

# Exercises

## Building Molecules

Practice building molecules first using pencil and paper followed by building them as a Z-matrix or graphical molecular editor. The information in the following tables will be helpful.

**Table 1:** Point Groups of Several Molecules

Molecule	Symmetry
CH <sub>4</sub>	T <sub>d</sub>
C <sub>2</sub> H <sub>6</sub>	C <sub>3v</sub>
C <sub>2</sub> H <sub>4</sub>	D <sub>2h</sub>
C <sub>2</sub> H <sub>2</sub>	D <sub>∞h</sub>
H <sub>3</sub> COH	C <sub>s</sub>
H <sub>2</sub> CO	C <sub>2v</sub>
HCOOH	C <sub>s</sub>
CO <sub>2</sub>	D <sub>∞h</sub>
CO	C <sub>∞v</sub>
LiH	C <sub>∞v</sub>
LiF	C <sub>∞v</sub>
NH <sub>3</sub>	C <sub>3v</sub>
H <sub>2</sub> O	C <sub>2v</sub>
HF	C <sub>∞v</sub>
H <sub>2</sub> NCOOH	C <sub>1</sub>

**Table 2:** Standard Bond Distances

Bond	Distance (Å)
C–C	1.54
C=C	1.34
C≡C	1.22
C–O	1.40
C=O	1.20
C≡O	1.13
C–H	1.10
N–H	1.05
O–H	1.00
Li–F	1.57
Li–H	1.62

## Dipole Moments, Partial Charges, Population Analysis, and Koopman's Theorem

Using the molecules that were constructed in the previous exercise, perform an RHF calculation with the SVP basis set.

1. Obtain the results of the population analyses and create a table of partial charges of the carbon atoms in a series of molecules. How do the numbers compare with your intuition?
2. View the frontier orbitals of the molecules using a visualization program, and classify the MOs as  $\pi$ ,  $\pi^*$ ,  $\sigma$ ,  $\sigma^*$ , or lone pair.
3. Construct a quantitative MO diagram for one of the molecules studied.

This should consist of the occupied and the first three unoccupied MOs. Find the irreducible representations of all MOs, and label them. Are degenerate MOs unique?

4. Determine the ionization potentials predicted by Koopman's theorem and the dipole moments.

Compare the results of these calculations with the experimental data collected in Table 3.

5. Perform a regression analysis of the computed data. Determine the average absolute error, the largest absolute error, the average deviation from experiment and the standard deviation. These quantities are indicative of the reliability of the calculations and the tendency to over- or underestimate a given quantity.

Molecule	Dipole Moment Debye	Ionization Potential (eV)
CH <sub>4</sub>	0.000	12.61±0.01
C <sub>2</sub> H <sub>6</sub>	0.000	11.56±0.02
C <sub>2</sub> H <sub>4</sub>	0.000	10.51±0.015
C <sub>2</sub> H <sub>2</sub>	0.000	11.41±0.01
H <sub>3</sub> COH	1.700	10.84±0.07
H <sub>2</sub> CO	2.330	10.86
HCOOH	1.410	11.31
CO <sub>2</sub>	0.000	13.778±0.002
CO	0.112	14.0142±0.0003
LiH	5.880	7.9±0.3
LiF	6.330	11.3
NH <sub>3</sub>	1.470	10.07±0.01
H <sub>2</sub> O	1.850	12.6188±0.0009
HF	1.820	16.06
Glycine	1.095	8.9

**Table 3:** Experimental Dipole Moments and Ionization Potentials of the Small Molecules. The direction of dipole moments is such that the arrow points from negative charge to the positive charge. The Experimental data is taken from <http://srdata.nist.gov/cccbdb/> and <http://webbook.nist.gov/chemistry/>

## Walsh Diagrams

1. Perform calculations on the following molecules using the Hartree-Fock method and SVP basis set, and examine the variation of the total energy as a function of H-A-H angle by performing a rigid scan, and plot the results.

- $\text{LiH}_2^+$  (Li-H = 1.7 Å)
- $\text{BeH}_2$  (Be-H = 1.34 Å)
- $\text{CH}_2$  (S=0; RKS calculation; C-H = 1.078 Å)
- $\text{CH}_2$  (S=1; ROHF calculation; keyword ! ROHF; C-H = 1.078 Å)
- $\text{H}_2\text{O}$  (O-H = 0.956 Å)

2. A summary of the total energy as a function of angle will be printed at the bottom of the output file. Examine the orbitals and their energies at the bent geometry and the linear geometry, and plot them.

Discuss the variation of the orbital energies and the total energy as a function of bond angle. Are the Walsh Diagram results consistent with the *ab initio* results?

3. Plot the variation of the nuclear repulsion energy, the one-electron and two-electron energies, as well as the kinetic energy, of each molecule as a function of angle.

Also plot the sum of the occupied MO energies weighted by their occupancy as a function of bond angle. For each triatomic species, explain why the most stable geometry is either linear or bent.

## Geometry Optimization of Molecules

In order to draw definitive conclusions on structural trends for this exercise, it is necessary to perform calculations on more than five molecules.

1. Choose at least five of molecules that were constructed for the exercise on building molecules, and perform geometry optimization calculations on them with an SVP basis.
2. Compare the optimized structures with experimental data, and summarize these results in [Table 4](#)

Parameters	Exp.	Calc.	Parameters	Exp.	Calc.
rCH in CH <sub>4</sub>	1.094		rOH in H <sub>3</sub> COH	0.956	
aHCH in CH <sub>4</sub>	109.47		rCO in H <sub>3</sub> COH	1.427	
rCC in C <sub>2</sub> H <sub>6</sub>	1.536		rCH in H <sub>3</sub> COH	1.096	
rCH in C <sub>2</sub> H <sub>6</sub>	1.091		aHCH in H <sub>3</sub> COH	109.03	
aHCH in C <sub>2</sub> H <sub>6</sub>	108.0		aHOC in H <sub>3</sub> COH	108.87	
aHCC in C <sub>2</sub> H <sub>6</sub>	110.91		dHCOH in H <sub>3</sub> COH	180.0	
rCC in C <sub>2</sub> H <sub>4</sub>	1.399		rCH in H <sub>2</sub> CO	1.111	
rCH in C <sub>2</sub> H <sub>4</sub>	1.086		rCO in H <sub>2</sub> CO	1.205	
aHCH in C <sub>2</sub> H <sub>4</sub>	117.6		aHCH in H <sub>2</sub> CO	116.133	
aHCC in C <sub>2</sub> H <sub>4</sub>	121.2		aHCO in H <sub>2</sub> CO	121.9	
rCH in C <sub>2</sub> H <sub>2</sub>	1.063		rCO in HCOOH	1.202, 1.343	
rCC in C <sub>2</sub> H <sub>2</sub>	1.203		rCH in HCOOH	1.097	
aHCC in C <sub>2</sub> H <sub>2</sub>	180.0		rOH in HCOOH	0.972	
rCC in C <sub>6</sub> H <sub>6</sub>	1.397		aOCO in HCOOH	124.9	
rCH in C <sub>6</sub> H <sub>6</sub>	1.084		aHCO in HCOOH	124.1	
aCCC in C <sub>6</sub> H <sub>6</sub>	120.0		aHOC in HCOOH	106.3	
aHCC in C <sub>6</sub> H <sub>6</sub>	120.0		rCO in CO <sub>2</sub>	1.162	
rLiH in LiH	1.596		aOCO in CO <sub>2</sub>	180.0	
rLiF in LiF	1.564		rCO in CO	1.128	
rNH in NH <sub>3</sub>	1.012		rCN in glycine	1.469	
aHNN in NH <sub>3</sub>	106.67		rCC in glycine	1.532	
aXNH in NH <sub>3</sub>	112.15		rCO in glycine	1.207, 1.357	
rOH in H <sub>2</sub> O	0.958		rOH in glycine	0.974	
aHOH in H <sub>2</sub> O	104.48		rNH in glycine	1.014	
rHF in HF	0.917		rCH in glycine	1.096	
			aCCN in glycine	113.0	
			aCCO in glycine	125.0, 111.5	
			aHOC in glycine	110.5	
			aHNC in glycine	113.27	
			aHNN in glycine	110.29	
			aHCH in glycine	107.04	

**Table 4:** Experimental Geometric Parameters of Selected Molecules.

Perform regression and error analysis for this data.

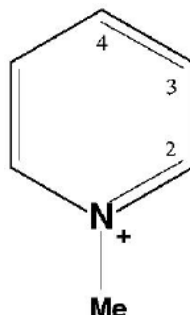
3. Perform optimizations of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>, and deduce whether the bonds are single, double, or triple.

Compare the calculated bond orders obtained from Mulliken, Mayer or Löwdin population analysis with the chemical nature of the bonds.

Plot the bond order versus the bond distance for a given bond type, i.e. the C-C bonds in these three molecules.

## Qualitative Molecular Orbital Analysis of Organic Molecules

As an example of employing the techniques of qualitative molecular orbital analysis to an organic molecule, the reactivity of the pyridinium cation, shown in **Figure 1**, will be studied.



**Figure 1:** The Pyridinium Cation

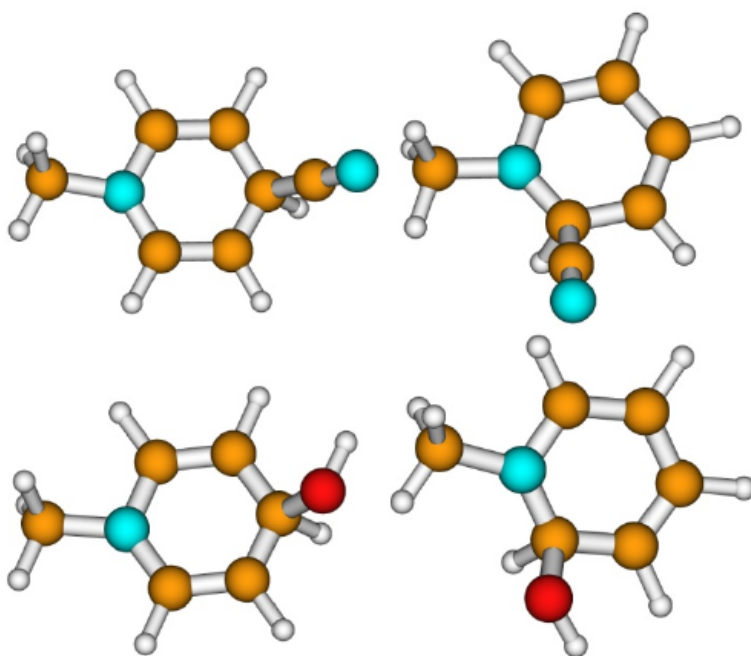
1. Build the molecular structure of the pyridinium cation as described in the exercise on building molecular structures using a Z-matrix.
2. Use one of the methods, including RHF, B3LYP, or BP86 to perform an optimization on the unsubstituted structure, and analyze the wavefunction of the final, optimized structure.
3. Predict the hard/soft nucleophile substitution by analyzing Mulliken net charges and LUMO coefficients.

Determine if the Mulliken net charges and the shape of the LUMO change, if the basis set is increased from SVP to TZVP. Will the qualitative results of the frontier orbital analysis change?

4. Instead of analyzing the MO coefficients numerically, use visualization software to obtain a qualitative view of important valence orbitals.
5. Calculate the most reactive sites of the pyridinium cation in a reaction with hard ( $\text{OH}^-$ ,  $\text{NH}_2^-$ ) and soft ( $\text{CN}^-$ ,  $\text{CH}_2\text{--CO}^-$ , and  $\text{Ph--CO}^-$ ) nucleophiles, respectively.

Experimentally, it is known that hard nucleophiles prefer site C(2), while soft nucleophiles prefer site C(4).

Verify the relative reactivity of the two sites for  $\text{OH}^-$  and  $\text{CN}^-$ , as models of hard and soft nucleophiles, by calculating the energy difference of the four transition structures, CN(2) versus CN(4) and OH(2) versus OH(4), as shown in **Figure 2** below. In this case, it is sufficient to fully optimize the four structures, and TS search is not necessary.



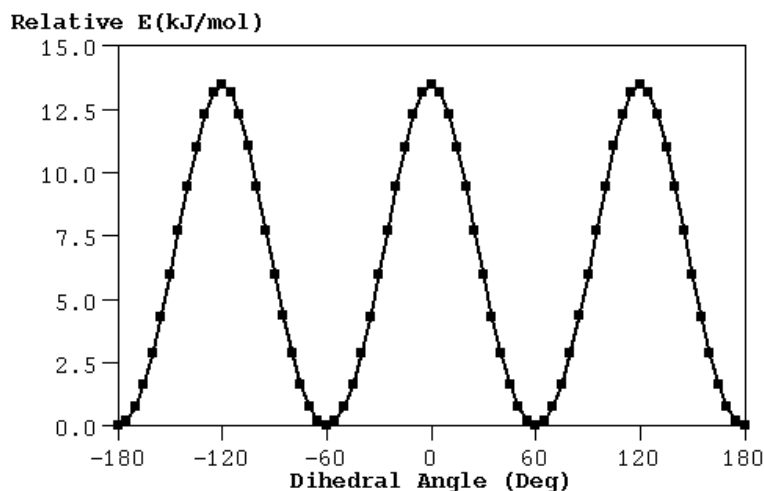
**Figure 2:** Structures of the Reaction Products to be Optimized.

# Conformations of Organic Molecules

## Conformational Analysis

Organic molecules can assume different spatial arrangements (**conformations**) which are generated by rotation about single bonds. A detailed analysis of the various conformations adopted by individual molecules is termed **Conformational Analysis**. Conformational analysis is an important tool for chemists trying to unravel the complex structure of both organic and bio-organic molecules in an effort to obtain a clearer understanding of the reactivity and interaction with other molecules.

As the simplest example of conformational analysis, the rotation of the two methyl groups about the **C-C** bond in **ethane** ( $\text{H}_3\text{C} - \text{CH}_3$ ) is shown in the **Rotational Energy Profile** given below:



## Conformers versus Conformations

The terms **conformers** and **conformations** are associated with conformational analysis.

Conformers are structures that differ by rotation around one or more bonds. Examples of conformers include minima, maxima, and transition states. In the figure above, the **H-C-C-H** torsion angles (or dihedral angles) at  $\pm 180^\circ$  and  $\pm 60^\circ$  are minima and are designated as *staggered* conformations. Those at  $\pm 120^\circ$  and  $0^\circ$  are maxima and are *eclipsed* conformations.

Conformations structures correspond to any point on the **Potential Energy Surface** as shown in the **Rotational Energy Profile** given above. If a specific value of the dihedral angle ( $\Phi$ ) is chosen from the curve above, this corresponds to a **Conformation**. This term usually applies to a molecule which has one or more bonds about which rotation can take place. In the figure above, any value of the **H-C-C-H** torsion angle will produce a **conformation** for ethane.

## 1. Rotational Barrier of Ethane

In this exercise, the rotational barrier of ethane will be studied.

- Build the ethane molecule using the Z-matrix format.
- Perform a relaxed and an unrelaxed potential energy surface scan and plot the results.
- Determine the energies of the eclipsed and staggered conformations.
- What generally happens, if one does not relax all the degrees of freedom during the surface scan.  
Will the rotational barrier be over- or under-estimated by an unrelaxed surface scan?
- Compare the calculated results to the available experimental data. The rotational barrier of ethane is approximately  $1024\text{ cm}^{-1}$  (12.25 kJ/mol); Weiss, S. and Leroi, G.E. J. Chem. Phys., 48, 962 (1968).

## 2. Butane ( $\text{CH}_3\text{CH}_2\text{—CH}_2\text{CH}_3$ )

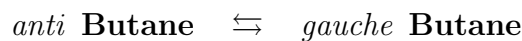
Butane has three conformers defined by the **C—C—C—C** torsion angle ( $\Phi_{\text{C—C—C—C}}$ ). These include the ***anti or trans*** (**a**) conformation where  $\Phi_{\text{C—C—C—C}} = \pm 180^\circ$  and the two ***gauche*** ( $\text{g}^+$ ,  $\text{g}^-$ ) conformations defined by  $\Phi_{\text{C—C—C—C}} = \pm 60^\circ$ . There are also three different maxima present:  $\Phi_{\text{C—C—C—C}} = \pm 120^\circ$  and  $\Phi_{\text{C—C—C—C}} = 0^\circ$

### Rotational Energy Profile for Butane

- Obtain the rotational energy profile (the energy versus torsion angle) of the butane molecule as a function of the **C—C—C—C** torsion angle from  $-180^\circ$  to  $+180^\circ$ .
- On the graph, designate the minima (**a**,  $\text{g}^+$ ,  $\text{g}^-$  conformations) and maxima (***eclipsed*** conformations).
- Determine if two conformations ( $\text{g}^+$  and  $\text{g}^-$ ) are superimposable, and explain the relationship between these conformations.
- Comment on the relative stability of the minima as well as the relative barrier heights for the maxima. Then provide an explanation of the rotational energy profile for the **butane** molecule.

### The *anti-gauche* Equilibrium for Butane

For the equilibrium between the ***anti*** (**a**) and ***gauche*** (**g**) conformations of **butane**:



the equilibrium constant is given by



$$K = \frac{[gauche \text{ Butane}]}{[anti \text{ Butane}]}$$

The equilibrium constant (**K**) can be related to the **Free Energy** ( $\Delta G$ ) between reactants and products by the equation:

$$\Delta G = -R T \ln K$$

where **R** is the gas constant (**8.31451 J mol<sup>-1</sup> K<sup>-1</sup>**), and **T** is the temperature in degrees Kelvin.

The **Free Energy** change for the reaction is then given by

$$\Delta G \approx E(gauche \text{ Butane}) - E(anti \text{ Butane})$$

- Calculate the fractions of **a**, **g<sup>+</sup>**, and **g<sup>-</sup>** at equilibrium for **T = 25° C** and **T = 225° C**.
- Discuss what happens to the fraction of the ***anti*** conformation of **butane** as the temperature is **increased** and explain why this happens.

### 3. Methylethyl Ether (**CH<sub>3</sub>CH<sub>2</sub> – OCH<sub>3</sub>**)

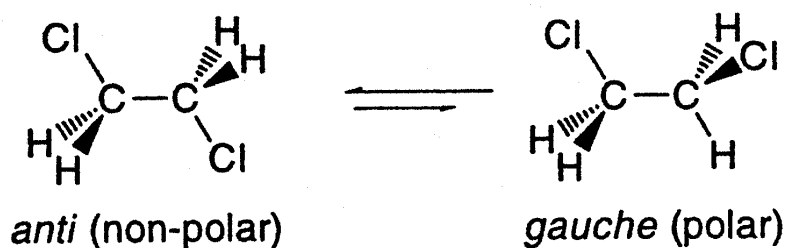
One way to think of the rotation about the **C-O** bond in **CH<sub>3</sub>CH<sub>2</sub> – OCH<sub>3</sub>** is that one **CH<sub>2</sub>** group in **CH<sub>3</sub>CH<sub>2</sub>–CH<sub>2</sub>CH<sub>3</sub>** is replaced by an **O** atom. The two lone pairs on the **O** atom point out in space similar to hydrogen atoms attached to the **C** atom.

- Obtain the rotational energy profile for **CH<sub>3</sub>CH<sub>2</sub> – OCH<sub>3</sub>**.  
On the graph, designate the minima (**a**, **g<sup>+</sup>**, **g<sup>-</sup>** conformations) and maxima (***eclipsed*** conformations).
- Provide an explanation for the differences (e.g. higher or lower rotational barrier) and similarities (e.g. rotational energy periodicity) for **CH<sub>3</sub>CH<sub>2</sub> – CH<sub>2</sub>CH<sub>3</sub>** and **CH<sub>3</sub>CH<sub>2</sub> – OCH<sub>3</sub>**.

#### 4. 1,2-Dichloroethane ( $\text{ClCH}_2\text{CH}_2\text{Cl}$ )

##### The Role of Solvent on Conformation

Solvent can significantly change the conformation of molecules. In general, polar solvents such as  $\text{H}_2\text{O}$  will stabilize a polar conformation to a greater extent than a non-polar conformation. The *anti* and *gauche* conformers of 1,2-dichloroethane ( $\text{ClCH}_2\text{CH}_2\text{Cl}$ ) shown in the equilibrium below:

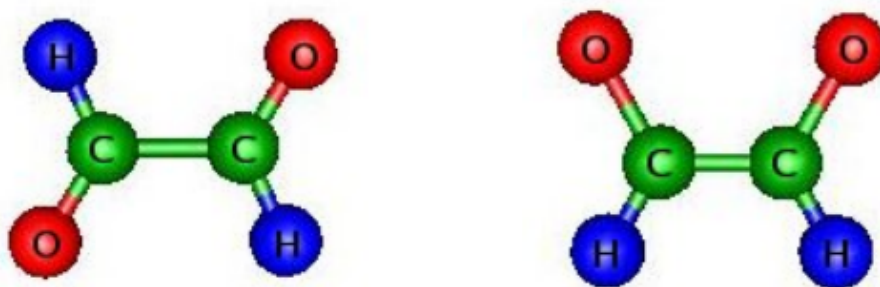


shift with the polarity of the solvent.

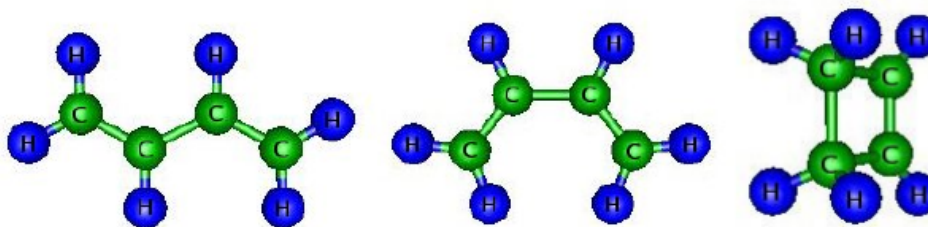
- Obtain the rotational energy profiles of 1,2-dichloroethane in the gas phase and polar solvent.
- Calculate the dipole moments for *anti* and *gauche* conformations of  $\text{ClCH}_2\text{CH}_2\text{Cl}$ , and place the results in a table.
- Label the *anti* and *gauche* conformations of  $\text{ClCH}_2\text{CH}_2\text{Cl}$ , and include a vector to show the direction of the dipole moment.  
Explain the origin of the dipole moment observed for each of these conformations.
- What happens to the energy difference between *anti* and *gauche* conformations of  $\text{ClCH}_2\text{CH}_2\text{Cl}$  in polar solvent?
- Calculate the ratio of the *anti*/*gauche* conformational equilibrium for  $\text{ClCH}_2\text{CH}_2\text{Cl}$  in going from the gas phase to polar solvent at room temperature.
- Comment on the effect of a non-polar solvent on the *anti*/*gauche* conformational equilibrium.

## 5. Conformations of Glyoxal and Butadiene

This exercise consists in performing a frequency analysis at the stationary points of the potential energy surface. The goal of this exercise is to get a feeling for how to locate different minima on a given potential energy surface, to characterize their nature using frequency calculations, and to understand the chemical implications of the different minima. Vibrational and thermal corrections to the total energy will be needed.



**Figure 3:** The two isomers of glyoxal: trans (left) and cis (right).



**Figure 4:** Three isomers of  $C_4H_6$ : trans (left) and cis (middle) butadiene and cyclobutene (right).

	$C_2H_2O_2$	$C_4H_6$
<i>trans</i>	0	0
<i>cis</i>	16 <sup>a</sup>	17 <sup>b</sup>
<i>cyclo</i>	-	46 <sup>c</sup>

**Table 5:** Relative Energies  $C_2H_2O_2$  and  $C_4H_6$  Isomers in kJ/mol; (a) Butz KW, Krajnovich DJ, Parmenter CS, *Journal of Chemical Physics*, **93**, 1557-1567 (1990); (b) Engeln R, Consalvo D, Reuss J, *Chemical Physics*, **160**, 427-433 (1992); (c) Spellmeyer DC, Houk KN, *J. Amer. Chem. Soc.*, **110**, 3412-3416, (1988); Wiberg KB, Fenoglio RA, *J. Amer. Chem. Soc.*, **90**, 13, 3395-3397 (1968).

- Build the *cis* and *trans* geometric conformers of glyoxal, as well as for the *cis* and *trans* conformers of butadiene, along with the cyclobutene isomer using Z-matrices.

- Perform a full geometry optimization using B3LYP/SVP for all conformers and stationary points on the potential energy surface.

Determine whether the obtained stationary points are local minima. To this end, frequency calculations should be performed.

Compare the relative energies of each isomer.

Does the inclusion of zero-point energy improve the relative energies significantly?

Compare the magnitude of the thermal correction to that of the ZPE corrections.

Which contribution is more significant for relative isomer energies?

- Use chemical intuition in order to guess a starting geometry that leads to convergence to first-order saddle points, and confirm the results by performing frequency analyses.

For either butadiene or glyoxal, a reasonable starting geometry for a transition state structure can be obtained by rotating one  $\text{—HC=CH}_2$  or  $\text{—C=O}$  group by 90 degrees, so that it is arranged perpendicular to the other  $\text{—HC=CH}_2$  or  $\text{—C=O}$  group.

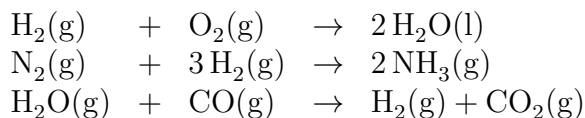
- Calculate the fractional population of each isomeric form using Boltzmann statistics.

Will the calculated ratios of the different isomers be in the same proportion as the experiment? Discuss possible sources of deviations from the expected ratios.

- Using the optimized geometries of the glyoxal isomers, which have been calculated previously, determine how quickly glyoxal interconverts at room temperature by calculating the activation energy and the rate constant.

## Free Energy Calculations

In this exercise, simple chemical systems will be investigated, and the change in in Gibbs free energy,  $\Delta G_0$  will be determined. The reactions include the Haber-Bosch reaction, the Knallgas reaction of hydrogen and oxygen to produce water, and the gas-phase reaction between water and carbon monoxide:



Experimental data on free energies is available in [Table 6](#).

1. Optimize the geometry of all participating reactants, using DFT with the B3LYP functional and SVP basis set.
2. Perform a frequency analysis for the optimized geometries, and look for the relevant thermochemical data in the output file
3. Calculate the change in free energy for the above reactions, and compare the results to experimental data.

## Bond Strengths and Dissociation Energies

The strength of different C–H bonds will be examined for simple organic molecules, and the atomization energy of these compounds will be determined. As sample systems, the following molecules can be compared: methane, acetylene, benzene, and acetaldehyde.

1. Employ the B3LYP/SVP combination, and optimize the structures of all molecules.
2. Determine the bond dissociation energies of all C-H bonds and the C-H binding energy in methane, as well as the atomization energies for all molecules.

Compare the calculated bond energies to experimental data given in [Table 7](#).

3. Repeat the calculations for an enlarged basis sets TZVP and TZVPP, and observe any basis set effects.

**Table 6:** Free Energies of Reactions

Reaction	$\Delta G_0(\text{kJ/mol})$
$\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$	-572.0
$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$	-92.3
$\text{H}_2\text{O}(\text{g}) + \text{CO} \rightarrow \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$	-41.2

**Table 7:** C-H Bond Dissociation Energies

Bond	$D_{298\text{K}}^0(\text{kJ/mol})$
H–CH <sub>3</sub>	438.9
H–CH <sub>2</sub>	462.0
H–CH	424.0
H–C <sub>6</sub> H <sub>5</sub>	473.1
H–CCH	556.1
H–CH <sub>2</sub> CHO	394.6
H–COCH <sub>3</sub>	373.8

# Symmetry Allowed and Forbidden Reactions

## Photochemical Dissociation of Formaldehyde

1. Optimize the following structures employing the 6-311G\* basis, and visualize the both the valence and lowest unoccupied orbitals.

- $\text{H}_2\text{C}=\text{O}$ ,  $\text{H}_2$ , and  $\text{CO}$

2. Investigate the orbital symmetry with respect to the operations of the  $C_{2v}$  point group, and classify the valence and lowest unoccupied orbitals according to their irreducible representations.

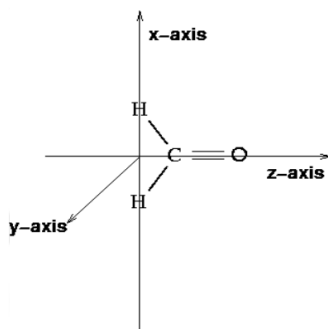
- Identity ( $E$ )
- two-fold rotation axis ( $C_2$ )
- mirror plane ( $xz$ )
- mirror plane ( $yz$ )

3. Draw an MO diagram for  $\text{H}_2\text{C}=\text{O}$  (left side) transforming to  $\text{H}_2+\text{CO}$  (right side).

Connect those orbitals which belong to the same irreducible representation.

Repeat these steps for  $C_s$  symmetry with the symmetry elements  $E$  and  $\sigma$ . There are two possibilities for the orientation of formaldehyde in this point group. What should attract your attention?

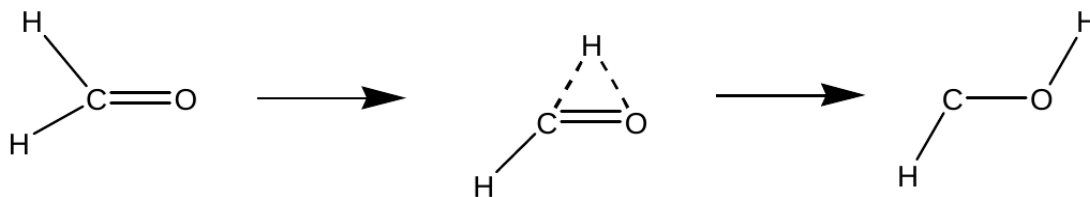
4. Determine whether  $C_{2v}$  or  $C_s$  symmetry, would yield an allowed photochemical decomposition of  $\text{H}_2\text{CO}$  to  $\text{H}_2 + \text{CO}$  products.



**Figure 5:** Coordinate System for  $\text{H}_2\text{C}=\text{O}$ .

$C_{2v}$	$E$	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$		
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_x$	$yz$

**Table 8:** Character Table for the  $C_{2v}$  Point Group.



**Figure 6:** Hydrogen Migration in Formaldehyde

5. Another problem involves the transition state for hydrogen migration in formaldehyde shown in **Figure 6**:

First optimize the reactants and products, and then guess a transition-state geometry.

Hydrogen migration in formaldehyde presents a difficult case for determining an initial structure for the transition state.

Once a transition state is obtained, a calculation of vibrational frequencies for the proposed transition state structure should produce one imaginary frequency.