

Particle in a box experiment: visible absorption spectra of dyes

Introduction

The one dimensional particle in a box model discussed in lectures provides one of the simplest methods of demonstrating quantum effects. It would be worthwhile seeing if there is, in fact, any real system that approximates this very simple model. Although real systems are three dimensional, it appears, as alluded to in the lectures, that there are real systems that may be approximated as a one-dimensional problem for certain purposes.

For example in the dye molecule-ion structures shown in Figure 1, the double bonds between the two nitrogen atoms can be thought of as being spread out over the molecule ions i.e. they are not localised in one bond area but rather appear to be spread out over the entire length of the double bond chain. These electrons, the so-called π – electrons, “move” along the chain between the terminal nitrogen atoms and are highlighted in yellow in Figure 1. If it is assumed that the potential encountered by the electrons due to the carbon centres is constant over the length of the chain, the potential may for convenience be taken as zero. This is of course just like the one dimensional particle in a box that is free ($V=0$) to move along the x direction between $x=0$ and $x=L$, where L is the length of the box. In the real molecule or ion the electrons are free to move along the chain (x) between the limits $x=0$ and $x=L$, where L is the length of the chain. The energy values for this particle in a box are as derived in the lectures:

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

In the real molecule, there are several one-dimensional particles (electrons) all confined to the one box. Each such particle must be described by a particular wavefunction and because of spin a maximum of two oppositely paired electrons only can occupy each energy level. This means that in the ground state, the n -electrons would fill up the energy levels in pairs or more generally for a case of N electrons the first $N/2$ energy levels would be filled.

In visible absorption spectroscopy, energy is absorbed by an electron in the highest occupied level, n to promote it to the next highest level, $n+1$. For the particle in a box model the energy absorbed would be given by,

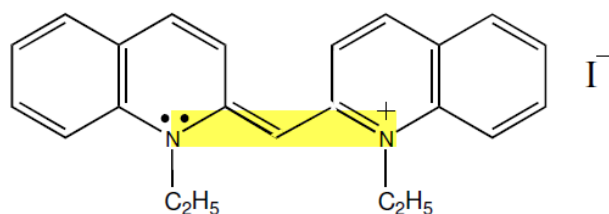
$$\Delta E = E_{n+1} - E_n = \frac{h^2}{8mL^2} (2n + 1)$$

$\Delta E = E_{\text{photon}} = \frac{hc}{\lambda}$ and the wavelength λ of the absorbed radiation is therefore

$$\lambda = \frac{8mL^2}{h(2n + 1)}$$

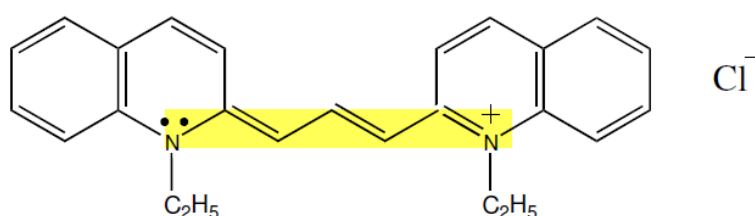
The three dye compounds used in this experiment are shown in Figure 1 below. The conjugated system modelled by the particle in a box extends from one nitrogen atom to the other and is highlighted in yellow.

Compound (I)



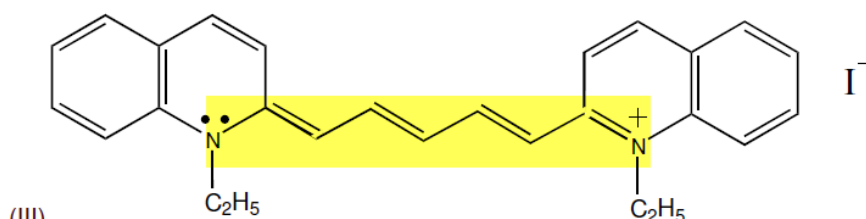
1,1'-DIETHYL-2,2'-CYANINE IODIDE

Compound (II)



1,1'-DIETHYL-2,2'-CARBOCYANINE CHLORIDE

Compound (III)



1,1'-DIETHYL-2,2'-DICARBOCYANINE IODIDE

Figure 1

For compound (I) therefore the conjugation system encompasses the two N atoms and three carbon atoms. Each carbon atom will contribute one electron to the system while the two nitrogen atoms contribute three electrons between them. So, knowing the number of carbon atoms we can predict the visible wavelength value for each of the dye compounds shown using the expression for the wavelength we derived above.

Exercise 1

Draw an energy level diagram for each dye in its ground state. Work out the number of π -electrons for each dye (one for each carbon atom and three for the two nitrogen atoms present) and place two of opposite spin in each energy level derived from the particle in a box model.

Exercise 2

Then use the formula for the wavelength given above to calculate λ in nanometres (nm) for each dye compound. The L values to use for each dye compound are as follows:

Dye 1: 10.6 angstrom

Dye 2: 12.9 angstrom

Dye 3: 15.2 angstrom

Exercise 3

Now go to the virtual laboratory to view the preparation of the dyes for the spectroscopy experiment and then use the simulated spectrometer to record the visible absorption spectrum for the three dyes. Record the wavelength of the peak maximum, λ_{max} , for each dye in nanometres (nm) and compare your experimentally determined values with your calculated values in Exercise 2 above. Reflect on the agreement between experimental and calculated values and discuss in the forums the suitability and limitations of the model to this particular problem.

Assessment question

The *calculated energy* in eV and *experimental* λ_{max} value measured for Dye, Compound (III) are respectively:

- a) 1.0 eV and 626 nm
- b) 3.4 eV and 702nm
- c) 1.7 eV and 626 nm
- d) 1.7 eV and 702 nm
- e) 3.4 eV and 626 nm
- f) 2.5 eV and 702 nm