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Sinhgad College of Engineering, Vadgaon Bk,Pune-41

Subject – Engineering Chemistry

Unit 5 (18 marks-7,6,5)

Spectroscopic Techniques (UV and IR spectroscopy)

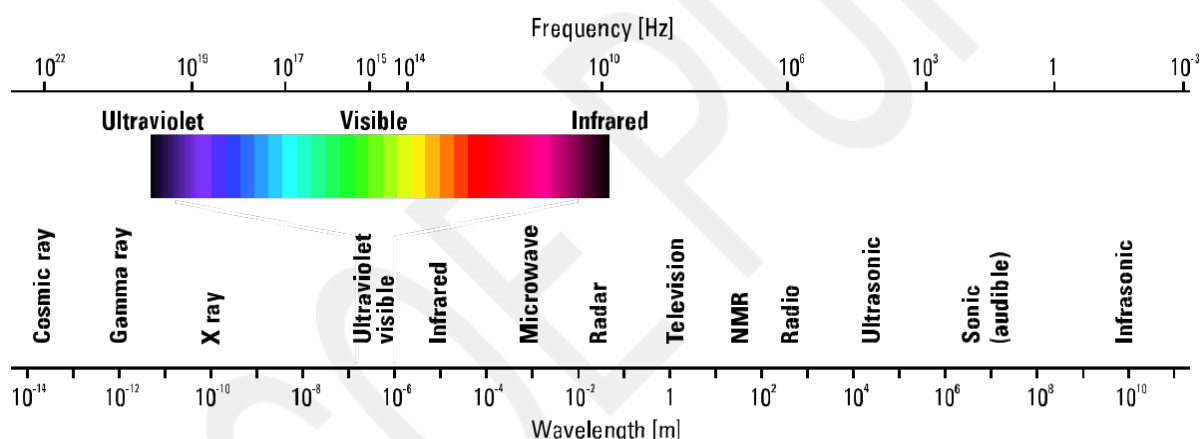
Spectroscopy is the study of molecular structure and dynamics through the absorption, emission, and scattering of light.

The mechanism of absorption energy is different in the Ultraviolet, Infrared, and Nuclear magnetic resonance regions. However, the fundamental process is the absorption of a certain amount of energy.

The energy required for the transition from a state of lower energy to a state of higher energy is directly related to the frequency of electromagnetic radiation that causes the transition.

The absorption of ultraviolet radiation by molecules is dependent upon the **electronic structure** of the molecule.

So the ultraviolet spectrum is called the electronic spectrum.



$$E = h\nu$$

$$E = hc/\lambda$$

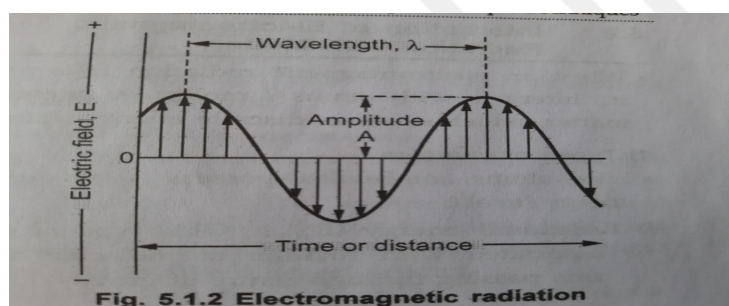
This spectroscopy is based on **Absorption Spectroscopy**.

Part 1: UV-Visible spectroscopy

Q.1) Give characteristics of electromagnetic radiation. Explain the interaction of electromagnetic radiation of matter with the type of energy levels involved in it. {7 mks-(2+1+3+1)}

Ans: Characteristics of Electromagnetic radiations: It is branch of science that deals with the study of electromagnetic radiation with matter. Electromagnetic waves show dual nature i.e. particle as well as wave forms. Particles are nothing but photons.

Electromagnetic radiation consist of discrete packets of energy which are called as photons. A photon consists of an oscillating electric field (E) and magnetic field (M) which are perpendicular to each other.



Frequency is the no of times electrical field radiation oscillates in one second. Hz is the unit

Wavelength is the distance between the 2 successive crest or troughs

$$C = \nu\lambda$$

As photon is subjected to energy, so

$$E = h\nu = hc/\lambda$$

Different types of energy when molecule is subjected to UV radiation : When electromagnetic radiation falls on the matter, it interacts with atoms or molecules present in the matter which exist in discrete energy states.

There are molecular energy levels which include electronic, vibrational, rotational energy levels.

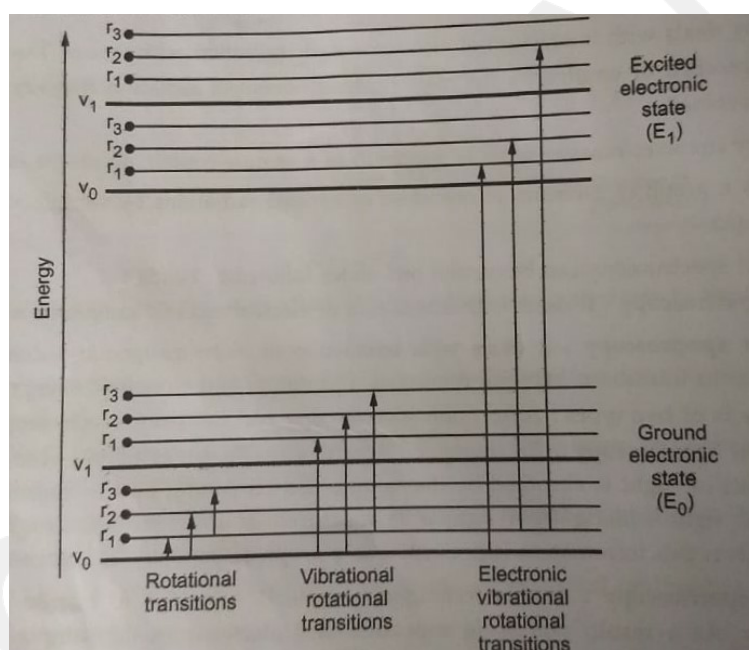
Rotational energy levels are closely spaced and occur in the microwave region

Vibrational energy levels are spaced further apart. They occur in the infrared region.

Vibrational transitions are accompanied by rotational transitions

If further higher energies are required which may take place from GS to ES, it occurred in the UV-visible region. Electronic transitions are accompanied by vibrational, rotational and electronic transitions.

The molecule accepts energy only in quanta of appropriate value to cause an excitation from one energy level to another.



Q.2) State and derive Beer Lambert's law involved in UV spectroscopy. {5 mks-(1+1+3)}

Ans: Beer's Law - When a beam of monochromatic light is passed through a homogenous solution, then the rate of decrease in intensity with the concentration of the medium is directly proportional to the intensity of incident light.

Lambert's Law - When a beam of monochromatic light is passed through a homogenous solution, then the rate of decrease in intensity with thickness or path length of the medium is directly proportional to the intensity of incident light.

By the combination of above laws,

Absorbance is proportional to the concentration and thickness of the medium

$$A = \epsilon L C$$

Where, A = Absorbance

L = Path length

ϵ = Molar absorptivity

C = Concentration

Beer's Law

$$-dI \propto I$$

$$-\frac{dI}{dc} = k \cdot I$$

Rearranging above eqⁿ

$$I = I_t \quad c = c$$

$$-\int \frac{dI}{I} = k \cdot \int dc$$

$$I = I_0 \quad c = 0$$

Integrating on both sides

$$-\frac{I_t}{I_0} = k \cdot c$$

Taking log on both side

$$-\ln \frac{I_t}{I_0} = \ln k \cdot c$$

$$\log_{10} \frac{I_0}{I_t} = \frac{k}{2.303} \cdot c$$

$$A = \epsilon \cdot c$$

$$\therefore A \propto c$$

\therefore By combination of Beer-Lambert's law

$$A \propto c \cdot t$$

$$\therefore A \propto c$$

Lambert's Law

$$-dI \propto I$$

$$-\frac{dI}{dt} = k' \cdot I$$

Rearranging above eqⁿ

$$I = I_t \quad t = t$$

$$-\int \frac{dI}{I} = k' \cdot \int dt$$

$$I = I_0 \quad t = 0$$

Integrating on both sides

$$-\frac{I_t}{I_0} = k' \cdot t$$

Taking log on both sides

$$-\ln \frac{I_t}{I_0} = \ln k' \cdot t$$

$$\therefore \log_{10} \frac{I_0}{I_t} = \frac{k'}{2.303} \cdot t$$

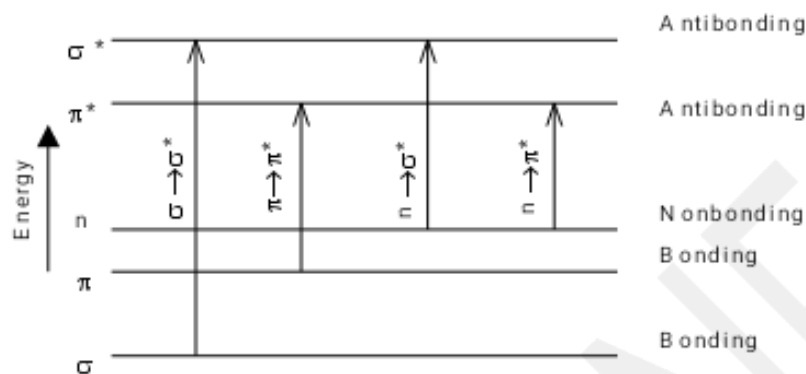
$$A = \epsilon \cdot t$$

$$\therefore A \propto t$$

t - constant (thickness or path length)

Q.3) Explain different types of electronic transitions that occur in an organic molecule after absorbing UV radiation. {6 mks- (4 transitions 1.5 each)}

Ans: Electronic Excitations in UV spectroscopy - The absorption of light energy by organic compounds in the visible and ultraviolet region involves the promotion of electrons in σ , π , and n -orbitals from the ground state to higher energy states. This is also called the energy transition. These higher energy states are molecular orbitals called antibonding.

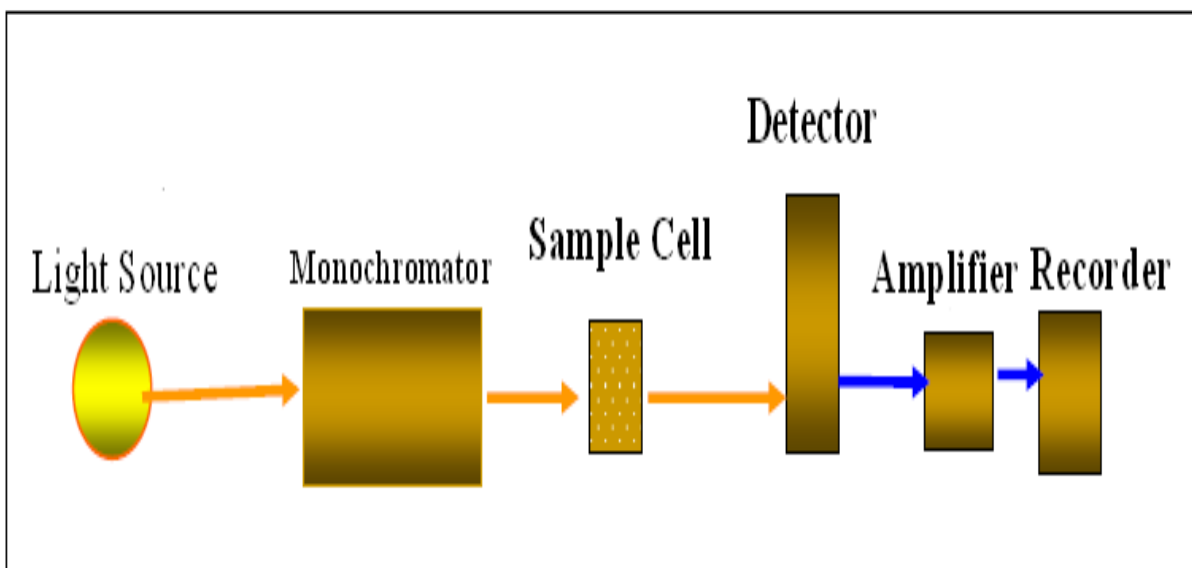


UV (wavelength range) 200-400 nm and Visible range 400-800 nm

- 1) $\sigma \rightarrow \sigma^*$ transitions – σ electron from bonding orbital is excited to the corresponding antibonding orbital. The energy required is large for this situation. All saturated hydrocarbons e.g. alkane (methane, ethane, etc.) This transition is below 200 nm so it is not easily detected by UV visible spectrophotometer
- 2) $\pi \rightarrow \pi^*$ transitions – π electrons in a bonding orbital is excited to corresponding antibonding orbital π^* . All unsaturated hydrocarbons e.g. alkene, alkynes, aromatic compounds, etc.
- 3) $n \rightarrow \sigma^*$ transitions – saturated compounds containing atoms with lone pairs on heteroatoms like N, O, S, X, etc. are capable of $n \rightarrow \sigma^*$ transition. These transitions usually require less energy than $\sigma \rightarrow \sigma^*$ transition e.g. alcohol, ether, amines, etc
- 4) $n \rightarrow \pi^*$ transitions – An electron from nonbonding orbital is promoted to antibonding π^* orbital. Compounds containing unsaturated structures containing heteroatoms like N, O, S, X, etc. e.g. esters, ketones, amide, acids, etc. These transitions usually require minimum energy.

Q.4) Give principle and instrumentation of Single beam UV visible spectrophotometer with block diagram. Give functions of each component of a single-beam spectrophotometer. {7 mks – (1+1+5)}

Ans: Principle – UV and Visible electromagnetic radiations are more energetic. Absorption of UV-visible radiations by sample brings about electronic excitations. Electronic excitations are accompanied by vibrational and rotational changes. The absorption spectrum is a graph of absorption Vs wavelength of light.



1) Source - Tungsten lamp (350-2500 nm), Deuterium (200-400 nm), Xenon Arc lamps (200-1000 nm) can be used.

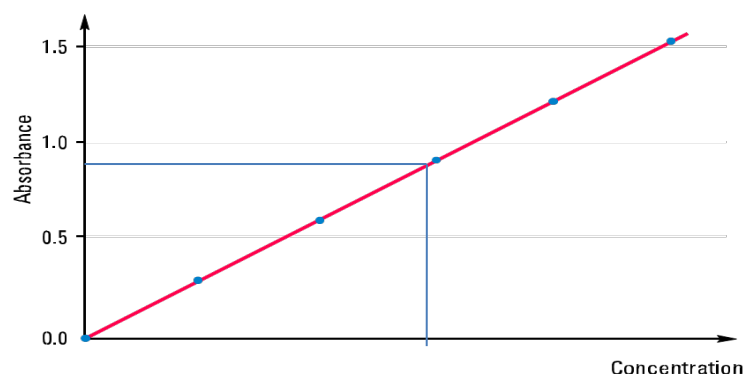
2) Monochromator – It is composed of the entrance slit, dispersion medium (grating or prism) and monochromator. It disperses radiations according to wavelength. Quartz prism or grating are used as dispersing elements of the monochromator.

3) slits – Entrance slit and exit slit are placed on opposite sides of prism or grating. Exit slit can be movable. Exit slit helps in selecting the desired wavelength of the desired wavelength from dispersed light obtained from prism or grating.

4) sample cell or cuvette – For UV Spectrophotometer, Quartz (crystalline silica) and for Visible Spectrophotometer, Glass cuvette can be used.

5) detector- Transmitted light from sample cuvette falls on the detector where it is converted into electric current. (light energy to electrical energy). The output current of the photodetector is directly proportional to the intensity of light falling on it. For UV-visible spectroscopy, commonly used detectors are photomultiplier tubes, phototubes, photovoltaic cells, etc.

6) Amplifier and recorder system – signals received from the detector are amplified and read on the recorder. Recorder can record output in the form of digital values or graphical manner.



Q.5) Define the terms with suitable example {any 4 for 4 mks-1 each}}

OR

Give a reason – {6 mks-(2 marks each)}

- 1) Benzene shows λ_{max} at 255 nm whereas phenol shows λ_{max} at 270 nm
- 2) 1,5 hexadiene shows λ_{max} at 178 nm whereas 2,4 hexadiene shows λ_{max} at 227 nm
- 3) Aniline shows a blue shift in acidic medium
- 4) In alkaline medium, p-nitrophenol shows redshift.
- 5) 1,3 butadiene possess higher λ_{max} than ethylene

Ans: Chromophore – chromophore is a functional group containing multiple bonds capable of absorbing radiations above 200 nm due to $\pi - \pi^*$ and $n - \pi^*$ responsible for electronic absorption

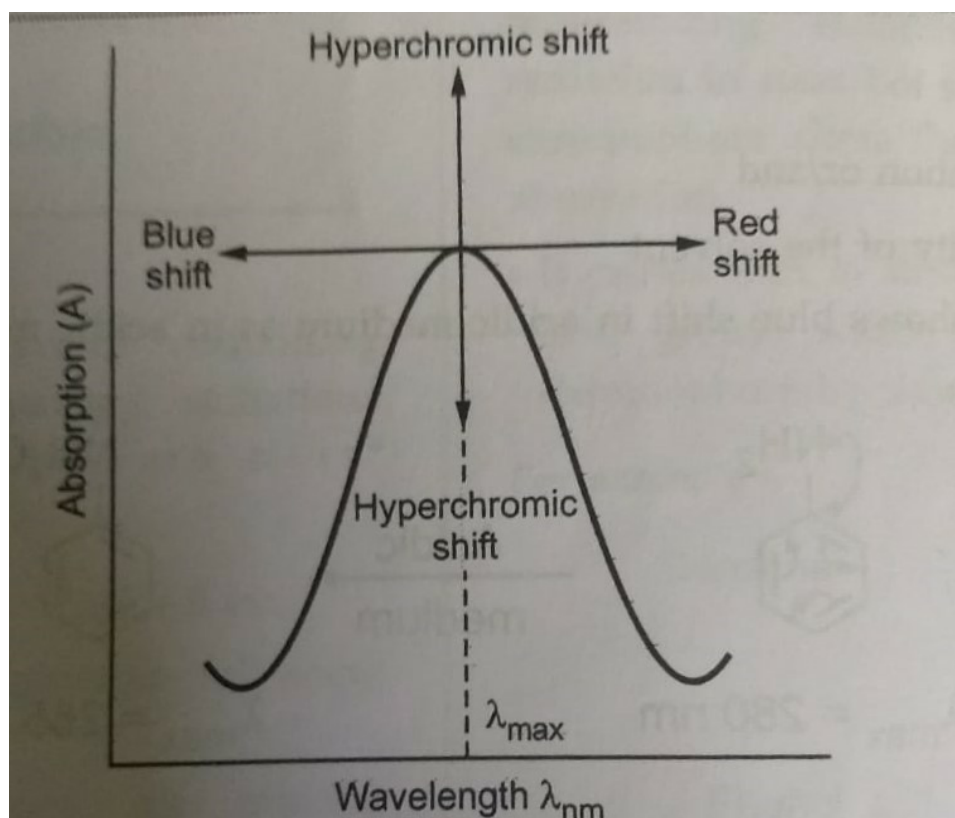
Auxochrome– auxochrome is a **saturated** functional group (OH, OCH₃, NH₂) with nonbonding electrons, when attached to chromophore alters the wavelength and responsible for the change in Absorption

Bathochromic Effect (**Red Shift**) – When λ_{max} of compound shifts to a longer wavelength due to the presence of an auxochrome or by the change of solvent..(**Longer Wavelength**)

Hypsochromic Effect (**Blue Shift**) – When λ_{max} of compound shifts to a shorter wavelength due to change in polarity of the solvent or removal of conjugation. (**Shorter Wavelength**)

Hyperchromic Shift – (Higher Absorbance) introduction of an auxochrome increases the intensity of absorption

Hypochromic Shift - (Lower Absorbance) due to the introduction of a group that distorts the original geometry of the molecule.



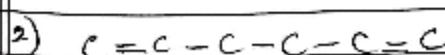
Give reasons



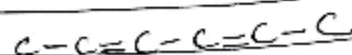
$\lambda_{\max} = 255 \text{ nm}$

$\lambda_{\max} = 270 \text{ nm}$

-OH is saturated functional group attached to chromophore i.e. benzene, shifts absorption to longer wavelength

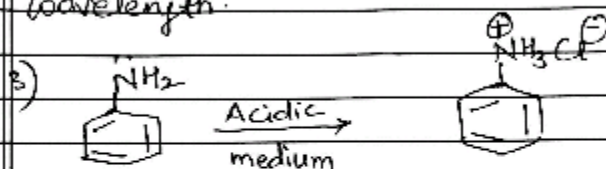


$\lambda_{\max} = 178 \text{ nm}$



$\lambda_{\max} = 227 \text{ nm}$

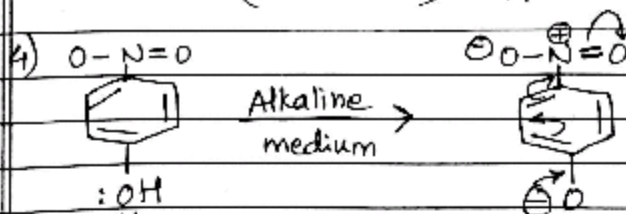
Extended conjugation shifts absorption to longer wavelength.



$\lambda_{\max} = 280 \text{ nm}$

$\lambda_{\max} = 265 \text{ nm}$

In acidic medium, it loses conjugation & forms salt, therefore shifts absorption to shorter wavelength called as (blue shift) Hypsochromic shift.



p-nitrophenol shows red shift, because -vely charged oxygen delocalises electron more effectively than unshared pair of e^- on -OH group.

5) In 1,3 butadiene, due to extended conjugation, it shows higher λ_{\max} than ethylene.

Q.6) Explain Applications of UV-visible spectroscopy. {5 mks (1 for each)}

Ans:

1) Qualitative – Detection of functional group, conjugated compounds show absorption at a longer wavelength and non-conjugated compounds show absorption at a shorter wavelength.

The unknown compound can be compared with known compound, can be determined by qualitative analysis

2) Quantitative analysis - using UV-visible absorption spectroscopy, the concentration of an unknown solution can be calculated by Beer Lambert's law

3) Detection of impurities – IT is used for the determination of impurities in organic compounds. If additional peaks are observed, it can be compared with standard material. By measuring absorbance at a particular wavelength, impurities can be detected.

4) Determination of molecular weight – Molecular weight of the compound can be determined by recording absorbance. Using Beer Lambert's law, if conc. is known then molecular weight can be calculated

4) Detection of cis and trans isomers – Trans isomer shows higher λ_{max} values than cis isomer, so it can be easily distinguished.

5) Study of kinetics of chemical reactions – Kinetic study of chemical reactions is done by measuring changes in concentration of reactant/product that show presence in the UV-visible spectrum.

Part 2 - IR SPECTROSCOPY

IR Spectroscopy is also based on **absorption** spectroscopy

Q.1) What are the conditions for the absorption of IR radiations by the molecule? {3 mks}

Ans:

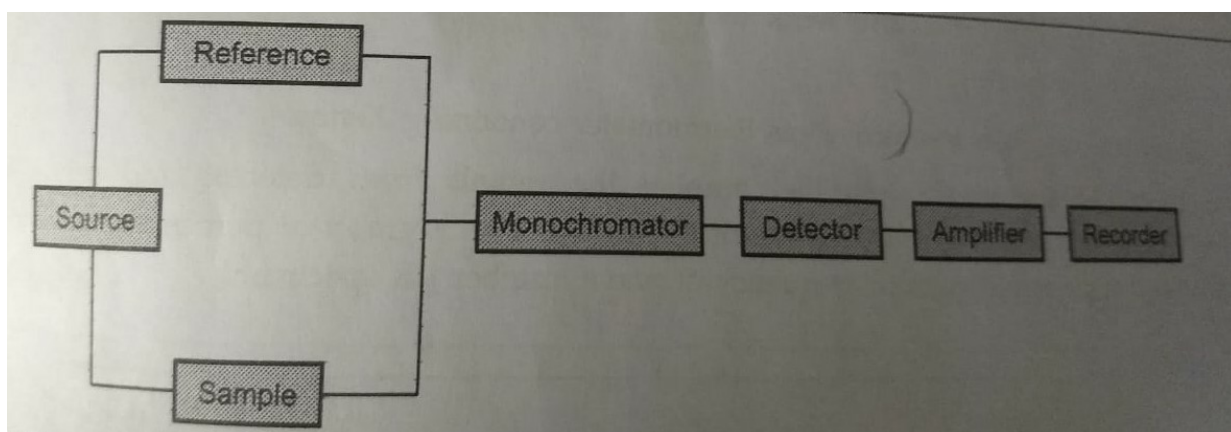
a) A molecule absorbs radiations only when the frequency of vibration of a bond and frequency of IR radiation used for excitation match perfectly.

b) A molecule can only absorb IR radiation when its absorption causes a change in electric dipole (dipole moment)

Q.2) Give the principle and instrumentation of the IR spectrophotometer with a block diagram. Give functions of each component of a double beam IR spectrophotometer. {7 mks – (1+1+5)}

Ans: Principle of IR spectrophotometer - A molecule is not rigid. The atoms in the molecule are always in vibrating motion. Each vibration requires different energy (vibrational energy levels)

If a molecule absorbs IR radiation, it gets excited to higher vibrational energy level. It depends on the type of atoms and bonds in the molecule.



1) Source – One of the following sources can be used.

Nernst filament, globar, incandescent wire or mercury arc can be used

2) Monochromator – Prism or grating can be used. Prism is made up of metal halides like NaCl or KBr

3) Sample cell and sampling of substances – Infrared spectra can be obtained for solids, liquids or gases. Material containing sample must be transparent to the IR radiation so the material made up of certain salt like NaCl or KBr are used.

Sampling of solid can be done by film technique or pressure pellet technique. Liquid samples can be sandwiched using sample cells of KBr or NaCl.

4) Detectors – different types of thermal detectors can be used

Thermocouple, Bolometer or Golay detector can be used

5) Amplifier and recorder – Amplifier amplifies the signals from the detector and sends these signals to the recorder. In the recorder system, IR spectra are obtained as a graph of percentage transmission of IR Vs wave no.

Q.3) How many fundamental modes of vibrations are possible in IR spectroscopy
OR

Explain different types of fundamental modes of vibrations in IR spectroscopy.

{6 mks – (2 + 4)}

Ans: Molecules consist of atoms that are bonded by a covalent bond, which is not rigid. The covalent bond between the atoms is elastic and behaves like a spring.

i.e. covalent bonds in the molecule behave as molecular spring and are constantly vibrating with a certain frequency.

Vibrations are of 2 types-

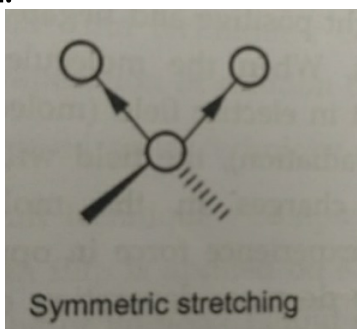
- a) Stretching vibrations
- b) Bending vibrations

a) Stretching vibrations: They are characterized by a **change in internuclear distance**. The distance between the two atoms increase or decrease but atoms remain in the same plane.

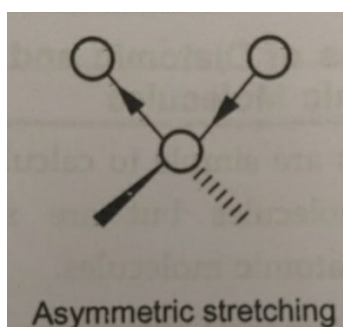
The stretching vibrations are of 2 types.

1) Symmetric stretching vibration: Movement of the atom w.r.t. a particular atom in a

molecule in **the same direction**.



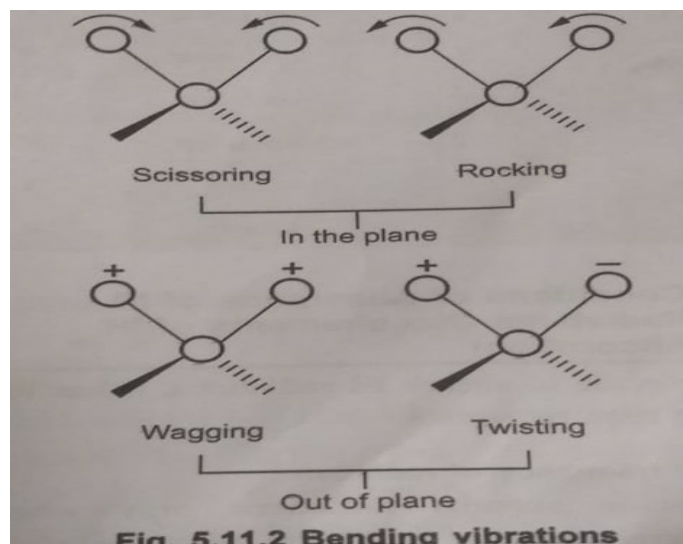
2) Asymmetric stretching vibration: Movement of the atom w.r.t. a particular atom in a molecule in the same plane but **not in the same direction**.



b) Bending vibrations: They are characterized by a **change in the angle between two covalent bonds**, due to change in the position of the atoms relative to the original axis.

The bending vibrations are of 4 types-

- 1) Scissoring vibrations: It involves the movement of two atoms in the opposite direction. This vibration is on the plane.
- 2) Rocking vibrations: It involves the movement of two atoms in the same direction in the same plane. This vibration is in the plane.
- 3) Wagging vibrations: It involves movement of atoms up the plane or below the plane w.r.t. central atom. This vibration is out of the plane.
- 4) Twisting vibrations: It involves movement of one atom up and the other atom down the plane w.r.t central atom. This vibration is out of the plane.



Q.4) Calculate possible no. of fundamental modes of vibrations for linear and nonlinear molecules. {6 mks-(any 3-2 mks each)}

Ans: Number of fundamental vibrations in the molecule can be calculated from its degree of freedom.

1) For linear molecule, the formula is $3N-5$, (N is no. of atoms)

In a linear molecule, only two degrees of freedom are required to describe rotation and three describe translation. Thus the remaining $(3N-5)$ degrees are vibration degrees of freedom

2) For nonlinear molecule, the formula is $3N-6$, (N is no. of atoms)

For a nonlinear molecule, out of the $3N$ degrees of freedom, three describe rotation and three describe the translation and remaining $(3N-6)$ degrees are vibration degrees of freedom.

molecule	No. of atoms(N)	Geometry of molecule	Fundamental modes of vibrations
H ₂ O(water)	3	Non-linear	3
NH ₃ (ammonia)	4	Non linear	6
CH ₄ (Methane)	5	Non linear	9
C ₂ H ₆ (Ethane)	8	Non linear	18
C ₆ H ₆ (Benzene)	12	Non linear	30
NO(nitric oxide)	2	linear	1
CO ₂ (carbon dioxide)	3	linear	4

Q.5) Explain Applications of IR spectroscopy. {5 mks(1 each)}

Ans:

- 1) Determination of structure & functional group – By using a functional group and fingerprint region structure can be determined.
- 2) Study of kinetics of chemical reaction – A comparison between IR spectra of reactants and products can help to determine the progress of a reaction.
- 3) The distinction between intra & intermolecular hydrogen bonding – IR spectroscopy can also distinguish between inter and intramolecular hydrogen bonding
- 4) Detection of impurities – IR spectra of the impure sample will show extra absorption bands. By comparing with pure compounds, the presence of impurity can be detected.
- 5) The study of isomerism – keto-enol tautomerism can be studied by IR spectra.
- 6) Detection of the size of ring ketones – Ring strains in cyclic ketones shift the carbonyl group (stretching frequency) to a higher wavelength.

Q.6) Explain parts of IR spectrum with the range of wavenumber and their significance(6 mks- (2 each))

Ans: The electromagnetic radiations having wavenumber range 12800 to 50 cm^{-1}
IR region is divided into 3 regions-

- a) Near IR region : $12800 - 4000\text{ cm}^{-1}$
- b) Middle IR region : $4000 - 667\text{ cm}^{-1}$
- c) Far IR region : $667 - 50\text{ cm}^{-1}$

This middle IR region further subdivided into functional group region, fingerprint region, aromatic region

- 1) Functional group region – The region extending from 4000 to 1500 cm^{-1}

This part contains absorption bands due to stretching vibrations of functional groups such as O-H, N-H, etc.

- 2) Fingerprint region – The region extending from 1500 to 909 cm^{-1}

This part contains bands due to stretching and bending vibrations.

This region is useful for the identification of compounds.

- 3) Aromatic region –

The region extending from 909 to 67 cm^{-1}

This region is useful for the detection of the aromatic character of the compound.

This part contains bands due to bending vibrations.