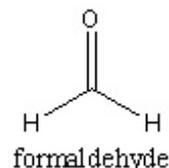# 7 Infrared, Thermochemistry, UV-Vis, and NMR

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

Build a molecule of formaldehyde using the C Trivalent and the O
   Trivalent fragments. Click the Clean icon.
Optimize the structure and determine the vibrations energies using AM1
   and choosing Opt+Freq. Save as formAM1.chk and formAM1.cjf.
Close everything except the main Control Panel and the original View
   workspace.
Open the formAM1.log file with a text editor such as WordPad, scroll to the bottom of
   the file, and move up about 150 lines by clicking the scroll bar five times.
Record all frequencies in the table below.

Motion	AM1	PM3	HF/ 6-31G(d)	B3LYP/ 6-31G(d)	Experimental values (cm^{-1})
b_1: CH$_2$ a-stretch					2843
a_1: CH$_2$ s-stretch					2782
a_1: CO stretch					1746
a_1: CH$_2$ scissors					1500
b_1: CH$_2$ rock					1249
b_2: CH$_2$ wag					1167

Repeat the calculations at the PM3 level saving the files as formPM3.chk and
   formPM3.cjf. Record the results in the table above.
Repeat the calculations at the HF/6-31G(d) level saving the files as formHF.chk and
   formHF.cjf. Record the results in the table above.
Repeat the calculations at the B3LYP/6-31G(d) level saving the files as formDFT.chk
   and formDFT.cjf. Record the results in the table above.

To improve the agreement between the calculated values and experimental values, try
multiplying each frequency by the respective scaling factor: 0.9532 for AM1, 0.9761 for
PM3, 0.8929 for HF/6-31G(d), and 0.9613 for B3LYP/6-31G(d).

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.

$$H_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}H + H_3C\text{-}CH_3 \longrightarrow H_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + CH_4$$
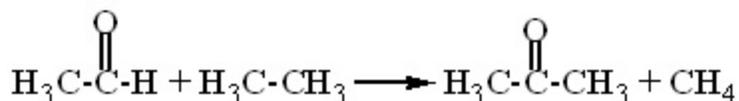
Build a molecule of acetone. Use the C Trivalent and O Trivalent fragments and the C Tetravalent fragment. Click the Clean icon.
Minimize at the PM3 level using Opt+Freq. Save as acetone.chk and acetone.cjf.
Close everything except the main Control Panel
From the acetone.log file, record the value of "Sum of electronic and thermal Enthalpies" = H(acetone) = _____ Eh.
Likewise, build a molecule of methane and perform the same calculations. Save as methane.chk and methane.cjf. Record the value H(methane) = _____ Eh.
Also build molecules of acetaldehyde and ethane and perform the same calculations. Save the files with appropriate names. Record the values of H(acetaldehyde) = _____ Eh and H(ethane) = _____ Eh.
To find $\Delta_r H$ for the reaction use Hess's law $\Delta_r H = \sum H(\text{products}) - \sum H(\text{reactants}) =$ (_____ Eh)(625.5095 kcal mol^{-1}/1 Eh) = _____ kcal mol^{-1} (-9.9 ± 0.3 kcal mol^{-1} literature).

Exercise 3 Electronic Transitions of Polyene Aldehydes.

Carbonyl compounds have two principal UV transitions, the allowed $\pi \rightarrow \pi^*$ transition and the forbidden $n \rightarrow \pi^*$ transition. Two polyene aldehydes,
$$CH_3\text{-}CH\text{=}CH\text{-}CHO \qquad CH_3\text{-}(CH\text{=}CH)_2\text{-}CHO$$
will be constructed, optimized, and the UV-Vis spectrum of each will be determined.
Build the first aldehyde and minimize at the PM3 level. Save the files as poly1pm3.chk and poly1pm3.cjf.
Open the output file and click the MO Editor icon. Under the View tab, click HOMO,LUMO and Update. Record the number and identify the type of each orbital. HOMO #_____, _____; LUMO #_____, _____.
Close the editor. With the output file View window still open, click Calculate / Gaussian and choose Energy for the Job and ZINDO for Method. Save the files as poly1zindo.chk and poly1zindo.cjf.
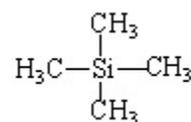After the completion of the calculations, close everything except the main Control Panel.

Open the poly1zindo.log file and working up from the bottom of the file, locate the
electronic transition data predictions. Record the wavelength of the transition
corresponding to the orbital numbers from above λ = _____ nm (225 nm
literature).
Repeat the above calculations for the second aldehyde. Save the files as poly2pm3.chk,
poly2pm3.cjf, poly2zindo.chk, and poly2zindo.cjf.
Record the number and identify the type of each orbital and record the corresonding
wavelength. HOMO #_____, _____; LUMO #_____, _____;
_____ nm (270 nm literature).

Exercise 4   NMR Chemical Shift Calculations.

Build a molecule of tetramethylsilane. Minimize at the B3LYP/6-31G(d)
level. Save the files as tmsb3lyp.chk and tmsb3lyp.cjf.
Use the output file as input to the calculation of the NMR shifts. Choose
Job: NMR and GIAO at the B3LYP/6-31G(d) level. Save the files
as tmsnmr.chk and tmsnmr.cjf.
Open the tmsnmr.log file and scroll down to the list of NMR peaks. Record the values
for the four C atoms and the twelve H atoms. Find an average for the C atom
_____ and for the H atom _____.

Build a molecule of benzene. Run the minimization and NMR calculations as above.
Save the files with appropriate names. Record the values for the six C atoms and
the six H atoms. Find an average for the C atom _____ and for the H atom
_____.

Build a molecule of CH_3CH_2Cl. Run the minimization and NMR calculations as above.
Save the files with appropriate names. Record the values for each of the two C
atoms, the two methylene H atoms, and the three methyl H atoms. List the two
C atom values _____ and _____, the average for the methylene H
atoms _____, and the average for the methyl H atoms _____.

Build a molecule of CH_3CH_2OH. Run the minimization and NMR calculations as above.
Save the files with appropriate names. Record the values for each of the two C
atoms, the hydroxyl H atom, the two methylene H atoms, and the three methyl
H atoms. List the two C atom values _____ and _____, the hydroxyl
H atom _____, the average for the methylene H atoms _____, and the
average for the methyl H atoms _____.

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

Benzene	Calc.	Exp.	CH$_3$CH$_2$OH	Calc.	Exp.
H's		7.16	Methyl H's		1.16
C's		128.4	Methylene H's		3.59
			Hydroxyl H		4.00
CH$_3$CH$_2$Cl			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			