10.675 Assignment #3

due 10/14/04

(1) *Pose a simple problem to address using G03, and solve it.*

Solution:
Since this is any case chosen by yourself, there will be no solution for this one.

(2) *Using the same methods that you used in Assignment 2, for the isomerization reaction below, use transition-state theory in G03 to compute the barrier height for reaction. Confirm that you have only one complex mode (negative frequency) and visualize it to get the pathway for isomerization.*

cis-CHD=CHD → *trans-CHD=CHD*

Solution:
This problem looks easy, but it is actually pretty complicated. The reason is that the transition state for this isomerization reaction is a singlet diradical. You have to treat it specially, otherwise, you will not be able to get the right transition state. Please refer to the following procedures about how to get the correct transition state (The input files will also be posted on website).

Step 1: Treat the system as a normal one, obtain its wavefunction
 # b3lyp/6-31g scf

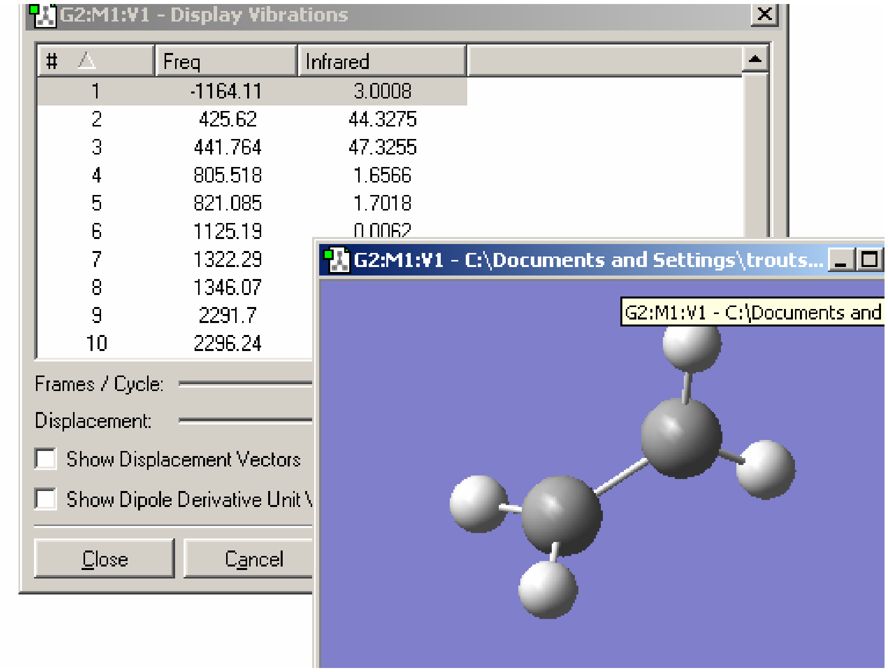
Step2: Alter one virtual and one occupied orbital to get the correct wavefunction for the singlet diradical (see more details from Gaussian menu)
 # ub3lyp/6-31g scf geom=Allcheck guess(Tcheck, Alter)

Step 3: Use the correct wavefunction to do geometry optimization and frequency calculations
 # opt=(calcall, ts, noeigentest) freq=readiso ub3lyp/6-31g scf=qc geom=Allcheck guess=(Tcheck, nosymm)

Another two alternative ways are: a). Iop(4/15=3) Alter; or, b). Guess=Mix

From the above procedures, we can obtain the transition state as below (The Hs rotate around the c-c axis).
The free energy barrier can be calculated from the difference between free energy of transition state and that of reactant:

$$Barrier = \Delta G = G(TS) - G(cys) = -78.455558 - (-78.549272) = 0.093714 a.u. = 58.8 kcal/mol$$



#	Freq	Infrared
1	-1164.11	3.0008
2	425.62	44.3275
3	441.764	47.3255
4	805.518	1.6566
5	821.085	1.7018
6	1125.19	0.0062
7	1322.29	
8	1346.07	
9	2291.7	
10	2296.24	

(Courtesy of Gaussian, Inc.. Used with permission.)

*(3) Compare the results from (2) to the experimental data (at 770 K), log A = 13 s^{-1}, and E = 65 kcal/mol (JCP, **23**, 315 (1955)).*

Solution:

Now we can calculate prefactor A as below:

$$A = \frac{kT}{h} e^{-\frac{\Delta S}{R}}$$

$$= \frac{1.38\times10^{-23}(J/K)\cdot770(K)}{6.63\times10^{-34}(J\cdot S)} \times \exp(-\frac{(57.958-56.391)(cal/mol\cdot K)}{1.99(cal/mol\cdot K)})$$

$$= 7.29\times10^{12}$$

Therefore, $\log A \approx 12.9$ (Exp. logA=13)

The calculated energy barrier is about 60 kcal/mol, while the experimental energy barrier is about 65 kcal/mol. The difference between calculated result and experimental results could be caused by the following reasons:

a. finite basis set
b. approximate method
c. finite temperate and pressure effects
d. experimental uncertainty