

Lab #6: Modeling in Solution

Exercise 1 - Determine the Enthalpy of Vaporization of Water.

Build a molecule of H₂O.

Perform a geometry optimization using PM3 (Job Name: H2OGas) and record $\Delta_f H =$ _____ kcal mol⁻¹ (-57.796 kcal mol⁻¹ literature).

Click on “New Job Using This Geometry”. Click the blue “continue” arrow, choose Mopac, and Type in/Choose the following:

Job name: H2OLiq

Calculation: Geometry Optimization

Theory: PM3

Charge: 0

Multiplicity: Singlet

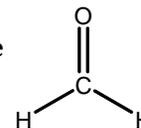
Click the Advanced tab. In the Solvent pull-down menu, choose Water. Click the blue “continue” arrow. You should see your job listed.

Record $\Delta_f H =$ _____ kcal mol⁻¹ (-68.315 kcal mol⁻¹ literature).

The difference between the two enthalpies of formation is the enthalpy of vaporization

$\Delta_{\text{vap}} H =$ _____ kcal mol⁻¹ (10.519 kcal mol⁻¹ literature).

Exercise 2 - Determine the Frequency Shift for C=O for Formaldehyde Dissolved in Acetonitrile.



Build a molecule of CH₂O and choose Clean-Up > Comprehensive – Mechanics.

Perform a geometry optimization using PM3 (Job Name: CH2Ogas).

Click on “New Job Using This Geometry”. Click the blue “continue” arrow, choose Mopac, and Type in/Choose the following:

Job name: CH2OgasPM3

Calculation: Vibrational Frequencies

Theory: PM3

Charge: 0

Multiplicity: Singlet

Once the calculation is complete, scroll to Vibrational Modes and click on the filmstrip next to each frequency to animate that frequency. Identify the frequency for the C=O stretch and record it here: _____ cm⁻¹ (literature 1746.07 cm⁻¹).

Click on “New Job Using This Geometry”. Click the blue “continue” arrow, choose Mopac, and Type in/Choose the following:

Job name: CH2OLiqPM3

Calculation: Vibrational Frequencies

Theory: PM3

Charge: 0

Multiplicity: Singlet

Click the Advanced tab. In the Solvent pull-down menu, choose Acetonitrile. Click the blue “continue” arrow. You should see your job listed.

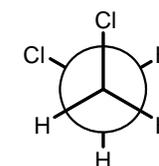
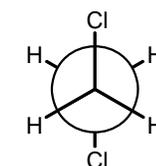
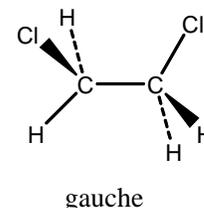
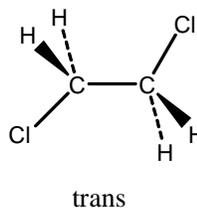
Follow the instructions above, find the frequency for the C=O stretch, and record it here: _____ cm^{-1} (literature 1723 cm^{-1}).

The difference between these frequencies is the effect on the vibrational frequency as a result of the solvation process. $\Delta\nu =$ _____ cm^{-1} (literature 23 cm^{-1}).

Exercise 3 - Determine the stable form of 1,2-dichloroethane.

Build a molecule 1,2-dichloroethane and clean-up the structure.

Choose Tools > Z-Matrix. In the pull-down menu to the right of the Cl-C-C-Cl dihedral angle, choose “S” as shown below. Use the atom numbers to help identify this angle.



Order	Atom	Na	Length	Opt	Nb	Angle	Opt	Nc	Dihedral Opt
1	C1								
2	Cl2	1	1.800	0					
3	C3	1	1.535	0	2	110.605	0		
4	Cl4	3	1.800	0	1	110.624	0	2	-179.979 S
5	H5	3	1.115	0	1	111.653	0	2	-61.468 O
6	H6	3	1.115	0	1	111.673	0	2	61.517 O
7	H7	1	1.115	0	2	106.579	0	3	121.570 O
8	H8	1	1.115	0	2	106.559	0	3	-121.558 O

Start: -180.0 Stop: 180.0 # Steps: 72

Buttons: ReOrder, ReConnect, Opt All, Fix All, OK

As shown above, enter the Start (-180) and Stop (180) scan values, along with 72 steps, then click OK to close the Z-matrix Editor window.

Click Close Editor, then click the blue “continue” arrow. Choose Mopac.

Use the following Job Options:

Job Name: C2H4Cl2Gas

Calculation: Coordinate Scan

Theory: PM3

Charge: 0

Multiplicity: Singlet

Click the blue “continue” arrow. Your job should appear in the queue.

When the job is complete, click on the linked name. Scroll down to the Coordinate Scan table and click on the magnifying glass on the table title bar.

A Coordinate Scan window opens showing the plot of Energy vs. dihedral angle.

Choose Options > Axes, and in the Options window change the x-axis setting to Start (-180), Stop (180), and Interval (60). Click OK.

Use your mouse to place the cursor on the graph. Displayed above the graph are the x-y coordinates of the cursor. Use the cursor and record the energy values for the following conformers: *Trans* conformer ($\sim \pm 180^\circ$): _____ kcal mol⁻¹, the maxima of the two rotation barriers ($\sim \pm 120^\circ$): _____ kcal mol⁻¹ and ($\sim 0^\circ$): _____ kcal mol⁻¹, and the energy of the *gauche* conformer ($\sim \pm 60^\circ$): _____ kcal mol⁻¹.

Which conformer is more stable in the gas phase, and by how much energy? _____ conformer by _____ kcal mol⁻¹ (literature 1.1 kcal mol⁻¹).

Close the Coordinate Scan window and click “New Job Using This Geometry”.

Open the Editor, choose the “adjust” tool (arrow 6th down on the left), and click on one of the green Cl atoms. Hold down the shift key and click on the attached carbon, the other carbon, and the remaining Cl atom. Click on “Adjust” in the pull-down menu, and choose ‘Dihedral Angle’. Type in 180, click ‘Apply’ followed by ‘OK’. Close the Editor, choose Mopac, and use the following Job Options:

Job Name: C2H4Cl2Liq180

Calculation: Geometry Optimization

Theory: PM3

Charge: 0

Multiplicity: Singlet

Click the Advanced tab. In the Solvent pull-down menu, choose Water. Click the blue “continue” arrow. You should see your job listed.

When the job is complete, click on the filename and scroll down to find the heat of formation. Record the value in the table below.

Repeat the above process for the other angles listed in the table.

Dihedral Angle	$\Delta_f H$ (kcal mol ⁻¹)
180°	
120°	
0°	
60°	

Which conformer is more stable in the aqueous solution and by how much energy? _____ conformer by _____ kcal mol⁻¹ (literature 0.3 kcal mol⁻¹).

What might you predict for the preferred structure in the pure liquid C₂H₄Cl₂ ($\epsilon = 10.36$)? The literature indicates the trans conformer by 0.31 kcal mol⁻¹.