Chapter 1

General introduction

Spectroscopy is the field of study of the interaction between matter and radiations. Molecular spectroscopy deals with mainly absorption, emission and scattering of electromagnetic radiation by molecule. It reveals structural information, dynamics and wide range of properties of the molecule. During the last century, significant and substantial progress has been made in experimental investigations and their theoretical explanations [1–13]. The different regions (e.g. ultraviolet–visible, infrared and microwave) of electromagnetic radiation are used to investigate various molecular processes. Each molecule produces unique spectrum because of its unique set of electronic, vibrational and rotational levels. The analyses of these spectra provide information regarding the quantized energy levels of the molecules and that can be used for qualitative and quantitative chemical analysis as well as for test of quantum chemical calculations.

The various kinds of spectroscopy are used to investigate molecules but the present study is restricted to vibrational spectroscopy which is most important tool in the multidisciplinary areas of sciences. This spectroscopy involves the transitions between quantum states that are evolved due to vibrational motion of the nuclei around their mean position. The accurate measurements of these transitions have become possible due to the advance developments in instrumentations that produce the reliable spectroscopic information by measuring the vibrational spectra of molecules [1–5]. The vibrational spectroscopy provides information like molecular structure, molecular vibrations, isomerism, thermodynamic properties, strength of chemical bonds, intermolecular and intramolecular interactions of molecules in solid, liquid and gas phase [9, 14–17]. It is commonly used for characterisation and
identification of materials, structure elucidation, reaction monitoring and quality control in industries.

Molecule possesses energy due to its translation, rotational and vibrational motions. All nuclei of a molecule vibrate periodically about their equilibrium position. This periodic motion is known as molecular vibration. During molecular vibration, all nuclei of a molecule are in periodic motions with same frequency and same phase but with different amplitudes. Because of the equality of phase and frequency, all nuclei reach their positions of maximum displacement at the same time and pass through their equilibrium positions at the same time. A mode of vibration having all these characteristics is called a normal mode, and its frequency is known as a fundamental frequency of the mode [9]. An \( N \)-atom non-linear (or linear) molecule has \( 3N-6 \) (or \( 3N-5 \)) normal modes of vibrations. In general, a normal mode of vibration involves motions of all the atoms of the molecule. There are some conditions in which normal modes are localized in a part of the molecule.

The infrared (IR) and Raman spectroscopy are the two main techniques used to obtain vibrational spectra. The success of vibrational spectroscopy in the field of sciences is due to technical developments, for instance, availability of laser as an excitation source for Raman spectroscopy and the development of interferometers for measuring accurate vibrational spectra. These are the important milestones in the development of vibrational spectroscopy. These techniques involve the interaction of radiation with molecule by different mechanisms (absorption or scattering) which change the vibrational state of molecule. The complete vibrational analysis requires both IR and Raman spectroscopy because they have different selection rules and sensitivity to molecular vibrations. The infrared absorption spectroscopy is a direct absorption process in which the radiation of frequencies equal to those of the normal modes of vibrations of a molecule is absorbed from continuous infrared sources. In Raman spectroscopy, the molecular vibrations are excited by the inelastic scattering of monochromatic radiation by the molecule.

The transitions between the vibrational states are governed by the vibrational selection rules i.e., electric dipole and Raman selection rules [18]. The charge distribution over molecule undergoes a periodic change during the vibrational motion and, therefore, in general, the dipole moment changes periodically. The vibrations,
connected with a change of dipole moment, show absorption in the infrared region and are known as infrared active. The integral

\[ R^{v'}_{v''} = \int \psi_{v'}^* \mu \psi_{v''} \, d\tau \]  

(1.1)

where \( \mu \) is the dipole moment vector; \( \psi_{v'} \) and \( \psi_{v''} \) are the wave functions of the upper \((v')\) and lower \((v'')\) vibrational state respectively; is known as the electric dipole transition moment for a vibrational transition and the intensity of transition is proportional to the square of the magnitude of this integral. The vibration is said to be IR active when at least one of the components of the electric dipole transition moment is non–zero. The symmetry considerations are also important in dipole selection rules. There are symmetry requirements for the integral (Eq. 1.1) to be non–zero. The symmetry requirement for the transition between states, which are non–degenerate, is that the symmetry of the quantity to be integrated is totally symmetric which can be given as:

\[ \Gamma(\psi_{v'}) \times \Gamma(\mu) \times \Gamma(\psi_{v''}) = A \]  

(1.2)

where \( A \) is the totally symmetric species of any point group. The symmetry requirement for the transition between states, of which at least one is degenerate, is that the symmetry species of the quantity to be integrated contains the totally symmetric symmetry species. It can be written as:

\[ \Gamma(\psi_{v'}) \times \Gamma(\mu) \times \Gamma(\psi_{v''}) \supset A \]  

(1.3)

The vibrational modes, connected with change in polarizability, which arises due to the oscillating electric field of the incident radiation on the molecule, appear in Raman spectrum of a molecule. The intensity of scattered Raman light is proportional to the square of the transition moment,

\[ R^{v'}_{v''} = \int \psi_{v'}^* \mu^0 \psi_{v''} \, d\tau \]  

(1.4)

The amplitude of dipole moment, \( \mu^0 = \alpha' Q_k E^0 \), where \( Q_k \) is the normal coordinate for the vibration \( k \) and \( \alpha' \) is the derivative of polarizability tensor which has the six different components. The vibration is said to be Raman active when at least one of the six components of the integral, \( \int \psi_{v'}^* \mu^0 \psi_{v''} \, d\tau \), remains non–zero. The symmetry requirement for transitions between non–degenerate vibrational states is that the
product of the symmetry species of the quantities inside the integral must be totally symmetric. This can be written as:

\[ \Gamma(\psi'_i) \times \Gamma(\alpha_{ij}) \times \Gamma(\psi''_p) = A \quad (1.5) \]

Since,

\[ \Gamma[(d\alpha_{ij}/dQ_k)Q_k] = \Gamma(\alpha_{ij}) \quad (1.6) \]

The symmetry requirement for the transition between two vibrational states (one of which is degenerate) becomes:

\[ \Gamma(\psi'_i) \times \Gamma(\alpha_{ij}) \times \Gamma(\psi''_p) \supset A \quad (1.7) \]

The molecules having the center of inversion follow the rule of mutual exclusion. According to this rule, the fundamental vibrations which are active in the Raman spectrum are inactive in the infrared spectrum and vice versa. However, the converse is not always true: there are some vibrations which are inactive in both the IR and Raman spectra [18, 20]. The IR and Raman spectra have many similarities of intensities but also have some differences. The Raman spectrum provides some additional information regarding symmetry of vibrations. The measurement of the depolarization ratio of Raman band gives the degree to which polarization properties of the incident radiation may be changed after scattering.

The molecular vibrations are anharmonic in nature. Therefore, combinations and overtone bands may appear in the vibrational spectrum in addition to the fundamentals. However, these bands are generally weaker than the fundamentals [19, 20]. Vibrational spectra of polyatomic molecules of medium size are generally very complex due to large number of bands. The bands, which appear in vibrational spectra, are characterized by their frequencies, intensities and band shapes, which give the information of energies, polar characters or polarizabilities and environmental effects respectively [16]. The vibrational spectra of the organic polyatomic molecules can be split in two spectral regions for the convenience of its interpretation. These are functional group (higher wavenumber) and fingerprint regions (lower wavenumber) or region of skeletal vibrations. The normal modes corresponding to the skeletal vibrations involve strong coupling between stretching or bending motions of atoms in a chain or ring. The two different molecules may have the same band positions in the functional group region due to a common functional groups but different in the
fingerprint region. The fingerprint region has unique signature for a molecule. The wavenumbers and their intensities of group vibrations are fairly constants from one molecule to another. Many transferable group vibrations occur in functional group region. The appearance of Raman band depends on the magnitude of the change of the amplitude of the induced dipole moment. This change is less sensitive than the change of dipole moment due to the environment of the vibrating group. Therefore, intensities of group vibrations are more accurately transferrable from one molecule to another or from one phase to another in the Raman than the IR spectrum. The group vibrations are termed as symmetric and asymmetric stretching, in-plane and out-of-plane bendings (or deformation), rocking, twisting, scissoring, wagging, torsion, ring breathing, inversion (or umbrella) and Kekule type [18].

Practically, it is very difficult task, almost impossible, to get isolated molecule. In nature, the molecules occur within the intermolecular networks. Therefore, the structure, vibrational frequencies and other properties of the molecule are affected due to influence of intermolecular interactions. Factors such as anharmonic mode-mode coupling interactions [21–23], intramolecular and intermolecular hydrogen bonding [24–26], Fermi resonance and Darling-Dennison resonance [18–20, 27–29] affect the bands of vibrational spectra. The studies of intermolecular and intramolecular hydrogen bonding interactions are important because they stabilize the structure of molecules [30]. Many people have studied the tera–Hertz time domain (THz–TD) spectra (0.1–3.0 THz or 3–100 cm⁻¹) of DNA and amino acids that reveal the signature as vibrational modes of intermolecular and intramolecular hydrogen bond networks [30–32]. It is still not easy to distinguish between intramolecular and intermolecular vibrational modes experimentally since they have similar frequencies. The ab initio theoretical models play crucial role in understanding the vibrational spectra under influence of the intramolecular and intermolecular interactions, resonances and mode-mode coupling.

The molecular vibrations are associated to the force constants which can be derive from the fundamental vibrational frequencies. The bond stretching and angle bending type of force constants are associated to a molecule. The bending force constants are more sensitive than stretching one. The force constants for stretching and bending vibrations of groups of atoms are invariant to the neighbouring atoms of
the molecule. Therefore, force constants can be transfer from one molecule to other similar molecule [18].

In 1955, Wilson et al. [9, 33] developed FG matrix method for normal coordinate analysis (NCA) [33]. This provides the normal coordinates, force constants, vibrational frequencies and the potential energy distribution of the various modes. These calculations have played a vital role in making assignments of vibrational bands. The NCA method assumes the fore information of the equilibrium molecular geometry, atomic masses and vibrational frequencies. In this method, the secular determinant, \(|FG - \lambda I| = 0\), is solved where the \(F\), \(G\), \(I\) are matrices. The matrix \(F\) defines the harmonic force constants; \(I\) is the unit matrix; \(G\) is invert kinetic energy matrix and \(\lambda\) is related to frequency \((\nu)\) of the mode by the expression, \(\lambda = 4\pi^2c^2\nu^2\). The \(FG\) calculations involve the internal coordinates and start with the adhoc assignments of bands of vibrational spectra [34].

In the field of vibrational spectroscopy, the quantum chemical methods play very crucial role for interpreting and assigning the vibrational spectra of medium sized polyatomic molecules. Moreover, based on equilibrium molecular geometry, the quantum chemical methods provide various properties of molecules in their ground and excited states. Improvements in computational power along with quantum chemical programs enable the utilization of ab initio quantum mechanical calculations for vibrational analysis. The vibrational analysis of molecules takes into accounts both the vibrational frequencies and intensities to assure reliable assignments of experimentally observed vibrational bands. The ab initio quantum chemical methods are based on first principle calculations, which are used to solve Schrödinger equations without reference to experimental parameters except physical constants. These are mathematically rigorous and accurate, but computationally expensive. Among these methods, DFT is very popular because it is more accurate and computationally less expensive. This method comprises variety of gradient-corrected exchange-correlation functionals such as BLYP, B3LYP and B3PW91 that generate reliable theoretical molecular data. HF method is important due to its legacy but the results deviate much from experimental results due to negligence of electron-electron correlations. In post HF methods e.g., multi-configuration self-consistence field (MCSF) and Moller-Plesset perturbation (MPn) methods, such correlations have been
included. Currently, high-speed computing systems, numerical algorithms and the quantum chemical methods [35–39] have been efficiently used to solve many chemical and biological problems.

1.1 Motivation

Vibrational spectroscopy technique is an effective and sensitive tool to probe the basic process of life and it has proven itself a valuable contributor in the field of medicine, biochemistry, materials science, analytical chemistry and pharmaceutical science etc [40, 41]. In addition to this experimental technique, the \textit{ab initio} HF, MP2 and DFT methods are used to describe the structural and vibrational properties of medium to large sized molecules. The vibrational spectra of medium to large size organic molecules are very complex and appear with many overlapping fundamental as well as non–fundamental bands. Therefore, the analysis of vibrational spectra becomes very difficult and tedious. The theoretical calculations using \textit{ab initio} approach play key role in assigning the vibrational spectra with good accuracy. The \textit{ab initio} HF method is a fundamental approach but show large deviations from experimental results due to ignorance of electron–electron correlation effects. This has motivated to do the calculations using methods that include these effects. The MP2 and DFT methods include these effects and reproduce the results with great accuracy. The molecules show anharmonicity in nature. Therefore, the combination and overtone bands appear along with fundamentals in vibrational spectra of molecules. The harmonic force field calculations by these methods are useful to interpret vibrational spectra due to its low computational cost but are not of sufficient accuracy. This approach does not include the anharmonic terms in potential energy function that is itself of great interest. Therefore, such calculation does not give the information regarding combination and overtone bands. The harmonic vibrational calculations generally overestimate the frequency with respect to the experimental one. Various scaling procedures are used to compensate discrepancies between theoretical and experimental frequencies. These are useful to assign vibrational spectra but are not based on first principle. The advantages of anharmonic calculations motivate to do simulation of vibrational spectra in the anharmonic approximations within MP2 and DFT framework. These calculations give the reliable and accurate data that help in assigning the fundamentals as well as combination and overtone bands without any
scaling. The vibrational modes are coupled due to anharmonicity and, therefore, affect the vibrational spectrum. The vibrational modes show anharmonicity due to mode–mode coupling along with intrinsic anharmonicity. It has motivated to do mode–mode coupling computation to study the anharmonic nature of vibrational modes. In nature, the molecules are found in hydrogen bond networks. In order to achieve the theoretical results close to solid phase or matrix–isolated data, it is necessary to define structure within intermolecular hydrogen bond network for the calculations. Therefore, present thesis also comprises quantum chemical calculations on intermolecular complexes of associated molecule to investigate the effect of associations.

1.2 Objectives and scope of the present work

The present work aims to study some polyatomic molecules of biological, pharmaceutical and industrial importance (L–aspartic acid, o–, m–, p–iodonitrobenzene, 3–methyladenine and allantoin) using FTIR, Raman spectroscopy and quantum chemical calculations. The objectives of the present thesis include the computation of vibrational spectra in the harmonic and anharmonic approximations, molecular structures and mode–mode coupling strengths. Molecular simulations for the intermolecular complexes of associated molecules have been performed including some molecular properties. The quantum chemical approaches do help in solving various chemical problems. The FTIR and Raman spectroscopy along with efficient algorithm and theoretical models are very effective in analysing the molecules. The present investigations of molecular vibrations provide the site for the new research for understanding the physics of complex biological system. The vibrational spectroscopy has very broad range of application to the biomedical, biochemical, genetic engineering etc. The elucidation of the structure and monitoring of vibrations of the molecules of biological importance using spectroscopy and high–level theoretical calculations, help to understand the various biochemical and biological processes. The research on molecules are of high demands because these are utilized in pharmaceutical, polymer and chemical industries. The biochemical components of a cell can be observed with the help of their inherent vibrational signatures. Any changes in the structure and biochemical composition due to stress, injury or any disease at cellular level can be understood with the help of vibrational
spectroscopy [40]. It proves to be a potential tool in diagnosing various clinical disorders and can be used to identify the foreign molecular species, bacteria, cancerous cells and metabolites in living cells. This has increased the utility in different field of research due to advance development in FTIR and Raman spectroscopies.

1.3 Thesis overview

The work presented in thesis mainly deals with the studies of vibrational spectroscopy of polyatomic molecules. It also includes molecular structure and properties. The molecules for investigations are L-aspartic acid [42], o-, m-, p-iodonitrobenzene [43], 3-methyladenine [44] and allantoin [45]. These are chosen because of their biological, pharmaceutical and industrial importance. The short summary of each thesis chapter are given as follows.

In the above sections of Chapter 1, a brief introduction of the molecular vibrations, vibrational spectroscopy and quantum chemical methods are presented. It includes the importance of vibrational spectroscopy and quantum chemical calculations which are used for investigating the polyatomic molecules. It also comprises the motivation, objectives, scope of the work and the thesis structure.

Chapter 2 is devoted to methodology of vibrational spectroscopy that includes experimental and theoretical methods used for the present work. The instrumentation and advantages of FTIR and Raman spectroscopy techniques have been discussed in this chapter. On the other hand, the brief descriptions on the quantum chemical methods like \textit{ab initio} Hartree–Fock (HF), Moller–Plesset second order perturbation (MP2) method and density functional theory (DFT) along with basis sets are presented. The structures of the calculations are presented in terms of geometry optimization, vibrational frequencies calculations and potential energy distribution calculations. The anharmonic force field calculations that include second order perturbation (PT2), vibrational self-consistent field (VSCF) and correlation corrected VSCF (CC–VSCF) approaches have been discussed. In addition to these, the calculation of mode–mode coupling strengths based on 2-mode coupling representation of the quartic force field (2MR–QFF) approximation as well as estimation of IR and Raman intensities are also described. The theory regarding
molecular properties like molecular electrostatic potential (MEP), thermochemistry, non-linear optical properties, atomic charges, chemical reactivity indices and natural bond orbitals (NBO) have been also included in this chapter.

Chapter 3 mainly deals with the vibrational and quantum chemical studies of L-aspartic acid. The experimental vibrational spectra were fully studied with the aid of quantum chemical calculations. The molecular structure and vibrational spectra were computed using DFT/B3LYP, MP2 and HF calculations in the harmonic as well as anharmonic approximations with triple zeta Pople's and Dunning basis sets. The anharmonic vibrational frequencies were obtained using PT2, VSCF and CC-VSCF approaches. The correlation plots, root mean square (RMS) and mean absolute deviation (MAD) values are obtained that reveal the good agreement between theoretical and experimental data. The vibrational spectra have been assigned accurately using potential energy distribution (PED) values and with the help of animated modes. The non-fundamental bands of the FTIR spectrum have been also assigned with the help of anharmonic computations. To study the anharmonic mode–mode coupling, the coupling integrals have been computed using 2-mode coupling representation of the quartic force field (2MR–QFF) approximation within DFT framework. The simulations on L-aspartic acid dimers (D1 and D2) have been performed at B3LYP/6–311G(d,p) level of theory to investigate the effect of the intermolecular interactions on the structure and vibrational frequencies. The anharmonic vibrational frequencies of monomer and scaled frequencies of dimer, D1, are found close to experimental values. Moreover, various molecular properties such as atomic charges, non-linear optical (NLO) properties, molecular electrostatic potential (MEP) diagram, thermodynamic properties, natural bond orbital (NBO) analysis, etc. are also presented.

Chapter 4 presents the studies on ortho–, meta–, para–iodonitrobenzene using vibrational spectroscopy and quantum chemical calculations. The molecular structure and vibrational spectra were computed using DFT/B3LYP, MP2 and HF methods in the harmonic as well as anharmonic approximations. The basis sets 6–311G(d,p), 6–311++G(d,p) and cc–pVTZ were used on each atoms except iodine in iodonitrobenzenes. The basis sets for the heavy elements beyond the fourth row in the periodic table, are relatively limited. The basis sets 3–21G* and LANL2DZ were
used for iodine atom. To determine the stable conformations of these molecules, the
torsional angle T (C–C–N–O) was varied and energy profiles were obtained. The
assignments of vibrational modes of isomeric iodonitrobenzenes were done by using
potential energy distribution (PED) and vibrational assignments of benzene,
nitrobenzene and iodo benzene. The anharmonic vibrational frequencies were obtained
using PT2 approach within HF, MP2 and DFT framework. The correlation plots,
RMS and MAD values were used to compare between theoretical and experimental
data. The combination and overtone bands appeared in the FTIR spectra are also
assigned. This chapter demonstrates the comparative studies of o−, m−,
p−iodonitrobenzene. Moreover, atomic charges, MEP mapping, HOMO–LUMO,
NBO analysis, thermodynamics quantities and other molecular properties are
presented.

Chapter 5 describes the experimental and theoretical investigations on
3–methyl adenine molecule. This chapter presents complete vibrational analysis using
FTIR, FT–Raman and anharmonic force field calculations. The molecular geometry
and vibrational spectra of 3–methyl adenine in the ground state are computed by using
DFT (B3LYP and B3PW91), MP2 and HF methods in the harmonic as well as
anharmonic approximations with 6–311G(d,p), 6–311++G(d,p) and cc–pVTZ basis
sets. The anharmonic vibrational frequencies were obtained using PT2, VSCF and
CC–VSCF approaches. The PT2 approach was used within HF, MP2 and DFT
frameworks while VSCF and CC–VSCF algorithms were employed at
B3LYP/6–311G(d,p) level of theory. The correlation plots, RMS and MAD values
were used to compare between theoretical and experimental data. The vibrational
spectra have been assigned accurately using literature and with the help of animated
modes. In order to know the coupling between pairs of modes, the magnitude of
mode–mode coupling for the ground state has been estimated. The 2MR–QFF
potential energy function was used for calculating anharmonic mode–mode coupling
strengths. The coupling between some important pairs of vibrational modes has been
discussed. The intermolecular hydrogen bonding interactions affect the molecular
structure, vibrational spectra and other molecular properties of monomer. Therefore,
in order to make good correlation between theoretical results and solid phase
experimental data, the simulations have been performed also on dimeric and trimeric
structures of 3–methyl adenine at DFT/6–311G(d,p) level of theory in the harmonic
approximation. Moreover, atomic charges, HOMO–LUMO analysis, NBO analysis, NLO properties and various other molecular properties have been also presented. The chemical behaviour and the reactivity of the isolated 3–methyladenine were investigated using HOMO (ionization potential) and LUMO (electron affinity) energy eigenvalues calculated at DFT level. These values have been used to compute chemical reactivity descriptors.

Chapter 6 comprises the investigations on the molecular structure and vibrational spectra of allantoin molecule using experiments as well as quantum chemical calculations. FTIR and FT–Raman spectra were recorded and analysed using HF, MP2 and DFT(B3LYP) method along with 6–311G(d,p), 6–311++G(d,p) and cc–pVTZ basis sets. The molecular structure, anharmonic vibrational spectra, natural atomic charges, non–linear optical properties, etc. have been computed for the ground state of allantoin molecule. The anharmonic vibrational frequencies are calculated using PT2 algorithm (Barone method) as well as VSCF and CC–VSCF methods. The PT2 approach was used within HF, MP2 and DFT frameworks while VSCF and CC–VSCF algorithms were employed at B3LYP/6–311G(d,p) level of theory. These methods yield results that are in remarkable agreement with the experiments. The coupling strengths between pairs of modes are also calculated using coupling integral based on 2MR–QFF approximation. The simulations on allantoin dimers have been also performed at B3LYP/6–311++G(d,p) level of theory to investigate the effect of the intermolecular interactions on the molecular structure and vibrational frequencies of the monomer. Vibrational assignments are made with the great accuracy using PED calculations and animated modes. The combination and overtone bands have been also identified in the FTIR spectrum with the help of anharmonic computations. The important global quantities such as electro–negativity, electronic chemical potential, electrophilicity index, chemical hardness and softness based on HOMO, LUMO energy eigenvalues are also computed. NBO analysis has been performed for monomer and dimers of allantoin at B3LYP/6–311++G(d,p) level of theory. The correlation plots, RMS and MAD values were used to compare between theoretical and experimental data.

The final chapter of this thesis, Chapter 7, includes the overall conclusion of thesis.
References


