Title: UV-Vis

Alan Yu*, Harrison, Dante, Joshua, Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08901.

Abstract

In the experiment, the particle in a 1-D box was considered to predict a wavelength at peak absorption and the change in energy compared to experimental results using conjugated pi systems of cyanine dyes. From the experiment, the peak absorption wavelengths of DTC, DTCC, DTDC, and DTTC were 425nm, 560nm, 650nm, and 765nm respectively. Using these wavelengths the change in energy for the four compounds were 2.91eV, 2.21eV, 1.91eV, and 1.62eV respectively. For the approximations, the peak absorption wavelengths of DTC, DTCC, DTDC, and DTTC were 201nm, 266nm, 343nm, and 411nm respectively. Using these wavelengths, the approximated change in energy was found to be 6.17eV, 4.67eV, 3.61eV, and 3.02eV respectively. From quantum dots, the band edge was found to be 577.7nm, the band gap was found to be 2.15eV, the bulk band gap was found to be 1.74eV and the radius of CdSe was found to be 2.72nm.

*To whom correspondence should be addressed.

Introduction

There were two sections to this experiment. The first section was to determine the accuracy of calculating the peak absorbance wavelength and the change in energy using the derived particle in a 1-D box approximation.

$$\Delta E = \frac{h^2}{8mL^2}(N + 1) = \frac{hc}{\lambda} \tag{1}$$

This equation contains E being the energy, h being Planck's constant, m being the mass of an electron, L being the length of the molecule, N being the number of pi electrons in the molecule, c being the speed of light and λ being the wavelength. For our molecules, DTC has 22 pi electrons, DTCC has 24 pi electrons, DTDC has 26 pi electrons, and DTTC has 28 pi electrons. This equation can also be used without using the 1-D approximation yielding:

$$\Delta E = \frac{hc}{\lambda_{exp}} \tag{2}$$

with λ_{exp} being the experimental wavelength. Having these wavelengths, the Beer-Lambert law is used to decipher the relationship between concentration and the absorbance of a substance.

$$A = \varepsilon cL \tag{3}$$

Where A is the absorbance, ε is the molar absorptivity, c is the concentration and L is the cell path length.

Moving on to the second section of the experiment being quantum dots. To find the radius of a quantum dot, R, a lot of other information must be calculated or known. The first equation being

$$\Delta E_g = E_g(R) - E_g(\infty) \tag{4}$$

Where $E_g(R)$ is the energy of the band gap, and $E_g(\infty)$ is the energy of the bulk band gap. After finding this,

$$\Delta E_g = \frac{\pi^2\hbar^2}{2R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{\varepsilon R} \tag{5}$$

can be used with R being the radius of the quantum dot, ε being the semiconductor dielectric constant, m_e being the effect mass of the electron, m_h being the effect mass of the hole, $\hbar$ being the reduced Planck's constant, and e being the .

Methods

Since the labs are cancelled, the data was provided by the professor so there will be no method explanation.

Results

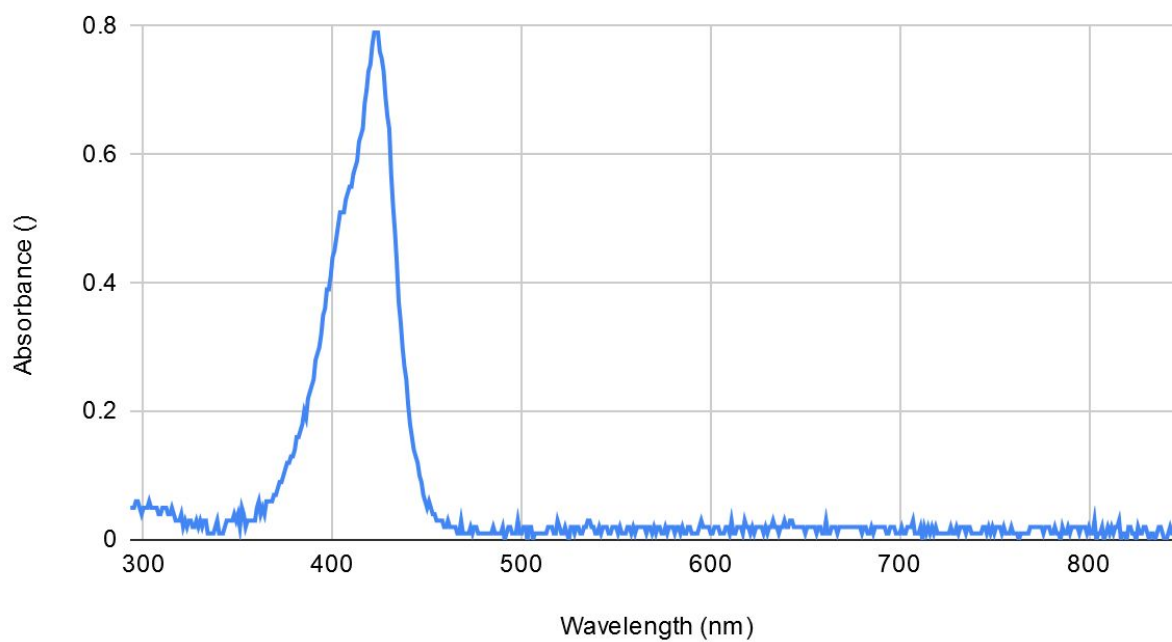## Absorbance vs Wavelength (nm) for DTC Yellow

Figure 1. Absorbance vs Wavelength plot for DTC Yellow.

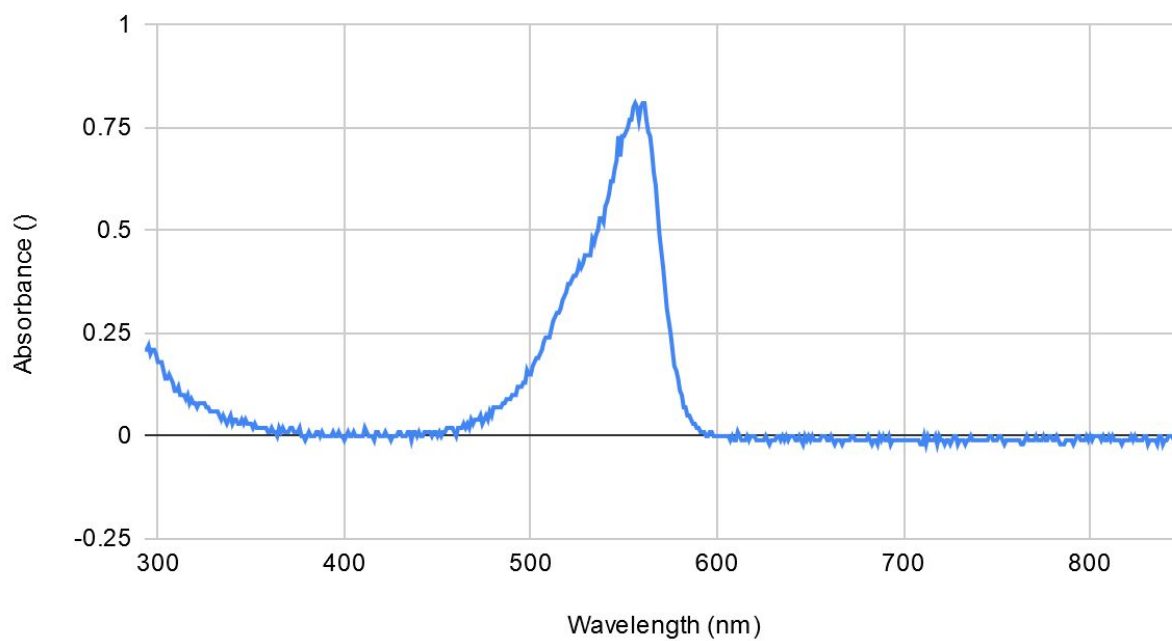## Absorbance vs Wavelength (nm) for DTCC Pink

Figure 2. Absorbance vs Wavelength for DTCC Pink.

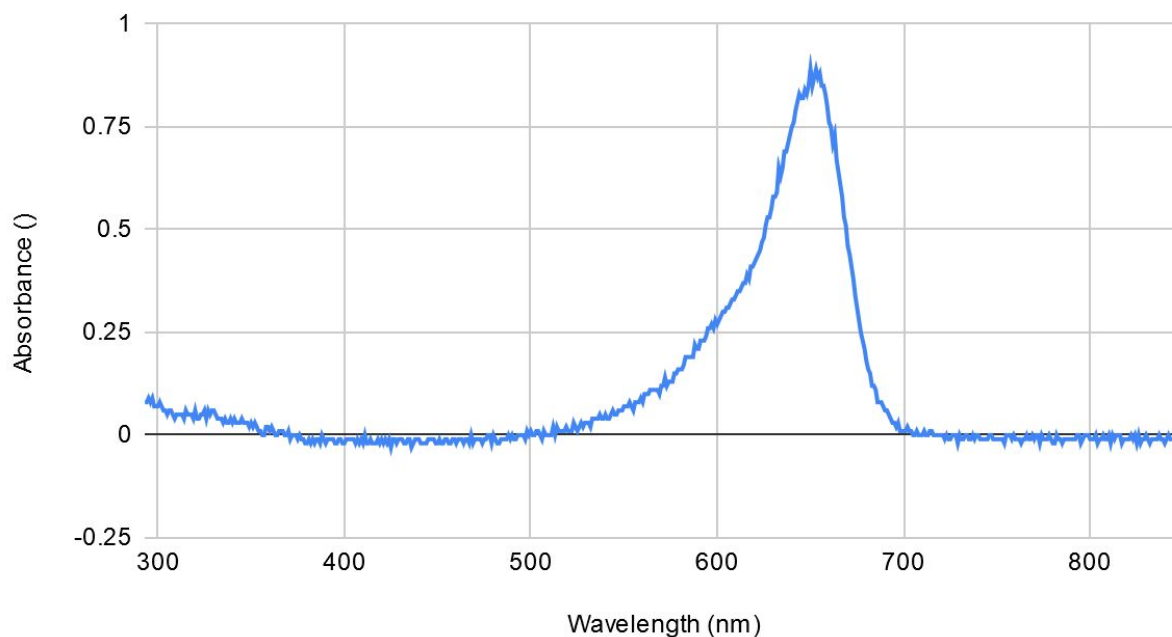# Absorbance vs Wavelength (nm) for DTDC Blue

Figure 3. Absorbance vs Wavelength for DTDC Blue.

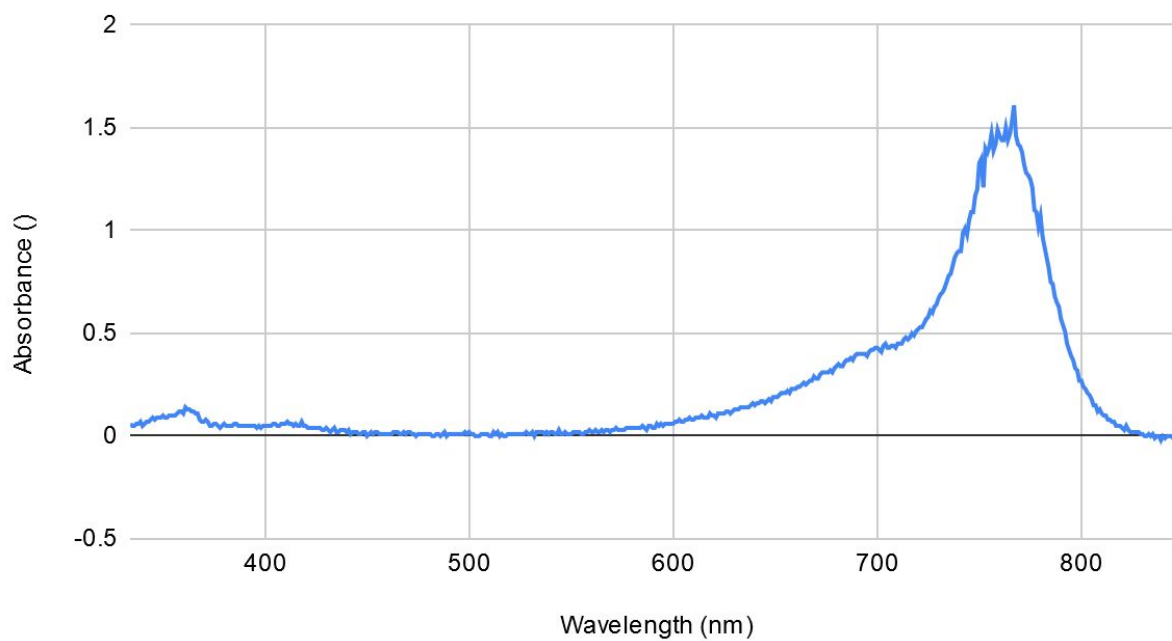# Absorbance vs Wavelength (nm) for DTTC Green

Figure 4. Absorbance vs Wavelength for DTTC Green.

Table I: Cyanine Dyes

Molecule	Length Å	Exp Wavelength nm	Calc Wavelength nm	Change in E Exp eV	Change in E Calc eV
DTC	11.84	425	201	2.91	6.17
DTCC	14.19	560	266	2.21	4.67
DTDC	16.76	650	343	1.91	3.61
DTTC	19.01	765	411	1.62	3.02

Sample calculations:

For DTC:

Using equation 1 from the introduction:

$$\Delta E = \frac{h^2}{8mL^2}(N+1) = \frac{hc}{\lambda}$$

Calculated Values:

N = 22 pi electrons

$L = 11.84\text{Å} * \frac{1\,m}{1*10^{10}\text{Å}} = 1.184*10^{-9}\text{m}$

$\Delta E = \frac{(6.626*10^{-34}J/s)^2}{8*(9.11*10^{-31}kg)*(1.184*10^{-9}m)^2}(22+1) = 9.88*10^{-19}$ J $* \frac{1\,eV}{1.60218*10^{-19}J} = 6.17$ eV

$\Delta E = \frac{hc}{\lambda} \rightarrow \lambda = \frac{hc}{\Delta E} = \frac{(6.626*10^{-34}J/s)*(2.998*10^8 m/s)}{9.88*10^{-19}J} = 2.01*10^{-7}$ m = 201nm

Experimental Values:

Using equation 2 from the introduction:

$$\Delta E = \frac{hc}{\lambda_{exp}}$$

$\lambda_{exp} = 425\text{nm} * \frac{1\,m}{1*10^9 nm} = 4.25*10^{-7}\text{m}$

$\Delta E = \frac{(6.626*10^{-34}J/s)*(2.998*10^8 m/s)}{4.25*10^{-7}m} = 4.67*10^{-19}$ J $* \frac{1\,eV}{1.60218*10^{-19}J} = 2.91$ eV
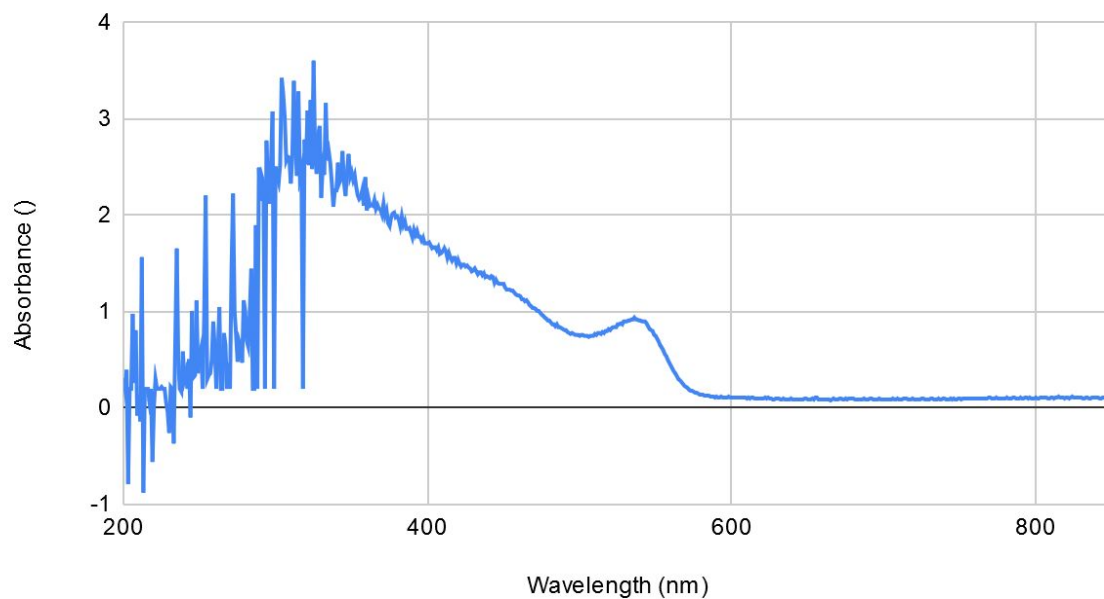
Absorbance vs Wavelength (nm) for CdSe

Figure 5. Absorbance vs Wavelength for CdSe.

To find the band edge, we use the method as suggested from Nedeljkovic[1] et al. where an intersection of the tangent with the wavelength axis is found/calculated.
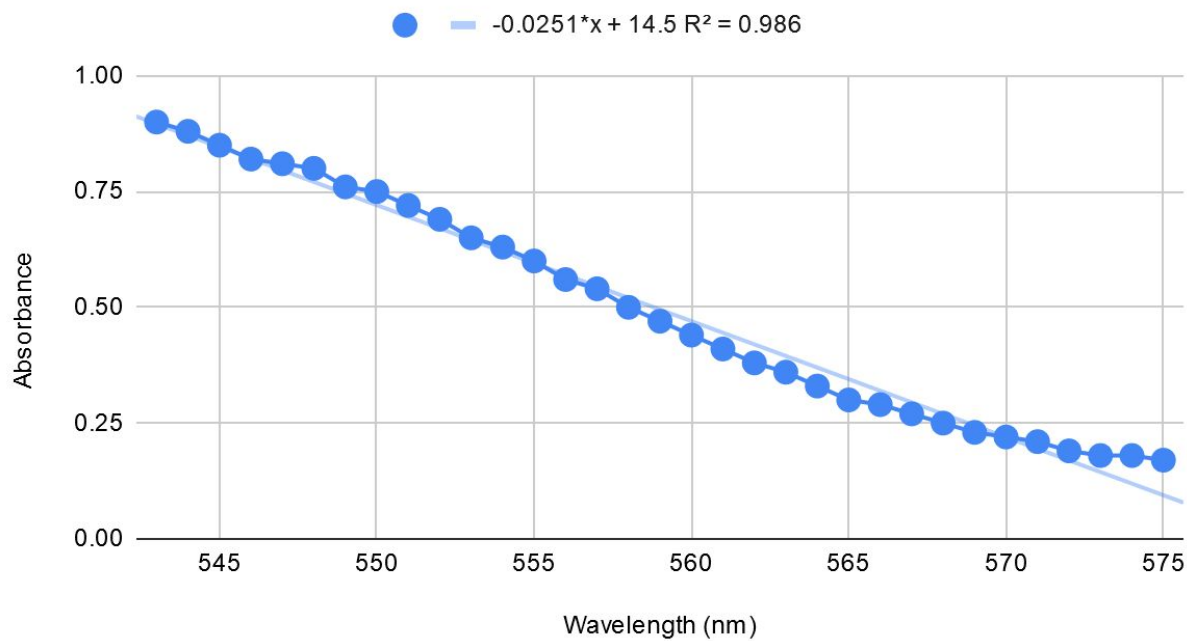
Absorbance vs Wavelength (nm) for CdSe

-0.0251*x + 14.5 R² = 0.986

Figure 6. Plot to find band edge of CdSe.

Table II: Quantum Dot

Nanoparticle	Band edge nm	Band gap eV	Bulk band gap eV	Radius nm
CdSe	577.7	2.15	1.74	2.72

Calculations:

From Figure 6, the equation of the line is found to be:

$$Y = -0.0251x + 14.5$$

X = 14.5 / 0.0251

X = 577.7nm

Finding E_g:

$$E_g = \frac{hc}{\lambda_g} = \frac{(4.14*10^{-15}eV*s)*(2.998*10^8 m/s)}{(5.777*10^{-7}m)} = 2.15 \text{ eV}$$

Using equation 4:

$$\Delta E_g = E_g(R) - E_g(\infty) = 2.15 \ eV - 1.74 \ eV = 0.41 \ eV$$

Now back to equation 5:

$$\Delta E_g = \frac{\pi^2\hbar^2}{2R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{\varepsilon R} = \frac{\pi^2*(6.58*10^{-16})^2}{2R^2} * \left(\frac{1.6018*10^{-19}}{9.11*10^{-31}}\right) * \left(\frac{1}{.13} + \frac{1}{.45}\right) - \frac{1.8*(1.60*10^{-19})^2*(6.24*10^{18})}{10.2*R*(8.85*10^{-12})*(4\pi)}$$

Rearranging for R to get:

0.41 = 3.72*10^-18/R² - 2.53*10^-10/R

$$0 = 0.41R^2 + 2.53 * 10^{-10}R - 3.72 * 10^{-18}$$

Solving for R to get: 2.72 nm.

Conclusion

From the experiment it was concluded that the margin of error for using the particle in a 1-D box was found to be around 50% for each trial. In order to decrease the margin of error, we need to not assume that the electron density is within a line. As the professor suggested at the end of the lecture video, a particle in a 2-D box approximation can help decrease the error that was found from this experiment.

For the quantum dots segment, it was found that the band edge was found to be 577.7nm, the band gap was found to be 2.15eV, the bulk band gap was found to be 1.74eV and the radius of CdSe was found to be 2.72nm.

Acknowledgements

I used the lecture video, the lecture slides, and the document about quantum dots that the professor posted.

Discussion Questions

1. Explain what HOMO, LUMO, valence band, and conduction band mean.

The HOMO is the highest occupied molecular orbital and the LUMO is the lowest unoccupied molecular orbital. A valence band is the band of electron orbitals that electrons can jump from into the conduction band, where it is the band of orbitals that accept excited electrons. These two bands represent the LUMO and HOMO respectively.

2. Set up, but do not solve, Schrdinger's equation for a particle in a 1-D box of length L. What is the potential energy inside and outside of the box? What boundary conditions do you impose on the wave-function for this model? Why is this model relevant to our system?

$$\hat{H}\psi = E\psi \rightarrow \frac{-\hbar^2}{2m} * \frac{d^2\psi}{dx^2} = E\psi$$

The potential energy within the box is 0 and the potential energy outside the box is infinite. For the boundary conditions, we impose from $x = 0$ to $x = L$, which is the 1-D box length. This model is relevant for our system because we're creating this 1-D box where L is the length of the molecule starting from $x = 0$.

3. Prepare five graphs of your experimental results: one graph each for the conjugated thiacyanine dyes DTC, DTCC, DTDC and DTTC and another graph for the quantum dot. How is the band gap determined from your data?

The band gap is determined by substituting the experimentally determined absorption onset into equation 5 from the introduction.

4. Fill in Table I. Note: Exp stands for experimental, and Calc stands for calculated. The experimental wavelength is the location of the peak absorption measured in the experiment. Use the particle in a box energies to calculate the theoretical change in energy. From which you obtain the calculated wavelength. The location of the peak absorption for DTC is presented in the table since the spectrum can become noisy in this region.

5. Using the Beer-Lambert Law, calculate the absorption for DTC at λ_{max}. The molar absorptivity of DTC at λ_{max} is $8.5*10^4$ L/(mol·cm), while the concentration of the solution is $1.5*10^{-5}$ M.

From the introduction, equation 3 is presented:
$$A = \varepsilon cL$$
$$A = 8.5*10^4 \text{ L/(mol·cm)} * 1.5*10^{-5} \text{ M} * 1 \text{ cm}$$
$$A = 1.28$$

6. Fill in Table II. Here the bulk band gap is the band gap of the bulk CdSe, you need to look this up. Also, the effective electron mass m_h is 13% of the mass of an electron and the effective hole mass m_h is 45% the mass of an electron. To understand how to complete this table you must read the journal article on quantum dots posted on Sakai.

References

1. Nedelijkovic, J. M.; Patel, R. C.; Kaufman, P.; Joyce-Pruden, C.; Oleary, N. Synthesis and Optical Properties of Quantum-Sized Metal Sulfide Particles in Aqueous Solution. *Journal of Chemical Education* **1993**, *70* (4), 342.
2. Professor's lecture slides, lecture video, and lab manual.