6 Modeling in Solution

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

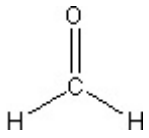
Using the "ball and cylinder" view, build a molecule of C_6H_6 using the Benzene Ring fragment.
Near the benzene molecule, build a molecule of H_2O using the Oxygen Tetravalent fragment.
Using this representation of the molecules, does it look like there is an empty space in the center of the benzene molecule through which the water molecule can pass? _____
Click View / Display Format / Molecule. Type in 150 for the Scale Radii and click Use van der Waals Radii.
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 the Oxygen Tetravalent fragment.
Minimize at the B3LYP/6-31G(d) level. Save as h2ogas.chk and h2ogas.cjf.
From the summary of results, record the energy E(gas) = _____ Eh.
Close all windows except the main Control Panel and the original View workspace.
Click Calculate / Gaussian, change the title to reflect liquid water, and click Solvation / Default / Model in Water. Submit saving as h2oliq.chk and h2oliq.cjf.
Record E(liq) = _____ Eh.
The enthalpy of vaporization $\Delta_{vap}H$ = [E(gas) - E(liq)](625.5095) + (298)(1.987/1000) = _____ kcal mol^{-1} (10.519 kcal mol^{-1} literature).

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

Build a molecule of CH_2O using the C trivalent fragment and the O Trivalent fragment.

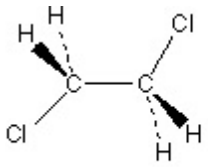


Minimize at the B3LYP/6-31G(d) level choosing Opt+Freq for the job type. Save as ch2ogas.chk and ch2ogas.cjf.
Open the ch2ogas.log file with a suitable text editor such as WordPad, scroll to the bottom of the file, and move up about 150 lines by clicking in the scroll bar five times. The six vibrational frequencies will be listed. The peak for the C=O stretch is #4 with A1 symmetry. Record the value $\tilde{\nu}$ = _____ cm^{-1} (literature 1746.07 cm^{-1}).

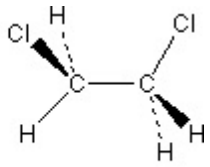
Close everything but the main Control Panel and the original View workspace.
For the solution, minimize and calculate the vibrational frequencies at the B3LYP/6-31G(d) level choosing Default and Acetonitrile on the Solvation panel. Save the files as ch2osoln.chk and ch2osoln.cjf.
Locate the peak for the C=O stretch in the log file 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} (literature 23 cm^{-1}).

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

Build a molecule 1,2-dichloroethane using the Carbon Tetravalent fragment twice and the Chlorine Terminal fragment twice to replace two of the original H atoms that are trans.

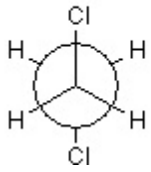


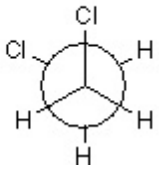
trans



gauche

Use the Redundant Coordinate Editor to define the Cl-C-C-Cl dihedral angle and choose Freeze Coordinates. Set the value at 180 °.
Minimize at the B3LYP/6-31G(d) level and save as c2h4cl2trans.chk and c2h4cl2trans.cjf. Record the energy _____ Eh from the results summary.





Close everything except the main Control Panel.
Build the gauche conformer, freeze the dihedral angle at 60 °.
Minimize saving as c2h4cl2gauche.chk and c2h4cl2gauche.cjf. Record the energy _____ Eh.
Close everything except the main Control Panel.
Which conformer is more stable in the gaseous phase _____ and by how much energy? _____ kcal mol^{-1} (literature 1.1 kcal mol^{-1})
Build the trans conformer, freeze the dihedral angle at 180 °.
Minimize in water using the Default solvation model. Save as c2h4cl2transaq.chk and c2h4cl2transaq.cjf. Record the energy _____ Eh.
Close everything except the main Control Panel.
Build the gauche conformer, freeze the dihedral angle at -60 °.
Minimize saving as c2h4cl2gaucheaq.chk and c2h4cl2gaucheaq.cjf. Record the energy _____ Eh.
Close everything except the main Control Panel.
Which conformer is more stable in aqueous solution _____ and by how much energy? _____ kcal mol^{-1} (literature 0.3 kcal mol^{-1})
The dielectric constant of water is 78.4. What might you predict for the preferred structure in the pure liquid $C_2H_4Cl_2$ (ϵ = 10.36)? The literature indicates the trans conformer by 0.31 kcal mol^{-1}.