Exercise

QS1

QUANTUM MECHANICS AND SPECTROSCOPY: PARTICLE-IN-A-BOX

AIMS

(a) To measure the visible absorption spectra of a series of three organic dyes.

(b) To determine, from the spectrum, the wavelength and frequency of the lowest-energy intense absorption band, the absorbance, and the molar absorptivity.

(c) To apply the particle-in-a-box model to the electronic energy levels in a long-chain conjugated hydrocarbon and, using the observed spectra, estimate the length over which the delocalised electrons are free to move and compare this with the geometrical lengths of the molecules.

Under the heading AIMS, in your lab book, paraphrase the above to record why you did this experiment.

SKILLS USED IN THIS EXERCISE

- Measuring visible absorption spectra using a compact single–beam spectrophotometer.
- Applying the particle-in-a-box energy level expressions.
- Making critical comparisons between experimental and model (calculated) values.

INTRODUCTION

In this exercise you will examine the electronic absorption spectra of a series of three polymethine dyes which differ only in the number of =CH– units linking the terminating ring groups (see structures in Figure 1):

(a) 1,1'–diethyl–2, 2'– cyanine iodide (1 CH unit)

(b) 1,1'–diethyl–2, 2'– carbocyanine iodide (3 CH units)

(c) 1,1'–diethyl–2, 2'– dicarbocyanine iodide (5 CH units).

These dyes will be referred to as (a), (b), and (c) to simplify the text. All three dyes have delocalised π electrons between the two nitrogen atoms, illustrated in Figure 2 where two resonance forms of dye (b) are shown.

Make sure you understand the structures of the three dyes. The conjugated carbon chain connecting the nitrogens consists of alternating single and double bonds. Each carbon atom and each of the two terminal nitrogen atoms is bonded to three adjacent atoms through sigma bonds. This leaves one valence electron on each carbon atom and a total of three valence electrons on the two nitrogen atoms available for π bonding; these electrons can be considered to be delocalised over the length of the N–C– ⋯ –C–N chain (plus half a bond at each end – see your lecture notes!). The total number of electrons in π orbitals is therefore $p + 3$, where p is the number of carbon atoms in the chain; *e.g.* for dye (b) $p = 5$ and the number of electrons in π orbitals is 8 (look at figure 1 to make sure you understand how these numbers were determined).

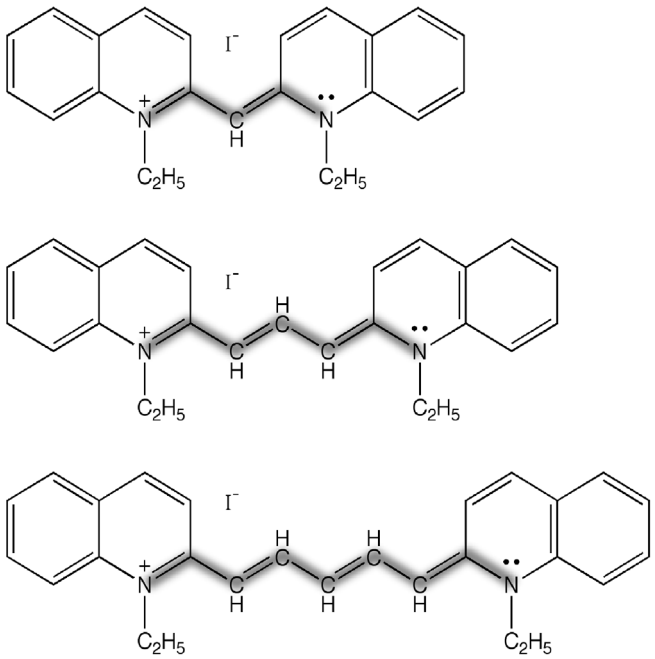

Figure 1 – The structures of dyes (top to bottom) (a), (b), and (c) showing the assumed path accessible by the delocalized electrons (shaded).

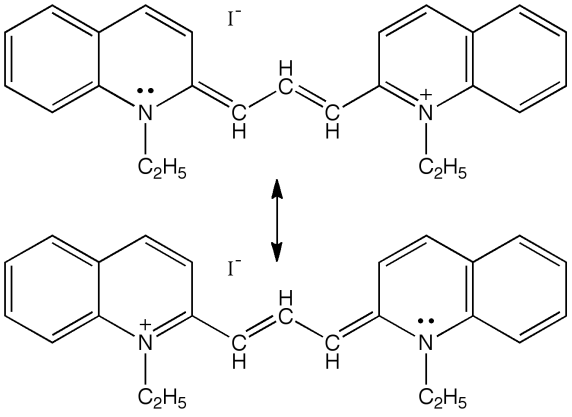

Figure 2 – Two resonance forms of dye (b) illustrating the delocalized electrons.

The particle-in-a-box model supposes that these electrons in π orbitals occupy the energy levels appropriate to a particle confined in a 1–dimensional box of length, L, equal to the length of the N–C– ⋯ –C–N chain (plus half a bond at each end). The lowest-energy electronic transition observed in the ultra-violet – visible spectrum of the molecule then corresponds to the promotion of an electron from the occupied level with highest energy to the lowest energy unoccupied level (in molecular orbital theory these are respectively the HOMO and LUMO). The particle-in-a-box model allows the absorption intensity to be calculated. However, in this experiment you will study only the wavelength of the light absorbed.

The energy levels for a particle-in-a-box are given by:

$$E_n = \frac{n^2h^2}{8mL^2} = Cn^2, \qquad \text{Equation 1}$$

$C = h^2/8mL^2$, m is the mass of the electron, h is the Planck constant, the quantum number n = 1, 2, 3 *etc.* and the value of C depends only on the particular dye used (because L changes between the dyes). Figure 3 shows the first five energy levels in terms of C.

The Pauli exclusion principle limits the number of electrons to two per level. For a molecule with N π electrons the highest occupied level will have quantum number $n_1 = N/2$, the lowest-energy unoccupied level will have quantum number $n_2 = N/2 + 1$.

Hence, the longest wavelength (lowest energy) band in the UV–visible spectrum, which corresponds to the transition of an electron from the highest occupied level to the lowest unoccupied level, will have an energy:

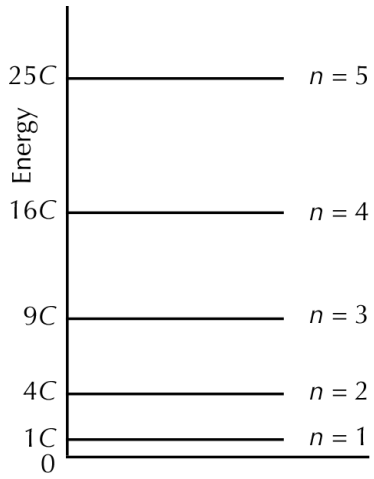

Figure 3 – The energy levels for a particle in a one–dimensional box.

$$\begin{aligned}\Delta E &= C(n_2^2 - n_1^2) \\ &= C\left(\left(\frac{N}{2}+1\right)^2 - \left(\frac{N}{2}\right)^2\right) \\ &= C(N+1)\end{aligned} \qquad \text{Equation 2}$$

C and N both vary between the dyes used in this experiment. Hence, their absorption spectra will be different, and by determining ΔE and knowing N, the constant C can be calculated and thus L can be determined. This value of L can be compared with the geometric value of L, calculated from bond lengths.

ΔE is obtained from the wavelength of maximum absorption which is estimated from the spectrum. Using the Planck equation $\Delta E = h\nu$ together with $\nu\lambda = c$ gives $\Delta E = hc/\lambda$.

The colour of the light absorbed is not the same as the colour you perceive for a substance. The retina of the eye consists of three colour-sensitive "cone cells", which are respectively more sensitive to red, green and blue light. The relative levels that these cones are excited determine the perceived colour. This is the basis of the RGB additive colour used by television, computer monitors and other devices such as smart phones. Equal levels of red, green, and blue create the perception of white light. Absorption of any one colour (from white light) by a substance will result in the substance being coloured, and that colour will be the one complementary to the colour being absorbed. This is the basis of subtractive colour used by newspapers and colour printers (CMY). The complementary colours of the primary additive colours are given below. For example, a substance absorbing blue light (450 nm) will appear yellow when illuminated by white light.

Additive Colour		**Complementary Subtractive Colour**	
Blue (~450 nm)		Yellow	
Green (~550 nm)		Magenta	
Red (~650 nm)		Cyan	

A computer monitor or television creates a cyan colour by lighting up blue and green picture elements (pixels). Printers create a red colour by mixing the two CMY colours that "contain red", i.e. magenta and yellow. A black ink is also required.

RISK ASSESSMENT AND HEALTH AND SAFETY INFORMATION

Apparatus	*Risk*	*Safety precautions*
Compact UV-Vis spectrophotometer	Electric shock	Do not spill solutions on electrical apparatus. Apparatus tested and tagged annually.
Polystyrene cells	None	
Chemicals	**See MSDS and label on bottle**	**Wear safety glasses. Do not ingest any chemical.**
1,1'–diethyl–2, 2'–cyanine iodide	Fatal if swallowed (LD_{50} 5 to 50 mg/kg). Harmful in contact with skin. Causes skin irritation. Causes serious eye irritation.	Avoid contact with skin: wear gloves and safety glasses.
1,1'–diethyl–2, 2'–carbocyanine iodide	Toxic if swallowed. Toxic in contact with skin. Toxic if inhaled.	Avoid contact with skin: wear gloves and safety glasses.
1,1'–diethyl–2, 2'–dicarbocyanine iodide	Harmful if swallowed. Harmful in contact with skin. Causes skin irritation. Causes serious eye irritation.	Avoid contact with skin: wear gloves and safety glasses.
Methanol	Toxic by inhalation, toxic in contact with skin, toxic if swallowed. May cause eye irritation. Highly flammable liquid and vapor. Causes damage to organs.	Avoid skin contact and do not breathe vapor. Wear safety glasses. Keep away from sources of ignition.
Other hazards	None identified	
Control measures	Eye protection to be worn at all times.	
Clean up	Spilled chemicals should be mopped up with a damp cloth, followed by thorough rinsing with water. Broken glass to 'glass only' container.	

Overall Risk assessment: Significant risk that may be effectively controlled.

Risk assessment by: Prof. Timothy Schmidt **Date:** 2 March, 2017

REFERENCES

(1) Engel, T. and Reid, P., *Physical Chemistry*, Pearson New International Edition, Pearson 2014.

PROCEDURE

Make sure you read all of this material before coming to the laboratory.

Using cuvettes

Cuvettes are used to hold liquids while in a spectrophotometer. The cuvettes you will be using are made of plastic (polystyrene) and have a 1.00 cm pathlength.

* The cuvettes have two possible pathlengths. You will use the **long** path length. Hold the cuvettes by the opaque panels. Do not touch the optical (clear) faces with your fingers.
* Fill cuvettes to 1cm below full. Use a lint-free tissue to dry the outside of the cuvettes after filling, taking particular care that the optical faces are clean.
* Remove any water droplets or marks from the optical faces by wiping the optical faces with a lint-free tissue before putting the cuvette into the instrument.
* Make sure you place the cuvette with the **correct orientation** in the instrument so the light beam passes through the optical faces (from *USB-ISS-UV-VIS* to *Red Tide USB650UV*).
* Fill one cuvette (the reference cell) with methanol and fill the other cuvettes with the dye solutions. Do *not* fill cuvettes while they are in the spectrophotometer. In this experiment we make the assumption that the cuvettes are all identical. However, if you wish, you can reuse the same cuvette and rinse with methanol and the solution to be delivered before recording each spectrum. **Discuss with your demonstrator, and note what you did in your lab book.**

Using the Red Tide USB650UV Compact Spectrophotometer

The spectrophotometer used in this experiment is the OceanOptics Red Tide USB650UV (shown on the right). The instrument comprises a light source (USB-ISS-UV-VIS) and a spectrometer (USB650UV). The light source must be connected to power, and the spectrometer should be connected to a computer by a USB cable.

Open the SpectraSuite Software. Ensure that the spectrometer is recognized in the **Data Sources** box (top left). If not, contact a demonstrator.

Ensure that the **Integration Time** is set to 100 ms, and that **Scans to Average** is set to 9.

- Enable the light source by checking the **Strobe/Lamp Enable** checkbox (**NOT Auto-Toggle**).
- Place the solid black dummy cuvette in the holder. Record the "dark spectrum" by clicking on the **grey lightbulb** (next to the yellow one).
- Replace the black dummy cuvette with a blank (methanol).
- The light source spectrum should now be displayed. If it is at all saturated (very flat plateau), reduce the integration time.

- Record the reference spectrum by clicking on the **yellow lightbulb**. Subtract the dark spectrum by clicking on the **minus-grey lightbulb**. The spectrometer is now set-up for recording spectra.
- Check that upon clicking T, the transmission spectrum is 100% across the 200-850 nm range, and that upon clicking A, the absorption spectrum is 0 across the 200-850 nm range.
- Replace the blank solution with the one whose absorbance is to be measured.

Recording the spectra

Take care of the Dye Solutions! Stock solutions of each of the three dyes are provided in the laboratory. The dyes are *expensive and susceptible to contamination and decomposition* on exposure to light. You should avoid contaminating the stock solutions, and *avoid leaving them in daylight* for longer than necessary. Use clean and dry disposable Pasteur pipettes for all transfers; *never return solutions to the stock bottles.*

1. **Record the concentration of each dye solution and the perceived colour of each dye in your lab book.**
2. Record the spectrum of each dye and save the **processed spectrum** by pressing the **3.5" floppy-disk** icon as a **Tab Delimited .txt** file in an appropriate folder.
3. **Plot your results as they are obtained** by pasting the data from the generated **`.txt`** file into an **Excel** spreadsheet and **ask the demonstrator to check your work** before discarding your solutions (into the appropriate waste solvent container).
4. **Plot all absorbance spectra on the one graph, print and tape it into your lab book under the heading RESULTS.** For each dye plot the absorbance against wavelength from 400-800 nm. Make sure the vertical scale is appropriate. The wavelength of the maximum absorbance of the longest-wavelength peak is λ_{max}.
5. For each dye, tabulate λ_{max}, the wavelength for maximum absorbance, and A_{max}, the absorbance at λ_{max}.

Tidy your area and dispose of solutions and solid waste appropriately.

CALCULATIONS

Answer each of the following questions in your lab book under the heading CALCULATIONS. You may wish to tabulate the answers.

Applying the particle-in-a-box model to estimate *L*

1. Beer's law relates the absorbance A to c the concentration (mol L^{-1}) of the absorbing species, l the pathlength of the cuvette in cm and ε the molar absorption coefficient (the conventional units of ε are L mol^{-1} cm^{-1}): $A = \varepsilon.c.l.$ For each dye use Beer's law to calculate the molar absorption coefficient at λ_{max}.
2. Calculate the frequency of light absorbed at λ_{max} from $c = \nu\lambda$, then calculate ΔE from ν using the Planck equation $\Delta E = h\nu$.

3. Write down the number of carbon atoms in the N-C-…-C-N chain (p), and the number of π electrons ($N = p + 3$).
4. Use equation 2 with ΔE and N to calculate C.
5. From C calculate the length over which the π electrons are delocalised according to the particle-in-a-box model used here.

Calculating *L* from molecular geometry

The resonance structures which can be drawn for these dyes (see Figure 2) suggest each carbon–carbon (or carbon-nitrogen) bond has a bond order of 1.5 (*i.e.* similar to the carbon–carbon bonds in benzene) and the CC bond length may be assumed the same as in benzene *i.e.* 0.140 nm. The average of the carbon–nitrogen single and double bond lengths is also 0.140 nm. If it is assumed that the "box" ends half a bond beyond the nitrogen nuclei the length of the zig–zag path is therefore $(p + 2) \times 0.140$ nm, where p is the number of carbon atoms in the chain. Calculate the value of L for each dye from this geometrical approach.

DISCUSSION

Answers the following questions in your lab book under the heading DISCUSSION.

For each dye you have two estimates of L: one from the geometry of the molecule using average bond lengths, and the other from the particle-in-a-box model applied to the spectral data. Compare the two estimates of L. Interpret any differences and also the variation (or otherwise) of these differences between the dyes. Note: answering this question is central to the aims of this experiment.

List the essential features of the potential well used in the particle-in-a-box model and for each feature describe how it could be modified to better reflect the potential function experienced by the delocalized electrons in these dye molecules.

LAB BOOK WRITE-UP

Ensure that your lab book is **complete.**

Before leaving the laboratory, submit your lab book to a demonstrator for stamping and signing off.

QS1

PRE – LABORATORY QUESTIONS (PASTE INTO LAB BOOK)

1. State the Beer – Lambert law; define all symbols used.

2. Calculate the frequency (Hz) and energy per photon (J and eV) for 500 nm radiation.

3. List the parameters which determine the energy of a particle in a 1-dimensional box. Note: 'parameters' do not include fundamental constants; parameters are quantities which at least, in principle, can be varied in an experiment, *i.e.* properties of the particle and the box.

4. A 'particle in a 1-dimensional box' model is used in this exercise to describe the electronic state of a molecule. How many electrons can occupy each energy level?

5. Calculate the lowest allowed energy for an electron in a 1-dimensional box of length 1.0 nm. Record the mass of the electron and the value of the Planck constant as part of your calculations, so you have these values at hand in the laboratory.

6. What colours are absorbed by chlorophyll, the principal pigment of leaves?