# Assignment 1

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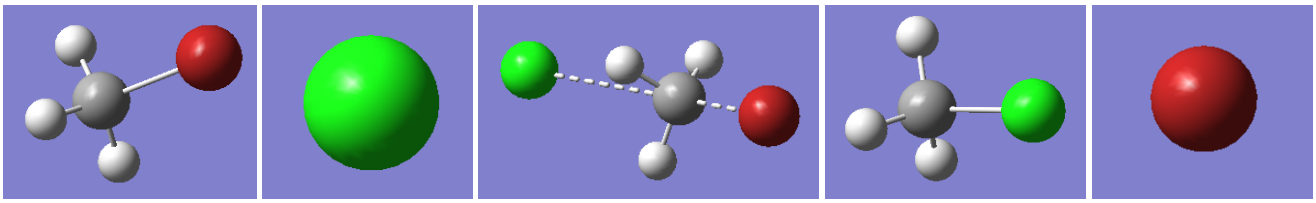
**Note:** 1 a.u. = 1 Hartree = 2625 kJ/mol = 627.51 kcal/mol = 27.21 eV (source).

## Question 1

Take five organic reactions of your choice, calculate the reaction energies (in kcal/mol), and include the reactions with structures.

### Reaction 1

$CH_3Br + Cl^- \rightarrow CH_3Cl + Br^-$



Images from left to right: Bromo Methane, Chloride Ion, Transition State, Chloro Methane, Bromide Ion.

| Molecules | Energy (in a.u.) |
|---|---|
| $CH_3Br$ | -2583.81369428 |
| $Cl^-$ | -454.48042161 |
| $(CH_3ClBr)^-$ | -3038.30454810 |
| $CH_3Cl$ | -493.72311643 |
| $Br^-$ | -2544.53229064 |

Energy of Reactants = -3038.29411589 a.u.

Energy of Transition State = -3038.30454810 a.u.

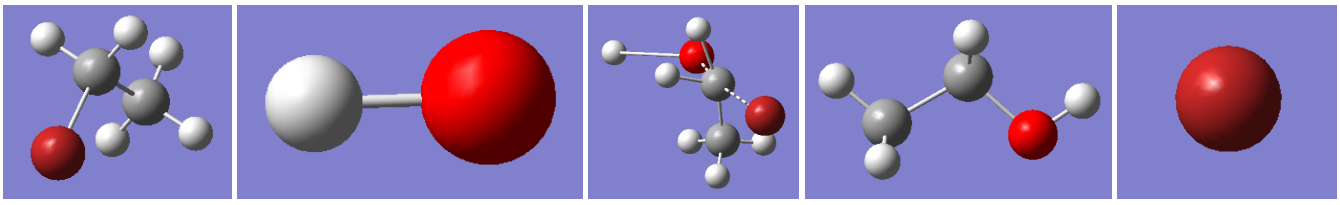
Energy of Products = -3038.25540707 a.u.

Reaction Energy = 0.03870882 a.u. = 24.2901716382 kcal/mol

Activation Energy = -0.01043221 a.u. = -6.5463160971 kcal/mol

### Reaction 2

$C_2H_5Br + OH^- \rightarrow C_2H_5OH + Br^-$



Images from left to right: Bromo Ethane, Hydroxide Ion, Transition State, Ethyl Alcohol, Bromide Ion.

| Molecules | Energy (in a.u.) |
|---|---|
| $C_2H_5Br$ | -2622.39474053 |
| $OH^-$ | -74.06501719 |
| $(C_2H_5BrOH)^-$ | -2695.89152909 |
| $C_2H_5OH$ | -152.13267481 |
| $Br^-$ | -2544.53229064 |

Energy of Reactants = -2696.45975772 a.u.

Energy of Transition State = -2695.95511133 a.u.

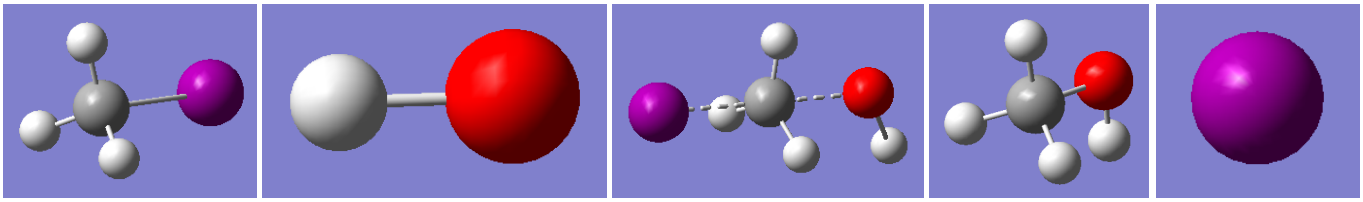
Energy of Products = -2696.66496545 a.u.

Reaction Energy = -0.20520773 a.u. = -128.7699026523 kcal/mol

Activation Energy = 0.56822863 a.u. = 356.5691476113 kcal/mol

## Reaction 3

$CH_3I + OH^- \rightarrow CH_3OH + I^-$



Images from left to right: Iodo Methane, Hydroxide Ion, Transition State, Methyl Alcohol, Iodide Ion.

| Molecules | Energy (in a.u.) |
|---|---|
| $CH_3I$ | -6889.83984463 |
| $OH^-$ | -74.06501719 |
| $(CH_3IOH)^-$ | -6963.70894514 |
| $CH_3OH$ | -113.54919323 |
| $I^-$ | -6850.60517305 |

Energy of Reactants = -6963.90486182 a.u.

Energy of Transition State = -6963.70894514 a.u.

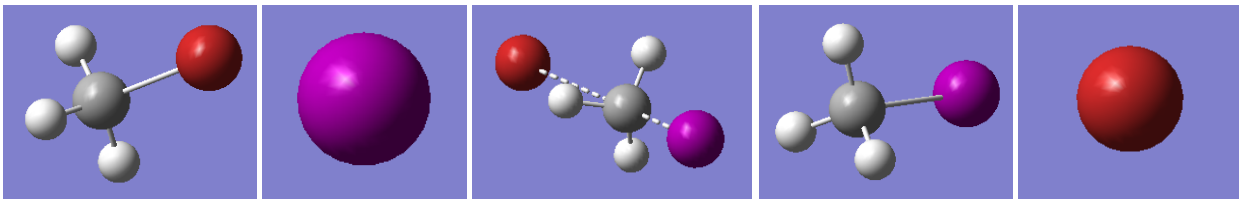
Energy of Products = -6964.15436628 a.u.

Reaction Energy = -0.24950446 a.u. = 156.5665436946 kcal/mol

Activation Energy = 0.19591668 a.u. = 122.9396758668 kcal/mol

## Reaction 4

$CH_3Br + I^- \rightarrow CH_3I + Br^-$



Images from left to right: Bromo Methane, Iodide Ion, Transition State, Iodo Methane, Bromide Ion.

| Molecules | Energy (in a.u.) |
|---|---|
| $CH_3Br$ | -2583.81369428 |
| $I^-$ | -6850.60517305 |
| $(CH_3BrI)^-$ | -9434.38345603 |
| $CH_3I$ | -6889.83984463 |
| $Br^-$ | -2544.53229064 |

Energy of Reactants = -9434.41886733 a.u.

Energy of Transition State = -9434.38345603 a.u.

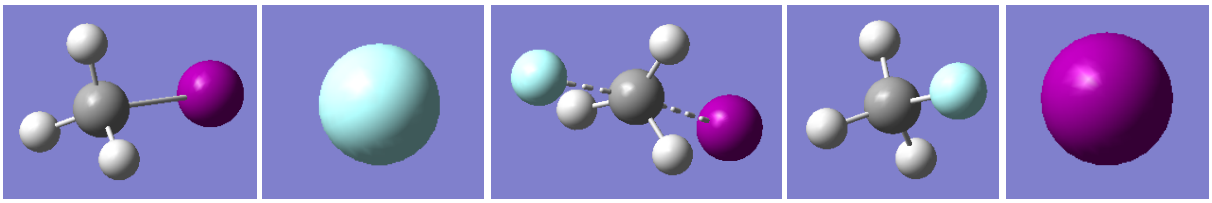
Energy of Products = -9434.37213527 a.u.

Reaction Energy = 0.04673206 a.u. = 29.3248349706 kcal/mol

Activation Energy = 0.0354113 a.u. = 22.220944863 kcal/mol

### Reaction 5

$CH_3I + F^- \rightarrow CH_3F + I^-$



Images from left to right: Iodo Methane, Fluoride Ion, Transition State, Fluoro Methane, Iodide Ion.

| Molecules | Energy (in a.u.) |
|---|---|
| $CH_3I$ | -6889.83984463 |
| $F^-$ | -97.61331475 |
| $(CH_3IF)^-$ | -6987.49081589 |
| $CH_3F$ | -137.16905607 |
| $I^-$ | -6850.60517305 |

Energy of Reactants = -6987.45315938 a.u.

Energy of Transition State = -6987.49081589 a.u.

Energy of Products = -6987.77422912 a.u.

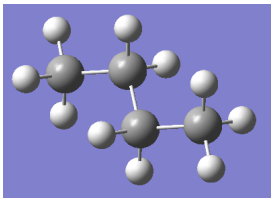
Reaction Energy = -0.32106974 a.u. = -201.4744725474 kcal/mol

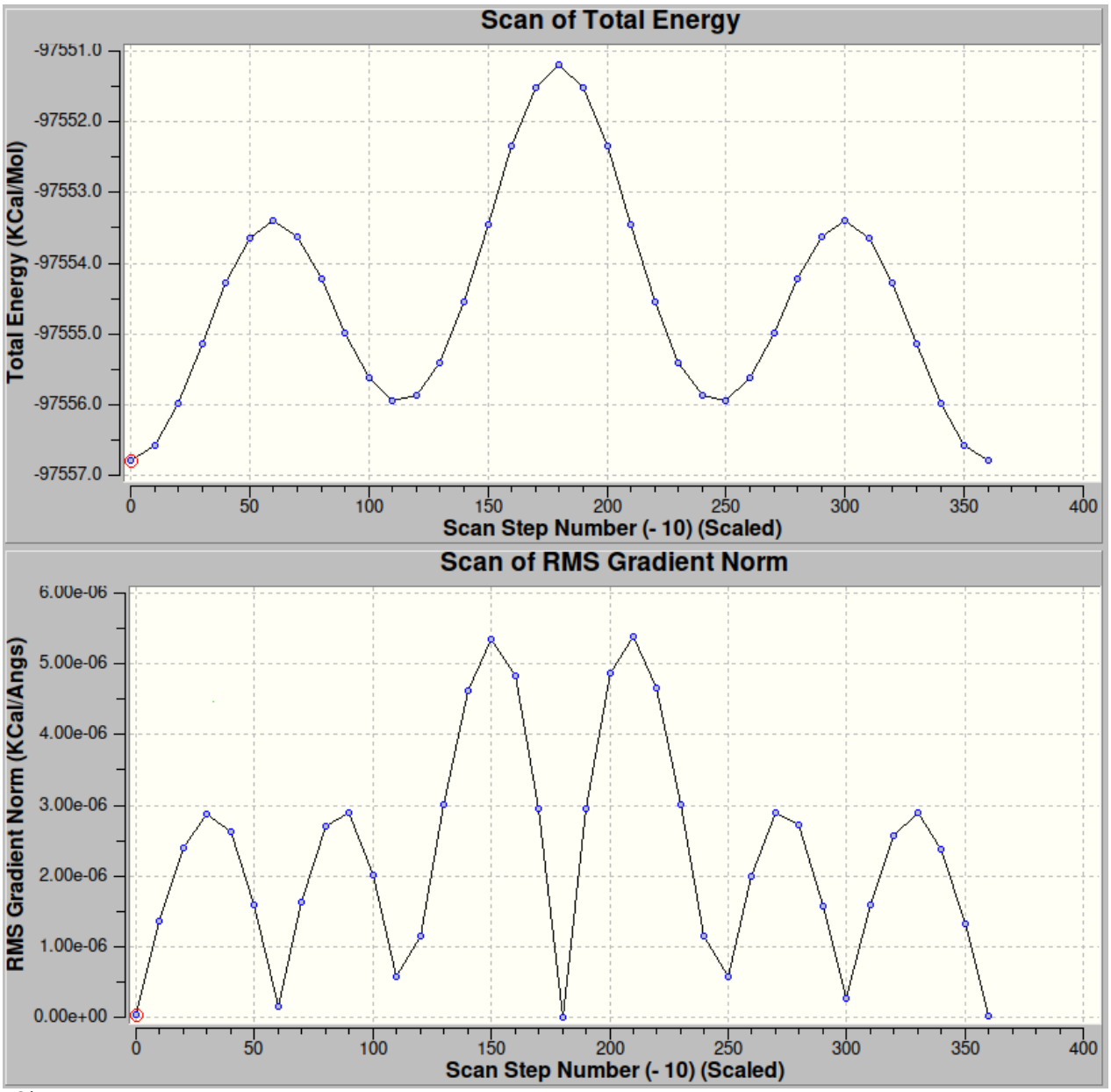
Activation Energy = -0.03765651 a.u. = -23.6298365901 kcal/mol

**Note:** The transition states for reactions 2, 3 and 5 could not be optimized due to errors in Gaussian.

## Question 2

Perform conformational analysis of butane and plot the energy (in kcal/mol) as a function of the rotation angle.



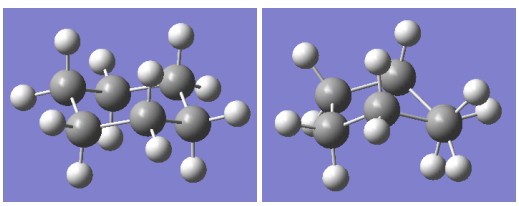


q2/1.png

We can observe the most stable conformation is the antiperiplanar at 180 degrees and the least stable conformation is the synperiplanar at 0 or 360 degrees. The gauche confirmations at 60 and 300 degrees are the second most stable, while the eclipsed at 120 and 240 degrees are the second least stable.

## Question 3

Calculate the energy difference between the chair and boat forms of cyclohexane.



Images from left to right: Chair Cyclohexane, Boat Cyclohexane.

Energy of Chair Cyclohexane = -231.48267163 a.u.

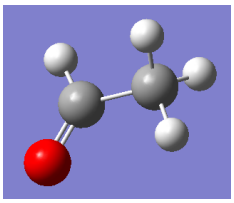
Energy of Boat Cyclohexane = -231.47297425 a.u.

Energy Difference = 0.00969738 a.u. = 6.0852029238 kcal/mol = 25.46kJ/mol

The boat form is thus less stable than the chair form. The energy difference calculated to be 25.46kJ/mol is close to the theoretical value of 23kJ/mol (source).

## Question 4

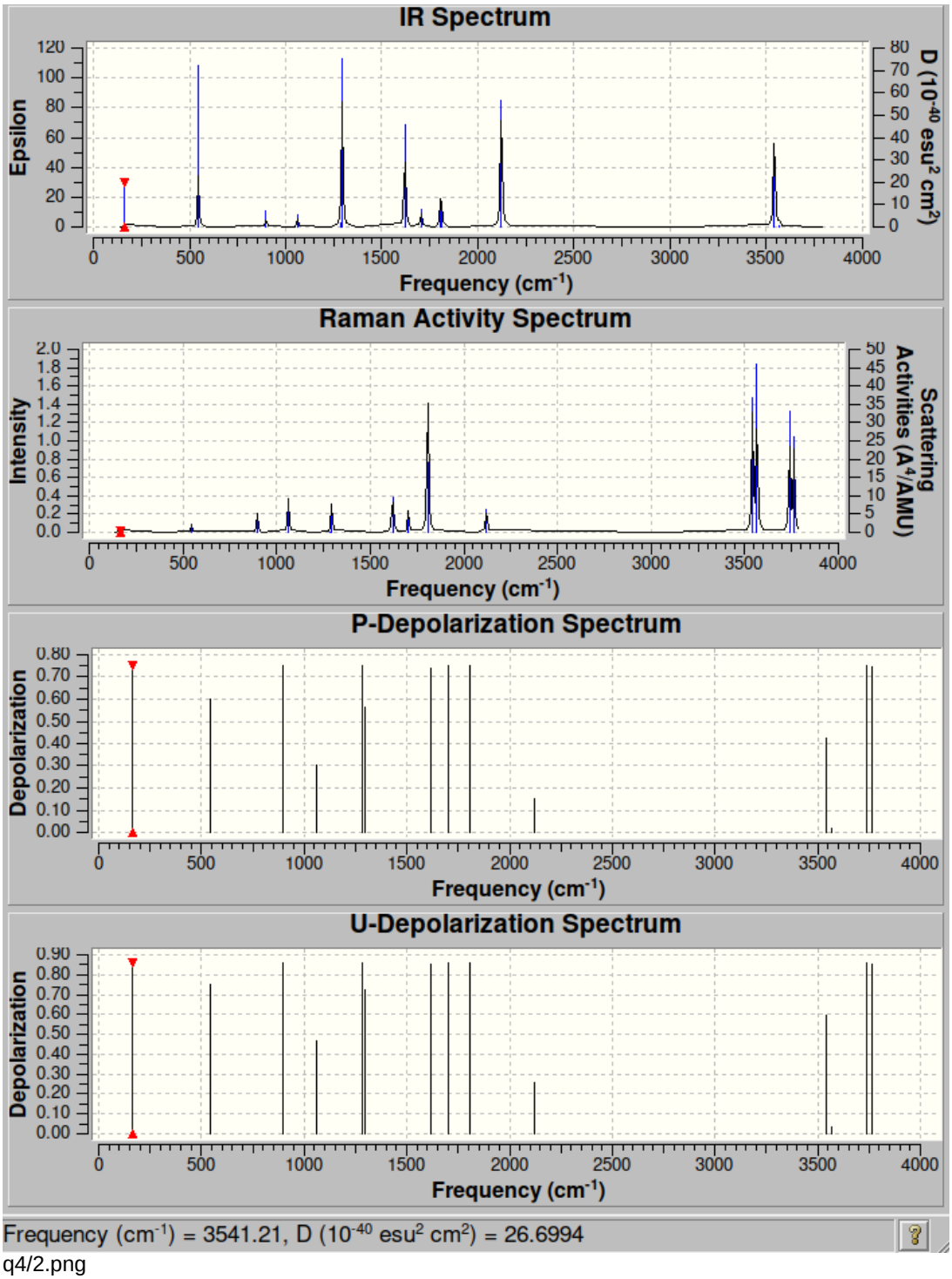
Calculate the vibrational spectrum of Acetaldehyde, obtain the experimental spectrum and compare the two.



## Vibrational Spectrum

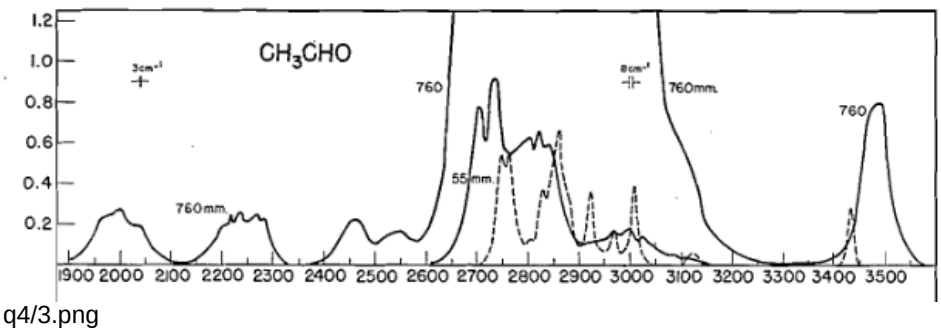
| Mode # | Freq | Infrared | Raman Activity | Depolar-P | Depolar-U |
|---|---|---|---|---|---|
| 1 | 162.92 | 0.7998 | 0.4962 | 0.7500 | 0.857 |
| 2 | 545.36 | 9.8541 | 1.1334 | 0.6011 | 0.750 |
| 3 | 896.42 | 1.5578 | 3.3816 | 0.7500 | 0.857 |
| 4 | 1062.42 | 1.4973 | 5.7264 | 0.3032 | 0.465 |
| 5 | 1284.95 | 0.5148 | 0.0008 | 0.7500 | 0.857 |
| 6 | 1294.00 | 24.3848 | 5.6211 | 0.5646 | 0.721 |
| 7 | 1619.59 | 18.5906 | 9.6927 | 0.7381 | 0.849 |
| 8 | 1703.87 | 3.3477 | 4.9540 | 0.7499 | 0.857 |
| 9 | 1806.42 | 4.0288 | 15.0184 | 0.7500 | 0.857 |
| 10 | 1808.14 | 4.7065 | 19.2270 | 0.7402 | 0.850 |
| 11 | 2121.60 | 30.0689 | 6.2810 | 0.1490 | 0.259 |
| 12 | 3541.21 | 23.6999 | 36.7894 | 0.4259 | 0.597 |
| 13 | 3564.81 | 0.7282 | 46.0108 | 0.0160 | 0.031 |
| 14 | 3739.50 | 0.0025 | 33.1865 | 0.7500 | 0.857 |
| 15 | 3763.15 | 0.1421 | 26.0496 | 0.7480 | 0.855 |

q4/1.png

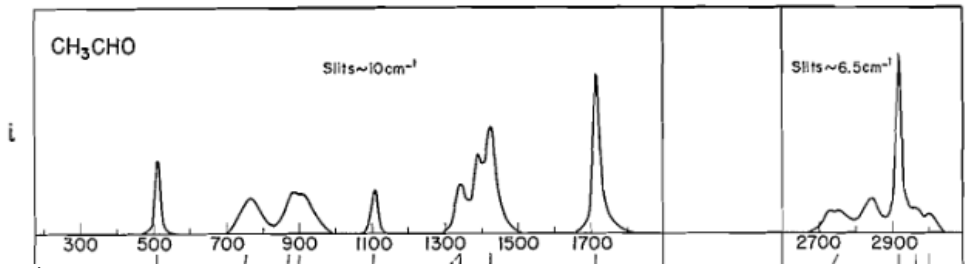



q4/2.png

**Experimental Spectrum**




q4/3.png



q4/4.png

Images from top to bottom: Experimental IR Spectrum, Raman Activity Spectrum (Source: https://cdnsciencepub.com/doi/pdf/10.1139/v56-141).

### Comparision

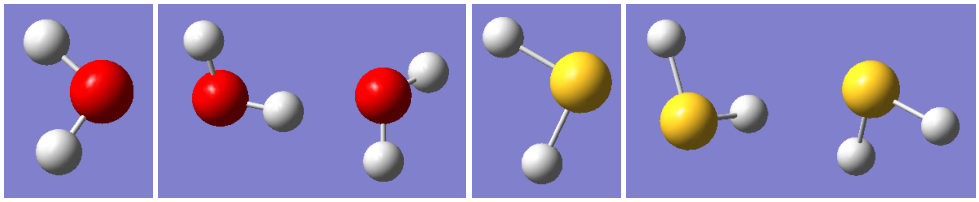
We notice several common peaks in the vibrational and experimental spectra, e.g. around $2200cm^{-1}$ and $3500cm^{-1}$ for the IR spectrum, around $500cm^{-1}, 900cm^{-1}, 1100cm^{-1}, 1700cm^{-1}$ for the Raman spectrum.

However, there are several patterns observed only in one of the two spectra. For example, the peak around $2900cm^{-1}$ in the experimental Raman spectrum is missing in the vibrational counterpart. Similarly, the sharp peak around $2200cm^{-1}$ is observed only in the vibrational IR spectrum.

These can be attributed to a wide spectrum of issues, such as approximations employed at different stages of the computation, numerical issues, limitations of physical apparatus, etc.

## Question 5

Hydrogen bond between two water molecules are stronger than that between two hydrogen sulfide molecules. Prove.



Images from left to right: Water Monomer, Water Dimer, Hydrogen Sulphide Monomer, Hydrogen Sulphide Dimer.

| Molecules | Energy (in a.u.) |
|---|---|
| Water Monomer | -74.96590117 |
| Water Dimer | -149.94124350 |
| Hydrogen Sulphide Monomer | -394.31163006 |
| Hydrogen Sulphide Dimer | -788.62430206 |

Energy change in Water due to H-bonding = -0.00944116 a.u. = -5.9244223116 kcal/mol

Energy change in Hydrogen Sulphide due to H-bonding = -0.00104194 a.u. = 0.6538277694 kcal/mol

We notice that the change in energy is 9 times more in case of Water than in case of Hydrogen Sulphide. This can be attributed to hydrogen bonding, which is evident in the optimized structure of the dimers. We can thus argue experimentally that the hydrogen bond between two water molecules is stronger than that of two hydrogen sulphide molecules.