6 Modeling in Solution

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

Using the Text Tool, build a molecule of C_6H_6.
Build a molecule of H_2O using the Text Tool.
Does it look like there is an empty space in the center of the benzene molecule through which the water molecule can pass? _____
Select the water molecule. Move it to the edge of the workspace by dragging.
Click View / Solvent Accessible Surfaces / Show Surface.
Is there an empty space in the center of the benzene molecule through which the water molecule can pass? _____
Close.

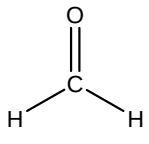
Exercise 2 Determine the Enthalpy of Vaporization of Water.

Build a molecule of H_2O using the Text Tool.
Minimize using PM3 and record $\Delta_f H$ = _____ kcal mol^{-1} (-57.796 kcal mol^{-1} literature).
Save as h2ogas.c3d.

Save as h2oliq.c3d and minimize using PM3 geometry in water. Click MOPAC / Minimize Energy / Theory: PM3 / Property: Heat of Formation and Cosmo Solvation in Water and click Run.
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 $\Delta_{vap} H$ = _____ kcal mol^{-1} (10.519 kcal mol^{-1} literature).

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

Build a molecule of CH_2O using the Text Tool.
Minimize using PM3 and save as ch2ogas.c3d.
Determine the vibrational/IR spectrum by clicking MOPAC / Spectral Analysis / Theory: PM3 and click Run.



Click the triangle on the Message Window, locate the frequency for Vibration 4 which corresponds to the peak for the C=O stretch, and record the value $\tilde{\nu}$ = _____ cm^{-1} (literature 1746.07 cm^{-1}).
Save.

Save as ch2osoln.c3d. Minimize choosing a modified PM3 geometry in water. Click MOPAC / Minimize Energy / Theory: PM3 / Properties: Heat of Formation, Gradient Norm, Cosmo Solvation in Water and click Run.

Save.

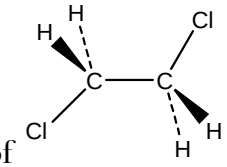
Determine the vibrational/IR spectrum using a modified PM3 geometry in water. Click MOPAC / Minimize Energy / Theory: PM3 / Properties: Heat of Formation, Gradient Norm, Cosmo Solvation in Water / General: type FORCE in the Additional Keywords box. Click Run.

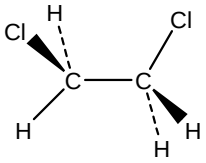
Navigate to c:\Documents and Settings\Default\Local Settings\Temp\CSMOPACOutput. Open ch2osoln.arc and record the value $\tilde{\nu}$ = _____ cm^{-1} (literature 1723 cm^{-1})

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

Exercise 4 Determine the Stable Form of 1,2-dichloroethane.

Build a molecule 1,2-dichloroethane using the Text Tool. The *trans* conformer will be produced.

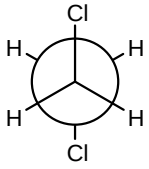


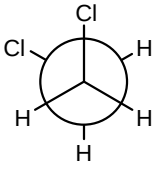


trans gauche

Minimize at the PM3 level and save as c2h4cl2gastranspm3.c3d. Record the value of the energy $\Delta_f H$ = _____ kcal mol^{-1}.

Change the *trans* conformer to the *gauche* conformer by clicking the CC bond and clicking and dragging on the Internal Rotation Bar at the left of the workspace. (Note that the angle of rotation appears at the bottom left and should be about 120°.)





Minimize at the PM3 level and save as c2h4cl2gasgauchepm3.c3d. Record the value of the energy $\Delta_f H$ = _____ kcal mol^{-1}.

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

Close.

Open c2h4Cl2gastranspm3.c3d and save as c2h4Cl2solntranspm3.c3d.

Minimize the molecule in aqueous solution. Click MOPAC / Minimize Energy / Theory: PM3 / Properties: Heat of Formation, Gradient Norm, Cosmo Solvation in Water and click Run.

Save and record the energy _____ kcal mol^{-1}.

Close and Open / New Model. Open c2h4cl2gasgauchepm3.c3d and save as c2h4cl2solngauchepm3.c3d.

Minimize the molecule in aqueous solution as above, save, and record the energy _____ kcal mol^{-1}.

Which conformer is more stable in the gaseous phase and by how much energy?

_____ conformer by _____ kcal mol^{-1} (literature 0.3 kcal mol^{-1}). Close.