Optical Properties of Quantum Dots:
An Undergraduate Physics Laboratory

Aaron Jones (Engineering Physics)
Nick Verlinden (Engineering Physics)
WPI Department of Physics
Professor R. Quimby
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Abstract
An undergraduate laboratory module was designed to study the optical properties of quantum dots. Transmission data yielded the absorption coefficient of a quantum dot solution when analyzed using Beer’s Law and baseline subtraction. Theoretical quantum well calculations confirmed the observed onset of absorption. Additionally, Beer’s Law was proven using multiple path length and concentration measurements. By completing this laboratory module, students will be exposed to a number of fundamental concepts and gain valuable experience in data manipulation and analysis.
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Extended Abstract

The aim of this project was to develop an undergraduate laboratory experiment for the photonics laboratory course based upon the optical properties of quantum dots. The lab module must be comprehensible to sophomore level physics students, all of the experimental work should fit within the time allowed by the course, and provide an opportunity for students to apply concepts learned in lecture.

Plots of the absorption coefficient for a 1 cm path length of a solution and a 2 cm path length of half the concentration exhibited nearly identical behavior in terms of both numerical value and shape. This data demonstrates that, in addition to varying with wavelength, the absorption coefficient, $\alpha$, is directly proportional to the concentration of quantum dots in a solution. Doubling the concentration in solution is equivalent, in terms of absorption, to doubling the path length of the light beam through the solution.

$$\frac{hc}{\lambda} = E_{bg} + \frac{h^2(n_1^2 + n_2^2 + n_3^2)}{8m^*d^2} + \frac{h^2(n_1^2 + n_2^2 + n_3^2)}{8m^*d^2} - \frac{e^2}{8\pi \varepsilon}$$

Additionally, the onset of absorption, as wavelength is decreased, occurs close to the value which the three dimensional quantum well model predicts, based upon the energy band gap of cadmium telluride and the size of the dots provided by the manufacturer. The theoretical calculation, using the above equation, predicted the minimum energy in a photon required to excite an electron, and therefore be absorbed, to be between 614.3 and 618.5 nm. Experimentally, absorption begins to increase at approximately 625 nm. Using the same calculations, it is therefore possible to determine the size of quantum dots in a sample based upon their absorption spectrum and material band gap energy.

A lab module was successfully created that focuses on the absorption properties of quantum dots, with supplementary work on blackbodies and other semiconductor absorption. Based on the time required to complete scans using the optical spectrum analyzer and setup any required components, the experimental work can be finished within lab time allowed by the course while allowing some room for error. Students will be exposed to Beer’s law, basic semiconductor physics, quantum well calculations, and computer data manipulation with sufficient background to learn the necessary concepts. There is also the opportunity to gain experience with a more capable, yet complex, measurement device; the scanning spectrometer with a lock-in amplifier.
Background

1. Other Quantum Dot Labs

The first step in beginning our project was to do a literature research on whether or not there were any other programs that had already implemented the study of quantum dots into their undergraduate physics curriculum. What we found was that there was really only one other school that had been able to accomplish the implementation of such labs. Siena College recently received an NSF grant and partnered with Evident Technologies, the leading producer in quantum dots, in order to formulate laboratory modules that would study quantum dots and be comprehensible to undergraduate physics students. They were able to develop five experiments dealing with various optical properties of quantum dots:

- Optical Absorption of CdSe Quantum Dots
- Bandgap Measurements; ZnSe Quantum Dots
- Fluorescence and Quantum Yield of Core and Core-Shell Quantum Dots
- Effect of Oxidation on Fluorescence and Size of Quantum Dots
- X-ray Diffraction Measurements on Quantum Dots

The first two of these labs covered the same two major concepts that we examined in our experiment: absorption properties of quantum dots, and how quantum dots behave compared to bulk quantities of the same material.

2. Semiconductors

All materials have discrete energy bands in which electrons can exist. When no electrons are excited, they will be in lowest possible energy band, however, due to the Pauli Exclusion Principle, each energy band can only accommodate a finite number of electrons. For this reason, it is the outermost two energy bands, the valence band and the conduction band, which have the greatest effect on the material’s electrical properties. Metals have a full valence band, and a number of electrons in the conduction band that are free to move, enabling them to conduct charge. The energy difference between these two states is referred to as the band gap energy. For an electron to change energy states, it
must receive an amount of energy at least equal to the band gap energy. An insulating material has an empty conduction band while in its ground state and has a large band gap energy, making it difficult to excite an electron out of the valence band. When in its lowest energy, or ground, state semiconductors have a full valence band and empty conduction band and behave, electrically, exactly like an insulator. The difference is that semiconductor materials have much smaller band gap energies on the order of 1 eV.

The band gap energy is low enough that it is possible for photons to excite electrons from the valence band into the conduction band. For a photon to excite an electron, it must have a minimum energy, $h\nu$, equal to the band gap energy of the semiconductor in which case the photon is absorbed. A photon with energy less than the band gap cannot be absorbed by the semiconductor. Photodiode detectors are based upon this principle. When photons strike the semiconductor, electrons are excited into the conduction band where they are free to move. An induced potential is applied causing the electrons to flow in a photocurrent, which is then detected.

![Figure 1: Semiconductor Energies][Quimby, 2006]

When an electron is excited into the conduction band, it leaves behind a hole, which can be treated as a positive particle. It is possible for a photon to have more energy than the band gap energy and still be absorbed, in which case the electron is excited from lower in the valence band to higher in the conduction band. This excess energy is lost, however, through inelastic collisions as the electron settles to the bottom of the conduction band and the hole rises to the top of the valence band. Since materials will always return to their ground state if possible, the hole and the electron will then recombine emitting a photon with energy equal to the band gap energy. A schematic of the energy band gap, a semiconductor absorbing a photon, and a semiconductor emitting a photon is shown above.
Due to the minimum energy required to excite an electron, at very long wavelengths, which correspond to low photon energies, the semiconductor will not be absorbent at all. However, as wavelength is decreased, there will come a point at which the material will suddenly begin to absorb.

3. Quantum Wells

Quantum wells are structures characterized by a region of low potential of width $d$ surrounded by essentially infinite potential, confining any and all particles within the well. By convention, the potential inside the well is set to zero in order to simplify solving the Schrödinger equation, and since the sides are infinite, it has no effect on the solution. According to quantum theory, only discrete values of energy are allowed to exist within a quantum well. Every particle has a deBroglie wavelength based upon its mass and energy, and the energy states allowed in a quantum well correspond to the energy levels that cause the deBroglie wavelength to form a standing wave. The deBroglie wavelength and the condition for a standing wave are given below.

$$\lambda_{dB} = \frac{\hbar}{mE}$$

$$n\lambda_{dB} = 2d$$

Substituting for the wavelength and solving for energy yields an expression for energy as a function of the integer $n$.

$$E_n = \frac{\hbar^2 n^2}{8md^2}$$

Each value of $n$ corresponds to one of the allowed energy states, with $n=1$ being the lowest. The standing wave in the quantum well will have $n$ half-wavelengths.
This expression can also be found by solving the Schrödinger equation within the quantum well and applying boundary conditions. The time-independent Schrödinger equation is as follows:

$$-\frac{h^2}{8\pi^2 m} \frac{\partial^2 \psi}{\partial x^2} = (E - V)\psi$$

When the potential, $V$, is zero, solving this simple differential equation yields a periodic expression for the wave function that is shown below.

$$\psi = A \sin \left( \frac{8\pi^2 mE}{h^2} x \right) + B \cos \left( \frac{8\pi^2 mE}{h^2} x \right)$$

The boundary conditions are that the wave function is equal to zero when $x=0$ and when $x=d$, which immediately shows that $B=0$. Unless the particle does not exist, $A$ must not equal zero, therefore the expression inside the sine function must equal an integer value of $\pi$. Once that condition is met, one can solve for $E$ as a function of $n$.

$$0 = A \sin \left( \frac{8\pi^2 mE}{h^2} d \right)$$

$$n\pi = \sqrt{\frac{8\pi^2 mE}{h^2}} d$$

$$E_n = \frac{n^2 h^2}{8md^2}$$

The Schrödinger approach, while lengthier, is useful for finding the energy states when the sides of the quantum well do not rise immediately to infinity at the boundaries or the potential is non-uniform within the well.
Returning to the standing wave model, in a three dimensional cubic well, standing waves, or modes, can exist in all three dimensions independent of one another. Thus, the expression for allowed energies is modified and now contains three values for \( n \), one corresponding to each direction.

\[
E_n = \frac{\hbar^2 (n_1^2 + n_2^2 + n_3^2)}{8md^2}
\]

If the width is not the same in each direction, the energy will be a sum of three of the energy equations for one dimension; one with the energy level and width for each dimension.

4. Quantum Dots

Quantum dots are semiconductor nanocrystals that exhibit unique optical properties due to a combination of their material band gap energy and quantum well phenomena, discussed in the previous section. Due to their extremely small size, on the order of a few nanometers, the dots behave similarly to three dimensional quantum wells. When an electron is excited by a photon striking the quantum dot, it behaves as a particle confined in an infinite potential well, since the electron cannot escape from the quantum dot. The hole, created by the excited electron, behaves in the same fashion.
Figure 3: Energy diagram of a semiconductor quantum dot

The figure above is a schematic diagram of energy states within a quantum dot. The electron, when excited, exists in the conduction band in one of the \( n \) energy states, and the hole exists in the valence band, also in one of the \( n \) energy states. Therefore, the minimum difference in energy between the electron and hole is not simply the band gap, but the energy difference between the \( n=1 \) energy state of the hole in the valence band, and the \( n=1 \) energy state of the electron in the conduction band. This difference is equal to the quantum well energy equation for the electron, plus the quantum well energy equation for the hole, plus the material band gap energy.

\[
\Delta E = \frac{hc}{\lambda} = E_{BG} + \frac{h^2 (n_1^2 + n_2^2 + n_3^2)}{8m_e^*d^2} + \frac{h^2 (n_1^2 + n_2^2 + n_3^2)}{8m_h^*d^2}
\]

A photon must have this amount of energy to excite an electron and be absorbed. In a semiconductor material, the hole and the electron have difference effective masses to use in the above equation, and these values can be obtained from a semiconductor materials handbook.
There is one other factor that affects the energy required to excite an electron, referred to as the exciton effect. The two charge carriers, the hole and the electron, do not exist in isolation. They interact with each other, creating a negative potential energy term shown below.

\[ V = -\frac{e^2}{4\pi \varepsilon} \]

The two charge carriers orbit each other, similar to the interaction between a proton and electron in a hydrogen atom, and this leads to an additional kinetic energy term. Since the proton is much more massive in the atom, it is considered to be fixed with the electron orbiting around it. A similar assumption will be made about the hole, although it is not nearly as massive as a proton, it is still heavier than the electron. The centripetal force confining the electron to its orbit is the Coulomb force, and knowing the relation between acceleration and velocity for circular motion, it is possible to solve for \( \frac{1}{2} mv^2 \), the kinetic energy.

\[ a = \frac{v^2}{r} \]

\[ \frac{e^2}{4\pi \varepsilon r^2} = m_e \frac{v^2}{r} \]

\[ \frac{1}{2} mv^2 = \frac{e^2}{8\pi \varepsilon r} = KE \]

The total energy of the electron hole combination is then equal to the kinetic energy plus the potential energy.

\[ E_x = KE + V = \frac{e^2}{8\pi \varepsilon r} - \frac{e^2}{4\pi \varepsilon r} = -\frac{e^2}{8\pi \varepsilon r} \]

Including this factor, the final expression for the energy of an absorbed or emitted photon is as follows:

\[ \frac{hc}{\lambda} = E_{BG} + \frac{h^2 (n_1^2 + n_2^2 + n_3^2)}{8m_e d^2} + \frac{h^2 (n_1^2 + n_2^2 + n_3^2)}{8m_h d^2} - \frac{e^2}{8r \pi \varepsilon} \]

The quantum dots used for this report were obtained from American Dye Source in a water solution, and were composed of cadmium telluride (CdTe). The product number on the dots used for the majority of the experimentation was ADS-QD620. The number 620 at the end indicates the wavelength, 620 nm, at which the dots are expected to emit and
begin absorbing light. ADS-QD820 quantum dots were also used in portions of the experiment as a contrast to the QD620 dots. The dots had a coating of molecules that allowed them to be stable in water, for a time, which can be seen in the picture provided by the manufacturer.

![Diagram of quantum dot with coating that allows water solubility](image)

**Figure 4: Diagram of quantum dot with coating that allows water solubility**

The material specific values for CdTe used in the above equations are:

- Band gap energy: 1.51 eV at room temperature [Berger, 1997]
- Electron effective mass: 0.096 [Berger, 1997]
- Heavy hole effective mass: 0.84 [Berger, 1997]
- Dielectric constant: 10.392 [Zanio, 1978]

Based purely on the band gap energy, the onset of absorption for a bulk sample of CdTe, would occur when \( h\nu = E_g \). Plugging in the band gap energy listed above, the associated wavelength would be approximately 821.11 nm.

![Manufacturer-provided quantum dot spectrum, arrow indicates absorption and 620 nm](image)

**Figure 5: Manufacturer-provided quantum dot spectrum, arrow indicates absorption and 620 nm**

[American Dye Source]

The line increasing from right to left in the graph above indicates the absorption of the quantum dots. On the graph, the onset of absorption occurs between 600 and 650 nm, with the point of steepest ascent at about 620 nm. This represents a shift of 200 nm from the wavelength of a photon emitted at the band gap energy.
One of the more common applications of quantum dots is in biological research where the quantum dots are used as tracers inside living cells. The quantum dots that have been injected into the tissue can be excited using short wavelength light and the dots can then be observed fluorescing at their peak frequency. For this application, water soluble quantum dots are very important. For the purposes of this report, water solubility is a critical factor because it means pure distilled water can be used to normalize the transmission data, and the students will not need to work with more hazardous substances.

5. Beer’s Law

Beer’s Law is a formula relating transmitted light intensity, $I$, to incident intensity as a function of the absorption coefficient, $\alpha$, as well as the path length. The absorption coefficient is equal to the number of particles per unit volume in the path of the light beam, $N$, multiplied by their optical cross section, $\sigma$. It is also equal to the fractional decrease in intensity over a differential path length, $dL$.

Figure 6: Diagram showing intensity change over a differential path length, $dL$

\[
\frac{I_1 - I_2}{I} = -\frac{dI}{I} = \alpha dL
\]

Integrating both sides yields:
\[
\ln(I) = -\alpha L + C
\]

According to Beer’s Law, transmitted intensity decreases exponentially as path length increases. In order to satisfy boundary conditions, \( C' \) is equal to the incident intensity, \( I_o \), in the simple approximation of Beer’s Law. In practice, however, the constant \( C' \) is equal to \( I_o \) multiplied by a reflection factor, \((1-R)^2\), and a scattering term, \( f_s \), yielding the following final equation.

\[
I = I_o (1-R)^2 f_s e^{-\alpha L}
\]

While the scattering and reflection terms do not depend on \( L \), they do vary with wavelength, as does the cross section, and therefore absorption coefficient.

6. Optics

Optical fibers are composed of two materials, the core and the cladding, and operate based on the principle of total internal reflection. Snell’s law states that when light propagates from one medium to another, the angle with which it strikes the boundary on the two regions, A, is related to the angle which the propagated beam makes with the normal, B.

![Light propagating from one medium to another of higher index of refraction](image)

Figure 7: Light propagating from one medium to another of higher index of refraction

The relation between these two is a function of the indices of refraction and is given by the equation below, referred to as Snell’s Law.
\[ n_1 \sin(A) = n_2 \sin(B) \]

A portion of the incident light is reflected at an angle equal to the angle at which it struck the surface. The fraction that is reflected is based upon the indices of refraction of the two media and the angle of incidence.

In the drawing above, it is assumed \( n_1 \) is smaller than \( n_2 \) and therefore has a larger angle, with respect to the normal. When light is propagating from higher medium to lower medium, the angle on transmission is greater than the angle of incidence. However, the angle of transmission cannot be greater than 90 degrees, meaning that there is some critical angle at which light cannot be transmitted and it totally reflected. Plugging in 90 degrees for angle \( B \) in the above equation, we can solve for the critical angle, \( \theta_c \).

\[
\sin(\theta_c) = \frac{n_2}{n_1}
\]

In an optical fiber, the core material has higher index of refraction than the cladding, and therefore when the light strikes the boundary between the core and cladding at an angle equal or greater than the critical angle, the light is totally internally reflected down the length of the fiber. The angle the light strikes the core-cladding boundary at is dependent on the angle at which it enters the fiber, shown below.

**Figure 8:** Diagram showing light being coupled into a fiber using a lens. The light does not necessarily enter the fiber at the center of the core, but is shown that way in this diagram to view the angles clearly.
The greatest angle between the axis of the fiber and the incoming light beam that yields total internal reflection inside the fiber is the maximum acceptance angle, \( \alpha_{\text{max}} \). Snell’s law can be used to calculate \( \alpha_{\text{max}} \) based upon the indices of refraction for the core, cladding, and the medium outside the fiber. When dealing with air outside the fiber, the index of refraction is 1 and can therefore be omitted from the calculations.

\[
\sin(\alpha_{\text{max}}) = n_1 \cos(\theta_i) = \sqrt{n_i^2 - n_2^2} = NA
\]

NA is termed the numerical aperture of the fiber, and is a commonly supplied parameter when purchasing fibers. The numerical aperture for the optical fiber used by the optical spectrum analyzer is 0.27 which corresponds to an acceptance angle of 15.7 degrees when used in air.

As can be seen from the figure shown above, the maximum acceptance angle determines how close a lens can be placed when coupling light into a fiber. Once the location of the image is determined, at the aperture of the fiber, the location of the object being imaged can be calculated using the lens equation.

\[
\frac{1}{s_1} + \frac{1}{s_2} = \frac{1}{f}
\]

In the above equation, \( f \) is the focal length of the lens. For the setup used to couple light into the optical fiber for the OSA, two lenses are used.

![Figure 9: The positions of the two lenses and light source with distances and heights labeled](image-url)
The position of the second lens can be easily determined because the ratio of the radius of the lens to the distance of the image is the same for both lenses when they are setup so no light is lost between the two.

\[
\frac{h_1}{d_1} = \frac{h_2}{d_2}
\]

Knowing all of these positions, the location of the light source can be determined by a second use of the lens equation.

Accepting the assumption that the light source is emitting equally in all directions, it is possible to calculate the percentage of light being emitted that is collected by the first lens. In three dimensions, it is important to introduce the solid angle concept. In two dimensions, an angle measured in radians is related to the radius and the arc length it traces along the circumference of a circle, and there are \(2\pi\) total radians in a circle. Solid angles are measured in steradians, and are related to the radius of a sphere and the area projected on the surface of the sphere. There are \(4\pi\) total steradians in a sphere. When an object with radial symmetry, such as a lens, is placed such that the central axis of the lens is in line with the center of a light source, the total solid angle, \(\Omega\), defined by the lens is given by the following expression.

\[
\Omega = 2\pi(1 - \cos \theta)
\]

In this equation, \(\theta\) is the angle between the horizontal and a line drawn from the center of the source to the top of the lens.

![Figure 10: Angular collection of a lens as a portion of the total emitted light](image)

This solid angle can then be converted into a fraction of the total emitted light by dividing by \(4\pi\).
Methodology

1. Experimental Setup

The majority of measurements taken for this experiment will be performed using the optical spectrum analyzer, or OSA. The basic layout for the experiment, shown in the figure below, consists of a bulb, two lenses, an optical fiber, a sample, and the OSA. Light from the bulb is collected by a lens, directed through a sample, collected by the second lens, and focused into a fiber. The fiber then connects to the OSA, which will produce a spectrum of the input signal as a function of wavelength.

![Setup for Primary Procedure](image)

Before we took any measurements, we first had to position the optical components to yield the highest signal strength. We did this by taking the free end of the optical fiber, that we would later attach to the OSA, and placing it in front of a photodetector. We then sent the signal from the photodetector to a digitizing oscilloscope on which we could view a value for the DC signal. We then slightly shifted each of the components of our setup until the signal on the oscilloscope was at its maximum value. Once we maximized the signal, we connected the fiber to the OSA and began familiarizing ourselves with this apparatus. Parameters that we could alter for each scan included the scan range (min and max wavelength), the wavelength resolution, the detector sensitivity, and the number of
data points taken within the interval. The parameters that we determined were most efficient, and thus became standard throughout the majority of the lab, were a scan range of 600-1600 nm, a resolution of 2.0 nm, a sensitivity of High 2, and 5000 data acquisition points.

2. Primary Procedure
After completing both setups, we were ready to begin taking data. However, before just throwing the quantum dots in the path of the beam and starting a scan, we wanted to understand a few concepts about how our setup would be functioning, and the process we would be using to determine certain optical properties. Thus to begin our experimentation, we took several spectra of the light emitted from our light source, a tungsten bulb, with no sample in place. We then took an average of all these spectra in order to reduce the random noise that may have been prevalent in any one scan. In addition, we calculated an average spectrum of the background signal by blocking the light from the bulb and taking several scans. We then subtracted it out to account for any ambient light that may have been entering our optical fiber. We then were left with a plot for the tungsten bulb that we could compare with the theoretical spectrum of a blackbody emitter.

![Figure 12: Average of Experimental Blackbody Spectra](image-url)
There are two methods for comparing Figure 12 and Figure 13. The first is to compare the general shape of the curve. We can assume the temperature of our tungsten bulb to be between 3000 and 3300 Kelvin, so it should appear to have the same shape as the theoretical 3500-Kelvin curve. We can quickly see this is the case; both have a very broad peak, and only a slight decrease as wavelength increases. The second way to compare these two graphs is quantitatively using Wien’s Displacement Law. It states that \( \lambda_{\text{peak}}T = 2.90 \times 10^6 \text{ nm K} \)

If we use the above range of temperatures, we get a range of 878 to 966 nm for the maximum wavelength, and if we examine Figure 12 closely we see that the peak stretches from about 840 to 975 nm. This agrees very well, and thus it is safe to conclude that our tungsten bulb is acting as a blackbody emitter.

Next, we wanted to measure the optical properties of our first sample. The simplest way to do this was to just take a thin piece of any material and place it in the path of the beam. So we took a thin wafer of silicon and made sure to place it between the two lenses at a point where the beam had converged enough to be focused within the sample. As above
we took several scans in order to average them into a single plot that showed a transmission spectrum through a bulk silicon material.

![Figure 14: Average Transmission Through a Thin Wafer of Silicon](image1)

We then proceeded to use the results of our blackbody spectrum as the normalization factor in measuring the transmission through a thin silicon wafer. That is to say, we took the average transmission spectrum for the silicon wafer and divided it by the average blackbody spectrum in order to expose solely the effects that the silicon had on the transmitted light.

![Figure 15: Average Silicon Spectrum Normalized to Average Blackbody Spectrum](image2)
This graph quickly became one of the most puzzling results in our entire experiment. We would expect the graph to look exactly like it does right up until about 1200 nm, completing absorbing up to a certain cutoff wavelength around 1000 nm, and then transmitting after that. However, we would expect the transmission to be constant at the longer wavelengths, there should not be any more absorption until about 9 microns. We tried long and hard to come up with an explanation for the slight decrease in transmission at the longer wavelengths, but in all our research of the properties of silicon nothing indicated that this result would ever be expected. Furthermore, we even measured a different wafer of silicon just to check if we would see the same results, and indeed we did.

The next major portion of our experiment dealt with measuring the optical properties of an empty cuvette, and a cuvette filled with distilled water. Since the quantum dots that we purchased came mixed in a water solution, and we would be placing them in the plastic polystyrene cuvettes, then it was necessary that we examine and understand exactly how each of these components interact with the incident light separately. First, we found an average transmission spectrum for the empty cuvette.

![Figure 16: Average Transmission Through an Empty Cuvette](image-url)
Then, we normalize this to our average blackbody spectrum to get an idea of how they relate to one another.

As you can see, when dividing the two spectra, the result is very close to a horizontal line. This tells us that the shapes of the two curves were very similar, as we would expect since the light is passing through a transparent plastic cuvette. However, there are two distinct features on this graph to take note of. The first is the dip near 1150 nm, this is the only portion of the graph that differs from that of the blackbody spectrum, and it is due to the optical properties of the polystyrene. The second is the value on the vertical axis that roughly corresponds to the horizontal line that we see. It is about 0.75, this means only 75 percent of the light emitted from the bulb is being transmitted through the cuvette. Conversely, it means that 25 percent of our signal is already lost, due to the cuvette alone.

Next, we wanted to see how the absorption properties of water would affect our signal. In order to do this, we now used the plot of the empty cuvette as our normalization factor. We found an average spectrum for the transmission through water, divided it by the empty cuvette spectrum, and thus pulled out only the effects of water on the beam of light.

![Figure 17: Empty Cuvette Transmission Normalized to Blackbody Spectrum](image)
Figure 18: Average Transmission Through a Cuvette of Water

A few characteristics of this plot to make note of are the two dips in transmission/peaks in absorption at about 990 nm and 1200 nm, and also the onset of “complete” absorption at about 1400 nm. In this region, the absorption of the water is so strong that the OSA is not sensitive enough to detect a signal.

Figure 19: Water Transmission Normalized to Empty Cuvette Transmission

This is now the final transmission spectrum for water. To compare this with some theoretical curves of water, it is more convenient to do the conversion into a plot of the absorption coefficient. In order to do this we need to closely examine Beer’s Law, which states:
\[ I = I_0 (1-R)^2 f_s \exp(-\alpha L) \]

We can rewrite this as:

\[ \frac{I}{I_0} = (1-R)^2 f_s \exp(-\alpha L) \]

We can then replace the term on the left side with \( T \), the fraction of transmission, and since both \( R \) and \( f_s \) change very gradually with respect to wavelength, we can replace them with a single constant \( C \). This leaves us:

\[ T = C \exp(-\alpha L) \]

The \( T \) in this equation is what we have represented in the graph above, so now we want to solve this equation for \( \alpha \) in order to find how we must alter our plot.

\[ \frac{1}{T} = \frac{1}{C} \exp(\alpha L) \]

\[ \ln \left( \frac{1}{T} \right) = \ln \left( \frac{1}{C} \right) + \alpha L \]

\[ \alpha = \frac{1}{L} \ln \left( \frac{1}{T} \right) - C' \]

where \( C' \) is just another constant representing \( \ln \left( \frac{1}{C} \right) \)

As a result, we see that in order to transform our plot, we must first take the inverse of our data, and then take the natural log of this. Finally, we would have to divide by the path length, which in this case is just 1 cm, and subtract the baseline \( C' \). The baseline is found by separating a portion of the graph where you expect there to be no absorption, fitting a curve to this series of points, and extrapolating it over the entire range.
Figure 20 is what results when performing this transformation on the normalized transmission plot for water. As you can see the plot had to be cut at around 1400 nm because this was where the transmission signal was very close to zero, thus when taking the inverse in this region these values became infinite. However, we can still compare this to an expected plot of the absorption coefficient of water, seen below in Figure 21.
From first glance these graphs do not appear to be all that similar, but if we take a closer look at the magnitudes of the absorption coefficient we can see they compare quite well. In both graphs the value for $\alpha$ at 1000 nm is about 0.1 cm$^{-1}$ and about 10 cm$^{-1}$ right around 1400 nm. This means that within that relatively short span of wavelengths the absorption coefficient has increased by a factor of 100. Another way to compare the two graphs is to examine the wavelengths at which the distinct peaks occur. Within our experimental region, there are two peaks that agree quite nicely, a sharper one at about 1000 nm, and a broader shoulder at about 1200 nm.

**Quantum Dot Procedure:**

We then took this same type of analysis to examine the optical properties of the quantum dots we had purchased. Since our quantum dots were stored in a water solution, the necessary normalization factor for this portion of our experiment would be the cuvette
filled with distilled water. Using this would eliminate all absorption and/or reflection caused by the both the polystyrene cuvette and the water, thus leaving us with spectra showing only how the light interacted with the quantum dots.

The first step was to transfer the quantum dots from their original bottles into the cuvettes. Taking appropriate precautions, we did this in another lab, under a fume hood and wearing protective gloves. After preparing our quantum dot samples, we began taking transmission spectra for the quantum dots. The first measurements we took were of the quantum dot solution directly out of the bottle, what we considered to be a “pure” concentration, of course this was actually a relative concentration as the company did not supply us with any information regarding the original proportions of water and quantum dots. Once we completed our first few scans, we could see that this was a bit too opaque, meaning that in the region we were interested in it was absorbing so strongly that we were getting a zero signal for the transmitted light.

As you can see in Figure 22, even in the region that the dots are fully transmitting, the transmission fraction is still only about 0.5. Even this is already only about 30 percent of the original blackbody signal, so when you get into the region of absorption, about 600-650 nm, the signal is too small to measure. However, there is a very easy way of
correcting this. If we dilute the sample further, the transmission fraction relative to water will continue to increase as we add more and more water. This will bring the signal in our absorption range up to a value that can easily be measured, and then we can get an idea of how the absorption coefficient behaves in this region. Just as an example, we tried a relative concentration of 1/5 quantum dots, that is one part quantum dots and four parts water. This plot is shown below.

![Normalized Transmission](image)

**Figure 23: 1/5 Concentration of Quantum Dots Normalized to Water**

When we zoom in on the region between 600 and 700 nm, and perform all the necessary analysis to convert this to a plot of the absorption coefficient, we see the following.

![Absorption Coefficient](image)

**Figure 24: Absorption Coefficient for 1/5 Concentration of Quantum Dots**
Continuing along the same lines, we wanted to then examine how these graph of the absorption coefficient would change for various concentrations. So we made a series of concentrations from pure all the way down to 1/10 of quantum dots, and then even a couple that were more diluted including 1/15 and 1/30 of quantum dots. To see how these relate to one another, the following graph shows normalized transmission plots for a number of different concentrations.

![Graph showing normalized transmission plots for different concentrations](image)

*Figure 25: Transmission for a Series of Concentrations Ranging from 1/3 to 1/6*

As you can see, decreasing the concentration yields greater transmission. Conversely, we can say that decreasing the concentration decreases the absorption. This makes sense because as we put fewer and fewer dots in the same volume, light is obviously going to pass through the solution easier.

To conclude our experiment we wanted to examine how changes in one more variable would affect the quantum dot spectra. If you remember from the solving of Beer’s Law for $\alpha$:

$$\alpha = \frac{1}{L} \ln \left( \frac{1}{T} \right) - C'$$
The variable $L$ is the length of the path that the light must be transmitted through. For all examples previous to this we only used one cuvette, thus $L$ was equal to 1 cm, and did not affect our values for $\alpha$ at all. Now we chose a few concentrations to examine with path lengths of two and three centimeters. The following shows the transmission through various path lengths for a concentration of 1/9 quantum dots.

![Figure 26: Transmission for Series of Path Lengths (1, 2 and 3 cm) for a 1/9 Concentration of Quantum Dots](image)

As expected, from the graph we see that the transmission decreases significantly as the path length increases. Next we wanted to normalize these plots and then convert them to plots of the absorbance and absorption coefficient. Where absorbance is just equal to $\alpha L$. In order to do this we had to be sure to change our normalization factor for each path length, meaning for our 2 cm quantum dot data the proper normalization factor would be 2 cm of water.
Finally, we divide each of the curves by their respective path lengths and end up with a plot of the absorption coefficient. Since we used the same concentration for all three path lengths, we would expect the absorption coefficient to remain constant as we alter the path length. This is shown in Figure 28 below.
3. Scanning Spectrometer

The second apparatus used to collect data for this report was the scanning spectrometer. The spectrometer was used in conjunction with a lock-in detector and the Spec1 software on the laboratory computer. The light source used was a tungsten bulb, identical to the bulb used for the OSA. Light from the bulb was collected by a lens, directed through a sample and chopping wheel, collected by a second lens, and focused into the input slit on the spectrometer. The output signal was gathered by a photodiode, which was connected to the lock-in detector and, from there, the computer.

![Diagram of the setup for the scanning spectrometer](image)

**Figure 29: Diagram of the setup for the scanning spectrometer**

The drawing above is a basic schematic of the setup of the scanning spectrometer when viewed from the top. It was necessary to set up the optical components and maximize the input signal before any data could be collected. The bulb was placed approximately 32.7 cm from the slit on the spectrometer. The first lens, diameter 35 mm and focal length 50 mm, was then placed approximately 7.9 cm from the light source and adjusted such that the center of the lens lined up, both horizontally and vertically, with the slit and the filament of the bulb. Placing an index card in the path of the beam, the 5 cm where the beam was narrowest were reserved to place the sample. Just before that point, the
chopping wheel was placed to cut the beam. After the sample space, approximately 4.0 cm from the slit, a second lens with diameter 25 mm and focal length 25 mm was placed in the path of the light beam. These distances were based upon a calculation using Lens’s law and the maximum acceptance angle of the spectrometer and a collection efficiency calculation for the bulb and first lens. Once these components were in place, a silicon photodiode was pressed against the outgoing slit on the spectrometer and connected to the lock-in detector.

With the chopping wheel turned on and the reference signal sent to the lock-in detector, the final lens position was adjusted and placed in a position that yielded the maximum signal on the lock-in detector.

The scanning spectrometer has two knobs that are used to control scan rate and can also be used to manually rotate the diffraction grating. Their position, whether pulled out or pushed in, relates to scan rate by the chart printed on the right side of the spectrometer. Due to the diffraction grating used in the lab, the actual scan rate is double what is given on the chart. Similarly, the value on the display given for the current wavelength is also half of the actual wavelength currently being transmitted.

The lock-in detector is used to improve signal to noise ratio. A reference signal is supplied to the lock-in by the chopping wheel controller. The lock-in then filters out all signals that do not have the same frequency as the reference signal. Those signals that do have the same frequency are then separated into an in-phase and an out-of-phase component, or quadrature. The lock-in detector has a number of parameters that can be adjusted based upon the details of the scan. The phase should be adjusted so the quadrature needle reads zero, which maximizes the in-phase signal strength. The phase angle may vary based upon the detector being used and the frequency with which the chopping wheel is rotating. Based on the strength of signal, the sensitivity of the lock-in can be varied in order to observe a clear signal. Exceeding a reading of 1 on the lock-in should be avoided, and when samples or detectors were changed, a scan was always taken on low sensitivity in order to determine what the peak signal strengths were in a particular scan range. Finally, the time constant could be varied to control signal to noise ratio. Increasing the time constant improves signal to noise ratio at the expense of data...
collection rate. Since signal noise was not an issue with the time constant set at 1 second, this parameter was not adjusted between scans.

The lab computer data collection software was used to perform a scan once the desired parameters had been set on the lock-in detector and scanning spectrometer. Scan range and speed parameters were entered into the program and the start condition was a falling trigger. Starting the spectrometer would automatically start the collection on the computer. At the completion of a scan, the data was saved as a .csv file. Failing to save at the end of a scan, or when closing the program, causes the data for the previous scan to be lost.

In order to determine which parameters would yield the clearest absorption data, dozens of scans were taken with a different combination of variables. Each scan was conducted a minimum of three times and then averaged. The Si photodetector is sensitive in the visible region of the spectrum and in the near-infrared out to approximately 1000 nm. The InGaAs detector is not optimized for lower wavelengths, but extends farther in the infrared. Due to the phenomena of second order effects from the diffraction grating inside the spectrometer, a long-pass filter was needed in conjunction with the InGaAs detector to observe wavelengths in the 1000 to 1600 nm range. The spectrum of the filter itself was measured using another long-pass filter to determine what magnitude of losses could be expected. Once a sample of the quantum dots was scanned at longer wavelengths, it became evident that the quantum dot absorption was very low at high wavelengths and further measurements were concentrated at wavelengths under 1000 nm. The silicon photodetector is sensitive in this region and therefore the InGaAs detector, and the accompanying filter, was not required.

Multiple path lengths of water were scanned over the range from 400 nm to 1000 nm in order to determine the strength of the reference signal as a function of wavelength.
Samples of quantum dots were prepared varying in concentration from pure solution, straight from the bottle, to 1/6 concentration. After performing a scan on each of these concentrations, it was noticed that the quantum dots absorbed very strongly for wavelengths less than approximately 650 nm and greater dilution would be required to see more detailed structure. New samples were created, varying in concentration from 1/10 to 1/50 quantum dots/water. From these measurements, it was determined that the 1/30 concentration would yield suitable results for 1, 2, and 3 cm path lengths. In addition to three samples of 1/30 concentration, one sample of 1/15 concentration was also created. Scans were conducted across the 400 nm to 1000 nm wavelength range, and after dividing by scans conducted with an equivalent path length of water, the absorption coefficient was calculated using Beer’s law. As can be seen from the above graph, the signal strength of the water is very low for wavelengths below 575 and this caused the data for the absorption coefficient in this range to be very noisy. Therefore, additional scans conducted with higher sensitivity were conducted from 400-575 for both water and all four quantum dot samples. Scans were also taken of the same samples from 800-1000 nm, a region where the quantum dots are known to be non-absorbent, and this data was used to form a baseline to subtract from the absorption coefficient at lower wavelengths. A linear baseline fit was used because Excel’s curve fitting algorithm for higher order polynomials is not exact enough when
creating a function of numbers on the order of 800-1000. Additionally, in order to eliminate electrical noise interference, a scan was taken with the light source switched off and that scan was subtracted from the averages of the water and quantum dot scans. The calculated absorption coefficient for the 400-575 nm range was merged with the absorption coefficient for the 575-1000 nm range and the baseline was subtracted producing complete absorption coefficient graphs from 400-1000 nm for three path lengths of 1/30 concentration and 1 cm of 1/15 concentration.

4. Additional Experimentation:

Within the progression of our experiment, we did also measure a number of other samples, none of which proved to produce any vital results. Nevertheless, they were stepping stones along the way. The first of these was a sample of red food coloring. This was something we measured very early on in our experiment, and when we went about analyzing it is when we realized that we needed to constantly be altering our normalization factor throughout the experiment. When we tried to normalize the food coloring to our blackbody spectrum, the shape of the curve did not change at all because what we should have used as a basis was a cuvette filled with water.

Another step we took along the way was to measure the transmission through a filter of which we already had a graph of its transmission. This was kind of just a checkpoint or a calibration of sorts to ensure that we were measuring everything properly. The filter was a long pass filter designed to “cut off” at 800 nm, that is to say it allowed all light of longer wavelengths to pass through cut out any light of shorter wavelengths. This is what our plot below showed.
Furthermore, we did also purchase one other type of quantum dots. We started out with the intention of also measuring all the same properties for the ADSQD820 dots, but midway through the experiment we realized that these dots seemed to be decaying at a faster rate than the red ADSQD620 dots, so we decided to shift our focus to only the more stable of the two. However, we were able to get a few measurements of the pure concentration before scrapping this portion of our experiment. Figure 32 below shows the normalized transmission of the 820 nm quantum dots.
Then converting this plot to that of the absorption coefficient.

In the latter stages of our experimentation, we did also attempt to measure the emission spectrum for our ADSQD620 dots using the OSA to see if it would be something that we could include as a supplementary portion of our lab module. We used a large green HeNe laser to excite the fluorescence, and then attempted to collect the light into our optical fiber. Unfortunately, even on the highest sensitivity, the OSA can only read signals down to about 0.1 pW, and our emission signal must have been smaller than that.
Data Analysis

The following graphs show the experimentally observed absorption for the quantum dot solutions. The first graph shows the absorption for the 1/30 concentration solution for 1, 2, and 3 cm path lengths followed by the same data divided by the respective path lengths to illustrate the absorption coefficient. The third graph displays the 1 cm of 1/15 solution data with the 2 cm of 1/30 data. Finally, the fourth figure is the absorption and emission spectrum for the quantum dots provided by the manufacturer.

Figure 34: Absorbance for three path lengths of 1/30 concentration

Examining the above graph, the relationship between the 1, 2, and 3 cm path length absorption is clearly linearly proportional to path length. The three curves all exhibit the same shape, however at corresponding wavelengths, the absorption of 2 cm of solution is double the absorption of 1 cm. Likewise, the absorption of 3 cm of solution is triple the absorption coefficient of 1 cm. The small jump at 575 nm in the 1 cm curve, and the larger jump at the same wavelength on the 3 cm curve, is from a slight inconsistency in matching the 400-575 nm high sensitivity scan with the 575-1000 nm scan data. This could be a result of the linear baseline fitting when the true baseline may exhibit some other shape. The 2 cm curve, however, does not exhibit this jump and transitions smoothly. The data values in the previous graph can all be divided by their path length in order to show only the absorption coefficient.
While there are some minor inconsistencies, the curves are very close to one another. A possible cause for the discrepancy is reflection by the quantum dots in solution that is less prominent at higher wavelengths and thus was not subtracted out during baseline analysis. Another possible source of error is the differing age of the samples. At the time these scans were taken, the quantum dot solutions would begin to become unstable in a matter of hours with particulates visible in the solution. Data collection on the spectrometer took approximately 20-30 minutes per scan, depending on the wavelength range being scanned, and when three scans are averaged, it amounts to more than one hour between different path length measurements.

More puzzling is the sharp dip occurring at approximately 415 nm that is present in all of the final absorption coefficient data regardless of path length or concentration. The feature is too large and is common in all of the graphs, which rules out noise. Based on the material and structure of the quantum dots, the reason for this sharp drop in absorption is unknown and is not mentioned in literature references for CdTe. Due to this uncertainty, the focus of this analysis will be on the shoulder, or half-peak that occurs just below 600 nm. This feature is consistent in shape to data found in (Cadmium Telluride Semiconductor materials book) and is also apparent in the absorption spectrum provided by the manufacturer with the quantum dots.
Figure 36: Graph contrasting the absorption of 1cm of 1/15 concentration with 2cm of 1/30 concentration

Comparing the plots of the absorption coefficient for 1cm of 1/15 concentration and 2cm of 1/30 concentration, one can see that they exhibit nearly identical behavior in terms of both numerical value and shape. This data demonstrates that, in addition to varying with wavelength, the absorption coefficient, $\alpha$, is directly proportional to the concentration of quantum dots in a solution. As shown below, doubling the concentration in solution is equivalent, in terms of absorption, to doubling the path length of the light beam through the solution. In the equation below, $\alpha_1$ represents the 1/15 concentration and $\alpha_2$ represents the 1/30 concentration.

$$C \exp[- \alpha_1 L] = C \exp[- \alpha_2 2L]$$

$$\alpha_1 = 2 \alpha_2$$

Given the fact that the absorption is equal in both cases, which is experimentally verified above to a reasonable degree of accuracy, the absorption coefficient of the 1/15 concentration solution is double that of the 1/30 concentration solution. This is the expected result, knowing that $\alpha$ is a linear function of the number of particles present. Examining the structure of the absorption graph above, the onset of absorption as energy increases and wavelength decreases, can be observed at approximately 650 nm. The middle of the initial increase at the point where the graph is steepest occurs at about 625
nm. The theoretical minimum absorbed energy can be calculated using the formula below, which is further explained in the background section on page 11.

\[
\frac{hc}{\lambda} = E_{bg} + \frac{h^2 (n_1^2 + n_2^2 + n_3^2)}{8m_e d^2} + \frac{h^2 (n_1^2 + n_2^2 + n_3^2)}{8m_h d^2} - \frac{e^2}{8\pi\varepsilon}
\]

For CdTe, the band gap energy is 1.51 eV, the electron effective mass is 0.096*m\(_e\), the hole effective mass is 0.84*m\(_e\) [Berger, 1997], and \(\varepsilon\) is 10.392*\(\varepsilon_0\) [Zanio, 1978]. Varying \(r\) from 2.5 nm to 5 nm, half the diameter to the full diameter of the quantum dot, and plugging in the values listed above, the theoretical onset of absorption should occur between 614.3 and 618.5 nm. These values correspond very closely to the center of the steep slope between 600 and 650 nm. The initial onset at 650 nm can be explained by the non-homogenous size of the quantum dots in the solution. The quantum dots vary in width from 4.5 to 5.5 nm, and an average value of 5 nm was used in the above calculation. Both the experimental data and theoretical calculations agree with the manufacturer provided spectrum, shown below.

Figure 37: Manufacturer-provided spectra [American Dye Source]
Creation of Laboratory Module

In order for an undergraduate laboratory module to be created studying quantum dots, it was necessary to confirm that suitable data could be collected using the available equipment. By following the procedure outlined in the previous section of this report, it was possible to gather data showing a clear onset of absorption for the quantum dots. The observation of this onset of absorption confirmed that the concept is feasible for an undergraduate laboratory experiment and that positive results could be attained.

Laboratory experiments in the photonics laboratory course offered at WPI span four lab sessions of two hours apiece. The second criteria for a lab module studying the absorption of quantum dots was that it must fit within the eight hours allowed for each experiment.

The scanning spectrometer was deemed impractical for the bulk of the measurements by the following analysis. To compare three path lengths and two difference concentrations, it was necessary to perform scans of 4 different quantum dot samples. Three different path lengths of water also needed to be scanned as a reference. Each scan was performed a minimum of three times to obtain an average. Multiplying the total number of scans by the wavelength range and the scan rate used on the spectrometer yielded a total time of 8.4 hours. This estimate did not account for the fact the lab time is broken up into 4 sections, nor did it allow for any time to setup the experiment, switch samples, or reset the spectrometer and computer between scans.

The optical spectrum analyzer takes considerably less time to perform a scan, and therefore will be the primary apparatus for the laboratory experiment. Once the setup has been completed and the signal coupled into the optical fiber has been maximized, measurements of the blackbody spectrum and an empty cuvette are conducted in order to gain familiarity with the OSA. Next, the scans of the multiple path lengths and concentrations of quantum dots, and the accompanying reference scans of water, are conducted. Finally, the scanning spectrometer can be used to perform scans on one path length or concentration as a contrast to using the OSA. The four lab periods were outlined in the table below showing estimates of the time required for each step.
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<th>Day 2</th>
<th>Day 3</th>
<th>Day 4</th>
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<td>Check setup</td>
<td>Start spectrometer</td>
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<td>2cm water</td>
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<td>3cm water</td>
<td>1cm chosen concentration 3 scans</td>
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</table>

Figure 38: Table showing time required for each step of the experiment and how the steps fit into the 4 lab periods

Background information on semiconductor band gap energies and quantum well states is provided in the lab instructions handout, included in Appendix A. The information in the handout is designed so the students have a basic understanding of the physical phenomena affecting the absorption spectrum of the quantum without requiring prior knowledge of quantum mechanics or photonics. Clear instructions, along with comprehension questions, follow the background section to guide students through the experiment. Students completing the lab experiment will be experimentally verifying Beer’s Law and theoretical calculations based upon quantum well and band gap energies. Additionally, they will gain experience in data manipulation on the computer, and data collection with two different pieces of equipment, the OSA and the scanning spectrometer.
Conclusions

There were two key concepts of physics that we were able to verify through the work outlined in this report. The first was Beer’s Law, which describes how absorption relates to both concentration and path length. We were able to show that indeed absorption does increase when either the path length or the concentration is increased. In addition, we were able to show that the two are in fact related, and that if you double the path length for a given concentration, it is the same as doubling the concentration for the original path length. From our data, we saw that 2 cm of the 1/30th concentration was the same as 1 cm of the 1/15th concentration. Secondly, through an analysis of our particular semiconductor’s (CdTe) band gap energy, the 3-D quantum well effect, and the exciton effect, we were able to calculate, for a particular size of quantum dots, a range of values for the wavelength at which the onset of absorption would take place. We found that this onset of absorption should occur between 614.3 and 618.5 nm, which agrees respectably with our experimental data given that there was actually a range of different size dots in the solution we purchased.

The laboratory module that was created as a result of all of our experimentation was designed to take the most key results from all of our work and present them in a way that they will be comprehensible to a student just beginning to learn about photonics. It should give each student a brief introduction to the phenomenon of quantum dots, in addition to giving him/her a complete understanding of how to measure the absorption of any given material. It is certainly short enough to fit into the allotted 8 hours leaving room for some inevitable student errors, but with the optional scanning spectrometer section, it is also ensured to keep even the most effective students busy for the entire time.

As far as fully implementing our lab module into the undergraduate physics curriculum, there seem to be some substantial road blocks in how feasible that would be: the single greatest issue being the stability of the quantum dots. Even in ideal circumstances quantum dots only have a shelf life of about 6 months, and as we noticed in practice they tend to show characteristics of instability even earlier than that. On several different
occasions, we would enter the lab and find the dots to look nothing like we left them. Whether it be small black particles floating around in the liquid, a white sort of milky substance floating around at the bottom of the cuvette, or even a complete separation from the water causing all of the quantum dots to be clumped at the bottom under a layer of water. With all of these unknown factors, and most quantum dot companies having strict proprietary rules about sharing information, it makes coming to any extremely confident results near impossible. In addition, there would be cost issues that would arise. New quantum dots would have to be purchased every year that the lab would be used, and they are definitely not cheap. However, though not incredibly feasible, implementation is certainly possible. One school, Siena College, was not only able to get an NSF grant, but also a direct partnership with Evident Technologies, the leading producer of quantum dots, and they were able to create five lab modules which are now a part of their undergraduate curriculum. The most probable solution to each of the issues above is to work conjunctly with the chemistry department, in which they could develop an undergraduate laboratory that would synthesize quantum dots that the physics department would then be able to examine all the properties of. This way, we would know specifically under what conditions they were manufactured.
References


Appendices

Appendix A: Lab Module Handout

1. Introduction

In this laboratory experiment, we will be examining the absorption properties of quantum dots in solution. The optical spectrum analyzer will be used to collect spectra of light transmitted through a variety of samples, which will then be used to find the absorption coefficient as a function of wavelength.

Quantum dots are semiconductor nanocrystals that exhibit unique optical properties due to a combination of quantum well-type effects and their base material band gap structure. According to quantum theory, particles can only have a discrete set of energy levels defined by their environment. For an electron in a semi-conductor material, there are certain energy bands in which the electrons can exist. Due to the Pauli Exclusion Principle, each energy band can accommodate a finite number of electrons, so for an electron to change states, there must be space in one of the adjacent energy bands. We will therefore concern ourselves with the outermost energy bands, the conduction band, and the valence band. In a semiconductor material, the valence band is the highest energy band electrons are found in when in their ground state. When unexcited, the valence band is full and the conduction band, one energy level higher, is empty. The material’s band gap energy is the difference between the energy of an electron in the bottom of the conduction band and the energy of an electron in the top of the valence band. No electrons can exist with energies between these two values.

For a semiconductor material to absorb a photon, the photon must have a minimum energy $h\nu$ equal to the band gap energy to be absorbed and excite an electron. For photons with energy less than the band gap energy, there can be no absorption. An electron moving up to the conduction band leaves a “hole” in the valence band, which can be treated as a positive particle. If the incoming photon’s energy is greater than the band gap energy, the excess energy is lost in collisions (heat) as the electron settles to the bottom of the conduction band, and the hole moves to the top of the valence band. Since
electrons naturally move into their lowest energy, or ground, state, the hole in the electron will recombine emitting a photon with energy equal to the band gap energy.

A quantum well is a feature in which the potential energy is zero for a certain region, and essentially infinity everywhere else. This has the effect of confining particles to exist only within the quantum well, the width of which is given by d.

The discrete energy levels allowed in the quantum well correspond to the kinetic energies of electrons whose deBroglie wavelength yields a standing wave in the well.

$$n \lambda_{dB} = 2d$$

Where n is a positive integer and r is the radius of the quantum well. The deBroglie wavelength, as a function of the particle’s energy is:

$$\lambda_{dB} = \sqrt{\frac{\hbar^2}{2mE}}$$

Combining these two equations yields the energy levels, as a function of n, in a one dimensional quantum well:

$$E_n = \frac{\hbar^2 n^2}{8md^2}$$

For a cubic three dimensional quantum well, the formula changes to include three values of n, representing the three directions:

$$E_n = \frac{\hbar^2 (n_1^2 + n_2^2 + n_3^2)}{8md^2}$$
Due to the small size of the quantum dots, the radius is on the order of 5nm, they are essentially spherical three dimensional quantum wells. This means that electrons, and holes, have discrete energy levels given by the above equation. The two particles, or charge carriers, therefore do not remain at the border of the conduction in valence bands, they have additional energy. It is important to keep in mind that in a semiconductor, the hole and the electron have different effective masses.

When a photon is emitted from a quantum dot, its energy is not simply equal to the band gap energy, but the energy of the band gap, plus the ground state energies ($n=1$) of both the hole and the electron. This same phenomena has an effect on absorption as well. A photon must have a minimum energy equal to the sum mentioned above, greater than the band gap energy, to be absorbed. In this laboratory experiment, we will be determining the absorption coefficient of the quantum dots provided. The absorption coefficient, $\alpha$, is related to intensity by Beer’s law.

$$I = I_0 C \exp[-\alpha L]$$

$$\alpha = N \sigma$$

$C$ represents the losses due to reflection and scattering. The absorption coefficient is a linear function of the effective optical cross section, $\sigma$, and the number of particles per
unit volume in the path of the beam, N. What effect would doubling the number of quantum dots in a solution have on the transmitted intensity?

2. Setting up the Experiment

The majority of measurements taken for this experiment will be performed using the optical spectrum analyzer, or OSA. The basic layout for the experiment, shown in the figure below, consists of a bulb, two lenses, an optical fiber, a sample, and the OSA. Light from the bulb is collected by a lens, directed through a sample, collected by the second lens, and focused into a fiber. The fiber then connects to the OSA which will produce a spectrum, as a function of wavelength, of the light in the fiber.

Before measurements can be taken, we must first position the optical components to yield the highest signal strength. As the light source for the absorption measurements we will be using a tungsten lamp. Other optical components include a 40mm diameter lens with a focal length of 50mm, a 25mm diameter lens with focal length 25mm, and an optical fiber with radius X and an acceptance angle of Y. To maximize signal, we will also be using a chopping wheel, a silicon photodetector, and an oscilloscope.

Begin by placing the tungsten bulb and screwing it down. The filament and the point of the glass should be perpendicular to the direction you intend on focusing the beam. Next, place the larger diameter lens approximately 11cm from the bulb. An index card can be held in the path of the beam to observe the spot size. Keep in mind the closer the lens is to the bulb, the greater the collection efficiency. The center of the lens should be lined up
vertically and horizontally with the bulb filament. Examine your setup from the side and from the top to ensure that it is. Once the lens is in place, screw it down as well. What fraction of the light emitted from the bulb is the lens collecting?

Place the second lens in line with the first at a position after the focused point approximately 15.5 cm from the larger lens, allowing room to place a sample. Once again, adjust the position so the light is focused to as small a point as possible. Make sure one of the ends of the optical fiber is placed up against a photodetector and the detector is connected to the oscilloscope. Position the other end of the fiber at the position where the light is focused from the second lens. While watching the oscilloscope signal, move the fiber to the position where the signal is the largest, and then screw it down.

Once this is complete, you may remove photodetector and connect the other end of the fiber to the OSA.

3. Blackbody Spectrum

Now that you have completed your set up and have the maximum amount of light coupled into the optical fiber, it is time to begin taking data. You will first want to familiarize yourself with the operation of the OSA. Parameters that can be set for each scan include the scan range (min and max wavelength), the wavelength resolution, the detector sensitivity, and the number of data points taken within the interval. You should experiment systematically changing each of these parameters to achieve a good understanding for how each of them affects the results of your scan. For example, set a scan range of 800-850 nm, and take multiple scans varying the resolution, sensitivity and number of data points. Comment in your report how each change affects the quality and time of your scan.

Next, we want to examine how close the tungsten bulb is to an ideal blackbody emitter. Begin by setting the scan range to 600-1600 nm, the resolution to 2.0 nm, the sensitivity to High 2, and the number of data points to 5000. These will be the standard settings throughout the majority of this lab. After you acquire the spectrum, you will want to save it into one of the 32 memory locations on the OSA. To do this, press the MEMORY button, then choose SAVE, and finally pick the location you wish to save to and press
ENTER. You will also want to save all of your data directly to a floppy disk to analyze outside of the lab. To do this, press the FLOPPY button, choose WRITE, then be sure to give each scan a unique file name so that you will be able recognize it later. For example, your first blackbody spectrum could be BB1. Once you have named the file choose EXECUTE.

NOTE: Always wait for the green light below the floppy drive to go off before removing the disk.

You should then repeat your measurement two more times, so that you now have three blackbody spectra. In your analysis, you will want to average the data from each of these, and come up with one average blackbody spectrum. This practice of taking multiple scans and averaging them is a good way to reduce random noise that could be prevalent in any single scan.

Another good practice is to account for any background signal that could be getting into the fiber from the ambient light in the room. To do this, you should take two or three scans in which you block the light from the tungsten bulb. After averaging these, you will have a spectrum of the average background signal. If you then subtract that from your average blackbody spectrum, you will have the true spectrum that is result of only the tungsten bulb.

How does this final spectrum compare to that of a theoretical blackbody assuming the temperature of the tungsten bulb is approximately 2700 Kelvin? Is the wavelength at which the peak signal occurs what you would expect it to be? Why or why not?

4. Transmission through a Silicon Wafer

You will now study how the light from your tungsten bulb interacts with your first sample, a small wafer of silicon. Carefully place the wafer in the holder provided, and position it in the path of the beam between the two lenses. Be sure the image of the filament (the small brighter spot) is centered on the wafer. As you will notice, it
“appears” that no light is passing through the wafer, that is why this is a good test for you to understand that the majority of light we will be working with is not visible to the human eye. Take this scan three times with the same settings as above, saving each time.

Now to analyze these results you want to take from this scan solely the effects of the silicon wafer. In order to do so you must normalize the average spectrum with the wafer in place by dividing it by the average blackbody spectrum. You now have a normalized transmission curve that you could compare with a theoretical transmission curve of bulk silicon material. Do your results agree, particularly the cutoff wavelength? Is the behavior of your scan at the longer wavelengths what you would expect? Why or why not?

5. Absorption of Water
Next you will repeat the above measurements except you will replace the silicon wafer with an empty cuvette and then with a cuvette filled with distilled water. This time in your analysis you will divide the average spectrum for the cuvette filled with water by the average spectrum for the empty cuvette. This will give you a spectrum characterizing the transmission of light through the water itself. Explain why we must use the spectrum of the empty cuvette instead just using the blackbody spectrum as our normalization factor.

REMINDER: Be sure to be giving unique file names to your scans as the number of individual scans is increasing, you will not want to get them mixed up and have to retake all of your data.

In order to convert this plot of normalized transmission into a plot that gives the absorption coefficient as a function of wavelength, you need to closely examine Beer’s law and find the relationship between T and α. Beer’s law states that

\[ T = \frac{I_1}{I_0} = (1-R)^2 f_s e^{-\alpha L} , \]

Where \( \alpha \) is the absorption coefficient, \( l \) is the length of the path the light travels through, \( R \) is the reflection at each surface, and \( f_s \) is a constant due to scattering. Since the
reflection, and scattering constant remain constant throughout, we can replace them with a single constant and call it C. Beer’s law then becomes

\[ T = \frac{I_1}{I_0} = C \ e^{-\alpha l} \]

For now, ignore the constant C (that is, let it equal one) and find how you must alter your current plot to result in plot of \( \alpha(\lambda) \). We will see how this constant affects our results later in the lab. Show this calculation in your report.

BONUS: Does the strong absorption of water in the infrared have any major impacts on our everyday life? How so?

6. Absorption of Quantum Dots

Now take the sample of quantum dots that has been prepared for you and place it in the path of the beam, and repeat the multiple scans with the same settings as above. This time, because the quantum dots are in a water solution, you will want to use the average spectrum of a cuvette of water as your normalization factor, and divide your quantum dot spectrum by it. You should repeat the same process to convert this spectrum into an absorption spectrum. At the start of your next lab period, rescan the same cuvette of quantum dots and compare your two spectra. Is there any difference? If so, what do you think could be the cause?

Next, we will account for the constant that we ignored above. After carefully working through Beer’s Law, you should come up with a result that looks like the following:

\[ \alpha = \frac{1}{L} \ln \left( \frac{1}{T} \right) - C' \]

The constant C' is called the baseline, and in order to correctly account for it, you must analyze your curve in the area where you expect there to be no absorption due to the dots, thus at very long wavelengths. Fit a curve to this portion of your graph, display the equation, and then subtract that equation from your entire data set to come up with a final plot for the absorption coefficient.

7. Measure Different Relative Concentrations

The instructor will now have prepared for you a series of relative concentrations. Since we have no way of knowing the concentration of quantum dots in the original solution, there is no way to know the absolute concentration, but we will consider the given
solution to be pure, thus all the cuvettes of mixed concentrations are relative to this statement. For example, a concentration labeled 1:4 means one part of original quantum dot solution mixed with four parts distilled water, this can also be described a concentration made up of one fifth quantum dots. Either notation is acceptable, just be sure to be consistent throughout the experimentation. You should repeat all the above steps until you complete absorption spectra for each of the concentrations, including baseline analysis.

8. Measure for Different Path Lengths
In beginning this section of the lab, you should check to see that your beam is well collimated about the point where you have been placing your sample. When you add multiple cuvettes into the path of the beam, you will want to be sure that the light is focused enough to pass through your maximum path length (3-3.5 cm) without significant divergence. That is to say, you need to make sure the beam is smaller than the width of the cuvette for the entire path length. If this is clearly not the case, you will need to readjust your optics a bit to make it work. You do not want any light in getting into your data that has no passed through the sample. Once you are sure the beam will pass through all path lengths, you should repeat the above process for one, two, and three cuvettes of quantum dots.

IMPORTANT: What do you think you should use for a scan to normalize the scans of two and three cuvettes of quantum dots? Why is this important?
NOTE: When converting to a plot of the absorption coefficient, do not forget to account for l, the path length, in your calculations. How does this factor in to your spectra? Do your plots turn out to be what you would expect from part 7? Why or why not?

9. Using the Scanning Spectrometer
In this section, the scanning spectrometer will be used to confirm data taken by the OSA. The advantages of the scanning spectrometer used in conjunction with a lock in detector include greater scan range, greater sensitivity, and improved signal to noise ratio. The
scanning spectrometer works by rotating a diffraction grating as it scans. As the grating
rotates, one wavelength from the incident signal at a time is directed out through the
second slit to the detector. Along with a reference signal, the signal from the photodector
is input into the lock in detector. The lock in detector filters out all signals that do not
share a common frequency with the reference signal. The light beam is chopped in order
to make it periodic.
It will not be necessary to setup the optics yourself for this portion of the experiment,
having already done it for the OSA.

On the laboratory computer, open the program Spec1 on the desktop. Set the scan range
to 600nm to 1000nm, the scan rate to 250 Å/min and the trigger (Ext. Trig. Start) to
“falling.”
Due to the diffraction grating in the spectrometer, the number on the external dial, given
in angstroms, is half of what is actually being transmitted. Likewise, the actual scan rate
is double the given value. In order to manually wind the scanning spectrometer, move the
Hi-Lo Shift knob out to its middle position, then turn the Scan Speed knob until 3000 Å,
the equivalent of 600nm, is showing on the dial.
Push the Hi-Lo Shift knob back in and move the Scan Speed knob to the position corresponding to 125 Å/min on the chart on the right of the spectrometer. On the lock in detector, choose a sensitivity of 2.5mV and a time constant of 0.3s. Varying the time constant will adjust how narrowly the lock in defines allowed frequencies at the expense of response time. Finally, set the reference angle to 90 degrees and turn the phase knob until the quadrature needle is at zero.

Select one of the path length or concentration measurements from earlier in the experiment. With the appropriate path length of water in place as the sample, click start on the computer program and then turn the +/- knob to the left on the spectrometer to start the scan. At the completion of the scan, click stop scan on the computer and return the +/- knob to its vertical position. Save the scan as a .csv file and manually wind the spectrometer back to the starting wavelength. Repeat this step three times for water and another three times for the quantum dot sample. Do the results obtained from these measurements agree with those obtained using the OSA?
Appendix B: Equations and Constants

Beer’s Law:
\[ I = I_0 (1 - R)^2 f_s e^{-\alpha L} \]
Absorption coefficient:
\[ \alpha = \alpha N \]
Snell’s Law:
\[ n_1 \sin(A) = n_2 \sin(B) \]
Critical angle for total reflection:
\[ \sin(\theta_c) = \frac{n_2}{n_1} \]
Numerical aperture of an optical fiber:
\[ \sin(\alpha_{\text{max}}) = n_1 \cos(\theta_c) = \sqrt{n_1^2 - n_2^2} = NA \]
Lens equation:
\[ \frac{1}{s_1} + \frac{1}{s_2} = \frac{1}{f} \]
Solid angle formula:
\[ \Omega = 2\pi (1 - \cos \theta) \]
Energy of a photon:
\[ E_r = h\nu = \frac{hc}{\lambda} \]
DeBroglie wavelength:
\[ \lambda_{dB} = \sqrt{\frac{h^2}{2mE}} \]
Standing wave condition:
\[ n\lambda = 2d \]
One dimensional Schrödinger equation:
\[ -\frac{h^2}{8\pi^2m} \frac{\partial^2 \psi}{\partial x^2} = (E - V)\psi \]
Quantum well energy states in one dimension:
\[ E_n = \frac{\hbar^2 n^2}{8md^2} \]
Three dimensional cubic quantum well energy states:
\[ E_n = \frac{\hbar^2 (n_1^2 + n_2^2 + n_3^2)}{8md^2} \]
Energy difference between n=1 state in the valence band and the n=1 state in the conduction band for a quantum dot:
\[ \Delta E = \frac{hc}{\lambda} = E_{\text{so}} + \frac{\hbar^2 (n_1^2 + n_2^2 + n_3^2)}{8m_e d^2} + \frac{\hbar^2 (n_1^2 + n_2^2 + n_3^2)}{8m_h d^2} \]
Potential energy between two charge carriers:
\[ V = \frac{-e^2}{4\pi \varepsilon r} \]

Kinetic energy of an electron in the hydrogen atom:

\[ KE = \frac{e^2}{8\pi \varepsilon r} \]

Exciton total energy including potential and kinetic terms:

\[ E_x = \frac{-e^2}{8\pi \varepsilon r} \]

Total energy of an emitted or absorbed photon in a quantum dot:

\[ \frac{hc}{\lambda} = E_{bg} + \frac{h^2 (n_1^2 + n_2^2 + n_3^2)}{8m_e^*d^2} + \frac{h^2 (n_1^2 + n_2^2 + n_3^2)}{8m_h^*d^2} - \frac{e^2}{8\pi \varepsilon} \]

Constants

Planck’s constant:

\[ h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} = 4.1357 \times 10^{-15} \text{ eV} \cdot \text{s} \]

Permittivity of free space:

\[ \varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m} \]

Speed of light:

\[ c = 2.998 \times 10^8 \text{ m/s} \]

Mass of an electron:

\[ m_e = 9.1 \times 10^{-31} \text{ kg} \]

Charge of an electron:

\[ q = 1.609 \times 10^{-19} \text{ C} \]

Electron effective mass in CdTe:

\[ m_e^* = 0.096 m_e \]

Heavy hole effective mass in CdTe:

\[ m_h^* = 0.84 m_e \]

Dielectric constant in CdTe:

\[ \varepsilon = 10.392 \varepsilon_0 \]

CdTe band gap energy at room temperature:

\[ E_g = 1.51 \text{ eV} \]
Appendix C: Equipment Used

- DC Power Supply
  
  Typical currents and voltages applied to the bulb were about 3 Amperes and 6 Volts respectively.

- Tungsten Light Bulb
  
  Should function as ideal blackbody with temperature ranging from about 3000 to 3300 Kelvin. Coiled filament with approximate height of 3 mm.

- Lenses
- Optical Fiber
  
  GIF625 Multimode Fiber: Diameter of 62.5 microns, Numerical Aperture 0.27, Collection Angle 15.7 degrees.

- Optical Spectrum Analyzer (OSA)
  
  - Wavelength Range 600 to 1750 nm
  - Wavelength Accuracy ± 0.05 nm
  - Wavelength Resolution 0.02 nm
  - Sensitivity ~ 0.1 pW

  Standard parameters used throughout our experiment were: wavelength range of 600 to 1600 nm, wavelength resolution of 2.0 nm, sensitivity of High 2, and number of data points to 5000.

- Digitizing Oscilloscope
- Chopping Wheel and Controller
  
  Typical driving frequency of 30 Hz, sent directly to the Lock-in amplifier as the reference signal.
• Photodetectors
  
  o Si: Response 320 to 1100 nm with peak response at 960 nm

  Used in Scanning spectrometer setup. Large detector area made it ideal for the light exiting the small slit of the spectrometer.

• Scanning Spectrometer
  
  o Focal Length 0.5 m
  o Grating 590 grooves/mm
  o Collection Angle 11.5 degrees

  Unlike the OSA, the spectrometer does not have a built in data acquisition and analysis tool. For this reason, the signal from the scanning spectrometer must be sent to either the digital oscilloscope or to a specialized program on the lab computer for processing. The advantage of the spectrometer is its sensitivity to a wider range of wavelengths. Although the light does not have to be focused into an optical fiber, it still must pass through a small slit within a limited acceptance angle.

• Lock-in Detector

  The Lock-in detector receives a reference signal from the driving frequency of the chopping wheel, and then reads all other signal as either in phase or out of phase to this reference signal. It then sends the reading for the in phase signal to the computer.

• Computer Software

  The computer program takes the data sent from the lock-in detector and plots the signal as a function of wavelength. However, it is necessary to correlate the starting wavelength with that of the scanning spectrometer.

• He-Ne lasers
  
  o Green- Wavelength: 543.5nm- Beam Diameter: 0.70mm
INTRODUCTION

American Dye Source, Inc. is now offering from gram to kilogram quantity aqueous solution of semiconducting quantum dots, which emit strong fluorescent light from blue to red upon exposure to ultraviolet radiation.

DESCRIPTION

ADS620QD is CdTe quantum dot dispersed in water. This product can be used for various applications that include sol gel coatings, polymer coatings, biomedical probes, biosensors and fluorescent water based inks.

TECHNICAL DATA

- Appearance: Red solution
- Concentration: 0.25 % based on Cd
- pH: 10 - 11
- Excitation wavelength: 465 nm
- Emission wavelength: 620 ± 10 nm
- Quantum yield: ~ 50 %
- Particle size: 4.5 – 5.5 nm
- Package: in N2 sealed bottle
- Shelf life: 6 months

CONTACT INFORMATION

American Dye Source, Inc.
555 Morgan Boulevard
Baie d’Urfé, Quebec, Canada H9X 3T6
Tel. 514 457-0070
Fax 514 457-0071
Website: www.adsdyes.com
E-mail: info@adsdyes.com

DISCLAIMER

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**PRODUCT BULLETIN**

**CdHgTe NEAR INFRARED EMISSION QUANTUM DOT**

**ADS820QD**

**INTRODUCTION**

American Dye Source, Inc. is now offering from gram to kilogram quantity aqueous solution of semiconducting quantum dots, which emit strong fluorescent light from blue to near infrared upon exposure to ultraviolet radiation.

**DESCRIPTION**

**ADS820QD** is CdHgTe quantum dot dispersed in water. This product can be used for various applications that include sol gel coatings, polymer coatings, biomedical probes, biosensors and fluorescent water based inks.

**TECHNICAL DATA**

- Appearance: Brownish solution
- Concentration: 0.25 % based on Cd
- pH: 10 - 11
- Excitation wavelength: 465 - 550 nm
- Emission wavelength: 820 ± 10 nm
- Quantum yield: > 30 %
- Particle size: 5.5 – 7.5 nm
- Package: in N₂ sealed bottle
- Shelf life: 6 months

**CONTACT INFORMATION**

American Dye Source, Inc.
555 Morgan Boulevard
Baie d'Urfe, Quebec, Canada H9X 3T6
Tel. 514 457-0070
Fax 514 457-0071
Website: www.adsdyes.com
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Absorption and emission spectra of ADS820QD quantum dot in aqueous solution.
Price List – September 2006

QUANTUM DOTS – ADS620QD

American Dye Source, Inc. is now offering from gram to kilogram quantity aqueous solution of semiconducting quantum dots, which emit strong fluorescent light from blue to red upon exposure to ultraviolet radiation.

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Please contact us for additional information on the pricing and availability of the above product.
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