Assignment 3: Molecular Orbital Calculations
(50 points)

In this assignment, you will carry out some molecular orbital calculations to explore the capabilities of these methods. You will investigate the calculation of thermochemical properties, reactivity trends via LUMO energy, and determination of reaction paths.

The software package that you will use for these calculations is called *Gaussian*, one of the most widely used quantum chemistry packages available. The graphical interface that we will use is a program called *GaussView*. To start the program, simply type "gv &" in the terminal window after logging on to the departmental cluster, sauron.che.ilstu.edu. A tutorial illustrating the use of *GaussView* and *Gaussian* previously was distributed and demonstrated in class.

THIS ASSIGNMENT IS DUE MONDAY, OCTOBER 26, 2015.

PART A (15 points) - Thermochemistry of Hydrogen Fluoride

In this part of the assignment, you will investigate the use of molecular orbital calculations to predict enthalpies of reaction and enthalpies of formation. In particular, you will study the dissociation of hydrogen fluoride, HF, as well as the formation of HF. You will (hopefully) see that the use of methods that include electron correlation give good predictions of these enthalpies.

In order to calculate an enthalpy change of reaction, we must know its relationship to the electronic energy determined from a molecular orbital calculation. For a gas phase reaction, the relationship is

$$\Delta H_{rx} = \Delta E_e + \Delta(PV) + \Delta H_{vib} + \Delta H_{rot} + \Delta H_{trans} \, . \tag{1}$$

In the equation, ΔE_e is the difference in electronic energies of the products and reactants. This is the quantity obtained by solving the Schrödinger equation. In most quantum chemistry software packages, the electronic energy is reported in atomic units (or hartrees); to convert to kcal/mol, use 1 a.u. = 627.51 kcal/mol. The term $\Delta(PV)$ is included to convert from internal energy to enthalpy ($H = U + PV$, or $H = E + PV$). Assuming that the gases behave ideally, we have that $\Delta(PV) = \Delta \nu RT$, where $\Delta \nu$ is the difference between the number of moles of gaseous products and reactants. The terms ΔH_{vib}, ΔH_{rot}, and ΔH_{trans} represent the vibrational, rotational, and translational contributions to the enthalpy of reaction. The vibrational contribution is determined from calculation of the vibrational frequencies; the rotational contribution is determined from calculations of the moments of inertia (which depend upon the equilibrium geometry of the molecule), and the translational contribution is determined from the number of degrees of freedom of the system. The various contributions to the enthalpy are reported by the *Gaussian* program when a frequency calculation is requested, and are lumped together into one term,

$$E_e + H_{corr} \;=\; E_e + H_{vib} + H_{rot} + H_{trans} \, . \tag{2}$$

The only term in Eq. (1) not included in the $E_e + H_{corr}$ factor is the $\Delta(PV)$ term, which has to be taken into account separately.

The enthalpy change of a reaction then can be written as

$$\Delta H_{rx} = \Delta(E_e + H_{corr}) + \Delta \nu RT ,$$

$$\text{or} \quad \Delta H_{rx} = \sum_{products}(E_e + H_{corr}) - \sum_{reactants}(E_e + H_{corr}) + \Delta \nu RT , \tag{3}$$

where it is assumed in the sums over products and reactants that the appropriate stoichiometric factors are included.

Procedure – Part A

1. Using *GaussView*, build the hydrogen fluoride molecule, HF. Set up a Hartree-Fock/6-31+G(d) calculation in which you optimize the geometry and determine the vibrational frequencies. By selecting *Calculate* → *Gaussian* from the main menu, a window will open where you can set the parameters for the calculation. The Job Type is Opt+Freq, the Method is Hartree-Fock, and the basis set is 6-31+G(d); select Basis: 6-31G with added "+" and "d". Make sure to set the memory to 4GB and the number of processors to 8 in the Link0 tab as well. Complete the calculation by retaining the calculation information, saving a .com file, and submitting your job using the **qg09** command as illustrated in the *Gaussian/GaussView* tutorial.

    When the optimization/frequency calculation is complete, you will open the results file directly with a text editor. To do this, type the following in the terminal window:

    > **gedit   filename.log**

    Here, 'filename' is the name of the .com file that you saved.

    To find the vibrational, rotational, and translational enthalpies from the frequency calculation, search for the section of the file that lists "Thermochemistry". The value that you need to record is the "Sum of electronic and thermal Enthalpies". Note that in *Gaussian*, this value is given by the equation

    $$\text{Sum of electronic and thermal Enthalpies} = E_e + H_{corr} = E_e + H_{vib} + H_{rot} + H_{trans} .$$

   This value is also adjusted to be at 298 K rather than 0 K.

2. Repeat the optimization and frequency calculation at the MP2/6-31+G(d) level. It is best to start from scratch and rebuild the HF molecule, saving it with a new file name. Once the optimization/frequency calculation is complete, record the MP2 value for the sum of electronic and thermal enthalpies (it is located in the log file for the calculation as described in step 1).

3. Next, build and perform a calculation on the F atom. Select an <u>energy</u> calculation as the Job Type (*not* an optimization) and use the 6-31+G(d) basis set and the Hartree-Fock level of theory. Once the calculation is complete, this time open the checkpoint file in *GaussView*. Record the electronic energy, E_e (available in this case from *Results* → *Summary*). Note that the vibrational and rotational enthalpy corrections for atoms are zero. The translational enthalpy for any atom is 3/2 RT. Use this to calculate H_{corr} for the atom at 298 K.

4. Repeat the calculation for F atom that you completed in step 3 at the MP2/6-31+G(d) level. Again, it is best to start from scratch and rebuild the F atom, saving it with a new file name. Once the calculation is complete, open the checkpoint file in *GaussView*. Record the electronic energy E_e (again available from *Results* → *Summary*). The value of H_{corr} for the atom is determined in the way same as in step 3.

5. Repeat the calculation that you performed in step 3 for the H atom. For H atom, the MP2 and Hartree-Fock results are identical because H atom has only one electron, so you only have to do the Hartree-Fock calculation. The value of H_{corr} for the H atom is determined in the way same as in step 3.

6. Use the results from steps 1-5 to calculate the bond dissociation enthalpy of HF,

$$\text{HF} \quad \rightarrow \quad \text{H} + \text{F} .$$

You should have two sets of calculations: Hartree-Fock/6-31+G(d) and MP2/6-31+G(d). Use Equation (3) and do not forget to add in the $\Delta(PV)$ term.

7. Use a similar procedure to that given in steps 1-6 to calculate the enthalpy of formation of HF,

$$\tfrac{1}{2}\text{H}_2 + \tfrac{1}{2}\text{F}_2 \quad \rightarrow \quad \text{HF} .$$
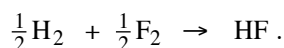
You should carry out the calculations at both the Hartree-Fock/6-31+G(d) and the MP2/6-31+G(d) levels. You may use the results from steps 1 and 2 above for the HF molecule. In this case, you also will have to carry out geometry optimization/frequency calculations for the H_2 and F_2 molecules using *Gaussian/GaussView*.

Results and Discussion – Part A

1. For the bond dissociation enthalpy of HF (step 6), include a table listing $E_e + H_{corr}$ for each atom or molecule at the Hartree-Fock and MP2 levels of theory. Also list the $\Delta(PV)$ term. Give the result for the bond dissociation enthalpy in kcal/mol for each level of theory. Compare your results for the bond dissociation enthalpy to a literature value; make sure that the literature value is an experimental one, not one from some computational method. Discuss which level of theory, Hartree-Fock or MP2, gives better agreement with experiment.

2. For the formation enthalpy of HF (step 7), include a table listing $E_e + H_{corr}$ for each molecule at the Hartree-Fock and MP2 levels of theory. Give the result for the enthalpy of formation in kcal/mol for each level of theory. Note that to calculate the reaction enthalpy, you must include the coefficients in the balanced chemical reaction. If a factor of $\frac{1}{2}$ appears in the balanced reaction, then you must multiply the sum of electronic and thermal enthalpies for that species by $\frac{1}{2}$ in your calculation of the overall reaction enthalpy. Compare your results for the formation enthalpy to a literature value. Again, discuss which level of theory, Hartree-Fock or MP2, gives better agreement with experiment.

Note: The literature values that you should compare your calculations to can be found in the *CRC Handbook of Chemistry and Physics* or the NIST Chemistry Webbook (webbook.nist.gov). Calculate the experimental enthalpies of reaction from the literature values of enthalpies of formation.

Part B (10 points) - Reactivity Trends in Diels-Alder Cycloaddition Reactions

A Diels-Alder cycloaddition reaction involves the reaction of a diene with a dienophile to form a new ring system. The most common example is the reaction between 1,3-butadiene (the diene) and ethylene (the dienophile) to yield cyclohexene, Figure 1.

Figure 1. Diels-Alder reaction between 1,3-butadiene and ethylene.

The mechanism of the reaction is thought to involve an interaction between the highest occupied molecular orbital (the HOMO) of the diene and the lowest unoccupied molecular orbital (the LUMO) of the dienophile. The most favorable Diels-Alder reactions generally occur between electron-rich dienes and electron-poor dienophiles. It is especially helpful to attach functional groups to the diene which are good π-electron donors because the HOMO of the diene is a π-type orbital. For the dienophile, it is helpful to attach functional groups which are good π-electron acceptors because the LUMO of the dienophile is a π^*-type orbital.

One condition for a favorable interaction between diene and dienophile is that the energy difference between the diene HOMO and the dienophile LUMO is small. A second condition for favorable interaction between the diene and dienophile is that the overlap integral between the two molecular orbitals is large. These two conditions come from the second-order perturbation theory result for the interaction energy, E_{int}, which is given by

$$E_{int} \propto \frac{\left| \int \phi^*_{HOMO,diene} \, \phi_{LUMO,dienophile} \, d\tau \right|^2}{\varepsilon_{HOMO,diene} - \varepsilon_{LUMO,dienophile}} . \tag{4}$$

Here, ϕ denotes the molecular orbital (HOMO or LUMO), and ε denotes the orbital energy. The integral that appears in the numerator of Eq. (4) is just the overlap between the diene HOMO and the dienophile LUMO, while the term in the denominator gives the energy difference between the molecular orbitals. Experimental data for rates of Diels-Alder cycloaddition reactions are shown in Table 1.

Table 1. Relative rates (measured relative to cyanoethylene)[1] for cycloaddition reaction between cyclopentadiene and substituted ethylene dienophiles.

Dienophile	Relative Rate
ethylene	6×10^{-6}
cyanoethylene	1
trans-1,2-dicyanoethylene	81
cis-1,2-dicyanoethylene	91
1,1-dicyanoethylene	4.55×10^4
tricyanoethylene	4.8×10^5
tetracyanoethylene	4.3×10^7

1. N. S. Isaacs, *Physical Organic Chemistry*, John Wiley and Sons, New York, 1987, p. 661.

In this part of the project, you will attempt to correlate the experimental rates of reaction between cyclopentadiene (the diene) and cyano-substituted ethylenes (the dienophiles) with LUMO energies of the substituted ethylenes.
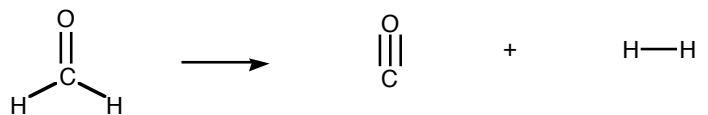
Procedure – Part B

1. Using *GaussView*, build the cyclopentadiene and ethylene molecules. Perform geometry optimization calculations (Job Type: Optimization) using the Hartree-Fock method with a 3-21G basis set for each molecule. Again, remember to set the memory to 4GB and processors to 8 in the Link0 tab. Submit the cyclopentadiene and ethylene calculations using the qg09 command as described in the *Gaussian/GaussView* tutorial. Once the calculations are complete, open the checkpoint file for each molecule in GaussView, and record the energy of the HOMO of cyclopentadiene and the energy of the LUMO of ethylene. These values will be given in hartrees.

2. Using the Molecular Orbtial editor in *GaussView*, generate and display the HOMO of the cyclopentadiene moleule. Sketch the shape of the HOMO and describe what type of orbital it corresponds to (i.e., indicate whether it is sigma or pi type and whether it is bonding or antibonding).

3. Repeat step 2 for ethylene, except generate and display the LUMO of ethylene. Sketch the shape of the LUMO and describe what type of orbital it is.

4. In order to see the trends in reactivity related to the energy difference between the diene HOMO and dienophile LUMO, we will keep the HOMO the same and vary the LUMO by looking at different dienophiles. Build and carry out equilibrium geometry calculations of the molecules cyanoethylene, *trans*-1,2-dicyanoethylene, *cis*-1,2-dicyanoethylene, 1,1-dicyanoethylene, tricyanoethylene, and tetracyanoethylene. Perform the equilibrium geometry calculations using the Hartree-Fock method and a 3-21G basis set. Set the memory to 4GB and processors to 8 in the Link0 tab. Once the calculations complete, open the checkpoint file of each substituted ethylene in *GaussView* and obtain the LUMO energy.

Results and Discussion – Part B

1. Tabulate the HOMO energy of cyclopentadiene along with the LUMO energies of the substituted ethylenes. Use eV for the units [1 hartree = 27.2114 eV].

2. Prepare a graph correlating the LUMO-HOMO energy difference to reaction rate (note that we are assuming that the orbital overlap is essentially constant). Plot the LUMO-HOMO energy difference in eV on the *y*-axis and log(base 10) of reaction rate on the *x*-axis. The log is used for reaction rate because the relative rates span so large a range.

3. Discuss any trends observed in the graph from #2. What does adding CN groups do to the LUMO energy of the substituted ethylene? Explain the trends observed in reaction rates on the basis of qualitative arguments like those presented in the introduction to this problem.

*PART C (10 points) – Transition State in the Dissociation of Formaldehyde*

In this part of the assignment, you will locate the transition state in the dissociation of formaldehyde. In the reaction that you will study, formaldehyde breaks apart into to carbon monoxide and diatomic hydrogen,

Figure 2. Decomposition reaction of formaldehyde to form carbon monoxide and diatomic hydrogen.

Procedure – Part C

1. The first step in a transition state search is to obtain optimized geometries for the reactants and products. Build formaldehyde, carbon monoxide, and diatomic hydrogen. Set up and perform geometry optimization / frequency calculations at the Hartree-Fock/ 6-31G(d) level (note that this basis set is not quite the same as the one employed in Part A; therefore, you will have to repeat the calculations on H_2 with this basis set). Set the memory to 4 GB and the processors to 8. Retain the calculation information, save a .com file, and submit the calculation using the qg09 command. When the calculations are complete, open the log file using the gedit command, and record the sum of electronic and thermal enthalpies for each molecule (follow the procedure outlined in Part A, step 1 to locate this value for each molecule).

2. Open the checkpoint file for each structure in *GaussView*. Measure and record the equilibrium bond lengths and bond angles for formaldehyde, carbon monoxide, and diatomic hydrogen.

3. The next step is to build an approximate guess for the structure of the transition state. In formaldehyde, the two hydrogens are approximately 1.8 Å apart, while the distance is much closer in H_2. So one possible structure for the transition state might have the hydrogen atoms further from the carbon, but closer to each other. An example initial guess at the transition state is sketched below,
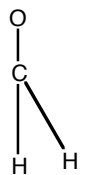
Figure 3. Approximate transition state for decomposition of formaldehyde.

Use *GaussView* to build your own approximate guess for the transition state. Set up a calculation to locate a transition structure at the Hartree-Fock/6-31G(d) level of theory. The Job Type is Opt+Freq. You must also change the first two pull-down menus on the Job Type panel to read: "Optimize to a": TS (Berny); "Calculate Force Constants": Once. Finally, in the space for "Additional Keywords" enter OPT=(Noeigentest). In the Link0 tab, set the memory to 4GB and processors to 8. Save a com file, and submit the job using the qg09 command.

4. Once your transition state calculation is complete, open the checkpoint file with *GaussView*. Verify that you actually have a transition state by checking the vibrational frequencies. You can do this by selecting *Results → Vibrations*. There should be only one imaginary frequency listed, since a system that possesses a single imaginary frequency corresponds to one direction that is concave down (a saddle point) on the potential energy surface. Imaginary frequencies are listed in the vibrations results as negative frequencies. So, if you have one negative frequency in the listing, you have found the transition state. If you do not have a transition state, try redrawing your initial guess for the transition structure and repeating step 3.

Once you have a transition state, view the animation of the vibrational motion corresponding to the imaginary frequency. This is the mode that corresponds to the reaction path.

5. Measure the equilibrium bond lengths and bond angles for the transition state. Make sure that you measure both the C-H and H-H distances.

6. Open the log file for the transition state calculation using the gedit command, and record the sum of electronic and thermal enthalpies for the transition state (open the log file and find this value as per Part A, step 1).

Results and Discussion – Part C

1. Report the equilibrium bond lengths and angles of formaldehyde, diatomic hydrogen, and carbon monoxide and compare to literature values. Discuss the agreement.

2. Include a table listing $E_e + H_{corr}$ for each molecule. Also list the $\Delta(PV)$ term. Compute the enthalpy of reaction using the formula given in Equation (3), and compare to literature values. You should use the CRC or the NIST Webbook to obtain an experimental literature value. In addition, you should compare with the computational results at the CCSD(T) level found Li, Millam, and Schlegel [*J. Chem. Phys.* **113,** 10062 (2000)]. Discuss your agreement.

3. Report the equilibrium bond lengths and angles of the transition state. Discuss whether or not the transition state structure is what you expected.

4. Describe in words or with a sketch what is happening along the reaction path in this reaction based on your viewing of the motion in step 4 of the procedure.

5. Provide a listing of $E_e + H_{corr}$ for the transition state. Use this along with the value of $E_e + H_{corr}$ for the reactants and products to calculate the enthalpy of activation for both the forward and reverse reactions. Compare your result to literature values from Li, Millam, and Schlegel [*J. Chem. Phys.* **113,** 10062 (2000)]. You should compare to both the computational CCSD(T) results and to experiment. Discuss your agreement.

PART D (15 points) – A Gas Phase S$_N$2 Reaction Path

The *S$_N$2* reaction involves the attack of a nucleophile, X^-, on a tetrahedral carbon opposite a leaving group, Y^-,
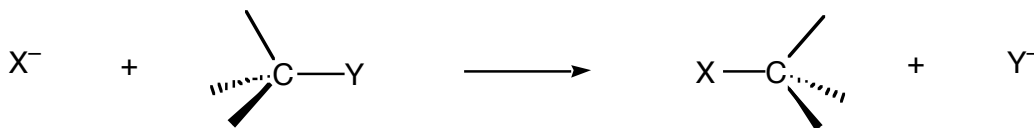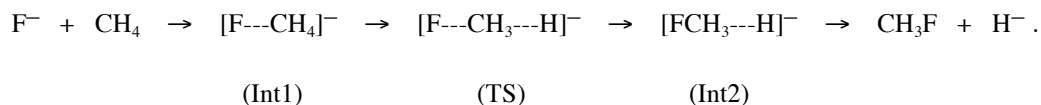

Figure 4. An example of an *S$_N$2* reaction.

In this section, you will examine the reaction

$$F^- \;+\; CH_4 \;\rightarrow\; CH_3F \;+\; H^-.$$

From ab initio calculations, you will obtain the energy difference between reactants and products, along with the geometries of reaction intermediates and the transition state. In general, to determine the lowest energy reaction path, many different approaches of the F^- anion toward the methane molecule should be considered. For this project, we will consider a constrained approach in which the F^- anion attacks along a path collinear with the leaving group.

In this reaction, there are two intermediates in addition to a transition state in the reaction path,

$$F^- \;+\; CH_4 \;\rightarrow\; [F\text{---}CH_4]^- \;\rightarrow\; [F\text{---}CH_3\text{---}H]^- \;\rightarrow\; [FCH_3\text{---}H]^- \;\rightarrow\; CH_3F \;+\; H^-.$$

$$\text{(Int1)} \qquad\qquad \text{(TS)} \qquad\qquad \text{(Int2)}$$

In the reaction shown above, the structures $[F\text{---}CH_4]^-$ and $[FCH_3\text{---}H]^-$ represent intermediates, denoted Int1 and Int2, respectively. These intermediates correspond to local minima on the potential energy surface that describes the reaction. The structure $[F\text{---}CH_3\text{---}H]^-$ corresponds to a transition state.

Procedure – Part D
1. First, obtain optimized geometries (frequency calculations are not necessary) for CH_4 and CH_3F using the *GaussView/Gaussian* software packages. Use the Hartree-Fock method with a 6-31+G(d) basis set, along with 4 GB and 8 processors for all the calculations in this part. Once the calculations are complete, open the checkpoint files in *GaussView*, and measure the equilibrium bond lengths, along with the H-C-H angle for methane and the H-C-F angle for fluoromethane. You should also report the electronic energy in hartrees (atomic units) for each species; to get this, select *Results* → *Summary* from the *GaussView* menu once you have loaded the checkpoint file.

    Next, perform *single point energy* calculations (Job Type: Energy) for H^- and F^-. Use a 6-31+G(d) basis set along with the Hartree-Fock method and record the electronic energies of the two ions. Don't forget to set the total charge to –1 when you set up each calculation.

2. The next step is to carry out calculations to determine the structures of the two reaction intermediates, $[F\text{---}CH_4]^-$ (Int1) and $[FCH_3\text{---}H]^-$ (Int2). To build these structures, start from methane and use the "Add Valence" button in the *GaussView* builder. Make sure that the F^- or H^- is arranged in a collinear fashion with respect to the carbon and the leaving group (as shown in Figure 5). Also make sure that the ion is between 2.0 and 2.5 Å from the carbon. Remember to set the total charge to –1. Perform Hartree-Fock/6-31+G(d) geometry optimizations for both intermediates.

The [F---CH$_4$]$^-$ intermediate is sometimes difficult to obtain. If the geometry at the end of your calculation shows the F$^-$ interacting directly with one of the H atoms, try again. You want a structure in which the F$^-$ is attacking the C atom. It may take a couple of tries to get the intermediate geometry to converge. The structure should look something like that shown in Figure 5.
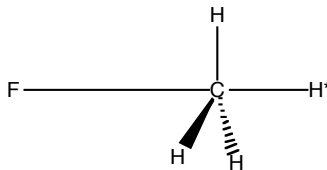
Figure 5. Approximate starting structure of the [F---CH$_4$]$^-$ intermediate.

In the builder, try setting the F-C distance to 3 Å and the C-H distance for the opposite H to about 1.3 Å. Set up and submit the geometry optimization.

When your calculations of the intermediates are complete, record the electronic energy in hartrees, the F-C distance, and the C-H distance for the opposite hydrogen. Also, measure the H*-C-H angles (where H* corresponds to the hydrogen that is opposite the fluorine atom) and the H-C-F angles.

3.   The final step in the calculation is to determine the geometry of the transition state. You can build a starting structure for the transition state again by using *GaussView*. Start from an approximately trigonal bypyramidal geometry with carbon at the center and F and H at either end, as is shown in Figure 5 above. You can get this using "Add Valence" to the central carbon.

Set the C-F and C-H* distances to around 2 Å (here, H* is the hydrogen that is opposite the fluorine atom). To perform the transition state calculation, select "Opt+Freq" as the Job Type. You must also change the first two pull-down menus on the Job Type panel to read: "Optimize to a": TS (Berny); "Calculate Force Constants": Once. Finally, in the space for "Additional Keywords" enter OPT=(Noeigentest). Again, use the Hartree-Fock/6-31+G(d) level, and set the charge to –1.

When the calculation is complete, record the electronic energy in hartrees, the F-C distance, the C-H* distance for the opposite hydrogen (H*), and the H-C-H* and H-C-F angles.

Results and Discussion – Part D
1.   Report the electronic energies and geometries of the reactants and products. Compare the total energy of the reactants. F$^-$ and CH$_4$, to the total energy of the products, H$^-$ and CH$_3$F. Compute the energy difference ΔE in kcal/mol as the total energy of the products minus the total energy of the reactants. Does the reaction release energy or does it require energy to be input? Is this result in agreement with what you would expect from the electronegativities of the species involved in the reaction? Explain.

2.   Provide a table of geometries of the two intermediates, Int1 and Int2. Discuss what happens to the C-F and C-H* bond lengths and also what happens to the bond angles (which way does the central CH$_3$ "umbrella" point?) as the reaction progresses.

3.   Make a sketch of the transition state structure. Provide a listing of the geometrical parameters. Is the central carbon planar at the transition state? If not, is it closer to planar or closer to tetrahedral?

4. Determine and report the activation energy of the forward reaction of F^- and CH_4 in kcal/mol. This is obtained by taking the energy of the transition state minus the energy of the $[F\text{---}CH_4]^-$ intermediate (Int1).

5. Also, determine and report the energy of activation of the reverse reaction of H^- and CH_3F in kcal/mol. This is obtained by taking the energy of the transition state minus the energy of the $[FCH_3\text{---}H]^-$ intermediate (Int2).

6. Compare your energies and geometries of the various species to the computational results found in Z. Shi and R. J. Boyd, *J. Am. Chem. Soc.* **1989,** *111,* 1575. Be quantitative in your comparisons whenever possible.

7. Sketch an energy level diagram, including the energies of the reactants, products, intermediates, and transition state for the reaction. Use the F-C distance as an approximate reaction coordinate. Discuss the mechanism and energetics of the reaction.