

UV-Visible Absorption Spectroscopy

Physical Chemistry Laboratory - CHEM 329

References

Shoemaker/Garland/Nibler, "Customized Experiments in Physical Chemistry", 6e
Absorption Spectrum of a Conjugated Dye

Sime, "Physical Chemistry"
Spectrum of a Particle in a Box

Lowe, "Quantum Chemistry", 2e

Nedeljković/Patel/Kaufman/Joyce-Pruden/O'Leary, "Synthesis and Optical Properties of Quantum-Size Metal Sulfide Particles in Aqueous Solution", *J. Chem. Edu.*, **1993**, 70, 342.

Safety

In this experiment, we will work with four thiocyanine dyes and two types of CdSe quantum dots (QDs). These chemicals are toxic, and some are probably carcinogenic. Wear gloves, handle with care, and immediately wash any contact of chemicals or their solutions with soap and water.

Theory

The absorption bands observed in these systems are due to *electronic transitions* from the ground state to an excited state. During such a transition in a molecule, electrons are promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (Figure 1a). In a semiconductor bulk solid or nanoclusters, the transitions occur between the valence band (VB) and conduction band (CB), as shown in Figure 1b. The VB and CB are the solid state analogue of the HOMO and LUMO of a molecule. E_g is the band gap or energy difference between the valence and conduction bands.

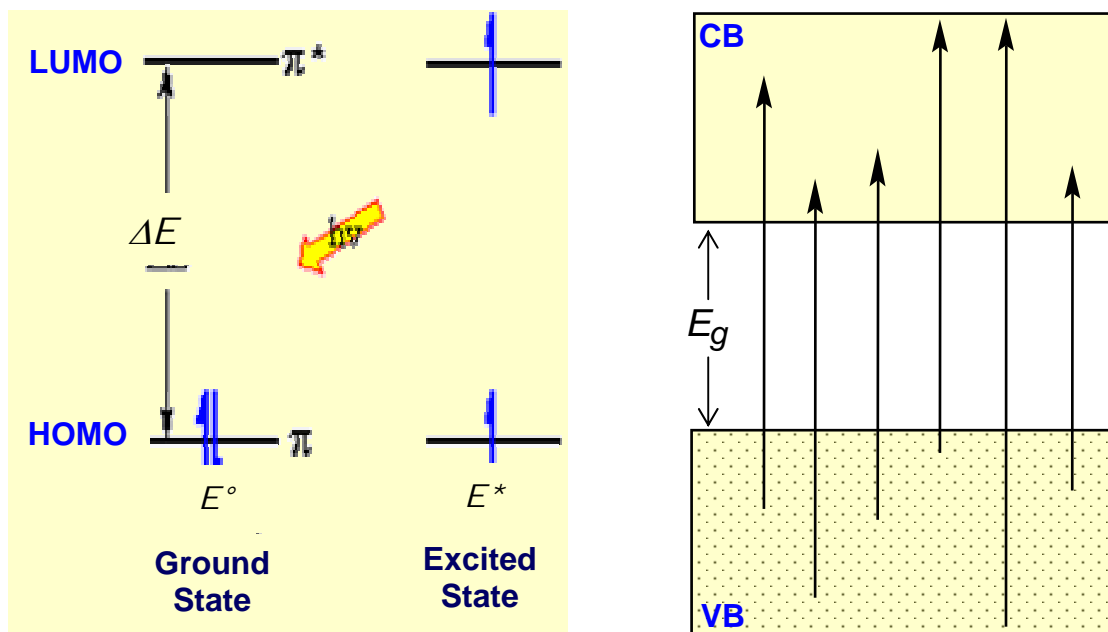


Figure 1. Energy diagram and electronic transitions in (a) a molecule, and (b) a bulk solid.

The energy absorbed:

$$\Delta E = (E^* - E^0) = h\nu = (hc)/\lambda$$

$$\text{UV region} \quad \Delta E = 190\text{-}400 \text{ nm}$$

$$\text{VIS region} \quad \Delta E = 400\text{-}800 \text{ nm}$$

The electronic energy levels in these systems can be estimated using a very simple “particle-in-a-box” model.

Dyes: One-dimensional (1D) Box

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

$$\Delta E = E_{n+1} - E_n = \frac{h^2 (2n + 1)}{8m_e L^2}$$

Where,

n = quantum number (1, 2, 3 ...)

h = Planck's constant

m_e = electron mass

L = length of the 1D box

E_{n+1} = energy of LUMO

E_n = energy of HOMO

For a dye molecule having N π -electrons:

$$\Delta E = \frac{h^2 (N + 1)}{8m_e L^2} \quad \text{for } N = \text{even}$$

$$\Delta E = \frac{h^2 (N + 2)}{8m_e L^2} \quad \text{for } N = \text{odd}$$

Where,

$N = 2n$ for $N = \text{even}$

$N = 2n - 1$ for $N = \text{odd}$

n = number of *occupied* π -type orbitals (assuming each atom contributing one orbital)

QDs: Three-dimensional (3D) Box

Semiconductor quantum dots are very small particles of semiconductors. These particles are clusters of atoms ranging typically from 1 nm to 10 nm in diameter. They exhibit quantum-like

properties that differ from those present in the bulk form of the same material due to the confinement of electrons in the dots. The phenomenon is called *quantum confinement*. Other terms such as ‘nanocrystal’, ‘nanocluster’, or ‘nanoparticle’ are also used. Nanoparticles can be just about anything whose dimensions are on the nanometer scale, while nanocrystals usually refer to nanometer-sized inorganic solids such as metals, insulators or semiconductors. ‘Quantum dot’ is a term usually applied to semiconductor nanocrystals in a size limit whose volume is smaller than the volume defined by *Bohr radius* of that particular semiconductor.

The electronic energy levels of quantum dots can be estimated using the elementary electron-hole in a three-dimensional box model.

For an electron in a 3D cubic box, the energy levels can be written as:

$$E_n = \frac{h^2}{8m_e L^2} (n_x^2 + n_y^2 + n_z^2)$$

Where;

$$L = L_x = L_y = L_z$$

$n_x, n_y, n_z =$ quantum numbers

For a spherical semiconductor quantum dot, the energy expression can be derived using the confined Wannier exciton Hamiltonian:

$$E_n = E_g + \frac{n^2 h^2}{8m^* R^2} - \frac{e^2}{4\pi\epsilon_0 \epsilon R}$$

Where;

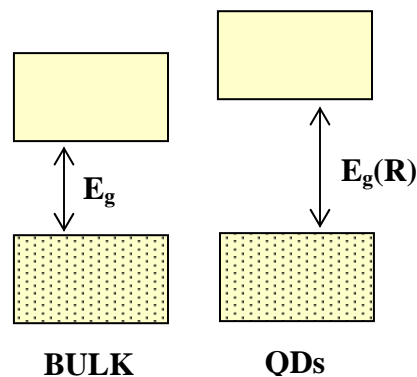
$E_g =$ band gap of the bulk semiconductor
 $n =$ quantum number (1, 2, 3 ...)
 $h =$ Plank’s constant
 $m^* = (m_e \times m_h)/(m_e + m_h)$
 $m_e =$ effective mass of electron, $m_h =$ effective mass of hole
 $R =$ radius of the QDs
 $\epsilon =$ semiconductor dielectric constant

For the electronic transition from the valence band to conduction band ($n = 1$), ignoring small contributions from $1/R$ term:

$$E_g(R) = E_g + \frac{h^2}{8R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right)$$

and;

$$\Delta E_g = E_g(R) - E_g = \frac{h^2}{8R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right)$$



Where;

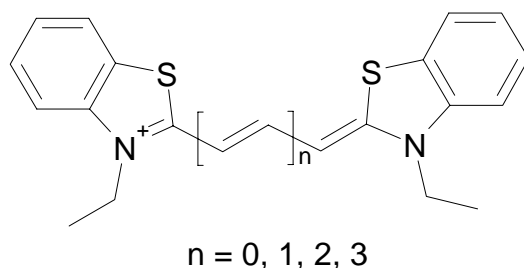
$E_g(R)$ = band gap of the QDs

ΔE_g = change in band gap energy due to quantum-size effect

From the above equations, it is clear that the absorption energy of quantum dots will shift to higher frequency [$E_g(R) > E_g$] with decreasing diameter of the dots with a dependence of $1/R^2$.

Paet I: Conjugated Dyes

You will work with four thiacyanine dyes with a general structure shown below:

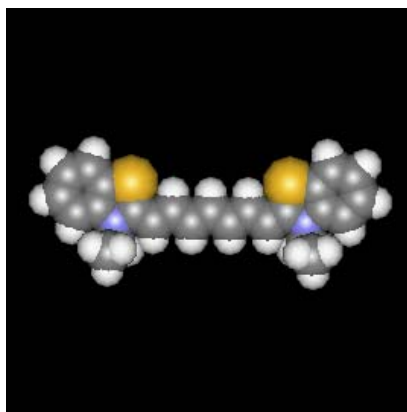


As the conjugated chain length increases from $n = 0, 1, 2,$ and $3,$ or 1 to $3, 5,$ then 7 carbon atoms, the energy of the electronic transition is reduced (see Figure 2). In terms of molecular orbital theory, the energy gap between the HOMO and LUMO decreases.

You will measure the transition energy (defined as the peak of the absorbance spectrum), and correlate this with the length of the conjugated π -electronic system of the molecule.

To assist you in learning about these molecules, we have placed a program called WebLab Viewer Pro (3.5 Trial) on the computers in the p-chem. lab, WL-165. The molecule files are found in the C:\PchemLab directory, and are called DTC_pm3.msv, DTCC_pm3.msv, DTDC_pm3.msv, and DTTC_pm3.msv for $n = 0, 1, 2,$ and 3 cases, respectively. Using WebLab ViewerPro you can rotate the molecules, display the van der Waals surfaces (or ball-and-stick, or other representations), and measure distances between atoms. The "Spin" function from the View menu is particularly fun. To measure distances between atoms, Shift-select two atoms with the Arrow tool, then use the Tools -> Monitors -> Distance to draw a labeled distance vector between the atoms.

For each molecule, choose several different distance measures: Use the furthest distance between carbon atoms on opposite rings, the distance between the two nitrogen atoms, the distance between the two sulfur atoms etc. From these data, you will determine the extent of conjugation by comparing measured electronic transition energies and those predicted by the solutions to the Schrodinger equation for an electron in a one-dimensional infinite potential box. The molecules are planar (with the exception of the $n = 0$ case, and the diethyl groups), as shown in the 'CPK' representation below.



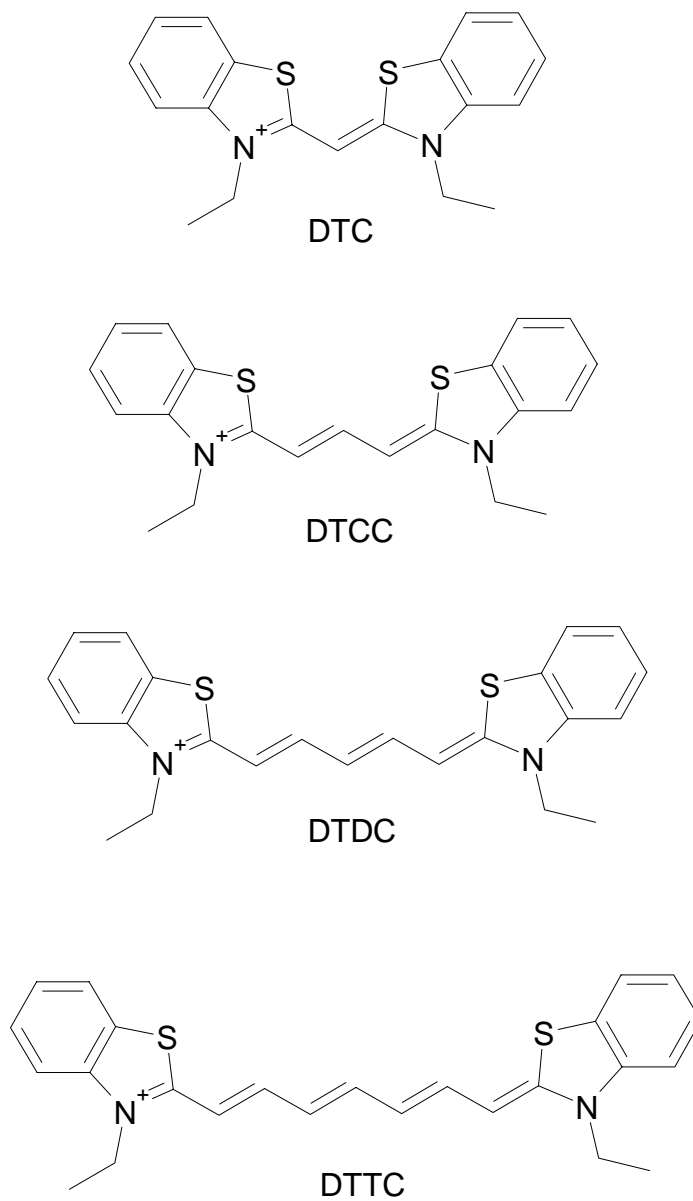


Figure 2. Structures of the four thiocyanine dyes

DTC (n=0):	[2197-01-5]	3,3'-diethylthiocyanine iodide
DTCC (n=1):	[905-97-5]	3,3'-diethylthiacarbocyanine iodide
DTDC (n=2):	[514-73-8]	3,3'-diethylthiadibocyanine iodide
DTTC (n=3):	[3071-70-3]	3,3'-diethylthiatribocyanine iodide

Paet II: CdSe Quantum Dots (QDs)

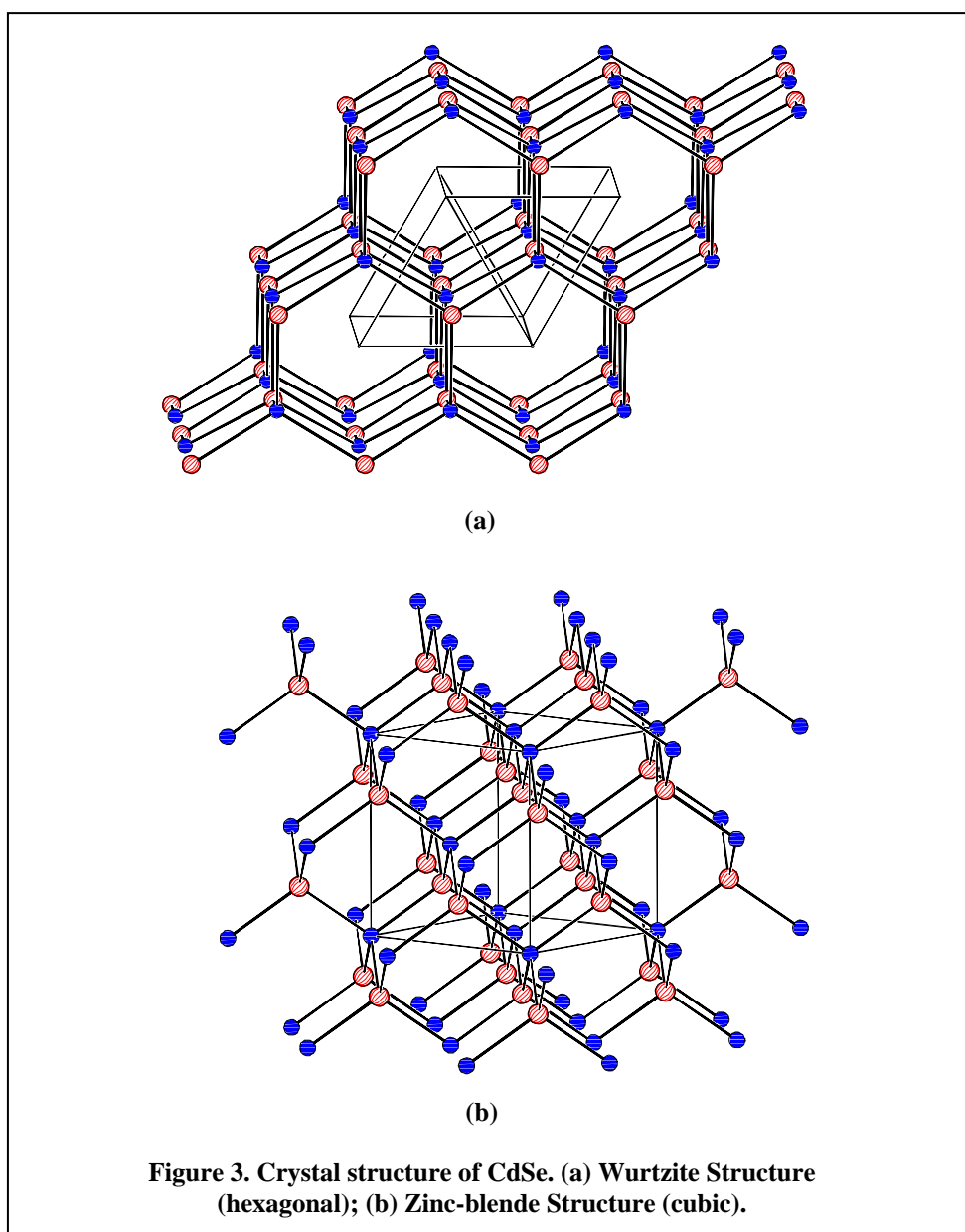
You will take absorption spectra of CdSe quantum dots of two different sizes.

Green dots in a toluene solution

Red dots in a toluene solution

You will calculate the band gap of each QD and compare them with the value of the CdSe bulk and report the observed blue shift (band gap shifting to higher energy) in each case. You will then calculate the size of each dot and understand the size effect on the band gap shift.

The crystal structure of CdSe semiconductor can be either wurtzite or zinc-blende (see Figure 3). You will need to find the band gap values from literature.



Use of Ocean Optics, Inc. Chem2000 Computer-based Spectrometers

1. Turn on spectrometer lamp using toggle switch at rear of blue housing. The lamp must stabilize for at least 15 minutes after turn-on.
2. From the Start menu on the PC to which the blue fiber optic cable is attached (at rear), run the program OOIChem from the Start menu.
3. Select "Scope" from the "Mode of Operation" pull-down menu.
4. Check that the instrument settings at the right of the screen read as follows:
Integ. Period 5 ms
Average 1
Boxcar Smooth 0
5. Carefully place the sample "blank" (cuvette containing only solvent, no dye) in holder.
6. Make sure lamp is not blocked. Click "Reference" to acquire a reference (or I(0)) spectrum. Adjust integration period to fill the screen, but not to overflow. If your spectrum in "Scope" mode has a flat top, you have saturated the detector. Reduce the Integration period in increments of 1 ms at a time until there are no further flat spots. Remember that the instrument uses a 12-bit Analog/Digital converter, and thus can't count beyond the range of 0 to $2^{12} - 1$ (or 4095). When a good reference spectrum has been obtained, click "Store" to save the reference spectrum.
7. Block the lamp (*e.g.*, using a piece of scrap metal or other thin, opaque material). Now click "Dark" to acquire a dark background, and "Store" to save the background. Click the check box underneath the "Dark" button labelled "Subtract Dark". Unblock the lamp.
8. Remove the blank, and insert the sample cuvette containing the thiocyanine dye solution into the holder. Change "Mode of Operation" to "Absorbance".
9. Click "Scan" to record the absorption spectrum.
10. Now increase the signal to noise ratio (S/N) by increasing the number of scans. Do this by changing the value of "Average" from 1 to 500. (Recall that S/N increases proportional to the square root of N). Repeat steps 5 - 9.
11. Save the absorption spectrum. Go to the "File" menu, and select "Save Spectral Values". Choose the PchemLab sub-directory with your TA's name on the C:\ drive.
12. Repeat until you have the absorption spectra for each of the cyanine dyes. Copy your spectra to a 3.5" floppy diskette.