

## Chem 260 Laboratory 1

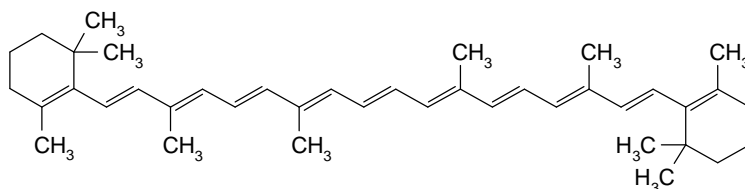
This lab uses the example of the electronic spectroscopy of conjugated polyenes to demonstrate some features of the “Particle in a Box”. The conjugated bond system is “the box”, and the electrons are “the particles”. In the ground state of the molecule, energy levels are filled from the lowest upwards, with two electrons in each level. The lowest spectroscopic transition corresponds to promotion of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

You will use HyperChem Lite software to calculate the LUMO-HOMO energy gap ( $\Delta E$ ) for several different molecules, convert  $\Delta E$  to the corresponding frequency and wavelength of light, and plot the results using Excel. If there is time you may create other polyene structures by editing one of the supplied files. Structures should be optimized with the molecular mechanics routine (MM+). A single point calculation using Extended Hückel Theory (EHT) provides the energy levels and can also be used to plot molecular orbitals.

### DETAILED PROCEDURE

1. Copy the following files from the network directory F:\COURSES\CHEM260 to your local hard drive, C:\CHEM260.  
260lab1.xls, ethene.hin, buta2ene.hin, hexa3ene.hin, carotene.hin.
2. Start HyperChem Lite. You *must* have the CD in the drive while running the program.
3. Open the file ethene.hin. Use Edit/Setup Image to select Metafile, not Bitmap as file type.
4. Make sure the structure is optimized by clicking Setup/Molecular Mechanics followed by Compute/Geometry Optimization.
5. Perform a single point EHT calculation with Setup/ Extended Hückel followed by Compute/Single Point.
6. Display results with Compute/Orbitals. Note that there are 12 energy levels. Two are very close together. If necessary, expand the energy level diagram by click-dragging a box in the energy level window.
7. Click the Labels box to add electrons. There are 4 electrons (1 each) from the H atoms and 4 electrons from each carbon. The Extended Hückel method ignores the carbon 1s electrons as they have little effect on bonding.
8. Click on the HOMO level in the energy level diagram to find its energy. Record this in the Excel file 260lab1.xls (supplied).
9. Click on the LUMO and record the energy.
10. Expand the energy level diagram so that only the LUMO and the three highest occupied levels are shown in the window. Click Copy to capture the picture on the Windows clipboard. Paste it into your report (create a Word file such as 260lab1.doc).
11. Click Cancel to return to the main (molecular structure) window. If you click OK instead of Cancel you will get a plot of the selected molecular orbital. We'll play with that another day! If you couldn't resist trying the orbital plot (did you discover how to rotate it?) you can switch it off by clicking the display with the select tool (bull's eye icon).

12. Measure the C–C bond length by using the select tool to click the bond. If you miss the bond you will select the whole molecule – click the right mouse button to de-select. Record the bond length (0.01 Å precision), which is displayed at the bottom of the screen.
13. When you are finished with ethene, clear the HyperChem window with File/New.
14. Open the butadiene file (buta2ene.hin).
15. Optimize structure, do EHT calculation and display energy levels (see steps 4-6).
16. Measure and record the HOMO and LUMO energy levels.
17. Find and record the distance along the carbon chain by clicking each bond and adding the lengths.
18. Measure and record the direct distance between the carbons at the ends of the chain by first clicking on one atom with the select tool and then the other. If you can only select one carbon at a time you need to switch on Select/Multiple Selections.
19. Clear the window and load hexatriene (hexa3ene.hin)
20. Repeat steps 15-18 for the new molecule. Note the similarity of the bond lengths.
21. Clear the window and load  $\beta$ -carotene (carotene.hin).



22. Repeat steps 15-18 for the new molecule. Notice that the C–C bonds in the polyene chain are significantly shorter than the others (single bonds).
23. Use your Excel spreadsheet to calculate the frequencies ( $\nu$ ) and wavelengths ( $\lambda$ ) of the lowest spectroscopic transition for each molecule.
24. Try plotting  $\nu$  and  $\lambda$  against the  $(\text{length})^2$  of the polyene chain (does it matter which length measure: direct or along the chain?). Does one plot look like a straight line? Find the best line through the points (called the “trendline” in Excel). Try using length (not squared) as the  $x$ -axis of your plot. Is there any improvement?

#### OPTIONAL EXERCISES

25. Try removing the ring CH<sub>2</sub> and methyl groups from carotene so that the simple polyene is left. (Select bits of the molecule and press the delete key.) Optimize the structure. Has the spectroscopic transition changed?
26. Make intermediate size polyenes by deleting portions of the molecule you made in step 25. Check if their spectroscopic transitions lie on the graph you made in step 24.