Chapter X

CONCLUSIONS AND SCOPE FOR FUTURE WORK

The important conclusions and the scope for future work based on the research findings reported in this thesis are summarized below.

The optimized geometry and vibrational spectral investigations of non-centrosymmetric NLO crystals and potential push-pull conjugated NLO chromophore have been comprehensively carried out to elucidate the correlation between molecular structure and NLO property and other factors that influence the normal modes of vibration. The basic strategy of using electron-donor and electron-acceptor substituents to polarize the \( \pi \)-electron system of organic materials, thereby creating the possibility of second-order nonlinear optical response has been analyzed.

Theoretical modeling and vibrational spectroscopic study of p-hydroxy benzoic acid dimer (PHBA) and its contributions to NLO activity were analyzed from the optimized molecular structure and vibrational spectral analysis with the aid of density functional theory (DFT) methods. Vibrational spectral investigation confirms the formation of cyclic dimers in the crystal along with the carboxyl groups of each acid molecule which are bonded to those of adjacent molecules. Analysis of phenyl ring modes shows that the C-C stretching mode 8 is found equally active as strong bands in both IR and Raman, which can be interpreted as the evidence of intramolecular charge transfer between OH and C=O groups. The conjugated ring path is responsible for hyperpolarizability enhancement, which leads to NLO activity. The comparative study of normal Raman spectrum with the SERS along with the B3PW91/lanl2dz calculations predicts the
adsorption geometry of PHBA bound to silver through carboxyl group at a perpendicular orientation with respect to the surfaces.

The concept of intramolecular charge transfer interaction and their influence on NLO property has been analyzed for the hydrogen bonded NLO crystal p-bromoacetanilide (PBA) using geometry optimization and vibrational spectra supported by HF/6-31G(d) ab initio computations. The resemblance between IR and Raman spectra reveals the existence of intramolecular charge transfer (ICT), thus the molecule behaves as an effective push-pull NLO system. Ab initio quantum chemical computations predict the existence of intramolecular C-H⋯·O bonds. In addition, NBO analysis confirms the presence of strong intermolecular N-H⋯·O hydrogen bonds in PBA dimer. The SERS spectrum predicts that the PBA molecules is adsorbed and lie flat on the silver surface.

The optimized geometry and structural features of the most prospective electro-optic crystal Ethyl-3-(3,4-dihydroxyphenyl)-2-propenoate (EDP) and its vibrational spectral investigations have been carried out based on its vibrational and electronic spectra. DFT computations were used to elucidate the contribution of vibrational modes to the linear electro-optic effect. The effect of intramolecular charge transfer interaction, inter- and intramolecular hydrogen bonding and hyperconjugative interactions on molecular geometries have been studied by NBO analysis. The influence of electronic effects such as hyperconjugation and backdonation on the C-H stretching vibrations of the methyl groups have been examined from their optimized molecular structure and vibrational spectral features. The concurrent intense activation of Raman and IR activity significantly contributes to the linear electro-optic effect resulting from the strong electron-phonon coupling. The simultaneous activation of “effective conjugate coordinate”
mode in both IR and Raman spectra have been inferred from the push-pull NLO chromophores. These modes of vibrations involve the intramolecular charge transfer from the donor to the acceptor and gives rise to a large variation of the dipole moment, thus gaining a strong infrared activity. This vibration carries out the phenomenon of the electron-phonon coupling in these conjugated materials, which mimics the evolution from an aromatic to a quinoid structure in the π-conjugated path, what provokes to be very intense in the Raman spectrum.

Single crystals of Sarcosinium oxalate monohydrate (SOM) were grown by the slow evaporation technique. The geometry optimization of SOM carried out by *ab initio* quantum computation reveals that the sarcosinium ion, oxalate ion and water molecule lie not on the same plane. The IR, and Raman spectral analysis indicates the presence of C = O, COO⁻ and NH₂⁺ stretching and bending frequencies. Imino group of sarcosine is protonated at the expense of hydrogen from the oxalic acid. The oxalic acid molecule exists in a monoionic state in the crystal maintaining an overall charge neutrality. Lowering of NH₂⁺ symmetric and asymmetric stretching vibration is due to the N - H · · · O hydrogen bonding. The existence of ‘blue-shift or improper’ C-H · · · O hydrogen bonding and the intense low wavenumber Raman vibrations corresponding to the stretching of H-bond modes due to electron-phonon coupling and non-bonded interactions make the molecule, NLO active. The occurrence of strong intra- and intermolecular N-H · · · O and C-H · · · O hydrogen bonds have been confirmed by NBO analysis. The SERS spectrum exhibits a tilted ‘side on’ orientation of the molecule.

The single crystals of Bis glycyl glycinium oxalate (BGGO) were grown by slow evaporation technique and vibrational spectral analysis was carried out using NIR-FT Raman, FT-IR and SERS spectra. The *ab initio* quantum
computations were also performed to derive the optimized geometry, atomic charges and vibrational frequencies of the BGGO molecule. Vibrational analysis indicates the presence of peculiar intermolecular N-H ÷ ÷ ÷ O and C-H ÷ ÷ ÷ O hydrogen bonding interaction producing ‘blue shift’ of N-H and C-H stretching wavenumber. The predicted nonlinear optical (NLO) properties of BGGO are much greater than the reference compound urea. The NLO properties are due to the molecular frontier orbitals and π-electron conjugative effect.

The concept of intramolecular charge transfer interaction and their influence on NLO property were analyzed for the hydrogen bonded NLO crystal L-Histidinium Dihydrogenmonophosphate Monohydrate (LHDM) using geometry optimization and vibrational spectra supported by ab initio computations. The SHG efficiency was calculated by Kurtz-Perry powder experiment, which is around 0.5 times that of urea and the calculated first hyperpolarizability of LHDM is found to be $5.104 \times 10^{-30}$ e.s.u. The effects of intramolecular charge transfer interaction and hyperconjugative interactions on the molecular geometries were analyzed by means of Mulliken population analysis. The elucidation of considerable changes in the endocyclic and exocyclic angles between the phenyl ring and the hydroxyl substituted diethylamino group was carried out based on the DFT computations. The correlation between molecular structure and NLO property relationship for the donor-acceptor (D-A) system containing heteroaromatic π-bridging unit (imidazole) is described. The existence of strong intra- and intermolecular hydrogen bonds facilitates the intramolecular charge transfer between the negative and positive charged species within the molecule throughout the crystal. The NBO analysis clearly reveals the existence of C-H ÷ ÷ ÷ O, N-H ÷ ÷ ÷ O and O-H ÷ ÷ ÷ O inter and intramolecular hydrogen bonding.
The lowering of wavenumbers and the increasing intensity of C-H stretching modes of the \( \text{CH}_2 \) in histidinium cation points the influence of back-donation in the ring owing to the presence of nitrogen atom.

Vibrational spectral investigation using FT-IR, NIR FT Raman and SERS spectra aided by accurate ab initio and DFT quantum chemical computational method has emerged as an effective tool to get deeper insight into the structural and bonding features of molecules. These studies are aimed to provide the molecular structure-property correlation of biological molecules and NLO materials. Vibrational modes are assigned on the basis of intra- and intermolecular hydrogen bonding, vibrational interactions, intramolecular charge transfer, etc. The techniques used in this report could well be utilized in engineering new drugs as well as simulating natural medicinal products with desired medicinal activity, to provide insight into biological and quantitative structural activity relationship of biomolecules and to design high efficient organic and semi organic NLO materials by optimizing the molecular hyperpolarizability.

The in-depth understanding of vibrational contributions of low wavenumber hydrogen bond stretching Raman modes to the first and second hyperpolarizabilities of the molecules in hydrogen bonded NLO systems is a vibrant area for future research.