

CHEM3023 “Spins, Atoms and Molecules”

Computational quantum chemistry practical

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1 Introduction

Chemical reactions involve the making or breaking of chemical bonds between atoms. Only quantum theory is able to describe such processes as the electrons and nuclei are microscopic particles and do not obey the laws of classical mechanics. In quantum mechanics observable properties of molecules can be obtained from the wavefunctions, which are the solutions of Schrödinger's equation. Schrödinger's equation can be solved exactly, on paper, only for simple problems such as the particle in a box, the harmonic oscillator and the hydrogen atom. To study problems in Chemistry computational approaches are necessary.

Most approaches begin with the separation of electronic from nuclear motion via the Born-Oppenheimer approximation. A variety of *ab initio* (meaning "from the beginning" in Latin, to emphasise that no experimental input is required) methods are available for solving the electronic problem. The Hartree-Fock theory, which we have covered in the lectures, is an *ab initio* method. The solution of the electronic problem yields various electronic experimental observable properties and the Potential Energy Surface (PES). The PES is the potential energy operator in the nuclear Schrödinger equation. In what follows we will perform Hartree-Fock calculations and use the PESs obtained to study molecular structure, molecular vibrations (IR spectra) and simple chemical reactions.

The following constants and conversion factors will be useful:

$$1 \text{ Hartree} = 27.2116529 \text{ eV}$$

$$1 \text{ Hartree} = 2625.516 \text{ kJ/mol}$$

$$R = 8.31447 \text{ J K}^{-1}\text{mol}^{-1}$$

$$h = 6.62608 \cdot 10^{-34} \text{ J s}$$

$$c = 2.9979 \cdot 10^8 \text{ m/s}$$

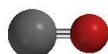
2 The Potential Energy Surface of CO

Let's start by performing Hartree-Fock calculations to generate "by hand" the Potential Energy Surface of a CO molecule as a function of bond length.

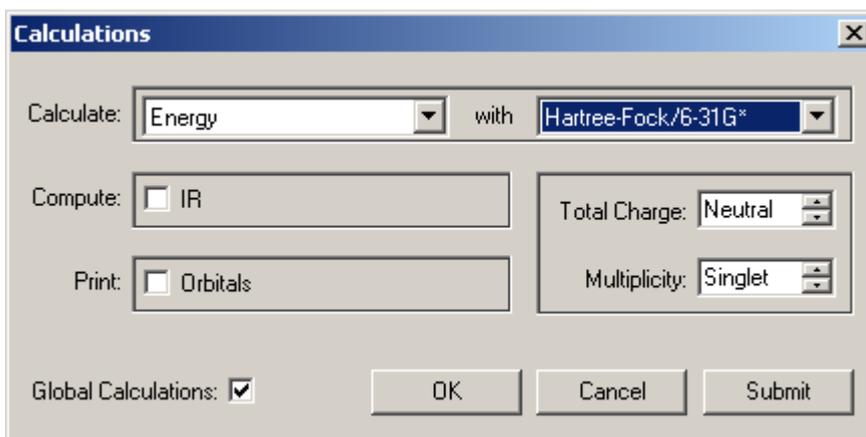
- Generation of PES and determination of equilibrium geometry
 1. Run Spartan (Log in with your account on the PC and select: Start->All Programs->Your School Software->Chemistry->Spartan->PC Spartan)
 2. Click File->New
 3. Select the "Inorganic" molecule builder tab on the left, then from the "Ligands" drop-down box under the periodic table select  and then click in the middle of the screen to draw a carbon monoxide molecule:



4. Use the delete function  to remove the "spoke" that appears attached to the carbon atom:



- Use the distance tool  to click on the C-O bond and display its length on the bottom right hand side of the screen. Click in this window and type "0.5" to set the bond length to 0.5 Å. **Length(Bond1) = 0.500 Å**.
- Go to Setup->Calculations and select to perform a single-point energy Hartree-Fock calculation with the 6-31G* basis set :



Press "Submit" and save the "Spartan.spartan" file on the Desktop. The calculation should complete in a few seconds.

- Open the output file ("Display -> Output") and note the energy of the molecule reported as "SCF total energy" in atomic units. Note that this is actually the PES energy as the program reports the sum of the electronic and nuclear-nuclear repulsion energy.
 - Open a Microsoft Excel sheet and fill in the bond length in one column and the PES energy in a second column.
 - Repeat the calculation with a bond length of 1 Å (by re-setting the bond length as in step 5 and following the next steps). **Make sure that you perform the calculation on the same molecule and do not open a new file.**
 - Continue steps 5-8 incrementing the bond length by 0.5 Å each time until you reach a bond length of 3.5 Å. **Perform the calculations on the same molecule, one at a time, and do not open a new file.**
 - Make a plot of the PES (energy on the y-axis and bond length on the x-axis) in your Excell spreadsheet.
 - Perform more calculations, using the "bisection method", to approximate the point of minimum energy on the PES and hence the equilibrium bond length R_e of CO. Each step of the bisection method involves performing a calculation at a bond length which is the average of your two current bond lengths of lowest energy. Iterate for 2 or 3 bisection steps.
 - Note that searching for the minimum of the PES is not related to the variational principle: the electronic Hamiltonian changes with the C-O distance (due to the nuclear attraction operator), while the variational principle involves varying a wavefunction until it minimises the energy of a **fixed** Hamiltonian. You do however apply the variational principle in each of your "single-point" Hartree-Fock calculations where you use the SCF procedure to minimise the electronic energy and obtain the best Slater determinant electronic wavefunction **for each C-O distance** (i.e. a single point on the PES).
- Calculation of IR vibrational frequency

Calculate the second derivative of the PES with respect to bond length by “finite differences” about R_e as follows:

1. Compute the first derivative from the left and from the right of R_e as

$$\left. \frac{dE_{PES}}{dR} \right|_{left} \simeq \frac{E_{PES}(R_e) - E_{PES}(R_e - l)}{l} \quad \text{and} \quad \left. \frac{dE_{PES}}{dR} \right|_{right} \simeq \frac{E_{PES}(R_e + l) - E_{PES}(R_e)}{l}$$

where l is a small distance (say 0.05 Å) to the left or right of the R_e you have determined. Now compute the second derivative, as the derivative of the first derivatives:

$$\frac{d^2 E_{PES}}{dR^2} \simeq \frac{\left. \frac{dE_{PES}}{dR} \right|_{right} - \left. \frac{dE_{PES}}{dR} \right|_{left}}{l} = \frac{-2E_{PES}(R_e) + E_{PES}(R_e + l) + E_{PES}(R_e - l)}{l^2}$$

2. The value you obtain for the second derivative of the PES at R_e can be used to solve the nuclear Schrödinger equation for the diatomic

$$\left[-\frac{1}{2\mu} \frac{d^2}{dR^2} + E_{PES}(R) \right] \Psi_{nuc}(R) = E' \Psi_{nuc}(R)$$

which after the harmonic approximation (see lecture notes) turns into the equation for a harmonic oscillator (spring) of force constant k

$$\left[-\frac{1}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2} k (R - R_e)^2 \right] \Psi_{nuc}(R) = E \Psi_{nuc}(R)$$

where k is the value of the second derivative of the PES at R_e that you have calculated.

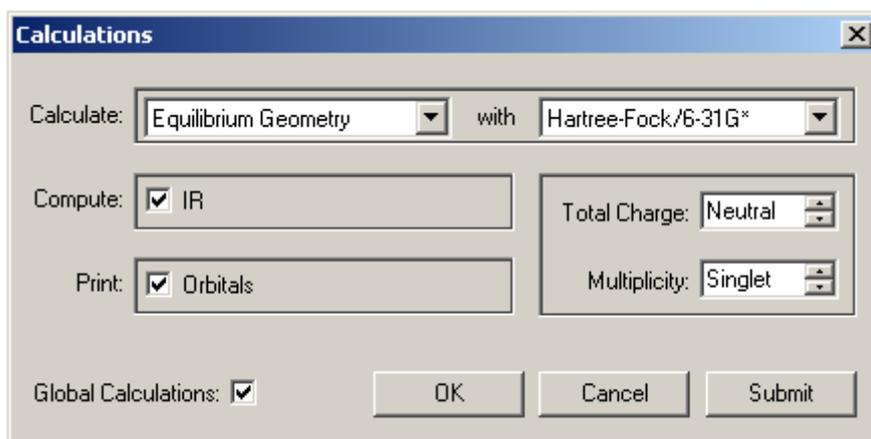
3. You can now compute the vibrational frequency of the CO molecule using the harmonic oscillator formula:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{and} \quad \mu = \frac{M_C M_O}{M_C + M_O}$$

where M_C is the mass of the carbon nucleus and M_O the mass of the oxygen nucleus.

4. Convert the frequency you computed to cm^{-1} and compare with the experimentally determined IR vibrational frequency of CO which is 2169.8 cm^{-1} . Also compare your computed equilibrium bond length R_e with the experimental value which is 1.128 Å . Compute the zero-point energy (ZPE) of the molecule from the vibrational frequency you calculated.

5. It would be extremely difficult to attempt to generate a PES in more than one dimension. Quantum Chemistry programs are able to explore rather complicated multi-dimensional PESs by employing efficient function optimisation techniques. Use the techniques available in the Spartan program to perform a geometry optimisation and vibrational frequency calculation as follows:

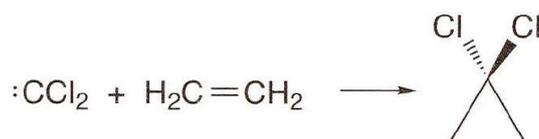


Press "Submit".

6. Examine the vibrational frequency you obtain from this calculation by selecting the menu "Display->Spectra". The vibrational frequency and the optimised bond length that you will obtain from this calculation should be close to the values that you obtained from your "manual" scanning of the PES.
7. Notice that the computed frequency is an overestimate of the experimental value (why?). In practice the computed Hartree-Fock frequencies are scaled by a factor of 0.9 to obtain better agreement with experiment (try this with the frequency you computed). You can also repeat this calculation with methods such as DFT and MP2 which include electronic correlation and produce better results.

3 Addition of dichlorocarbene to ethylene

Singlet dichlorocarbene adds to ethylene to yield 1,1-dichlorocyclopropane:



We will use Hartree-Fock calculations to study the mechanism of this reaction and examine how it is affected by different functional groups.

3.1 Electrostatic potential of singlet dichlorocarbene

- Build a structure for dichlorocarbene
Select File->New.

Click on the “Organic” molecule builder tab (top of right hand side) and then click on the tetrahedral carbon symbol . Click on the middle of the screen to get

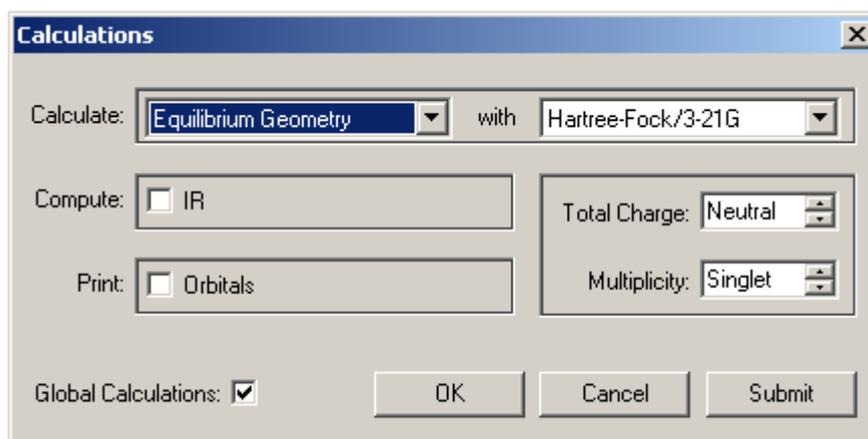


Add chlorine atoms to two of the “spokes” by selecting the  button from the organic model builder on the right and then clicking on a free “spoke” of the carbon. Delete the other two spokes by selecting the delete button  and clicking on them. Your molecule should now look like this:



- Optimise the structure of dichlorocarbene

Use the techniques available in Spartan for exploring the PES to minimise the energy along each coordinate and find an equilibrium geometry for the molecule (a minimum of the PES). For computational speed, we will work with the PES generated by restricted closed-shell Hartree-Fock (RHF) calculations with the 3-21G basis. Select the menu “Setup->Calculations” and set up the following parameters:



Press OK and then “Setup->Submit”.

- Molecular electrostatic potential

We saw in the lectures that the total (electronic & nuclear) electrostatic potential of a molecule is given by the formula:

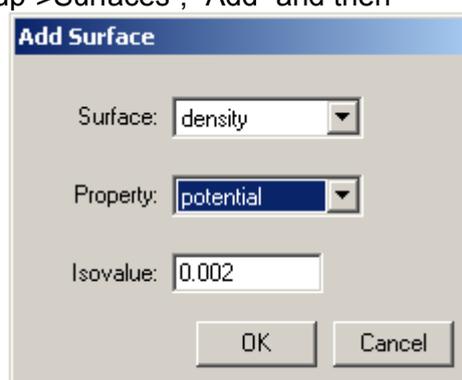
$$V_{ES}(\mathbf{r}) = \sum_{I=1}^{N_{atom}} \frac{Z_I}{|\mathbf{r} - \mathbf{r}_I|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

1. Re-write this formula in terms of

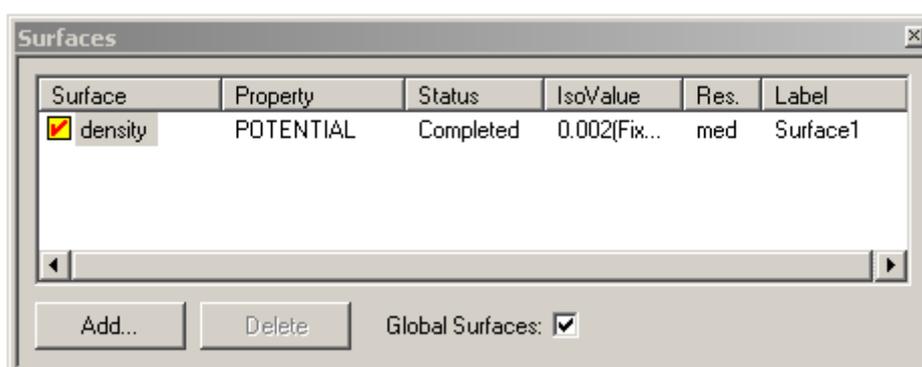
i. Molecular orbitals:

i. Basis functions:

2. Calculate the electrostatic potential as a colour-map on an isosurface of the electronic density by selecting "Setup->Surfaces", "Add" and then



Press "OK" and then "Setup->Submit". After the calculation has finished, display the surface by ticking the "density" box



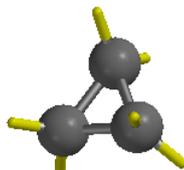
Examine the surface, bearing in mind that red regions correspond to low (more negative) values of the electrostatic potential (therefore less attractive for negative-charged particles like electrons) while blue regions correspond to high values of the electrostatic potential (more attractive for electrons). Where is the "electrophilic site", in the C1C1 plane or out of the plane? How would you expect dichlorocarbene to approach ethylene?

3.2 Transition state for addition reaction

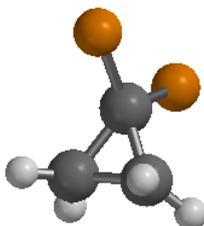
- Build a “guess” for the transition state

1. Select File->New.

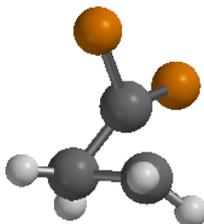
Click on the “Organic” molecule builder tab (top of right hand side) and then click on the “rings” drop-down box and select “Cyclopropane” . Then click in the middle of the screen to create this structure



2. Add 4 H and 2 Cl atoms to build 1,1-dichlorocyclopropane

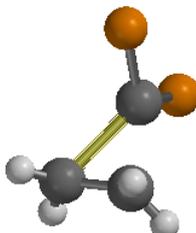


3. Delete one of the $\text{CH}_2\text{-CCl}_2$ bonds with the break bond tool  and remove the empty spokes with the delete tool  to get

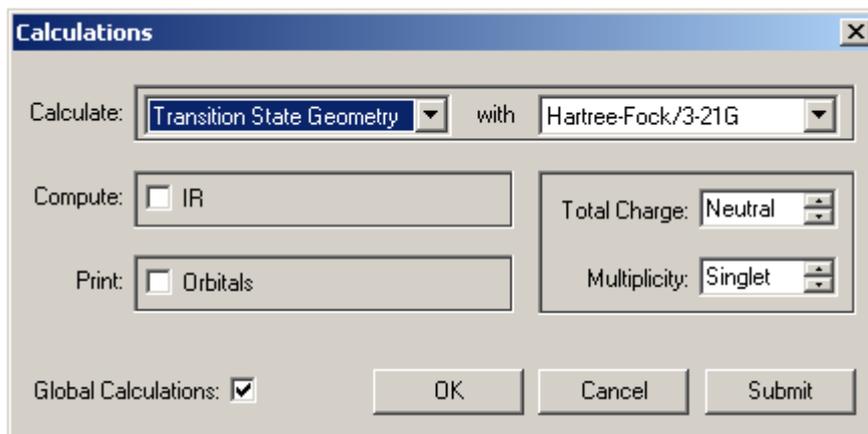


4. Select the $\text{CH}_2\text{-CCl}_2$ bond with the distance tool  and reset the bond length:

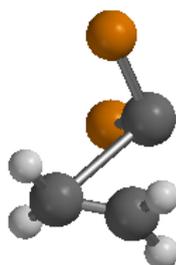
Length(Bond2) = to obtain



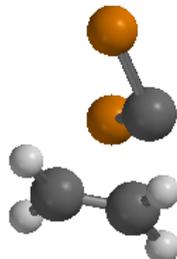
5. Now you have a reasonable initial guess. Search for the transition state with the following settings:



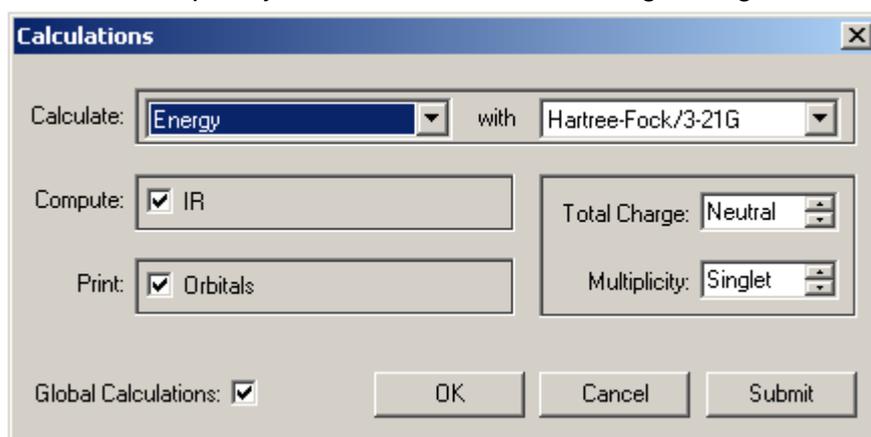
After the calculation has completed, your optimised transition state geometry should look like this



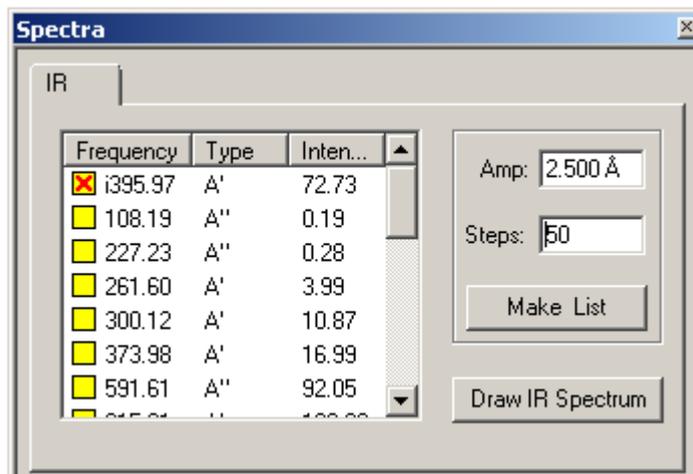
Delete the $\text{CH}_2\text{-CCl}_2$ "bond" to avoid confusion:



- Calculate the normal coordinates and their energies (frequencies)
 1. Perform a vibrational frequency calculation with the following settings:



2. After the calculation has completed examine the normal mode frequencies (Select menu "Display->Spectra") and confirm that this is indeed a transition state structure (one of the frequencies is imaginary). Select the imaginary frequency:

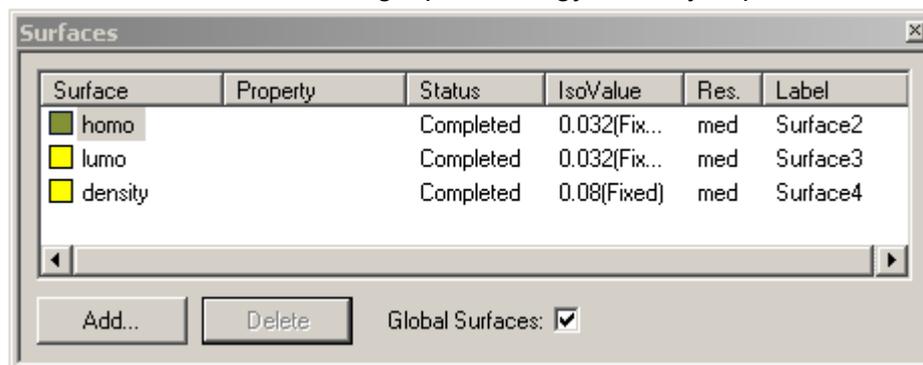


and observe the motion of the atoms along the normal coordinate (it is more clear if you set Amp:2.5Å and Steps:50). Does this look like a motion that would lead from the reactants to the products in the reaction you are studying?

Feel free to also animate and observe other normal modes.

View the output file "Display->Output" from the frequency calculation. **Note down in an Excel spreadsheet the SCF total energy (given in Hartrees) and the zero-point energy (ZPE) (in kJ/mol).**

3. Make plots of the molecular orbitals HOMO, LUMO and of the bonding density (make sure you have set the calculation to single point energy before you press "submit"):

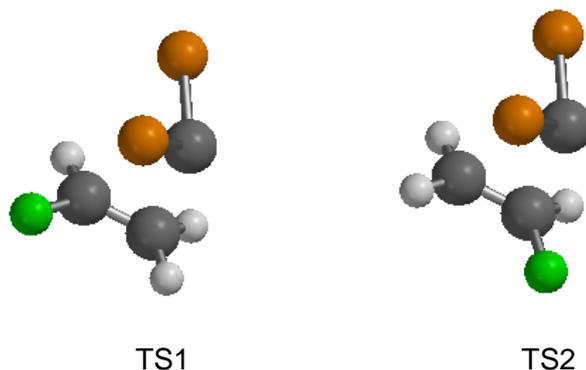


Observe the bonding density and the molecular orbitals. Can you see where/how the bond between ethylene and CCl₂ is forming?

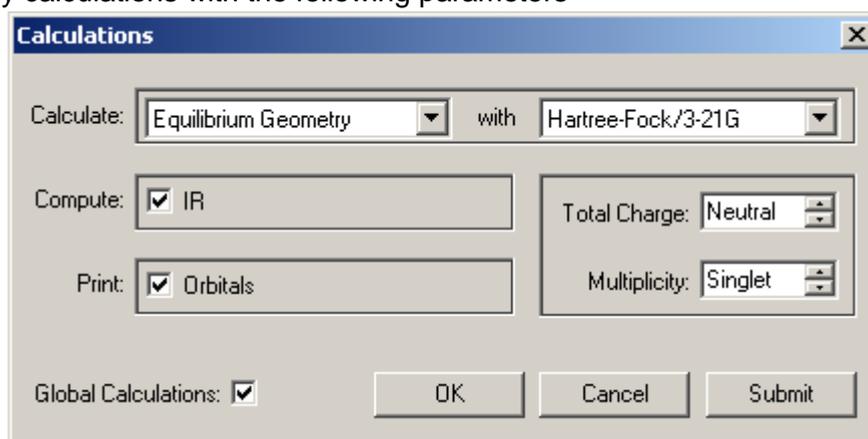
3.3 Relative reaction rates for addition of singlet CCl₂ to ethylene and fluoroethylene

We will also perform calculations for the addition of CCl₂ to fluoroethylene CH₂=CHF and compare the rate of this reaction with the rate of addition to ethylene.

- Use the transition state that you determined in the previous step to prepare an initial "guess" for the two possible transition states for the reaction of CCl₂ with fluoroethylene CH₂=CHF



1. Optimise each of these two transition states, again with HF/3-21G, including calculations of vibrational frequencies.
 2. After each optimisation completes examine if the normal mode with the imaginary frequency corresponds to the addition reaction and note down in your Excel spreadsheet the total energy and ZPE of each transition state.
- Perform also geometry optimisation and frequency calculations for the two reactant alkenes.
 1. Open a new file for each molecule (“File->New”) and perform geometry optimisation and frequency calculations with the following parameters



for (1) $\text{CH}_2=\text{CH}_2$ and for (2) $\text{CH}_2=\text{CHF}$:



2. Note the energies and zero-point (vibrational) energies (ZPE) of each alkene in your spreadsheet.

- The reaction rate constant is given by the Arrhenius equation

$$k = Ae^{-E_a/RT}$$

Where A is the pre-exponential factor and E_a is the activation energy.

- Assuming that A is the same for all reactions, calculate the ratio of the rate constants k at 300K, for the reaction with ethylene



with respect to the two possible reactions of fluoroethylene



- i.e. calculate k/k_1 and k/k_2 . Include zero-point vibrational energy corrections in your activation energies. Observe what “speed-up” ethylene offers in this reaction compared to fluoroethylene.
- Are the relative rates k/k_1 and k/k_2 as you would expect based on your chemical knowledge of electronic effects of F as a functional group and of its possible steric effects between the different transition states?
 - We assumed that the energies of CCl_2 molecules are the same in all reactions and will therefore cancel out from the reactant energies when we compare the relative rates. Examine if this is an approximation and if yes how can you avoid it?
 - Discuss what other parameters you can change to improve the quality of the PES and hence of the relative rate calculations (at the expense of computational speed).

3.4 Optional further work

- Compute IR spectra, ionisation energies (via Koopmans’ theorem), electron affinities and optimised molecular structures for some of the above molecules and compare with experimental measurements which you can find at <http://webbook.nist.gov/chemistry/>
- Use Hartree-Fock calculations to study the mechanism of some chemical reaction of your choice.

4 Finishing the tutorial

Exit Spartan, (File->Exit, you do not need to save your changes), delete all the .spartan files from your Desktop and logout from your PC. Click the “Log off” icon on the Desktop.

The time allocated for this tutorial is 2 hours; If you don’t finish it in this time you are welcome to complete it in your own time in the Physical Chemistry computer room.