7 Infrared, Thermochemistry, UV-Vis, and NMR

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

Open the file ch2ogas.c3d saved in Exercise 3 of Session 6.
Record the values of the vibrational frequencies determined at the PM3 level listed in the Message Window in the table.

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

Motion	AM1	Scaled AM1	PM3	Scaled PM3	B3LYP	Experimental values (cm^{-1})
						2843
						2782
						1746
						1500
						1249
						1167

Save as ch2ogasam1.c3d.
Minimize at the AM1 level and save.
Determine the IR/vibrational spectral values at the AM1 level by clicking MOPAC / Spectral Analysis, click Run, and save.
Record the values in the table of the spectral transitions found in the Message Window.

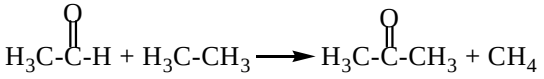
Chem3D does not have *ab initio* capabilities. However, Chem3D serves as a graphical interface to Gaussian ′03 for various *ab initio* calculations.

Using Gaussian ′03

Save ch2ogasam1.c3d as ch2ogaussian.c3d.
Minimize by clicking Gaussian / Minimize Energy / Theory. Choose Method: B3LYP, Basis Set: 6-31G, Polarization: Heavy Atom d.
Click Run and save.
Click Gaussian / Spectral Analysis / Theory B3LYP 6-31Gd and click Run.
Save the structure and record the values in the table for the vibrational transitions that appear in the Message Window.

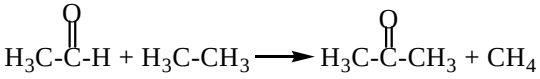
Exercise 2 $\Delta_r H$ for an Isodesmic Reaction.

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 using the Text Tool and save as acetoneam1.c3d.
Minimize at the AM1 level and record the $\Delta_f H$ = _____ kcal mol^{-1}.
Save.
Save as acetonepm3.c3d and minimize at the PM3 level. Save and record the $\Delta_f H$ = _____ kcal mol^{-1}.
Close.
Repeat the above calculations for methane. Save the results as methaneam1.c3d and methanepm3.c3d. $\Delta_f H$(AM1) = _____ kcal mol^{-1}, $\Delta_f H$(PM3) = _____ kcal mol^{-1}.
Repeat the above calculations for acetaldehyde. Save the results as acetaldehydeam1.c3d and acetaldehydepm3.c3d. $\Delta_f H$(AM1) = _____ kcal mol^{-1}, $\Delta_f H$(PM3) = _____ kcal mol^{-1}.
Repeat the above calculations for ethane. Save the results as ethanem1.c3d and ethanepm3.c3d. $\Delta_f H$(AM1) = _____ kcal mol^{-1}, $\Delta_f H$(PM3) = _____ kcal mol^{-1}.

To find $\Delta_r H$ for the reaction:



use $\Delta_r H = \sum \Delta_f H$(products) - $\sum \Delta_f H$(reactants).
Place your results in the table below and compare with the experimental value.

AM1	PM3	*ab initio*	Experimental (kcal mol^{-1})
			-9.9 ± 0.3

Chem3D does not have *ab initio* capabilities. However, Chem3D serves as a graphical interface to Gaussian ′03 for various *ab initio* calculations and to GAMESS for Hartree-Fock *ab initio* calculations.

Open acetonepm3.c3d and save as acetonegaussian.c3d.
Click Gaussian / Minimize Energy / Theory. Choose Method: B3LYP, Basis Set: 6-31G, Polarization: Heavy Atom d.
Click Run. (This calculation may take several minutes.) Record the value of E = _____ h.
Close and save the structure.
Repeat the calculations for methanepm3.c3d, acetaldehydepm3.c3d, and ethanepm3.c3d. Record the value of $E(CH_4)$ = _____ h, $E(CH_3CHO)$ = _____ h, $E(CH_3CH_3)$ = _____ h.
Calculate $\Delta_r H$ using $\Delta_r H = \Delta_r E = [\sum E(\text{products}) - \sum E(\text{reactants})](627.51 \text{ kcal mol}^{-1}/\text{h})$ = _____ kcal mol^{-1}.

Using GAMESS

Open acetonepm3.c3d and save as acetonegamess.c3d.
Click Gamess / Minimize Energy / Theory. Choose Method: Hartree-Fock, Basis Set: 6-31G, Polarization: Heavy Atom d.
Click Run. (This calculation may take several minutes.) Record the value of E = _____ h.
Close and save the structure.
Repeat the calculations for methanepm3.c3d, acetaldehydepm3.c3d, and ethanepm3.c3d. Record the value of $E(CH_4)$ = _____ h, $E(CH_3CHO)$ = _____ h, $E(CH_3CH_3)$ = _____ h.
Calculate $\Delta_r H$ using $\Delta_r H = \Delta_r E = [\sum E(\text{products}) - \sum E(\text{reactants})](627.51 \text{ kcal mol}^{-1}/\text{h})$ = _____ kcal mol^{-1}.