Spectroscopy is a necessary tool and experimental technique for determining the electronic structure of atoms and molecules. Among the various types of spectroscopy, vibrational spectroscopy is a valuable tool for the elucidation of molecular structure. It also provides important information about the intramolecular forces acting between the atoms in a molecule, the intermolecular forces in condensed phase and nature of the chemical bond.

Vibrational spectroscopy gives a dynamical picture of the molecule. Vibrational spectra can be utilized directly and simply as molecular fingerprints to characterize and identify the molecule. Information about the symmetry and vibrational energies of the molecules can be obtained to a reasonable accuracy from their Raman & Infrared (IR) spectra. The information obtained from structural parameters, conformational stabilities, force constants, vibrational frequencies as well as infrared and Raman band intensities represent significant contributions to the field of vibrational spectroscopy. Rapid developments in Fourier transform have led to higher resolution, total wavelength, coverage, higher accuracy in frequency and intensity measurements.

The philosophy of sophisticated and cost effective computational methods of vibrational spectroscopy significantly changed after the introduction of quantum chemical calculations. This has made it possible to perform a complete vibrational analysis on relatively large polyatomic molecules. For a proper understanding of IR and Raman spectra, a reliable assignment of all vibrational bands is essential. For this purpose, quantum chemical methods are invaluable tools. Among them,
Density Functional Theory (DFT) methods have evolved as a powerful quantum chemical tool for the determination of the structure of molecules.

In the present work, the FTIR and FT-Raman spectra of various compounds of some specific applications have been chosen for vibrational spectroscopic analysis. Samples are procured in the spectroscopic pure form from Lancaster and Alfa Aesar chemical company, and used as such for the spectral measurements. The room temperature FTIR and FT-Raman spectra of the samples were recorded in the regions 4000-400 and 4000-50 cm\(^{-1}\) respectively at a resolution of ±1 cm\(^{-1}\).

The density functional theory calculation with B3LYP method and 6-31G*, 6-31G** and 6-311+G** basis sets have been carried out to obtain the optimized geometrical parameters, energy calculations, force fields and prediction of intensities. The molecular geometry optimization and vibrational frequencies calculations of the selected molecules are performed with the Gaussian 98W software package. The transformation of force field and the subsequent normal coordinate analysis including the least square refinement of the scaling factors, calculation of total energy distribution (TED), prediction of IR and Raman spectra were performed by the MOLVIB software package. The DFT computations provide vibrational frequencies usually in Fourier agreement with the experiment. The proposed thesis is organized in ten chapters.

Chapter one deals with the preliminary concepts of vibrational spectroscopy, group theory in determining the symmetry and normal modes of vibration and also the selection rules for IR and Raman spectroscopy are discussed.

In chapter two, the procedure of quantum chemical calculations and normal coordinate analysis of the vibrational spectra are explained.
The recording of spectra, the instrumentation of FTIR and FT-Raman spectrophotometers and the sample handling techniques are the subject matter for chapter three.

In chapter four the FTIR and FT-Raman spectra of 1,3-dibromo 2,4,5,6-tetrafluoro benzene and 1,2,3,4,5-pentafluoro benzene are discussed. The fluorine and bromine substitutions in the aromatic ring produced a remarkable effect on the geometric and spectroscopic properties of the title compounds which are highly electronegative. The results of the SQM studies of structure and vibrational spectra are also analyzed.

Chapter five focuses on the density functional theory calculations and vibrational analysis of 3,5-dichloro hydroxy benzaldehyde and 2,4-dichloro benzaldehyde. Vibrations of OH and CHO groups reflect the effect of strong intra molecular hydrogen bonding. All the vibrations affected by this hydrogen bonding are described satisfactorily by the scaled DFT force fields.

The effect of hydrogen bonding on the structure and vibrational frequencies of benzoic acid, salicylic acid and chlorine substituted benzoic acid and salicylic acid are analyzed form the subject matter for chapter six. Quantum chemical calculations involving carboxylic acids have to account for the electron rich carboxyl group. Intra and inter molecular factors affect the carbonyl absorption due to inductive, mesomeric, field and conjugation effects.

Chapter seven is devoted to simulation of IR and Raman spectra based on DFT force fields and the assignments of vibrational bands of naphthalene and octafluoro naphthalene. The activity of octafluoro naphthalene is greater than naphthalene due to the presence of fluorine which is highly electronegative.
Chapter eight is concerned with the quantum chemical calculation and normal coordinate analysis of 1-hydroxy naphthalene. The peak is broader and its intensity is higher than that of a free OH vibration which indicates involvement in an intermolecular hydrogen bond. Hydroxyl compounds, containing active hydrogen grouping undergo self association and their spectra are accordingly very dependent on the state of the sample.

In chapter nine, a detailed theoretical and spectral analysis of 6-bromo 2-naphthoic acid and 2-naphthoic acid was made. The results obtained and their significance are also discussed elaborately. The influence of carbonyl group in the vibrational frequencies of the title compounds is discussed.

In the last chapter, the normal modes of 1-napthyl acetic acid has been identified and assigned on the results of total energy distributions obtained from normal coordinate analysis. The influences of carbonyl and methylene groups in the vibrational frequencies of the title compound are discussed.