

## 7 Infrared, Thermochemistry, UV-Vis, and NMR

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

Open the file ch2ogas.HIN saved in Exercise 2 of Session 6.

Click Setup / Semiempirical: AM1 and click OK.

Click Compute / Geometry Optimization.

Click Compute / Vibrations. Click Compute / Vibrational Spectrum.

Save.

Record the values of the vibrational frequencies determined at the AM1 level in the table.

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

Motion	AM1	Scaled AM1	PM3	Scaled PM3	B3-LYP	Experimental values (cm <sup>-1</sup> )
						2843
						2782
						1746
						1500
						1249
						1167

Minimize at the PM3 level and save as ch2opm3.HIN.

Determine the IR/vibrational spectral values at the PM3 level and record the values in the table.

Click Setup / Density Functional. Choose 6-31\* for the Orbital Basis Set. Click Exchange Correlation / B3-LYP and click OK. Click OK.

Click Compute / Geometry Optimization. Click Run. (The calculation will take a few minutes.)

Determine the IR/vibrational spectral values at the B3-LYP level and record the values in the table.

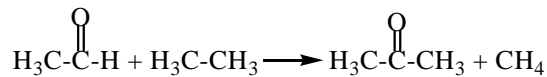
Save as ch2odft.HIN.

### 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 and save as acetoneam1.HIN.

Minimize at the AM1 level and record the  $\Delta_f H = \underline{\hspace{2cm}}$  kcal mol<sup>-1</sup>.

Save.

Save as acetonepm3.HIN and minimize at the PM3 level. Save and record the  $\Delta_f H = \underline{\hspace{2cm}}$  kcal mol<sup>-1</sup>.

Close.

Repeat the above calculations for methane. Save the results as methaneam1.HIN and methanepm3.HIN.  $\Delta_f H(\text{AM1}) = \underline{\hspace{2cm}}$  kcal mol<sup>-1</sup>,  $\Delta_f H(\text{PM3}) = \underline{\hspace{2cm}}$  kcal mol<sup>-1</sup>.

Close.

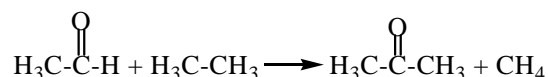
Repeat the above calculations for acetaldehyde. Save the results as acetaldehydeam1.HIN and acetaldehydep3.HIN.  $\Delta_f H(\text{AM1}) = \underline{\hspace{2cm}}$  kcal mol<sup>-1</sup>,  $\Delta_f H(\text{PM3}) = \underline{\hspace{2cm}}$  kcal mol<sup>-1</sup>.

Close.

Repeat the above calculations for ethane. Save the results as ethanem1.HIN and ethanepm3.HIN.  $\Delta_f H(\text{AM1}) = \underline{\hspace{2cm}}$  kcal mol<sup>-1</sup>,  $\Delta_f H(\text{PM3}) = \underline{\hspace{2cm}}$  kcal mol<sup>-1</sup>.

Close.

To find  $\Delta_r H$  for the reaction:



use  $\Delta_r H = \sum \Delta_f H(\text{products}) - \sum \Delta_f H(\text{reactants})$ .

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

AM1	PM3	B3-LYP	Experimental (kcal mol <sup>-1</sup> )
			-9.9 ± 0.3

Open acetonepm3.HIN and save as acetonedft.HIN.

Minimize at the B3-LYP/6-31G\* level. (This calculation takes several hours.) Record the value of  $E = \underline{\hspace{2cm}}$  kcal mol<sup>-1</sup>.

Close and save the structure.

Repeat the calculations for methanepm3.HIN, acetaldehydep3.HIN, and ethanepm3.HIN. Record the value of  $E(\text{CH}_4) = \underline{\hspace{2cm}}$  kcal mol<sup>-1</sup>,

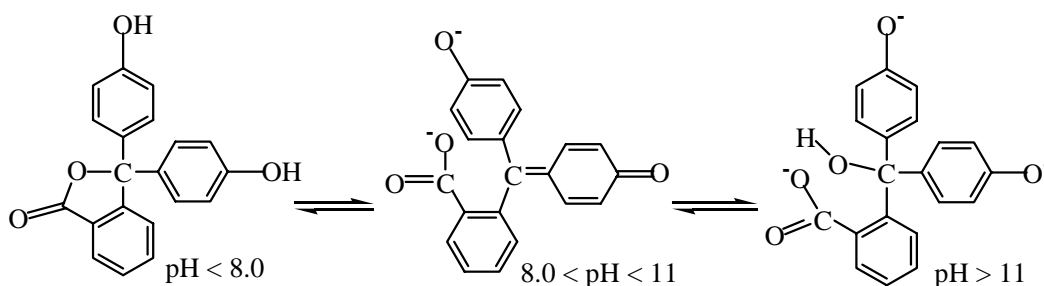
$$E(\text{CH}_3\text{CHO}) = \text{_____ kcal mol}^{-1}, E(\text{CH}_3\text{CH}_3) = \text{_____ kcal mol}^{-1}.$$

(Note that the acetaldehyde calculation takes a few hours.)

Calculate  $\Delta_r H$  using  $\Delta_r H = \Delta_r E = [\sum E(\text{products}) - \sum E(\text{reactants})] = \text{_____ kcal mol}^{-1}$ .

### 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. Double click the Select Tool to clean up the structure. Save as indicatorlowph.HIN.

Click Setup / Semiempirical / ZINDO/S. Click Options and click Configuration Interaction. Choose Singly Excited and enter 3, 3 for Orbital Criterion. Click OK three times.

Calculate the UV-Vis spectrum by clicking Compute / Single Point and then click Compute / Electronic Spectrum. Record the range of wavelengths \_\_\_\_\_ nm.

Build the center structure in the equilibrium. Double clicking each bond in the O-C-O group will form equivalent bond represented by dashed lines. To put the -1 charge on the O atom at the top, click the Select Tool, click Select / Atom and be sure Multiple Selections is on, click the O atom, click Build / Set Charge and enter -1 and click OK. Right click in the workspace. To put the charges on the O atoms connected to the C, select both O atoms, click Build / Set Charge and enter -0.5 and click OK. Right click in the workspace.

Save as indicatormidph.HIN.

Click Setup / Semiempirical / ZINDO/S. Click Options and enter -2 for the charge and 2 for multiplicity. Click Configuration Interaction. Choose Singly Excited and enter 3, 3 for Orbital Criterion. Click OK three times.

Click Compute / Single Point and then click Compute / Electronic Spectrum. Record

the range of wavelengths \_\_\_\_\_ nm.

Build the high pH structure on the right and save as indicatorhighph.HIN.

Calculate the UV-Vis spectrum. Use -3 for the charge and 1 for the spin.

Record the wavelength of the lowest energy (longest wavelength) transition here:

\_\_\_\_\_ nm.

Which of the above structures have color? \_\_\_\_\_ Does this make sense?

\_\_\_\_\_

#### Exercise 4 NMR Chemical Shift Calculations.

Build a molecule of tetramethylsilane. Optimize at the PM3 level.

Save as tms.HIN.

Click Compute / Invoke NMR. (Ignore warning message.)

Click View / Rendering and choose Atoms: Labels and Atom Labels:

Numbers and click OK. Keep track of the numbers of equivalent atoms.

Click View / Rendering and choose Atoms: Labels and Type and click OK. If any of the atoms are indicated by \*\*, click Edit / Atom Types.

Click Setup / Shielding&Coupling. Choose TNDO/2, Shielding Constants, Fermi spin-spin, and Special Slater.

Click Quantum Atoms. Click Select All / Add and click OK.

Click NMR Atoms. Click Select and select the proton atoms and carbon atoms. Click OK. Click Add and click OK.

Click Equivalent Atoms. Select all of the H atoms and click Add. Click Apply. Change the Set Number to 2 by clicking the up arrow and select and assign all the C atoms. Click Apply. Click OK.

Click Labeled Atoms. Select the C atoms and click Add. (Do not select the H atoms.) Click OK.

Click SCF. Settings should be 0 for Charge, 1 for Multiplicity, 0.01 for Convergence, 50 for Iterations. Click OK.

Click OK to close the Shielding&Coupling Options.

Click Compute / Shielding&Coupling.

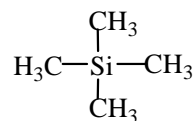
Click View / Shielding Constants. Record the chemical shifts for  $^1\text{H}$  \_\_\_\_\_ and  $^{13}\text{C}$  \_\_\_\_\_.

Save as tms.NMR and close HyperNMR. Save and close.

Build a molecule of benzene and save as benzene.HIN. Record the chemical shifts for  $^1\text{H}$  \_\_\_\_\_ and  $^{13}\text{C}$  \_\_\_\_\_.

Build a molecule of chloroethane and save as chloroethane.HIN.

Note that there will be two types of C atoms and two types of H atoms. Record the



chemical shifts for  $^1\text{H}$ : methyl \_\_\_\_\_, methylene \_\_\_\_\_ and  $^{13}\text{C}$ :  
methyl \_\_\_\_\_, other \_\_\_\_\_.

Build a molecule of ethanol and save as ethanol.HIN.

Note that there will be two types of C atoms and three types of H atoms. Record the  
chemical shifts for  $^1\text{H}$ : methyl \_\_\_\_\_, methylene \_\_\_\_\_, hydroxyl  
\_\_\_\_\_ and  $^{13}\text{C}$ : methyl \_\_\_\_\_, other \_\_\_\_\_.

To calculate the  $^1\text{H}$ - or  $^{13}\text{C}$ -NMR chemical shift for a given atom, take the H or C shift  
from TMS and subtract the shift for that atom. Fill in the values below and  
compare with the experimental values.

<b>Benzene</b>	<b>Calc.</b>	<b>Exp.</b>	<b><math>\text{CH}_3\text{CH}_2\text{OH}</math></b>	<b>Calc.</b>	<b>Exp.</b>
H's		7.16	Methyl H's		1.16
C's		128.4	Methylene H's		3.59
			Hydroxyl H		4.00
<b><math>\text{CH}_3\text{CH}_2\text{Cl}</math></b>			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			