ bandedge exciton (**Figure 3**-

6d). In the one-electron picture, the energy of the $1P_{e(h)}$ state for a given size PbS QD can be approximated as the sum of the energies of the $1S_{h}-1S_{e}$ exciton (GSB) plus the energy of the $1S_{e(h)}-1P_{e(h)}$ intraband transition measured in the nanocrystal. The energy of the $1D_{e(h)}$ states of the PbS QDs can be similarly estimated using the corresponding $1S_{e(h)}-1d_{e(h)}$ intraband transitions.

The direct measurements of the line shapes of the intraband transitions in the various sized PbS QD films through broadband IR TA, permitted the estimation of the energy range spanned by the $1S_{e(h)}$, $1P_{e(h)}$ and $1D_{e(h)}$ states. From these estimations, it was possible to construct the energy diagrams represented in **Figure 3-10** and **3-11** using a relative energy scale for all oleate



Figure 3-10. Experimentally obtained spectral density for 2.9 nm, 3.1 nm, 3.7 nm and 4.9 nm oleate capped PbS QD films. The lineshapes and intensities were obtained directly from fits to the transient absorption spectra. Their alignment on the same energy axis is possible because the transitions share a common state, the 1Se-1Sh exciton. The 1S state energies (green) were set to 0 eV along the y-axis while the 1P (violet) and 1D (cyan) states remained unchanged, maintaining their respective energy separations from the 1S state.

capped PbS films and solutions, respectively. To do this quantitatively, the centers of the lognormal functions used to fit the $1S_h-1S_e$ excitonic absorption peaks for each size QD were aligned to the origin of a relative energy axis for each sample. The log-normal functions used to fit the $1S_{e(h)}-1P_{e(h)}$ and $1S_{e(h)}-1D_{e(h)}$ were then aligned to this zero energy point to capture the spectral overlap of the electronic transitions among the states. In the **Figures 3-10** and **3-11**, the lineshape functions used to fit the transient spectra are presented rather than the experimental data for clarity for film and solution data, respectively.

The widths of the spectral densities of each transition measured in the near-IR to mid-IR transient absorption spectra characterize the breadth of the transition energies between the states in the PbS QDs. Therefore, the energy spectra represented in **Figures 3-10** and **3-11** provide an experimental estimation of the widths of the densities of states of the $1S_{e(h)}$, $1P_{e(h)}$ and $1D_{e(h)}$ states. The spectral densities measured in the $1S_{h}$ - $1S_{e}$, $1S_{e(h)}$ - $1P_{e(h)}$, and $1S_{e(h)}$ - $1D_{e(h)}$ transitions include the absorption cross sections, which determines their amplitudes. Nevertheless, for spectral density to be observed at a particular transition energy, electronic states must be available for those transitions to occur, even if only transiently in the case of homogeneous broadening due to vibronic coupling. Therefore, the spectral densities measured in the three



Intensity from Log-Normal Fits to TA Spectra (a.u.)



Lower spectral density overlap

Figure 3-11. Experimentally obtained spectral density for 2.9 nm, 3.1 nm, 3.7 nm and 4.9 nm oleate capped PbS QD solutions for The lineshapes and intensities were obtained directly from fits to the transient absorption spectra. The 1S state energies (green) were set to 0 eV along the y-axis while the 1P (violet) and 1D (cyan) states remained unchanged, maintaining their respective energy separations from the 1S state.

different transitions can be utilized to identify the energetic distributions of the densities of states of the $1S_{e(h)}$, $1P_{e(h)}$ and $1D_{e(h)}$ states for oleate capped PbS QDs.

The energy diagrams represented in **Figures 3-10** and **3-11** highlight an important trend that provides insight about the possible origin of fast carrier cooling rates that have been measured in smaller, more strongly quantum confined PbS nanocrystals. Namely, the spectral density of intraband transitions in the smaller PbS colloidal QDs were significantly broader in comparison to the larger QDs. This increase in spectral width caused greater overlap of the density of states of the 1S_{e(h)}, 1P_{e(h)}, and 1D_{e(h)} states in both films and solutions consisting of smaller diameter PbS QDs. As a consequence, charge carriers initially excited to higher energy states could find resonant electronic relaxation pathways from $1D_{e(h)}$ to $1P_{e(h)}$ states and even from $1P_{e(h)}$ to $1S_{e(h)}$ states in the smallest dots studied, leading to the potential for rapid-carrier cooling. In contrast, the spectral density overlap creating these resonant relaxation paths is reduced in the larger, but still quantum confined, PbS QDs because of the decreased coupling of the electronic states to vibrational modes. This investigation reveals that the energy overlap of the electronic states is suppressed in the larger PbS QDs. A decrease of the electronic overlap of higher energy intraband states would be expected to slow the rate of carrier cooling in larger quantum confined systems, in accord with prior measurements of fast energy relaxation pathways in lead chalcogenide systems.¹⁸⁻²⁰ The data lead to the counter-intuitive conclusion that the more strongly quantum confined PbS nanocrystals actually exhibit more energetic overlap among their higher energy states, which increases overall pathways for fast electronic relaxation processes. This conclusion explains the phenomenon of faster carrier thermalization in smaller diameter PbS ODs.²¹

An implication of these findings has bearing on the selection of quantum confined systems that may enable more efficient utilization of MEG and HCE in solar cells. In particular, quantum confined systems exhibiting lower exciton-vibrational coupling such as Type I or Type II core/shell architectures³⁶⁻³⁹ may provide the opportunity to reduce structural disorder that often characterizes interfaces of nanomaterials by anchoring the surfaces of the nanocrystalline cores through covalent bonding to their shells. Such disorder can lead to greater coupling of electronic and nuclear coordinates. Consequently, core/shell architectures have the potential to reduce such coupling. Furthermore, if vibronic coupling is controlled by ligand vibrational degrees of freedom, then correct utilization of core/shell architectures can act to decouple the ligands from the exciton states of the QD. These findings suggest that continued investigation of more complex nanostructures may reveal approaches which can be utilized to develop next generations MEG and HCE photovoltaic devices.

3.6 Conclusion

Broadband IR TA spectroscopy²⁶⁻²⁸ was used to identify and examine the $1S_{e(h)}$ - $1P_{e(h)}$ and formally forbidden $1S_{e(h)}$ - $1d_{e(h)}$ intraband transitions in PbS CQDs of different sizes in order to gain insight about the origins of fast electronic relaxation processes that have been observed in quantum confined systems. The absorption strengths of the $1S_{e(h)}$ - $1D_{e(h)}$ transition features in the PbS QDs increased markedly with decreasing QD diameter. Within the strong confinement regime, a shift of the crystalline lattice away from the QD center breaks the symmetry of the wavefunctions that then relaxes the parity selection rules, causing the $1S_{e(h)}$ - $1D_{e(h)}$ transition to be allowed in smaller QDs. Taking advantage of the shape of the intraband spectral features, the spectral linewidths of the transitions were analyzed and related to the energetic overlap of higher energy electronic states in the strong confinement regime. The spectral density of the intraband

transitions in smaller PbS colloidal QDs was significantly broader in comparison to the larger QDs. This is because stronger confinement in the smallest nanocrystals enhances the excitonvibrational coupling. The increased spectral and energetic overlap of higher energy electronic states of the smallest PbS QDs leads to resonant energy relaxation pathways which effectively bypass the predicted hot-phonon bottleneck. The larger but still quantum confined nanocrystals investigated in this study exhibited decreased vibronic coupling and less energetic overlap of the higher energy electronic states. The size-dependent differences in the spectral and energetic overlap of higher energy electronic states in the PbS QDs were consistent with the variation of charge carrier cooling rates in PbS QDs of varying sizes.²¹ The study indicated that there exists a balance between carrier-phonon interactions and electronic energy level separation for QDs. Optimization of this balance will be necessary to reduce overall carrier cooling rates for device application. The investigation also highlights the development of novel experimental tools that can help identify new quantum confined systems capable of exhibiting lower exciton-vibrational coupling. Such new systems may enable more efficient charge carrier multiplication for high performance device applications.

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CHAPTER 4

SURFACES MEDIATE CARRIER COOLING IN LEAD SULFIDE QUANTUM DOTS

ABSTRACT: Electron-phonon coupling plays a significant role in rapid carrier thermalization that has made it challenging to observe the phonon bottleneck in PbS colloidal quantum dots (QDs). Two potential sources of this coupling include phonons of the QDs and their surfaces or vibrational modes of the ligands that passivate QD surfaces. Here, inorganic surfaces are found to be the principal source of phonons that broaden the density of excitonic states in PbS QDs and permit fast carrier cooling via resonant energy relaxation channels. Time-resolved mid-infrared spectroscopy reveals the differences in ligand surface chemistry and bonding in iodide/mercaptopropionic acid capped PbS QD films versus PbS QD films passivated with their original oleate ligands. Oleate ligands with only one surface active functional group undergo marked changes in bonding when PbS QDs are excited to higher energy states, indicating significant structural perturbation of the QD surfaces. However, the bidentate structure of mercaptoproprionic acid prevents this reorganization. Despite these differences in ligand surface chemistry and excited state properties, both types of PbS QD films exhibit identical carrier cooling rates and electron-phonon coupling strengths. The data suggest that surface modification techniques that reduce the coupling of electronic states to surface phonons may enable quantum confined structures with slower carrier cooling rates. Such surface modifications may include the use of thin inorganic shells or controlled composition gradients to reduce dangling bonds and tune the lattice strain at QD surfaces tailored for applications requiring efficient multi-exciton generation or hot carrier extraction.

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4.1 Introduction

Colloidal quantum dots (QDs) have attracted considerable interest in the optoelectronics device community due to their size-tunable electronic properties and potential in solution processed solar cells.¹⁻⁸ For example, solar cells which utilize QDs as a light absorbing layer have the potential to overcome the theoretical efficiency limit of single junction solar cells (~32.7%)⁹ through multiple exciton generation (MEG) or hot-carrier extraction (HCE).¹⁰⁻¹⁵ Both MEG and HCE processes reduce overall thermal losses in a device by utilizing the excess energy of high energy photons, yielding theoretical maximum efficiencies of $\sim 42-47\%^{2, 16-17}$ and $\sim 67\%^{18}$ respectively. However, achieving a high MEG or HCE photoconversion efficiency requires the lifetime of the hot-carriers in the QD be maximized, increasing the probability of either impact ionization or extraction before thermalization occurs.¹⁹ Quantum dots are theorized to be particularly well suited to extend hot-carrier lifetimes in a working device due to the large energy spacing between the discrete excitonic states that make up the conduction and valence bands of the material.²⁰⁻²² This energy spacing is significantly larger than the energy of a single phonon, causing cooling to occur in principle via a low probability multi-phonon scattering mechanism.^{20,} ²³⁻²⁴ This predicted slowed carrier cooling in QDs was thus termed the phonon bottleneck. ^{20, 24}

Despite the appeal of MEG and HCE in boosting photovoltaic device efficiencies, MEG and HCE devices have yet to reach their full potential. For example, several spectroscopic measurements of hot-carrier lifetimes have shown that hot-carrier cooling rates in both colloidal QDs and bulk materials are similar, suggesting that an effective mechanism exists in colloidal QDs that allows hot carriers to bypass the phonon bottleneck.^{19, 25-28} Auger recombination has been identified as a highly efficient pathway for carrier cooling in CdS and CdSe QDs, and significant efforts have focused on finding ways to circumvent this relaxation process by

decoupling the electron and hole from each other. ^{19, 29-30} However, unlike CdS and CdSe, the Auger mechanism is not expected to be an efficient cooling channel in PbS and PbSe QDs because of the similar effective masses of both electrons and holes within the material.³¹⁻³² Even though the Auger mechanism can be effectively ruled out as a significant relaxation pathway in PbS, the measured hot-carrier relaxation times in PbS semiconductor QDs are comparable to bulk PbS cooling rates, suggesting that another mechanism is responsible for rapid carrier cooling in this class of material.^{20, 33-35}

Size-dependent vibronic coupling to excitonic states has been demonstrated to be a possible route for carrier cooling in colloidal QDs.³⁶⁻³⁸ For example, a recent work on strongly quantum confined PbS QDs revealed that exciton-vibrational coupling activates resonant energy relaxation pathways within the nanocrystals, allowing charge carriers to rapidly thermalize to the material's band edge (see **Chapter 3**).³⁹ However, although the above mentioned work suggested that vibrational modes play a role in carrier cooling, a clear understanding of the source of this vibronic coupling remains elusive.

Significant effort has been spent studying the underlying mechanism of thermalization and vibronic coupling in CdSe QDs.⁴⁰⁻⁴⁴ For instance, early research on CdSe QDs proposed that excitonic states couple to the vibrational modes of surface ligands.⁴¹ That is, when the surfaces of the QDs were modified by ligand exchange, hot carrier lifetimes were extended. Recent studies have supported these earlier predictions, indicating that the ligands on the surface of CdSe QDs are vibronically coupled to excitonic states in the material's core.⁴⁵⁻⁴⁸ Though these efforts have provided evidence that the ligand vibrations may play a significant role in vibronic coupling to excitonic states, they suffer from the inability to elucidate the interplay between the vibrational dynamics of ligands and surface properties of the QD. In part, this is because ligands are known to control the electronic properties of QDs and therefore any modification of the ligands or surfaces will inevitably affect the electronic properties of the QD as well, complicating the assignment of vibronic coupling.⁴⁹⁻⁵³ Therefore, the ability to distinguish the vibrational degrees of freedom which couple to electronic states in PbS QDs is critical to understanding and controlling hot-carrier lifetimes in this class of material.⁵⁴

Using nanosecond transient absorption (TA) spectroscopy, the origins of phonons coupled to electronic states in PbS QDs of varying sizes and ligand chemistries were investigated. Combining electronic and mid-infrared spectroscopy enables the examination of the vibrational dynamics of distinct types of ligands at PbS QD surfaces and decouple these signatures from the broad electronic transitions of the excitonic states. This chapter builds upon work outlined in **Chapter 3** which demonstrated that electron-phonon coupling broadens the density of states in strongly confined PbS QDs and creates resonant relaxation channels by which highly excited electronic states can cool to the band edges.³⁹ The work in this chapter reveals the origins of the phonon modes that cause such broadening, which identifies pathways to overcome the associated fast cooling.

Time-resolved mid-IR spectroscopy was used to examine changes of the ligand surface chemistry and bonding to nanocrystal surfaces of PbS QD films passivated with iodide/mercaptopropionic acid (I/MPA) ligands *versus* PbS QD films passivated with their original oleate ligands. The data reveal significant changes of bonding of the carboxylate groups of oleate ligands when the QDs are optically excited to their excitonic states, indicating that their surfaces undergo significant structural perturbation upon excitation. The bidentate structure of MPA ligands prevents such bonding changes because of their additional anchoring through the thiol groups. Despite these differences of ligand surface chemistry, PbS QD films passivated

with both types of ligands exhibit carrier cooling rates and electron-phonon coupling strengths that cannot be distinguished within experimental precision. Furthermore, while the electronphonon coupling strengths that broaden the density of electronic states are strongly size dependent, the transient vibrational features of both types of ligands do not depend on size. This indicates that the vibrational modes of the ligands do not figure prominently in the phonons that are coupled to the excitonic states in PbS QDs. Instead, the perturbation of the oleate ligand surface chemistry in the excited state suggests that surface phonons of the PbS QDs are strongly coupled to the excitonic states and that the size dependence of the density of states is a consequence of the coupling of excitonic states with the QD surfaces. It is likely that surface modifications such as thin inorganic shells or controlled composition gradients may be effective means to slow the rates of carrier cooling in PbS QDs. These modifications may reduce the coupling of excitonic states with surface phonons by tuning the strain and removing dangling bonds at surfaces away from core electronic states to enable applications where efficient multiexciton generation or hot carrier extraction are required.

4.2 Steady State Properties of PbS Quantum Dot Ligands

To determine the origins of the phonon modes coupled to the excitonic states of PbS QDs, nanocrystalline thin films were examined due to the ability to exchange the native oleate ligands for I⁻/MPA. Oleate capped PbS QDs were synthesized and cast from octane, onto BaF₂ substrates coated with a thin mesoporous alumina adhering layer. Iodide/mercaptopropionic acid treated films were prepared using the ligand exchange procedure detailed previously.⁵⁵ All films were cast in air and immediately placed into a sealed cryostat under nitrogen atmosphere for all optical measurements. The diameters of the QDs measured were found to be 2.9 nm, 3.1 nm, 3.7

nm, and 4.9 nm, determined by fitting the visible/near-infrared (Vis/near-IR) absorption spectra and confirmed through high-resolution TEM images (see **Figures 3-1** and **3-3**).

Both the original oleate ligands and MPA have surface active carboxylate groups that bind to PbS surfaces and exhibit distinct vibrational signatures corresponding to the various bonding geometries they can adopt. **Figure 4-1** illustrates three common bonding geometries that carboxylates can adopt when they interact with metals.⁵⁶⁻⁵⁷ The bridging and chelating geometries are characterized by symmetric v_{sym} and antisymmetric v_{as} stretch modes that differ in frequency by approximately 150 and 100 cm⁻¹, respectively. The unidentate bonding geometry possesses formal double-bonded C=O and single-bonded C-O moieties with a much larger frequency difference $v_{C=O} - v_{C-O}$ near 300 cm⁻¹.



Figure 4-1. Illustrations of common carboxylate binding motifs and the corresponding frequency differences of their symmetric and antisymmetric stretch modes.

Vibrational features corresponding to these bonding geometries appear in the Fourier transform infrared (FTIR) spectra of the oleate and Γ /MPA passivated PbS QD films examined here (**Figure 4-2**). Vertical lines serve as guides to the eye highlighting the lower frequency v_{sym} stretch of carboxylate groups around 1400 cm⁻¹ and the v_{as} stretch around 1525 cm⁻¹ in **Figure 4**-

2a. The vibrational signatures of the bridging and chelating geometries are not well resolved in the oleate passivated films across the range of PbS QD sizes from 2.9 nm to 4.9 nm. The spectra have been offset for clarity. The long aliphatic chains of the oleate ligands contribute a C-H bend



Figure 4-2. Cartoons depicting the structures of oleate and I⁻/MPA ligands and their interactions with PbS quantum dots. FTIR spectra of four different size PbS QD films with (a) oleate ligands and (b) treated with I⁻/MPA. Distinct vibrational modes including symmetric v_{sym} and antisymmetric v_{as} stretches are labeled with corresponding structures. Bridging vibrational frequencies are identified with blue lines an chelating ligands identified using red lines.

vibrational feature between the v_{sym} and v_{as} modes. FTIR spectra of other prominent vibrational

modes including the aliphatic and alkene C-H stretch modes around 2900 cm⁻¹ appear in Figure

4-3.

The C-H bend feature does not appear in the FTIR spectra of the I/MPA passivated films (**Figure 4-2b**), which is consistent with quantitative removal of the oleate ligands by the ligand exchange chemistry in the solid state as previously reported.^{58 59}Again, the spectra have been offset for clarity. Furthermore, the v_{sym} and v_{as} vibrational features of bridging and chelating



Figure 4-3. Full FTIR spectra for 2.9 nm diameter PbS QD films capped with oleate and I/MPA ligands.

bonding geometries are more clearly resolved in the I/MPA passivated film, which demonstrates that both the thiol and the carboxylate groups of MPA molecules are attached to the PbS surfaces. The bidentate structure of MPA on PbS is further confirmed by the absence of a S-H stretch mode around 2500 cm⁻¹ in the FTIR spectra represented in **Figure 4-3**. Because some of the Pb sites on the PbS surfaces are passivated by iodide ions in the I/MPA treated film, a fraction of MPA ligands interact with the QD surfaces only through their thiol groups. These MPA ligands give rise to the "free" carboxylic acid feature around 1700 cm⁻¹, which corresponds to the protonated form of the functional group. It is possible that a small fraction of MPA molecules may not be coordinated to PbS surfaces but may remain in the film after the washing steps. These may also contribute to the 1700 cm⁻¹ peak. Finally, the vibrational features around 1300 cm⁻¹ are indicative of a mixture of MPA molecules that either have free carboxylic acid groups or that engage in unidentate bonding of their carboxylate groups to PbS surfaces.

It is noteworthy that neither the FTIR spectra of the oleate or I'/MPA capped PbS QD films exhibit significant size dependence. This indicates that interactions the ligands have with the QD surfaces do not differ substantially with changing nanocrystalline size. The FTIR spectra of the oleate capped films were fit with Lorentzian functions corresponding to the v_{sym} and v_{as}



Figure 4-4. FTIR spectra for 2.9 nm diameter PbS QDs capped with oleate and I⁻/MPA ligands, highlighting the region of the v_{sym} and v_{as} vibrational frequencies. Dashed black lines show the individual Lorentzian functions used to fit the data (solid blue curves) and the solid green traces represent the sum of the Lorentzian functions.

modes of the bridging and chelating bonding geometries to quantify their relative populations (see **Figure 4-4**). From the intensity ratios of the bridging and chelating symmetric stretching frequencies in these samples, it can be estimated that ~70% of ligands adopt a bridging bidentate binding geometry in the ground state for oleate capped QDs, while ~60% of ligands adopt a bridging adopt a bridging geometry in the ground state of I/MPA capped samples.

4.3 Excited State Surface properties of PbS Quantum Dots

Transient absorption (TA) spectroscopy was used to characterize the spectral shapes of the excitonic transitions and the origins of the phonons to which they are coupled in PbS QD films of different sizes and passivated with different ligands. **Figure 4-5a** and **Figure 4-5b**



Figure 4-5. Transient absorption spectra recorded at 40 ns following optical excitation of PbS films at 532 nm and 10 μ J/cm². Films treated with oleate ligands with PbS quantum dot sizes of 2.9 and 4.9 nm are represented in **A** and **B**, respectively. The same size PbS quantum dots treated with I/MPA ligands appear in **C** and **D**, respectively. The excitonic and intraband transitions in the spectra are color coded with corresponding log-normal fit functions shaded under each peak. The smooth curves through the data represent the best fits to the spectra.

represent TA spectra measured 40 ns after 532 nm excitation of films of 2.9 and 4.9 nm PbS QDs passivated with oleate ligands. The spectra are plotted on an energy (eV) scale and span the mid-IR to the visible spectral region. Transient absorption spectra of the 3.1 and 3.7 nm oleate capped PbS QD films can be found in **Figure 3-1** while I/MPA may be found in **Figure A-19**. Three transitions are prominent in the spectra and are highlighted by shading: the negative-going bleach of the excitonic transition $(1S_h-1S_e)$, the $1S_{e(h)}-1P_{e(h)}$ intraband transition on the lower end of the energy scale, and the $1S_{e(h)}-1D_{e(h)}$ transition that spans the mid-IR to the near-IR spectral region (~0.2 - 1 eV). These assignments are based on analysis of similar spectra that were reported previously.³⁹

Figure 4-5c and **Figure 4-5d** represent similar TA spectra also measured 40 ns after 532 nm excitation of PbS QD films. However, these films were passivated with I/MPA ligands. The spectra were measured in films formed from the same 2.9 and 4.9 nm QDs that were used to

deposit the films capped with oleate ligands. The spectra exhibit subtle changes in the transition energies of the excitonic and intraband transitions that arise from stronger interactions between PbS QDs due to replacement of the long oleate ligands with much smaller Γ and MPA ligands. Such stronger interactions cause the Γ/MPA capped films to conduct electrical charges between QDs following photon absorption, which leads them to form some of the highest efficiency PbS QD devices.^{55, 60} Aside from these differences, the TA spectra of the Γ/MPA capped films are remarkably similar to the TA spectra of the oleate capped films. The spectra measured in films of both types of ligands exhibit the marked size dependence that was observed previously and that arises from the coupling of the excitonic transitions with phonons in the QDs.³⁹

The vibrational features of ligands attached to the PbS QD surfaces were examined in order to gain insight about the origin of the phonon modes that couple to the excitonic transitions. The grey shaded boxes in **Figure 4-5** highlight the spectral region below 0.2 eV where the carboxylate features of oleate and MPA ligands appear. Transient absorption spectra measured in this region between 1150 and 1800 cm⁻¹ in PbS QD films passivated with oleate ligands are represented in **Figure 4-6**. Vibrational TA spectra for PbS QD films treated with Γ /MPA are presented in **Figure 4-7**. The spectra exhibit narrow vibrational features that are superimposed onto broad electronic feature that arises from the $1S_{e(h)}$ - $1P_{e(h)}$ intraband transitions of the PbS QDs.

Figure 4-8a depicts the transient vibrational features obtained from the TA spectra of oleate capped films composed of PbS QDs of a range of sizes. The broad $1S_{e(h)}$ - $1P_{e(h)}$ intraband transition has been subtracted from the spectra in order to isolate the vibrational features. The FTIR spectrum of the 2.9 nm PbS QD film capped with oleate ligands appears below the transient vibrational spectra for comparison. The vertical lines in **Figure 4-8a** mark the

frequencies of the v_{sym} and v_{as} carboxylate stretch modes around 1400 and 1520 cm⁻¹, respectively. Vertical lines are also included as guides to the eye to mark where the doublebonded C=O and single-bonded C-O moieties absorb with frequencies $v_{C=O}$ and v_{C-O} around 1600 and 1250 cm⁻¹, respectively. These vibrational features are not prominent in the ground state FTIR spectrum but do appear in the transient vibrational spectra of the oleate capped films following optical excitation.



Figure 4-6. Transient absorption spectra measured at several delay times following 532 nm excitation of (a) 2.9 nm, (b) 3.1 nm, (c) 3.7 nm, and (d) 4.9 nm PbS QD films passivated with oleate ligands. The spectra consist of narrow vibrational features that are superimposed on broad electronic features corresponding to the $1S_{e(h)}$ - $1P_{e(h)}$ intraband transitions.

The pattern of transient vibrational features measured in the oleate capped PbS QD films reveal several photophysical processes occurring simultaneously following optical excitation. A prominent negative-going ground state bleach feature is observed between the v_{sym} and v_{as}

stretch modes of the carboxylate groups in the FTIR spectrum. Superimposed on this is a positive-going transient absorption feature that coincides only with the v_{sym} stretch mode. To understand this pattern of positive- and negative-going features, it is helpful to recall that the ground state bleach reflects the vibrational spectrum that the oleate ligands had before they were perturbed by formation of the excitonic excited state following the optical excitation. Therefore, the ground state bleach must include both the v_{sym} and v_{as} modes of the oleate ligands that are perturbed in the excited state. The ground state bleach feature can differ from the FTIR spectrum if there are overlapping transient absorption features that interfere with the negative-going bleach. It can also differ from the FTIR spectrum if a sub-population of oleate ligands on the PbS



Figure 4-7. Transient absorption spectra measured at several delay times following 532 nm excitation of (a) 2.9 nm, (b) 3.1 nm, (c) 3.7 nm, and (d) 4.9 nm PbS QD films with I/MPA ligands. The spectra consist of narrow vibrational features that are superimposed on broad electronic features corresponding to the $1S_{-0.5}$ - $1P_{-0.5}$ intraband transitions.

QDs is preferentially perturbed in the excited state while other sub-populations are not.

The pattern of vibrational features in the transient spectra in Figure 4-8a reveals that



Figure 4-8. (a) Vibrational TA spectra of PbS QD films capped with oleate ligands measured at 40 ns time delay. The broad electronic $1S_{e(h)}$ - $1P_{e(h)}$ transition has been subtracted from the data in order to clearly see the vibrational features. FTIR spectra for a 2.9 nm diameter QD are shown beneath the size-dependent spectra for clarity. Vertical lines mark the symmetric v_{sym} and antisymmetric v_{as} stretch modes as well as the single and double bond C-O stretch modes of unidentate binding geometries. **(b)** Cartoon depiction of how transition dipoles from symmetric v_{sym} and antisymmetric v_{as} stretch modes of carboxylate groups can interact with image dipoles from polarizable excited states.

oleate ligands having the smallest frequency difference between their v_{sym} and v_{as} stretch modes are selectively perturbed by optical excitation of the PbS QD films. These are oleate ligands that adopt the chelating bonding geometry to Pb atoms on the QD surfaces. This causes the ground state bleach feature to appear between the v_{sym} and v_{as} stretch modes in the FTIR spectrum, which includes contributions from oleate ligands adopting both chelating and bridging bonding geometries. The ground state bleach feature may include contributions from the C-H bend mode around 1460 cm⁻¹, but this narrow band is not resolved in the bleach feature. The data also reveal that the oscillator strength of the v_{sym} mode is selectively enhanced in comparison to its absorption strength when the PbS QDs are in their ground electronic state. Consequently, the superposition of the negative-going ground state bleach and the positive going transient absorption of the v_{sym} mode results in a net positive feature around 1400 cm⁻¹.

The selective bleaching of the v_{as} mode with corresponding enhancement of the v_{sym} modes in the transient vibrational spectra can be understood in terms of the effect of image dipoles in the polarizable excited state of the PbS QDs. It is helpful to recall that the exciton binding energy of bulk PbS is small in comparison to thermal energy at room temperature so that excitons readily dissociate to form charge carriers in bulk PbS. Quantum confinement of excitons in the few nanometer diameter nanocrystals examined here increases their binding energy. However, the delocalized nature of the excitonic states that leads to their small binding energy in the bulk causes their charge distributions to be highly polarizable even in quantum confinement. Such polarizable charge distributions lead to the formation of image dipoles in response to the presence of dipoles near the QD surfaces.

Figure 4-8b illustrates the effect that the transition dipoles of the v_{sym} and v_{as} stretch modes of carboxylate groups have on the formation of image dipoles in the excited electronic state of the PbS QDs. In particular, the transition dipole of the v_{sym} stretch is parallel to the bisector of the O-C-O bond angle. The image dipole formed in response to this transition dipole oscillates in phase and in the same direction (**Figure 4-8b**, left), leading to an overall enhancement of the oscillator strength of the v_{sym} when the carboxylate group adopts a near-

normal orientation with respect to the quantum dot surface. In contrast, the transition dipole of the v_{as} stretch is perpendicular to the O-C-O bisector. The corresponding image dipole oscillates at the same frequency but in the opposite direction, leading to suppression of the v_{as} mode. These interference effects give rise to the enhanced v_{sym} and suppressed v_{as} that appear in the transient vibrational spectra of the oleate capped PbS QD films.

Two additional transient absorption vibrational features appear in the oleate capped PbS QD spectra represented in **Figure 4-8a**. These features correspond to the double-bonded C=O and single-bonded C-O moieties that appear around 1600 and 1250 cm⁻¹, respectively. These vibrational features are indicative of the unidentate bonding geometry represented in **Figure 4-1** where the carboxylate group adopt formal C=O and C-O bonds. Note that the 1600 cm⁻¹ transient absorption feature is significantly lower in frequency than the absorption of free carboxylic acid groups, indicating that the oleate ligands contributing to this feature remain attached to the PbS QD surfaces in the excited state.

Taken together, the transient vibrational features of oleate ligands in **Figure 4-8a** reveal complex responses to optical excitation of PbS QD to their excitonic excited state. A fraction of oleate ligands that originally adopted chelating bonding geometries are perturbed, leading to the formation of more bridging and unidentate bonding geometries. Oleate ligands that either remain in bridging bonding geometries or that came to adopt this geometry following photoexcitation interact with image dipoles of the polarizable excited states, leading to enhancement of their v_{sym} and suppression of their v_{as} modes. In either case, the data reveal significant changes of the interactions that oleate ligands have with the surfaces of PbS QDs in the excited state in comparison to their interactions in the ground state.

Figure 4-9a depicts the transient vibrational features obtained from the TA spectra of I⁻/MPA capped films composed of PbS QDs of a range of sizes. As before, the broad $1S_{e(h)}-1P_{e(h)}$ intraband transition has been subtracted from the spectra in order to isolate the vibrational



Figure 4-9. (a) Vibrational TA spectra of PbS QD films capped with I[/]/MPA ligands measured at 40 ns time delay. The broad electronic $1S_{e(h)}$ - $1P_{e(h)}$ transition has been subtracted from the data in order to clearly see the vibrational features. FTIR spectra for a 2.9 nm diameter QD are shown beneath the size-dependent spectra for clarity. Vertical lines mark the symmetric v_{sym} and antisymmetric v_{as} stretch modes as well as the single and double bond C-O stretch modes of unidentate binding geometries. **(b)** Cartoon depiction of how transition dipoles from symmetric v_{sym} and antisymmetric v_{as} stretch modes of carboxylate groups can interact with image dipoles from polarizable excited states.

features, and the FTIR spectrum of the 2.9 nm PbS QD film capped with I/MPA ligands appears below the spectra for comparison. The vertical lines mark the frequencies that are prominent in the oleate transient vibrational spectra (**Figure 4-8a**) and are reproduced here to facilitate quantitative comparison of the data measured in films passivated with the two types of ligands.

Note that the frequency scale differs slightly in **Figure 4-9a** *versus* **Figure 4-8a**, which affects the position of the vertical lines as guides to the eye in the figures.

The transient vibrational features of MPA ligands in **Figure 4-9a** differ markedly from those of oleate ligands in **Figure 4-8a** even though both correspond to carboxylate groups attached to PbS surfaces. In particular, the broad ground state bleach feature is not observed, that in the oleate system spanned both v_{sym} and v_{as} modes of carboxylate groups adopting the chelating geometry. Furthermore, the selective enhancement of the v_{sym} mode around 1400 cm⁻¹ is not apparent in the I-/MPA capped PbS QD films. Finally, the transient absorption feature at 1600 cm⁻¹ that is indicative of the formation of unidentate carboxylate groups is not observed among the transient vibrational features of MPA ligands.

These differences highlight the distinct structures of the I-/MPA *versus* oleate ligands and how they bond with PbS QD surfaces. For example, MPA is a bidentate ligand that bonds to PbS surfaces through both its thiol and carboxylate groups. Thiols are known to dissociate excitons by localizing holes at metal chalcogenide surfaces in shallow traps which suppresses photoluminescence from thiol capped quantum dots.⁶¹⁻⁶² The vibrational features in **Figure 4-9a** exhibit a derivative-like structure in which a transient absorption feature appears ~30 cm⁻¹ lower in frequency than the ground state bleach for both the v_{sym} and v_{as} stretch modes. The shift to lower frequency is consistent with the vibrational Stark effect in which holes localized at the PbS QD surfaces by the thiol groups cause a large red-shift of the vibrational frequencies of the neighboring carboxylate groups. Furthermore, the absence of the enhanced v_{sym} stretch suggests that the carboxylate groups of MPA ligands are not able to adopt near-normal bonding geometries to the PbS QD surfaces. **Figure 4-9b** illustrates, in cartoon fashion, that conformational restrictions imposed by the bidentate binding geometry of MPA ligands makes it unlikely that the carboxylate groups could orient in such near-normal orientation. Depending on the specific bonding angle, image dipoles from the electronic excited state would experience greater destructive interference with the transition dipole of the v_{sym} stretch, leading to the absence of the enhancement at 1400 cm⁻¹. Finally, the absence of the 1600 cm⁻¹ transient absorption feature indicates that the carboxylate groups of MPA ligands do not experience the same perturbation in the excited electronic state in comparison to the ground state that occurs in oleate capped PbS QDs. This difference could arise from the excitons being dissociated by the presence of the thiol groups or because the thiol groups anchor the MPA ligands to the QD surfaces and prevent the carboxylate groups from changing their bonding geometries in the excited state.

The transient vibrational spectra in **Figure 4-8a** and **Figure 4-9a** reveal that oleate ligands experience substantially different interactions with PbS QDs in their excitonic excited state in comparison to PbS QDs passivated with Γ' MPA ligands. It was therefore interesting to examine the effect these differences in bonding characteristics may have on electron-phonon coupling and carrier cooling rates in the PbS QDs. To quantify the effects of electron-phonon coupling in the oleate *versus* the I-/MPA capped PbS QD films, the fitting routine was adopted that was developed previously to describe excitonic transitions in similar TA spectra.³⁹ Lognormal distributions were used to describe the excitonic transition $(1S_h-1S_e)$, the $1S_{e(h)}-1P_{e(h)}$ intraband transition, and the $1S_{e(h)}-1D_{e(h)}$ transition that appear in the spectra represented in **Figure 4-5**.

Prior work demonstrated that the variance of the log-normal distributions (related to their widths) describing the excitonic transitions in oleate capped PbS QDs increases with decreasing nanocrystal volume following a power-law dependence.^{39, 63} This dependence is consistent with

the widths of the transitions being dominated by electron-phonon coupling. Figure 4-10 represents a comparison of the variance of the log-normal functions describing the $1S_h-1S_e$, $1S_{e(h)}-1P_{e(h)}$, and $1S_{e(h)}-1D_{e(h)}$ transitions that were measured in the oleate and I-/MPA capped



Figure 4-10. Comparison of the width parameters (variance) of the log-normal functions of the GSB (black), $1S_{e(h)}$ - $1P_{e(h)}$ (red), and $1S_{e(h)}$ - $1D_{e(h)}$ (blue) characterizing the excitonic transitions in different sized PbS quantum dots. The width parameters measured in I/MPA capped PbS are indistinguishable from those measured in oleate capped PbS despite the differences in surface chemistry of these systems.

PbS QD films. The numeric values of the variances are tabulated in **Table 4-1**. The comparison demonstrates that despite the differences of the interactions that oleate *versus* I/MPA ligands experience with PbS surfaces in their excited state, the electron-phonon coupling that dominates the widths of the excitonic transitions is unchanged within experimental precision.

The differences of the interactions of oleate *versus* I-/MPA ligands have with PbS surfaces, which might influence the rates of carrier cooling to the lowest energy $1S_{e(h)}$ states of the QDs, were also investigated. To do this, the rate of carrier cooling was measured directly using ultrafast mid-IR pump-probe spectroscopy to monitor the growth of the $1S_{e(h)}$ - $1P_{e(h)}$ transition. Using an optical excitation at 532 nm (2.3 eV) creates highly excited excitonic states well above the minimum $1S_h$ - $1S_e$ excitonic energy of 0.9 eV and 1.36 eVfor the 4.9 nm and 2.9 nm QD films, respectively. It was therefore possible to observe the dynamics of carrier cooling

by monitoring the growth of the $1S_{e(h)}$ - $1P_{e(h)}$ transition at 2000 cm⁻¹ for 4.9 nm oleate and Γ /MPA capped and Γ /MPA capped 2.9 nm and 4.9 nm PbS QD films. Figure 4-11 compares the transient absorption kinetics of the $1S_{e(h)}$ - $1P_{e(h)}$ transitions measured in the oleate and I-/MPA

Diameter	Ligand	1S _h -1S _e	$1S_{e/h}$ - $1P_{e/h}$	$1S_{e/h}$ - $1D_{e/h}$
2.9 nm	Oleate	0.0031	0.0178	0.0943
	I ⁻ /MPA	0.0027	0.0160	0.1347
3.2 nm	Oleate	0.0029	0.0144	0.0643
	I ⁻ /MPA	0.0023	0.0132	0.0998
3.7 nm	Oleate	0.0019	0.0068	0.0308
	I ⁻ /MPA	0.0016	0.0066	0.0312
4.9 nm	Oleate	0.0013	0.0017	0.0092
	I ⁻ /MPA	0.0008	0.0019	0.0139

Table 4-1. Comparison of the variances calculated from the model used to fit the electronic transitions in the TA spectra at 40 ns.

capped PbS QD films following ultrafast optical excitation at 532 nm along with corresponding fits to the data. From the fits to the data in **Figure 4-11a**, it was determined that the carrier relaxation times for both types of ligands were identical within experimental precision, with cooling rates of 0.8 ± 0.1 ps and 0.9 ± 0.1 ps for oleate and Γ /MPA ligands respectively. Despite their differences in surface chemistry, passivation with oleate *versus* Γ /MPA ligands does not influence the dynamics of carrier cooling in PbS QDs. In **Figure 4-11b**, the carrier cooling rate for 2.9 nm diameter QDs capped with Γ /MPA was found to be 0.5 ± 0.1 ps, compared to 0.9 ± 0.1 ps for the 4.9 nm sample. This nearly two-fold decrease in hot-carrier lifetime is a result of the size-dependent electron-phonon interactions for smaller diameter QDs that were identified in **Chapter 3**.

Although the types of ligands on PbS QD surfaces do not influence the electron-phonon coupling or carrier cooling dynamics observed here, the surface chemistry of the ligands does



Figure 4-11. Ultrafast pump-probe kinetics using 532 nm pump and 2000 cm⁻¹ wavelengths for (a) comparison of a 4 .9 nm PbS QD film capped with oleate and I/MPA ligands, and (b) 2.9 nm and 4.9 nm diameter QD capped with I/MPA.

influence their response to optical excitation of the QDs. Oleate ligands that attach to PbS surfaces via only one functional group experience significant perturbations of their bonding geometries in response to formation of the excitonic excited state. In contrast, MPA ligands that are anchored by strong thiol bonds to surface Pb atoms do not exhibit such changes in bonding geometry. The implication is that the surfaces of the PbS QDs undergo significant structural changes during promotion to excitonic excited states of the nanocrystals. This indicates that surface phonons of the nanocrystals are strongly coupled to the electronic states of PbS QDs.

The phonon spectrum of the surfaces of the QDs is expected to be poorly defined and significantly broadened due to excess crystal strain, exposed facets and dangling bonds.⁶⁴⁻⁶⁹ Because the phonon spectrum at the surface is significantly broad, it can interact strongly with the excitonic states of the QD and cause the significant state broadening that we observe in the experimental data. This state broadening has been demonstrated to be highly size-dependent and results in an effective means to bypass the phonon-bottleneck in PbS QDs (**Figure 4-11b**).³⁹

Because the surface area to volume ratio increases with decreasing particle size, the electronic properties of smaller QDs are more strongly controlled by surface effects. Additionally, smaller QDs exhibit a greater degree of exposed facets at the surface and increased strain as they deviate from a spherical approximation.⁷⁰ Finally, the conclusion that surface phonons couple strongly to electronic states of PbS QDs and create resonant energy relaxation pathways for hot-carrier cooling suggests that efforts to slow carrier cooling should focus on controlling surface properties such as strain, dangling bonds, and exposed facets. Effective strategies to control these properties may include the use of thin inorganic shells or controlled composition gradients to move dangling bonds and surface phonons away from the core electronic states of the nanocrystals.

4.4 Conclusion

Using electronic and vibrational TA spectroscopy the effects of ligand and surface vibronic coupling to excitonic states in PbS QDs have been decoupled. Despite the significant variations in the vibrational character of the ground and excited states of oleate and Γ /MPA ligands, identical vibronic coupling through broadband TA spectroscopy and observed matching thermalization times for both ligands were measured. The magnitude of vibronic coupling measured was not affected by the strength of the interaction between the QD excitonic states and the ligand. It was also found that there were no size-dependent vibrational trends in either the ground or excited state that coincided with the strong size-dependence of the inhomogeneous linewidths in the electronic spectra.

These observations ruled out the possibility that vibronic coupling was mediated via ligands. Instead, it was shown that electron density localizes at the Pb-rich surface of the PbS QD films resulting in reversible changes to the ligand binding structure in the excited state of oleate

capped QDs without affecting vibronic coupling of excitonic states. It is this localization of the electron on the surface of the QDs that is responsible for the thermalization mechanism of PbS QDs. QD surfaces are known to suffer from strain, dangling bounds, and exposed facets, all of which result in a broad phonon spectrum at the surfaces, which interact with the excitonic states to create resonant energy relaxation pathways for carrier cooling. The surfaces of significantly small diameter QDs have a phonon spectrum that is especially broadened modes due to increased strain, and a greater number of exposed crystalline facets, thus interacting strongly with the excitonic states to effectively bypass the phonon bottleneck.

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CHAPTER 5

EXCITON DELOCALIZATION IN PERYLENE DIIMIDES

ABSTRACT: Ultrafast vibrational spectroscopy in the mid-infrared was used to directly probe the delocalization of excitons in two different perylenediimide (PDI) derivatives that are predicted to preclude the formation of excimers, which acts as a trapping mechanism for excited state energy in organic semiconductors. Vibrational modes within the conjugated C-C framework of PDI molecules were identified whose frequencies directly reported the interactions of molecules within delocalized excitonic states. The vibrational linewidths of these modes, termed intermolecular coordinate coupled (ICC) modes, provided a direct probe of the extent of exciton delocalization among the PDI molecules, which was confirmed using X-ray diffraction and electro-absorption spectroscopy. It was shown that a slip-stacked geometry among the PDI molecules in their crystal structure promotes delocalized charge-transfer (CT) excitons, while localized Frenkel excitons tend to form in crystals with helical, columnar stacking geometries. Because many organic molecules possess vibrational modes which are sensitive to electronic properties, the use of ultrafast mid-infrared spectroscopy to measure ICC vibrational modes offers a new approach to examine exciton delocalization in a variety of small molecule electron acceptors for optoelectronic and organic photovoltaic applications.

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5.1 Introduction

Perylenediimide (PDI) molecules are a class of organic N-type materials that have been explored as alternatives to fullerenes in organic photovoltaics (OPVs) due to their high electron mobilities.¹⁻³ Typical mobilities for PDI molecules are ~1 cm² V⁻¹ s⁻¹, at least one order of magnitude higher than comparable fullerene mobilities.⁴⁻⁷ PDIs also have added advantages over fullerene based acceptors in that they are relatively inexpensive, light and air stable, and their electronic properties and crystal packing geometries are easily tuned.^{1, 8-14} Furthermore, PDIs have high extinction coefficients in the visible region, allowing both donor and acceptor molecules to contribute to photocurrent in photovoltaic device applications.^{11, 13, 15}

Despite their major advantages, significantly lower power conversion efficiencies have been realized to date using PDIs as electron acceptors in OPV devices in comparison to those using fullerene-based acceptors.¹⁻³ Reduced efficiency has largely been attributed to phase separation between polymer-donors and PDI-acceptors, as well as the formation of large PDI crystalline domains in organic blend devices.⁴⁻⁸ In addition to these morphological matters, PDI molecules in crystalline films can form strong π - π interactions that favor the formation of localized excimer states.⁹⁻¹² While strong π - π interactions are generally associated with high charge carrier mobility, these excimer states can localize excitons and act as trapping sites for excited state energy, which hinder excitation transport donor/acceptor interfaces in the active layers.¹³⁻¹⁵ The formation of these self-trapped excimers is predicted to be controlled through the geometric arrangement of PDI molecules, effecting the intermolecular electronic coupling.^{16, 17} Therefore, understanding the influence of molecular packing on excimer formation in PDI molecules can provide insight into the formation of similar charge-trapping mechanisms in other small molecule organic photovoltaic materials, resulting in the development of new design strategies which maximize exciton mobility and create delocalized excitations.

Current strategies for circumventing excimer states in PDIs films have focused on tuning π - π interactions by choosing molecules that adopt either helical or slip-stacked geometries.^{7, 13, 15, 18, 19} While these packing motifs have generally been found to reduce the formation of excimers by decoupling neighboring PDI molecules, it is unclear how they affect the delocalization of excited states in crystalline films.²⁰⁻²² This is particularly relevant because even subtle changes in the crystal packing geometries can have significant impact on organic semiconductor materials and therefore device properties.^{8, 22-26} Additionally, delocalized excited states are predicted to be more favorable for photovoltaic devices because the exciton binding energy should be lower than a localized state with a smaller radius.²⁷⁻²⁹ More delocalized excited states should exhibit smaller reorganization energies associated with excited state energy transfer among molecules, leading to higher exciton diffusion lengths and more efficient diffusion of excitons to donor/acceptor (D/A) interfaces.

In this chapter, ultrafast vibrational spectroscopy in the mid-infrared (mid-IR) spectral region is used to gain insight into the influence that molecular packing geometry has on the delocalization of excited excitonic states in PDI films. Motivation for this work stemmed from research showing that the conjugated C-C ring stretch modes of the perylene core are particularly sensitive to electronic coupling between molecules in covalently tethered dimers.³⁰ This sensitivity has also been used to examine the charge transfer character in exciplexes formed between conjugated molecules in solution.³¹⁻³³ The transient vibrational spectra of PDI molecules in solution at various concentrations were first investigated to identify unique vibrational modes of the perylene cores whose frequencies report on the interactions of molecules in delocalized

excited states. The vibrational modes that were identified through this research were termed ICC vibrational modes since these modes report directly on the intermolecular electronic interactions of coupled PDI molecules. The ultrafast vibrational spectroscopy studies were then extended to examine PDI molecules in crystalline films, revealing that the vibrational linewidths and frequencies of the ICC modes provided a direct probe of the extent of exciton delocalization among PDI molecules. These studies were complemented by X-ray diffraction and electro-absorption experimental measurements that revealed a transition from Frenkel-like to CT-like excitons as the PDI packing geometry was changed from helical to slip-stacked arrangements. This works findings suggest that PDI molecules adopting slip-stacked packing geometries may be better suited for photovoltaic device applications by enhancing exciton delocalization while still suppressing excimer formation. The approach of identifying ICC vibrational modes using ultrafast mid-IR spectroscopy and using them to investigate exciton delocalization should be applicable to a variety of organic semiconductor materials because the electronically coupled vibrational modes are not specific to only PDI molecules.

5.2 Assignment of Intermolecular Coordinate Coupled Vibrational Nodes in Perylene Solutions

Two different PDI molecules were chosen to investigate using ultrafast vibrational spectroscopy and are presented in **Scheme 5-1**. The PDI derivatives selected for this study were chosen because they crystallize in either helical (Molecule 1: (N,N'-Bis(3-pentyl))perylene-3,4,9,10-bis(dicarboximide))) or slip-stacked (Molecule 2: (N,N'-Bis(1-pentyl))perylene-3,4,9,10-bis(dicarboximide))) packing arrangements that have been shown to suppress the formation of excimers in PDI derivatives.^{7, 13, 15, 18, 19} Molecule 1 consists of a "swallowtail" five carbon chain located at the imide position of the PDI core. This "swallowtail" structure represents a class of PDIs that form helical columns in single crystals as well as in thin films.³⁴ Molecule 2 consists of



Scheme 5-1. Molecular structure of the PDIs used in this study.

a linear five carbon alkyl chain at the imide position and crystallizes in a slip-stacked geometry.^{35, 36} The 'swallowtail' structure of the alkyl substituent of Molecule **1** imbues increased solubility of the molecule in organic solvents,³⁷ which was utilized to analyze the concentration-dependence of the excited state dynamics and spectra in solution to aid in the identification of vibrational signatures in the corresponding PDI films. Molecule **2** has a significantly lower solubility in non- π -interacting solvents, causing it to aggregate even at very low concentrations. Consequently, Molecule **2** was not chosen for solution-phase studies which enabled the identification of vibrational modes that specifically report on intermolecular interactions.

Ultraviolet/visible (UV/Vis) absorption spectra of Molecule **1** in chloroform are represented in **Figure 5-1a** at a range of concentrations from 0.5 mM to 95 mM. The UV/Vis spectra do not show significant changes to the linewidth, frequency, or intensity of the vibronic progression up to 40 mM, indicating that the PDI molecules do not aggregate to a significant extent in their ground states.^{22, 24} At a concentration of 95 mM, significant changes in the peak



Figure 5-1. (a) Uv/Vis spectra for solutions of molecule **1** in chloroform normalized to the 0-0 vibronic band and **(b)** photoluminescence spectra normalized to the 0-1 vibronic feature at ~580 nm. **(c)** Photoluminescence decays of the monomer and excimer species. The monomer decay was produced by spectrally integrating the 0.5 mM sample data from 500–750 nm. The excimer decay was produced by spectrally integrating the 40 mM sample data from 650–850 nm.

intensities and full width at half maximum (FWHM) of the vibronic signatures were observed in the UV/Vis spectrum due to aggregation. The 95 mM solutions is presented in **Figure 5-1a** to contrast the UV/Vis spectra of weakly interacting PDI molecules at low concentrations to aggregates which form at high concentration. The 95 mM solution was not used in the subsequent studies described below to ensure that any delocalized excited states observed in the solution studies occurred by only by collisional encounters rather than through preformed aggregates. In this way, the interactions of delocalized excited state species were dominated by the interactions of no more than two molecules in solution. Fourier transform infrared (FTIR) spectroscopy of the solutions was also measured (**Figure 5-2**). The spectra of the 40 mM solution and below remained unchanged in the conjugated C-C stretch and the carbonyl stretch regions (1500-1800 cm⁻¹), further suggesting the absence of aggregation for these concentrations of Molecule **1**.

Figure 5-1b depicts fluorescence spectra of solutions of Molecule 1 at varying concentrations from 0.5 mM to 40 mM following excitation of the sample by a ~1 ns duration 450 nm laser pulse generated by pumping a dye cavity (Coumarin 450 dye) with a nitrogen laser. The samples were measured in a liquid cell between two 0.5 mm thick sapphire optical flats with a pathlength of 10 µm set by a Teflon spacer. At the lowest concentrations of 0.5 mM and 2 mM, the fluorescence spectra exhibit clear vibronic structure that is characteristic of emission from isolated PDI molecules in solution. At higher concentrations however, a broad red shifted emission band grows in, revealing the interactions of the PDI molecules in their excited states. Although the fluorescence spectra in Figure 5-1b have been normalized at 580 nm to aid in comparison of their shapes, the quantum yield of the emission decreased markedly as the concentration is increased. Similar changes in emission spectra have been associated with excimer formation in other PDI molecules.^{22, 24, 38-40} Furthermore, the time-dependence of the fluorescence was examined for the solutions of Molecule 1 with varying concentrations (Figure 5-1c). The data indicate a factor of four increase in the fluorescence lifetime of the broad and featureless emission band of the 40 mM solution in comparison to the monomer emission from the 0.5 mM solution. Because the absorption spectra of the solutions of Molecule 1 in this concentration range demonstrate a lack of aggregation in their ground states (Figure 5-1a), the

broad emission band in the 40 mM solution resulted from molecules that encountered each other within their excited state lifetimes. Consequently, the spectral signatures at high concentrations were assigned to the formation of excimers and the broad featureless emission spectra at these concentrations are a result of no more than the interaction of two molecules.



Figure 5-2. FTIR spectrum of the C-C and carbonyl vibrational regions for Molecule **1** in CHCl₃. Significant spectral changes are not observed which indicates that significant electronic coupling in the ground state is not occurring.

Taking advantage of this control over the formation of excited state dimers, vibrational modes associated with either monomer or excited dimer states of Molecule **1** were identified using ultrafast vibrational transient absorption (TA) spectroscopy. **Figure 5-3a** displays the mid-IR TA spectra for a monomer in a 2 mM solution of Molecule **1** in chloroform following excitation of the sample by a 100 fs duration 532 nm laser pulse generated by pumping an optical parametric amplifier (OPA) with the output of a Ti:Sapphire laser at 800 nm. These vibrational measurements were made on Molecule **1** in a liquid cell consisting of 2 mm thick CaF₂ windows separated by a 10 μ m Teflon spacer. The spectra exhibit ground state bleach peaks (GSBs) of the symmetric (1655 cm⁻¹) and antisymmetric (1690 cm⁻¹) carbonyl stretch modes along with the conjugated C-C stretch modes of the perylene core at 1580 cm⁻¹ and 1595 cm⁻¹. These features



Figure 5-3. Transient absorption spectra measured for solutions of molecule 1 in chloroform having concentrations of (a) 2 mM and (b) 30 mM. Samples were excited using 532 nm excitation. (c) FTIR spectrum of molecule 1 in chloroform, shown for reference.

correspond closely to the ground state vibrational modes present in the FTIR spectrum of the sample in **Figure 5-3c**. In addition, new excited state absorption (ESA) peaks are present at lower frequencies and with opposite sign in comparison to the corresponding GSB features. Most pronounced are the ESA features corresponding to the symmetric stretch of the carbonyl groups at 1645 cm⁻¹ and the ESA features of the conjugated modes of the perylene core at 1502 and 1550 cm⁻¹, respectively. The lower vibrational frequencies of these modes arise from a change in charge distribution of the excited state in conjunction with anharmonic coupling to lower frequency modes that are also perturbed by the change in charge distribution.

Figure 5-3b represents mid-IR TA spectra of a 30 mM solution of Molecule **1** in chloroform for comparison to the spectra of the 2 mM solution. In the higher concentration solution, new vibrational features appear on the nanosecond time scale at 1525 cm⁻¹ and 1580 cm⁻¹ that are not present in the 2 mM solution. Because the 30 mM solution of Molecule **1** exhibits excimer emission while the 2 mM solution does not, the vibrational features that appear

only in the 30 mM solution are assigned to those of excited state dimers. These vibrational features at 1525 and 1580 cm⁻¹ were assigned to ICC modes due to their specificity to intermolecular interactions between PDI dimers.

In addition to ultrafast concentration dependent TA measurements, global target analysis was also performed using the Glotaran software package to further support the assignment of vibrational features of the monomer and excited state dimer states of Molecule **1** in solutions



Figure 5-4. (a) Species associated spectra for the monomer and excimer in molecule 1 solutions at varying concentrations from global target analysis performed using Glotaran software. (b) Model used to calculate the species associated spectra and format the 2x2 matrix in Glotaran.

with concentrations of 2, 20, 30 and 40 mM in chloroform.⁴¹ The species associated spectra (SAS) shown in **Figure 5-4** demonstrate the individual spectral signatures that arise from the monomer and excimer that combined model the total TA data measured on the ultrafast

timescale. The analysis reveals that the ICC vibrational modes are nearly identical at all concentrations of Molecule 1 and that the 1525 cm⁻¹ vibrational signature provides a clear, unobstructed spectroscopic feature that is distinct for the excited state dimers in all solutions of concentration greater than 2 mM. The second ICC mode centralized at 1580 cm⁻¹ mode overlaps other vibrational features, complicating further analysis. Therefore, the ICC vibrational mode at 1525 cm⁻¹ was used as a distinct marker for the formation of excited state dimers. It is noteworthy that the vibrational ICC modes were shifted by $\sim 25 \text{ cm}^{-1}$ to higher frequency and were significantly broader than the ESA features of the monomer that appear in the spectra of the 2 mM solution. A significant blue-shift of the conjugated C-C stretch modes of PDI molecules has been observed previously in molecular dimers with increasing J-type electronic interaction in their excited states, consistent with the assignment of these features to intermolecular coupled modes.³⁰ The broader linewidth also supports the same conclusion since delocalization of an excited state over a greater number of molecules decreases the dephasing time, resulting in broader vibrational signatures of modes which are coupled to the electronic states.

Further substantiation for the assignment of the 1525 cm⁻¹ vibrational feature to the ICC vibrational mode of PDI molecules in an excited state dimer was provided by examining the rate of formation of this feature as a function of the concentration. **Figures 5-5a** and **5-5b** highlight the concentration dependence of the 1525 cm⁻¹ vibrational feature in the mid-IR TA spectra of solutions of Molecule **1** ranging between 2 mM and 40 mM in chloroform. Spectra at select time delays for each sample are represented in **Figure 5-5a**, while surface plots including all measured time points for each sample appear in **Figure 5-5b**. The data confirm the absence of excited state dimer formation in the 2 mM solution, while the rate of growth of the 1525 cm⁻¹

feature increases as the concentration of Molecule **1** increased from 20 mM to 40 mM. **Figure 5-5c** compares the kinetic decay of the 1502 cm⁻¹ vibrational mode of the excited state monomer to the growth of the 1525 cm⁻¹ mode of molecules in the excited state dimer for a 30 mM solution. The anticorrelation of these vibrational features demonstrates the population transfer that is expected for the decay of monomer states as they interact with ground state molecules to form excited state dimers. Finally, **Figure 5-5d** highlights the concentration dependence of the growth kinetics of the 1525 cm⁻¹ vibrational feature. The data identify that growth of this feature occurs more quickly in solutions of higher concentration as expected for the bimolecular process of excited dimer formation. Higher concentrations of molecules in solution, increases the probability that an excited state PDI molecule will encounter another molecule in the ground



Figure 5-5. (a) Time-resolved C=C ring mode vibrational spectra for solutions of molecule 1 in chloroform with varying concentrations ranging from 2 - 40 mM. **(b)** Corresponding TA intensity maps for each solution measured. **(c)** Vibrational absorption kinetics for the monomer and excimer features for the 30 mM solution. **(d)** Excimer absorption growth kinetics for each solution measured.

state before it relaxes back to the ground state. Taken together, these data confirm the 1525 cm⁻¹ vibrational feature as an ICC vibrational mode that results from the formation of excited state dimers and represent a vibrational probe of intermolecular interactions.

The ICC vibrational signatures arise from perturbations of the monomer vibrational modes when a molecule in the excited state electronically couples with a ground state molecule to form the excited state dimer. It is noted that there is greater conformational flexibility in the intermolecular coordinates between two coupled molecules than there is within the intramolecular nuclear coordinates of individual molecules. This is because Van der Waals interactions are much weaker than covalent bonds and are therefore subject to larger amplitude motions during thermal fluctuations. As a consequence, the coupling of the 1525 cm⁻¹ mode to the intermolecular interactions between molecules in the dimers (that cause the ~25 cm⁻¹ blueshift) is expected to cause greater frequency fluctuations due to thermal motion of the molecules in the dimers. These frequency fluctuations cause the broader linewidths of the ICC vibrational modes at 1525 and 1580 cm⁻¹ in comparison to those of the monomers at 1502 and 1550 cm⁻¹ (**Figure 5-3b**). Additionally, there may be some degree of perturbation of the carbonyl modes for the excited state dimer; however observation of these differences is obstructed by overlapping bleach and ESA features and therefore further interpretation of these signatures is excluded.

5.3 Molecular Packing in Perylene Diimide Thin Films

Having identified a distinct ICC vibrational mode among the conjugated C-C stretch modes of the perylene cores, this mode could be subsequently used to probe intermolecular interactions and exciton delocalization in two homologous PDI molecules that adopt different crystal packing structures.³⁴⁻³⁶ Crystal packing was controlled without effecting electronic structure of the materials by taking advantage of the fact that subtle changes of the alkyl groups

located at the imide position of the perylene do not significantly affect the electronic properties of the individual molecules.²³ It was reasoned that the homologous structures and similar vibrational spectra of Molecules 1 and 2 (Figure 5-6) would enable the use of the ICC



Figure 5-6. FTIR spectrum for Molecule 1 and Molecule 2 spray-cast films on CaF₂ windows

vibrational mode observed in the solution studies of Molecule **1** to examine intermolecular interactions and exciton delocalization of both Molecules **1** and **2** in their spray-coated thin films.



Figure 5-7. Images of PDI films spray-cast from CHCl₃

Thin films of Molecules 1 and 2 were prepared by spray-coating 1 and 2 from HPLC grade chloroform solutions with a concentration of 2 mM onto heated CaF_2 substrates at 150 °C. The film thicknesses were built up through successive, overlapping coats. Images demonstrating the optical quality of the films can be found in the supporting information (**Figure 5-7**). Molecules of 1 and 2 have previously been shown to adopt helical, columnar³⁴ and slip-stacked^{35, 36} packing geometries in their molecular crystals, respectively. The molecular structures



Figure 5-8. (a) Molecular structures of **1** and **2** generated using Mercury software package of the published single crystal structures from references 46 and 48, respectively. Measured grazing incident X-ray diffraction, measured Bragg-Brentano powder X-ray diffraction and calculated powder X-ray diffraction data for **(b)** molecule **1** and **(c)** molecule **2**.

represented in **Figure 5-8a** illustrate the differences in these packing arrangements and were obtained from analysis of crystallographic information files published in references ³⁴ and ³⁶ for Molecules of **1** and **2**, respectively. The structures in the figure were generated using the Mercury software package. Verification of the crystalline packing structure was the same for the spray-cast films was accomplished by performing GIXRD of the thin films of each type of PDI. **Figure 5-8b** depicts the GIXRD patterns measured in a thin film of Molecule **1** spray-coated onto CaF₂ substrates under identical conditions as those used to prepare the samples of optical characterization. For reference, a Bragg-Brentano X-ray powder diffraction pattern appears in the figure along with a calculated powder diffraction pattern obtained from analysis of the corresponding crystallographic information file. The comparison confirms that Molecule **1** adopts the helical, columnar packing geometry that has been observed previously. Similar XRD analysis of the spray-coated film and powder sample of Molecule **2** in comparison to the calculated powder diffraction pattern in **Figure 5-8c** confirms that Molecule **2** adopts a slip-stacked packing geometry in the spray-cast films.

In addition to grazing incidence X-ray diffraction presented in the main text, Bragg-Brentano X-ray measurements were also conducted and are shown in **Figure 5-9**. The measured powder data is in close agreement with the powder diffraction pattern calculated from published crystallographic information files using Mercury software.³⁴⁻³⁶ In general, while there can be small local variation in the stacking and tilt of molecules, the similarities between the grazing incidence and Bragg-Brentano to the powder and simulated data suggest that they have similar unit cells and likely similar packing as a result. If large deviations in d-spacing or 20 in the Bragg-Brentano data are observed (~1-2°), then possible polymorph formation could be considered due to large changes in the lattice parameters. For the data presented in **Figure 5-8**, the absolute peak positions for the grazing incidence data cannot be determined; however, the Bragg-Brentano data in **Figure 5-9** satisfies the Bragg condition and can be used in that manner.



Figure 5-9. Comparison of Bragg-Brentano XRD measurements for (a) Molecule 1 and (b) Molecule 2

The grazing incidence does inform that the expected planes are present in the sample.

For Molecule **1**, the Bragg-Brentano data (**Figure 5-10**) displays that there is orientation in the molecule as evidenced by the loss of many of the peaks associated with the plane of the PDI core. This indicates that the molecules are stacking perpendicular to the plane of the PDI core along the (200), (002), and (20-2) planes. As PDI molecules stack tilted to the surface with end groups in contact with the surface, the peaks present give an indication that rotation is occurring. Should molecular rotation not be occurring, one would expect that either (h00) or (001) to be present which correspond to cores extending vertically away from the substrate. However, a (20-2) peak is also observed which is depicted above as a plane between two partially tilted molecules. Partial rotation likely increases unfavorable stacking along the PDI



Figure 5-10. Selected planes showing compound orientation on the surface and intermolecular stacking in molecule **1**.

core allowing the retention of its relative intensity compared to (200). In the grazing incidence, there are many additional reflections not observed in Bragg-Brentano which are normal to the plane of the PDI core. Specifically, the high angle reflections correspond to the tilt and layering as seen above with the (221) plane. In comparison to the powder and simulated data, most of the peaks are preserved, supporting the conclusion that not only is the symmetry of the rotation retained, but also the molecular packing.

For Molecule 2, the same orientational frustration does not exist based on the molecular



Figure 5-11. Selected planes showing compound orientation on the surface and intermolecular stacking in molecule 2.

packing when considering surface orientation because the slip stacking leads to the end groups aligning in the same direction. Therefore, significant increases in peak intensity are observed corresponding to the planes parallel to the end groups. A good example of this is the increased relative intensity of the (010) peak compared to the (01-1) reflection when compared to the calculated pattern. This is significant because the (01-1) corresponds to a plane closer to the length of the PDI whereas (010) would enable aligning the hydrocarbon end to the surface, as seen below. In terms of slip-stacking versus other possible molecular packing, the (104) and (01-1) peaks which correspond to rows of PDI molecules (**Figure 5-11**) fall on top of the calculated and powder pattern. These observations provide confidence that though there is significant ordering to the substrate, the consistent peak positions in Bragg-Brentano with the calculated pattern mean planes of molecules lie in the same location as in the single crystal data from literature.^{42, 43, 44}

5.4 Influence of Molecular Packing on Delocalization of Excited States

Having confirmed that Molecules of 1 and 2 adopt distinct molecular packing geometries in their crystals, ultrafast vibrational spectroscopy studies of Molecules 1 and 2 in their spraycast films were undertaken and used the ICC vibrational mode as a probe of the electronic interactions among the molecules in their excited states. Figure 5-12a reproduces mid-IR TA spectra of Molecule 1 in a 30 mM solution of chloroform at select time delays for comparison to the mid-IR TA spectra of the films. Figure 5-12b and Figure 5-12c depict mid-IR TA spectra of Molecules 1 and 2, respectively in their spray coated films following excitation at 532 nm by a 100 fs pulse with 120 μ J/cm² energy density. The grey shaded spectra in the lower portions of the panels in Figure 5-12 show the corresponding FTIR spectra of the samples. The comparison highlights the GSB features of the conjugated C-C stretch modes of the perylene cores between 1575 and 1600 cm⁻¹ in both the solution and film spectra. Lower intensity vibrational features at ~1510 and ~1480 cm⁻¹ are also present with corresponding small GSB features in the transient spectra of the films. Comparison of the mid-IR TA spectra of the 30 mM solution and the film of Molecule **1** highlight the similarity of both the GSB and ESA features of the molecules in their excitonic states in the region of the conjugated C-C stretch modes. For example, an ESA peak similar to the vibrational mode of the excited monomer in solution at 1502 cm⁻¹ is apparent in the thin film. Furthermore, the ICC vibrational mode observed in dimers in solution also appears in the thin film with a peak at 1528 cm⁻¹. However, because the molecules in the thin film are in intimate contact with one another, this mode appears instantaneously, in contrast to the delayed formation of this peak in 30 mM solution. The overlap of several spectral features in the 1550 cm⁻¹ region obscure the higher frequency ESA feature of the conjugated C-C stretch modes in the thin film. The striking similarity of the mid-IR spectra of Molecule **1** in both solution and thin film samples suggests that excitons in Molecule **1** are delocalized over only one or two molecules in their



Figure 5-12. Ultrafast vibrational spectra in the region of the conjugated C-C stretch modes of **(a)** 30 mM solution of molecule **1** in chloroform, **(b)** film of molecule **1**, and **(c)** film of molecule **2**. The FTIR spectra of the corresponding samples are represented as the grey shaded spectra in each panel.

crystals since the solution spectra represent the interaction of no more than two molecules in their excited state.

Figure 5-12c reveals that the mid-IR TA spectra of Molecule **2** in its spray-cast film are markedly different in comparison to Molecule **1** even though the FTIR spectra (**Figure 5-6**) of these samples are nearly identical. While similar GSB features are observed in the transient spectra of Molecule **2**, no monomer ESA peaks were observed around 1500 or 1550 cm⁻¹.



Figure 5-13. Results of the spectral modeling of the excimer absorption peak of (a) the 30 mM solution of molecule **1** in chloroform taken at 1000 ps with the monomer spectrum plotted at 1 ps for comparison. Film spectrum averaged from 1–10 ps for (b) molecule **1**, and (c) molecule **2.** All electronically coupled vibrational features were fit using Gaussian functions.

Instead, the lower frequency portion of the spectra is dominated by a broad feature with a maximum intensity at ~1530 cm⁻¹. Motivated by the assignment of this feature in the 30 mM solution and film of Molecule 1, this feature corresponds to the ICC vibrational mode of molecules of 2 that interact in their excitonic states in the film.

Figure 5-13 provides a more detailed comparison of the mid-IR TA spectra of the 30 mM solution and films of Molecules **1** and **2** to highlight the differences in the positions and linewidths of the ICC vibrational modes in 1525 to 1530 cm⁻¹ region. The ICC vibrational signatures were found to be 1525, 1528, and 1530 cm⁻¹ in the 30 mM solution and films of Molecules **1** and **2**, respectively after fitting. Fitting the data allowed for the quantification of the changes observed in linewidth and position of the ICC modes for each sample. The best fit functions are overlaid on the mid-IR TAspectra in **Figure 5-13**, revealing that the line widths of the peaks were 18 ± 1 , 25 ± 3 and 50 ± 10 cm⁻¹ in the 30 mM solution and films of Molecules **1** and **2**, respectively. Because these vibrational modes are specific to coupled molecules interacting in their excitonic states, the increase in linewidth provides information about the properties of these intermolecular states.

The line width of the ICC vibrational mode measured in the thin film of Molecule 2 is substantially larger in comparison to that of excitons in the film of Molecule 1 or in the 30 mM solution. Furthermore, no evidence of the excited monomer vibrational features at either 1502 and 1550 cm⁻¹ appear in the TA spectra of Molecule 2, in contrast to the spectra of the thin film of 1 (Figure 5-12). Two possibilities suggest themselves and are illustrated in Scheme 5-2 to explain this behavior: The first possibility, which is referred to as the Greater Fluctuation Model, suggests that molecules of 2 may have greater conformational flexibility in comparison to molecules of 1 in their film or in solution, leading to faster dephasing of the ICC vibrational



Greater Fluctuation Model Greater Delocalization Model

Scheme 5-2. Generic cartoons illustrating possible origins for the greater vibration linewidth of the ICC modes in the excited excitonic states of molecule 2.

mode because its frequency depends on the intermolecular coordinates. Such large fluctuations would imply that molecules of **2** experience much more free volume than do molecules of **1**, which is often encountered in amorphous phases. However, this possibility is difficult to rationalize in light of the nearly identical density and corresponding similar free volume of molecules of 670 and 650 Å for Molecule **1** and **2**, respectively in their molecular crystals. Furthermore, molecules of **2** adopt more ordered crystalline domains in comparison to Molecule **1**, as can be observed qualitatively through the narrow peaks in the powder X-ray diffraction patterns in **Figures 5-8** and **5-9**. Therefore, this model can be effectively ruled out as a possible explanation for the broader line width of the 1530 cm⁻¹ mode in **Figure 5-13**.

An alternative explanation, the Greater Delocalization Model, depicted in Scheme 5-2, suggests that excitons in the more highly ordered films of 2 are delocalized over more molecules than in films of Molecule 1. This greater degree of delocalization could arise from either highly mobile, small radius excitons or excitons which possess a larger radius and envelope a greater number of molecules. A large radius would cause all the molecules within the exciton to exhibit the ICC vibrational mode at 1530 cm⁻¹. This model predicts that the vibrational free-induction decay time (which determines the dynamic line width of the vibrational mode) would be

determined by the time-scale over which the vibrational motions of the individual molecules could maintain their initial coherence. Consequently, this model predicts that molecules involved in more delocalized excitons should exhibit faster dephasing (and broader line widths) of their ICC vibrational modes because of the faster rate at which phase errors can be accrued within a coherent state overlapping more molecules. Additionally, exciton migration could cause rapid relaxation of the ICC vibrational population, resulting in fast dephasing and consequently a broadened lineshape. These explanations are consistent with the increased crystalline order adopted by molecules of **2** in comparison to Molecule **1**. As a consequence, the width of the ICC vibrational mode can be assigned as a reporter of a greater degree of delocalization of excitons in films of Molecule **2** in comparison to films of Molecule **1**.

The combination of greater crystalline order, different crystal structure, and greater exciton delocalization observed in spray coated films of Molecule 2 suggests that excitons in crystals of 2 may have significantly different character in comparison to Molecule 1. Using electro-absorption (EA) spectroscopy of thin films of 1 and 2 in the visible spectral range the properties of excitons in the corresponding molecular crystals were examined. Electro-absorption spectroscopy has been used to characterize the types of excited states formed in materials on the basis of their response to an applied electric field.^{45-47,48} In the particular geometry of a thin film sandwiched between a transparent indium-tin-oxide (ITO) electrode and a reflective metal electrode, the change in absorbance of the sample $\Delta \alpha$ is related to the change in reflectivity, ΔR , via $-\Delta R/R \approx 2d\Delta \alpha/\cos\theta$, where *d* is the active layer thickness, θ is the incidence angle, and interference effects are neglected. The lowest order perturbations to the absorption spectrum of a given transition by application of an electric field *F* arise from the change in dipole moment, $\Delta \mu$, and the change in polarizability, $\langle \Delta \bar{p} \rangle$, (averaged over the tensor) between the ground and excited

states. For example, excited state species with significant Frenkel excitonic character have little CT character. Therefore, the change in polarizability typically dominates, leading to EA spectra that resemble the first derivative of their corresponding linear absorption spectra α ' according to:

$$\Delta \alpha = -\frac{1}{2} \langle \Delta p \rangle F^2 \alpha' \tag{5.1}$$

In contrast, the response of excited state species having largely CT excitonic character to an applied electric field is typically dominated by the change in dipole, leading to EA spectra that are dominated by the second derivative of the absorption spectrum α '' according to:

$$\Delta \alpha = -\frac{1}{6} (\Delta \mu F)^2 \alpha'' \tag{5.2}$$

Assuming that the dipole moments are isotropically oriented.

Figure 5-14a represents the EA spectrum ($\Delta \alpha$) of a film of Molecule 1 following application of a time-varying electric field. Overlaid on the data is the first derivative of the visible absorption spectrum of the sample (- α '). The comparison demonstrates that the EA spectrum of the film of 1 is qualitatively described by the first derivative of the absorption spectrum, indicating that excitons in Molecule 1 are dominated by Frenkel character (Eqn. 5.1). The EA spectrum of a film of Molecule 2 measured under identical conditions appears in Figure 5-14b with a qualitatively different shape than the film of 1. Overlaid on the EA spectrum of Molecule 2 is the second derivative of the absorption spectrum of the sample (α ''). The comparison reveals that excitons in Molecule 2 are best described by CT character (Eqn. 5.2).

CT excitons can be considered intermediate between more localized Frenkel excitons and more delocalized Wannier-Mott excitons.⁴⁹ Therefore, the results of the EA study provide additional support for the conclusions about exciton delocalization drawn from analysis of the vibrational linewidths of the ICC vibrational mode of the PDI molecules. From the solution study described above, it was found that the ICC vibrational modes report the coupling of two

molecules. Therefore, a shared excited state spanning two molecules is the minimum basis needed to describe molecules that exhibit a ICC vibrational mode. The appearance of this mode in the thin films of Molecule 1 was only slightly broader in comparison to the 30 mM solution. Furthermore, the vibrational mode at 1502 cm^{-1} of localized excited states was also observed in the thin film of Molecule 1. Taken together, these results confirm that Frenkel excitons in thin films of 1 were delocalized over a range of only one to two molecules.



Figure 5-14. Electro-absorption of PDI films (black data points) and **(a)** first derivative absorption spectrum for molecule **1** (blue) and **(b)** second derivative absorption spectrum for molecule **2** (red).

In contrast, the greater line width of the ICC vibrational mode of CT excitons in the film of Molecule **2** indicates that these excitons were more delocalized. For example, the absence of

the vibrational mode of a localized excited state at 1502 cm⁻¹ in the TA spectra of Molecule 2 (**Figure 5-13c**) is consistent with CT excitons being delocalized over two or more molecules. Considering a shared excited state spanning two molecules as the minimum basis, CT excitons in the film of 2 should be described by a superposition of more than one basis function spanning multiple pairs of molecules (**Scheme 4-2**).

It should be noted that the EA spectrum of the film of Molecule 2 indicates the delocalization of excitons in the film was limited, albeit greater than in the film of 1 as described above. This is because the EA spectrum was dominated by the change in dipole of the excited state (Figure 5-14b). However, in the limit of extreme delocalization of a CT exciton, the EA spectrum should again be dominated by the polarizability term. The CT excitons in the film of Molecule 2 were not near this limit. Unfortunately, these results are not able to evaluate the extent of the delocalization of excitons in Molecule 2 without performing high level ab-initio calculations of the electronic-vibronic coupling that established the dephasing rate of the ICC vibrational mode combined with calculations of the polarizability and change in dipole moments of CT excitons delocalized over several molecules. While such calculations would be very computationally intensive, they may provide quantitative insight about the nature of excited electronic states in organic semiconductors that can be compared with the experimental results reported here. Taken together, these findings suggest that PDI molecules such as Molecule 2 that adopt a slip-stacked geometry in their crystals may be better suited to optoelectronic device applications because they simultaneously facilitate greater exciton delocalization while effectively avoiding the excimer state as reported by others.^{7, 13, 15, 18, 19}

5.5 Conclusions

The influence that crystalline packing geometry has on exciton delocalization was investigated for small molecule organic semiconductors being targeted as non-fullerene electron acceptors in optoelectronic and photovoltaic material applications. Two homologous perylenediimide (PDI) molecules were investigated that adopt distinct packing geometries that have been targeted for their potential to avoid the formation of excimer states in their molecular crystals. The PDI molecules differed only in the structures of their imide side groups without efffecting the molecular weight of electronic properties. Using ultrafast vibrational spectrocopy in conjunction with electro-absorption spectroscopy, unique vibrational modes were identified within the conjugated C-C framework of the perylene cores that are coupled to the intermolecular coordinate between neihboring molecules in delocalized excitonic states. These vibrational features, termed intermolecular coordinate coupled modes, provided an incisive probe of the extent of delocalization of the excitonic states in the molecules. PDI molecules forming the slipstacked crystalline geometry exhibited the greatest extent of excitonic delocalization with charge transfer character. In contrast, molecules adopting a helical geometry exhibited more localized Frenkel excitonic character. These findings suggest that PDI molecules adopting a slip-stacked packing geometry may be better suited for photovoltaic applications because they form more delocalized excitons while avoiding the formation of excimers. The approach of using ultrafast vibrational spectroscopy to identify intermolecular coordinate coupled vibrational modes to probe excitonic delocalization is expected to be applicable to a variety of other organic semiconductors because all molecules possess vibrational modes.

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CHAPTER 6

OUTLOOK AND FUTUR DIRECTIONS

6.1 Lead Sulfide Quantum Dots

Quantum dots have the potential to overcome the Shockley-Queisser limit for single junction solar cells by taking advantage of hot carriers created by high energy excitons through the processes of either hot carrier extraction (HCE) or multiple exciton generation (MEG).¹⁻⁵ The efficiency of both of these processes is proportional to the rate of thermalization of the hot carriers, which has been predicted to be slow in QDs due to the large energy separation between the atomic-like states which make up the bands.⁶ This predicted slowed carrier cooling has been termed the phonon-bottleneck and, except for a few unique cases, has not been observed experimentally.⁷⁻⁸ The absence of the phonon bottleneck has been explained by an Auger mechanism in CdS and CdSe QDs in which excess energy from an electron is transfer to a hole which is able to readily thermalize due the much smaller effect mass of holes in these materials.⁹⁻ ¹¹ The electrons and holes in PbS QDs, on the other hand, have nearly identical effective masses and this Auger mechanism cannot explain the rapid cooling that has been experimentally measured.⁷ The absence of a phonon bottleneck in PbS QDs limits their potential for use in high efficiency, third generation solar cells since the probability of HCE and MEG are greatly reduced.

In **Chapters 3** and **4** the fast hot-carrier thermalization in PbS QD materials was found to be mediated by vibronic coupling of the excitonic states to surface phonon modes, likely a result of the poorly defined phonon spectrum at the disordered surfaces of the particles and was found to be highly dependent on nanocrystal size. These results imply that in order to slow carrier relaxation in these and other QDs, the excitonic states must be decoupled from the surfaces of the nanoparticles. This is not a simple feat however, owing to the large surface area of QD materials, and the fact that the electronic wavefunctions of the core states extend beyond the surfaces of the dots, especially for smaller diameters. From the results obtained in this work, one possible method to alleviate some vibronic coupling is to maximize the diameter of the QDs used. Larger QDs were found to be less effected by vibronic coupling, in large part due to their smaller surface area to volume ratio and because the surfaces of the dots are more well defined and less strained. This result is somewhat counter intuitive, in that slower cooling rates would be observed in QDs with smaller energy separation between the states which make up the bands. Simply increasing the diameter of the QDs in attempt to slow carrier cooling can also have a negative effect on the MEG process however. In order to increase the likelihood of MEG, strong carrier-carrier interactions are needed. Since smaller dots confine electrons and holes to a greater extent, smaller dots should have higher MEG efficiencies. Likely there exists an ideal QD diameter which maximizes carrier interactions while minimizing phonon coupling. Furthermore, the diameter of the QD must be chosen in accordance with the desired bandgap for the application. With the interplay between these various trade-offs, it is unlikely that size alone can be controlled to achieve slowed carrier cooling in PbS QDs.

Since size alone cannot be utilized to observe the phonon bottleneck and thus increase the potential application of PbS QDs to be used in third generation solar cells, alternative controls must be taken advantage of to control vibronic coupling. One such way in which exciton-vibrational coupling may be controlled is through the addition of a shell on the PbS QDs. The shell that would need to be added to the QD would need to be insulating, with a bandgap larger than the bandgap of the core dot and also adopt a rock salt packing structure with similar crystal parameters of PbS. This would effectively force both the electron and hole to be localized on the

core of the dot while minimizing strain and defects at the core/shell interface. By minimizing defects at the interface, the phonon spectrum can be sharpened and the shell can act to spatially separate the excitons from the vibrational modes responsible for phonon interactions. In order for this method to be tested, experiments would need to be performed in which the vibronic coupling was measured for different shell thicknesses. By varying the shell thickness, exciton-phonon coupling may be able to be tuned in QDs and the effect measured. Furthermore, exciton-phonon interactions may be controlled through the use of chemical gradients at the surface of the QDs, in which the crystalline strain and concentration of dangling bonds are reduced while still strongly confining the excitonic wavefunctions.¹²

In addition to the work outlined in this thesis, additional experimental work is needed to further the knowledge base of exciton-phonon interactions and understand the thermalization mechanisms in PbS QDs. To gain more knowledge regarding the mechanism of carrier relaxation, pump-push optical probe spectroscopy should be utilized to selectively monitor cooling in QDs. With this technique, the pump pulse should be tuned to the first excitonic transition of the QD sample, while the push pulse should be tuned to selectively excite the band edge carriers to either the P or D states. Then, the thermalization process back to the band edge of the hot carriers can be monitored through either of the intraband transition identified. This experiment should allow for additional details about the mechanism of cooling to be elucidated. For example, doe cooling from high energy states occur via a step-wise mechanism D-P-S, or does thermalization from the D state occur directly to the S state. Furthermore, because of the high fidelity of this type of experiment, select portions of the broad electronic transitions can be interrogated. If the initially excited band edge exciton is given sufficient time to cool into the lowest vibrational energy level of the 1S_e state, then a finely tunable push pulse can excite the

electron into various vibrational energy levels of the P and D states. Knowing the precise location of the electron relative to the QD density of states should allow for new details about the mechanisms of carrier cooling, as well as enhance the knowledge of exciton-phonon interactions.

Finally, the $1S_{e(h)}-1P_{e(h)}$ and $1S_{e(h)}-1D_{e(h)}$ transitions that have been identified in this work should be subject to two-dimensional electronic spectroscopy in order to quantitatively identify the amount of homogenous and inhomogeneous broadening in PbS QDs. Using the methods available, the degree of homogenous broadening in the PbS samples could only be estimated by comparing the linewidths of the intraband transitions to the variance of the $1S_h-1S_e$ exciton. In performing the analysis in such a manner, predictions were able to be made that longitudinal optical phonons were responsible for the vibroninc coupling measured in the TA spectra. However, determining quantitative values for homogenous and inhomogeneous broadening in the samples using two-dimensional spectroscopy would allow for a more confident assignment of the types of vibrational modes which couple to the excitonic states. If the phonon modes can be well defined, then methods may be possible to minimize the presence of such phonon modes in QDs.

6.2 Intermolecular Coordinate Coupled Vibrational Modes

Singlet fission (SF) is a process that occurs in organic chromophores, where an excited singlet state is converted into two triplet states with half the energy. ¹³ This process has been studied extensively recently, due to its potential applications to improve the efficiency of solar cells beyond the Shockley-Queisser limit.¹⁴⁻¹⁹ One of the challenges that researchers face in SF is elucidating the mechanism of triplet pair separation. Separating triplets is a critical step in SF because, until separated, they have the potential to annihilate with one another to reform the singlet state and decrease overall yield of carriers. ¹⁹ Since the triplet pair has both singlet and

triplet character, it is difficult to study the separation mechanism because the spectral signatures overlap those of the triplet and singlet absorptions.¹⁷ Without the ability to understand the mechanism of triplet separation in SF, designing materials which have efficient triplet separation becomes a blind search. Therefore the identification of new spectroscopic signatures is necessary which are able to distinguish between the singlet, triplet and triplet pair states.

In Chapter 5, Perylene diimide (PDI) molecule derivatives were utilized to identify a new type of intermolecular vibrational modes which are only sensitive to intermolecular interactions.²⁰ These intermolecular coordinate coupled (ICC) vibrational modes were used to determine the degree of exciton delocalization in different films of PDI molecules and aided in the assignment of the types of excitons present in each sample. It is believed that the ICC modes should be present in any intermolecular bound chromophores which have IR-active C=C aromatic ring modes, including SF chromophores. Therefore these vibrational frequencies are ideal candidates to interrogate the mechanism of triplet separation in molecules that undergo SF. Using these vibrational signatures will be able to provide researchers with a direct probe of both the presence and degree of coupling between triplet pairs. Performing time-resolved spectroscopy of SF chromophore by interrogating ICC modes will allow accurate calculations of the yield of free triplet excitons from singlet fission, as well as determine the rate constants for triplet separation. With the ability to measure these processes directly, new design rules for controlling the coupling between molecules can be developed which optimize the processes of SF and triplet pair separation.

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APPENDIX

A.1 Experimental Methods for PbS Quantum Dots

QD SYNTHESIS: PbS QDs were synthesized according to the procedure outlined by Hines and Scholes.¹ For 2.9 nm dots, 0.45 g of PbO, 2 g of oleate and 10 g of 1-octadecene (ODE) were heated to 110 °C under vacuum for 20 minutes to degass the precursors. The reaction flask was then purged with N₂ gas and cooled to 85 °C. 210 μ L of bis(trimethylsilyl)sulfide ((TMS)₂S) in 5 mL of ODE was injected and the flask was removed from heat and allowed to cool to room temperature. After cooling, the QDs were precipitated from the reaction liquor using ethanol and then washed twice using hexane/ethanol as the solvent/antisolvent pair. The final QD product was dispersed in octane with a final concentration of 30 mg/mL. Larger sizes of PbS QDs were synthesized following the same procedure, but with slight modifications to the amount of oleic acid and the injection temperature as noted in **Table A-1**.

QD Diameter	Oleic Acid	Temperature
nm	g	°C
2.9	2	85
3.1	2	120
3.7	8	95
4.9	12	120

Table A-1. Injection temperatures and oleic acid amounts for synthesis of PbS QDs.

SAMPLE PREPARATION: Oleic acid capped films were prepared by concentrating the solutions in octane through evaporation of the solvent under a flow of nitrogen gas. The solutions were then filtered through a 0.22 μ m PTFE filter and spin-cast at 2000 rpm onto CaF₂ substrates with ~100 nm thick mesopourous AlO₃ adhering layer that were vigorously cleaned with 2-propanol and DI water. I/MPA capped films were prepared as detailed previously.² For the I /MPA films, solutions of 30 mg/mL were used, and spin-cast at 2000 rpm. Solid state ligand

exchange of the native oleate ligands for Γ was performed by spinning a layer of oleate capped QDs, and then dipping this film into 10 mM PbI₂ solution in DMF for 3 minutes. The film was then rinsed in acetonitrile. This process was repeated four consecutive times to build up a thick film. After the Γ ligand, two consecutive layers of MPA ligands were added following the same procedure by spin coating the QD layer from octane and then dipping the film into a 10 vol % MPA in methanol solution for 4 seconds.

Solutions of PbS QDs were prepared by evaporating the octane solution using a flow of nitrogen gas and re-suspended in carbon tetrachloride. Solutions were filtered through a 0.22 μ m PTFE filter and bubbled with nitrogen before loading into the liquid cell.

TRANSIENT ABSORPTION: Broadband transient absorption experiments were conducted on two separate systems. Measurements in the visible to near-IR spectral regions were performed using a transient absorption instrument (enVISion, Magnitude Instruments, State College, PA), which consisted of a pulsed, frequency doubled (532 nm) Nd:YAG laser as the excitation source and a tungsten-halogen lamp as the probe light source. The probe light source was filtered through a monochromator and detected using photodiodes optimized for detection in the visible and near-IR ranges to collect the entire spectral region. Measurements in the mid-infrared region were performed using a mid-infrared transient absorption spectrometer (inspIRe, Magnitude Instruments, State College, PA), which also utilized a pulsed, frequency doubled (532 nm) Nd:YAG laser as the excitation source and a broadband glow bar as the probe light source. The probe light was dispersed in a monochromator and detected with a mercury cadmium telluride (MCT) photovoltaic detector. PHOTOLUMINESCENCE: PL measurements were conducted on the same instrument that was used for the nanosecond near-IR transient absorption measurements. PL was collected at a 90° angle relative to the excitation laser.

All film samples were measure inside of a crysostat under vacuum to avoid prolonged exposure to oxygen during the measurements. Temperature dependent spectra were collected in the cryostat, which was cooled using liquid nitrogen. Measurements on solutions were carried out using a home built liquid cell which was composed of two 1.5 mm thick CaF_2 windows sandwiched together with the sample and a 1 mm Viton spacer, which was used to set the sample path length. The solutions were bubbled with nitrogen for 15 minutes prior to loading into the liquid cell to minimize the exposure of the QDs to oxygen.

A.2 Additional Data For PbS Quantum Dots

A.2.1 Characterization of Quantum Dot Size and First Excitonic Transitions.

Vis/NIR absorption spectroscopy was performed on PbS QD films and colloidal solutions with native oleate ligands, as well as films that had been passivated with I/MPA ligands and are shown in **Figure A-1** for the four different size QDs used in this study. The absorption spectra show clear first excitonic transitions that are characteristic of quantum confined nanoparticles.³ Fitting the spectra using log-normal distributions allowed the approximate size of the dots to be determined through comparison of sizing curves calculated using the K•P four band envelope method.⁴ The film absorption spectra have large etalons which are caused by high sample reflectivity, yet distinct first excitonic transitions are still able to be fit well using log-normal distributions. The center frequency of the log-normal distributions was used to fit the first excitonic transition in colloidal solutions with oleate ligands to calculate representative dot sizes of the QD samples since these solutions had the lowest probability of interdot electronic



Figure A-1. Vis-NIR absorption spectra of (a) colloidal PbS QD solutions capped with oleate and suspended in chloroform, (b) oleate capped, and (c) I/MPA capped PbS QD films. Corresponding log-normal fits to each absorption spectrum are shown for reference. Spectra for the various size dots are offset by 0.2 O.D. for clarity.

coupling. Interdot coupling is apparent in I/MPA ligand exchanged films which exhibited a strong red-shift, when compared to the oleate capped films and solutions.^{2, 5} The colloidal solutions of PbS QDs with oleate ligands yielded dot diameters of 2.9 nm, 3.1 nm, 3.7 nm, and 4.9 nm which are used throughout the remained of this chapter to identify the different size

samples. Error in each of these diameters was found to be 0.1 nm, from the uncertainty associated with fitting the absorption spectra along the X-energy axis.

A.2.2 Time-Evolution of PbS Quantum Dot Transient Absorption Spectra

Time-resolved transient absorption measurements were conducted on oleate capped films, colloidal solutions and Γ/MPA films of PbS QDs. **Figures A-2** through **A-4** demonstrate the time-evolution of the spectra, in which the overall shape of the spectra is unchanged over the entire excited state lifetime. Using the same log-normal distributions that were used to fit to the different spectra at 20 ns and modifying only the intensity, the TA spectra at every time slice are able to be accurately modeled. Fits to every diameter QD sample at every time slice have been omitted for clarity, however **Figure A-5** highlights the ability to fit the data sets varying only intensity for a 2.9 nm PbS QD film capped with oleate ligands.



Figure A-2. Nanosecond, broadband transient absorption spectra of (a) 2.9 nm, (b) 3.1 nm, (c) 3.7 nm, and (d) 4.9 nm PbS QD films capped with oleate ligands taken at select time slices.



Figure A-3. Nanosecond, broadband transient absorption spectra of (a) 2.9 nm, (b) 3.1 nm, (c) 3.7 nm, and (d) 4.9 nm PbS QD solutions capped with oleate ligands taken at select time slices.



Figure A-4. Nanosecond, broadband transient absorption spectra of (a) 2.9 nm, (b) 3.1 nm, (c) 3.7 nm, and (d) 4.9 nm PbS QD films capped with I /MPA ligands taken at select time slices.



Figure A-5. Nanosecond broadband transient absorption spectra for an oleate capped 2.9 nm PbS QD film with fits for multiple time slices using the sum of two positive and one negative log-normal distributions.

A.2.3 Kinetic Comparison of Transient Absorption Signatures with Photoluminescence

Using the flash-photolysis spectrometers, the complete ground state recovery of each component comprising the TA spectrum was able to be resolved on a nanosecond timescale. Time-resolved PL measurements were also possible with the enVISion instrument, therefore integrated PL decay traces were measured for the QD samples to compare the TA data. Analysis of the PL kinetics was particularly useful in assigning the low and high energy ESAs to the $1S_{e(h)}-1P_{e(h)}$ and $1S_{e(h)}-1D_{e(h)}$ transitions. All of the states that were assigned in the TA spectra have a common initial energy state, the $1S_{e(h)}$ state, and thus should all have matching kinetics for this assignment to hold true. **Figures A-6** through **A-7**, demonstrate that in both of the oleate capped QD samples measured, the kinetic traces for the $1S_{e(h)}-1P_{e(h)}$ and $1S_{e(h)}-1D_{e(h)}$ match the recovery of the GSB, supporting the claims made in **Chapter 3**. In addition, the PL lifetime also matches lifetime of the bleach recovery, within experimental error, eliminating the possibility that one of the transitions observed in the TA spectra is caused by defect states.

For I/MPA capped PbS OD films, the ESAs and the GSB are longer lived than the PL (Figure A-8). This difference in the lifetimes for the TA and PL is likely a result of either trap states or the presence of free carriers in the films. Traps states mediate non-radiative recombination and could cause the bleach to outlive the radiative decay, similar to previous reports.⁶ Previous reports have also shown that performing ligand exchange procedures in PbS QDs can result in imperfect passivation and the formation of trap states at the surface of the OD.⁷⁻⁸ In addition to potential defect-states, free carriers may be also be present in these films. These films were specifically chosen due to their photovoltaic efficiency and are known to be electronically coupled resulting in the possibility to spate excitons into free electrons and holes.², ^{5, 9} Free carriers are able to recombine nonradiatively which can also explain the deviation of the kinetics traces from exponential such is measured in oleate capped samples. The kinetics for I /MPA capped samples take on power law decays. Such power law relaxation dynamics are expected for bimolecular processes, such as free carrier recombination and highly suggests that the samples are separating excitons.⁶ Whether trap states or free carriers are present in the I⁻ /MPA films, the TA spectra is consistent with oleate capped samples and therefore the technique is not highly sensitive to these species in the samples studied.



Figure A-6. Transient absorption kinetics for each measured TA transition and PL decays for (a) 2.9 nm, (b) 3.1 nm, (c) 3.7 nm, and (d) 4.9 nm PbS QD films capped with oleate ligands.



Figure A-7. Transient absorption kinetics for each measured TA transition and PL decays for (a) 2.9 nm, (b) 3.1 nm, (c) 3.7 nm, and (d) 4.9 nm PbS QD solutions capped with oleate ligands.



Figure A-8. Transient absorption kinetics for each measured TA transition and PL decays for (a) 2.9 nm, (b) 3.1 nm, (c) 3.7 nm, and (d) 4.9 nm PbS QD solutions capped with I/MPA ligands.

A.2.4 Comparison of Experimental $1S_{e(h)}$ - $1P_{e(h)}$ and $1S_{e(h)}$ - $1D_{e(h)}$ Values to Theory

The final method used to identify the low energy and high energy transitions as the $1S_{e(h)}$ - $1P_{e(h)}$ and $1S_{e(h)}$ - $1D_{e(h)}$ was comparing the measured transition energies to the calculated energies predicted from the K•P four band envelope function model. **Figure A-9** shows the measured transition energies plotted with the predicted energies as a function of the first excitonic transition (optical bandgap). The measured transition energies quantitatively agree with the calculated energies within experimental error for oleate solutions and Γ /MPA films. Due to the spectral breadth of the ESA features and the small energy separation between predicted electron

and hole specific transitions, identification of these specific transitions is not possible with the available data. Therefore the assigned transitions are expected to have contributions from both electrons and holes. The $1S_{e(h)}$ - $1P_{e(h)}$ and $1S_{e(h)}$ - $1D_{e(h)}$ transitions are represented by the dashed and solid lines in **Figure A-9**.



Figure A-9. Measured intraband transition energies for (a) oleate capped colloidal solutions and (b) I/MPA capped films of PbS QDs with their optical bandgaps compared to calculated $1S_{e(h)}$ - $1P_{e(h)}$ and $1S_{e(h)}$ - $1D_{e(h)}$ transition energies using the K-P method.

A.2.5 Temperature Dependent Transient Absorption

As an alternate explanation for the observation of the formally forbidden $1S_{e(h)}-1D_{e(h)}$ transition in the TA spectra, the possibility that the feature was allowed due to an indirect transition involving intervalley scattering of phonons within the conduction band was considered.⁴ To test this hypothesis, a temperature dependent TA study was conducted to investigate whether the intraband $1S_{e(h)}-1D_{e(h)}$ transition was allowed due to coupling to excited state phonons. By eliminating the total number of phonon modes present in the sample through lowering the temperature, it was expected that the observed oscillator strengths of the $1S_{e(h)}-1D_{e(h)}$ transitions would be reduced if exciton-phonon coupling was responsible for breaking down the selection rules in the samples. **Figure A-10** depicts TA spectra measured under identical conditions to those depicted in **Chapter 3** but at temperatures of 298 and 77 K. By performing TA experiments at 77 K, a majority of the vibrational modes which have been identified in the resonant Raman and far infrared absorption spectra for PbS QDs were removed.¹⁰⁻¹² Specifically, at such low temperatures, the available energy of the system (6.6 meV) was below the predicted energy of the X-point phonon mode (~10 meV) responsible for intervalley scattering from one L point in the valence band to another L point in the conduction band.⁴ Despite a large reduction in the occupied phonon population, the amplitude of the measured $1S_{e(h)}$ - $1D_{e(h)}$ transition in the QDs was unchanged when compared to the room temperature TA spectra. The fact that a significant difference in intensity or line shape of the $1S_{e(h)}$ - $1D_{e(h)}$ transition was not observed for such a change in density of excited phonon modes indicated that the transition was not the result of an indirect excitation. Noteworthy increases in the lifetimes of the GSB and ESAs at low temperatures were observed which may be attributed to shallow trapping below the band edge in the sample (**Figure A-11**). These results suggested that the transition was a direct absorption event and supported the claim that the transition originated from a breakdown of parity selection rules within the QD.



Figure A-10. Broadband transient absorption spectra of an oleate capped PbS QD film at (a) 77 K and (b) 298 K.



Figure A-11. Normalized transient absorption kinetics for the GSB, $1S_{e(h)}$ - $1P_{e(h)}$, and $1S_{e(h)}$ - $1D_{e(h)}$ of the 2.9 nm oleate capped PbS QD film at 77 K.

A.2.6 Additional Size Dependences of Intraband Transitions

The $1S_{e(h)}$ - $1D_{e(h)}$ transition if formally forbidden due to parity selection rules and so the cause for its strong absorption signature in our data was sought out. The low and high energy ESA features in the TA spectra in Chapters 4 and 5, and in the Appendix were observed to be highly dependent on nanocrystal size, with both transitions becoming narrower as the QD radius increases. Additionally, the intensity of the $1S_{e(h)}-1P_{e(h)}$ and $1S_{e(h)}-1D_{e(h)}$ transitions appeared to be shrinking with increasing dot size. To quantify this effect in I/MPA capped samples, the relative oscillator strengths of the 1S_{e(h)}-1P_{e(h)} and 1S_{e(h)}-1D_{e(h)} transitions were plotted as a function of the QD volume. This comparison is shown in Figure A-11. In Figure A-11, the areas of the measured transitions have been normalized to the bleach. In normalizing in such a way, size dependent differences in extinction coefficients and normalization of the excited state concentrations across the samples can be taken into consideration. Additionally, normalizing in such a manner eliminates increased area of a transition due to inhomogenous broadening as a result of non-uniform QD size distributions in the sample. This procedure causes the bleach area to always be one and it has been included in the figure for reference. The $1S_{e(h)}$ - $1D_{e(h)}$ transition is shown to increase as the QD volume decreases, while the $1S_{e(h)}$ - $1P_{e(h)}$ transition has the opposite trend. This variation is characteristic of "oscillator strength borrowing" that can arise from coupled, nearly degenerate transitions that form a Fermi resonance¹³ or from systems in which a break of symmetry allows a formally forbidden transition to become allowed. In the latter case, the break of symmetry can also suppress the oscillator strength of the normally symmetry allowed transition. A break in symmetry has been predicted to occur in PbS QDs¹⁴ and such a break in symmetry is consistent with the strong size-dependence measured throughout the data. It was concluded that the $1S_{e(h)}$ - $1D_{e(h)}$ transition becomes allowed due to a break in

inversion symmetry in small QDs as the crystal lattice shifts away from the center of the nanocrystal.



Figure A-12. Area calculated from the log-normal fits to the transient absorption spectra at 20 ns and normalized to the area of the bleach for I/MPA capped PbS QD films. Solid lines represent the line of best fit for the data points to emphasize trends.

A.2.7 Size-Dependent Spectral Linewidth of Quantum Dot Samples

Broadening of electronic transitions in semiconductor nanocrystals is controlled by homogenous and inhomogenous broadening. Inhomogenous broadening is largely regulated by the size distribution of QD samples while homogenous broadening has been presented to be dominated by electron-phonon interactions.¹⁵⁻¹⁶ Quantum confined systems have been shown to exhibit strong size dependence on electron-phonon coupling.¹⁵ To determine the strength of electron-phonon coupling in Γ /MPA samples, the size-dependent variances of the functions used to fit the measured GSB ($1S_h-1S_e$), $1S_{e(h)}-1P_{e(h)}$, and $1S_{e(h)}-1P_{e(h)}$ transitions measured in the TA experiments were compared in the same manner as in **Chapter 3** (**Figure A-13**).¹⁵ Additional analysis to linearlize the data by plotting the variance against $1/R^3$ was performed (**Figure A-14**) in order to predict the type of phonon modes present in the sample and compared to oleate capped QD samples.



Figure A-13. Variance of the $1S_{e(h)}$ - $1P_{e(h)}$, $1S_{e(h)}$ - $1D_{e(h)}$ and bleach features from the fits to the TA data for I/MPA capped PbS QD films.



Figure A-14. Linearlized variance plot of the $1S_{e(h)}-1P_{e(h)}$, $1S_{e(h)}-1D_{e(h)}$, and bleach transitions measured in TA spectra for I/MPA capped films.

A.2.8 Photoluminescence Spectra of Quantum Dots

Transient photoluminescence spectra of all of the samples studied were measured in addition to the TA data that was collected. The time-resolved spectra are given in **Figures A-15** through **A-17**. All samples had strong emission, with radiant lifetimes that depended on the

diameter and type of ligand on the QD sample. Colloidal solutions with oleate ligands had the longest PL lifetimes while films capped with Γ /MPA ligands had the shortest lifetime. The emission spectra also displayed a dynamic shift to lower frequency. This shift was likely a result of energy transfer to the largest diameter nanocrystals in the sample and was on the order of ~50 meV.



Oleate Capped Films

Figure A-15. Photoluminescence decay traces for (a) 2.9 nm , (b) 3.1 nm, (c) 3.7 nm, and (d) 4.9 nm oleate capped PbS QD films.



Figure A-16. Photoluminescence decay traces for (a) 2.9 nm , (b) 3.1 nm, (c) 3.7 nm, and (d) 4.9 nm oleate capped, colloidal PbS QD solutions in chloroform.



Figure A-17. Photoluminescence decay traces for (a) 2.9 nm , (b) 3.1 nm, (c) 3.7 nm, and (d) 4.9 nm PbS QD films capped with I/MPA ligands.

A.2.9 Modeling Density of States for Quantum Dots with I/MPA Ligands

Spectral density of state plots were constructed for PbS QD films capped with I/MPA ligands. These plots are shown in **Figures A-18**. The plots exhibit identical, size dependent trends which were showcased in Chapter 3 for oleate capped QD samples. Small diameter QDs have increased spectral breadth that causes a large overlap area between the $1P_{e(h)}$ and $1D_{e(h)}$ states. In addition to a large overlap of the higher energy density of states, there is also an overlap of the $1S_{e(h)}$ and $1P_{e(h)}$ states. Such large spectral overlap is the direct result of electronic state coupling to vibrational modes. This energetic overlap provides resonant relaxation pathways between high energy states to the band edge. Through this mechanism, carriers are able to thermalize rapidly, approaching bulk cooling rates. Larger diameters of QDs maintain spectral overlap between $1D_{e(h)}$ and $1P_{e(h)}$ states, yet this overlap is reduced as the magnitude of excitonphonon coupling decreases. The 1S_{e(h)} and 1P_{e(h)} states also have minimal overlap in such large diameter quantum confined systems. Large diameter systems which minimize exciton-phonon interactions have narrower densities of intraband states and therefore are more suitable for slowed-carrier cooling. Slowed carrier cooling in PbS QD samples is predicted to increase the efficiency of MEG or HCE for application in photovoltaic devices.



Figure A-18. Experimentally obtained spectral density for 2.9 nm, 3.1 nm, 3.7 nm and 4.9 nm I/MPA capped PbS QD films. The lineshapes and intensities were obtained directly from fits to the transient absorption spectra. The 1S state energies (green) were set to 0 eV along the y-axis while the 1P (violet) and 1D (cyan) states remained unchanged, maintaining their respective energy separations from the 1S state.

A.2.10 Broadband Transient Absorption Spectra of I'/MPA Capped PbS Quantum Dots

In addition to the broadband spectra of oleate capped films and solutions, TA spectra of PbS QD films capped with Γ /MPA ligands were also measured, to determine the effects of ligands on the exciton-phonon coupling. The size-dependent spectra presented in **Figure A-19** have slight differences in peak energies due to interdot electronic coupling caused by the conducting ligands used to passivate the surfaces. The overall spectral signatures however are identical to the oleate capped spectra measured, with the calculated variances from log–normal fits to the data having no significant differences between the ligand sets. This indicates that Γ /MPA ligands do not alter the exciton-phonon coupling in PbS QDs, suggesting ligands are not responsible for vibronic coupling. Instead, the data reveals that the broad phonon spectrum of the QD surfaces are responsible for exciton-vibrational interactions which significantly broaden the QDs electronic states, leading to resonant relxation pathways.



Figure A-19. Transient absorption spectra of PbS QD films capped with I /MPA ligands at 20 ns for (a) 2.9 nm, (b) 3.1 nm, (c) 3.7 nm, and (d) 4.9 nm diameter dots. Red lines show the fit to the data using the sum of three log-normal functions representing the $1S_{e(h)}$ - $1P_{e(h)}$ (violet) and $1S_{e(h)}$ - $1D_{e(h)}$ (cyan) transitions, along with the bleach (green). Orange spheres represent the diameter of the QDs.

A.2.11 Power Dependent Vibrational Spectroscopy of Quantum Dots

The intensity of the vibrational modes of the different diameter QDs, presented in **Figure** 4-7 exhibit what appears to be a size-dependent trend, with smaller dots having less intense vibrational signatures. To determine whether this variation in the vibrational intensities was due to size-dependent properties, or a change in the concentration of photons absorbed per QD in the samples, mid-IR TA was performed on the 2.9 nm PbS QD samples capped with native oleate ligands and varying absorbed energy densities of the pump laser. These power-dependent data are presented in Figure A-20. At the lowest energy densities measured, the vibrational spectrum matches the spectrum of the 2.9 nm diameter QDs in 4-7. At higher energy densities however, the spectrum of the 2.9 nm diameter dots look nearly identical to the 4.9 nm dots in Figure 4-7, with the growth of the C-O vibrational mode being highly dependent on the energy density of the measurements. The power-dependent vibrational signatures are likely highly sensitive to the number of photons absorbed per QD. As the number of excitons is increased in the QD film, the surfaces of the QDs become less electronegative as the electrons localize on them. This decrease in electronegativity decreases the interaction between Pb atoms on the QD surface and the carboxylate groups of the oleate ligands. Such decrease in interaction reduces the bond order of the Pb-O bond causing the ligands to adopt more unidentate character in the excited state. The reorganization of the ligands binding geometry is a reversible process that returns to steady-state geometry as the excitonic states of the QDs decay.



Figure A-20. Transient absorption spectra after the removal of the $1S_{e(h)}$ - $1P_{e(h)}$ electronic feature at 40 ns for a 2.9 nm diameter QD film capped with oleate ligands. The different spectra correspond to different absorbed pump energy densities at 532 nm. Also shown is the ground state FTIR of the sample for reference.

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VITA

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During his time at Penn State Eric had the opportunity to present his work at seminars and professional conferences including: The College of Engineering Research Symposium at Penn State where he won a second place paper/presentation award, The ACS National Meeting and Exposition in New Orleans, and The ACS National Meeting and Exposition in Boston. Eric was also awarded the Dr. John Randall Shuman Troxell Scholarship in Chemistry for his work. This dissertation serves to complete his work as a doctoral candidate at Penn State University.