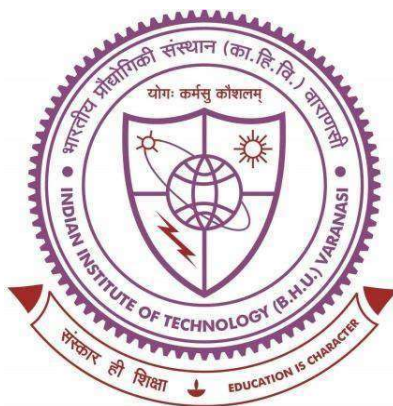


***Ab initio* conformational studies of selected alkanethiols and their clusters**



**THESIS SUBMITTED IN PARTIAL FULFILLMENT
FOR THE AWARD OF DEGREE**

DOCTOR OF PHILOSOPHY

By

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Year of Submission: 2022

Chapter 6
**Summary and future
scope**

6.1 Summary

In summary, we have explored the conformational and structural stability of sulfur containing molecules and their clusters through quantum chemical calculations. Current thesis addressed three major objectives that were outlined in the first chapter and realized through details entailed in four different chapters. Briefly recalling we had the following objectives:

1. Revisiting the conformational analysis and structural stability conformers of ethanethiol, and propylthiol (i.e. 1-propanethiol (1P), and 2-propanethiol (2P)).
2. Revisiting the conformational analysis along with unraveling the nature and strength of sulfur centered hydrogen bonding in homo dimeric and trimeric clusters of methanethiol molecule.
3. To rationalize the strength and nature of sulfur centered hydrogen bonds in hetero dimeric, trimeric and tetrameric cluster system of the methanethiol with water.

Summary of Objective 1

1. Rotational barriers of ethanethiol molecule calculated at the CCSD/cc-pVTZ are in good agreement with the experimentally reported values.
2. Rotational barriers for the C-S and C-C bond rotation are 1.42 kcal/mol and 3.75 kcal/mol respectively as obtained from the one dimensional potential energy curve and 1.44 kcal/mol & 3.61 kcal/mol obtained from the two dimensional potential energy surface.
3. Gauche conformer was found to be more stable compared to the anti-conformer by 0.5 kcal/mol and 0.70 kcal/mol at the CCSD(T)/CBS limit and CCSD(T)/cc-pVDZ level of theory, respectively.

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4. NBO results provided a clear evidence for the stability of the gauche conformer in comparison of anti-conformer by highlighting the presence of strong charge transfers in the gauche conformer and the absence of the same in the anti-conformer.
5. Four (T–G, G–G, T–T, and G–T) and two (anti and gauche) minimum energy conformers were found for nP and 2P molecules.
6. Out of four conformers of the nP molecule, T–G was the global minima with three local minima G–G, T–T, and G–T.
7. In the conformational analysis of nP, the role of the C–C and C–S bonds was seen to be highly crucial in determining the energy of the conformer.
8. Conformational analysis of nP molecule with T–T conformer as the starting geometry matched well with the experimental values vis-à-vis the G–G conformer as the starting geometry.
9. Conformational stability of nP and 2P molecules was corroborated through NBO, FMO, MCA, ESPM, and NCI analysis.
10. Our calculated geometrical parameters and rotational barriers for nP and 2P molecules excellently matched with the experimental results.

Summary of Objective 2

1. Strength and nature of SCHBs in methanethiol cluster system were studied by applying quantum chemical calculations.
2. Three minima corresponding to dimer and trimer cluster system of methanethiol were identified as against the previously reported 5 minima.

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3. Interaction energy corresponding to the cluster system was observed to decrease with an increase in the size of the basis set.
4. Results corroborated well with the earlier reported experimental values but significantly differed from the previous computational predictions.
5. Local energy decomposition study suggested electrostatic energy to be dominant contributor to the interaction energy of the SCHBs in homo dimeric and trimeric clusters of methanethiol.

Summary of Objective 3

1. Strength and nature of SCHB involved in the M_mW_n clusters were studied by applying quantum chemical calculation. Optimized geometries were free from imaginary frequency and the normal modes of vibrations matched exceedingly well with earlier reported experimental values.
2. The computed interaction energy, geometrical parameters, and vibrational frequencies display a trend that is similar to its homologous methanol-water cluster. With increase of cluster size, length of S-H---S, O-H---S, S-H---O, and O-H---O interactions decreased, and the corresponding interaction energies increased.
3. It was found that the sulfur atom has the potential to act as both a donor and acceptor of hydrogen bond in all the cluster systems.
4. It was found that the interaction energy corresponding to O-H---S hydrogen bond was larger than the S-H---O hydrogen bond.

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5. Local energy decomposition module suggested the electrostatic component to be a dominant contributor to the interaction energy in all instances of SCHB observed in the clusters studied herein.

6.2 Future scope:

In future, we would like to explore our study around the following motifs-

- Sulfur centered hydrogen bonds (SCHBs) with different molecular cluster systems where sulfur atom acts as both a donor and an acceptor.
- Conformational analysis of alkanedithiols their hetero-structures (organic molecules containing both sulfur and oxygen atom) and their interactions with water, ammonia, hydrogen sulfide and other specific molecular systems those are directly or indirectly involved in to biological system by computational means.
- Carrying out Raman spectroscopy and SERS to experimentally measure the SCHBs of the clusters studied herein as well as some new clusters.