

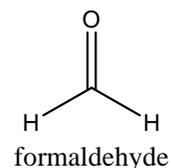
7 Infrared, Thermochemistry, UV-Vis, and NMR

Exercise 1 Method Dependence and Scaling for the Infrared Spectrum of Formaldehyde.

Build a molecule of formaldehyde using sp^2 C and O atoms. Clean up the structure by selecting Beautify / Comprehensive.

Save as formaldam1.csf in the CACheUser\cachetmp directory.

Optimize the geometry by selecting Experiment / New and selecting chemical sample optimized geometry using AM1 geometry. Close the two experiment windows.



Calculate the infrared spectrum by selecting Experiment / New and selecting chemical sample IR transitions using MOPAC AM1 FORCE. Close the two experiment windows.

View the infrared spectrum by selecting Analyze / IR Transitions. How many transitions are shown (count the white triangles)? _____ Is this the number expected? _____ Fit both windows (one with the molecule, the other with the IR spectrum) onto the screen by choosing Windows / Tile. Click and drag on the sides and/or lower right corner of each window as needed.

On the IR spectrum, *single click* on a white triangle. The type of motion associated with the chosen transition is superimposed on the molecule. You may want to use the View / Line option to more clearly see the vectors. Try to identify the type of motion for each transition. (The molecule can be rotated to assist with this.) Record your results in the table on the next page.

On the IR spectrum, *double click* on a white triangle. Record the wavenumber value for each transition in the table on the next page.

Navigate to the C:\CACheUser\cachetmp\formaldam1.io folder and investigate the contents of the mopac.OUT file (Word document).

Build a molecule of formaldehyde using sp^2 C and O atoms. Clean up the structure by selecting Beautify / Comprehensive.

Save as formaldpm3.csf in the CACheUser\cachetmp directory. Optimize the geometry by selecting Experiment / New and selecting chemical sample optimized geometry using PM3 geometry. Close the two experiment windows.

Calculate the infrared spectrum by selecting Experiment / New and selecting chemical sample IR transitions using MOPAC PM3 FORCE. Close the two experiment windows.

View the infrared spectrum by selecting Analyze / IR Transitions. Fit both windows onto the screen by choosing Windows / Tile.

Record the wavenumber value for each transition in the table on the next page.

Build a molecule of formaldehyde using sp^2 C and O atoms. Clean up the structure by selecting Beautify / Comprehensive.

Save as formalDDFT.csf in the CACheUser\cachetmp directory. Optimize the geometry by selecting Experiment / New and selecting chemical sample optimized geometry using B88-LYP DFT geometry. Close the two experiment windows.

Calculate the infrared spectrum by selecting Experiment / New and selecting chemical sample IR transitions using B88-LYP DFT IR Spectrum. Close the two experiment windows.

View the infrared spectrum by selecting Analyze / IR Transitions. Fit both windows onto the screen by choosing Windows / Tile.

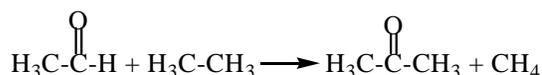
Record the wavenumber value for each transition in the table below.

Navigate to the C:\CACheUser\cachetmp\formaldDFT.io folder and investigate the contents of the dgauss.OUT file (Word document) and the dgauss.log file (using WordPad).

Try the scaling factors (AM1 = 0.9532; PM3 = 0.9761) if you would like.

| Motion | AM1 | Scaled AM1 | PM3 | Scaled PM3 | B88-LYP | Experimental values (cm ⁻¹) |
|--------|-----|------------|-----|------------|---------|---|
| | | | | | | 2843 |
| | | | | | | 2782 |
| | | | | | | 1746 |
| | | | | | | 1500 |
| | | | | | | 1249 |
| | | | | | | 1167 |

Exercise 2 $\Delta_r H$ for an Isodesmic Reaction.



An isodesmic reaction is one in which the total number of each type of chemical bond is the same in both reactants and products. Because of this equality in bond type, results of calculations using such a reaction should benefit from cancellation of errors.

Build a molecule of acetone. Clean up the structure by selecting Beautify / Comprehensive.

Save as acetone.csf in the CACheUser\cachetmp directory.

Build a molecule of methane. Clean up the structure by selecting Beautify / Comprehensive.

Save as methane.csf in the CACheUser\cachetmp directory.

Build a molecule of acetaldehyde. Clean up the structure by selecting Beautify / Comprehensive.

Save as acetaldehyde.csf in the CACheUser\cachetmp directory.

Build a molecule of ethane. Clean up the structure by selecting Beautify / Comprehensive.

Save as ethane.csf in the CACheUser\cachetmp directory.

Using Project Leader

In addition to the CAChe workspace where you have been building molecules, performing calculations, and visualizing results, the software also has a separate application called Project Leader. Project Leader allows the user to perform calculations on several chemical samples in series and to carry out mathematical analyses on the results of the calculations. It automates and greatly simplifies the process where the results of a number of calculations are required.

From the Start Menu choose All Programs, CAChe, Project Leader. A spreadsheet appears.

Double click in cell A1, and navigate to C:\CACheUser\cachetmp\acetone.csf. Click Open.

Double click in cell A2, and navigate to C:\CACheUser\cachetmp\methane.csf. Click Open.

Double click in cell A3, and navigate to C:\CACheUser\cachetmp\acetaldehyde.csf. Click Open.

Double click in cell A4, and navigate to C:\CACheUser\cachetmp\ethane.csf. Click Open.

The name of each file appears in the corresponding cell of Project Leader.

Double click in the topmost (gray) cell of Column B. Choose Property of chemical sample (next), Kind of Property heat of formation (next), Using H_f at AM1 geometry (O.K.).

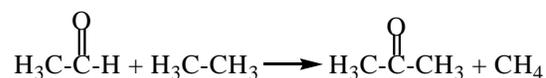
Double click in the topmost (gray) cell of Column C. Choose Property of chemical sample (next), Kind of Property heat of formation (next), Using H_f at PM3 geometry (O.K.).

Double click in the topmost (gray) cell of Column D. Choose Property of chemical sample (next), Kind of Property heat of formation (next), Using H_f at PM5 geometry (O.K.).

Place the cursor in Cell B1, Click and Drag down to Cell D4. The 12 cells should be highlighted.

Choose Evaluate / Cell. Results will appear in the spreadsheet as they are calculated.

To find $\Delta_r H$ for the reaction



take the values from each Column, and find $\Delta_r H = \sum H_f(\text{products}) - \sum H_f(\text{reactants})$ (i.e. $\Delta_r H(\text{AM1}) = [\text{B1} + \text{B2}] - [\text{B3} + \text{B4}]$)

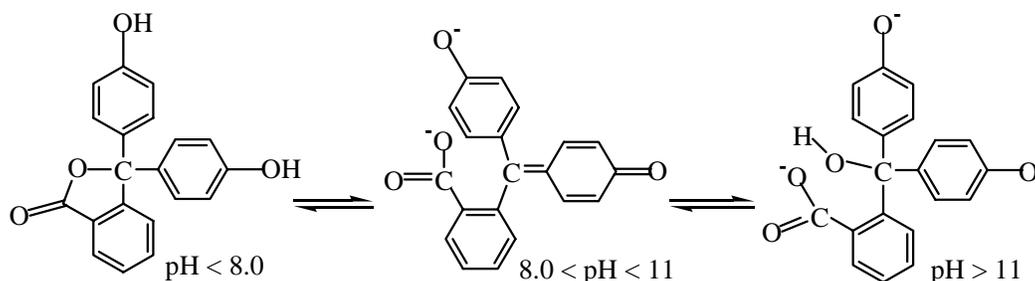
Place your results in the table below and compare with the experimental value.

| AM1 (Column B) | PM3 (Column C) | PM5 (Column D) | Experimental (kcal/mole) |
|-------------------|-------------------|-------------------|-----------------------------|
| | | | -9.9 ± 0.3 |

(If you wish to view the molecular structures, double click on the desired sketch in Project Leader. The CAChe Workspace opens with the chosen structure displayed).

Exercise 3 Electronic Transitions of Phenolphthalein at Various pH.

Phenolphthalein is a widely used acid-base indicator. Three forms of the molecule, shown below, will be constructed and the UV-Vis spectrum of each will be calculated. Each optimized structure will be investigated to determine the correlation between structure and absorbance of light.



Build the protonated structure on the left of the equilibrium above. Be careful to choose the proper hybridization for all atoms. Clean up the structure by selecting Beautify / Comprehensive.

Save as indicatorlowph.csf in the CACheUser\cachetmp directory. If you have overlapping atoms at this point, perform a structure optimization using the MM2 method.

Calculate the UV-Vis spectrum by choosing Experiment / New and selecting chemical sample UV-visible transitions using ZINDO CI at MM/PM3 geometry. Close the two experiment windows.

View the UV-Vis spectrum by selecting Analyze / UV-visible Transitions. Fit both windows onto the screen by choosing Windows / Tile. *Single click* on the white triangles in the spectrum. The orbitals involved in each transition are shown superimposed on the structure. Rotate the structure if needed to study the

orbitals involved.

Double click on a white triangle to observe the wavelength of each transition. Record the wavelength of the lowest energy (longest wavelength) transition here:

_____ nm.

Carefully build the center structure in the equilibrium. Make the appropriate oxygen atoms negatively charged. Clean up the structure by selecting Beautify / Comprehensive.

Save as indicatormidph.csf in the CACheUser\cachetmp directory. If you have overlapping atoms at this point, perform a structure optimization using the MM2 method.

Calculate the UV-Vis spectrum by choosing Experiment / New and selecting chemical sample UV-visible transitions using ZINDO CI at MM/PM3 geometry. Close the two experiment windows.

View the UV-Vis spectrum by selecting Analyze / UV-visible Transitions. Fit both windows onto the screen by choosing Windows / Tile. Record the wavelength of the lowest energy (longest wavelength) transition here: _____ nm. Does this number make sense? _____ What orbitals are involved in this transition?

Carefully build the high pH structure on the right. Make the appropriate oxygen atoms negatively charged. Clean up the structure by selecting Beautify / Comprehensive.

Save as indicatorhighph.csf in the CACheUser\cachetmp directory. If you have overlapping atoms at this point, perform a structure optimization using the MM2 method.

Calculate the UV-Vis spectrum by choosing Experiment / New and selecting chemical sample UV-visible transitions using ZINDO CI at MM/PM3 geometry. Close the two experiment windows.

View the UV-Vis spectrum by selecting Analyze / UV-visible Transitions. Fit both windows onto the screen by choosing Windows / Tile. Record the wavelength of the lowest energy (longest wavelength) transition here: _____ nm.

Based on the lowest energy transition, which of the above structures have color?

_____ Does this make sense? _____

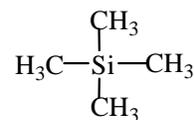
Open all three of the structures in the workspace. Fit the three windows onto the screen by choosing Windows / Tile. Focus on the phenolic rings of each structure. What is the difference in the position of these rings between the structures?

_____ For the structure with an absorbance in the visible region, what unique property does this structure possess?

Navigate to the C:\CACHeUser\cachetmp\indicatorhighph.io directory (and the other two similar directories) and examine the contents of the zindo.OUT file (Word document).

Exercise 4 NMR Chemical Shift Calculations.

Build a molecule of tetramethylsilane. Clean up the structure by selecting Beautify / Comprehensive.



Save as tms.csf in the CACHeUser\cachetmp directory.

Build a molecule of benzene. Clean up the structure by selecting Beautify / Comprehensive.

Save as benzene.csf in the CACHeUser\cachetmp directory.

Build a molecule of chloroethane. Clean up the structure by selecting Beautify / Comprehensive.

Save as chloroethane.csf in the CACHeUser\cachetmp directory.

Build a molecule of ethanol. Clean up the structure by selecting Beautify / Comprehensive.

Save as ethanol.csf in the CACHeUser\cachetmp directory.

From the Start Menu choose All Programs, CACHe, Project Leader. A spreadsheet appears.

Double click in cell A1, and navigate to C:\CACHeUser\cachetmp\tms.csf. Click Open.

Double click in cell A2, and navigate to C:\CACHeUser\cachetmp\benzene.csf. Click Open.

Double click in cell A3, and navigate to C:\CACHeUser\cachetmp\chloroethane.csf. Click Open.

Double click in cell A4, and navigate to C:\CACHeUser\cachetmp\ethanol.csf. Click Open.

The name of each file appears in the corresponding cell of Project Leader.

Double click in the topmost (gray) cell of Column B. Choose Property of atom (next), Kind of Property LORG chemical shift (next), Using LORG chemical shift at DFT B88-LYP geometry (O.K.).

Place the cursor in Cell C1, Click and Drag down to Cell C4. The four cells should be highlighted.

Choose Evaluate / Cell. Results will appear in the spreadsheet as they are calculated. (This may take several minutes).

The spreadsheet assigns a number and calculated chemical shift to each atom. To see the atom numbers, double click on the small sketch of a molecule in Column A. This will open the .csf file in the CACHe Workspace. Choose Analyze / Atom

Attributes, click on the Label tab, and check the Atom Number box. In the space next to the table below, sketch each molecule, and include the atom numbers.

To calculate the ^1H - or ^{13}C -NMR chemical shift for a given atom, take the average H or C shift from TMS and subtract the shift for that atom (some atoms are equivalent, but may have slightly different values). Fill in the values below and compare with the experimental values.

| Benzene | Calc. | Exp. | CH₃CH₂OH | Calc. | Exp. |
|---------------------------------------|--------------|-------------|---------------------------------------|--------------|-------------|
| H's | | 7.16 | Methyl H's | | 1.16 |
| C's | | 128.4 | Methylene H's | | 3.59 |
| | | | Hydroxyl H | | 4.00 |
| CH₃CH₂Cl | | | Methyl C | | 17.6 |
| Methyl H's | | 1.48 | Other C | | 57.0 |
| Methylene H's | | 3.57 | | | |
| Methyl C | | 18.7 | | | |
| Other C | | 39.9 | | | |