Energetics and Dynamics in Quantum Confined Semiconductor Nanostructures

Jessica Hoy
Washington University in St. Louis

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WASHINGTON UNIVERSITY IN ST. LOUIS

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Energetics and Dynamics in Quantum Confined Semiconductor Nanostructures

by

Jessica Hoy

A dissertation presented to the
Graduate School of Arts and Sciences
of Washington University in
partial fulfillment of the
requirements for the degree
of Doctor of Philosophy

May 2013

St. Louis, Missouri
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>$a_B$</td>
<td>Bulk exciton bohr radius</td>
</tr>
<tr>
<td>$a_e$</td>
<td>Electron bohr radius</td>
</tr>
<tr>
<td>$a_h$</td>
<td>Hole bohr radius</td>
</tr>
<tr>
<td>$\sigma_{\text{abs}}$</td>
<td>Absorption cross-section</td>
</tr>
<tr>
<td>$\chi_{\text{abs}}$</td>
<td>Absorption cross-sectional density</td>
</tr>
<tr>
<td>1D</td>
<td>One-dimensional (quantum confinement)</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional (quantum confinement)</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional (quantum confinement)</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>EED</td>
<td>Excitation-energy dependence</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest-occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest-unoccupied molecular orbital</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-infrared</td>
</tr>
<tr>
<td>NPL</td>
<td>Nanoplatelet</td>
</tr>
<tr>
<td>ODA</td>
<td>Octadecylamine</td>
</tr>
<tr>
<td>OLA</td>
<td>Oleylamine</td>
</tr>
<tr>
<td>Ox1</td>
<td>Oxazine1 (3,7-bis(diethylamino)phenoxazin-5-iium perchlorate)</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PLE</td>
<td>Photoluminescence excitation</td>
</tr>
<tr>
<td>QB</td>
<td>Quantum belt</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum dot</td>
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<tr>
<td>QW</td>
<td>Quantum wire</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>PL QY</td>
<td>Photoluminescence Quantum yield</td>
</tr>
<tr>
<td>Rh6G</td>
<td>Rhodamine 6G (2-[6-(ethylamino)-3-(ethylimino)-2,7-dimethyl-3H-xanthen-9-yl]-benzoic acid)</td>
</tr>
<tr>
<td>TCSPC</td>
<td>Time-correlated single-photon counting</td>
</tr>
<tr>
<td>TOP</td>
<td>Tri-octylphosphine</td>
</tr>
<tr>
<td>TOPO</td>
<td>Tri-n-octylphosphine oxide</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>W</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>ZB</td>
<td>Zinc-blende</td>
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</table>
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Finally, thank you to my mom, my dad and my sister, Debbie, Peter, and Rebecca Hoy. I rely on you for your guidance and advice. You have always been sources of my determination and dedication. Thank you for always placing such an important emphasis on my education and for the sacrifices you have made for it. I know that it made a difference in the work I’ve done. I love you very much.
To Mom and Dad
ABSTRACT OF THE DISSERTATION

Energetics and dynamics in quantum confined semiconductor nanostructures

By
Jessica Hoy

Doctor of Philosophy in Chemistry
Washington University in St. Louis, 2013
Professor Richard A. Loomis, Chairperson

The ability to tune the band-gap energies of semiconductor quantum dots, nanoplatelets, and quantum wires, their significant absorption cross sections, and high photoluminescence quantum yields make these nanostructures promising moieties for use in optoelectronic devices, solar concentrators, chemical sensors, and biological labels. The variable dynamics of the electron-hole pairs that occur within semiconductor nanostructures, however, can complicate the utility of these devices. The variability of the dynamics is born from the different paths accessible for the charge carriers to endure. In this work, three pathways are proposed to be of primary consequence, namely, electronic intraband relaxation, coupling to surface-mediated processes, and tunneling to the external environment. The dominance of these paths will depend on the sample. More importantly, within a sample, the contributions of the available pathways are found to change with excitation energy.
To this end, I investigated the dependence of the photoluminescence (PL) quantum yields (QYs) on excitation energy for numerous semiconductor nanoparticles with quantum confinement in varying dimensions. A strong dependence of the PL QY on excitation energy is observed in quantum dots (QDs), nanoplatelets (NPLs), and quantum wires (QWs). The highest PL QYs are within the first 300 meV above the band edge, and there is a severe drop in the PL QY towards the highest excitation energies investigated, ~3.1 eV. These high PL QYs are 91 % for CdSe/ZnS QDs, 24 % in CdSe NPLs, which are dispersed in toluene and 25 % in CdTe/CdS QWs, which is dispersed in TOP. These values drop to 12, 8, and 8 % by 3.1 eV, respectively. The decreases are not monotonic, and there are some recognized trends to the shape of this dependency. Local minima in PL QY values occur when intraband relaxation is restricted and ligand or surface mediated transitions are available. For example, the energy spacing between charge carrier states of QDs with diameters of ~ 5.7 nm large enough that the coupling to the surface states effectively competes with intraband relaxation and a minimum in the PL QY results. These variations in PL QY are reduced when a shell is added to produce a type-I heterostructure. QWs are more weakly confined systems with large surface areas. Their saw-like densities of states that result from the long, unconfined dimension of the QWs and increased valence state mixing yields a higher density of states which leads to a smoother PL QY dependence of the excitation energy. The minimal undulations in the PL QYs that do still exist in these QWs, are further minimized with the addition of a shell to create a type-I heterostructure. This result reveals the role of surface-related processes in QWs. The pseudo-2D confinement and atomic flatness of NPLs results in narrow, discrete bands of states separated by large energies, ~ 200 meV. This electronic structure restricts intraband relaxation and promotes coupling to other pathways that sponsor non-radiative recombination even more efficiently than
QDs. Exciting with high energies in the near-visible region severely diminishes PL QYs in all samples as these energies generate highly excited charge carriers that can access environmental pathways.
Chapter 1:

Introduction
1.1 Semiconductors and excitons

In atomic and molecular systems, energy transfer can occur within a molecule via intramolecular vibrational energy redistribution and electronic state coupling. Energy transfer between molecules can occur through coupling of rotations, vibrations, or electronic excitation. In all of these energy transfer mechanisms, the probability for the coupling depends on the relative energies of the states being coupled. Within a molecule, the energy between the first excited state and the ground state depends on the build up of atomic orbitals to form molecular bands, the highest occupied molecular orbital (HOMO) being the ground state, and the lowest unoccupied molecular orbital (LUMO) being the first exited state. In solid state systems, the magnitude of the energy difference between the HOMO and LUMO, referred to as the band gap or $E_g$, can be separated into one of the following three types: metals, semiconductors, and insulators. In a metal the energies of the HOMO and LUMO orbitals overlap, and electron promotion occurs with very little or no impetus. In insulators, $E_g$ is very large and electronic excitation is a weak or unlikely process. Semiconductors, as their name suggests, have a measurable band gap but not so significant as to limit electronic excitation. The states that lie at or below the HOMO are in the valence band (VB) and the states that lie at or above the LUMO are in the conduction band (CB). In large-scale semiconductor materials, the build up of the atomic orbitals in forming the molecular orbitals includes many, many atoms each with slightly different energies. In the case of heteroatom semiconductors, the VB can be comprised of metal atomic orbitals and the CB is comprised of non-metal atomic orbitals.\textsuperscript{1-3}

Electronic excitation can occur in a semiconductor when a photon with energy equal to or greater than $E_g$ is absorbed. The promoted electron leaves behind a vacancy and there is less electron density than there is the ground state of the system.\textsuperscript{4} The electron deficient region
behaves as a positively charged particle with an effective mass greater than that of the electron, and is referred to as a hole. Depending on the crystal structure of a semiconductor, the dispersion or energy distribution of the VBs can lead to three types of hole states, a heavy-hole, light-hole and split-off hole state. The materials investigated as part of this thesis have either Zinc-blende (ZB) or Wurtzite (W) crystal structures, both of which have these three hole-states. It has been shown, however, that transitions from the heavy-hole state tend to dominate the optical spectra, and it will thus be the primary focus of any discussions.[Landsberg, 1991 #660] The energy and distribution of the photogenerated electrons and holes are described quantum mechanically by their wavefunctions, probability distributions, and permitted energies. The breadth of the probability distributions of the electrons and holes determine their effective size and are referred to as the electron $a_c$ and hole $a_h$ Bohr radii. As for all charged particles, there are Coulombic interactions between the electrons and holes, and the strength of these interactions determine if the electrons and holes can be treated separately or as Coulombically bound electron-hole pairs, termed excitons. There is a preferred separation distance between the electron and hole probability distributions in an exciton, and this distance is termed the exciton Bohr radius, $a_B$.

1.2 Quantum confinement

Decreasing the size of a semiconductor particle in one, two or all three physical dimensions can change the electronic structure of the material by confining the spatial distribution of the exciton, electron, or even hole wavefunctions. There are many reports on the role of nanoparticle size on the energetics of the excitons, electrons, and holes. In this thesis, I investigate how the properties and dynamics of excitons, electrons, and holes depend on the degree of confinement of the semiconductor material. The samples characterized include...
quantum dots (QDs), quantum wires (QWs), and nanoplatelets (NPLs) that exhibit quantum confinement in 3D, 2D, and pseudo-2D, respectively. All of the materials studied are direct-band gap materials. The density of states in the VBs and CBs of a bulk semiconductor form continua above the lowest energies of the bands, as depicted in Figure 1A. The electronic states in the CBs and VBs of a semiconductor become quantized, or discrete, as the size of the material in at least one dimension is reduced to that of the exciton, electron, and hole probability distributions. Since there is a continuum of states for each of the dimensions that do not exhibit quantum confinement, the density of states depend on the dimensionality of the material, as shown in Figure 1. The states of a QD become discrete with energies of a few hundred meV between the quantized states, Figure 1D, and there is a similar shift of the band gap to higher energy than the bulk $E_g$. In a 2D system (Figure 1C), the states resemble a saw-like quasicontinuum, the energy between these states can be a few hundred meV, and the band gap can also shift a few hundred meV above $E_g$. The free degree of freedom along the long dimension gives rise to a distribution of kinetic energies for the charge carriers that is dictated by the temperature of the sample and tails spanning to higher energy accompany each discrete state so that a saw-like pattern of states is formed. Contrary to the QDs, the QWs can have significant state mixing in the VB due to the increased energetic proximity of the hole states. This mixing leads to a more complicated energy pattern, and clusters or groups of transitions can result that further increase the density of states.
Figure 1-1. The density of states in energy for a semiconductor as the degree of quantum confinement increases. On the left, a), shows the continuous nature of the bulk material, b) depicts confinement in 1 dimension, c) in two and d) the density of states becomes discrete for confinement in all three dimensions.

Another semiconductor nanostructure investigated as part of this thesis is the NPL. Charge carriers in NPLs are considered to exhibit pseudo-2D confinement. Here, the confinement in the dimensions are not the same, and there is one small dimension that exhibits strong confinement, one larger dimension that leads to weaker confinement, and the third dimension has no confinement.

The strong, medium, and weak confinement terms mentioned are a result of the specific size in each dimension relative to $a_B$, $a_e$, and $a_h$. In the case of strongly-confined systems, the restricted dimension(s) are smaller than both $a_e$ and $a_h$. In an intermediate-confinement regime, the size of the confined dimension is smaller than $a_e$ but greater than $a_h$. In a weakly confined system, the restricted dimension(s) are larger than both $a_e$ and $a_h$ but small enough that the wavefunction of the exciton is perturbed, and an energetic shift of this state to higher energy results. The QDs and QWs investigated in this thesis are sufficiently small that photogenerated charge carriers in them are all intermediately confined. Charge carriers in the NPLs, however, are strongly confined in one degree of freedom, X, intermediately confined in another, Y, and are weakly confined in the last, Z. In NPLs, then the density of states is similar to 2D QWs, in that there is a saw-like distribution to the states. The quantized energies of the NPLs are observed to be separated by several hundred meV, and the band-gap energy is also shifted to
higher energy in accord with the extent of confinement. The NPLs are further dissimilar from the QDs and QWs investigated due to the near atomic flatness and an extremely small inter-platelet diameter distribution. The high quality of the NPLs synthesized in the Buhro laboratory gives rise to little inhomogeneous broadening in absorption and photoluminescence spectra in comparison with those of other semiconductor nanomaterials.

The extent of confinement also affects the spatial overlap of the electron and hole wavefunctions and the Coulombic interactions between them. Bound electron-hole pairs, or excitons, should also be treated as quantum-mechanical systems with wavefunctions that resemble this simple H-atom system. The photogenerated electron-hole interactions are weak in bulk semiconductors, and the binding energies are sufficiently small that the electron-hole pairs are not bound at room temperature. Instead, they dissociate into separate electrons and holes. The dependence of the oscillator strength and the binding energy depends on how many degrees of confinement there are. The energy interactions due to quantum confinement are often large compared to the coulomb interaction term. Furthermore, the dimensionality may not permit the electrons and holes to be stabilized at a preferred length within the coulombic potential, and excitons may not be formed. Such is the case for small QDs, where the electrons and holes are forced to occupy the same volume and the electrons and holes weakly interact and can be considered as independent systems. In QWs with 2D quantum confinement, the electrons and holes are quantum confined in the radial dimension, but not along the long axis. The electrons and holes interact strongly along the long axis, and can be bound, even at room temperature, as 1D excitons. Binding energies for 1-D systems are predicted to be tens of meV’s for typical QWs. Exciton levels with wave functions resembling simple particle-in-a-1D Coulombic potential are associated with these bound D excitons, and such levels have recently been
observed for CdSe QWs in our laboratory.$^{19}$ Much less is known about the properties of electron hole pairs in pseudo-2D semiconductor systems, although large oscillator strengths have recently been predicted and observed for CdSe NPLs.$^{12,15}$ The pseudo-2D structure of the NPLs should result in bound excitons and some translational kinetic energy of the excitons.

1.3 Electronic structure and optical measurements

The resolution of the optical spectra recorded in the room-temperature experiments presented here is not sufficient to resolve the individual transitions that are permitted based on quantum-mechanical selection rules. The size distributions within the ensemble samples provide further broadening the permitted transitions. Calculations on the excitation spectra of CdTe QWs indicate that numerous electronic transitions with varying oscillator strengths tend to fall within single absorption features.$^{10}$

The absorption of a single photon at the excitation energies utilized in these experiments produces one electron-hole pair typically associated with the CB and VB states that are closest in energy to the photon energy and that are optically allowed. $^2$ Varying the excitation energy dictates the specific states that are accessed. Conservation of momentum must be obeyed for the QW and NPL systems, so the excitons, as well as the electron and hole within each exciton, are initially prepared with very little kinetic energy. The initially prepared electrons and holes promptly relax via interband relaxation that is enhanced by phonon and momentum coupling.$^{20}$

$^{21,22,23}$ Under low-power exciton conditions, the electrons and holes tend to efficiently relax to the lowest energies within the CB and VB and radiative recombine, giving off photons near the band gap energy, $E_g$. The measure of the number of photons emitted versus the number of photons absorbed is the photoluminescence (PL) quantum yield (QY) directly conveys the efficiency for both relaxation of the charge carriers and radiative recombination.
1.4 Intraband relaxation

Once the electron-hole pair is photogenerated at energies above the band gap, relaxation efficiently competes with emission from these excited states. Radiative rates are typically on the order of 20 MHz to 1 GHz, but relaxation processes tend to occur with rates of 1 to 10 THz.\textsuperscript{24} As just mentioned, the process of relaxation involves charge carrier coupling to phonons (vibrational modes in the crystal lattice) in addition to coupling to electronic and/or exciton states. Increasing the energy spacing between the electronic features increases the number of phonons required for charge relaxation from one state to the next lower state. It is hypothesized that above a certain energy difference, the probability for phonon-mediated relaxation between these states will become negligible, as the coupling to multiple phonons becomes improbable.\textsuperscript{20,25} The energetic threshold where phonon coupling becomes so inefficient that the rate for interband relaxation becomes low is known as the phonon bottleneck.\textsuperscript{26} In general, the density of states is lower and the energy spacing between adjacent states is higher near the band edge in comparison with those at energies well above the band gap. Both effects mean more phonons are required for charge carrier relaxation from one state to the next. As a result, differences in the efficiency for relaxation to the band gap should be more prevalent for excitation energies accessing this low-density regime near the band gap.

1.5 Competing pathways

There exist numerous charge carrier relaxation pathways and mechanisms that compete with interband relaxation and radiative recombination, and these will result in a reduction in the PL QY. The roles of these competing pathways become even more prevalent when inter- and intraband relaxation becomes less efficient, such as when there is a phonon bottleneck.\textsuperscript{26} Typical pathways that efficiently compete with intraband relaxation of the charge carriers to the
band gap include coupling to bound ligand states,\textsuperscript{20,25} coupling to surface traps,\textsuperscript{27-29} or tunneling into the environment.\textsuperscript{30-32} The nanoparticles investigated in this thesis are single crystalline, but there may be imperfections in the QDs, QWs, or NPLs that would result in variations in the potential-energy landscape. The potential minima can trap or localize the excitons, and even separate the electrons from the holes in the QWs or NPLs. The proximity of the ligands bound to the surface of a nanoparticle to the charge carriers photogenerated within the nanoparticle can also influence the dynamics and the PL QYs. The energetic alignment of the ligand states relative to the CB and VB states of the semiconductor nanoparticle can result in the formation of donor or acceptor states that will influence the relaxation dynamics. For the larger nanoparticles, such as QWs, incomplete surface passivation by the ligands can result in localized charge carrier traps and an irregular potential-energy landscape along the QWs. The formation of Type I semiconductor systems can be achieved by forming a shell of a higher-energy semiconductor on the nanoparticle. This shell acts as an energetic barrier between the charge carriers generated in the core of the semiconductor nanoparticle and the surface of its surface and the local environment. Depending on the offsets of the core and shell VBs and CBs, the charge carriers may still interact with varying degrees with the surface ligands and environment via tunneling of the charge carriers through the shell.\textsuperscript{33} The environment can consist of the solvent as well as any free ligands from the synthetic reaction. The tunneling efficiency of the charge carriers depends to some extent on the specific electronic states of the electrons and holes. The radial probability distribution of the lower-energy S-like states will have a lower probability for tunneling through the shell than higher-energy states, such as the P-like and D-like states that have extended probability to longer radial distances.\textsuperscript{10,24,34} As a result of these probability distributions and the lower potential barrier for tunneling, the dynamics of
charge carriers prepared well above $E_g$ will tend to be more strongly influenced by the surface and environment than those prepared near $E_g$.

The last alternative relaxation pathway arises from the surrounding environment of the sample. For ensemble measurements the nanoparticles are typically suspended in a solvent, such as toluene, hexane, etc. However, colloidal synthetic techniques that are used for making the semiconductor nanoparticles, often have other byproducts and residual ligands remaining in the sample. Most of the residual ligands are short chain alkyl, amine, or phosphine chemicals. These compounds, as well as the solvent itself, can both absorb photons and interact with the charge carriers photogenerated with the semiconductor nanoparticles. The typical onsets for absorption of these types of molecules are typically in the blue spectral region, and as a result they may overlap transitions associated with excitation of the QDs, QWs, and NPLs. Even if not directly excited, the offsets between the HOMOs and LUMOs of these compounds relative to the energies of the CB and VB states of the nanoparticles may result in additional relaxation pathways along which the charge carriers photogenerated within the semiconductor nanoparticle can evolve.

The schematic energy-level diagram included in Figure 2 depicts the relaxation pathways that may be followed for charge carriers prepared in CdSe/ZnS QDs.
Figure 1-2. A representative absorption spectrum for a CdSe/ZnS QD is shown in the black data. Three lines indicate hypothetical excitation energies, red, blue and black, in order of increasing energy. Above this absorption spectrum, a simplified energy level diagram for the electronic transitions is shown. The red, blue and black excitation arrows reflect the relative energy above the band edge. The possible energetic pathways for the excited charge carriers changes for the red versus the blue versus the black excitation.

This diagram is representative for a single CdSe/ZnS QD. The absorption spectrum is shown at the bottom, the black data. Each of the three lines on the absorption curve, red, blue, and black are proposed excitation energies. The simplified energy-level diagram above the absorption displays the proposed charge carrier pathways for each of the three excitation energies, and is color-coded to correspond to each. Due to the variations in sample, surface passivation, and environments, the efficiencies for the competing pathways may contribute to varying degrees. At the band edge, charge carriers can radiatively recombine. However, some surface traps are present and coupling to these states can occur leading to an increased probability for non-radiative recombination. As the excitation energy is increased, the charge carriers can interact with electronic transitions, bound-ligand states, and surface trap states. The ability to couple to the electronic transitions to relax to the band edge, requires coupling to phonon modes. With
large confinement and large $\Delta E$ between electronic transitions, phonon coupling becomes less efficient while coupling to other pathways become more probable. At the highest excitation energies new pathways exist due to the presence of free ligands. Highly excited charge carriers can couple to these and leave the QD permanently resulting in decreased radiative recombination. $^{27,35,32}$

For a type-I heterostructure, such as CdSe/ZnS, the ZnS shell creates an energetic barrier for the electron and hole. $^{36,37}$ The energy of the barrier is determined by the relative band offsets. $^{33}$ The barrier confines the electron and hole to the core of the QD, restricting their interaction with surface trap states and bound-ligand states. In theory, this should create the highest probability for intraband relaxation. In reality, some tunneling through the shell can occur that will occur to a higher degree for smaller QDs than larger QDs. However, the net effect is improved intraband relaxation, which promotes radiative recombination.

1.6 Photoluminescence quantum yield and excitation energy

As mentioned above, the PL QY is a measure of the number of photons emitted versus the number of photons absorbed. The typical procedure for determining a PL QY of a sample, termed the Relative PL QY method, involves two consecutive measurements. $^{38}$ First, the absorption of a sample is measured to determine the absorbance or number of photons absorbed by the sample at a given excitation energy. Second, the PL is collected for excitation at that same excitation energy for which you have an absorbance value. The integrated intensity of the sample PL spectrum is then compared to the integrated PL intensity measured for a standard sample with a known PL QY. Numerous measurements are repeated using different sample concentrations. The QY of the sample can then be calculated using
\[ Q_Y^{(\text{UNKNOWN})} = Q_Y^{(\text{Dye})} \left( \frac{m^{(\text{UNKNOWN})}}{m^{(\text{DYE})}} \eta^2_{\text{UNK}} \right) \]

Here, the subscripts represent variable for the sample, unknown, and the standard, dye. The variable \( m \) is the slope of the line obtained by fitting the plot of integrated PL intensity versus absorbance value, and \( \eta \) is the refractive index of the solvent used. Using appropriate conditions, the dye does not have an excitation energy dependence of the PL QY.\(^{38,39}\) Specific procedural details of this method as employed in this thesis can be found in Chapter 2 and Appendix II.

As has been discussed, the variety of relaxation pathways accessible depends on the excitation energy. It has been shown that this variability can cause changes in the relaxation process for both QDs and quantum rods. Since the process of PL emission first requires relaxation to the band edge, it is expected that, for a given sample, varying the excitation energy and collected several PL QYs will yield different values. This is the primary focus of the present work.

In contrast, the process of recombination from the band edge should involve the same pathways regardless of excitation energy. Charge carriers will leave the band edge by either recombining radiatively or will couple into surface traps. In this regard the PL lifetimes should not change with excitation energy within a given sample. From one sample to another, the relative amounts of trapping will likely change. Each sample will have a slightly different surface quality and can either be passivated with ligand or a shell. Therefore the process of relaxing from \( E_g \) to a trap state will vary from sample to sample, causing the radiative recombination to change. Deviations between samples will be discussed presently.
One final optical study that allows for probing of PL QY changes instigated by excitation energy is photoluminescence excitation (PLE). PLE is measured by setting the emission energy to that equal to or near the band edge and varying the excitation energy. The spectrum produced displays the changing emission intensity across a variety of excitation energies. For a molecule with no EED of the PL QY, the shape of the PLE data should match the absorption data. Dividing the normalized PLE by the normalized absorption produces a PL efficiency spectrum, which has recently been referred to as a photoactivation spectrum. These data can be plotted with the PL QY data to demonstrate reproducibility of any trend shapes.

1.7 Excitation energy and sample variability

There appear to be four dominant relaxation pathways that can efficiently compete with radiative recombination within semiconductor nanoparticles. These are the extent and dimensionality of quantum confinement, the degree of surface passivation and the chemical identity of the passivating ligands, and the local environment. In this thesis, I focus on the roles of dimensionality and excitation energy in dictating the PL QYs. Due to the 3D quantum confinement of charge carriers in QDs, the energy spacings between the VB and CB states are the largest of the samples. As a result, the efficiency for coupling to other non-radiative relaxation pathways may result in significant variances in the PL QY values as a function of excitation energy. Even though lower PL QYs are expected for QWs due to the sampling of larger surface areas along the QWs, the lower-energy spacings between the electronic states and the continua from the kinetic energies of the 1D excitons are expected to yield smaller variances in the PL QYs with excitation energy. In NPLs, the inefficient mixing of the heavy-hole and light-hole states and the near-atomic flatness of the sample make for a much more discrete
version of the saw-like continuum of states. The NPLs are therefore expected to show higher variations in the PL QYs than for the QWs.

The physical properties of the surfaces and the chemical nature at the interface of the semiconductor with the environment will play dominant roles in the efficiencies for charge carrier intra- and interband relaxation and radiative recombination near the band gap. The surface-to-volume ratio for QDs is smaller than for QWs, but the total surface area sampled by the delocalized 1D excitons is larger for the QWs. As a result, the relative contributions from surface-related relaxation processes will likely be greater for QWs than QDs. The NPLs also have a large surface-to-volume ratio, but it has been shown that the faces of these types of lamellar structures, which comprise ~85 % of the total surface, have a very low occurrence of surface traps. Additional reports have measured efficient band-gap emission with a minimal amount of low-energy surface-trap emission for similar NPL samples.

The work presented as part of this thesis indicates that there is indeed an excitation-energy dependence (EED) of the PL QYs in quantum dots, quantum wires, and nanoplatelets. While the overall shape of this dependence is similar with decreasing PL QYs towards the highest photoexcitation energies utilized, there are subtle differences between the EEDs that arise from the dimensionality of the samples. Numerous experiments reported in the literature utilize the intensity of the PL to monitor synthetic parameters and progress, chemical environment, as well as energy transfer phenomena. Although these reports do not state it explicitly, most of these experiments rely on a constant PL QY regardless of the excitation energy above the band gap. As a result, any experiments that probe effects of the varying size of the nanoparticles or varying the surface passivation, it may be necessary to map out the entire EED of the PL QY to truly identify what has truly changed within the sample.
1.8 References


Chapter 2:

Experimental methods and Validation of Spectroscopic Techniques
2.1 Synthetic Details:

A. Nanoplatelets (1.4 nm thickness)

The procedure for synthesizing NPLs has been reported previously,\textsuperscript{1-5} and our modifications to this method are described.

Cadmium acetate (Cd(OAc)\textsubscript{2}-2H\textsubscript{2}O, 65 mg) was dissolved in di-octylamine (5.7 g, 0.024 mol) in a N\textsubscript{2} purged Schlenk reaction tube. The selenium precursor was prepared by dissolving selenourea (SeC(NH\textsubscript{2})\textsubscript{2}, 50 mg, 4.06E\textsuperscript{-4}) in n-octylamine (CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{7}NH\textsubscript{2}, 1.2 g, 0.0093 mol) in a septum capped vial. Then the selenium precursor was injected into the cadmium precursor via syringe at room temperature. The reaction tube was left at room temperature under N\textsubscript{2}. After 2 days without stirring, CdSe NPLs were formed as indicated by a yellow precipitate mixed with a pale red supernatant. The samples were then annealed at an elevated temperature (70°C) for 40 min, during which the supernatant turned to deep red. Tri-n-octylphosphine (TOP, P(C\textsubscript{8}H\textsubscript{17})\textsubscript{3}) (0.25-0.50 mL) was injected into the round-bottom flask which reacts with elemental Se, resulting in a colorless solution with yellow precipitate. The mixture can then be centrifuged to remove the Se. The final product contained a matrix of CdSe NPLs. Unbundling this matrix into NPLs could be accomplished either by five to ten minutes of sonication in the presence of Oleylamine (OA, CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{7}CH=CH(CH\textsubscript{2})\textsubscript{8}NH\textsubscript{2})/toluene solution (1:1, v/v) or suspension in OA/toluene solution (1:1, v/v) for one day. The unbundled process transforms the product from many rows of NPLs to single NPLs. The sample was stored in a vial in OA/toluene solution for PL measurement.
B. Synthetic Detail: CdSe QDs (4.8 nm diameter)

The procedure for synthesizing QDs has been reported previously and our modifications to this method are described. 6-8

Specifically, 10 mg of cadmium oxide, CdO, 37 mg of Di-n-octylphosphinic acid, (DOPA, C_{16}H_{35}O_2P), 17 mg of tetradecylphosphonic acid (TDPA, CH_{3}(CH_{2})_{13}P(O)(OH)_2), and 5044 mg of tri-n-octylphosphine oxide (TOPO, OP(C_{8}H_{17})_{3}) were added to a Schlenk reaction flask in a glove box. A separate vial containing 505 mg of tri-n-octylphosphine selenide (TOPSe), 103 mg of TOP, and 56 mg of gold nanoparticles (diameters of 1-2 nm) was also prepared inside the glove box. The Schlenk reaction flask containing the cadmium mixture was heated in a salt bath and degassed for ~30 min at ~100°C in a clean, dry N\textsubscript{2} atmosphere. After 30 minutes the flask temperature was raised to 286°C. Once the temperature was stable, the TOP mixture was injected into the Schlenk flask and allowed to react for 5 minutes with no stirring. The solution was taken out of the salt bath and allowed to cool for ~1 min before decanting into a storage vial.

C. Synthetic Detail: CdSe QDs (5.7 nm diameter)

The CdSe QD sample was synthesized using modifications to the method described by Qu and coworkers. 6-8 Specifically, 10 mg of Cd(OAc)_2, 90 mg of cadmium stearate (C_{36}H_{70}CdO_4), 406 mg of oleylamine, and 5299 mg of tri-n-octylphosphine oxide (TOPO) were added to a Schlenk reaction flask in a glove box. A separate vial containing 164 mg of TOPSe and 404 mg of TOP was also prepared inside the glove box. A Schlenk reaction flask containing the cadmium mixture was heated in a salt bath and degassed for ~30 min at ~100°C in a clean, dry N\textsubscript{2} atmosphere. After 30 minutes the flask temperature was raised to 304°C. Once the temperature
was stable, the TOP mixture was injected into the Schlenk flask and allowed to react for 2.5 minutes with no stirring. The solution was taken out of the salt bath and allowed to cool for ~ 1 min before decanting into a storage vial.

**D. Synthetic Detail: CdSe/ZnS QDs (4.9 nm core diameter, 6.9 nm total diameter)**

The CdSe/ZnS core/shell QDs were purchased from NN Labs. Part No. CZ600-25.

**E. Synthetic Detail: CdTe quantum wires (5.3 nm and 7.9 nm diameter)**

The CdTe QWs were synthesized by Yihsin Liu using the solution-liquid-solid growth mechanism. The protocol established for synthesizing the 5.3 nm and 7.4 nm ligand passivated wires is referred to as the “ODPA protocol”, it typically generates QW with frequent alternations of W and ZB within a wire, and can be found in the following references.

The general synthetic procedure utilizes ~15 mg of CdO and 50 mg of octadecylphosphonic acid (ODPA, C_{18}H_{37}P(O)(OH)_{2}) are dissolved in 5 g of distilled TOPO in a Schlenk reaction tube. ~ 25 mg of Bi nanoparticles of a specific diameter (5.8 nm Bi for 5.3 nm wires, 12.4 nm Bi for the 7.9 nm wires) and 1.25 g trioctylphosphine telluride (TOPTe) are combined in a vial. The components in the Schlenk tube were heated to 340 °C in a salt bath for ~ 5 min. The temperature is then lowered to a specific value (250 °C for 5.3 nm wires, 275 °C for 7.9 nm wires). After the temperature equilibrates, the mixture in the vial is injected into the Schlenk tube. After 5 min, the reaction tube is withdrawn from the salt bath and allowed to cool. Dried toluene was added, and the sample was stored in a glove box.

**F. CdTe/CdS quantum wires: (6.8 nm diameter core)**

The CdTe/CdS QWs studied in this work were synthesized by Fudong Wang. The procedure is referred to as the “OA-TDPA-DOPA” procedure and primarily produces Wurtzite crystal structure. The procedure utilizes ~15 mg of CdO, 100 mg of OA, 12 mg TDPA, 12 mg
DOPA are dissolved in 4.15 g of recrystallized TOPO in a Schlenk reaction tube. ~ 20 mg of 10.3 nm diameter Bi and 0.750 g TOPTe are combined in a vial. The components in the Schlenk tube were heated to 320 °C in a salt bath for ~ 80 minutes. The temperature is then lowered to 248 °C. After the temperature equilibrates, the mixture in the vial is injected into the Schlenk tube. After 5.5 minutes, the reaction tube is withdrawn from the salt bath and allowed to cool. ~ 3 mL dried toluene was added and the sample was stored in the glove box.

The process of adding the CdS shell occurs via a thermal enhancing process. First, an aliquot of the as-synthesized QWs in dried toluene are placed in a borosilicate test tube and removed from the glove box. Then ethane thiol is added. Typically amounts used are, 1 mL of QWs and 1.5 mL of ethane thiol. The sample is deliberately exposed to air for 1 - 2 s. The test tube is then placed into a hot sand bath (100 °C) for 23.5 hours. After this time, the sample is precipitated via centrifugation, and the supernatant is discarded using a syringe. The remaining sample is suspended in TOP for storage.

Both the CdTe and the CdTe/CdS QWs were further passivated by a photoenhancing process. An aliquot of wires were loaded into a cuvette and suspended in TOP. The volume chosen is done so to maintain absorbance values are between 0.02 and 0.1 across the excitation energy region of interest. From a typical reaction mixture this is typically < 0.5 mL of the total synthetic product. This cuvette is then placed ~5 cm from a 100 W incandescent light bulb for a given amount of time. The photoenhancing times for the samples studied here will be reported in Chapter 4, where the data is discussed.

2.2 Absorption Spectroscopy

Absorption measurements were collected on a PerkinElmer lambda 950 spectrometer equipped with a scattering sphere. The absorption measurement is a dual beam experiment in
which a sample path and a reference path are compared side by side. A blank scan is collected first, during which both paths contain a solvent cuvette. The blank scan is utilized by the instrument software to remove any absorption of the solvent while also monitoring spectral variations. Then a sample scan is collected by placing a sample cuvette in the sample path and a matched cuvette containing the solvent in the reference path. The scattering sphere is utilized to minimize losses attributed to scattering. The sphere integrates the light exiting the sample in the forward direction. This light may be light scattered from the cuvette or from the sample, emission from the sample, and the excitation light transmitted through the sample. It was imperative to use the scattering sphere when measuring accurate absorbance values since the nanoparticles can scatter the excitation light, and a traditional attenuation spectrum would not differentiate between losses due to scattering from those due to absorption by the sample.

An graph comparing absorption and attenuation is shown in Appendix III.

Details of the procedure followed when recording accurate absorption spectra are included in Appendix III. All optical measurements are performed using matched quartz cuvettes for the sample and reference paths (spectra of the matched cuvettes are included in Appendix III.). The slit widths are maintained for a bandwidth of 5 nm for all measurements, and this resolution matches the resolution utilized in the PL measurements. The absorbance values are utilized in calculating the PL QYs as a function of excitation energy. Care was taken in these studies to minimize the possible role of other absorbing compounds present in the sample on the PL QY measurements. The major constituents that may remain in the sample and may perturb the PL QY and PL efficiency measurements are OLA, TOP, and TOPO. The absorption spectra of pure samples of these compounds are included in Figure 1.
TOPO is the major constituent in the sample, but pure TOPO in dry toluene has negligible absorbance throughout the spectral region over which the PL QYs are performed.

![Absorption Spectra Graph](image)

**Figure 2-1.** This graph includes the absorption spectra for a few ligands prevalent in the synthesis of the CdSe QDs, CdSe/ZnS QDs, CdSe NPLs and CdTe and CdTe/CdS QWs.

The OLA and TOP each comprise ~1.2% of the total moles of molecules in the sample cuvette after dilution in toluene for the spectroscopy experiments. Using the absorbance values of the pure OLA and TOP samples at 3.1 eV, 0.063 and 0.045, respectively, the maximum absorption from these ligands is 0.00076 and 0.00054, or a total of 0.0013. The QD samples are typically prepared so that the absorption is ~0.1 near 3.1 eV. For a PL QY of ~11% at 3.1 eV, the error resulting from the absorption of the OLA and TOP in the solution would be less than 0.2%, which is less than the error associated with each of the PL QY measurements. For NPLs, oleylamine is in slightly higher concentration, 5 % of the total moles. The TOP is however, only present in residual amounts. The maximum absorption from these ligands is 0.0031. For a PL QY of 9.5 % at 3.1 eV, the error from absorption of OLA in the solution is ~ 0.8 which is close to the error of the measurement.
2.3 Photoluminescence Spectrometer

The PL and PLE were collected on a home-built spectrometer that was calibrated using a NIST-traceable light source (AvaLight-HAL-CAL, from Avantes). The calibration file is validated by comparing the data from two standards, Rh6G and Ox1. Matched quartz cuvettes are used to collect the Photoluminescence (PL) spectra and photoluminescence excitation (PLE) spectra of all samples. Specific details of the spectrometer can be seen below and in Appendix II.

Overview of spectrometer specifications:

This overview is a general description of the spectrometer from light source to detector. The general layout for any fluorescence spectrometer requires an excitation source to excite the sample and for the detected light to be collected at 90 degrees from the incident beam path. However, there are some specific details that are very important to this spectrometer. The first is that the excitation source, being a 250W QTH filament, produces a rectangular beam shape. This affects the focal lengths required and as can be seen, traditional focal lengths are not always used. The bulb has a parabolic mirror behind it and 1.5” telescoping lens at the output of the lamp housing. These filaments are meant to have a lifetime of 50 hours but my studies have shown that beyond 15 hours the S/N is steadily increasing (see Appendix II. for details). The way to monitor lamp lifetime is to run the program entitled QTH Bulb Lifettime.vi when the lamp is turned on. (See section 5.3 to ensure proper lifetime acquisition). The way to monitor lamp lifetime is to run the program entitled QTH Bulb Lifettime.vi when the lamp is turned on. The component after the lamp is the first monochromator (hence forward to be referred to as the Excitation Monochromator or MonoExc) and we use is a 2150i. This MonoExc requires as FL 4 optic at the input and output. Due to the rectangular beam shape, there are specific equations for determining the distance from lamp to optic and these were verified by Newport.
and these details are shown in Appendix II.). The second lens (first mobile lens) is 6 inches away from the output of the lamp and 4 inches away from the entrance slit of the excitation monochromator. The lens is a 2” diameter lens with an 8” focal length.

Each turret in the 2150i monochromators has 2 grating options. The excitation monochromator has 3 different turret options in order to span the visible through the near infrared (NIR) wavelengths regions. Turret 1 has 2 visible grating options (utilized from 375nm – 900nm), turret 2 has 2 NIR grating options (utilized from 900nm – 2200nm), and Turret 3 has 1 NIR option (utilized from 1200nm – 2800nm). The grating positions and specs are displayed in section Appendix II. At the exit of this monochromator there is another F4 lens, this time diameter = 1”. The next item is a shutter from Vincent Associates. The purpose of the shutter is to only allow excitation light to interact with the sample when data needs to be collected. Otherwise the shutter is closed leaving the sample in darkness.

After the shutter there is a 25.4mm = d lens with a 1” focal length that focuses the light down tightly through a Stanford Research Systems (SRS) optical chopper wheel. The frequency of the chopper wheel is typically set to 1kHz and the set value output is fed into the lock-in amplifiers so that only signal with this set frequency is collected while the rest is attenuated. The resolution of this attenuation is determined by a setting on the front face of the lock-in amplifier. 28db/octave is what we typically use. The complimentary 25.4 mm = d, 1” focal length lens is on the other side of the chopper wheel, collecting the diverging light and re-collimating it (although the light is never perfectly re-collimated). Next there is a piece of flat CaF$_2$ that is used as a beam splitter reflecting, on average 9% of the incident light to a detector. The detector for the visible range is a Hamamatsu photomultiplier tube (PMTs), model R3896 and for the NIR, this is an liquid nitrogen cooled, InSb detector. In front of the PMT, there is a gold flip
mirror in place to switch the excitation detectors from visible to NIR. From this gold plated flip mount mirror, the beam is directed along a path of 2 gold parabolic mirrors that direct and focus the beam size down to the \( \sim 0.4\text{cm}^2 \) detector active area of the InSb detector. This detector monitors lamp fluctuations that can later be removed from the data during when the analysis program processes the data. Finally, there is a F3 lens, \( l'' = d \) that focuses the transmitted light down into the sample. The beam size at the middle of the sample holder = 0.185 \( \text{cm}^2 \).

The light passes straight through the sample holder. Any emission (and scatter) can then be collected at 90 degrees of the center of the sample holder. The best configuration was determined to be: first a 2” F4, is aligned 1.25” from the center of the cuvette; proceeded by a 1.5” F3 lens, 3.25” from the first lens; and finally a 1” F4 lens, 6.75” from the second lens and 2.75” from the entrance slit of the second monochromator used for detection (MonoDet). This second monochromator can be either a 2150i or a 2300i, both have been used and yielded both precise and accurate data. However, the 2300i is the standard and has a wider wavelength range, due to the purchased gratings. There are two turrets available. The first turret has 2 visible grating options (350-900nm); G1 is standard plane-ruled and G2 is Holographic to reduce effects from multiple orders of diffraction, in addition to a mirror. The second turret has 3 NIR options (900nm – 2500 + nm). The grating positions and specs are displayed in Appendix II. The second detector on the exit slits of this monochromator is also an R 3896. To collect NIR emission, the PMT simply needs to be removed from the exit slit and the gold parabolic mirrors are in place to guide the light into the second InSb detector. When working in the NIR, the last item that needs to be adjusted is the BNC cable out put from both the PMTs.

This system is calibrated by collecting an instrument response function (IRF) using the aforementioned NIST-traceable light source. The correction file includes corrections for
detector and pre-amplifier gain and slit width differences. As it is described in Appendix II, the calibration procedure commences with collection of absorption and emission data of two standard dyes, Rh6G (Exciton, 95 % = QY) and Ox1 (Exciton, 11 % = QY).\textsuperscript{18,19} The ratios of the QYs of these dyes is $\sim 8.6$. Any error in alignment or calibration will result in a different value.

The signal from either the PMTs or the InSb detectors, goes through a current pre-amplifier and then into the lock-in amplifier. Using the program entitled, \textit{Excitation Energy Dependence II.}, one can collect single PL(or PLE) spectra, several repeat PL (or PLE) spectra, several PL(or PLE) spectra at a variety of excitation wavelengths, Depending on the sample rate, a certain number of data points are taken and averaged together for each read-out value. This program requires that the computer write commands to: 2 monochromators, the shutter, and the BNC 2090 (into the back of the lock-in amplifiers to trigger the start of data collection); additionally, the computer will need to read data from the lock-in amplifiers and the monochromators. Once a spectrum is obtained, the numerical data as well as the text file is saved in the folder entitled “PLscans” (or “PLE scans”) on the desktop.

This data must then be corrected for instrument response and normalized to the NIST intensity values. The program entitled \textit{“Total Data Analysis”} performs this function. This program makes use of the NIST data sent to us with the calibrated lamp, the NIST data we collect with the lamp for both the excitation and the detection side of the spectrometer, and the voltage gain files for each of the PMT power supplies. The excitation arm is corrected for separately from the detection arm first. The final data is in excel format with column 1 with wavelength, column 2 with detection divided by excitation, column 3 with excitation data and column 4 with detection data. The second column of data is what should be reported and is
essentially unit-less as it is a ratio of $\mu$W/cm$^2$nm (OUT) versus $\mu$W/cm$^2$nm (IN). Any final data you would like to plot requires that you open in excel and then you have the choice to copy and paste in origin or continue to modify and plot in excel.

If you have collected emission of a sample as well as absorption you can proceed to calculating the quantum yield (QY) provided that the standard dye data has been collected recently. The program entitled Quantum Yield Estimator will allow you to determine the quantum yield of your sample within seconds (see appendix II. and III. on program protocols). This program simply requires you to select the values necessary from the most recent dye data (which is saved in a chart in this program) and then enter your absorbance value and integrated emission intensity for your unknown sample. One second after you push run, the output QY and error bar will appear. These values are not saved but simply displayed by an indicator on the front panel.

Appendix II. provide more specific details on the spectrometer set-up, how to calibrate the instrument, how the programs work, how to collect and analyze data and some advice on troubleshooting the instrument.
2.4 Photoluminescence Spectra

The PL spectra were collected on the aforementioned home-built spectrometer. For the excitation energy dependence measurements, the samples were prepared followed by collection of absorption spectra to verify appropriate optical densities for collecting emitted light at 90 degrees from excitation. For a PL measurement, the excitation energy is fixed and the emission energies being detected are varied. The choice of excitation energy in a standard experiment might be known. However, in this work, the choice of excitation energy is the main focus of the experiments.

Typical set-up parameters include 5 nm slit widths for every excitation energy and detection energy and use of the 1200 groove/mm, blazed at 500 nm. Electronic parameters utilized are typically, 1 KHz frequency for the optical chopper, < 600 V of gain for the excitation and emission PMT, 1 mA/V pre-amplifier gain for the excitation detector and 50 nA/V gain for the emission detector. The sensitivity on the excitation (emission) lock-in amplifiers is usually set to 100 mV – 1 V (1 mV – 500 mV). For any spectra that will scan near or over the excitation color, the PMT gain must be reduced and tested for these particular scans.

PL spectra were recorded at systematically by varying excitation energies. The excitation increments were 10 nm, which is associated with steps of 30 meV at low energies (near the band edge) of 75 meV at the highest excitation energies. The shape of the PL QY dependence using 5 nm step sizes were also collected for a few data sets to validate the shape. Any excitation scatter (or orders of excitation scatter) that appears in the PL spectrum must be removed and the methods described for this are shown in Appendix II.

Within each experimental data set, at least one of PL spectra is collected two or three times, non-sequentially, using the same exact parameters for each. This is to verify that the
sample is stable across the window of time for the entire experiment to run. In this regard it is recommended that the first PL spectrum collected using the first excitation energy is the taken again, as the last spectrum collected for the data set. For any repeat scans, whether for stability testing or concentration testing it is important to maintain and make note of the parameters to ensure they are the same. In this regard, the automatic text file that is generated for each scan is highly useful. Please see Appendix II for details.

2.5 Photoluminescence excitation spectra (PLE)

A PLE measurement requires that the emission energy is fixed and the excitation energy is varied. This is data reveals the amount of emission that occurs when exciting at each of a variety of excitation energies. For a mono-disperse sample with a narrow emission feature, a single emission energy is easily chosen – it is the peak of the emission line. In the case of the present work, all but one of the samples is poly-disperse. As will be discussed presently, the source of the dispersion comes from size distributions of the sample and potential energy traps that lie near $E_g$. Due to the band selection of the monochromators used in this experiment, PLE can then be used to select out size sub-sets, if the slits are narrow enough. The peak of the PL, or PL $X_c$, is utilized to collect one PLE spectrum. Similarly, several PLE spectra are collected by varying the center of the emission energy. These PLE spectra typically shift according to the different sized sub-set of total sample being studied. An example of several PLE spectra can be seen below for a batch of 5.7 nm CdSe QDs and 4.93 nm core CdSe QDs in Figure 2. The determination of the usefulness of each PLE spectrum is discussed further in proceeding sections.
2.6 Photoluminescence quantum yield measurements

Standard protocols have been established for calculating the emission QY for an unknown sample. There are however, several considerations that are often overlooked in everyday practice. These items are accounted for either by the set-up or in the protocol I have established (Appendix II. and III.). These items are: differences in solvent refractive index, concentration dependence of the dye or of the unknown, and the overlap of dye and unknown emission.

The first use of QY calculation is to validate the calibration file. This requires direct comparison of two standard dyes. Rhodamine 6G (Rh6G) has a known QY of 95 % and Oxazine1 a QY of 11 %. Plotting the absorbance versus integrated emission fits well to a straight line, the slope of which is proportional to each dye’s respective QY.

\[
\Phi_{PL}^A = \frac{\text{Slope}_A \cdot n_A^2}{\text{Slope}_B \cdot n_B^2} \cdot \Phi_{PL}^B
\]
The ratios of these two dyes in theory should be 8.6 and in practice remained within ~ 7% of this value. There is a known concentration dependence of these molecular dyes and it originates with the absorption of emitted photons.\textsuperscript{19,21} Therefore, the absorbance values were kept between 0.01 and 0.02 by using dilute concentrations.

To determine the QY of unknown samples we used a modified method. In order to collect these data in a timely and efficient matter, a modified version of QY calculation is used. The spectra take a few minutes each to collect and for each sample 25 to 45 spectra are collected. The traditional method of calculating PL QY requires the same data to be collected multiple times for each of several concentrations. This fairly large number of data sets will take several hours to collect (for a representative experiment, 35 PL spectra, at 2 minutes each, and 6 different concentrations, would take 7 hours) and this does not include the analysis. The method developed is described below and simplifies the entire process. In addition, it allows for using appropriately low concentrations for all the data collected (at each excitation energy) which has been shown to be very important in calculating PL QY.\textsuperscript{22} To address the important factors of sample stability and concentration dependence, single studies were done to test these effects. Repeating a few of the PL QY measurements at the beginning and end of the study validated the stability of the samples. The PL QYs were found to remain the same within the error of the measurement. The lack of concentration dependence on any of the PL QY data is discussed below.

The measured value of the absorption for the sample (X) is used in conjunction with the known values from fitting the dye data in the equation, $Y = mX + b$. The values for slope, $m$, and intercept $b$ are those found from fitting the dye data. Solving for $Y$ provides a “calculated integrated intensity” for the sample with the assumption that it has a QY equal to the dye.
ratio of this calculated integrated intensity to the dye QY can be set equal to the measured PL integrated intensity to X, the unknown QY. Solving for X provides the QY for the unknown. The choice of which dye to use in this measurement depends on the overlap of the emission spectra. For the samples studied in this work, both Rh6G and Ox1 were utilized to accomplish these measurements. The 5.7 nm CdSe QDs and the 4.9 nm-core CdSe/ZnS QDs and the CdTe and CdTe/CdS QWs emit in a range that spans energies under the Ox1 emission window. The 4.8 nm QDs and the 1.4 nm-thick NPLs emit in ranges closer to the emission of Rh6G. Thus, the corresponding dye data was used in the calculation of each sample PL QY.

The concentration dependence of the samples was studied by repeating this study for a few concentrations of each sample. These data can be seen below for one batch of NPLs, QDs and QWs. Since the dyes are suspended in methanol and each of the samples in either toluene or TOP, the refractive index is corrected for. The step is part of the LabView program, Quantum Yield Estimator.vi. Finally, plotting them together tests the precision of these two emission efficiency measurements. These data are shown below again for NPLs and QWs in Figure 3.
Figure 2-3. The top graph shows the EED of the PL QY for 2 different concentrations of the CdSe NPLs. The bottom graph shows the EED of the PL QY for 3 different concentrations of 5.5 nm diameter CdTe QWs.

2.7 Photoluminescence Efficiency measurements

PL efficiency spectrum is the PLE divided by the absorption. In quantum dots, size selection has been shown to affect the shapes of PL spectra and can therefore cause shape changes in the PLE spectrum. To investigate the potential size-selecting shape effects we compare PL efficiency curves calculated by two different methods to generate the numerator – the PLE data – divided by absorption. First, by using an average of a few PLE collected across a few detection energies versus the PLE collected at the peak of the PL spectrum (PL $X_c$) were investigated. The deviation between these two PL efficiency curves was minimal for QD samples as can be see in the figure below. The datum in black was collected using one PLE spectrum collected with an
emission wavelength centered on the $X_c$ of the PL, 1.92 eV (CdSe) and 2.00 eV (CdSe/ZnS). The red PL efficiency spectra were collected using an average of three PLE spectra. The deviations are detectable but not grievous.

![Graph of PL efficiency profiles](image)

**Figure 2-4.** PL efficiency profiles collected using one PLE spectrum (black) and using an average of the three PLE spectra (red) for CdSe (top) and CdSe/ZnS (bottom), respectively. The PLE spectra are included in Figure S5. The single PLE spectra used for the CdSe and CdSe/ZnS profiles were recorded by monitoring emission at 1.92 and 2.00 eV, respectively.

To test the reproducibility of the PL efficiency with respect to the traditional PL QY measurement, the results of both are plotted side by side. These results can be seen in the Figure 5. The results show reasonable agreement between the two methods.
Figure 2-5. The PL QY data and the PL efficiency data are plotted together for CdSe NPLs (top graph), CdSe QDs (middle graph), and 7.4 nm CdTe QWs (bottom graph). The right Y-axis displays the calculated PL QY values and the left Y-axis is left as normalized values.

The normalized PL efficiency values can be scaled to the calculated PL QY values so that instead of plotting each PL QY data point, only the PL efficiency (blue line) is displayed. It can be scaled so that the Y-axis portrays the appropriate values.
2.8 Time-resolved Studies

PL decays are studied in each of the proceeding studies on NPL, QD and QW samples. The excitation energy dependence was initially hypothesized to be purely an effect of the relaxation processes and therefore should not affect the recombination process from the band edge. Collecting PL lifetimes using a variety of excitation energies allows this hypothesis to be tested. Similarly, deep surface traps were suspected to be present in a variety of samples, a hypothesis generated from the small asymmetry to the severe shoulders in some of the PL spectra. Emission from shoulders, or surface traps, is typically on a longer time-scale. Therefore, the PL lifetimes were collected using a variety of detection energies at a fixed excitation energy to test the validity of the presence of surface trap emission.

The PL Lifetimes were recorded using the doubled output of a tunable, Ti:Sapphire oscillator laser, 400 to 455 nm at a repetition rate of 0.16 MHz, and a time-correlated single-photon counting system with an MC PMT detector (Hamamatsu, R928 P) for detection. These power densities were also kept low. For 2.92 eV (425 nm), $2.14 \times 10^{12}$ photons/s or $1.3 \times 10^7$ photons per pulse were generated. To collect the photons with energies corresponding to each sample’s $E_g$, a PI Acton 2150i monochromator was used. The detection slit widths were adjusted to help improve the ratio of the signal to SYNC counts but were always kept between 0.62 nm and 0.25 nm, for QDs and NPLs, and were kept $\leq 2$nm for QWs.

All of the PL decay curves collected are multi-exponential. Origin fitting produced improved $R^2$ values by increasing the sum of exponentials. In order to determine the most appropriate function these data were analyzed using a Bayesian statistical software package. The software determines the posterior probabilities for the parameters in each of a variety of applicable models. The probabilities are utilized to determine the most likely model. In each
case, QD decay profiles fit to a sum of three exponentials with 100 % probability. The NPLs and QWs have a more multi-exponential behavior. Their decay profiles fit best to a sum of 3 exponentials with high probability (+ 80%), as compared to a sum of two and four and five exponentials. Below is displayed an example of a lifetime decay, the best fit (a sum of three exponentials), the residual of the fit, and the probability distributions for each the three $\tau$ values. Below we display an example of a lifetime decay, the best fit (a sum of three exponentials), the residual of the fit, and the probability distributions for each the three $\tau$ values.

![Example of lifetime decay](https://example.com/figure2-6.png)

**Figure 2-6.** This figure depicts the results of fitting using parameters chosen by the Bayesian software. The data used for this specific example is the decay profile from exciting the CdSe QDs at 3.06 eV (405 nm) and detecting at 1.93 eV (642 nm). The top graph is the raw data (black) with the fit of a sum of three exponentials. The middle graph shows the difference or
residual of the fit (green). The bottom graph shows the probability distributions for each of the $\tau$ lifetime values chosen.

The average PL intensity decay lifetime was calculated using the equation below. $f_n$ is fraction of photon counts associated with the lifetime parameter $\tau_n$.

$$\langle\tau_{\text{ave}}\rangle = \sum_n f_n \tau_n$$

$$f_n = \frac{A_n \tau_n}{A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3}$$

The parameters obtained when fitting and analyzing the PL intensity decay profiles recorded as a function of excitation energy and of detection energy are included in tables in chapter 4.
2.9 Calculation of exciton densities

The photon density used in each experiment was maintained at low levels to as to keep the number of excitons used per QD, NPL, or QW lower than 1. In this way, any exciton-exciton interactions will not affect the results. The estimates for the number of excitons per QD, NPL and QW are shown below.

A. Steady-state PL: Number of excitons per QD:

From previously determined absorption cross section values we estimate our absorption cross sections (\(\sigma_{xc}\)) for our CdSe and CdSe/ZnS QDs, exciting at 3.1 eV (400 nm), to be \(2.3 \times 10^{-15} \text{ cm}^2\) and \(4.2 \times 10^{-15} \text{ cm}^2\), respectively. Using a variation of Beer’s law (\(l\) is the path length):

\[
\frac{n}{\text{volume}} = \frac{\text{absorbance}}{\sigma_{xc} \cdot l}
\]

we determine the volume of QDs in a cuvette average is \(4.3 \times 10^{13} \text{ CdSe QDs/cm}^3\) and \(2.6 \times 10^{13} \text{ CdSe/ZnS QDs/cm}^3\). At this energy, a typical incident power of 0.1 mW/cm\(^2\) is equal to a photon flux of \(3.7 \times 10^{13} \text{ photons/s}\).

\[
\left(\frac{\text{# incident photons}}{\text{power}}\right) = \frac{\text{incident power}}{\hat{\alpha}_{\text{beam}} \cdot \left(\frac{\lambda}{hc}\right)}
\]

With this photon flux, and maintaining the absorbance values ≥ 0.1 at the highest excitation energies, there are \(~3.7 \times 10^{12} \text{ photons/s}\) absorbed by the CdSe and CdSe/ZnS samples, respectively.

\[
\text{photons absorbed} = \left(\frac{\text{# incident photons}}{\text{volume}}\right) \cdot \frac{n}{\sigma_{xc} \cdot l}
\]
The number of electron-hole pairs photogenerated per QD is then $3 \times 10^{-2}$ s$^{-1}$ and $5 \times 10^{-2}$ s$^{-1}$, respectively. Since the lifetimes are in on the order of 10s of nanoseconds and in 1 second less than one electron-hole pair exists, the probability is very high for less than one exciton generated per quantum wire at any instant.

**B. Steady-state PL: Number of excitons per QW:**

From values previously determined absorption cross sections,$^{31}$ we estimate our absorption cross sections for our 5-μm long wires, exciting at 2.12eV (585nm), to be $6 \times 10^{-12}$ cm$^2$. Using a variation of beers law we could determine the volume of CdTe in a cuvette and then divide by the single wire volume to determine that on average we have $1 \times 10^{10}$ quantum wires/cm$^3$. From an incident power of 0.3 mW/cm$^2$ (or incident photons of $1.6 \times 10^{14}$ photons/s) we calculated $1 \times 10^{13}$ photons/s absorbed by the ensemble and from this, the number of excitons photogenerated per QW to be 3000 s$^{-1}$. With ~90 ns of nanoseconds lifetime, the probability is very high for less than one exciton generated per quantum wire at any instant.

For the purposes of comparison, this calculation is repeated for 3.1 eV (400 nm) excitation. The total photons absorbed (which as shown above for 400 nm and 0.1 absorbance units) is $3.7 \times 10^{12}$ photons/s. The number of excitons photogenerated per QW to be 400 s$^{-1}$ which is still very low with respect to the average length of time the exciton remains in the QW.

**C. Steady-state PL: Number of excitons per NPL:**

Recently, Tessier et al. experimentally determined the absorption cross section for 7 ML thick CdSe NPLs using optical data and inductively coupled mass spectrometry.$^{2,5}$ The volume of each of these NPLs = $5.1 \times 10^{-19}$ cm$^3$ and the $C_{abs} = 2.5 \times 10^{-13}$ cm$^3$. The CdSe NPLs we synthesized have single volumes = $7 \times 10^{-19}$ cm$^3$. The estimated for our NPLs to be, $C_{abs} = 3.5 \times 10^{-13}$ cm$^3$. The total volume in a cuvette = $2.9 \times 10^{11}$ NPLs/cm$^3$. The total photons absorbed
(which as shown above for 400 nm and 0.1 absorbance units) is $3.7 \times 10^{12}$ photons/s. For our experiments then, there are an average of 4.3 excitons per NPL per second. This is very low with respect to the average length of time the exciton remains in the NPL, ~10 ns. (See Chapter 4).

**D. PL decay: excitons per pulse:**

The average excitation power density at 400 nm ($2.014 \times 10^{18}$ joules/photon) is 5 $\mu$W/cm$^2$. With a rep rate of 0.16 MHz, this is equivalent to $1.3 \times 10^7$ photons/pulse. For each of the above mentioned volumes of samples in a cuvette we then have: $\sim 9 \times 10^{13}$ QDs, $1.4 \times 10^{-7}$ excitons per pulse per QD; $3 \times 10^{10}$ QWs, $4 \times 10^{-4}$ excitons per pulse per QW; $9 \times 10^{11}$ NPLs, $1.4 \times 10^{-5}$ excitons per pulse per NPL. With less than one exciton per pulse and average lifetimes that are faster than the rep rate, the probability is very low for more than one exciton to exist in a QD, QW or NPL at any instant.
2.10 References


Chapter 3.

Excitation-energy dependence of the photoluminescence quantum yields of three-dimensionally quantum confined semiconductors

Portions of this chapter are in preparation for publication, by: J. Hoy, P. Morrison, L. Steinberg, W. Buhro, R. Loomis* as “Excitation-energy dependence of the photoluminescence quantum yields of core and core/shell quantum dots”
3.1 Introduction

The ability to tune the band-gap energies ($E_g$) of semiconductor quantum dots (QDs), as well as their significant absorption cross sections and high photoluminescence (PL) quantum yields (QYs) make these nanostructures promising moieties for use in optoelectronic devices,\(^1\)-\(^6\) solar concentrators,\(^7\) chemical sensors,\(^8\) and biological labels.\(^9\)-\(^11\) The variable dynamics of the electron-hole pairs that occur within semiconductor QDs, however, can complicate the utility of these devices. Consider for instance, the intermittency of the PL intensity trajectories, PL blinking, that is observed from single QDs under continuous excitation.\(^12\) The unpredictable nature of PL blinking can hinder the temporal and spatial tracking of individual QDs. Furthermore, the PL blinking trends depend on their immediate environments and synthetic preparation.\(^13\),\(^14\) The blinking behavior in CdSe/ZnS core/shell QDs was also found to depend on excitation energy.\(^12\) This excitation-energy dependence (EED) of the PL blinking dynamics was explained by a higher probability for accessing non-emissive trap states with increasing excitation energy above $E_g$.\(^12\) This inconstant probability for trapping charge carriers suggests there is also an EED of the PL QY for these core/shell QDs since electrons and holes localized in traps have a higher propensity for non-radiative recombination that leads to lower PL QYs.

The energetics and dynamics of electron-hole pairs photogenerated in CdSe core-only and CdSe/ZnS core/shell quantum dots (QDs) are characterized using steady-state and time-resolved spectroscopy. Using two different techniques, the photoluminescence (PL) quantum yields (QYs) of the room-temperature QDs suspended in toluene are found to have a strong dependence on excitation energy, up to at least 1 eV above the band gap, $E_g$. The PL QYs of the CdSe and CdSe/ZnS QDs are measured to be 25-31% and 79-91% within the first 200 meV above $E_g$. The PL QYs monotonically decrease to ~5% and ~11% with increasing energies. The
time-resolved PL intensity decay profiles for band-gap emission of both samples are nearly the same for excitation energies over the range of 0.75 eV to 1.10 eV above $E_g$. These results indicate the varying efficiencies of internal relaxation to $E_g$ dictate the observed changes in the PL QYs. The average PL lifetimes are found to increase with decreasing emission energy when excited at a fixed energy, indicating an enhanced role of trap emission at the energies below $E_g$.

There is strong evidence for the EED of the PL QYs in the optical spectra recorded for numerous types of QDs, including CdSe, CdTe, InP, CdSe/ZnS, and CdSe/ZnS/CdSe QDs. Hoheisel et al. found a strong deviation between the photoluminescence excitation (PLE) and absorption spectral profiles acquired at 77 K for five samples of CdSe QDs with different mean diameters. The differences observed at excitation energies just above the band gap were attributed to the narrowing of spectral features in the PLE spectra due to the distribution of diameters in the CdSe-QD sample and subsequent size selection resulting from collection of emission over a finite portion of the PL feature. The differences between the absorption and PLE spectra observed at higher excitation energies, 300 meV above $E_g$ and higher, were explained by the opening of a continuum of higher-energy, non-radiative states. Significant differences between the scaled amplitudes of the absorption and PLE spectra were also observed for CdSe/ZnS core/shell QDs, with the largest differences observed at excitation energies 500 meV to 600 meV above $E_g$. The results from transient absorption measurements on InP QDs revealed a dependence of the fraction of charge carriers that relax to the band edge on excitation energy. These changes in the relaxation efficiencies were again attributed to the opening of surface or external energy states that charge carriers energetically and spatially access, thereby influencing the PL QYs of the QDs.
Other results seemingly contradict this evidence for an EED of the PL QYs for semiconductor QDs. Tonti et al\textsuperscript{21} suggest that the observed differences between the absorption and PLE spectra acquired for five different samples of CdSe QDs, with diameters between 2.6 and 5.0 nm, are due to scattering from aggregates of the QDs, ligand absorption, and size selection of the QDs that result from the narrow emission window detected during the acquisition of the PLE spectra. They conclude that once these effects are considered there is no EED of the PL QYs for CdSe QDs. More recently, Cruz et al\textsuperscript{22} measured the EED of the PL QYs for CdSe/ZnS QDs using the technique of thermal lens spectrometry. In this method, the fraction of the absorbed energy converted into heat is monitored as a function of excitation energy. They measured no changes in the heat dissipation into the sample, and thus found no evidence for an EED of the PL QYs.

Due to the potential impacts that utilizing an incorrect or varying value of the PL QY could have on experiments performed when monitoring the PL intensity from QDs, we have investigated the EED of the PL QYs for CdSe and CdSe/ZnS QDs. We measured the integrated intensity of the PL spectra as a function of excitation energy as well as the ratios of the PLE to absorption spectra to track the EED of the PL QYs. The results indicate there are small variations in the PL QYs at energies near $E_g$, but the PL QYs monotonically decrease with increasing excitation energy, up to 1 eV above $E_g$.

3.2 Experimental

Measurements were performed on a sample of CdSe QDs with a mean diameter of 5.7(1.3) nm and a sample of CdSe/ZnS core/shell QDs with a mean diameter of 6.9(1.2) nm, core diameters of ~4.9 nm, and shell thicknesses of ~1.0 nm. See chapter 2 for additional details of the samples, sample preparation, instrumentation, and data acquisition. Absorption spectra
were recorded using a commercial UV/VIS spectrometer equipped with an integrating sphere to minimize losses due to scattering, and matching cuvettes were used for the sample and reference paths. The PL and PLE spectra were recorded on a home-built, fluorimeter, and were corrected for the instrument response function of the instrument. Excitation power densities were kept low, ≤0.3 mW/cm², in order to ensure that there is on average much less than one exciton within a QD at any time, thereby minimizing charge-charge interactions and multi-photon effects. Nevertheless, spectra were recorded as a function of power density and sample concentration to verify the linearity of the signals. Multiple measurements were also performed as a function of time in order to ensure the samples were stable, and the PL intensities at a given excitation energy and power density remained constant throughout a set of experiments.

3.3 Results and Discussion

An absorption spectrum, black, and a PL spectrum, blue, of the CdSe QD sample are shown in Figure 1A). The lowest-energy feature in the absorption spectrum is at 1.97 eV, and is associated with $1S_{3/2} - 1S_e$ transitions at $E_g$. The additional weak features noticeable in the
**Figure 3-1.** Spectra and PL QY data for CdSe QDs. A) The absorption spectrum is shown as black, and the PL spectrum acquired with excitation at 2.36eV (525nm) is shown as blue. The black tics indicate the energies of the calculated lowest-energy transitions. The magenta tics above the PL spectrum indicate energies at which emission was detected when acquiring PLE spectra. B) The PL QY data are shown as blue circles, and the PL efficiency profile, acquired by dividing average of the PLE spectra by the absorption spectrum, are shown as grey.

The absorption spectrum is associated with transitions that access excited electron or hole states. The calculated lowest-energy transitions are shown as black tics for comparison. The PL spectrum shown in Figure 1A) was recorded using an excitation energy of 2.36eV (525nm). The intensity profile of the PL feature is slightly asymmetric with a maximum intensity at 1.93 eV, which is Stokes shifted by ~45 meV from $E_g$. The PL spectra recorded as a function of excitation energy from 1.97 to 3.1 eV, have nearly identical shapes, albeit with varying intensities. The total integrated intensity of each PL spectrum was compared to that of a standard in order to obtain the PL QY of the CdSe QDs at each excitation energy, blue circles in Figure 1B). The highest PL QY measured is 31(1)% at an excitation energy of 2.00 eV, ~30 meV above $E_g$. There is a local minimum in the PL QYs near 2.10 eV, and the PL QY steadily drops to 4.5(2)% by 3.1 eV, which is 1.1 eV above $E_g$.

The EED of the PL efficiency was also measured by dividing the PLE spectrum by the normalized absorption spectrum collected for the same sample. In order to avoid preferentially sampling the emission from different diameter QDs within the sample, PLE spectra were acquired by detecting emission at three energies spanning the PL spectrum, 1.89 eV (655 nm), 1.92 eV (645 nm), and 1.95 eV (635 nm); these energies are shown as magenta ticks above the PL spectrum in Figure 1A). The PLE spectra acquired with detection at each of the energies are included in the thorough discussion in chapter 2. Each PLE spectrum was scaled by the intensity of the PL at the emission window monitored when collecting the spectrum, and the three PLE
spectra were averaged. The absorption spectrum was normalized to have the same intensity as the average PLE spectrum at an excitation energy of 2.016 eV. The PL efficiency spectrum of the CdSe QDs, obtained by dividing the average PLE spectrum by the normalized absorption spectrum, is shown as a grey line in Figure 1B). The profile of the PL efficiency spectrum overlaps exceptionally well the PL QY data. The PL efficiency profile is also consistent with the deviations in absorption and PLE data for CdSe nanocrystals reported previously.\textsuperscript{17} The data in this work by Hoheisel, et al was absorption and PLE spectra of CdSe QDs, mean diameter of 1.6 nm, at a temperature of 77 K.\textsuperscript{4} The spectral data, Figure 2, were digitized so that the PL efficiency profile, PLE divided by absorption as function of excitation energy, could be calculated for their sample.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3-2.png}
\caption{Figure 3-2. Left, the absorption and PLE spectra of CdSe QDs (mean diameter of 1.6 nm) recorded at 77K. The data was digitized from reference 17. Right, the PL efficiency profile calculated by dividing the PLE data by the absorption data is shown. The structure present at low excitation energies was attributed to size selection when acquiring the PLE spectrum. The deviations between the absorption and PLE spectra and the low values of the PL efficiency profile were attributed to competing relaxation pathways from the local environment.}
\end{figure}

The local minimum observed near 2.10 eV in the PL QY and PL efficiency data for the CdSe QD sample is between the first and second lowest-energy features observed in the
absorption spectrum. Calculations of the excitation energies and transition strengths of CdSe QDs with a diameter of ~6 nm \(^{23}\) indicate that the two dominant transitions, near 1.98 and 2.17 eV, may be associated with the \(1S_{3/2}-1S_e\) and \(1P_{3/2}-1P_e\) transitions. The observed decrease in the PL QYs occurring between these transition energies is likely due to the low density of hole and electron states coupled with the presence of surface-mediated pathways and trap states that effectively compete with intraband relaxation to the band gap when the QDs are excited in this energy region.\(^ {16,20,26,27}\) These surface-mediated pathways may also contribute to the significant decrease in the PL QYs observed at even higher excitation energies, above 2.45 eV. Lastly, at these excitation energies, charge carriers in high-lying electron and hole states can couple directly to states of the organic ligands used to passivate the surface of the QDs.\(^ {28-30}\) Although the relative offsets between the bands of the CdSe QDs and the organic ligands are not accurately known, the absorption spectra of these molecules, Figure 2-2 in chapter 2, indicate that these pathways may be open. The absorbance of oleylamine, for instance, increases significantly for excitation above \(~2.4\) eV, and the absorbance of tri-\(n\)-octylphosphine has a similar increase above \(~2.8\) eV. As a result, either the electrons or holes prepared in high-lying states within the conduction or valence bands of the CdSe QDs may couple to the organic ligands that are either bound to or interacting with the surface of the QDs. These charge-transfer pathways compete with relaxation of the charge carriers to the band edge where radiative recombination occurs, and can result in a decrease in the PL QY. Note that possible errors in these PL QY measurements that can be attributed to direct electronic excitation of the ligands are small, \(<0.2\%\), since the maximum absorbance of the ligands is only \(~0.003\), as explained in chapter 2.
The Type-I band structure of the CdSe/ZnS QDs should minimize the role of surface-mediated relaxation pathways and of charge transfer to the organic ligands by confining the electrons and holes to the core of the QD, especially at low excitation energies. As a result, the overall PL QYs of these QD heterostructures should be higher. The confinement should also minimize the role of surface-mediated relaxation pathways, and there should be less-pronounced variations in the PL QYs for excitation near $E_g$.

![Figure 3-3. Spectra and PL QY data for CdSe/ZnS core/shell QDs. A) The absorption spectrum is shown as black, and the PL spectrum acquired with excitation at 2.36eV (525nm) is shown as red. The black tics indicate the energies of the calculated lowest-energy transitions. The magenta tics above the PL spectrum indicate energies at which emission was detected when acquiring PLE spectra. B) The PL QY data are shown as red squares, and the PL efficiency profile, acquired by dividing average of the PLE spectra by the absorption spectrum, are shown as grey.](image)

The experimental results obtained for the sample of CdSe/ZnS QDs are shown in Figure 2. The energy of the first feature in the absorption spectrum, black spectrum in Figure 2A), indicates $E_g = 2.04$ eV for these core/shell QDs, and several other higher-energy features are distinguishable. The PL spectrum, red, was recorded with excitation at 2.36 eV (525 nm) and
has a maximum that is Stokes shifted by 40 meV from $E_\text{g}$. Numerous PL spectra were recorded with excitation energies ranging from 2.0 to 3.1 eV, and the profiles of the spectra were nearly identical with varying overall intensities. The PL QYs obtained by integrating the PL spectra and comparing with a known standard are included in Figure 2B), red squares. The highest PL QY, 91(7)%, is at an excitation energy of 2.10 eV, ~50 meV above $E_\text{g}$. The PL QYs decrease with increasing excitation energy, down to 10.6(4)% by 1.1 eV above $E_\text{g}$. The PL efficiency spectrum for these CdSe/ZnS QDs, grey line in Figure 2B, was obtained in the same manner as described above, and by averaging the PLE spectra acquired with emission detection at 1.95 eV (635 nm), 2.00 eV (620 nm), and 2.05 eV (605 nm). Once again, the PL QY data and the PL efficiency spectrum match within error throughout the entire spectral region investigated.

As expected, the addition of the protective ZnS shell on the CdSe core results in consistently higher PL QYs than measured for the CdSe core-only QDs across the energy range investigated. Somewhat surprisingly, the overall shape of the EED of the PL QYs for the CdSe and CdSe/ZnS QDs are quite similar at higher excitation energies with both exhibiting monotonically decreasing values up to 3.1 eV. The similar profiles suggest non-radiative pathways at these energies that are common to both samples. The PL QY and PL efficiency data for the CdSe/ZnS QDs, however, do not have a local minimum just above $E_\text{g}$. This result suggests that the ZnS shell does efficiently minimize the role of the non-radiative, surface-mediated relaxation pathway proposed for the CdSe QDs.

The pathways that compete with relaxation of the charge carriers to the band edge and radiative recombination from the lowest states of the hole and electron, $1S_{3/2}/1S_e$, are schematically illustrated in Figure 3. The probability for intraband relaxation to the $1S_{3/2}/1S_e$ states following photoexcitation of CdSe QDs just above $E_\text{g}$, panel A), is largely dictated by the
coupling of the charge carriers to the surface traps and ligands. The total number of non-radiative states that can be accessed increases with higher excitation energies, panels B) and C), and the probability for relaxation to the band edge, and thus the PL QY, is lowered. The shell of the CdSe/ZnS QDs gives rise to an overall decrease in the probability for accessing the trap and ligand states and the higher PL QYs, especially at lower excitation energies. With increasing excitation energies, the electrons at first and then the holes can sample the shell region of the CdSe/ZnS QDs, and the likelihood for accessing the non-radiative traps increases. This generalizaiton appears to be true, even despite the fast timescales for intra- and interband processes. 

**Figure 3-4.** Schematics of the competing non-radiative relaxation pathways that reduce the PL QYs in QDs. Following photoexcitation of CdSe QDs to energies just above the lowest states of the hole and electron, A), coupling to surface traps and ligands can compete with relaxation to the $1S_{3/2}/1S_e$ states, and give rise to varying PL QYs. The number of non-radiative states is higher with increasing excitation energy, B) and C), and the fraction of charge carriers that relax to the $1S_{3/2}/1S_e$ states decrease. Due to the Type-I heterostructure of the CdSe/ZnS QDs, the pathways to the ligands and traps are minimized, especially at lower excitation energies. The conduction-band offset between CdSe core and ZnS shell permits electrons to sample the ZnS shell and surface for excitation energies near the $1P_{1/2}/1P_e$ transition. 

C), and the probability for relaxation to the band edge, and thus the PL QY, is lowered. The shell of the CdSe/ZnS QDs gives rise to an overall decrease in the probability for accessing the trap and ligand states and the higher PL QYs, especially at lower excitation energies. With increasing excitation energies, the electrons at first and then the holes can sample the shell region of the CdSe/ZnS QDs, and the likelihood for accessing the non-radiative traps increases. This generalizaiton appears to be true, even despite the fast timescales for intra- and interband processes.
interband relaxation to the band edge. As a result, the overall shape of the EED of the PL QY for the CdSe/ZnS QDs resembles that of the CdSe QDs at the higher excitation energies.

The charge carrier dynamics that give rise to the observed EED of the PL QYs are thus dictated by the pathways that the electrons and holes follow during relaxation down to the band edge. The resultant dynamics of the charge carriers in the emitting $1S_{3/2}$ and $1S_e$ states should thus be independent of excitation energy. We have recorded the time-resolved PL-intensity decay profiles using time-correlated single-photon counting as a function of excitation energy to verify this conclusion. The PL-intensity decay profiles for the CdSe QD sample obtained with photoexcitation at 2.85 and 3.06 eV and detecting emission at 1.93 eV are shown in Figure 4A) as blue and magenta, respectively. The PL-intensity decay profiles for the CdSe/ZnS QD sample obtained with photoexcitation at 2.76 and 3.10 eV and collecting emission at 2.00 eV are shown as red and black, respectively, in Figure 4B). All of the decay profiles collected are clearly multi-exponential, but do not appear to vary significantly with excitation energy.

Although it is common to report half-life, $t_{1/2}$, or 1/e times to characterize multi-exponential decay profiles, we have found that such times tend to be dominated by the short-time components, even when the fraction of photons associated with the short-time components are not the major contributors to the decay profile. As a result, average lifetimes calculated by fitting each decay profile to a sum of exponential decays tends to be more informative in characterizing the PL dynamics. The issue of how many exponential decays should be utilized when fitting a PL-intensity decay profile can still be ambiguous. We utilized a Bayesian software package\textsuperscript{35-39} to statistically compare models for sums of different numbers of exponential decays for each profile in order to identify the most appropriate model to be used in the fitting. The analyses indicate the PL-intensity decay profiles of the CdSe and CdSe/ZnS QDs
collected as either functions of excitation or emission energy fit best to a sum of three exponentials. The amplitudes, lifetimes, and relative contributions of the exponentials determined in the analysis of

Figure 3-5. Time-resolved PL-intensity decay profiles and lifetime data. The decay profiles for CdSe and CdSe/ZnS QDs recorded at two different excitation energies are shown in A) and B), respectively. The excitation energies associated with each profile are shown, and emission was collected at the maximum of the PL spectrum. The average PL lifetimes measured for the CdSe (blue circles) and CdSe/ZnS (red squares) QDs at varying excitation energies and with fixed emission energies of 1.93 and 2.00 eV are included in C) and D), respectively. The PL QYs for the CdSe and CdSe/ZnS QDs presented in Figure 1B) and 2B) are shown as open symbols. The average PL lifetimes measured for the CdSe (blue circles) and CdSe/ZnS (red squares) QDs at varying emission energies, but with fixed excitation energies of 3.06 and 3.10 eV are included in E) and F), respectively. The lifetimes are superimposed on the emission profiles of the QDs for reference.

the decay profiles recorded at different excitation energies are included in Table 1 below.
Table 1. Dependence of PL intensity decay components on excitation energy. The emission from the CdSe and CdSe/ZnS QD samples was collected at 1.931 and 2.003 eV, respectively, when exciting at the indicated energies, in eV. The profiles were fit to a triple-exponential decay with coefficients, $A_i$, and time constants, $\tau_i$, in ns. The fraction of the total photons detected within each exponential, $f_i$, are also included. The average lifetimes, $\tau_{Ave}$, are plotted in Figure 3-5 (C and D).

The mean lifetimes of the decay profiles recorded are all 38-40 ns for the CdSe QD sample, independent of excitation energy, as shown in Figure 4C). The mean lifetimes for the CdSe/ZnS QD sample fall in the range of 22.0(1.0) to 25.9(1.7) ns with only a slight increase in lifetime measured with increasing excitation energy, Figure 4D). The observation of nearly constant PL lifetimes for the CdSe and CdSe/ZnS QDs measured with photoexcitation at energies well above the band gap, where the PL QYs change by more than a factor of two, verifies that the photoexcitation energy does not significantly affect the electron-hole recombination dynamics occurring near the band edge.

These PL lifetimes, as well as those reported previously for CdSe \(^{40}\) and CdSe/CdS QDs,\(^{41}\) are significantly longer than the estimated radiative lifetime of ~3 ns for CdSe QDs.\(^{42}\)
Such long PL lifetimes are typically associated with surface-trap emission, even when high PL QY values are measured.\textsuperscript{40,43,44} While the emission from hole traps is typically associated with PL that is shifted by several hundred meV below the band-gap energy, shallow electron traps with energies lying very close to the edge of the conduction band have also been identified for CdS QDs.\textsuperscript{26,27} The PL-intensity decay profiles that result from the dynamic filling and emptying of these traps have lifetimes of \textasciitilde20 ns. The specific depths of these traps should most likely dictate the trapping dynamics, and thus the PL lifetimes.

We recorded the PL-intensity decay profiles as a function of emission energy and with fixed excitation for the CdSe and CdSe/ZnS QD samples. The decay profiles again fit well to a sum of three exponential decays with best-fit parameters included in Table 2. Below.
Table 2. Dependence of PL intensity decay components on detection energy. The CdSe QD sample was excited at 3.061 eV, and the CdSe/ZnS QD sample was excited at 3.100 eV. The PL intensity decay profiles were recorded at the indicated detection energies, in eV. The profiles were fit to a triple-exponential decay with coefficients, $A_i$, and time constants, $\tau_i$, in ns. The fraction of the total photons detected from each exponential, $f_i$, are also included. The average lifetimes, $\tau_{\text{ave}}$, are plotted in Figure 3-5 (E and F).

<table>
<thead>
<tr>
<th>Detection Energy</th>
<th>$A_1$</th>
<th>$\tau_1$</th>
<th>$f_1$</th>
<th>$A_2$</th>
<th>$\tau_2$</th>
<th>$f_2$</th>
<th>$A_3$</th>
<th>$\tau_3$</th>
<th>$f_3$</th>
<th>$\tau_{\text{ave}}$</th>
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<tr>
<td>CdSe</td>
<td></td>
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<tr>
<td>1.993</td>
<td>7.79E-4</td>
<td>4.86</td>
<td>0.020</td>
<td>0.00524</td>
<td>24.2</td>
<td>0.68</td>
<td>8.81E-4</td>
<td>62.7</td>
<td>0.30</td>
<td>35.4(1.0)</td>
</tr>
<tr>
<td>1.931</td>
<td>7.64E-4</td>
<td>5.64</td>
<td>0.023</td>
<td>0.00482</td>
<td>26.4</td>
<td>0.68</td>
<td>8.00E-4</td>
<td>68.3</td>
<td>0.29</td>
<td>37.9(1.6)</td>
</tr>
<tr>
<td>1.873</td>
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<td>5.94</td>
<td>0.024</td>
<td>0.00373</td>
<td>29.9</td>
<td>0.60</td>
<td>9.12E-4</td>
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<td>0.38</td>
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</tr>
<tr>
<td>1.818</td>
<td>7.41E-4</td>
<td>5.54</td>
<td>0.022</td>
<td>0.00316</td>
<td>32.3</td>
<td>0.55</td>
<td>9.34E-4</td>
<td>85.6</td>
<td>0.43</td>
<td>54.7(1.4)</td>
</tr>
<tr>
<td>CdSe/ZnS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td>0.00174</td>
<td>4.42</td>
<td>0.047</td>
<td>0.00759</td>
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<td>0.82</td>
<td>3.92E-4</td>
<td>53.7</td>
<td>0.13</td>
<td>21.8(1.4)</td>
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<tr>
<td>2.003</td>
<td>0.00175</td>
<td>9.32</td>
<td>0.13</td>
<td>0.00650</td>
<td>22.0</td>
<td>0.81</td>
<td>1.56E-4</td>
<td>105.4</td>
<td>0.065</td>
<td>25.9(1.7)</td>
</tr>
<tr>
<td>1.953</td>
<td>0.00133</td>
<td>4.85</td>
<td>0.039</td>
<td>0.00602</td>
<td>20.7</td>
<td>0.76</td>
<td>6.02E-4</td>
<td>54.2</td>
<td>0.20</td>
<td>26.8(9)</td>
</tr>
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</table>

The average lifetimes recorded for the CdSe QDs with an excitation energy of 2.92 eV, shown as blue circles in Figure 4E), increase from 35.4(1.0) ns at 1.99 eV up to 54.7(1.4) ns at 1.82 eV, which is within the low-energy tail of the PL spectrum. This trend was also observed for the CdSe/ZnS QDs, red squares in Figure 4F), and for any excitation energy utilized for either sample. Increasing PL lifetimes with decreasing emission energies were also reported for CdS QDs. In all of these QD systems, the PL QYs are largely dictated by the relaxation pathways down to the low-lying emitting states. While these lowest-energy states may be associated with shallow electron traps on the surface of the QDs, and thus the PL QYs will be
influenced by the dynamics in the trap states, these states will not contribute to the EED of the PL QYs.

3.4 Conclusions

The repercussions of not taking into account the EED of PL QYs when monitoring the PL from QDs could lead to incorrect interpretations and erroneous conclusions. Due to experimental constraints and data acquisition times, it is common to utilize fixed excitation energies to measure PL QYs and PL-intensity decay profiles for semiconductor nanocrystals. For instance, PL spectra and QYs are often measured on aliquots of a sample mixture during synthesis or passivation procedures to monitor the growth of the QDs and to identify the optimal parameters for producing high-quality QDs.\(^{19,41,45-47}\) During the synthesis of CdSe QDs, \(E_g\) can vary from 2.80 eV down to 2.00 eV as the diameter of the QDs increase. The data presented here indicate that if the PL QYs were measured using a fixed excitation energy of 3.00 eV during the synthesis of the QDs, the QYs could decrease by a factor of four as a result of the increase in the photoexcitation energy above \(E_g\). When exciting near \(E_g\), the local minima in the EED of the PL QYs could result in further misinterpretations. Thus, whether characterizing the growth or passivation of colloidal QDs, monitoring energy transfer using QDs as donors or acceptors,\(^{48,49}\) investigating blinking and charging dynamics within QDs,\(^{12,50-52}\) or simply measuring the PL QYs of QD samples, correctly characterizing the EED of the PL QYs is essential for developing accurate interpretations of the results.
3.5 References:


Chapter 4.

Excitation-energy dependence on the photoluminescence quantum yields of semiconductor nanostructures: The role of dimensionality

Portions of this chapter are in preparation for publication, by: J. Hoy, P. Morrison, F. Wang, Y. Wang, W. Buhro, R. Loomis* as “Role of dimensionality and excitation-energy dependence on the photoluminescence quantum yields of semiconductor nanostructures”
4.1 Introduction

Quantum-confined semiconductors have very unique optical and electronic properties that depend on their degree of confinement. These characteristics of quantum dots (QDs), which exhibit quantum confinement in three dimensions, namely, tune-ability of the band gap energy ($E_g$), large absorption cross-sections, and high photoluminescence (PL) quantum yields (QY) have been utilized in optoelectronic devices, $^{1-6}$ utilized in chemical sensing, $^7$ and monitored in biological labeling.$^{8-10}$ In recent years, methods for synthesizing nanoplatelets (NPLs), which are pseudo-1D confined structures. They posses strong confinement in 1 dimension, intermediate in 1 dimension and weak confinement in the last dimension. These lamellar structures have large absorption cross-sections, high quantum yields, and are proposed to have diminished surface trapping. For these reasons, they have been developed for their use in quantum cascade lasers and for fluorescent labeling have been suggested.$^{11-14}$ Several studies on quantum wires (QWs), which have confinement in 2D and are fully free in the third, indicate that they may be particularly useful, especially in optoelectronic devices, since the band-gap energies are tunable, yet they should provide efficient charge transport over microscopic distances.$^{15-20}$ The applications of these nanoparticles require efficient photogeneration of the charge carriers and detailed understanding of the dynamics incurred by the charges. The optimization of the properties of these nanoparticles and of their utility in devices depends on gaining a solid understanding of the variables that alters the charge carrier dynamics.

As discussed in Chapter 3, an excitation-energy dependence (EED) of the PL QY exists for CdSe and CdSe/ZnS QDs. The PL QY data were obtained by measuring the PL spectra as a function of excitation energy above $E_g$ and comparing these values to known standards. The spectral dependence of the PL efficiency was also obtained by direct comparison of the
absorption spectrum to the photoluminescence excitation spectrum collected for a sample. The two methods yielded the same EED of the PL QYs.

In order to further characterize the charge carrier dynamics, we have continued these experiments on nanoparticles with different dimensionality and paying attention to the type of surface passivation and the presence and energetic availability of the surrounding environment. Specifically, we measure the EED of the PL QYs or the PL efficiency profiles of samples of CdSe QDs (diameter ~4.8 nm), CdSe NPLs (thickness ~1.4 nm), CdTe QWs (diameters of ~5.5 nm and ~7.5 nm), and CdTe/CdS core/shell QWs (diametercore ~ 6.8 nm). The roles of quantum confinement, surface passivation, and the local nanoparticle environment are considered in interpreting the observed trends. The synthetic details of each sample are discussed in Chapter 2.

It was found in the previous chapter, that the EED of the PL QYs and the PL efficiency profiles of the CdSe and CdSe/ZnS QDs agree to within error. Since the data acquisition times are significantly shorter for collecting PL efficiency profiles, we often collect the PL efficiency profiles. In order to appropriately scale the PL efficiency profiles to indicate PL QY values, a single PL QY data point is included at a single excitation energy to scale each profile. So, the PL QY and PL efficiency are reporting the same values.

4.2 Results and Discussion: Quantum Dots

The absorption spectra, PL spectra, and PL efficiency profiles obtained for CdSe QDs (diameters of ~4.8 and 5.7 nm) and CdSe/ZnS core/shell QDs (core diameter of ~4.9 nm) are included in Figure 1. The PL efficiency is scaled to the PL QY values as discussed above. Figure 1a displays data from CdSe QDs (4.8 nm ~ d). The PL QY of this sample varies from ~25 % near $E_g$ down to ~7 % at 3.1 eV. Exciting at low energies near $E_g$, the undulations of the
PL efficiency are similar to those observed for the larger diameter CdSe QDs. Specifically, there are minima at both 2.55 eV and 2.80 eV, and both of these energies lie between energies of the electronic transitions. At high energy, the PL QYs decrease, as is observed in both the CdSe (5.4 nm) QDs and the CdSe/ZnS QDs.

In figure 1c, PL efficiency values (blue line) of the CdSe/ZnS QDs, (4.93 nm = d_{core}), have an overall higher PL QY values ranging from 91 % (< 100 meV + E_g) to 10.9 % (1.1 eV + E_g). There is not any significant structure in the PL efficiency spectrum. In contrast, the 5.7 nm core-only dots (1b) have PL QYs ranging from 30.9 % at 2.00 eV (30 meV + E_g) down to 4.5 % at 3.1 eV (~1.1 eV + E_g). There is some variation of the PL efficiency varies from 25 – 30 % within 300 meV above E_g. The deviations of the PL QY numbers across these energies are indeed significant in that they are outside of the error of the measurement, as can be viewed in Chapter 2. All samples have strongly diminishing PL efficiencies at high excitation energy.
Figure 4-1. Spectra and PL Efficiency data for QDs. A) contains data from CdSe ~4.8 nm diameter CdSe QDs, B) from ~5.7 nm CdSe QDs, C) from ~4.9 nm diameter core CdSe/ZnS QDs. The absorption spectrum is shown as black, and a representative PL spectrum is shown in magenta. The black tics indicate the energies of the calculated lowest-energy transitions. The PL efficiency data is shown as a blue line and a singular PL QY value indicating the error is displayed as a red circle.

The local minimum in PL QY, observed in both sets of core-only CdSe QDs (1A and 1B), within the first few hundred meV above the band edge. This shape is attributed to two factors, the strong quantum confinement leading to large ΔE and well-separated, discrete transitions and the coupling of the charge carriers to ligand acceptor states on the QD surface. In the 5.7 nm QDs, the PL efficiency remains relatively high over the first and second transitions which lie ~60 meV apart and the second transition has weaker oscillator strength in comparison. A local
minimum exists between these transitions and the third. The $\Delta E$ between the first and third transitions is large, $\sim 200$ meV. This decrease in PL QY then is associated with the decreased probability for phonon coupling between these states. Instead, relaxation can rely on ligand mediated pathways, which are often times sources of non-radiative pathways. For the 4.8 nm QDs, the first and second transition are shifted farther apart in $E$, $\sim 188$ eV. With comparable energy spacing, the phonon relaxation is again restricted leading to reliance on ligand-mediated paths. The recovery of the PL efficiency over the second transition could be due to the weaker oscillator strength.

In contrast, these PL efficiency fluctuations are not present between the first three transitions in the core-shell CdSe/ZnS QDs spectrum. Also, these QDs have significantly higher overall PL QY. We have hypothesize that both of these effects are largely due to presence of a shell creating a type-I heterostructure. The energetic barrier restricts the interaction of the electron and hole wavefunctions with the surface. Therefore between two transitions with large $\Delta E$, coupling with surface-mediated transitions are less likely to occur. In this way, interactions with these typically non-radiative processes are avoided.

All samples show a general overall decrease in PL QY with increasing excitation energy. This has been attributed to an increase in the probability for tunneling of the charge carriers out of the QD into the shell or further, in part due to the small diameter of the QDs and the strong confinement of the electron and hole wavefunctions. It has been hypothesized that in QDs the charge carrier tunneling outside the core can lead to decreases in emission.\(^{10}\) If the amount of tunneling is significant in a sample it can blur threshold energies for other processes. A sharp threshold at 620 meV above $E_g$, the energy of the valence band offsets for CdSe and ZnS, is expected but not found. In some large CdSe/ZnS QDs, a threshold is distinct.\(^{10,21}\) The smaller
the core of the QD, the more the wavefunctions will tunnel into through the shell. We propose that in these core shell QDs, which have a similar diameter to those studied by Ghosh and coworkers, that tunneling is occurring to some extent across a range of excitation energies leading to blurring of the increased tunneling at the turn on of the ZnS valence band edge.

An alternate relaxation pathway exists, that of charge carrier coupling to residual free ligands in the sample cuvette. In the case of these QDs, the most abundant ligands are TOP and OLA. The absorption spectra for concentrated samples of these two ligands are shown in the grey solid (TOP) and dashed (OLA) spectra. The type of free ligand present for the 4.8 nm QDs, 1a, is likely to be only TOP (solid gray line indicates the absorption spectrum). These electronic transitions from the environment provide an energetic pathway for highly excited charge carriers to take. Charge carriers coupling to the environmental transitions will have a high probability for leaving the QD permanently and reducing emission efficiency. The band offsets of the ligands relative to those of the QDs are unknown. The onset of the absorptions of these ligands near the higher excitation energies investigated here suggest that ligand states may be energetically accessible, and coupling to these states may efficiently compete with inter- or intraband relaxation of the charge carriers to the band gap within the QDs.

The shapes of the EED of the PL QY can be supported by a few previous studies investigating charge carrier relaxation dynamics. Previous reports validate the changing charge carrier relaxation paths at low excitation energy, specifically, for samples with a large energy spacing between the first two transitions. The decreased efficiency for phonon-relaxation increases the probability for surface-mediated relaxation. It has been hypothesized that electrons can couple to the acceptor states of ligands bound to the surface of a QD. Specifically, it was observed that varying the type of ligand acceptor states in CdSe QDs alters the relaxation time from the 1P, to
the 1S, transition. However, the presence of the shell that generates a type-I heterostructure should restrict surface interactions, and decrease the probability to use this pathway. A previous report investigated the 1Pe to 1Se relaxation rate in CdSe/ZnS QDs with varying QD diameter. The change of QD size will affect the energetic overlap between the 1Pe transition and the bound ligand acceptor states. This study revealed a stable relaxation rate with size change.

Additional reports also support the results observed when exciting at high excitation energy. PL intermittency, or blinking, in both CdSe QDs and CdS quantum rods showed a decrease in the probability for long on-time at higher excitation energy versus lower excitation energy. Following suit, a study of PbS QD charging using low versus high excitation energy showed increased charging at the higher excitation energies. Additionally, the band edge transient absorption in InP QDs with varying excitation energy displays a similar decrease in charge carrier relaxation at higher excitation energies.

4.3 Results and Discussion: Nanoplatelets

The EED of the PL efficiency for the CdSe NPLs is shown in Figure 2. NPLs are hypothesized to follow a templated growth, creating a rectangular grid of CdSe nanoclusters. The final product can be unbundled vertically to create either quantum belts (QBs) or ribbons, or laterally to create nanosheets, or nanoplatelets (NPLs). The unbundling process is performed by suspending the NPLs in a few drops of oleylamine. The dimensions of these NPLs are 1.4 nm thick, 10 nm wide and ~50 nm long. These dimensions create pseudo-1D confinement with a step-like density of states. The first two electronic transitions are the first electron state coupled with the 1Se-S_{hh} (heavy-hole) and 1Se-1S_{lh} (light hole) respectively. These NPLs are also extremely flat with high quality intra-platelet thickness distribution. The absorption features and the PL feature are very narrow as is expected. The highest PL QY is
observed at an excitation energy $= E_g$ and is $\sim 23\%$. Between the two electronic transitions there is a strong decrease down to $12\%$ over the second transition. The dominant residual ligand present from the synthetic protocol is oleyelamine and it will not affect the absorbance values, as is discussed in Chapter 2.

![Graph](image)

**Figure 4-2.** Spectra and PL Efficiency data for NPLs. These platelets are $\sim 1.4$ nm thick, $\sim 10$ nm wide and $\sim 50$ nm long. According to the TEM images and optical data, the platelets are likely 5 monolayers thick. The absorption spectrum is shown as black, and a representative PL spectrum is shown in magenta. The black tics indicate the energies of the calculated lowest-energy transitions.\(^{12}\) The PL efficiency data is shown as a blue line and a singular PL QY value indicating the error is displayed as a red circle.

The similar PL efficiency drop observed in NPLs (Figure 1a) between the first and second apparent transitions could be due to a similar characteristic despite the significantly different electronic structure. NPLs are deep pseudo-2D wells created by the lamellar structures of ligand and CdSe\(^{13}\). Nanoplatelets are defined as being strongly confined in x, weakly confined in y and unconfined in z.\(^{11,12,13,14}\) Such confinement results in a saw-like density of states. In the case of 5 ML thick CdSe NPLs, the first electronic transition at 2.78 eV, is the $1\text{Se}-S_{\text{hh}}$ (1S electron with the 1 S heavy hole) and the second transition is 170 meV higher in energy ($1\text{Se}-1S_{\text{lh}}$, 1S electron with the 1 S light hole).\(^{12}\) Importantly, in addition to this is large $\Delta E$, these structures are atomically flat producing extremely narrow features. The significant decrease in PL QY, by more than half ($\sim 23\%$ to $\sim 12\%$) over the first transition to the second transition could be an effect of the large energy difference again providing a restriction for efficient charge carrier
relaxation via traditional phonon coupling. Additionally, giant oscillator strength (GOST) has been suggested for this lowest energy transition.  

The most prominent similarity between the QDs and the NPLs are the overall decrease upon using higher excitation energy. There are synthetic similarities that could produce this trend. These NPLs are likely to have some free TOP and OLA present from the synthetic work-up. Again, relative band offsets with respect to the NPLs are not known, free ligand provides a channel in the high-energy region. Highly excited charge carriers can couple to these, escape the NPL permanently and result in a diminished PL efficiency. Oleylamine has slightly lower energy transitions. If the band offsets are indeed small, then the charge carriers in the NPLs can begin to tunnel outside the platelets from as low as the first electronic transition.

4.4 Results and Discussion: Quantum Wires

In NPLs and QDs, the type of surface passivation affects the overall PL efficiency. In conjunction with the surface passivation, degree of quantum confinement can lead to measurable variability in the PL efficiency at low excitation energy. Surface passivation using a shell in a 3D quantum confined sample reduces this variability. Last, the presence of free ligand can produce decreases in PL efficiency, if using an excitation energy similar to the energy of the ligand(s) transition.

In contrast, quantum wires (QWs) are strict 2-D confined systems. The density of the electronic transitions has saw-like density of states. These theoretical values for electronic transition for CdTe QWs were determined by Sun et al. As they found, there is significant valence band mixing and thus each transition line shown represents a cluster of transitions. In addition, bound excitons exist in QWs and therefore excitonic states associated with each electronic state. These circumstances could lead to greater ease of phonon relaxation through
this denser ladder of states, suggesting that the local minima and maxima in PL QY experimentally determined in QDs and platelets will be minimized. In contrast, the surface-to-volume ratio in QWs is much larger than QDs and in this regard interaction of the exciton with the surface defects will be increased which in turn suggests any effects from ligand mediated processes on the PL efficiency will be stronger. Finally, the long z-dimension in QWs allows for exciton delocalization as has been previously shown. Any exciton generated in excess of $E_g$, will have some translational kinetic energy associated with it. Exciton translation along the QW length will allow it to experience different potential energy landscapes caused by different densities of traps. The ability to sample more than one region of the wire could lead to variation in PL QY with varying degrees of excess ($+E_g$) excitation energy. Generating a type-I heterostructure by shell addition to these wires would likely produce similar results as observed for the QDs; higher quantum yields as the surface traps are made less accessible.

First, the results of the ligand-passivated wires are discussed. Figure 3a and 3b display the absorption, one PL spectrum, and PL efficiency spectrum for two different diameters of ligand-passivated CdTe wires: (3a) 5.5 nm = d and (3b) 7.5 nm = d. The PL efficiency is scaled to the PL QY values as discussed above. The grayed absorption spectrum of TOP is included since these QW were suspended in TOP. To appropriately collect the absorption data for these CdTe wires, TOP was used in the blank scan, which is collected prior to the sample absorption measurement and removed from the sample scan. The black lines beneath the absorption again represent electronic transitions. In that case for QWs, there is significant valence band mixing. For simplicity, we use 1 black line to represent the cluster of strong transitions associated with each the coupling of multiple hole states with each electron state and the basic description of the first four lines is listed next to Figure 3 and Figure 4. The full PL efficiency spectrum (shown in
blue in panel a)) for the smallest wires (5.5 nm) have PL QYs ranging from 5.6 % (~1.82 eV = $E_g$) to 1.8 % (~ 2.8 eV). The PL spectrum for these low PL QY wires is very broad and contains both high and low energy shoulders. The first two electronic transitions lie within this region at ~1.80 eV and ~2.05 eV respectively. The PL efficiency remains stable within error from 2.1 to 2.3 eV, although there is a slight decrease. Above this energy, the PL efficiency decreases.

![Figure 4-3. Optical spectra and PL Efficiency data for CdTe QWs. These QWs are ~5.5 nm and 7.5 nm diameter for 3a and 3b respectively. The absorption spectrum is shown as black data, and a representative PL spectrum is shown in magenta. The straight black lines beneath the absorption indicate the energies of the calculated lowest-energy transitions. The PL efficiency data is shown as a blue line and a singular PL QY value indicating the error is displayed as a red circle. In contrast, the PL from the 7.5 nm CdTe QWs has only a low energy shoulder and higher overall PL efficiency. There are some fluctuations to the PL efficiency that create a local minimum near ~ 1.81eV; to slightly lower energy, 1.73 eV, the PL QY = 15.2 % and to slightly higher energy, 1.89 eV, the PL QY is 15.3 %. Although the PL efficiency is slightly decreased it remains stable within error from ~ 1.89 eV to ~ 2.10 eV. From 2.1 eV up through higher energy, the PL efficiency decreases.]
energies the decline continues and is slightly sharper. At the highest excitation energy, the PL QY = 5.9 %.

In this QW study there are some contradictions and some consistencies in the hypothesized affects of the available pathways on the PL efficiency. One clear consistency is the local minimum between cluster (cluster of transitions)1 and 2 in the 7.5 nm diameter wires. At 1.73 eV ($E_g$) the PL QY is 15.2 %, at 1.81 eV the PL QY is 13.8 %, at 1.89 eV the PL QY is 15.3 %. In QDs, this shape is associated with charge carriers coupling to bound ligand states due to the decreased probability for phonon relaxation. Such a shape change was shown to be more severe in the QDs. However, since clusters 1 and 2 are different in energy by ~ 150 meV and each has low mixing associated with them, any ligand-mediated deviations are expected to be minimal. As can be seen in Chapter 2, this local minimum is within the error of the measurement but consistently repeatable. Interestingly, between the 2nd and 3rd clusters there is no significant change in the PL efficiency. This excitation energy region will be discussed presently.

In the 5.5 nm diameter wires the lower PL efficiencies are likely due to a higher density of traps. As is shown, the PL spectrum is broad with both and low energy shoulders, which are likely due to surface traps as, discussed in chapter three and reference 60. So although traps can promote non-radiative decay excitons can also emit from them. The trend of PL efficiency for 5.5 nm wires is slightly different than what was observed for the 7.5 nm wires. From $E_g$ (1.82 eV) to the 2nd ($E_g + 280$ meV) cluster of transitions there is a consistent decline in PL efficiency. Instead of a decline, a local minimum would be predicted in this region. This local minimum is based on increased probability for phonon coupling from one transition to the HOMO of the bound ligand states and from this HOMO state through phonons to $E_g$. Such a high density of
trap states indicates fewer ligands are bound to the surface. Therefore this pathway is restricted and it is hypothesized that the inefficient intraband relaxation pathway is relied upon.

Between clusters 2 and 3 the PL efficiency remains stable within error. This is a similar circumstance to the 7.5 nm QWs. This similarity is likely an effect of the increased density of states. The second transition, 1Π, has two strong transitions associated with it and the third, 2Σ and 1Δ, have a total of four transitions associated with them. Higher densities of states allows for ease of phonon relaxation.

In both the 5.5 nm and 7.5 nm QWs both show a continued decrease in PL efficiency at high excitation energies. The states associated with the 3rd and 4th transition are a mixtures of hole states with 2Σe and 1Δe transitions (3rd) and 1Φe and 2Πe transitions (4th). The radial probability distribution is lower near the QW center with these higher energy transitions allowing for increased interactions with non-radiative surface states. In addition, an electronic transition is present for TOP at high energies. It provides an escape pathway for excitons to take. Removal of excitons from the QW produces decreased PL.

Figure 4-4. Optical spectra and PL Efficiency data for CdTe/CdS QWs. These QWs are estimated to have a core diameter ~ 6.8 nm. The absorption spectrum is shown as black data, and a representative PL spectrum is shown in magenta. The straight black lines beneath the absorption indicate the energies of the calculated lowest-energy transitions.38 The PL efficiency data is shown as a blue line and a singular PL QY value indicating the error is displayed as a red circle.
Next, a CdS shell can be added to the CdTe wires. This creates a type-I heterostructure, with the bulk valence band offset = 1 eV and the bulk conduction band offset = 110 meV. The process by which the shell is added is requires oxidation of the surface Te\textsuperscript{2} atoms and generation of a CdS shell. This is explained further in Chapter 2 and the following reference.\textsuperscript{39} This process allows for cleaving of dangling bonds. The $E_g$ as determined by the absorption spectrum is used to validate the diameter of these QWs after addition of the shell and is found to be $\sim$ 6.8 nm.\textsuperscript{40,41} The PL line shape shows the most narrow line shape of the QWs with no prominent high or low energies shoulders. The overall PL QYs can be as low as $\sim$17% (at $E_g$ $\sim$ 1.75 eV) and $\sim$ 4 % at 3.1 eV and can reach up to $\sim$25 % at $\sim$2.15 eV. There are no undulations in the PL efficiency across the low excitation energies. There is a slow rise from $E_g$ up to the maximum value, spanning the first 3 transitions. From 2.15 eV on there is a decline that is gradual at energies near this and then becomes sharpest at high excitation energies. The TOP used for these particular QWs is displayed by the grey absorption spectrum.

Based on previous results observed for the QDs, the alteration to a type-I heterostructure by shell addition is expected to reduce any of the local minima/maxima in the PL efficiency shape. The band offset for the valence band (hole) states is $\sim$ 1.00 eV and for the conduction band (electron) states is $\sim$ 0.11 eV.\textsuperscript{42} These offsets create an energetic barrier for energies roughly spanning the first two clusters of transitions. Interactions between the excitons and ligand states are therefore restricted over these energies, which will likely remove the local minimum observed at these energies. The data shows no signs of depleted PL efficiency between the two transitions and there is instead a slight increase.

In the region between the 2\textsuperscript{nd} and 3\textsuperscript{rd} transitions the PL efficiency of these CdTe/CdS QWs continues to increase. A second sample replicated this PL efficiency trend (see Chapter 2).
QWs the exciton is bound. An exciton generated with an excess of energy \((E + E_g)\) will have some probability for translation along the QW length. With increasing amounts of kinetic energy, some of which is translational, the exciton can sample more of the potential energy landscape. As the data indicates, increased probability for excitons delocalization in these core-shell QWs leads to improved exciton relaxation and higher PL efficiency. It is hypothesized that in the process of sampling different potential energy landscapes, the delocalized exciton can find a “good” or flat region, amenable for the relatively long process of exciton recombination.

In ligand passivated QWs, the PL efficiency does not increase in a similar energetic region, indicating that exciton delocalized is not efficient enough to afford improved exciton relaxation. So, the delocalization process appears to be dependent on the nature of the surface passivation. As was shown for CdSe QWs, for efficient exciton delocalization to take place, the deep potential energy minima needed to be photo-filled, to generate energy landscapes with less harsh variability.\(^{37}\) In the case of these CdTe ligand-passivated wires, surface traps are likely present, as can be observed in the PL spectra shapes. Te\(^2\)-dangling bonds have been shown to act as hole traps.\(^{43}\) In the CdTe/CdS QWs, the process of adding the shell likely cleaves dangling bonds. Any remaining hole-traps on the surface of the wires will still be difficult for the hole to access as the band offsets for the holes are 1.00 eV above \(E_g(\text{CdTe})\). Therefore, it is hypothesized that the ability to delocalize can be severely restricted by poor surface passivation but in a sample where delocalization is obtainable it can promote improved PL efficiency.

Exciting with increasingly higher energy, similar effects are expected as were observed in the QDs; a general decrease in PL efficiency. The excitons in these QWs are confined in the radial dimension but some tunneling can occur. In line with this the radial probability distribution is different at the lower energy transitions than the higher transitions. The majority of the radial
probability density is closer to the center of the QW core. Higher energy transitions have increasing nodes and lobes to the probability density.\textsuperscript{34} These changes in probability density shift the electron and hole density away from the core and allow for increased interactions with non-radiative surface states. This notion was described previously for a few diameters of CdSe/ZnS QDs.\textsuperscript{10} Next, the band offsets for CdS will allow the exciton to access the shell at \( \sim 2.75 \) eV. The PL efficiency is decreasing in this region however, as was observed in the QDs with intermediate confinement, threshold energy is not stark. Last, the TOP used for this particular study was partially oxidized leading to a slightly higher but still energetically accessible transition. Excitons coupling to the free environmental ligands will leave the QW permanently, producing reduced PL.

\textbf{4.5 Results and Discussion: Photoluminescence Lifetimes}

The types of pathways available, which can change with excitation energy, will affect the relaxation process and in turn will affect the number of charge carriers that reach the band edge. In contrast, the emission process, whereby the electron and hole at \( E_g \) recombine to produce a photon, is affect by the type of pathways available from the band edge only. Therefore, collecting the \( E_g \) emission at \( E = E_{\text{PL peak}} \) with a variety of excitation energies should not this will not change with excitation energy. PL lifetimes are collected for CdSe QDs (5.7 nm = d), CdSe NPLs and CdTe QWs (d = 7.5 nm) with a few different energies ranging from 2.75 eV to 3.1 eV. All decay profiles are multi-exponential and show limited variability with excitation energy. So, in order to quantitatively compare these decays, the data was fit using software that applies Bayesian theory to ascertain the best fitting parameters based on their statistical significance. Most data fits best to a sum of three exponentials. Utilizing the amplitude (\( A_i \)) and lifetime (\( \tau_i \)) parameters obtained from the fit, it is possible to calculate the fraction of photons
contribute $(f_i)$ to each lifetime component and then the average lifetime. The comprehensive results can be displayed in Table 1 through Table 3.

<table>
<thead>
<tr>
<th>Excitation Energy</th>
<th>$A_1$</th>
<th>$\tau_1$</th>
<th>$f_1$</th>
<th>$A_2$</th>
<th>$\tau_2$</th>
<th>$f_2$</th>
<th>$A_3$</th>
<th>$\tau_3$</th>
<th>$f_3$</th>
<th>$\tau_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe QDs (5.7 nm)</td>
<td>3.061</td>
<td>7.64E-4</td>
<td>5.64</td>
<td>0.023</td>
<td>0.00482</td>
<td>26.4</td>
<td>0.68</td>
<td>8.00E-4</td>
<td>66.3</td>
<td>0.29</td>
</tr>
<tr>
<td>2.988</td>
<td>7.40E-4</td>
<td>5.68</td>
<td>0.023</td>
<td>0.00485</td>
<td>26.5</td>
<td>0.69</td>
<td>7.71E-4</td>
<td>68.5</td>
<td>0.29</td>
<td>38.6(2.1)</td>
</tr>
<tr>
<td>2.917</td>
<td>6.20E-4</td>
<td>4.75</td>
<td>0.016</td>
<td>0.00462</td>
<td>24.8</td>
<td>0.62</td>
<td>0.00114</td>
<td>60.2</td>
<td>0.35</td>
<td>37.2(1.4)</td>
</tr>
<tr>
<td>2.850</td>
<td>0.00146</td>
<td>11.2</td>
<td>0.087</td>
<td>0.00444</td>
<td>31.7</td>
<td>0.75</td>
<td>3.19E-4</td>
<td>93.4</td>
<td>0.16</td>
<td>39.7(4.7)</td>
</tr>
</tbody>
</table>

**Table 4-1.** The results from fitting four separate PL decay curves for the 5.7 nm diameter CdSe QDs. Each decay curve was generated by exciting at four different energies and detecting at the PL peak energy (detection ~ 1.92 eV). The average lifetime is displayed in the far right column, highlighted blue. Values range from 37.7 ns to 37.9 ns. The max PL QY ~ 32 %.

<table>
<thead>
<tr>
<th>Excitation Energy</th>
<th>$A_1$</th>
<th>$\tau_1$</th>
<th>$f_1$</th>
<th>$A_2$</th>
<th>$\tau_2$</th>
<th>$f_2$</th>
<th>$A_3$</th>
<th>$\tau_3$</th>
<th>$f_3$</th>
<th>$\tau_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe NPLs (1.4 nm)</td>
<td>3.02</td>
<td>8.93E-5</td>
<td>21.14</td>
<td>0.311</td>
<td>7.98E-4</td>
<td>3.672</td>
<td>0.483</td>
<td>9.55E-4</td>
<td>1.308</td>
<td>0.206</td>
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<tr>
<td>2.95</td>
<td>4.67E-5</td>
<td>28.55</td>
<td>0.249</td>
<td>4.89E-4</td>
<td>4.713</td>
<td>0.430</td>
<td>11.14E-4</td>
<td>1.511</td>
<td>0.321</td>
<td>9.6 (0.6)</td>
</tr>
<tr>
<td>2.88</td>
<td>4.35E-5</td>
<td>34.22</td>
<td>0.261</td>
<td>4.63E-4</td>
<td>5.220</td>
<td>0.423</td>
<td>1.14E-4</td>
<td>1.587</td>
<td>0.316</td>
<td>11.6 (0.6)</td>
</tr>
<tr>
<td>2.82</td>
<td>5.83E-5</td>
<td>26.35</td>
<td>0.280</td>
<td>6.04E-4</td>
<td>4.170</td>
<td>0.460</td>
<td>9.75E-4</td>
<td>1.458</td>
<td>0.260</td>
<td>9.7 (0.5)</td>
</tr>
<tr>
<td>2.79</td>
<td>5.82E-5</td>
<td>26.36</td>
<td>0.296</td>
<td>5.76E-4</td>
<td>4.058</td>
<td>0.451</td>
<td>9.23E-4</td>
<td>1.418</td>
<td>0.253</td>
<td>10.0 (0.5)</td>
</tr>
</tbody>
</table>

**Table 4-2.** The results from fitting five separate PL decay curves for the 1.4 nm thick CdSe NPLs. Each decay curve was generated by exciting at five different energies and detecting at the PL peak energy (detection ~ 2.75 eV). The average lifetime is displayed in the far right column, highlighted blue. Values range from ~ 9 ns to ~ 12 ns. The max PL QY ~ 23 %.

<table>
<thead>
<tr>
<th>Excitation Energy</th>
<th>$A_1$</th>
<th>$\tau_1$</th>
<th>$f_1$</th>
<th>$A_2$</th>
<th>$\tau_2$</th>
<th>$f_2$</th>
<th>$A_3$</th>
<th>$\tau_3$</th>
<th>$f_3$</th>
<th>$\tau_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe QWs (7.5 nm)</td>
<td>2.73</td>
<td>5.108E-4</td>
<td>114.6</td>
<td>0.746</td>
<td>9.546E-4</td>
<td>18.53</td>
<td>0.225</td>
<td>0.00102</td>
<td>2.146</td>
<td>0.0280</td>
</tr>
<tr>
<td>2.71</td>
<td>4.814E-4</td>
<td>124.3</td>
<td>0.749</td>
<td>8.308E-4</td>
<td>21.50</td>
<td>0.224</td>
<td>7.146E-4</td>
<td>3.017</td>
<td>0.0270</td>
<td>98.0 (5.7)</td>
</tr>
<tr>
<td>1.74</td>
<td>6.601E-4</td>
<td>102.5</td>
<td>0.858</td>
<td>7.26E-4</td>
<td>13.79</td>
<td>0.127</td>
<td>7.137E-4</td>
<td>1.685</td>
<td>0.0152</td>
<td>89.7 (13.4)</td>
</tr>
<tr>
<td>1.69/1.68</td>
<td>7.264E-4</td>
<td>101.1</td>
<td>0.886</td>
<td>9.581E-4</td>
<td>13.53</td>
<td>0.107</td>
<td>9.942E-4</td>
<td>1.587</td>
<td>0.00701</td>
<td>88.5 (15.1)</td>
</tr>
</tbody>
</table>

**Table 4-3.** The results from fitting five separate PL decay curves for the 7.5 nm diameter CdTe QWs. Each decay curve was generated by exciting at five different energies and detecting at the PL peak energy (detection ~ 1.69 eV). The average lifetime is displayed in the far right column, highlighted blue. Values range from ~ 87 ns to ~ 98 ns. The max PL QY ~ 16 %.

As is observed here, the excitation energies do not significantly affect the average lifetimes for the QDs or for the QWs. The NPLs produce decay times that are similarly steady although, have some limited variation outside of the error. This is in good agreement with our hypothesis.
Other studies have reported PL lifetime values.\textsuperscript{10,23,44,45,46,47} Some are in reasonably good agreement with the average values we have determined here. However, it is important to determine whether the average lifetime or $\tau_{1/2}$ lifetime is reported. For example, for the CdSe NPLs studied here, the $\tau_{1/2} = 1.5$ ns which is quite different than the mean $\sim 10$ ns. Also, in some cases intensity coefficient ($f_i$) is inappropriately generated.\textsuperscript{14,12}

The differences in the average PL lifetimes between QWs, $\sim 91$ ns, to QDs, $\sim 38$ ns, to NPLs, $\sim 10.0$ ns, is interesting. The multi-exponential behavior that was mentioned above, indicates that there are a large variety of emitting species present. Based on what has been seen in the PL efficiencies, different pathways are expected to dominate in different samples. Of these three samples, the 7.5 nm QWs are hypothesized to have significant strong surface traps producing the prominent low energy shoulder on the PL and overall lowest PL QY values. The QD PL spectra displayed a low energy shoulder that was weaker and overall higher QYs. The PL spectrum for the NPLs is sharp and narrow, indicated minimal surface trapping, although the PL QYs are intermediate. Emission from surface traps is known to occur on longer timescales than $E_g$ emission.\textsuperscript{48-50} The PL decay profile should reflect the changing contribution to the long lifetime if the emission energy is varied and one excitation energy is used. This is studied in the CdSe QDs and CdTe QWs. The results of these studies are shown in Table 4 and 5 below.

Due to the extremely narrow PL feature, this experiment was not run for the CdS NPLs. Decreased surface trapping is expected in these atomically flat NPLs. Low defective surface areas have been shown in similar CdSe lamellar structures and based on the comparability of the total area of the two, is predicted to be the same for these NPLs.\textsuperscript{32}
Table 4-4. The results from fitting four separate PL decay curves for the 5.7 nm diameter CdSe QDs. Each decay curve was generating by exciting at ONE energies (E = 2.75 eV) and detecting emission at a variety of energies spanning the PL peak center energy, ~1.92 eV. The average lifetime is displayed in the far right column, highlighted blue. The range of values is larger from ~35 ns to ~55 ns. Longest time components in this graph are labeled as $\tau_3$.

Table 4-5. The results from fitting four separate PL decay curves for the 7.5 nm diameter CdTe QWs. Each decay curve was generating by exciting at ONE energies (E = 2.75 eV) and detecting emission at a variety of energies spanning the PL peak center energy, ~1.69 eV. The average lifetime is displayed in the far right column, highlighted blue. The range of values is larger from ~70 ns to ~108 ns. The longest time components in this graph are labeled as $\tau_1$.

As was anticipated, the average PL lifetime at the shoulders is found to increase. In the case of these CdSe QDs and CdTe QWs, these were both significant low energy shoulders. The factor increase of the lifetimes for both the QDs and the QWs from detecting above $E_g$ to at the prominent shoulder, lower energy than $E_g$, is ~1.6.

This information provides further validity to the types of pathways present for each dimensionally different sample. We use this to depict the role of dimensionality on the EED of the PL QY. Any process that is efficient from $E_g$ (recombination, trapping, or tunneling to the environment) will affect the PL lifetime. Figure 5 displays the representative PL decay profiles for (1.4 nm thick) CdSe NPLs, CdSe QDs (5.7 nm) and CdTe QWs (7.4 nm). A representative PL spectrum is displayed above each decay profile. The respective energy level diagrams depict the available pathways to each type of sample. The processes that have been shown to affect the
PL and the decay rate of the PL are in competition with band edge recombination. These processes are coupling to surface traps and escaping into the external environment. The former depends on the prevalence of surface traps and type of surface passivation and the latter depends on the transition energy of the molecular environment. For a single emitting species, the relaxation path has a radiative and a non-radiative component associated with it. However, each ensemble sample will have a variety of emitting species and each will relax and emit via any one of the aforementioned pathways or an additional pathway. Each species will contribute to the average PL lifetime based on the dominance of each.
Figure 4-5. The types of available pathways have been predicted by the PL efficiency data. The affects of these pathways on the PL lineshape and PL decay profiles are displayed. The PL spectra with significant shoulders show increased contribution from the long-time component. In these cases, the density and ease of coupling to surface traps is increased. The energy offsets for the ligand states and electronic transitions indicate the relative probabilities for charge carriers tunneling out into the environment.

The shape of the PL of the NPLs indicates limited surface trapping but the organic environment was shown to have a transition that lies at a similar energy to the band edge. In
addition, the shape of the EED and the results of previous studies indicate high oscillator strength of the heavy-hole ($E_g$) transition. This insinuates an increase in $E_g$ recombination. The 5.7 nm QDs display evidence for some surface trapping in the slightly asymmetric shape of the PL and the drop in PL QY at low energy in the EED PL QY spectrum. The 7.5 nm QWs indicate severe surface trapping as observed in the PL line shape and the PL QY dependence on excitation energy near these low and high-energy surface traps. For both the QDs and the QWs the external environment is not energetically accessible from each respective $E_g$.

### 4.6 Conclusions

For a variety of nanostructures an excitation energy dependence of the PL efficiency (PL QY) is found to exist. In extremely narrow, CdSe nanoplatelets, charge carriers respond to the high oscillator strength of the first transition but can also escape directly into environment. QDs passivated with ligands have more surface mediated processes resulting in undulations in the PL efficiency at low excitation energies. QDs with a type-I heterostructure are hypothesized to have fewer surface mediated processes and less PL QY variation at low excitation energy. Ligand passivated wires have increased surface trap interaction due to increase in surface-to-volume ratio. This affects allows for similar surface-mediated process to take place. With a CdS shell, CdTe QWs have decreased interactions with the surface, which produces overall improved PL spectrum and is hypothesized to promote efficient exciton delocalization. This leads to significantly improved and smoother PL efficiency spectrum.

The information provided here gives some insight into the effects of available pathways on the PL efficiency in a few different nanostructures. The results indicate the importance of determining the PL efficiency as well as elucidating the options for modifying the trend shape. Without knowledge of the complete PL QY other experiments that rely on carrier relaxation
efficiency, emission efficiency or energy transfer can produce convoluted results. Beyond utilizing this experiment for determining accurate and precise PL QY values, controlling this trend can lead to an expansion and improvement of applicable experiments. One example is in cascaded photovoltaic devices. These are solar cells that convert solar energy to electricity by utilizing varying band gap materials to energetically favor electron transport in a circuit. Manipulating the characteristics of the quantum confined nanomaterial, such as surface or strength of confinement, could be used to favorably alter the transport properties.
4.7 References


Chapter 5:

Conclusions
5.1 Summary:

In this work, the PL QY was carefully studied with respect to the excitation energy in QDs, QWs and NPLs. It was found that the PL QY value is not constant across all excitation energies and values were found to change by as much as a factor of 8, in CdSe/ZnS QDs. The changes in PL QY are hypothesized to be due to the changes in the available charge carrier paths as the excitation energy changes. The three most dominant paths are seen to be intraband relaxation, bound ligand-mediated relaxation, and coupling to transitions in the external environment. Efficient intraband relaxation promotes charge carrier recombination and a high PL QY. Inefficient intraband relaxation increases the probability for utilization of other pathways. For example, increasing the degree of confinement affects the ability for intraband relaxation due to large $\Delta E$ between transitions and inefficient phonon coupling. Instead, a different pathway is viable for the charge carriers, ligand-mediated relaxation. This will be less sufficient in systems with a shell. The energetic barrier for the charge carriers restricts to access the bound ligand states. In intermediately confined systems, such as our QDs and QWs, where the electron is bound but the hole is not, a certain degree of tunneling is expected at any excitation energy. Finally, at the highest excitation energies, any ligands present can provide an energetic transition to which the charge carriers can couple with changing efficiency depending on the energy with which the charge carriers are prepared; the excitation energy.

5.2 Ramifications and Applications

The ability to carefully study the EED of PL QYs when monitoring the PL from any quantum confined semiconductor sample, can be exploited to elucidate the trend and clarify potentially convoluted results. Due to experimental constraints and data acquisition times, it is common to utilize fixed excitation energies to measure PL QYs and PL intensity decay profiles
for semiconductor nanocrystals. For instance, PL spectra and QYs are often measured on aliquots of a sample mixture during synthesis or passivation procedures to monitor the growth of the QDs and to identify the optimal parameters for producing high-quality QDs.\textsuperscript{1-5} During the synthesis of CdSe QDs, $E_g$ can vary from 2.80 eV down to 2.00 eV as the diameter of the QDs increase. The results presented here indicate that if the PL QYs were measured using a fixed excitation energy of 3.00 eV during the synthesis, the PL QYs could decrease by a factor of four just due to the increase in the energy above $E_g$. Additionally, when exciting near $E_g$, the local minima in the EED of the PL QYs exist. Thus, whether characterizing the growth or passivation of QDs, monitoring energy transfer using QDs as donors or acceptors,\textsuperscript{6,7} investigating blinking and charging dynamics within QDs,\textsuperscript{8-11} or simply measuring the PL QYs of QD samples, mapping out the EED of the PL QYs is essential for developing a more complete foundation of the sample and is a useful tool for providing aid to interpreting the results.

Similarly, the PL efficiency trends can be exploited to optimize different applications. For example, an optimal solar photovoltaic device can utilize the entire spectrum of light that the sun emits. Quantum confined semiconductors are useful to this end, in that their $E_g$ can be tuned. The PL QY of a sample is one of several aspects that must be optimized to allow for high overall efficiency of a solar cell. Thus, it is important to know the range over which this efficiency remains constant and at its highest. Utilizing the studies found here, this can be determined.

Solar cells also require efficient charge carrier capture. This requires that the charges be transported from the QD or QW to an anode or cathode. The unconfined $z$ dimension of QWs makes them excellent candidates for PV cells. Being able to maximize the PL QY with a shell in
QWs, which has also been shown to generate more stable PL efficiency spectra, makes this an excellent opportunity for PV cells.

5.2 Future directions:

**A. NPLs:** Giant oscillator strength has been predicted for the 1Se-1Shh transition for NPLs. In the 5 monolayer thick platelets studied in this work, the maximum PL QY is over this first transition. It is also a very singular local maximum in that the PLQY maintains a high over only $< 100$ meV. The PL QY drops rapidly and is half its original value by the second transition. This could insinuate high oscillator strength for this transition. However, the free ligand present begins to absorb near $E_g$. The charge carriers are then facing competition of relaxation with tunneling, probably in addition to ligand-mediated paths as well. However, varying the number of monolayers of these NPLs will change the confinement, shifting the two lowest energy transitions to lower values, below the energetic turn on for the free ligand. By varying the quantum confinement of these CdSe NPLs, the shape of the PL efficiency can be studied to validate the giant oscillator strength of the first transition.

Recently, single CdSe NPL PL and PL decays were collected and very little inhomogeneous broadening was found. This same group has begun efforts to create a type-I heterostructure with either a CdS shell or a CdZnS shell. This would also be a beneficial next step to take. This would provide feedback on the EED trends in these NPLs.

**B. CdTe/CdS QWs:** The process of CdS shell growth on the CdTe QWs via thermal enhancing is described as being an oxidative substitution of the surface $Te^2$. The QWs studied in the recent work generated only one layer thick CdSe shell and this was validated by TEM, absorption and XRD. In summary, the growth of the shell causes a shift to slightly higher
energy as the CdTe core diameter decreases. The corresponding diameter for the shifted $E_g$ insinuated a single monolayer of CdS had grown. The highest QYs generated from thermal shell growth were 25% and the shift of absorption was even further increased from the carefully studied sample that generated $\sim 15\%$ PL QY. On closer examination of a few studies, the following shifts were found:

- 0 hour thermal enhancement: 1.71 eV
- 17 hour thermal enhancement: 1.72 eV
- 24 hour thermal enhancement: 1.73 – 1.75 eV

The $E_g$ is determined using the equation found using a modified equation, $\Delta E_g = (2.97)d^{-1.31}$.\textsuperscript{15}

The lattice parameter for a CdS bond = 0.21 nm and is used to estimate the monolayers of thickness for the CdS shell. As can be seen, the longest photoenhancing times produces an increased $E_g$ shift and indicate $\sim 2$ monolayers of CdS. It would be beneficial to perform a more careful study of the effects of varying thermal enhancing time on the CdS shell thickness. It would also be more comprehensive to include TEM and XRD data of each sample as well.

**C. Low energy materials, PbS:** A very large portion of the solar irradiance spectrum covers the UV through the near-IR energy ranges. The materials studied in this work have bulk band gaps in the visible (1.82 eV, CdSe and 1.5 eV, CdTe). Several NIR materials have been used to synthesize QWs, such as InAs, PbSe and PbS.\textsuperscript{16-20} The effects of the EED of the PL QY is better understood in the visible materials. This dependence should likewise be investigated in these low energy materials for the purpose to optimizing their applications. Also, due to their large bohr radii, the strong, intermediate, and weak regimes of quantum confinement can be easily examined. It will be interesting to see how the EED of the PL QY responds to different confinement regimes. Synthesis of PbS wires has been achieved by Jianwei Sun, in Dr. Buhro’s
lab. In summary, he utilized a single source precursor to synthesize PbS QWs via the solution-liquid-solid (SLS) growth mechanism.\textsuperscript{21} The diameters obtained ranged from 8 nm – 33 nm. Upon his completion of the graduate program, I began synthesizing some PbS QWs. One new development was, that it was found that the solvent, tri-n-octylphosphine oxide (TOPO), utilized in the SLS growth of CdSe QWs requires careful examination in order to optimize the QWs growth.\textsuperscript{22} TOPO is also the primary solvent in the synthesis of PbS QWs. I began some work to elucidate the best TOPO for PbS wire growth. I synthesized QWs ranging in diameter from 6.7 nm – 34.2 nm and collected several absorption spectra as well. This initial work can be found in Appendix I.
5.4 References


Appendix I.

Investigation of TOPO impurities for PbS nanowires and their NIR absorption
IA. Overview:

Synthesis of solution-liquid-solid (SLS) grown lead sulfide quantum wires was achieved by the focused efforts of Jianwei Sun, with diameters ranging from 6.9 nm (±1.3) – 31.2 nm (±3.9) \(^1\) In subsequent synthesis, I was able to achieve a similar diameter distribution, 6.7 nm (±1.0 %) - 33.7 nm (±6.4). Specifically, the method developed requires a single-source precursor. This precursor is Lead Diethylthiocarbamate \((\text{Pb(S}_2\text{CNEt}_2)_2)\). It can be synthesized following the procedure set forth by Trindade and coworkers in 1997, see reference seven. A typical synthetic procedure, set out by Jianwei is as follows. In the glove box 4g (0.01 mol) trioctylphosphine oxide \((\text{TOPO})\) is loaded into a Schlenk reaction flask. (~20 mg) 0.04 mmol of the \(\text{Pb(S}_2\text{CNEt}_2)_2\) is combined with 0.8 g phenyl ether in a septum-capped vial. Roughly 15 mg of bismuth catalyst nanoparticles are dissolved in 0.5 g tri-n-octylphosphine \((\text{TOP})\) in a separate septum-capped vial. The range of bismuth nanoparticle sizes used are 4.3 nm – 10.3 nm (J. Sun) (diameters I used: 7.7 nm – 11.1 nm). The contents are removed from the glove box.

The Schlenk reaction flask is heated using a pre-heated salt bath \((\text{NaNO}_3/\text{KNO}_3)\) to the desired reaction temperature. Temperatures in the range of 232°C – 290°C were successfully used by both Jianwei and myself for generating high quality wires. The vial of precursor is then heated with a heat gun. The gun was set to >200°C and held several inches away for ~1 minute. Proper heating of this mixture results in a color change from white and cloudy to clear and yellowish. (If the mixture turns black, often times nanocubes are made.) This mixture and the bismuth mixture are drawn into a syringe and injected into the reaction flask. Efficient reaction times are in the range of 2 to 5 minutes. Specific protocols for Jianwei’s synthesis can be found in the following references. The batches I synthesized will be discussed presently.
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**II. TOPO impurities:**

In the SLS growth mechanism, variability in different batches of the primary solvent, TOPO have been found to change the quality of the wires produced in CdSe wire synthesis.\textsuperscript{2,3} Subsequent studies on the types of impurities, and their affects on wire growth indicated that for CdSe wires DOPA was often the best impurity. Inappropriate ratios of impurities resulted in poor intra- and inter-diameter distributions to cone-like wires, rods, or branched wires. It is therefore important to understand the primary impurity of interest for PbS QWs.

The successful synthesis of the several batches of PbS wires indicated the TOPO utilized likely has the best presence and ratios of impurities. All these QWs were synthesized with a specific batch 90% TOPO that was distilled twice, that will hereafter be referred to as TOPO\textsubscript{032407}. Both Jianwei and I utilized this TOPO\textsubscript{032407}. The impurities can be elucidated using $^{31}$P NMR. The $^{31}$P NMR taken of TOPO\textsubscript{032407} (in deuterated chloroform) is shown below.
Figure I-1. $^{31}$P NMR of TOPO$_{032407}$ The other impurities are DOPO (Di-n-octylphosphine Oxide), DOPA (Di-n-octylphosphinic acid), OPA (n-octylphosphonic acid), and MOPA (mono-n-octylphosphinic acid).

This TOPO$_{032407}$ contains small amounts of DOPA, DOPO and MOPA and each peak is labeled according to the specific impurity. The relative amounts of each of these impurities in a total of 4 g of TOPO are listed above. Therefore, synthesis was performed attempting to use different amounts of (TOPO$_{032407}$) + impurities and (new, distilled TOPO) + impurities. The results can be seen in Table 1. below. Interestingly, the largest and smallest diameter wires were synthesized using some extra impurity. Several TEM images are displayed as well, with their corresponding diameters listed.
Mimicking Good TOPO (~3mg MOPA, ~21mg DOPA and ~26mg DOPO in 4g pure TOPO), produces wires but lack in smoothness and length when compare to the wires made with TOPO$_{032407}$. This can be seen by the bottom set of TEM images.
Table I-1: Synthetic details

<table>
<thead>
<tr>
<th>TOPO Type / (g)</th>
<th>Impurity Type / (g)</th>
<th>Pb(S₂CNEt₂)² (g)</th>
<th>Phenyl Ether (g)</th>
<th>Bismuth Size (nm) / (g)</th>
<th>TOP (g)</th>
<th>Rxn T (°C) / time (min)</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure/4.04</td>
<td>DOPA/0.01</td>
<td>0.021</td>
<td>0.872g</td>
<td>8.8/0.015</td>
<td>0.503</td>
<td>240/2</td>
<td>6.7 nm (±1.0)</td>
</tr>
<tr>
<td>TOPO₀₃₂₄₀₇/4.00</td>
<td></td>
<td>0.030</td>
<td>1.00g</td>
<td>8.8/0.034</td>
<td>0.520</td>
<td>232/2</td>
<td>10.8 nm (±1.5)</td>
</tr>
<tr>
<td>TOPO₀₃₂₄₀₇/3.934</td>
<td></td>
<td>0.023</td>
<td>0.826g</td>
<td>8.8/0.019</td>
<td>0.505</td>
<td>240/4</td>
<td>11.7 nm (±1.9)</td>
</tr>
<tr>
<td>TOPO₀₃₂₄₀₇/3.934</td>
<td></td>
<td>0.023</td>
<td>0.826g</td>
<td>8.8/0.019</td>
<td>0.505</td>
<td>240/2</td>
<td>11.7 nm (±1.9)</td>
</tr>
<tr>
<td>TOPO₀₃₂₄₀₇/4.043</td>
<td></td>
<td>0.019</td>
<td>0.808g</td>
<td>8.8/0.015</td>
<td>0.509</td>
<td>250/4</td>
<td>12.2 nm (±3.3)</td>
</tr>
<tr>
<td>Pure/1.145 + TOPO₀₃₂₄₀₇/3.262</td>
<td>*</td>
<td>0.034</td>
<td>0.835g</td>
<td>8.8/0.016</td>
<td>0.600</td>
<td>235/2</td>
<td>12.3 nm (±1.7)</td>
</tr>
<tr>
<td>TOPO₀₃₂₄₀₇/4.372</td>
<td></td>
<td>0.050</td>
<td>0.900g</td>
<td>8.8/0.015</td>
<td>0.600</td>
<td>246/2.5</td>
<td>12.3 nm (±2.3)</td>
</tr>
<tr>
<td>TOPO₀₃₂₄₀₇/4.043</td>
<td></td>
<td>0.019</td>
<td>0.808g</td>
<td>8.8/0.015</td>
<td>0.509</td>
<td>250/2</td>
<td>12.7 nm (±2.5)</td>
</tr>
<tr>
<td>Pure/3.053 + TOPO₀₃₂₄₀₇/1.143</td>
<td>*</td>
<td>0.020</td>
<td>1.047g</td>
<td>8.8/0.019</td>
<td>0.501</td>
<td>237/2</td>
<td>12.9 nm (±2.3)</td>
</tr>
<tr>
<td>Pure/2.5 + TOPO₀₃₂₄₀₇/1.411</td>
<td>DOPA/0.05</td>
<td>0.020</td>
<td>0.830g</td>
<td>8.8/0.015</td>
<td>0.531</td>
<td>250/5</td>
<td>13.4 nm (±2.01)</td>
</tr>
<tr>
<td>TOPO₀₃₂₄₀₇/4.445</td>
<td></td>
<td>0.023</td>
<td>1.0g</td>
<td>8.8/0.028</td>
<td>0.500</td>
<td>242/2</td>
<td>13.6 nm (±2.6)</td>
</tr>
<tr>
<td>TOPO₀₃₂₄₀₇/4.045</td>
<td></td>
<td>0.035</td>
<td>0.900g</td>
<td>8.8/0.022</td>
<td>0.510</td>
<td>250/2.5</td>
<td>14.2 nm (±2.4)</td>
</tr>
<tr>
<td>Pure/1.916 + TOPO₀₃₂₄₀₇/2.027</td>
<td>*</td>
<td>0.024</td>
<td>1.08g</td>
<td>8.8/0.015</td>
<td>0.503</td>
<td>242/2</td>
<td>14 nm (±2.4)</td>
</tr>
<tr>
<td>TOPO₀₃₂₄₀₇/4.176</td>
<td></td>
<td>0.026</td>
<td>0.900g</td>
<td>11.1/0.030</td>
<td>0.530</td>
<td>264/2</td>
<td>15.2 nm (±2.3)</td>
</tr>
<tr>
<td>Pure/3.872</td>
<td>DOPA/21 DOPO/26 MOPA/03</td>
<td>18 (0917)</td>
<td>795</td>
<td>7.7/0.017</td>
<td>508</td>
<td>250/4</td>
<td>~16 nm</td>
</tr>
<tr>
<td>Pure/4.165</td>
<td>MOPA/0.14/8</td>
<td>0.034</td>
<td>0.812g</td>
<td>8.8/0.017</td>
<td>0.520</td>
<td>241/2</td>
<td>33.7 nm (±6.4)</td>
</tr>
<tr>
<td>Pure/4.12</td>
<td>DOPA/20 DOPO/36</td>
<td>29</td>
<td>1.250 g Oleyel - amine</td>
<td>7.7/22</td>
<td>623</td>
<td>253/5†</td>
<td>~50 nm Cubes</td>
</tr>
</tbody>
</table>

* Some TOPO₀₃₂₄₀₇ is mixed with pure TOPO, the reaction is anticipated to have additional impurity.
† As discussed in the text, it is hypothesized that the cubes were made while heating the precursor with the heat gun. During the additional reaction time (5 minutes in TOPO) it is unclear what this step may or may not contribute.
IC. Attenuation Spectroscopy:

The cleanest absorption information was obtained using the attenuation detectors. Achievement of attenuation spectra was met with some issues. Jianwei was able to obtain three clean, good attenuation spectra of PbS wires. He did so by first washing in Toluene/Methanol (MeOH) and Hexanes/Acetone. Before suspending in dried carbon tetrachloride, he dried the wires, under the flow of N\textsubscript{2}. The attenuation spectra he was able to obtain were using very high concentrations.\(^1\) However, in order to perform PL, PLE and PL QY measurements, as discussed in Chapter 2 and Appendix II, it is important to use low concentrations. I attempted to collect attenuation spectra of the samples I synthesized at lower concentrations. The wires need to be suspended in dry a dried solvent. Washing can be performed in non-dried solvents as long as the wires are dried with N\textsubscript{2} before suspended in dry carbon tetrachloride.

Attenuation spectra of the wires I synthesized using dry carbon tetrachloride and low concentrations of PbS wires still displayed several very strong spurious features making the band edge was difficult to determine. It was difficult to determine the starting energy for the fitting range. The most successful wash procedure, for obtaining clean attenuation spectra, involved both washing and drying the wires. After a few washes, with the supernatant decanted, the wires were left in the bottom of a test tube, capped with a rubber septum and dried under N\textsubscript{2}. A secondary needle is used to allow proper ventilation. The appearance of the wires at the bottom of the test tube changes from glassy and wet to powdery and dry in just a few minutes. However, drying was always performed for many more hours. The best attenuation spectra obtained are shown below. These were dried for no less than 2 hours.
Figure 1-3. Attenuation spectra of four different samples of PbS QWs. The samples were suspended in dry carbon tetrachloride. The washing and drying procedures are discussed in the text.
The water spike at 0.459 eV (2700 nm) is a strong feature that is most easily removed with longer drying times and is not permanent. This can be seen in the two representative attenuation spectra in the figure below.

![Figure 4. Two attenuation spectra of a batch of 13.4 nm diameter PbS QWs with respect to the time at which the data was collected after completion of the drying process. The arrow indicates the prominent water vibration. The wires were washed twice and then dried for ~ 4 hours. The black attenuation spectrum is taken within 15 minutes of completion of the drying process. The red attenuation spectrum is taken 24 hours after the drying process, while being stored, in the borosilicate test tube in which they were dried. The attenuation spectra were fit by first, subtracting a scattering background. The residual was subsequently fit to a sum of Gaussian functions to determine the energies of the electronic features. The values were obtained for the band edge $E_g$. These numbers were compared to those obtained from the wires Jianwei collected and are shown below.](image)
<table>
<thead>
<tr>
<th>Mean Diameter</th>
<th>Estimated $E_g$</th>
<th>Method for fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.2 nm (± 2.5)</td>
<td>0.615 eV</td>
<td>1</td>
</tr>
<tr>
<td>10.8 nm (± 1.5)</td>
<td>0.560 eV</td>
<td>4</td>
</tr>
<tr>
<td>11.2 nm (± 2.3)</td>
<td>0.529 eV</td>
<td>1</td>
</tr>
<tr>
<td>11.7 nm (± 1.9)</td>
<td>0.490 eV</td>
<td>4</td>
</tr>
<tr>
<td>13.4 nm (± 2.0)</td>
<td>0.477 eV</td>
<td>4</td>
</tr>
<tr>
<td>14.2 nm (± 2.4)</td>
<td>0.465 eV</td>
<td>4</td>
</tr>
</tbody>
</table>

Table I-2. The measured $E_g$ for different diameter PbS quantum wires. Some fitting was performed by Jianwei and some by myself. The literature for the fitting procedure is listed. The difference between the two fitting methods is that Sun and Buhro use an exponential decay to fit the background and Kuno et. Al. use a wire scattering term plus a bulk scattering term.

As was suggested in chapter 5, it would be interesting to study the confinement effects in PbS, since the exciton bohr radius is so large. The strong, intermediate, and weak confinement regimes could be studied within the range of diameters what were synthesized. Using origin one can digitize previous data from a document. In this way J. Sun attenuation spectra can be fit using the same procedure as I have used. The $E_g$ from both methods can be compared. Plotting the $E_g$ with $1/d^2$ can be used to display the transition between the intermediate and strong confinement regimes.\textsuperscript{5,6}
References


Appendix II.

Details of the Photoluminescence Spectrometer

This section can serve as a manual for the home-built photoluminescence spectrometer.
IIA. WARNINGS: READ THIS SECTION BEFORE USING THE SPECTROMETER

a. SAFETY RULES:
- When working directly on the spectrometer, uncovered, at the laser table, use the LASER SAFETY GOGGLES. When aligning and you need to remove goggles, remember to keep a mildly lit room and refer to lab specific safety training for alignment tips.
- When working with the InSb detectors you will need to fill these with liquid N2. Remember to use CRYOGENIC gloves, eye protection and to wear closed toed shoes, long pants, and long sleeves.
- The power supplies for the InSb detectors have some soldered wires. Before connecting these to power, always be sure that the electrical tape and INSULATING covers are properly covering these supplies.

b. REMINDERS TO PREVENT DAMAGE TO THE SPECTROMETER:
(1) Lock-In amplifiers display error: OVLD – this means signal overload. This can permanently damage the lock-ins and must be fixed IMMEDIATELY. Most likely you have too much signal from the lamp letting too much light in or the PMT voltage being too high. The quickest fix is to close the shutter to block the light: Go to front panel of shutter control box. The switches are labeled “N.O. / N.C.” and “Local / Remote” and are both DOWN. Flip the one switch from “N.C.”/down to “N.O.”/up. This closes the shutter, blocking the beam and will provide a temporary fix to you problem. (Note: before running the data collection program, you need to flip the switch back for the computer to communicate with the shutter.) Even if you do fix it quickly, you might want to test for damage. To do this: go to the “testing” section of the Lock-in manual and perform test # 10.
(2) Whenever moving either the chopper wheel for any reason – ALWAYS unplug the motor and ALWAYS test the motion of the wheel BY HAND before plugging it back in and turning it on.

(3) Sometimes the oscilloscope is used to monitor the shape of a weak signal and parameters are adjusted. ALWAYS return the parameters back to their original settings when you return the BNC cables to their original layout. If necessary, you may then gradually adjust the parameters to the new setting, while monitoring the Lock-In amplifier display.

(4) If the lock-in amplifier is off but (any) detector is on and uncovered damage can be caused to the detector. Therefore, (any) detector active area should ALWAYS remain covered or within the spectrometer housing when it is ON.

(5) The switches are labeled “N.O. / N.C.” and “Local / Remote” and both should be DOWN to allow the program to communicate with the shutter.

(6) BNC 2090 is being used to trigger the start of data collection by the lock-in amplifier. The connections go to “Trig In” in the back of the Lock-in amplifiers. Similarly the BNC 2090 is used to trigger open and close of the shutter. These wires should connect the front of the BNC 2090 to the front of the shutter control box.
IIB. Layout:

Figure II-1.
IIC. PROCEDURES

A. PROCEDURE FOR: SPECTROMETER CALIBRATION

Each optical component of the spectrometer has an optical efficiency that will affect the amount of signal to varying degrees at each wavelength. We purchased a NIST calibrated lamp and it has a Correction file that lists the total power expected to be transmitted at each wavelength. If we shine this lamp through our spectrometer and collect the light at the output we can set up a ratio between the expected intensity at each wavelength and the actual intensity of light that is transmitted through the spectrometer.

(i.) Wavelength Calibration

A neon pen lamp can be used to validate the grating wavelengths. This is typically a procedure performed when a new monochromator or a new grating is implemented, if a turret is switched, or if the monochromator has just been returned from being serviced. Whether calibrating the 2150i or the 2300i, there are a few important steps necessary to ensure that the procedure is done without problems.

First, the pen lamp will need to be set up the correct distance away from the entrance slit of the monochromator to ensure that the image of the lamp lines are clear and sharp on the other side of the focusing lens (on the entrance slit). Second, because the pen lamp is extremely bright and strongly diverging, 2 irises are required to keep a good signal-to-noise ratio. The first iris usually is placed somewhere between the pen lamp and the focusing lens to block a majority of the diverging light. CAUTION: this iris can get HOT. The second iris should be placed at the entrance of the monochromator to allow only 1 clean, sharp line through the entrance slit. Last, because you are using a Lock-In amplifier to collect your data, you will need to place one of the chopper wheels in the optical path. Since the slits in the chopper wheel are relatively small, the
The best place for the chopper is between the second iris and the entrance slit. This will require some CAREFUL arrangement of the wheel and TESTING out its motion by turning the wheel BY HAND before plugging it back in.

You can utilize the wavelengths in the CRC handbook on the position of Neon lines. Create two columns in origin: one of the measured wavelengths and one of the standard wavelengths (form CRC). Find the difference between the two for several data points. Find the average of the difference between the two. From the two columns of data, find a set of values is “different” by roughly the average amount, you will need these two (measured and standard) wavelength values. Now, you can use the information to adjust the wavelengths in the Acton software (STIK, on desktop). Use the procedure from the monochromator control software entitled “SpectraPro v.3.37” -> help -> Software manual.

(ii.) Instrument Response Calibration

Introduction:
The NIST lamp is sent to Avantes who send the lamp to the Netherlands to be calibrated on a NIST spectrometer. It calibrated from 300nm to 2500nm. It is returned to us with both a hard and digital copy of the Correction File that gives us how much power (in \( \mu \text{W/cm}^2 \text{nm} \)) the lamp should emit at each wavelength and this calibration file is good for 60 hours of use. The lamp is aligned through the excitation arm and data is collected at the input of the sample holder. Then it is aligned through the detection arm, with the lamp at the sample holder position, and data is collected at the output of the detection monochromator. After a few required steps to treat the data (discussed further in the next section), an instrument response function (IRF) can be made
by creating a ratio between the Calibration File that was sent and the Collected Avantes data. This data can be used to correct any sample data in the following way:

\[
\frac{X}{SampleData} = \frac{NIST_{\text{Correction File}}}{NIST_{\text{RALdata}}}
\]

**User notes:**

1. Locate and unpack the NIST lamp (located above the laser table in a box), the plastic baggie labeled “AVANES LAMP POSTS” (from the black file cabinet), and open the “QTH Bulb Lifetime” program.

2. Ensure that both PMTs are completely off. Remove the PMT that is located on the output of the second/emission monochromator. Keep the front face covered until this step is complete. Use the posts in the bag to attach this PMT to the tall post. Remove the cuvette holder by pulling the posts out of their holders – but leaving the post holders fixed to the table. Fix this PMT/post to the laser table at the position where the sample-holder had been. Ensure that all the proper connections are still attached.

3. The NIST lamp does not have a holder nor does it have any threaded holes with which you can secure it to the laser table. Instead, we use flat posts that are located in the black file cabinet next to the laser table. These posts are in a plastic baggie and are labeled “AVANES LAMP POSTS”. One post is higher than the other because the lamp has 2 levels on its encasement. Each post is placed under the appropriate ridge to get the lamp to be the appropriate height and to be level. The lamp can be used in the right-side-up or up-side-down position and in the latter case the posts will need to be in the reversed order so as to hold the lamp up to an inappropriate
height to the rest of the optics in the beam path. Be careful to arrange the power cable so that it will not be bumped or jostled as this will lead to misalignment.

(4) To calibrate the excitation side, first the QTH lamp is removed from its original position to allow room for the Avantes lamp. (The replacement procedure can be found in paragraph 1 of section 2.3.2). Next, the 1.5” lens that was in the bag with the posts must be placed in front of the 2” F/4 lens in front of the monochromator. (This is a “replacement” for the telescoping lens inside the lamp housing.) Then, place the NIST lamp on the posts in front of this lens. Turn the lamp on. Return to the computer and in the program window – enter the current date into the LOWER box, labeled “Avantes Lamp”. Select the Run button, which will turn green AND push the Run white arrow. (See section 2.4.1 for details.)

(5) Align the lamp left and right with ONLY the second lens in place. Then put the first lens in place; first align the height by adjusting the neck of the lens or adding/removing spacers on the posts for the lamp; second align back/forth so that the spot is focused and sharp on the entrance of the monochromator. The only height adjustment that should be needed should be once it is focused and sharp check to make sure that the lamp is level – place the level on top of the lamp on the flat section. The posts have been adjusted so that the lamp should be level. The second lens might need some minor adjusting in HEIGHT ONLY. The beam will be focused when you can see a small circle (1 cm = d) on the entrance slit of MonoExc.

(6) The NIST light will progress through the monochromator, through the lenses and chopper on the output side of the monochromator, 9% will reflect off of the beam splitter into PMT #1 and the transmitted portion will be detected by PMT #2. Make sure there is nothing blocking the beam path. Then replace the cover over the beam path.
(7) Turn on the pre-amplifiers, lock-in amplifiers and PMTs. The signal from the NIST lamp is weak and there is likely no cause for OVLD (signal overload). If you see this – close the shutter immediately and determine the cause of the OVLD. You can probably just adjust your PMT voltage settings to fix this.

(8) The slit widths for the MonoEXC for NIST data collection are typically set wider than for sample data collection. This is necessary to ensure reasonable signal-to-noise for both PMT’s. Wider slits will require lower PMT voltage settings and vice versa. Typical settings for the NIST lamp are: 1.5mm slits, 900V excitation PMT, 450V transmission PMT (this PMT is currently at the transmission point, replacing the sample holder). The Pre-amplifier/Amplifier settings typically used are: 500nA/1V (transmission) and 50nA/100mV (excitation).

(9) You should not need to adjust the pre-amplifier settings – if you do it is VERY important to RECORD these numbers in your notebook and electronically in the auto-generated text file.

(10) Open the “Photoluminescence and Photoluminescence Excitation.vi.” Program. Select a name for the scan you are collecting – in this case the name should include be: “Date_NIST_Excitation_GratingName”.

(11) Turn off the room lights. Start the program (click white arrow). Enter the appropriate values in when prompted (See section 2.4.2) (REMEMBER TO ENTER THE SLIT WIDTHS). The raw data will then be saved in an excel file and the text file containing all of the appropriate parameters will be saved with it.

(12) The data will not be dealt with yet. Next, you need to calibrate the emission arm of the spectrometer. In this case, a few parts will need to be adjusted. The first is the PMT at the sample holder – that will need to be replaced back to its original position on the exit port of MonoEm. Next, the NIST lamp will take the place of the PMT you just moved. It will be aimed
to shine light down the path towards the MonoEm and ensure proper alignment again. Finally, you need a chopper wheel placed along this arm of the spectrometer. The easiest route is to unplug the power chord from the current chopper and use a screwdriver to CAREFULLY remove the wheel currently set in place. Then locate the spare chopper system in the file cabinets and CAREFULLY attach the wheel. Bolt this system to the laser table at the location between the last optic and the MonoEm. Once this is in place and you have made certain that the wheel is touching nothing, plug the motor back in and turn the chopper back on.

(13) Once you are certain that the alignment is set you will want to adjust the slits on the entrance and exit slit of this MonoDet. Since this pathway is shorter with fewer optics, less light is lost. So, in order to not overload the detector or lock-in amplifier the typical slit widths are ~ 0.25 mm and the PMT voltage ~ 650 V.

(14) You should not need to adjust the pre-amplifier settings – if you do it is VERY important to RECORD these numbers in your notebook and electronically in the auto-generated text file.

(15) Use the “Photoluminescence and Photoluminescence Excitation.vi.” Program again. Select a name for the scan you are collecting – in this case the name should include be: “Date_NIST_Detection_GratingName”.

(16) Start the program (click white arrow). Enter the appropriate values in when prompted (See section 2.4.2) (REMEMBER TO ENTER THE SLIT WIDTHS). The raw data will then be saved in an excel file and the text file containing all of the appropriate parameters will be saved with it.

(17) You now have 3 different data sets for the calibration of the spectrometer. Use the information in the next section to get these data prepared for use in the Data Analysis file.
(iii.) Treatment of the Instrument Response Calibration data and Application of these data to Analysis programs

Introduction:

Before these calibration files can be used to analyze any unknown/sample data, they need to be corrected to match the same parameters that are used to collect unknown/sample data. An example of the following detailed procedure can be seen in the origin project: “D:/Hoy/Calibration/MarchNIST_datafile.opj”.

User Notes:

(1) Each data set needs to be adjusted for (a) slit width differences, (b) voltage, (c) pre-amp settings (if they were switched) and (d) smoothing. Last, each data set will be placed in an excel file and its file name will be entered into the appropriate locations within the analysis program.

(2) The average slit widths across all wavelengths used for the MonoExcitation are 0.94 – 0.96 mm (to get 5 nm) and the average slit widths used for MonoEmission are 1.93 – 2.00 mm (to get 5 nm). Correct the calibration data by multiplying by the factor relationship (that will reduce the excitation data and increase the detection data). The data the lists the slit width translations can be found in table: “desktop:/Slit Width Data 111710.ogw” and these slit calculations can be found in: “D:\Hoy\Calibration Files\SlitWidths_082510.opj” and Raw data found in July 2011. Do this for all three data sets.

(3) To correct for the voltage differences you will need the voltage translation chart found in: D:\Hoy\CalibrationFiles\Old\Data_Obtained_2calculate_GAIN_ogw.zip. This step is simple. Find the voltage that was used to collect the calibration file, determine the gain, and then divide the calibration data by the gain amount. Do this for all three data sets.
If the pre-amp settings are changed then a correction should be made. Take the typical Pre-amp setting and divide by the pre-amp setting used to collect the calibration data. This should be a whole number on the orders of 10’s, 20’s, 25’s or 50’s. What ever this number is, divide the calibration data by it. Do this for all three data sets.

Finally, all data sets should be smoothed. For these data, because we cover the full range of instrument sensitivity in one single scan, but we do not have the option of adjusting the lock-in amplifier sensitivity, the resulting data can have regions where the local fluctuations are step-wise in nature. Savitzky-Golay smoothing can remove this. This can be done in an origin program. Don’t use large “Points of Window”; < 20. Do this for all three data sets.

From these finished products, three separate excel documents must be created. These will be saved in a location specific to this calibration date and any sample data collected after this date will want to be able to refer back to all of it. To this end, set up a folder within calibration folders, entitled “Calibration_Date”. Save the origin project used to prepare the calibration data here as well.

Excitation data collected from the PMT detecting reflected photons can be the first. Column A of the excel document should be wavelength – but it must be in whole numbers in order for the analysis program to run properly – so you will need to change this. The typical file name is “Exctation_Transmitted_G1.txt”. Repeat this for the Detection data. Last, the reflected excitation data divided by the transmitted excitation data will be used to generate the final excel document, again with wavelength in column A. (typical file name is “Excitation_Ratio_G1.txt”).

Open the “Total Data Analysis” LabView program. On the front panel there are three ‘control’ boxes. Use these to choose the calibrations files necessary for correcting the sample
data. Choose the appropriate files depending on the headings above each control box. Repeat this for the other two files. When you have completed this, put your cursor over each of these control boxes separately, right click, select “data operations”, then select “Make Current Value Default”. When you have done this, save the entire program and you can close the program.

(iv.) Validation of the Calibration

The validation step requires collecting data for two standard dyes, analyzing these data, and checking the ratios of the quantum yields. NOTE: PROCEDURE C provides more details on the data collection process necessary to perform THIS VALIDATION.

(1) The two dyes used for this process are rhodamine 6 G (Rh6G) ($C_{28}H_{31}N_{2}O_{3}Cl$) and oxazine 1 (Ox1) ($C_{20}H_{26}ClN_{3}O_{5}$). R6G has a known quantum yield (QY) of 95 % and Ox1 has a known (QY) of 11%.¹ [ Sens, R, 1981, # ]

(2) First, one cuvette of each dye is made. The concentrations of these dyes must be kept very low, below 0.01 absorbance units across the standard excitation wavelength range. From R6G this is 450 nm to 490 nm and for Ox1 this is 560 nm – 600 nm. Concentration dependencies due to re-absorption of emitted photons have been found to contribute significantly above 0.01.[Kubin, 1982, Journal of Luminescence, 27, 455 - 462] Once these have been made, you will collect one absorption spectrum for each. Use the procedure for the absorption spectrometer outlined in appendix II.

(3) Next, collect at least 5 different emission spectra by exciting at 5 different wavelengths for R6G. Use the procedure outlined in the next section (2.3.2) for sample data collection. The 5 different wavelengths should span the range suggested above and each excitation wavelength will be exciting the sample with different absorbance values. The step size between these should
be 5 nm as the slit widths used will be 5 nm. To determine how to set 5 nm slits, utilize the chart “Desktop/Slit Width Data 111710.ogw”. Do the same for Ox1.

(4) Once the emission data has been collected, use the “Total Data Analysis” program to correct the data for the instrument response. The procedure for using this program is detailed in Program Details section 2.4.3.

(5) Finally, you want to determine that the ratios of the QY’s are correct and so the QY’s must be calculated. Create an origin project with the absorption and corrected emission data for both dyes in it. Generate a new X-column for the emission data that is energy (NOT wavelength). Be sure that these emission spectra do not contain any excitation scatter in them. If they do, use the procedure outlined in section 2.5 to remove it. Next, integrate the total emission for each spectrum obtained and record this value in the column next to the absorbance value column, corresponding to the appropriate wavelength of excitation. Add a new set of values to this: go to the bottom of these 2 columns and append a new row with 0 as the absorbance value and 0 as the integrated emission. Change the absorbance column “X” values. Now, select the integrated emission and plot these values. They should make roughly a straight line. Fit these data to a straight line. Perform this procedure for both R6G and Ox1. Record the slopes for each.

(6) Verify that the ratio of the slopes between R6G : Ox1 ~ 8.60 (95 / 11 = 8.60). The closeness of the values should be within 7 % error (8.60 ± 0.60)

(7) Assuming that these values are within this range, you will now need to open “Quantum Yield Calculator” program. On the front panel of this program there is a chart in the bottom, right-hand quadrant. In this chart you can enter the slope, intercept, standard deviations of both of these, the type of dye and the date the dye data was collected. First, enter this information in the chart. Next, this information will need to be entered into the ‘control boxes’ corresponding to
each. Typically, for the visible samples we study, Ox1 is used to calculate QYS and so, in the left-hand side of the front panel, enter the slope, intercept, standard deviation of slope and intercept, in addition to 11% for the known QY. You must then right click over each box, select “data operations”, then select “Make Current Value Default”. Finally, save the program.

This is the end of the calibration procedure. The data analysis program and the quantum yield calculator program are now set for analyzing new unknown sample data.
B. INSTRUCTIONS FOR CHANGING QTH BULB OR BULB SOCKET

The procedure for changing a QTH bulb can be found in the manual. Be sure to turn the lamp off when replacing the bulb. Be sure to wear gloves when handling the new bulb. The bulb has some variability in how it sits in the socket. WEARING LASER GOGGLES, investigate the relative position of the new filament on the entrance slit of the monochromator. Turn the bulb off and perform one or two gross adjustments by shifting the bulb up or down. The procedure to perform the alignment of the filament and its reflection from the parabolic mirror are found in the manual.

To replace a socket – FIRST, DISCONNECT THE POWER SUPPLY. Again, wear gloves while handling the socket and replacing it. The replacement sockets were purchased from City Lighting as detailed in section VIII. The picture in the manual will give you the information needed to replace the socket.
C. PROCEDURE FOR: DATA COLLECTION

(1) Before you turn on the QTH bulb, open the program entitled: “QTH Bulb Lifetime”. Follow the instructions in section 2.4.1 for utilizing this program efficiently.

(2) If you are collecting data after calibrating with the NIST lamp, you will first need to replace the QTH lamp to its original position. ALWAYS USE LASER GOGGLES WHEN WORKING WITH THIS LAMP. This position is marked on the laser table in red marker. Make sure that the beam is aligned and centered on the entrance port of the MonoExc. For a discussion and to see the equations used to determine the distances from this rectangular beam, see section, IIE, page 139. To properly focus light out of lamp utilize the telescoping lens on the exit port of the lamp. To find the “focused” point, first dial the lens completely forward; then bring it back (counter clockwise) a few millimeters from the fully forward position.

(3) Next, you will need to set the appropriate slit widths. This will depend on the excitation and emission wavelengths you will be using, which will inherently depend on the sample of interest. Once you determine the single excitation wavelength, look up the necessary setting for the slits to produce 5 nm of bandwidth (Desktop/ Slit Width Data 111710.ogw). For the emission scan range, determine the middle wavelength, and use the setting necessary to produce 5 nm of bandwidth for that value.

(4) Always collect absorption first to ensure that the absorbance values remain below 0.05 (for quantum nanostructures)\(^2\) and below 0.01 (for dyes)\(^1\). Insert the sample into the sample holder. Ensure that the entire set up is covered properly. Turn on the PMTs (main power switch only), turn on pre-amplifiers and lock-in amplifiers, turn on the chopper and the shutter system. The chopper wheel typically starts at a frequency higher than it is set to and gradually reaches its set frequency after about 30 minutes.
(5) Open the “Photoluminescence and Photoluminescence Excitation.vi” program and create a name for your data. Typically, this should include “Date_Sample name_Batch Number_Name of Person that synthesized it/company from which the sample was purchased”. Often times, an additional appendage is included if necessary but this information can also be included in the text file notes. Follow the rest of the instructions for using this program in the section 2.4.2. As a reminder, the raw data collected in this program is not corrected for the instrument response. In order to utilize the data, you must next open the “Total Data Analysis” program. Enter the name of the file you just collected and follow the steps detailed in the proceeding section for running this program.

(6) When the “Total Data Analysis” program is done running, the data is completely ready. You should close the analysis program and the excitation energy dependence program. One you turn off the QTH bulb you can stop the “QTH Bulb lifetime” program – make sure you follow the appropriate steps to ensure that you save the data properly.

(7) Open a new Origin project. Create an X column of the energy range over which you scanned. Copy and paste column B from the analyzed file of the data you just collected and analyzed into a column next to the X column.

(8) This step is for removing the excitation scatter from the scans taken near the emission wavelengths scanned:

First, determine the excitation wavelength for the spectrum you are dealing with. Highlight the data at the excitation wavelength. Delete the data 5 nm above and 5 nm below the excitation value. If you are unsure of the bandwidth, plot the data and delete the values until the excitation scatter is completely removed. This procedure was found to be more efficient than fitting the excitation spike and emission feature, collecting the integrated intensity of the two
and subtracting them. The results of this study can be seen in:

D:\Hoy\Origin\FittingexcitationScatter.opj

IF YOU ARE EXCITING AT 630 or 650 nm, YOU WILL NEED TO examine the excitation scatter closely. Often times these two colors require that A FEW EXTRA DATA POINTS are deleted (on the shorter and longer wavelength sides, respectively).

D. PROCEDURE FOR: CHANGING MONOCHROMATOR TURRET

The procedure for changing a turret is important as you will use this process to run the instrument from the far UV to the NIR. The majority of this procedure involves instructions written by the company PI Acton. The procedure can be found at the URL listed below but PLEASE NOTE – this procedure was written only for the short path-length monochromator (2100i series). For the 2300i series, the procedure is different in ONE VERY IMPORTANT WAY: Step 2, that asks you to change the wavelength the grating is set to – for the 2300i – you must change the grating to the longest wavelength – not to zero as is the case for the 2150i.

The procedure can be found in Section IV-E of the document below:

**IID. Program Details**

**A. QTH Bulb Lifetime**

*Overview:*

This purpose of this program is to generate a text file that records the date and length of time that either a QTH bulb or the Avantes NIST lamp was used for. The program uses a counter and will either generate a new text tile or append data to a previously generated text file. The average length of time that Newport says that their bulbs last is 50 hours. Typically the signal-to-noise increases significantly from 15-20 hours. The Avantes Lamp calibration is good for 60 hours according to the company. After this point, the lamp should be returned for calibration. Since the lamp is sent overseas, this process takes a while; previously, it has never taken less than 3 weeks.

*User notes:*

When you open the program, there are 2 text boxes for entering a file name. One is listed as being for the QTH bulb and the other is listed as being for the NIST lamp. If you just replaced the QTH bulb and you wish to monitor its usage time, change the file name in the UPPER grey box to be the “QTH_current date.txt” If you are using the Avantes NIST lamp for the first time since it returned from being re-calibrated, change the name in the LOWER grey box to be “NIST_current date.txt”.

Next you click the button in the center for the front panel so that it is illuminated (green). Finally, push the standard, white RUN arrow (upper left hand side of menu bar) to begin the program and turn on the lamp you are monitoring.

The most **important** step is this last step, when you are done using your lamp. To tell the program to stop, you must click the button in the center of the screen. You will be asked 2
questions. The first is if you want to save the data. You will select YES. The second question asks if you are using the Avantes NIST lamp. You will either answer YES or NO depending on what you are using.

**Program details or Frequent issues:**

The text files are generated in D://Hoy/QTH Bulb Lifetime. The date + start time and date + stop time are entered all together on one line, and each time the program is run a new line is added. Therefore, to determine the total number of hours the program has been running, one must find the difference for each date and then add them up. Typically, after 10 or so, I add them and then edit the document with a dashed line and the total after the first 10.

If you forget to turn on the program (and you have no documented account of the time) or if you forget to turn off the program (and you have a severely wrong over estimate of the time), you can also, just estimate based on data collection files, how long the lamp was used for and then edit the text file with the date and a time estimate.

B. Photoluminescence and Photoluminescence Excitation.vi

**Overview:**

This program collects PL or PLE data and creates an excel document with the data in it. As was previously mentioned, there are 2 detectors in the spectrometer. One monitors the lamp fluctuations and the data from this detector can be related to the photons exciting the sample. This data is therefore referred to as the excitation data. The second detector is at the end of the beam path that is collecting photons emitted from the sample at 90 degs to the incident light and is referred to as the detection data. The shutter is also used to get an average amount of background scattering contributing to the total photon count. This average amount can then be subtracted from the data. Any PL or PLE data that is collected is put into an excel file. These
collected excel documents that have not been analyzed (or raw data) contains 4 columns: 1: wavelength, 2: detection normalized by dividing by excitation, 3: excitation only, and 4: detection only. The data collection program also generates a text file to keep track of the day, time and parameters used to collect the data.

**User Notes:**

There are 2 large tabs with the heading: “Go To Wavelength” and “Collect Data”.

When you click the white RUN arrow starting the program to collect data a series of grey boxes appears, one after the other, in which you are asked a series of questions. The answers to the questions are placed in a text file that is required for the necessary data analysis.

Once the last question is answered the program begins the scan and the data is collected.

**C. Total Data Analysis**

**Overview:**

This program uses the NIST collected data and the accompanying calibration file to correct any sample data for the instrument response function (IRF). The shape of the IRF comes from the wavelength dependence of the lenses, monochromator (grating) and detectors. The program can correct both PL data and PLE data.

This analysis program first opens the text file containing all the important parameters, corrects the last 2 columns separately, divides the analyzed detection data by the analyzed excitation data, and then generates an analyzed file that is similar to the original file: column 1 is wavelength, and then detection divided by excitation, then excitation, then detection.

**User Notes:**

The base path for the file that will be opened is set. Enter the rest of the file name in the indicated box. Ensure that the calibration files chosen are the most recent. If the file a PL
spectrum, you can push the arrow to start the program. If the file is PLE, change the base path from “C:\Documents and Settings\admin\Desktop\PL scans” to “C:\Documents and Settings\admin\Desktop\PLE” and change the Control switch from PL (green) to PLE (red).

Program details or Frequent issues:
Often times, a file name is entered incorrectly. It can be as small a detail as a space missing. It can be a calibration file, data file, or text file.

D. Quantum Yield Calculator
The slope of absorbance versus integrated emission intensity is a straight line proportional to the quantum yield. Typically to collect this data one makes several cuvettes with various concentrations of a known dye, collects absorption, and then collect emission by exciting at the same excitation color and integrating the intensity.

The math required to determine an unknown quantum yield:

\[
\frac{QY_{(DYE)} \eta^2}{m_{(DYE)}} = \frac{QY_{(UNKNOWN)} \eta^2}{m_{(UNKNOWN)}}
\]

For a sample that does not have an excitation energy dependence on the quantum yield, another way to collect this data is to vary the excitation color (essentially varying the absorbance values) and collect the emission and integrate. Here again, we have the values to plot absorption versus integrated intensity. The graph in the bottom right had corner of the front panel provides a list of slopes and intercepts for either Rhodamine 6G (R6G) and/or Oxazine1 (Ox1) at the dates that they are collected. Beneath the slope and intercept the standard deviations of the numbers are also reported.
Sometimes we work with unknown samples that do have a energy or wavelength dependence of their QY’s. In this case, we need another method for calculating the quantum yields of such samples. So, we use a method where we compare integrated intensities of unknown samples to the slopes and intercepts of known dye slope, intercept values.

\[ Y_{(\text{INTEGRATED\_INTENSITIES})} = m X_{(\text{ABSORBANCE\_VALUES})} + b \]

Slope is m and intercept b, as usual. The know dye slope and intercept are plugged in. Since there is an unknown sample we wish to determine the QY of, we use the unknown sample absorbance value in place of X and solve for Y.

\[ \text{INTEGRATED\_INTENSITY}_{(\text{CALCULATED})} = m_{(\text{DYE})} X_{(\text{MEASURED\_ABSORBANCE})} + b_{(\text{DYE})} \]

This (calculated) integrated intensity is proportional to the QY of the known dye and this ratio can be set equal to the measured integrated intensity over the unknown QY value we are trying to calculate.

\[ \frac{\text{INTEGRATED\_INTENSITY}_{(\text{CALCULATED})}}{QY_{(\text{DYE})}} = \frac{\text{INTEGRATED\_INTENSITY}_{(\text{MEASURED})}}{QY_{(\text{UNKNOWN})}} \]
This process has been tested with two standard dyes, wherein the second dye is the “QY (UNKNOWN)” we are solving for. Then this calculated value is compared the literature value. For example, Oxazine1 has a QY reported to be between 10 and 16% and again reported to have a QY of 11%. [Brouwer, 2011 #10] We determine a QY of ~11%. This number does vary a small amount. If it has been a while since the system was recalibrated the value might fluctuate more. If it is outside of the error of previous measurements then the system should be recalibrated.

The program itself simply performs the aforementioned math. Additionally, it uses the standard deviation values to determine the error bars for the QYs. The standard deviations are propagated through each step of the calculation utilizing the appropriate procedure in Chapter 3.5 of Harris, [Harris, D., Quantitative Chemical Analysis, 6th Edition, 2003, W.H. Freeman and Company, NY], yielding an absolute and percent relative error.

User Notes:
Enter the corrected absorbance value in the appropriate indicator box. Enter the integrated intensity of the PL in the appropriate indicator box. Select run. The values will appear in the boxes labeled QY and % relative error.

Program details or Frequent issues:
Refer to the chart on the front panel to ensure that the appropriate dye data entered for “slope”, “intercept”, “standard deviation in slope”, and “standard deviation in intercept”. Make sure that if you are using oxazine1 (rhodamine 6G) data, the QY entered below for the dye information is 11 (95).
IIE. SPECIFIC CHARACTERISTICS THAT ARE INTEGRAL TO THE SET-UP

A. APPROPRIATE USE OF OPTICS WITH THE NON-COLLIMATED NEWPORT LIGHT SOURCE

The light source purchased for the photoluminescence spectrometer is a quartz-tungsten-halogen source. The reason for purchasing this 250 W bulb was is smooth and wide spectral output, which can be seen here: http://assets.newport.com/webDocuments-EN/images/Light_Sources.pdf (page: 30). The lamp was advertised as a collimated light source indicating that the optic required for focusing the light into the monochromator would be the standard F/4 plano-convex lens. However, upon purchasing the lamp it was determined that the lamp was not collimated, rather it was diverging. At 1 foot away from the output of the lamp, the 1 cm x 4 cm filament creates a ~ 15 cm diameter beam.

Replacing the lamp didn’t seem like a good idea. Smaller filaments were an option or arc lamps were an option. However, the sacrifice would have been power (smaller filaments) or monitoring and removal of noise (arc lamp). Newport has a calculation to accompany their “gently-diverging” QTH lamp. The equation can be seen in the Newport document on the “desktop\Getting_Light_into_a_Monochromator.pdf” on pages 5,6 and 7. This equation verifies that the focusing optic must be at ~28 cm away from the focusing lens. In our case, the focusing lens is a 2” F/4 plano-convex lens which is then 8” away from the entrance slit of the monochromator.

Email discussions took place between, myself, Rich, Roger Milson and Lana Pryde during the months of September and October 2007.
B. EXTRA SCATTER FROM MONOCHROMATOR GRATINGS

A plane ruled diffraction grating is a type of reflection grating that will diffract white light with different intensity distribution depending on the wavelength(s) and angle of incidence as well as the spacing of the grooves. The blaze angle of the grating characterizes the angle of reflection. It is related to the groove spacing (d) and incident wavelength(s) by the equation: \( m\lambda = 2dsin\theta \). [Moore, Building Scientific Apparatus, 2nd Edition, 1989, Addison-Wesley Publishing Company, Inc.] Any integer value (m) of a particular wavelength is permissible. In any commercial spectrometer, exciting at 350 nm allows the second order diffracted light to be detected at 700 nm. However, in the spectrometer I built it was found that some extra scatter was appearing in some of our scans. This scatter occurred at roughly 1.48 – 1.40 times the excitation light, and in this case, was detectable when exciting from 450 – 500 nm. An example of this can be seen below. Upon using a 550 SWP filter, this scatter will be reduced.

Upon examining the beam at a point in the spectrometer where it was diverging creating a large spot size, a small dot of the scattered light could be seen. Upon addition of a 550 LWP filter, this scatter will be depleted.

Over the course several months from February 2010 through May 2010, I worked with Bill Fischer at PI Acton to determine the source of this problem as well as a solution. Initially, they were unable to replicate our data. I determined the difference between our set-up and theirs: they were using a CCD and we use a PMT. When they switched detectors, they were able to reproduce our data. They determined that this scatter was due to the grating coating and that a holographic grating will reduce this scatter. Their data, plane ruled (top) and holographic (bottom) is shown below. The holographic grating does cause a further reduction in the intensity
of light that makes it through the monochromator. Therefore, 1 holographic grating is utilized on the emission side when this spurious scatter is interfering with data collection.
LIST OF SPECTROMETER COMPONENTS AND COMPANY CONTACTS

1. Newport Oriel Lamp
   Part number
   (66506; 250W QTH Light Source, 06/25/2007, $3,457.80)
   Subcomponents:
   Power Supply
   Bulb part number
   (6334NS; QTH 250Watt Filament, $34.00)
   Socket part number
   (No option to purchase JUST the socket from Newport; So, we purchased from City Lighting on 4307 West Papin Street, St. Louis, MO)
   (01/17/11 MILL80054Z, MILLER L80054 round mr16 SCKT round mr16 socket g53 base, $1.51)
   Communication on appropriate focal lengths for this rectangular filament
   Age of bulbs, noise data
   Age of sockets
   (Start using in fall 2007, needed replacement in January 2011)

2. Princeton Instruments 2100i Monochromator
   Part number
   (SP 2155, PI Acton, $4750.00)
   Subcomponents:
   Part No’s Turret 1: Grating 1, Grating 2
   (1) 150-120-500; Plane ruled, 32x32mm, 1200g/mm 500nm blaze, $300.00
   (2) 150-120-300; Plane ruled, 32x32mm, 1200g/mm 300nm blaze, $
   Turret 2: Grating 1, Grating 2
   (1) 150-060-1; Plane ruled, 32x32mm, 600g/mm 1um blaze, $275.00
   (2) 50-030-2; Plane ruled, 32x32mm, 300g/mm 2um blaze, $275.00
   Turret 3, Grating 1
   (1) 300g/mm at 3um blaze
   Scattering data for slit width determination
   Communication to computer: RS232 connection
   Labview Handle number: 1
   Contact = Bill Fisher = bfisher@princetoninstruments.com

3. Vincent Associates Single Channel Shutter Driver
   Part Number
   (VCM-D1, 02/23/10, $850.00)
   Typical physical set up (front switches)

4. Stanford Research Systems Optical Chopper (5/6 and 25/30 slot blades)
   Part Number (SR 540, 06/01/12, $1095.00)
This device requires no computer communication. It does need to be connected to the Lock-In amplifiers so that these devices receiving signal are only locking on to signal at the frequency set by this chopper. The connections are through a wire then alligator-to-bnc input to the front panel of each lock-in.

5. Stanford Research Systems Pre-Amplifiers
Part Number
(SR570, 10/13/08, $2,295.00 each)
Front panel settings
Excitation Pre-Amp needs less gain than Detection pre-amp
Any data on optimal settings

6. Stanford Research Systems DSP Dual Phase Lock-In Amplifiers
Part Number (SR830, 06/01/07 and 09/26/08, $4200.00 each)
GPIB number 7 and 8 (Do not change these)
Front Panel settings:
   Input: use A only
   The time constant is typically 30 ms with a 24dB/octave slope
   Sensitivity/Dynamic Reserve (see the Manual for conversion)
   Line Filter and Linex2 filter – both on Have them on
Back Panel Settings:
   A connection from the BNC 2090 goes into the back of each lock-in to tell the lock-ins for the purpose of a triggered start for data collection.

1 Repair: Thought we blew out an op amp: tried replacing, with Greg Potters help, 01/10/08, part no.’s AD 645 (U101) and NPD 5564 (U102). This didn’t work so we sent the Lock-In back for repair to front panel - $450.00.

7. Princeton Instruments 2300i Monochromator
Part number
(SP2355, spectraPro monochromator, 06/25/07, $7950.00)
Subcomponents:
   Part No’s Turret 1: Grating 1, Grating 2, grating 3
      (1) 1-120-500, Plane ruled, 68x68mm, 1200g/mm 500nm blaze, $700.00
      (2) Holographic Grating – Visible “1200@500nm”-like
      (3) Visible coating mirror
   Turret 2: Mirror, Grating 2, grating 3
      (1) 1-060-1, Plane ruled, 68x68mm, 600g/mm 1um blaze, $650.00
      (2) 1-030-2, Plane ruled, 68x68mm, 300g/mm 2um blaze,
      (3) 1-030-3, Plane ruled, 68x68mm, 300g/mm 3um blaze,
Labview Handle number: 2

Contact = Bill Fisher = bfisher@princetoninstruments.com

8. Hamamtsu Photomultiplier Tubes*
There are 2, one for excitation and the other for detection. This is a high quantum efficiency, 28 mm detector active area, side-on PMT. Manual and gain information can be found in: Desktop/pmt_handbook_applications.pdf

Good Technical Contact: Kate Pritchard: Kpritchard@hamamatsu.com (908-252-7660)

9. InSb NIR detectors w/MSL-12 Dewar from IR Associates
(2 total of both)
   IS-1.0 ($1500.00) (06/25/07 and 06/24/09)
Matched Pre-Amp
   IAP-1000IS ($475.00) (06/25/07 and 06/24/09)
Pre Amp Power Supply
   ($150.00) (06/25/07 and 06/24/09)

Suggested Power Supplies for the detector:
Linear Regul Power Supply, AC-DC dual tracking outputs, ±15V out, 0.3Amps, Acopian Technical Company
(DB15-30, 01/05/11, $132.00 each)

10. UV/Vis/NIR lenses and mirrors
all from CVI Melles Griot Corporation
   All lenses made of Calcium Flouride for vis and IR (CFIR); 180nm – 8um
   All mirrors are coated with GOLD; 95.5% average reflectance (650nm-1.7um) and 98%
   average reflectance from 2um-16um)

Contact = Jake Jamarillo = jjaramillo@civmellesgriot.com

11. NIST traceable Halogen Lamp
with calibration file: CC-UV/VIS-CAL
(purchased separately, extended CAL to 2500nm)
   AvaLight-HAL-CAL, 09/29/09, $952.00
   HL-Recal-NIR, 09/29/09, $273.00

Contact = Greg Neece = gregn@avantes.com

12. LabView Analysis Programs
LabView version 8.6*
   QYH Bulb Lifetime
   Photoluminescence and Photoluminescence Excitation.vi
   Data Analysis
   Quantum Yield Calculator

Contact procedure: call the NI support line from the lab phone. Tell them what version of LabView you have and what you specific question is (questions are, bullet). Have the program
in front of you ready to run. They will either likely tell you a change to make then test OR they will ask you to send a screen shot of the trouble. Once an email chain has started there is a customer **service number** associated with your emails. You will need this number to enter if you need call them back. The person you work with usually will solve your trouble within as quickly as a few minutes to a few days.
II. LIST MANUALS AND THEIR FILE LOCATION

(1) Origin: Monochromator slit width determination:
D:\Hoy\Calibration Files\SlitWidths_082510.opj

(2) Origin: Voltage gain determination, compared with documented gain:
D:\Hoy\Calibration Files\Old\Data Obtained_2calculate_GAIN_ogw.zip ( Determined in house)
D:\Hoy\Calibration Files\Old\3896Gain ObtainedByFit_ogw.zip ( Determined by Hamamatsu)

(3) Origin: example of calibration file analysis:
D:\Hoy\Calibration\MarchNIST_datafile.opj

(4) Newport manual:
Hard copy on the desks in the office

(5) Newport Rules for determining first focal length:
Desktop\Getting Light into a Monochromator.pdf

(6) Lock-in manual:
Hard copy on the desks in the office
Desktop\www.thinksrs.com\downloads\PDFs\Manuals\SR830m.pdf

(7) Pre amp manual:
Hard copy on the desks in the office

(8) PMT manual:
Desktop\pmt_handbook_applications.pdf

(9) STIK software manual:
Desktop\SpectraPro v.3.37 -> help -> Software manual

(10) Vincent associates manual
Hard copy on the desks in the office
Appendix III.

Absorption Spectroscopy Details
The PerkinElmer lambda 950 is an attenuation or extinction spectrometer. It measures the amount of light transmitted through the sample. It does not account for non-absorptive losses such as scattering. It was upgraded in September of 2010 to include an integrating sphere coupled with the detectors. This component can be easily swapped out with the attenuation detectors have the capability to collect scattering off the front face of the cuvette. The scattering sphere provides a more reliable absorption spectra as it accounts for some of the scattering. The differences between attenuation and absorption for QDs and QWs are shown below.
Figure III-1. The top graph displays attenuation (red) and absorption (black) for some large CdSe/ZnS QDs purchased from NN Labs. The bottom graph displays attenuation (red) and absorption (black) for some CdTe QWs. The insets provide a smaller wavelength range near the band edge. These data were all corrected for by the procedure explained below.

However, it was found that from scan to scan, the absorbance values can shift by a randomly varying amount, creating an offset. The exact reason for this is unknown. An example is shown below.
Figure III-2. The data in the top graph display two absorption spectra of Oxazine 1 that were taken 25 minutes apart from each other. There is an offset of the data and the inset displays a smaller wavelength range to enunciate the values. The bottom graph displays two absorption spectra for the large diameter CdSe/ZnS QDs that were taken 10 minutes apart from each other. These are the same QDs that were studied in figure 1. The inset displays the smaller wavelength range to enunciate deviations between the two spectra.

The deviations in time between the two Oxazine 1 spectra are ~3E-3. This is outside of the acceptable noise for the lambda 950. Although the deviations between the two QD absorption
spectra are small, the overall offset is off by -0.05. As can be seen by the data in figure 1, and from our knowledge of these samples, this is highly inappropriate.

When relying on absorbance values to generate comparative spectra or to calculate QYs, it is important that the values are accurate. False variability can indicate a single sample changing in time. False variability between two different samples can also lead to inappropriate conclusions. Therefore, a modified procedure is used to treat these absorption data. This is shown below. The significant step is 8.

(1) Let the instrument warm up for 30 minutes.

(2) Set up Parameters.

(3) Click "set wavelength" button. It's at the top of the screen. Choose 630nm.

(4) Open the lid and turn the overhead light on about 1/2 way. Take the "background" cuvette (make sure that the outside has been wiped clean and DRY and carefully slide it in - NOTE: the cuvette holder has the capacity to move (meant to be helpful but not so much here). Use a piece of business card to make sure that the light is going through the sample holder appropriately. You should check this with a cuvette in place to make sure that the light is NOT clipping the meniscus. You will get faulty overall offsets if the light is too close to the meniscus.

(5) Close lid and collect autozero when you have time to collect both autozero and sample scan.

(6) Collect sample scan. Again, take your time when replacing cuvettes.

(7) If you have any additional samples - even if they have the sample "background" cuvette - you must re-collect the background scan. The lamps tend to drift. This is why it is good to leave NO delay time between collecting the autozero and the sample scan (step 5 and 6).

(8) Once you have the data, check the region where there should be NO absorption (i.e.: Band
gap = 705, look at the region: 890-775). Chose a region with a representative amount of noise as well. There will likely still be an offset of some sort. The absorption values in this offset should be no more than $|10E^{-3}|$. This is within the realm of acceptable noise for the PerkinElmer UV/Vis. If it is larger, either positive or negative, first check the beam height relative to the meniscus of your sample. If that appears fine, you should shut down the instrument for ~30 minutes and start over. Remember to close the program down too.

What to do with an appropriate offset: take at least 50 data points where there should be NO ABSORPTION, and average them together. Then subtract this average value from the entire absorption spectrum.

Advice If you want to start your scan from 890nm, a good way to do this is to change the “detector switch” wavelength to 900nm. This is the highest it will go.

Another way to minimize error is to use matched cuvettes. We have purchased a total of 16 cuvettes over the course of the fall of 2010 and spring of 2011. The matched-ness of the cuvettes was tested at the end of the spring 2011. The graph containing the absorption spectra for these cuvettes is shown below.
**Figure III-3.** Each line is the absorption spectrum for each of the 16 cuvettes we purchased from Starna.

These cuvettes are expected to have ~90% transmittance across the experimental range and 50% by 150 nm. The purple and the red curves are quite deviant. The highly unmatched cuvette is labeled as “Unmatched” and stored in the cuvette containers in the wet lab. The other slightly deviating curve (purple) was re-run and found to match.