

**CHEM 3420 Pchem II, Fall Semester**  
**Group Lab Research Project: Particle-in-a-Box and Particle-on-a-Ring**

**Overall Goals:**

- To learn the steps involved in setting up a research project
- To calculate the  $\lambda_{\max}$  of various conjugated systems via QM models, to execute the spectrophotometric experiments to determine the same  $\lambda_{\max}$ , and to compare these data to QM literature values to determine the percent error of the QM models
- To learn how to write scientific articles for publication in a peer-reviewed journal

**I. Particle-in-a-Box**

**Goal:** To determine how well the particle-in-a-box model models the absorption spectrum for conjugated systems (To 1. calculate the absorption spectrum (uv-vis) for several conjugated molecules using the particle-in-a-box model, 2. measure the  $\lambda_{\max}$  using spectroscopy, and 3. compare both the theoretical and experimental results to literature values for  $\lambda_{\max}$  to determine how well the particle-in-a-box model works and the percent error of the experimental results)

**Introduction and Theory:**

Please see the following references:

Sime, R. J. *Physical Chemistry: Methods, Techniques, and Experiments*; Saunders College: Philadelphia, **1988**. (Theory)

Garland, C. W.; Nibler, J. W.; Shoemaker, D. P. *Experiments in Physical Chemistry*, 8<sup>th</sup> Ed.; McGraw Hill: New York, **2003**, pp 393-398. (Experimental Method)

**Procedure**

Please see the above references.

**Data Analysis**

Please see the above references.

Questions and thoughts to be pursued and included in the formal lab report...

1. Discuss the theory of quantum mechanics and the particle-in-a-box explaining why these molecules can be modeled with this theory.
2. *For each compound*, (a) take the experimental  $\lambda_{\max}$  and calculate the experimental energy of the electronic transition, (b) take the literature  $\lambda_{\max}$  and calculate the experimental energy of the electronic transition, and (c) calculate the experimental energy using the particle-in-a-box model. In addition, (d) compare the calculated and literature values of the energies of the electronic transition and (e) compare the experimental and literature values of the energies of the electronic transition. Show all your work (e.g. all of your calculations, etc.). Finally, (e) compare the experimental and calculated values of the energies of the electronic transition.
3. Comment on the agreement between the model and your experiment. What assumptions are most likely to be incorrect? Is there any trend with an increase in the number of conjugated rings?

## II. Particle-on-a-Ring

Adapted from "Physical Chemistry Lab Manual" from William West and John Pojman at the University of Southern Mississippi

**Goal:** To determine how well the particle-on-a-ring model (the 2-D rigid rotor) models the absorption spectrum for benzene, naphthalene, and anthracene (To 1. calculate the energy associated with the absorption spectrum (uv-vis) for several conjugated molecules using the particle-on-a-ring model, 2. then convert this energy to a wavelength, 3. measure the  $\lambda_{\text{max}}$  of each compound using spectroscopy, 4. compare both the calculated and experimental results to literature values to determine the percent error of the position of the spectral transition, and 5. compare the calculated and experimental results to one another)

### Introduction and Theory:

This experiment is very similar to the experiment for a particle-in-a-box where conjugated dyes were used as the box and where one electron was the particle in the box. For this experiment, the conjugated systems of benzene, naphthalene, and anthracene will be used as the ring, and an electron of each molecule will be considered as the particle on said ring. The particle-on-a-ring concept is a "practical" application of the rigid rotor, which is discussed in class. Atkins (ps. 297-308) has an excellent discussion on the rigid rotor and is required reading for this lab.

The jist of Atkins' discussion is as follows: When a particle of mass  $m$  is confined to a ring, its energy contains angular momentum ( $J$ ) and the moment of inertia ( $I$ ).

$$E = \frac{J^2}{2I} \quad (1)$$

where  $J = m_l\hbar$  and where  $I = mr^2$ . Substituting quantum mechanical operators reduces the equation to:

$$E = \frac{m_l^2\hbar^2}{2mr^2} \quad (2)$$

where  $m_l$  is a quantum number,  $m$  is the mass of the particle, and  $r$  is the radius of the ring. It is evident that the energy is quantized in regards to the quantum number  $m_l$ .

In order to test the particle in a ring problem in regards to these conjugated compounds, one first needs to know the radius of motion. Since the electrons in conjugated compounds revolve around the centers of the molecules, one can assume that the radius of the molecule is equivalent to the radius of motion. However, since the molecules are not perfect circles, it is difficult to obtain a definite radius. For this reason, the radii used are the average of the smallest possible radius and the largest possible radius for each molecule.

The second major hypothesis is the construction of the energy levels of the electrons in the ring structure. In a conjugated structure, the energy levels can be viewed as subsequent levels of increasing energy each containing one orbital. In this unexcited state, the angular momentum quantum number  $m_l$  would be zero. When this system is excited, the change in the angular momentum quantum number must be +1, 0, or -1. Thus, the only change that could occur that would apply to our model is  $\Delta m_l = 1$ , from  $0 \rightarrow 1$ . Combining this fact with equation (2) yields an equation for the predicted energy of transition

$$E = \frac{\hbar^2}{mr^2} \quad (3)$$

If one knows the radii for a molecule from the above method, one can predict the energy of a transition for a conjugated cyclical structure.

The next task is to obtain the actual energies of transition to compare with the theoretical model (equation 3). The actual energies can be obtained via UV-Vis spectroscopy (or the literature). By obtaining the spectra for benzene naphthalene, and anthracene, one can convert the wavelength of the primary peak to an energy.

$$E = h\nu = \frac{hc}{\lambda} \quad (4)$$

where  $c$  is the speed of light and where  $\lambda$  is the wavelength of light. Once the energy of the predominant peak is obtained it can be compared to the theoretical energy calculated from equation 3.

### Procedure

Obtain the UV spectrum for benzene, naphthalene, and anthracene in a 1.0 cm standard cuvette. Determine the  $\lambda_{\max}$ .

### Data Analysis

One can calculate the energy of the transition for the  $\lambda_{\max}$ . To calculate the predicted transition energy from the model, we need to estimate the effective radius of each compound. The bond length for benzene is 1.39 Å. Draw the structure carefully and show that a circle of radius equal to the bond length will circumscribe the structure. Calculate the energy for the transition and compare to the experimental value. For naphthalene and anthracene, draw the structures carefully and determine the average radii.

Questions and thoughts to be pursued and included in the formal lab report...

4. Discuss the theory of angular momentum and the rigid rotor explaining why these molecules can be modeled with this theory.
5. For each compound, compare the measured (or literature) value of the energy of the electronic transition and compare it to value you calculate. Show all your work (e.g. all of your calculations, etc.).
6. Comment on the agreement between the model and experiment. What assumptions are most likely to be incorrect? Is there any trend with an increase in the number of conjugated rings?
7. How would the agreement between the model and experiment change if the model used the largest radii for the molecules? The smallest radii?