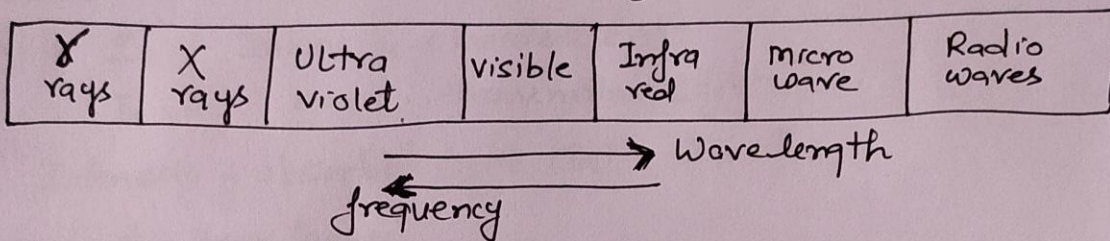# Spectroscopy

Spectroscopy is the analysis of the electromagnetic radiation scattered, absorbed or emitted by molecules.

Electromagnetic spectrum:

The arrangement of all types of electromagnetic radiation in order of their increasing wave-lengths ordecreasing frequency is known as complete electromagnetic spectrum.

γ rays	X rays	Ultra violet	Visible	Infra red	Micro wave	Radio waves

→ Wavelength

← frequency

Ultra-Violet (UV) and visible absorption spectroscopy

UV and visible spectroscopy (electronic spectroscopy) is used to measure the multiple bonds or aromatic conjugation within molecule. The U.V region can also be divided into near & far (vacume) U.V region. The word vacume is used because the molecule of air [O_2 & N_2] obsorbs in this region and thus this region is acceptable only with special vacuum equipments.

		Visible
Far U.V	U.V	V I B G Y O R

1500A° 2000A° 4000A°   8000A°

→ wave length.
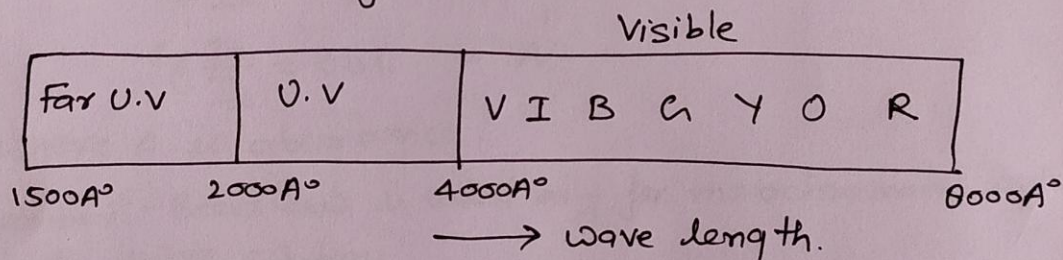
From 4000 A° — 8000A° we get visible region se the compound in this region appears coloured to human eye.

Absorption law :-

When a beam of monochromatic
radiation of suitable frequency
passes through a solution. It
is absorbed by the solution,
as a result the intensity of
the light when it is finally
emerges from the solution is
considerably reduced.
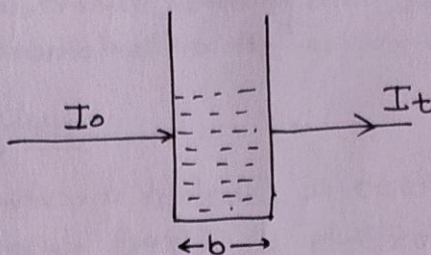
If I_0 — Intensity of incident light
I_t — " " transmitted light

Intensity of absorbed light $(I_a) = I_0 - I_t$

Lambert - Beer law :-

According to this law, the intensity of a beam of a monochro-
matic radiation decreases exponentially with increase in thickness
(b) and the concentration(c) of the absorbing medium.

$$\frac{I_t}{I_0} = e^{-\epsilon bc} \qquad \epsilon - \text{molar absorption coefficient}$$

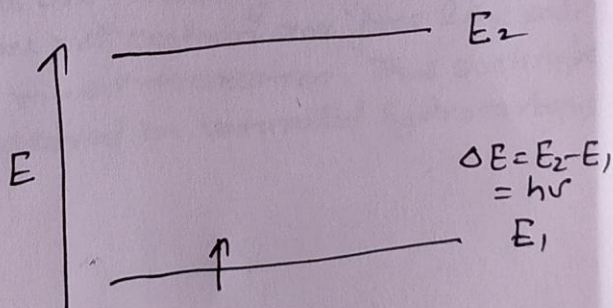$$\log \frac{I_t}{I_0} = -\epsilon bc$$

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

where A is absorbance.

Lambert - Beer's law is valid only for monochromatic light
and for dilute solutions.
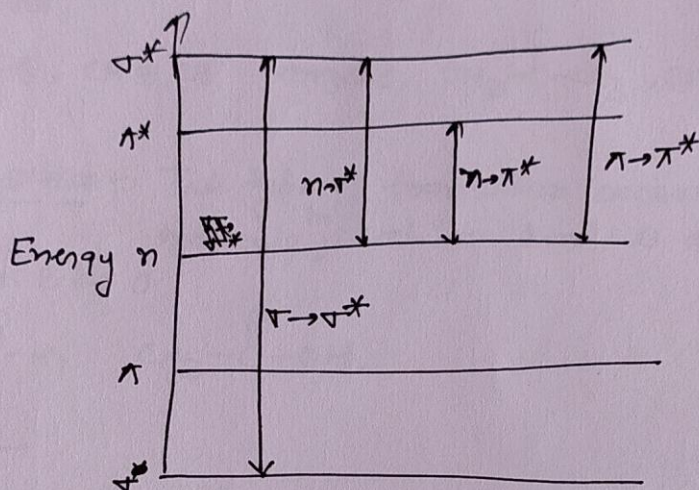
Electronic transition :-

Since the energy levels of
a molecule are quantized, the
energy required to bring about
the excitation is a fixed value.
~~If the radi~~
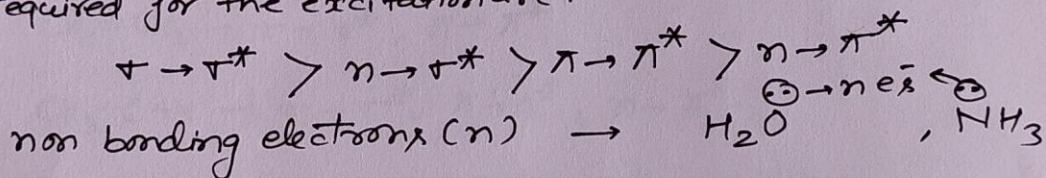
E

E_2

$\Delta E = E_2 - E_1$
$= h\nu$

E_1

If the radiation of the correct of desired frequency is passed through the sample of the substance, energy will be absorbed and the electrons will be promoted to the higher energy level.

Types of electronic transition :-

According to M.O theory, when a molecule is excited by the absorption of energy (U.V or visible light), its electron are promo -ted from a bonding to anti bonding M.O's.

from above it is clear that four electronic transition it may occur in a molecule. The decreasing order of energy required for the excitation are.

$$\sigma \to \sigma^* \; > \; n \to \sigma^* \; > \; \pi \to \pi^* \; > \; n \to \pi^*$$

non bonding electrons (n) → $H_2\overset{\cdot\cdot}{O} \overset{\oplus \to nes \ominus}{}$, NH_3

$\underline{\sigma \to \sigma^* \text{ transition}}$:- Its a high energy process since σ bonds are generally very strong. The organic compounds which does not contain any free lone pair of electron normally undergo $\sigma \to \sigma^*$ transition. Thus such type of transition are normally observed in saturated hydrocarbons eg CH_4, C_2H_6 etc.
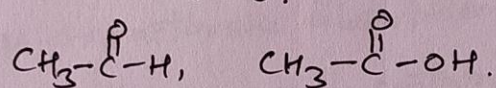
$\underline{n \rightarrow \sigma^* \text{ transition}}$:- This type of transition takes place in saturated compounds containing one hetro atom (N, S, O, Cl etc.) which contains at least one lone pair of electron.
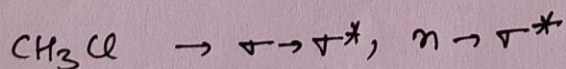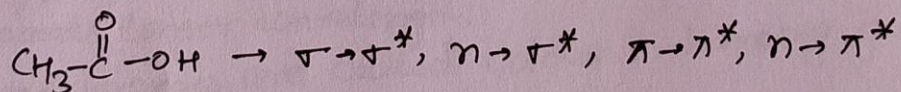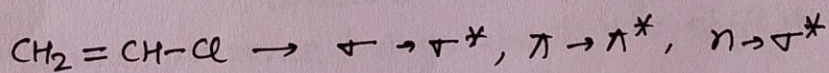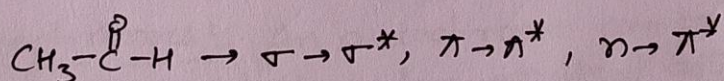
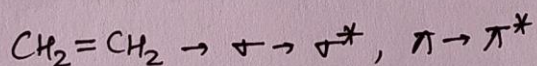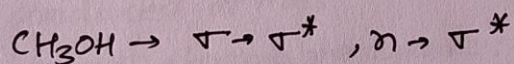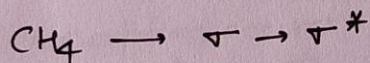eg CH_3OH, CH_3Cl, CH_3NH_2 etc.

$\underline{\pi \rightarrow \pi^* \text{ transition}}$:- This type of transition occurs in the molecule that contains at least one $= \text{ or } \equiv$ bond.

eg $CH_2=CH_2$, $CH\equiv CH$, benzene, $CH_3-\overset{O}{\overset{||}{C}}-CH_3$, $CH_3-\overset{O}{\overset{||}{C}}-OH$ etc.

$\underline{n \rightarrow \pi^* \text{ transition}}$:- This type of transition occurs in the molecule which $=$ bond is attatched to hetro atom like σ.

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

Examples $\rightarrow$

$CH_4 \longrightarrow \sigma \rightarrow \sigma^*$

$CH_3OH \rightarrow \sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$

$CH_2=CH_2 \rightarrow \sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$

$CH_3-\overset{O}{\overset{||}{C}}-H \rightarrow \sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$

$CH_2=CH-Cl \rightarrow \sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$

$CH_3-\overset{O}{\overset{||}{C}}-OH \rightarrow \sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$

$CH_3-\overset{O}{\overset{||}{C}}-NH_2 \rightarrow$ "   "   "   "

$CH_3Cl \rightarrow \sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$

Electronic transition Range :-

$\sigma \to \sigma^*$ — $< 160 \, nm$

$n \to \sigma^*$ — $160 - 180 \, nm$

$\pi \to \pi^*$ — $180 - 220 nm$

$n \to \pi^*$ — $220 - 320 \, nm$

UV range — $200 - 400 nm$

Visible " — $400 - 800 nm$

* $\sigma \to \sigma^*$ & $n \to \sigma^*$ electronic transition — do not absorb
  UV or visible light.

* $n \to \pi^*$ & $\pi \to \pi^*$ → Absorbs UV & vibt visible light.

Chromophores :-

It is defined as any isolated covalently bonded group that shows characterstic absorption is the UV or visible region.

Generally the compounds containing $=$ or $\equiv$ bond will absorb UV or visible light.

The absorption occurs irrespective to the fact whether colour is produced or not.

Important chromophores are :- $=$, $\equiv$, $\overset{\circ}{\underset{\circ}{C}}$, $\overset{\circ}{\underset{\circ}{C}} - OH$, $C \equiv N$
$-NO_2$ etc.

Auxochromes :-

An auxochrome can be defined as any group which does not itself acts as an chromophore but whose presence brings about the shift of absorption band towards longer wavelength.

Auxochromes are called colour enhancing group.

Imp. Auxochromes are :- $-OH$, $-NH_2$, OR, $-SH$ etc.

Absorption and Intensity shifts :-
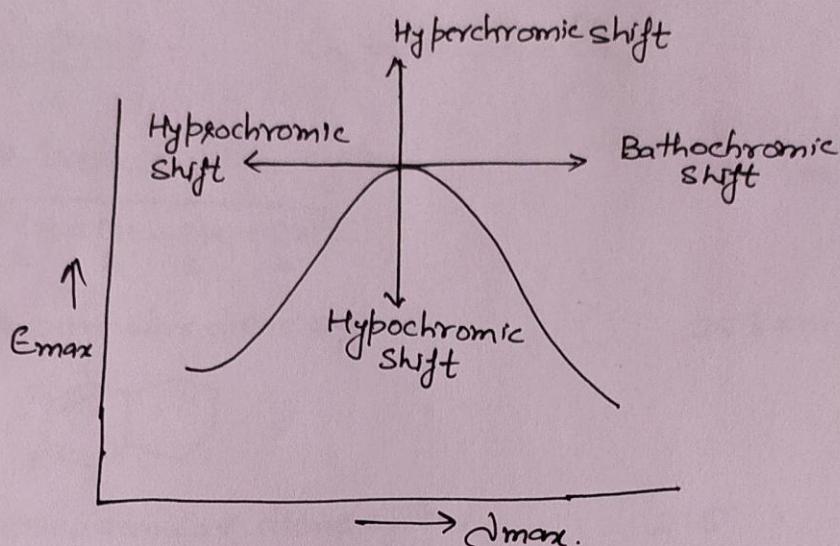
[a] __Bathochromic shift__ :- It is an effect due to which the λ_{max} is shifted towards longer wave length. It happens due to the presence of an auxochrome. It is also called red shift.

[b] __Hypochromic shift__ :- It is an effect due to which the λ_{max} is shifted towards shorter wavelength. It happens due to removal to auxochrome or conjugation. It is also called blue shift.

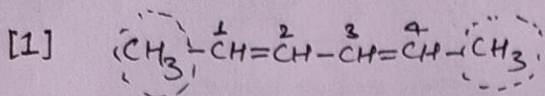[c] __Hyperchromic shift__ :- It is an effect due to which intensity of λ_{max} increases.

[d] __Hypochromic shift__ :- Due to which intensity of λ_{max} decreases.

λ_{max} :-

It is the wavelength at which compounds absorbs maximum light.

Calculation of λ_{max}

[1] $\underset{(CH_3)}{}-\overset{1}{C}H=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H-(CH_3)$
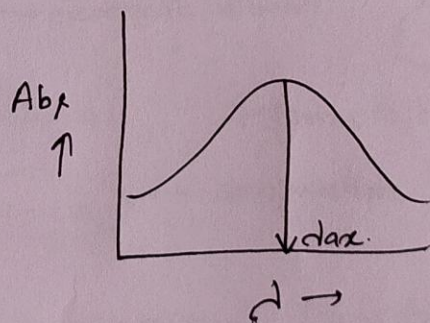
Basic value = 217 nm

alkyl substituent (2) = +10 nm

$\overline{\qquad\qquad\qquad}$

λ_{max} = 227 nm

[2] (ring)$\overset{1}{=}\overset{2}{C}H-\overset{3}{\underset{(CH_3)}{C}}=\overset{4}{C}H-(CH_3)$
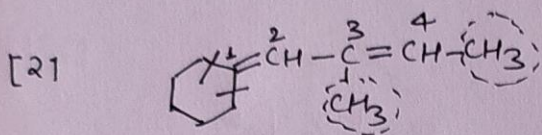
Basic value = 217 nm

1 exocyclic =bond = +5 "

2 alkyl subs = +10 "

2 Ring Residues = +10 "

$\overline{\qquad\qquad\qquad}$

λ_{max} = 242 "

[3]

$$\underset{CH_3}{}\underset{1}{}C H=\underset{\overset{|}{CH_3}}{\overset{2}{C}}=\overset{3}{C}H-\overset{4}{C}H=\overset{5}{C}H-CH_3$$

$\overset{1}{CH_3}-\overset{2}{C}H=\overset{3}{\underset{(CH_3)}{C}}-\overset{4}{C}H=\overset{5}{\underset{(CH_3)}{C}}-\overset{6}{C}H=CH-(CH_3)$
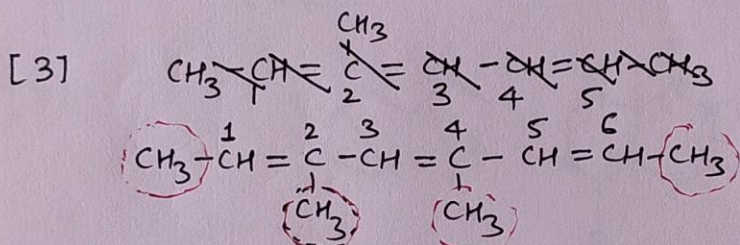
Basic value = 217 nm

1 = bond extending conjugation = +30 "

4 alkyl subs = +20 "

$\overline{\qquad\qquad\qquad}$

λ_{max} = 267 nm

[4] $\overset{1}{CH_2}=\overset{2}{C}H-\overset{3}{\underset{(CH_3)}{C}}=\overset{4}{C}H-(CH_2-CH=CH-CH_3)$ [No conjugation]
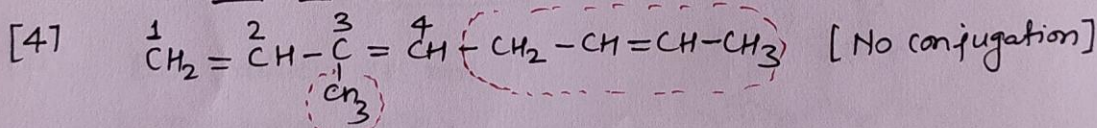
Basic value = 217 nm

2 alkyl subs = +10 "

$\overline{\qquad\qquad\qquad}$

λ_{max} = 227 "

[5]
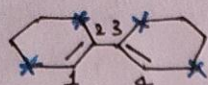
hetero annular diene
Basic value = 215 nm
4 Ring Residue = +20 "
λ_{max} = 235 "

[6]

Basic value = 215 nm
1 exo cyclic =bond = +5 "
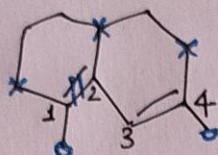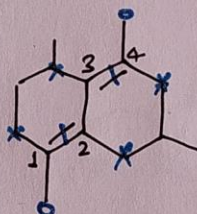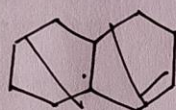2 alkyl subs = +10 "
3 Ring Residue = +15
λ_{max} = 245 nm

[7]

Basic value = 215 nm
2 exo = +10 "
2 alkyl = +10 "
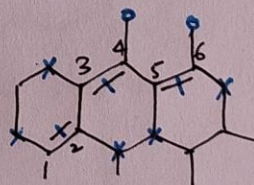4 R.S = +20 "
λ_{max}. 255 "

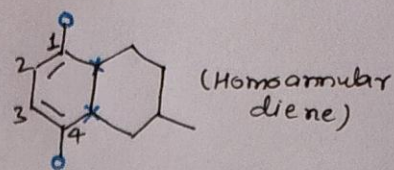[8] Basic value = 215 nm
1 conjugation = +30 "
3 exo = +15 "
2 alkyl = +10 "
5 R.S = +25 "
λ_{max} = 295 "
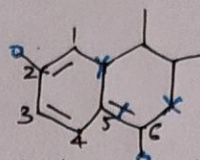
[9] Basic value = 253 nm
    2 alkyl   = +10 "
    2 R·S   = +10 "
    ─────────────────────
    λ_{max} = 273 "

(Homoannular diene)

[10] Basic value = 253 nm
    1 conjugation = +30 "
    1 exo   = +5 "
    2 alkyl   = +10 "
    3 R·S   = +15 "
    ─────────────────────
    λ_{max} = 313 "
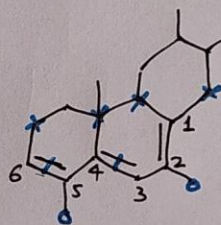

It have both homo & hetro annular diene.
basic value of Homo will be taken.

[11] Basic value = 253 nm
    1 exo   = +5 "
    1 alkyl   = +5 "
    3 R·S   = +15 "
    ─────────────────────
    λ_{max} = 278 "
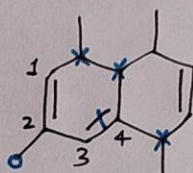
[12] Basic value = 253 nm
    1 conjugation = +30 "
    2 exo   = +10 "
    2 alkyl   = +10 "
    4 R·S   = +20 "
    ─────────────────────
    λ_{max} 323 "

[13] Basic value = 253 nm
    2 conjugation = +60 "
    1 exo   = +5 "
    1 alkyl   = +5 "
    5 R·S   = +25 "
    ─────────────────────
    λ_{max} = 348 nm