CHAPTER – I

INTRODUCTION TO VIBRATIONAL SPECTROSCOPY

Abstract

The preliminary concepts of vibrational spectroscopy and its application to polyatomic molecules are discussed. Various types of force fields with their relative merits and limitations are given briefly. The symmetry elements and the associated symmetry operations are explained. The application of group theory in determining the normal modes of vibrations and the selection rules for Infrared and Raman activities are also outlined.
INTRODUCTION TO VIBRATIONAL SPECTROSCOPY

1.1 INTRODUCTION

Spectroscopy is the branch of science dealing with the study of interaction of electromagnetic radiation with matter. Electromagnetic radiations are produced by the oscillation of electric charge and magnetic field residing on the atom. Spectroscopic methods are generally used to measure the energy difference between various molecular energy levels and to determine the atomic and molecular structures. The most important consequence of such interaction is that energy is absorbed or emitted by the matter in discrete amounts called quanta. The various branches of spectroscopy generally involve the measurement of two important experimental parameters. i.e.

1. The energy of the radiation absorbed or emitted by the system and
2. Intensity of the spectral lines.

These data are correlated with the molecular and electronic structure of the substance and with intra and intermolecular interactions. Molecular spectroscopy explains various methods for the better understanding of molecular motions. Information regarding molecular structure, chemical properties and thermodynamic properties can be obtained from the molecular spectra.

An isolated molecule in space has various forms of energy by virtue of different kinds of motion and intramolecular interactions. The molecule possesses translational energy by virtue of the motion of the molecule as a whole. It possesses rotational energy due to bodily rotation of the molecule
about an axis passing through the centre of gravity of the molecule. The molecule possesses vibrational energy due to periodic displacement of its atoms about their equilibrium positions. It also possesses electronic energy since the electrons associated with each atom and bond is in constant motion. It also possesses nuclear energy due to nuclear and electron spins. As a first approximation, the total energy of a molecule can be expressed as the sum of the constituent energies, that is
\[ E_{\text{total}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} + \ldots \] ... (1.1)

It is assumed that the various types of energy associated with different motions of the molecule are independent of one another. Among the various types of spectroscopy, Vibrational spectroscopy gives valuable insight into the structural feature of molecules. It provides vital information about molecular structure, inter and intra molecular forces, crystalline environments, vibrational interactions, distortion of molecules, hydrogen bonding, isomerism, molecular rotations, etc.

Vibrational spectroscopy is concerned with vibrational transition due to absorption and emission of electromagnetic radiations. These transitions appear in the \(10^2\) to \(10^4\) cm\(^{-1}\) region and originate from the vibrations of nuclei constituting the molecule. The vibrational energies of the molecule can be studied by infrared and Raman spectroscopy. The infrared and Raman spectroscopic methods frequently yield complementary types of information. For a complete vibrational analysis, both methods should be necessarily used \([1 - 4]\).

The study of vibrational spectroscopy has resulted in a large volume of data on the vibrations of polyatomic molecules. Vibrational spectroscopy
gives a dynamic picture of the molecule. With the introduction of Fourier transform infrared spectrometers and lasers as source for recording Raman spectra, vibrational spectroscopy has become an effective tool for the elucidation of molecular structure [5,6].

Vibrational spectroscopy has contributed significantly to the growth of different areas as polymer chemistry, catalysis, fast reaction dynamics and charge – transfer complexes [7]. The use of spectroscopy as a means of probing the structure of simple and even complex molecules has been of inestimable value in the field of structural study of organic, inorganic and organometallic compounds, biological molecules, polymers and minerals [5, 6, 8-17].

1.2 INFRARED SPECTROSCOPY

Infrared spectroscopy is widely used for the identification of organic compounds because of the fact that their spectra are generally complex and provide numerous maxima and minima that can be used for comparison purposes. Infrared spectroscopy is generally concerned with the absorption of radiation incident upon a sample. IR technique when coupled with intensity measurements may be used for qualitative and quantitative analysis. Currently, this technique has become more popular as compared to other physical techniques (X-ray diffraction, electron spin resonance, etc.,) in the elucidation of the structure of unknown compounds.

1.2.1 Infrared Activity

A normal mode of vibration to be infrared active, there must be a change in the dipole moment of the molecule during the course of vibration. During the vibrational motion of a molecule, a regular fluctuation in the dipole
moment occurs, and field is established which can interact with the electrical field associated with radiation. For the absorption of infrared radiation, and change in the amplitude of the molecular vibration, a molecule must undergo a net change in its dipole moment as a result of its vibrational or rotational motions.

**1.3 QUANTUM THEORY OF RAMAN EFFECT**

A simple method for obtaining vibrational and rotational frequencies of molecule is through observation of Raman effect. Quantum mechanics gives a qualitative description of the phenomenon of Raman effect. A schematic energy level diagram is shown in Fig. 1.1. The interaction of a photon of the incident light beam with the molecule in its ground electronic and vibrational state (v=0) may momentarily raise the molecule to a time dependent quasi-excited electronic state (or a virtual state) whose height is above the initial energy level. Virtual states are those in which the molecule has a very short mean lifetime and hence the uncertainty in energy is large according to the Heisenberg uncertainty principle.

In the case of stokes line, the molecule at ground electronic state (v=0) is excited to the virtual electronic state, then radiates light in all directions except along the direction of the incident light. On return to the ground electronic state, quantum vibrational energy may remain with the scattering species and there will be a decrease in the frequency of the scattered radiation.

Anti-Stokes lines arise when the molecule is already in an excited vibrational state (say v=1) and is raised to quasi-excited state and reverts to ground electronic state (v=0) on scattering of photon. Scattered photon is the
sum of the energy of incident photon and the energy between the vibrational levels $v = 1$ and $v = 0$.

In another instance, a molecule in the ground state on interacting with a photon and attaining the virtual state may leave the unstable electronic state and return to the ground electronic state. In this case, scattered photon has the same energy as the incident radiation and the result is Rayleigh scattering.

![Energy Levels Involved in Raman and Rayleigh Scattering](image)

**Fig. 1.1 Energy levels involved in Raman and Rayleigh Scattering**

### 1.3.1 Raman activity

For a molecular vibration to be Raman active, there must be a change in the polarizability of the molecule during this vibration. This change can be considered as being a change in the shape of the electron cloud surrounding the molecule (polarization ellipsoid). In a molecule without any symmetry elements, all the normal vibrations are accompanied by polarizability changes and the corresponding frequencies appear in the Raman spectrum. But in a symmetric molecule, some of these vibrations may not produce any change in
polarizability and the corresponding normal frequencies are not observed. Such vibrations are Raman inactive [1, 5, 10, 18-26].

Raman spectrum gives information about molecular symmetry, which can then be used to determine the molecular configuration. There are various chemical problems, which have been successfully solved with the help of Raman spectra.

1.4 SELECTION RULES FOR IR AND RAMAN SPECTRA

Rules that limit the number of transition between energy levels are called selection rules. All the transitions may not be active in both IR and Raman spectra. Some may be active in IR while inactive in Raman or vice versa. Some of the transitions may be inactive in both IR and Raman spectra. In a molecule having a centre of symmetry, Raman active transitions are IR inactive and IR active modes are inactive in Raman.

1.4.1 Selection Rule for IR

According to quantum mechanics, the selection rule for the infrared spectrum is determined by the integral

$$\left[ \mu \right]_{v',v''} = \int \psi_{v''}^\ast(Q_a) \mu \psi_{v'}(Q_a) dQ_a \quad \ldots \quad (1.2)$$

Here $\mu$ is the dipole moment in the electronic ground state. $\psi$ is the vibrational eigen function, $v'$ and $v''$ are the vibrational quantum numbers of the states before and after transition respectively and $Q_a$ is the normal coordinate whose activity is to be determined. The dipole moment can be resolved into three components in the $x$, $y$ and $z$ directions, as

$$\left[ \mu_x \right]_{v',v''} = \int \psi_{v''}(Q_a) \mu_x \psi_{v'}(Q_a) dQ_a$$

$$\left[ \mu_y \right]_{v',v''} = \int \psi_{v''}(Q_a) \mu_y \psi_{v'}(Q_a) dQ_a$$

$$\left[ \mu_z \right]_{v',v''} = \int \psi_{v''}(Q_a) \mu_z \psi_{v'}(Q_a) dQ_a$$
For the vibrations to be infrared active, at least one of the components of the derivative of the dipole moment with respect to the normal coordinate, taken at the equilibrium position, should be non-zero. If all the integrals are zero, the vibration is infrared inactive [11,12].

1.4.2 Selection Rule for Raman Spectra

The selection rule for the Raman spectrum is determined by the integral.

$$[\alpha]_{\nu'\nu} = \int \psi_{\nu'}^*(Q_a) \alpha \psi_{\nu'}(Q_a) dQ_a \quad ... (1.3)$$

The polarizability of the molecule consists of six components $\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$, $\alpha_{xy}$, $\alpha_{yz}$ and $\alpha_{xz}$. For the vibration to be Raman active, at least one of these integrals should be non-zero. If all the integrals are zero, the vibration is said to be Raman inactive.

1.5 MOLECULAR FORCE CONSTANTS AND ITS SIGNIFICANCE

The force constant is defined as the restoring force per unit displacement of a bond. Force constants serve as a basis for probing chemical bonding and structural characteristic of molecules. It is possible to calculate the interatomic distances from the knowledge of the force constants using the empirical relations of Badger [27]. By using force constants the other important molecular constants can be evaluated.

The changes in the energy of the electrons binding the nuclei together give the “Force field”. Hence the force constant gives a measure of the strength of the chemical bonding between the atoms.

Since the force constants of a molecule and its isotopic analogues have almost the same set of force constants, it is possible to deduce the fundamental wave numbers of the isotopic substitutes when the force field of
the molecules is known. Since the force constants are the characteristic of
 certain group vibrations, they can be transferred from molecule to molecule. Hence we can suggest the nature of force fields in large molecules from those of smaller ones.

The force constant depends on the bond order and the mass of atoms. The variation of force constants with bond order indicates that the force constants yield information regarding the valence state of atoms in the molecule. Force fields help to know the normal coordinates associated with each vibrational frequency essential for the absolute intensity studies. Infrared and Raman intensities have been used along with the force constants successfully to obtain the bond dipole moments, polarizabilities and their derivatives. [28].

1.6 TYPES OF FORCE FIELDS

1.6.1 Central Force Field (CFF)

Dennison [29] assumed that the force acting on a given atom in a molecule is the result of the attraction and repulsion by all other atoms (i.e) only central force acts between the atoms in a molecule. The attraction and repulsion depend only on the distance from other atoms and act along the lines connecting them with the atom under consideration. This is equivalent to assuming the potential energy to be purely a quadratic function of the change in distance between the nuclei. But this force field is rarely used due to its limitations and fails to account for the bending vibrations in linear molecules. It also fails to account for the out-of-plane vibrations. This type of force field is applicable only if ionic forces hold the atoms together. Further the frequencies predicted by this force field often differ from the observed ones.
1.6.2 Simple Valence Force Field (SVFF)

Simple valence force field developed by Bjerrum [30] involves a restoring force in the line of every valence bond; if the distance between the two bonded atoms is changed and restoring force opposing the change of the angle between two valence bonds connecting one atom with two others. In this force field, the potential function includes terms involving changes in interatomic distances and also changes in angles between two valence bonds. But this force excludes the forces between non-bonded atoms.

The potential energy function under this model is expressed as

\[ V = \frac{1}{2} \sum_i f_r(r_i)^2 + \frac{1}{2} \sum_i f_\alpha(\alpha_i)^2 \]  

(1.4)

Where \( r \) and \( \alpha \) are the changes in bond lengths and bond angles respectively, \( f_r \) and \( f_\alpha \) are the respective stretching and bending force constants.

Shimanonchi et al., [31] have applied this model successfully to a number of molecules containing hydrogen atoms and a single heavy atom such as \( \text{H}_2\text{O} \), \( \text{NH}_3 \) and \( \text{CH}_4 \). However, this model is not suitable for molecules having more than one heavy atom. This force field is superior to the central force field and chemically more meaningful, yet often fails to reproduce the observed frequencies.

1.6.3 General Valence Force Field (GVFF)

The simple valence force field potential functions can be modified in order to get more accurate description of the vibrational frequencies, by introducing some judiciously chosen interaction constants.

In this model the potential energy function, which includes all interaction terms in addition to the valence forces is given by the expression (1.4). It is expressed in its most general form as,
\[ V = \frac{1}{2} \sum f_r (r_i) + \frac{1}{2} \sum f_a (\alpha_i)^2 + \frac{1}{2} \sum f_{rr} (r_{ij}) + \sum f_{aa} (\alpha_i \alpha_j) + \sum f_{ra} (r \alpha) \] ..(1.5)

Where \( r \) and \( \alpha \) are the changes in bond lengths and bond angles, respectively. In the expression (1.5), the force constants \( f_r \) and \( f_a \) refer to principal stretching and bending force constants respectively and \( f_{rr}, f_{aa} \) and \( f_{ra} \) refer respectively to stretch-stretch, bend-bend and stretch-bend interactions. This is a convenient force field from practical point of view since the force constants can be straight forwardly transferred from one molecule to other.

1.6.4 Urey Bradley Force Field (UBFF)

The Urey-Bradley force field [32] is a combination of central force field and valence force field. The UBFF adds interactions terms between non-bonded atoms to the simple valence force field.

It includes the bond stretching force constants \( K \), angle bending force constants \( H \), torsional force constants \( Y \) and repulsive force constants \( F \). The potential energy function under this model is written as [33].

\[ V = \frac{1}{2} \sum K_{ij} (r_{ij})^2 + \frac{1}{2} \sum H_{ijk} (\alpha_{ijk})^2 + \frac{1}{2} \sum Y(t_{ijk}) + \frac{1}{2} \sum F_{ij} (R_{ij})^2 \] ..(1.6)

Where \( r \), \( \alpha \), \( t \) and \( R \) are the changes in bond lengths, bond angles, angle of internal rotation and distance between non-bonded atom pairs, respectively.

The general validity of this type of field has been demonstrated by Shimanouchi [31]. In this model, the VFF is supplemented by forces between non-bonded nuclei. The advantages of this force field are:

- It requires only a few parameters to describe the potential energy completely.
• Force constants of similar bonds can be transferred from related molecules.

• Determination of force constants of complex molecules is also possible.

It has its own limitations. Sometimes the force constants may not give a good estimate of the frequencies for certain types of vibrations, such as vibrations involving hydrogen atoms. In such cases, modifications have been suggested [34-42]. The resulting force field is known as Modified Urey-Bradley Force Field (MUBFF).

1.6.5 Orbital Valence Force Field (OVFF)

This force field is a modified form of valance force field devised by Health and Linnet [43]. OVFF eliminates the difficulty of introducing separate angle bending constants for the out-of-plane vibrations and makes use of the same constants as those used for in-plane vibrations and strictly in accordance with modern theory of direct valency [44].

In this field, it is assumed that the bond forming orbitals of a atom X are at definite angles to each other and a most stable bond is formed when one of these orbitals overlaps the bond forming orbitals of another atom Y to the maximum extent possible. If now Y is displaced perpendicular to the bond, a force will be set up tending to restore it to the most stable position. The potential energy function is expressed as,

\[ V = \frac{1}{2} K \Sigma (r_i)^2 + K' \Sigma (\beta_j)^2 + A \Sigma (R_{jk})^2 - B \Sigma (R_{jk}) + B' \Sigma (r_i) \]  \hspace{1cm} (1.7)

Where \( r \) and \( R \) are the changes in bond lengths and the distance between non-bonded atom pairs, respectively, the \( \beta \) is the angular displacement. The
symbol $K$, $K'$, $B$ and $A$ stands for the stretching, bending and non-bonding repulsion force constants respectively.

This model was shown by Health and Linnet [43] to be a very satisfactory one for tetrahedral XY$_4$ and planar XY$_3$ types of molecules and ions. Later on, it has been shown by Kim et al., [45] and Rai et al., [46] to be a superior model to the usual one using interbond angles for a series of octahedral hexahalides.

Considerable attention has been focused in recent years on the application of this model to different types of systems [47-54]. A modified form of OVFF known as modified orbital valence force filed has been successfully applied to octahedral systems [29, 30, 34, 47, 55].

1.6.6 Hybrid Orbital Force Field (HOFF)

Mills [56] proposed this model by incorporating the idea of changes in the hybridization orbitals because it attributes the molecular deformation to changes in bond angles. Therefore, it accounts for the stretch-bend interactions. The relation between stretching force constants under this model is given by [56]

$$F_y = -\frac{\delta R_j}{\delta \lambda_i} \left[ \frac{\delta \lambda_i}{\delta \alpha_j} \right] F_{ij}$$

Hence $R_j$, $\lambda_i$ refer to internal stretching and bending coordinates, respectively, and $\lambda_i$ is the hybridization parameter associated with $R_j$.

The HOFF has been applied successfully by several workers [57-60] to a variety of compounds. It is evident that the simplified force fields cited above are essential when one has to evaluate the force constants from frequency data alone. The approximation involved in framing the models are arbitrary.
and empirical, though the degree to which they are so is varied. Different groups of molecules or ions are found to obey different force fields, depending on how perfectly the assumptions made correspond to the actual state of affairs.

1.7 VIBRATIONS OF POLYATOMIC MOLECULES

In a polyatomic molecule, each atom is having three degrees of freedom in three directions, which are perpendicular to one another. Consequently, a polyatomic molecule is requires three times as many degrees of freedom as the number of its atoms. Thus, a molecule of \( n \) atoms has \( 3n \) degrees of freedom. For a non-linear molecule, three of the degrees of freedom describe rotation and three describe translation; the remaining \( 3n-6 \) degrees are vibrational degrees of freedom or fundamental vibrations. In a linear molecule, only two degrees of freedom are required to describe rotation. Thus, a linear molecule has \( 3n-5 \) vibrational degrees of freedom [61].

The number of degrees of freedom possessed by the molecule is the number of co-ordinates required to completely specify the positions of the nuclei. The number of normal modes is equal to the number of vibrational degrees of freedom possessed by the molecule. In any one normal vibration, every atom performs a simple harmonic motion with the same characteristic frequency.

The theoretical number of fundamental vibrations or absorption frequencies given by \( (3n-6)/(3n-5) \) will seldom be observed because overtones and combination tones increase the number of bands, while some other phenomena reduce the number of bands.

The theoretical number of bands is reduced by following reasons:
• Some of the fundamental frequencies fall beyond the range of the instruments.
• Some fundamental bands are too weak to be observed.
• Fundamental vibrations, which are very close, may overlap.
• Occurrence of a degenerate band from several absorptions of the same frequency in symmetrical molecule.
• Certain vibrational bands do not appear in the infrared region due to lack of required change in dipole character of the molecule.

1.8 GROUP THEORY AND MOLECULAR VIBRATIONS

A knowledge of the point group symmetry of a molecule and application of group theory concept is useful in the classification of the normal vibrations, determination of their normal vibrations and determination of their spectral activity. Molecule of different symmetries has qualitatively different spectra [3, 62-64].

A very important property of the normal vibrations is that they transform according to the irreducible representations of the molecular point group. Because of their relationship with the normal coordinates, the vibrational wave function associated with the vibrational energy levels also behaves in the same way. Hence, the normal coordinates and the vibrational wave functions can be classified according to their symmetry properties.

1.8.1 Normal modes of vibrations

Normal modes (or fundamental modes) of vibrations of any molecule are internal atomic motions in which all the atoms move in phase with the same frequency but with different amplitudes. The amplitude and direction of each atom may be represented by a displacement vector. The various
displacements of the atoms in a given normal mode of vibration may be
represented by a linear combination of atomic displacements known as
normal coordinates which are functions of angles and distance [65]. A very
important property of these vibrations is that for non-degenerate normal
modes of vibration, the normal coordinates and the vibrational wave functions
are either symmetric or antisymmetric with respect to the symmetry
operations of the point group symmetry of the molecule in its mean position.
For degenerate normal mode of vibration, the symmetry operation will
transform the degenerate set of vibrations into a linear combination of
mutually degenerate normal coordinates. A normal mode in a molecule is
equivalent to a simple harmonic motion of certain mass and force constant,
and can vibrate independently without exciting any other mode for small
amplitude motion. The number of molecular vibrations of a chemical
compound depends upon the number of atoms in its molecular composition,
and the molecular vibration allowed in the IR or Raman depends upon its
molecular symmetry. Thus, the number of vibrational modes is 3N-6 or 3N-5,
respectively, depending on whether the molecule is non-linear or linear [66].

1.8.2 Molecular symmetry and point groups

Symmetry is a visual concept as reflected by the geometrical shapes of
molecules such as benzene, methane etc. Symmetry defines the mutual
relationship of parts of something in respect of magnitude and position. Its
importance in very many theoretical problems in chemistry and physics arises
from the reflection, exchange or inversion of equivalent features of the
system. The consideration of the role of symmetry in chemistry is basically a
consideration of its role in quantum mechanics.
In spectroscopy, the symmetry possessed by a molecule may be used with advantage to simplify the calculation of energy levels of the system and to determine which transitions are allowed or forbidden.

The symmetry of a rigid system is easily defined in geometric terms. The molecular symmetry is systematized quantitatively by introducing the concept of 'symmetry operation'. It is an action, which moves the nuclear framework into a position equivalent to the original one. Related to the symmetry operation is the 'symmetry element'. The symmetry element is a geometrical entity such as a point, an axis or a plane about which action takes place. The symmetry operation is applied to the molecule and the symmetry operation should leave the molecule, physically indistinguishable.

All the axes and planes of symmetry of a molecule must intersect at least at one common point. Thus, the symmetry operation performed on molecule must leave at least one point unaffected. Such groups of operations are called point groups. In a point group, the symmetry of space about a point is uniquely described by a collection of symmetry elements about that point. Point groups are used to describe the symmetry of isolated molecules.

1.9 VIBRATIONAL ASSIGNMENT AND GROUP FREQUENCIES

The observed vibrational spectrum of any molecule consists of a large number of bands and a band is said to have been assigned. The normal vibrations of a molecule are associated with appropriate Raman and infrared frequencies and this process is referred to as vibrational assignment. The applications of infrared and Raman Spectroscopy rest largely on the correct assignment of the spectra. The assignment of the infrared and Raman spectra is generally made on the basis of the group frequency concept.
By comparison of the spectra of large number of compounds, it has been observed that the presence of certain groups, for example C-H, O-H, N-H, C=O, C=N etc. in various molecules may be correlated with a constant occurrence of absorption bands in the infrared spectra whose positions are only slightly altered on going from one compound to another. The atomic group vibrates independently of the other groups in the molecules and has its own frequency. These frequencies are called characteristics group frequencies [7]. The vibration of the group is assumed to occur independently of the rest of the molecule. A number of characteristic group absorptions have been established. The group frequency concept is extremely useful as an aid to the interpretation of vibrational spectra. The force constant of a bond changes with its electronic structure, the resulting characteristic small shifts in the vibrational frequency enable us to gather more information about the respective bond. A number of characteristic group absorptions have been established. The general technique of assigning new group frequencies begins with the vibrational assignments of small molecules and proceeds to the assignments of larger molecules. If certain vibrations retain fairly constant spectral positions, they can be considered as good group frequencies.

Frequency shifts generally result from mechanical or electronic effects. Mechanical effects arise from changes in mass or from coupling of the vibrations. They do not affect the force constant of the bond. Electronic effects affect the vibrations by altering the force constants by inductive, conjugative and other effects. The electronic effects are generally transmitted through chemical bonds. In some instances, steric effects may occur,
resulting in either the hindrance to electronic effects or to dipolar effects transmitted through space (field effect).

1.9.1 Factors influencing vibrational frequencies

Many factors influence the precise frequency of a molecular vibrational and it is usually impossible to isolate one effect from another. Each molecular group is influenced by the structure of the molecule or different electronic environments [5, 11]. Some of the important factors which are responsible for shifting the vibrational frequencies of certain groups from their normal value are discussed below:

(a) Coupled Interactions

The energy of a vibration and thus the wavelength of its absorption peak may be influenced by other vibrators in the molecule [61]. The extent of coupling is influenced by the following important factors.

- Strong coupling between stretching vibrations occurs only when the vibrations have a common atom.
- Interaction between bending vibrations occurs only when a common bond is present between the vibrating groups.
- Coupling between a stretching and a bending vibration can occur if stretching bond forms one side of the angle that varies in the bending vibrations.
- Interaction is greatest when the coupled groups have individual energies that are approximately equal.
- If groups are separated by two or more bonds, little or no interaction occurs.
- Coupling occurs when vibrations are of the same symmetry species.
(b) Hydrogen bonding

Hydrogen bonding can occur in any system containing a proton donor group (X-H) and a proton acceptor (Y), if the s-orbital of the proton can effectively overlap the p or π orbital of the acceptor group. Atoms X and Y are electronegative with Y possessing lone pair of electrons. In organic molecules, the common proton donor groups are carbonyl; hydroxyl, amine or amide group and common proton acceptor atoms are oxygen, nitrogen and the halogens. The strength of the hydrogen bond is at its maximum, if the proton donor group and the axis of the lone pair orbital are collinear. The force constant of both the groups X and Y is altered as a result of hydrogen bonding [7]. Hence frequencies of both stretching as well as bending vibrations are altered because of hydrogen bonding. The X-H stretching bands move to lower frequencies usually with increased intensity and band widening. The X-H bending vibration usually shifts to higher frequencies or shorter wavelength when bending occurs. Thus hydrogen bonding changes the position and shape of an infrared absorption band.

Inter-molecular hydrogen bonding involves association of two or more molecules of the same or different compound, and it may result in dimer molecules as in carboxylic acids. Intra-molecular hydrogen bonds are formed when the proton donor and acceptor are present in a single molecule under special conditions that allow the required overlap of orbitals, e.g. formation of a 5- or 6-membered ring. The extent of both inter-molecular and intra-molecular hydrogen bonding depends upon the temperature. In general, inter-molecular hydrogen bonds given rise to broadband, while intra-molecular
hydrogen bonds give sharp and well-defined bonds. Hydrogen bonding also involves interaction between functional groups of solvent and solute.

(c) Fermi resonance

When interactions take place between fundamental vibration and overtones or combination tones vibrations, such interactions are known as Fermi resonance. This phenomenon may occur when two vibrational transitions have nearly the same energy and both belong to the same symmetry. In such a case, instead of strong band due to the fundamental and a weak intensity band due to the overtone, two nearly equal intense bands may be observed. The two energy levels involved repel one another so that both the levels are perturbed. Evidence of Fermi resonance may be obtained by taking the spectra in different solvents and from the spectra of isotopically substituted molecules.

(d) Electronic effects

Apart from external factors such as hydrogen bonding and molecular association, various internal factors may affect the electronic structured of the carbonyl group. The nature of the substituent group X in carbonyl compounds of the formula RCOX may influence the frequency of C=O stretching by inductive and mesomeric effects. Inductive effect arises due to the different electronegativities of the carbonyl carbon and of the substituent in compounds of the type RCOX. It involves the electrons in the sigma bonds. The mesomeric effect involves the electrons in the π and nonbonding orbitals and it operates in general opposite to that of inductive effect. These effects cannot be isolated from one another and the contribution of one of them can only be estimated approximately.
Electron withdrawing groups (such as chloro and nitro) suppress the polar contribution with an effective increase in the double bond character and consequently an increase in the force constant of the C=O bond. In other words, the inductive effect reduces the length of the C=O bond and thus increases its force constant and consequently the frequency of absorption. Electron releasing groups, such as amino and methyl, attached to the carbonyl group tend to favour the polar contribution by mesomeric effect and thus lower the force constant of the C=O bond, consequently resulting in a decrease of the carbonyl stretching frequency.

In Introduction of alkyl group causes +I effect, which results in weakening of the bond and hence the force constant is lowered and wave number of absorption decreases. The introduction of an electronegative atom (or) group causes –I effect, which results in the bond order to increase. Thus, the force constant increases and hence the wavenumber of absorption rises [67].

In most of the cases, mesomeric effect works along with inductive effect and cannot be ignored. It is important to note that only inductive effect is considered when the compound in meta is substituted [67]. In para substitution, both inductive and mesomeric effects become important and the domination of one over the other will decide the wavenumber of the absorption. In ortho substitution, inductive effect, mesomeric effect along with steric effect is considered. In ortho substituted compounds, the lone pairs of electrons on two atoms influence each other through space interactions and change the vibrational frequencies of both the groups. This effect is called field effect.