

Particle in a Box : Absorption Spectrum of Conjugated Dyes

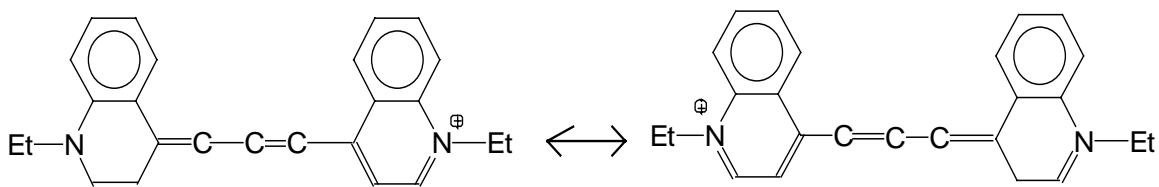
Part A – Recording the Spectra and Theoretical determination of λ_{\max}

Theory

Absorption bands in the visible region of the spectrum (350 - 700 nm) correspond to transitions from the ground state of a molecule to an excited electronic state which is 160 to 280 kJ above the ground state. In many substances, the lowest excited electronic state is more than 280 kJ above the ground state and no visible spectrum is observed. Those compounds which are colored (i.e., absorb in the visible) generally have some weakly bound or delocalized electrons such as the odd electron in a free radical or the electrons in a conjugated organic molecule. In this experiment we are concerned with the determination of the visible absorption spectrum of several symmetrical polymethine dyes and with the interpretation of these spectra using the "free-electron" model.

The visible bands for polymethine dyes arise from electronic transitions involving the π electrons along the polymethine chain. The wavelengths of these bands depends on the spacing of the electronic energy levels. Bond orbital and molecular orbital calculations have been made for these dyes, but the predicted wavelengths are in poor agreement with the observed values. We shall present here the simple free-electron model first proposed by Kuhn; this model contains some drastic assumptions but has proved reasonably successful for molecules like a conjugated dye.

As an example, consider a dilute solution of 1,1'-diethyl- 4,4'-carbocyanine iodide:



The cation can "resonate" between the two limiting structures; that is, the wave function for the ion has equal contributions from both states. Thus all the bonds along this chain can be considered equivalent, with bond order 1.5 (similar to the C-C bonds in benzene). Each carbon atom in the chain and each nitrogen at the end is involved in bonding with three atoms by three localized bonds. The extra valence electrons on the carbon atoms in the chain and the three remaining electrons on the two nitrogens form a mobile cloud of electrons along the chain (above and below the plane of the chain). We shall assume that the potential

energy is constant along the chain and that it rises sharply to infinity at the ends; i.e., the electron system is replaced by free electrons moving in a one-dimensional box of length a . The quantum mechanical solution for the energy levels of this model is:

$$(1) \quad E_n = h^2 n^2 / 8ma^2 \quad \text{where } n = 1, 2, 3, \dots$$

and m is the mass of an electron and h is Planck's constant.

The Pauli exclusion principle limits the number of electrons in any given energy level to two and these two electrons must have opposite spins: $+1/2$ and $-1/2$. The ground state of a molecule with N electrons will have the $N/2$ lowest energy levels filled and all higher levels empty. When the molecule (or ion in this case) absorbs light, one electron jumps from the highest filled level ($n_1 = N/2$) to the lowest empty level ($n_2 = N/2 + 1$). The energy change for this transition is

$$(2) \quad \Delta E = \frac{h^2(n_2^2 - n_1^2)}{8ma^2} = \frac{h^2(N+1)}{8ma^2}$$

Since $\Delta E = hv = hc/\lambda$, where c is the speed of light and λ is the wavelength, we have:

$$(3) \quad \lambda = \frac{8ma^2}{hc(N+1)}$$

The polymethine chain stretches from the one nitrogen atom to the other nitrogen atom. Let us denote the number of double bonds within in the chain by j ; then $N = (2j + 2)$. In our example dye, $j = 5$, therefore $N = 12$; count the π electrons to check. Huhn assumed the length a was the length of the chain between nitrogen atoms plus one bond distance on each side; thus, $a = (2j + 2)L$, where L is the bond length between atoms along the chain. Therefore,

$$(4) \quad \lambda = \frac{8mcL^2(2j+2)^2}{h(2j+3)}$$

Where $L = 1.39 \times 10^{-10}$ meter (the bond length in benzene, a molecule with similar bonding). This is the fundamental equation to theoretically calculate the wavelengths of absorption of the dyes.

Experimental

Turn on the Unicam spectrometer and allow it to warm up for at least 10 minutes prior to use. For most instruments, such a warm-up period is necessary to achieve stable, drift-free operation.

Prepare solutions of three dyes in methanol. The concentrations of these stock solutions are listed on the labels; please copy them into your lab notebook. You will need to quantitatively dilute the solutions to about 10^{-6} M to obtain good spectra.

The dyes to be studied are:

pinacyanol chloride

1,1' - diethyl - 2,2' - cyanine iodide

1,1' - diethyl - 2,2' - dicarbocyanine iodide

The structures of these dyes are shown later.

Obtain a baseline spectrum over the wavelength range of interest (400 - 800 nm). A baseline is obtained by placing pure solvent in both the reference and sample cells and running the instrument over the wavelength range of interest. This baseline will be subtracted from all your dye spectra.

Prepare your first dye solution (10 mL) and obtain the absorbance spectrum from 400 to 800 nm. If necessary, dilute the initial solution and redetermine the spectrum. Repeat this procedure until a spectrum is obtained with a maximum absorbance between 0.8 and 0.6. The band shape will change with concentration, since these dyes dimerize. At the final concentration used, the monomer band (higher wavelength band) will be much more prominent than the dimer band, which will remain as a shoulder on the low wavelength side of the main peak.

Make up solutions (10 mL) of the other dyes at approximately the same molar concentration that gave the best results previously. Obtain their spectra in the same way.

Rinse the cells with solvent and return them to the instructor. Turn off the spectrometer.

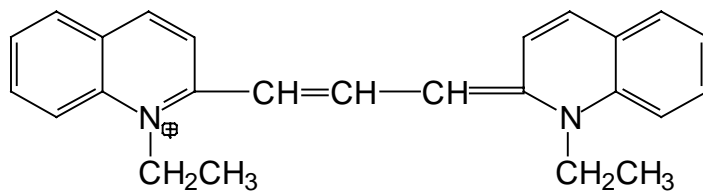
Calculations – Part a

Structures and molar masses of the dyes are shown on the next page.

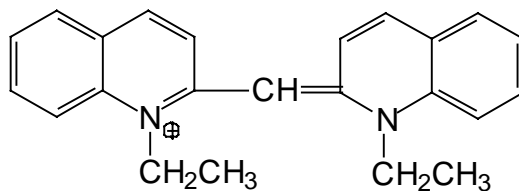
For each dye, calculate the wavelength of maximum absorption and compare with the experimental result. Present your results in tabular form along with the molar absorptivities of the dyes at the maximum wavelength. Discuss the experimental results and their agreement with the model.

A reasonable modification to the model would remove the restriction that the potential energy rises abruptly at the ends of the box (the nitrogen atoms). To allow for a less drastic change in the potential energy, let us introduce a parameter, s , into the expression for the box length. The length of the box then becomes $a = (2j + 2 + s)L$. Use your data for the dye with the longest

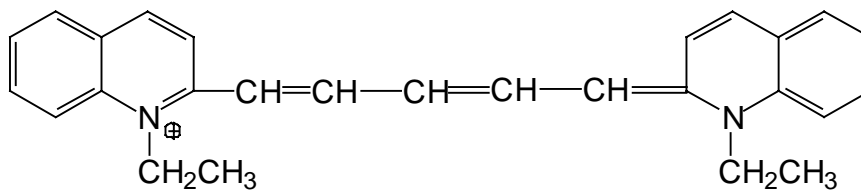
wavelength to calculate s ; then use this optimum value of s to calculate the wavelengths for the other two dyes. Comment on any improvement.



Pinacyanol Chloride MM = 388.94



1,1'-Diethyl-2,2' cyanine iodide MM = 454.36



1,1'-Diethyl-2,2'-dicarbocyanine iodide MM = 506.43

Part 2: Theoretical Calculation of the Oscillator Strength of an Electronic Transition and Comparison with Experiment

If the Schrödinger equation is applied to the particle in the box problem, the Hamiltonian is simply the kinetic energy operator (recall that $V = 0$):

$$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (1)$$

Since there are no time dependent terms in this Hamiltonian, the wavefunctions obtained describe the stationary states (probability density is time independent) of the system. If, however, the Hamiltonian contains a time dependent component, the wavefunctions will depend on the time and nonstationary (time dependent) states of the system will result. If the perturbation energy is equal to the difference in energies between two stationary states, there is a probability that the system, originally described by state 1, can be transformed into state 2. In other words, because of the perturbation, a transition is induced between states 1 and 2.

All spectroscopy is based on these transitions between states of the system. During a spectroscopic event, the molecule interacts with the electromagnetic radiation impinging on the sample. The time dependent perturbation for an electron in a radiation field is:

$$\hat{H}' = -ezE_o \cos(2\pi\nu t) \quad (2)$$

Where e is the charge on the electron, z is the z -coordinate of the electron, E_o is the amplitude of the electric field vector of the radiation, ν is the frequency of the radiation, and t is the time.

If the initial (stationary) state of the system has ψ_k and eigenvalue E_k , and the final state of the system has wavefunction ψ_n and eigenvalue E_n , then the transition probability per unit time and per unit radiation density is given by B_{kn} , the Einstein coefficient for induced absorption:

$$B_{kn} = \frac{D^2}{6\epsilon_o \hbar^2} \quad (3)$$

B_{kn} is a measure of the probability of producing the transition. The term D is the transition moment integral and is related to the wavefunctions through:

$$D = \int \psi_k \hat{\mu} \psi_n d\tau \quad (4)$$

Obviously, the value of the transition moment integral determines the strength of the transition. If, for example, $D = 0$, the transition is said to be forbidden and no spectrum would be observed. The transition moment integral is the basis for selection rules that are used to predict the intensity of spectral peaks. Using particle-in-the-box wavefunctions in equation (4), a selection rule can be derived for electronic transitions in a conjugated dye.

Other quantities can characterize the intensity of spectroscopic transitions: one such measure is the oscillator strength, f . It is related to the transition moment (and therefore the Einstein coefficient) by the following expression:

$$f = \frac{4m_e \pi \nu}{3e^2 \hbar} D^2 \quad (5)$$

Since the oscillator strength depends on the frequency of the transition, it can be anticipated that ultraviolet (electronic) transitions are, all things being equal, more strongly allowed than infrared (vibrational) transitions, which, in turn, are stronger than microwave (rotational) transitions. In equation (5), ν represents the frequency at the *maximum* absorption.

It can also be shown that there is a relationship between the oscillator strength and the experimental integrated absorption coefficient, A , which is defined by:

$$A = \int \epsilon(\nu) d\nu \quad (6)$$

The integrated absorption coefficient is an experimental measure of the intensity of a transition because it is the area under the spectral curve. The integrated absorption coefficient is related to the oscillator strength by:

$$f = 1.44 \times 10^{-19} \int \epsilon(\nu) d\nu \quad (7)$$

where ν is the frequency, and $\epsilon(\nu)$ is the molar absorptivity at each frequency in units of $\text{L mol}^{-1} \text{cm}^{-1}$. The integrals in (6) and (7) cover the entire absorption band corresponding to the transition. Thus, the oscillator strength can be determined from the area under the quantitative absorption spectrum of a given transition.

Experimental and Calculations – Part B

Previously, you had measured the spectrum of a series of conjugated dyes. Import the spectral data for the dyes into Excel.

Using your calculated concentrations, convert the absorbances into $\epsilon(\nu)$; also convert the wavelengths into ν . Copy the new data to the clipboard. Paste your data to ORIGIN and plot it. If the data consist of a single peak, you can obtain the area by fitting to a Gaussian. If the data appear to be multiple peaks or overlapping peaks, you will have to separate the data and obtain the area of the peak of interest. ORIGIN accomplishes this from the FIT menu to select multiple Gaussian. Use HELP as needed. For each of the absorption spectra, calculate the respective oscillator strengths by applying equation (7). Calculate both the Einstein coefficient and the transition moment integral for each dye. Express the transition moment integral in Debye units.

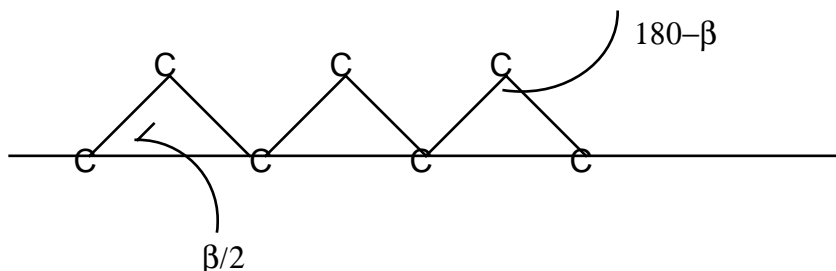
Questions

1. Show that for the particle in a box model, the frequency of the lowest energy electronic transition is given by:

$$\nu = h(N + 1)/(8ma^2)$$

where N is the number of π electrons, and a is the 'length' of the molecular box. Recall that there are two electrons in each energy level.

2. The conjugated system is not linear but actually zigzag and the displacement of the electron follows the zigzag path.



s is the projection of on on the z -axis

Therefore $z = s \cos(\beta/2)$ where $\beta = 56^\circ$. The wavefunction for state $N/2$ (the highest filled state) is:

$$\psi_{N/2} = (2/a)^{1/2} \sin(N\pi s/2a)$$

The transition moment (eq.7) is then (after much math and gnashing of teeth)

$$D_{kn} = \frac{2eaN(N+2)(\cos(\beta/2))}{\pi^2(N+1)^2}$$

Use the expression for frequency, D (given above) and equations (3) and (5) to show that the theoretical oscillator strength is:

$$f = \frac{4N^2(N+2)^2 \cos^2(\beta/2)}{3\pi^2(N+1)^3}$$

3. Compare the experimental oscillator strengths with the theoretical values and comment on the agreement.
4. The oscillator strength is a measure of the allowedness of a transition. An oscillator strength ~ 1 implies that a transition is completely allowed. Comment on the "allowedness" of your transitions.
5. Prepare a table of maximum absorbance, maximum molar absorptivity, integrated area, and oscillator strength for your dyes. All of these values are measures of transition intensity. Are there any trends in these data?
6. Which dye has the most intense transition? Which measure is most precise in determining intensity of a transition? Why? Which measure is easiest to compute?
7. Using the oscillator strength, calculate the Einstein coefficient and transition moment integral.
8. Prepare a table to list, for each dye, λ_{\max} , ϵ_{\max} , A , f , B , and D . Note the relation of the last five quantities.