CHAPTER - IX

SUMMARY, CONCLUSION AND SCOPE FOR FUTURE WORK

Vibrational Spectroscopy is a valuable tool for the elucidation of molecular structure. In the recent years, DFT has proved its efficiency in investigating the medium and large sized compounds of biological and pharmaceutical importance. In the present work, the efficiency of DFT in elucidating the molecular properties and the complete vibrational picture of some of the medium and large sized compounds chosen was again proved. The present work is aimed in bringing out the complete vibrational picture of the polyatomic molecules chosen using experimental (FTIR and FT-Raman) spectra and theoretical DFT Quantum Chemical calculations. The molecules taken for investigation are 2-nitroso-1-napthol, 2,6-Dihydroxy acetophenone, 3,5- Dihydroxy acetophenone, 2-methoxy benzoyl chloride, Diphenyl carbazide and Cinnamylidene acetone.

The chosen compounds were put under investigations using the tools of DFT like structure optimization procedure, Potential energy surface scan analysis, Vibrational analysis, influence of hydrogen bonding on molecular parameters, UV-Visible analysis, HOMO-LUMO analysis and Natural bond orbital analysis by using suitable combination of methods and basis sets. A satisfactory assignment of most of the fundamentals has to be done in order to achieve a close agreement between the experimentally observed and theoretically calculated vibrational wavenumbers, for which the effective use of scaling procedure is essential. In the present work, we have employed three types of scaling procedure namely uniform scaling, initial scaling and final scaling. The selective scaling procedure enabled us to bring the close agreement between the calculated and experimental counterparts which in turn helps in doing the vibrational assignments of most of the fundamentals satisfactorily.

In the present work, Vibrational Spectroscopy has been effectively utilized in analyzing the molecules in following aspects:

1. Exploration of large molecule
2. Depicting the most stable geometry
3. Effect of substitution
4. Conformal stability
5. Effect of Hydrogen bonding
6. S-cis and S-trans conformers
7. Investigation on synthesized compound and
8. Suitable choice of method & basis set for a specific molecule.

In the present work, the following DFT based computational analysis performed:

1. Energy optimization
2. Vibrational analysis
3. UV-Visible analysis
4. Potential Energy Surface scan analysis
5. Natural bond orbital analysis
6. Homo-Lumo analysis
7. Mulliken charge analysis &
8. Calculation of thermodynamical parameters.

For the molecule 2-nitroso-1-napthol, the most stable conformer was identified using DFT optimization procedure and potential energy scan analysis. The geometrical parameters of the most stable conformer reveals that the substitution of nitroso group into the 1-napthol has produced remarkable changes in the structural parameters. A weighted RMS deviation of 9.6 cm\(^{-1}\) obtained from the SQM results indicates the good agreement between experimental and calculated wavenumber. The clear picture of electronic absorption of the molecule was given by ultraviolet visible spectra. The Natural bond orbital analysis reveals that the charge transfer from the lone pair to bond pair was found to be greater than bond pair to bond pair and this contributes to the stabilization of the chosen system.

The various possible conformers, their respective energies, optimized geometry, vibrational wavenumbers and the intramolecular interactions of 2,6- and 3,5-Dihydroxyacetophenone were investigated with aid of B3LYP/631-G** method. The most stable conformers of DHAP I and DHAP II were identified using DFT optimization procedure and potential energy surface scan analysis. From the comparative study made on the geometrical parameters, a strong intramolecular hydrogen bond formation between one of the
hydroxyl group and carbonyl group of DHAP I was identified. The RMS deviation of 7.26 cm\(^{-1}\) and 5.7 cm\(^{-1}\) between experimental and calculated wavenumber for DHAP I and DHAP II respectively has been achieved by employing the SQM methodology and selective scaling. The results from the frontier molecular orbital analysis establishes that, the molecule DHAP II is having slightly higher energy gap of about 0.1456 eV when compared to DHAP I. The electronic absorption of both the molecules was given by UV-Vis analysis. The results from NBO analysis confirms that the stabilization of DHAP I was seen to be highly dependent on the charge transfer from the lone pair to lone pair in and it differs as bond pair to bond pair interactions in case of DHAP II.

The most stable geometry among the synperiplanar (S-cis) and antiperiplanar (S-trans) conformers of 2-Methyl benzoyl chloride was obtained from the DFT (B3LYP and B3P86) structure optimization calculation and PES scan analysis. An intramolecular hydrogen bond formation between one of the CH group and chlorine atom of that S-cis conformer was found from the geometrical parameters obtained. The SQM methodology and selective scaling results in a weighted RMS deviation of 8.27 (S-cis) and 9.45 (S-trans) cm\(^{-1}\) between experimental and calculated wavenumber. The results from the frontier molecular orbital analysis establishes that, the S-trans conformer of 2MBC possesses slightly higher energy gap of about 0.0948 eV when compared to S-cis conformer. The theoretical UV-Vis spectra agree very well with its experimental counterpart in terms of absorption wavelength. The stabilization of the title compound seems to be highly dependent on the charge transfer from the lone pairs of oxygen (O8, O10) and chlorine (Cl9) atoms onto the bond pairs.

The most stable conformer of Diphenyl Carbazide have been identified using DFT optimization procedure. The scaling procedure ends up with a weighted RMS deviation of 9.8 cm\(^{-1}\) between experimental and calculated wavenumber. The results form NBO analysis reveals that the charge transfer from the lone pair to bond pair and bond pair to bond pair equally contribute to the stabilization of the molecule.

Cinnamylidene acetone (CA) was successfully synthesized through a single step base catalyzed aldol type condensation between acetone and cinnamaldehyde. The prepared molecule’s structure has been confirmed using \(^1\)H and \(^13\)C NMR Spectral analysis. The structure optimization performed on CA using the DFT/ B3LYP/6-31G** method the most stable geometry was identified. The complete vibrational characterization of the molecule was done by using experimental (FTIR and FT-Raman) spectra and calculations at DFT level. The
SQM methodology results in a RMS deviation of 6.53 cm\(^{-1}\) by adopting selective scaling procedure. The energy gap of 3.80103 eV was found for the chosen system from the frontier molecular orbital analysis. The absorption wavelength was identified from the UV-Vis spectral analysis. The NBO analysis confirms that, stabilization of CA seems to be highly dependent on the charge transfer from bond pairs (\(\pi\)) of the ring atoms to its antibonding (\(\pi^*\)) orbitals and from the lone pair (LP) of oxygen atom (O21) into the bond pairs.

Thus, DFT has been effectively utilized in analyzing all the chosen compounds. Various analysis were performed and the results were properly reported. The present work has made an earnest effort to solve molecule specific vibrational problems by employing various DFT tools.

**Suggestions for future work**

The results of the present investigation gives a pathway and scope for future investigations as outlined below:

Attempts can be made to synthesize more compounds of biological and pharmaceutical importance and their vibrational characterization can be done using DFT theoretically, which can save money before it goes to wet lab.

2d NMR spectrum and COSY spectrum for the synthesized compounds can be done getting more clarity on product confirmation. The surface quality can be tested using Scanning electron microscopy (SEM) for the molecules having industrial importance.

More complicated systems, having similar environment with different substituents or substituents at different positions which can change the entire vibrational property of the molecule can be synthesized and their entire vibrational property can be studied.

Molecular docking studies can be done for the molecules of biological importance using theoretical calculations at DFT level. DFT has proved its ability in reproducing various molecular properties and vibrational picture of them. It helps to save money and time before it goes into the wet lab or to a pharmaceutical industry.