# CHAPTER - 9

# SUMMARY AND SUGGESTIONS FOR FUTURE WORK

## 9.1 SUMMARY

Growth and spectroscopic studies of NLO materials have been an emerging area used in understanding its structure-activity relationship. The extensive use of spectroscopic techniques for structural elucidation such as infrared, Raman, and electronic in the field of NLO compounds, to look into the active sites of these molecules is having much significance. Quantum chemical calculations predicting harmonic wavenumbers are essential when interpreting experimental spectrum, particularly for large molecules in which the high density state results in spectral complexicity. Much effort has been put in this work to disentangle the physical basis for the NLO activity of certain molecules such as LLS, ZNS, TONP, PDNB and ZNB. The important conclusions and the scope for future work based on the research work reported in this thesis are summarized below.

Single crystals of LLS were grown by the slow evaporation technique. The single-crystal XRD result confirms that the crystal structure has the monoclinic system and $P2_1$ space group. The first-order hyperpolarizability is found to be $4.72 \times 10^{-30}$ e.s.u., which is 18 times greater than that of urea. The structural parameters and vibrational assignments were carried out using DFT computation at B3LYP/6-311++G(d,p) level of basis set. Blue-shifting of the

C-H stretching wavenumber is due to the formation of the improper C-H···O hydrogen bonding. The red-shift of the N-H stretching wavenumber indicates the formation of N-H···O hydrogen bonding. The experimental values and the theoretical values were in good agreement. NBO and the HOMO-LUMO energy gap explain the presence of ICT within the molecule, which is responsible for the optical non-linearity of the crystal. The Hirshfeld surface analysis with fingerprint plots and electrostatic potential map reveals the percentage of intermolecular interactions and distribution of electrostatic potential of the title compound.

The structural parameters, vibrational assignments and NBO were carried out using DFT computation at B3LYP/6-311++G(d,p) level of basis set. FT-IR and FT-Raman spectra were compared with the computational wave numbers. The experimental values and the theoretical values are in good agreement. The simultaneous occurrence of IR and Raman bands of C=C explain the presence of intramolecular charge transfer within the molecule, which is responsible for the optical non-linearity of the crystal. The Hirshfeld surface analysis with fingerprint plots and electrostatic potential map reveals the percentage of intermolecular interactions and distribution of electrostatic potential of the title compound. NBO and NPA analyses reveal the intramolecular O-H···O hydrogen bonding and charge distribution takes place within the molecule. The calculated value of second-order hyperpolarizability and low value of

HOMO-LUMO energy gap exposes the non-linear optical properties of the ZSD.

The most stable molecular structure of the compound triphenylphosphine oxide 4-nitrophenol (TONP) was optimized by DFT/B3LYP method using 6-311++G(d,p) basis set. The lowering of calculated bond length (O36-H50) indicates the formation of intramolecular O36-H50···O2 hydrogen bonding. The intramolecular hydrogen bond formation produced significant red shift in vibrational wavenumber associated with hydroxyl stretching. UV-vis spectrum reveals that the maximum absorption arises due to the n→π* electronic transition of the TONP molecule. FMOs analysis reveals the reactive nature and the presence of ICT within the molecule. NBO analysis supports the possible intramolecular interactions and hydrogen bonding, which are responsible for the NLO activity of the TONP molecule. The observed increase in electron density of antibonding orbital σ*(O36-H50) also confirms the formation of intramolecular hydrogen bonding. The intermolecular interactions are studied by Hirshfeld surface analysis. Non-linear optical activity of the TONP molecule was also examined by the second-order hyperpolarizability calculations and Kurtz Perry method. The obtained results reveal that the TONP molecule is a potential NLO agent and can be used for NLO applications.

The optimized molecular structure of the PDNB molecule was obtained by DFT/B3LYP method using 6-311++G(d,p) basis set. The IR, Raman and

UV-vis spectra of the molecule were recorded and analysed. The optical band gap of the PDNB molecule is 4.5 eV. Frontier molecular orbital analysis reveals the reactive nature of the PDNB molecule and the presence of ICT within the molecule which enhance the NLO activity. Intramolecular charge transfer interactions from σ to σ* interactions also contribute significantly to the stabilization of the PDNB molecule. NBO analysis confirms the intramolecular charge transfer interactions in the molecule which leads to the stability of the molecule. Non-linear optical activity of the PDNB molecule was examined by first-order hyperpolarizability calculations. The calculated dipole moment was found to be 13.59 debye. The crystal has 1.4 times the conversion efficiency of KDP. Hirshfeld surface analysis of PDNB shows the strong close and weak longer intermolecular interactions in the crystalline state. The obtained results show that PDNB molecule is potential candidate for NLO applications.

A systematic study has been conducted on the structural characteristics of ZNB by spectroscopic methods along with quantum chemical calculations. The IR, Raman and UV-vis spectra of the molecule were recorded and analyzed. The theoretical model of ZNB obtained by DFT calculation describes the non-planarity of the structure and Jahn-Teller effect. NBO and vibrational analyses confirms the intramolecular interaction with in the molecule, which is in turn to the NLO activity of ZNB. Frontier molecular orbital analysis supports this result. The UV-vis spectrum of the molecule

demonstrate that strong absorption band observed is due to $\pi \rightarrow \pi^*$ transition at 282 nm. The band gap of ZNB is found to be 4.85 eV, which shows least consistency with the DFT calculated HOMO-LUMO gap (3.44 eV).The estimated SHG efficiency of ZNB crystal was found to be 1.3 times that of KDP crystals.

**9.2 SUGGESTIONS**

The grown organic and semi-organic optical crystals can be used to fabricate optoelectronic and NLO applications. For all the crystals obtained in this thesis, one can study HRXRD, birefringence and laser damage threshold. The laser damage threshold studies can be carried out on the grown crystals with improved optical quality and the variation of laser damage threshold with beam energy can be correlated. Temperature dependent conductivity experiments can be done in future and the results can be correlated with thermal studies. The particle size may be one of the factors which influence the SHG efficiency. The nano-particle size of the crystal may change the NLO efficiency of the crystal. Hence, attempts could be made in future to synthesis the crystals in nano-crystalline form. The physicochemical properties of the nano-crystalline materials can be investigated and the influence of their size, in particular, can be studied for NLO efficiency. Attempts can be made to identify suitable dopants which could provide better optical properties and enhance the NLO property of the crystals. Hence more work must be done to

investigate the nonlinear optical properties to make these crystals into a reality to replace the conventional material used in the laser applications.