

2. INFRARED (IR) SPECTROSCOPY

2.1 Introduction

Infrared (IR) spectroscopy is one of the most powerful and important analytical techniques mainly used in the structure elucidation of organic compounds. The technique is based on the marked absorption of radiation by a chemical substance in the infrared region.

Infrared radiation is the electromagnetic radiation in the wavelength range that is adjacent to visible radiation. The name infrared is derived from the fact that radiation in this region is less (infra) energetic than that of visible red radiation. IR spectroscopy is based on the selective absorption of IR radiations by a molecule which induces a change in its vibrational and rotational levels. Atoms or atomic groups in a molecule are in continuous motion with respect to one another. IR absorption occurs when the frequency of the alternating electric field associated with the incident radiation matches the natural frequency of atoms or groups to bring about a possible change in the vibrational or rotational frequency of the absorbing molecule.

These vibrational-rotational transitions produce closely packed absorption bands called IR spectra that is characteristic to the bonds and functional groups or atoms present in the molecule. The IR spectrum of a compound is considered as a fingerprint for its identification since no two compounds except optical isomers have identical spectra. Hence, it is used for the identification and structural elucidation of compounds.

Infrared Region

The IR region of the electromagnetic spectrum extends from the red end of the visible region to the microwave region (0.7 to $500 \mu\text{m}$ or 14000 to 20 cm^{-1}). It is further divided into smaller regions according to energetic proximity to the visible region.

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1. Near-Infrared Region

This region extends from the end of the visible region ($0.7 \mu\text{m}$ or $14,000 \text{ cm}^{-1}$) to about $2.5 \mu\text{m}$ (4000 cm^{-1}). Low energy electron transitions as well as changes in vibrational and rotational levels take place in this region. Near IR region is restricted to the study of compounds containing OH, NH and CH groups.

2. Mid-Infrared Region

This region extends from $2.5 \mu\text{m}$ (4000 cm^{-1}) to about $50 \mu\text{m}$ (200 cm^{-1}). Since changes in the vibrational levels of most molecules occur in this region, it is widely used for the analysis of organic compounds.

This region is subdivided into two regions,

(a) Group Frequency Region

This region extends from $4000\text{-}1300 \text{ cm}^{-1}$ or $2.5\text{-}7.69 \mu\text{m}$. In this region the principle absorption bands are assigned to vibration units consisting of only two atoms of a molecule that are dependent on the functional group that gives the absorption band and not on the complete molecular structure.

Absorption bands between $4000\text{-}2500 \text{ cm}^{-1}$ are characteristic of hydrogen stretching vibrations with elements of mass 19 or less. This region helps in the identification of the type of compound (unsaturated, aliphatic, aromatic) present.

Frequency range from $2500\text{-}1540 \text{ cm}^{-1}$ is called the unsaturated region. Triple bond frequencies occur from $2500\text{-}2000 \text{ cm}^{-1}$ and double bond frequencies appear from $2000\text{-}1540 \text{ cm}^{-1}$.

(b) Fingerprint Region

This region extends from $7.69 \mu\text{m}$ (1300 cm^{-1}) to $50 \mu\text{m}$ (200 cm^{-1}). The major factors in the spectrum i.e., single-bond stretching and bending frequencies of polyatomic molecules that involve rotational vibrational transitions occur in this region. The absorption bands in this region aid in establishing the identity of the compound hence it is called the fingerprint region.

3. Far Infrared Region

This region ranges from $50 \mu\text{m}$ (200 cm^{-1}) to $500 \mu\text{m}$ (20 cm^{-1}). It contains bending vibrations of atoms heavier than mass 19 and additional vibrations in cyclic or unsaturated systems. The molecular vibrations in this region are sensitive to changes in the overall structure of the

molecule thus the absorption bands in this region differ for different isomers of the same basic compound. This region is used for the study of organometallic or inorganic compounds whose atoms are heavy and whose bonds are weak.

Interpretation of IR Spectrum

IR spectrum is a graph of absorption band intensities on ordinate versus position of band on abscissa. Band intensities can be given in terms of transmittance (T) or absorbance (A). The position of band can be expressed in terms of wave number or wavelength. IR spectrum is usually plotted using transmittance, hence absorption bands appear as dips rather than maxima. Each dip is called a band or peak.

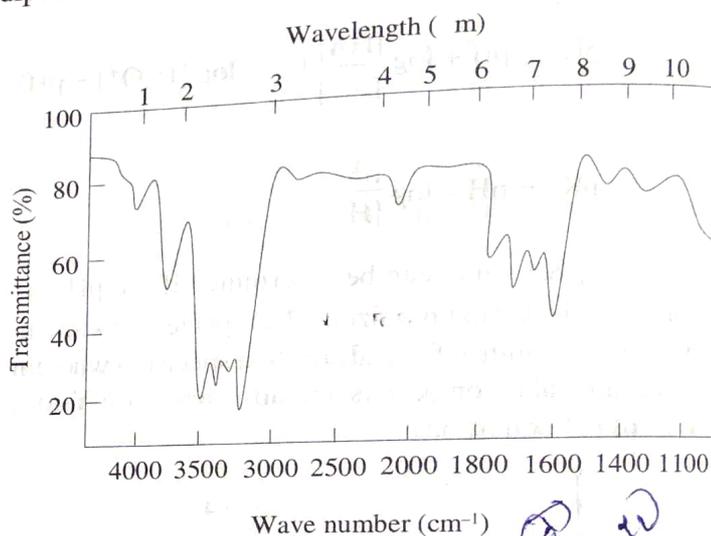


Figure: IR Spectrum

Before running an infrared spectrum, information about the compound or mixture that includes the physical state, appearance, melting point, solubility, flame tests should be obtained.

After the spectrum is run, if the compound is organic, the C - H stretching region is investigated to determine if it is aromatic, aliphatic or both. Presence or absence of functional groups is ascertained by further examination in the group frequency region. Once the category is established, spectrum of the unknown is compared with the spectra of appropriate compounds to find the exact match from the available collections of standard spectra and characteristic group frequencies.

If the exact compound is not documented, then particular structural variation within the category may help in arriving at possible answers and eliminating others.

2.2 Theory

Absorption in the infrared region is due to changes in the vibrational and rotational levels of a molecule. The absorbed energy brings about changes in the vibrational energy that depends upon masses of the constituent atoms, strength of the bonds and arrangement of the atoms constituting the molecule. Vibrational motion induces the displacement of the atoms from their equilibrium positions causing distortion in the bond length and bond angle. Changes in the bond length produce a change in the dipole moment of the molecule (heteronuclear) which will give rise to absorption bands in the IR region.

The molecules of a sample are in the lowest vibrational state. Upon absorption of radiation of suitable energy the molecules become excited to the second vibrational energy level where the amplitude of vibration is greater. Absorption of IR radiation can occur only if the dipole moment is different in the two vibrational levels so as to give absorption bands.

A molecule in its ground state possess three energy levels, electronic (e_E), vibrational (v_E) and rotational (j_E).

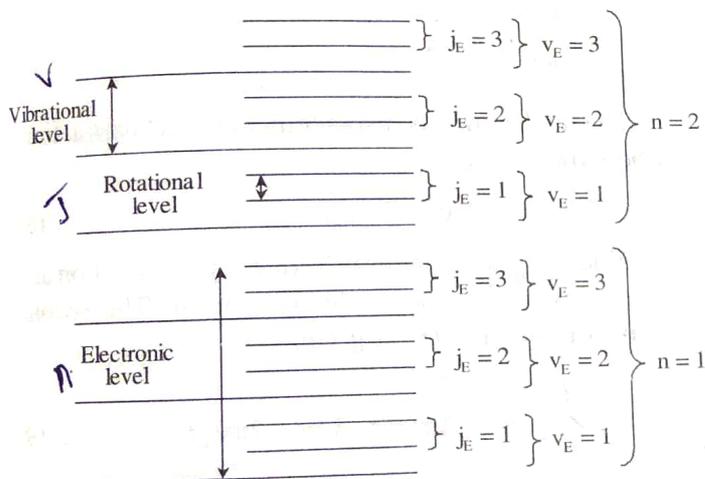


Figure: Diagrammatic Representation of Different Energy Levels in a Molecule

When the molecule absorbs energy, the electron jumps from the lower energy level to the higher energy level. Depending upon the energy of incident IR radiations, various transitions may occur. When an electron absorbs less energy, rotational transitions take place. These transitions occur between the rotational quantum levels within the same vibrational level due to which changes take place in the rotational quantum number (j). The spectrum observed is called rotational spectrum which is obtained in far IR region or rotation region (25 to 300 - 400 μ).

Absorption in the infrared region is due to changes 3.33

When an electron absorbs still higher energy, vibrational transitions take place between the vibrational quantum levels within the same electronic level. As a result, changes take place in the vibrational quantum number (v). Vibrational transitions are accompanied with rotational transitions. The spectrum observed is called vibrational-rotational spectrum which is obtained in near IR region or vibration region (2.5 to 25 μ).

When the electron absorbs energy, sufficient to cause electronic transitions which occur between the electronic quantum levels ($n = 1, 2, 3, \dots$ etc.), changes take place in the principle quantum number (n). These transitions are accompanied by both vibrational and rotational transitions. The spectrum observed is called electronic band spectrum and is obtained in UV and visible region.

Vibrational-rotational spectra helps in predicting the energy required to distort the bond length and bond angles from their equilibrium positions and hence the flexibility of the molecule. Vibrational-rotational spectra is given by heteromolecular diatomic molecules with permanent dipole moment and polyatomic molecules with or without permanent dipole moment. Homonuclear molecules do not show vibrational-rotational spectra as they do not have dipole moment.

Vibrations in a Diatomic Molecule

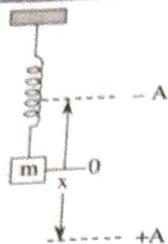
The theory of vibrational rotational spectra can be best explained by approximating a mechanical model that consists of two masses connected by a spring (diatomic molecule). As a first approximation, the vibrations of a diatomic molecule are considered as the vibrations of a simple harmonic oscillator showing simple harmonic motion resulting when one of these masses is disturbed along the axis of the spring.

To understand the mode of vibrations better, consider the vibrations of a "single mass" (atom) attached to a spring (bond) hung from an immovable object.

According to Hooke's law, if the mass is displaced by a distance x from its equilibrium position by applying a force along the axis of the spring, the restoring force F is proportional to the displacement.

$$F \propto -x$$

$$F = -kx \quad \dots (1)$$



Where F is the restoring force and k is the force constant that depends upon the stiffness of the spring. The negative sign indicates that the direction of restoring force is opposite to the direction of displacement, thus restoring the mass to the original position.

Potential Energy

Hooke's law implies that the potential energy of a particle exhibiting a simple harmonic oscillation increases parabolically in either direction from the equilibrium position. The potential energy of the mass and spring at equilibrium position or rest is assigned a value of zero. As the spring is compressed or stretched, the potential energy of the system increases by an amount equal to the work required to displace the mass. If the mass is moved from a position x to say $x + dx$, then the work done and hence the change in potential energy dE is equal to the force F times the distance dx . Thus,

$$dE = - Fdx \quad \dots (2)$$

Combining equations (1) and (2),

$$dE = kx dx \quad \dots (3)$$

Integrating equation (3) between the equilibrium position, $x = 0$ and x ,

$$\int_0^E dE = k \int_0^x x dx$$

$$E = \frac{1}{2} kx^2 \quad \dots (4)$$

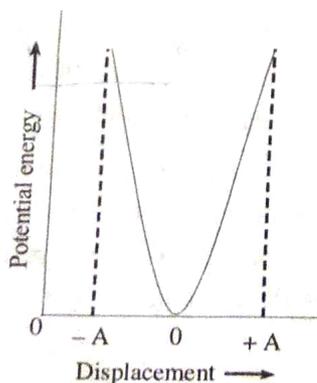


Figure: Potential Energy Curve

Potential energy curve for a simple harmonic oscillator derived from equation (4) shows that the potential energy is maximum when the spring is compressed or stretched to its maximum amplitude A and decreases parabolically to zero at the equilibrium position.

Vibrational Frequency

The vibrational frequency or motion of the mass as a function of time t can be derived from the classical mechanics. According to Newton's second law,

$$F = ma \quad \dots (5)$$

Where m is the mass and a is its acceleration. Since acceleration is the second derivative of distance with respect to time. It is expressed as,

$$a = \frac{d^2x}{dt^2}, \text{ equation (5) can be written as,}$$

$$F = m \cdot \frac{d^2x}{dt^2} \quad \dots (6)$$

Substituting the above value of F in equation (1),

$$m \cdot \frac{d^2x}{dt^2} = - kx \quad \dots (7)$$

The instantaneous displacement of the mass at time t can be expressed as,

$$x = A \cos 2\pi v_m t \quad \dots (8)$$

Where v_m is the natural frequency of vibration and A is the maximum amplitude of motion. The second derivative of equation (8) is given as,

$$\frac{d^2x}{dt^2} = - 4\pi^2 v_m^2 A \cos 2\pi v_m t \quad \dots (9)$$

On substituting equations (8) and (9) in equation (7) we have,

$$- 4\pi^2 v_m^2 A \cos 2\pi v_m t m = - k A \cos 2\pi v_m t$$

$$4\pi^2 v_m^2 m = k$$

$$v_m^2 = \frac{k}{4\pi^2 m}$$

$$v_m = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \dots (10)$$

In case such asymmetric vibration always takes place with the symmetric vibration then it is known as coupled vibration

Where v_m is the natural frequency of the mechanical oscillator which depends on the force constant of the spring and mass of the attached body. The natural frequency however is independent of the energy imparted to the system. Changes in energy causes a change in the amplitude A of the vibration but does not affect the frequency of vibration.

Vibrational energy for a diatomic molecule, consisting of two masses m_1 and m_2 attached by a spring can be explained by modifying equation (10) and by substituting the reduced mass μ for a single mass m .

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \dots (11)$$

Thus, the vibrational frequency of a diatomic system is given by,

$$v_m = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$= \frac{1}{2\pi} \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}} \quad \dots (12)$$

Wave number ($\bar{\nu}$) can be estimated by a simple addition to equation (12),

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$= 5.3 \times 10^{-12} \sqrt{\frac{k}{\mu}}$$

Where,

$\bar{\nu}$ = Wave number (cm^{-1})

c = Velocity of light (cm/sec)

m_1, m_2 = Mass of atoms (g)

k = Force constant (dynes/cm)

The behaviour of a molecular vibration is analogous to the mechanical model described above. Hence the vibrational frequency of any molecular system is calculated from equation (12) after substituting the respective masses of the two atoms for m_1 and m_2 . The quantity k is the force constant of the chemical bond which defines the stiffness of the bond.

Factors Influencing Vibrational Frequencies

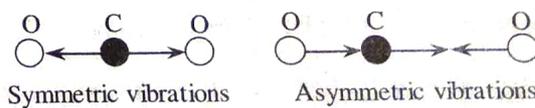
1. Vibrational Coupling

The energy of a vibration and wavelength of the corresponding absorption maximum is influenced by or coupled with other vibrations in the molecule. Factors that influence such coupling are given below.

- Strong coupling between stretching vibrations occur when there is an atom common to the two vibrations.
- Coupling between bending vibrations occur when there is a common bond between the vibrating groups.
- Coupling between a stretching and bending vibration can occur when the bond that is stretching and shrinking is also one of the bonds involved in the bending.
- Interaction is maximum when the individual energies of the coupled groups are approximately equal in magnitudes.
- Coupling is not observed between groups separated by two or more bonds.
- Vibrational coupling occurs between molecules of same symmetry.

Vibrational coupling can be best explained by taking the example of a triatomic molecule such as carbon dioxide. If no coupling occurs between the two C=O bonds, an absorption band will result at the same wave number as that for the C=O stretching vibrations in an aliphatic ketone (1700 cm^{-1}). But experimentally, carbon dioxide exhibits two absorption maxima at 2350 cm^{-1} and 667 cm^{-1} respectively.

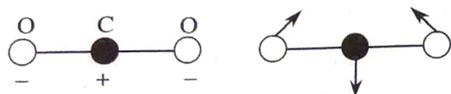
CO_2 is a linear triatomic molecule ($n = 3$), therefore it has $(3 \times 3) - 5 = 4$ normal modes of vibrations, which includes two stretching and two bending vibrations. Stretching vibrations further include asymmetric and symmetric vibrations.



Furthermore, coupling between these two may occur as the bonds involved in vibration are associated with a common carbon atom. Due to symmetrical stretching vibrations, the C=O bond contracts. It is a known fact that stretching vibrations require more energy and hence occur at shorter wavelengths.

But due to coupling, absorption of symmetrical stretching vibrations occur at longer wavelengths when compared to C=O group of aliphatic ketones. This mode of vibration causes no change in the dipole moment of CO₂, hence it is inactive to infrared radiations. In asymmetric stretching vibrations, one of the C=O contracts while the other stretches out of the plane. As a result, a change in dipole moment occurs which makes this mode of vibration infrared active. Absorption occurs at shorter wavelength (2350 cm⁻¹) when compared to C=O group of aliphatic ketones. The variation in absorption frequency seen in C=O group of CO₂ is due to strong interaction or coupling existing between the vibrating groups.

The remaining two vibrational modes of carbon dioxide involve in plane and out of plane scissoring. The two vibrations are identical in energy and thus produce a single absorption band at 667 cm⁻¹.



2. Electronic Effects

Electronic effects like inductive, mesomeric, conjugation etc., affect the frequency shifts from the normal position of absorption due to changes in the bond strength and force constant.

Introduction of an alkyl group causes positive inductive effect which results in the lengthening or weakening of the bond causing the absorption to take place at a lower wave number. For example, formaldehyde (HCHO) shows absorption band at 1750 cm⁻¹ whereas acetaldehyde (CH₃CHO) exhibits at 1745 cm⁻¹.

Introduction of electronegative atoms in a molecule induces negative inductive effect that results in absorption taking place at higher wave number. For example, acetone (CH₃COCH₃) gives absorption band at 1715 cm⁻¹ whereas chloroacetone (ClCH₂COCH₃) exhibits the same at 1725 cm⁻¹.

Mesomeric effect works in a similar manner as inductive effect while conjugation lowers the wave number of absorption.

3. Hydrogen Bonding

Hydrogen bonding gives downward frequency shifts. Stronger the hydrogen bonding, greater is the absorption shift towards the lower wave number.

Intermolecular and intramolecular hydrogen bonding can be distinguished from the IR absorption bands. Generally, intermolecular hydrogen bonds give broad absorption bands compared to the sharp and well defined bands given by intramolecular hydrogen bonds.

Moreover, intermolecular hydrogen bonds are concentration dependent. Upon dilution, the intensities of such bands decrease and eventually they disappear. Intramolecular hydrogen bonds are independent of concentration.

Types of Molecular Vibrations ✓

In a molecule, the relative positions of atoms are not fixed but fluctuate continuously because of different types of vibrations and rotations about the bonds.

In simple diatomic and triatomic molecules, the number and nature of vibrations is easy to define and relate with the energies of absorption. However for polyatomic molecules such analysis becomes difficult because they have large number of vibrating centres and interact among themselves.

Molecular vibrations fall into two basic categories, stretching and bending. When the molecules vibrate, the covalent bonds behave as tiny springs connecting the atoms. The atoms in a molecule vibrate back and forth about an average value of interatomic distance. Thus the vibrational motion is quantized and various stretching and bending vibrations of a bond occur at certain quantized frequencies. The energy required for stretching vibrations is more than bending vibrations. Therefore, stretching vibrations occur at shorter wavelength (higher wave number) than bending vibrations that require less energy and occur at longer wavelength (lower wave number).

1. Stretching Vibrations

These type of vibrations involve the movement of atoms within the same bond axis such that the bond length changes without any change in bond angle at regular intervals. Symmetrical molecules like O=C=O are not IR active because their dipole moment does not change upon stretching vibrations.

Stretching vibrations are subdivided into two types,

(a) Symmetrical Stretching Vibrations

In this type, the movement of atoms with respect to the central atom is in the same direction such that the bond length increases or decreases symmetrically without any change in the bond angle or bond axis.

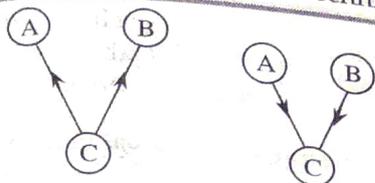


Figure: Symmetrical Stretching Vibrations

(b) Asymmetrical Stretching Vibrations

In this type of vibration, the atoms move with respect to the central atom such that one moves away and the other moves towards the central atom.

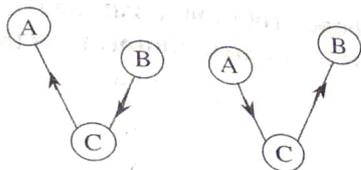


Figure: Asymmetrical Stretching Vibrations

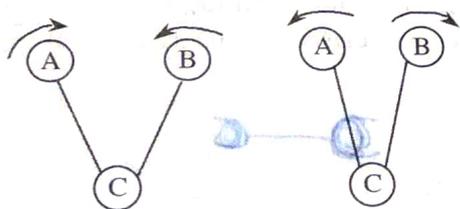
2. Bending or Deformation Vibrations

In this the position of atoms change with respect to the original bond axis, such that there is a change in the bond axis and bond angle of each individual atom without any change in their bond lengths.

These are further divided depending on in-plane and out-of-plane bending of atoms.

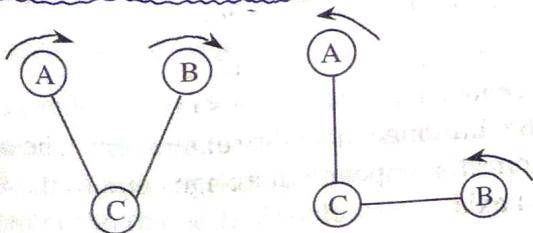
(a) Scissoring Vibrations

In this type of vibrations, in-plane bending of atoms occur wherein they approach each other or move apart.



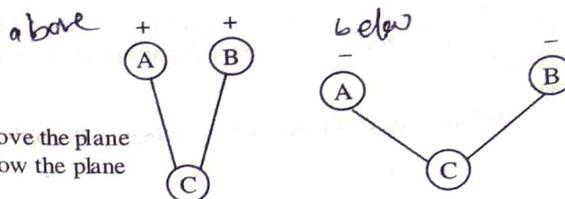
(b) Rocking Vibrations

In this type, in-plane bending of atoms occur wherein they swing back and forth in the same direction with respect to the central atom, maintaining the bond angle.



(c) Wagging Vibrations

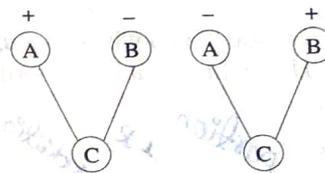
In this type of vibrations, out-of-plane bending of atoms occur wherein they either move above or below the plane with respect to the central atom.



+ = Above the plane
- = Below the plane

(d) Twisting Vibrations

In this type of vibrations, out-of-plane bending of atoms occur wherein they twist around the bond which joins the central atom such that one of the atom moves above the plane while the other moves below the plane with respect to the central atom.



Modes of Vibration

The total possible number and kinds of vibrations in a molecule can be calculated if the number of atoms in the molecule is known. For a molecule containing N number of atoms, three coordinates (x, y and z) are required for each atom to completely specify the position and orientation of the molecule in space at a particular instant. Therefore, for each molecule 3N degrees of freedom exists, where each coordinate is a degree of freedom for the molecule.

Every molecule is associated with three kinds of motion,

1. Translational motion of its centre of gravity i.e., motion of the entire molecule through space
2. Rotational motion around its centre of gravity
3. Vibrational motion due to motion of each of its atoms relative to the other atoms.

Therefore, the total number of degrees of freedom for a molecule is given as,

$$\text{Total number of degrees of freedom (3N)} = \text{Degree of freedom for vibrational motion} + \text{Degree of freedom for translational motion} + \text{Degree of freedom for rotational motion}$$

Since all the atoms in a molecule are constantly in motion in space, therefore translational motion is common and requires three of the 3N degrees of freedom.

For non-linear molecules, another three degrees of freedom are required to define the rotational motion. Therefore the degrees of freedom required for vibrational motion that represent the number of possible vibrations in a molecule is given by,

$$\text{Degree of freedom for vibrational motion} = 3N - 3 - 3 = 3N - 6$$

In case of linear molecules, all the atoms lie in a single straight line, hence rotation about the bond axis is not possible. Therefore only two degrees of freedom is sufficient to describe their rotational motion. Thus the number of vibrations is given by,

$$\text{Degree of freedom for vibrational motion} = 3N - 3 - 2 = 3N - 5$$

Each of the 3N - 6 and 3N - 5 vibrations is called normal mode of vibration.

For example the possible number of vibrational modes for water (H₂O) which is a non-linear triatomic molecule is $3 \times (3) - 6 = 3$.

For carbon dioxide (CO₂) which is a linear triatomic molecule, the number of vibrational modes are $3 \times (3) - 5 = 4$ and for hexane (C₆H₁₄) which is a linear molecule containing 20 atoms, the number of possible vibrational modes are $3 \times (20) - 5 = 55$.

2.3 Principle

Absorption of IR radiations corresponds to a change in the vibrational and rotational levels in a molecule. These changes are characterized by changes in the rate or direction of vibration of a portion of a molecule with respect to the remaining molecule or a change in the rotation of the molecule about its centre of gravity.

IR spectroscopy is based on the principle that when a compound is exposed to IR radiations, the atoms selectively absorb the radiations of specific wavelength resulting in vibration of the molecule. The multitude of vibrations occurring simultaneously produce a highly complex absorption spectrum that is characteristic of the functional groups and bonds that constitute the molecule and also its overall configuration.

Requirements for IR Radiation Absorption

The two important criteria for a molecule to absorb IR radiation are,

1. Frequency of Applied Radiation

Atoms or atomic groups in a molecule are in continuous motion with respect to one another. Every bond and atom in a molecule thus possesses an inherent natural frequency of vibration that is characteristic to the energy portion of the molecule. When a compound is exposed to IR radiation, a portion of the incident radiation is absorbed at specific wavelengths. Absorption occurs only when the frequency of the electric field associated with the incident radiation is equal to the natural frequency of vibration thus causing a change in the rate of rotation and amplitude of vibration of the absorbing molecule.

2. Dipole Moment

A molecule will absorb IR radiation only when its absorption causes a change in its dipole moment. The positive and negative charges on the atoms of the molecule experience forces in opposite directions due to the electric field of the IR radiations. As a result, the spacing between the charged atoms (electric dipoles) of the molecule

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charged
spacing As a forces opposite direction

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position IR radiation



also decreases. As the electric field of the IR radiation changes its polarity periodically, the spacing between the electric dipoles of the molecule also changes periodically which results in vibrations. When these charged atoms vibrate they absorb IR radiation. The amount of IR radiation absorbed by the molecule is proportional to the rate of vibration. If the rate of vibration in charged atoms is fast, they exhibit intense absorption and vice versa.

Symmetrical diatomic molecules (O_2 , N_2 , etc.) do not possess electric dipole. They cannot be excited by IR radiations and hence do not give IR absorption spectra. Symmetrical compounds such as ethylene

—C=C— exhibit dipoles, but do not show any change in the dipole moment, upon C=C stretching. Since there is no change in the dipole moment, the bond does not absorb IR radiation. However if the symmetry of the compound is destroyed, it exhibits dipole moment and absorbs strong IR absorption.

For example, substitution of bromine for hydrogen of ethylene destroys the symmetry around the double bond. Stretching of the double bond now generates a change in the dipole moment and strong IR absorption takes place.

If the atoms in the molecule are close to each other, then the rate of change of electric dipole is fast. This increases the frequency of vibration and in turn increases the intensity of IR absorption.

When a polar molecule is exposed to IR radiations, stretching vibrations along the internuclear axis of the polar bond are seen. Hence, electron distribution changes and a change in the dipole moment is seen resulting in the absorption of IR radiations.

2.4 Instrumentation

1. Radiation Sources

Radiation sources used in IR spectroscopy are hot bodies whose emissions are equivalent to black body radiator. The various radiation sources used are,

(a) Incandescent Lamp

Incandescent lamp consists of a closely wound nichrome coil enclosed in a glass covering. Upon heating, a black oxide film is formed on the nichrome coil which gives acceptable emissions of

IR radiations. The intensity of IR radiations emitted is less compared to others. It cannot give far IR radiations and has low spectral emission.

(b) Nernst Glower

Nernst glower consists of a hollow rod made up of fused mixture of rare earth metal oxides like thoria, yttria and zirconia. Nernst glower remains non-conducting at room temperature and should be heated (between 1000-1800°C) by suitable external means to make it conductive in nature. The energy output from Nernst glower ranges in between 1-10μ.

Advantages

1. The intensity of radiations emitted is 3 times more than that of incandescent lamp and global source.
2. It emits wide range of radiations without any fluctuations in intensity over prolong period of time.
3. It does not get oxidized by air.

Disadvantages

1. It is extremely fragile.
2. It require heaters for preliminary heating.
3. Requires frequent repairs.

(c) Globar Source

It consists of a silicon carbide rod about 50 mm long and 6-8 mm in diameter. It can be operated to a temperature of about 1300°C. The radiations emitted by globar source is equivalent to 80% of a black body radiator. Its intensity of radiation is less below 10 μm but high above 15 μm.

Disadvantages

1. It undergoes exhaustion with time i.e., its resistance increases. This can be overcome by increasing the voltage.
2. It is less intense than Nernst glower.

(d) High Pressure Mercury Arc

For radiations in far IR region, high pressure mercury arc is used which consists of a double-jacketed quartz lamp filled with mercury vapour under high pressure. At shorter wavelengths, the heated quartz jacket gives out intense radiations equivalent to that of black body sources.

2. Monochromator and Collimating Systems

The radiation source emits IR rays of varying frequencies. Since the sample absorbs IR radiations of a definite frequency, the radiations of desired intensity are selected using a monochromator.

Monochromators are of 2 types i.e., prism monochromators and grating monochromators.

(a) Prism Monochromator

Prisms made up of alkali metal halides like NaCl, KBr etc., are used as they are transparent to IR radiations. Quartz prisms can be used in near IR region (0.8-3 μ) only. Prisms made up of lithium fluoride (LiF) can be used in near IR region (1-5 μ). Crystalline NaCl prisms are widely used which show high dispersion in the region between 5-15 μ and satisfactory dispersion up to 2.5 μ . They are used for mid IR region, Crystalline KBr and CsBr are used in far IR region (15-40 μ).

Prism monochromators are of two types,

(i) Single-Pass Monochromator

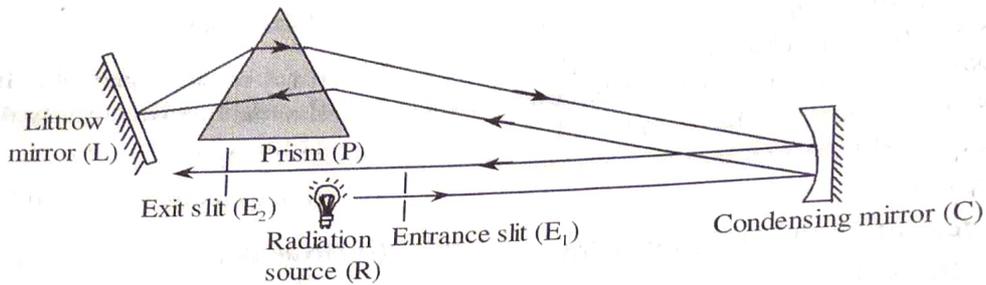


Figure: Single-pass Monochromator

In a single-pass monochromator, a single beam of light from the radiation source (R) enters into the sample cell (not shown). After passing through the sample, it passes through the entrance slit (E_1) and strikes the condensing mirror (C), which directs the radiations towards the prism (P). The prism disperses the radiation that strikes the littrow mirror (L) and is reflected back to the condensing mirror via prism and finally exits through the exit slit (E_2).

(ii) Double-Pass Monochromator

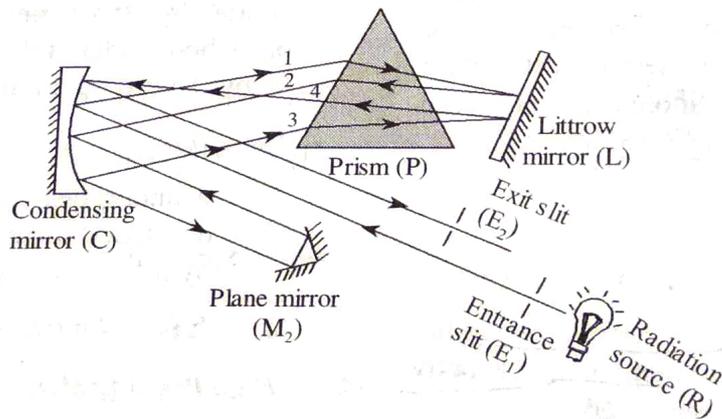


Figure: Double-pass Monochromator

In a double-pass monochromator, a single light beam from the radiation source undergoes four passes (1, 2, 3, 4) through the prism as shown in the figure. The double pass of the light beam through the monochromator results in its better resolution before it reaches the detector thereby producing fairly good results compared to single-pass monochromator.

Grating Monochromator

(b) Refer Page No. 3.19.

Mirrors

(c) In IR spectrophotometry, concave mirrors which are made up of metals or glass coated with aluminium are used. These mirrors are used for collimating and for focussing the radiations.

Sample Handling System/Sampling Techniques

3. IR spectroscopy helps in the identification and determination of solids, liquids and gases.

Narrow sample cells (0.1-1mm) made up of NaCl, KBr, ThBr are used. Silver chloride cells are used for aqueous and moist samples. Polyethylene cells can be used when absorption frequency is less than 600 cm^{-1} .

IR spectra varies with the physical state of the sample. It is therefore mandatory to indicate the state of the sample in the IR spectroscopy.

Example: IR spectra of stearic acid in solution shows broad peaks making it difficult to characterize them whereas IR spectra of stearic acid in solid film shows definite peaks.

(a) Solid Samples

Solid samples can be analyzed using IR spectroscopy by the following ways,

(i) Solution of SolidIn this technique, the solid sample is dissolved in an inert solvent and the solution is analyzed in liquid sample cell. Some of the solvents which are used in IR spectroscopy are CCl_4 , CHCl_3 , CH_3COCH_3 , cyclohexane etc. To avoid absorption band due to single solvent, two solvents having complimentary absorption regions are used (E.g.s: CCl_4 and CS_2).**Disadvantages**

1. Solid sample may react with the solvent resulting in undesirable spectra.
2. This method cannot be used for all solids because suitable solvents are limited and there is no single solvent which is transparent in the entire IR region.

(ii) Sample Film

In this technique, an amorphous solid sample is dissolved in a suitable volatile solvent. A

drop of this solution is placed in NaCl or KBr sample cells. The solvent is evaporated by gentle heating, which leaves a thin film on the surface of the cell. The resultant film is used for qualitative analysis.

(iii) Mull Method

In this technique a thick paste of finely powdered sample and mineral oil (nujol oil) is sandwiched between two salt plates (NaBr/KBr).

Mineral oil widely used is nujol oil, but it shows absorption maxima at 2915 cm^{-1} , 1462 cm^{-1} , 1376 cm^{-1} and 719 cm^{-1} which interferes with sample absorbance. This interference can be avoided using hexachlorobutadiene with nujol oil which absorbs in the regions of $1630 - 1510$, $1200 - 1140$ and $1010 - 760\text{ cm}^{-1}$ thus permitting the recording of IR spectra of only the sample. This method is applied for qualitative analysis of crystalline compounds.**Disadvantage**

Grinding of the crystalline sample may lead to degradation and polymorphic changes.

(iv) Pressed Pellet Technique

In this technique, a small amount of finely powdered solid sample is mixed with about 100 times its weight of powdered potassium bromide. The mixture is passed under a mini press and compressed at high pressure (25,000 psig) to form a small pellet of about 1-2 mm thick and 1 cm in diameter. The resulting pellet is transparent in the IR region.

Advantages

1. Absorption bands due to mineral oil can be avoided.
2. KBr pellets can be stored for longer periods.
3. Spectrum obtained from this technique helps in easy characterization when compared to mull method.

Disadvantages

1. The absorption spectrum always shows a band at 3450 cm^{-1} due to hydroxyl (OH) group of the moisture which is always present in the sample.

3.42

2. Inorganic crystalline complexes may undergo decomposition or polymorphic changes due to exposure to heat and high pressure while forming a pellet.
3. Bromide ion of the KBr may substitute the ligand of the inorganic molecules.
4. Applicable to only those substances which can be powdered along with KBr.

(b) **Liquid Samples**

The samples which are liquid at room temperature are directly introduced in the sample cell such that the sample thickness is 0.01-0.05 mm with a transmittance of 15-20%.

Viscous liquids are sandwiched between two salt plates of NaBr or KBr as the sample cannot be introduced directly in a pre-assembled cell.

(c) **Gas Samples**

Gas sample cells consist of glass or metal cylinder, about 10 cm to 1 m long and are made up of NaCl, KBr etc. These are equipped with internal gold plated or stainless steel metal components and gold-surfaced mirrors. These components cause multiple reflection of the radiation thereby increasing the effective path length of the cell several times longer than the actual cell length. The gas sample is introduced into the cell through a stop cock under a pressure of 5-50 mm of Hg.

Disadvantages

1. High pressure in the gas cell may broaden the absorption peaks.
2. Analysis of gases by IR spectroscopy is less commonly employed due to its low sensitivity.
3. Moisture should be avoided as it interferes with the analysis.

4. **Detectors**

(a) **Thermal Detectors**

When IR radiations fall on a thermal detector, its temperature increases due to heating. This increase in temperature produces a potential difference which is proportional to the amount of radiations falling on the detector.

The properties which are measured in thermal detectors are expansion of solid, gas or fluid (Golay cell), electrical resistance (thermistor), voltage induced at the junction of two dissimilar metals (thermocouple and thermopile) and electric polarization (pyroelectric detectors).

(i) **Thermocouple**

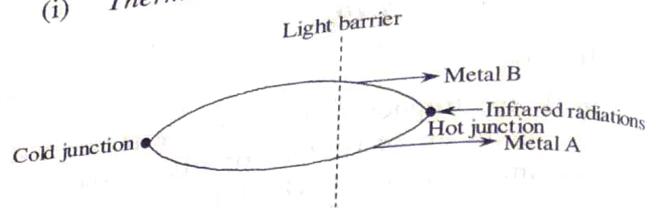


Figure: Thermocouple

It is the most widely used detector in IR spectrophotometry. Its working is based on the fact that when two different semiconductor or metal wires are connected together at both ends and kept at different temperatures, then an electric current flows through them. The thermocouple is enclosed in an evacuated steel casing which consists of a window made up of KBr or CsI to prevent energy loss by convection. One end of the thermocouple is exposed to IR radiation and is called as hot junction. The other end called cold junction is maintained at constant temperature. When the IR radiations fall on the hot junction, its temperature increases which results in the development of an electric potential difference between the two junctions. The magnitude of potential difference generated is proportional to the amount of IR radiations falling on the hot junction.

(ii) **Bolometer**

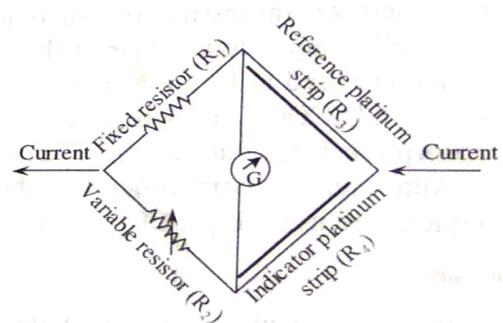


Figure: Bolometer

It is based on the principle that electrical resistance of a metal increases for every one degree rise in temperature. A bolometer is based on Wheatstone bridge arrangement.

In bolometer two arms of the bridge are made up of platinum strips coated with lamp black. One arm is exposed to radiations (indicator

strip) and other arm is protected from radiations (reference strip). The two platinum strips are initially connected to a sensitive galvanometer, then to a battery in Wheatstone bridge arrangement. When radiations fall on the exposed platinum strip, its temperature increases, resulting in a change in the degree of resistance of the conductor, which makes the bridge unbalanced and causes the current to flow through the galvanometer. The amount of current flowing through the galvanometer is proportional to the amount of radiations falling on the exposed platinum strip. The response time of bolometer is 4 millisecond.

(iii) Pyroelectric Detector

Pyroelectric detector consists of a thin flake of pyroelectric crystal (which shows permanent dipole moment) of $0.25-12 \text{ mm}^2$ in size. This crystal flake is placed between two electrodes which are connected to an external electric circuit. When the crystal is exposed to IR radiations, it absorbs heat leading to a change in its dipole moment. This change results in the generation of electrical charges which are attracted towards the electrodes. Accumulation of charge at the electrodes creates a potential difference hence producing electric current in the external circuit. Various pyroelectric crystals used are barium titanate, lead zirconate, lithium tantalate (LiTaO_3), lithium niobate (LiNbO_3), triglycerine sulphate (TGS) and deuterated triglycerine sulphate (DTGS).

Use

Pyroelectric detectors are increasingly used in Fourier transform spectrometer as they require rapid responses.

Advantages

1. It has faster response time (10 μ sec) when compared to other detectors.
2. It can be used with radiations that are chopped at high frequency order (10^5 Hz).

Disadvantages

1. Expensive.
2. These respond only to those radiations that have been suitably modulated or chopped but are unresponsive towards steady radiations.

(iv) Golay Cell

Golay cell consists of a small metal cylinder filled with xenon gas. One end of the cylinder is sealed with a rigid blackened metal foil (2 mm^2) while the other end is sealed by a flexible silvered diaphragm which acts as a mirror. The blackened metal plate is exposed to IR radiations. The heat produced due to absorption of radiation causes the gas present inside the cylinder to expand and deform the flexible diaphragm. Light from the lamp is made to fall on the diaphragm which in turn reflects it onto the phototube. When the diaphragm is at rest no light passes through it. However when the diaphragm flexes, varying amounts of light reaches the phototube. The signal received by the phototube is modulated according to the intensity of the radiation falling on the cell and is displayed on the readout device.

Advantages

1. It can be used over wide wavelength range.
2. It has a faster response time (10^{-2} sec) compared to bolometer and thermocouple.

Disadvantage

It is expensive and bulky, hence less convenient to use.

(b) Photon Detectors

When photons from IR radiations fall on the semiconductor, the interaction produces electrons and holes (internal photoelectric effect). The energetic photons strike the electrons of semiconductor causing its excitation and render it conductive from non-conducting state.

The most commonly used semiconductors are lead sulphate, lead telluride or germanium which do not conduct at low energy state but conduct electricity when excited to high energy state.

(i) Photoconductivity Cell

Photoconductive detectors are made up of photosensitive materials like cadmium sulphide, lead sulphide etc., supported on glass and enclosed in an evacuated glass casing.

When IR radiations fall on the detector, the electrical conductivity of the photosensitive

material increases due to excitation of electrons by the incident light. During the process, current is produced which is proportional to the amount of incident IR radiations. Photoconductivity cell is highly sensitive and has good speed of response (0.5 msec).

(ii) *Semiconductor Detectors*

A semiconductor is a material that behaves as an insulator when no radiations fall on it but becomes a conductor when exposed to radiation. Exposure to radiation causes a rapid change in its electrical resistance and therefore produces a very rapid response to the IR signal. The response time is the time required to change the semiconductor from an insulator to a conductor.

Semiconductor detectors work on the basic principle that the electrical conductivity changes significantly when the energy of a single photon of IR radiation displaces an electron in the detector to a higher energy level.

These detectors are made by depositing a layer of semiconductor material on an evacuated sealed glass envelope. Exposure to radiation produces a rapid change in the conductivity. These detectors are very fast and very sensitive with response time as short as 1 nsec.

2.5 Working

IR spectrophotometers are of the following types,

1. Dispersive Instruments

Dispersive instruments utilize prisms or gratings. These are further classified as single beam and double beam IR spectrophotometers.

(a) *Single Beam IR Spectrophotometer*

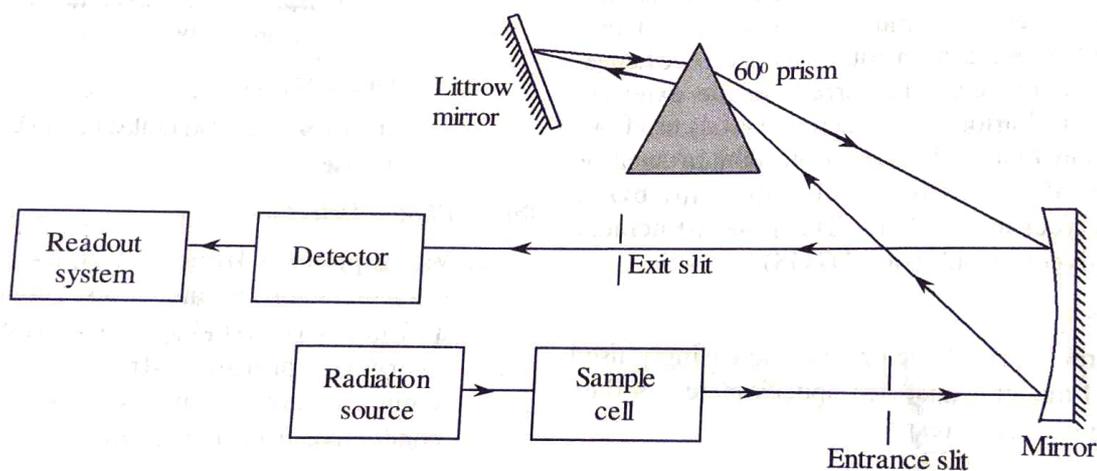


Figure: Single Beam IR Spectrophotometer

In single beam IR spectrophotometer, radiations from the radiation source is allowed to fall on the sample cell. The sample absorbs the radiations and transmits some of it via the entrance slit onto the mirror. Radiations from the mirror are directed towards the prism and then towards a rotating littrow mirror. The littrow mirror selects the desired wavelength, reflects it back to the mirror and through the exit slit onto the detector. The detector sends signals to the readout device which gives the transmittance of the sample as a function of its wavelength.

Disadvantages

1. The emission intensity of radiation source is not uniform, which results in deformed IR absorption spectra.
2. The IR spectrum of the sample solution shows extra bands due to solvent. In such cases, pure spectrum of the sample is obtained by subtracting the resultant spectrum from the spectrum of the solvent.

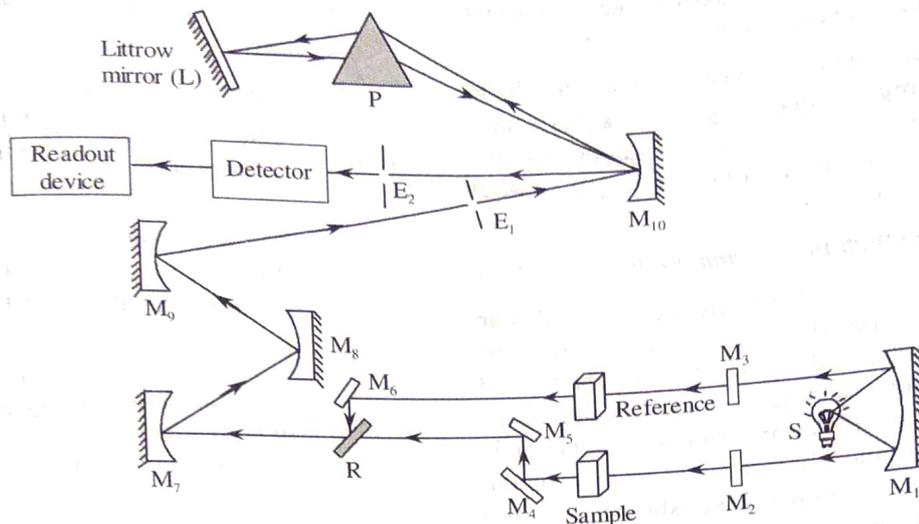


Figure : Double Beam IR Spectrophotometer

In double beam IR spectrophotometer, Nernst glower is used as a radiation source (S). The radiations emitted by it split into two beams which are identical in their intensities. The beam pair is reflected by the mirror M_1 on mirrors M_2 and M_3 where they undergo further reflection. After being reflected by mirror M_2 , one of the beam passes through the sample cell while the other beam (reflected by mirror M_3) passes through the reference cell. Two mirrors M_4 and M_5 reflect the transmitted light beam from the sample cell to the rotating sector mirror (R). The transmitted beam from the reference cell is also passed onto the rotating sector via mirror M_6 .

During one half of its rotation, the rotating sector mirror reflects the sample beam and blocks the reference beam, while in the other half rotation, the reference beam is reflected and the sample beam is blocked. As the two beams are of equal intensity, any change in their intensity would lead to an imbalance in the detector signal. The sample beam now undergoes reflection by mirrors M_7 , M_8 and M_9 . The beam is then passed through the entrance slit (E_1) into the monochromator consisting of mirror M_{10} , prism (P) and Littrow mirror (L) where it undergoes dispersion. The dispersed beam is again reflected back to M_{10} which selects the beam of desired wavelength. The selected beam exits through the exit slit (E_2) and falls on the detector. Signal from the detector is then passed onto the readout device. In the next rotation, the rotating sector blocks the sample beam and transmits the reference beam which undergoes similar process. The alternate sample and reference signal reaching the detector is amplified and sent to the readout device which records the transmittance of sample as a function of its wavelength.

2. Non-Dispersive Instruments

Non-dispersive IR spectrometers utilize interference filters, tunable laser sources or interferometer.

Fourier Transform Infrared Spectrometer

FTIR spectrometer has been discussed under FTIR spectroscopy.

2.6 Applications

1. Analysis of Organic Compounds

(a) Identification of Organic Compounds

IR spectra of two organic compounds cannot be identical unless they are optical isomers because no two organic compounds produce the same spectrum of absorption bands. However, two enantiomers of the same compound give identical IR spectra. Thus, IR spectroscopy cannot differentiate between two enantiomers.

3.46

The IR spectra depends upon the physical state of the sample, solvent used to dissolve the sample and concentration of the solution.

A particular functional group gives absorption band in a definite region depending upon the molecules surrounding it. This in turn leads to variation in the intensity of absorption band that may be either strong, moderate or weak.

(b) **Structural Elucidation of Compounds**

Molecular structure of unknown compounds can be determined from IR spectrum. IR spectroscopy plays an important role in determining the type of functional groups by observing the position of the absorption bands. If the spectrum does not contain an absorption band characteristic of a particular functional group, then the substance does not contain that group.

Example : Presence of strong absorption band at a frequency of 1717 cm^{-1} indicates the presence of carbonyl group.

(c) **Study of Rates of Reactions**

The rate and extent of reaction can be determined by analyzing the IR spectra of sample at different intervals during the reaction. The rate of disappearance of a particular absorption band of a reactant or the rate of increasing absorption bands due to the formation of product can help in determining the reaction rate.

Example : In the oxidation of alcohol to carbonyl compound, there is a gradual disappearance of an absorption band of OH at $3600\text{--}3650\text{ cm}^{-1}$ and appearance of an absorption band $\text{C}=\text{O}$ at $1680\text{--}1760\text{ cm}^{-1}$.

(d) **Determination of Purity of Sample**

IR spectrum of a sample can be compared with that of the pure compound to detect the presence of impurities. The spectrum of an impure sample does not show sharp bands, has many additional bands, and is generally blurred.

Example : Presence of blurred absorption band of ketone in the IR spectrum of alcohol indicates the presence of ketone as impurity in alcohol. Moreover, the sample gives an absorption band at 1720 cm^{-1} which is the characteristic frequency of carbonyl group indicating the presence of ketone as impurity.

(e) **Identification of Isomers**
IR spectroscopy helps in studying the following isomers.

(i) **Functional Isomers**

The analysis of functional isomers (compounds having the same molecular formula but different functional groups) can be carried out using IR spectroscopy as the different functional groups of two functional isomers give different absorption spectra.

(ii) **Cis-trans Isomers or Geometric Isomers**

Cis-trans isomers can be identified if spectra of both are available. *Trans*-isomers are more symmetric and the vibrations may or may not change the dipole moment of the compound, thus IR spectra of *Trans*-isomer is simple compared to *cis*-isomer. *Trans*-isomers appear at a higher frequency range than *cis*-isomers (nearly $5\text{--}10\text{ cm}^{-1}$ higher).

If a heteroatom (like O, N, S etc.), is present then *trans*-isomer has $20\text{--}40\text{ cm}^{-1}$ higher frequency than *cis*-isomer.

(iii) **Rotational Isomers or Conformers**

Conformers are the compounds that can be interconverted by rotation about a single bond. They differ slightly in their energy content and hence require sensitive techniques for identification. In general, difference in frequency of 1 cm^{-1} corresponds to energy of about 3×10^{-3} kcal/mole. Hence, high resolution IR spectrophotometer is required for their identification.

Example : Conformers of ethanol and α -haloketone esters can be assessed using IR spectroscopy.

(iv) **Tautomerism**

IR spectroscopy helps in the identification of tautomers due to the presence of different absorption bands in their spectra.

Example : Thiocarboxylic acid exhibits tautomerism wherein the keto group is in equilibrium with enol group. Thiocarboxylic acid tautomers are identified by the presence or absence of bands characteristic of O—H or S—H and $\text{C}=\text{O}$ or $\text{C}=\text{S}$.

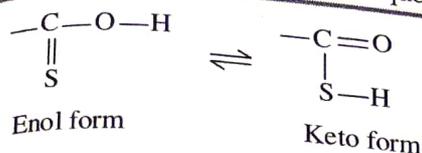


Figure: Thiocarboxylic acid

Miscellaneous Applications

2. (a) Shape and Symmetry of a Molecule

The shape and symmetry of a molecule can be determined by IR spectroscopy.

Examples

- (i) The structure of NO_2 can be determined from the fact that if NO_2 is a linear molecule, it will exhibit two bands like CO_2 , if it is bent like H_2O it will exhibit three bands. In practice IR spectra of NO_2 produces three bands at positions 750 , 1323 and 1616 cm^{-1} indicating its bent structure.
- (ii) IR spectra has also been used to elucidate the structure of large molecules like xenon fluorides which possess various types of symmetry. The IR spectra of XeF_2 , XeF_4 and XeF_6 has elucidated their linear, square planar and octahedral structure respectively.

(b) Detection of Water in a Sample

IR spectrum can detect the presence of water in a sample. If the sample contains lattice water, it can be detected by three characteristic bands in the regions $3600\text{--}3200 \text{ cm}^{-1}$, 1650 cm^{-1} and $600\text{--}3000 \text{ cm}^{-1}$.

If the sample contains water coordinated to a metal ion it can be detected by an additional band at $890\text{--}660 \text{ cm}^{-1}$.

(c) In Pharmaceutical Industry

Applications of IR spectroscopy in pharmaceutical industry can be seen as follows,

- (i) Detection of impurities
- (ii) It helps in determining the composition and the amount of product present in the sample.
- (iii) Identification of samples in research centres
- (iv) Waxes like beeswax, carnauba wax and other waxes can be identified by IR spectroscopy for the presence of impurities like cheaper petroleum wax.

- (v) Flavouring agents and colouring components which are used in food materials can also be identified using IR spectroscopy.

(d) Analysis of Paints and Varnishes

Paints and varnishes are analysed by reflectance analysis wherein the sample is irradiated with IR radiations and the amount of light reflected by the paint is allowed to enter the IR instrument. This helps in identifying the paint on automobiles or appliances without destroying the surface.

(e) Examination of Paintings and Artifacts

IR spectroscopy is employed in the examination of old paintings and artifacts. Information regarding the varnish used on the painting, the pigments present in the paint and the textile of the canvas can be obtained by IR spectroscopy that can be used to detect fake masterpieces.

(f) Assessment of Brain Function

Alteration of haemoglobin concentration with neural activity helps in assessing the brain function which is possible with near infrared spectroscopy (NIRS).

NIRS and optical topography are sometimes used as synonyms, but optical topography involves detection of spectroscopic reflection and scattering from multiple measurement point and the results are obtained in the form of a map whereas NIRS involves fewer measurement points.

2.7 Fourier Transform Infrared (FTIR) Spectroscopy

Principle

FTIR spectroscopy is a versatile tool in pharmaceutical sciences with wide range of applications. It operates on a different principle called *Fourier transform*. Fourier transform is a mathematical operation demonstrated by Jean Fourier. It converts the frequency domain into time domain. The mathematical expression for Fourier transform is,

$$F(\omega) = \int_{-\infty}^{+\infty} F(x) e^{i\omega x} dx$$

Where,

ω = Angular frequency

x = Optical path difference