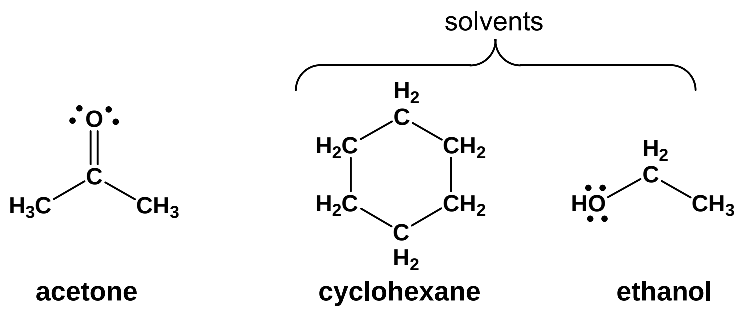
LAB 02: SOLVENT EFFECT ON UV ABSORPTION OF A CARBONYL GROUP

Assigned Reading
Read chapter 15 (section regarding UV-VIS) in Wade,

NOTE: Allow approximately 8 pages in your record book for this experiment.

Pre-Lab Planning
After reading this handout and the assigned reading mentioned above, prepare your notebook so as to include a Title, Introduction, Haz-Mat, and an outline of the Procedure in your notebook.

Introduction
Spectroscopy is the study of the interaction of light with matter. Ultraviolet/visable spectroscopy investigates changes in electronic transitions. The UV/Vis spectra of gas-phase molecules can be related directly to orbital energies of the particular molecule. For example, λ_{max} for acetone in the gas phase is 265.4 nm and is due to an $n \rightarrow \pi^*$ transition. However, solvent interactions can affect the energy associated with electronic states of molecules. This will be detected, in this experiment, by measuring ultraviolet absorption spectrum of **acetone** in two different solvents, ethanol and cyclohexane. Data obtained from the spectra will enable you to calculate the electronic transition energy for acetone in each solvent.



Procedure:
Note:: When preparing the following solutions, you must be certain ***not to contaminate one solution with the other*** *(water or* ***excess*** *acetone).*

You will need to prepare two separate test solutions:

1) Acetone in ethanol solvent

   - Measure 5.0 mL of anhydrous ethanol using a 10 mL graduated cylinder.
   - Add to this solution, 20.0 µL of anhydrous acetone using a a 500 µL syringe.

2) Acetone in cyclohexane solvent

   - Measure 5.0 mL of the anhydrous solvent contained in a 10 mL graduated cylinder.
   - Add to this solution, 20.0 µL of anhydrous acetone using a a 500 µL syringe.

*NOTE: Be careful to use either a dry cylinder or rinse the cylinder with solvent first. Thoroughly mix each separate solution by transferring each solution back-and-forth from the graduated cylinder to a small **clean & dry** test tube labeled acetone in EtOH or acetone in C_6H_{12} .*

In addition you will need three more small ***labelled*** test tubes (be sure they start clean). One is two-thirds filled with ethanol, another two-thrids filled with cyclohexane, and the last nearly filled with DI-water. Each of the pure solvents (*ethanol* and *cyclohexane)* will be used to flush the sample compartment of the UV/VIS spectrophotometer *and* determine the background of each pure solvent. All remaining extra ethanol and water are to be used for flushing the cell at the end of the experiment. Be sure all test tubes are labeled.

After your instructor has demonstrated the use the Beckman DU640 spectrophotometer obtain the required spectra.

Using the Beckman DU640 Spectrophotometer

1) Getting started:

a) Before beginning, be sure that the UV source is turned on.

b) Near the upper right side of the screen, where Autosave name: [B;\]NAME? Appears, select Name?

c) When the keyboard appears, type your initials and the last two digits of your lab station. For example, BZR38. Select OK button and proceed.

d) You will use the following main functions: FLUSH, FILL BLANK, FILL READ, AUTOSCALE, TRACE, ANNOTATE and PRINT.

2) Loading your **acetone/ethanol** sample (three steps: FLUSH, FILL BLANK, FILL READ)

a) Step One: FLUSH with pure ethanol:

- Making sure the sipper tube is at the bottom of the test tube, use the FLUSH button to rinse the spectrometer cell with about one third of your sample of pure ethanol.

b) Step Two: FILL BLANK with pure ethanol.

- Without removing the sipper tube, use the FILL BLANK button to fill the cell with pure ethanol. This will not only fill the cell but also record the background intensity, I_0, over the entire wavelength range. The background is not displayed but instead is stored in memory.

c) Step Three: FILL READ with ethanol acetone:

- Place the sipper tube in your test tube containing the acetone in ethanol solution and then press the FILL READ button. This action will rinse and fill the cell with your solution, measure the intensity, I, passing through the solution at each wavelength, calculate $-\log(I/I_0) = A$, and finally plot absorbance, A, vs. wavelength, λ.

3) Loading your **<u>acetone/cyclohexane</u>** sample (three steps: FLUSH, FILL BLANK, FILL READ)

a) Step One: FLUSH with pure cyclohexane

- Making sure the sipper tube is at the bottom of the test tube, use the FLUSH button to rinse the cell with about one third of your sample of pure cyclohexane.

b) Step Two: FILL BLANK with pure cyclohexane

- Next, use the FILL BLANK button to measure background intensity of pure cyclohexane.

c) Step Three: FILL READ with acetone cyclohexane:

- Finally use the FILL READ button to obtain the spectrum of acetone in cyclohexane solvent. This second spectrum will now overlay the first spectrum of acetone in ethanol.

4) Fine tuning and printing your UV-VIS spectra:

a) Use the AUTOSCALE screen-button if necessary, and then use the TRACE screen-button to determine λ_{max} of acetone in each solvent. Record these values immediately in your lab notebook in the following format:

λ_{max} of **acetone** in ***EtOH*** ___________
corresponding absorbance _______________

λ_{max} of **acetone** in ***C_6H_{12}*** ___________
& corresponding absorbance ___________

b) Use the ANNOTATE button to label the first curve ETOH & the second curve C6H12.

c) Next print your annotated spectrum using the PRINT button that appears near the middle right-hand-side. (*Be careful; there are two print buttons. Use the correct one and only print ONCE. Be patient. The print command is slow to activate.)*

d) After printing is complete use the SAVE/CLEAR button at the top to save and clear the screen.

e) NOW USE THE FLUSH BUTTON TO RINSE THE CELL FIRST WITH ALL REMAINING ETHANOL AND THEN FLUSH THOROUGHLY WITH PLENTY OF DI WATER.

f) Leave the sample-cell filled with DI-water.

Post lab Questions

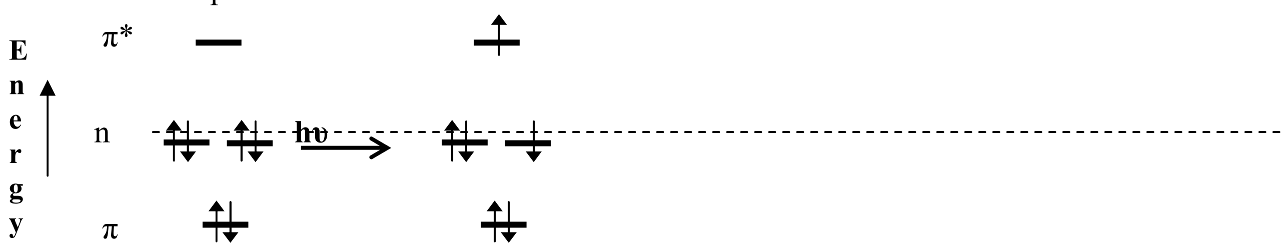
Answer the following questions in your lab notebook before your conclusion section.

1) According to your *spectra,* of the two acetone solutions (note the respective $\lambda_{\mathbf{max}}$ of each), in which solution is the energy of electronic excitation greater?

2) Calculate ΔE for n → π* energy of excitation in kJoule/mole for electronic excitation for acetone in each solvent. For which solvent was $\Delta E_{n\rightarrow\pi^*}$ the largest, $\Delta E^{\text{ethanol}}_{n\rightarrow\pi^*}$ or $\Delta E^{\text{cyclohexane}}_{n\rightarrow\pi^*}$? You can do scratch work elsewhere but neat, organized , labeled work should be in your lab book. Don't forget to use the correct units.

3) Why is ΔE for n → π* for acetone slightly different in the two different solvents? Here is the main reason: The lone-pair electrons of acetone are not so lonely afterall, especially in *one of the solvents*. In which solvent would you expect the strongest interact with the lone-pair electrons of acetone? Answer by drawing structures of acetone interacting with cyclohexane and of acetone interacting with ethanol. Label the type of intermolecular interaction involved in each case and which is likely to be the stronger.

4). Shown below is a partial orbital energy diagram for both ground and electronically excited acetone in the *cyclohexane enviornment*. The dotted line represents the reference energy of electrons in non-bonded p-orbitals of isolated atoms. Notice the non-bonded electrons of acetone in cyclohexane are *slightly more stable* than the dotted line. Presumeabley this is due to the weak dipole / induced dipole interaction between the non-bonded e⁻-pair on oxygen with the electron clound of cyclohexane. Sketch a similar diagram illustrating your best guess of orbital energy for acetone in ethanol. Be sure that your sketch is consistent with your answer to questions 3.



ground-state excited-state ground-state excited-state
acetone orbital energy in C_6H_{12} acetone orbital **energy** in C_2H_5OH

5. Calculate the energy difference for the two different transitions, $\Delta E^{\text{ethanol}}_{n\rightarrow\pi^*} - \Delta E^{\text{cyclohexane}}_{n\rightarrow\pi^*}$

6. Remember that only *one electron* was excited during the electronic transition. Calculate the strength (in kJoule/mol) of the ethanol-acetone interaction involving an *electron pair*. What is the name given to this type of solvent-solute interaction that occurs with acetone & ethanol?

7. Assuming that volumes are additive and obtaining a numerical value of density from Lange's Handbook, calculate the molarity (mmol/mL) of acetone in your ethanol soln. Be sure to include a general formula and calculation is clearly labeled.

8. Calculate the molar absorptivity, ε, for acetone in ethanol. The cell is 1.00 cm thick, and the molarity equals the value calculated in question 7.