Homework 4
Lectures 5: Potential Energy Sufaces
(CBE 60547)

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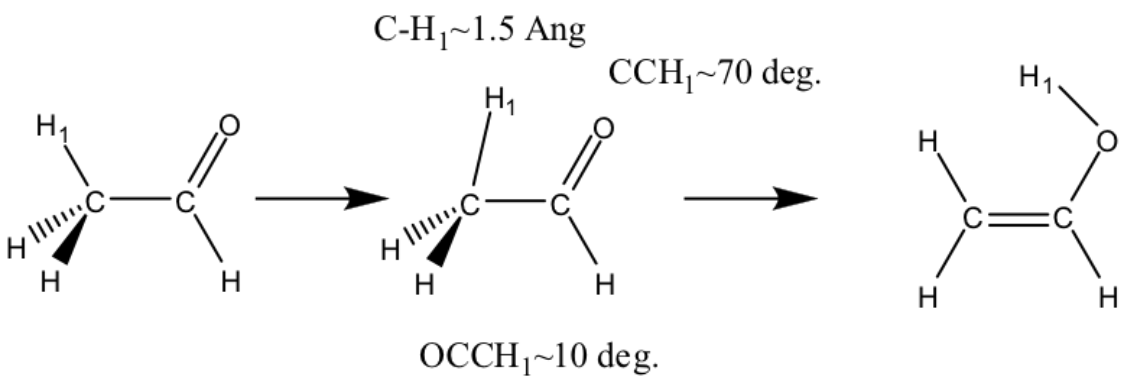
Due: November 2017

In this assignment you will determine some of the properties of **acetaldehyde** (CH_3CHO), its isomer **vinyl alcohol** ($H_2C{=}CH(OH)$), and the **transtion state** (TS) that interconverts the two:



1 Characterizing the reactant and product

(a) First, optimize the structures of the reactant acetaldehyde and product vinyl alcohol at the Hartree-Fock level with the 6-31G(d) basis set. Make a table of the key internal coordinates in the two (note you will figure out the TS below):

	Acetaldehyde	Transition State	Vinyl alcohol
H_1–C (Å)	1.08	–	2.47
C–C (Å)	1.50	–	1.32
C–O (Å)	1.19	–	1.35
O-H_1 (Å)	2.55	–	0.95

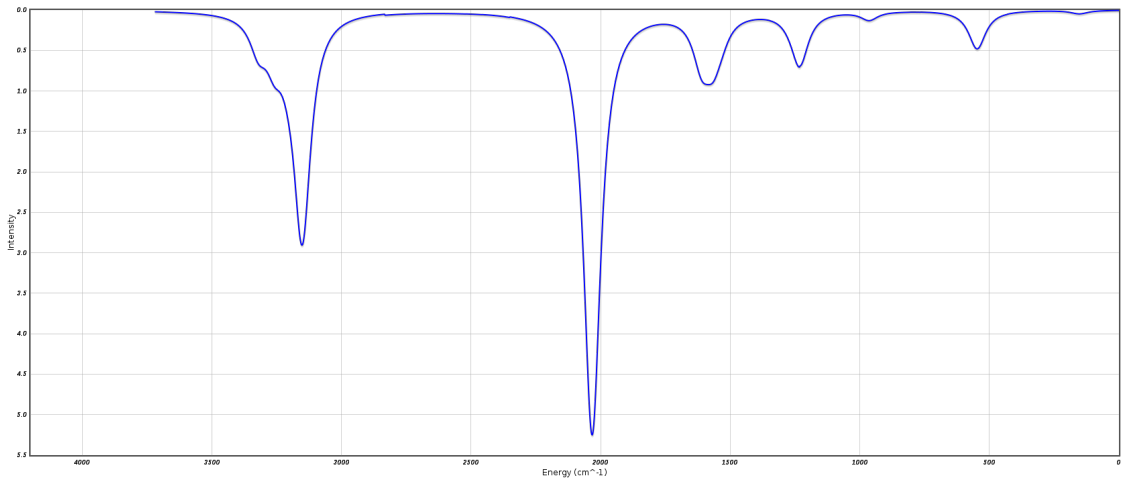
(b) Which geometry optimization method did you use in (a)? What type of coordinate system? What were the convergence criteria?

The Quasi-Newton Raphson method with BFGS Hessian updates was used to optimize the geometry of the molecules. Coordinates were described in a Z-matrix format. Optimization convergence was reached when the density matrix update was less than 1E-5.

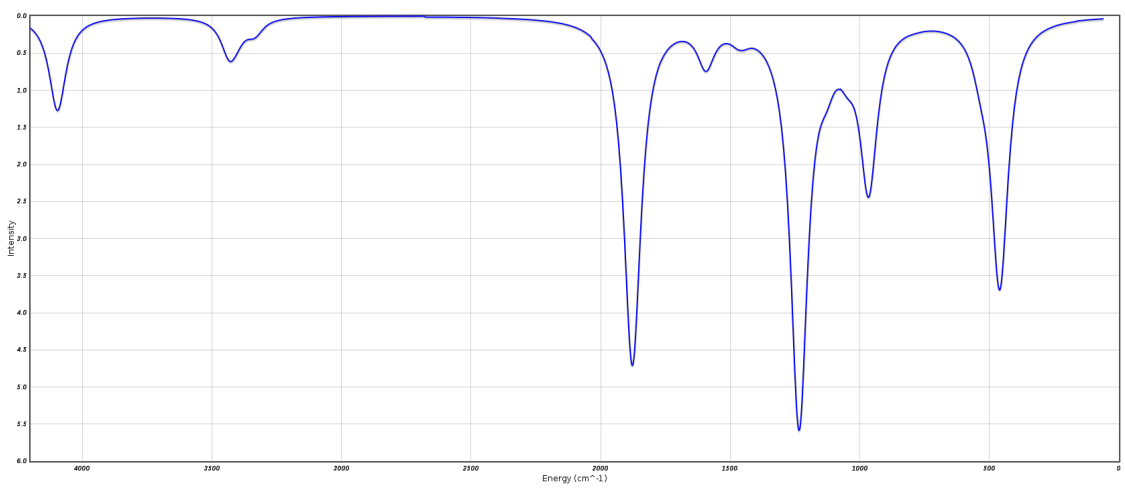
(c) Calculate the vibrational spectra of the reactant and product. Confirm that both are true minima (if not, adjust and recalculate). Identify the most prominent (intense) infrared vibrational modes in the two. Could you distinguish these two by their vibrational spectra?

The vibrational frequencies are different for the two molecules. The most prominent frequencies are 2032 cm^{-1} and 1233.84 cm^{-1} for the reactant and product respectively. The spectra are easily distinguishable.

Reactant IR Spectra:



Product IR Spectra:



(d) Perform single-point energy calculations on the reactant and product at the MP2/6-31G(d) level. Use the results to complete the table below:

	Product − reactant (kJ/mol)	TS − reactant (kJ/mol)
HF/6-31G(d)	71.09	368.44
MP2/6-31G(d)	70.89	309.72
ZPE	3.0	-12.01
MP2 + ZPE	73.89	297.71

react HF = -152.9159655 hart prod HF = -152.888888 hart

prod MP2 = -153.32002 hart react MP2 = -153.34692 hart

prod ZPE = 160.4 kJ/mol react ZPE = 157.4 kJ/mol

(e) From the frequency calculations on the reactant and product, extract $H^\circ(298) - H(0)$ for each. Combine with the MP2 + ZPE results to estimate the 298 K reaction enthalpy.

Heat capacity functions of T: Cp(reactant) = 0.0772T + 31.832 Cp(product) = 0.0722T + 30.553

	Reactant (kJ/mol)	Product (kJ/mol)	Rxn (kJ/mol)
H(0)	-402612	-402541	71
Integrated Heat Cap.	12904.9	12794	–
$H^\circ(298)$	-389707.1	-389747.4	-40.3

2 Transition state by scanning

(a) Do a rigid scan about the H_1-C-C-O dihedral in acetaldehyde. It is easiest to do this using a z-matrix representation of acetaldehyde. Construct a z-matrix based on your optimized acetaldehyde structure and do a series of energy evaluations as you vary the dihedral angle. Approximately how large is the barrier to rotation about the C–C bond, in kJ/mol?

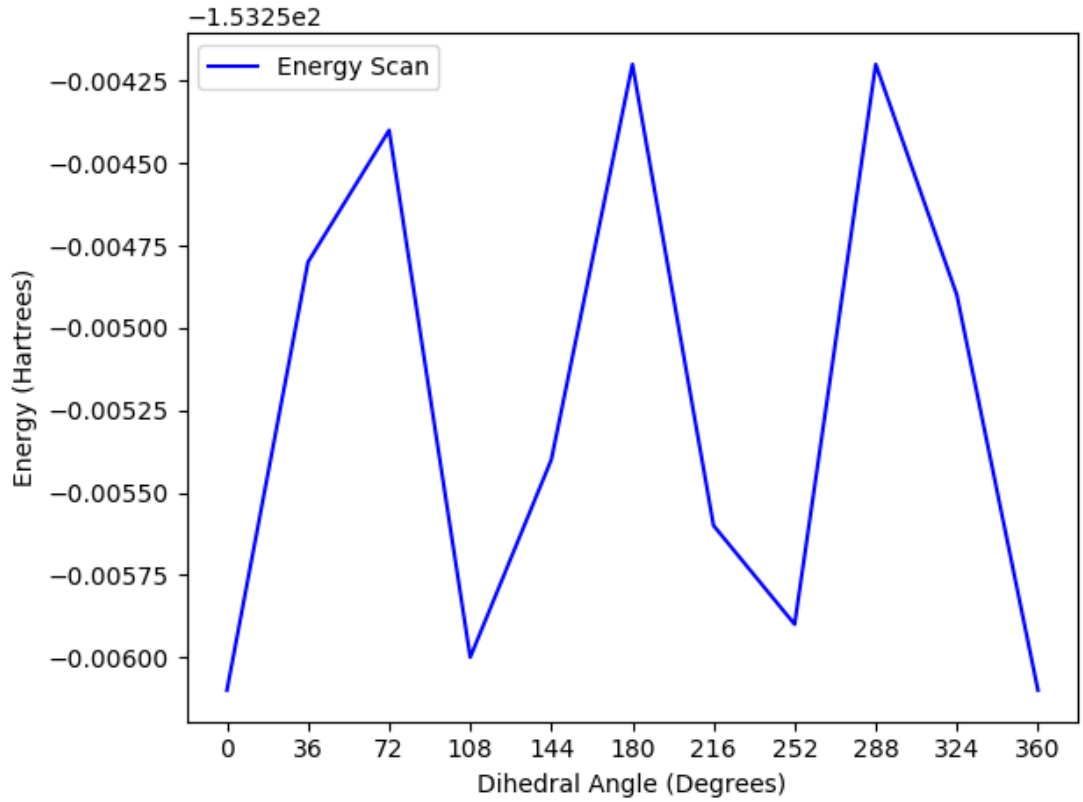
All single-point energy calculations performed in Orca using the MP2 method. The rotation barrier is approximately 4.6 kJ/mol.

0	-153.2561
36	-153.2548
72	-153.2544
108	-153.2560
144	-153.2554
180	-153.2542
216	-153.2556
252	-153.2559
288	-153.2542
324	-153.2549
360	-153.2561

```python
import matplotlib.pyplot as plt

dihedrals = [entry[0] for entry in table]
energies = [entry[1] for entry in table]


plt.plot(dihedrals, energies, 'b', label='Energy Scan')
#,spline1,Rxn_label,spline2)
plt.xticks(dihedrals)
plt.xlabel('Dihedral Angle (Degrees)')
plt.ylabel('Energy (Hartrees)')
plt.legend(loc='best')
plt.tight_layout()
plt.savefig('./energy_scan.png')
plt.show()
```



3 Transition state optimization

(a) Guess a structure near the transition state that connects acetaldehyde to vinyl alcohol (note I gave you some hints in the figure) and compute the Hessian at the HF/6-31G(d) level to make sure you are near a saddle point. Once you have a satisfactory guess, search from this starting point for the transition state. Make sure your calculation converges, and calculate the vibrational spectrum again to make sure you landed at the saddle point. Add the key internal coordinates to the Table in 1(a).

(b) What is the magnitude of the imaginary vibrational mode at the transition state?

(c) Perform a single-point MP2/6-31G(d) calculations on this transition state. Add the results to the Table in 1(c).

(d) Use transition state theory to estimate the rate constant for this reaction at 298 K. From the frequency calculations on the reactant and transition state, extract $G^{\circ}(298K) - G(K)$ for each. Combine these results with the MP2 + ZPE energies to estimate $\Delta G^{\ddagger}(298)$. Evaluate the rate constant using the TST expression:

$$k(T) = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}(T)/k_B T} \tag{1}$$

3.1 Solution

3.1.1 a)

Input file of GAMESS for TS structure guess

```
 $CONTRL SCFTYP=RHF RUNTYP=HESSIAN
       ICHARG=0 MULT=1 COORD=ZMTMPC $END
 $BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
 $DATA
C2H4O
C1 1
C 0.0000000 0 0.0000000 0 0.0000000 0 0 0 0
C 1.5400000 1 0.0000000 0 0.0000000 0 1 0 0
O 1.2750000 1 120.00000 1 0.0000000 0 2 1 0
H 1.0900000 1 117.38979 1 -161.69239 1 2 1 3
H 1.0900000 1 109.47122 1 -110.00000 1 1 2 3
H 1.5049141 1 69.873799 1 -11.355914 1 1 2 3
H 1.0900000 1 109.47122 1 130.00000 1 1 2 3
 $END
```

The vibrational modes for the guessed TS structure

Mode	Frequency (cm^{-1})
1	1170.63841 I
2	220.80887
3	0.01753
4	0.00648
5	0.00508
6	232.68365
7	382.62252
8	531.21061
9	708.46004
10	822.0281
11	952.78115
12	1193.26027
13	1274.08053
14	1335.08057
15	1398.97709
16	1504.56455
17	1570.71896
18	1722.9671
19	3196.77908
20	3228.2914
21	3262.89519

Input file of GAMESS for finding TS structure

```
 $CONTRL SCFTYP=RHF RUNTYP=SADPOINT
       ICHARG=0 MULT=1 COORD=ZMTMPC $END
 $BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
```

```
 $STATPT HESS=CALC NSTEP=100 $END
 $DATA
C2H4O
C1 1
C 0.0000000 0 0.0000000 0 0.0000000 0 0 0 0
C 1.5399999 1 0.0000000 0 0.0000000 0 1 0 0
O 1.2750004 1 120.00001 1 0.0000000 0 2 1 0
H 1.0899999 1 117.38978 1 -161.69236 1 2 1 3
H 1.0899999 1 109.47118 1 -109.99999 1 1 2 3
H 1.5049143 1 69.873796 1 -11.355956 1 1 2 3
H 1.0900000 1 109.47123 1 129.99998 1 1 2 3
 $END
```

Then, perform a single-point calculation to confirm the vibrational modes of converged structure

Input file of GAMESS for finding TS structure

```
 $CONTRL SCFTYP=RHF RUNTYP=HESSIAN
       ICHARG=0 MULT=1 COORD=ZMTMPC $END
 $BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
 $DATA
C2H4O
C1 1
C 0.0000000 0 0.0000000 0 0.0000000 0 0 0 0
C 1.4205123 1 0.0000000 0 0.0000000 0 1 0 0
O 1.2517072 1 109.17749 1 0.0000000 0 2 1 0
H 1.0807165 1 131.54793 1 -177.24197 1 2 1 3
H 1.0846693 1 110.03343 1 -73.713743 1 1 2 3
H 1.5184653 1 65.616181 1 7.9326391 1 1 2 3
H 1.0785697 1 120.71715 1 152.43909 1 1 2 3
 $END
```

Mode	Frequency (cm^{-1})
1	2573.824 I
2	4.724
3	3.454
4	3.069
5	0.034
6	0.347
7	0.461
8	541.747
9	719.07
10	896.329
11	1078.011
12	1161.812
13	1270.518
14	1312.98
15	1432.017
16	1613.097
17	1729.381
18	2088.627
19	3254.42
20	3339.587
21	3357.344

The key internal coordinates

	Acetaldehyde	Transition State	Vinyl alcohol
$H_1 - C$ (Å)		1.51846	
$C - C$ (Å)		1.42051	
$C - O$ (Å)		1.25171	
$O - H_1$ (Å)		1.23416	

3.1.2 b)

The magnitude of the imaginary vibrational mode at the transition state is 2573.824.

3.1.3 c)

Input file of GAMESS for single-point MP2/6-31G(d) calculations on the transition state

```
 $CONTRL SCFTYP=RHF MPLEVL=2 RUNTYP=ENERGY
       ICHARG=0 MULT=1 COORD=ZMTMPC $END
 $BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
 $DATA
C2H4O
C1 1
C 0.0000000 0 0.0000000 0 0.0000000 0 0 0 0
C 1.4205115 1 0.0000000 0 0.0000000 0 1 0 0
O 1.2517074 1 109.17751 1 0.0000000 0 2 1 0
H 1.0807169 1 131.54793 1 -177.24200 1 2 1 3
H 1.0846694 1 110.03348 1 -73.713741 1 1 2 3
```

```
H 1.5184649 1 65.616187 1 7.9326351 1 1 2 3
H 1.0785700 1 120.71714 1 152.43909 1 1 2 3
 $END
```

Product - reactant (kJ/mol)	TS - reactant (kJ/mol)
HF/6-31G(d)	(-397204) - (-397582) = 377.3846
MP2/6-31G(d)	(-402285) - (-402606) = 321.1754
ZPE	(142.325482) - (157.354624) = -15.0291
MP2 + ZPE	306.1463

3.1.4 d)

Thermochemistry at T = 298.15 K

Using ideal gas, rigid rotor, harmonic normal mode approximations.

from the vibrational calculation of TS

	E	H	G	CV	CP	S
	KJ/MOL	KJ/MOL	KJ/MOL	J/MOL-K	J/MOL-K	J/MOL-K
ELEC.	0.000	0.000	0.000	0.000	0.000	0.000
TRANS.	3.718	6.197	-40.298	12.472	20.786	155.948
ROT.	3.718	3.718	-23.019	12.472	12.472	89.678
VIB.	143.472	143.472	141.989	14.551	14.551	4.975
TOTAL	150.909	153.388	78.671	39.495	47.809	250.601

from the vibrational calculation of reactant

	E	H	G	CV	CP	S
	KJ/MOL	KJ/MOL	KJ/MOL	J/MOL-K	J/MOL-K	J/MOL-K
ELEC.	0.000	0.000	0.000	0.000	0.000	0.000
TRANS.	3.718	6.197	-40.298	12.472	20.786	155.948
ROT.	3.718	3.718	-23.218	12.472	12.472	90.347
VIB.	159.926	159.926	155.471	19.320	19.320	14.943
TOTAL	167.363	169.842	91.954	44.263	52.577	261.237

Thus, we can compute $\Delta G^{\ddagger}$

Compound	(MP2 + ZPE) + G_{corr} (kJ/mol)
TS - reactant	(306.1463) + (78.671 - 91.954) = 292.8633

$$k(T) = \frac{k_B T}{h} e^{-\Delta G(T)^{\ddagger}/k_B T}$$

$$k(298K) = \frac{(1.380662 \times 10^{-23})(298)}{6.626176 \times 10^{-34}} e^{\frac{-292.8633 \times 1000}{(8.314472) \times (298)}} = 2.88298 \times 10^{-39} s^{-1}$$

4 Bronsted-Evans-Polanyi relations

Your colleague wants to know if replacing one of the methyl H's with an F will speed-up or slow down the isomerization. You know from experience that it is much easier to calculate relative rates than absolute ones.

(a) Perform additional calculations to determine whether the reaction is more or less exothermic with the F substituent.

(b) Perform additional calculations to determine whether the reaction barrier is higher or lower with the F substituent.

(c) Do your answers to (a) and (b) conform to expectations from the BEP relationship?

4.1 Solution

4.1.1 a)

Using the same method as we used in the first three questions, we optimized the geometry of the reactant, the product and the transition state at the HF/6-31G(d) level, then calculated the single-point energies at the MP2/6-31G(d) level. Zero point energies were obtained from vibrational frequency calculations using the optimized geometries. All calculations were done using Gamess in WebMO. (1 Hartree = 2625.50 kJ/mol)

Energy (kJ/mol)	Reactant	Product	TS	TS - Reactant	Product - Reactant
HF/6-31G(d)	-660991	-660925	-660599	391.20	63.64
MP2/6-31G(d)	-662548	-662492	-662222	325.56	55.14
ZPE	139.28	122.83	141.21	1.93	-16.45
MP2 + ZPE	-662408	-662370	-662081	327.49	38.69

Product - Reactant = 38.69 kJ/mol for F substituent. Compared with the original reaction, the reaction with the F substituent is less exothermic.

4.1.2 b)

TS - Reactant = 327.49 kJ/mol for F substituent. Compared with the original reaction, the reaction barrier with the F substituent is higher.

4.1.3 c)

BEP relationship: the difference in activation energy between two reactions of the same family is proportional to the difference of their enthalpy of reaction. Our answers to (a) and (b) conform to expectations from the BEP relationship.

5 Useful Templates

5.1 Frequency calculation:

```
$CONTRL SCFTYP=RHF RUNTYP=HESSIAN $END
$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
$FORCE METHOD=ANALYTIC VIBANL=.TRUE. $END
$GUESS GUESS=MOREAD NORB=xxx $END ! use if you have a converged SCF wavefunction to read in
$DATA
...
$END
```

5.2 Geometry optimization using redundant internal coordinates:

```
$CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE NZVAR="3n-6" $END
$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
$STATPT NSTEP=xx $END
$ZMAT DLC=.TRUE. AUTO=.TRUE. $END
$GUESS GUESS=MOREAD NORB=xxx $END ! use if you have a converged SCF wavefunction to read in
$DATA
 ...
$END
$VEC ! converged SCF wavefunction, if you have it
...
$END
```

5.3 Transition state search:

```
$CONTRL SCFTYP=RHF RUNTYP=SADPOINT NZVAR="3n-6" $END
$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
$STATPT HESS=READ NSTEP=xx $END
$ZMAT DLC=.TRUE. AUTO=.TRUE. $END
$GUESS GUESS=MOREAD NORB=xxx $END ! use if you have a converged SCF wavefunction to read in
$DATA
...
$END
$HESS
...
$END
$VEC
...
$END
```

5.4 MP2 calculation:

```
$CONTRL SCFTYP=RHF RUNTYP=ENERGY MPLEVL=2 $END
$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
$DATA !
...
$END
```

5.5 CIS calculation:

```
$CONTRL SCFTYP=RHF RUNTYP=ENERGY CITYP=CIS $END
$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
$DATA !
...
$END
```