CONCLUSIONS

Conclusions

The work reported in the thesis mainly involve the computational investigation of the molecular properties such as Geometry optimization, Conformer analysis, Vibrational analysis, NBO analysis, HOMO-LUMO analysis, Molecular electrostatic potential surface, Non linear optical behavior, Global reactivity descriptors, UV-vis spectra, Thermodynamical properties, Mullikan charges analysis etc. for the following applicable molecules:

- 2-Amino- 5-(m-Nitrophenyl)-1,3,4-Thiadiazole (AMNT)
- 3-(3,4-dimethoxyphenyl)-1-(pyridine-2-yl)prop-2-en-1-one (DPP)
- 2-Aminopyridinium p-Toluenesulfonate (APPTS)
- 1-[4-(methylsulfanyl) phenyl]-3-(4-nitrophenyl) prop-2-en-1-one (4MPNP)

A detailed normal coordinate analysis of all the normal modes along with PED very clearly indicates the composition of each normal mode in terms of internal coordinates. Discrepancy between the experimental and the calculated wavenumbers may be attributed to neglect of anharmonicity and also isolated molecule model for molecular geometry. Thus, some reasonable deviations from the experimental values seem to be justified. Despite of some discrepancy, theoretical investigation helps a lot in understanding experimental data.

Electrostatic potential surface provides the information about the hydrogen bonding and chemical reactive sites as well as NBO and HOMO-LUMO calculations may help in making understanding of biological and nonlinear activity and set guidelines for experimentalists for the synthesis of new materials.

The thesis as a whole contributes to the knowledge generation by theoretically computing various parameters and properties for some useful molecules. A detailed interpretation of computed data will help in understanding these molecules at broader level and help in looking for new applications. The molecule wise important conclusions are summarized below:

- DFT calculations for 2-Amino- 5-(m-Nitrophenyl)-1,3,4-Thiadiazole (AMNT) suggests that,
  - The basis set 6-311++G(d,p) with B3LYP functional is found most suitable for the computation.
Optimized geometry of titled molecule provides the structural parameters, which are in good agreement with experimental values. Some deviations from x-ray data are observed for thiadiazole ring parameters. It may be attributed to isolated molecule (gas phase) model.

Potential energy surface scan, performed by minimizing the potential energy in all geometrical parameters suggests one less stable conformer.

Electrostatic potential surface provides the information about the hydrogen bonding and chemical reactive sites as well as NBO and HOMO-LUMO calculations may help in making understanding biological activity and in synthesis of new thiadiazole derivatives.

Theoretical investigation for the molecule 3-(3,4-dimethoxyphenyl)-1-(pyridine-2-yl)prop-2-en-1-one (DPP) suggests that,

- The use of basis set 6-31G(d,p) employing B3LYP functional is found more appropriate out of various basis sets for the computation of molecular properties of titled molecule.
- Potential energy scan suggests a stable conformer at a combination of dihedral angles [$\Phi_1$(C9-C7-C6-N1) = 0.0° and $\Phi_2$(C12-C11-C10-C9) = 0.0°].
- Optimized geometry of the DPP molecule was found in good agreement experimental data. Significant differences were not obtained and, therefore, geometry optimized by DFT is used for further investigations.
- The calculated first hyperpolarizability $\beta_{tot}$ comes out to be 53.54704×10^{-30} esu, which is about 143 times greater than urea making DPP a potential material for NLO applications.

For the NLO molecule 2-Aminopyridinium p-Toluenesulfonate (APPTS) our computation shows that,

- The basis set 6-31G(d,p) with B3LYP functional is most suitable basis set out of various basis sets for the computation of molecular properties of the titled molecule.
- Calculated values of static hyperpolarizability confirm good nonlinear behavior of the molecule.
- Electronic behavior and global reactivity descriptors parameters are calculated and analyzed through HOMO-LUMO analysis. Energy band gap and simulated UV-visible Spectrum show good agreement with experimental results.
The computational analysis of NLO molecule 1-[4-(methylsulfanyl) phenyl]-3-(4-nitrophenyl) prop-2-en-1-one (4MPNP) reflects that,

- The basis set 6-31G(d,p) with B3LYP functional out of various basis sets provides more accuracy than other basis sets for the molecule APPTS.
- Calculated values of static and dynamic hyperpolarizability components confirm good nonlinear behavior of the title molecule.
- Predictive values of thermodynamic properties like rotational constant, zero point vibrational energy, total energy at room temperature and pressure and Mulliken atomic charge and natural atomic charge distribution are again very important for understanding this molecule and play a guiding role for experimentalists.

The work reported in the thesis is primarily based on the calculation of molecular properties using DFT and HF methods. All these studies are based on certain assumptions and as such have their own limitations.

- The experimental data, which have been used, also have their dependability within certain limits. Density functional theory (DFT) calculations are the most common type of calculations, though they are subject to limitations in the accuracy of the functional employed, and the ability to chemically interpret the result.
- The choice of functionals is intimidating and can have a real impact on the calculations.
- Another important limitation to density functional theory is DFT's characteristically poor treatment of long-range noncovalent interactions. Although DFT is enjoying ever increasing popularity in Solid State Physics and Quantum Chemistry but it is generally known that HF overestimates the HOMO-LUMO gap whereas DFT/B3LYP underestimates it.
- In the present work one of the important limitations in the evaluation of spectroscopic data lies in the fact that an isolated model has been used in place of three dimensional systems. This leads to a shift of few wave numbers in the calculated frequencies. Calculations on a three dimensional system together with intermolecular interactions will fully interpret the vibrational modes, but the calculation with three dimensional system becomes computationally very costly and cumbersome.
Despite of the limitations mentioned above, the computed results, based on simplified model, matches very well with experimental data and can serve well, up to an extent, for understanding molecular system and its properties.