unit II

spectroscopy It is a technique for chemical analysis of molecules or compounds

Earlier. molecular formula & chemical rxn. (classical technique)

Now days chemical analysis through spectroscopy
(Qualitative & Quantitative analysis)

spectroscopic techniques

1) electronic spectroscopy
2) vibration & Rotational spectroscopy

principle of spectroscopy ① It is a branch of science which deals with the study of interaction of EMR & matter

② It deals with the transition that a molecule undergoes b/w its energy level.

spectrum

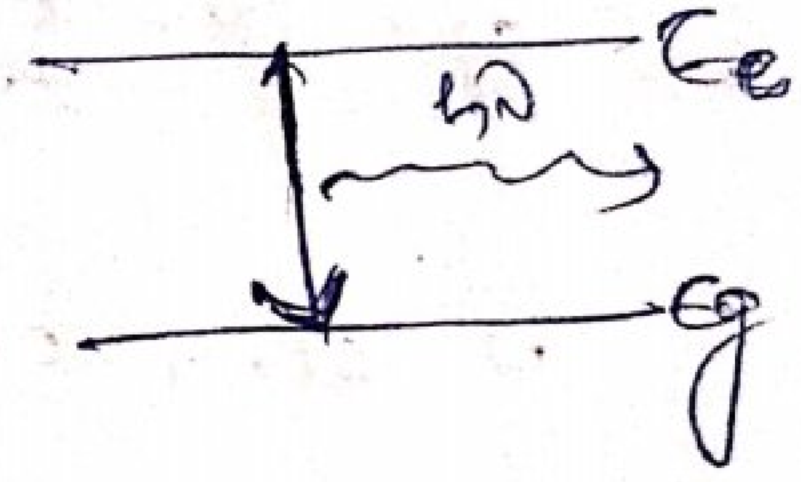
consider two energy level of an atom & molecule

1) Ground state energy level (E_g)
2) Excited energy level (E_e)

Emission spectrum

higher $\xrightarrow{h\nu}$ lower

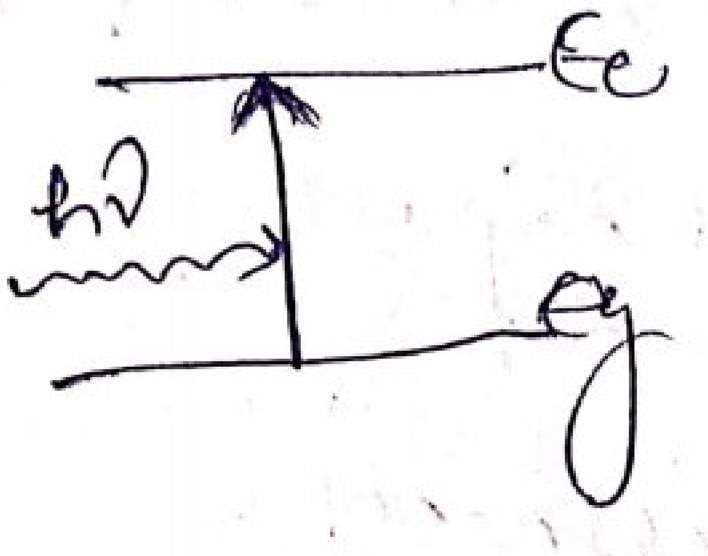
$\Delta E = E_e - E_g$



Absorption spectrum

lower $\xrightarrow{h\nu}$ higher

$\Delta E = E_e - E_g$

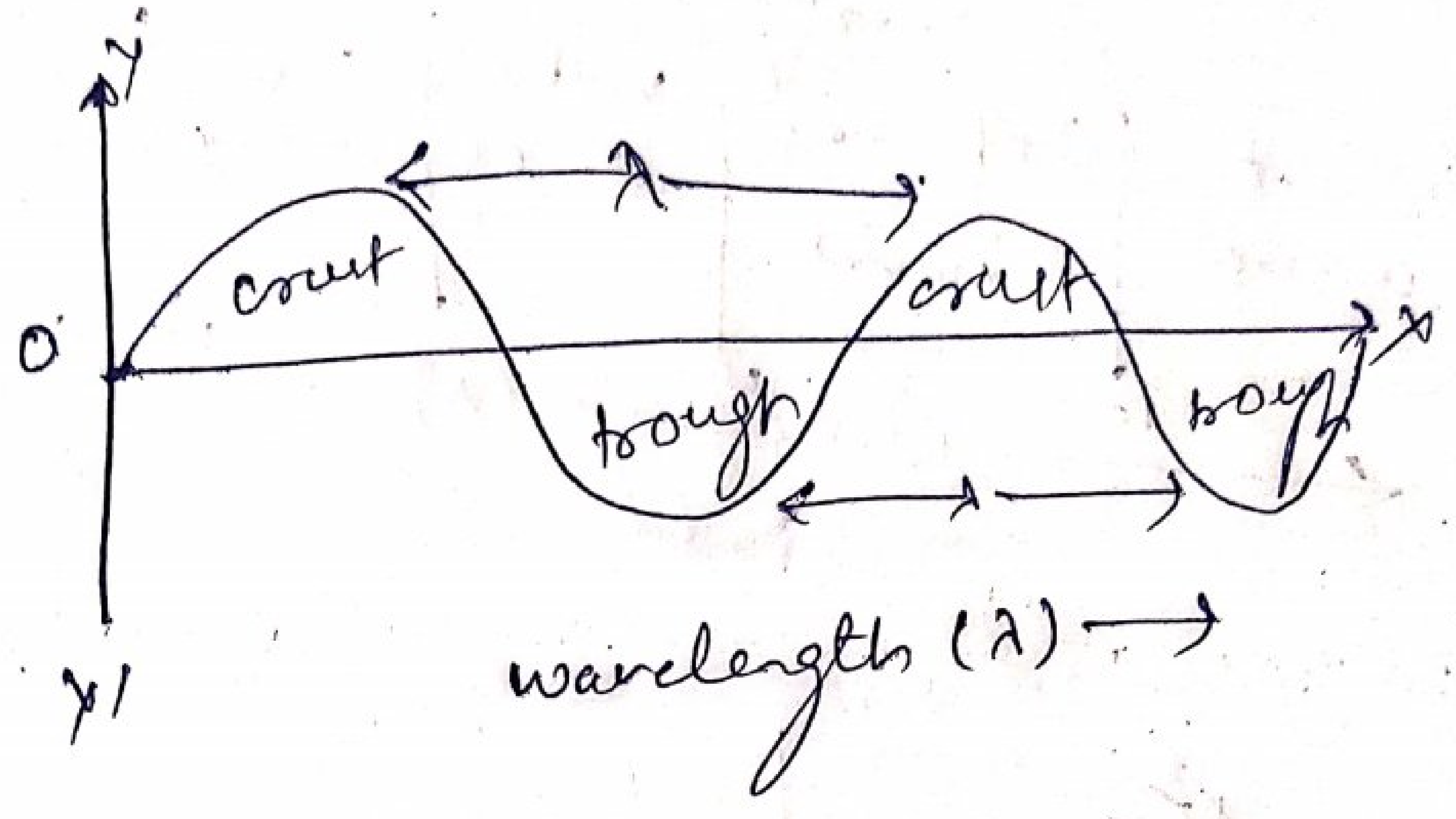


Importance of spectroscopy

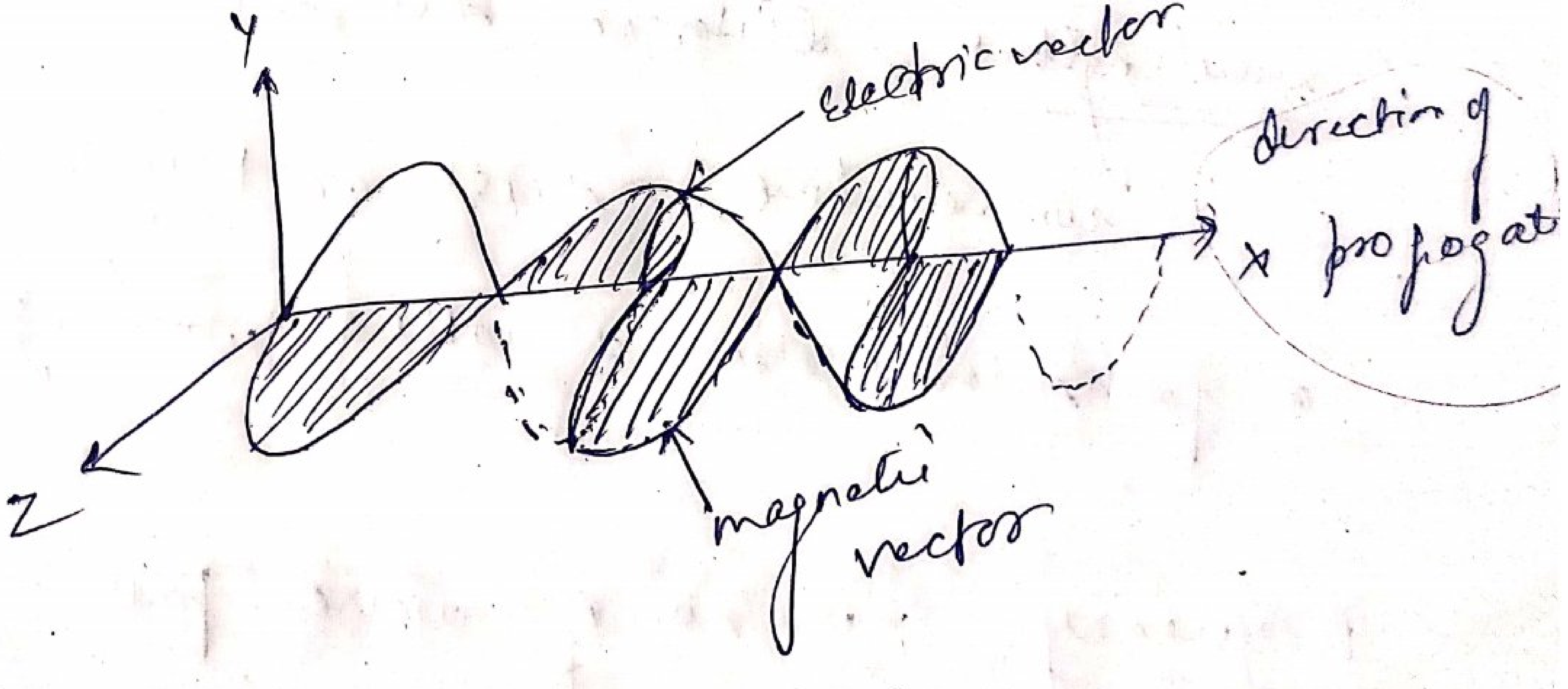
1) They require very small amount for investigation.
2) They take much lessest time.
3) They are cheap in the long run.

EMR

EMR radiation are oscillating or wave like electric & magnetic field in space.



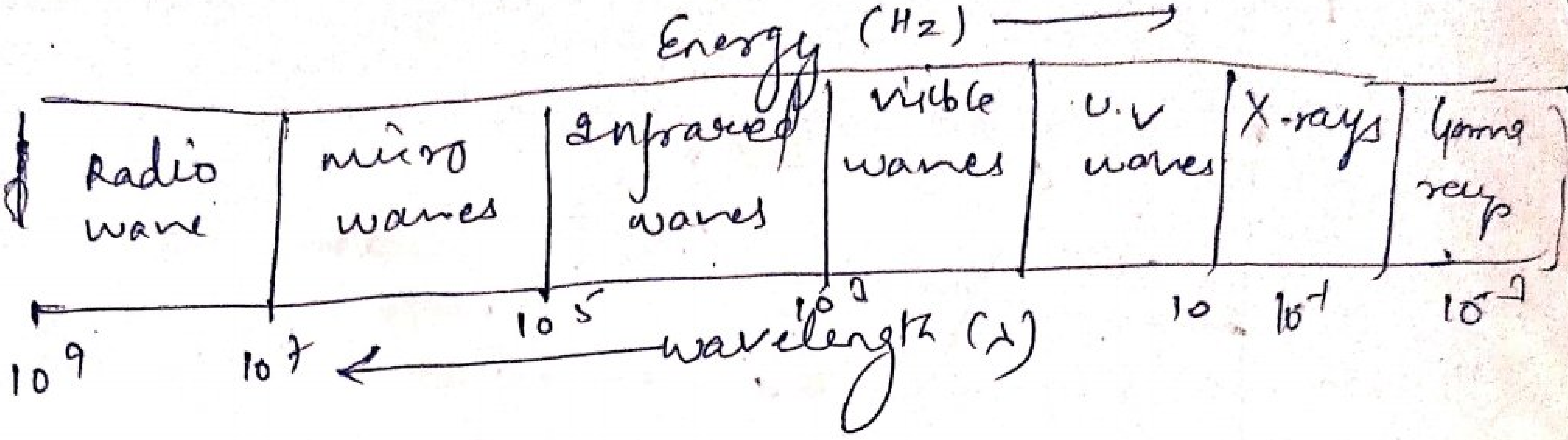
(wave motion)



EM wave

Spectrum of EMR radiation :-

RMIVUVXY

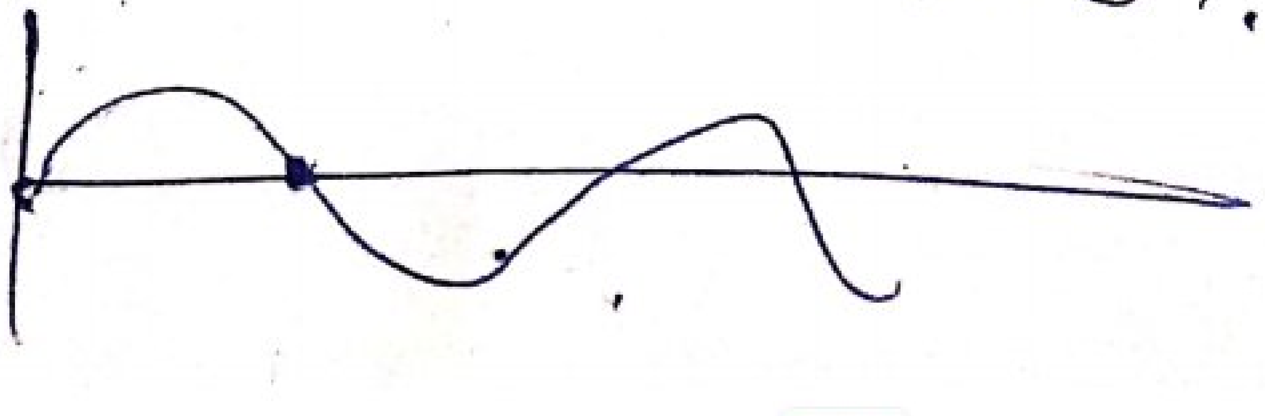


$$\boxed{\bar{\nu} = \frac{1}{\lambda}}$$

wavelength : Distance b/w two consecutive crust or trough in a particular wave is called wavelength

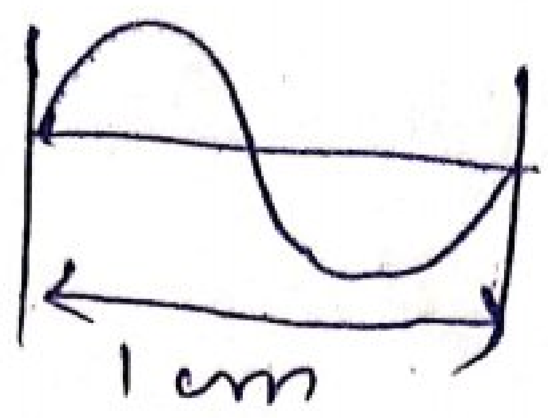
ferequency f. the no. of waves pass through a pt. in one second It is expressed as cycle/sec or Hz or sec^{-1}.

(ν)



the total no. of waves that are represented in unit length (1 cm). The symbol is ($\bar{\nu}$) is expressed as cm^{-1}.

$\boxed{\bar{\nu} = \frac{1}{\lambda}}$



$\boxed{\bar{\nu} \propto \frac{1}{\lambda}}$

velocity (c) = velocity is the linear distance travelled by a wave in one sec. It is expressed in m/s.

$c = \lambda \times \nu$

$\boxed{\nu = \frac{c}{\lambda}}$ $\quad \bar{\nu} = \frac{1}{\lambda}$ $\quad \nu = c \times \frac{1}{\lambda}$

$\boxed{\nu = c\bar{\nu}}$ $\quad \nu = c\bar{\nu}$

Energy expressed by wave

Acc. to Planck's eqn

$\boxed{E = h\nu}$

$\boxed{h = 6.625 \times 10^{-34}\ Js}$

$\boxed{\text{velocity of wave } c = 3 \times 10^{10}\ cm/s}$

λ = wavelength

$\nu = \frac{c}{\lambda}$ $\quad E = \frac{hc}{\lambda}$

$\boxed{E \propto \frac{1}{\lambda}}$

Selection rule or transition rule

selection rule decides whether transition is allowed or not allowed (forbidden)

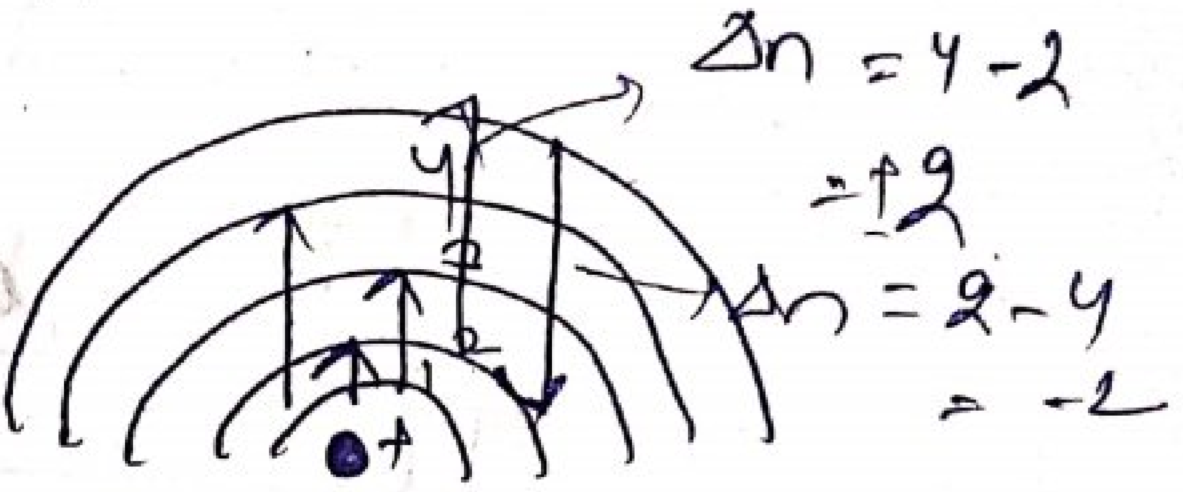
1) allowed transition
2) forbidden transition

Rule I

change in energy level or (Principal Quantum no)
transition in any energy level

anything
$\Delta n = \pm 1, \pm 2, \pm 3, \pm 4$

e⁻ can jump to any energy level.



Rule 2 Laporte's selection rule (azimuthal Quantum no)

change in orbital ~~Quantum~~ angular momentum (l)

orbital changes like s, p, d, f

can jump only to next level.

$s \longleftrightarrow p$
$p \longleftrightarrow d$
$d \longleftrightarrow f$
} allowed transition

$s \longleftrightarrow d$
$p \longleftrightarrow f$
} forbidden transition

$\boxed{\Delta l = \pm 1}$ only $\Delta l \neq \pm 1$ not allowed

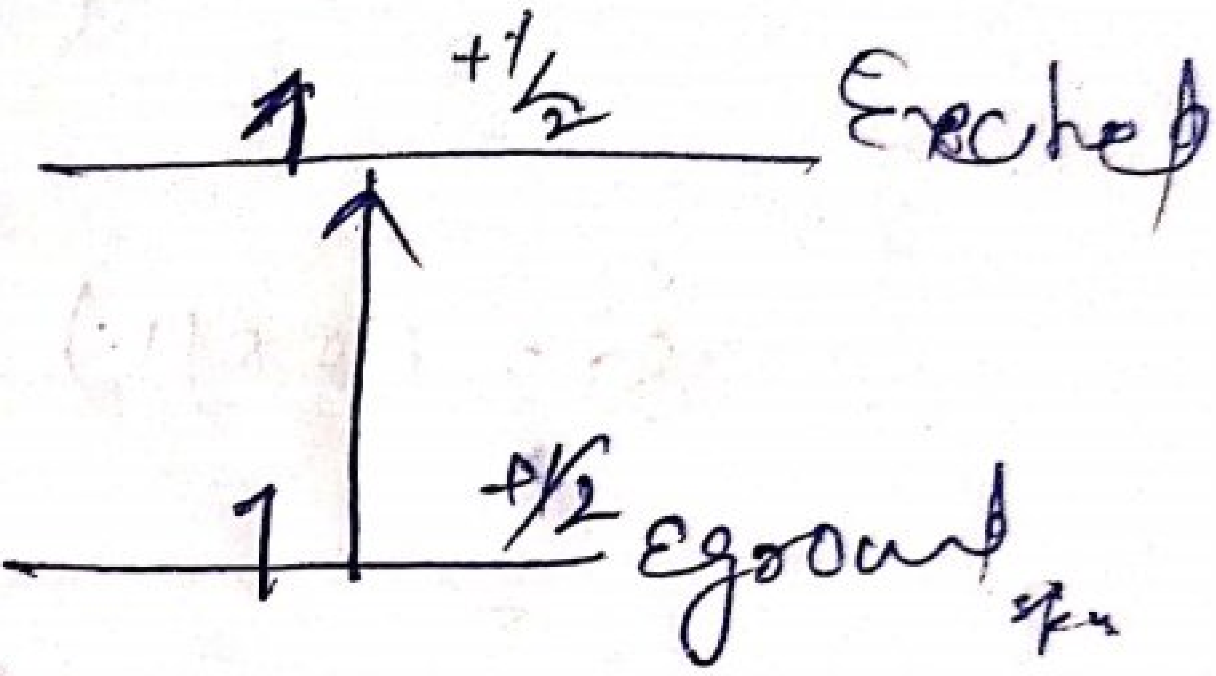
Rule 3 spin selection rule (S) spin q. no.

spin angular momentum (S)

$\boxed{\Delta S = 0}$ allowed

spin multiplicity of e⁻ should not change then it is allowed transition.

$\boxed{\Delta S \neq 0}$ forbidden



Rule 4 total angular momentum change rule

$\boxed{\Delta J = 0, \pm 1}$ allowed

$\Delta J \neq 0, \pm 1$ → forbidden.

total angular mom = orbital angular momentum (L) + spin angular mom (S)

Term symbol

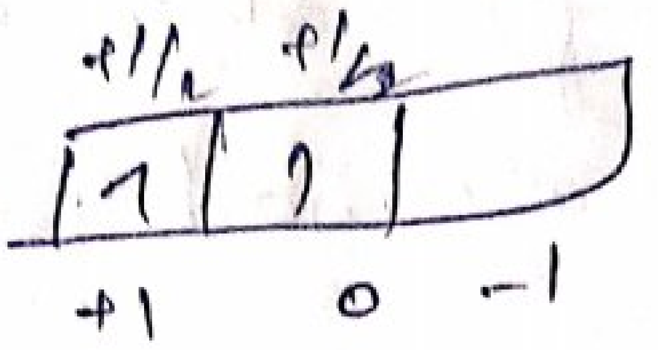
$$\boxed{{}^{(2S+1)}L_J}$$

→ spin angular momentum

→ orbital ang. mom

→ Total ang. mom

p^2



$s = (+1/2) + (+1/2) = 1$

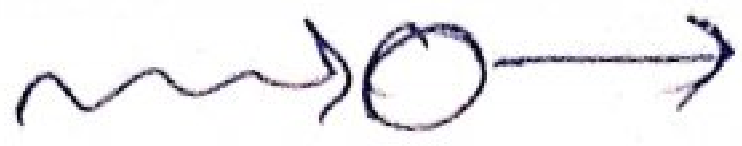
$S = (2s+1) = (2 \times 1 + 1)$
$= 3$

L =

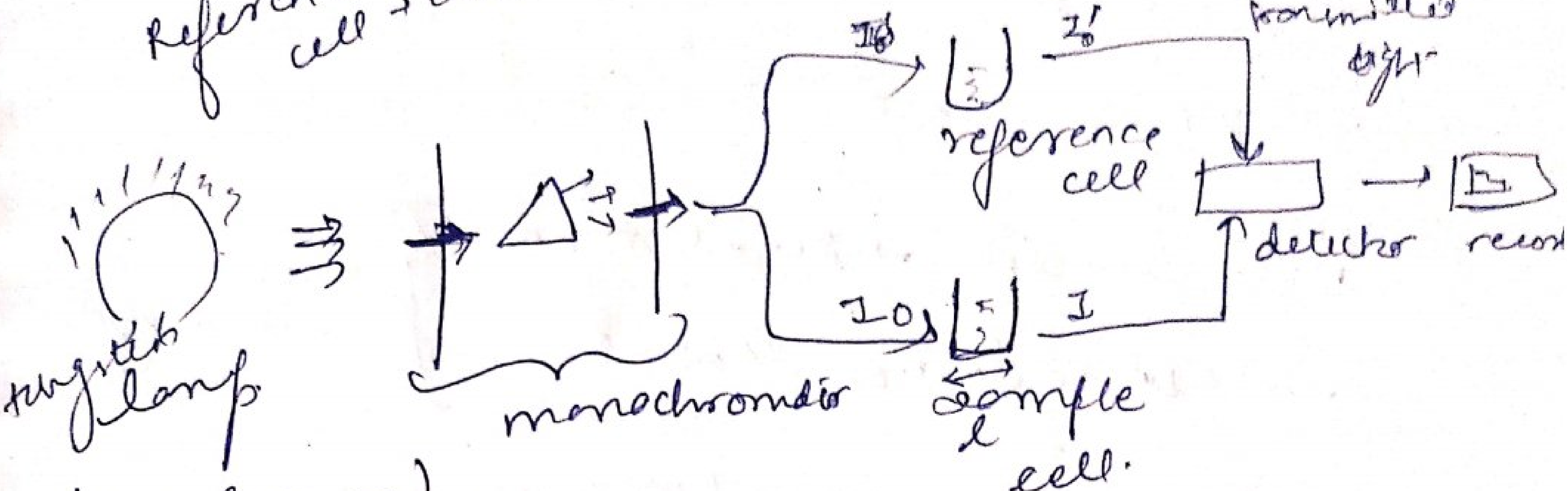
s	p	d	f
0	1	2	3

$J = L + S =$

U.V visible spectroscopy



Reference cell + cuvette



UV- radiation

200 - 400 nm - U.V

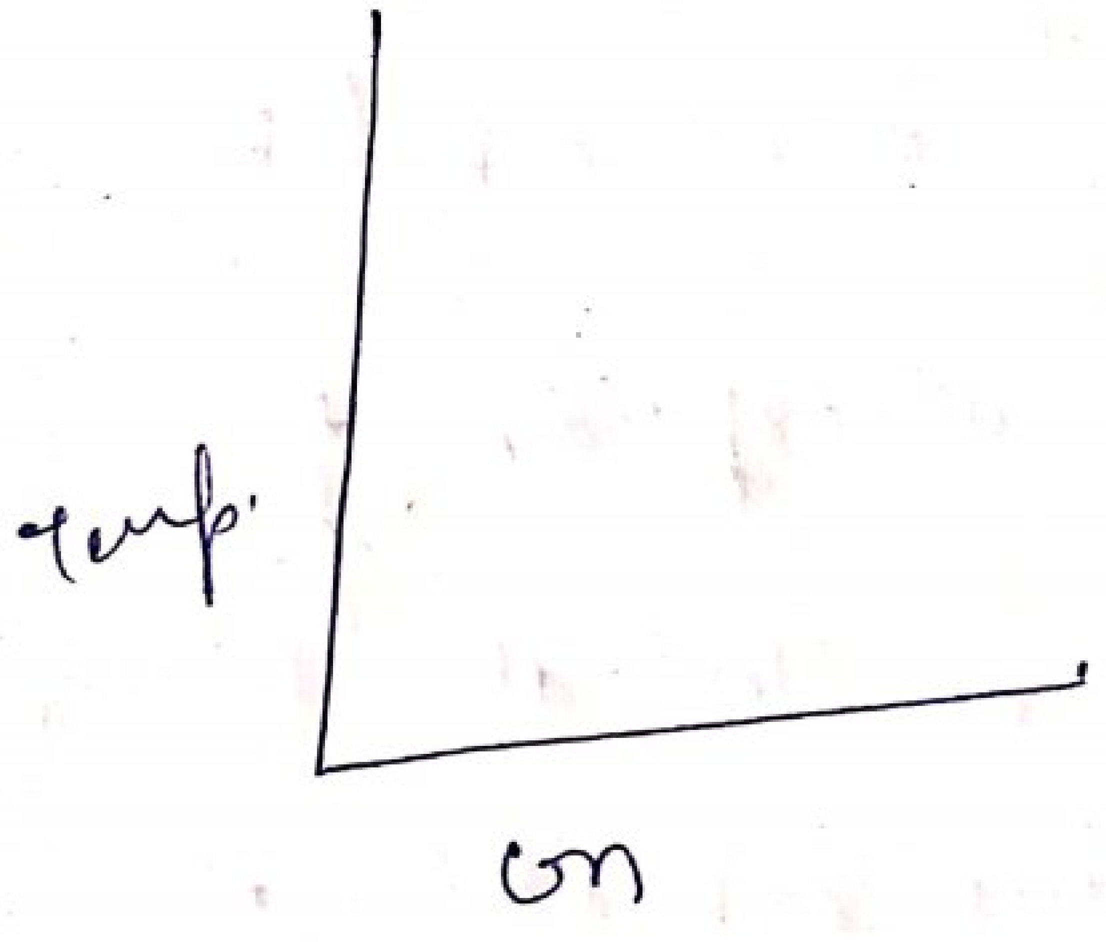
400 - 800 nm - visible

shorter wavelength radn

$A \propto C$ (Beer's law)

$A \propto L$ (Lambert's law

detector → transmittance detect.



U.V visible spectroscopy.

Introduction

→ wavelength range

UV radiation → 200 - 400 nm } shorter wavelength
visible radiation → 400 - 800 nm }

→ It is type of absorption spectroscopy

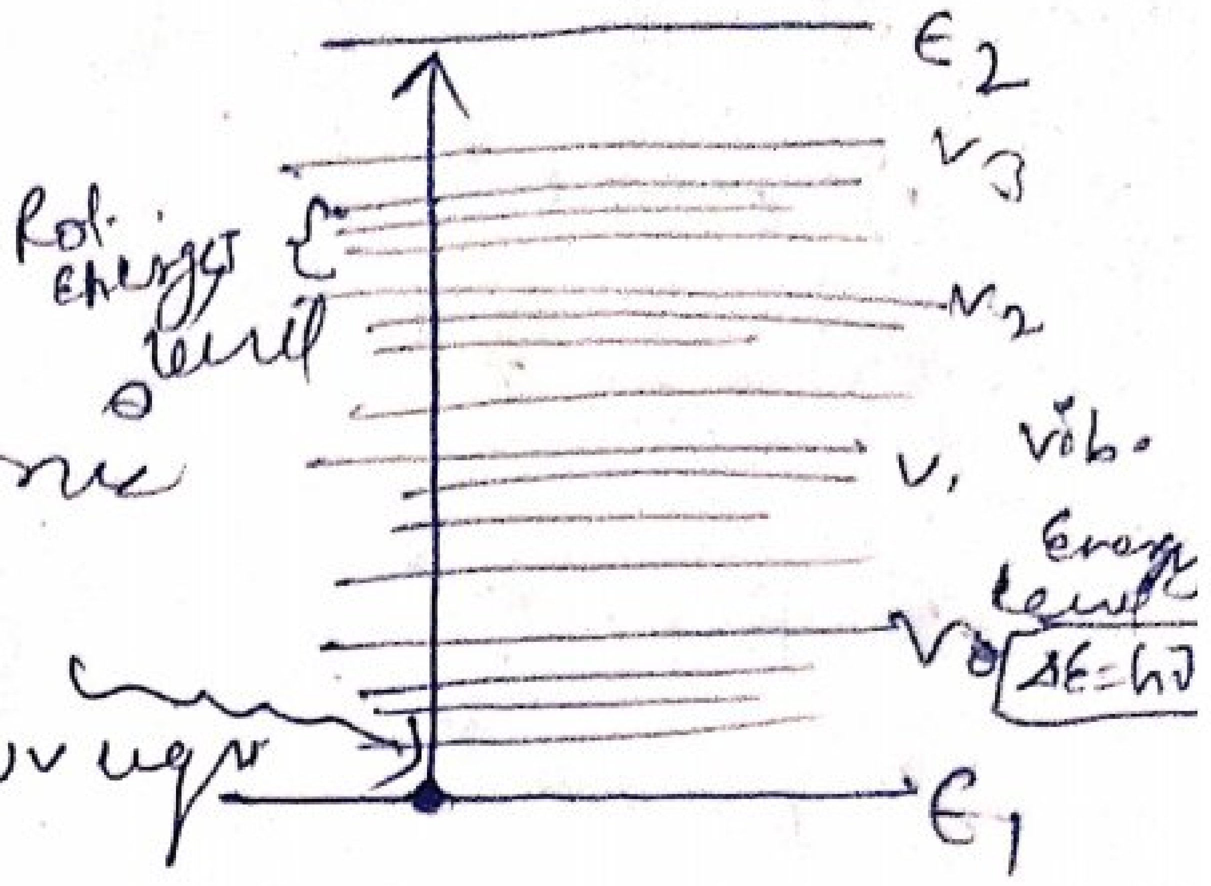
→ electronic transition takes place so it is called electronic spectroscopy.

Principle

On passing emR (UV-vis range 200-800 nm) to compound a part of radⁿ is absorbed by the compound after the absorption of energy the e⁻s in the orbital at lower energy are excited to the orbital at lower energy are excited to the orbital of higher energy level.

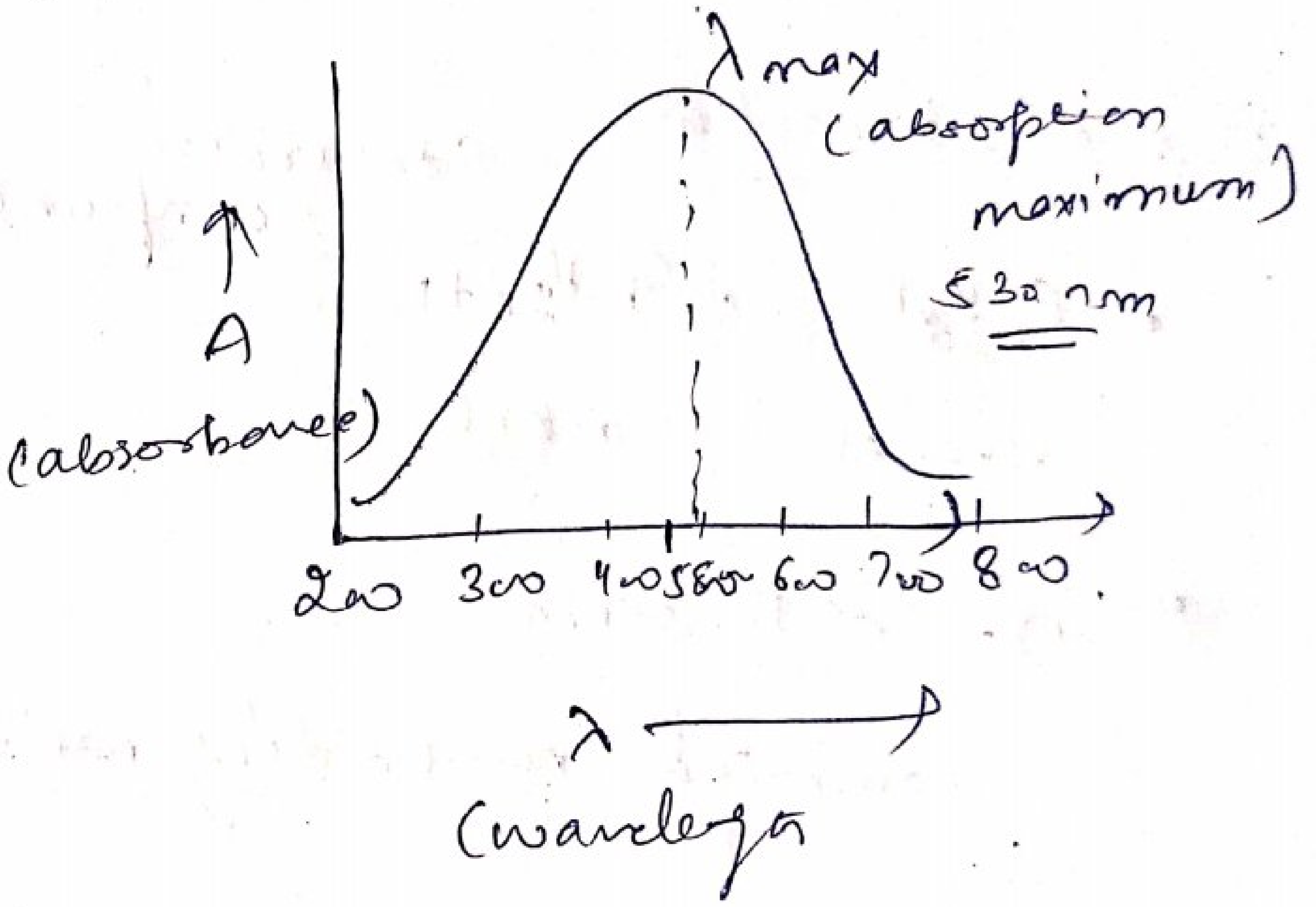
The energy absorbed by the e⁻s will equal to the energy difference b/w two energy levels.

$$\boxed{\begin{array}{l}\Delta E = E_2 - E_1 = h\nu \\ \text{or} \\ \Delta E = h\nu\end{array}}$$



during this stage, electronic excitation occur and we get absorption spectra

hence it is also called "electronic spectroscopy"



electronic transition

ground state (E_0) ⟶ excited state

(HOMO) ⟶ (LUMO)

types of electron

σ, π, non bonding e's (n)
(not participating in bonding)

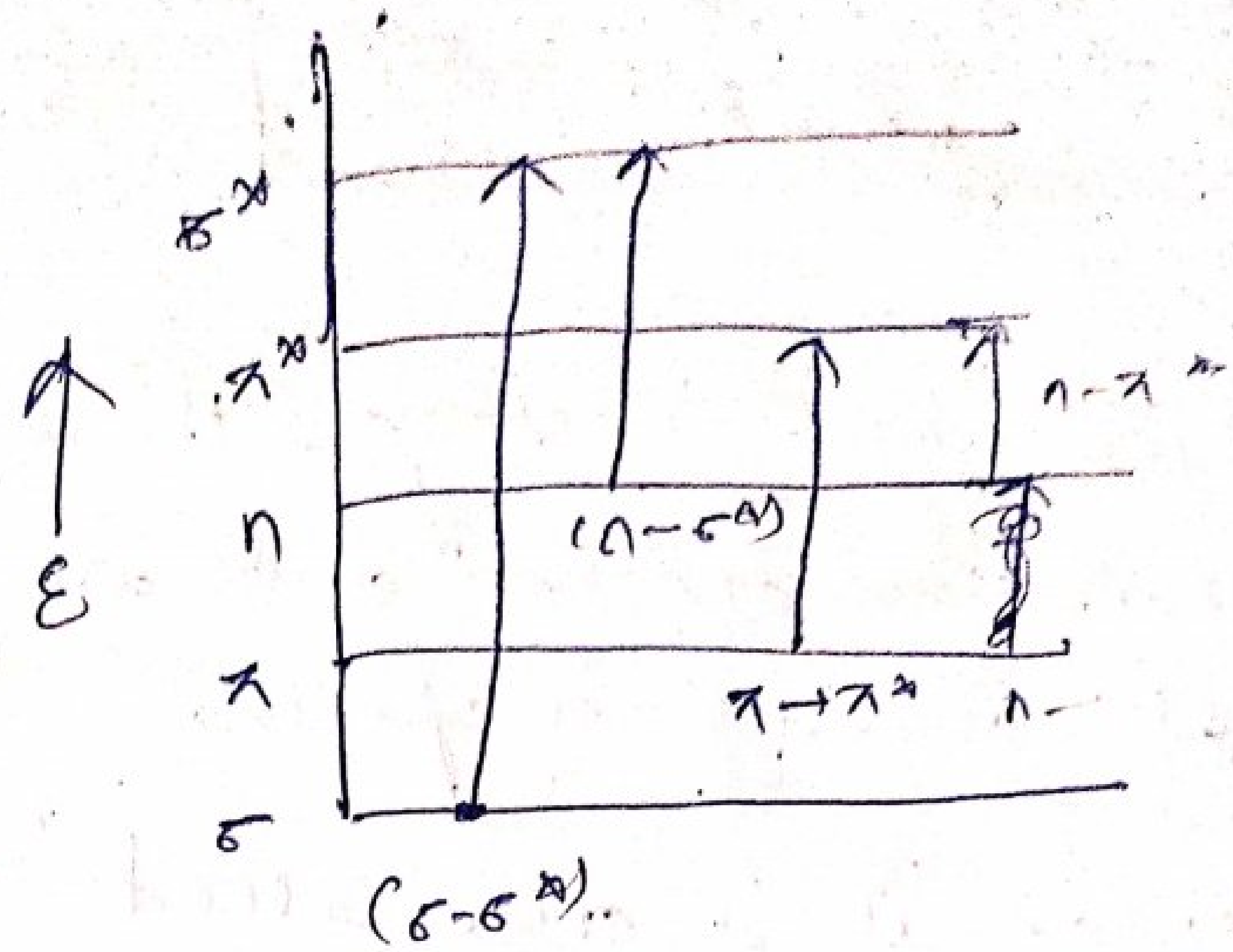
σ → saturated (single bond) CH_4

π → un-saturated (=, ≡) C_2H_2

O, N, Cl, F (heteroatoms)

Types of transition

1) σ → σ*
2) π → π*
3) n → σ*
4) n → π*



1) σ-σ* transition (saturated compound.)

• C_nH_{2n} , C_nH_{2n+1}

alkanes alkyl

2) n → σ* transition

saturated, non-bonding ~~molec~~ e^- (N, O, S, Cl, F)

Ex. $C_2H_5NO_2$, C_2H_5Cl , C_2H_5OH

3) π → π* transition

unsaturated

C_nH_{2n} C_nH_{2n-2}

Energy order

σ → σ* > n-σ* > π-π* > n-π*

4) n→ π* transition

unsaturated , non-bonding

Ex. $C_3-\overset{O}{\overset{||}{C}}-H$, $CH_3-\overset{O}{\overset{||}{C}}-CH_3$

Beer's law

It states that conc. and absorbance is directly proportional to each other

$$A \propto C \quad \text{—①}$$

Lambert law

It states that absorbance & path length is directly prop. to each other.

$$A \propto L \quad \text{—②}$$

Beer Lambert law

It states that for a given material sample path length and concentration is directly proportional to the absorbance of light.

$$A \propto L$$

$$A \propto C$$

$$\boxed{A = \varepsilon L C}$$

A → amount of light absorbed

C → conc. of absorbing specie

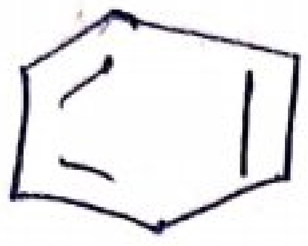
L → path length.

ε → molar extinction coeff.

Chromophores and Auxochromes

$\underbrace{\text{chromo}}_{\downarrow\ \text{colour}}\ \underbrace{\text{phores}}_{\downarrow\ \text{bearing gp.}}$

Ex- Benzene



(colourless)

Nitrobenzene

coloured
(Yellow)

chromophores are unsaturated group (covalently bonded), responsible for electronic absorption.

Ex. $>C=C<$, $>C=O$, $-NO_2$

Auxochrome.

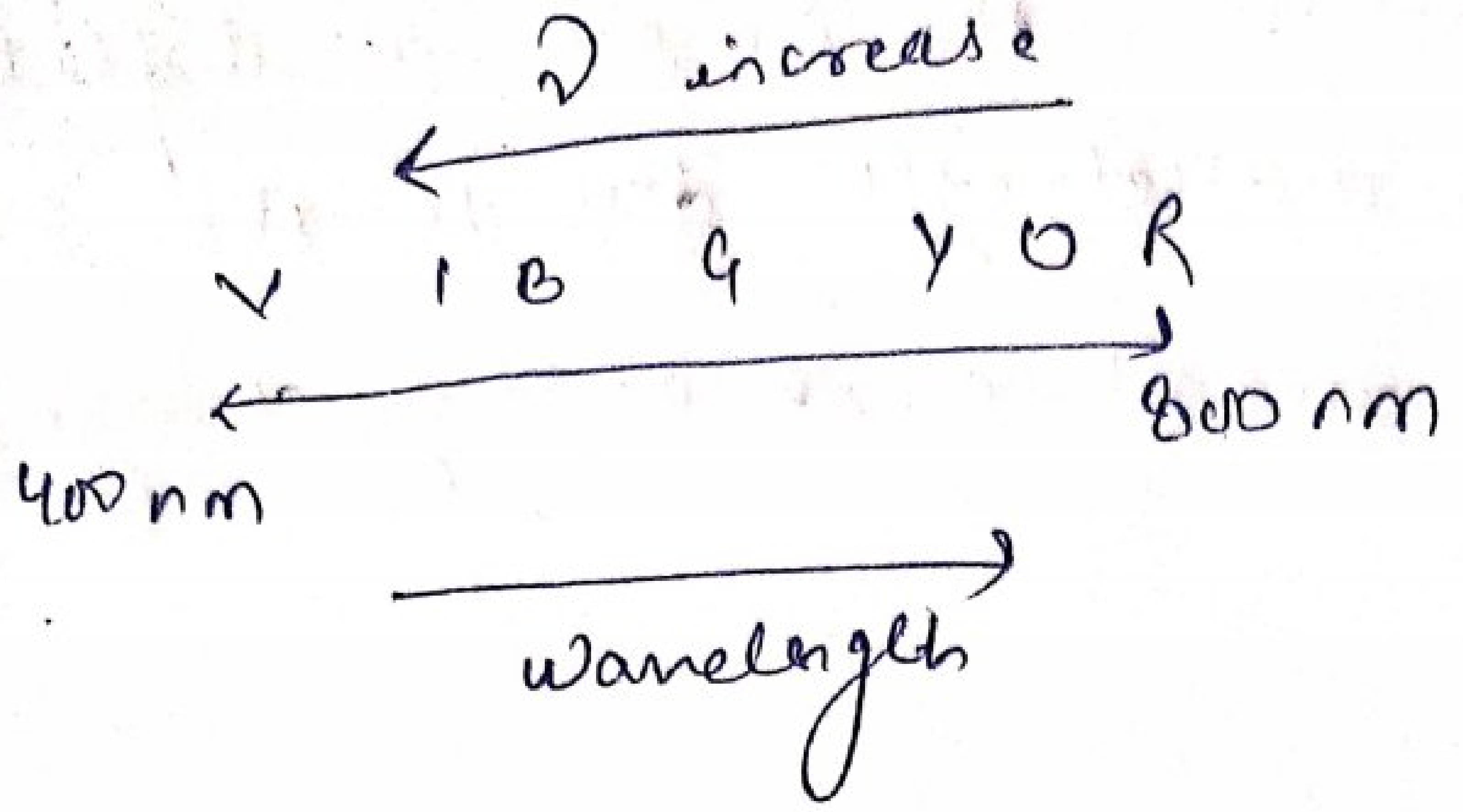
An auxochrome is a saturated group which are not chromophore themselves but their presence can cause the increase in colour intensity of compounds.

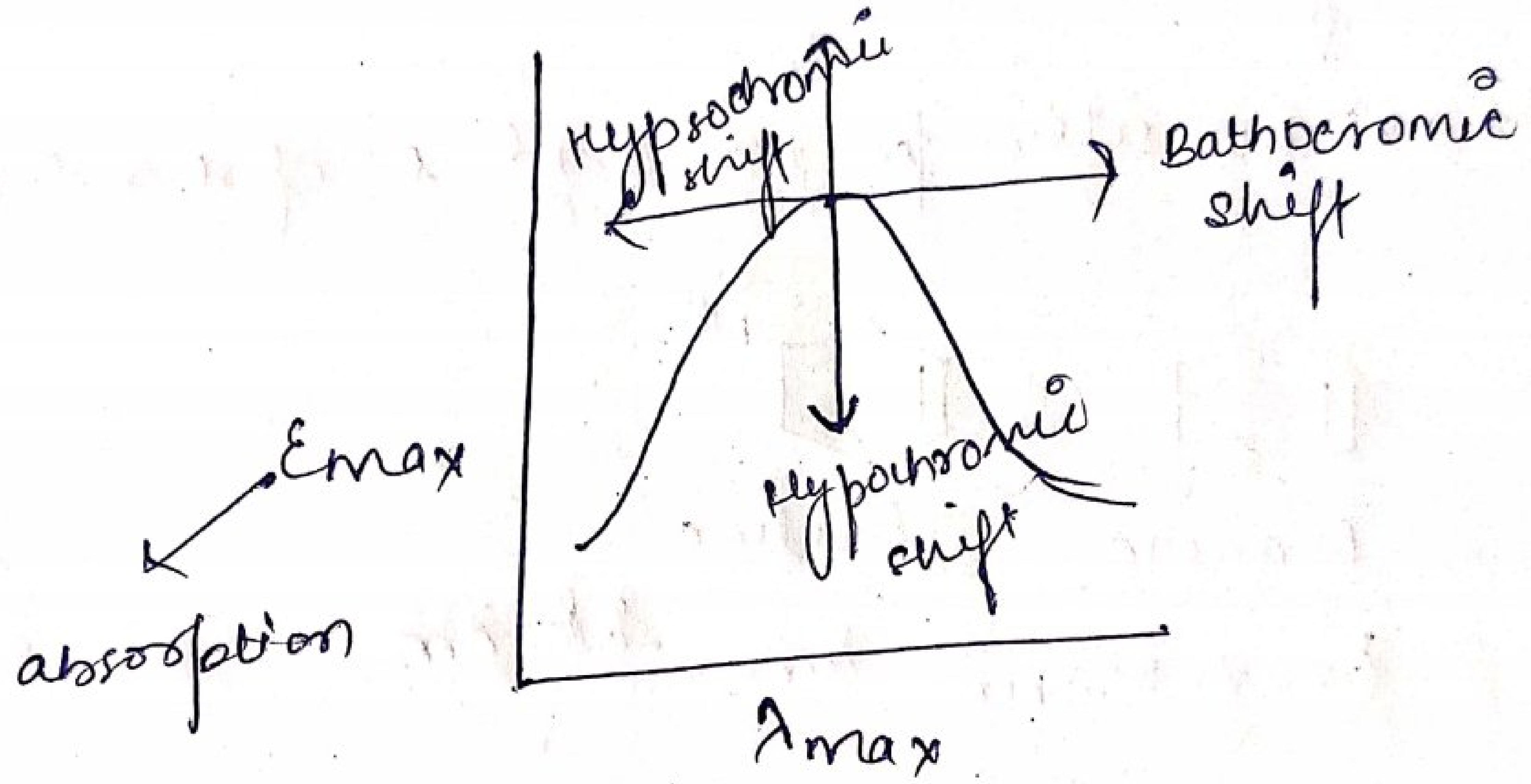
Eg. Amino gp. (NH_2), OR, NR_2, $-NHR$, $-SH$ etc.

(Basically they have non bonding e's)

(dark yellow)

Absorption and intensity shifts





λ_{max} → wavelength at which there is max. absorption

εmax → the intensity of maximum absorption

Reasons

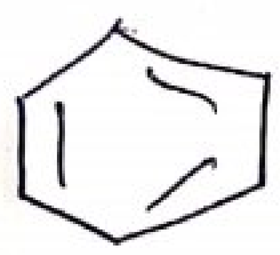
1) chromophore & auxochrome
2) change in solvent
3) Effect of conjugation

1) **Bathochromic shift**

The shift in which the λmax is shifted towards longer wavelength due to the presence of an auxochrome or by change of solvent.

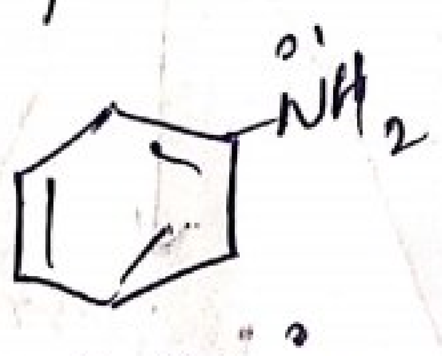
→ Red shift.

→ Eg. $\pi \rightarrow \pi^*$ transition for carbonyl compound or Amines



Benzene

λmax - 250 nm



Aniline

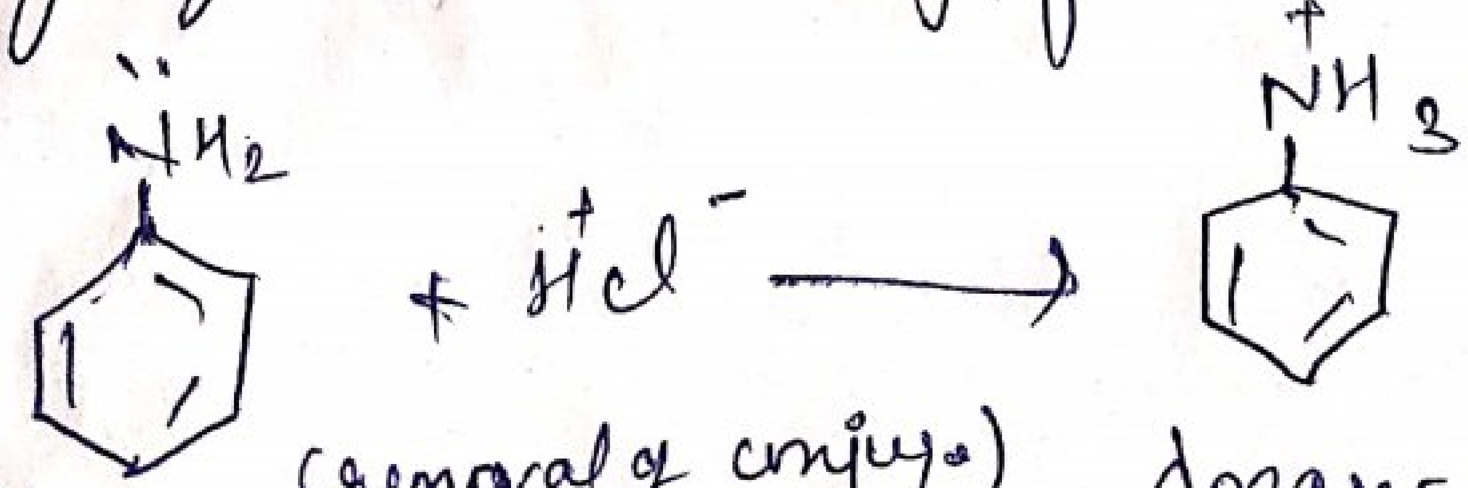
λmax - 280 nm

2) **Hypsochromic shift** In this shift, the absorption maximum shifts toward shorter wavelength.

→ λmax shifts towards shorter wavelength called Blue shift.

→ It is caused by the removal of conjugation & by changing the polarity of solvent.

Aniline



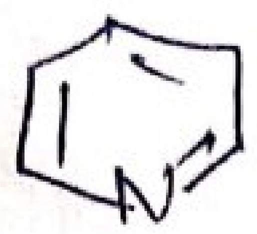
(Anilium salt)

λmax - 280 nm (removal of conjug.) λmax - 200 nm

3) Hyperchromic shift :-

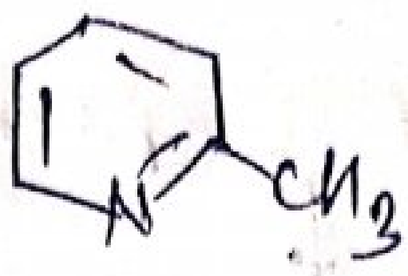
In this shift the intensity of absorption maximum increases i.e. ϵ_{max} increases.

Ex.



Pyridine

ϵ_{max} - 2750



2-methyl pyridine

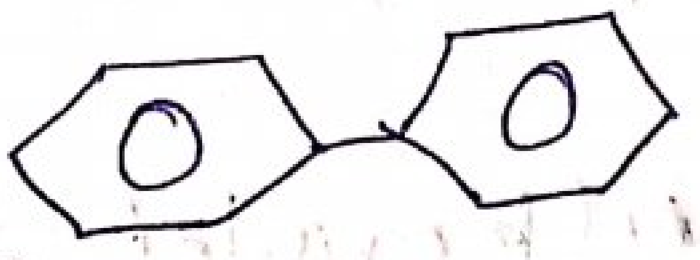
ϵ_{max} - 3560

(auxochrome added)

4) Hypochromic shift :-

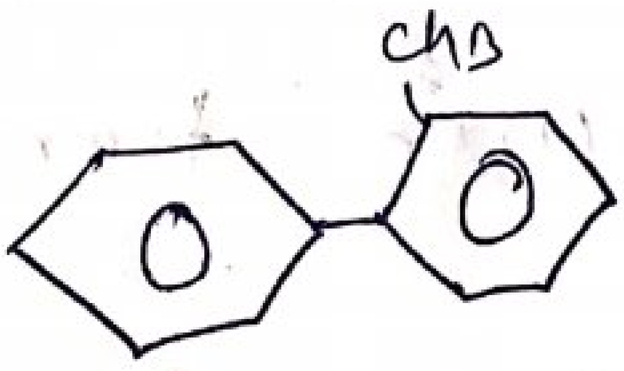
In this shift, the intensity of absorption maximum decreases i.e. ϵ_{max} decreases.

Ex -



Biphenyl

ϵ_{max} - 19000



methyl biphenyl.

ϵ_{max} - 10250

Fluorescense and Phosphorescence.

- Light-matter interaction
  - scattering
    - Elastic (wavelength not change)
    - Inelastic (λ change
  - Absorption ↓
    - types of emission after absorption
      - Photo luminescence
        - Fluorescence
        - Phosphorescence
      - Electroluminescence
      - Thermoluminescence
      - Chemiluminescence
      - Bioluminescence etc

Principle of fluorescence and phosphorescence :-

many compounds absorb ultraviolet or visible light and undergo electronic transition from low electronic energy levels to high electronic energy level. This absorption of light requires 10^{-15} sec.

The instant re-emission of the absorbed energy is called Fluorescence.

while delayed re-emission of the absorbed energy is called phosphorescence.

Fluorescence:- A process in which a part of energy (U.V. visible) absorbed by a substance is released in the form of light as the stimulating radiation is continued.

The fluorescence emission took place from a singlet excited state.

[avg. lifetime from $<10^{-10}$ to 10^{-7} sec].

Phosphorescence:- A process in which energy of light absorbed by a substance is released relatively slowly in the form of light.

The phosphorescence emission took place from a triplet excited states.

[avg. lifetime from 10^{-15} to $>10^{+3}$ sec].