PREFACE

In this thesis work, quantum chemical calculations were done by utilizing various methods like DFT, Møller-Plesset perturbation method, and coupled-cluster method using Gaussian16 suite of program with basis sets of different sizes. In the following paragraphs, the summary of each chapter of the thesis is presented.

Chapter 1 introduces different aspects of conformational analysis and non-covalent interactions. We have discussed the nature and strength of different kinds of non-covalent interactions. To probe the conformations and non-covalent interactions, we discuss various spectroscopic techniques and the utility of computational chemistry. This chapter also includes detailed information on quantum chemical methods, basis sets, computational tools and server credentials of quantum chemical calculations used to deduce various molecular properties. This chapter ends by stating the objectives of the thesis work.

Chapter 2 presents the conformational analysis of ethanethiol molecule. The rotational barriers were calculated for the first time and they were found to be in good agreement with the experimentally measured rotational barrier reported in literature. Results pertaining to the thermodynamic parameters, normal modes of vibration, and rotational barriers were in good agreement with the previously reported experimental finding about the existence of two conformers. Furthermore, our calculations at the CCSD/CBS limit revealed gauche conformer to be the most stable conformer with a higher relative abundance (49.82% & 64.07% corresponding to the dihedral angle HCCS and CCSH rotation parameters, respectively) at 298 K. The gauche conformer was 0.70 kcal/mol more stable with respect to the anti-conformer. The rotational barriers around the C-C bond and C-S bond rotations calculated at the CCSD/cc-pVTZ level of theory were 1.42 kcal/mol and 3.62 kcal/mol, respectively. NBO, Mullikan charges, and frontier molecular orbital calculations supported these results very well.

Chapter 3 is a revisit to the conformational and structural stability of n-propanethiol (nP). Hitherto prevailing literature was ambiguous and inconclusive on the conformational aspects of nP and there existed no physical chemistry insight to the stability of the conformers of 2-propanethiol (2P) and the same was brought to a decisive conclusion in this chapter. Based on the rotation around the C–C and C–S bonds, four conformers for nP and two conformers for 2-propanethiol (2P) were found to have the lowest energies at the CCSD/cc-pVDZ level of theory. The two conformers of 2P are anti (T), and gauche (G), and those of nP are T–G, G–G, T–T, and G–T. Rotational barriers, geometrical parameters, fundamental vibrational modes, and energy parameters reported herein agree exceedingly well with the reported experimental values for nPand 2P molecules. Furthermore, natural bond orbital (NBO), frontier molecular orbital (FMO), Mullikan charge (MC), electrostatic potential charge (ESP), and vibrational mode analyses were carried out to get a better understanding of both the thiols.

Chapter 4 discusses the conformation and structural stability of methanethiol molecular cluster. B3LYP/cc-pV(D/T/Q)Z and CCSD/cc-pVDZ levels of theory predict three minima for both dimers and trimers of methanethiol. Predictions at B3LYP/cc-pVDZ corroborate exceedingly well with the earlier reported experimental values but significantly differ from the previous computational predictions. It was observed that the interaction energy between the molecules decreased with an increase in the size of the basis set for both the dimer and trimer. The dipole moment of methanethiol dimer got reduced at the B3LYP/cc-pVDZ level of theory relative to all minima conformations, and the same was seen for trimer also. These new predictions were well supported by atoms in molecules (AIM), frontier molecular orbital (FMO), Mullikan charge (MC), and natural bond orbital (NBO) analysis.

Chapter 5 deals the nature and strength of noncovalent interaction in methanethiol-water clusters. Herein, methanethiol (M) and water (W) clusters like dimers (M_1W_1, M_2 and W_2), trimers (M_1W_2, M_2W_1, M_3 and W_3) and tetramers (M_1W_3, M_2W_2, M_3W_1, M_4 and W_4) were

studied to assess the strength of the sulfur centered hydrogen bonding using different levels of theories viz HF, MP2, MP3, MP4, B3LYP, B3LYP-D3, CCSD, CCSD(T)-F12, and CCSD(T)) along with aug-cc-pVNZ (where N= D, T, Q) basis sets. Interaction energies were found to be in the range 3.3-5.3 kcal/mol for the dimers, 8.0-16.7 kcal/mol for the trimers and 13.5-29.5 kcal/mol for the tetramers at B3LYP-D3/CBS limit level of theory. Normal modes of vibrations computed at B3LYP/cc-pVDZ level of theory were seen to be in good agreement with the experimental values. Local energy decomposition (LED) calculations using DLPNO-CCSD(T) level of theory indicated the domination of electrostatic interactions' contribution to the interaction energy in all cluster systems. Furthermore, atoms in molecules (AIM) and natural bond orbital (NBO) calculations both carried out at B3LYP-D3/aug-cc-pVQZ level of theory aided in visualizing the hydrogen bonds besides proving a rationale for the strength of the hydrogen bonds and thereby the stability of these cluster systems.

The thesis ends with a summary of the findings of the considered three objectives along with a brief discussion on the future scope of this work.