6 Modeling in Solution

Exercise 1 Will a molecule of Water Pass through the Center of a Molecule of Benzene?

Build a molecule of C_6H_6 using the draw tool to construct a hexagon of C atoms, using the add bond tool to create alternate C=C bonds, clicking the add H tool, and clicking Mark / Pi Atoms. Click the add H tool to remove the H atoms.

Near the benzene molecule, build a molecule of H_2O on a blank portion of the screen by clicking the draw tool, clicking in the workspace, clicking the periodic table tool, choosing O, and clicking the small gray circle. Close the periodic table.

Click the add H tool to add H atoms to both structures.

Minimize.

Using this representation of the molecules, does it look like there is an empty space in the center of the benzene molecule through which the water molecule can pass? _____

Change to the "space filling" view to generate the van der Waals surface by clicking View / CPK Surface.

Is there an empty space in the center of the benzene molecule through which the water molecule can pass? _____

Save and Close.

Exercise 2 Determine the Enthalpy of Vaporization of Water.

Note that the calculation may take several minutes.

Build a molecule of H_2O. Save as H2Ogas.pcm.

Minimize using MMX and record $\Delta_f H$ = _____ kcal mol^{-1} (-57.796 kcal mol^{-1} literature).

Click Edit / Build Solvent Box/Solvate. Choose 50 molecules of water and click OK.

Save as H2Oliq.csf and minimize. Record $\Delta_f H$ = _____ kcal. Divide this value by 51 to get $\Delta_f H$ = _____ kcal mol^{-1} (-68.315 kcal mol^{-1} literature).

Note the H-bonding between the molecules.

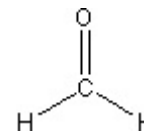The difference between the two enthalpies of formation is the enthalpy of vaporization $\Delta_{vap} H$ = _____ kcal mol^{-1} (10.519 kcal mol^{-1} literature).

Save and Close.

Exercise 3 Determine the Frequency Shift for C=O for Formaldehyde Dissolved in Water.

This Exercise requires the program PCM-Vibrate to visualize the calculated spectra–however, the values of the IR spectral peaks may be read from the output file.

Note that the calculation may take several minutes.

Build a molecule of CH_2O. Use the draw tool to construct two C atoms, use the add bond tool to generate a double bond, click the periodic table tool and choose O, click one of the C atoms to change it to an O atom, close the periodic table, and use the add H atoms tool. Save as ch2ogas.pcm.

Click Force Field / MM3 and minimize at the MM3 level. Save.
Click Compute / Normal Vibrational Modes. Save as ch2ovib.vib.
The values of the vibrational frequencies can be obtained by opening the ch2ovib.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 ch2ovib.vib file and click OK. A "stick" spectrum appears on the screen. Clicking on the spectral lines will produce a animation of the respective vibration. Locate the peak for the C=O stretch and record the value $\tilde{v}$ = _____ cm⁻¹ (1746.07 cm⁻¹ literature).
Click Edit / Build Solvent Box/Solvate. Choose 50 molecules of water and click OK. Minimize. Note the H-bonding to the O atom in formaldehyde by the water molecules.
Click Compute / Normal Vibrational Modes. Save as ch2oaqvib.vib. The stick spectrum will have many closely spaced vibrational lines for water, but the formaldehyde lines will be visible. Locate the peak for the C=O stretch and record the value $\tilde{v}$ = _____ cm⁻¹.
The difference between these frequencies is the effect on the vibrational frequency as a result of the solvation process. $\Delta\tilde{v}$ = _____ cm⁻¹.
Be sure to click Force Field / MMX.
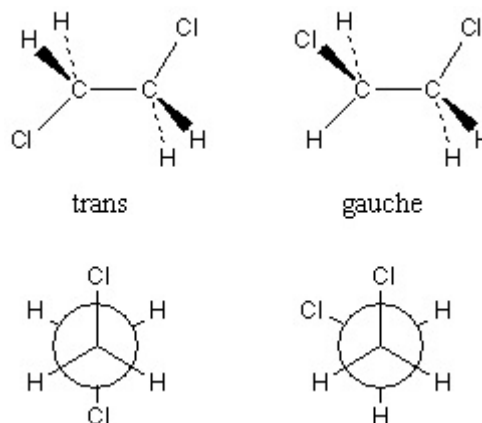Save and Close.

Exercise 4 Determine the stable form of 1,2-dichloroethane.
Note that this calculation may take up to 1.5 hr.

Build a molecule 1,2-dichloroethane using the build tool and the periodic table tool choosing Cl to replace a H atom at each end of the molecule. Save as c2h4cl2gas.pcm. Minimize and Save.
Define a dihedral angle consisting of the Cl-C-C-Cl atoms and choose Compute / Dihedral Driver. Choose -180, 180, and 10. Save as c2h4cl2gasrot.pcm.
Record the values of the energy of the trans conformer _____ kcal mol⁻¹, the maxima of the rotation barriers _____ kcal mol⁻¹ and _____ kcal mol⁻¹, and

trans   gauche

the energy of the gauche conformer _____ kcal mol^{-1}. Which conformer is more stable in the gaseous phase and by how much energy? _____ conformer by _____ kcal mol^{-1} (1.1 kcal mol^{-1} literature).

Save the structure as c2h4cl2aq.pcm and prepare a model of the molecule in 50 molecules of water by clicking Edit / Build Solvent Box/Solvate. Minimize and Save.

Run Compute / Dihedral Driver and save as c2h4cl2aqrot.pcm.

Record the values of the energy of the trans conformer _____ kcal mol^{-1}, the maxima of the rotation barriers _____ kcal mol^{-1} and _____ kcal mol^{-1}, and the energy of the gauche conformer _____ kcal mol^{-1}. Which conformer is more stable in the aqueous solution and by how much energy? _____ conformer by _____ kcal mol^{-1} (0.3 kcal mol^{-1} literature).

Save and Close.

The dielectric constant of water is $\epsilon = 78.4$. What might you predict for the preferred structure in the pure liquid $C_2H_4Cl_2$ ($\epsilon = 10.36$)? The literature indicates the trans conformer by 0.31 kcal mol^{-1}.