CHEMISTRY 162

Experiment 5 - ELECTRONIC SPECTROSCOPY OF POLYENES AND NANOPARTICLES

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Adapted from

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Possible Pre lab Questions

1. The C=C bond length in Part B is linear alkanes is 1.3Å. Show how this bond length was determined.
2. Show calculations for zinc acetate and tetra methyl ammonium hydroxide for part D

I. Introduction

Solar Energy

Solar cells work by converting sunlight into usable energy. Photons in sunlight hit the solar cell and are absorbed by a semiconductor. The semiconductor can be silicon, an organic molecule (organic photovoltaics or OPVs), or nanoparticles such as ZnO or CdSe. Electrons in the semiconductor are excited to a higher energy. In this higher energy state the electrons are free to move. Importantly though the electrons only move in one direction. Thus, the electrons are able to generate a current. The special structure of the materials is very important to keep the electrons moving in one direction and is often accomplished by adding small amounts of other chemicals such as boron or phosphorus to the silicon in a process called doping.

Solar cells are typically named after the semiconductor material from which they are composed. First generation solar cells were based on crystalline silicon. Second generation (thin film solar cells) utilize silicon, CdTe and CIGS (copper- indium-gallium-selenium). Many third-generation solar cells are still in the research and development stage. One type of third generation solar cell that is a particularly active area of research is semiconductor nanoparticles. Semiconductor nanoparticles are nanometer-sized crystals of semiconductors such as CdSe or ZnO with particle sizes ranging from 1 – 20 nm. Nanoparticles – also called quantum dots - are a very active area of research and offer methods to increase the efficiency of the harvesting of light energy in the design of solar cells.

Using Spectroscopy to examine bonding and nanoparticles

A basic understanding of quantum mechanical principles allows us to use spectroscopy to examine principles of bonding and estimate nanoparticle size from absorption spectra.

Electron transitions between different quantum mechanical states in atoms, molecules and solids typically take place in the UV-visible-near infrared region of the electromagnetic spectrum. Light absorption takes place when a photon excites an electron from one electronic state to another state at a higher energy.

We can use absorbance spectra generated from these electron transitions to examine phenomena such as bond type/length and nanoparticle size.

Bond type/length: Behavior of electrons in bonds changes depending on the bond type (sigma vs pi) and the length of the bond being examined. The wavelength of light absorbed to excite an electron in these different types of bonds is different and by examining the absorption spectrum we can gain information about the type of bond and bond length under examination.

Nanoparticle size: The electronic absorption spectra of nanoparticles depends on particle size. Because the size dependence of the absorption spectra arises from quantum-mechanical confinement effects, semiconductor nanoparticles are often called “quantum dots”. The size-dependent absorption spectra of these materials provide a simple and convenient way to monitor particle size during growth.

In this lab, you will use absorption spectroscopy of electronic transitions in molecules or nanoparticles to examine these two different aspects of molecular structure: linear alkenes with increasing numbers of bonds and nanoparticle quantum dots of increasing sizes

You will analyze your spectroscopy data for both the linear alkenes and the quantum dots in the context of the quantum mechanical model known as the “particle in a box model”.

Spectrophotometer and diffraction grating.

All spectrometers contain a few basic design elements in common (Figure 1)

A Light source
B Sample chamber where incident light passes through the sample
C A diffraction grating where output light is split into individual wavelengths
D A detector (which converts photons to a readout).

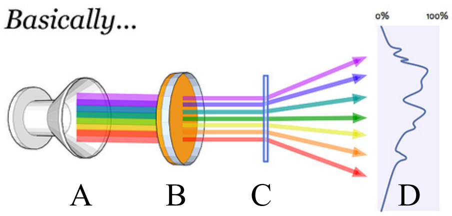


Figure 1 Schematic of Spectrophotometer

In considering how the diffraction grating works, it is useful to consider an incoming light wave incident on the diffraction grating as breaking up into many little wavelets (Fig. 2) which interfere constructively with each other at specific places given by the diffraction equation, $n\lambda = d\sin\theta$. In this relationship, d is the spacing between the openings, θ is the angle of diffraction, and n is an integer corresponding to the "order" of the diffracted wave. The diffraction equation says that the extra distance, dsinθ, traveled by adjacent waves must be a whole number of wavelengths, nλ in order for constructive interference to occur. In order for a grating to be useful, the slit or groove spacing must be smaller than the incident wavelengths. The inverse of the slit spacing is known as the grating constant, which is the quantity to be measured in the first part of the laboratory. It is typically measured in units of lines/mm.

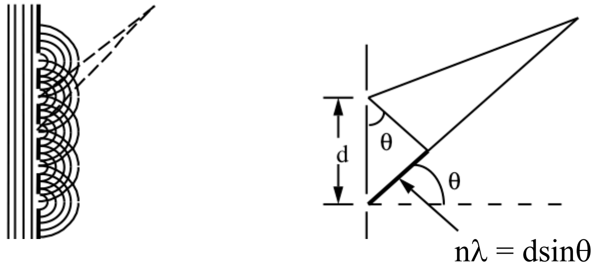


Figure 2

Left: Waves enter from the left and interfere after passing through the slits.

Right: Graphical representation of the diffraction equation.

In this laboratory, you will work with a diffraction grating mounted on a laser pointer to reinforce the operating principle behind the spectrometer.

Particle in a box model

The solutions to the equations that describe the energies of electrons in a hydrogen atom are for a system with a single electron. To solve these equations for complex multielectron systems the math becomes much more complex. There are many simplifications and assumptions that are required to make the math work. In this introduction, the math has been streamlined to show only the essential equations for relating the energy of an electronic transition to the bond length or particle size.

In this laboratory, you will investigate the optical properties of both one-dimension systems (linear alkenes) and three-dimension systems (semiconductor nanoparticles) using the particle in a box model.

One dimensional box – linear alkenes

The dependence of an absorption spectrum on particle size can be understood using the particle-in-a-box model. For a particle in a one-dimensional box of length *L*, the energy (E) is given by:

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

Equation 1

Where h is Planck's constant, and m is the mass of the particle. Figure 3 shows the energies, wave functions and associated probabilities for the first three energy levels.

Notice that the number of nodes in the wave functions (points where the wave function equals zero) increases as the energy increases.

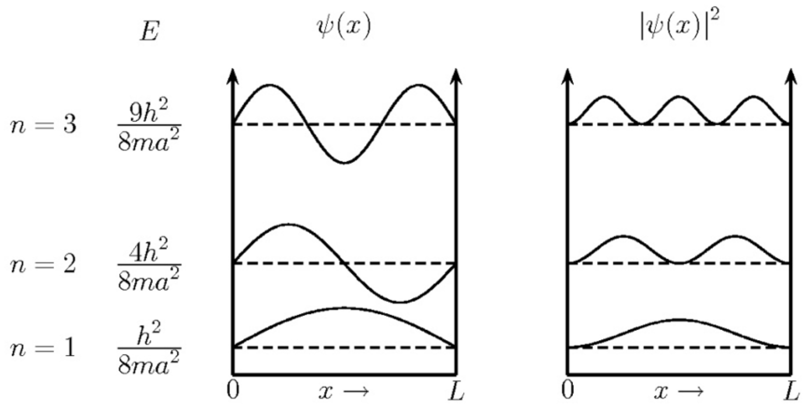


Figure 3 Particle in a box energies, wave functions and probabilities.

Application of the Particle in a Box Model to Linear Alkenes

Chemical bonding can be described using molecular orbitals (MO) constructed from linear combinations of atomic orbitals. As an example, consider ethene (CH_2=CH_2). In ethene, the carbons are sp^2 hybridized such that the 2s, $2p_x$, and $2p_y$ atomic are combined to produce sp^2 orbitals localized on each carbon. Carbon-hydrogen bonds is formed by the overlap of one of the C (sp^2) orbitals with the H(1s) orbital. The σ-bond between the two carbons is formed by overlap of the C (sp^2) orbitals from each carbon. Two $2p_z$ orbitals remain on each carbon atom, labeled $2p_{z1}$ and $2p_{z2}$, and these orbitals overlap to form a π bond. There are two ways to combine the p orbitals as illustrated in Figure 3: ($2p_{z1}$ + $2p_{z2}$) and ($2p_{z1}$ − $2p_{z2}$). When the orbitals are combined as ($2p_{z1}$ + $2p_{z2}$) a π bonding orbital is formed, and when combined as ($2p_{z1}$ − $2p_{z2}$) a π anti-bonding orbital is formed. The anti-bonding orbital has a reduced electron density between the carbon atoms in comparison to the bonding orbital; therefore, the energy of the anti-bonding orbital is greater as shown in Figure 4.

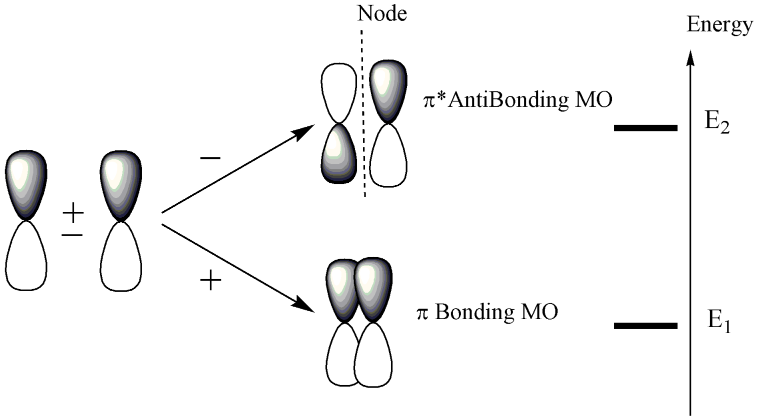


Figure 4 π bonding in ethene.

Figure 5 presents a qualitative energy diagram for ethene. Since σ bonds are stronger than π bonds, the σ bonds are located at lower energy relative to the π bonds. Also, since the C-H bond is stronger than the C-C bond (413 kJ/mole vs 347 kJ/mole) the C-H bond are placed at lowest energy.

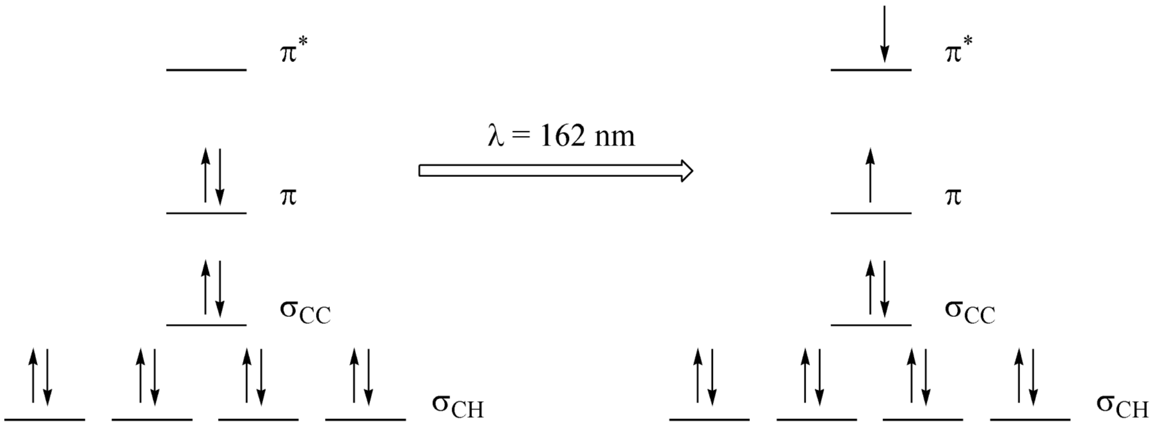


Figure 5 Qualitative energy level diagram for ethene. Left diagram is the ground state and the right diagram is the first excited state.

The 12 valence electrons in ethene are added to these energy levels according to the Aufbau principle and Hund's rules. Since the π electrons are "delocalized" between the carbon atoms, we can describe the energetics of the π orbitals using the particle-in-a-box model. The lowest-energy transition corresponds to the advancement of an electron from the highest occupied π orbital to the lowest unoccupied π orbital. The energy difference between these levels can be defined in terms of the quantum numbers j and n as:

$$\begin{aligned}\Delta E_{jn} &= E_j - E_n \\ &= \frac{j^2h^2}{8mL^2} - \frac{n^2h^2}{8mL^2}\end{aligned}$$ **Equation 2**

The lowest-energy transition corresponds to j = n+1; therefore, that the energy difference is:

$$\begin{aligned}\Delta E_{n+1,n} &= E_{n+1} - E_n \\ &= \frac{(2n+1)h^2}{8mL^2}\end{aligned}$$ **Equation 3**

For ethene, the highest occupied π orbital corresponds to n = 1 so that:

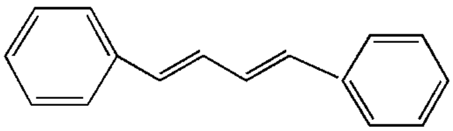
$$\Delta E_{21} = \frac{3h^2}{8mL^2}$$ **Equation 4**

This difference in energy is related to the wavelength of light corresponding to this transition (162 nm as indicated in Figure 4), corresponding to a "box" length of:

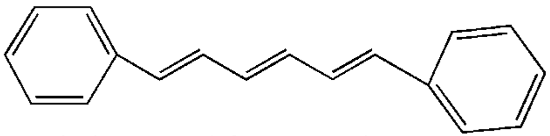
$$\begin{aligned}L^2 &= \frac{3h\lambda}{8mc} \\ L &= \sqrt{\frac{3h\lambda}{8mc}} = 3.8 \text{ x} 10^{-10} \text{ m}\end{aligned}$$ **Equation 5**

This length (3.8 Å is quite different from the C=C bond length of 1.34 Å (184% error!). The particle-in-a-box model assumes an electron has a 0% chance of escaping the box. However, the π orbitals extend past the centers of the carbon nuclei such that this model is only approximate This is a simplification that is required to be able to solve equations but is not really all that accurate. After all the description of a quantum mechanical orbital is a region of space where there is a 90% probability of finding the electron.

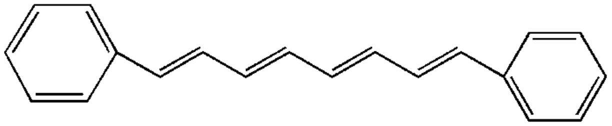
How does this model work for linear alkenes of variable size or box length? To address this question, we will apply the one-dimensional particle-in-a-box model to the following diphenyl substituted alkenes:



1,4 diphenyl-1,3-butadiene



1,6 diphenyl-1,3,5 hexatriene



1,8 diphenyl-1,3,5,7 octatetraene

The electrons in the π orbitals of the alkene chains are localized to a “box” defined by the distance between the phenyl rings. To calculate a theoretical box length, we will use 1.39 Å as the average length of a carbon-carbon bond in these molecules. For 1,4 diphenyl-1,3-butadiene, there are 5 bonds between the two phenyl rings such that the length of the box is 5 × 1.39 Å = 6.95 Å. The number of electrons in the box is the number of electrons in the π-bonding orbitals. For 1,4 diphenyl-1,3-butadiene, there are 2 double bonds corresponding to 4 electrons in the box. In the ground state electron configuration, there are two electrons in the n = 1 level and two in the n = 2 level. Therefore, the lowest-energy electronic transition corresponds to an advancement of an electron from the n = 2 (the highest occupied molecular orbital) to the n = 3 (the lowest unoccupied molecular orbital) level. According to the particle in a box model, the difference is energy between these levels is given by:

$$\begin{aligned} \Delta E_{32} &= \frac{5h^2}{8mL^2} = h\frac{c}{\lambda} \\ L &= \sqrt{\frac{5h\lambda}{8mc}} \end{aligned} \qquad \textbf{Equation 6}$$

By measuring the location of the lowest-energy the absorption band of 1,4 diphenyl-1,3-budatiene, one can determine λ and use this information to determine L. This process is repeated for the other two diphenyl alkenes.

Three-dimensional box – semiconductor nanocrystal quantum dots

The dependence of an absorption spectrum on particle size can also be understood using the particle-in-a-box model. Since the quantum dots are 3D spheres, and are filled with a crystalline semiconductor, solving the equations is a bit more complicated, but an approximate solution for the energy of the lowest energy absorption or emission peak in a small semiconductor quantum dot can be derived.

If we shine light on a macroscopic (bulk) semiconductor with energy larger than the band gap, E_{gap}, we can excite electrons from the valence band into the conduction band. ***What energy is required to excite electrons from the valence band to the conduction band in a small semiconductor nanoparticle?*** The energy of the lowest energy absorption transition is given by

$$E = E_{gap} + \frac{\hbar^2\pi^2}{2r^2}\frac{1}{m_e^*} + \frac{\hbar^2\pi^2}{2r^2}\frac{1}{m_h^*} - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 r} \quad \textbf{Equation 7}$$

In this equation E_{gap} is the energy of the band gap between the valence and the conduction band which is 1.74 eV for CdSe at room temperature.

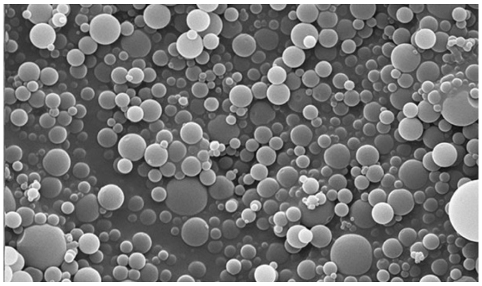
$\hbar$ is a special form of planks constant

r is the radius of the nanoparticle

m_e and m_f are the effective mass of the electron and the hole it leaves behind when it moves from the conduction to the valence band

ε ε_0 are constants that have to do with how electrons move.

Researchers were able to solve this equation by obtaining images of actual nanoparticles



http://en.farsnews.com/newstext.aspx?nn=13930507000184

Utilizing experimental values for the radius yields a much simpler equation for the relationship between the **energy (or wavelength) of the electron required to excite electrons from the valence band to the conduction band in a small semiconductor nanoparticle**.

Equation 7 becomes

$$\frac{1240}{\lambda_{half}} = A + \frac{B}{4r^2} - \frac{C}{2r} \quad \textbf{Equation 8}$$

the analysis and calculations section explains how to use this formula to solve for the radius.

In this laboratory, you will be studying CdSe and ZnO nanocrystals and will test how well the above discussion describes the behavior of real particles. You will measure the absorption and spectra of a series of CdSe quantum dots. You will make a plot of energy as a function of radius, and then use that as a calibration curve to estimate the sizes of the ZnO quantum dots you made in lab. You will also calculate the values of the radius of the ZnO particles using Equation 8. You will be able to compare your estimated values to your calculated values and discuss any variation.

IV. EQUIPMENT

To Bring: A flash drive if you have one. You may utilize the internet and email your data if you wish.

From drawers: Test Tubes
Set of 2 0.5 cm quartz cuvettes
Glass pipets
beakers
10-ml graduated cylinder
250 mL Erlenmeyer (for waste)
Stopwatch

The beaker, bottles and test tube should be cleaned before use. Rinse well with deionized water and then rinse two or three times with a little ethanol (the goal is to rinse out all of the water). Dispose of the ethanol in your Erlenmeyer flask until you have a chance to empty it into the bottle labeled " nanoparticle waste". Place the beaker, test tube and bottles upside down on some tissue until dry. The ZnO crystals will be grown at 50°C with temperature maintained using the appropriate water bath in the laboratory. Check to be sure the water bath is on and set to the correct temperature. Find a test tube clamp which will hold your test tube firmly and mount the clamp so it is just above the top of the tank.

V. OUTLINE OF THE EXPERIMENT

You will take spectra of 5 sets of samples (steps 3, 4, 5 and 6 outlined below). The spectra will be taken using Spectra Vis UV/VIS spectrophotometer. You must save an Excel file for all of the spectra you collect. In addition to taking spectra of the prepared samples.

1. Clean the bottles and test tube and leave to dry while you weigh out your zinc acetate and tetramethyl ammonium hydroxide
2. The synthesis of ZnO nanoparticles will take approximately 30 minutes and 90 minutes once all the solutions are prepared. Prepare solutions of Zinc Acetate and Tetramethyl Ammonium Hydroxide in ethanol. The Zinc Acetate solution will precipitate over time and thus should not be made up in advance.
3. Timed growth of ZnO nanoparticles in ethanol at room temperature. The growth will be done in the cuvette.
4. Timed growth of ZnO nanoparticles in ethanol at an elevated temperature. The reaction will be run in the test tube clamped into the water bath. The samples will be withdrawn from the test tube and diluted/cooled to room temperature.
5. A set of diphenyl polyenes in cyclohexane. Take one spectrum of each sample using the cuvette with cyclohexane as the reference. These will be analyzed using a one-dimensional particle-in-a-box model.
6. A set of CdSe nanoparticles in toluene. Take one spectrum of each sample using the cuvette with toluene as the reference. These will be analyzed using a three-dimensional particle-in-a-box (sphere) model.

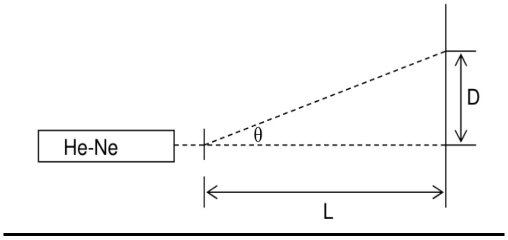
VI. PROCEDURES

A. Measuring the grating constant (lines/mm)

Find the laser/grating set-up. Measure the distance between the grating and the screen or wall. This distance is L.

Measure the distance between the zeroth order (undiffracted) and the other visible lines. This distance is D.

Use D and L to determine the angle θ. (See analysis and calculations)



B. Spectra of Diphenyl polyenes

Diphenyl polyenes. There should be 4 sealed quartz cuvettes. One will contain cyclohexane, which you will use as the reference. The others will contain one of the three diphenyl polyenes in cyclohexane. Plan to take spectra of the three diphenyl polyenes versus cyclohexane covering the region from 300 to 420 nm. Use the cursor to determine the wavelength of the peak corresponding to the lowest energy electronic transition and write the number into your lab book.

The wavelength of the photon from this transition is correlated with the energy of the transition using the equation 6.

C. Spectra of CdSe Nanoparticles (Prepared Samples)

CdSe nanoparticles. There should be 6 sealed plastic cuvettes. One will contain a blank, which you will use as a reference. The others will contain one of the CdSe/ZnS nanoparticles listed in the table below. The CdSe/ZnS nanoparticles were purchased from Navillum Nanotechnologies. The data in **Table 2** is from Navillum's catalog. We will refer to the samples by the name given to them by the manufacturer. Use the cursor to determine the wavelength of the peak corresponding to the lowest energy transition and write the number into your lab book.

Table 2. Properties of CdSe/ZnS nanoparticles

QD - Identifier	1st Exciton Peak (nm)	Diameter (nm)[1]	Molecular Weight (μg/nmol)
CZ-BLUE	480	2.3	8.4
CZ-GREEN	515	2.6	14
CZ-YELLOW	568	3.5	38
CZ-ORANGE	587	4.1	78
CZ-RED	620	5.6	200

1. Estimates from Navillum Nanotechnologies.
2. Units are Liters/(Mole cm)

Take absorption spectra of the five CdSe nanoparticles versus the given blank covering the region from 350 to 700 nm.

D. Synthesis and spectra of ZnO nanoparticles

ZnO(s) is formed from Zn^{2+} and OH^- via the reaction[3]:

Zn^{2+} (aq) + $2OH^-$ (aq) → ZnO (s) + H_2O $\Delta G° = -0.39$ kJ/mol

Water catalyzes this reaction and is also a product, making the reaction autocatalytic. The negative ΔG^{o} means that this reaction is spontaneous under standard conditions. One difficulty in making nanoparticles is that if the reaction is not controlled, the reaction will proceed to yield large macroscopic particles instead of the desired nanoparticles. There are various steps one can take to control the rate of nanoparticle growth. First, the reaction is conducted in ethanol at relatively low concentrations (< 20 mM). Second, although the stoichiometry of the reaction indicates that 2 moles of OH^- are required for each mole of Zn^{2+}, ≤ 1.5 equivalents of the base are added to the solution containing the Zn^{2+}. The growth of the nanoparticles will be monitored at both room temperature and an elevated temperature.

The ZnO nanoparticles are formed from the reaction of Zinc Acetate dihydrate with Tetramethyl Ammonium Hydroxide, pentahydrate in ethanol. The first set of spectra you will collect will be series of spectra taken as the ZnO nanoparticles form over approximately 32 minutes. The low concentrations used in this reaction result in a relatively slow reaction, which makes it easy to follow in a 1-cm path length cuvette. However, the resulting particles are fairly small and little is known about them. Therefore, a reaction will be run at higher concentration and temperature, and at set intervals, and small aliquot of the reaction mixture will be diluted to slow the rate of particle growth providing you time to create samples and take their absorption spectra.

1. Waste solutions. Label an Erlenmeyer flask "nanoparticle waste". Any waste solutions should be placed in there temporarily until you have a chance to empty the flask into the nanoparticle waste bottle in the hood.

Ethanol. Fill a clean beaker with 100% ethanol from the bottle in the flammable storage cabinet. Refill as needed, discard any excess at the end of the period.

Tetramethyl Ammonium Hydroxide ($N(Me)_4OH$). This should be supplied as the pentahydrate. Weigh out approximately 0.07 grams of $N(Me)_4OH{\cdot}5(H_2O)$, record the weight to three significant figures and place it in a specimen bottle. Using the molecular weight of 181.2 gram/mole, calculate how much ethanol must be added to make a solution which is 0.05 M in $N(Me)_4OH$ (the result should be around 7 ml). Add the ethanol, cap the bottle and swirl gently until all the $N(Me)_4OH$ is dissolved. Note: the Tetramethyl Ammonium hydroxide tends to stick to the weighing paper, so weigh the sample on the weighing paper, transfer as much as possible to the bottle and then reweigh the weighing paper. The difference will be the actual amount of base added to the bottle.

Zinc Acetate. This should be supplied as the dihydrate. Weigh out approximately 0.03 grams*** of $Zn(Acetate)_2{\cdot}2(H_2O)$, record the weight to two significant figures and place it in one of the specimen bottles. Using the molecular weight of 219.5 gram/mole, calculate how much ethanol must be added to make a solution which is 0.02 M in Zinc Acetate (the result should be around 7 ml). Add the ethanol, cap the bottle, and swirl gently until all the Zinc Acetate is dissolved. The solubility of Zinc Acetate in ethanol is low, so this process may take 10 to 15 minutes. This can be sped up somewhat by heating. Insert the end of the bottle into the water bath while gently swirling the liquid in the bottle until the Zinc Acetate is dissolved. Be sure the solution has cooled to room temperature before using it. If you store this solution until your next lab period, it may form ZnO precipitate. Before using, check any old solutions for signs of any white precipitate. If any white precipitate or cloudiness is seen, discard the solution into the appropriate waste container, clean the bottle and make a fresh solution.

3. Cleaning the cuvette. Impurities in the cuvette can cause the ZnO to precipitate out of solution. At the start of lab, rinse the cuvette well with DI water, dry the outside with tissue, and invert the cuvette onto a clean tissue. Blot the cuvette against the tissue until most of the water is gone. Add a small amount of ethanol (½ to 1 ml, it isn't necessary to be precise) to the cuvette. Tilt the cuvette so as to rinse all four walls of the cuvette with the ethanol. Pour off the ethanol, and invert the cuvette on a piece of tissue and blot until most of the ethanol is gone. Repeat the ethanol rinse three times. This is most important for part 4, where you will grow the ZnO nanoparticles in the cuvette. For part 5 it is not necessary to do this between samples, only once before you start taking spectra of your nanoparticles.

4. Growth of ZnO at room temperature. Be sure you have enough time to complete this before starting. These directions assume a 1-cm path length cuvette is being used. Place 1.25 ml of the Zn(acetate) solution and 5.0 ml of ethanol in a clean cuvette. Place the cuvette in the spectrometer cuvette holder and use it as a reference. Set the software to collect absorbance. Set the display to show wavelengths from 230 to 400 nm, and absorbances from 0 to 1.5. Add 0.50 ml of the Tetramethyl Ammonium Hydroxide solution. Stopper the cuvette and shake gently for a few seconds to mix (do not shake the cuvette so much that the solution splashes). Place the cuvette back in the spectrometer cuvette holder and save an absorbance spectrum. Take additional spectra at approximately 1 min, 2 min, 4 min, 8 min, 16 min, and 32 minutes after you added the base solution (7 spectra in all, the times do not need to be exact just record the actual value.)

Write instructions here for collecting data using Logger pro.

Do a dry run before you start so you are comfortable using the spectrometer software and you have usable saved data.

5. Growth of ZnO at 50°C (corrected) Be sure you have enough time to complete this before starting. These directions assume a 1-cm path length cuvette is being used. Take 8 small vials and label them 1 through 8 using the labeling tape. The aliquots removed from the reaction mixture will be diluted with room temperature ethanol in these vials. Put 5.75 ml of ethanol in each vial. Place 5.00 ml of the Zn(acetate) solution in a clean test tube (it is not necessary to preheat this solution). Draw up 3.00 ml of the tetramethyl ammonium hydroxide solution in the pipet. Insert the pipet into the test tube until the pipet tip is about one cm above the surface of the Zn(acetate) solution and gently add the base solution. Mix by swirling the tube for several seconds and then clamp the test tube in the water bath (do not shake the cuvette so much that the solution splashes). Get the tube as far into the water as possible. Start the stopwatch. After 1 minute, remove 0.50 ml of the reaction mixture and place it in vial 1. Cap vial 1 and mix gently. 2 minutes after the tube was placed in the water bath, remove 0.2 ml of the reaction mixture and place it in vial 2. Cap vial 2 and mix gently. Continue taking samples at 4, 8, 16, 30 ,60 and 120 min (note that the times are not evenly spaced). The time between withdrawals increases as the reaction proceeds, because the rate at which the particle diameter increases slows as the reaction proceeds. You do not need to use a different pipet for each sample. Just make sure you have expelled all the ethanol from the previous sample before taking a new sample.

Take the absorbance spectrum of each of your samples as before, using ethanol as a blank. You do not have to wait until all the samples have been collected to start taking the absorbance. After sample 4 or 5, there should be enough time for you to start collecting absorbance spectra for some of your samples. If the absorbance of the peak is greater than 1.2, dilute the sample with ethanol until it is less than 1.0 (add ethanol to the cuvette). See Figure 6 for an example of a peak.

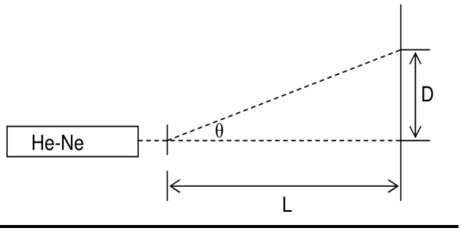
Since we are not going to be analyzing the kinetics of the growth, the times do not need to be very exact. They were chosen to yield a reasonable range of particle sizes. Just be sure to record your actual time.

6. Troubleshooting. Be sure the outside of the cuvette is clean and that you have properly stored the dark spectrum and reference spectrum for your cuvette. If the spectra do not look like the spectrum **in Figures 6 – 7**, but instead show a nearly flat absorbance everywhere, it probably means that the ZnO is forming large particles which are scattering light. Check first to make sure you are using the correct reference spectrum. If you are, clean the cuvette. If the problem persists, stop the reaction and remake the Zinc Acetate solution. When the sample scatters light, it shows up as an absorption, which is larger for small wavelengths than long wavelengths. Therefore, in an absorbance spectrum, scattering appears as a sloping baseline which decreases with increasing wavelength. Do not shake the cuvette so much that the solution splashes. When you shake the cuvette or test tube you nucleate the reaction. Shaking a lot creates more nanoparticles, but not larger ones. Too many nanoparticles can drive the absorbance off scale. Gentle shaking is sufficient.

Analysis and Calculations

A. Analysis of Diffraction Grating to determine Grating Constant d (lines/mm)

Use D and L to determine the angle θ.



Use the equation, $n\lambda = d\sin\theta$ To determine the spacing between the slits in the diffraction grating (d)

In this relationship, d is the spacing between the openings, θ is the angle of diffraction, and n is an integer corresponding to the "order" of the diffracted wave

B. Analysis of Diphenyl alkenes.

1. Determine the peak wavelength of the lowest-energy transition for each diphenyl alkene.

2. Determine the “box length” for each diphenyl alkene using the particle in a 1- dimensional box model using Equation 6.

3. Compare the results with the actual lengths calculated from the average lengths of the carbon-carbon bonds.

4. Include a single plot showing all your spectra for all the alkenes.

5. Your results table should include the lengths calculated from the spectra and the actual lengths of the alkene chain and a percent error.

Spectra of nanoparticles. There are two characteristic wavelengths which you will extract from the spectra of the nanoparticles, λ_{peak} and λ_{half}. For the CdSe nanoparticles you will determine λ_{peak}. For the ZnO nanoparticles you will need λ_{half} and λ_{peak}. Figures 6 and 7 illustrate how to determine λ_{peak} and λ_{half} , respectively.

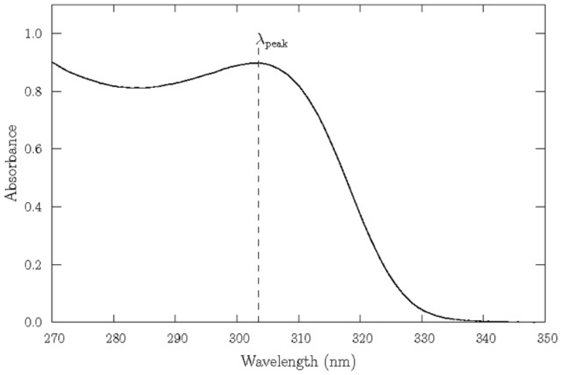


Figure 6. Definition of λ_{peak}.

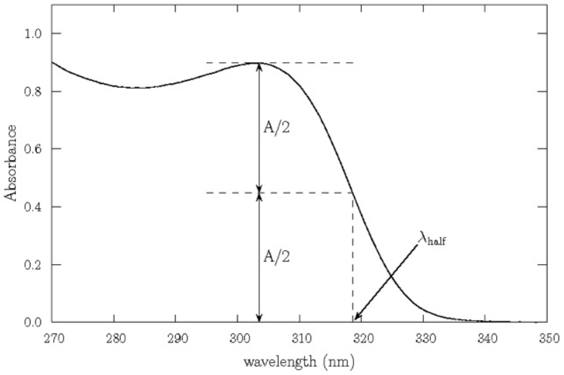


Figure 7. Definition of λ_{half}.

C. Analysis of CdSe nanoparticles.

1. Include a single plot showing all your spectra for the CdSe nanoparticles. Be sure to indicate λ_{peak} for each spectrum.
2. Prepare a plot of calculated E versus $1/r^2$. Equation 8 suggests that the first transition energy should scale with particle radius as $1/r^2$. Test this prediction. Convert your measured λ_{peak} into energy and make a plot of peak E versus $1/r^2$. These values of E are your experimental values and this curve is your experimental curve.

D. Analysis of ZnO nanoparticles. For each ZnO nanoparticle synthesis time point determine the values of λ_{half}, λ_{peak}, E, and the predicted nanoparticle radius. You will use an empirical equation which has been adjusted to size calibrated particles to determine the radii[4]:

$$\frac{1240}{\lambda_{half}} = A + \frac{B}{4r^2} - \frac{C}{2r} \quad \textbf{Equation 8}$$

where $A = 3.301$, $B = 294.0$, $C = -1.09$, λ_{half} is in nm, and r is the particle radius in nm. Note: the model is only applicable for particles with absorbances between $330 \text{ nm} < \lambda_{half} < 370 \text{ nm}$.

1. Include a plot showing all your spectra for the ZnO nanoparticles for each experiment (room temperature and 50 degrees). Indicate determination of λ_{half} and λ_{peak}.

2. Prepare a plot of radius vs time for each experiment (room temperature and 50 degrees)

3. Provide a sample calculation of the determination of a radius using Equation 8.

4. Predict the radius of the ZnO samples using use your CdSe standard curve. Calculate a percent error based on your experimental value and the predicted values from the CdSe standard curve.

5. Prepare a graph of E vs 1/r2 for each experiment (room temperature and 50 degrees)

6. For each ZnO nanoparticle experiment compile a table summarizing your measured values of λ_{half}, λ_{peak}, E, and the experimental and predicted nanoparticle radius at each time point.

XI. ADDITIONAL QUESTIONS (May use these)

1. R.B. Laughlin, Phys. Rev. B22, 3021 (1980) reports the Band Gap of crystalline quartz to be 8.9 eV. Use this information to explain why quartz is transparent in the visible. Based on this number, what is the longest wavelength of light that you would expect quartz to absorb due to an electronic excitation?

2. Electrons will generally only be excited thermally from the valence band to the conduction band when the thermal energy is comparable to the band gap. Calculate kT for room temperature and compare it to the band gaps of ZnO and CdSe. At what temperature is kT equal to the band gaps of ZnO and CdSe?

3. Why is the effective mass for an electron in a solid different from that of an electron in vacuum? What is the meaning of the effective mass of a hole?

4. Examine the plots showing the spectra of samples taken on different days. Are your samples at equilibrium? If not, what would you expect the spectra to look like if the solutions were at equilibrium?

5. Carefully compare your CdSe data with the theoretical prediction from Eqn. 3 and comment on any similarities and differences. Does your experimental data for CdSe show the theoretically predicted $1/R^2$ dependence on energy? What reasons could you give for any discrepancies in both the shape and position of the curve?

6. Try to improve the agreement between theory and experiment that you discussed in Additional Question 5. Perhaps the values we chose weren't the best selection possible. Fig. 5 clearly shows that the effective mass (band curvature) changes with E, while the values of 0.13 m_e and 0.45 m_e were taken at the band minimum. Improve the agreement between theory and experiment by adjusting the appropriate values in Equation 3. (Hint: it will be helpful to set up an Excel spreadsheet that lets you replot the data by typing different values for the parameters in Eqn. 3 into one or more cells).

XII. REFERENCES

1. T. Engel and P. J. Reid, "Physical Chemistry", 3rd edition, Prentice Hall, Upper Saddle River, NJ, 2013.

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3. D. A. Schwartz, N. S. Norberg, Q. P. Nguyen, J. M. Parker and D. R. Gamelin, "Magnetic quantum dots: Synthesis, spectroscopy, and magnetism for Co2+ and Ni2_ doped ZnO nanocrystals, J. Am. Chem. Soc, 2003, *43*, 13204-13218.

4. E. A. Meulenkamp, Synthesis and Growth of ZnO Nanoparticles, J. Phys. Chem. B. **1998**, 102, 5566-5572.

5. A. Wood, M. Giersig, M. Hilgendoff, A. Vilas-Campos, L. M. Liz-Marzán, and P. Mulvaney, Size Effects in ZnO: The Cluster to Quantum Dot Transition. Australian Journal of Chemistry, **2003**, 56, 1051-1057.

Background References.

S. V. Gaponenko, Optical Properties of Semiconductor Nanocrystals, **1998**, Cambridge University Press, New York.

XIII. APPENDIX

Table of Physical constants and units

Symbol	Value	Name
h	$6.626\text{x}10^{-34}$ J•s	Planck’s constant
e	1.602×10^{-19} Coulombs	Electron charge
c	3.00x108 m/s	Speed of light
1eV*	$1.602 \text{ x } 10^{-19}$J	electron volt
m_e	$9.109 \text{ x } 10^{-31}$ kg	Mass of an electron

*The electron volt is a unit of energy which is defined as the energy associated with moving an electron through a potential of one volt.

$$1\text{ eV} = \left(1.602 \times 10^{-19}\text{ Coulombs}\right)\left(1\text{ Volt}\right) = 1.602 \times 10^{-19}\text{ Joule}$$

I. HAZARDS

Ethanol is flammable and should be kept away from flames. Zinc Acetate, Zinc Oxide and Tetramethyl Ammonium Hydroxide are toxic, and should be disposed of as described below.

II. WASTE DISPOSAL

The product of the reactions is ZnO in ethanol. It should be disposed in the marked bottle in the hood. Take a 250 ml Erlenmeyer flask and label it nanoparticle waste. Collect the waste solution in the flask until you have a chance to empty the flask into the waste bottle in the hood.