

REF BOOKS: Basic concepts of Analytical chemistry - SM Knopku

Engg. Chem - O.G. Palan

Instrumental methods of chemical analysis
UNIT - 5

Page:

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- GR Chatwal

SPECTROSCOPIC TECHNIQUES (18M)

UV Visible

Infra Red

Spectroscopy

Spectroscopy

(9M)

(9M)

Q.5] a - 7M — UV visible OR i normally IR

b - 6M - GR — IQ - 2M UV-visible

2Q - 4M - IR

c - 5M - IR

OR

Q.6] a - 7M — IR

b - 6M - GR — IQ - 2M - IR

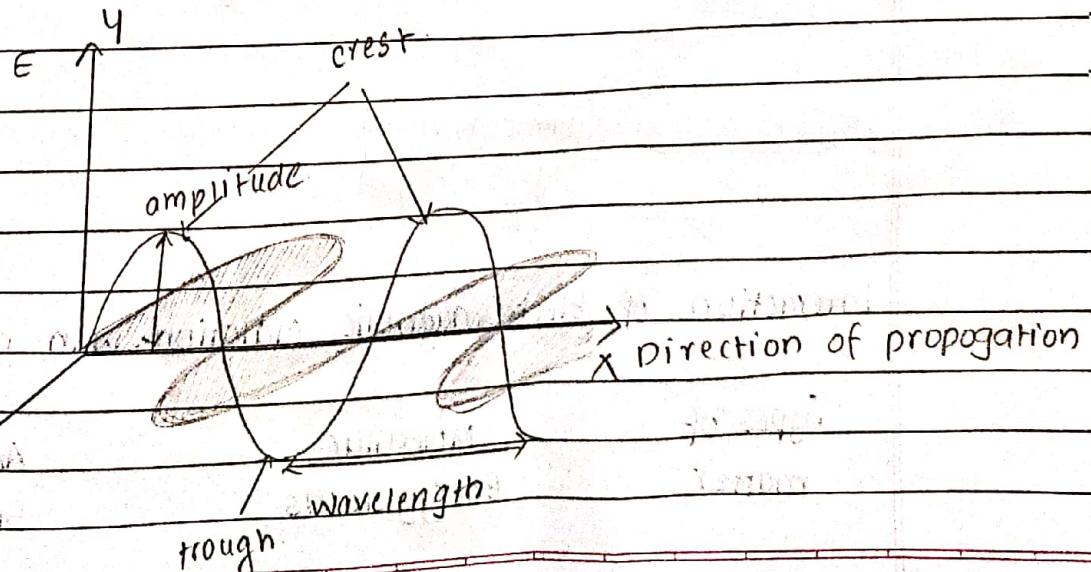
— 2Q - 4M - UV visible

c - 5M - UV visible

NOT IMP

Spectroscopy

It is the branch of science which deals with study of interaction of EMR (Electro Magnetic Radiation) with the substance, matter.



Characteristics of EMR:

- 1) EMR travels along the direction of propagation in presence of electric and magnetic field which is mutually perpendicular to each other.
- 2) It travels with speed of light, i.e. $3 \times 10^8 \text{ m/sec}$
- 3) It consists of discrete energy packets called as photons.
- 4) It possess characteristics of both particle and wave.
- 5) Energy of photon is given by $E = h\nu$ = freq. of radiation.

$$E = h\nu = hc/\lambda \quad \text{where } E: \text{Energy}$$

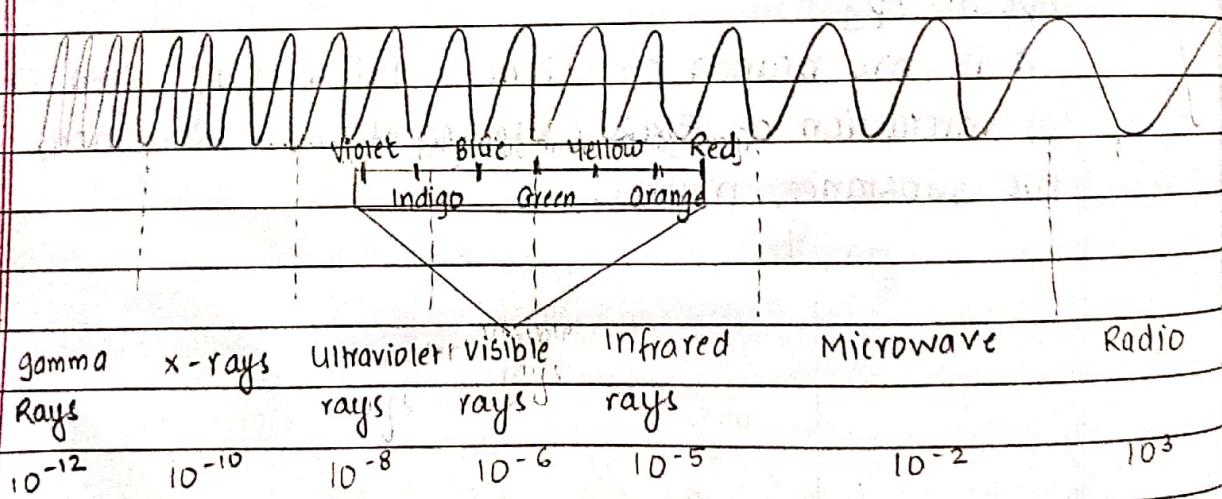
h : Plank's constant

λ : wavelength

c : velocity of light.

Electromagnetic spectrum

It is the entire distribution of electromagnetic radiation according to frequency or wavelength.



Interaction of Electromagnetic radiation with matter:

↓
Types of
matter

↓
Molecular
Energy levels

↓
Absorption
Spectrum

(a) Types of Energies

- ↓
Rotational Energy (Erot)
vibrational Energy (Evib)
Electronic Energy (Eelec)
- Rotation of molecule about the axis passing through centre of gravity - vibration of molecule such as bending or stretching of bonds.
 - Electrons from ground state to excited state.

$$E_{elec} > E_{vib} > E_{rot}$$

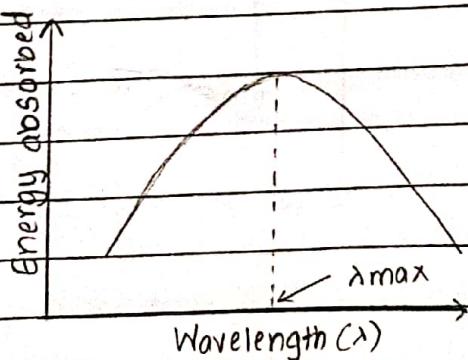
$$E_{total} = E_{elec} + E_{vib} + E_{rot}$$

(b) Molecular Energy levels:

- V. N. Patil MMCOE, Pune
- Rotational Energy level: It requires little energy and occurs in microwave region.
 - Vibrational Energy level: It requires more energy and occurs in IR region.
 - Electronic Energy level: It requires higher energy and occurs in Visible region.

(c) Absorption Spectrum:

At a particular wavelength, absorption is maximum which is called as " λ_{max} " i.e. wavelength of maximum absorption.



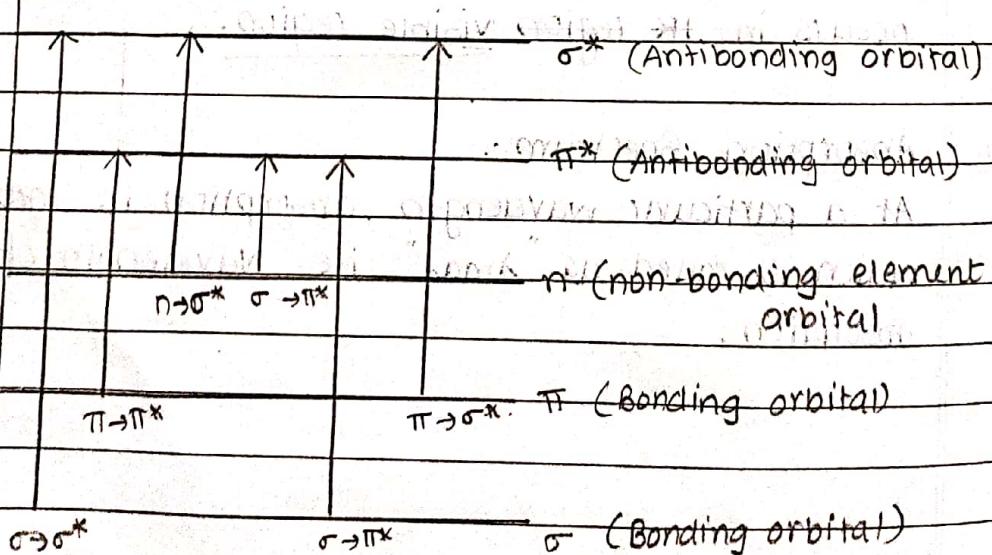
UV visible Spectroscopy.

Range (in nm)	Region
0 - 200	near vacuum or far region
200 - 400	UV
400 - 800	visible
800 onwards	IR

Principle:

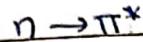
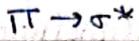
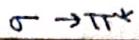
Absorption of UV visible radiations by the sample to be analysed causes electronic excitations, i.e $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ transitions by following Beer's law of absorbance, i.e absorbance is directly proportional to conc. of solution at constant pathlength/ thickness of the solution i.e $A \propto c$ at constant x where x is pathlength or thickness.

Electronic transitions.



Theoretically and
Practically possible
transition

Only theoretically possible
transition.



$\sigma \rightarrow \sigma^*$ transition:

An electron from bonding σ orbital is excited to its antibonding σ^* orbital.

for example: saturated hydrocarbons, i.e. alkanes.

$\pi \rightarrow \pi^*$ transition.

An e⁻ from π orbital is excited to its antibonding π^* orbital.

for example: unsaturated hydrocarbons i.e., alkenes, alkynes, etc.

$\pi \rightarrow \sigma^*$ transition

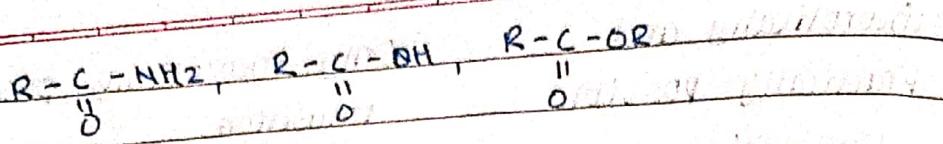
An e⁻ from non-bonding elemental orbital i.e., heteroatoms, halogens is excited to σ^* orbital.

for example: saturated compounds containing N, O, S, halogens like F, Cl, Br, I, etc., ~~etc.~~, R-OH, R-O-R, R-NH₂, R-SH, etc.

$\pi \rightarrow \pi^*$ transition.

An e⁻ from non-bonding elemental orbital i.e., heteroatoms halogens is excited to π^* orbital.

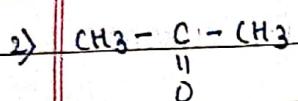
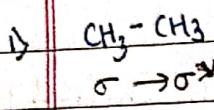
for example: non-saturated compound containing non bonding elements such as O, S, N, Halogens, etc.



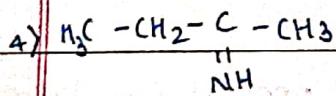
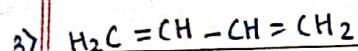
$\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ transitions.

These are not possible practically. Hence they are called as forbidden transitions.

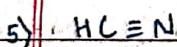
Q) State the possible transitions in following compounds.



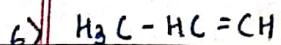
$n \rightarrow \pi^*$



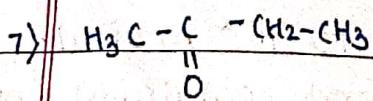
$n \rightarrow \pi^*$



$n \rightarrow \pi^*$

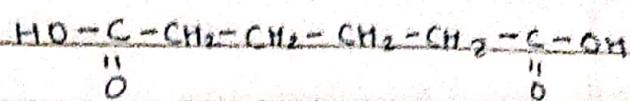


$\pi \rightarrow \pi^*$

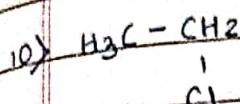


$n \rightarrow \pi^*$

8) Adipic acid

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

9) Hexamethyl diamine.

 $n \rightarrow \sigma^*$  $\rightarrow n \rightarrow \sigma^*$

Absorption laws.

(i) Beer's Law: When a beam of monochromatic light is passed through a transperant solution, decrease in intensity of radiation, i.e. absorbance (A) is directly proportional to concentration (C) of the solution at constant pathlength or thickness (x) of solution.

$$\frac{-dI}{I_0} \propto dC$$

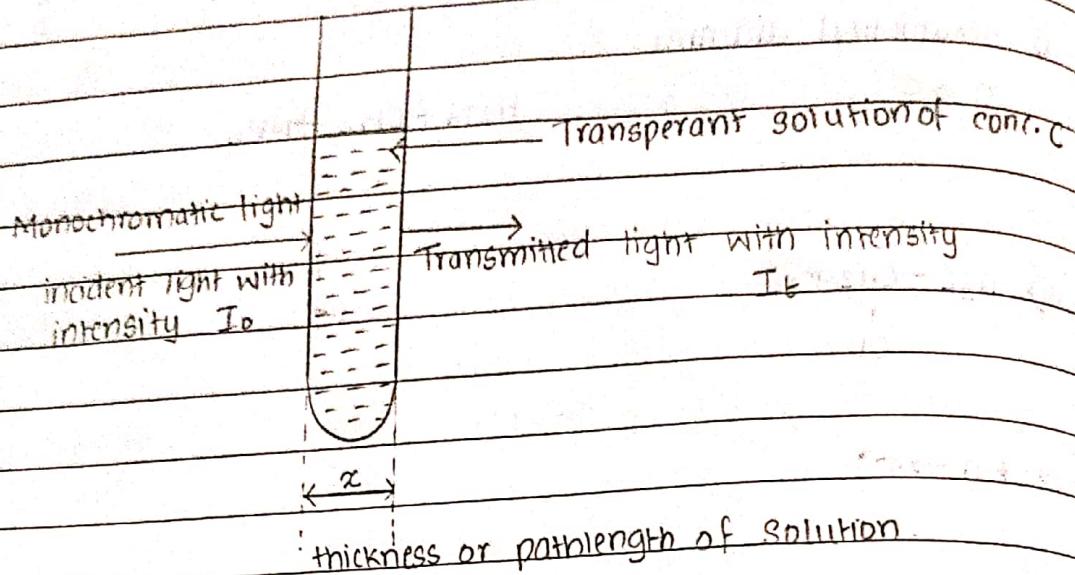
$$A \propto C \text{ at constant } x$$

2) Lambert's law: When a beam of monochromatic light is passed through a transperant solution, decrease in intensity of radiation i.e. absorbance (A) is directly proportional to pathlength or thickness (x) at constant concentration (C) of solution.

$$A \propto x \text{ at concentration } C$$

$$\frac{-dI}{I_0} \propto dx$$

3) Beer Lambert's law.



$$A \propto x \cdot C$$

$$A = a \cdot x \cdot C$$

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where a : absorptivity constant, coefficient

A : Absorbance

x : pathlength

C : concentration

but if x in cm, C is in mol/lit

$$\text{then } A = E \cdot x \cdot C$$

where E is molar extinction coefficient

or molar absorptivity coefficient.

$$A = -\log T$$

$$T = \frac{I_t}{I_0}$$

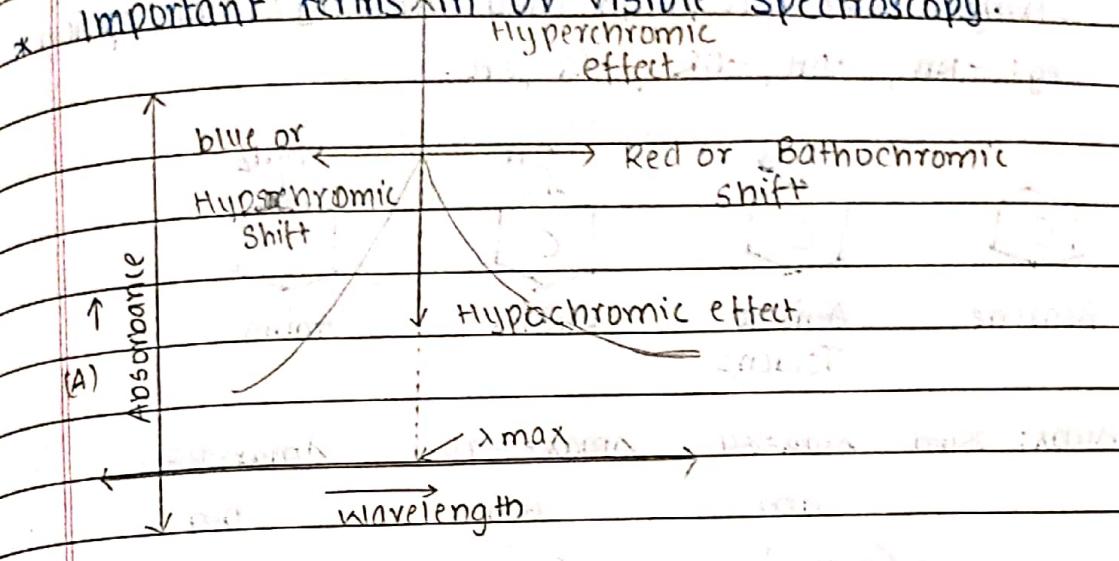
where T is transmittance

I_0 : incident light

I_t : transmitted light.

Statement: When a beam of monochromatic light is passed through transperant solution, then absorbance (A) is directly proportional to the pathlength (x) and concentration (c) of solution.

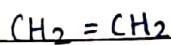
* Important terms in UV visible Spectroscopy.



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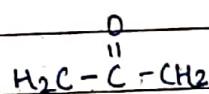
Define the following terms (in each)

1) Chromophore: It is the functional group responsible for $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions i.e. unsaturated compounds containing either $C=C$, $C \equiv C$, $C=O$, $C \equiv N$, $C=S$, NO_2 , etc.



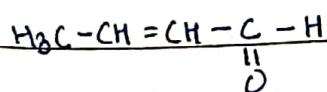
Ethene

$$\lambda_{max} = 171\text{nm}$$



Acetone

$$\lambda_{max} = 279\text{nm}$$

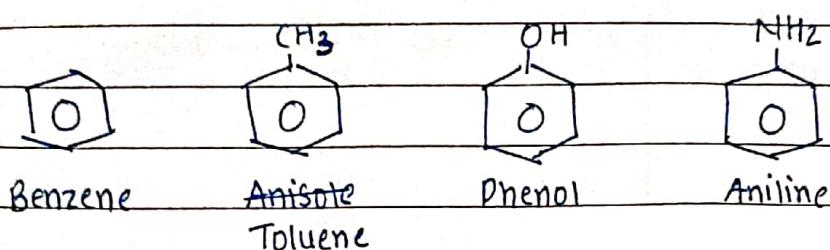


Crotonaldehyde

$$\lambda_{max} = 290\text{nm}$$

2) Auxochrome

It is a functional group with non bonding electrons that does not absorb U-V radiations in near UV region (200-400 nm) but when attached to chromophore, it changes both wavelength and intensity of absorption.
eg: $-\text{NH}_2$, $-\text{OH}$, $-\text{OR}$, $-\text{Cl}$, etc.



$$\lambda_{\max} = 225 \text{ nm} \quad \lambda_{\max} = 269 \text{ nm} \quad \lambda_{\max} = 270 \text{ nm} \quad \lambda_{\max} = 280 \text{ nm}$$

($-\text{CH}_3$ is auxochrome) ($-\text{OH}$ is auxochrome) ($-\text{NH}_2$ is auxochrome)

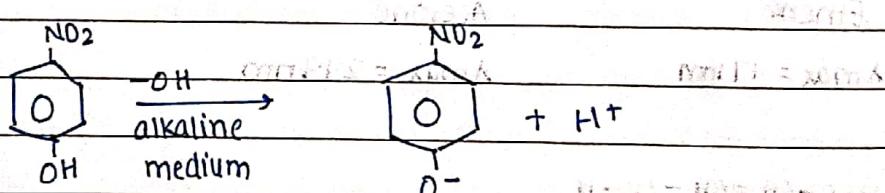
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3) Red or Bathochromic shift.

The shift of absorption ^{to} the longer wavelength.

It occurs due to presence of an auxochrome or by the change of solvent

It is also known as red shift.



p-nitrophenol

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

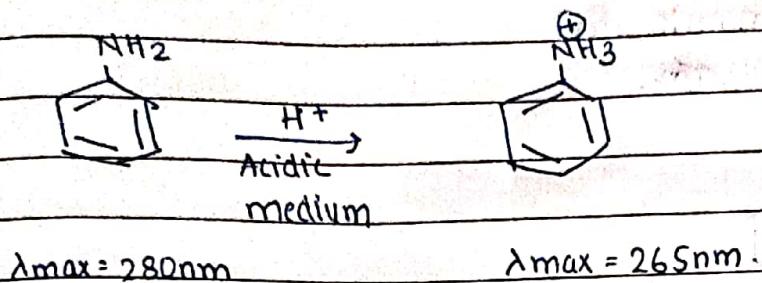
p-nitrophenoxide ion

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

Hypsochromic4) Hypsochromic or Blue shift.

The shift of absorption to the shorter wavelength.

It occurs due to removal of conjugation or change in polarity of solvent.

5) Hyperchromic shift / effect.

An increase in absorption intensity.

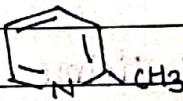
It occurs due to introduction of auxochrome which increases intensity of absorption.

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Pyridine

$$\epsilon = 2750$$



2-methyl pyridine

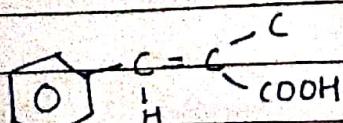
$$\epsilon = 3560 \text{ nm}$$

(-CH₃ auxochrome)

6) Hypochromic effect / shift.

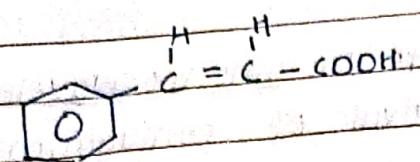
Decrease in intensity of absorption.

It occurs due to introduction of groups which distorts / changes geometry of molecule.

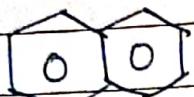


trans-cinnamic acid.

$$\epsilon = 15900$$



cis-cinnamic acid
 $\epsilon = 10700$



naphthalene

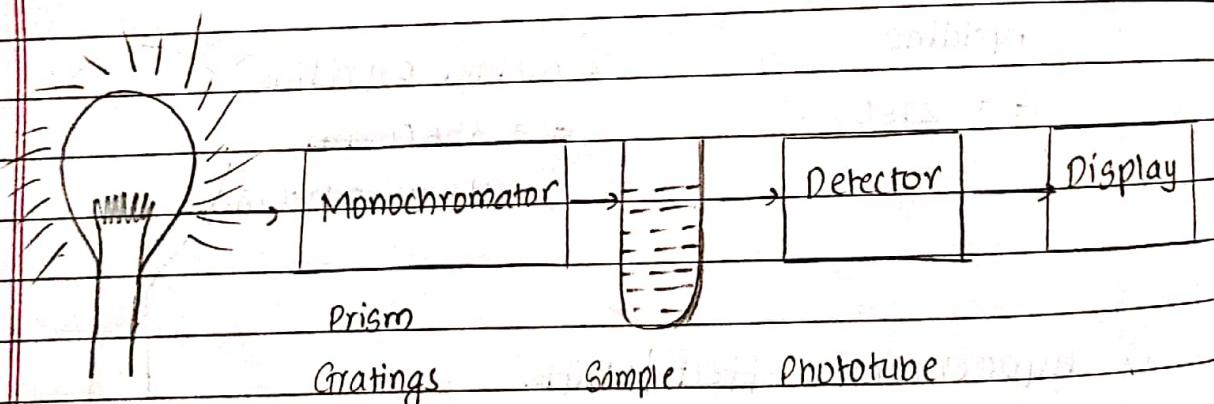
$\epsilon = 19000$



2-methyl naphthalene

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Single beam UV-visible Spectrophotometer:-



Polychromatic source (light)

1) Polychromatic source: (Source of Radiation)

It should have high intensity with desired range of wavelength.

eg: Tungsten filament lamp \rightarrow visible radiation (400-800 nm)

Quartz halogen lamp \rightarrow UV radiation (200-400 nm)

2) Monochromator: It disperses polychromatic light according to wavelength.

eg: Quartz, Prism, Gratings, Coloured filters.

3) Sample Holder | Cuvettes: It is used to hold sample or ref. solution chosen.

eg: Glass cuvettes - for visible Spectroscopy.

Corex or Quartz - for UV Spectroscopy.

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4) Detectors: It converts light energy directly into electric energy.

eg: Photomultiplier tube, phototubes, photovoltaic cells, etc.

5) Amplifier or Recorder: It gives digital values or graphical presentation as absorbance or transmittance.

Applications of UV Visible Spectroscopy

1) Qualitative Analysis \rightarrow

(i) Detection of functional groups.

(ii) Distinguishing conjugated and non-conjugated double bonds.

(iii) Identification of unknown compounds.

2) Detection of geometry of compounds i.e cis & trans isomers.

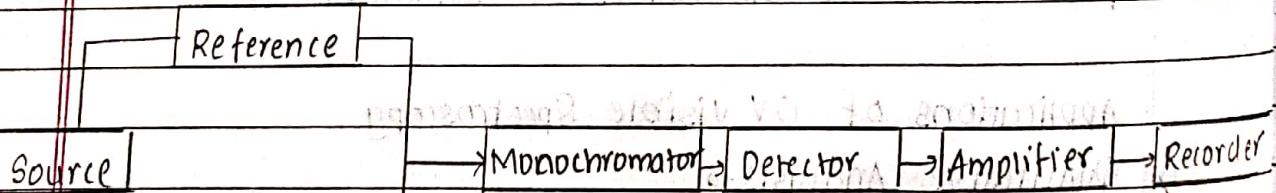
- 3) Determination of mole wt.
- 4) Detection of impurities
- 5) Quantitative analysis - unknown concentration of solution.
- 6) Study of kinetics of chemical reaction

IR (Intra Red Spectroscopy)

It is defined as study of interaction between IR radiations and matter.

Principle: IR is concerned with study of absorption of IR radiations which causes vibrational transition in the molecule, hence it is also known as Vibrational Spectroscopy.

Instrumentation in IR spectroscopy:



Reference

Source → Monochromator → Detector → Amplifier → Recorder

Sample

Source → Monochromator → Detector → Amplifier → Recorder

1) Source of Radiation

(i) a nichrome wire (ii) Nernst glower (iii) Mercury arc
When electrically heated up to 2000°C, they produce mid-IR radiations.

2) Monochromator:

Prisms and gratings are used to disperse different wavelength radiations and lenses/mirrors are used to intensity monochromatic radiations.

3) Sample Cell -

Solid sample - (i) by deposition of solid film by evaporating solvent on KBr plate.

(ii) Solid sample pasted with nujol oil.

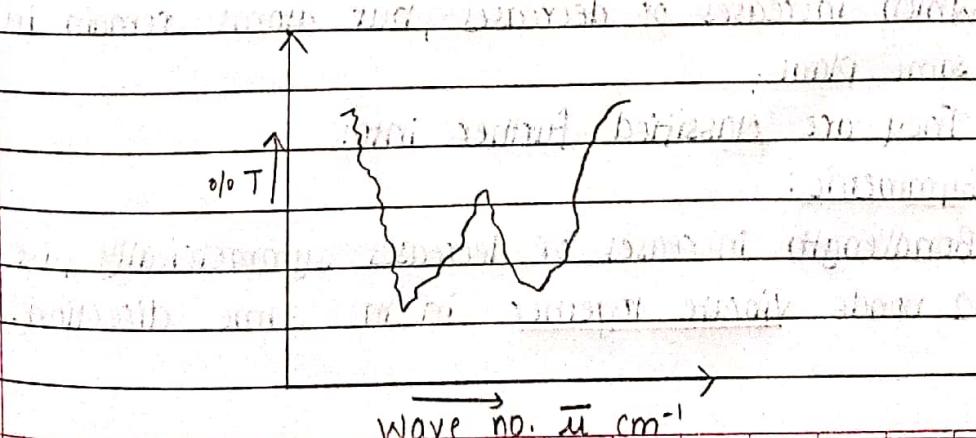
Liquid sample - direct or in the form of solution in suitable solvent, kept in rectangular cell of KBr.

Gas sample - in 10-20 cm long tube.

4) Detector

Photoconductivity cell, Thermocouple, Pyroelectric detector.

5) Recorder - Modern IR instrument which directly give IR spectrum of compound.



Applications of IR spectroscopy.

- 1) Identification of functional group.
- 2) Identification of organic compound.
- 3) Detection of purity of sample.
- 4) Study of kinetics of reactions.
- 5) Crystallinity of polymers.
- 6) Quantitative estimation.
- 7) Detection of geometrical isomers of compound (cis-trans).

Types of vibration in IR spectroscopy.

- Q] Explain modes of vibrations with stretching and bending vibrations in IR spectroscopy.

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Molecular vibrations

Stretching \downarrow vibrations

Bending \downarrow Vibrations.

Stretching vibrations.

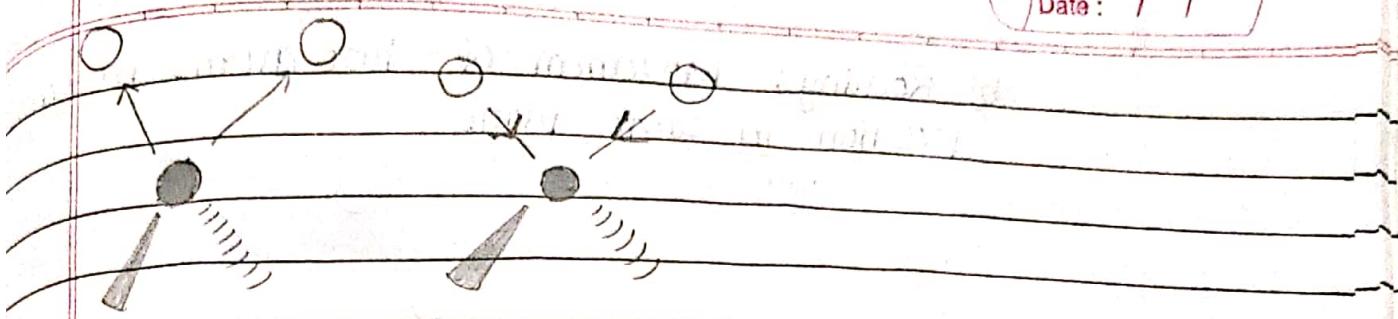
Due to change in internuclear distance between 2 atoms which increases or decreases, but atoms remain in the same plane.

They are classified further into:

- I) Symmetric:

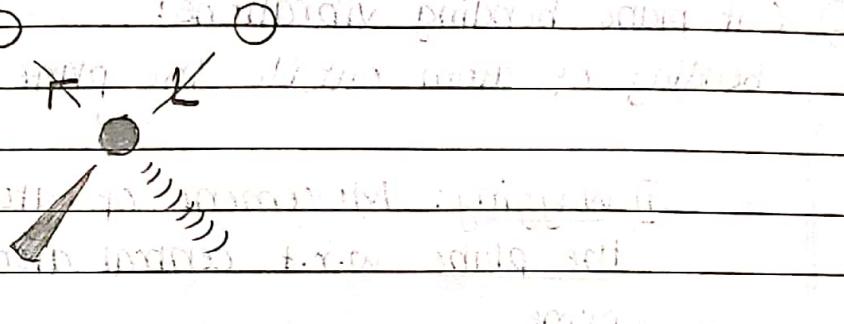
Bond length increases or decreases symmetrically, i.e.

2 bonds vibrate together in the same direction.



2) Asymmetric stretching:

Bond length of one atom increases and the other one decreases, i.e. vibration in same plane but not in same direction.



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Bending vibrations:

Due to change in angle between two covalent bonds.

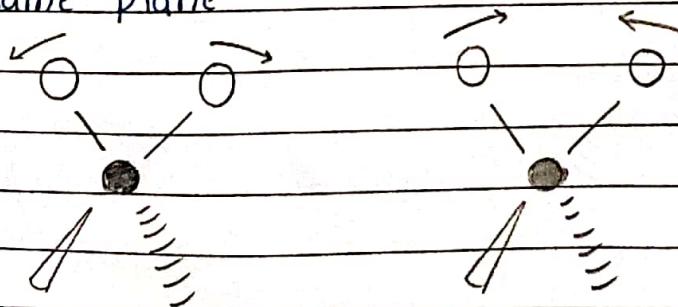
They are classified into 2 types:

i) In plane bending vibrations.

Change of bond angle within the same plane

a) Scissoring:

Movement of 2 atoms in opposite direction i.e. towards each other or away from each other in the same plane



b] Rocking: Movement of two atoms in same direction in same plane

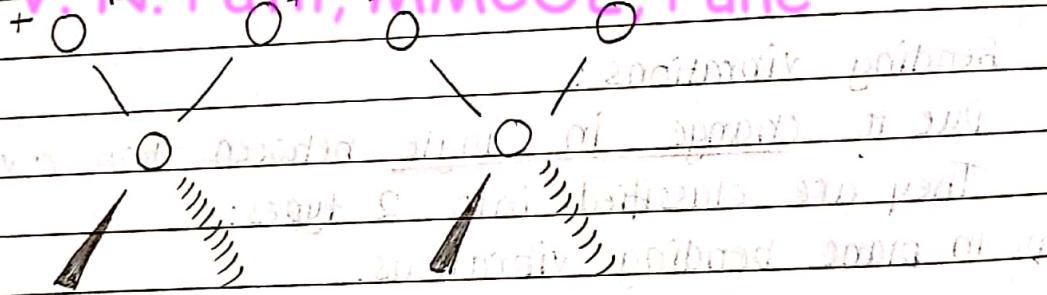


2) Out plane bending vibrations:

Bending of atom outside the plane of the molecule

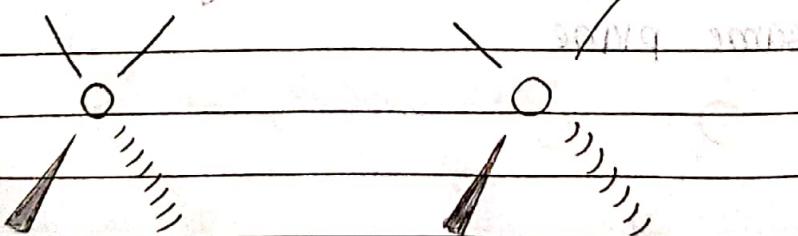
i] Wagging: Movement of atoms up or below the plane w.r.t central atom but out of the plane.

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ii] Twisting: Movement of one atom up and one atom down wrt central atom but out of the plane.

in addition to the above two modes



vibrations of diatomic and polyatomic molecule.

Q] Explain how fundamental modes of vibrations of linear and non linear molecules are calculated with examples.

No. of fundamental vibrations,

Linear	($3N - 5$)
(where N is no. of atoms in the molecule)	

eg: NO, CO₂
for NO, (N = 2)
 $\therefore 3N - 5 = 1$

for CO₂, (N = 3)
 $\therefore 3N - 5 = 4$

Non-linear	($3N - 6$)
(where N is no. of atoms in the molecule)	

eg: H₂O, NH₃, CH₄
For H₂O, (N = 3)

$\therefore 3N - 6 = \underline{\underline{3}}$
For NH₃, (N = 4)

$\therefore 3N - 6 = \underline{\underline{6}}$
For CH₄, (N = 5)

$\therefore 3N - 6 = \underline{\underline{9}}$

For CHCl₃, (N = 5)

$\therefore 3N - 6 = \underline{\underline{9}}$

Parts of IR spectrum with the range of wave number and its significance.

(i) Explain parts of IR spectrum (6M)

IR spectrum (i.e EMR) shows wavelength range 0.78 to 200 μ or wave number range 12800 to 50 cm⁻¹

IR range

Near IR

region

12,800 to 4000
 cm^{-1}

Middle IR

region

4000 to 667
 cm^{-1}

Far IR

region

667 to 50
 cm^{-1}

0.8 to 2.5 μm

2.5 to 15 μm

15 to 200 μm

Middle IR region.

Functional group
region

Finger Print
region

Aromatic Region

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4000 - 1500 cm^{-1}

1500 - 909 cm^{-1}

909 - 667 cm^{-1}

2.5 to 6.5 μm

6.5 to 11 μm

11 to 15 μm

The IR region is further divided into 3 regions,

i.e i) near IR region

2) Middle IR region

3) Far IR region

Middle IR region is further subdivided into

1) Functional group region

2) Finger Print region

3) Aromatic Region

to identify structure of compound.

1) Functional group region. has the

In this region, the range extends from $4000 - 1500 \text{ cm}^{-1}$
($2.5 - 6.5 \mu$)

Region having above range is called functional group region.

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

2) Fingerprint region

In this region, the range extends from $1500 - 909 \text{ cm}^{-1}$
($6.5 \text{ to } 11 \mu$)

Region having above range is called Fingerprint region.

This is the most complex part of IR spectrum which contains large no. of absorption bands due to stretching and bending vibrations.

This region can be used for identification of compounds.

3) Aromatic region.

In this region, the range extends from $909 - 667 \text{ cm}^{-1}$
($11 \text{ to } 15 \mu$)

This part of IR spectrum contains absorption bands due to bonding vibrations in the molecule.

This region is used for detection of aromatic character of compound. It provides information about aromatic compounds containing ortho, meta, para substitution.

Give Reasons.

1) UV spectra are relatively broad as compared to IR spectra.

→ (i) UV visible electromagnetic radiations are more energetic which shows absorption about electronic excitations which are accompanied by vibrational & rotational changes resulting in broad spectra.

(ii) IR electromagnetic radiations are comparatively less energetic which shows absorption about vibrational & rotational changes.

Hence, UV spectra are relatively broad as compared to IR spectra.

2) HCl can undergo stretching vibrations only whereas CO₂ undergoes stretching as well as bending vibrations.

→ (i) HCl is linear diatomic molecule

where N=2

$$\therefore (3N-5) = 1$$

Therefore it can undergo only stretching vibrations which maybe symmetric or asymmetric.

(ii) CO₂ is linear triatomic molecule

where N=3

$$\therefore (3N-5) = 4$$

Therefore it can undergo stretching as well as bending vibrations.

Hz

3) Methane does not absorb IR radiation.

→ 4) Methane has only C-H bonds and can undergo transition for which higher energy is required

- 3) H₂ does not absorb IR radiations
- (i) The ability of molecule to absorb radiations during particular vibration depends on its electrical geometry.
- (ii) There is no net change in dipole moment during vibration of homonuclear molecule like H₂.
- Hence, H₂ does not absorb IR radiations.

- 4) Chloroform gives prominent bands in IR spectrum while CCl₄ does not.
- (i) A molecule is said to be IR active when it undergoes change in dipole moment on exposure of IR radiation.
- (ii) As CCl₄ has symmetrical structure, its net dipole moment is zero.
- (iii) Hence it does not give prominent peak in IR spectrum, whereas chloroform is less symmetrical molecule and shows net dipole moment.
- Thus it gives prominent peak in IR spectrum.

- 5) Acetone and ethanol can be distinguished by using IR spectroscopy.
- (i) Acetone is ketone.
- (ii) Its IR spectra shows characteristic peak at 1715 cm⁻¹ due to carbonyl stretching.
- (iii) Ethanol is an alcohol.
- (iv) It shows characteristic broad peak at 3391 cm⁻¹ due to -OH stretching.

Thus acetone and ethanol can be distinguished by using IR spectroscopy.

6] $\text{H}_2, \text{O}_2, \text{N}_2, \text{Cl}_2$ - these molecules do not absorb IR radiation.

→ (i) One of the most important condition for IR absorption is that the molecule can only absorb IR radiation when its absorption causes a change in dipole moment, i.e. electric dipole.

(ii) $\text{Cl}_2, \text{H}_2, \text{O}_2, \text{N}_2$ molecules do not possess electric dipole, i.e. it does not show dipole moment.

Hence these molecules do not absorb IR radiation.

7] Fundamental modes of vibration for H_2O are 3.

→ fundamental modes of vibration for H_2O are 3 because H_2O is non-linear molecule.

(i) To calculate fundamental modes of vibration for non-linear molecule, the formula is $(3N-6)$, where N is no. of atoms, i.e. 3.

(ii) Thus the answer for $3N-6$ for H_2O is 3.

Hence it is proved.

8] $\text{KBr}, \text{NaCl}, \text{LiF}$ are used for repairing samples for IR Spectroscopy.

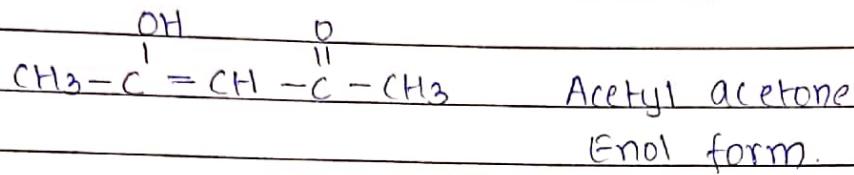
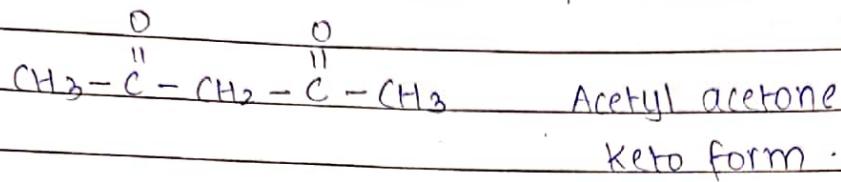
→ (i) Material containing sample must be transparent to the IR radiation, so that the material made out of certain salts like KBr, NaCl and LiF etc are used which do not absorb IR radiation.

9] Keto and enol form can be distinguished by IR spectroscopy.

→ (i) One of the application of IR spectroscopy is to study isomerism.

(ii) Keto-enol tautomerism can be studied by IR spectra.

(iii) IR spectra shows characteristic absorption of carbonyl group for keto form whereas a broad -OH band and C=C stretching frequencies for enol form.



[iv] Intermolecular and intramolecular hydrogen bonding can be identified by IR spectroscopy.

→ (i) One of the application of IR spectroscopy is distinction between intermolecular and intramolecular Hydrogen bonding.

(ii) This is done by taking series of IR spectra of a compound at different dilutions.

(iii) As dilution increases, the absorption band due to intermolecular hydrogen bonding disappears while that of intramolecular hydrogen bonding remains unchanged.

Thus, intermolecular and intramolecular hydrogen bonding can be identified by IR spectroscopy.