→ Spectroscopy - Introduction स्पेक्ट्रोस्कॉपी -परिचय :→

→ Electromagnetic Radiations (विद्युत चुम्बकीय विकिरणें) :→

- It was believed that light travels in a straight line (particle nature) कण प्रकृति
- Some important phenomena like Interference (व्यतिकरण), Refraction (अपवर्तन) and Diffraction (विवर्तन) Can not explain on the basis of particle nature of light.
- To explain these phenomena, light is supposed to travel in wave (तरंग)
- All the properties of light can be explained on the basis of particle (कण) and wave nature. (Dual Nature) (द्वैत प्रकृति)
- Maxwell reveals that light waves are associated with electric and and magnetic field. (विद्युत व चुम्बकीय क्षेत्र)
- like light, there are various form of radiation which are associated with electric and magnetic fields. these radiations are called Electromagnetic Radiations.

→ Properties of EMR :→

- These are produced by oscillation (दोलन) of electric charge (विद्युत आवेश) and magnetic field (चुम्बकीय क्षेत्र) residing on the atom.
- The electric and magnetic components are mutually perpendicular (परस्पर लम्बवत) to each other and are coplanar.

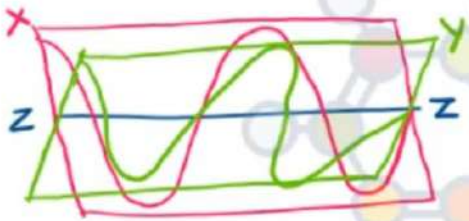


fig:- planes of Electromagnetic waves

- These are characterised by their wavelength (तरंगदैर्ध्य) or frequencies (आवृत्ति) or wave number (तरंगसंख्या)
- The energy carried by an EMR is directly proportional to its frequency.

$$\text{energy of EMR} \propto \text{Frequency}$$

- The emission (उत्सर्जन) or absorption (अवशोषण) of radiation is quantised (क्वांटीकृत) and each quantum of radiation is called Photon (फोटोन) or quanta (क्वांटा)

- All types of radiations travel with same velocity.
- No medium is required for their propagation. They can travel through Vacuum.
- When white light is passed through a prism, it is split into seven colours. this phenomena is called dispersion (विक्षेपण).

⇒ units :-

ⓐ Wave length (तरंग दैर्ध्य) (λ) :→

- The distance b/w two crests (शीर्ष) or troughs (गर्त) in a particular wave is called wave length.

unit (इकाई) A° or $m\mu$ or nm

$1 A^\circ = 10^{-8}$ cm

$1 m\mu = 10^{-7}$ cm

$1 nm = 10^{-9}$ m

ⓑ Wave number (तरंग संख्या) ($\bar{\nu}$):→

- The reciprocal (व्युत्क्रम) of wavelength is called wave number $\bar{\nu} \propto \frac{1}{\lambda}$
- the total no of wave which can pass through a space of 1cm.

unit = cm^{-1} ✱ used in Infrared technique.

ⓒ Frequency (आवृत्ति) (ν) :→

– Number of waves which can pass through a point in one second.

unit :- Hertz $\quad 1\,Hz = 1\,cycle\ sec^{-1}$

$$\text{Frequency} \propto \frac{1}{\text{Wave length}}$$

ⓓ Energy (ऊर्जा) (E):→

Energy of a particular radiation is given by

$$E = h\nu$$

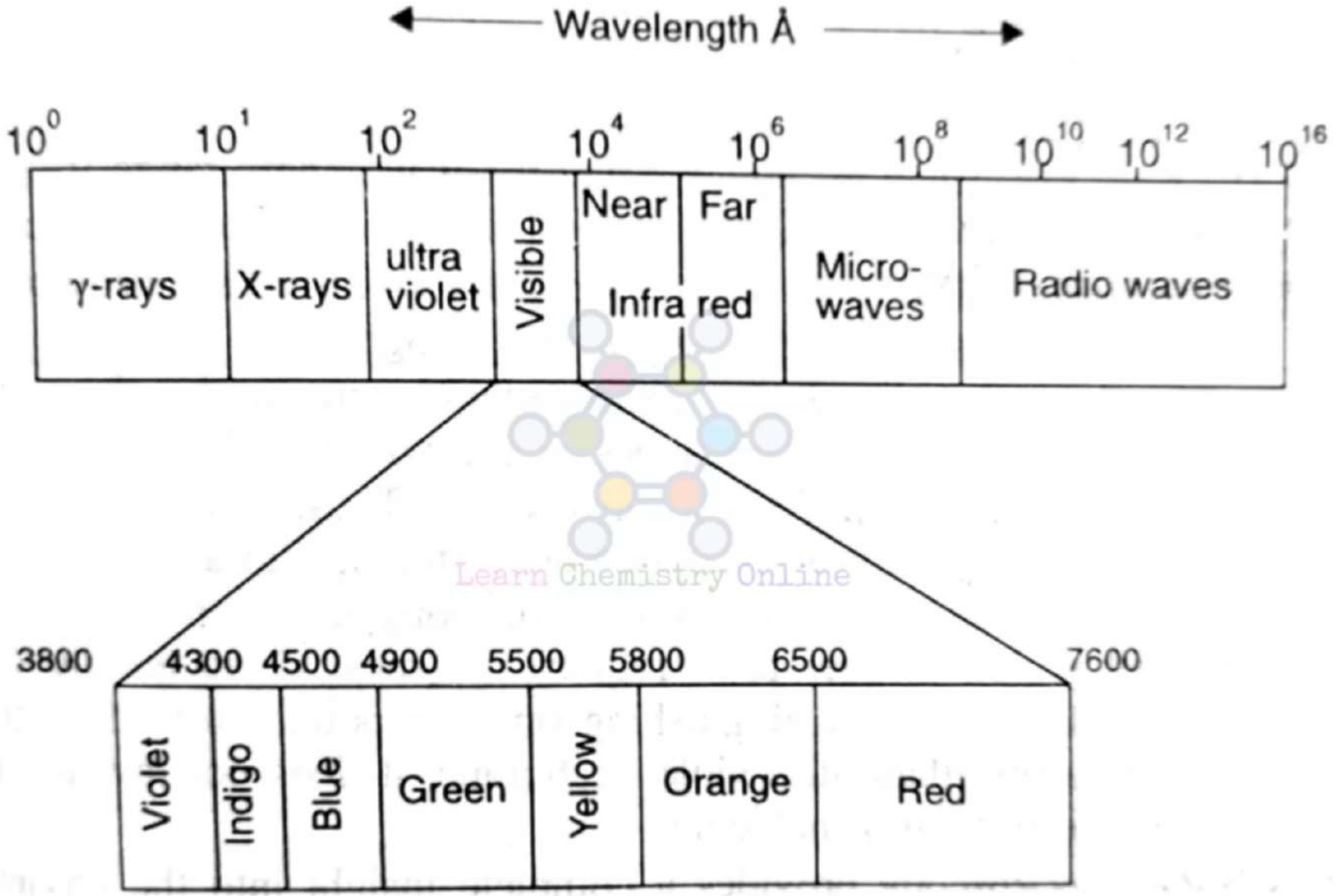
or $\quad E = h \cdot \frac{c}{\lambda} \quad \because \nu = \frac{c}{\lambda}$

h = planck's constant

ν = Frequency

c = Velocity of EMR

λ = Wavelength



⇒ Spectroscopy :→

- Spectroscopy may be defined as interaction (अन्तक्रिया) between matter (द्रव्य) and electromagnetic radiation.
- The study of Spectroscopy deals with emission spectra (उत्सर्जन स्पेक्ट्रा) and absorption spectra (अवशोषण स्पेक्ट्रा)
- Absorption spectra:- is produced by absorption of radiant energy (विकिरण ऊर्जा)
- Emission spectra :- is produced by emission of radiant energy
- The wavelength of absorbed or emitted radiation is measured by spectrometer.

Summary of Spectroscopic Techniques			
S.No.	**Radiation Absorbed**	**Changes in the Molecule of a Substance**	**Information Obtained**
1.	Infra red 667–4000 cm^{-1}	Changes in the vibrational and rotational movements of the molecule.	Detection of almost all functional groups which have specific vibrational frequencies, e.g., C=O, O—H, C≡ C, NH_2 etc.
2.	Ultraviolet 190–400 nm Visible 400–800 nm	Changes in electronic energy levels within the molecule.	Conjugated unsaturation, conjugation with non-bonding electrons. Extent of π-electron system.
3.	Radio-frequency 60–300 MHz	Nuclear magnetic resonance induces changes in the magnetic properties of certain atomic nuclei, notably that of hydrogen.	Hydrogen atoms in different environments can be detected, counted and analysed for structure determination.
4.	Electron Beam Impact 70 eV, 6000 kJ mol^{-1}	Ionisation and fragmentation of the molecule into a spectrum of fragment ions.	Determination of molecular weight and deduction of molecular structure from the fragments obtained.

→ Ultra-violet Spectroscopy :→ पराबैंगनी स्पेक्ट्रोस्कॉपी :→

- This is also called Electronic spectroscopy. (इलेक्ट्रॉनिक स्पेक्ट्रोस्कॉपी)
- Ultra-violet spectroscopy involves promotion of e^- from ground state (आद्य अवस्था) to higher energy state. (उच्च ऊर्जा अवस्था)
- Ultra-violet spectroscopy involves absorption of radiations (विकिरण) of Ultra-Violet and visible region (दृश्य क्षेत्र) of electromagnetic spectrum. (विद्युत चुम्बकीय स्पेक्ट्रम)
- following e^- are promoted in UV spectroscopy -
  - (a) σ e^-
  - (b) π e^-
  - (3) n e^-

- Since the energy levels of a molecule are quantised (क्वांटीकृत), the energy required for excitation (उत्तेजित) of e^- is a fix quantity. thus, the EMR with only a particular Value of frequency will be able to cause excitation.
- If the substance is exposed to radiation of some different Value of frequency, energy will not be absorbed and there is no loss of intensity (तीव्रता)

- If the radiation or light of correct or desired frequency is fall on the compound or sample, energy will be absorbed and electrons will be promoted to higher energy states.
- After absorption of radiation, its intensity will be less or may be completly lost.
- Substance absorbing in the visible range (दृश्य परास) will appear coloured to human eye.
- The wavelength of particular radiation absorbed canbe expressed in the terms of frequency or energy in Kcal/mole.

1500 A° 2000 A° Ultraviolet 4000 A° Visible 8000 A°
150 (पराबैंगनी) (दृश्य) 800 mμ

— Wavelength ⟶

- A record of the amount of light absorbed by the sample as a function of the wavelength of light in mμ or nm units is called absorption spectrum. (अवशोषण स्पेक्ट्रम). which generally consist of absorption bands (अवशोषण बैण्ड या पट्टी)
- The far UV region (below 2000Å or 200 mμ) is not much studied due to absorption by oxygen and nitrogen. Moreover, studies in these regions require Vacuum instruments.

→ Use of UV Spectroscopy :→

- used to measure conjugation (संयुग्म) and aromatic conjugation in molecule.
- used to differentiate-
  - (a) Conjugated and non-conjugated system.
  - (b) α, β- unsaturated (असंतृप्त) Carbonyl compounds from β, γ- analogues. (संगत)
  - (c) Homoannular (समवलय) and Heteroannular (विषम वलय)

→ The Absorption Law :- (अवशोषण नियम) :→

- There are two laws which explain the absorption of light by the molecules.-

① Lambert's Law (लैम्बर्ट नियम) ② Beer's Law (बीयर नियम)

① Lambert's Law :→

- When a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intenstiy of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation.
- जब किसी एकवर्णी प्रकाश की किरण को संमागी अवशोषक माध्यम में से गुजारा जाता है तो अवशोषक माध्यम की मोटाई के साथ विकिरण की तीव्रता में कमी की दर, आपतित विकिरण की तीव्रता के समानुपाती होती है।

Mathematically.

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

- Mathematically, the law expressed as

$$-\frac{dI}{dx} \propto I \quad \text{—(1)}$$

I = Intensity of radiation after passing

x = thickness

dI = Small decrease in intensity

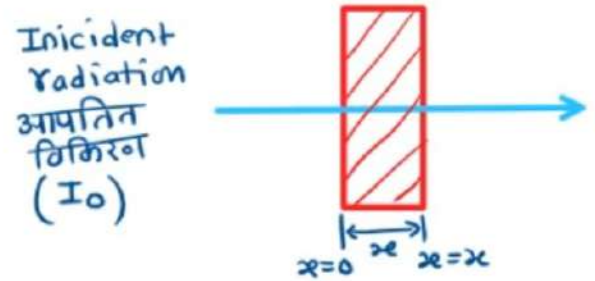
dx = Small thickness

$\frac{-dI}{dx}$ = rate of decrease of intensity of radiation with thickness of absorbing medium

or $$-\frac{dI}{dx} = KI \quad \text{—(2)}$$

K = proportionality constant or absorption Coefficient (समानुपातिक स्थिरांक या अवशोषण गुणांक)

- value of K depends upon nature of absorbing medium.



eq. (2) can be written as

$$\frac{dI}{I} = -K\,dx \quad \text{—(3)}$$

integrate eq. (3) b/w the limits

or $$\int_{I_0}^{I} \frac{dI}{I} = -\int_{x=0}^{x=x} K\,dx \left[\because \int_a^b \frac{dx}{x} = [\ln x]_a^b = \log b - \log a = \log\frac{b}{a}\right]$$

or $$\ln\frac{I}{I_0} = -Kx \quad \text{or} \quad \frac{I}{I_0} = e^{-Kx}$$

or $$\boxed{I = I_0 e^{-Kx}} \quad \text{—(4)}$$

- Intensity of radiation absorbed (I_{abs}) is given by -

$$I_{abs} = I_0 - I$$

from eq. ④

$$I_{abs} = I_0 - (I_0 e^{-kx})$$

or $$\boxed{I_{abs} = I_0(1 - e^{-kx})} \quad - ⑤$$

on changing natural log to base 10 eq. ④ can be written as

$$I = I_0 10^{-\frac{k}{2.303}x}$$

or $$\boxed{I = I_0 10^{-ax}}$$

where $a = \frac{k}{2.303}$

a = extinction coefficent of the absorbing medium
(विलोपन गुणांक)

→ **Beer's law** :→

- When a beam of monochromatic light is passed through a solution of an absorbing system, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the conc^n of the solution.

- जब किसी एकवर्णी प्रकाश की किरण को संमागी अवशोषक माध्यम में से गुजारा जाता है तो अवशोषक माध्यम की मोटाई के साथ विकिरण की तीव्रता में कमी की दर, आपतित विकिरण की तीव्रता तथा विलयन की सान्द्रता के समानुपाती होती है।

- Mathematically, this law is expressed as

$$-\frac{dI}{dx} = k'IC$$

k' = molar absorption coefficient
~~मोलर अवशोषण गुणांक~~
its value depends upon the nature of absorption medium

C = conc^n of Sol. in moles/litre

or $\int_{I_0}^{I} \frac{dI}{I} = -\int_{x=0}^{x=x} k'C\,dx$

or $\boxed{I = I_0 e^{-k'Cx}}$

or $\boxed{I = I_0 10^{-a'Cx}}$

I_0 = Intensity of Incident Radiation
I = Intensity of trasmitted Radiation
x = thickness of medium

$a' = \frac{x}{2.303}$ = molar extinction coefficient of Solution

→ Chromophore :- (क्रोमोफोर)

- All those compounds which absorb light of wavelength between 400-800 mμ (visible range) appear Colour to human eye. Exact colour depends upon the wavelength of the light absorbed by the compound.
- It is defined as any isolated covalenty bonded group (विलगित सहसंयोजी बंधित समूह) that shows a characteristic absorption in the ultra violent or the visible reason.
- The absorption occurs irrespective of the fact whether colour is produced or not.
- Some important chromophores are –

① Ethylenic ② Acetylenic ③ Carbonyls ④ Acids ⑤ Esters

⑥ Nitrile etc.

* Carbonyl group is an important chromophore, although, the absorption of light by an isolated group does not produce any Colour in UV spectroscopy.

- There are two types of chromophore —

① chromophore in which group contains π e^- and undergo $\pi - \pi^*$ transition

example :- $>C=C<$ Ethylene

$-C\equiv C-$ Acetylene etc.

② Chromophore which contains both π e^- and n e^- and undergo $\pi-\pi^*$ and $n-\pi^*$

example :- $>C=\ddot{O}$ Carbonyls

$-C\equiv \ddot{N}$ Nitriles

$-\ddot{N}=\ddot{N}-$ Azo compounds

✱ - In compounds like $>C-C<$ and $>C-H$, absorption occurs around 150 mμ (Vacuum UV Region) as result of $\sigma \rightarrow \sigma^*$ transition.

- In compounds like $-\ddot{O}-$, $-\ddot{S}-$, $>\ddot{N}-$ etc., absorption occurs around 190 mμ as result of $n \rightarrow \sigma^*$ transition.

✱ There are no set rules for the identification of chromophores. The change in position as well as the intensity of absorption depends upon large no. of factors.

⇒ Auxochrome (ऑक्सोक्रोम) :→

- An auxochrome can be defined as any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards red end of the spectrum (longer wavelength)
- The absorption at longer wavelength is due to combination of a chromphore and an auxochrome to give rise to another chromophore.

  Chromophore + auxochrome → New Chromophore.
- Auxochromic group is also called colour enhancing group. (वर्ण वर्धक समूह)
- Auxochromic group do not show characteristic absorption above 200 mμ.

exameples $-OH$ (Hydroxy), $-OR$ (Alkoxy), $-NH_2$ (amine), $-NHR$ (2° amine), $-NR_2$ (3° amine)
$-SH$ (Thiol) etc.

- The effect of auxochrome is due to extension in conjugation of chromophore by sharing of non bonding e⁻

example

Benzene $\lambda_{max} = 255$ mμ

Aniline $\lambda_{max} = 430$ mμ

→ Types of Electronic Transitions :→ (इलेक्ट्रॉनिक संक्रमण के प्रकार)

– According to MOT, when a molecule is excited by the absorption of energy (UV or Visible), its e^- promoted from a bonding to an antibonding orbital.

① $\sigma \rightarrow \sigma^*$ transition
② $n \rightarrow \sigma^*$ transition
③ $\pi \rightarrow \pi^*$ transition
④ $n \rightarrow \pi^*$ transition

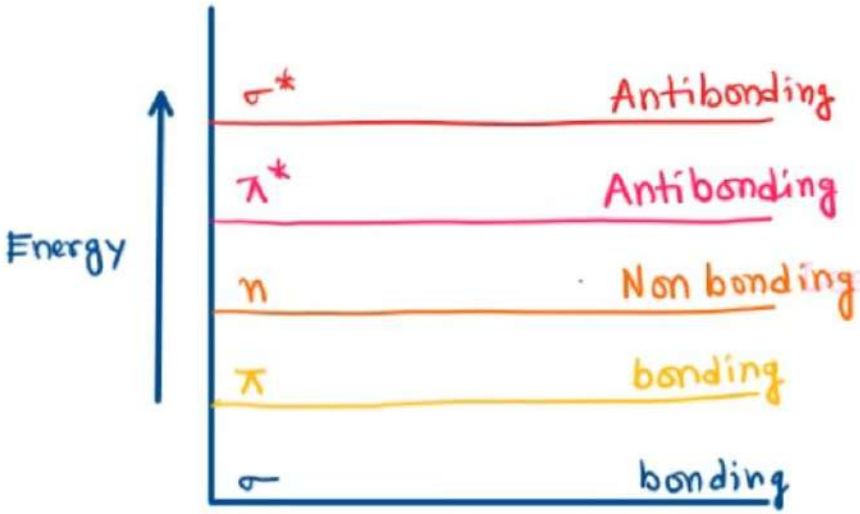


Fig:→ Various electronic energy levels

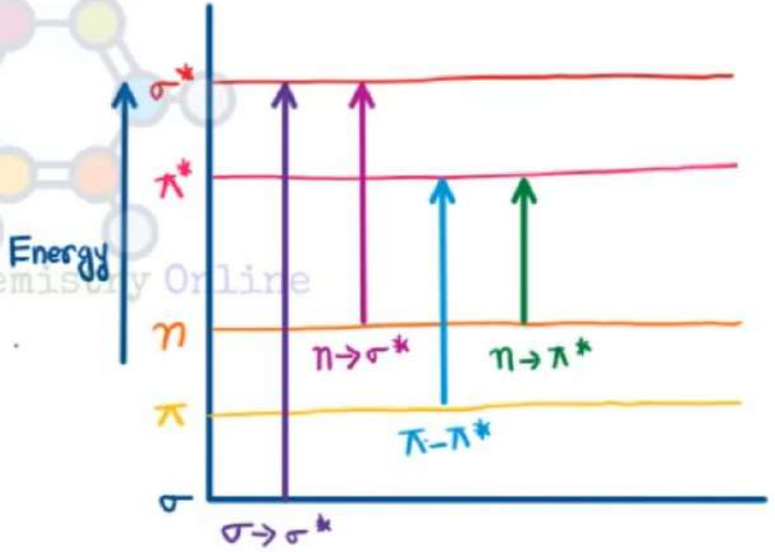


Fig:→ Electronic excitation energies

* Order of energy for transitions → $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$

① $\sigma \rightarrow \sigma^*$ transitions :→

- It is high energy process because σ bonds are strong.
- Saturated compound (संतृप्त यौगिक) do not show absorption in the normal UV region, i.e 180–400 mμ.
- Saturated compound like methane, propane etc. show absorption near 150 mμ (high energy or short wavelength)
- Consider a $\sigma \rightarrow \sigma^*$ transition in a saturated hydrocarbon

- The usual spectroscopy can not be used below 200mμ, since oxygen (present in air) begins to absorb strongly.
- To study such high energy transitions, the entire path must be evacuated (aire must be excluded). Thus, region below 200 mμ is called Vacuum UV Region.
- The excitation of sigma bond e⁻ to σ^* level occurs with net retention of electronic spin. This is called excited singlet state.

(2) $n \rightarrow \sigma^*$ transitions :→

- This type of transition occurs in Saturated compound containing one hetero atom (विषम परमाणु) with unshared pair (असाझित युग्म) of e^-.
- examples - Saturated halides ($R-\ddot{X}:$), alcohol ($R-\ddot{O}-H$), ether ($R-\ddot{O}-R$), Aldehyde ($R-\underset{:O:}{\overset{\|}{C}}-H$), ketone ($R-\underset{:O:}{\overset{\|}{C}}-R$), amine ($R-\ddot{N}H_2$) etc.
- This transition requires less energy than $\sigma \rightarrow \sigma^*$.

$$\text{>C}-\ddot{X}: \xrightarrow{n \rightarrow \sigma^*} \text{>C}-\ddot{X}:$$

- In Saturated alkyl halides, the transition energy decreases with the increase in the size of halogen atom (or decrease in Electonegativity of atom)

	CH_3-Cl		CH_3-I
E.N.	Cl	>	I
λ_{max}	172 - 175 mμ		λ_{max} - 258 mμ (longer wavelength or lower energy)

- Similarly, amine absorbs at higher wavelength as compare to Alcohol.
- Hydrogen bond shift UV absorption to shorter wavelength (due to non bonding e^-)

③ $\pi - \pi^*$ transitions :→

- This type of transition occurs in unsaturated centre of the molecules, i.e. double or triple bonds and also in aromatics.
  example - alkenes, alkynes, carbonyl compounds, cyanides, azo compounds etc.
- The excitation of π e^- requires smaller energy (π is weaker than σ) hence transition occurs at longer wavelength.
- Consider an alkene -

- This transition requires less energy than $n \rightarrow \sigma^*$
- Absorption usually occurs within region of ordinary UV region.
- In unconjugated alkene, absorption band appear around 170 - 190 mμ.
- In Carbonyl compounds, absorption band appear around 180 mμ.
- Extension in conjugation also shifts absorption towards longer wavelength.
  example. ethen $\lambda_{max} = 180$ mμ 1,3 - Butadiene $\lambda_{max} = 217$ mμ.

④ $n \rightarrow \pi^*$ transitions :→

- In this type of transition, an e⁻ of unshared e⁻ pair on hetero atom gets excited to π^* antibonding orbital.
- This type of transition required less energy out of all transitions and hence occurs at longer wavelength.

example :-

shows both type of transition

$\pi \rightarrow \pi^*$ – 180 mu

$n \rightarrow \pi^*$ – 290 mu

$n \rightarrow \sigma^*$ - also occurs

- In Saturated Carbonyl compounds, two types of transitions take place -

ⓐ High energy transitions

(i) $n \rightarrow \sigma^*$ (Intense)

(ii) $\pi \rightarrow \pi^*$ (Intense)

ⓑ Low energy transitions

(i) $n \rightarrow \pi^*$ (weak)

* In Carbonyl compounds, shift in the absorption depends on the polarity of the Solvent.

→ Theory of Electronic spectroscopy :→

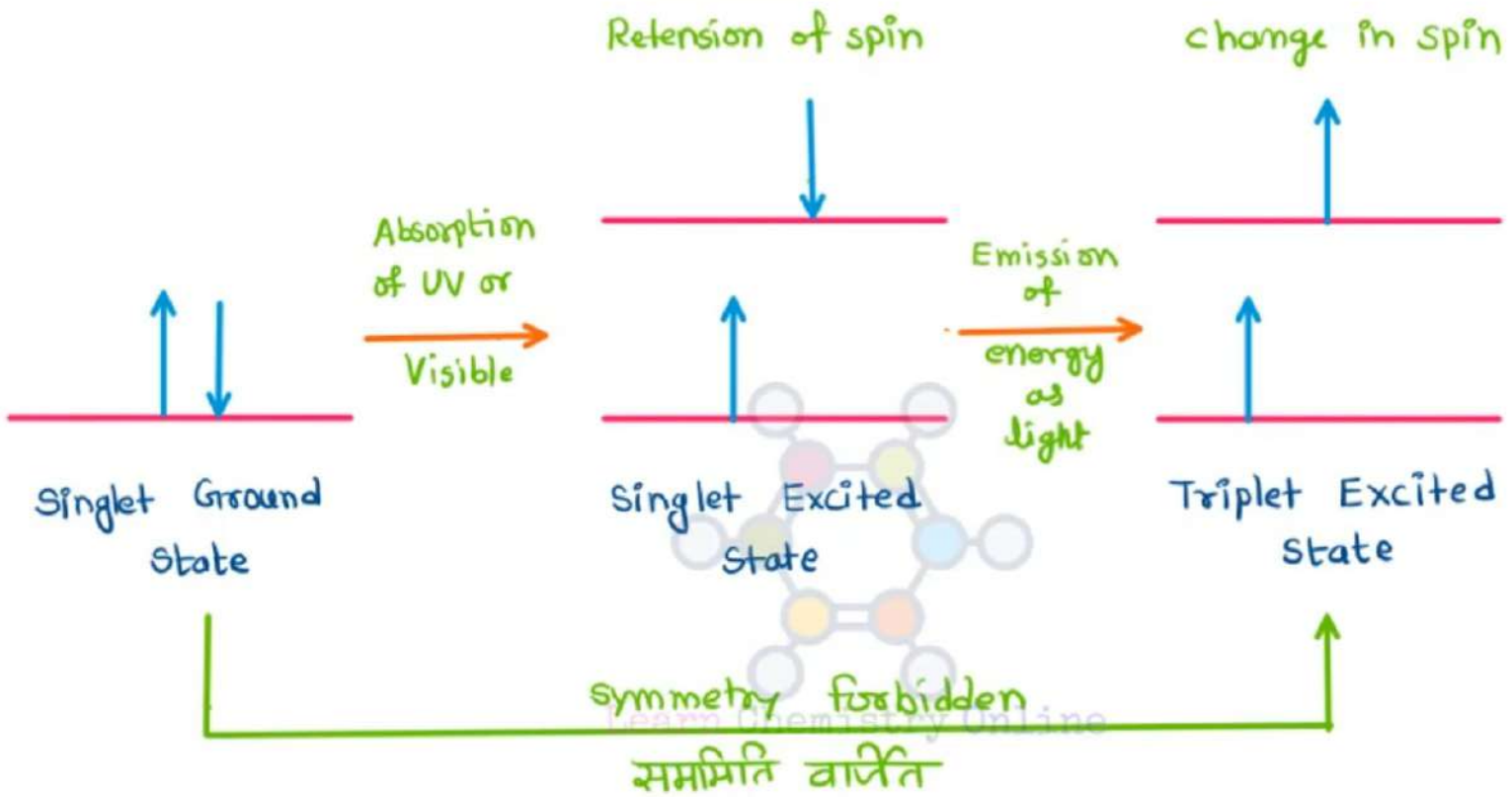
- When the molecule absorbs UV or visible light, its electrons gets promoted from the ground state to the higher energy state
- In the ground state, the spins of the e^- in molecular orbital are paired

- In the higher state, there are two possibilites

① Singlet Excited state
- e^- are paired ↓ ↑
- higher energy
- lower stability

② Triplet Excited State
- e^- are parallel ↑ ↑
- lower energy ($e^- - e^-$ repulsion minimum, e^- are far apart)
- higher stability

- Multiplicity of State = $2S+1$ S = Sum of spin quantum no.



→ Absorption and Intensity shifts :- (अवशोषण व तीव्रता विस्थापन) :→

⇒ Absorption shifts

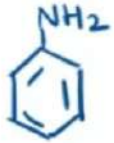
① Bathochromic shift (वर्णोत्कर्षी विस्थापन) :→

- In this shift, absorption maximum (λ_{max}) is shifted towards longer wavelength due to presence of an auxochrome or by change of solvent.
- This is also called Red Shift, because absorption shifts towards longer wavelength
- Extension of Conjugation also Cause this shift.
- example ①  λ_{max} = 254 nm  λ_{max} = 261 nm

② The $\pi \rightarrow \pi^*$ transition for carbonyl comp. experiences bathochromic shift when the polarity of solvent is decrease.

② Hypsochromic shift (वर्णोपकर्षी विस्थापन) :→

- In this shift, absorption maximum is shifted towards shorter wavelength due to removal of conjugation and also by changing polarity of the solvent.
- This is also called Blue Shift

example :-  Aniline  Aniliniumion (Acidic medium)

⇒ Intensity shift :→

① Hyperchromic shift (अतिवर्णक विस्थापन)

- In this shift, intensity (तीव्रता) of absorption maximum increases i.e. ε_{max} increases. ε_{max} = Extinction Coefficient
- The introduction of an auxochrome usually increases intensity of absorption.

example :-

Pyridine

$\varepsilon_{max} = 2750$

$\lambda_{max} = 257$ nm (mμ)

2-Methy pyridine

$\varepsilon_{max} = 3560$

$\lambda_{max} = 262$ nm (mμ)

② Hypochromic Shift (अधोवर्णक विस्थापन)

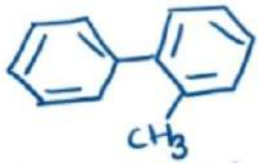
- In this shift, intensity of absorption maximum decreases i.e. ε_{max} decreases
- The introduction of group which distort (विकृत) the geometry of the molecule, decreases intensity of absorption

example :-

Biphenyl

$\varepsilon_{max} = 19000$

$\lambda_{max} = 250$ nm



2-Methyl biphenyl

$\varepsilon_{max} = 10250$

$\lambda_{max} = 237$ nm

↳ it is due to distortion (~~विकृति~~) caused by $-CH_3$ (Methyl group)

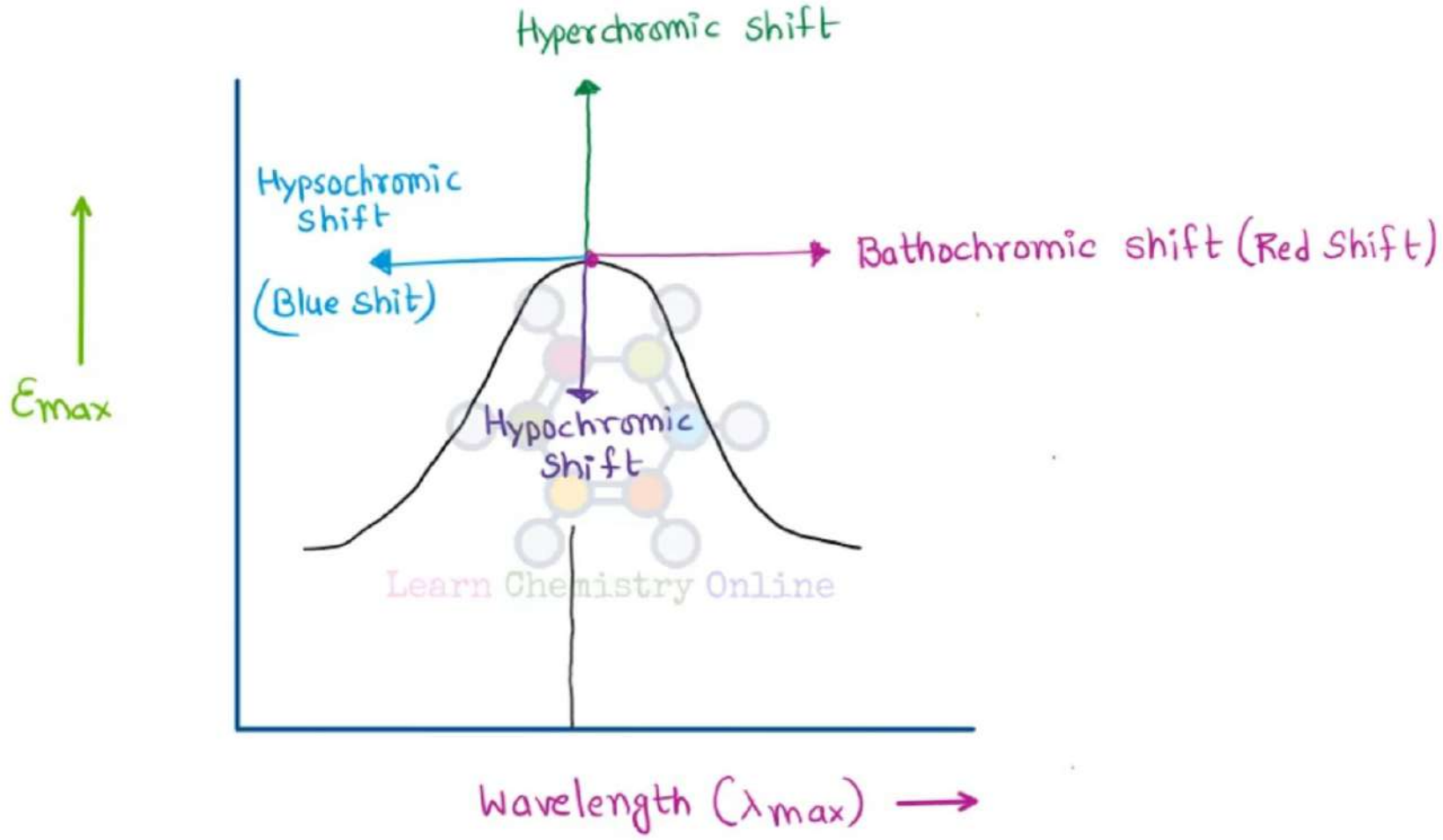


Fig. Absorption and Intensity shift

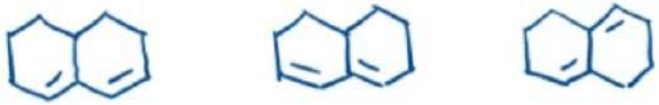
→ Woodward - Fieser rules for calculating absorption maximum (λ_{max}) in Dienes :→

- Absorption maximum (λ_{max}) ∝ Length of conjugated system.
- The conjugated polyene system appears coloured to the eye if there are more than five double bond in conjugation (संयुग्म) and absorption occurs above 400 mμ or nm (Visible range) (दृश्य क्षेत्र)
- Types of double bond in conjugation are-

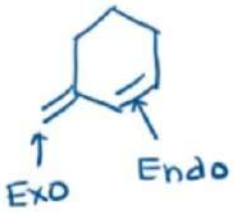
ⓐ Alicyclic dienes (अचक्रीय डाइईन) or dienes contained in open chain system.
- basic unit is butadiene system

ⓑ Homo-annular (समवलय) conjugated double bonds (Homodienes)
- when conjugated double bonds present in same ring

ⓒ Hetero-annular (विषमचक्रीय) conjugated double bonds
- when conjugated double bonds are not present in same ring



© Exocyclic and Endocyclic conjugated double bond.



Exocyclic to ring A

Contains two Exocyclic bonds.

- Woodward formulated certain rules for Calculating λ_{max} in case of dienens. These rules were modified by Fieser in 1948.
- According to these rules, each type of diene has a fixed basic value and value of λ_{max} (Absorption max.) depends upon :-

① The no. alkyl group or ring residue (वलय अवशेष) on the double bond.

② No. of double bonds extending conjugation

③ The presence of polar group such as
-Cl, -Br, -SR, -OR etc

Conjugated dienes and Trienes.

Solvent–Ethanol Transition involved—$\pi \rightarrow \pi^*$	
Parent value for Butadiene System or a cyclic conjugated diene	217 mμ (nm)
Acyclic Triene	245 mμ (nm)
Homoannular conjugated diene	253 mμ (nm)
Heteroannular conjugated diene	215 mμ (nm)
Increment for each substituent	
Alkyl substituent or ring residue	5 mμ (nm)
Exocyclic double bond	5 mμ (nm)
Double bond extending conjugation	30 mμ (nm)
Auxochrome	
—OR	+ 6 mμ (nm)
—SR	+ 30 mμ (nm)
—Cl*, —Br*	+ 5 mμ (nm)
$—NR_2$	+ 60 mμ (nm)
$OCOCH_3$	0 mμ (nm)

* In case of cyclic or open chain diene, 17 mμ are added

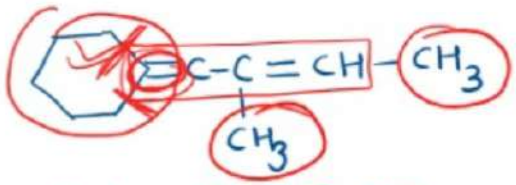
→ Examples :-

① $CH_3-CH=CH-CH=CH-CH_3$

Basic value :- 217 nm

2 Alkyl group :- 10 nm

λ_{max} = 227 nm

② 

B.V. ⇒ 217 nm

2 Alkyl group ⇒ 10 nm

2 R.R ⇒ 10 nm

1 Exo cyclic ⇒ 5

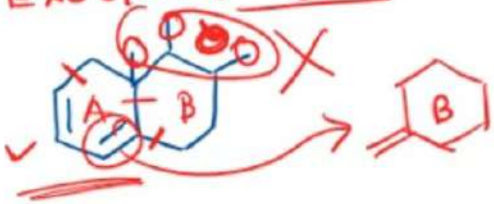
λ_{max} = 242 nm

③ 

B.V. = 215 nm

4 R.R. = 20 nm

λ_{max} ⇒ 235 nm

④ 

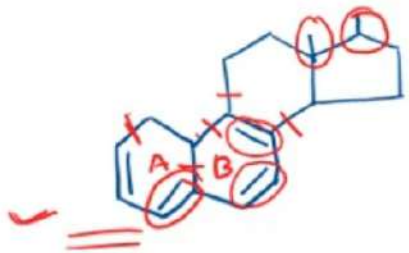
B.V. ⇒ 253 nm.

3 R.R. ⇒ 15 nm

1 Exo ⇒ 5 nm

λ_{max} 273 nm

(5)



B.V. = 253 nm

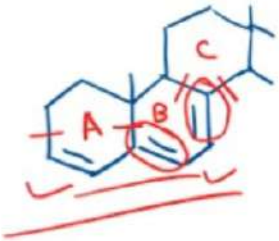
5 R.R. = 25 nm

1 Exo = 5 nm

2 Extension = 60 nm

λ_{max} = 343 nm

(6)



B.V = 253 nm

4 R.R = 20 nm

2 Exo = 10 nm

1 Extension = 30 nm

λ_{max} = 313 nm

→ Woodward - Fieser rules for Calculating absorption maxium (λ_{max}) in α,β- unsaturated Carbonyl compounds.

- Woodward and fieser framed certain rules for estimating the absorption maximum (λ_{max}) for α,β- unsaturated Carbonyl compounds. (α,β - असंतृप्त कार्बोनिल यौगिक)
- These rules were later modified by scott.
- Rules are -

ⓐ The basic value for α,β- unsaturated Ketone → 215 nm (mμ)

* Ketone maybe cyclic or six membered

X = Alkyl group → 215 nm

X = H (Aldehyde) → 207 nm

X = -OH or -OR → 193 nm

ⓑ If the double bond and the carbonyl group are contained in five membered ring (cyclopentenon) → 202 nm

The structural increments for estimating λ_{max} for a given α, β-unsaturated Carbonyl compound are as follows :

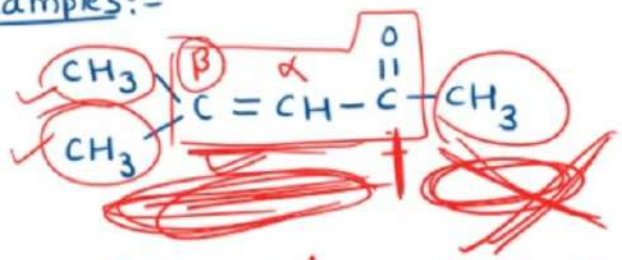
(*i*) For each exocyclic double bond	+ 5 mμ
(*ii*) For each double bond endocyclic in five or seven membered ring except cyclo-pent-2 enone	+ 5 mμ
(*iii*) For each alkyl substituent or ring residue at the	
α-position	+ 10 mμ
β-position	+ 12 mμ
γ- or δ- or higher position	+ 18 mμ
(*iv*) For each double bond extending conjugation	+ 30 mμ
(*v*) For a homoannular conjugated diene.	+ 39 mμ

Chromophore increments in Carbonyl Compounds

Chromophore	Increment in nm (or mμ) for position w.r.t. the carbonyl group			
	α-	β-	γ-	δ- or higher
—OH	+35	+30	—	+50
—OAc	+6	+6	+6	+6
—Cl	+15	+12	—	—
—Br	+25	+35	—	—
—OR	+35	+30	17	31
—SR	—	+85	—	—
$—NR_2$	—	+95	—	—

Examples:-

(1)

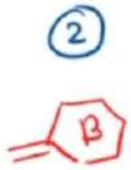


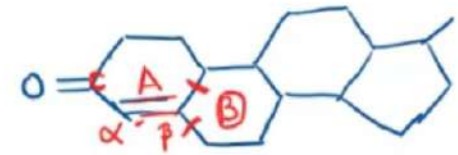
Basic value → 215 nm

2 β- alkyl group → 24 nm (12)

λ_{max} → 239 nm

(2)



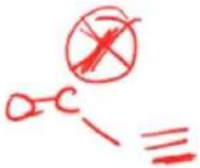


Basic value → 215 nm

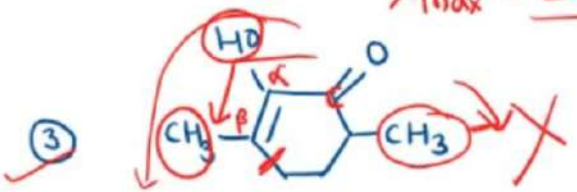
2β- RR (2×12) - 24 nm

1 exocyclic = 5 nm

λ_{max} → 244 nm



(3)



Basic V - 215 nm

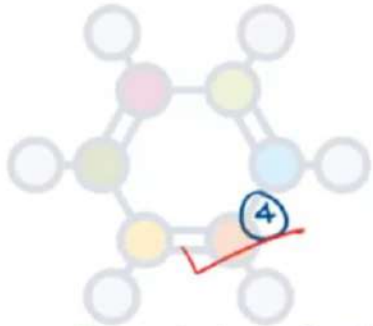
1 β - Alkyl grp - 12 nm

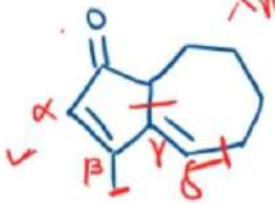
1 β - RR - 12 nm

1 -OH @ α 35 nm

λ_{max} → 274 nm

(4)





Basic value = 202 nm

1 - β - alkyl = 12 nm

1 exocyclic = 5 nm

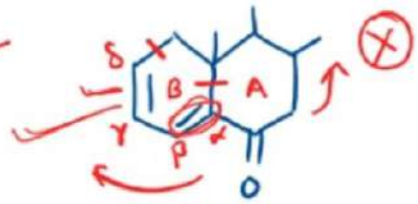
1 double bond exte = 30 nm

1 γ - RR = 18 nm

1 δ - RR = 18 nm

× 285 nm

(5)



Basic V = 215 nm

1 α - RR = 10 nm

1 δ - RR = 18 nm

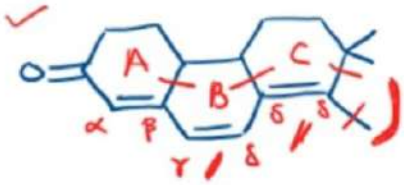
1 exocyclic = 5 nm

Homoannular = 39 nm

1 extention = 30 nm

λ_{max} → 317 nm

(6)



B.V ⇒ 215 nm

1 β - RR ⇒ 12 nm

1 δ - RR ⇒ 18 nm

2 δ - RR = 36 nm

2 double = 60 nm (30 × 2)

2 exocyclic = 10 nm

λ_{max} ⇒ 351 nm

→ Molar absorptivity or Molar extinction coefficient (ε):→

- The molar extinction coefficient is a measure of intensity of absorption.
- It is the measurement of absorption efficiency at the given wavelength.

OR

$$A = \varepsilon l c = \log_{10} \frac{I_0}{I} \quad \text{OR} \quad \varepsilon = \frac{A}{cl}$$

Where :- I_0 = Intensity of the incident light

I = Intensity of the transmitted light

ε = Molar absorptivity or molar extinction coefficient.

c = concentration (mole/l)

l = path length (cm)

- The intensity of absorption is directly proportional to the transition probability. A fully allowed transition will have ε value greater than 10^4 while those with low transition probability will have ε value less than 10^3.

→ Unit of ε :→

$$\varepsilon = A/cl$$

$$\varepsilon = L/(\text{mol } L^{-1}) \times (\text{cm})$$

$$= L \text{ mol}^{-1} \text{ cm}^{-1}$$

→ Effect of conjugation on UV spectra of dienes:→

- A conjugated system requires lower energy (higher wavelength) for $\pi - \pi^*$ transition than unconjugated system.
- Example:→ λmax for Butadiene ($CH_2=CH-CH=CH_2$) ⇒ 217 nm
  λmax for Ethylene ($CH_2=CH_2$) ⇒ 175 nm
- Higher the number of double bonds in conjugation, longer will be the wavelength of absorption which can move into the visible region, i.e. the compound is coloured.
- Further the conjugation of two chromophores not only produces a bathochromic shift but also increases the intensity of the absorption bands.

(a) Effect of conjugation in Acyclic dienes:→

- Ethylene absorbs at 175 nm while 1,3-butadiene absorbs at 217 nm. The effect of conjugation may be explained as follows -

A double bond consist of two π-MOs, one bonding and one antibonding. But when two double bonds are brought into conjugation, four new MOs are formed - two of these (ψ_1 and ψ_2) are bonding and are occupied by pair of electron each while other two (ψ_3 and ψ_4) are antibonding.

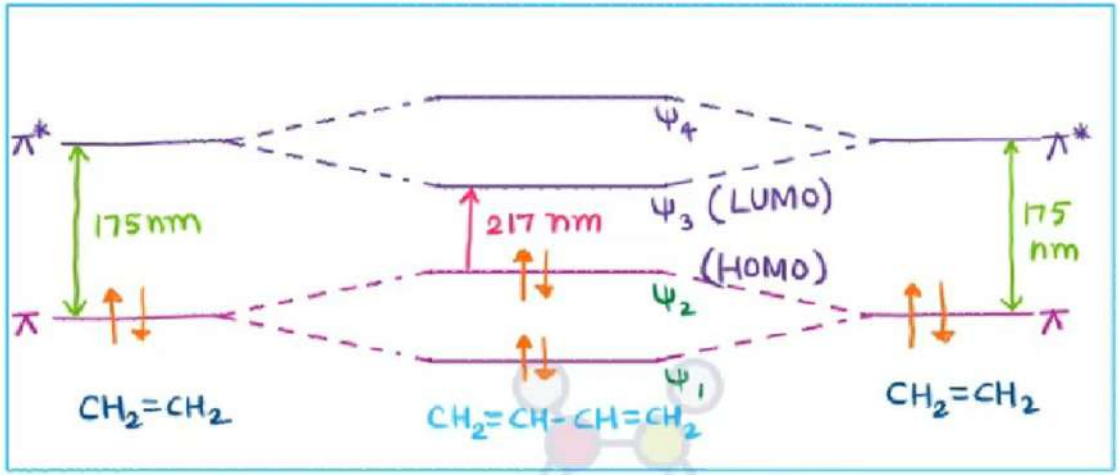


fig:- MOs of 1,3-Butadiene

LUMO = Lowest unoccupied molecular orbital

HOMO = Highest occupied molecular orbital

- It is clear that energy of LUMO (Ψ_3) is decreases while that of HOMO (Ψ_2) is increases. due to this the energy levels involved in $\pi-\pi^*$ transition come closer and lesser amount of energy is required.
- Similarly when three double bonds are brought into conjugation, the energy gap b/w LUMO and HOMO becomes smaller and the $\pi-\pi^*$ absorption band shows a further bathochromic shift (higher wavelength) with further increase in ε_{max} of the absorption band.

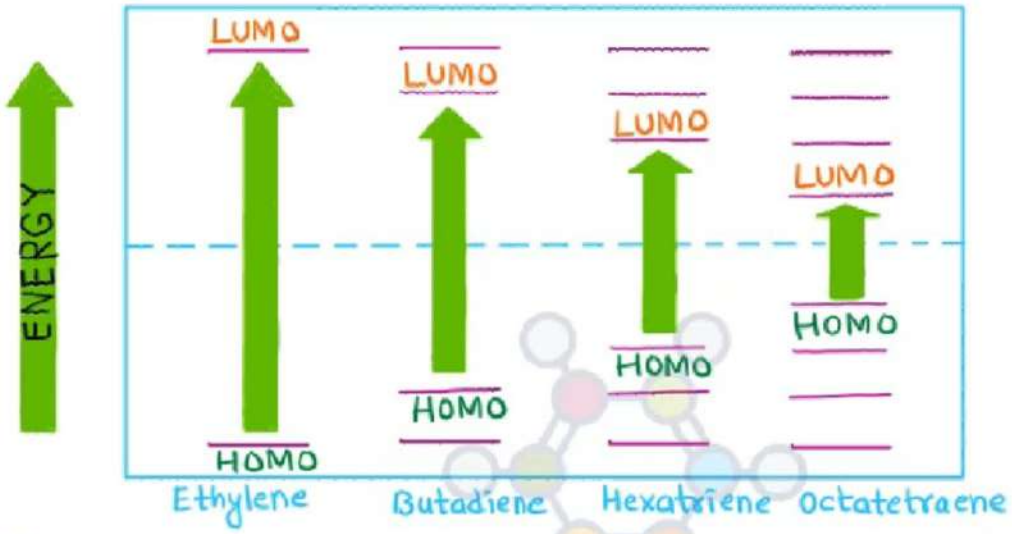
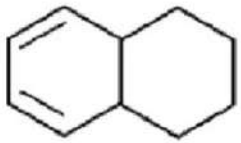


fig:- As the conjugation increases energy gap b/w HOMO and LUMO increase and absorption shifts to longer wavelength.

⑥ Effect of conjugation in cyclic dienes :→

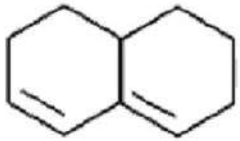
- Homoannular dienes (two double bonds in same ring) absorb at longer wavelength but with lesser intensity as compared to heteroannular dienes (two double bonds in different rings) which absorb at shorter wavelength but with higher intensity.



Homoannular diene

λ_{max} = 263 nm

(ε_{max} = 5,000 - 8,000)

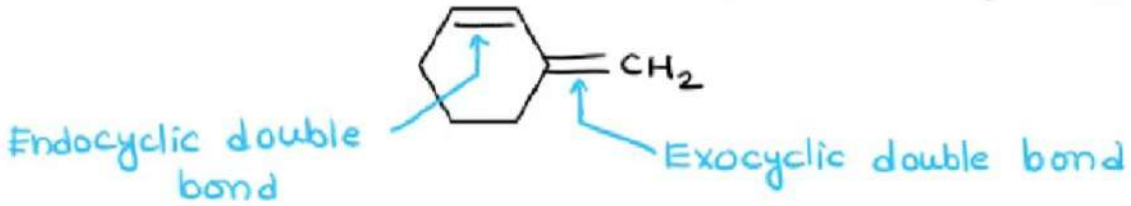


Heteroannular diene

λ_{max} = 234 nm

(ε_{max} = 18,000 - 20,000)

- Each exocyclic double bond increases λ_{max} of given cyclic conjugated diene or polyene by 5 nm. This small bathochromic shift is due to fact that an exocyclic double bond distorts the strainless staggered conformation of the chair form of cyclohexane more than an endocyclic double bond and hence energy gap between HOMO and LUMO decreases thereby λ_{max} shifted towards longer wavelength.



→ Presentation and analysis of UV spectra :→

① Presentation of UV spectra :→

- An UV spectrum is a plot of a wavelength (λ) versus the Absorbance (A) or optical density.

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

here A = Absorbance

I_0 = Intensity of radiation before passing through solution.

I = Intensity of radiation after passing through solution.

- The absorption intensity can also be measured in the terms of molar absorptivity (ε) or its logarithm, $\log \varepsilon$. It is also called molar extinction coefficient.

$$\varepsilon = \frac{A}{cl}$$

here ε = molar absorptivity

A = Absorbance

c = conc^n of solution (mol/lit)

l = thickness of sample (cm)

- Peaks in UV or visible spectrum is quite broad. That is, they span many wavelengths. it is convenient to specify the molar absorptivity (ε) at the wavelength of greatest intensity of absorption within a broad peak.
- Wavelength of greatest intensity is represented by λ_{max} and at this wavelength molar absorptivity is shown by ε_{max}.
- ε is replaced by $\log \varepsilon$ if ε is very large.

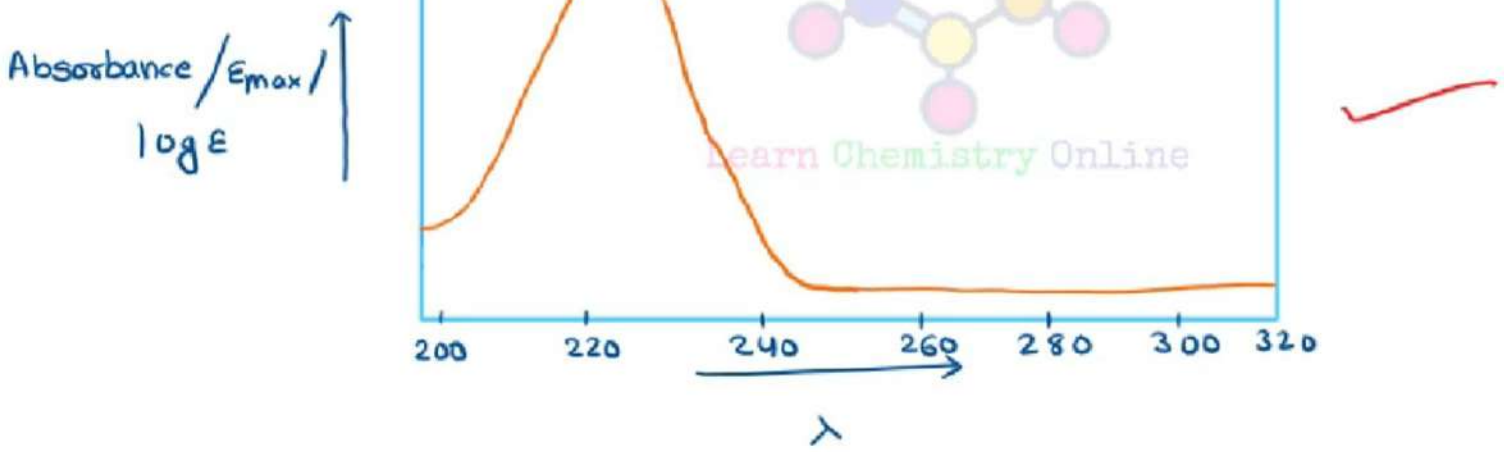


fig:- UV spectrum of Isoprene (in methanol) $CH_2=C(CH_3)-CH=CH_2$

② Interpretation (Analysis) of UV spectra :→

① A single absorption of low intensity ($\varepsilon > 100$) in the region 250-350 nm, without any major absorption at shorter wavelength (200-250 nm) indicates $n \rightarrow \pi^*$ transition.

e.g. $-N=N-$, $-NO_2$, $>C=O$, $>C=N$, $-COOR$, $-COOH$, $-\langle\bigcirc\rangle-NH_2$ etc.

② A single absorption of low to medium intensity ($\varepsilon = 100 - 10000$) in the region < 220 nm indicates $n \rightarrow \sigma^*$ transition.

e.g. amines, alcohols, ethers, triols, haloalkanes etc.

③ Two bands of medium intensity ($\varepsilon = 100 - 10000$) in the region > 200 nm indicate a aromatic system.

④ High intensity band ($\varepsilon = 10000 - 20000$) in the region > 210 nm indicates α, β-unsaturated ketone or diene or a polyene.

⑤ Two absorption of low intensity in the region > 300 nm ($n \rightarrow \pi^*$) & < 250 nm ($\pi - \pi^*$) indicate unconjuated ketones, acids, esters, amides etc.

⑥ An absorption in visible region indicates highly coloured compound likely to contain a long-chain conjugated non-aromatic system, benzenoid system or polynuclear aromatic chromophore.

→ Applications of UV spectroscopy :→

(A) Qualitative Analysis :→

1. Detection of functional groups :→

- The ultraviolet spectroscopy has been used to detect the presence or absence of certain groups in the organic molecules.
- For example, if an organic compound shows no λ_{max} above 200 nm, it cannot have a conjugated chromophore, and aldehyde or ketone, benzene ring or halogen. However it may possess fluorine or chlorine, carboxy group, cyano group etc.

2. Detection of impurities :-

- Compounds with large λ_{max} values can be detected when present as impurities, even at low impurities, in sample of substance having no absorption in the region of the sample.
- Example - Benzene can be detected as low concentration impurity in ethanol using UV spectroscopy. Benzene absorpts at 254 nm but ethanol does not absorb in this region.

3. Study of charge transfer complex :-

- The colour of the charge transfer complex can be explained on the basis of UV spectroscopy

Example :- Brown colour of Benzene-iodine ($C_6H_6-I_2$) complex.

4. Distinction between conjugated and non-conjugated compounds:-

- Conjugted compounds absorb at a longer wavelength than non-conjugated compounds.

5. Determination of extent of conjugation:-

- Greater the number of conjugated double bonds, higher will be the wavelength of absorption.

6. Study of geometrical isomerism:-

- Trans isomer absorbs at a longer wavelength with higher intensity than corresponding cis isomer.
- This is due to more effective π-orbital overlap possible in the trans isomer whereas in the cis-isomer, the coplanarity is lost due to steric effect.

7. Study of keto-enol tautomerism:-

- Keto and enol forms exist as tautomeric mixture and their UV spectra will show absorption characteristics of both keto and enol forms.
- Keto form shows weak absorption due to $n \rightarrow \pi^*$ transition.
- Enol form shows strong $\pi \rightarrow \pi^*$ absorption due to conjugated double bond.

8. Progess of a reaction:-

- The progress of a reaction can be studied by measuring UV spectra of aliquots (a portion of a larger whole or a sample taken for chemical analysis) taken from the reaction mixture time to time.

9. Determination of Strength of Hydrogen bond :-

- When a carbonyl compound is dissolved in polar, protic solvents, such as water, hydrogen bonds are formed between the solvent and n electrons of carbonyl oxygen and causes hyposochromic shift.
- On the basis of hyposochromic shift it is possible to determine the strength of the hydrogen bond. The shift is equal to a decrease in energy which may considered to be equivalent to the strength of the hydrogen bond.

(B) Quantitative analysis:-

- Quantitative UV spectroscopy is based on Beer-Lambert law.
- Using Beer-Lambert law Conconcentration of a compound can be determined.

Example:- Concentration of anthracene and naphthalene in anthracene-naphthalene mixture can be determined using quantitative UV spectroscopy (Beer-Lambert law)