

The Electronic Spectrum of β -Carotene

In this laboratory exercise, you will measure the electronic spectrum of β -carotene, which is the plant pigment that gives rise to the distinctive color of the carrot. This polyene is used as a yellow coloring agent in foods and is a precursor of vitamin A in all species except cats. (It is not surprising that this most excellent of mammals has evolved its own biochemical pathway.) You will then rationalize the nature of the spectrum by (1) applying the particle-in-a-box Hamiltonian to the π electrons in this molecule, and (2) using the Schrodinger equation to predict the electronic excitation energy.

Experimental Procedure

Shave a few pieces off the exterior of the carrot. Avoid using the light yellow center portion, which contains higher concentrations of xanthophyll, another plant pigment. Grind the carrot pieces in a clean test tube with a stirring rod. Pour about 5 mL of hexane into the test tube and swirl to extract the yellow β -carotene. A few seconds will suffice to extract sufficient pigment to obtain a UV-visible spectrum. Acquire the UV-visible spectrum (300–800 nm) of this pigment in hexane solution, against a neat hexane reference. Turn off the spectrometer, monitor and printer when done. Dispose of the hexane solutions in an organic waste container and clean up the cuvettes and the test tube.

Analysis

You will be submitting a written report (as you did in Chemistry 55 Lab) in which you present your experimental data and your results for the following calculations:

I. The Free Electron Molecular Orbital Model

Look up the structure of β -carotene and determine how many π electrons this molecule has. Assume (rather crudely) that the π electrons in the molecule are particles confined to a one-dimensional infinite well, with the energy levels given by the result we learned in Chapter 11. Further assume that the aufbau and Pauli exclusion principles determine the ground electronic state of β -carotene (that is, two π electrons fill each of the lowest available energy levels of the box). This is the so-called Free Electron Molecular Orbital Model.

The first excited state of β -carotene involves promotion of one electron from the highest occupied molecular orbital (the HOMO) to the lowest unoccupied molecular orbital (the LUMO). Derive an expression for the separation in energy between the HOMO and the LUMO. This energy will depend on L , the length of the box. Then derive an expression (in terms of L) for the wavelength of light required to excite this transition. Using these results, derive a "spectroscopic" value of L from the value of λ_{\max} you observed for β -carotene.

Next, calculate a "structural" value of L by assuming the π electrons are required to "travel" along the backbone of the molecule; use the known average values for the lengths of carbon-carbon single and double bonds in your calculation. Compare the structural and spectroscopic values by computing a percent difference. In your report, try out at least one alternate way of determining the structural value of L that may improve the agreement with the spectroscopic value. For example, use trigonometry to calculate the "through space" length of the box ("as the crow flies").

II. A More Realistic Quantum-Mechanical Model

The most accurate way to interpret the electronic spectrum of β -carotene is to solve the Schrodinger equation for the molecule. Such a calculation takes into account both σ and π electrons. This cannot be done analytically, but software programs like MacSpartan Pro can do an excellent job of solving the Schrodinger equation numerically. We will use this program (which is loaded on the iMacs in the department computer lab) in two ways. First, we will "optimize" the geometry of β -carotene—that is, we will have MacSpartan predict all the bond lengths and angles in the molecule. This should give us an accurate value for L . This calculation will also generate a prediction of the HOMO-LUMO energy gap completely independent of the Free Electron Molecular Orbital Model.

MacSpartan Pro Instructions

1. Find the program in the "Macalester Applications" folder and run it.
2. Select **New** from the **File** menu. The Model Kit window will appear.
3. Using the **Entry** mode of the Model Kit window, start building β -carotene. Choose a desired C hybridization, and click on the main window. The white "half-bonds" indicate sites where new fragments can be added. You can close a ring by clicking on the **Make Bond** button and then clicking on the white half-bonds of the atoms you wish to connect. Note that a white half-bond is assumed to be H unless you put another atom there.
4. You can control the conformation around bonds (*e.g.*, do you want your double bonds to be *cis* or *trans* to each other?) by choosing **Measure Dihedral** under the **Build** menu, clicking on the four consecutive atoms whose conformation you wish to set, and then entering the desired dihedral angle at the bottom of the main window. When you are done tweaking angles, choose **Add Fragment** under the **Build** menu to resume building your structure.
5. Note the following tools for manipulating your structure on the screen:
 - Enlarge/Reduce the Molecule: Depress the option and apple keys simultaneously while dragging the mouse in the appropriate direction to achieve the desired effect.
 - Molecule Representation: The way in which a molecule is displayed can be changed by switching between the "wire", "ball and wire", "tube", "ball and spoke", and "space filing" options under the **Model** menu.
 - Move the Molecule: Depress the mouse and option key simultaneously while moving the mouse.

- Rotate the Molecule in the X/Y Plane: Click on the background and drag the mouse in the desired direction.
 - Rotate the Molecule in the Z Plane: Depress the mouse and apple key simultaneously while dragging the mouse in the desired direction.
6. When you feel in the mood to save your work, choose **Save As** from the file menu, go to **UserFolder** on the hard drive, create and open a new folder with your group's name, and save your new MacSpartan Pro file(s). (Note that MacSpartan automatically creates a new folder.) If you close out of MacSpartan Pro, you can re-open your β -carotene file when you run the program again. Choose **Add Fragment** under the **Build** menu if you need to alter your saved structure.
 7. When you are all done building the molecule, click on the **Minimize** button. This will start a so-called molecular mechanics force field calculation that adjusts bond lengths and angles to match typical experimental values. This minimization does not solve the Schrodinger equation.
 8. Select **Calculations...** from the **Setup** menu. The resulting window can be used to establish appropriate parameters for the calculation. Under the "Calculate" heading select "**Equilibrium Geometry**" with "**Semi-Empirical**" and "**AM1**". The latter two terms refer to the method by which we will truly solve the Schrodinger equation. "**Initial geometry**" should be indicated under the "Start from" heading. Click OK once your selections in this window are complete. Then choose **Submit** under the **Setup** menu.
 9. The calculations will take a while. When they are over, measure the length of the β -carotene box by using **Measure Distance** under the **Build** menu. Compare this with the spectroscopic value.
 10. Then choose **Properties** under the **Display** menu. The **Molecule Properties** window that pops up will tell you the energies of the HOMO and LUMO. Use the difference in these energies to predict the wavelength of light that should match the HOMO-LUMO gap, and compare this with the experimental λ_{\max} value.

You may work in groups of 2 or 3 for all parts of this exercise: the experiment, the computation, and the write-up. Note that you will all share the same grade. All group members must share in the analysis of the data and the writing of the report.