Absorption spectra of conjugated dyes

Introduction

In this experiment you will measure the absorption spectrum of conjugated dye molecules in methyl alcohol using a UV-Visible spectrometer. The particle in a box model will be used to predict the location of the lowest energy electronic transition for the dye molecules (this is the most intense and longest wavelength transition observed in the spectrum). The oscillator strength for the transitions will also be calculated. Finally, the value for the vibrational constant for the active vibration in the upper electronic state will be found.

The three dye molecules you will work with are shown in Figure 1. Table 1 provides their molecular masses. Note that each structure gives one of two equivalent resonance structures for the molecule. The second resonance structure interchanges both the single and double bonds in the molecule and the location of the nitrogen atom with the positive charge. The actual structure of the molecule is, to a first approximation, a combination of the two resonance structures.

Figure 1. Structure of dye molecules.

Dye	Structure
1,1'-diethyl-2,2'-cyanine iodide	
1,1'-diethyl-2,2'-carbocyanine chloride (pinacyanol)	
1,1'-diethyl-2,2'-dicarbocyanine iodide	

Figure taken from Truman College, "Absorption Spectra of Conjugated Dyes"

Table 1. Molecular masses for dye molecules.

Dye	Molecular mass (g/mol)
1,1'-diethyl-2,2'-cyanine iodide	454.36
1,1'-diethyl-2,2'-carbocyanine chloride (pinacyanol)	388.94
1,1'-diethyl-2,2'-dicarbocyanine iodide	506.43

Particle in a box model

The π electrons in the conjugated bonds between the nitrogen atoms of the dye molecules can be (crudely) modeled as a one dimensional particle in a box, where the box is the length of the region containing the π electrons. This model ignores several important features of the real molecules, including the fact that the potential does not go to infinity at the ends of the box, that the potential does not have a constant value inside the box, that there is electron-electron repulsion between the π electrons, and that the box is three dimensional rather than one dimensional. Because of this, we expect the model to be at best qualitatively correct.

To use the particle in a box model we need to know the following:

Length of the box (L) – The "box" is defined as the region between the two nitrogen atoms in the dye molecules. The length of the box is taken as $(p+3)\ell$, where ℓ is the average bond length for a carbon-carbon or carbon-nitrogen bond, p is the number of carbon atoms between the two nitrogen atoms, and an additional length equal to one bond on each side of the terminal nitrogen atoms is added to account for the fact that the potential does not go to infinity at these points. Since there are p+1 covalent bonds between the nitrogen atoms, this gives $L = (p+1+2)\ell = (p+3)\ell$ as the length of the box. Since a C-C single bond has a typical bond length of 0.134 nm, and a C=C double bond has a typical bond length of 0.154 nm, we will use the average value, $\ell = 0.144$ nm, in the calculations.

Number of electrons in the box (N) – The carbon atoms in the carbon chain between the two nitrogen atoms all have sp^2 hybridization. These atoms each have a p_z orbital perpendicular to the chain, containing one electron per carbon atom. The terminal nitrogen atoms also have sp^2 hybridization and also have a p_z orbital perpendicular to the carbon chain. The neutral nitrogen atom has two electrons in the p_z orbital, while the positively charged nitrogen atom has a single electron in the p_z orbital.

If we combine the above, the number of π electrons in the box is equal to the number of carbon atoms in the carbon chain, plus the number of nitrogen atoms, plus one (since one of the nitrogen atoms contributes two electrons to the box). We can write the number of electrons in the box in terms of p, previously defined.

$$\# \ \pi \text{ electrons} = N = p + 3 \tag{1}$$

As a check, for 1,1'-diethyl-2,2'-cyanine iodide the length of the box is $L = 6\ell = 0.864$ nm and # pi electrons = 6.

The energy levels for the particle in a box are given by the expression

$$E_n = n^2 E_0 \qquad n = 1, 2, 3, \dots \tag{2}$$

where

$$E_0 = \frac{h^2}{8 m_e L^2} \tag{3}$$

Note that in the above equation m_e is the mass of an electron ($m_e = 9.109\times10^{-31}$ kg) and h is the Planck constant ($h = 6.626\times10^{-34}$ J·s).

The ground state (lowest energy) electron configuration for the π electrons in the dye molecule can be found by use of the Aufbau principle (electrons add to the lowest energy available orbital) and Pauli principle (a maximum of two electrons per energy level). The lowest energy excited electronic state can be found by moving one electron from the highest occupied energy level to the lowest unoccupied energy level. The difference in energy between these two electronic states corresponds to the lowest energy required to electronically excite the molecule. This energy, (ΔE), can be set to the energy of the photon needed to carry out the excitation

$$\Delta E = \frac{hc}{\lambda} \tag{4}$$

where c is the speed of light ($c = 2.998\times10^8$ m/s) and λ the wavelength of the absorbed photon.

The ground state of a molecule with N π electrons has $N/2$ lowest orbitals occupied. When the molecule (the ion in this case) absorbs light one electron gets excited from the level $n_1 = N/2$ to the level $n_2 = N/2 + 1$. Within the particle in a box model, the excitation energy ΔE is then the following:

$$\Delta E = \frac{h^2}{8 m_e L^2} (n_2^2 - n_1^2) = \frac{h^2}{8 m_e L^2} (N + 1) \tag{5}$$

Combining Eqs. (4) and (5), an expression for λ is derived:

$$\lambda = \frac{8m_e c}{h} \frac{L^2}{N+1} = \frac{8m_e c \ell^2}{h} \frac{(p+3)^2}{p+4} \tag{6}$$

After substituting for the constants in Eq. (6), the expression for λ simplifies to

$$\lambda(in\ nm) = (68.4\ nm) \frac{(p+3)^2}{p+4} \tag{7}$$

For each of the above dye molecules use the particle in a box model to predict the wavelength at which the first electronic transition should occur. Give sufficient details in your lab report to make it clear how you calculated the values for wavelength. You should compare your calculated values for wavelength to the values observed experimentally in two ways: qualitatively (is the trend in the values for wavelength predicted to occur as the size of the carbon chain increases the same as what is observed experimentally) and quantitatively (how well to the predicted values of wavelength compare to the values observed experimentally). Based on this, you should be able to make general comments on how well the data are modeled by the particle in a box.

Experimental

Stock solutions of each of the three dyes to be studied will be prepared by the instructor. Pipette few drops of a stock solution into cuvette filled with methyl alcohol and take the absorption spectrum on a UV-Visible spectrometer.

Oscillator strength

In addition to fitting your longest wavelength absorption peaks to the particle in a box model, you can use your spectra and the concentration of dye molecule to find the oscillator strength for the lowest energy electronic transition. The oscillator strength, f, is a semiclassical notion defined as the ratio between the actual (quantum mechanical) transition rate and the transition rate a single electron would manifest as a classical harmonic oscillator with the same frequency as that of the actual transition. Thus f is determined from the transition dipole moments as:

$$f = \frac{|\boldsymbol{\mu}_{12}|^2}{|\boldsymbol{\mu}_{12}|^2_{osc}} \tag{8}$$

where $|\boldsymbol{\mu}_{12}|^2$ and $|\boldsymbol{\mu}_{12}|^2_{osc}$ are the squares of the actual and the classical harmonic oscillator transition dipole moments, respectively. Evaluation of this definition gives:

$$f = \frac{4\varepsilon_0 m_e c^2 ln10}{N_A e^2} \int \varepsilon(v)dv = K \int \varepsilon(v)dv \tag{9}$$

$$K = \frac{4\varepsilon_0 m_e c^2 ln10}{N_A e^2} = 4.320 \times 10^{-9}\ mol \cdot cm^2/L \tag{10}$$

In the above expression ε_0 is the permittivity of free space, m_e is the mass of the electron, c is the speed of light, e is the fundamental electrical charge, and N_A is Avogadro's number. If we substitute values for the constants into Eq. (9) we get $K = 4.320 \times 10^{-9}\ mol \cdot cm^2/L$. The integral in Eq. (9) is in terms of frequency and is carried out over the absorption band being studied. Note that the concentration of dye molecule will be used to convert from A (absorbance) to ε (extinction coefficient), as discussed below. Equation 9 is derived from Einstein's model for light absorption and emission (Atkins and de Paula, pp. 477-478; Hollas, pp. 28-32).

The significance of the oscillator strength comes from the fact that the value for f is different for allowed and forbidden transitions. For an allowed electronic transition $f \cong 1$, while for a forbidden electronic transition f is typically around 10^{-3}.

In the present experiment we will calculate a value for f for the lowest energy electronic transition for each dye molecule. To find the value for the integral in Eq. (9), we can approximate the area of the spectrum (the grey area in Figure 2, below) by a triangle.

$$\int \varepsilon(v)dv \cong \frac{1}{2}\varepsilon_{max}\Delta v \qquad (11)$$

where

$$\varepsilon_{max} = \frac{A_{max}}{c\ell} \qquad \text{(units will be L/mol·cm)} \qquad (12)$$

A_{max} is the experimental absorbance of the dye at the peak of the spectrum, c is the concentration of dye molecule in solution (in units of mol/L) and ℓ is the pathlength of the cuvette (1.00 cm for a standard cuvette). Δv, the width of spectrum (in units of cm^{-1}) is found by converting the wavelengths corresponding to the base of the triangle used to approximate the absorption band into energies, in cm^{-1}, as shown in Figure 2. In this example, since the base of the triangle runs from 530. nm (18870. cm^{-1}) to 642. nm (15580. cm^{-1}), then $\Delta v = (18870. - 15580.) = 3290.$ cm^{-1}.
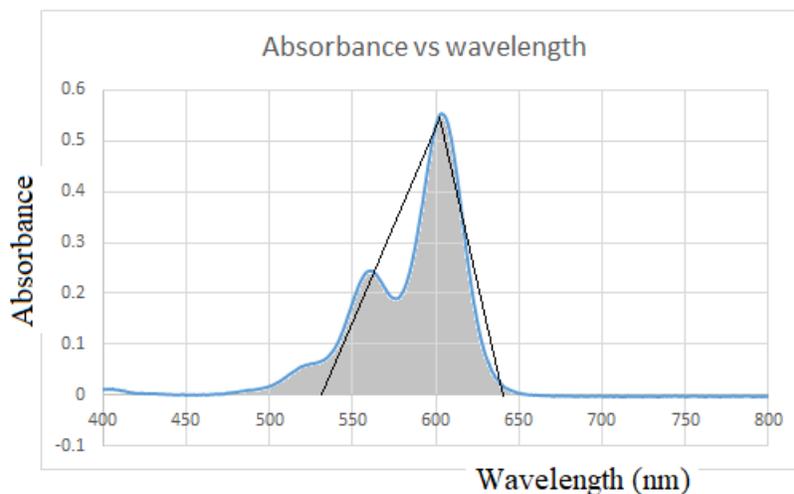

Figure 2. Example for finding Δv.

While the above method gives a rather crude approximation for the integral, and therefore the oscillator strength, it is more than sufficient for determining whether we are observing allowed or forbidden transitions in the dye molecules. This is because the difference in oscillator strength between an allowed and a forbidden transition is ~ 10^3.

We can also use the absorption spectrum to find an approximate value for ω', the vibrational constant for the active vibration in the upper electronic state of the molecule. The two most intense peaks in the spectrum correspond to transitions from $v'' = 0$ in the lower electronic state to $v' = 0$ and $v' = 1$ in the upper electronic state. The relative locations for these vibrational energy levels is given in Figure 3. If we convert the locations of the two lowest energy peaks in the spectrum from wavelength (in nm) to energy (in cm^{-1}), then the difference in energy will be equal to the value for ω'. For the spectrum in Figure 2, for example, the two lowest energy peaks and their assignment are:

$$v'' = 0 \;\rightarrow\; v' = 0 \qquad\qquad \lambda = 604. \text{ nm} \qquad\qquad E_{0,0} = 16556. \text{ cm}^{-1} \qquad (13)$$

$$v'' = 0 \;\rightarrow\; v' = 1 \qquad\qquad \lambda = 561. \text{ nm} \qquad\qquad E_{0,1} = 17825. \text{ cm}^{-1} \qquad (14)$$

$\Delta E = E_{0,1} - E_{0,0} = \omega' = 17825.$ cm^{-1} – 16556. cm^{-1} = 1270. cm^{-1} (to three significant figures).

Note that in the above calculations and in Figure 3 we have followed the usual convention of using a single prime (′) to indicate quantum numbers and constants for the upper electronic state, and a double prime (″) for quantum numbers and constants for the lower electronic state of the molecule.
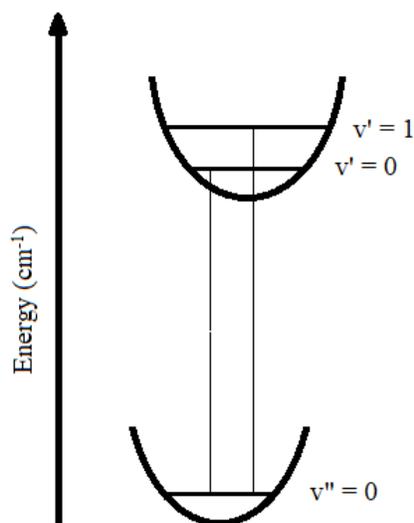
Figure 3. Relative locations for the v″ = 0 vibrational state in the lower electronic state, and the v′ = 0 and v′ = 1 vibrational states in the upper electronic state of the active vibration in the dye molecule.

Lab Report

(1) For each dye molecule give the calculation for the wavelength where the first maximum in the absorption spectrum is predicted to occur, based on the particle-in-a-box model. Compare the results predicted from this model to the experimental results. Discuss the degree of quantitative and qualitative agreement, as described in the last paragraph in the Introduction section of the handout (page 3).

(2) For each of the dye molecules, find the value for oscillator strength. Based on these values, determine whether the observed transition for each molecule is allowed or forbidden.

(3) For each of the dye molecules use the two longest wavelength peaks in the absorption spectrum to estimate the value for ω′, the vibrational constant for the active vibration in the dye molecule.

References

Atkins, P. W. and de Paula, J. Physical Chemistry, 10th Edition. New York: W. H. Freeman, 2014.

Garland, C. W., Nibler, J. W., and Shoemaker, D. P. Experiments in Physical Chemistry, 8th Edition. New York: McGraw-Hill, 2009.

Hollas, J. M. Modern Spectroscopy, 2nd Edition. New York: Wiley & Sons, 1992.

Pilar, F. L. Elementary Quantum Mechanics. New York: McGraw-Hill, 1968.

Truman College. http://chemlab.truman.edu/chemlab_backup/PChemLabs/ CHEM326Labs/ Conjugated Dyes.htm Retrieved 3/3/2014.

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