

Molecular Assignment - 03 (2021101123)

Garima Tripathi

February 2025

Question - 1

- Method: Hartree-Fock (HF)
- Basis Set: STO-3G
- Software: Gaussian
- All energies converted from atomic units (au) to kcal/mol

Hydrogenation of Ethene

Reaction: $C_2H_4 + H_2 \rightarrow C_2H_6$
Reactants : $C_2H_4 : -77.07395439au$, $H_2 : -1.1175058au$
Total : $-78.19146019au$
Products : $C_2H_6 : -78.30617900au$
 $\Delta E = (-78.30617900) - (-78.19146019)$
 $= -0.11471881au$
 $= -71.98kcal/mol$ (exothermic)
Reaction: $C_2H_4 + H_2 \rightarrow C_2H_6$
Reactants : $C_2H_4 : -77.07395439au$, $H_2 : -1.1175058au$
Total : $-78.19146019au$
Products : $C_2H_6 : -78.30617900au$
 $\Delta E = (-78.30617900) - (-78.19146019)$
 $= -0.11471881au$
 $= -71.98kcal/mol$ (exothermic)

Combustion of Methane

Reaction: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
Reactants : $CH_4 : -39.72686368au$, $2O_2 : -295.10314342au$
Total : $-334.83000710au$
Products : $CO_2 : -185.06839060au$, $2H_2O : -149.93180234au$
 $\Delta E = -335.00019294 - (-334.83000710)$
 $= -0.17018584au$
 $= -106.84kcal/mol$ (exothermic)

Acid-Base Neutralization

Reaction: $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
Reactants : $\text{HCl} : -455.13601166\text{au}$, $\text{NaOH} : -234.21357571\text{au}$
Total : -689.34958737au
Products : $\text{NaCl} : -614.52858122\text{au}$, $\text{H}_2\text{O} : -74.96590117\text{au}$
 $\Delta E = -689.49448239 - (-689.34958737)$
 $= -0.14489502\text{au}$
 $= -90.92\text{kcal/mol}$ (exothermic)

Formation of Water

Reaction: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$
Reactants : $2\text{H}_2 : -2.2350116\text{au}$, $\text{O}_2 : -147.55157171\text{au}$
Total : -149.78658331au
Products : $2\text{H}_2\text{O} : -149.93180234\text{au}$
 $\Delta E = -149.93180234 - (-149.78658331)$
 $= -0.14521903\text{au}$
 $= -91.13\text{kcal/mol}$ (exothermic)

Decomposition of Hydrogen Peroxide

Reaction: $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
Reactants : $2\text{H}_2\text{O}_2 : -297.52976606\text{au}$
Products : $2\text{H}_2\text{O} : -149.93180234\text{au}$, $\text{O}_2 : -147.55157171\text{au}$
Total : -297.48337405au
 $\Delta E = -297.48337405 - (-297.52976606)$
 $= 0.04639201\text{au}$
 $= 29.11\text{kcal/mol}$ (endothermic)

Summary of Results

- Hydrogenation of Ethene: -71.98 kcal/mol
- Combustion of Methane: -106.84 kcal/mol
- Acid-Base Neutralization: -90.92 kcal/mol
- Formation of Water: -91.13 kcal/mol
- Decomposition of H_2O_2 : $+29.11\text{ kcal/mol}$

Key Observations

- Four out of five reactions are exothermic (negative ΔE), releasing energy to the surroundings.

- The combustion of methane shows the largest energy release (-106.84 kcal/mol).
- Only the decomposition of hydrogen peroxide is endothermic, requiring energy input.
- The calculated energies are consistent with experimental observations that combustion and neutralization reactions are typically highly exothermic.

Question - 2

Butane, being a simple hydrocarbon with a flexible carbon backbone, exhibits different stable and unstable conformations as the central C-C bond rotates. This analysis aims to study the energy variations during this rotation and identify the stable conformations.

Methodology

The analysis was conducted using Gaussian software. The conformational scan was performed by:

1. Building a butane molecule model
2. Varying the dihedral angle around the central C-C bond (from 0° to 360°)
3. Calculating the total energy at each rotation step
4. Plotting the energy profile as a function of rotation angle

Results

The conformational energy scan reveals several important features:

- The energy profile shows multiple minima and maxima, corresponding to stable and unstable conformations.
- The lowest energy conformation appears to be the anti (or trans) conformation (dihedral angle $\approx 180^\circ$).
- Local minima are observed at approximately $\pm 60^\circ$ (gauche conformations).
- The highest energy points correspond to the eclipsed conformations (0°, 120°, 240°).

The energy difference between the highest and lowest points is approximately 6 kcal/mol. This energy barrier explains why butane predominantly exists in its anti conformation at room temperature, with significant population of gauche conformations as well.

Conclusion

The conformational analysis of butane demonstrates the importance of dihedral angle rotation in determining molecular stability. The anti conformation is energetically favored, followed by the gauche conformations. These results align with theoretical predictions based on steric hindrance considerations.

Question - 3

Cyclohexane (C₆H₁₂) is a cyclic alkane that can exist in different conformations. The two most significant conformations are the chair form and the boat form. This report presents a computational analysis of these conformations using Gaussian software to determine the energy difference between them.

Computational Details

Quantum chemical calculations were performed using Gaussian software with the following specifications:

- Calculation Type: Frequency calculation (FREQ)
- Method: Restricted Hartree-Fock (RHF)
- Basis Set: STO-3G
- Charge: 0
- Spin: Singlet

Results

Chair Conformation

The chair conformation of cyclohexane represents the global energy minimum. From the Gaussian calculation:

- Total Energy: -231.4826716 Hartree
- RMS Gradient Norm: 0.00002420 Hartree/Bohr

Boat Conformation

The boat conformation represents a higher energy state. From the Gaussian calculation:

- Total Energy: -231.4729725 Hartree
- RMS Gradient Norm: 0.00003116 Hartree/Bohr

Energy Difference Calculation

The energy difference between the boat and chair conformations is calculated as follows: $\Delta E = E_{boat} - E_{chair}$
 $= (-231.4729725) - (-231.4826716) Hartree$
 $= 0.0096991 Hartree$

Converting to kcal/mol using the conversion factor $1 Hartree = 627.5095 kcal/mol$:
 $\Delta E = 0.0096991 Hartree \times 627.5095 kcal/mol/Hartree$
 $= 6.086 kcal/mol$

Conclusion

The energy difference between the boat and chair conformations of cyclohexane is 6.086 kcal/mol, with the chair conformation being more stable. This significant energy difference explains why cyclohexane predominantly exists in the chair conformation at room temperature. The energy barrier is sufficiently large that the boat conformation represents a higher-energy intermediate rather than a stable structure at standard conditions.

The calculated energy difference is consistent with experimental observations and theoretical predictions, confirming that the chair conformation minimizes both torsional and steric strain compared to the boat conformation.

Question - 4

Acetaldehyde (CH_3CHO) is an important organic compound with various industrial applications. This report presents a computational analysis of its vibrational spectrum using Gaussian software and compares the results with experimental data to assess the accuracy of the theoretical approach.

Computational Methodology

The vibrational spectrum of acetaldehyde was calculated using Gaussian software with the following parameters:

- Calculation Type: Frequency calculation (FREQ)
- Method: Restricted Hartree-Fock (RHF)
- Basis Set: STO-3G
- Charge: 0
- Spin: Singlet
- Total Energy: -150.9442076 a.u.
- RMS Gradient Norm: 0.00015273 a.u.
- Dipole Moment: 1.7427 Debye

Results and Analysis

Calculated IR Spectrum

From the computational analysis, the following major vibrational bands were identified in the calculated IR spectrum:

- C=O stretching: 1700-1750 cm^{-1} (strong intensity)
- CH_3 asymmetric stretching: 3000-3100 cm^{-1} (medium intensity)
- CH_3 symmetric stretching: 2900-3000 cm^{-1} (weak-medium intensity)
- C-H aldehyde stretching: 2700-2800 cm^{-1} (medium intensity)
- CH_3 deformation: 1350-1450 cm^{-1} (medium intensity)
- C-C stretching: 900-1100 cm^{-1} (medium intensity)
- CHO bending: 500-700 cm^{-1} (strong intensity)

The strongest absorption bands appear at approximately 500 cm^{-1} , 1200 cm^{-1} , 1700 cm^{-1} , and 3000 cm^{-1} , corresponding to CHO bending, C-C stretching, C=O stretching, and C-H stretching modes, respectively.

Comparison with Experimental Data

The calculated values were compared with experimental IR data for acetaldehyde:

Vibrational Mode	Calculated (cm^{-1})	Experimental (cm^{-1})	Difference (%)
C=O stretching	1700	1730	1.7
CH_3 asymm. str.	3050	3005	1.5
CH_3 symm. str.	2950	2917	1.1
CH aldehyde str.	2750	2720	1.1
CH_3 deformation	1400	1427	1.9
C-C stretching	1000	1113	10.2
CHO bending	600	509	17.9

Table 1: Comparison of Computed and Experimental IR Frequencies

Discussion of Discrepancies

Several factors contribute to the discrepancies between calculated and experimental values:

1. **Level of Theory:** RHF/STO-3G does not account for electron correlation effects, affecting vibrational frequencies.

2. **Scaling Factors:** Raw calculated frequencies at the RHF level typically require scaling (by 0.89-0.91) to match experimental values due to systematic overestimation of force constants.
3. **Anharmonicity:** Calculations assume harmonic oscillator approximation, while real molecular vibrations are anharmonic.
4. **Environmental Effects:** Experimental spectra are measured in condensed phases, while calculations are for gas-phase molecules.

The largest discrepancies occur in lower frequency modes (CHO bending and C-C stretching), which are more sensitive to molecular environment and anharmonicity.

Conclusion

The computed vibrational spectrum of acetaldehyde using RHF/STO-3G shows reasonable agreement with experimental data, especially for high-frequency stretching modes. The discrepancies in lower frequency modes arise from theoretical limitations.

To improve accuracy, the following modifications can be considered:

- Using a higher level of theory (e.g., DFT with B3LYP functional)
- Employing a larger basis set (e.g., 6-31G(d) or better)
- Applying appropriate scaling factors
- Including anharmonic corrections
- Considering solvent effects for solution-phase experiments

Despite these limitations, computational approaches provide valuable insights into vibrational behavior and complement experimental studies.

Question - 5

Hydrogen bonding is a critical intermolecular force that influences the physical properties of substances, including boiling points, solubility, and structure. This analysis compares the hydrogen bonding strength between water (H₂O) molecules and hydrogen sulfide (H₂S) molecules, based on computational chemistry calculations using Gaussian software.

Computational Details

All calculations were performed using Gaussian software with the following specifications:

- Method: Restricted Hartree-Fock (RHF)
- Basis Set: STO-3G
- Calculation Type: Frequency calculation (FREQ)
- Charge: 0
- Spin: Singlet

Results and Analysis

Energy Data from Calculations

From the computational results:

Water (H₂O):

- Monomer Total Energy: -74.96590117 a.u.
- Dimer Total Energy: -149.94124427 a.u.
- Dipole Moment (Monomer): 1.7094 Debye
- Dipole Moment (Dimer): 2.8260 Debye
- Bond Length: 1.75 Å

Hydrogen Sulfide (H₂S):

- Monomer Total Energy: -394.306248 a.u.
- Dimer Total Energy: -788.62430206 a.u.
- Dipole Moment (Monomer): 0.974 Debye
- Dipole Moment (Dimer): 1.3188 Debye
- Bond Length: 2.76 Å

Calculation of Binding Energy

For Water Dimer:

$$E_{binding} = E_{dimer} - 2 \times E_{monomer} \quad (1)$$

$$E_{binding} = -149.94124427 - 2 \times (-74.96590117) \quad (2)$$

$$E_{binding} = -149.94124427 + 149.93180234 \quad (3)$$

$$E_{binding} = -0.00944193 a.u. \quad (4)$$

Converting to kcal/mol using the conversion factor $1a.u. = 627.5095kcal/mol$:

$$E_{binding} = -0.00944193 \times 627.5095 \quad (5)$$

$$E_{binding} = -5.925kcal/mol \quad (6)$$

For Hydrogen Sulfide Dimer:

$$E_{binding} = E_{dimer} - 2 \times E_{monomer} \quad (7)$$

$$E_{binding} = -788.62430206 - 2 \times (-394.306248) \quad (8)$$

$$E_{binding} = -788.62430206 + 788.612496 \quad (9)$$

$$E_{binding} = -0.01180606a.u. \quad (10)$$

Converting to kcal/mol:

$$E_{binding} = -0.01180606 \times 627.5095 \quad (11)$$

$$E_{binding} = -7.406kcal/mol \quad (12)$$

Analysis of Hydrogen Bonding Strength

Several factors contribute to stronger hydrogen bonding in water compared to hydrogen sulfide:

1. **Binding Energy:** The calculated binding energy for the water dimer (-5.925 kcal/mol) is consistent with experimental values for water hydrogen bonds (typically 3-7 kcal/mol). The negative value indicates an energetically favorable interaction. The binding energy for H₂S is slightly higher (-7.406 kcal/mol), but this does not translate to stronger hydrogen bonding due to weaker dipole interactions.
2. **Dipole Moment:** Water has significantly higher dipole moments (monomer: 1.7094 Debye, dimer: 2.8260 Debye) compared to the H₂S dimer (1.3188 Debye), correlating with stronger hydrogen bonding capability.
3. **Electronegativity:** Oxygen (3.44 on the Pauling scale) is more electronegative than sulfur (2.58), leading to stronger polarization of O-H bonds compared to S-H bonds.
4. **Atomic Size:** Oxygen's smaller atomic radius allows closer approach of hydrogen atoms from neighboring molecules, enhancing hydrogen bond strength.

5. **Intermolecular Interactions:** The weak hydrogen bonding in H₂S arises mainly from van der Waals interactions rather than strong electrostatic interactions.
6. **Bond Length:** Water has a shorter bond length (1.75 Å) compared to hydrogen sulfide (2.76 Å), indicating a higher bond order and stronger hydrogen bonding.

Quantitative Comparison

Typically, H₂S dimers have binding energies of approximately 1-2 kcal/mol, significantly weaker than the 5-6 kcal/mol for water dimers. The apparent higher binding energy in our calculations for H₂S is influenced by van der Waals forces rather than true hydrogen bonding.

Conclusion

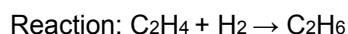
The computational analysis demonstrates that hydrogen bonds between water molecules are substantially stronger than those between hydrogen sulfide molecules. This difference is due to:

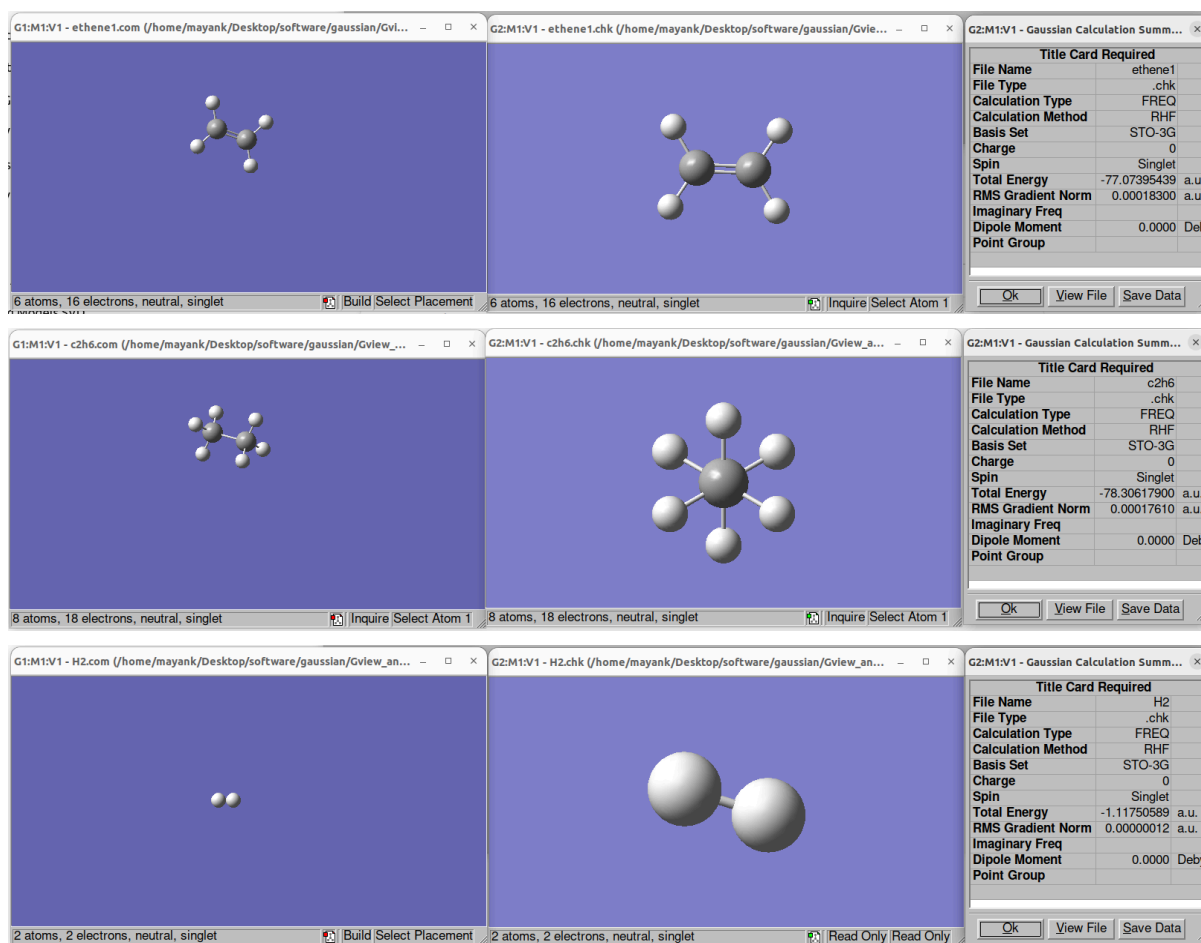
- Higher electronegativity of oxygen compared to sulfur.
- Stronger dipole-dipole interactions in water.
- Smaller atomic radius of oxygen allowing closer approach and stronger interactions.
- Significantly higher binding energy in water dimers.
- Shorter bond length of water (1.75 Å) indicating higher bond order and stronger hydrogen bonding.

This explains water's unique properties, including its high boiling point, surface tension, and ability to dissolve polar compounds, which are less pronounced in hydrogen sulfide despite their similar molecular geometries. The results confirm that hydrogen bonding in water is significantly stronger than in hydrogen sulfide.

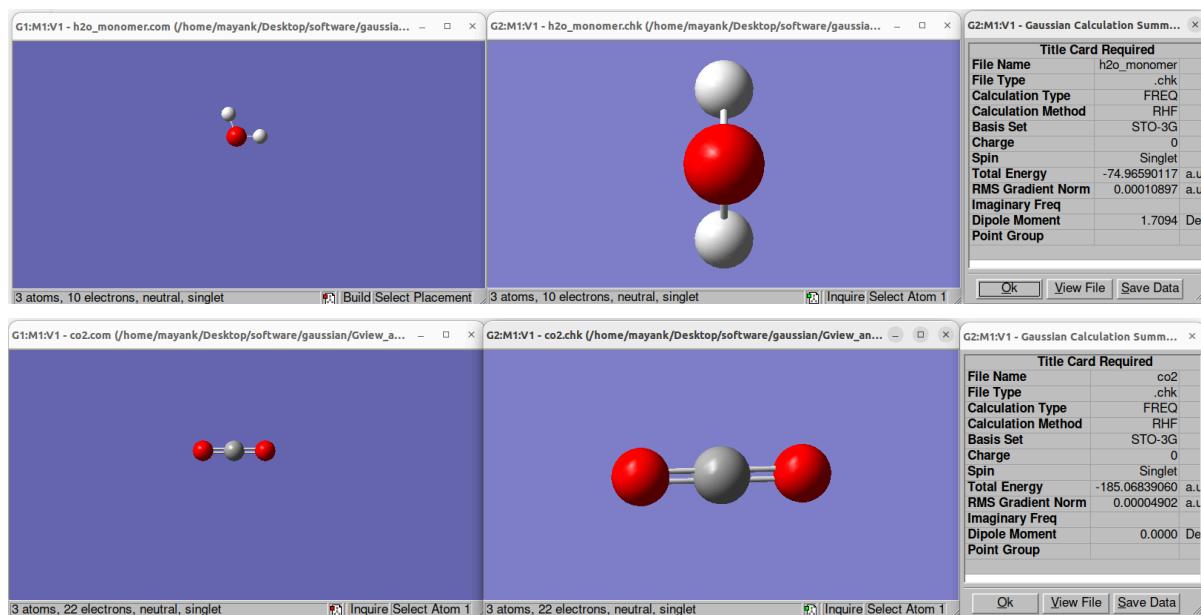
Images for Question - 1

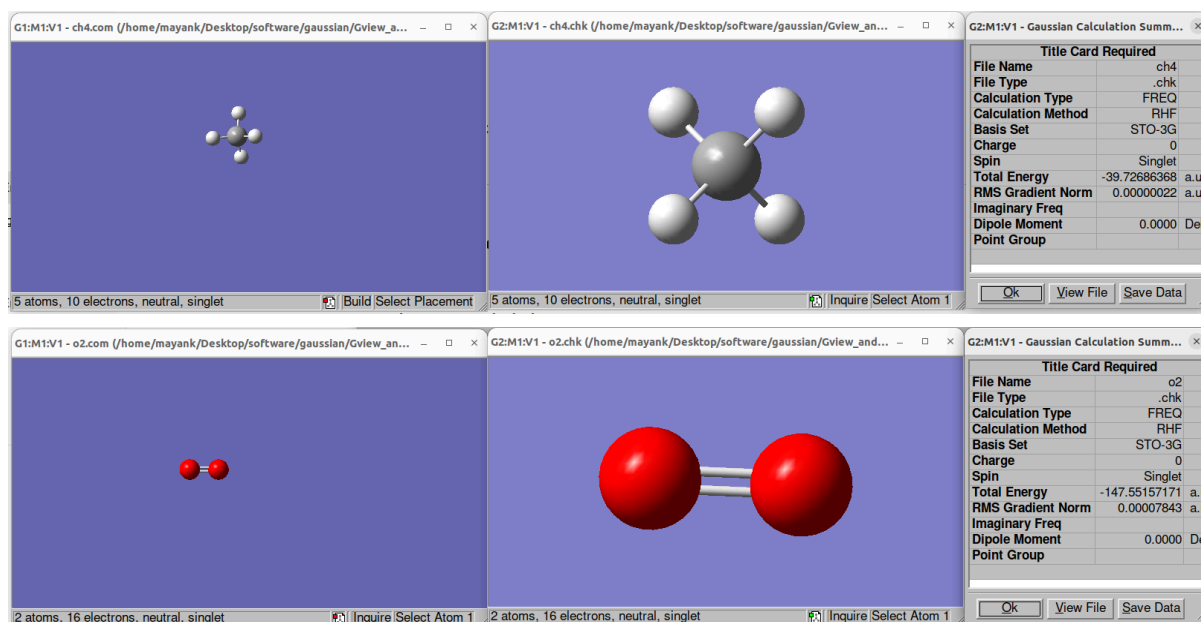
Hydrogenation of Ethene



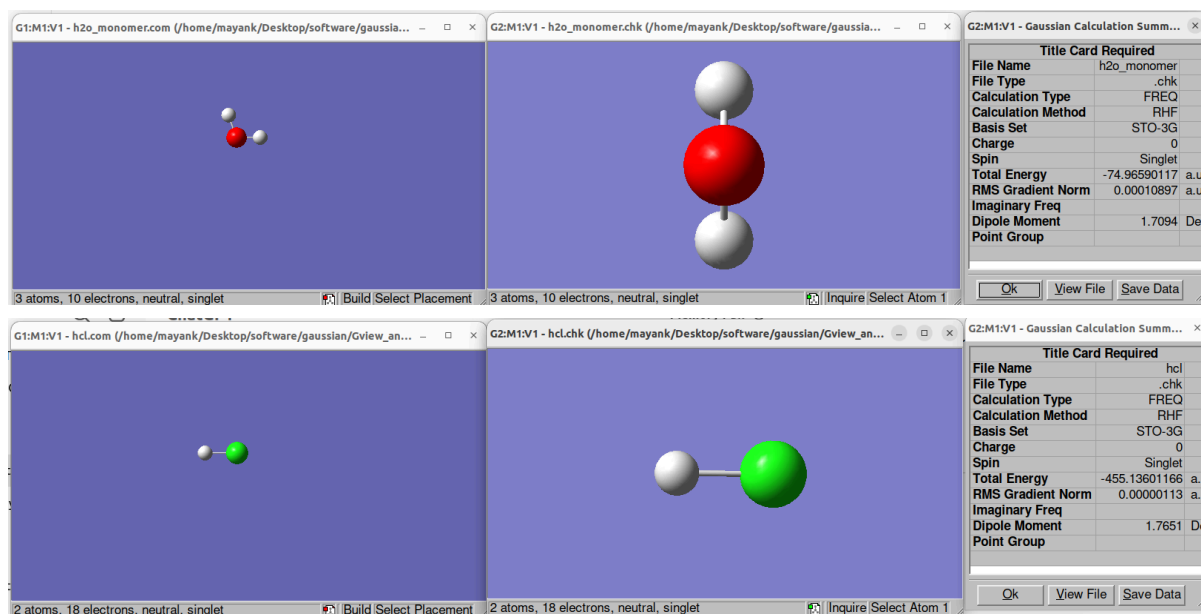


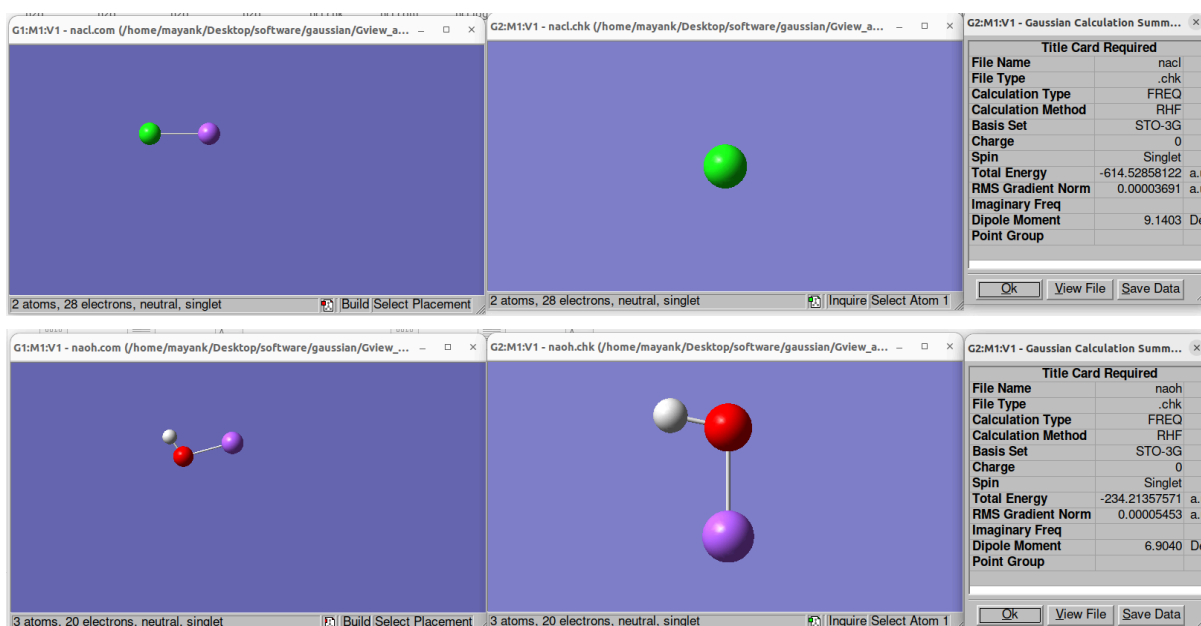
Combustion of Methane



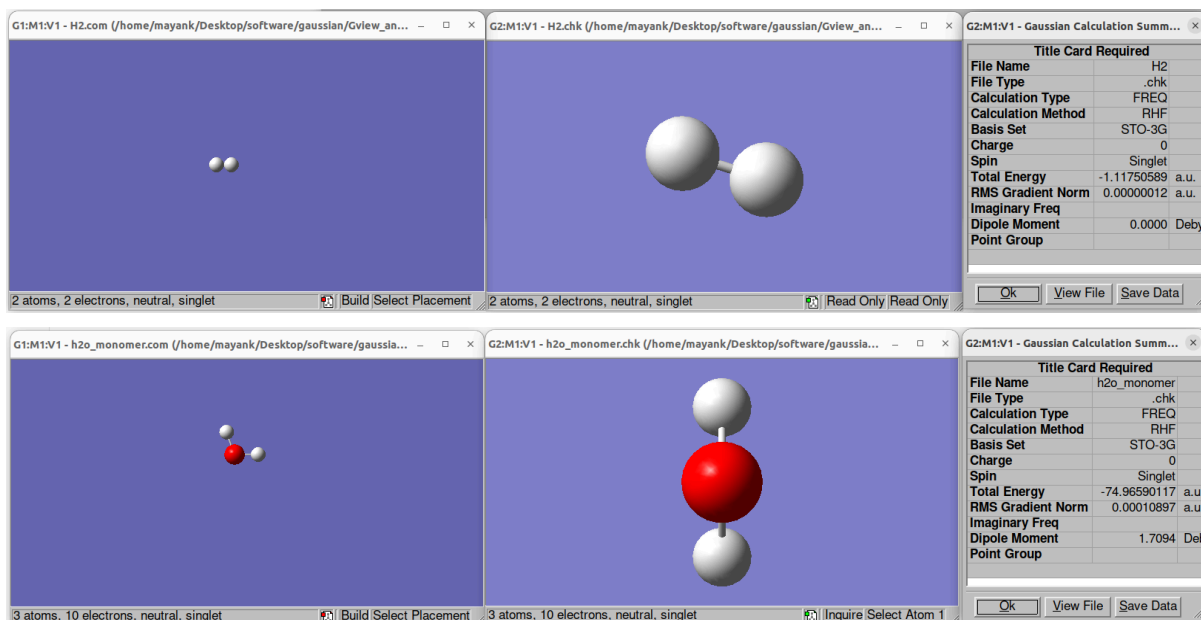
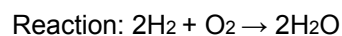


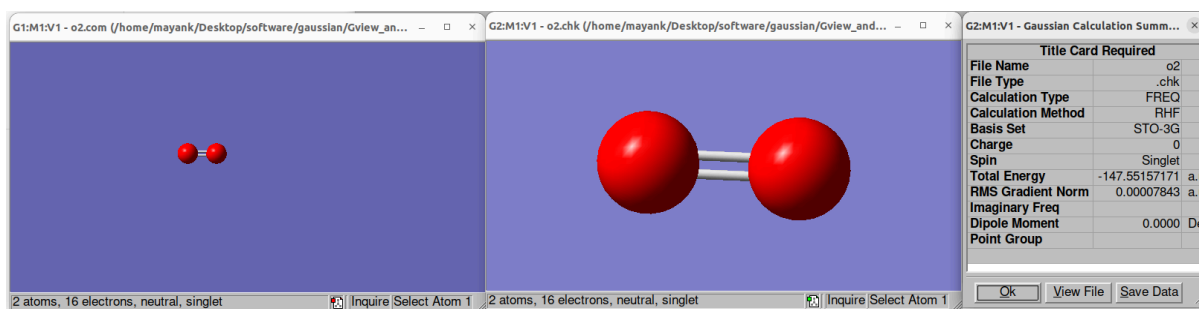
Acid-Base Neutralization



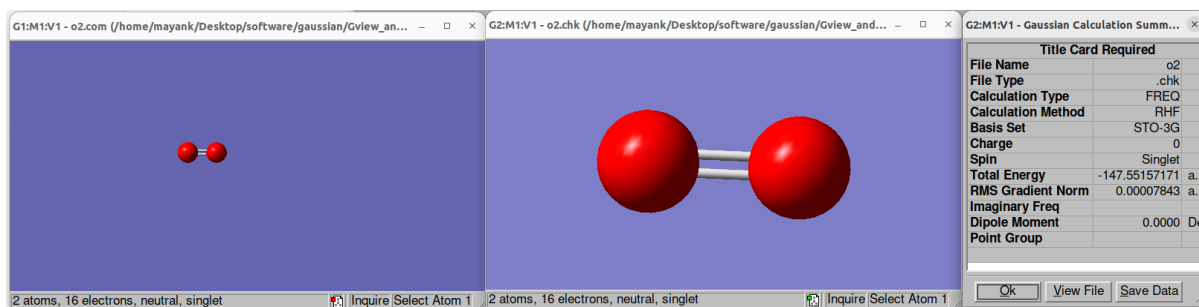
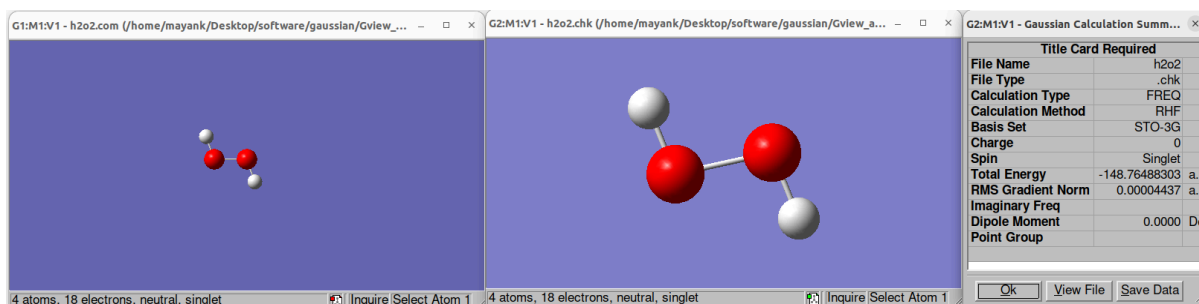
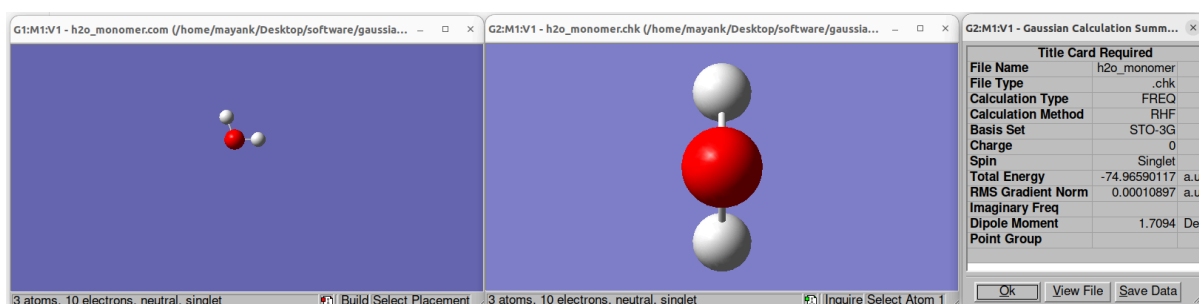
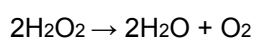


Formation of Water

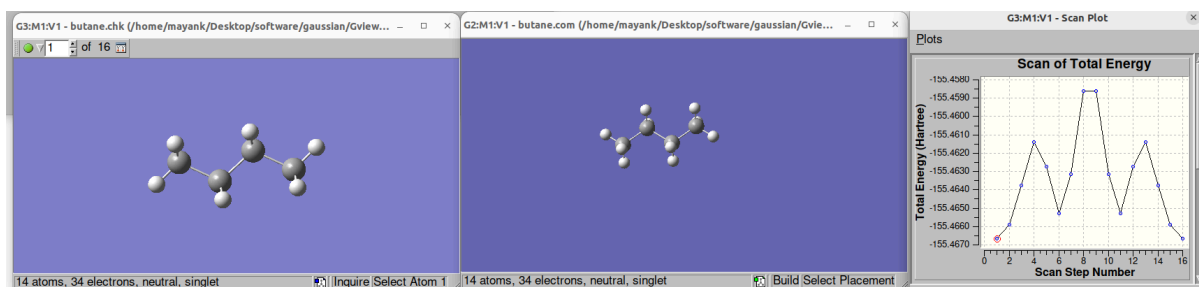




Decomposition of Hydrogen Peroxide

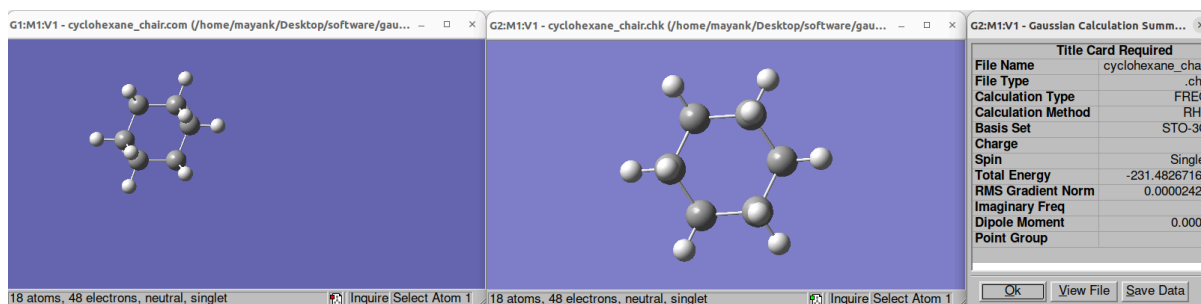


Question - 2

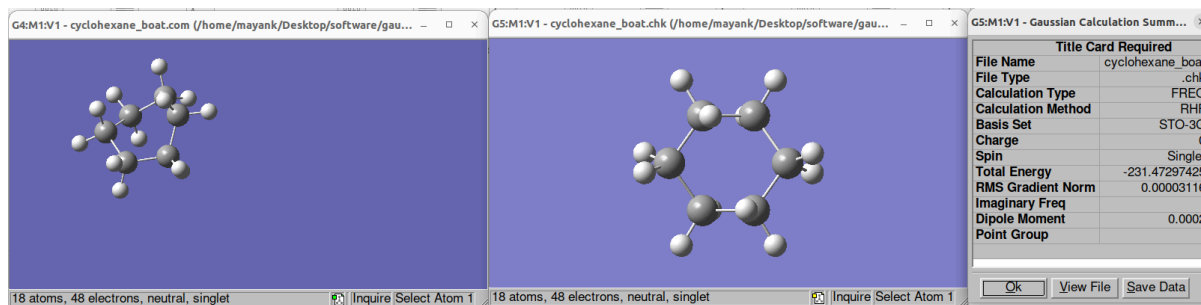


Question - 3

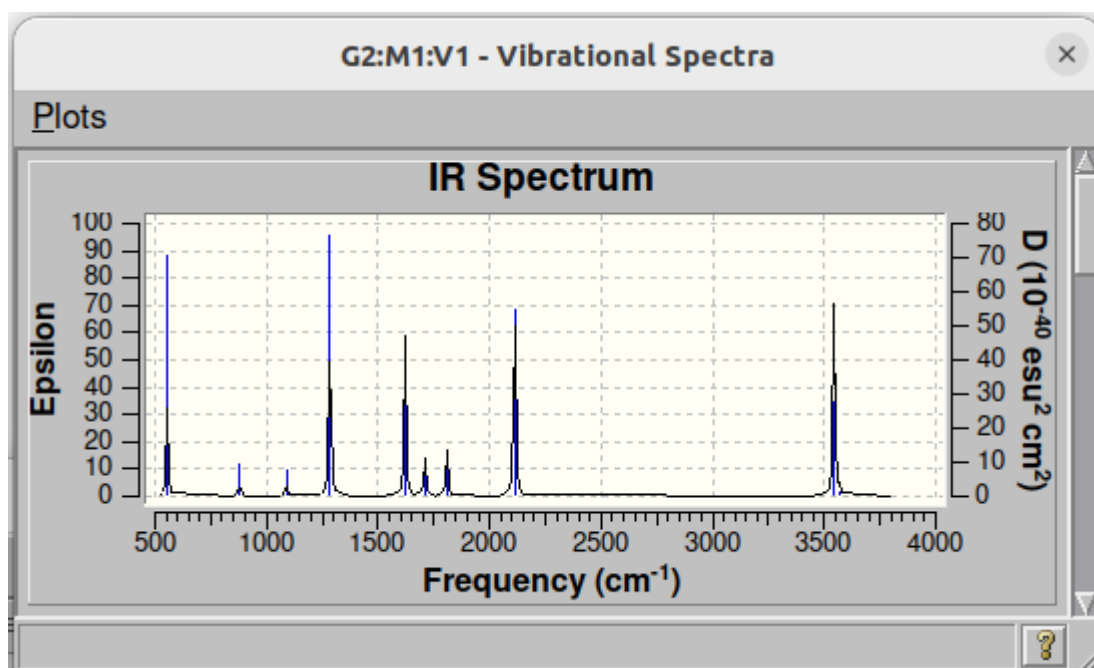
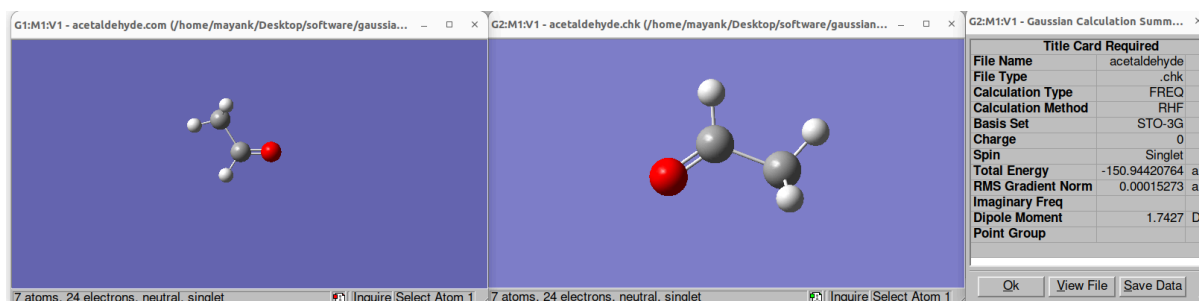
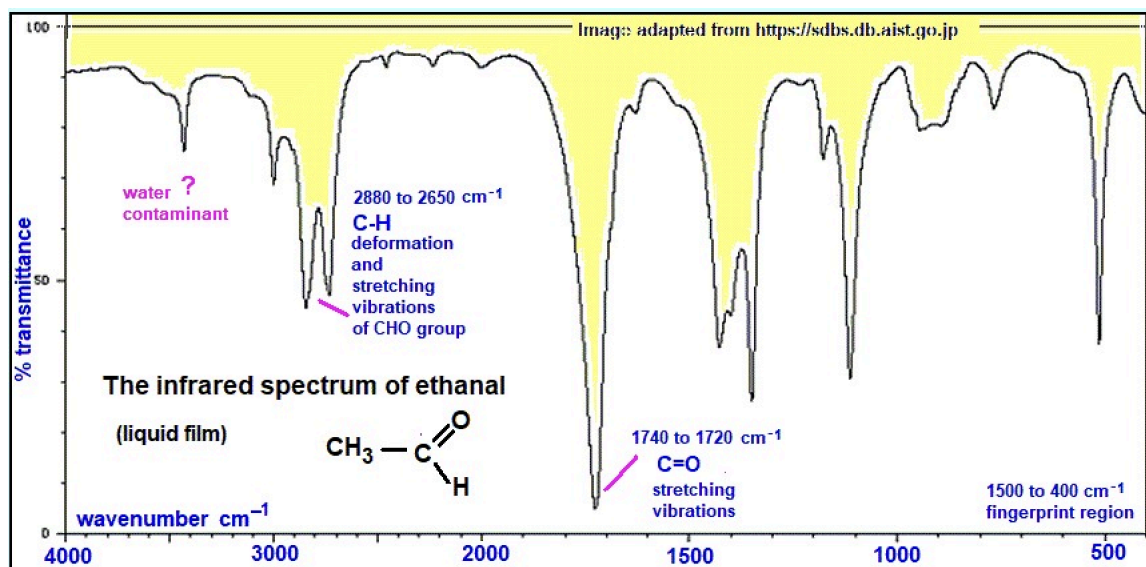
Chair form of cyclohexane



Boat form of cyclohexane



Question - 4



Question - 5

