

Module 2

Spectroscopy

Syllabus Content

Module-2 [08]

Spectroscopic techniques and Applications:

Elementary idea and simple applications of Rotational, Vibrational, Ultraviolet & Visible and Raman spectroscopy.

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1. Spectroscopy:-

It is the branch of science which deals with the determination of the structure of a compound through the interaction of electromagnetic radiation with the matter (**Figure 1**).

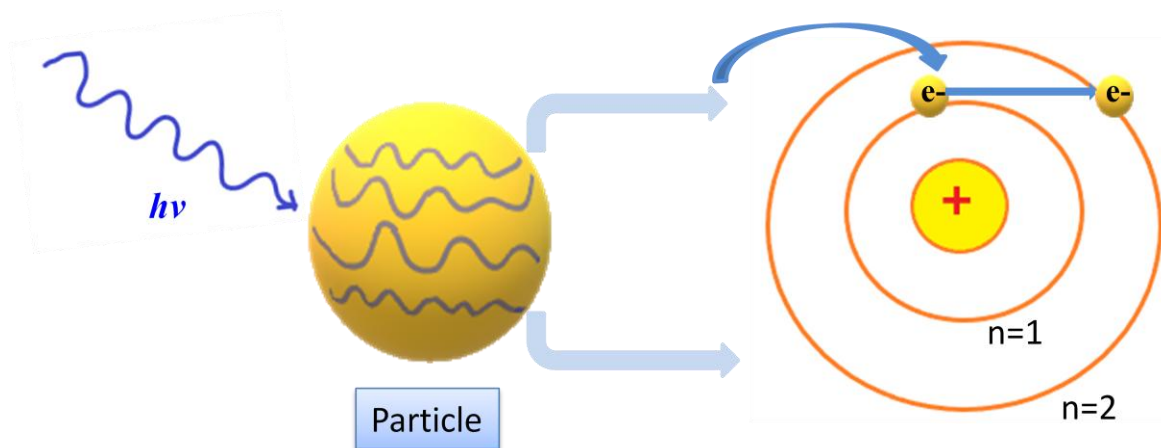


Figure1. Interaction of Radiation with particle of a matter

Classical methods for measuring physical properties of matter are: boiling point, melting point, solubility, optical rotation, refractive index and for chemical properties are: functional group analysis element analysis. Advantages of spectroscopy over other analytical technologies:-

1. It takes less time in the analysis.
2. It requires less amount of the sample.
3. The sample remains unaffected after analysis i.e. it can be reused.
4. This technique is more reliable.

1.1 Electromagnetic Radiations:-

It is a form of energy that is transmitted through space at an enormous velocity. Example is visible light. The quantum mechanics suggest that Electromagnetic radiation (EMR) has a dual character i.e. wave like and particle like. According to wave nature, electromagnetic radiations consist of oscillating electric and magnetic fields, which are mutually perpendicular to each other, does not require any medium to travel and travels with the velocity of light (**Figure 2**).

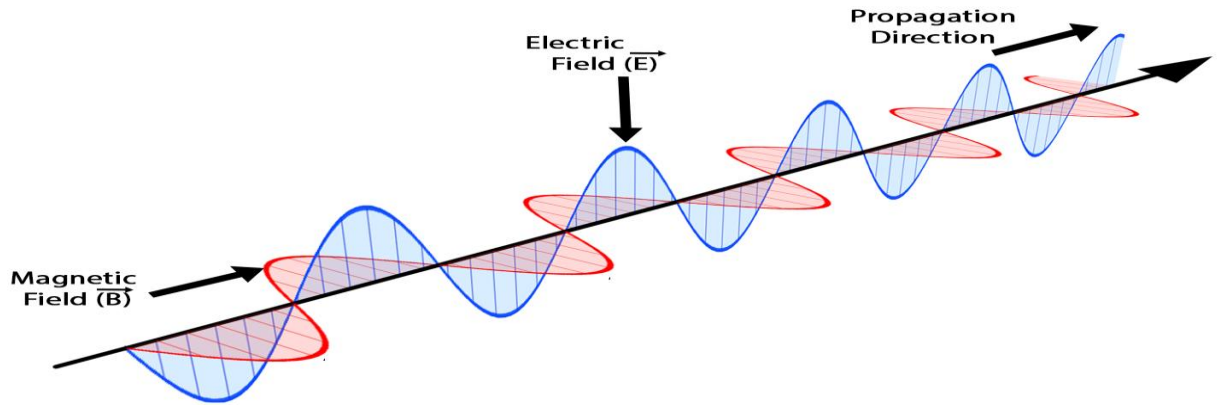


Figure 2. Electromagnetic radiation

They are characterized by following parameters:

1.1.1 Wavelength (λ):- It is a distance between the two adjacent crests or troughs (**Figure 3**) in a particular wave and expressed in Å or cm or m ($\text{Å} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$). Mathematically,

$$\lambda = \frac{v}{c} \quad \text{-----(1)}$$

where v is frequency and c is velocity ($3 \times 10^8 \text{ m/s}$).

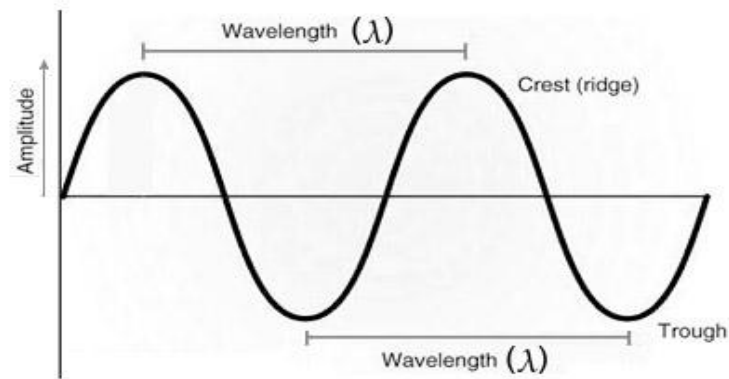


Figure 3. Propagation of a wave

1.1.2 Wave Number ($\bar{\nu}$):- It is the total number of waves which can pass through a space of one cm. It is a reciprocal of wavelength expressed in cm^{-1} . Mathematically,

$$\bar{\nu} = \frac{1}{\lambda} \text{ cm}^{-1} \quad \text{----- (2)}$$

1.1.3 Frequency (ν): It is defined as the number of waves which can pass through a point in one second and expressed in Hz or cycle per sec (1Hz = 1 cycle per sec). Mathematically,

$$\nu = \frac{c}{\lambda} \quad \text{----- (3)}$$

1.1.4 Energy (E): According to quantum mechanics an electromagnetic radiation consists of discrete energy packets called photons and quanta moving in direction of propagation and is perpendicular to both electrical and magnetic fields. Energy of a wave of a particular radiation is given by Plank's relation. Mathematically,

$$E = h\nu \quad \text{----- (4)}$$

$$\text{From equation (3)} \quad E = \frac{hc}{\lambda} \quad \text{----- (5)}$$

Where h is Plank's Constant = 6.62×10^{-34} J/s and ν is frequency given in cycle/s.

Example1. An Electromagnetic wave is transmitted with a frequency of 300 Hz, calculate the wavelength and energy of this radiation.

Solution. As given in question frequency $\nu = 300\text{Hz}$

We know **that speed of light** $c = 3 \times 10^8$ m/s

$$(1) \text{ From equation (3)} \quad \nu = \frac{c}{\lambda}$$

$$\text{Putting values in equation (3)} \quad 300 \text{ Hz} = \frac{3 \times 10^8 \text{ m/s}}{\lambda}$$

$$\lambda$$

$$\lambda = \frac{3 \times 10^8 \text{ m/s}}{300\text{Hz or sec}^{-1}}$$

$$(1\text{Hz}=1\text{sec}^{-1})$$

$$\text{Hence} \quad \lambda = 10^6 \text{ m}$$

$$(2) \text{ From equation (4)} \quad E = h\nu$$

$$E = 6.62 \times 10^{-34} \text{ J/s} \times 300\text{Hz or sec}^{-1}$$

$$E = 19.86 \times 10^{-32} \text{ J}$$

1.2 Electromagnetic Spectrum:-

It is the arrangement of EMR in order of increasing wavelength and decreasing frequency or vice versa (**Figure 4**). It ranges from cosmic waves (lower or shorter wavelength and higher frequency) to radio waves (longer wavelength and lower frequency). Energy of cosmic waves are very high whereas radio waves are very less.

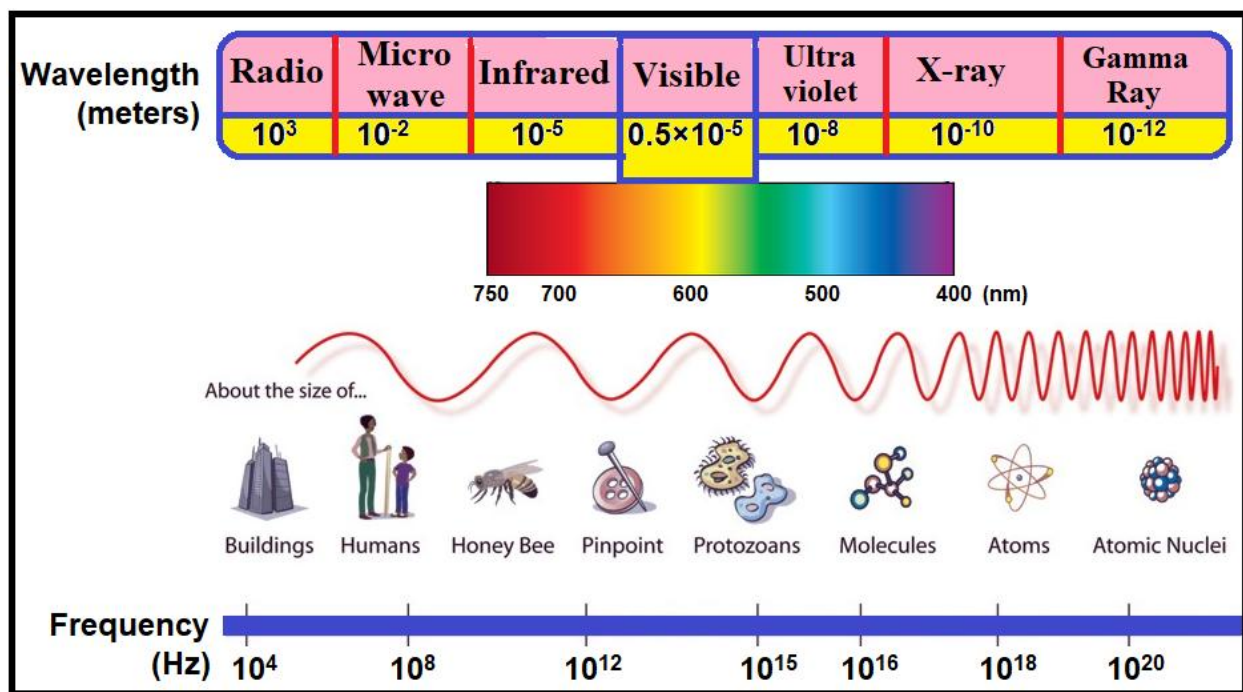


Figure 4. Electromagnetic spectrum

Table 1. Electromagnetic spectrum

Spectral Region	Wavelength	Types of Quantum change	Spectroscopic technique
Gamma rays	0.001 -0.1	Rearrangement of nuclear particles	Mossbauer
X rays	0.1 – 150	Change of inner electron of atom/molecules	X-ray Spectroscopy
UV rays	150 -3800	Separation between the energies of valence electrons	Electronic Spectroscopy
Visible region	3800 – 7600	Change of electronic distribution	Electronic Spectroscopy
IR region	7600 – 6×10^6	Change of vibration mode of molecules	Vibrational Spectroscopy

Microwave region	$6 \times 10^6 - 3 \times 10^9$	Change of rotation mode of molecules	Rotational Spectroscopy
Radio Wave region	$3 \times 10^9 - 3 \times 10^{16}$	Reversal of spin of nucleus or electron	NMR, ESR

1.3 The Born-Oppenheimer Approximation

In quantum chemistry and molecular physics, the **Born–Oppenheimer (BO) approximation** is the most known mathematical approximation in molecular dynamics. Specifically, it is the assumption that the motion of atomic nuclei and electrons in a molecule can be treated separately, based on the fact that the nuclei are much heavier than the electrons. The approach is named after Max Born and J. Robert Oppenheimer who proposed it in 1927. Energy Level in a molecule is associated with the following types of energy (**Figure 5**).

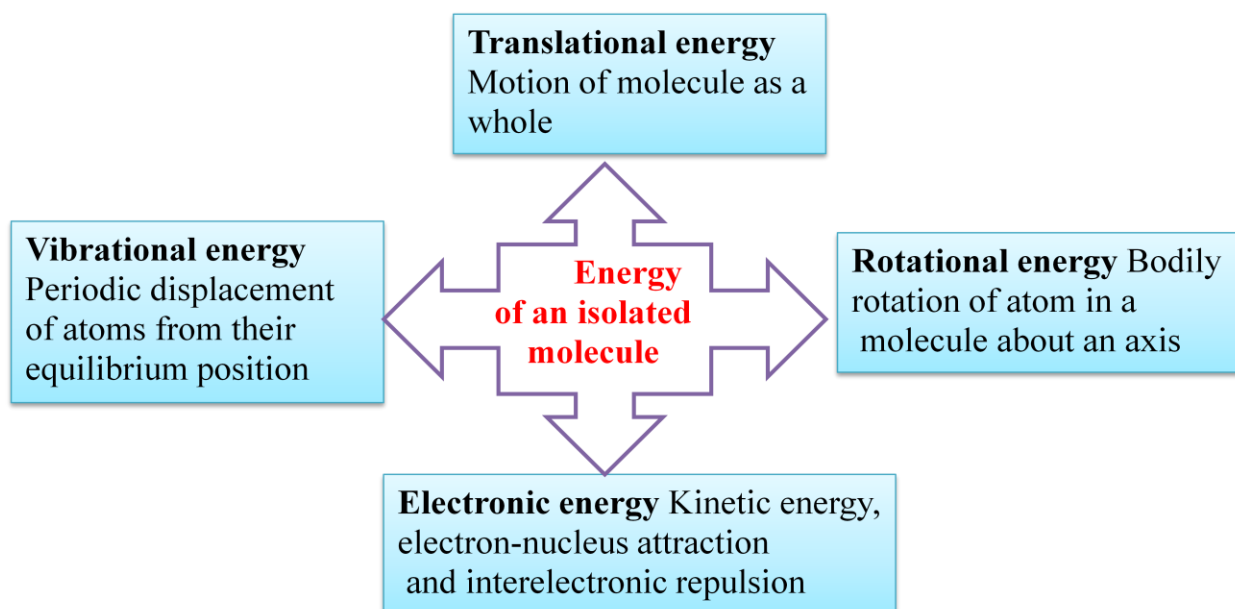


Figure 5. Energies of an Isolated molecule

In molecular spectroscopy, using the BO approximation means considering molecular energy as a sum of independent terms-

$$E_{\text{Total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{Rotational}} + E_{\text{translation}} \quad \text{-----(14)}$$

$E_{\text{translation}}$ is neglected due to small amount.

$$\text{Hence } E_{\text{Total}} = E_{\text{electronics}} + E_{\text{vibrational}} + E_{\text{Rotation}}, \quad \text{-----(15)}$$

$$E_{\text{electronic}} > E_{\text{vibrational}} > E_{\text{Rotational}}$$

All the energies are quantized except translational energy (**Figure 6**).

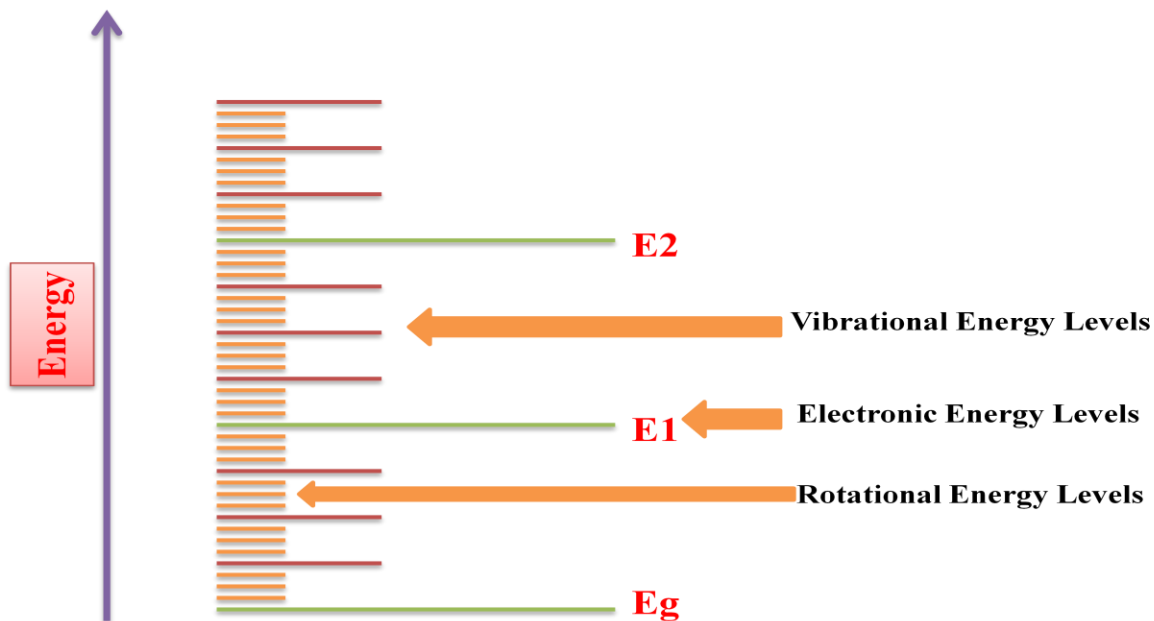


Figure 6. Quantization of Energies

1.4 Spectrum:-

The separation of a composite radiation into different wavelengths and frequencies constitutes a spectrum. Example is white light passes through a prism; a spectrum of seven colors is obtained. There are two types of spectra-

1.4.1 Absorption spectra: - It is obtained by a transition from lower level to higher level. When the radiation is passed through an absorbing substance and then observed through a spectroscope, it is found that certain wavelengths are missing and dark lines or bands appear at their places. The spectra so obtained are called Absorption spectra (**Figure.7**).

1.4.2 Emission spectra: - It is obtained by a transition from higher level to lower level. When the light emitted by a substance is passed through a prism and then examined by spectroscope the spectrum is obtained is called as emission spectra. The molecule is first excited to higher level by heating or passing electricity (**Figure.7**).

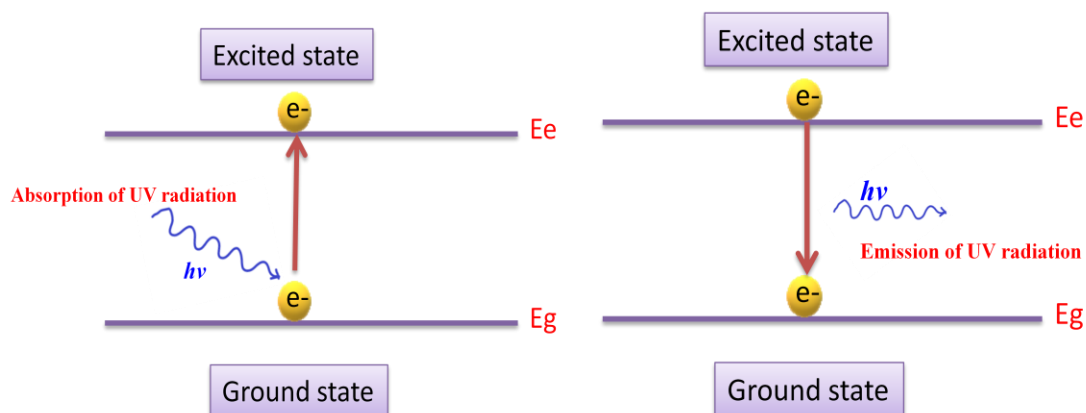


Figure7. Absorption and Emission spectra

Spectra can be classified into two classes on the basis of species

1. **Atomic Spectra:** - when the spectra are obtained in atomic state the resulting spectra is called Atomic spectra. Due the absence of $E_{\text{vibrational}}$, $E_{\text{rotational}}$ in atoms the spectra contains sharp lines corresponding to the electronic transition. eg. Hydrogen spectra.
2. **Molecular Spectra:-** when the spectra is obtained in molecular state the resulting spectra is called molecular spectra. Due the presence of $E_{\text{vibrational}}$, $E_{\text{rotational}}$ along with $E_{\text{electronic}}$ in molecules the spectra contains bands (**Figure 8**).

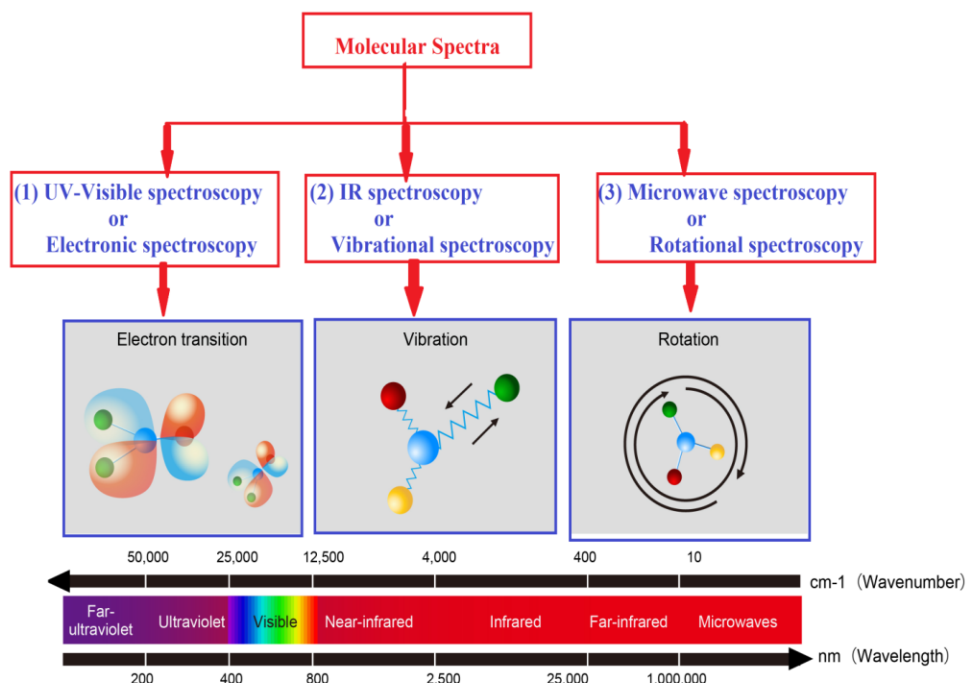


Figure 8. Types of molecular spectra

1.5 Beer-Lambert Law

When a beam of monochromatic light is passed through a solution of an absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is directly proportional to the intensity of radiation after passing through the medium as well as concentration of solution.

1.5.1 Transmittance and Absorbance:-

When radiations are passed through a sample of an organic compound some of the frequencies are absorbed while other are transmitted through the sample without being absorbed.

“Transmittance (T) of a solution is defined as the ratio of intensity of radiation after passing through the solution to the intensity of incident light”

$$T = \frac{I}{I_0} \quad \text{-----(6)}$$

Where I_0 is the intensity of incident light and I is intensity of transmitted light.

Absorbance (A) is the logarithm of inverse of transmittance-

$$A = \log \frac{1}{T}$$

$$A = \log \frac{I_0}{I} \quad \text{----- (7)}$$

1.5.2 Beer's law:-

It was stated by August Beer which states that concentration(C) and A are directly proportional to each other.

$$A \propto C$$

1.5.3 Lambert law:-

It was stated by Johann Heinrich Lambert which states that A and path length are directly proportional.

$$A \propto x$$

The Beer-Lambert law states that:

For a given material sample path length and C of the sample are directly proportional to the absorbance of the light.

$$A \propto xC$$

$$A = \epsilon Cx$$

where,

- A is the amount of light absorbed for a particular wavelength by the sample
- ϵ is the molar extinction coefficient
- x is the distance covered by the light through the solution
- C is the concentration of the absorbing species

The Beer-Lambert law is dependent on a beam of light being shone through a solution containing solutes which absorb a fraction of the light as it goes through the solution (**Figure 9**). As the solution absorbs some of the light, the intensity of the light that will come out of the other side of the solution will be decreased in intensity. This can be clearly represented using the following diagram where I_0 is the initial intensity of light, x is the total length of the path through which light travels and I is the intensity of light after it has travelled through the solution.

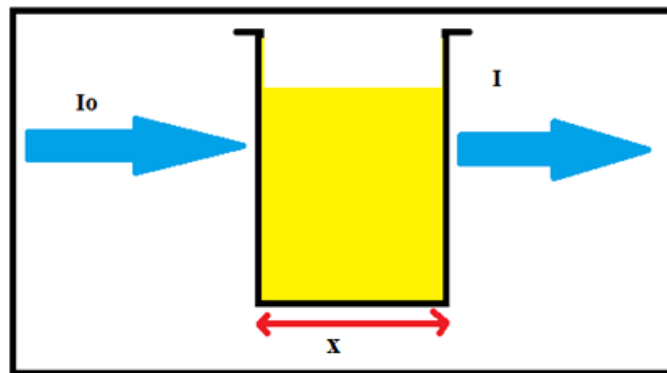


Figure 9. Absorption of light

1.5.4 Derivation:-

$$\begin{aligned}
 -\frac{dI}{dx} &\propto IC \\
 -\frac{dI}{dx} &= kIC \\
 \frac{dI}{dx} &= -kIC \quad \text{----- (8)}
 \end{aligned}$$

Integrating equation (8) on both sides as

$$\begin{aligned}
 \int_{I_0}^I \frac{dI}{I} &= -k \int_0^x C dx \\
 -\ln \frac{I}{I_0} &= kCx \quad \text{----- (9)}
 \end{aligned}$$

Converting natural \ln into $_{10}\log$ in equation (9)

$$\begin{aligned}
 2.303 \log \frac{I}{I_0} &= -kCx \\
 \log \frac{I}{I_0} &= -\frac{k}{2.303} Cx \quad \text{----- (10)}
 \end{aligned}$$

$$\text{In equation (10) } -\frac{k}{2.303} = \epsilon$$

$$\text{Hence equation (10) becomes } \log \frac{I}{I_0} = -\epsilon Cx \quad \text{----- (11)}$$

$$\text{We know from equation (7) } A = \log \frac{I_0}{I}$$

Hence equation (11) becomes

$$A = \epsilon Cx \quad \text{----- (12)}$$

Where A is the optical density or absorptivity of solution.

ϵ is the absorptivity coefficient/ extinction coefficient.

C is the concentration of solution in gm/l

x is the path length of the absorbing medium

$$\text{Similarly } A = \epsilon m C m x \quad \text{----- (13)}$$

Where A is the optical density or absorptivity of solution.

ϵm is the molar absorptivity coefficient/molar extinction coefficient.

C_m is the molar concentration of solution in mol/L $C_m = \frac{C}{M}$ ----- (14)

where M is the molar mass

X is the path length of the absorbing medium

Example 2. A compound having concentration 10^{-3} gm/L resulted absorbance value 0.20 at λ_{\max} 510nm using 1.0 cm cell. Calculate its absorptivity and molar absorptivity. Molar mass of compound is 400.

Solution. (1) Given Concentration(C)= 10^{-3} gm/L

Absorbance(A)= 0.20

Cell length(x)= 1.0 cm

Using equation (12) $A = \epsilon C x$

$$0.20 = \epsilon \times 10^{-3} \text{ gm/L} \times 1 \text{ cm}$$

$$\epsilon = \frac{0.20}{10^{-3} \text{ gm/L} \times 1 \text{ cm}}$$

$$\epsilon = 200 \text{ gm cm L}^{-1}$$

(2) Using equation (14) $C_m = \frac{C}{M}$

$$C_m = \frac{10^{-3} \text{ gm/L}}{400}$$

$$C_m = 2.5 \times 10^{-6}$$

Using equation (13) $A = \epsilon m C_m x$

$$\epsilon m = \frac{0.20 \times 400}{10^{-3} \text{ gm/L} \times 1 \text{ cm}}$$

$$\epsilon m = 80000 \text{ gm}^{-1} \text{ cm}^{-1} \text{ L}$$

2. UV-Visible Spectroscopy / Electronic Spectroscopy

The ultraviolet range can be divided into two spectral ranges-

1. **Near UV region**-- It has the range of 200nm to 400nm
2. **Far or vacuum region**-- below 200 nm

The range between 400nm to 800nm is called as visible range.

2.1 BASIC PRINCIPLE OF UV-VISIBLE SPECTROSCOPY:-

UV-Visible spectroscopy involves the electronic transition within a molecule from a lower level to higher level by the absorption of radiation falling in UV visible range of electromagnetic radiation or vice versa. This transition can take place only if the energy of the radiation will be equal to the energy difference between two electronic levels (**Figure 10**).

$$E_1 - E_2 = h\nu \quad \text{or} \quad \Delta E = h\nu$$

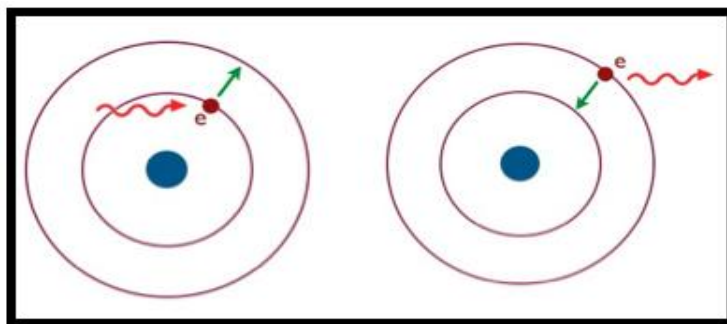


Figure 10. Principle of UV-visible spectroscopy

2.2 Types of electronic transitions:-

Absorption of UV radiation by an organic molecules leads to the electronic transition of an electron from HOMO (higher occupied molecular orbital) to LUMO (lower unoccupied molecular orbital) which can be of the following types (**Figure 11**).

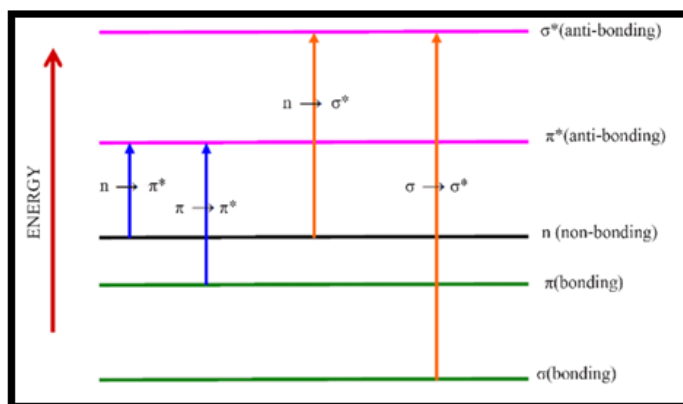


Figure 11. Types of electronic transitions

- i. **$\sigma \rightarrow \sigma^*$ transition:-** This transition occurs in only those compounds in which all electrons are in single bond (-) and has no lone pair. **eg. All saturated hydrocarbons.** This transition is possible in far UV region only.
- ii. **$\pi \rightarrow \pi^*$ transition:-** This transition is possible in compounds containing double or triple bonds(π bond). This transition takes place in near UV and visible region. eg. - C=C-,
- iii. **$n \rightarrow \pi^*$ transition:-** This transition occurs in compounds containing hetero atoms with lone pair of electron(non bonding e⁻) and bonded with double bond. This transition generally of weak intensities and occurs in visible region.eg. Aldehyde and ketones.
- iv. **$n \rightarrow \sigma^*$ transition:-** This transition is possible in compounds containing hetero atoms with lone pair of electron(non bonding e⁻) and bonded with single bond(-).eg. CH₃—Cl.

The relative energies required for various transitions follow the order-

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

Out of these $n \rightarrow \pi^*$ transition is forbidden according to the selection rule.

Example 3. Name the probable electronic transition in the following compounds.

- (1) Cyclopentane
- (2) Acetone
- (3) Pent-1-ene
- (4) Ethanol
- (5) Ethanal

Solution.

- (1) Cyclopentane = $\sigma \rightarrow \sigma^*$ transition
- (2) Acetone = $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$
- (3) Pent-1-ene = $\pi \rightarrow \pi^*$
- (4) Ethanol = $n \rightarrow \sigma^*$
- (5) Ethanal = $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$

2.3 Selection rule:-

It can be shown that $\epsilon_{\max} = 0.87 \times 10^{20} \times p \times a$ where p is probability with values 0 to 1 and a is area of chromophores. If $\epsilon_{\max} > 10^4$ the transition will be allowed and if $\epsilon_{\max} < 10^4$ then it will be forbidden transition.

2.4 Characteristics of UV-Visible spectra-

It carries two parameters.

1. **Absorption maximum (λ_{max}):**- The wavelength at which maximum absorption takes place. λ_{max} value is different for different molecules.
2. **Intensity (ϵ_{max}):**- It is the extent of absorption for a given concentration of a molecule at any given wavelength.

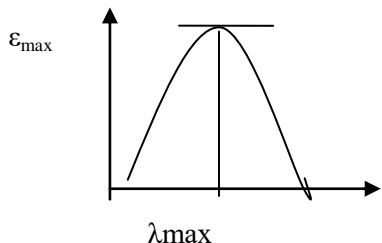


Figure 12. UV-visible spectra

2.5 Chromophores:-

Chromophores are also called as color imparting groups. Chromophores are the covalently bonded, unsaturated groups present in the molecules that show a characteristic absorption (due to $\pi \rightarrow \pi^*$ transition) in the UV-Visible region. This absorption occurs irrespective of the fact whether the color is produced or not.

Chromophores are of two types-

- (i.) Chromophores which contain π electrons and they undergo $\pi \rightarrow \pi^*$ transition only. eg. ethylenes, acetylenes etc.
- (ii.) Chromophores which contain both π electrons as well as non bonding electrons (n) and undergo $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition. eg carbonyls, nitriles, azo compounds and nitro compounds etc.

2.6 Auxochromes:-

Auxochromes are also called as color enhancing groups. These are the groups which contain only a lone pair of electron. They can not act as a chromophore i.e. they can not give the color (due to the lack of π and π^* orbital's) but their presence brings about a shift of absorption band towards red end of the spectrum (darkens the color). Auxochrome groups extend the conjugation of chromophores by sharing its lone pair of electron or by hyper conjugation effect. Example:- Hydroxyl group (-OH), Amino group (-NH₂), Aldehyde group (-CH₂) and the methyl mercaptan group (-SCH₃).

2 votes

2.7 Polar Solvent Effect:-

The position and intensity of absorption band is greatly affected by the polarity of solvent used.

(i) **Effect of polar solvent on $\pi \rightarrow \pi^*$ transition:-**

On addition of polar solvent, the λ_{max} for $\pi \rightarrow \pi^*$ transition will be increased i.e. shift towards red shift. As π^* orbital is more polar than the π orbital hence π^* is more stabilized due to polar-polar interaction with polar solvents as compared to π orbital and the energy required for the $\pi \rightarrow \pi^*$ transition becomes less and absorption moves to longer wavelength (**Figure 13**).

(ii) **Effect of polar solvent on $n \rightarrow \pi^*$ transition:-**

On addition of polar solvent, the λ_{max} for $n \rightarrow \pi^*$ transition will be decreased i.e. shift towards blue shift. As n orbital is more polar than the π^* orbital hence n is more stabilized due to polar-polar interaction with polar solvents as compared to π^* orbital and the energy required for the $n \rightarrow \pi^*$ transition becomes greater and absorption moves to smaller wavelength (**Figure 13**).

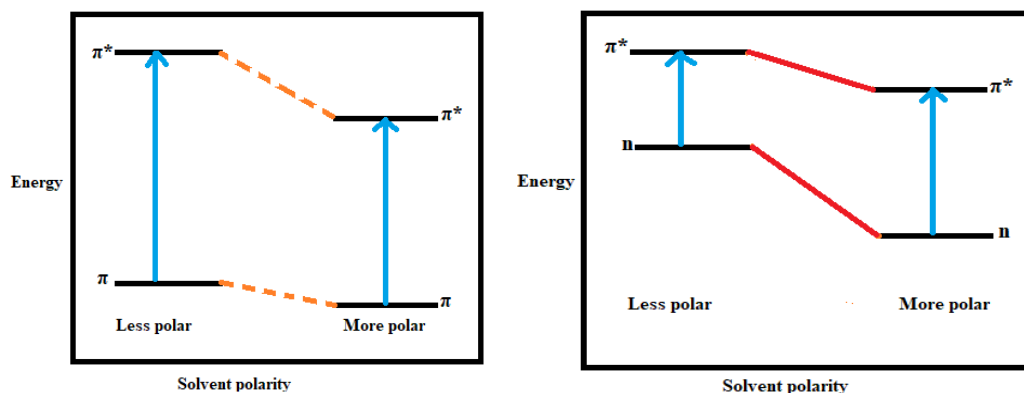


Figure 13. Polar Solvent Effect

2.8 Effect of conjugation on the λ_{max} value:-

A conjugated system requires lower energy for $\pi \rightarrow \pi^*$ transition than a corresponding non-conjugated system. As a transition takes place between HOMO to LUMO, the energy gap decreases on increasing the conjugation hence longer the conjugation, longer will be λ_{max} value due to decrease in the energy gap (**Figure 14**).

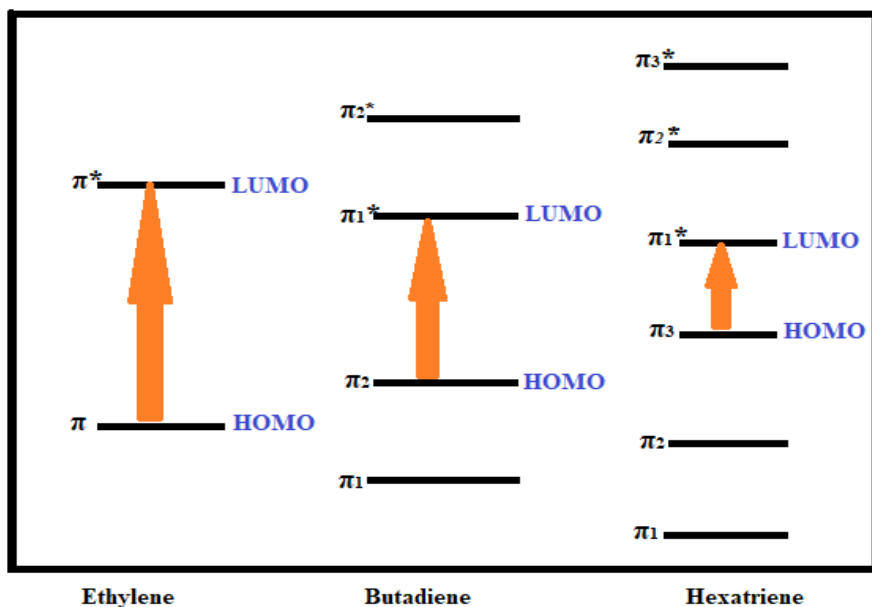
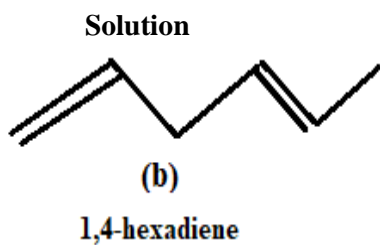
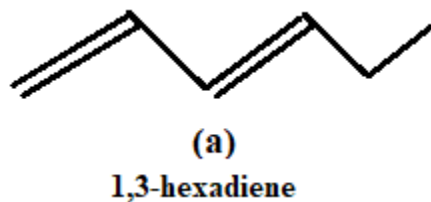


Figure 14. Effect of conjugation on the λ_{max} value

Example 4. Which molecule absorbs at longest wavelength-

1,3-hexadiene and 1,4-hexadiene



In both (a) and (b) the



(a)

1,3-hexadiene

has longest wavelength than



(b)

1,4-hexadiene

due to the conjugation.

2.9 Absorption and intensity shifts:–

A particular functional group absorbs a particular wavelength (λ_{max}) of UV-Visible light in different compounds provided the following two factors remain the same,

- i. Structural Environment
- ii. Solvent.

If they differ, the transition shifts towards either shorter or longer wavelength. The various shifts are (Figure 15)-

Table 2.

Nature of shift	Descriptive term
To longer wavelength	Bathochromic shift
To shorter wavelength	Hypsochromic shift
To greater absorbance	Hyperchromic shift
To lower absorbance	Hypochromic shift

1. Bathochromic shift/ Red shift:-

Shift of an (λ_{max}) to longer wavelength is called bathochromic shift or red shift. It may be due to the-

- (a) presence of an auxochrome
- (b) Decrease in the polarity of solvent (removing the polar solvent).

Example- Phenol to phenoxide anion cause bathochromic shift

2. Hypsochromic shift/Blue shift:-

Shift of an (λ_{max}) to smaller wavelength is called hypsochromic shift or blue shift. It may be due to the-

- (a) removal of an auxochrome
- (b) Increasing in the polarity of solvent (addition the polar solvent).
Example- Aniline to anilineum ion cause hypsochromic shift

3. Hyperchromic shift:-

When the intensity of absorption (ϵ_{\max}) is increased, it is called hyperochromic shift. It may be due to the-

- (a) presence of an auxochrome
- (b) Decrease in the polarity of solvent (removing the polar solvent).
Example- Pyridine to 2-methyl pyridine cause hypsochromic shift.

- 4. **Hypochromic shift**:-when the intensity of absorption (ϵ_{\max}) is decreased, it is called Hypochromic shift. The groups which distort the geometry of the molecule cause Hypochromic shift.
Example- Benzene to benzoate cause hypochromic shift.

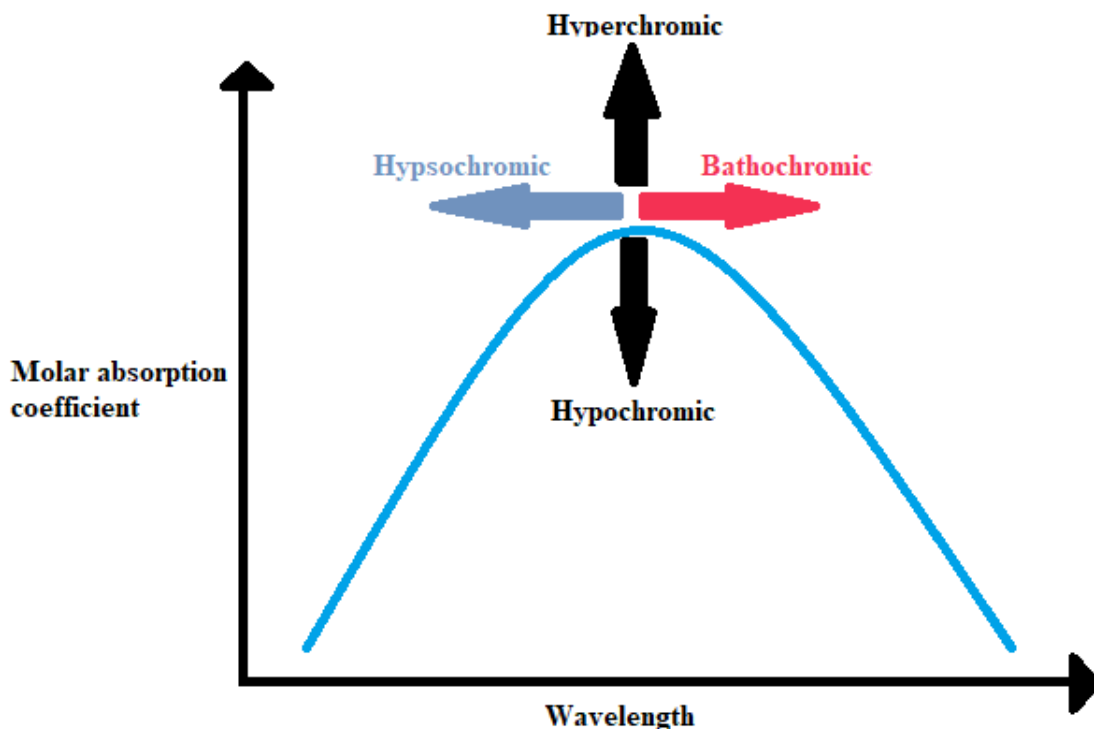


Figure 15. Absorption and intensity shifts

2.10 Instrumentation:-

The main components of instrument are mentioned below (**Figure 16**)-

- 1. **Radiation source**:- tungsten filament or hydrogen discharge lamp are used for UV-Visible radiation.

2. **Monochromator:-** it consists an entrance slit, a dispersing element(prism/grating) and slit.
3. **Sample and reference cell:-** two cells made up of Quartz or Silica are used .
4. **Detector:-** Generally Barrier layer cell, Photocell, Photomultiplier tube are used.
5. **Amplifier and recorder.**

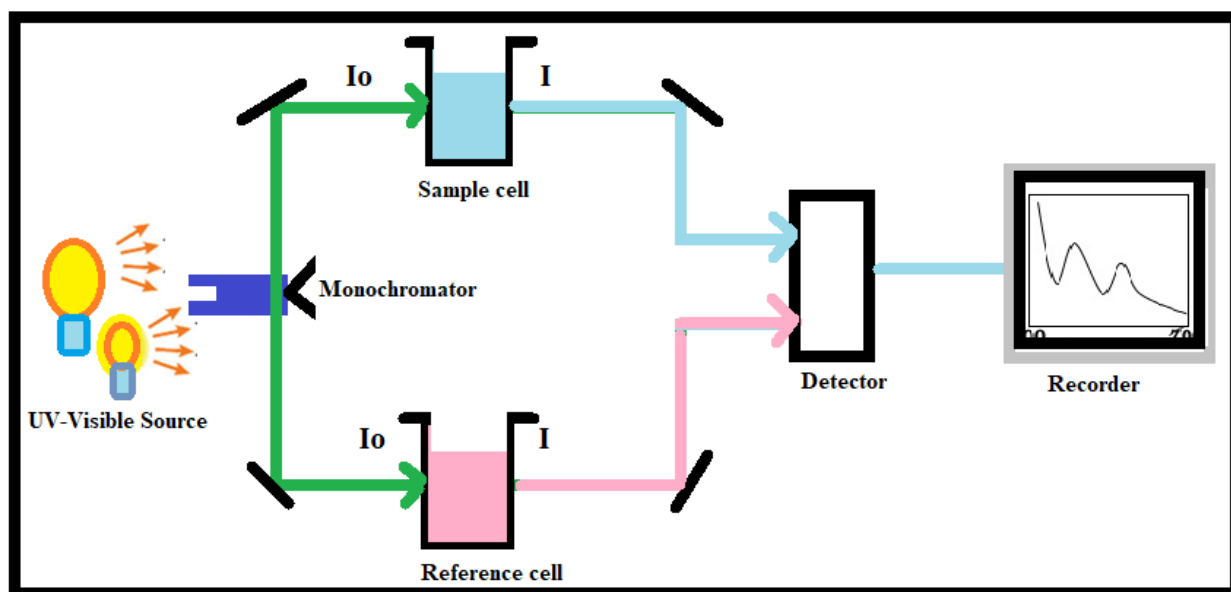


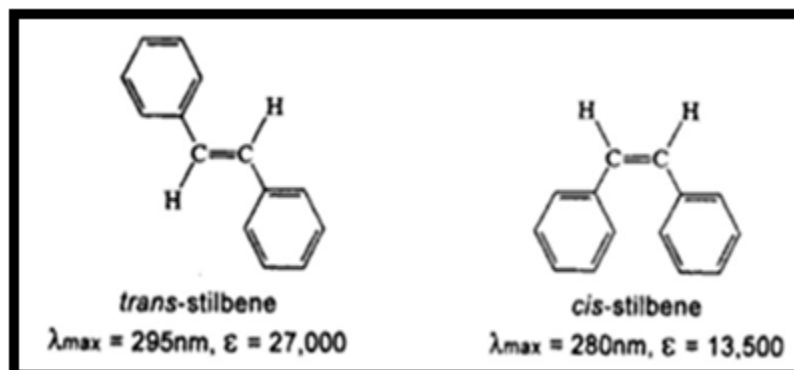
Figure 16. Instrumentation of UV-visible spectroscopy

2.11 Choice of solvent:- the solvent should be transparent to UV-Visible radiation and should be less polar. Most common solvent is 95% ethanol. Cyclohexane, water, chloroform and CCl_4 are some other examples.

2.12 Application of UV:- Visible spectroscopy-UV-Visible spectroscopy is used in various aspects-

1. Detection of geometrical isomerism:-

The trans isomers show λ_{max} at slightly longer wavelength than the cis isomers due to steric hindrance in the cis isomers, resulting in lack of co planarity and hence difficulty in conjugation that is why Trans Stilbene absorbs at longer λ_{max} as compared to cis isomer.



2. Detection of conjugated and non conjugated compounds:-

Compounds with conjugation absorb at longer wavelength as compared to compounds having no conjugation.

3. Detection of extent of conjugation:-

UV-Visible spectroscopy is useful to determine the conjugation extent in polyenes as more the conjugation more will be the shift of λ_{max} towards red end (**Figure 17**).

eg. 1, 3, 5 hexatriene absorbs at longer λ_{max} than 1,3 butadiene which in turn is greater than ethylene.

Compounds having more than 6 double bonds in conjugation show color due to shift of λ_{max} into visible range.

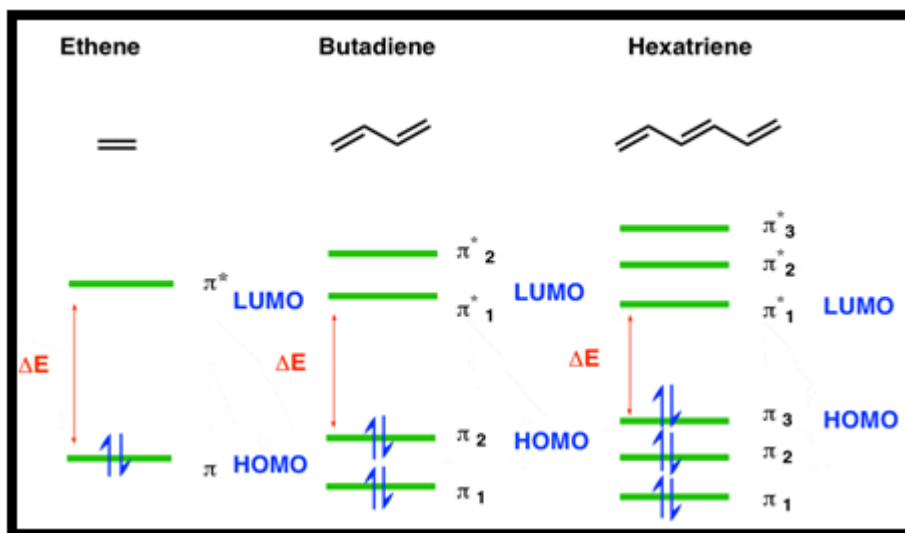


Figure 17. Detection of extent of conjugation

4. Qualitative analysis:-

Identification of unknown compounds can be done by comparing its absorption spectra with standard known compounds.

5. Quantitative analysis:-

we can find out the concentration of the sample from its absorbance by using Lambert-beer's law.

6. Detection of functional groups:-

Every functional group has a particular λ_{max} value in UV-Visible spectroscopy, using this data we can detect the presence of any functional group.

7. Detection of impurities.

3. IR Spectroscopy /Vibrational Spectroscopy.

The Branch of spectroscopy which deals with the interaction of a metal with the emr falling in the IR region (0.8 um to 200 um.) is called IR spectroscopy /Vibrational spectroscopy.

Near IR region 12500-4000cm⁻¹	Ordinary IR region/ Middle IR region 4000-600cm⁻¹		Far region 600-10 cm⁻¹
	Functional group Region 4000-1500 cm⁻¹	Finger print region 1500-600 cm⁻¹	

Due to the smaller amount of energy associated with the infrared radiation they can not cause electronic transition but can only induce vibrational – rotational transitions hence more accurately it should be called as Vibrational – Rotational spectroscopy

The molecules which show IR transition are called IR active molecule and the molecules which do not show IR transition are called IR inactive molecule .IR active molecule should have a net dipole moment during the vibration.

3.1 Selection rule of IR spectroscopy:-

Acc to this, to be a IR active molecule the dipole moment of the molecule must be changed during the vibration.eg. Homonuclear diatomic molecules are IR inactive as neither they have a dipole moment nor they have a change in dipole moment during the vibration whereas heteronuclear diatomic molecules are IR active as they have a change in dipole moment during the vibration. Symmetrical triatomic molecules which do not have a net dipole moment are ir active due to the change in dipole moment during the vibrations. eg. CO₂, H₂O, H₂S etc.

3.2 Vibrational frequency:-

The region where a stretching vibration occurs in a molecule can be calculated by Hook's law.The vibrating diatomic molecule with atomic mass m₁ and m₂ joined by a chemical bond vibrates as a 1-D Simple harmonic oscillator and hence according to the Hook's law the vibrational frequency will be –

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

$$\text{As } \mu = \frac{m_1 m_2}{m_1 + m_2} \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{cm}^{-1}$$



Where K is force constant (bond strength) of the bond. For a single bond it is approximately 5 X 10⁵ dynes /cm, for a double and triple bond, it becomes double and triple respectively.

u is the reduce mass and is equal to the $\mu = \frac{m_1 m_2}{m_1 + m_2}$.

3.3 Fundamental Vibration and Overtone:-

When the transition occurs from ground state to the first excited state then it is called Fundamental Transition. Energy required for Fundamental Transition is (Figure 19) –

$$\Delta E_{(0 \rightarrow 1)} = E_{(v=1)} - E_{(v=0)} = \frac{3}{2} h\nu_0 - \frac{1}{2} h\nu_0 = h\nu_0$$

Transition from ground state ($v=0$) to second and onwards excited state is called overtone Transition

$$\Delta E_{(0 \rightarrow 2)} = E_{(v=2)} - E_{(v=0)} = \frac{5}{2} h\nu_0 - \frac{1}{2} h\nu_0 = 2h\nu_0 \text{ (first overtone)}$$

$$\Delta E_{(0 \rightarrow 3)} = E_{(v=3)} - E_{(v=0)} = \frac{7}{2} h\nu_0 - \frac{1}{2} h\nu_0 = 3h\nu_0 \text{ (second overtone) and so on}$$

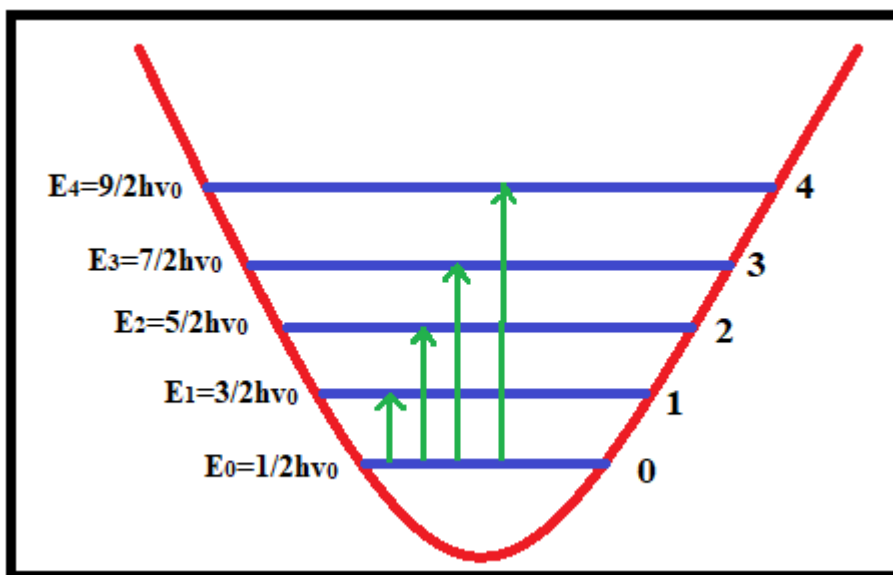


Figure 18. Fundamental Vibration and Overtone

3.4 Principle of IR spectroscopy:-

On passing an IR radiation a molecule can absorb it and can undergo a transition from lower vibrational level ($V=0$) to higher vibrational level ($V=1$) only if there is a change in dipole moment during the vibration (IR Active vibration).

Energy associated with a vibrational level can be calculated from the formula- $(V + 1/2) h\nu$ Where V is vibrational quantum no. ($V=0,1,2,3,\dots$). At room temperature, when a molecule exist in ground state ($V=0$), the energy will be $\frac{1}{2} h\nu$. This amount of energy is called zero point energy.

Conditions for IR spectroscopy:-

1. The molecule which undergoes a net change in dipole moment. $du/dq \neq 0$

2. The frequency of the vibration must be equal to the radiation frequency. $(\nu_0) = \nu$

3.5 Type of vibration:-

There are two types of fundamental vibrations (**Figure 19-23**)

1. **Stretching Vibration:** - In this type of vibration, the bond distance b/w two atoms changes but atoms remains in the same bond axis.
 - i. **Symmetrical stretching vibration:-** when the movement of atoms with respect to a central atom is in the same direction. It is called as Symmetrical stretching vibration.
 - ii. **Anti Symmetrical stretching vibration:-** When one atom approaches the central atom but other departs from it. Anti Symmetrical stretching vibration



Figure19. Stretching Vibration

2. **Bending vibration:** - In this type of vibration bond length remains same but the position of atoms changes relative to the original bond axis i.e. bond angle changes. Bending vibrations are called deformative vibration and they require less energy in comparison to stretching vibrations.
 - i. **Scissoring-** it is scissors like vibration in which two atoms approach each other.

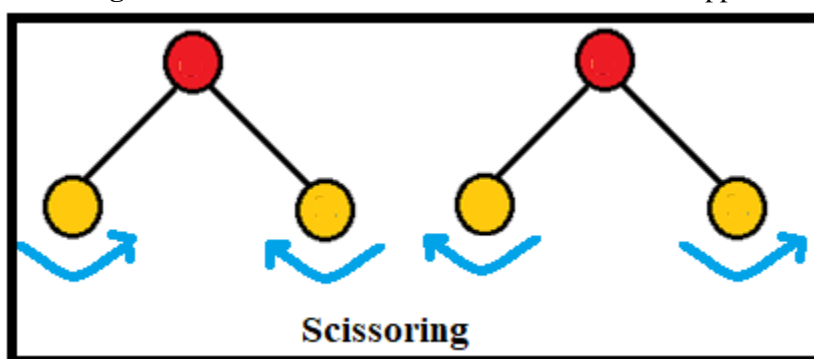


Figure 20. Scissoring

- ii. **Rocking-** when the movement of atoms takes place in same direction.

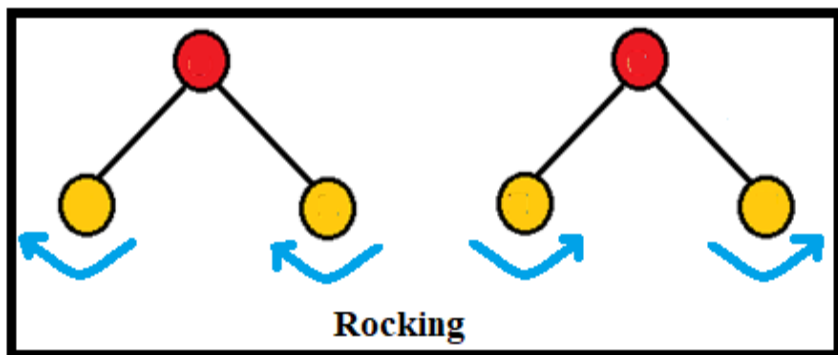


Figure 21. Rocking

- iii. **Twisting-** one atom moves up to the plane and moves down to the plane.

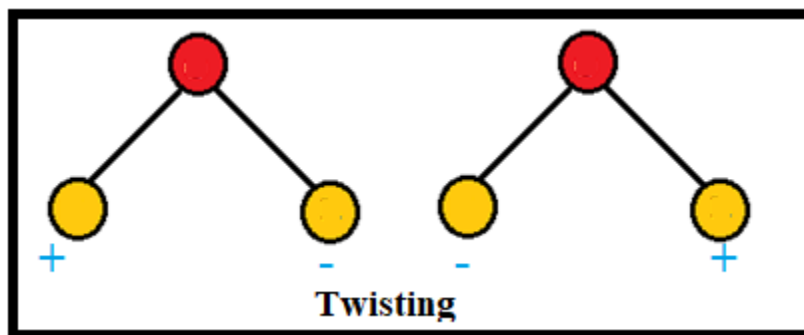


Figure 22. Twisting

- iv. **Wagging-** two atoms move up and down to the plane w.r.t. to the central atom.

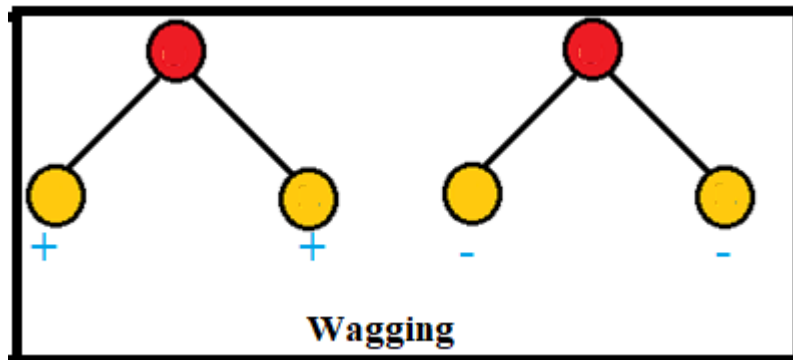


Figure 23. Wagging

3.6 Fingerprint region:-

The IR region below 1500 cm^{-1} ($1500\text{ cm}^{-1} - 600\text{ cm}^{-1}$) is known as finger print region. The region, above it, is the functional group region and is useful for identification of functional group. Functional group region show the absorption due to stretching mode whereas finger print region contains absorption due to bending vibrations. As there are many bending vibration in a molecule than the stretching vibration thus the spectra in this region becomes complex. Each organic molecule has its own unique absorption pattern in region. If two pure samples have same spectra in same medium and same condition then the samples are of same compound. If two different

molecules contain the same functional group, they show similar absorption above 1500 cm^{-1} (in functional group region) but their spectra differ in this region that is why it is called as finger print region.

3.7 Number of fundamental vibrations-

As we know for a molecule with (n) no. of atoms -

Total degree of freedom (3n) = Translational degree of freedom + Rotational degree + Vibrational degree of freedom

1. For linear molecules - Total degree of freedom (3n)

Translational degree of freedom = 3

Rotational degree of freedom = 2

So Vibrational degree of freedom = $3n - 3 - 2$

Vibrational degree of freedom = $3n - 5$

Example 5. Calculate vibrational degree of freedom of CO_2 molecule,

Solution. vibrational degree of freedom = $3n - 5 = 4$, as $n = 3$ (three atoms)

CO_2 should show 4 types of fundamental vibrations (**Figure 24**) which are as follows-

1. Symmetric stretching- IR Inactive
2. Antisymmetric stretching- IR active
3. In plane bending- IR active
4. Out plane bending- IR active.

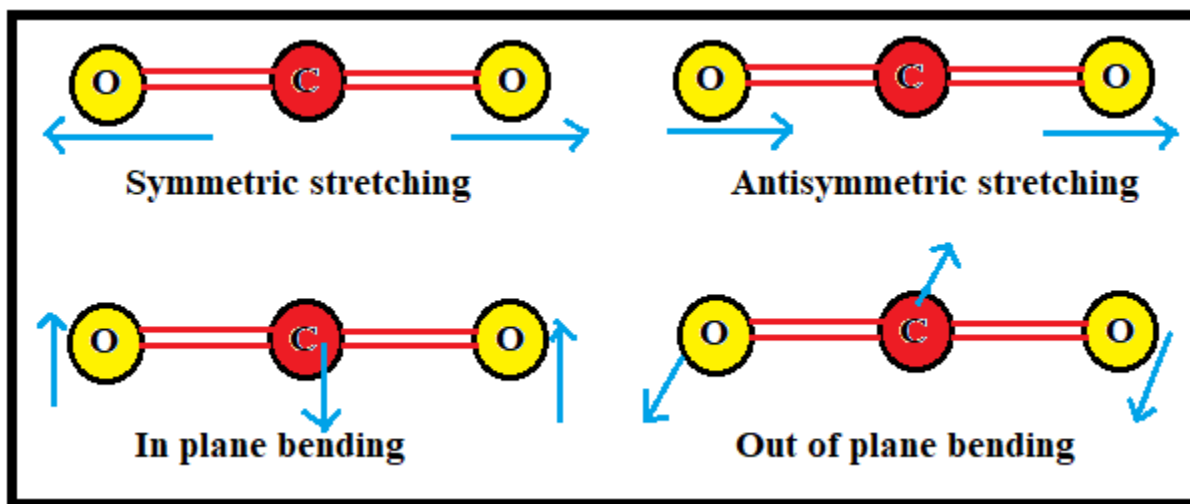


Figure 24. Degree of freedom of CO_2

2. For non linear molecules- Total degree of freedom (3n)

Translational degree of freedom = 3
 Rotational degree of freedom = 3
 So vibrational degree of freedom = $3n-3-3$

vibrational degree of freedom = $3n-6$

Example.6 Calculate vibrational degree of freedom of H_2O molecule.

Solution. H_2O (**Figure 25**) vibrational degree of freedom = $3n-6 = 3$

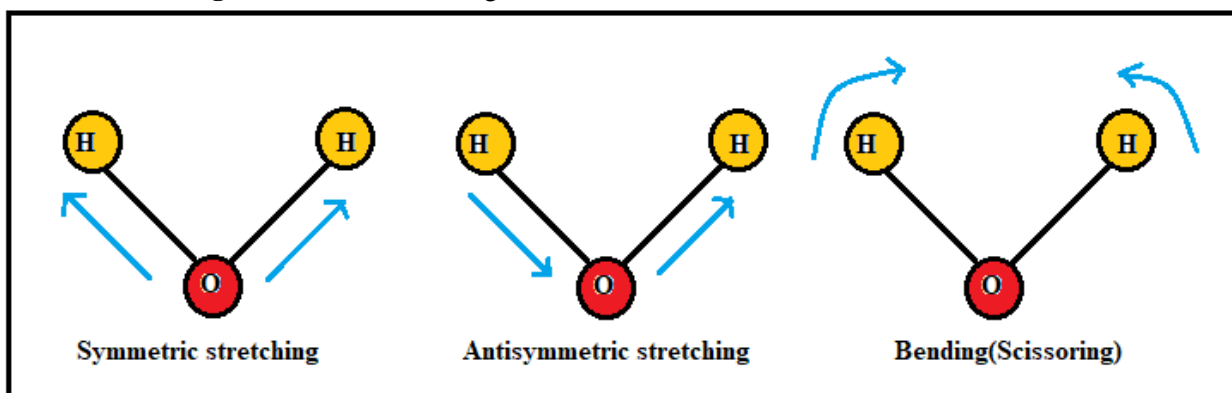


Figure 25. Degree of freedom of H_2O

3.8 Absorption values of some important functional groups:-

Table 3. Stretching frequency of important functional groups

Bond	Wave-number
C - H	2850-2950 (Alkane) 3000-3100 (Alkene) 3290-3310 (Alkyne) 3000-3040 (Aromatic)
C = C	1620-1680 (Alkene) 1400-1620 (Aromatic)
C triple bond C	2100-2260
C = O	1690-1740 (Aldehyde) 1710-1780 (Acid) 1630-1690 (Amide) 1680-1750 (Ketone) 1735-1750 (Ester)
N - H	3300-3500 (Amine) 3100-3500 (Amide)
O - H	2500-3200 (Acid) 3200-3700 (Alcohol/Phenol)
C triple bond N	2220-2260 (Nitrile)
C - N	1025-1220 (alkyl, amine, amide) 1250-1360 (aryl)
C - O	1040-1210 (alcohols/phenols) 1210-1320 (acid)
Nitro N - O bonds	1515-1560 and 1345-1385

Example 7. Determine the structure of the compound C_3H_6O which shows the following absorption bands in IR analysis-

- 1) 2950cm^{-1}
- 2) 1720 cm^{-1}
- 3) Negative Test with tallen's reagent

Solution. $\text{C}_3\text{H}_6\text{O}$ due to 1720 cm^{-1} band can be a carbonyl and due to 2950 cm^{-1} band it has C-H of alkane hence $\text{C}_3\text{H}_6\text{O}$ can exist in two structures as-

A) $\text{CH}_3\text{CH}_2\text{CHO}$ (Tallen's positive)

B) CH_3COCH_3 (Tallen's Negative)

But according to 3) compound gives negative test with tallen's reagent hence it can be a ketone only. Hence structure B) is correct.

Example 8. Two isomers A and B of the molecular formula $\text{C}_3\text{H}_6\text{O}$ gives IR spectrum at 1650 cm^{-1} and 1710 cm^{-1} respectively. Predict structural formula of A and B isomers?

Solution. $\text{C}_3\text{H}_6\text{O}$ due to 1650 cm^{-1} band and due to 1710 cm^{-1} band can be a carbonyl hence $\text{C}_3\text{H}_6\text{O}$ can exist in two structures as-

A) $\text{CH}_3\text{CH}_2\text{CHO}$

B) CH_3COCH_3 (+I effect group)

Hence due to +I effect, the structure B) has 1650 cm^{-1} and structure A) has 1710 cm^{-1} .

3.9 IR Spectrophotometer:-

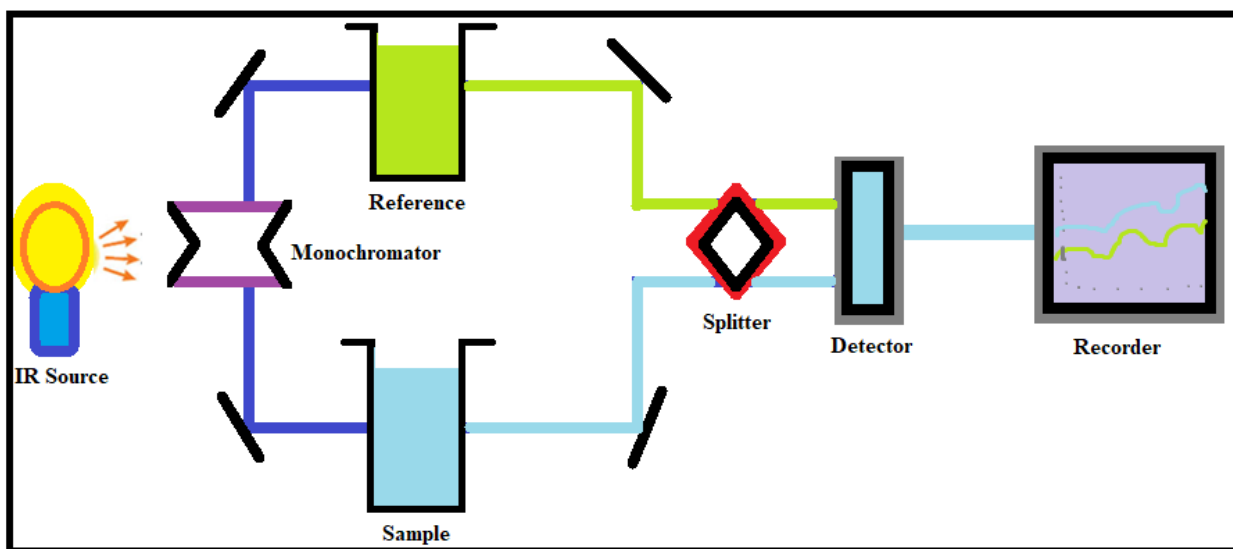


Figure 26. Instrumentation of IR

The main components of instrument are mentioned below (**Figure 26**)-

1. **Radiation source:** - Nernst glower (sintered mixture of oxide of Zr, Y, Er etc.) or Globar cell (silica carbide, heated up to 1800°C) are used for IR radiation.
2. **Monochromatic:** - it consist an entrance slit, a dispersing element (prism/grating) and slit. Generally rock salt prism is used.
3. **Sample and reference cell:** - Two cells made up of NaCl / KBr are used.

4. **Detector:** - Generally thermocouple detector is used are used.
5. **Amplifier and recorder.**

3.10 Choice of solvent:- the solvent should be transparent to UV-Visible radiation and should be less polar. Most common solvents are CS₂, chloroform and CCl₄. Water can not be used for this purpose.

3.11 Application of IR Spectroscopy:-

1. **Qualitative analysis:-**
2. **Quantitative analysis:-**
3. **Presence of water:-**

If sample contains water some bands at 3600 cm to 3200 cm⁻¹, - 1650 cm⁻¹ and 600 to 300 cm⁻¹ regions appear but if water molecules are present as ligand and coordinated with metal ion, then a band appears at the 880 cm⁻¹ to 650 cm⁻¹ region.

4. **Determination of force constant:-**

Force constant can be calculated by using IR spectroscopy as we know

$$\bar{\nu} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{cm}^{-1}$$

By using wave no., force constant can be calculated.

5. **Distinction between intra and intermolecular hydrogen bonding:-**

Intermolecular H-bonds show broad bands and are concentration dependent whereas intramolecular H-bonds show sharp and intense bands and they are concentration independent. So by increasing the concentration of solvent the bands, formed due to intermolecular H-Bonding, starts to weaken and finally disappear while that due to intramolecular H- Bonding remains unchanged.

6. **Identification of Functional groups:-** different functional groups absorb at characteristic frequencies in IR spectrum. Therefore from IR Spectrum of a compound, the presence or absence of certain groups in the compound is identified.

4. ROTATIONAL (MICROWAVE) SPECTROSCOPY

Spectroscopy in the microwave region is concerned with the study of rotating molecules. The energy associated with the rotating molecule is known as rotational energy. The rotational energy is quantized. This means that the molecule can not have any arbitrary amount of energy, but its energy is limited to certain definite values depending upon the shape and size of the molecule concerned. Rotational spectroscopy is concerned with the measurement of the energies of transitions between quantized rotational states of molecules in the gas phase. The spectra of polar molecules can be measured in absorption or emission by microwave spectroscopy or by far infrared spectroscopy. The rotational spectra of non-polar molecules cannot be observed by those methods, but can be observed and measured by Raman spectroscopy.

Rotational spectroscopy involves the transition between the rotational energy levels of a gaseous molecule having permanent dipole moment on absorption of radiations falling in the spectral range of $1-10 \text{ cm}^{-1}$ (microwave region)

Rotational spectroscopy is only really practical in the gas phase where the rotational motion is quantized. In solids or liquids the rotational motion is usually quenched due to collisions between their molecules.

4.1 Rotational spectra of diatomic molecules :

Assuming diatomic molecule AB behaves as a rigid rotator, it means, internuclear bond distances does not change during rotation. Let m_A and m_B are the masses of two atoms A and B respectively and r is the equilibrium internuclear distance between them that is $r = \text{bond length}$ (**Figure 27**).

Suppose r_A and r_B are the distances of atoms from the centre of gravity (Cg) of the molecule.

Moments of two atoms are equal around centre of gravity

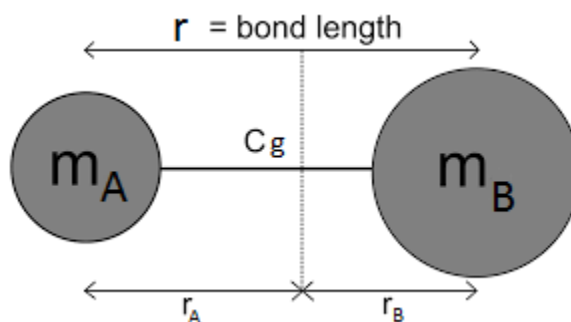


Figure 27. Rotational spectra of diatomic molecules

$$m_A r_A = m_B r_B \dots\dots\dots (1)$$

$$r = r_A + r_B$$

$$r_B = r - r_A \dots\dots\dots (2)$$

$$m_A r_A = m_B (r - r_A)$$

$$(m_A + m_B)r_A = m_B r$$

$$r_A = \frac{m_B r}{m_A + m_B} \dots\dots\dots (3)$$

$$\text{Similarly, } r_B = \frac{m_A r}{m_A + m_B} \dots\dots\dots (4)$$

$$\text{Now, the moment of inertia of diatomic molecule } (I) = m_A r_A^2 + m_B r_B^2 \dots\dots\dots (5)$$

Substituting the values of r_A and r_B from equation (3) and (4) into equation (5), we get

$$I = m_A \left(\frac{m_B r}{m_A + m_B} \right)^2 + m_B \left(\frac{m_A r}{m_A + m_B} \right)^2 = \frac{m_A m_B}{m_A + m_B} r^2 \quad \text{..... (6)}$$

$$= \mu r^2 \quad \text{..... (7)}$$

Where $\mu = \frac{m_A m_B}{m_A + m_B}$

μ is the reduced mass of the diatomic molecule.

Now, the angular momentum of rotating molecule is

$$(L) = I\omega \quad \text{..... (8)}$$

And Energy of a rotating molecule is

$$(E_J) = \frac{1}{2} I \omega^2 \quad \text{.....(9)}$$

Where

ω = Angular velocity

Let J = Rotational quantum number and it can have integral values from zero onwards

Then $L = \sqrt{J(J+1)} \frac{h}{2\pi}; J = 0, 1, 2, 3 \quad \text{.....(10)}$

Since angular momentum is quantized.

Now, $E_J = \frac{1}{2} I \omega^2 = \frac{(L\omega)^2}{2I} = \frac{L^2}{2I}$

Now the rotational energy levels allowed to the rigid diatomic molecule are given by the expression :

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ Joules} \quad \text{.....(11)}$$

Where $J = 0, 1, 2 \quad \text{.....}$

When energies expressed in cm^{-1} unit then it is normally reported as rotational term $F(J)$.

Thus, $F(J) = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1) \text{ cm}^{-1} \quad \text{..... (12)}$

Let $\frac{h}{8\pi^2 Ic} = B = \text{Rotational constant} \quad \text{..... (13)}$

Hence, $F(J) = BJ(J+1) \text{ cm}^{-1} \quad \text{..... (14)}$

Putting the values of $J = 0, 1, 2, \dots$ in equation (14)

We get the allowed rotational energy levels (**Figure 28**) of a diatomic molecule as follows:

J	0	1	2	3	4	5	6	7
$F(J) = BJ(J + 1) \text{ cm}^{-1}$	0	2B	6B	12B	20B	30B	42B	56B

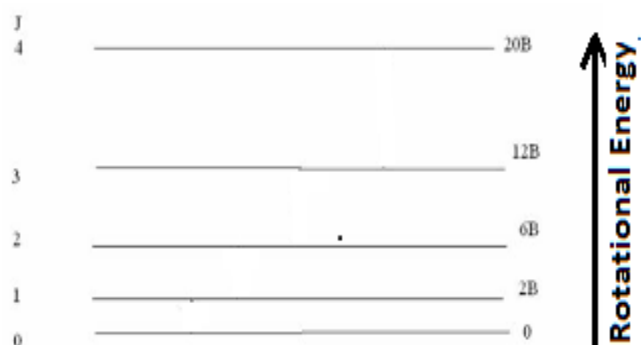


Figure 28. Allowed rotational energy levels

The rotational transitions for a rigid diatomic molecule are governed by the selection rule

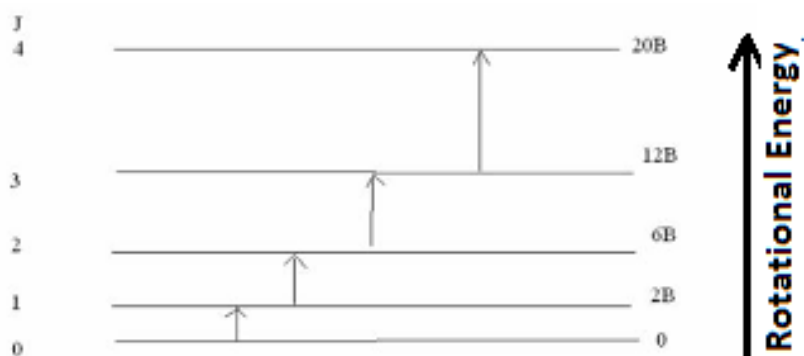
(i) $\Delta J = \pm 1$

For absorption of radiation $\Delta J = +1$ and for emission of radiation $\Delta J = -1$

(ii) Molecule should be in gaseous phase

(iii) There must be a change in dipole moment

Allowed transitions between rotational energy levels of diatomic molecules are shown in figure below.



In general, a transition taking place from J to $J + 1$, the rotational frequency is given by

$$\begin{aligned} \nu_{(J \rightarrow J+1)} &= F(J+1) - F(J) \\ &= B(J+1)(J+2) - BJ(J+1) \\ &= B(J+1)[J+2-J] \end{aligned}$$

$$\begin{aligned} \nu_{(J \rightarrow J+1)} &= B(J+1)[J+2-J] \text{ cm}^{-1} \\ &= B(J+1)(J+2) - BJ(J+1) \\ &= B(J+1)J+2-J \end{aligned}$$

$$\nu_{(J \rightarrow J+1)} = 2B(J+1) \text{ cm}^{-1}$$

Thus $\nu_{(0 \rightarrow 1)} = 2B$

$$\nu_{(1 \rightarrow 2)} = 4B$$

$$\nu_{(2 \rightarrow 3)} = 6B$$

$$\nu_{(3 \rightarrow 4)} = 8B$$

Hence the rotational spectrum of a rigid diatomic molecule consists of lines at $2B$, $4B$, $6B$ etc.

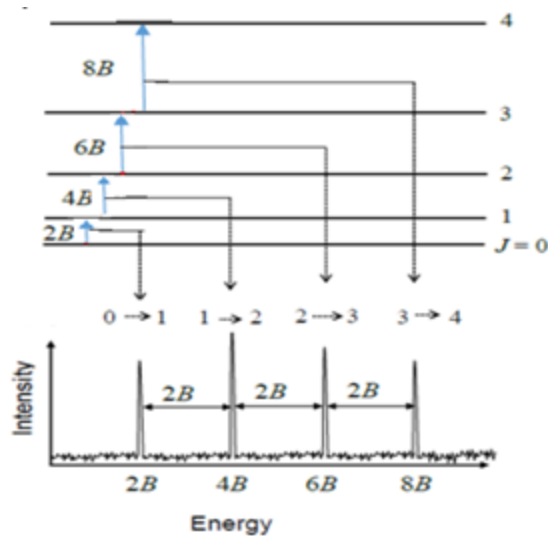
Now the distance between the two lines

$$\nu_{(1 \rightarrow 2)} \text{ and } \nu_{(0 \rightarrow 1)} \text{ is } 4B - 2B \text{ i.e. } 2B$$

$$\nu_{(2 \rightarrow 3)} \text{ and } \nu_{(1 \rightarrow 2)} \text{ is } 6B - 4B \text{ i.e. } 2B$$

$$\nu_{(3 \rightarrow 4)} \text{ and } \nu_{(2 \rightarrow 3)} \text{ is } 8B - 6B \text{ i.e. } 2B$$

Thus the distance between the two lines is $2B$



4.2 Determination of bond length from rotational spectrum:

From the rotational spectrum, we have

$$B = \frac{h}{8\pi^2 Ic}$$

$$I = \frac{h}{8\pi^2 Bc}$$

$$\text{Also } I = \mu r^2$$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{h}{8\pi^2 Bc\mu}}$$

4.3 Microwave active molecules:

The molecule with permanent dipole moment are microwave active. Heteronuclear diatomic molecules (such as HCl, HF, CO) – have permanent dipole moment (polar compound) - change of dipole occurs during the rotation – hence interaction with radiation takes place – Therefore, heteronuclear diatomic molecules are microwave active.

4.4 Microwave inactive molecules:

The molecule having no permanent dipole moment is microwave inactive. Homonuclear diatomic molecules (such as H_2 , O_2 , N_2 , Cl_2) – have zero dipole (non polar) - have zero change of dipole during the rotation, hence no interaction with radiation - hence homonuclear diatomic molecules are microwave inactive.

4.5 Applications:

1. Determination of bond length of a polar molecule :

From microwave spectroscopy, bond lengths can be determined with a correspondingly high precision, as illustrated in this example. From the rotational microwave spectrum of HCl, we find that $B = 10.59342 \text{ cm}^{-1}$. Given that the masses of H and Cl are 1.0078250 and 34.9688527 amu, respectively, determine the bond length of the HCl molecule.

We have

$$B = \frac{h}{8\pi^2 I c} = \frac{h}{8\pi^2 \mu r^2 c}$$

$$r = \sqrt{\frac{h}{8\pi^2 B c \mu}}$$

$$\mu = \frac{1.0078250 \times 34.9688527}{1.0078250 + 34.9688527} \times 1.67 \times 10^{-27} = 1.64 \times 10^{-27}$$

$$r = \sqrt{\frac{6.626 \times 10^{-34}}{8 \times (3.14)^2 \times 10.59342 \times 3 \times 10^{10} \times 1.64 \times 10^{-27}}}$$

$$r = 1.27 \times 10^{-10} m$$

$$r = 127 \text{ pm}$$

2. Determination of Symmetry in a molecule.
3. Determination of dipole moments of gaseous molecules is also possible by recording the spectra in the presence of electric field.
4. Microwave spectroscopy has been used in monitoring and control of industrial processes, such as;
 - (i) materials with low dielectric constants, such as plastics, glass, ceramics and composite materials.
 - (ii) determination of moisture in various tobacco types.
 - (iii) Monitoring of a batch esterification reaction as in the esterification of butanol by acetic acid.
 - (iv) Monitoring of the drying process in industry as it is one that is hard to monitor. For example, huge cakes of wet material when dried in big vessels.

EXERCISE :

1. What is the selection rule for the molecule to show rotational spectrum ?

(AKTU, sem II, 2018-2019)

Ans: The rotational transitions for a rigid diatomic molecule are governed by the selection rule

(i) $\Delta J = \pm 1$

For absorption of radiation $\Delta J = +1$ and for emission of radiation $\Delta J = -1$

(ii) Molecule should be in gaseous phase

(iii) There must be a change in dipole moment

2. Which of the following molecules will show rotational spectrum H_2 , HCl , CH_4 , CH_3Cl , CH_2Cl_2 , H_2O , SF_6 ?

Ans: HCl , CH_3Cl , CH_2Cl_2 , H_2O

(AKTU, sem I, 2018-2019)

3. What is the separation between adjacent lines in the microwave spectrum of rigid rotator ?

Ans: The separation between adjacent lines in the microwave spectrum of rigid rotator is $2B$.

4. Why is rotational spectra observed only in the gaseous phase ?

Ans: Rotational spectroscopy is only really practical in the gas phase where the rotational motion is quantized. In solids or liquids the rotational motion is usually quenched due to collisions between their molecules.

5. What are the applications of rotational spectra ?

Ans: 1. Determination of bond length of a polar molecule.

2. Determination of Symmetry in a molecule.

3. Determination of dipole moments of gaseous molecules is also possible by recording the spectra in the presence of electric field.

4. Microwave spectroscopy has been used in monitoring and control of industrial processes, such as;
- (i) materials with low dielectric constants, such as plastics, glass, ceramics and composite materials.
 - (ii) determination of moisture in various tobacco types.
 - (iii) Monitoring of a batch esterification reaction as in the esterification of butanol by acetic acid.
 - (iv) Monitoring of the drying process in industry as it is one that is hard to monitor. For example, huge cakes of wet material when dried in big vessels.

6. The pure rotational spectra of CN molecule in gaseous phase shows series of equally spaced lines with interspacing 3.8 cm^{-1} . Calculate the internuclear distance of CN molecule. Given, molar masses : C and N are 12 g/mol and 14 g/mol respectively.

Ans: Given $2B = 3.8 \text{ cm}^{-1}$

$$B = 1.9 \text{ cm}^{-1}$$

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.626 \times 10^{-34} \text{ Js}}{8 \times (3.14)^2 \times 1.9 \text{ cm}^{-1} \times 3 \times 10^{10} \text{ cm s}^{-1}}$$

$$= 1.47 \times 10^{-46} \text{ Kg m}^{-2}$$

$$\mu = \frac{(12 \text{ g/mol})(14 \text{ g/mol})}{(12+14) \text{ g/mol} \times 6.023 \times 10^{23} \text{ mol}^{-1}}$$

$$= 1.07 \times 10^{-23} \text{ g}$$

$$= 1.07 \times 10^{-26} \text{ Kg}$$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.47 \times 10^{-46} \text{ Kg m}^{-2}}{1.07 \times 10^{-26} \text{ Kg}}}$$

$$= 1.172 \times 10^{-10} \text{ m}$$

$$= 117 \text{ pm}$$

5. Raman Spectroscopy

Raman spectroscopy is a molecular spectroscopic technique that utilizes the interaction of light with matter to gain insight into a material's make up or characteristics. The information provided by Raman spectroscopy results from a light scattering process, whereas IR spectroscopy relies on absorption of light. Raman spectroscopy yields information about intra- and inter-molecular vibrations and can provide additional understanding about a reaction. Raman spectroscopy can provide both chemical and structural information, as well as the identification of substances through their characteristic Raman ‘fingerprint’. Raman spectroscopy extracts this information through the detection of Raman scattering from the sample.

5.1 The Raman Spectroscopy Principle

When light interacts with molecules in a gas, liquid, or solid, the vast majority of the photons are dispersed or scattered at the same energy as the incident photons. This is described as elastic scattering, or Rayleigh scattering. A small number of these photons, approximately 1 photon in 10 million will scatter at a different frequency than the incident photon. This process is called inelastic scattering, or the Raman effect, named after Sir C.V. Raman who discovered this and was awarded the 1930 Nobel Prize in Physics for his work.

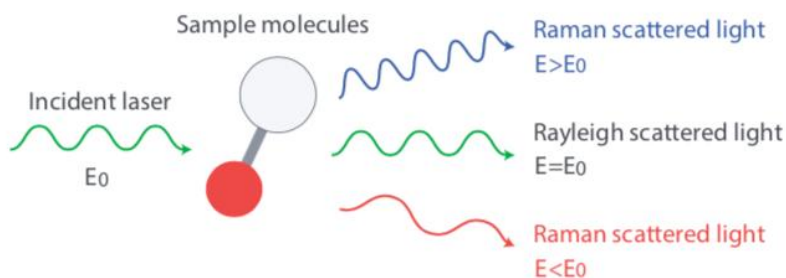
5.2 Raman Scattering Process

When a sample is irradiated with a beam of monochromatic light, usually from a laser in the visible, near infrared or near ultraviolet range is used. A very small fraction of it is scattered in all directions. If the scattered light in a direction perpendicular to the incident beam is spectrographed, it shows Rayleigh line corresponding to frequency of incident light and weak lines on either side of it. These weak lines are Anti-Stokes and Stokes lines

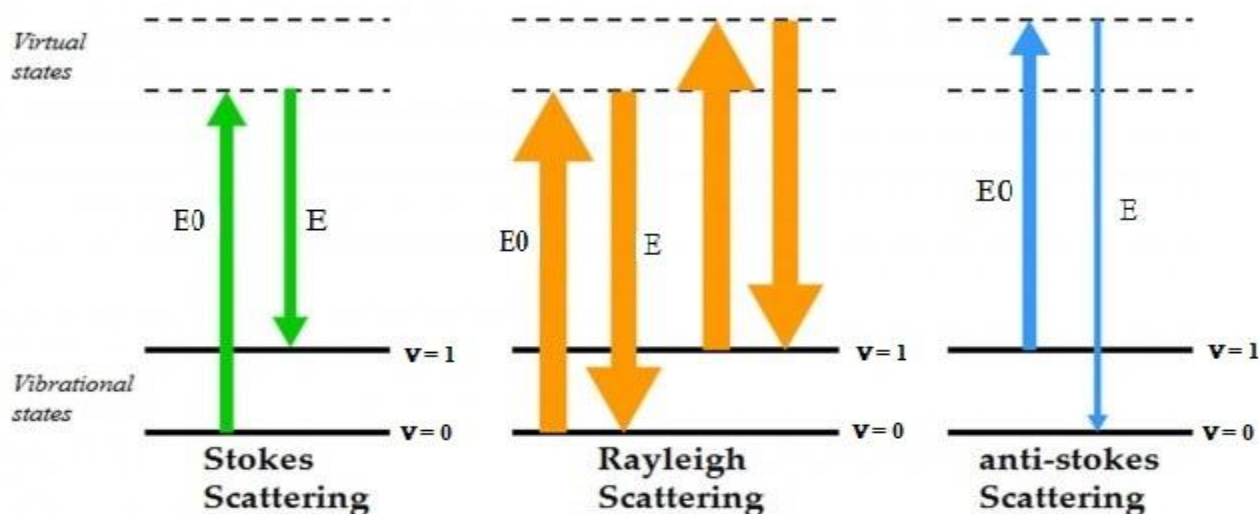
When photons interact with a molecule, the molecule may be advanced to a higher energy, virtual state. From this higher energy state, there may be a few different outcomes. One such outcome would be that the molecule relaxes to a vibrational energy level that is different than that of its beginning state producing a photon of different energy. The difference between the energy of the incident photon and the energy of the scattered photon is called the Raman shift.

When the change in energy of the scattered photon is less than the incident photon, the scattering is called Stokes scatter. Some molecules may begin in a vibrationally excited state and when they are advanced to the higher energy virtual state, they may relax to a final energy state that is lower than that of the initial excited state. This scattering is called anti-Stokes.

Scattering of light by molecules



When a sample molecule collides with a photon of energy E_0 i.e frequency ν_0 , it absorbs radiation and raised from ground state energy level to a virtual state energy level. Then scattering of light takes place. During scattering three types of lines are observed. Stokes lines ,Rayleigh lines and anti-Stokes lines.



Stokes lines : When molecule returns to different vibrational state after excitation from ground vibrational state . molecule emit radiation with lower frequency than the incident light and the Raman scattered lines observed with lower frequency are known as stokes lines

$$E_0 > E$$

$$\Rightarrow h\nu_0 > h\nu$$

$$\Rightarrow \nu_0 > \nu$$

$$\Rightarrow \Delta\nu > 0$$

where $\Delta\nu$ is Raman shift, as $\Delta\nu > 0$, it results in Raman scattering.

Rayleigh line : When molecule returns to original vibrational state after excitation from ground vibrational state . molecule emit radiation of same frequency as that of incident light and the lines observed with same frequency are known as Rayleigh lines.

$$E_0 = E$$

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where $\Delta\nu$ is Raman shift, as $\Delta\nu = 0$, it results in Rayleigh lines.

Anti-Stokes lines : When molecule is promoted from first excited vibrational state to virtual vibrational state from which it returns to different ground vibrational state . molecule emit radiation with higher frequency than the incident light and the Raman scattered lines observed with higher frequency are known as Anti-Stokes lines.

$$E_0 < E$$

$$\Rightarrow h\nu_0 < h\nu$$

$$\Rightarrow \nu_0 < \nu$$

$$\Rightarrow \Delta\nu < 0$$

where $\Delta\nu$ is Raman shift, as $\Delta\nu < 0$, it results in Raman scattering.

5.3 Criterion for a molecule to be Raman active

Raman looks at changes in a molecular bonds polarizability. Interaction of light with a molecule can induce a deformation of its electron cloud. This deformation is known as a change in polarizability. Molecular bonds have specific energy transitions in which a, giving change of polarizability occurs rise to Raman active modes. As an example, molecules that contain bonds between homonuclear atoms such as carbon-carbon, sulfur-sulfur, and nitrogen-nitrogen bonds undergo a change in polarizability when photons interact with them. These are examples of bonds that give rise to Raman active spectral bands.

Example : Symmetrical stretch in CO_2 molecule, giving change of polarizability occurs rise to Raman active modes.

Anti- Symmetrical stretch in CO_2 molecule, no change in polarizability occurs, we get Raman inactive modes.

5.4 Pure Rotational Raman Spectra of a diatomic molecules

When the polarizability of a molecule depends on the direction in which the applied field lies, Rotational transitions can also be observed by Raman effect. Since on every revolution, the polarizability of a molecule return to its initial value twice, the rotational selection rule in Raman spectra is therefore $\Delta J = \pm 2$

When molecule makes a transition with $\Delta J = +2$, the Raman scattered lines observed with lower frequency and we get the Stokes lines.

Similarly, When molecule makes a transition with $\Delta J = -2$, the Raman scattered lines observed with higher frequency and we get the Anti-Stokes lines.

When $\Delta J = 0$, only Rayleigh line observed with same frequency.

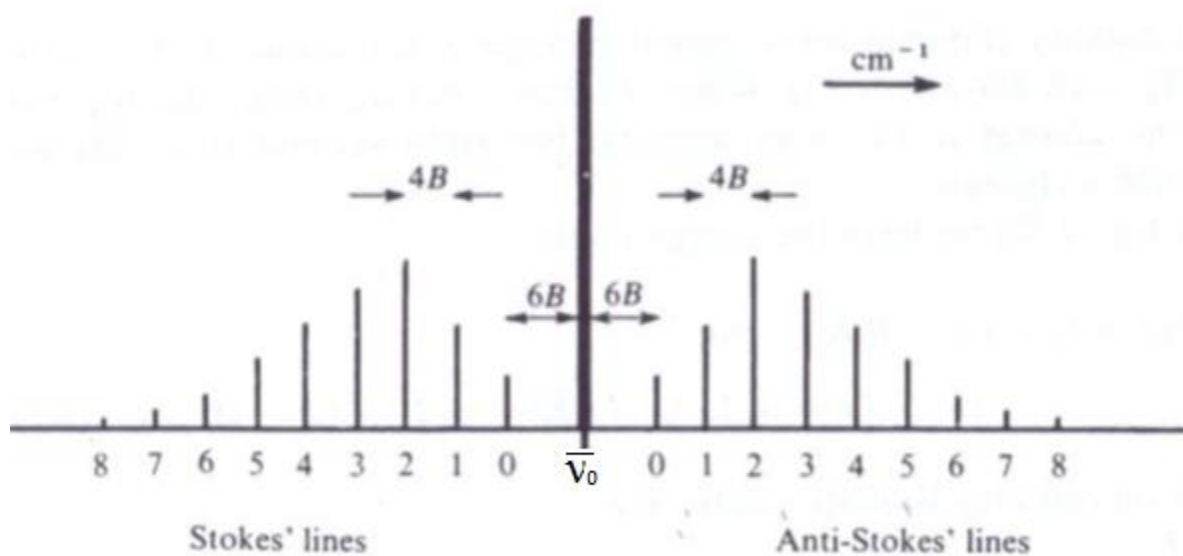
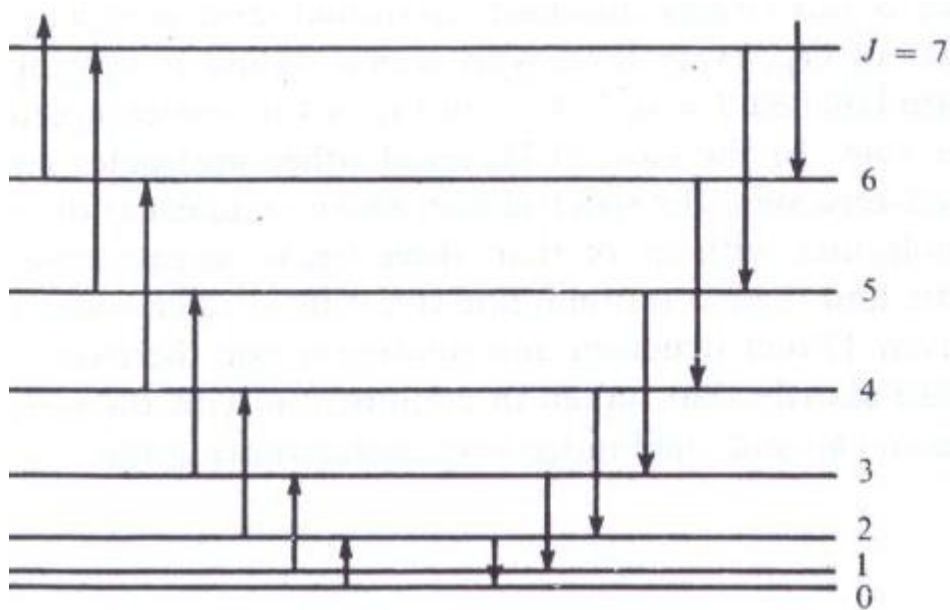
5.5 Vibrational Raman Spectra

The selection rule for vibrational Raman Spectra is $\Delta J = \pm 1$

When $\Delta J = +1$, the Raman scattered lines observed with lower frequency and we get the Stokes lines.

When $\Delta J = -1$, the Raman scattered lines observed with higher frequency and we get the Anti-Stokes lines.

Rotational energy levels of a diatomic molecule and the rotational Raman spectrum arising from transition between them.



Applications :

1. Raman spectroscopy is used in chemistry to identify molecules and study chemical bonding and intramolecular bonds.
2. Raman provides a fingerprint to identify molecules.

3. Raman and IR spectra were used to determine the vibrational frequencies of SiO , Si_2O_2 , and Si_3O_3 on the basis of normal coordinate analyses.
4. Raman spectra accessible without interference of gas phase.
5. Raman technology, which has been widely applied in detection of various substances in agriculture, food and biosystems, such as plant diseases identification, farm chemicals detection, food additives determination, and toxins analysis.

5.6 Difference between Infrared and Raman Spectra

S.No.	Infrared Spectra	Raman Spectra
1.	It results due the absorption of light by vibrating molecules.	It results due to the scattering of light by vibrating and rotating molecules.
2.	Change in dipole moment is essential condition. Water cannot be used as solvent for recording IR spectra.	Change in polarizability is essential condition. Water can be used as solvent for recording Raman spectra.
3.	Dilute solutions are generally preferred. Homonuclear diatomic molecules do not exhibit IR spectra.	Concentrated solutions must be utilized. Homonuclear diatomic molecules do not exhibit IR spectra.
4.	Application to aqueous biological sample is not possible.	Application to aqueous biological sample is possible . Example : Analysis of drugs in body fluids.
5.		
6.		

EXERCISE :

1.What is meant by the term polarizability in Raman spectra? (AKTU, sem I, 2018-2019)

Ans: Raman looks at changes in a molecular bonds polarizability. Interaction of light with a molecule can induce a deformation of its electron cloud. This deformation is known as a change in polarizability. Molecular bonds have specific energy transitions in which a, giving change of polarizability occurs rise to Raman active modes.

2.State the selection rule for Raman spectroscopy. What technological advances have enable the routine use of Raman spectroscopy? Which of the following spectroscopy (IR or Raman) would you use to measure the vibrational frequency of following bonds:

(i) The stretching frequency of ^{14}N -- ^{15}N

(ii) The $\text{C} \equiv \text{C}$ stretch in $\text{CH} \equiv \text{CH}$

(iii) The $\text{C} = \text{O}$ stretch in CH_3COCH_3

(iv) The Re-Re stretch in compound $(\text{CO})_5 \text{ Re-Re } (\text{CO})_5$

(AKTU, sem I,2018-2019) **Ans:** The selection rule for Raman spectroscopy is changes in a molecular bonds polarizability must be there. Interaction of light with a molecule can induce a deformation of its electron cloud. This deformation is known as a change in polarizability. Molecular bonds have specific energy transitions in which a, giving change of polarizability occurs rise to Raman active modes.

When the polarizability of a molecule depends on the direction in which the applied field lies, Rotational transitions can also be observed by Raman effect. Since on every revolution, the

polarizability of a molecule return to its initial value twice, the rotational selection rule in Raman spectra is therefore $\Delta J = \pm 2$

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The selection rule for vibrational Raman Spectra is $\Delta J = \pm 1$

When $\Delta J = +1$, the Raman scattered lines observed with lower frequency and we get the Stokes lines.

When $\Delta J = -1$, the Raman scattered lines observed with higher frequency and we get the Anti-Stokes lines.

Raman technology, which has been widely applied in detection of various substances in agriculture, food and biosystems, such as plant diseases identification, farm chemicals detection, food additives determination, and toxins analysis.

Raman spectroscopy is used to measure the vibrational frequency of following bonds:

- (i) The stretching frequency of $^{14}\text{N}-^{15}\text{N}$
- (ii) The $\text{C} \equiv \text{C}$ stretch in $\text{CH} \equiv \text{CH}$
- (iv) The Re-Re stretch in compound $(\text{CO})_5 \text{Re-Re} (\text{CO})_5$

IR spectroscopy is used to measure the vibrational frequency of following bonds:

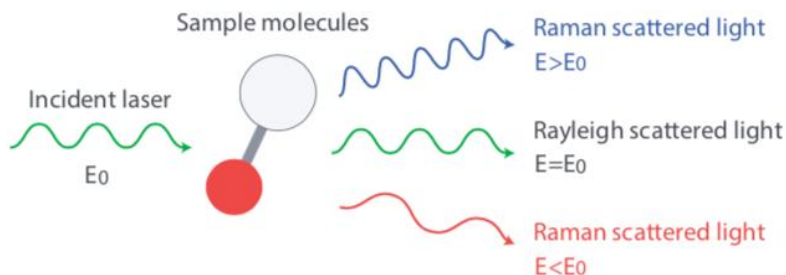
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Difference between Infrared and Raman Spectra

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4.	Dilute solutions are generally	Concentrated solutions must be utilized.
5.	preferred. Homonuclear diatomic molecules do not exhibit IR spectra.	Homonuclear diatomic molecules do not exhibit IR spectra.
6.	Application to aqueous biological sample is not possible.	Application to aqueous biological sample is possible . Example : Analysis of drugs in body fluids.

3. Discuss the quantum theory of Raman spectroscopy and how the stokes , Rayleigh line and anti- stokes lines appear in Raman spectroscopy. How does it differ from IR spectroscopy?
 (AKTU, sem II, 2018-2019) **Ans:** When a sample molecule collides with a photon of energy E_0 i.e frequency ν_0 , it absorbs radiation and raised from ground state energy level to a virtual state energy level. Then scattering of light takes place. During scattering three types of lines are observed. Stokes lines ,Rayleigh lines and anti-Stokes lines.

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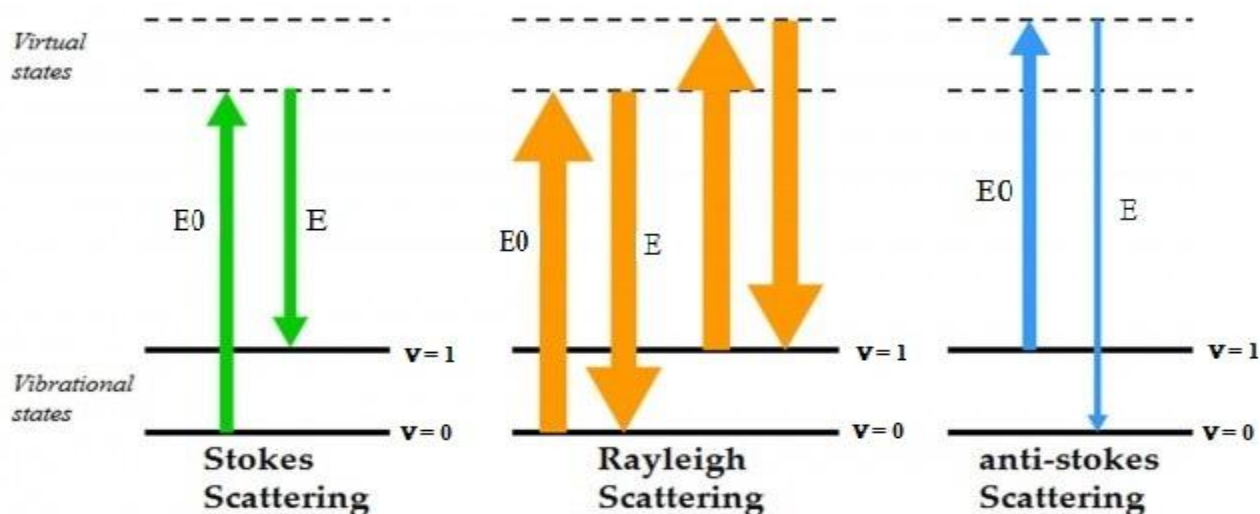
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Difference between Infrared and Raman Spectra

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Previous Year Questions:-

Ques.1 What is Beer-Lambert law in UV-Visible absorption spectroscopy? A compound having concentration 10-3g/l resulted absorbance value 0.20 at λ_{max} 510 nm using 1.0 cm cell. Calculate its absorptivity and molar absorptivity values. Molecular weight of compound is 400. Can ultra-violet spectral data be useful to distinguish the following compounds? Give reasons.

(i) Ethyl benzene and styrene. (ii) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$ and $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$.

(2018-19

AKTU)

Ques.2 What is finger print region and functional group region in IR spectroscopy? Two isomers A and B of the molecular formula $\text{C}_3\text{H}_6\text{O}$ gives IR absorption at 1650 cm^{-1} and 1710 cm^{-1} respectively. Assign structural formula to A and B isomers? (2018-19 AKTU)

Ques.3 Explain, which one will exhibit higher value of λ_{max} in UV/Visible spectra of CH_3COCH_3 and $\text{CH}_2=\text{CHCOCH}_3$. (2018-19 AKTU)

Ques.4 What type of electronic transitions is involved in UV-visible spectroscopy? Explain the Absorption and Intensity shift in UV spectroscopy and support with examples. Illustrate, the effect of polar and nonpolar solvent on $\pi \rightarrow \pi^*$ transition in acetone? (2018-19 AKTU)

Ques.5 Among H_2 , HCl , CO_2 and H_2O molecules identify which will be IR active and why? Explain different mode of vibrations observed in CO_2 molecule. Out of the following pairs which one is expected to absorb at higher frequency for stretching vibrations? Also state reason. (2018-19 AKTU)

- i. HCHO , CH_3CHO
- ii. $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$
- iii. $\text{O}-\text{H}$, $\text{C}-\text{C}$

References:-

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