

7 Infrared and Thermochemistry

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

Build a molecule of formaldehyde. Save as formaldMM3ir.pcm.

Minimize using the MM3 force field.

Calculate the IR spectrum by selecting Compute / Normal Vibration Modes using the MM3 force field. Save as formaldMM3vib.vib.

The values of the vibrational frequencies can be obtained by opening the formaldMM3vib.vib file with a text editor such as WordPad or represented on the screen by clicking Compute / Vibrations if the PCM-Vibrate program is installed.

Once the Vibration window is opened, choose the formaldMM3vib.vib file and click OK. A “stick” spectrum appears on the screen. Clicking on the spectral lines will produce an animation of the respective vibration. How many transitions are shown? ____ Is this the number expected? ____

Record the values of $\tilde{\nu}$ in the table below.

Repeat the above calculations at the MMX level. Save the files as formaldMMXir.pcm and formaldMMXvib.vib.

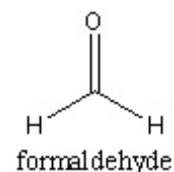
Repeat the above calculations at any of the other molecular mechanics levels in PCModel such as MMFF94 and if GAUSSIAN or GAMESS is available, repeat the calculations at the PM3 and B3LYP/6-31G(d) levels of theory.

Be sure to click Force Field / MMX when done.

Save and Close.

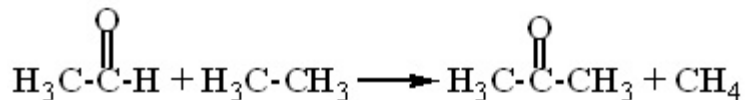
Compare the methods. (Note that MMX is not recommended for IR predictions!)

Motion	MM3	MMX	MMFF94	PM3	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



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. Save as acetone.pcm. Minimize. Record the value of $\Delta_f H$
= _____ kcal mol⁻¹.

Build a molecule of methane. Save as methane.pcm. Minimize. Record the value of
 $\Delta_f H$ = _____ kcal mol⁻¹.

Build a molecule of acetaldehyde. Save as acetaldehyde.pcm. Minimize. Record the
value of $\Delta_f H$ = _____ kcal mol⁻¹.

Build a molecule of ethane. Save as ethane.pcm. Minimize. Record the value of $\Delta_f H$ =
_____ kcal mol⁻¹.

To find $\Delta_r H$ for the reaction use Hess's law $\Delta_r H = \sum H_f(\text{products}) - \sum H_f(\text{reactants}) =$
_____ kcal mol⁻¹ (-9.9 ± 0.3 kcal mol⁻¹ literature).

Save and Close.