Chapter I

Introduction to Vibrational Spectroscopy
CHAPTER I

INTRODUCTION TO VIBRATIONAL SPECTROSCOPY

1.1. INTRODUCTION

Vibrational spectroscopy gives valuable insight into the structural features 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 [1-4]. As a first approximation, the total energy of a molecule can be separated into three additive components associated with the motion of electrons in the molecule ($E_{el}$), the vibrations of the constituent atoms ($E_{vib}$), and the rotations of the molecule as a whole ($E_{rot}$).

$$ E_{total} = E_{el} + E_{vib} + E_{rot} \quad \ldots \quad (1.1) $$

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.

Vibrational transitions can be observed from infrared (IR) and Raman spectra, though the origin of these two spectra is markedly different. Infrared (absorption) spectra arise when there is change in dipole moment of the molecule caused by photons in the infrared region that are absorbed as a result of transition between two vibrational levels of the molecule in the electronic ground state.

On the other hand, Raman (scattering) spectra have their origin in the change in polarisability caused by interaction of radiation with molecules. To get a complete knowledge of the energy levels of a system, a simultaneous study of both Infrared and Raman spectra is required. Thus, infrared and Raman spectroscopy together serve as a powerful tool for the investigation of physical and chemical properties of the molecules.
Vibrational spectroscopy has contributed significantly to the growth of different areas as polymer chemistry, catalysis, fast reaction dynamics, charge – transfer complexes etc., [5]. 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 [6-17].

1.2. INFRARED SPECTROSCOPY

Infrared spectroscopy is generally concerned with the absorption of radiation incident upon a sample. Infrared 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

For 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 a field which is established can interact with the electric field associated with incident radiation. For this interaction or absorption to occur, it is important that the dipole moment at one extreme of the vibration must be different from the dipole moment at the other extreme of the vibration in a molecule.

1.2.2 Selection rule for Infrared

Rules that limit the number of transition between energy levels are called selection rules. All the transitions may not be active in both Infrared and Raman Spectra. Some may be active in Infrared while inactive in Raman and vice versa. According to quantum mechanics, the selection rule for the infrared spectrum is determined by the integral,
Here $\mu$ is the dipole moment in the electronic ground state. $\psi$ is the vibrational eigen function and $v', v''$ 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

$$
\begin{align*}
[\mu_x]_{v',v''} &= \int \psi_{v'}^*(Q_a)\mu_x\psi_{v''}(Q_a)dQ_a \\
[\mu_y]_{v',v''} &= \int \psi_{v'}^*(Q_a)\mu_y\psi_{v''}(Q_a)dQ_a \\
[\mu_z]_{v',v''} &= \int \psi_{v'}^*(Q_a)\mu_z\psi_{v''}(Q_a)dQ_a
\end{align*}
$$

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. Accordingly, if $\partial \mu / \partial Q_k \neq 0$, then a normal mode $Q_k$ with frequency $\nu_k$ will be active in the infrared absorption spectrum. It must be emphasized that the molecule need not possess a permanent dipole moment but only a change in the dipole moment of the molecule during vibrations is necessary. If all the integrals are zero, the vibration is infrared inactive [11].

1.3. RAMAN SCATTERING

The Raman effect can be understood by considering the light scattering process as collision of the photons of the incident light with the molecules. The incident light consists of photons of energy $h\nu_o$. On collision with molecules, photons may be elastically scattered, where the photons neither gain nor lose energy in their collision with the molecules. This gives rise to the phenomenon of Rayleigh scattering. However, collision of photons with molecules may be inelastic. They may induce the molecules to undergo a transition to a higher energy level with a result that the photons lose energy and are scattered with a lower frequency. However, if the molecules are already in a higher vibrational
energy state, on collision with photons, they may undergo a transition to a lower energy level in which case the photons are scattered with increased frequency. The Raman lines on the low and high frequency sides of the Rayleigh line are called stokes and anti-stokes line respectively. The scattered photons have frequency shifts (10 - 4000 cm\(^{-1}\)) characteristic of the vibrational or rotational energies of the molecule. These weak lines of modified frequencies are generally referred to as the Raman lines.

### 1.3.1 Quantum theory of Raman effect

Quantum mechanics gives a qualitative description of the phenomenon of Raman effect. The 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 (\(\nu = 0\)), 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 (\(\nu = 0\)) is excited to the virtual electronic state and then radiates light in all directions except along the direction of the incident light. On return to the ground electronic state, quantum of 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 \(\nu = 1\)) and is raised to quasi – excited state and reverts to ground electronic state (\(\nu = 0\)) on scattering of photon. The energy of the scattered photon is equal to the sum of the energy of the incident photon and the energy difference between the vibrational levels \(\nu = 1\) and \(\nu = 0\).
In another instance, a molecule in the ground state on interaction 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)

**Figure 1.1 Energy levels involved in Raman and Rayleigh scattering**

### 1.3.2 Raman activity

For a molecular vibration to be Raman active, there must be a change in the polarisability of the molecule during its 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 polarisability 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 polarisability and the corresponding normal frequencies are not observed. Such
vibrations are Raman inactive [1, 9, 10, 17-25]. i.e., Molecules with a center of symmetry have no fundamental lines in common in the IR and Raman spectra.

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.

The advent of laser has revolutionised Raman spectroscopy. Today, with the development of optical spectrometers and new detection techniques, Raman spectroscopy has been developed as an extremely useful tool for material characterization.

### 1.3.3 Selection rule for Raman spectra

The selection rule for the Raman spectra is determined by the integral,

\[
[a]_{\nu,\nu} = \int \psi_\nu^* \cdot (Q_a) \alpha \psi_\nu (Q_a) dQ_a
\]

... (1.3)

The polarisability of the molecule \( \alpha \) consists of six components \( \alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}, \alpha_{yz}, \alpha_{xz} \). For the vibrations to be Raman active, atleast one of these integrals should be non-zero. If all the integrals are zero, the vibration is said to be Raman inactive.

### 1.4. MOLECULAR FORCE FIELDS

The fundamental vibrational frequencies of a molecule obtained from Raman and infrared spectra can be used to solve the secular equations to get the potential energy or force constants. Generally, the number of potential constants is larger than the number of normal vibrations and hence all the force constants of a particular molecule cannot be determined from the observed frequencies alone. The unique solution is then obtained either by introducing additional equations from isotopic cases which may be having the same force constants or by borrowing the initial set of force constants from molecules
having similar bonds and environment. A trial F matrix is set up and iterating those to give a weighted least square fit to all the observed frequencies.

Another solution is to make specific assumptions about the nature of the force in the molecules such that the number of force constants to be determined is not large. Several such force fields have been assumed and each of such fields has its own merits and limitations.

1.5. TYPES OF FORCE FIELDS

1.5.1 Central Force Field (CFF)

Dennison [26] 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 the atoms were held together by ionic forces. Further the frequencies predicted by this force field often differ from the observed ones.

1.5.2 Simple Valence Force Field (SVFF)

Simple valence force field, developed by Bjerrum [27], 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., [28] have applied this model successfully to a number of molecules containing hydrogen atoms and a single heavy atom such as H\(_2\)O, NH\(_3\) and 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.

### 1.5.3 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 an expression (1.4). It is expressed in its most general form as,

\[ V = \frac{1}{2} \sum_i f_r (r_i)^2 + \frac{1}{2} \sum_i f_\alpha (\alpha_i)^2 + \frac{1}{2} \sum_{i<j} f_{rr} (r_i r_j) + \sum_{i<j} f_{\alpha \alpha} (\alpha_i \alpha_j) + \sum f_{rr\alpha} (r \alpha) \]  

...(1.5)

Where \( r \) and \( \alpha \) are the changes in bond lengths and bond angles, respectively. The force constants \( f_r \) and \( f_\alpha \) refer to principal stretching and bending force constants respectively and \( f_{rr}, f_{\alpha \alpha} \) and \( f_{rr\alpha} \) 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 straightforwardly transferred from one molecule to the other.
1.5.4 Urey Bradley Force Field (UBFF)

The Urey-Bradley force field [29] is a combination of central force field and valence force field. The UBFF adds interaction 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 [30]

$$V = \frac{1}{2} \sum K_{ij} (r_{ij})^2 + \frac{1}{2} \sum H_{ijk} (\alpha_{ijk})^2 + \frac{1}{2} \sum Y_{ijk} (t_{ijk}) + \frac{1}{2} \sum F_{ij} (R_{ij})^2 \quad \ldots (1.6)$$

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 [30]. 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 [31-39]. The resulting force field is known as Modified Urey-Bradley Force Field (MUBFF).
1.5.5 Orbital Valence Force Field (OVFF)

This force field is a modified form of valance force field devised by Health and Linnet [40]. 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 [41].

In this field, it is assumed that the bond forming orbitals of an 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 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,

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

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

This model was shown by Health and Linnet [40] 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., [42] and Rai et al., [43] to be a superior model to the usual one using interbond angles for a series of octahedral hexahalides.

Considerable attention has been focussed in recent years on the application of this model to different types of systems [44-51]. A modified form of OVFF known as modified orbital valence force field has been successfully applied to octahedral systems [26, 31, 38, 44, 52].
1.5.6 Hybrid Orbital Force Field (HOFF)

Mills [53] 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 [53]

\[
F_{ij} = -\frac{\partial R_i}{\partial \alpha_{ij}} \left[ \frac{\partial \lambda_i}{\partial \alpha_{ij}} \right] F_{ij}
\]

...(1.8)

Hence, \( R_i \) and \( \alpha_i \) refer to internal stretching and bending coordinates, respectively, and \( \lambda_i \) is the hybridization parameter associated with \( R_i \).

The HOFF has been applied successfully by several workers [54-57] 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 are made correspond to the actual state of affairs.

1.6. 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 requiring 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 [58].
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.

1.7. **MOLECULAR SYMMETRY AND POINT GROUPS**

Symmetry is a visual concept as reflected by the geometrical shapes of molecules such as benzene, methane etc. The molecular symmetry is systematized quantitatively by introducing the concept of ‘symmetry operation’. A symmetry operation can be understood simply as some geometrical manipulation on the molecule in such a way that an ‘equivalent’ or ‘indistinguishable’ configuration of the molecule always results after the operation is performed. Symmetry operations and symmetry elements are
intricately related and the symmetry element is a geometrical entity such as a point, a line or a plane in the molecule about which action or operation takes place. All the symmetry elements contained in a molecules pass through a single point, and the operations generating all these elements leave just one point unmoved. This point is nothing but the centre of gravity of the molecule. Such groups of operations are called point group. Point groups are used to describe the symmetry of isolated molecules.

1.7.1 Symmetry and spectroscopy of molecules

Knowledge of the point group symmetry of a molecule and application of group theory concept is useful in the classification of the normal vibrations. It enables to determine the number of the fundamental frequencies, their degeneracies, the selection rules for the infrared and Raman spectra, the degrees of freedom of the secular equation, the numbering of independent constants in the quadratic part of the potential energy functions, the splitting of overtone levels, the nature of rotational structure of the infrared bands, the polarization properties of the Raman lines and other useful information. Molecule of different symmetries will have qualitatively different spectra [3, 59, 60].

1.8. VIBRATIONAL ASSIGNMENT AND GROUP FREQUENCIES

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 [5]. 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.

1.8.1 Factors influencing vibrational frequencies

It has been found that the calculated value of frequency of absorption for a particular bond is never exactly equal to its experimental value. This is due to the fact that each group is influenced by the structure of the molecule or different electronic environments [9, 11]. Following are some of the important factors, which are responsible for shifting the vibrational frequencies of certain groups from their normal values.

(a) Coupled Vibrations

The most important requirements for effective coupling interactions are:

- Strong coupling between stretching vibrations occur 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) Electronic Effects

Changes in the absorption frequencies for a particular group take place when the substituents in the neighborhood of that particular group are changed. The frequency shifts are due to the electronic effects, which include Inductive effects, Mesomeric effects, Field effects etc. These effects cannot be isolated from one another and the contribution of one of them can only be estimated approximately.

Introduction of alkyl group causes +I effect which results in weakening of the band 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 wave number of absorption raises [61].

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 is meta substituted [61]. 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.

(c) 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 colinear. The force constant of both the groups X and Y is altered as a result of hydrogen bonding [58]. 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 member rings. The extent of both inter-molecular and intra-molecular hydrogen bonding depends upon the temperature. In general, inter-molecular hydrogen bonds give rise to broad band, while intra-molecular hydrogen bonds give sharp and well defined bonds. Hydrogen bonding also involves interaction between functional groups of solvent and solute.

(d) Fermi Resonance

When interactions take place between fundamental vibration and overtones or combination tone 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.