INFRARED ABSORPTION SPECTROSCOPY

IR radiation refers to broadly to that part of the electromagnetic spectrum between the visible and microwave region i.e . 4000-667cm-1(2.5-1.5µ)

NEAR IR 0.8-2.5 µ (12500-4000cm-1)
MID IR 2.5-1.5 µ (4000-667cm-)
FAR IR 1.5-200 µ (-667-50cm-1)

The absorption of ir radiation can be expressed in term of wavelength λor in wave number (ʉ). Mostly ir spectra of organic compound are plotted as % transmittance vs wave number. (ʋ).
Wave-number (ʉ). = 1 / λin (cm)
if wavelength is 2.5 **µ= 2.5 X 10^{-4}cm then** wave number = 1/ 2.5 X 10^{-4}cm =4000cm^{-1}
(1 **µ = 10^{-6} meter =10^{-4}cm) so** wavelength in (cm^{-1}) = 10000/ wavelength in micron **µ.**

PRINCIPLE- The absorption of ir radiation cause an excitation of molecules from lower to higher vibrational leval. Ir spectroscopy or vibrational spectroscopy is concerned waith the study of ir radiadtion which result in vibrtional transition.
Energy of molecules = translational + vibrational +rotational energy.
The two atoms joined together by a chemical bond (may be single, double or triple bond), can be composed as two balls joined by a spring. The application of a force like **STRETCHING** of one or both the balls (atoms) away from each other or closer to each other (ii) **BENDING** of one of the atoms either vertically or horizontally and then release of the force results in the vibrations on the two balls (atoms). These vibrations depend on the strength of the spring and also the mode (stretching or bending) in which the force is being applied. We know that at ordinary temperature, molecules are in constant state of vibrations this is **called natural frequency of vibration.** When the frequency of incident electromagnetic radiations is equal to the natural frequency, the radiation is absorbed and vibrational levels of the molecule are excited and peak is observed.
Criteria for a compound to absorb IR radiation .
1-Change in dipole moment
2-Applied IR frequency = natural frequency of vibration.
Otherwise compound don't **give peak in I.R.**

Hooke's law and Absorption of radiations
The band positions in the IR spectrum are presented in wave numbers (□) whose unit is the reciprocal centimeter (cm^{-1}). □ is proportional to the energy of vibration.

$$\Delta E = h\upsilon = hc / \lambda = hc\ \square$$

Therefore, in principle, each absorption of radiation in the infrared region is quantized and should appear as sharp line. However, each vibrational transition within the molecule is

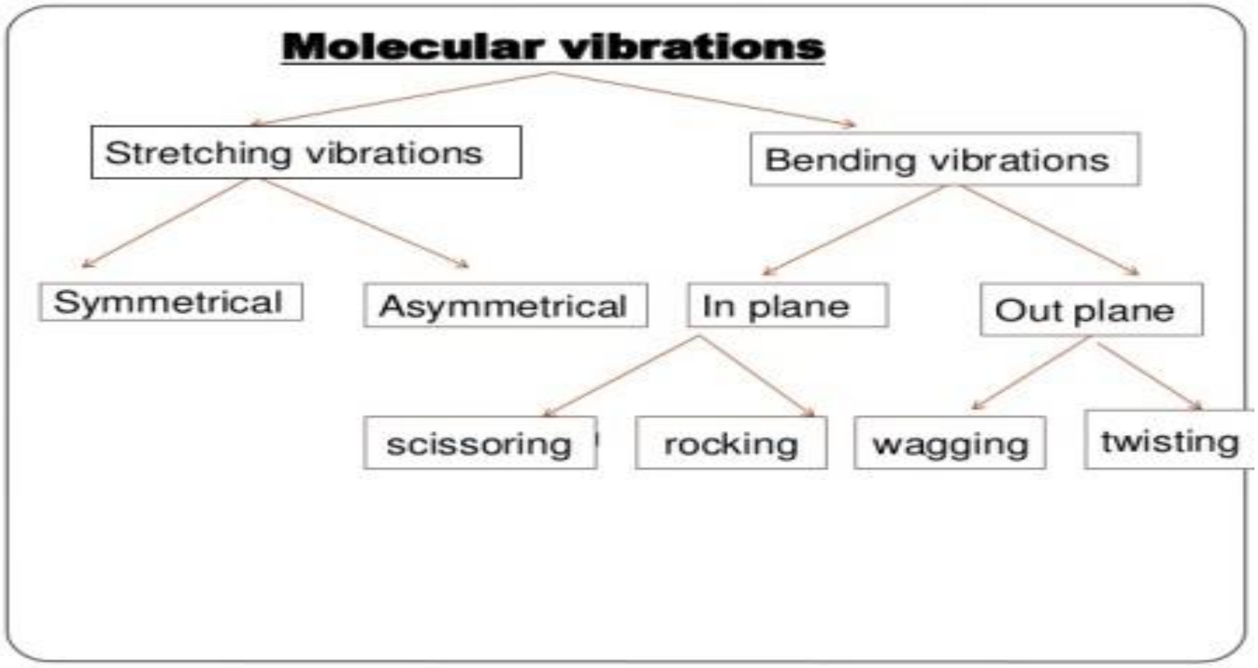
Associated with number of rotational energy changes and thus appears as combination of vibratioal -rotational bands.

The approximation to vibration frequency of a bond can be made by the application of Hooke’s law. In Hooke’s law, two atoms and their connecting bond are treated as a simple harmonic oscillator composed of two masses joined by a spring and frequency of vibration is stated as

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

Where $\bar{\upsilon}$ = the vibrational frequency (cm^{-1})
c = velocity of light (cm/s)
K = force constant of the bond (dyne/cm)
m1 and m2 = masses of the two atoms
The quantity (m1 m2) / (m1 + m2) is often expressed as μ, the reduced mass of the system.

TYPE OF VIBRATION.



(1) STRETCHING VIBRATION (2)- BENDING VIBRATION

These are vibration in which bond length is altered i.e. increased or decreased. There are 2 sub types

(a)- **Symmetrical stretching.** in which two bond. Increased or decreased in length symmetrically.

(b) **Asymmetrical stretching** in which when one bond length is increased the other one decreases

(2)- BENDING VIBRATION

(a) IN PLANE BENDING: in this vibration there is no change in bond angle. Bending of bonds takes place within the same plane.

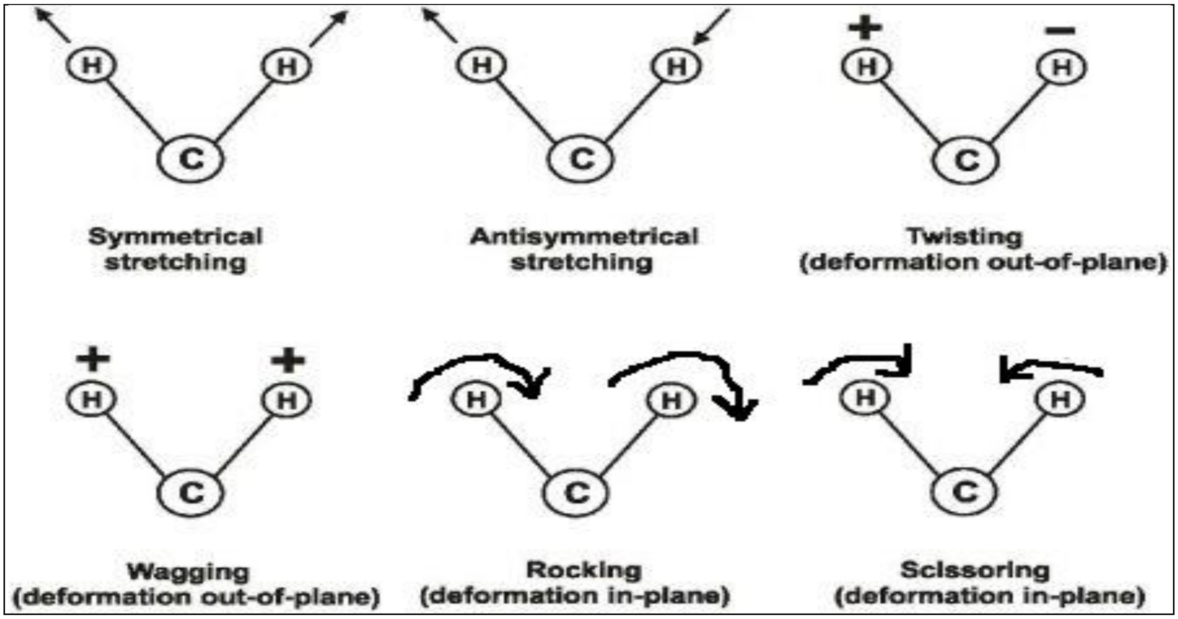
(i) **SCISSORING**: in which bond angle decreases.

(ii) **ROCKING:** in which bond angle is maintained. But both bonds move within plane.

(b). **OUT OF PLANE BENDING:** outside the plane of molecules

(i) **WAGGING**: in which both atom move to one side of plane.

(ii) **TWISTING:** in which one atom is above the plane and the other is below the plane.



Modes of molecular vibrations:
If a molecules conatin n atom ,the total number of fundamental vibration can be expressed as

(3n-6); for non-linear molecules
(3n-5) linear molecule

DEGREE OF FREEDOM FOR (**i) CO_2, (ii) H_20, (iii) C_6H_6**

For CO2 - it is a linear molecules n=3 DOF=3x3-5=4, for H_2O= it is non linear So DOF=3

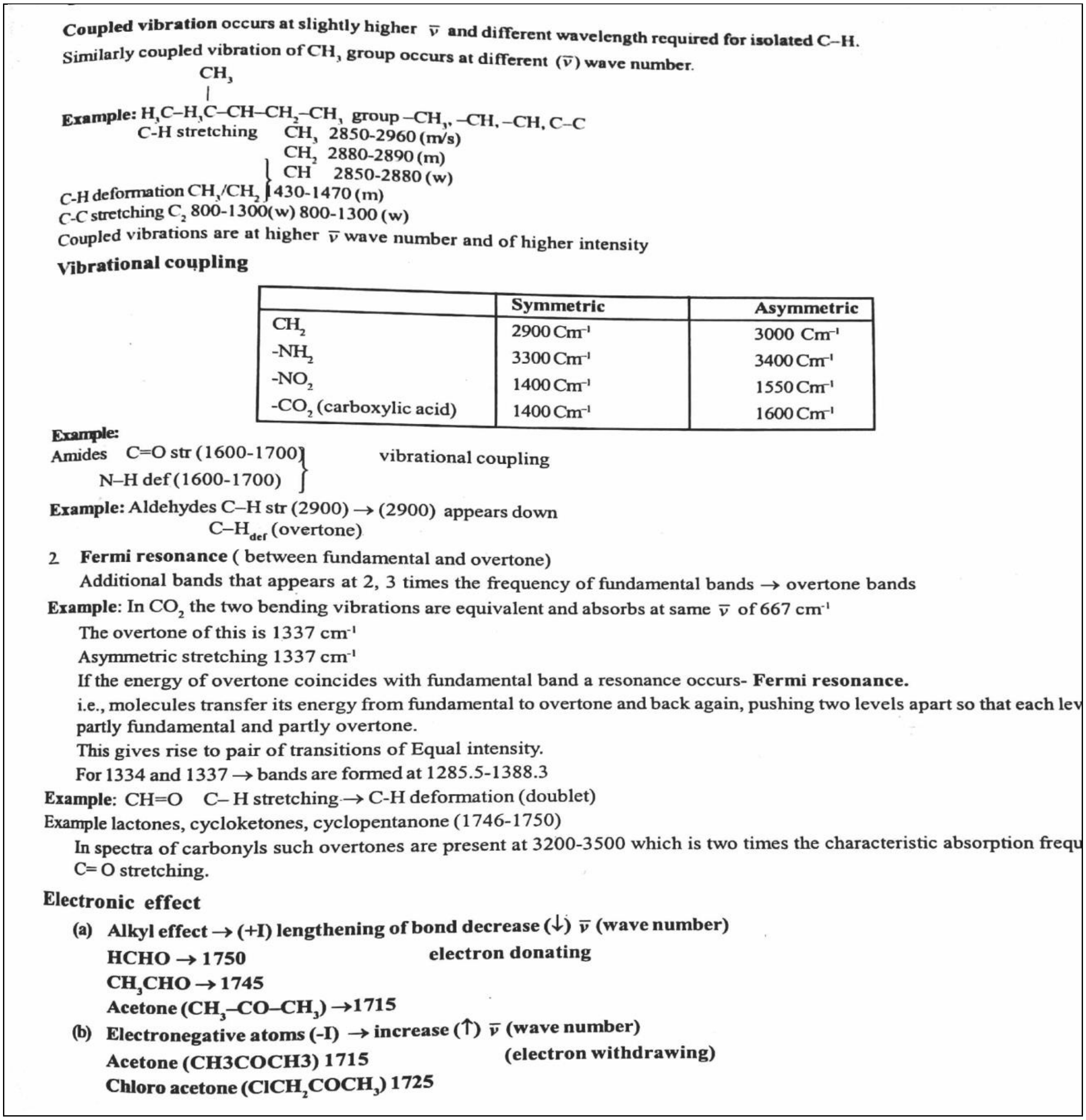
FOR C_6H_6 it is non linear n=12 3x12-6=30 So DOF=30

FACTORS AFFECTING ABSORPTION BAND-

1- VIBRATIONAL coupling **(**between fundamental bands**).** Actul band are called as fundamental and.

-CH- bond . (1) stretching **-CH2- (2) stretching(s+a)**

When asymmetric vibration ocuurs at slightly higher wave number compared to symmetric vibration known as coupled vibration.



Coupled vibration occurs at slightly higher $\bar{\nu}$ and different wavelength required for isolated C–H.

Similarly coupled vibration of CH_3 group occurs at different ($\bar{\nu}$) wave number.

Example: $H_3C-H_3C-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_3$ group $-CH_3$, $-CH$, $-CH$, C–C

C-H stretching CH_3 2850-2960 (m/s)

CH_2 2880-2890 (m)

CH 2850-2880 (w)

C-H deformation CH_3/CH_2 1430-1470 (m)

C-C stretching C_2 800-1300(w) 800-1300 (w)

Coupled vibrations are at higher $\bar{\nu}$ wave number and of higher intensity

Vibrational coupling

	Symmetric	**Asymmetric**
CH_2	2900 Cm^{-1}	3000 Cm^{-1}
$-NH_2$	3300 Cm^{-1}	3400 Cm^{-1}
$-NO_2$	1400 Cm^{-1}	1550 Cm^{-1}
$-CO_2$ (carboxylic acid)	1400 Cm^{-1}	1600 Cm^{-1}

Example:

Amides C=O str (1600-1700) } vibrational coupling

N–H def (1600-1700) }

Example: Aldehydes C–H str (2900) → (2900) appears down

$C-H_{def}$ (overtone)

2 **Fermi resonance** (between fundamental and overtone)

Additional bands that appears at 2, 3 times the frequency of fundamental bands → overtone bands

Example: In CO_2 the two bending vibrations are equivalent and absorbs at same $\bar{\nu}$ of 667 cm^{-1}

The overtone of this is 1337 cm^{-1}

Asymmetric stretching 1337 cm^{-1}

If the energy of overtone coincides with fundamental band a resonance occurs- **Fermi resonance.**

i.e., molecules transfer its energy from fundamental to overtone and back again, pushing two levels apart so that each lev partly fundamental and partly overtone.

This gives rise to pair of transitions of Equal intensity.

For 1334 and 1337 → bands are formed at 1285.5-1388.3

Example: CH=O C– H stretching → C-H deformation (doublet)

Example lactones, cycloketones, cyclopentanone (1746-1750)

In spectra of carbonyls such overtones are present at 3200-3500 which is two times the characteristic absorption frequ C= O stretching.

Electronic effect

(a) Alkyl effect → (+I) lengthening of bond decrease (↓) $\bar{\nu}$ (wave number)

$HCHO \rightarrow 1750$ **electron donating**

$CH_3CHO \rightarrow 1745$

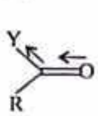
Acetone ($CH_3-CO-CH_3$) →1715

(b) Electronegative atoms (-I) → increase (↑) $\bar{\nu}$ (wave number)

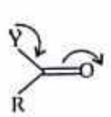
Acetone (CH3COCH3) 1715 **(electron withdrawing)**

Chloro acetone ($ClCH_2COCH_3$) 1725

(c) Conjugation decrease (↓) $\bar{\nu}$ of C=O and C=C



Inductive effect
eg. ester
(Stronger bond,
high frequency



Resonance effect
eg. Amides
(Weaker bond,
Lower frequency)

$R-\overset{O}{\overset{\|}{C}}-(O-R)$ o-CH$_3$

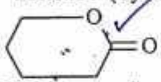
$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$

	Y	C = O
Inductive	Cl	1815
	Br	1812
	OH	1760
	OR	1705
Resonance	NH$_2$	1695
	SR	1720

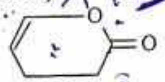
$CH_3-\overset{O}{\overset{\|}{C}}-Cl$ = 1815
↳Br → 1812
$CH_3-\overset{O}{\overset{\|}{C}}-(OH)$ → 1760
$CH_3-\overset{O}{\overset{\|}{C}}-(OCH_3)$ = 17
$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$
$CH_3-\overset{O}{\overset{\|}{C}}-S-CH_3$

OH > OCH$_3$

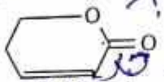
sp^3 Lactone :- (Cyclic esters) sp^2 Resonance (X) sp^2



1735 (Saturated)

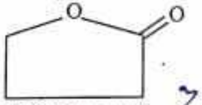


1760

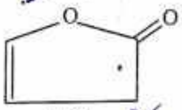


1720

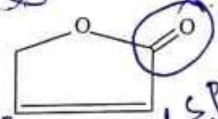
Ring size



1770 (Saturated) sp^3

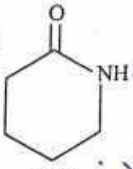


1800 sp^2

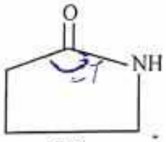


1770 α sp^2

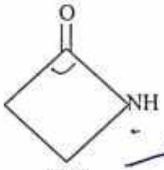
Lactam :-



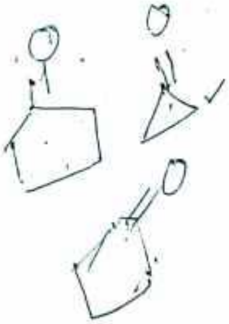
1660 six



1705 five



1745 → four



Hydrogen bonding

1. **Stronger the H$_2$ bond greater is wave number**
   O–H 3600 cm^{-1}
   N–H 3400 cm^{-1}
2. **Stronger the H$_2$ bond greater the frequency shifts**

	Normal	H$_2$ bonded.
O–H	3600	3300
N–H	3400	3300

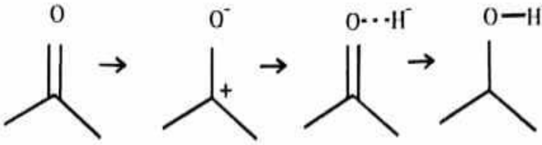
The H$_2$ bond can be regarded as resonance hybrid therefore H$_2$bond involves lengthening of original O–H bond. Bond is weakened (k↓) so stretching frequency is decrease (↓).

3. **Intermolecular H_2 → broad bands, concentration dependent**
Intermolecular H_2 bonds → sharp bands, concentration Independent

4.  –OH phenols: Strong H_2 bond → broadening

O- - - - OH
II I

5. CH_3–C–CH–CH–CH_3 Enols: H_2 bonding is strong and because of protonation and increase in single bond character and longer length → causes lowering of vibration (2800) ($\bar{\nu}$) wave number.



6. Use solvent CCl_4, $CHCl_3$, CS_2 → (No H_2 effect)
Benzene or acetone → influence OH, NH absorptions

7. Carbonyl group/ aromatic ring has same effects like H_2 bond

Finger print region

8μ-50μm (1250-200) cm^{-1} **vibrational + Rotational**

1. Doublet near 1380 → 3° butyl
2. Singlet near 1380 → Gem dimethyl
3. 1350 → Nitro
4. Primary alcohol/esters → 2 strong bonds → 1050 and 1350 (C–O)
5. Phenol (C–O) → 1200
6. Ethers (C–O) → 1070-1150
7. Cis alkenes (700) Trans alkenes (960)
8. Mono substituted benzene (700-750)

Instrumention

① IR radiation source
(II) Monochromator
(III) Sample cell
(IV) Detector.

- IR radiation can be produced by electrically heated a source.

(I) Nernst filament (II) Globar (III) Incandescent lamp.

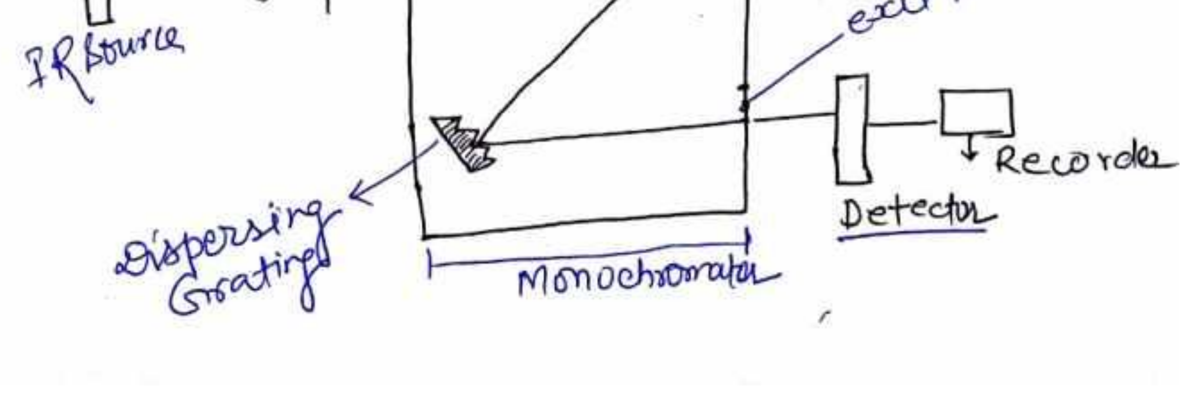
→ Nernst filament → It is fabricated from oxide of zirconium, thorium & cerium.

→ Globar source: → It is a rod of sintered (SiC)

: (Monochromator) → prism monochromator
→ Grating monochromator

→ prism is made up of LiF, KBr, NaCl, CsF

Grating is made up of alkali halide.

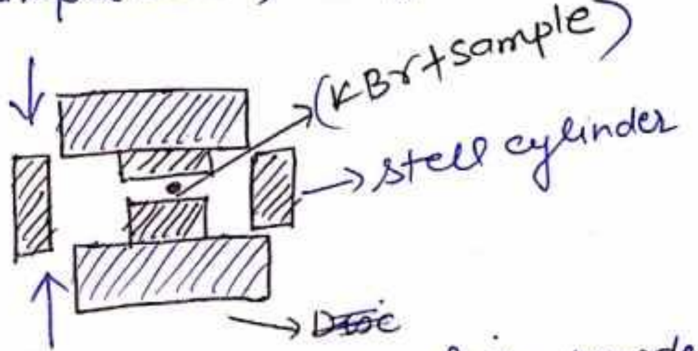


⇒ Sample handling Technique ->

Solid → pellet Technique
→ Mulling Technique.

-> pellet technique: sample is mixed with wt. Amt of powdered KBr and the mixture is Admitted to a pressure of several tones in a die to produces a highly transparent plate or Disc which can be introduced into the spectrophotometer.

$\text{KBr} + \text{sample} \xrightarrow{\text{pressed}} \text{to form Disc (pellete)}$



-> (mulling Technique) - In which powder sample is mixed with nujol (parafin oil)/mineral oil to form a paste. which is sandwich b/w salt plate.

-> (Liquid) -> Sample can be held using a Liquid sample cell made up of Alkali halide. (NaCl, KBr)

-> Gases: -> Absorption spectra of gases can be measured in a wide variety of Gases cell ranging from a few centimeter to several meter that can be directly placed in the path of infra-red beam.

Solvent → we use non-Aqueous solvent. b/c · Sample cell are made up of NaCl. when use aqueous solvent it dissolve NaCl or interfere in spectrum.

→ "CS_2, $CHCl_3$, CCl_4,"

(Detector -)

→ Detector used in IR spectrophotometer usually Convert the thermal radiant energy into electrical energy.

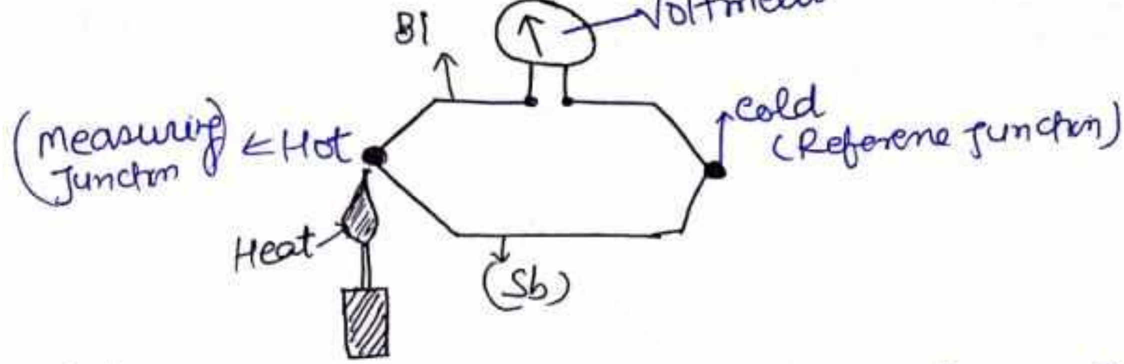
① Thermal Detector - In which IR radiation producing a heating effect that alters the some physical properties of the Detector.

Ⅱ (photon detector) - which use the Quantam effect of I.R. radiation to change the electrical properties of a semi-conductor.

(i) Thermo copule (ii) Bolometer (iii) Thermistor
(iv) Golay cell (v) photoconductivity ~~cell~~ detectors
(vi) semi-conductor Detector (vii) pyroelectric Detector.

- Thermal detector sense Temperature change by change in physical properties such as generation of voltage or change in Resistance. The Response of the Thermal detector is Independent of the wavelength of the incident radiation.

(Thermocouple) -



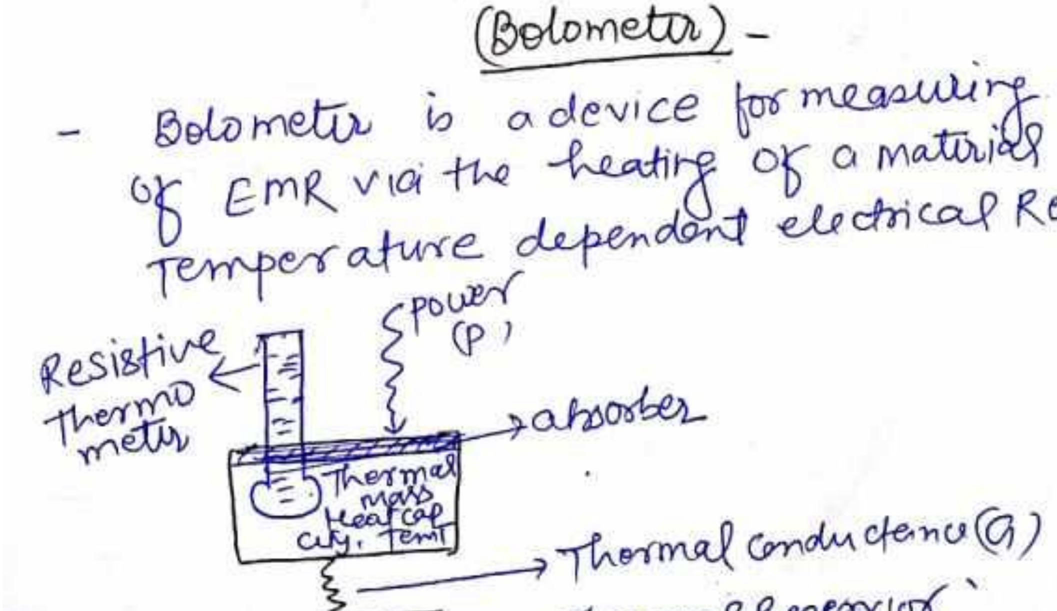
The Thermocouple is fabricated with two Dissimmila metal such as Bismuth & Antimony which produces a small voltage proportional to the temperature of Junction. Half of the junction is hot and alternative junction are cold. that are thermally bonded to the substrate and remain at lower Temperature.

Sensitivity of Thermocouple → [−240°C — 3000°C]

IR increses temperature of Junction. Due to Temperature Difference b/w two point potential Difference is created leads to flow of electricity.

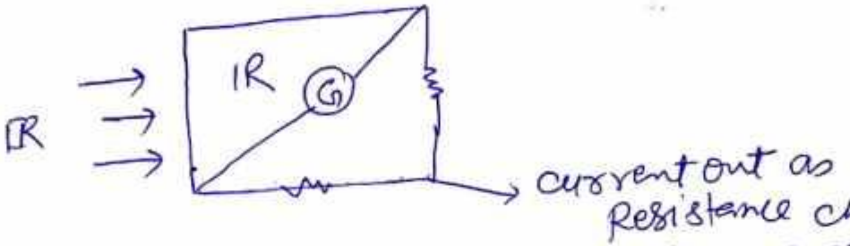
(Bolometer) -

- Bolometer is a device for measuring the power of EMR via the heating of a material with a Temperature dependent electrical Resistance.



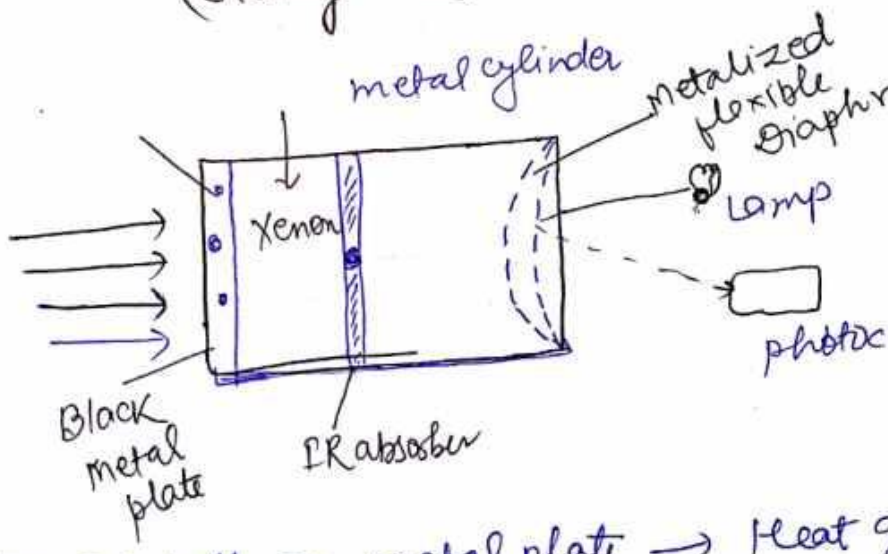
power 'p' from the incident signal is absorbed by the · Bolometer & heat up a thermal mass with capcity 'c' and temperature T. The Thermal mass is connected to a reservior of Constant Temperature through a link with Thermal Conductance G.

→ The charge in Temperature is Read out with a Resistive Thermameter ·



IR fall on the conductor, Temperature charge. As Temperature charge. Resistance charge, which is Determined by current.

(Golay cell)

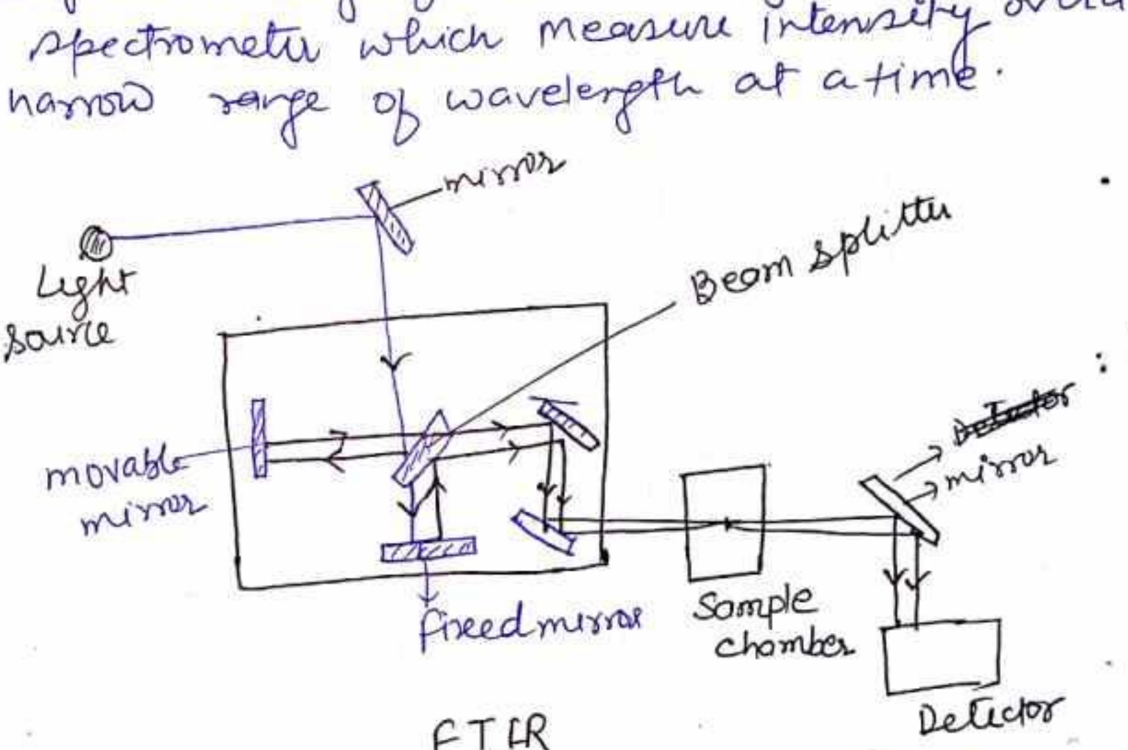


when IR falls on metal plate → Heat gas → expand → Deform diaphragm

Light from Lamp is made to fall on diaphragm → Reflect on photocell (Any deviation is determined.

FTIR (Interferometer)

Fourier transform infra-Red spectroscopy is a. Technique which is used to obtain an Infra-Red spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collect high spectral resolution data over a wide spectral range. This Conferes a significant advantage over a dispersive spectrometer which measure intensity over a narrow range of wavelength at a time.



FTIR

→ The michelson interferometer, which is core of FTIR spectrometer, is used to split one beam of light ~~in~~ into two so that the path of the Two beams are different. Then the two beam Recombine & conduct them into the Detector where the Difference of the Intensity of these two beams are measured as a function of the Difference of the path.

Advantage) - It is rapid, more sensitive and Accurate.

Fourier Transform I.R.	Dispersive I.R
① To improve Resolution a larger beam may be used	① small amount of IR. beam may be allow to pass through slit
② All frequency of radiation falls on the detector simultaneously	⑪ only radiation of narrow frequency range fall on the detector at any time
③ Straight line dont affect the detector, since all signal are modulated	(iii) cause spurious reading
④ Any emission of I.R. radiation by the sample will not be detected	(iv) Any emission of I.R. radiation falls on the detector is detected.
⑤ The sample is not subject to thermal heat	⑤ The ~~subject~~ sample is subject to thermal heat
⑥ Only the mirror moves during an experiment	many moving mirror are used
⑦ $4000 - 667\ cm^{-1}$	$2000 - 667\ cm^{-1}$

→ Application of I.R. spectroscopy -

① Identification of functional group & structure elucidation

The entire IR Region is divided into

Group frequency Region → $4000 cm^{-1}$ – $1500 cm^{-1}$

finger print Region → $1500 cm^{-1}$ – $500 cm^{-1}$

In the group frequency region, the peaks corresponding to different functional group can be observed.

→ Every part of the molecules has different atoms are connected by bonds, Each bond Requires different I.R. region for absorption and so characteristics peaks are observed. Hence this Region of IR spectrum is called as the finger print Region of the molecules

② Identification of Drug substance

③ Identifying the impurities in a drug sample.

④ Study of Hydrogen bonding
  - Intermolecular
  - Intramolecular

⑤ Study of polymer.

⑥ Structure elucidation

⑦ Identification of organic compound.

⑧ Study of chemical Rexn

⑨ study of Keto-enol tautomers

⑩ Conformational Analysis

⑪ Geometrical Isomers

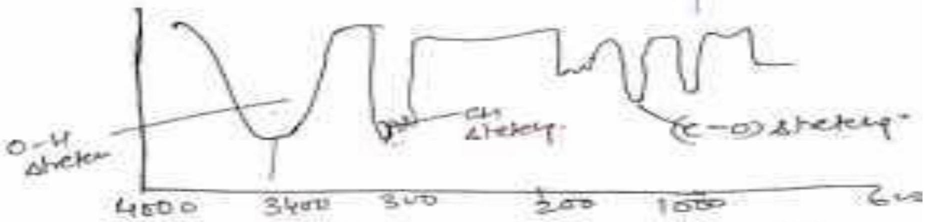
⑫ Ratio of cis-Trans isomers in a mixture of compounds

⑬ Qualitative Analysis ⑭ Quantitative Analysis

(IR spectra of ~~simple~~ compound) –

① CH_3-OH

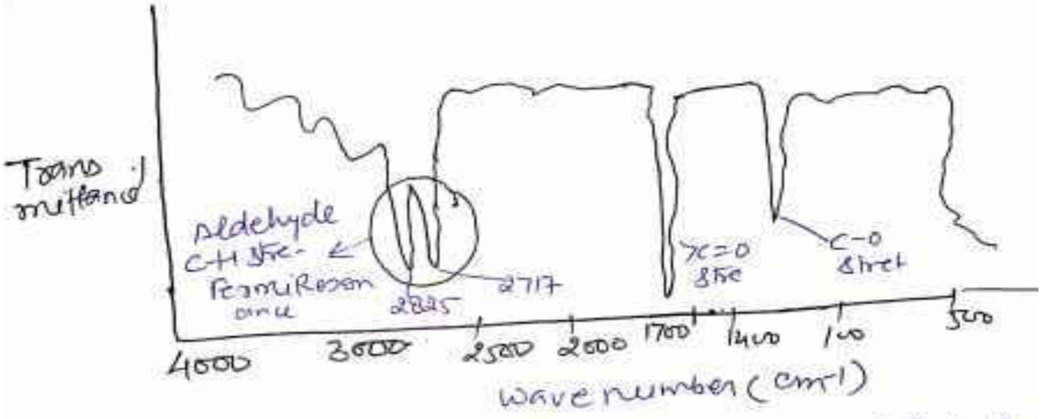
group	Stretching (wave number
$-O-H$	3400 cm⁻¹
$-C-H$ / str	2920 cm⁻¹
$C-O$	1138 cm⁻¹



(IR spectra of ethanol)

Ⓑ $C_6H_5-\overset{O}{\overset{\|}{C}}-H$

	wave number (cm⁻¹)
$-C-H$ stretching	2825, 2717 cm
$>C=O$	1710 cm⁻¹
$-C=C-$	1510 cm⁻¹
Aromatic C-H stretching	3010 cm⁻¹



(IR spectra of Benzaldehyde