Vibrational spectral investigations of biomolecules by means of infrared absorption, Raman and surface-enhanced Raman spectroscopy have become very active areas of recent research. These spectroscopic techniques are now established to be useful tools to derive valuable information about the structure and properties of molecules, hydrogen bonding, vibrational interactions, intramolecular charge transfer, etc from their vibrational transitions. The quantum chemical theoretical calculations can certainly assist to obtain a deeper understanding of the molecular geometry and vibrational spectra with surprising accuracy. This thesis reports the extensive study of vibrational spectral features of the certain biologically active molecules and organic nonlinear optic materials using infrared, Raman and Surface enhanced Raman scattering spectral data, along with density functional theoretical simulations.

The first chapter is of introductory nature and describes the basics of normal modes of vibrations, infrared absorption, Raman scattering, IR and Raman instrumentations, the theory of Surface enhanced Raman scattering and factors affecting the vibrational spectra and the recent advancements in the area of vibrational spectroscopy. A brief literature review of the structural and spectral features of the biomolecules under investigation, which are relevant to the present study are also included.

The second chapter is a general overview of computational and experimental methods employed in the present work. The different theoretical methods of quantum chemical computations, such as molecular mechanics, semi empirical methods, ab initio methods and density functional methods (DFT) are included. Special emphasis is given to DFT methods, along with the methods of optimization of molecular geometry and simulation of vibrational spectra are discussed. Details of the experimental work related to recording the FT-IR, NIR-FT Raman, SERS and NLO measurements are also included.

In the chapter 3, NIR FT Raman, FT-IR and SERS spectra of the biologically active compound Plumbagin (PLBN), have been analyzed, aided by the computed
geometry and their vibrational spectra using density functional theoretical (DFT) computations. Optimized geometry reveals that the contractions of carbonyl bonds are due to the increase of electron donating ability of the \(\text{CH}_3\) group. Vibrational analysis is used to investigate the electronic effects of hyperconjugation and induction of the methyl group with the \(\pi\) orbital of an aromatic ring system, resulting in increase of stretching mode wavenumbers and decrease of infrared intensities. The spectral characteristics of \(\text{C=O} \cdots \text{H}\) interactions are also analyzed. SERS spectra are analyzed to understand the spectroscopic behavior upon adsorption on colloidal silver particle.

In chapter 4, NIR-FT Raman, FT-IR and SERS spectral analysis of chloramphenicol (CLMP), a potential antibacterial drug for the treatment of typhoid fever, is carried out supported by density functional computations. The electronic effects on the vibrational modes of the methylene group resulting from induction have been discussed. The dependence of band positions of the carbonyl stretching modes on the strength of mesomeric effect has also been analyzed. The orientation of the adsorption of the CLMP molecule on silver surface is also inferred using SERS spectra.

The analysis of optimized geometry, computed vibrational spectra, FT-IR, NIR-FT, Raman and SERS spectral studies of the potential anti-cancer drug combretastatin-A1 (CA1), are included in chapter 5. The steric interaction resulting in the phenyl ring twisting is discussed based on the computed geometry. The spectral characteristics of the different effects of back donation and oxygen lone pair-aryl \(p_z\) orbital conjugation in CA1 are discussed. The calculated results have revealed, for the first time, that the synthesized molecule has microscopic nonlinear optical (NLO) behavior with non-zero hyperpolarizability \((\beta)\) values. The adsorption geometry of the molecules on silver surface is also confirmed using SERS spectra.

Chapter 6 describes the vibrational spectral features of dimerisation, nature of hydrogen bonding and other molecular interactions in \((S)\)-phenylsucciinic acid (SPSA) and \((RS)\)-phenylsucciinic acid (RSPSA) crystals. The presences of electronic interactions and Fermi resonance have been inferred from the spectral analysis. The adsorption behaviors of SPSA and RSPSA on silver nano-particles have been theoretically simulated and analyzed with experimental spectra.
The chapter 7 deals with the FT-IR, NIR-FT Raman and SERS spectral analysis of novel NLO material methyl 3-(4-methoxy phenyl) prop-2-enoate (MMP), supported by equilibrium geometry and vibrational spectra computed using Hartree Fock and density functional methods. The intramolecular charge transfer between the donors and the acceptor group through the $\pi$-system, responsible for NLO activities, is investigated from the vibrational spectra and the DFT computations. The effects of electronic interactions such as back donation and induction and Fermi resonance on the vibrational modes of the methoxy groups have also been discussed. The adsorption geometry of the molecule on silver surface is analyzed using SERS spectra.

The NIR-FT Raman, FT-IR and SERS spectral analysis of potential NLO material $\rho$-hydroxy acetophenone (PHA) and Methyl $\rho$-hydroxy benzoate (MPHB) along with density functional computations are included in chapters 8 and 9. Vibrational analysis is used to investigate the electronic effects of the methyl group with the $\pi$ orbital of an aromatic ring system. The spectral changes occurring in donor and acceptor moieties and in the conjugated path due to intramolecular charge transfer, responsible for NLO activity, have been analyzed. The large enhancement of in-plane ring stretching and ring stretching modes in the surface-enhanced Raman scattering spectrum indicates that the PHA and MPHB molecule are adsorbed on the silver surface in a stand on orientation.