CHAPTER-I

INTRODUCTION TO VIBRATIONAL SPECTROSCOPY

ABSTRACT

In the introductory chapter, some of the very basic concepts of vibrational spectroscopy and its applications to polyatomic molecules are discussed. As molecular symmetry and group theory plays an important role in the structure and characteristics of molecules, some of the concepts are discussed. Principles of UV–VIS absorption spectroscopy and the types of electronic transitions are given briefly. In addition, selection rules for IR, Raman, NMR and UV–VIS absorption spectra are outlined. Various types of force filed with their relative merits and limitations are dealt briefly. The concept of group frequency and the factors influencing the vibrational frequencies of polyatomic molecules are discussed
CHAPTER-I

INTRODUCTION TO VIBRATIONAL SPECTROSCOPY

1.1 FUNDAMENTALS OF SPECTROSCOPY

Spectroscopy is the study of the interaction of electromagnetic radiation with matter. When matter is energized (excited) by the application of thermal, electrical, nuclear or radiant energy, electromagnetic radiation is often emitted as the matter relaxes back to its original (ground) state. The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum, and the science is appropriately called emission spectroscopy [1].

Vibrational spectroscopy is the collective term used to describe two analytical techniques: infrared (IR) and Raman spectroscopy. IR and Raman spectroscopy are non-destructive, non-invasive tools that provide information about the molecular composition, structure and interactions within a sample. These techniques measure vibrational energy levels that are associated with the chemical bonds in the sample. The sample spectrum is unique, like a fingerprint and vibrational spectroscopy is used for identification, characterization, structure elucidation, reaction monitoring, quality control and quality assurance [2].

1.2 INFRARED SPECTROSCOPY

Infrared spectroscopy is generally concerned with the absorption or transmit 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 when compared with other physical techniques (X-ray diffraction, electron spin resonance, etc.) in the elucidation of the structure of unknown compounds [2].
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].

1.2.2 INFRARED SPECTROSCOPY

It has been noted that the covalent bonds of molecules are not rigid, but are like stiff springs that can be stretched and bent. Transitions between vibrational energy states may be induced by absorption of infrared radiation, whose photons have the appropriate energy. The stretching vibrations appear at higher wavenumbers than the bending vibrations, because more energy is required to stretch (compress) a bond than to bend it. The transition probability of infrared absorption is given by

\[ a^*(t) a(t) = \frac{1}{\hbar^2} \left| \langle m | \mu | k \rangle \right|^2 E_0^2 t. \]

(1.1)

The vibrations of a molecule result only in small deviations of the bond from its equilibrium length [2]. Hence, the dipole moment can be expanded as a power series in the displacement \( r \) around the equilibrium value \( r_0 \)

\[ \langle m | \mu | k \rangle = \int |m_0 + \left( \frac{\partial \mu}{\partial r} \right)_{r=r_0} (r-r_0) | \psi \, dr = \frac{1}{\hbar} \int \mu_m \psi \, dr. \]

(1.2)
The zero order of the expansion makes the integral non-zero only for \( m = k \), so no transition is taking place. For the second term, due to the orthogonality of the wave functions, the integral will only be \( \neq 0 \) for \( k = m + 1 \), which corresponds to a transition from a lower-energy level \( m \) to the next higher level \( (k = m + 1) \). In addition, a change in the dipole moment connected with the vibration is necessary to obtain a non-zero transition and, hence, absorption:

\[
\langle m | \mu | k \rangle \neq 0 \text{ if } \frac{\partial \mu}{\partial r} \neq 0 \text{ for } k = m + 1. \tag{1.3}
\]

Hence, it is evident that not all molecular vibrations lead to observable infrared absorption. In general, a vibration must cause a change in the electric dipole moment within a molecule to absorb IR light. The greater this change, the stronger will be the absorption [3].

1.2.3 SELECTION RULE FOR IR

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

\[
\left[ \mu^{\prime} \right]_{v^v} = \int \psi_{v^v}^\ast(Q_a) \mu \psi_{v^v}(Q_a) \, dQ_a, \tag{1.4}
\]

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

\[
\left[ \mu_x \right]_{v^v} = \int \psi_{v^v}^\ast(Q_a) \mu_x \psi_{v^v}(Q_a) \, dQ_a, \tag{1.5}
\]

\[
\left[ \mu_y \right]_{v^v} = \int \psi_{v^v}^\ast(Q_a) \mu_y \psi_{v^v}(Q_a) \, dQ_a, \tag{1.6}
\]

4
\[
[\mu_{\nu}]_{\nu'} = \int \psi_{\nu'}(Q_0) \mu \psi_{\nu'}(Q_0) \, dQ_0.
\] (1.7)

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 the
vibration is infrared inactive [1, 2].

1.3 RAMAN SCATTERING

Raman spectroscopy is an important method for investigating molecular
vibrations. The Raman effect can be understood by considering the light scattering
process as collision of photons of the incident light with the molecules. The
incident light consists of photons of energy \( \hbar \nu_0 \). 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
line on the low- and high-frequency sides of the Rayleigh line are called stokes and
anti-stokes line, respectively. The scattered phonons 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 Figure 1.1. The interaction of a photon of the incident 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 the ground electronic state \( V = 0 \) is excited to the virtual electronic state and then radiates light in all directions except along the direction of the incident light [5].

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 line 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. 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 \( V = 1 \) and \( V = 0 \).

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 [1,2].
1.3.2 RAMAN ACTIVITY

For a molecular vibration to be Raman active there must be a change in the polarizability 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 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 [3–14], 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 revolutionizes 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 spectrum is determined by the integral:

$$[\alpha]_{\nu,\nu'} = \int \psi_{\nu'}^* (Q_a) \alpha \psi_{\nu} (Q_a) \, dQ_a.$$  \hspace{1cm} (1.8)

The polarizability of the molecule $\alpha$ consists of six components $\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$, $\alpha_{xy}$, $\alpha_{yz}$, and $\alpha_{xz}$. For the vibrational to be Raman active, at least one of these integral should be non-zero. If all the integrals are zero, the vibration is said to be Raman inactive [5].

1.4 SELECTION RULE FOR IR AND RAMAN SPECTRA

A selection rule is a quantum mechanical rule that describes the type of quantum mechanical transitions that are permitted. Transitions not permitted by selection rules are said forbidden, which means they may occur, in practice, but with low probabilities. 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 IR and Raman spectra. In a molecule having a centre of symmetry, Raman active transitions are IR inactive and IR active modes inactive in Raman [6].

1.5 COMPARISON OF IR AND RAMAN SPECTROSCOPY

IR absorption spectroscopy together with Raman spectroscopy will give almost complete information about the vibrational spectrum of a molecule in the ground electronic state. The methods are complementary, which follows from the nature of the phenomena on which they are based. The complementarity of infrared
and Raman spectroscopy results from the different selection rules which determine the presence of a band corresponding to a given vibration of the molecule in the infrared and/or Raman spectrum. If the vibration causes a change in the dipole moment, which occurs when the vibration changes the symmetry of the charge density distribution, i.e. if \( \frac{\partial \mu}{\partial r} \neq 0 \), it is active in the IR spectrum. If the vibration is connected with a change of the molecular polarizability, i.e. if \( \frac{\partial \alpha}{\partial r} \neq 0 \), it is active in the Raman spectrum.

The fulfillment of one or both of these conditions is related to the symmetry of the molecule (If the molecule has a centre of symmetry, a vibration which is active in the infrared spectrum is inactive in the Raman spectrum and vice versa. This rule is called the rule of mutual exclusion) If the molecule does not possess a centre of symmetry, a number of vibrations appear in both spectra. The differences between the selection rules of both effects are related to the behavior of an anharmonic oscillator, used as a model for the vibrations of a molecule [7-9].

Band intensities in both types of spectra can be predicted with great reliability from some general rules. Non-polar or slightly polar groups tend to have strong Raman lines, whereas strongly polar groups show strong IR absorption. Overtones and combinatorial bands are stronger in the IR than in the Raman spectrum. In addition, there is a long list of relations for specific types of vibrations of certain molecular groups [8].

1.6 MOLECULAR FORCE CONSTANTS AND ITS SIGNIFICANCE

Force constant is used as a basis for probing the nature of chemical bonds and structural characteristics of molecules. The restoring force per unit displacement of a bond is known as force constant. From the empirical relations of
Badger, it is possible to calculate the inter-atomic distances by force constants [15]. The other important molecular constants can be evaluated from force constants.

The electrons are binding with nuclei together by electrostatic energy and the energy changes thus gives the “force field”. The force constant depends on the bond order and the mass of atoms. For the absolute intensity studies, force fields are used to identify the normal coordinates associated with each vibrational frequency. Infrared and Raman intensities have been used along with force constants in order to obtain the dipole moments, polarizabilities and their derivatives [16].

1.6.1 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. Thus, a molecule of \( n \) atoms has \( 3n \) degrees of freedom. For a nonlinear 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. For linear molecule, there is no rotation about the bond axis consequently two degrees of freedom are required to describe the rotation. Hence a linear molecule has \( 3n-5 \) vibrational degrees of freedom [17].

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. For each normal vibration, every atom performs a simple harmonic motion with the same characteristic frequency. The
(3n−6)/(3n−5) vibrations are called the internal vibrations or fundamental vibrations or normal vibrations of the molecule. During a normal vibration, the centre of gravity of the molecule remains unchanged. Because a molecule having n atoms has n−1 bonds, out of the (3n−6)/(3n−5) vibrations, (n−1) would be the bond stretching and (2n−5)/(2n−4) would be deformation vibrations. In large molecules the number of deformation vibrations becomes more involved. The theoretical number of fundamental vibrations or absorption frequencies given by (3n−6)/(3n−5) will rarely be observed because overtones and combination tones increase the number of bands [17].

The theoretical number of bands is reduced by following reasons:

1) Some fundamental bands are too weak to be observed.
2) Some of the fundamental frequencies fall beyond the range of the instruments.
3) Fundamental vibrations that are very close may overlap.
4) Occurrence of degenerate bands from several absorptions of the same frequency in symmetrical molecule.
5) Certain vibrational bands do not appear in the infrared region due to lack of required change in dipole character of the molecule.

1.6.2 GROUP THEORY AND MOLECULAR VIBRATIONS

Knowledge of point group symmetry of a molecule and application of group theory concept is useful in the determination of their normal vibrations and spectral activity. Molecule of different symmetries has qualitatively different spectra [18–21]. A very important property of the normal vibrations is that they transform according to the irreducible representations of the molecular point group.
The normal coordinates and the vibrational wave functions can be classified according to their symmetry properties.

1.6.3 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 and with the same frequency but 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 [22].

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 \(3n-5\) for nonlinear or linear molecule, respectively [23].
1.6.4 MOLECULAR SYMMETRY AND POINT GROUPS

Molecular symmetry plays an important role in the structure determination and characteristics of the molecules. 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 with respect to magnitude and position. Its importance in many theoretical problems in chemistry and physics arises from the reflection, exchange or inversion of equivalent features of the system [22].

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 the allowed and forbidden transitions. The symmetry of a rigid system is easily defined in geometrical 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. The symmetry element is a geometrical entity such as a point, or an axis or a plane about which a symmetry operation may be performed. The symmetry operation is applied on the molecule, thus the molecule is physically indistinguishable.

All the axes and planes of symmetry of a molecule must intersect at least at one common point [23]. 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.
1.6.5 VIBRATIONAL ASSIGNMENT AND GROUP FREQUENCIES

The observed vibrational spectrum of any molecule consists of a large number of bands. The normal vibrations of a molecule are associated with appropriate Raman and infrared frequencies and this process is referred to as vibrational assignment. The assignment of the infrared and Raman spectra is generally made on the basis of the group frequency concept.

By comparing 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 independent of the other groups in the molecule and has its own frequency. These frequencies are called characteristic group frequencies [24]. 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 in the interpretation of vibrational spectra. The force constant of a bond changes with its electronic structure, consequently small shifts in the vibrational frequency and this 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 large 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 such as inductive, conjugative, and other effects probably control the vibrations by altering the force constants. 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).

1.6.6 FACTORS INFLUENCING VIBRATIONAL FREQUENCIES

Many factors influence the precise frequency of a molecular vibrations and it is usually impossible to isolate one effect from another. Each molecular group is influenced by the structure of the molecule of different electronic environments [25,26]. 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 vibrations in the molecule [27]. The degree of coupling is influenced by the following important factors:

1. When the vibrations contain a common atom strong coupling occurs between stretching vibrations.

2. Interaction between bending vibrations occurs only when the common bond is present between the vibrating groups.
3. Interaction is at the peak when the coupled groups have individual energies that are approximately equal.

4. If groups are separated by two or more bonds, little or no interaction occurs.

5. Coupling occurs when the vibrations are of the same symmetric species.

(b) Hydrogen bonding

Hydrogen bonding can occur in any system containing a proton donor (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 hydroxyl amine or amide group and common proton acceptor atoms are oxygen, nitrogen and 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 [28]. 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. Intermolecular hydrogen bonding involves association of two or more molecules of same or different compound, and it may results in dimer. While intramolecular hydrogen bonds are formed by the interaction of proton donor and acceptor, which is present in a single molecule. In general, intramolecular hydrogen bonds give rise
to sharp and well-defined bonds, whereas intermolecular hydrogen results in a broadband. Hydrogen bonding also involves in an interaction between functional groups of the molecule and solvent.

(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 same energy and both belong to the same symmetry [28].

(d) Electronic effects

Apart from external factors such as hydrogen bonding and molecular association, various internal factors like electronic structure of the carbonyl group, etc., may influence the vibrational frequency. The nature of the substituent group X in carbonyl compounds of the formula R–C=O–X 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 group X in RCOX compounds. In addition, it involves the electrons in the sigma bonds. The mesomeric effect includes electrons in the π and non-bonding orbitals and it operates, in general, opposite to that of inductive effect [28]. These effects cannot be isolated from one another and the contribution of one of them can only be estimated approximately.

1.7 UV–VISIBLE OR ELECTRONIC SPECTROSCOPY

Electronic spectroscopy provides vital information about molecular structure such as nature of chemical bonds, functional groups, isomerism, tautomerism and extent of conjugation in organic compounds. Electronic spectra
arise due to the absorption of energy by the molecule in the ultraviolet region and make transitions between the electronic energy levels (Figure 1.2).

![Figure 1.2 Regions of the electronic spectrum and corresponding types of transitions.](image)

These transitions are quantized and depend on the electronic structure of the molecule. The energy differences between electronic energy levels in most molecules vary from 125 to 650 kJ/mol. When a molecule absorbs energy an electron is promoted from an occupied orbital to an unoccupied orbital of greater potential energy. Generally, the most probable transition is from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO) [29–32].

### 1.7.1 PRINCIPLES OF UV-ABSORPTION SPECTROSCOPY

When electromagnetic radiations of ultraviolet and visible wavelengths are passed through the compound with multiple bonds, a portion of radiation is normally absorbed. Amount of absorption depends on the wavelength of radiation and the structure of the compound. The amount of light absorbed by the sample is explained by the following empirical expression, known as the Beer–Lambert law,

$$ A = \log \left( \frac{I_0}{I} \right) = \varepsilon c l, $$

(1.9)
where A is the absorbance, I₀ is the intensity of light incident upon the sample cell, I is the intensity of light leaving the sample cell, c is the molar concentration of solute, l is the length of the sample cell and ε the molar absorptivity. The term log (I₀/I) is also known as absorbance and may be represented by A. The molar absorptivity ε (molar extinction coefficient) is a property of the molecule undergoing an electronic transition. The size of the absorbing system and the probability of electronic transition will control the absorptivity, which ranges from 0 to 10⁶ [33].

The Beer–Lambert law is strictly obeyed when a single species give rise to the observed absorption. The law may not be obeyed, due to the molecular properties of the sample such as complex formation or sample aggregation.

1.7.2 SELECTION RULES FOR UV SPECTRA

The conditions for occurrence of transitions between the energy levels are called selection rules. The most important requirement is that the electron must be promoted without change in spin orientation, i.e., ΔS = 0. The transitions that involve a change in the spin quantum number are not allowed to take place, they are forbidden transitions. One more condition is, the transition of electron occurs if the symmetry of the molecular orbitals (MOs) must change from g → u or u → g and change in symmetry g → g or u → u are not allowed (Laporte forbidden) [33].

1.7.3 TYPES OF ELECTRONIC TRANSITIONS

The ultraviolet absorption bands are associated with the chemical bonds containing the organic molecules. Ultraviolet absorption occurs due to the transitions of valence electrons in the molecule, i.e., the excitation of an electron from the occupied orbital (bonding orbital) to an unoccupied orbital (anti-bonding
orbital). The lowest energy occupied molecular orbitals are the σ-orbitals, which corresponds to σ-bonds. The π-orbitals have quite higher energy levels and holds unshared pairs. The non-bonding (n) orbitals are very higher energy levels. The unoccupied (anti-bonding) orbital of π* and σ* are the orbitals of highest energy. Electronic energy levels and transitions are shown in Figure 1.3. Thus, the promotion of an electron from a π-bonding orbital to an anti-bonding (π*) orbital is designated as π → π*.

![Figure 1.3 Electronic energy levels and transitions.](image)

As shown in Figure 1.3., it is clear that n → π* transition requires less energy compared with π → π* or σ → σ* transition. For many applications, the transition of lowest energy is the most essential. Saturated organic compounds such as alkanes provides σ → σ* transitions with λ_{max} around 190 nm. The saturated compounds with one heteroatom with unshared pair of electrons such as saturated halides, alcohols, ketones and amines may undergo n → σ* transition. The compounds with unsaturated centers such as alkenes, aromatics, carbonyl compounds gives π → π* transition. Unsaturated molecules that contain atoms such as oxygen or nitrogen may also undergo n → π* transition. These perhaps the
most interesting, particularly among carbonyl compounds. These transitions are
quite sensitive to the substitution on the chromophore structure. Most \( n \rightarrow \pi^* \)
transitions are forbidden and hence are of low intensity [34–36].
1.7.4. FACTORS AFFECTING THE POSITION OF \( \lambda_{\text{max}} \)

The position of \( \lambda_{\text{max}} \) depends on number of factors, including conjugation of
chromophores, auxochromes and solvent. A covalently unsaturated group such as
C=C, C=O and NO\(_2\) is responsible for electronic absorption in chromophore.
Auxochromes are saturated groups with non-bonding electrons. Furthermore,
auxochromes alter the wavelength and intensity of absorption while attached to
chromophores. The bathochromic shift (a shift to longer wavelength) occurs due to
the conjugation of chromophores, auxochromes and hyperconjugative effects. In
auxochromes, the resonance interaction of lone pair with the double bond increases
the length of the conjugated system. The exact position and intensity of the
absorption band of the conjugated system can be correlated with the extent of
conjugation in the system. Furthermore the hyperconjugative interaction takes
place due to the overlap of C–H bonding orbitals with the \( \pi \) system [37].

The choice of solvent can shift the peaks to longer or shorter wavelengths.
This will depend on the nature of the interaction of the particular solvent with the
environment of the chromophore. Additionally, solvent effect influences the fine
structure of the absorption spectrum. A non-polar solvent does not affect the fine
structure of the spectrum as it does not make hydrogen bond with chromophore.
Whereas polar solvents definitely influence the fine structure of the spectrum due
to the hydrogen bonding of solvents with chromophore, consequently solute–
solvent complex [38,39].
1.7.5 INTERACTION OF MOLECULES WITH ELECTROMAGNETIC RADIATION

Using the Born–Oppenheimer approximation, the energy of a molecule in one of its eigenstates can be written as the sum of four terms which correspond to different motions of the molecule:

\[ E = E_{\text{trans}} + E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}, \]  

(1.10)

where \( E_{\text{trans}} \) is the energy of the translation of the molecule, \( E_{\text{elec}} \) the electronic energy, \( E_{\text{vib}} \) the contribution of the vibrations of the atoms or atomic groups and \( E_{\text{rot}} \) that of the rotation of the complete molecule. Because the translational motion is not of interest, the \( E_{\text{trans}} \) term can be neglected. In addition, \( E_{\text{rot}} \) can be disregarded, because rotational transitions are not resolved in condensed matter.

Molecular spectroscopy is the study of the interaction of light with matter. The photons can interact with the molecules in three different ways: by absorption, emission and scattering. Absorption takes place if the photon energy corresponds to the difference between two energy eigenlevels of the molecule. The molecules are excited to a higher energy level when they absorb light. The type of excitation depends on the wavelength of this light (\( \lambda \)) [38]. For example, with UV and visible light (200–700 nm) electrons are promoted to higher orbitals, with infrared light (1000 nm–2.5 \( \mu \)m) vibrations are excited, and with far-IR and microwaves (25 \( \mu \)m–2.5 cm) rotations are excited. An absorption spectrum represents the absorption as a function of wavelength.

Emission occurs when the excited molecules decay to lower energy levels emitting a photon whose energy corresponds to the difference between two energy levels of the molecule. If the transition is between states with the same spin, the
emission is called fluorescence, if they have different spin, the emission is called phosphorescence. Also scattering of the irradiated light can occur but with less probability. The energy of the scattered photon does not correspond to the difference between two energy levels of the molecule. If the interaction is elastic, it is called Rayleigh scattering, if inelastic, Raman scattering [39]. This process takes place instantaneously (<10–12s). The different interactions of molecules with light: (a) UV–VIS absorption/emission, (b) IR absorption and (c) Raman scattering are shown in Figure 1.4.

![Diagram showing different interactions of molecules with light](image)

Figure 1.4 Comparisons of the different interactions of molecules with light: (a) UV–VIS absorption/emission, (b) IR absorption and (c) Raman scattering.

Transitions between energy levels of the molecular system can occur with absorption or emission of radiation, if the transition dipole moment between the initial and the final molecular state is non-zero. For light scattering, the polarizability of the molecule is the important quantity.

The Bouguer–Lambert–Beer law forms the mathematical–physical basis of light absorption measurements in the UV–VIS and IR region. This law relates the
decrease in the intensity of the radiation as it penetrates a distance \( dl \) in an absorbing sample, and reads

\[
-dI = \alpha (\omega) I X dl
\]

(1.11)

where \( X \) is the molar concentration and \( \alpha (\omega) \) the absorption coefficient.

The absorption band for a given transition usually extends over a range of frequencies. The total intensity of the band is obtained by measuring and integrating \( \alpha (\omega) \) in the region of the absorption [39].

\[
\Omega = \int_{\text{bound}} \alpha (\omega) d\omega
\]

(1.12)

The integrated form of Beer’s law is given by

\[
\ln \frac{I_0}{I} = \ln \frac{1}{T} = \alpha (\omega) X l \rightarrow \log \frac{I_0}{I} = \log \frac{1}{T} = \alpha (\omega) X l = A
\]

(1.13)

where \( I_0 \) is the intensity of the radiation before and \( I \) after passing through the sample, \( T = I/I_0 \) is the transmittance, and \( A \) the absorbance, which is given in units of the optical density (OD = \( \log (I_0/I) \)).

1.8. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance spectroscopy (NMR) is a non-invasive and robust tool for chemical structure determination [40]. In NMR, the local environment and properties of atomic nuclei are probed by inducing transitions between nuclear spin energy levels whose separation is determined by the Zeeman interaction. Subsequently, molecular structure is assigned by the energy spectrum of nuclear spins in a molecule, and by interpreting the symmetry and position of the resonance lines in the spectrum. Several parameters associated with NMR helps in the chemical structure determination, such as chemical shifts give information about the different chemical environments in a molecule. In addition, coupling
constants helps to establish connectivity between the different chemical environments in a molecule [41].

1.8.1 Quantum mechanical description of NMR

Atomic nucleus has an intrinsic property called spin which is a measure of the angular momentum of the nucleus. The spin angular momentum \( P \), of a nucleus is

\[
\frac{1}{2} \hbar, \\
\]  

(1.14)

where \( I = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots \) are spin quantum numbers and \( \hbar \) is reduced Plank’s constant. All nuclei with \( I > 0 \) have magnetic dipole moment \( \mu \), which is collinear with angular momentum vector \( P \),

\[
\mu = \gamma P, \\
\]  

(1.15)

where \( \gamma \) is the gyromagnetic ratio of the observed nucleus. When the nuclei is placed in magnetic field \( (B_0) \) the nuclei makes precessional motion about the applied field \( (B_0) \). The frequency of precession is known as the Larmor or resonant frequency \( (\omega_0) \) and depends on the type of nuclei and strength of applied magnetic field \( B_0 \). The equation is

\[
\omega_0 = \gamma B_0. \\
\]  

(1.16)

For a nucleus with \( I = 1/2 \), such as \(^1H\) and \(^{13}C\) there are two allowed state in the presence of an applied external magnetic field. One with its magnetic moment along the field direction and other opposite the field direction. The two orientations have corresponding energies \( \pm 1/2\gamma \hbar B_0 \) which results in an energy difference of \( \hbar B_0 \) as shown in Figure 1.5.

It is possible to make the nuclear transitions between two levels by injecting a photon with correct frequency.
\[ \Delta E = E_2 - E_1 = \nu B_0 = \hbar \omega. \]  \hspace{1cm} (1.17)

At room temperature, there are a slightly greater number of aligned nuclei than the anti-aligned and the difference is given as

\[ N_\uparrow - N_\downarrow = \]  \hspace{1cm} (1.18)

![Energy levels for protons](image)

Figure 1.5 Energy levels for protons.

In NMR spectroscopic method, a transition will be induced between two energy states when an electromagnetic wave is applied to the nuclei in the sample, provided the resonance condition \( \Delta E = \nu \) is satisfied. An additional oscillating exciting field \( (B_1) \) will be generated by irradiating the sample with a short pulse of radio frequency (RF) perpendicular to the main field \( (B_0) \). As a result, the nuclei will be subjected to a processional motion about a new effective field \( B_{\text{eff}} \), which is the sum of \( B_0 \) and \( B_1 \). Thus, Larmor precession of the transverse magnetization vector will produce a detectable signal by inducing an oscillating current in the receiver coil. When the RF pulse is removed, the precessions tend to decay back to the equilibrium state by relaxation process \( T_1 \) and \( T_2 \). This is known as free induction decay (FID) which is recorded as a function of time. By a mathematical treatment using Fourier transform (FT) function, the FID data are converted into standard NMR spectrum presented in the frequency-varying method [42].
1.8.2. Chemical shift

Nuclear magnetic resonance has great utility, because not all the protons in a molecule have resonance at the same frequency. This variability is due to diamagnetic shielding or diamagnetic anisotropy. As a result of diamagnetic anisotropy, each proton in a molecule is shielded from the applied magnetic field to an extent that depends on the electron density surrounding it. Each proton in a molecule is in a slightly different amount of electronic shielding, which results in a slightly different resonance frequency [42]. The position of the resonance signal for a molecule is shifted relative to the reference signal is termed as chemical shift and is expressed in parts per million.

1.8.3. Causes of Chemical shift

The variation in chemical shifts may arise due to the following factors:

The secondary fields produced by the circulating electrons about a nucleus in a molecule can oppose or reinforce the applied field. As a result, the resonance position in NMR spectrum moves up field or downfield, respectively. This is known as positive shielding and negative shielding.

The field experienced by a nucleus may be modified by field due to induced circulation of electrons localized on the nucleus. This is known as the local shielding. In aromatic compounds, the secondary field set up the induced circulation of $\pi$ electrons which often influence the fields experienced by nuclei not directly associated with the $\pi$ electrons. Due to this, additional shielding or deshielding effects may be included within the molecule [43, 44].
1.8.4 Spin–spin Coupling

The interaction between the spins of the neighboring nuclei in a molecule may cause the splitting of the lines in the NMR spectrum. This is known as spin–spin coupling that occurs through bonds by means of a marginal unpairing of the bonding electrons [44].

1.9 APPLICATIONS OF VIBRATIONAL SPECTROSCOPY

The applications of vibrational spectroscopy are extremely diverse and the techniques are making a contribution to many areas of science. Perhaps the most interesting areas are in materials science and in biomedical research where the early detection of cancer in human tissues is the primary goal. Industrial applications, both on- and offline are also receiving attention [45]. The use of chemometrics (statistical data processing techniques) has become a standard method for extracting maximum information from vibrational spectroscopic data.

Various spectroscopic techniques were used for the present work, the instrumentation of FT–IR, FT–Raman, UV-VIS and FT–NMR are discussed in the next chapter.
REFERENCES


