Abstract

In the present thesis, we have reported work on poly(4-methyl-2-pentyne) (PMP) and poly(2-methylbut-2-enylthiophene-3- carboxylate) (PMT), 4-chloro-4'dimethylamino-benzylidine aniline (CDMABA) and L-Lysine monohydrochloride dihydrate (LLMHCl.2H_2O).

Chapter 1 provides a brief introduction of the polymers and the nonlinear optical materials in general and those which have been studied in the thesis i.e. substituted polyacetylenes: PMP and PMT with nonlinear optical materials: CDMABA and LLMHCl.2H_2O. This chapter provides a general introduction to the different methods for studying structural, vibrational and electronic properties of the molecular systems.

Chapter 2 is divided into two sections. First part describes the theoretical details necessary for the vibrational dynamics reported in the chapters 3 and chapter 4 for PMP and PMT, while the second part deals with the theoretical details related with quantum-chemical *ab-initio* and DFT calculations reported in chapter 5 and chapter 6 for CDMABA and LLMHCl.2H_2O.

Chapter 3 gives the complete study of the vibrational dynamics of the poly(4-methyl-2-pentyne) (PMP) by studying its vibrational modes and their dispersion within the first brillouin zone. PMP shows high gas and vapor permeabilities with good resistant to organic solvent and offers promising applications in the manufacture of nanocomposite membranes for the separation of various hydrocarbon mixtures in industries. In the present work, we have examined the phonon dispersion profiles of PMP using Higgs method for evaluation of phase related normal modes. It leads to complete potential energy distribution and "best fit" Urey-Bradley force field. Characteristic features of the dispersion curves such as repulsion and bunching have been discussed.

The density-of-states have also been calculated from the dispersion curves of PMP to calculate its heat capacity.

In **Chapter 4** we have presented the vibrational dynamics of poly(2-methylbut-2-enylthiophene-3- carboxylate) (PMT). The PMT may refer to a very important class of electroactive polymers due to existence of polyacetylene backbone and electroactive thiophene group as a side chain moiety. We report here studies on the vibrational spectra (FTIR and FT-Raman). The complete normal mode analysis, phonon dispersion and density-of-states for PMT have been reported using Urey - Bradely force field. Some of the distinguished features of the dispersion curves such as cross-over and repulsion are discussed and possible explanations are given in terms of symmetry considerations. In addition, the heat capacity as a function of temperature in the region 10-450 K have been calculated.

Chapter 5 includes the quantum chemical *ab initio* and Density Functional Theory (DFT) study of third order nonlinear optical material 4-chloro-4'dimethylamino-benzylidine aniline (CDMABA). Vibrational spectroscopy has the potential to yield valuable structural and conformational information of molecules, if used in conjunction with accurate quantum mechanical vibrational calculations. Full geometry optimization using *ab initio* Hartree-Fock theory (HF) and DFT followed by a complete vibrational analysis of CDMABA is being reported in the present work. As expected, due to the inclusion of electron correlation, DFT calculations give us better result as compared to HF and are in excellent agreement with the experimental values. Our DFT calculations not only provides excellent match between the experimental FTIR and FT-Raman spectra enabling us assignments of all the bands even in the lower region of spectra but also provide the information about the other molecular properties such as charge distribution,

delocalization of π electrons within the molecule, molecular electrostatic potential, NMR shielding tensors and HOMO-LUMO energy band gap of CDMABA.

Chapter 6 provides the theoretical studies of molecular structure and vibrational spectra of L-Lysine monohydrochloride dihydrate (LLMHCl.2H_2O) using quantum chemical methods. L-Lysine monohydrochloride dihydrate shows large second order nonlinear optical (NLO) properties and good mechanical and thermal stabilities which are essential to use these materials in the fabrication of optoelectronic and photonic devices. Hartree-Folk (HF) and density functional theory (DFT) methods have been used in order to perform geometry optimization and to predict the vibrational spectra of title molecule. These results were then used to interpret the observed vibrational spectra and to elucidate the relationships between molecular structural features, nonlinear response and hyperpolarizability of the title molecule. NBO analysis has been done in order to understand intra- and intermolecular hydrogen bonding within the molecule. The charge distribution, molecular electrostatic potential, first hyperpolarizabilities and HOMO-LUMO energy band gap have also been calculated for this molecule.