

## **Particle in a Box**

Group Members: Kaffie Kirby, Cameron Lorenz, Sarayu Kondaveeti

November 8, 2024

PY203 Section 001

## **Introduction**

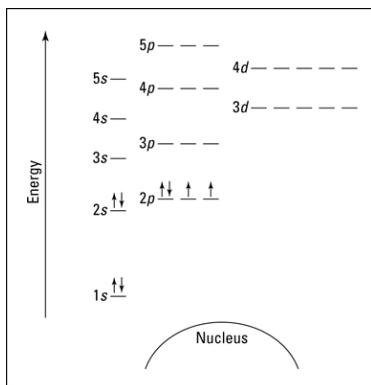
The objective of this experiment is to measure the wavelengths of the photons absorbed by the different substances and use those values to determine the values of certain energy transitions. This can be determined using the equation  $E = hc/\lambda$ . These experimental values will then be compared to the predicted values.

Before the experiment was conducted, the following questions were answered (in order to predict certain values):

*a) Find the correct ordering for each of the molecules. You can determine how many energy levels are needed by counting the number of double bonds ( $C=C$ ) in the molecule. There are 2  $\pi$ -electrons for every double bond ( $C=C$ ) in the molecule, so if, for instance, the molecule has 6 double bonds, then the molecule has 12  $\pi$ -electrons that will fill the first 6 energy levels in a pairwise fashion. As a result, the 6th energy level is the HOMO, and the 7th level is the LUMO.*

Naphthalene:

Naphthalene has 5 double bonds, so the molecule has 10  $\pi$ -electrons. According to Hund's rule, the electrons have to fill up every orbital in a sublevel before they start doubling in an orbit (see diagram).



HOMO: 5th level ( $n = 2$ )

LUMO: 6th level ( $n = 3$ )

Anthracene:

Anthracene has 7 double bonds so the molecule has 14  $\pi$ -electrons.

HOMO: 9th level ( $n = 3$ )

LUMO: 10th level ( $n = 3$ )

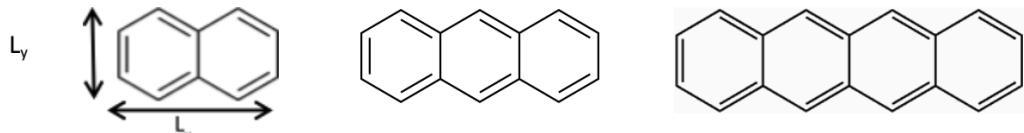
Tetracene:

Tetracene has 9 double bonds so the molecule has 18  $\pi$ -electrons.

HOMO: 9th level ( $n = 3$ )

LUMO: 10th level ( $n = 4$ )

b) For each molecule, calculate the approximate lengths of each molecule along the x and y directions. You may assume that each carbon-carbon (C-C) bond has a length of 0.14nm and that all angles are 120 degrees; use trigonometry to determine the approximate lengths of each molecule. Please calculate these lengths using x as the long dimension, as shown in Fig 6. Show your calculations and results in your lab report. The chemical structures of each molecule have been provided in Fig 6. Hint: find the dimensions of one ring first. C-C bond length is the length of one of the sides of the hexagonal units as in Fig 6.



**Fig 6.** Skeletal diagrams of naphthalene, anthracene, and tetracene, respectively. C=C bonds are represented by double lines, and hydrogen atoms are understood to be where necessary.

Naphthalene:

$$0.14 \cos(30^\circ) = \frac{x}{0.14 \text{ nm}}$$

$$0.14 \cos(30^\circ) = 0.1212 \text{ nm}$$

$$4(0.1212) = \boxed{0.485 \text{ nm} = L_x}$$

$$L_y = 2y + x$$

$$\sin(30^\circ) = \frac{y}{0.14 \text{ nm}}$$

$$y = 0.14 \sin(30^\circ) = 0.07$$

$$L_y = 2(0.07) + 0.1212 = \boxed{L_y = 0.2612 \text{ nm}}$$

Anthracene:

$$L_x = 6x = 6(0.1212) = \boxed{0.7275 \text{ nm} = L_x}$$

$$L_y = 0.2612 \text{ nm}$$

Tetracene

$$L_x = 8x = 8(0.1212) = \boxed{0.97 \text{ nm} = L_x}$$

$$L_y = 0.2612 \text{ nm}$$

c) Compute the various energy levels for each state in terms of the energy constant  $E_0$ , beginning with  $\{n_x = 1, n_y = 1\}$ . Calculate sufficient levels to ensure that you have captured the HOMO and LUMO levels. Sort the list to place the states in ascending order of energy. Include a printout of your calculation in your turned-in homework assignment for this lab.

The following equation was used for calculations:

$$E = E_x + E_y = \frac{\hbar^2 \pi^2}{2m_e} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

The python script used to calculate the energy levels can be found here:

<https://github.com/sara-k03/physics-computations/blob/master/PY203EIC/EICPreLab.py>

The text file with the list can be found here:

<https://github.com/sara-k03/physics-computations/blob/master/PY203EIC/PreLabOutput.txt>

The calculated energy values in the form of a table, where columns are  $n_y$ , rows are  $n_x$ , and energies are expressed in eV:

Naphthalene:

	$n_y = 1$	$n_y = 2$	$n_y = 3$
$n_x = 1$	7.12	11.91	19.91
$n_x = 2$	23.66	28.46	36.46
$n_x = 3$	51.24	56.04	64.04

Anthracene:

	$n_y = 1$	$n_y = 2$	$n_y = 3$
$n_x = 1$	6.23	8.36	11.91
$n_x = 2$	22.77	24.91	28.46
$n_x = 3$	50.35	52.48	56.04

Tetracene:

	$n_y = 1$	$n_y = 2$	$n_y = 3$	$n_y = 4$
$n_x = 1$	5.92	7.12	9.12	11.91

$n_x = 2$	22.46	23.66	25.66	28.46
$n_x = 3$	50.04	51.24	53.24	56.04
$n_x = 4$	88.65	89.85	91.85	94.65

### **Methods**

In this experiment, the Ocean Optics USB4000 spectrometer was utilized to obtain the absorption spectrum of Naphthalene, Anthracene, and Tetracene molecules. The aforementioned molecules were provided in the appropriate cuvettes for placement in the spectrometer. Our objective was to determine the absorption spectrum of each individual molecule and then compare our experimental peak wavelength with the predicted peak wavelength from the particle in a box model.

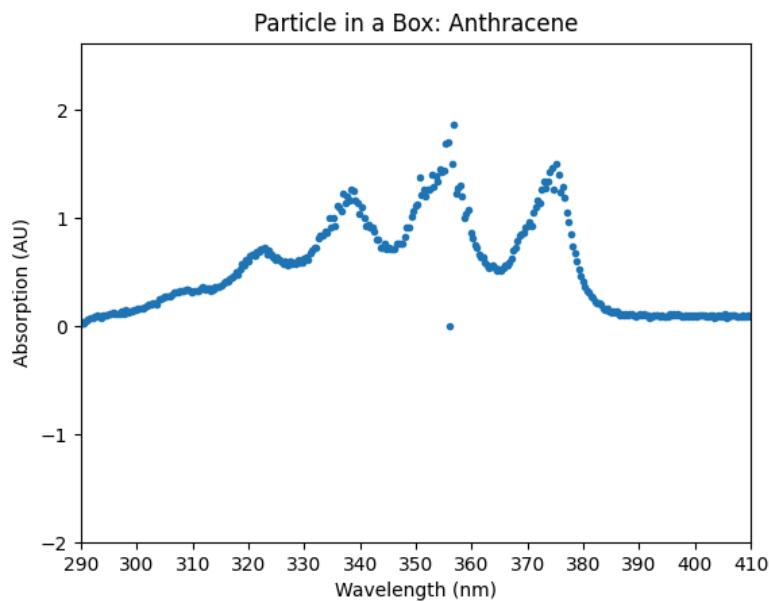
The spectrometer was already set up upon our arrival so we jumped straight into calibrating the machine. The OceanView software was utilized for this experiment so after we opened the software we performed an absorbance only measurement on the cuvette with octanol in it as a reference. Then, we saved a “dark” spectrum where we inserted a cuvette with black tape covering it into the machine and saved this in order to “zero” out the spectrum.

Once this setup was completed, we moved on to measuring the absorbance of our samples. Each cuvette containing either naphthalene, anthracene, or tetracene dissolved in octanol was wiped clean before being placed into the spectrometer one by one. Ten absorbance measurements were taken three times (for a total of 30 measurements) for each molecule and these files were then used to create the graphs shown in the results section below.

### **Results**

The graphs show absorption (AU) against wavelength (nm) and are zoomed in on the region where the peaks are located, showing the wavelengths of the photons that were absorbed. The parts of the graph that are not shown are either just noise or correspond to wavelengths that were not absorbed. As briefly mentioned in the introduction, the energies of the absorbed photons are determined by using the formula  $E = hc/\lambda$ , where  $h = 4.14 \times 10^{-15}$  eV s and  $c = 3 \times 10^8$  m/s. So,  $hc = 1.242 \times 10^{-6}$ .

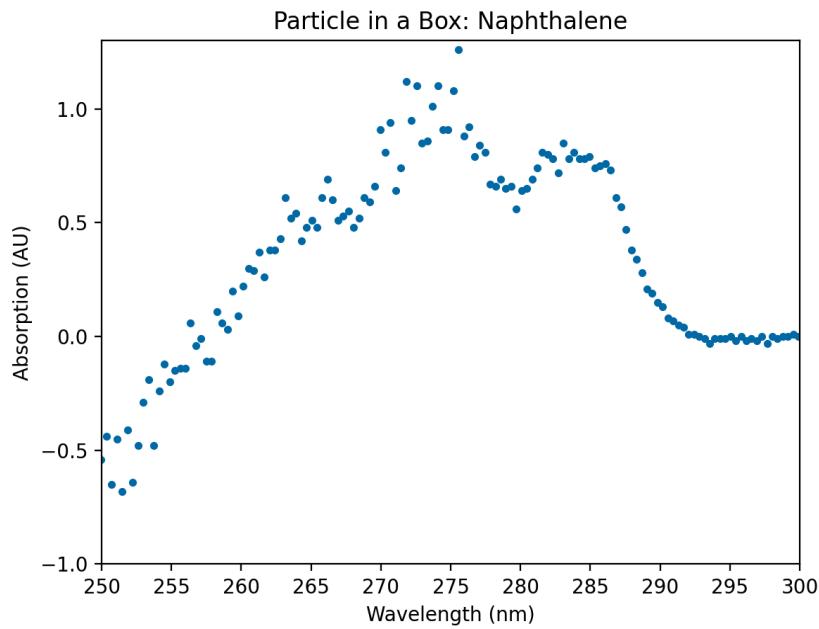
The Anthracene graph:



The peaks for Anthracene and their corresponding energies are roughly as follows:

Peak Coordinates (nm, AU)	Energy (eV)
(338.8, 1.265)	3.67 eV
(356.9, 1.871)	3.47 eV
(375.4, 1.478)	3.31 eV

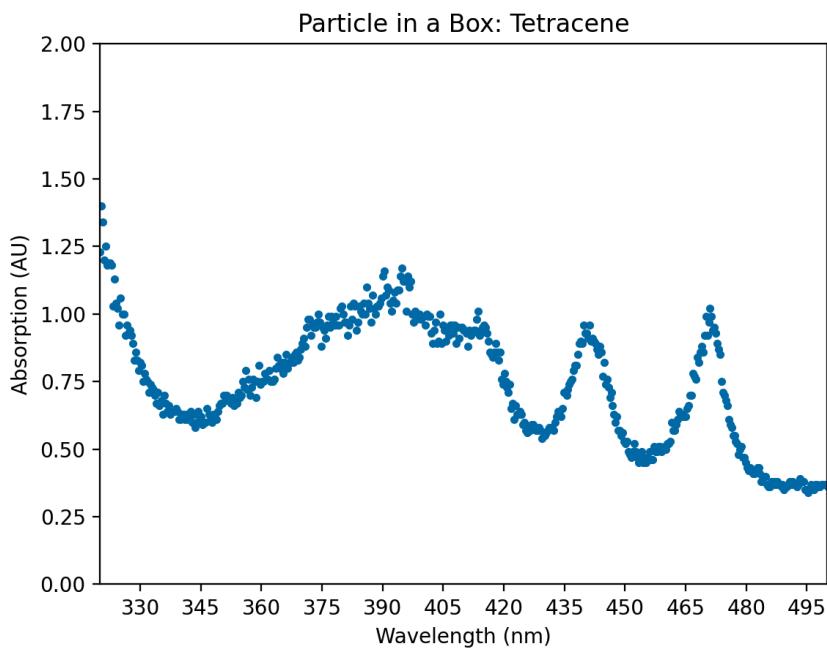
The graph for Naphthalene:



The peaks for Naphthalene and their corresponding energies are roughly as follows:

Peak Coordinates (nm, AU)	Energy (eV)
(266.03, 0.700)	4.66 eV
(275.66, 1.260)	4.51 eV
(283.11, 0.840)	4.39 eV

The graph for Tetracene:



A note about this graph—the left side of the graph starts off at a higher value because of noise. This does not correspond to an actual peak.

The peaks for Tetracene and their corresponding energies are roughly as follows:

Peak Coordinates (nm, AU)	Energy (eV)
(395.3, 1.162)	3.14 eV
(439.6, 0.970)	2.82 eV
(471.5, 1.018)	2.63 eV

## Conclusion

*Q1) Calculate the energy constant  $E_0$  from the pre-lab in units of electron-volts (eV).*

$$E = E_x + E_y = \frac{\hbar^2 \pi^2}{2m_e} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

$$E_0 = (\hbar^2 \pi^2) / (2m_e) = (6.58 \times 10^{-16})^2 \text{ eV}^2 \text{ s}^2 (\pi^2) / (2)(511000 \text{ eV}/(3 \times 10^8 \text{ m/s})^2)$$

$$E_0 = 3.76 \times 10^{-19} \text{ eV m}^2$$

The handwritten derivation shows the following steps:

$$\begin{aligned} \frac{\pi^2 \pi^2}{2m_e} &= (6.58 \times 10^{-16})^2 \text{ eV}^2 \cdot \frac{\pi^2}{m_e} \\ &\approx (2)(511000 \text{ eV}) / (3 \times 10^3)^2 \text{ m}^2 \\ &= (6.58 \times 10^{-16})^2 \text{ eV} \cdot \pi^2 \cdot m_e^2 \cdot (3 \times 10^3)^2 \\ &\approx (2)(511000) \\ &= 3.76 \times 10^{-19} \text{ eV} \cdot \text{m}^2 \end{aligned}$$

*Q2) Referring back to the pre-lab homework and Q1, construct a table of energies in eV while varying  $n_x$  and  $n_y$ . What energies would you expect for the lowest-energy excitations for each molecule? Which energy transitions do these correspond to?*

Tables were already constructed for the pre-lab, pasted below for reference. These values were generated by a python script (which is linked in the pre-lab).

Naphthalene:

	$n_y = 1$	$n_y = 2$	$n_y = 3$
$n_x = 1$	7.12	11.91	19.91
$n_x = 2$	23.66	28.46	36.46
$n_x = 3$	51.24	56.04	64.04

The lowest energy excitation for naphthalene would be 4.79 eV. Which corresponds to the transition between  $(x = 1, y = 1)$  to  $(x = 1, y = 2)$ .  $(x = 2, y = 1)$  to  $(x = 2, y = 2)$  and  $(x = 3, y = 1)$  to  $(x = 3, y = 2)$  also have similar transition energy transitions at 4.8 eV.

Anthracene:

	$n_y = 1$	$n_y = 2$	$n_y = 3$
$n_x = 1$	6.23	8.36	11.91
$n_x = 2$	22.77	24.91	28.46
$n_x = 3$	50.35	52.48	56.04

Similar to naphthalene, the lowest energy transitions are from (x = 1, y = 1) to (x = 1, y = 2), (x = 2, y = 1) to (x = 2, y = 2), and (x = 3, y = 1) to (x = 3, y = 2), with energies 2.13 eV, 2.14 eV, and 2.13 eV, respectively.

Tetracene:

	$n_y = 1$	$n_y = 2$	$n_y = 3$	$n_y = 4$
$n_x = 1$	5.92	7.12	9.12	11.91
$n_x = 2$	22.46	23.66	25.66	28.46
$n_x = 3$	50.04	51.24	53.24	56.04
$n_x = 4$	88.65	89.85	91.85	94.65

All the transitions from y = 1 to y = 2 (regardless of x energy level) emit photons of the same energy, 1.2 eV.

*Q3) From your collected absorption spectra, note the maximum-wavelength absorption lines for each sample. What are the energies of the absorbed photons? How do they compare to predicted values?*

For naphthalene, the maximum-wavelength absorption lines corresponded to the following energies: 4.66 eV, 4.51 eV, and 4.39 eV. This is very similar to the predicted values of 4.79 and 4.8.

For anthracene, the maximum-wavelength absorption lines correspond to the following energies: 3.67 eV, 3.47 eV, and 3.31 eV. This is also somewhat similar to the predicted values of 2.13 and 2.14. This is not quite as accurate as naphthalene, but it's still relatively close.

For tetracene, the maximum-wavelength absorption lines correspond to the following energies: 3.14 eV, 2.82 eV, and 2.63 eV. While these values are not very close to the predicted value of 1.2, they are still the lowest values out of the 3 molecules, which matches with the predicted values .

For both the measured and predicted values, naphthalene has the highest energy, followed by anthracene, then tetracene.

*Q4) Compare your measurements to the published data as in [3]. If the measured spectra are different from the literature spectra, do the literature spectra provide better agreement with your model?*

Our spectra seem to contain comparable shapes to the literature. However, some of our spectra's absorbance values (on the y-axis) seemed to have a different amplitude. This may likely be to the two graphs being made using different blanks, different machines, etc. The main piece of information we are going to focus on is the wavelength of each peak and the energy associated with that wavelength using the formula  $E = hc/\lambda$ , where  $h = 4.14 \times 10^{-15}$  eV s and  $c = 3 \times 10^8$  m/s. So,  $hc = 1.242 \times 10^{-6}$  eV m. A table for our determined wavelengths and the literature's determined wavelengths are shown below for each molecule.

Anthracene:

Our $\lambda$ (nm)	Energy (eV)	Experimental $\lambda$ (nm)	Energy (eV)
333.8	3.67	338	3.67
356.9	3.47	345	3.60
375.4	3.31	362	3.43

Naphthalene:

Our $\lambda$ (nm)	Energy (eV)	Experimental $\lambda$ (nm)	Energy (eV)
266	4.66	267	4.65
276	4.51	275	4.52
283	4.39	279	4.45

Tetracene:

Our $\lambda$ (nm)	Energy (eV)	Experimental $\lambda$ (nm)	Energy (eV)
395	3.14	~414	3.00
439	2.82	~440	2.82
472	2.63	~475	2.61

Each of these tables displays values for our wavelengths and the literature wavelengths that seem to agree fairly well with each other. There is some discrepancy between values of course, but I was also estimating the  $\lambda$  values for the literature graphs so I might have estimated incorrectly which would lead to slightly askew values.

One notable difference between our values and the literature values would be the lack of a fourth peak on our anthracene graph. In the literature graph, there is a fourth peak in between the peaks at 345 nm and 362 nm that isn't present on our graph. However, our graph does seem to have a bit of fluctuation occurring within that region between the two peaks which leads me to expect that the peak is present there but the graph is too condensed to show it.

Therefore, I would like to conclude that our values do match within experimental error with the literature values. If there is any notable difference then the literature values are more likely to provide better agreement with our model due to the age of our samples (which can cause the molecules to break down) and our spectrometer.

*Q5) What assumptions used to produce the predicted energy values do you suspect may have led to any discrepancies between the model and the measured or literature spectra? How would you modify the model to better describe the data?*

The model we used was a particle in a box model which makes many assumptions regarding the nature of the particles present in this experiment. Firstly, the particle in a box model assumes that there is one independent electron present in an infinitely high square well, which isn't the case in real life. The electron is assumed to be within this box and unable to get out of it. This model also (as a consequence of assuming there is only one particle present) neglects to consider how multiple electrons might affect each other.

To help rectify this, we could instead use a finite square well particle in a box model which would be more accurate in this circumstance. We could also adjust our equations to include the interactions between neighboring particles. These two adjustments would improve the accuracy of our model and align more closely with our results.