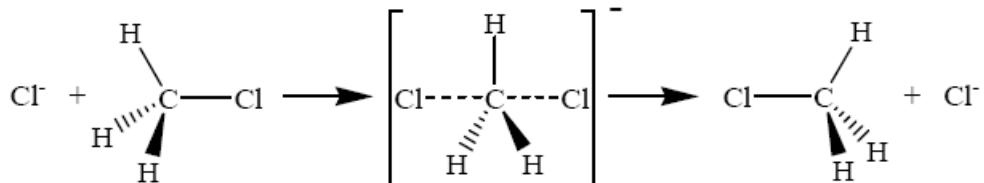


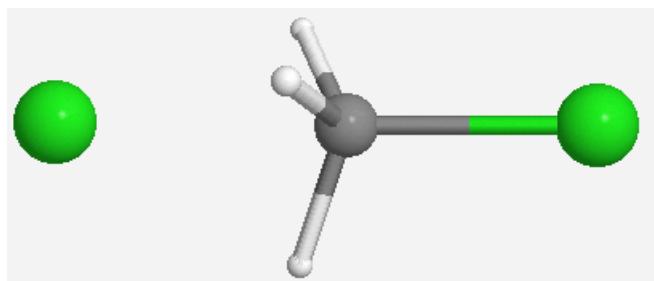
## Lab 9 Transition States (WebMO)

### Exercise 1 The Walden Inversion

This laboratory will study the S<sub>N</sub>2 reaction between Cl<sup>-</sup> and CH<sub>3</sub>Cl involving a Walden inversion:



In the WebMO Build Molecule window, draw a carbon atom, then attach a single chlorine atom. Choose Clean-Up > Comprehensive-Mechanics. You now have chloromethane. Add another Cl atom in the space opposite from the C-Cl bond, as shown below:



Select the Adjust tool (, 5<sup>th</sup> down on left) and click on the unbound Cl atom to highlight it. Choose Adjust > Charge and type in “-1” in the Adjust Charge window. Click Apply, then OK. Click the blue “Continue” arrow at the lower right. Select Gaussian as the computational engine and click the blue “Continue” arrow.

Type in/Choose the following:

Job Name: CH3Cl2(-1) Walden DFT  
Calculation: Transition State Optimization  
Theory: B3LYP  
Basis Set: Routine: 6-31G(d)  
Charge: -1  
Multiplicity: Singlet

**Click on the Preview tab.**

**Click the Generate button at the bottom of the window that opens.**

**Type in MaxCycles=200 after “NoEigenTest” in the OPT line, as shown below:**

#N B3LYP/6-31G(d) OPT=(TS,CalcFC,NoEigenTest,MaxCycles=200)

**Click Submit Job on the left hand side.**

You should see the submitted job in the Job Manager window.

When the job is complete, open it by clicking on the hyperlinked name.

Use the Select tool to measure the carbon chlorine distances (Lit. value 2.38Å):

C-Cl (bound): \_\_\_\_\_ Å      C-Cl (Unbound): \_\_\_\_\_ Å

Click “New Job Using This Geometry” at the bottom.

Click the blue “Continue” arrow. Choose Gaussian as the computational engine, and click the blue “continue” arrow again.

Type in/Choose the following:

Job Name: CH<sub>3</sub>Cl<sub>2</sub>(-1) Walden IR  
Calculation: Vibrational Frequencies  
Theory: B3LYP  
Basis Set: Routine: 6-31G(d)  
Charge: -1  
Multiplicity: Singlet

Click the blue “Continue” arrow and open the job once it is complete.

Scroll down and observe the Vibrational Modes listing.

How many imaginary (negative) frequencies are listed? \_\_\_\_\_ Is this expected? \_\_\_\_\_

Click on the “Animate” icon (film clip) to the right of the negative frequency listing and observe the corresponding motion. Was the transition state correctly located?

Save and close the file.

### Exercise 2    1,3 Hydrogen Shift in 3-fluoropropene

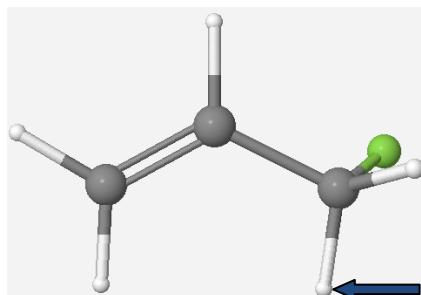
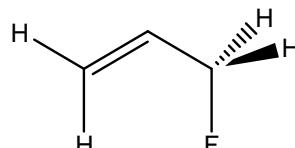
Draw 3-fluoropropene.

Choose Clean-Up > Comprehensive-Mechanics.

You will probably end up with the form shown to the right.

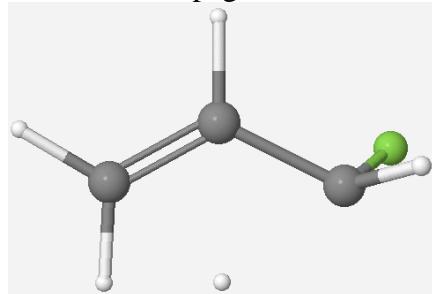
Choose the Adjust tool (), and click on the F atom to highlight it. HOLD DOWN THE SHIFT KEY, and click on the attached carbon, the central carbon, and the carbon on the left.

Choose Adjust > Dihedral Angle. Type in 120 in the Adjust Dihedral window, then click Apply and OK. You should now have the structure shown below:



Choose the Adjust tool, and click on the H atom (indicated in the above picture) to highlight it. Hit “delete” on your keyboard to remove the H atom.

Click on the Periodic Table icon, choose H, and place the H atom midway between the two terminal carbons as shown on the next page.



Click the blue “Continue” arrow, choose Gaussian as the engine, and click the arrow again.

Type in/Choose the following:

Job Name: C3H5F TSO DFT  
Calculation: Transition State Optimization  
Theory: B3LYP  
Basis Set: Routine: 6-31G(d)  
Charge: 0  
Multiplicity: Singlet

Click the blue “Continue” arrow. You should see the submitted job in the Job Manager window. When the job is complete, open it by clicking on the hyperlinked name.

Rotate the molecule and describe the approximate geometry at each of the terminal carbon atoms. Does this make sense?

Record the B3LYP Energy here (don’t round off!): \_\_\_\_\_ h

Click “New Job Using This Geometry” at the bottom.

Click the blue “Continue” arrow. Choose Gaussian as the computational engine, and click the blue “continue” arrow again.

Type in/Choose the following:

Job Name: C3H5F TSO IR  
Calculation: Vibrational Frequencies  
Theory: B3LYP  
Basis Set: Routine: 6-31G(d)  
Charge: 0  
Multiplicity: Singlet

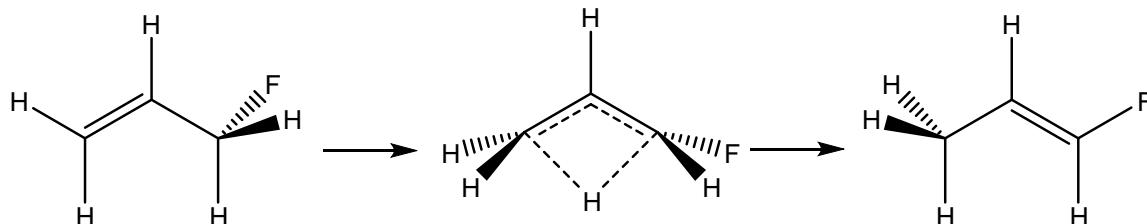
Click the blue “Continue” arrow and open the job once it is complete.

Scroll down and observe the Vibrational Modes listing.

How many imaginary (negative) frequencies are listed? \_\_\_\_\_

Click on the “Animate” icon (film clip) to the right of the negative frequency listing and observe the corresponding motion. Does the motion of the “unbound H” atom make sense? Explain.

What you are seeing is movement of the atoms (the H atom in particular) in going from 3-fluoropropene to 1-fluoropropene, as shown below:



Build a molecule of 3-fluoropropene (left structure above), perform a geometry optimization using Gaussian > B3LYP/6-31G(d), and record the B3LYP energy here (don't round off):

\_\_\_\_\_ h

Repeat the above process for 1-fluoropropene (right structure above) and record the B3LYP energy here (don't round off):

\_\_\_\_\_ h

Which compound is more stable? \_\_\_\_\_

From the three energies of reactant, transition state, and product you have found, use the conversion factor ( $627.51 \text{ kcal mol}^{-1} = 1 \text{ h}$ ) to **convert the energy differences between them into **kcal mol<sup>-1</sup>****. Draw a potential energy diagram for the reaction and indicate the size of the barrier in **kcal mol<sup>-1</sup>**.

