CHM5250 – Kinetics and Reaction Dynamics Fall 2007
Graded Homework #3 **Due Wednesday, 10/17/07, 5pm**

Please write solutions neatly on a separate sheet of paper and include appropriate computer printouts. Label any spreadsheets and/or graphs clearly. Show all of your work and report answers with the correct significant figures and units.

1. Steinfeld Problem 7.14 – instead of a contour diagram, use Excel to make a 3D plot (similar to Fig. 7-11) in which the two variables are $R_{F\text{-}H1}$ and $R_{H1\text{-}H2}$. Assume that the system is linear (so $R_{F\text{-}H2} = R_{F\text{-}H1} + R_{H1\text{-}H2}$). You will obtain a function V of both distances. It will be easiest to use Excel to calculate V for a range of values of $R_{F\text{-}H1}$ and $R_{H1\text{-}H2}$ and then use the 3D surface plot function (in the Chart Wizard) to make the graph. We will talk about how to do this in class, and there are also directions at: http://office.microsoft.com/en-us/excel/HA011179391033.aspx?pid=CL100570551033.

2. Download the following paper from the Journal of Physical Chemistry (available online from on-campus computers): "Complete Multidimensional Analytic Potential Energy Surface for Cl^- + CH_3Cl S_N2 Nucleophilic Substitution", *J. Phys. Chem.* **1990**, *94*, 2778-2788. Read the paper ***carefully*** and answer the following questions. There are several topics discussed in the paper that we have not yet gotten to in class. You are not expected to understand everything in the paper, but you should be able to figure out the answers to the questions below.

a. Make a sketch of the Cl^- + CH_3Cl system that shows the definitions of the internal coordinates listed in Table I.
b. What is the significance of the two coordinates g_a and g_b? Why are they useful?
c. What is the minimum number of internal coordinates that would be needed to fully describe this system? Do the researchers in the paper include any redundant coordinates? **Show/explain your reasoning.**
c. In the potential energy function given in equation (2), which terms are short range interaction terms?
d. In the potential energy function given in equation (2), which terms are long range interaction terms?
e. (The answer to this question is not necessarily in the paper!) The researchers used Hartree-Fock (i.e. Self Consistent Field or SCF) type ab initio calculations as a second way to probe the PES for the S_N2 reaction. It is known that SCF level calculations do not work well in cases where a covalent bond is broken or formed, such as the reaction $H_2 \rightarrow 2\ H^{\bullet}$. In this paper the SCF method was used without concern. What is different about the mechanism of the S_N2 reaction that allows it to be studied more reliably with this method?
f. Based on the contour diagram in Figure 7, what is the structure of the transition state? Give approximate values of the C-Cl distances.

3. We will discuss the paper in question #2 in class on Wednesday, 10/17. A list of points for you to consider as you prepare for the in-class discussion will be posted in the Handouts section of the course web page.