

## 6 Modeling in Solution

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

Using the “ball and cylinder” view, build a molecule of  $C_6H_6$  using  $sp^2$  C atoms and alternating double bonds. Add H atoms.

Near the benzene molecule, build a molecule of  $H_2O$  using a  $sp^3$  O atom. Add H atoms. 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.

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

### Exercise 2 Determine the Enthalpy of Vaporization of Water.

Build a molecule of  $H_2O$  using a  $sp^3$  O atom and add H atoms. Save as h2ogas.csf. Minimize using PM3 and record  $\Delta_f H =$  \_\_\_\_\_ kcal mol<sup>-1</sup> (-57.796 kcal mol<sup>-1</sup> literature).

Save as h2oliq.csf and minimize using PM3 geometry in water. Record  $\Delta_f H =$  \_\_\_\_\_ kcal mol<sup>-1</sup> (-68.315 kcal mol<sup>-1</sup> literature).

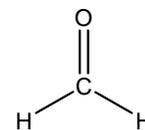
The difference between the two enthalpies of formation is the enthalpy of vaporization  $\Delta_{\text{vap}} H =$  \_\_\_\_\_ kcal mol<sup>-1</sup> (10.519 kcal mol<sup>-1</sup> literature).

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

Build a molecule of  $CH_2O$  using  $sp^2$  C and O atoms and add H atoms. Save as ch2ogas.csf.

Minimize using PM3. Determine the vibrational/IR spectrum using MOPAC PM3 Force. Locate the peak for the C=O stretch and record the value  $\tilde{\nu} =$  \_\_\_\_\_ cm<sup>-1</sup> (literature 1746.07 cm<sup>-1</sup>). The vectors representing the vibrational motion are easier to see using View / Lines. Double clicking the triangle for the peak brings up a small window listing the frequency.

Save as ch2osoln.csf. Minimize choosing a modified PM3 geometry in water. Modify the default parameters using the procedure editor by clicking edit / choose call MOPAC / open / edit / choose run Molecular Orbital... / open and change the name from water to acetonitrile and the dielectric constant from 78.4 ( $H_2O$  default) to 36.64 for acetonitrile. Click ok / close / yes / close / close and run the experiment.



Determine the vibrational/IR spectrum using a modified MOPAC PM3 Force. Modify the default parameters using the procedure editor by clicking simulate the solvent and using the same changes in the parameters as above. Locate the peak for the C=O stretch and record the value  $\tilde{\nu} = \underline{\hspace{2cm}}$   $\text{cm}^{-1}$  (literature  $1723 \text{ cm}^{-1}$ ).

The difference between these frequencies is the effect on the vibrational frequency as a result of the solvation process.  $\Delta\tilde{\nu} = \underline{\hspace{2cm}}$   $\text{cm}^{-1}$  (literature  $23 \text{ cm}^{-1}$ ).

Use the procedure editor to restore both the PM3 geometry in water and MOPAC PM3 Force settings to the original water values (remove the simulate solvent choice in MOPAC PM3 Force).

#### Exercise 4 Determine the stable form of 1,2-dichloroethane.

Build a molecule 1,2-dichloroethane using  $sp^3$  hybridized C and Cl atoms and add H atoms.

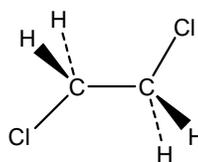
Define a dihedral angle consisting of the Cl-C-C-Cl atoms by holding down the shift key and clicking the four atoms. Click adjust / dihedral angle and select define geometry label and search. Accept the default angles by clicking ok.

Save as c2h4cl2gas.csf. Prepare an energy map by selecting chemical sample conformations

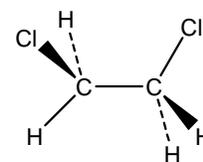
with an optimized map using PM3 energies (one label). Record the values of the energy of the trans conformer  $\underline{\hspace{2cm}}$   $\text{kcal mol}^{-1}$ , the maxima of the rotation barriers  $\underline{\hspace{2cm}}$   $\text{kcal mol}^{-1}$  and  $\underline{\hspace{2cm}}$   $\text{kcal mol}^{-1}$ , and the energy of the gauche conformer  $\underline{\hspace{2cm}}$   $\text{kcal mol}^{-1}$ . Which conformer is more stable in the gaseous phase and by how much energy?  $\underline{\hspace{2cm}}$  conformer by  $\underline{\hspace{2cm}}$   $\text{kcal mol}^{-1}$  (literature  $1.1 \text{ kcal mol}^{-1}$ ).

Save as c2h4cl2aq.csf and rerun the experiment using PM3 energies in water (one label). Record the energy values of the trans conformer  $\underline{\hspace{2cm}}$   $\text{kcal mol}^{-1}$ , the maxima of the rotation barriers  $\underline{\hspace{2cm}}$   $\text{kcal mol}^{-1}$  and  $\underline{\hspace{2cm}}$   $\text{kcal mol}^{-1}$ , and the energy of the gauche conformer  $\underline{\hspace{2cm}}$   $\text{kcal mol}^{-1}$ . Which conformer is more stable in the aqueous solution and by how much energy?  $\underline{\hspace{2cm}}$  conformer by  $\underline{\hspace{2cm}}$   $\text{kcal mol}^{-1}$  (literature  $0.3 \text{ kcal mol}^{-1}$ ).

What might you predict for the preferred structure in the pure liquid  $\text{C}_2\text{H}_4\text{Cl}_2$  ( $\epsilon = 10.36$ )? If you run this experiment, please remember to reset the dielectric constant value back to that of water. The literature indicates the trans conformer by  $0.31 \text{ kcal mol}^{-1}$ .



trans



gauche

