



# Chemistry

## Syllabus.

### Unit 1.

Electronegativity

Electron affinity

Ionisation Energy

P<sup>n</sup>.

Normality, Molarity, Molality.

] periodic Table basics

### Unit 2.

Pollution.

→ Air

→ Water

→ Soil

→ Marine

→ Any 1 case study.

### Unit 3.

Spectro-photometric Study

Chromatographic Study

Thermogravimetric analysis.

### Spectrophotometric studies

① Absorption

② Emission

based on wavelength :-

Lambert's law

a) Ultra-violet - Visible → Beer Lambert's law.

b) Infrared

c) NMR or H' NMR (Nuclear Magnetic Resonance  
or Proton " " " )

Based on  
source  
application  
find out

UV-VIS  
Laws

UV lamp

• Saturation

• Conjugation

• purity

IR  
theory

Wattson lamp

• functional groups

• purity

NMR

theory

Frequencies

• Number of H<sup>+</sup>

• Purity

⇒ Chromatography

• High pressure liquid chromatography (HPLC)

• TLC

• GLC

⇒ Thermogravimetric Analysis

• TGA

• DTA

• DSC

Unit 3  
Analytical Chemistry.

### Spectrophotometric Analysis.

This come under the branch of chemistry called spectroscopy.

We will study 3 types of spectroscopy:-

- 1) UV - Visible Spec. (Electronic)
- 2) Infrared Spectroscopy (Vibrational)
- 3) NMR. (Nuclear magnetic resonance)
  - a) H' NMR
  - b) C<sup>13</sup> NMR

### UV - Visible spectroscopy.

based upon 2 laws i.e.

- Lambert's law
- Beer - Lambert's law.

Since e<sup>-</sup>s are involved. it is called electronic spectroscopy  
 Radiation causes (e<sup>-</sup>)ic transition.

#### Lambert's law:

The loss of intensity of incident radiation is directly proportional thickness of sample.

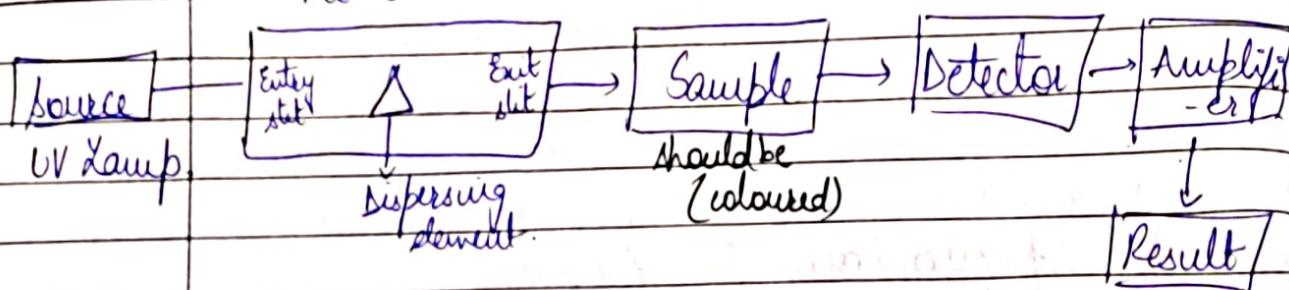
#### Beer & Lambert's Law:

Also proportional to concentration of material

#### Instrumentation

## Electronic Transitions Types / Type

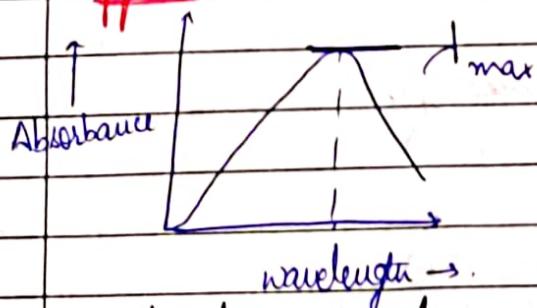
### Monochromator



Types:

- Single beam: Only a single wavelength beam is thrown on sample
- Dual beam: multiple beams of same wavelength used to study both reference & sample water/distilled water.

### Application



This  $\lambda_{\text{max}}$  is unique and using this  $\lambda_{\text{max}}$  we find the properties of soln.

Saturation, purity can be tested.

### # IR spectroscopy

- It is called vibration spectroscopy as the atoms undergo vibration
- Instrumentation is same. Just the source is IR
- Molecules with dipole are suitable.

- Q. Discuss the instrumentation of UV-visible spectrophotometer.
- Q. Explain the electronic transition in UV ~~ex~~ spectroscopy.
- Q. Discuss the fundamental modes of vibration in IR spectroscopy.
- Q. What are IR active or inactive molecule.
- Q. Discuss the significance of UV-visible or IR spectroscopy.

### U.V.-visible Spectroscopy (Sel)

Absorption of light occurs in the UV/visible region of spectrum. (210  $\rightarrow$  900 nm -1)

The absorbed energy from the radiation is used transition b/w electronic energy levels

The excited electrons come back to ground state by vibrational transition & hence absorbed ~~light~~ <sup>energy</sup> appears as heat!

### Effect of substituents on the absorption spectra.

a) Bathochromic shift (Red Shift)

Shift to lower energy / larger wavelength.

b) Hypsochromic shift (blue shift)

Shift to higher energy / shorter wavelength.

c) Hyperchromic effect

Increase in intensity

d) Hypo chromic effect

Decrease in intensity -

## # Energy states

- With more configuration, energy gap b/w ground state & excited state ↑.

- These energy states are quantised.

$$E = \frac{1}{2}mv^2 ; p^2 = m^2v^2$$

$$\Rightarrow E = \frac{p^2}{2m} = \frac{\hbar^2}{2m\lambda^2} \quad (p = \hbar)$$

But  $\lambda = \frac{2L}{n}$  (for standing wave)

$$\Rightarrow E = \frac{n^2\hbar^2}{8mL^2}$$

## \* Nuclear Magnetic Resonance Spectroscopy (NMR)

Types:

- 1)  $^1\text{H}$  NMR. (Proton number / In terms of hydrogen)
- 2)  $^{13}\text{C}$  NMR (Carbon number).

## # Principle Resonance.

## # Instrumentation

Terms:-

Chemical shift

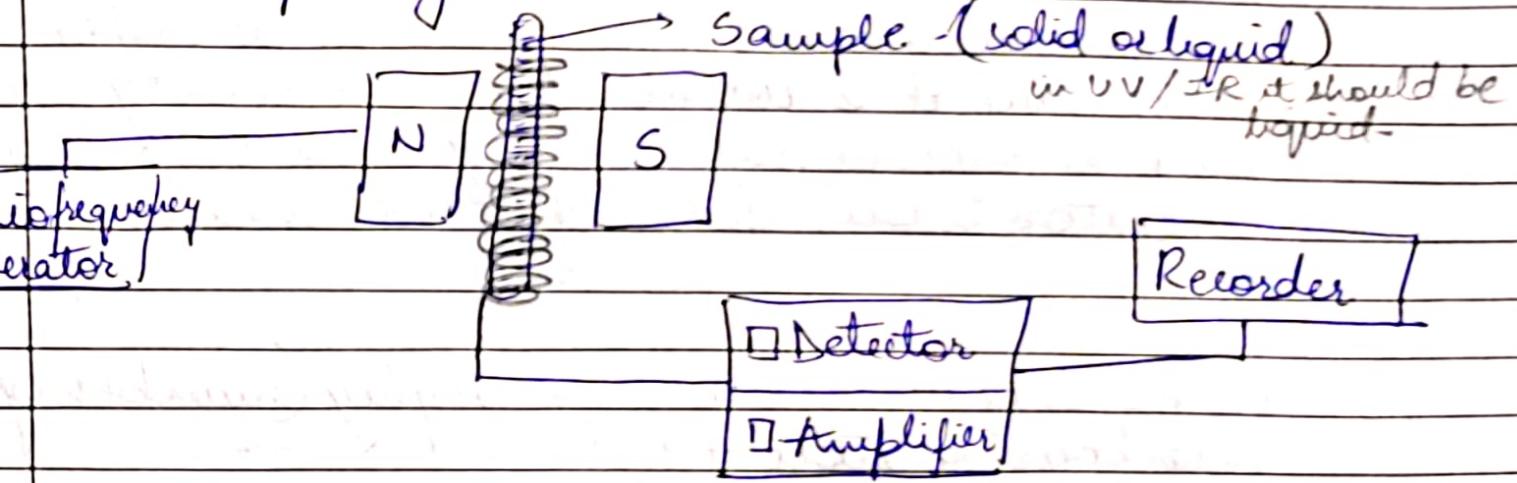
Coupling constant ( $J$ ) .

Spins

Spin interaction

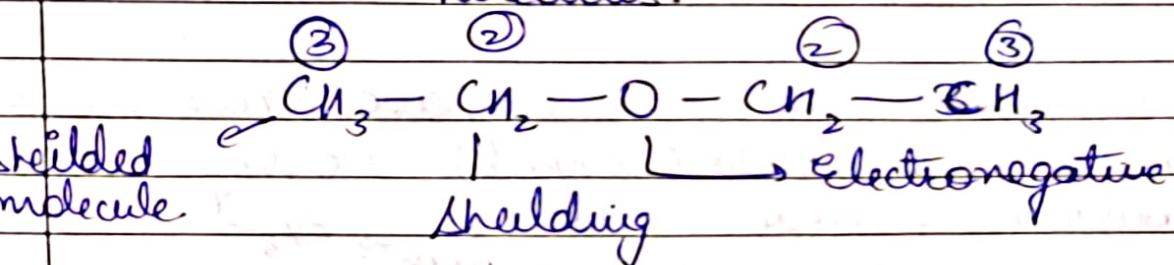
Peak Calculation

Peak Splitting



Peak Splitting ( $n+1$ ) Rule.

$n \Rightarrow$  number of Hydrogen atoms in neighbouring molecules.



Explanation

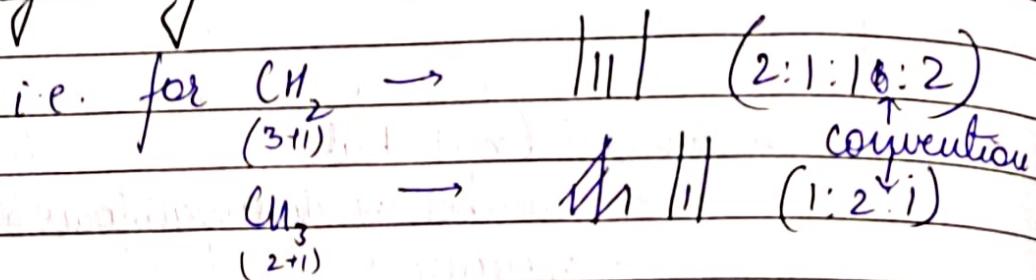
- charged particles on getting Radio frequency like small magnet start spinning. Because of spinning  $p^+$  neutrons also start spinning (spin interaction). Because of this spin, atom induces magnetic field around it!

If this induced magnetic field strengthen the

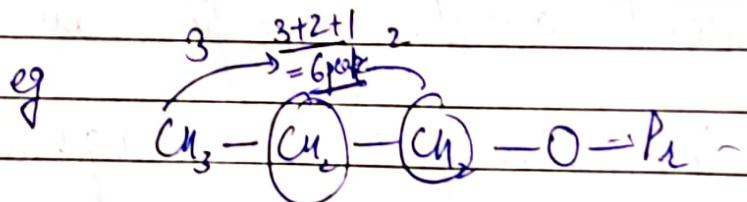
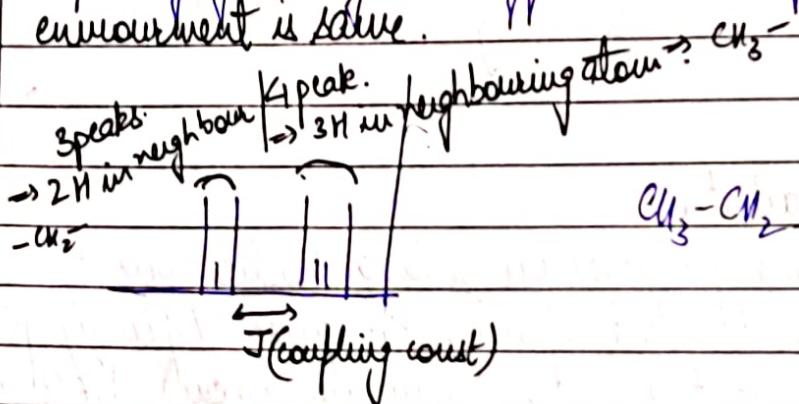
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existing magnetic field it is  $\alpha$  state of spin  
if it is opposite, it is  $\beta$  state of spin.

- On absorbing energy,  $e^-$  moves to higher energy state. Since it is unstable,  $e^-$  lose energy & come back to ground state. This goes on till frequency generator is on. That's what we mean by Resonance.
- Peaks shown by recording display (number of H in neighbouring atom + 1)



As on both side of O, we have same group (plane of symmetry @ Oxygen), we say chemical environment is same.



## Ultraviolet - Visible Spectroscopy -

UV - visible spectroscopy is used to measure the number of conjugated double bond & differentiate between conjugated and non conjugated systems.

Since energy levels are quantised, radiation of fixed frequency falls on a molecule, it absorbs energy & the electron are promoted to higher levels.

### Laws of absorption

The absorption of light by molecules are governed by :-  
**Lambert's Law**:

When a beam of monochromatic light passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to intensity of incident radiation.

$$-\frac{dI}{dx} = k I.$$

$$\Rightarrow \log \frac{I_0}{I_t} = k x.$$

$$\Rightarrow \log \frac{I_0}{I_t} = \frac{k}{2.303} x$$

$$\log \frac{I_0}{I_t} = \epsilon x.$$

$\epsilon$  = Absorption coefficient

$$\log \frac{I_0}{I_t} = A$$

A = Absorbance.

I<sub>0</sub> is the intensity of radiation before entering medium.

I is intensity coming out of radiation

## 2) Lambert's - Beer Law.

### Beer's Law

when parallel beam of monochromatic light enters  $\perp$  into dilute soln, absorbance  $\propto$  conc. of soln.

\* When a beam of monochromatic light is passed through a solution, the  $\downarrow$  in intensity of radiation with thickness of absorbing material  $\propto$  to intensity of incident radiation as well as conc. of soln.

$$A = \log \frac{I_0}{I} = \epsilon \times c.$$

$\epsilon$   $\Rightarrow$  molar absorption coefficient

if  $c=1$  and  $x=1$

$A = \epsilon =$  Extinction

$$\frac{I}{A} = \text{Transmittance}$$

## # Instrumentation

- 1) Light source: A tungsten filament lamp or Hydrogen/deuterium discharge lamp

Filter / monochromator : to isolate desired wavelength  
Sample : A Cuvette made of quartz containing the sample  
Radiation Detector : Detects the incoming radiation & converts it into electric signal.

### NOTE

Ordinary spectrophotometer do not work below 200 nm as the Oxygen is strongly absorbed below 200 nm

See previous notes for diagram.

### Electronic Transitions

$\sigma \rightarrow \sigma^*$  transition

$\sigma$  bonded e<sup>-</sup>s are firmly held in the molecules. Hence the transition requires large amounts of energy and therefore occurs in far UV region.  
Occurs in HCs like methane, propane etc.

$n \rightarrow n^*$  transition

These transitions occur in saturated compounds with one hetero atom having unshared electron like alcohol, ether, amine, ketone, aldehyde etc.

$\pi \rightarrow \pi^*$  transition

These transitions take place in compounds containing double and triple bonds. Since  $\pi$  e<sup>-</sup>s require less energy these transitions occur at higher energy.

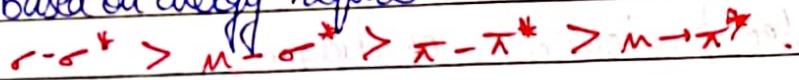
#### 4) $n \rightarrow \pi^*$ transition

e<sup>-</sup>s of unshared e<sup>-</sup> pair on hetero atom is excited to  $\pi^*$  anti bonding orbital. As non bonding e<sup>-</sup> are loosely held, this transition require least energy.

#### NOTE

as n e<sup>-</sup> are  $\perp$  to  $\pi$  bond plane, the probability is less.

Based on energy required:-



#### \* Chromophores & auxochromes -

An isolated covalently bonded group that shows a characteristic absorption in UV-visible region are called chromophores.

They are of 2 types:-

- i) Those which contain  $\pi$  electron & undergo  $\pi \rightarrow \pi^*$  transition
- ii) Those which contain  $\pi$  e<sup>-</sup>s & non bonding e<sup>-</sup>s. They undergo  $n \rightarrow \pi^*$  &  $\pi \rightarrow \pi^*$  transitions e.g. > C=O, -C≡N

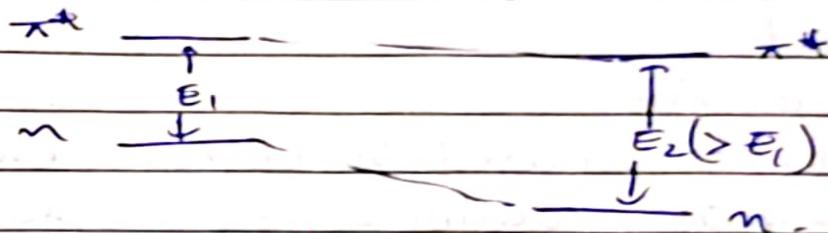
Any group which does not itself act as a chromophore but whose presence brings about a shift of absorption band towards the red end of spectrum

#### \* Solvent Effect

Non polar compounds like ethylene, butadiene etc experience no effect of solvent. But Polar compounds do.

#### 1) $n \rightarrow \pi^*$ transition

On T polarity of solvent,  $n-\pi^*$  transition experience blue shift as the polar solvents stabilise the  $n$  orbital more than  $\pi^*$  orbital.



### $\pi-\pi^*$ transition

On T polarity of solvent, the absorption band experiences a red shift as the dipole-dipole interaction with solvent lowers energy of excited state more than ground state.

In identification of  
Extend of conjugation

Determination of geometrical isomers

Identification of unknown compounds.

Distinction b/w conjugated & non conjugated compounds.

Detection of impurity

Detection of hydrogen bond

### Infrared Spectroscopy

It is also called as vibrational spectroscopy as it involves transitions b/w vibrational energy levels.

### Instrumentation

1) Light source

Infrared radiations are produced by electrically heating globar / Nernst filament.

2) Filter/monochromator

Optical prism / grating are used to obtain monochromatic light. Glass or quartz cannot be used as they absorb IR.

3) Sample

Gels are made of NaCl or alkali metal halides as they do not absorb IR. Solid samples are grounded with KBr & made into a disc. Sample should be dry as water absorbs strongly in IR region. Other solvents like chloroform,  $\text{CCl}_4$ , etc are used.

4) Detector

These analyse the light emitted by sample.

- Covalent bonds behave like tiny spring connecting atoms. This vibrational motion is quantised. When IR is passed, molecule absorbs radiation of appropriate energy & gets excited to a higher vibrational level.

NOTE IR gets absorbed only when dipole moment due to molecular vibration interacts with oscillating of molecule is different in 2 vibrational levels.

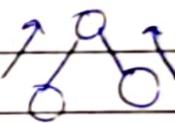
## # Types of vibration

### i) Stretching

Distance b/w atoms increase or decrease but atoms remain in same bond axis

#### 1) Symmetric

movement of atoms w.r.t particular atom is in same direction



#### 2) Asymmetric

One atom approaches the central atom & other departs.



### ii) Bending

Position of atoms changes w.r.t original bond axis but dist between atoms remains same

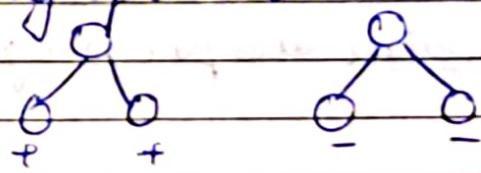
#### Out of plane bending

Atoms move out of nodal plane w.r.t central atom

They are of :-

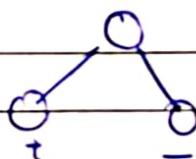
##### i) Wagging

both atoms swing up and down w.r.t central atom



##### ii) Twisting

One atom moves up the plane while other moves down w.r.t central atom



ii) In plane bending

Atoms remain in the same plane as the nodal plane.

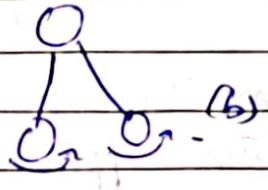
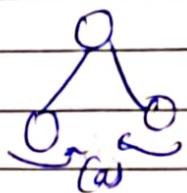
Of 2 types:-

a) Scissoring

2 atoms approach each other & move away like  
2 arms of scissors

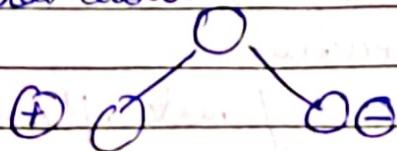
b) Rocking

both atoms move in same direction



3) Twisting

One arm moves up the plane and other moves down the plane w.r.t central atom.



NOTE:

Takes more energy in stretching than bending. Hence stretching vibration takes place at higher frequency

