

Chemistry 321: Physical Chemistry 2

Particle in a Box

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The write-up for this lab is due on 2006-02-06.

1 Background

You may already be aware that molecules and photons can interact in various ways. In large part, the nature of these interactions is dictated by the energy of the particular photons in question. For example, infrared photons may excite vibrational modes in molecules, while UV-B photons tend to knock electrons right out of their bonds (hence, ionizing radiation). Photons in the visible to near ultraviolet region have energies that can excite electrons out of their molecular orbitals into other bound states (formerly unoccupied molecular orbitals). So, each peak in a UV-vis spectrum corresponds to the excitation of an electron from some occupied molecular orbital to some unoccupied molecular orbital.

In this experiment, we will treat the molecular orbitals in a conjugated carbon-carbon system as one dimensional particle in a box wavefunctions. Transitions from one molecular orbital to another will be treated as transitions from one 1-D particle in a box energy state to another.

2 The experiment

You have been provided with stock solutions of three molecules in cyclohexane. The three molecules are 1,4-diphenyl-1,3-butadiene, 1,6-diphenyl-1,3,5-hexatriene, and 1,8-diphenyl-1,3,5,7-octatetraene. From these stock solutions, make up small samples diluted to $\approx 10^{-6}$ M.

Using the OceanOptics spectrophotometers, take absorption spectra of each of the three molecules. Be sure to save your data so you can include your spectra in your report. It may be wise to use the spectrophotometer software to take note of the locations of the peaks in your spectra.

3 Analysis

3.1 The experimental box length

3.1.1 Draw the molecules

Use a chemical drawing program to produce bond-line drawings of the molecules of interest for your report. All of the conjugated double bonds are in the “trans” configuration. It may help to just sketch them out by hand for now and “make them pretty” later.

3.1.2 Determine the particle in a box quantum numbers for each HOMO and LUMO

For each molecule, count the number of π electrons in the conjugated system (the phenyl rings don't count). Your bond-line drawing will help. Using this electron count, determine the 1-D particle in a box quantum number of the highest occupied molecular orbital (HOMO) for each molecule, assuming that a pair of electrons goes into each orbital. For example, if your system has two π electrons, then the particle in a box quantum number for the HOMO is $n = 1$. The corresponding 1-D particle in a box quantum number of the lowest occupied molecular orbital (LUMO) is one more than that of the HOMO. Therefore, the particle in a box quantum number for the lowest unoccupied molecular orbital (LUMO) in this example is $n = 2$.

3.1.3 Calculate the experimental box length

Using the expression for the energy of a particle in a one dimensional box, derive an equation for the energy difference between two 1-D particle in a box energy levels. For each molecule, find the peak in the spectrum that corresponds to the HOMO-LUMO transition. Use the Planck-Einstein equation for the energy of a photon to find the ΔE corresponding to the absorption of light with this wavelength. Plug this ΔE and the relevant particle in a box quantum numbers from 3.1.2 into your energy difference equation. The only unknown quantity should be the box length. Solve for the box length. This is your experimental box length.

3.2 The theoretical box length

One could go through a lot of trigonometry to try to figure out the box length from literature single bond lengths, double bond lengths, and bond angles, but that is more work than the rest of this lab so I will just give you these values. The distance from phenyl ring to phenyl ring in each of the molecules of interest is given in Table 1.

Table 1: Through space phenyl-phenyl distances

| Molecule | length (Å) |
|-----------------------------------|------------|
| 1,4-diphenyl-1,3-butadiene | 6.35 |
| 1,6-diphenyl-1,3,5-hexatriene | 8.83 |
| 1,8-diphenyl-1,3,5,7-octatetraene | 11.30 |

How do your experimental box lengths from 3.1.3 compare to the theoretical box lengths in Table 1?

4 Write-up

Start with a brief, simple introduction.

Briefly recount how you took the spectra, including what concentration of each molecule you used and any other relevant explanation, such as what you used as a blank. Include publication quality bond-line drawings of the molecules of interest. Present the spectra in a publication quality figure in your report.

Explain how you determined the HOMO and LUMO particle in a box quantum numbers for each molecule.

Explain which peaks you used in your calculations and how the calculations were done. Present the results of your calculated experimental box lengths for each molecule. How do your experimental box lengths compare to the theoretical box lengths?

End with a brief, coherent conclusion.