

### Homework Assignment 4

#### Question 1

a) Parameters (xyz coordinates, angle and bond length):

O    -2.10730    1.97533    -0.04557  
 H    -1.14844    2.03072    -0.28665  
 H    -2.54298    1.59113    -0.84755

HOH 104.51 degrees

O-H 0.990254 Angstrom

Energy – calculated using UFF method

5.38772e-13 kJ/mol = 1.2877e-13 kcal/mol,

Dipole

0.245 D

b)

	Energy (Hartree)	Energy (kcal/mol)	Dipole (Debye)
Avogadro	n/a	1.29e-13	0.245
PM3	-0.085	-53.35	1.7386
RHF/STO-3G	-74.966	-47041.82	1.7093
RHF/6-31G(d,p)	-76.024	-47705.55	2.1478
Experimental	n/a	n/a	1.85 <sup>1</sup> -1.86 <sup>2</sup>

Avogadro's prediction of the lowest energy state is higher than all the ones predicted theoretically using semi-empirical (PM3) and ab-initio (RHF) methods. As the difference between Avogadro's predictions and of the computational is large, it can be concluded that Avogadro's predictions are not accurate and cannot be fully trusted.

The lowest energy is reported by Ab-initio method: RHF/6-31G(d,p). As ab-initio methods are more accurate than semi-empirical method (PM3), it is not surprising that ab-initio methods give the lowest energy. 6-31G found a lower energy than STO-3G, perhaps because it takes into account the d and p orbitals. However, it is important to note that even if ab-initio methods found lower energy, they cannot always be implemented as they have limit on number of particles (and can take ages to calculate).

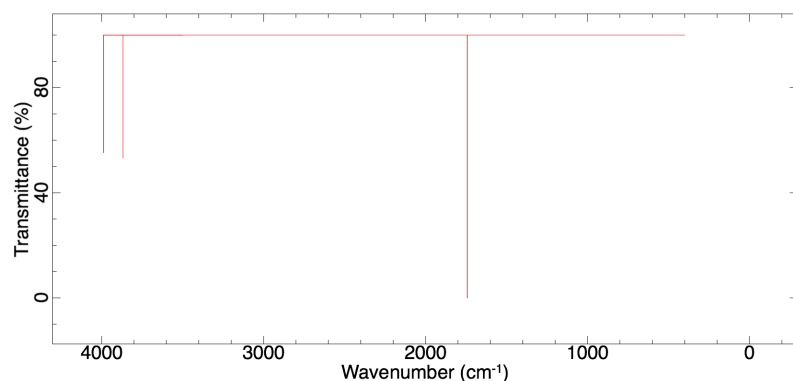
However, for dipole calculations, semi-empirical method, PM3, showed the closest value of dipole to experimental one. While ab-initio methods showed a close value to experimental one as well, Avogadro predictions showed to be way off the experimental value.

<sup>1</sup> R. D. Nelson Jr., D. R. Lide, A. A. Maryott "Selected Values of electric dipole moments for molecules in

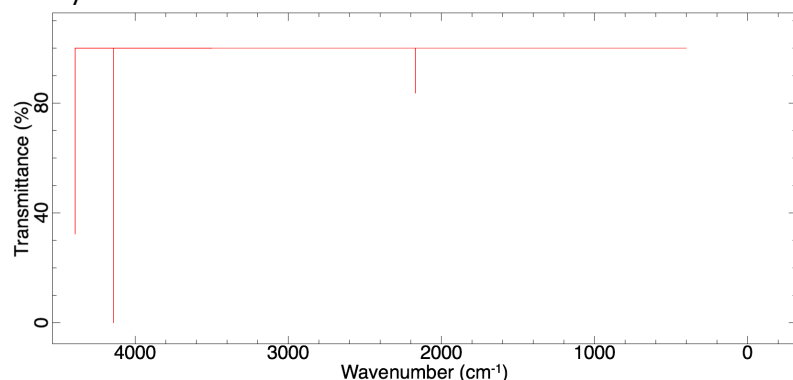
<sup>2</sup> P. L. Silvestrelli and M. Parrinello, *Physical Review Letters*, 1999, **82**, 3308-3311.

**c) Infrared spectra**

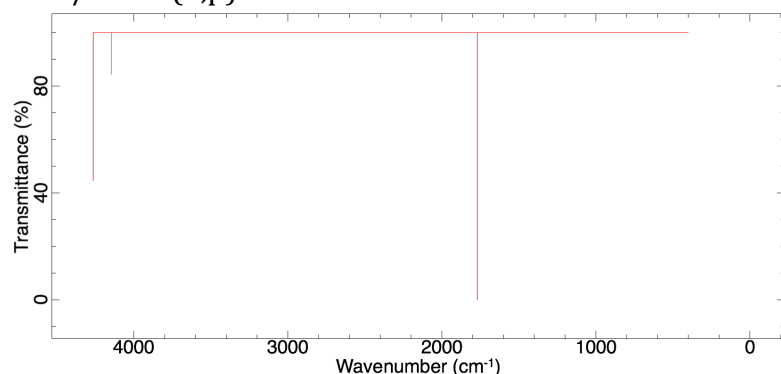
PM3



RHF/STO-3G



RHF/6-31G(d,p)

**Comparison of frequency**

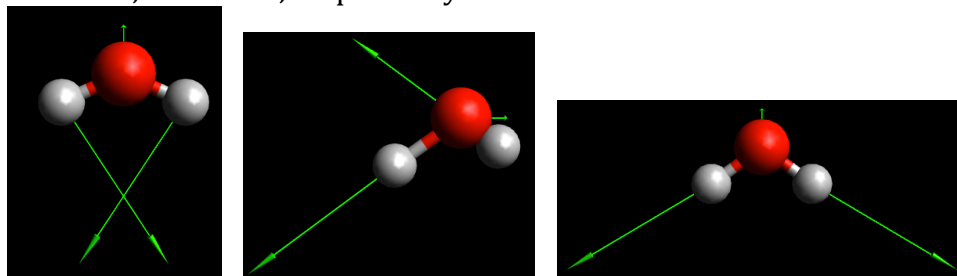
Name	v1 (cm-1)	v2 (cm-1)	v3 (cm-1)
PM3	1742.26	3867.79	3988.25
RHF6	1769.87	4146.76	4263.72
RHFS	2169.86	4140.93	4392.08

According to IR spectra of all three methods, there are three modes observed. Even though, all three predict three modes, all of them give different values for the frequency of modes, especially when PM3 and RHF are compared. RHF6 and RHFS seem to be closer in predictions of mode 2 and 3 frequencies, however, for mode 1 PM3 and RHF6 give similar predictions.

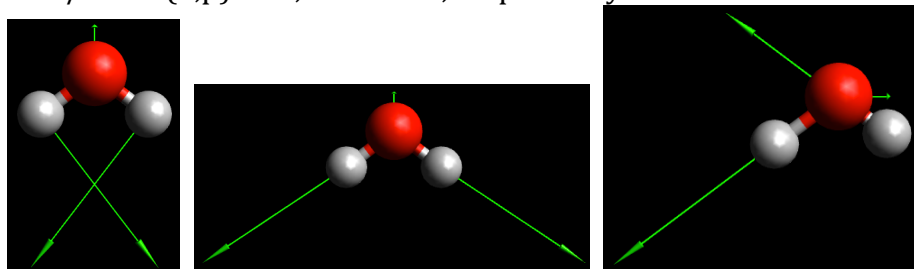
From the above spectra the intensity-differences should be noted as well. While RHF6 and PM3 intensify the first mode intensity, RHFS has dramatically lower intensity for the first mode.

### Vibrational modes

PM3 – v1, v2 and v3, respectively

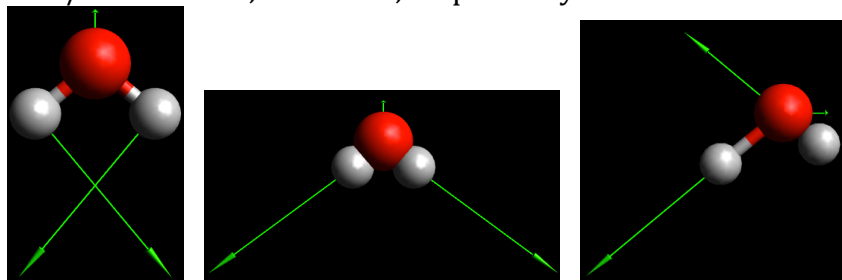


RHF/6-31G(d,p) – v1, v2 and v3, respectively



\*Let's say, first picture is mode 1, second is mode 2 and third is mode 3.

RHF/STO-3G – v1, v2 and v3, respectively



All three methods show the same vibrations. The only difference was noted with PM3 method, it switched the mode 2 with mode 3. In other words, in RHF mode 2 is in the middle of mode 1 and mode 2 (please see above), while in PM3, mode 2 comes at a frequency higher than mode 1 and mode 3.

## Question 2

**a)** Energies using MMFF94s in Avogadro:

Reactant = 31.4064 kJ/mol

Intermediate 1 = 9.91438 kJ/mol

Intermediate 2 = 5.23681 kJ/mol

Product 1 = 30.0454 kJ/mol

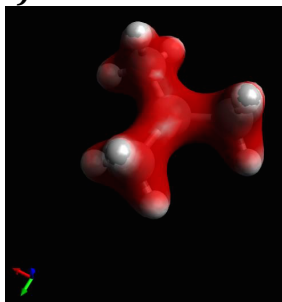
Product 2 = 9.05649 kJ/mol

**b)** SCF energies using RHF/6-31G(d,p)

Intermediate 1 = -156.4565501 Hartree = -410776.61 kJ/mol

Intermediate 2 = -156.4126803 Hartree = -410661.43 kJ/mol

Intermediate 1 is more likely to happen as it has a lower energy.

c) *Intermediate 1*

Mulliken charges:

1 C -0.421632 CH<sub>3</sub>

2 C 0.251799 Central carbon

3 H 0.217905

4 H 0.235166

5 H 0.217961

6 C -0.421632 CH<sub>3</sub>

7 H 0.217903

8 H 0.217964

9 H 0.235166

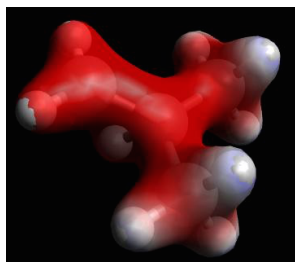
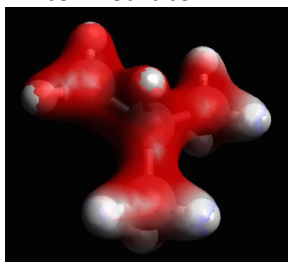
10 C -0.421631 CH<sub>2</sub>

11 H 0.217962

12 H 0.217904

13 H 0.235166

Sum of Mulliken charges = 1.00000

*Intermediate 2*

Mulliken charges:

1 C -0.143789 Central Carbon (CH)

2 C -0.346346 CH<sub>3</sub>

3 H 0.204196

4 H 0.170403

5 H 0.194929

6 C -0.346336 CH<sub>3</sub>

7 H 0.194925

8 H 0.170405

9 H 0.204201

10 C -0.076766 CH<sub>2</sub>

11 H 0.237421

12 H 0.268378

13 H 0.268378

Sum of Mulliken charges = 1.00000

Carbon to be attacked on *Intermediate 1* has a point charge of 0.251799, and the one on *Intermediate 2* has a point charge of -0.076766. As Chlorine is negatively charged, it is most likely to attack the carbon that has the most positive charge. As a carbon on *Intermediate 1* has a more positive charge than of the *Intermediate 2*, Chlorine is more likely to attack the *Intermediate 1*.

d)

	Theoretical					MM	
	Hartree	J	kJ	kJ/mol	kcal/mol	kJ/mol	kcal/mol
Reactant	-156.1238464	-6.80661E-16	-6.80661E-19	-409893.8484	-97969.11873	31.4064	7.506161006
Int1	-156.4565501	-6.82111E-16	-6.82111E-19	-410767.3422	-98177.8933	6.36615	1.521516216
Int2	-156.4126803	-6.8192E-16	-6.8192E-19	-410652.1646	-98150.3646	-0.633061	-0.151302212
Prod1	-616.2199957	-2.68656E-15	-2.68656E-18	-1617848.851	-386683.5933	30.0454	7.180880645
Prod2	-616.215044	-2.68654E-15	-2.68654E-18	-1617835.851	-386680.486	9.05649	2.164510166

For energies of all of them (reactant, intermediates and products), Theoretical calculations yielded a much lower energy, while MM showed almost exclusively positive energies. Out of all, according to *theoretical calculations*, Product 1 is shown to be the most stable, followed by Product 2. The least stable one (the one with the highest energy) surprisingly is the reactant. However, the order is different according to *MM calculations*, the most stable one is the intermediate 1 and the least stable one is the reactant.

Energy population of Product 1

$$\frac{\exp\left(-\frac{-616.2199957 \times 43.6 \times 10^{-19}}{300 \times 1.3806488 \times 10^{-23}}\right)}{\exp\left(-\frac{-616.2199957 \times 43.6 \times 10^{-19}}{300 \times 1.3806488 \times 10^{-23}}\right) + \exp\left(-\frac{-616.215044 \times 43.6 \times 10^{-19}}{300 \times 1.3806488 \times 10^{-23}}\right)}$$

$$= 0.994581...$$

Energy population of Product 2

$$\frac{\exp\left(-\frac{-616.215044 \times 43.6 \times 10^{-19}}{300 \times 1.3806488 \times 10^{-23}}\right)}{\exp\left(-\frac{-616.2199957 \times 43.6 \times 10^{-19}}{300 \times 1.3806488 \times 10^{-23}}\right) + \exp\left(-\frac{-616.215044 \times 43.6 \times 10^{-19}}{300 \times 1.3806488 \times 10^{-23}}\right)}$$

$$= 0.00541915...$$

Energy pop-n of Product 1/Product 2

$$= 181.53$$

e)

	H (H/part)	H (kcal/mol)	S (cal/molK)	S (kcal/mol)	G (H/part)	G
Reactant	-155.988983	-97884.56873	69.816	0.069816	-156.022154	-97905.38385
Int1	-156.309344	-98085.5983	73.564	0.073564	-156.344297	-98107.53164
Int2	-156.26392	-98057.09431	70.429	0.070429	-156.297383	-98078.09266
Prod1	-616.0674	-386588.1461	76.641	0.076641	-616.103814	-386610.9963
Prod2	-616.061612	-386584.5141	78.403	0.078403	-616.098864	-386607.8901

\*1 Hartree/particle = 627.5095 kcal/mol

$$f) k_1/k_2 = \exp(-E_{a1}/RT)/\exp(-E_{a2}/RT)$$

$$E_{a1} = E(\text{int1}) - E(\text{react}) = -98177.8933 - (-97969.11873) = -208.7745661 \text{ kcal/mol}$$

$$E_{a2} = E(\text{int2}) - E(\text{react}) = -98150.3646 - (-97969.11873) = -181.2458718 \text{ kcal/mol}$$

\*Note: weirdly enough, my activation energies are negative.

$$T = 300 \text{ K}$$

$$R = 1.9872041 \times 10^{-3} \text{ kcal/molK}$$

$$\text{Therefore, } k_1/k_2 = 1.3302 \times 10^{20}.$$

$$g) k = k_B T / c^n h \cdot \exp(-\Delta G / RT)$$

$$k_B = 1.3806488 \times 10^{-23} \text{ J/K}$$

$$T = 300 \text{ K}$$

$$c = 1 \text{ mol/L}$$

$$n = 2$$

$$h = 6.62606957 \times 10^{-34} \text{ J/s}$$

$$R = 1.9872041 \times 10^{-3} \text{ kcal/molK}$$

$$\Delta G_1 = G(\text{int1}) - G(\text{react}) = -98107.53164 - (-97905.38385) = -202.1477929 \text{ kcal/mol}$$

$$\Delta G_2 = G(\text{int2}) - G(\text{react}) = -98078.09266 - (-97905.38385) = -172.7088122 \text{ kcal/mol}$$

$$k_1 = \frac{1.3806488 \times 10^{-23} \times 300 \times \exp\left(\frac{202.1477929}{300 \times 1.9872041 \times 10^{-3}}\right)}{1^2 \times 6.62606957 \times 10^{-34}} = 1.14175 \times 10^{160} \text{ sM}^2 \text{ (sL}^2/\text{mol}^2\text{)}$$

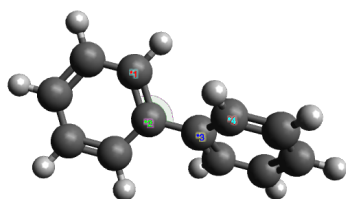
$$k_2 = \frac{1.3806488 \times 10^{-23} \times 300 \times \exp\left(\frac{172.7088122}{300 \times 1.9872041 \times 10^{-3}}\right)}{1^2 \times 6.62606957 \times 10^{-34}} = 4.08995 \times 10^{138} \text{ sM}^2 \text{ (sL}^2/\text{mol}^2\text{)}$$

$k_1$  is much faster than  $k_2$ . Therefore, it can be predicted that path 1 would be much more favored than path 2. It agrees with Markovnikov rule, where acid hydrogen (from HCl) attaches to the carbon with fewer substituents (ie.  $\text{CH}_2$  end of  $(\text{CH}_3)_3\text{C}=\text{CH}_2$ ) and the halide ( $\text{Cl}^-$ ) attaches to the carbon with more alkyl substituents (ie.  $\text{C}^+$  on Intermediate 1).

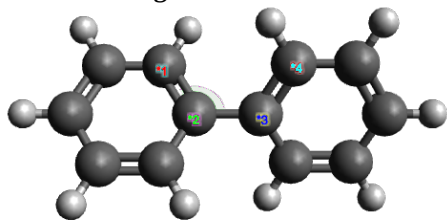
### Question 3

a) Minimum energy value: 164.664 kJ/mol

Dihedral angle: 53.9

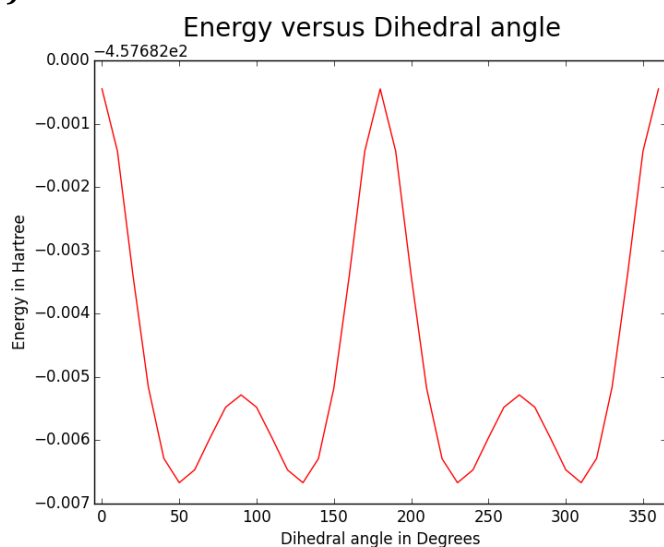


**b) Minimum energy value:** -460.2718448 Hartree = -288824.73 kcal/mol = -1.21e6 kJ/mol  
**Dihedral angle:** 45.5



↑ Dihedral Angle: 45.5°  
 Distances (Å): 1.383 Å 1.401 Å 1.383 Å

**c)**



Most stable when dihedral degree is 45.5, 134.5, 225.5 and 314.5. Most unstable when 0, 180 and 360.

**d) and e)** Professor, please find the code attached. Unfortunately, python could not calculate such high values. Energy of each angle is about -457.68 Hartree, kb is  $3.1668 \times 10^{-6}$  Hartree/K, and temperatures vary. For example, below I tried computing the energy of the first state (ie. Energy of angle 0).

$$\exp\left(-\frac{-457.682449}{3.1668114 \times 10^{-6} \times 270}\right), \text{ where } E \text{ equals to the energy of angle 0, kb as indicated above}$$

and K is 270 K. It results in  $4.93409... \times 10^{232467}$ . Python cannot read such information, and writes it as infinity resulting in no graph. Therefore, it becomes impossible to calculate the Q on python with such extremely low values of Energies.

\*Energy values are attached in a text.