

**Computational Chemistry  
Problem Set 5**

**Due Monday, March 9, 2009**

(note change from syllabus—you have two weeks to work on this assignment)

Total Possible Points = 113

Basic Technical Notes: (1) For security reasons, you are allowed to log into the Hope College computers only from a computer connected to the Macalester network. (2) On Macintosh computers, the WebMO software works with the Safari browser, but not with the (Macalester-endorsed!) Mozilla Firefox browser. On Windows computers, both Firefox and Internet Explorer should work.

**Material We Will Work on Together in Class**

Getting started:

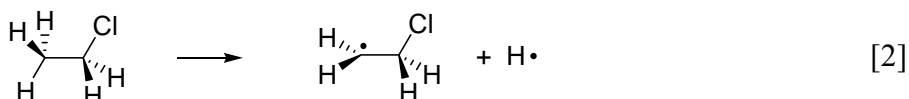
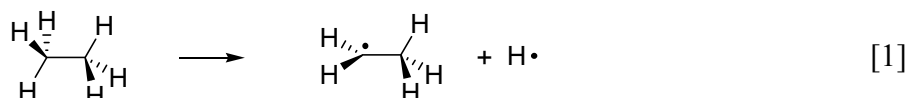
- Open the Safari web browser
- Go to [mu3c.chem.hope.edu/~kuwata/cgi-bin/webmo/login.cgi](http://mu3c.chem.hope.edu/~kuwata/cgi-bin/webmo/login.cgi)
- Login—Do you remember your Username and Password?

Using Vibrational Frequency Data in Spectroscopy and Thermochemistry

Do Optimize + Vib Freq B3LYP 6-31G(d) calculations on chloromethane, ethane, chloroethane, ethyl radical, and 2-chloroethyl radical. Also do a Vibrational Frequencies B3LYP 6-31G(d) calculation on H atom. (Even though an isolated atom obviously can't have any vibrations, this is the way we get Gaussian 03 to calculate the atom's enthalpy at 298 K.) Note that the radicals and H atom, all of which have one unpaired electron, have a Doublet Multiplicity.

We'll first examine together the effects of hyperconjugation on the C-Cl stretching frequency in the three chlorinated molecules, and the accuracy of the scaling factor of 0.9614 for B3LYP/6-31G(d) C-H stretching frequencies.

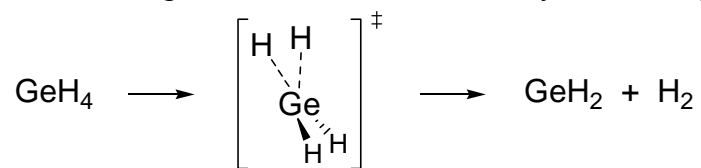
We will then compute the energy changes for the reactions



in three ways: (i) by differences in electronic energies, (ii) by differences in zero-point corrected electronic energies, (iii) by differences in enthalpies.



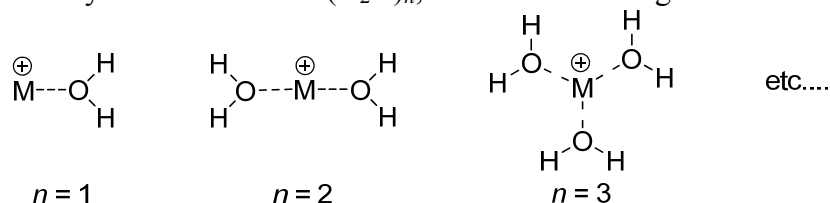
3. (20 points total) Consider the germane reaction that Jim Doyle and I may study in the future:



Using B3LYP Theory and the 6-31G(d) Basis Set, locate all the minima and the transition structure for the reaction. Use any method for locating the transition structure that you think will work. Confirm that you have located the desired transition structure by performing IRC (Forward) and IRC (Reverse) calculations. For the IRC calculations, remember to set a large number for `maxpoints` and use the `nosym` keyword.

- (2 points) Briefly describe the method(s) you used to locate the transition structure.
  - (2 points) Write down the imaginary (negative) frequency (in  $\text{cm}^{-1}$ ) of the transition structure, and briefly describe the motion associated with this vibrational frequency.
  - (6 points) Justify that you have located the correct transition structure by comparing the final geometries from your IRC calculations with the geometries of the reactants and products. Discuss both bond lengths and bond angles.
  - (3 points) Calculate the activation energy (in kcal/mol to two decimal places) for the reaction as (i) a difference of electronic energies, (ii) a difference of zero-point corrected electronic energies, and (iii) a differences of enthalpies at 298 K.
  - (4 points) Assume that the most accurate activation energy for the reaction is given by the differences of enthalpies at 298 K. By what factor would the predicted reaction rate differ if one calculated the activation energy as (i) a difference of electronic energies or (ii) a difference of zero-point corrected electronic energies?
  - (3 points) Go back to Problem Set 3 #4. Do you predict the dehydrogenation of silane or germane to be more favored kinetically? Briefly explain.
4. (63 points total) Note: One point of this problem is to help prepare you mentally and logistically for the kinds of calculations you will be performing for your final project. Some of the calculations for this problem could take **several hours!** **Do not wait until the day before the due date to tackle these non-trivial geometry optimizations!**

As discussed in Question 2 above,  $\text{H}_2\text{O}$  forms hydrogen bonds to anions. In contrast,  $\text{H}_2\text{O}$  forms ion-dipole complexes with cations. (You were introduced to ion-dipole complexes with the  $\text{S}_{\text{N}}2$  question in Problem Set 4.) We might guess that singly charged cationic clusters, generically referred to as  $\text{M}^+(\text{H}_2\text{O})_n$ , have the following structures:



In this simple model, the partially negative charged O's in the  $\text{H}_2\text{O}$ 's point directly at the cation, and the waters arrange themselves symmetrically about the cation, giving rise to  $\text{O} \cdots \text{M}^+ \cdots \text{O}$  bond angles consistent with VSEPR theory.

The data shown to the right are successive enthalpies of hydration (with the sign changed) for a series of Group I cations. (The data are taken from R. G. Keesee and A. W. Castleman, Jr., *Journal of Physical and Chemical Reference Data* **1986**, *15*, 1011-1071.)

Ion	$-\Delta H_{n-1,n}^{\circ}$ (kcal/mol)				
	1	2	3	4	5
<b>Li<sup>+</sup></b>	<b>(34)</b>	<b>25.8</b>	<b>20.7</b>	<b>16.4</b>	<b>13.9</b>
<b>Na<sup>+</sup></b>	<b>24.0</b>	<b>19.8</b>	<b>15.8</b>	<b>13.8</b>	<b>12.3</b>
	---	---	<b>14.9</b>	<b>12.6</b>	<b>10.6</b>
	---	---	---	<b>13.6</b>	<b>11.6</b>
	---	---	---	<b>12.6</b>	
	<b>26.5</b>				
<b>K<sup>+</sup></b>	<b>17.9</b>	<b>16.1</b>	<b>13.2</b>	<b>11.8</b>	<b>10.7</b>
	<b>16.9</b>				

Here's how you read the above table: For example, for the reaction  $\text{Na}^+ + \text{H}_2\text{O} \rightarrow \text{Na}(\text{H}_2\text{O})^+$ ,  $\Delta_{\text{rxn}}H^{\circ} = -24.0$  kcal/mol. For the reaction  $\text{Na}^+(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightarrow \text{Na}^+(\text{H}_2\text{O})_2$ ,  $\Delta_{\text{rxn}}H^{\circ} = -19.8$  kcal/mol. And so forth. Also note that when an ion has more than one row of numbers, use the top row—it contains the most reliable set of experimental measurements.

Your task is to calculate successive hydration enthalpies (at 298 K) for **two** series of ion-dipole clusters. Choose two different alkali metal cations, and vary the number of waters,  $n$ , from 1 to 5. Here are some more computational parameters:

- Use B3LYP theory and the 6-31+G(d,p) basis set for all calculations.
- Always check the vibrational frequencies to make sure you have located a minimum. If you have one (or more) imaginary frequencies, tweak the geometry manually or perform an IRC calculation to help Gaussian 03 find the minimum geometry.
- If you are having trouble getting a geometry to converge, consider replacing the keywords `opt freq` with `opt=calcall`

This will increase the time required for each geometry optimization step, but it will also increase the probability that the optimization will succeed in a reasonable number of steps.

- (23 points) Tabulate the successive hydration enthalpies you have calculated (in kcal/mol to two decimal places), the experimental successive hydration enthalpies, the absolute errors in the computed values (in kcal/mol), and the relative errors in the computed values (in %). Report errors to a reasonable number of significant figures.
- (8 points) Note and rationalize the trends in your computed hydration enthalpies. Consider both the effect of increasing the number of waters and the effect of increasing the size of the alkali metal cation.
- (20 points) Report the O---M<sup>+</sup>---O bond angles (in degrees, to one decimal place) in the optimized geometries for  $n = 2$  to 5, clearly labeling the angles in a drawing, ChemDraw, or printout of the geometry.) Rationalize any deviations greater than 5° in magnitude from the ideal VSEPR bond angles. (For  $n = 5$ , report and discuss only the angles whose nominal values are less than 180°.)
- (11 points) For the  $n = 2$  clusters you optimized, write down the charges (to three decimal places) on the alkali metal cations. Do the same for one series ( $n = 1$  to 5) of clusters. Rationalize the trends in these charges.