SPECTROSCOPY (Electronic Spectroscopy)

- UV spectroscopy (Ultraviolet - Visible)
- IR spectroscopy (Infra Red)
- NMR spectroscopy (Nuclear Magnetic Resonance)

Absorption Spectroscopy (Light, Electromagnetic waves)

Emission Spectroscopy (Light, Electromagnetic waves)

U.V spectroscopy :

→ Promotion of electrons ($\sigma, \pi, \underline{n^*}$) from ground state to excited state (higher energy level)

n^* → Antibonding

→ Uses : a) To measure no of conjugated double bonds.

b) Aromatic conjugation within molecules

c) To differentiate conjugated and non-conjugated system.

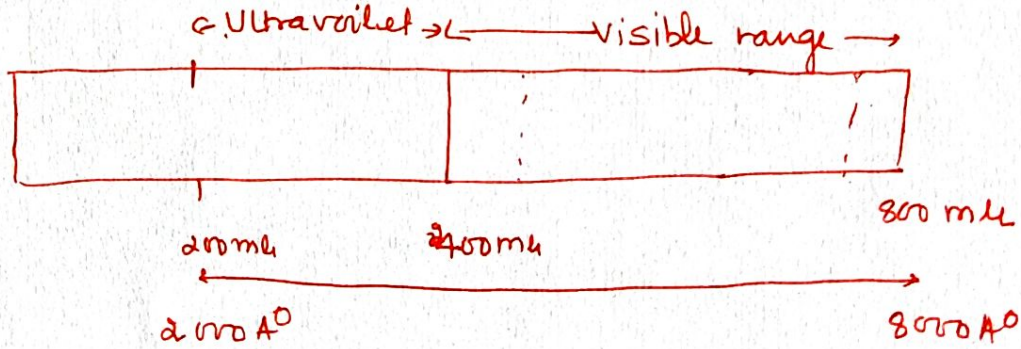
d) α- β- unsaturated compounds identification

e) Homoannuler or Heteroannuler compounds identification

f) Conjugated dienes identification

etc.

Ultraviolet Visible spectroscopy



→ Energy level of Molecules are quantised.

↓

Energy required to promotion to higher level should also be quantised.

$1\ \mu = 10^{-4}\ cm.$

$1\ m\mu = 1\ nm = 10^{-7}\ cm = 10\ A^{0}$

Q. Calculate the energy associated with radiations having 280 mμ.

$\lambda = 280\ m\mu = 280 \times 10^{-7}\ cm$

We know $E = h\frac{c}{\lambda} = h\nu$

$(h = 6.62 \times 10^{-27}$ ergs/sec$)$

4.18×10^{7} ergs = 1 calorie

$$E = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{280 \times 10^{-7} \times 4.18 \times 10^{7}}\ \text{Calorie}$$

$$E = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{280 \times 10^{-7} \times 4.18 \times 10^{7} \times 10^{3}}\ \text{KCal}$$

Energy per mole = E/Avagadro Number

$$E = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10} \times 6.02 \times 10^{27}}{280 \times 10^{-7} \times 4.18 \times 10^{7} \times 10^{3}}\ \text{KCal/mol.}$$

$$\boxed{E = 100\ \text{KCal/mole}}$$

Absorption – Governed by two laws

1. Lambert's Law
2. Beer's Law

1. <u>Lambert's Law:</u>

When a beam of monochromatic radiation passes through a homogenous absorbing medium, the rate of decrease of intensity of radiation with respect to thickness of absorbing medium is proportional to the intensity of incidant radiation.

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

I is intensity of light
dI is small decrease in intensity
dx is small thickness of homogenous sample.

$$-\frac{dI}{dx} = KI$$

K = proportionality constt.
↳ Absorption coefficient
↳ value depends upon medium.

Suppose I_0 = intensity of medium before entering in medium.

I = intensity after transmitance from medium

$$-\frac{dI}{dx} = KI$$

or $$-\frac{dI}{I} = K \cdot dx$$

Integrating this equation

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_{x=0}^{x=x} K\,dx$$

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

$$I = I_0 e^{-Kx}$$

So $\boxed{I_{abs} = I_0 - I = I_0(1 - e^{-kx})}$

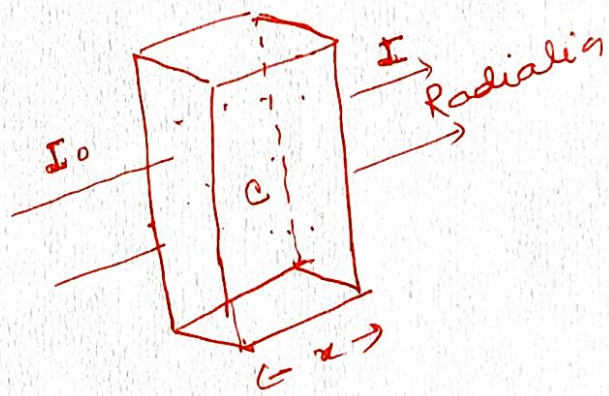
If we consider $\log_{10}$ then we can write

$$I = I_0 10^{-ax}$$ → extinction coefficient of absorbing medium.

$$\left(a = \frac{k}{2.303}\right)$$

Beer's Law:

When a light beam of monochromatic radiation is passed through a solution of absorbing substance the rate of decrease of intensity of radiation wrt thickness of absorbing solution is proportional to incident radiation as well as concentration of solution



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

$$-\frac{dI}{dx} = k' I c$$

$$-\frac{dI}{I} = k' dx \cdot c$$

On Integrating both sides

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_{x=0}^{x=x} k' dx \cdot c$$

$$\boxed{I = I_0 e^{-kcx}}$$

molar extinction coefficient $= a'$

then $\boxed{I = I_0 10^{-a' cx}}$

Limitation of Beer Lamberl Law:

- Not applicable when sample exist in more than one form.
- Not applicable for fluorescent compounds
- Not applicable when solute and solvent form complex compound.

'A' → For Absorbance.

a, a' → Molar extinction cofficient.

↓

ϵ

$$\log \frac{I_0}{I} = A = a c l (x)$$

Prob: 2.5×10^{-4} M solution of a substance in 1 cm cell length at λ_{max} 245 m has an absorbance of 1.17, calculate Molar extinction coefficient for this transition

Solu^n. We know

$$A = a c x$$

$$a = \frac{A}{c x}$$

$$a = \frac{1.17}{2.5 \times 10^{-4} \times 10^{-3} \times 1}$$

$$\boxed{a = 0.468 \times 10^{7} \ cm^2 mol^{-1}}$$

Prob: When a UV is passed through the given solution, the radiant Power is reduced to 50% calculate the absorbance.

Solu^n $I = \frac{1}{2} I_0$ or $2I = I_0$

$$A = \log \frac{I_0}{I} = \log \frac{2I}{I} = \log 2 = \underline{\underline{.3020}}$$

Problem: A 0.01 M solution of compound transmits 20% of radiation in a container having path length of 1.5 cm. Calculate molar extinction coefficient:

Solution:

$$\frac{I}{I_0} = \frac{20}{100} = 0.2$$

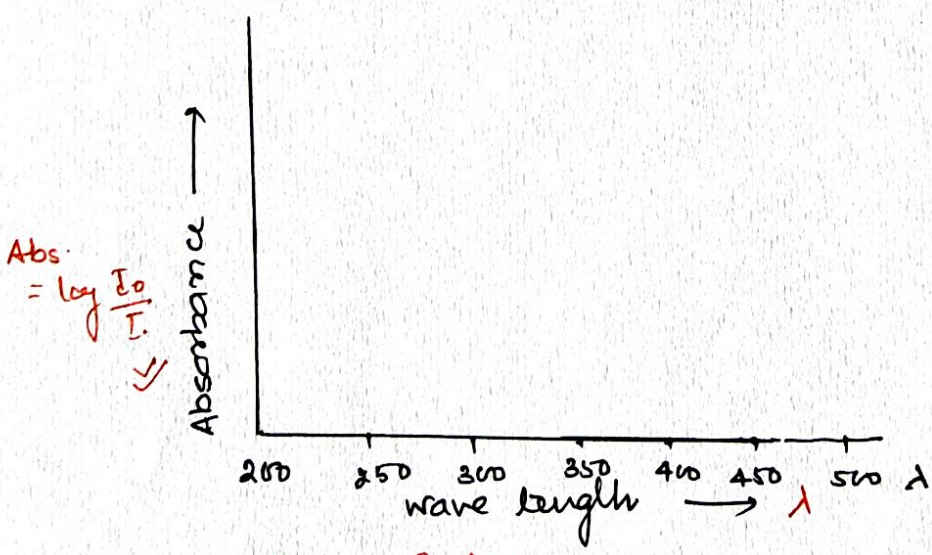
$$A = \log \frac{I_0}{I} = a c x$$

$$A = -\log \frac{I}{I_0} = -\log .2 = a \times 0.01\,M \times 1.5\,cm$$

$$a = \frac{-\log .2}{1.01 \times 10^{-3} \times 1.5\,cm}$$

$$\boxed{a = 46.598 \times 10^{3}\ cm^{-2}\ Mol^{-1}}$$

Absorption Intensity



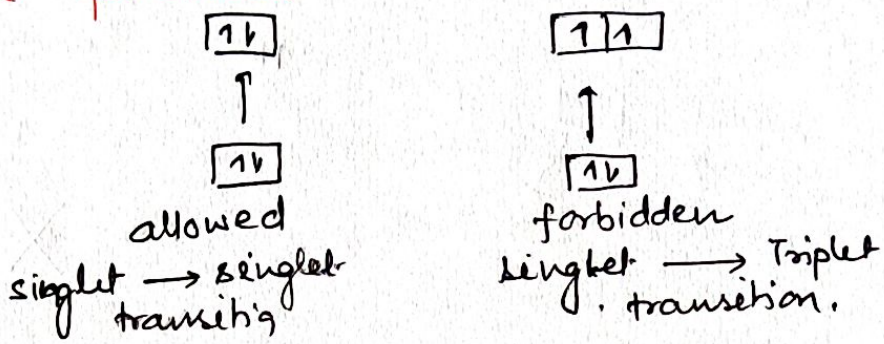
Selection Rules:

Singlet state → e^- are paired → higher energy [↑↓]

Triplet state - e^- are parrelly arranged [↑|↑] → Less energy

⇨ The transections involve change in spin quantum number during transition do not occur.

It means singlet - triplet transitions are forbidden.



⇨ Transition between orbitals of different symmetry do not occur

$\sigma \longrightarrow \pi^*$ or $\pi \longrightarrow \sigma^*$ are symmetry forbidden

$n \longrightarrow \pi^*$ → Always symmetry forbidden

Instrumentation:

Source
- Tungusten source → Red.
- Hydrogen - deuterium discharge lamp → Ultraviolet

200 — 800 nm

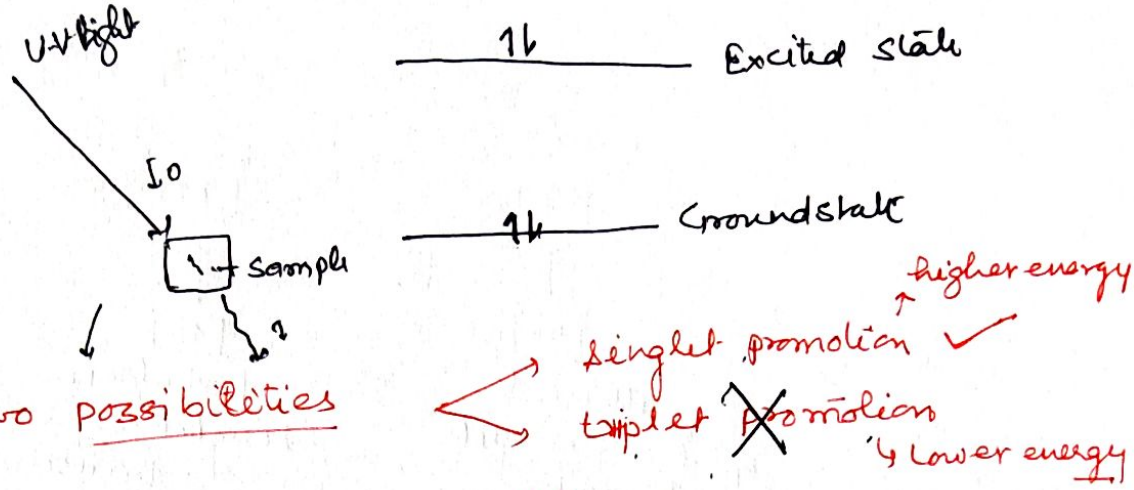
Monochromator
- 150 ← 200
- Vaccum →
- Fill this tube with nitrogen

detector

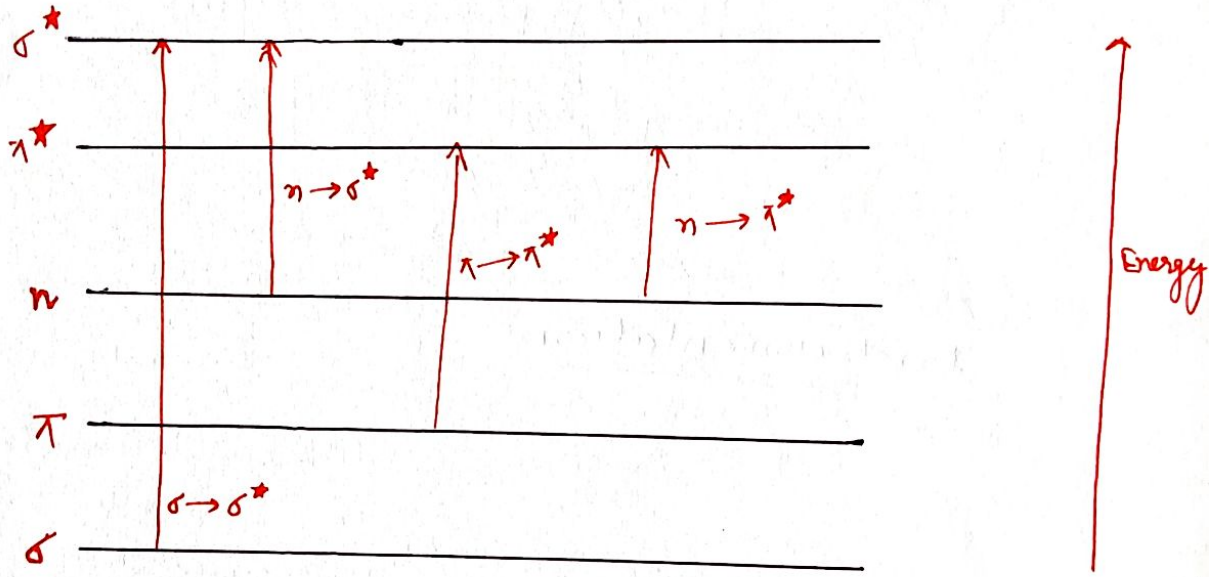
Amplifier

Recording device

Electronic Transitions:



Type of Electronic Transitions



Electronic transitions

1- $\sigma - \sigma^*$ Transition - 150 n.m.

→ Vaccum radiation

→ All the saturated hydrocarbons

Ethane, methane, propane, butane, cyclohexane etc.

→ Vaccum Ultraviolet region

2- $n \longrightarrow \sigma^*$ Transition :

→ 176 m.μ.

→ Such compounds show this transition which have at least one hetero atom.

→ Saturated compounds having heteroatom.

→ Groups like. halides, alcohols, thio alcohols ethers, aldehydes, ketones, amines, amides. etc.

→ Water (H_2O) → 167 mμ.

MeOH CH_3-OH → 174 mμ.

CH_3Cl → 169 mμ

CH_3-Cl CH_3-Br

require higher Lower wave length for transition → due to greater electronegativity

CH_3-NH_2 CH_3-OH

⇒ $n \longrightarrow \sigma^*$ transion also indicates about hydrogen bonding

⇒ In case of hydrogen bonding wave length will shift towards shorter wave length

③ $\pi \longrightarrow \pi^*$ Transition:

⇒ 200 mμ

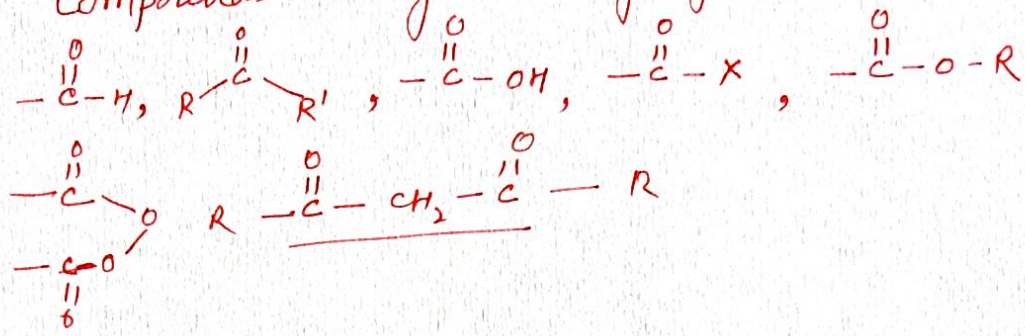
⇒ In all double, triple bonded unsaturated hydrocarbons, in aromatic compounds.

⇒ Alkenes, Alkynes, allenes cyanides, carbonyls azo compounds.

4- $n \longrightarrow \pi^*$ Transition:

⇨ more than 200 mμ.

⇨ Compounds having carbonyl group



Transition Probability:

Excitation coefficient:

$\epsilon_{max} = .87 \times 10^{20} \cdot P.a.$

P.a. → Target area of absorption system

P.a. → Transition probability with values 0 to 1

If ϵ_{max} 20,000 (252 mμ) Allowed transition.

ϵ_{max} 100 (325 mμ) Forbidden transition

★★ Chromophore:

Defined as any isolated covalent bonded group ~~that~~ which shows a characteristic absorption in ultraviolet or visible region

For eg. Ethylinic group, acetylenic, carbonyl acids, esters nitriles etc.

① Group ~~π~~ having π e⁻s — $n \longrightarrow \pi^*$ — hydrocarbons

② Group which contains π e⁻s as well as n (non bonding electrons)

$\pi \longrightarrow \pi^*$

$n \longrightarrow \pi^*$

(carbonyls, nitriles, azo compounds ~~ester~~ acids etc)

$-\ddot{O}-$ $-\ddot{S}-$ $>\ddot{N}$ (190 mμ)

transition $n \longrightarrow \sigma^*$

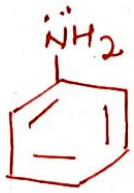
Auxochromes:

Auxochromes are defined as any group which does not itself act as chromophore but when present it brings about the shift of absorption towards red end. or (higher wave length)

Auxochromes → Colour enhancing group

absorption of auxochromic Groups. is above 200 mμ

$-\ddot{O}H$, $-\ddot{O}R$, $-\ddot{N}H_2$ $-\ddot{N}HR$, $-\ddot{N}R_2$ $-\ddot{S}H$



Aniline

λ_{max} = 280 nm.

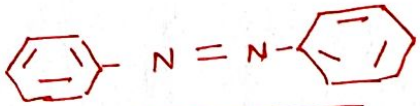
(ϵ_{max} = 1430)

Anilinium ion

λ_{max} = 254 nm

ϵ_{max} = (160)

(Azobenzen)



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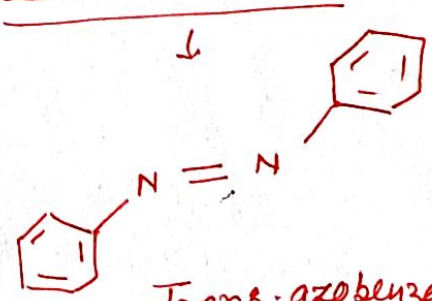
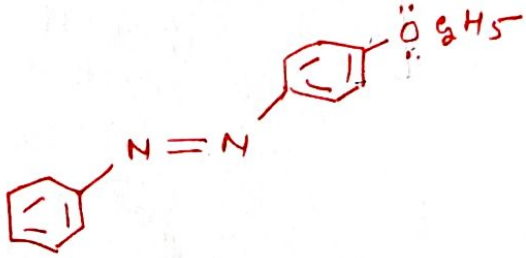


Trans. azobenzene

λ_{max} = 320 nm

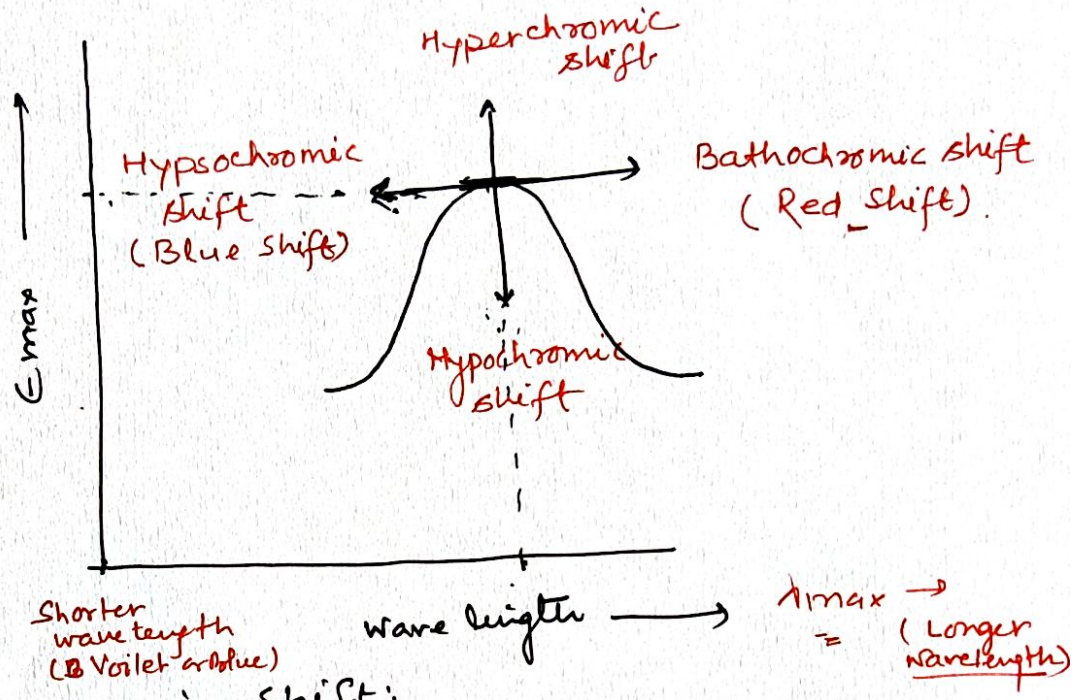
ϵ_{max} = 21000



λ_{max} = 385 nm.

ϵ_{max} = (42000)

★★ Absorption and intensity shifts



1- Bathochromic shift:

The effect by which absorption maximum is shifted towards red end is k/a. Bathochromic shift or red shift.

It is because of (i) auxochromes (ii) solvents

Shifting of λmax

2- Hypsochromic shift:

Effect by which absorption maximum is shifted towards shorter wavelength or Blue/Voilet end is known as Hypsochromic shift or Blue shift.

It is because of (1) Removal of conjugation → Removal of auxochrome or change in nature of auxochrom

(2) solvents.

3- Hyperchromic shift :

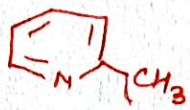
It is an effect due to which the intensity of absorption maximum increases.

It is because of insertion of auxochrome

pyridine.

λmax 257

& ϵmax 2750



2-methyl pyridine.

λmax 262

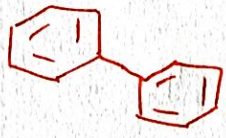
ϵmax = 3560

increase → Hyperchromic shift

4- Hypochromic shift :

Effect due to which absorption intensity decreases.

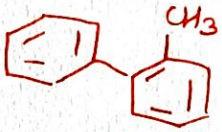
It is due to moity addition which distorts the geometry of molecule.



Biphenyl

λmax = 250 mμ

ϵmax = 19000



2-methyl biphenyl

λmax = 237

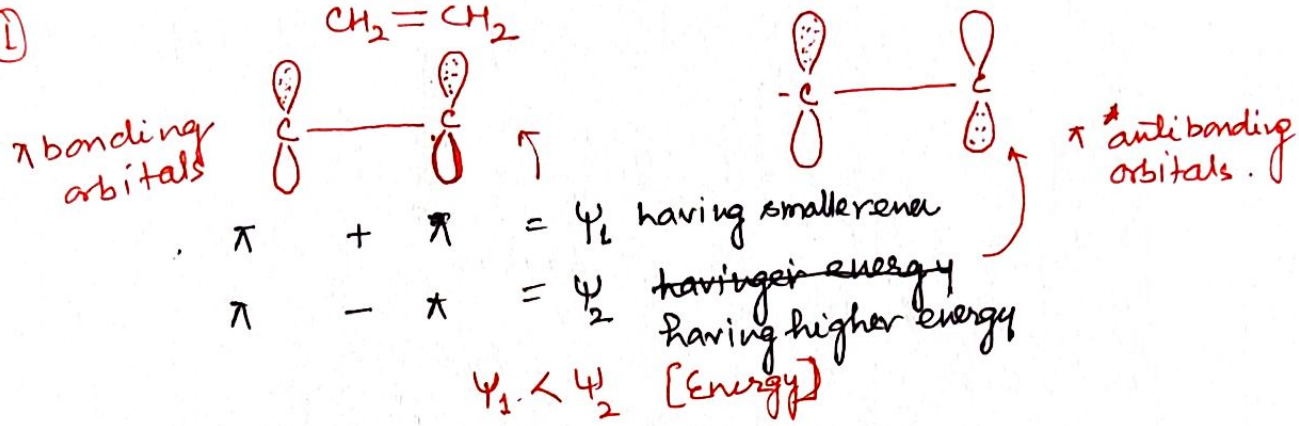
ϵmax = 10250

decrease → Hypochromic.

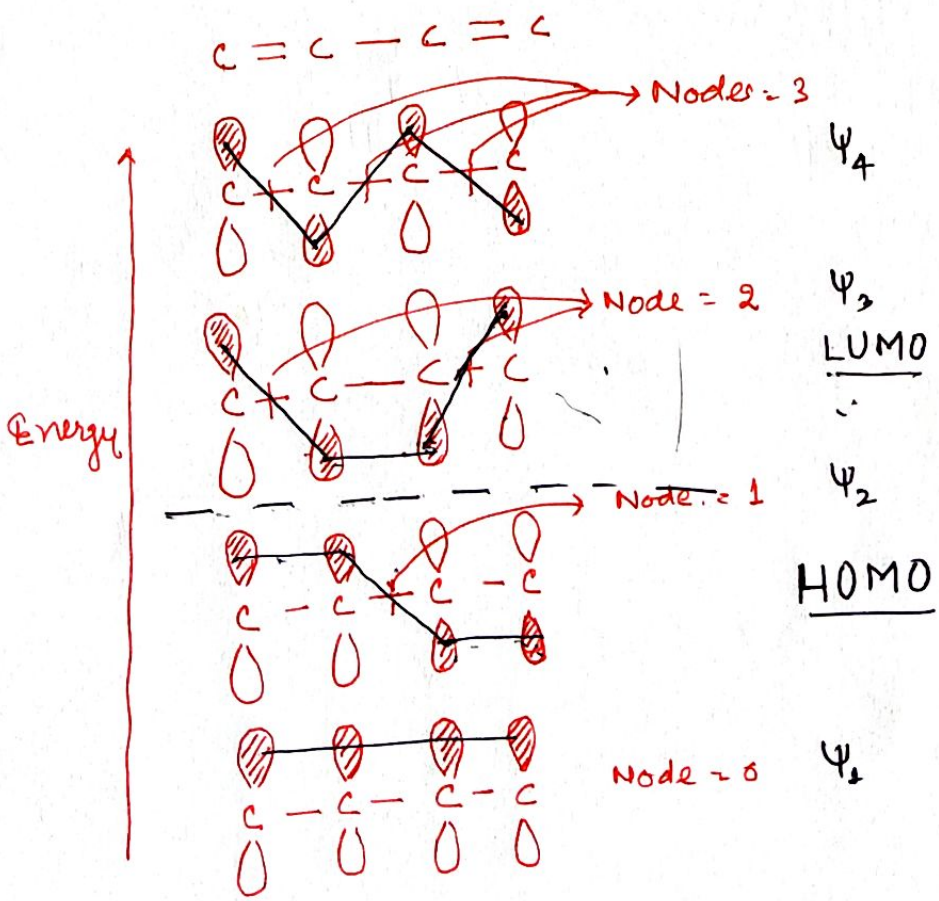
Conjugated diene systems and HOMO - LUMO concept

Simplest ene ~~Etene~~ Ethene

(1) $CH_2 = CH_2$



(2) 1, 3 - butadiene.



Woodward - Fieser Rules for calculating Absorbtion maximum

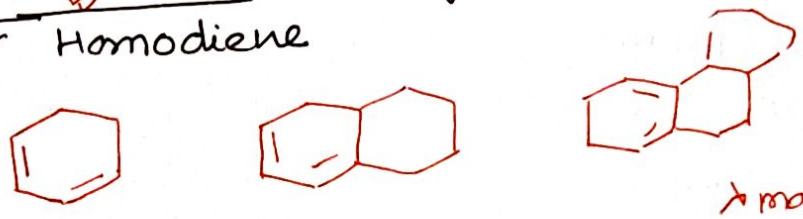
a- Alicyclic dienes or dienes in an open chain system.

Buta diene $\lambda_{max} = 217$ mμ

Acyclic triene.

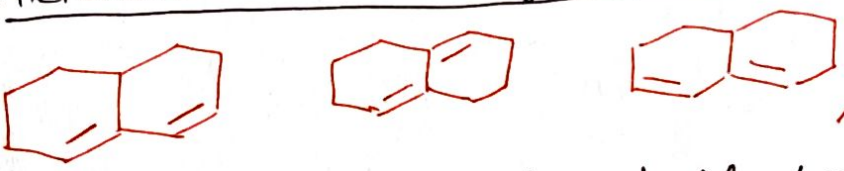
$\lambda_{max} = 245$ mμ.

b- Homo annular conjugated diene (double bond) or Homodiene



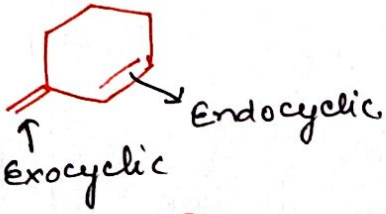
$\lambda_{max} = 253$ mμ

c- Hetero annular conjugated diene:

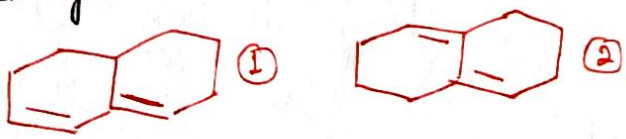


$\lambda_{max} = 215$ mμ

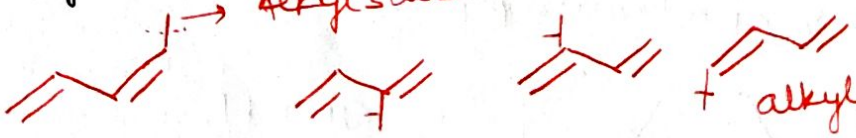
d). Exocyclic & Endocyclic double bond (conjugated)



Exocyclic $\lambda_{max} = 5$ mμ.

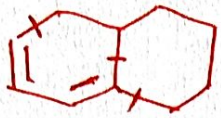


e) Alkyl substituent



$\lambda_{max} = 5$ mμ.

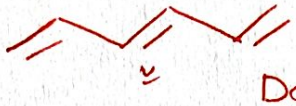
f) Ring residue



Ring residue $\lambda_{max} = 5$ mμ

Ring residue

g) Double bond extending conjugation



Double bond extending conjugation

$\lambda_{max} = 30$ mμ

h). Auxochromes

$-OR$	$\lambda_{max} = +6$ mμ
$-SR$	$\lambda_{max} = +30$ mμ
$-Cl, -Br$	$\lambda_{max} = +5$ mμ
$-NR_2$	$\lambda_{max} = +60$ mμ
$-O-\underset{\underset{O}{\parallel}}{C}-CH_3$	$\lambda_{max} = 0$ mμ

Prob: Calculate absorption maximum in UV spectra for 2,4-Hexadiene.

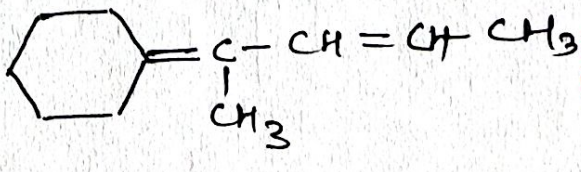
λ_{max} = ~~217~~

Basic Value = 217

2 alkyl subs. (2×5) = 10

λ_{max} = 227 mμ.

Prob: Calculate the absorption maximum in UV spectroscopy of



Basic Value = 217

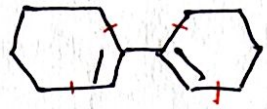
alkyl subst (2×5) = 10

Ring residue (2×5) = 10

Exocyclic = 5

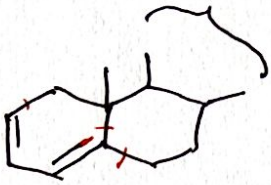
λ_{max} = 242 mμ

Prob: Calculate λ_{max} for



Hetro annular conjugated diene
Basic Value = 215 mμ
4 Ring Residue 4×5 = 20 = 20 mμ
λ_{max} = 235 mμ

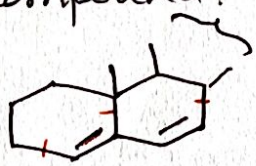
Prob:



calculate λ_{max} for given compound.

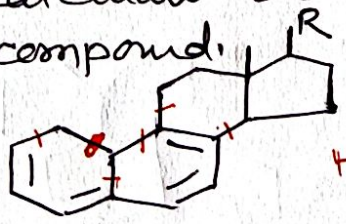
Homo annular conj. die
Basic Value = 253 mμ
3 Ring residue = 3×5 = 15
1 Exocyclic double bon = 5
λ_{max} = 273 mμ

Prob: calculate absorption maximum for following compound:



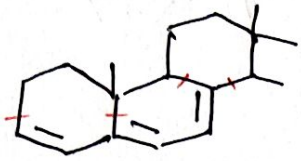
Heteroannular conj dien
Basic Value = 215 mμ
3 Ring residue 3×5 = 15 mμ
1 Exocyclic double bond = 5
λ_{max} = 235 mμ

Prob: Calculate absorption maximum for the compound:



Homoannular conj dien
Basic value = 253 mμ
2. double bond extending conjugation 2×30 = 60 mμ
5- ring residue. 5×5 = 25 mμ
1 Exocyclic 5 = 5 mμ.
λ_{max} = 343 mμ

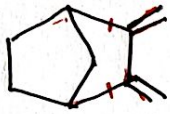
Prob: Calculate λmax for



Homoannular Conj. dien
Basic Value = 253 mμ
4 Ring Residue 4×5 = 20 mμ
1 Extending conjugation = 30 mμ
2 Exocyclic doublebond 2×5 = 10 mμ

λmax = 313 mμ

★★ **Prob:** Calculate λmax for the following

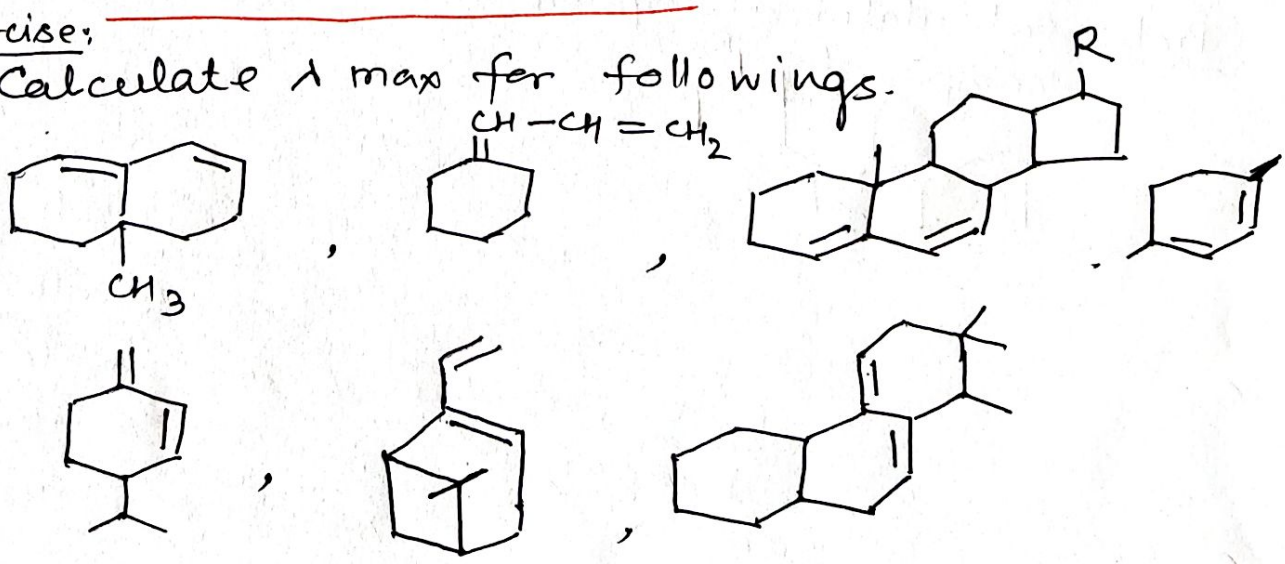


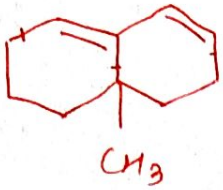
Basic Value = 217 mμ
2 Ring Residue 2×5 = 10 mμ
2 Exocyclic doublebond 2×5 = 10 mμ
1- bicyclic strain Correction 1×15 = 15 mμ

λmax = 252 mμ

Note: There is a strain correction when bicyclic ring is found the value for bicyclic ring strain correction is 15 mμ for each strain correction.

Exercise:
Calculate λ max for followings.





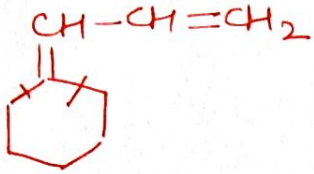
Hetero annulara Conj. diene.

Basic Vallue. = 215 mμ.

3. Ring Residue 3x 5 = 15

1 Exocyclic dublbal. = 5

λ max = 235 mμ



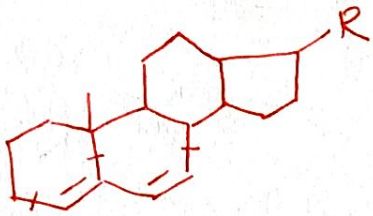
Alicyclic conj. diene.

Basic Value = 217

2 Ring Residue 2x5 = 10

1 Exocyclic double bond = 5

λmax = 232 mμ



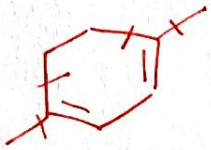
Hetero annular conj. diene

Basic vallue = 215

3 Ring Residue 3x5 = 15

1 Exo cyclic double bond = 5

λ max = 235 mμ



Homoannular conjugated dien

Basic Vallue = 253

4 Ring Residue 4x 5 = 20

λ max = 273 mμ

Basic vallue

(Alicyclic) = 217

2 Ring Residue 2x5 = 10

1 Exo cyclic = 5

λmax = 232 mμ

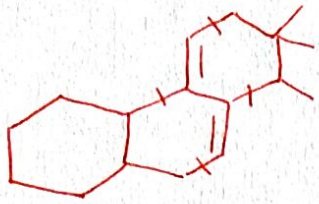
Alicyclic conju. diene

Basic value = 217

2 Ring Residue 2x5 = 10

~~Strain correction = 15~~

λmax = 242 mμ



Heteroannular conju. diene

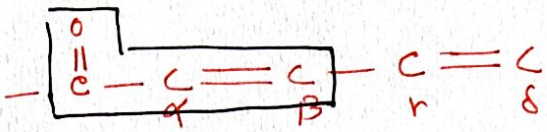
Basic Value = 215

4 Ring Residue 4×5 = 20

2 Exo cyclic 2×5 = 10

λ_{max} = 245 mμ

Absorption band for α-β unsaturated carbonyl compound



Base values

(i) α-β unsaturated acyclic or six membered ring ketone = 215 mμ/nm.

(ii) α-β unsaturated 5 membered ketone = 202 mμ/nm

(iii) α-β unsaturated aldehyde = 207 mμ/nm

(iv) α-β unsaturated acid/Ester = 197 mμ/nm.

(v) alkyl group or ring residue.

at α posion = 10 mμ/nm.

at β position = 12 mμ/nm.

at γ or higher = 18 mμ/nm

(vi) Double bond extending conjugation = 30 mμ/nm.

(vii) Exocyclic double bond = 5 mμ/nm

(viii) Homoannular diene compank = 39 mμ.

(ix) Auxochromes.

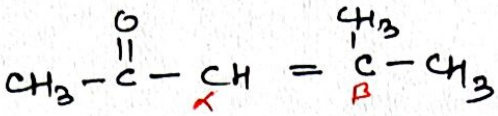
	α	β	γ	δ
—OH (Hydroxy)	35 nm.	30	30	50
—OR (Alkoxy)	35	30	17	31
—OCOCH$_3$ (Acetoxy)	6	6	6	6
—Cl	15	12	x	x
—Br	25	30	x	x
—NH$_2$	—x	95	x	x

Solvent EtOH (Ethanol)

Solvent other than EtOH → Solvent correction (provided)

Methanol - 0, $CHCl_3$ - +1, Ether - +7, Hexane/Cyclohexane +11, Dioxane +5, H_2O -8

Prob 1: Calculate λ_{max} for following compound.



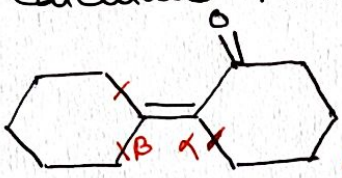
Acyclic α, β unsaturated diene (Ketone)

Basic Value = 215

2 Alkyl substituent at β 2×12 = 24

λ_{max} = 239 nm

Prob 2: Calculate λ_{max} for Given compound



Alicyclic α-β unsaturated diene (Ketone)

Basic Value = 215

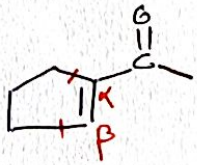
1 α Ring Residue = 10

2 β Ring Residue 2×12 = 24

2 Exo cyclic 2×5 = 10

λ_{max} = 259 nm.

Prob 3: Calculate λ_{max} for



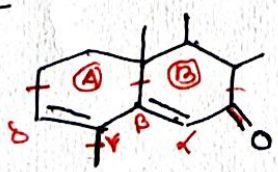
Basic Value = 215

1 α ring residue = 10

1 β ring residue = 12

λ_{max} = 237 nm.

Prob 4: Calculate λ_{max} for.



Six memberd ring α-β unsaturated Ketone

Basic Value = 215

1 double bond extending conj. = 30

1 ring residue at β = 12

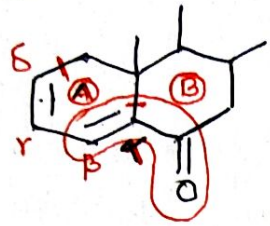
1 ring residue at γ = 18

1 " " " δ = 18

one Exo cyclic double bond = 5

λ_{max} = 298 nm.

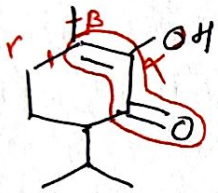
Prob 5: Calculate λ_{max} for given compound.



Basic Vallue = 215
1 extending Conju. = 30
1 homoannular diene = 39
1 α-ring residue = 10
1 δ- " " = 18
1 Exocyclic = 5

λ_{max} = 317 mμ.

Problem. 6: Calculate λ_{max} for compound.



Basic Vallue = 215
2, β ring residue. 2×12 = 24
α-OH = 35

λ_{max} = 274 nm