

## CHAPTER – 9

### SUMMARY AND CONCLUSIONS

Vibrational spectroscopic studies supported by density functional theory methods have been used in the interpretation of molecular structure, understanding different modes of vibration, intra and intermolecular charge transfer interactions of five important organic compounds. Much effort has been taken to explore the physiochemical properties of the organic compounds gemfibrozil, sulfasalazine, sulfamerazine, 2-methyl-4-nitrophenol, 3-methyl-4-nitrophenol and ethyl centralite.

In the vibrational spectroscopic investigation of gemfibrozil, the H $\cdots$ O distances shorter than the van der Waals separation indicates the existence of intramolecular C–H $\cdots$ O hydrogen bond in the molecule. Intramolecular C–H $\cdots$ O (C<sub>19</sub>–H<sub>20</sub> $\cdots$ O<sub>12</sub> and C<sub>19</sub>–H<sub>21</sub> $\cdots$ O<sub>12</sub>) interaction is further identified through NBO analysis, which shows the charge transfer between the oxygen lone pairs (O<sub>12</sub>) and antibonding orbitals. The broad and red shifted band around 3000 cm<sup>-1</sup> provides the spectral evidence for the existence of strong O–H $\cdots$ O hydrogen bonding. The carboxylic groups involved in the strong intermolecular hydrogen bondings increase the stability of the pharmaceutical compound. The lower energy gap between HOMO and LUMO orbitals is responsible for the bioactivity of the molecule.

Structural and hydrogen bonding features of sulfasalazine have been investigated by quantum chemical calculations and vibrational spectral studies. The elongation ( $\sim 0.01\text{\AA}$ ) of bond lengths N<sub>11</sub>–H<sub>12</sub> and N<sub>11</sub>–S<sub>13</sub> upon dimerization is due to N<sub>11</sub>–H<sub>12</sub> $\cdots$ O<sub>82</sub> hydrogen bonding. The bond length O<sub>38</sub>–H<sub>39</sub> bond is elongated to large

extent (0.05 Å) upon dimerization due to strong  $O_{38}-H_{39}\cdots N_{43}$  intermolecular interaction. NBO analysis of sulfasalazine monomer and dimer confirms the intramolecular  $O_{41}-H_{42}\cdots O_{40}$  interaction and intermolecular  $O_{38}-H_{39}\cdots N_{43}$  and  $N_{11}-H_{12}\cdots O_{82}$  hydrogen bonding. The broad and redshifted shallow band appeared in the region  $3200 - 2500\text{ cm}^{-1}$  in the IR spectrum provides spectral evidence for the effect of  $O-H\cdots N$  intermolecular interaction in the crystalline state. HOMA calculation reveals that the aromaticity values of pyridine and phenyl rings involved in hydrogen bonding are decreased. The intramolecular  $O-H\cdots O$ , intermolecular  $N-H\cdots O$  and  $O-H\cdots N$  hydrogen bonds enhance the stability of the antibacterial drug sulfasalazine.

Molecular structure and complete vibrational spectral analysis of sulfamerazine have been investigated using density functional theory methods. The stretching vibration of  $SO_2$  is downshifted to  $50\text{ cm}^{-1}$  due to the involvement of  $SO_2$  group in  $N-H\cdots O$  hydrogen bonding. Electron localization function analysis explains the delocalized nature of bonds in the molecule which contributes to the stability of the molecule.

In the vibrational spectroscopic investigation of 2-methyl-4-nitrophenol and 3-methyl-4-nitrophenol, molecular structure and spectra of the two molecules are compared. A frequency downshift of  $158\text{ cm}^{-1}$  in the OH stretching vibrations of PNMC when compared to PNOC and the variation of  $32^\circ\text{C}$  in the melting points reveals that PNMC is much stable compared to PNOC. The stability of the compound is increased as the methyl group is changed from second to third position in the phenyl ring.

Spectroscopic studies of ethyl centralite supported by DFT method reproduced its experimental geometry and vibrational frequencies excellently. Phenyl-N conjugation is explained by the stabilization energy in the NBO analysis. The calculated first order hyperpolarizability is five times that of urea. Simultaneous strong bands in both IR and Raman indicate that ethyl centralite may be a potential non-linear optical material.