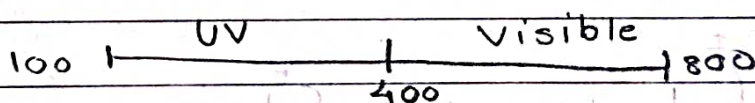


UV-Visible Spectroscopy

• Principle -

- The absorption study carried out using Ultraviolet and visible region are called UV-Visible spectroscopy.

- The UV-region extent from 100 to 400 nm while visible region extended from 400 to 800 nm. electromagnetic spectrum.



- The region from 100 to 200 nm are known as far-ultraviolet & region from 200 to 400 nm is known as near ultraviolet.

- The UV spectroscopy is studied under vacuum condition.

- The common solvent used for preparing sample solvent to be analyse is either ethyl alcohol or hexane.

- The UV light obtain from **duterium discharge lamp**

→ Lambert's Beer Law -

A beam of monochromatic light passing through a homogenous solution, decrease in intensity with thickness is directly proportional to concentration of solution & intensity of incidence radiation.

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

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

$$-\frac{1}{I} dI = k \cdot C \cdot dx$$

$$\int_{I_0}^I \frac{1}{I} \cdot dI = k \cdot C \cdot \int_0^x dx$$

$$[\ln I]_{I_0}^I = -k \cdot C [x]_0^x$$

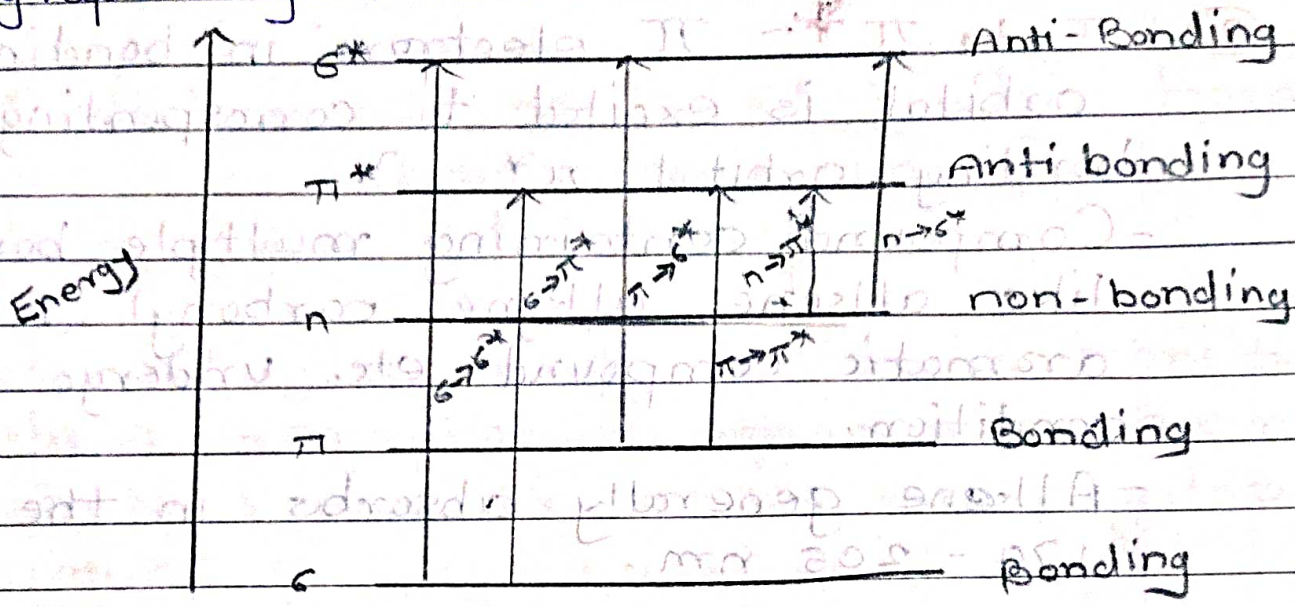
$$\ln I - \ln I_0 = -k \cdot C \cdot x$$

$$\ln \frac{I}{I_0} = -k \cdot C \cdot x$$

$$2.303 \log_{10} \frac{I}{I_0} = -k \cdot C \cdot x$$

$$\log_{10} \frac{I}{I_0} = \frac{-k \cdot C \cdot x}{2.303}$$

★ Electronic Transitions - about rare
 The possible electronic transitions are graphically shown as,



- Electronic transitions are -

- ① σ to σ^* (CH4) $\lambda = 125 \text{ nm}$
 - ② π to π^* (alkene, alkyne, carbonyl comp, aromatic)
 - ③ n to σ^* (saturated compound with heteroatom)
 - ④ n to π^* (C=O, C#N, -N=O)
 - ⑤ σ to π^*
 - ⑥ π to σ^*
- } practically forbidden

① σ to σ^* \rightarrow The σ electron from bonding orbital is excited to corresponding anti-bonding orbital of σ^* .

- The energy required is large for this transition.

- e.g. methane (CH4) has only C-H bond only

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f can undergo σ to σ^* transition f shows absorption maxima (λ) at 125 nm

② π to π^* - π electron in bonding orbital is excited to corresponding anti-bonding orbital π^* .

- Compound containing multiple bond like alkene, alkyne, carbonyl, nitrile, aromatic compound etc. undergo $\pi \rightarrow \pi^*$ condition.

- Alkene generally absorbs in the region 170 - 205 nm.

③ n to σ^* - Saturated compound containing atom with lone pair of electrons like O, N, S & halogen are capable of $n \rightarrow \sigma^*$ transition.

- These transitions usually define less energy than σ to σ^* transition.

- The no. of organic functional group with $n \rightarrow \sigma^*$ transition gives peak in uv. region is very small (150 - 250 nm)

④ n to π^* \rightarrow An electron from non-bonding orbital is promoted to anti-bonding π^* orbital.

- Compound containing double bond involving hetero atom $C=O$, $C \equiv N$, $-N=O$ undergo such transition.

- $n \rightarrow \pi^*$ transition required minimum energy & shows absorption of longer wavelength around 300 nm.

⑤ $\sigma \rightarrow \pi^*$ & ~~$\pi \rightarrow \sigma^*$~~ $\pi \rightarrow \sigma^*$ → This transitions are forbidden transitions & are only theoretically possible.

- $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ electronic transition shows absorption in region above 200 nm which is accessible to UV-Visible spectrometer.

★ Terms Used in UV-Visible Spectroscopy -

① Chromophores -

② Auxochromes -

③ Bathochromic Shift -

④ Hypsochromic Shift -

⑤ Hyperchromic Shift -

⑥ Hypochromic Shift -

① Chromophores -

- A chromophore is an unsaturated group of molecule that undergoes $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ transition.

- The compound containing chromophore are called chromogens.

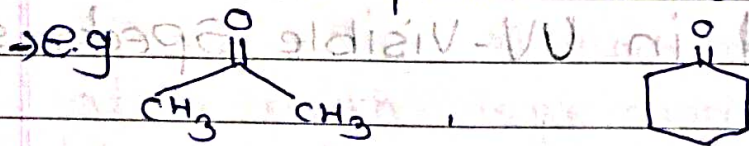
- The part of molecule responsible for

imparting colour are called chromophore
 - The functional containing multiple bond capable of absorbing radiation above 200 nm due to $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ transition.

→ eg - NO_2 , $-\text{N}=\text{O}$, $=\text{C}=\text{O}$, $\text{C}=\text{N}-\text{O}$, $\text{C}\equiv\text{N}$, $-\text{C}=\text{C}-$, $=\text{C}=\text{S}$.

- The non-conjugated alkene shows an **Auxochrome** - intense absorption below 200 nm therefore inaccessible to UV spectrophotometer.

- Non-conjugated carbonyl group gives a weak absorption band in the 200 to 300 nm



Acetone ($\lambda_{\text{max}} = 279 \text{ nm}$)

(Cyclohexanone) $\lambda_{\text{max}} = 291 \text{ nm}$

- When double bond are conjugated in compound λ_{max} shifted to the longer wavelength.

eg - \ominus 1,5-hexadiene has $\lambda_{\text{max}} = 178 \text{ nm}$
 & 2,4-hexadiene has $\lambda_{\text{max}} = 227 \text{ nm}$



1,5 hexadiene

(178 nm)



1,4 hexadiene

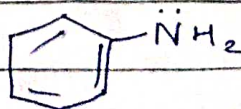
$\lambda_{\text{max}} = 227 \text{ nm}$

- Conjugation of $C=C$ & carbonyl group shifts the λ_{max} to the longer wavelength.
- e.g. - Acetone & ethylene.
Ethylene has $\lambda_{max} = 171 \text{ nm}$. ($CH_2=CH_2$)
Acetone has $\lambda_{max} = 279 \text{ nm}$. ($CH_3-\overset{O}{\parallel}C-CH_3$)

2] Auxochrome:-

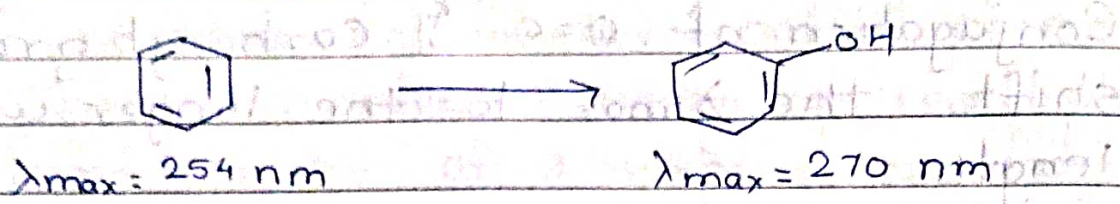
- Auxochrome is an atom or saturated group of containing non-bonded or lone pair of e^- .
- By itself it does not absorb radiation of wavelength greater than 200 nm but when couple with chromogen it shift the wavelength to the longer absorption & increase intensity of absorption peak.
- Some common auxochrome are $-SH$, $-OR$, $-OH$, $-Cl$, $-Br$, $-NH_2$, $-NHR$.
- An Auxochrome offered its lone pair of e^- for extending configuration of chromophore.
- They greatly lowers the transition energy (ΔE) & shift absorption to the longer wavelength.

e.g.,



$\lambda_{max} = 254 \text{ nm}$

$\lambda_{max} = 280 \text{ nm}$

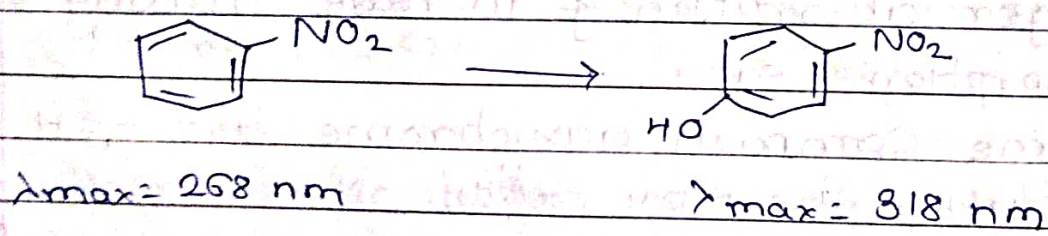


-NH₂ group does not absorb radiation of longer wavelength but when attach to benzene ring absorption shift to the longer side.

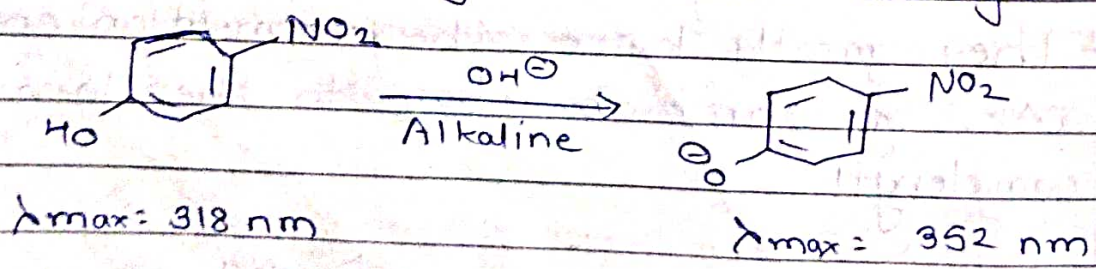
3] Bathochromic / Red shift -

- The shift of absorption band to the longer wavelength is called Bathochromic / red shift.
- The effect is due to presence of Auxochrome or by change of solvent.

e.g - 1] An auxochrome group attach to chromogen.



2] When surrounding medium is change.



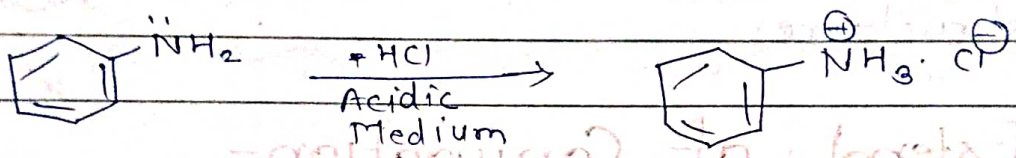
4] Hypsochromic Shift - (blue shift)

- When absorption shift to the shorter wave length

is called Hypsochromic/blue shift

- This effect is due to presence of group causes removal of conjugation by change of solvent.

e.g., - Aniline shows blue shift in acidic medium.



$\lambda_{max} = 280 \text{ nm}$

$\lambda_{max} = 265 \text{ nm}$

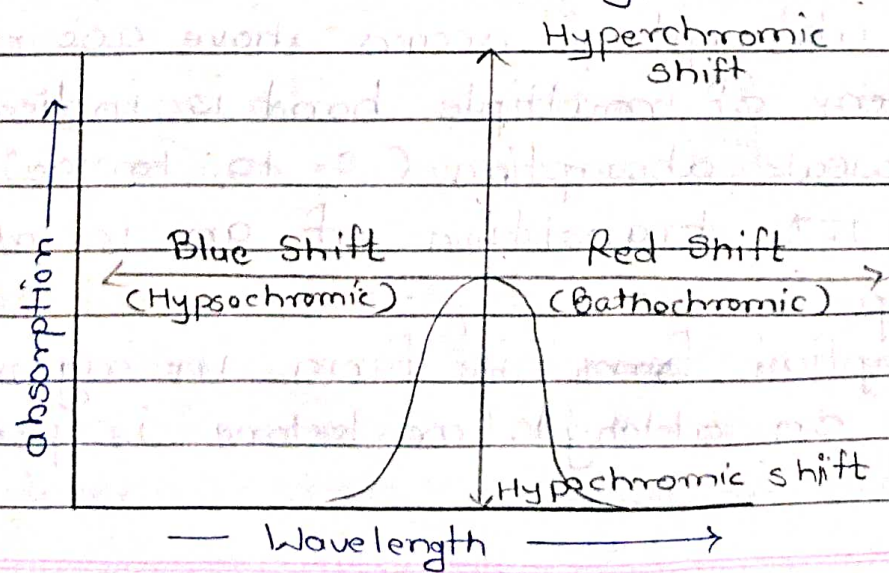
5] Hyperchromic Effect -

- When absorption intensity of compound is increase it is known as Hyperchromic effect.

e.g., When auxochrome introduced to the compound the intensity of absorption increases.

6] Hypochromic Effect -

- When absorption intensity of compound is decrease it is known as Hypochromic effect.



★ Applications of UV-Visible Spectroscopy -

- Applications of UV-spectroscopy for structural diagnosis are limited because it does not provide complete information about molecular structure.

① Extend of Conjugation-

- Higher the λ_{max} value longer the conjugation & vice versa so direct distinction between conjugated & non-conjugated structural analog can be made easily.

eg - -



$\lambda_{max} = 175 \text{ nm}$
(non-conjugated)



$\lambda_{max} = 217 \text{ nm}$
(conjugated)



$\lambda_{max} = 258 \text{ nm}$
(Extended conjugation)

② Detection of Chromophore - ($n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$)

- A strong absorption ($\epsilon = 10,000 - 20,000$) usually characteristics of $\pi \rightarrow \pi^*$ transition.

- If absorption occurs above 200 nm conjugated system of multiple bond is indicated.

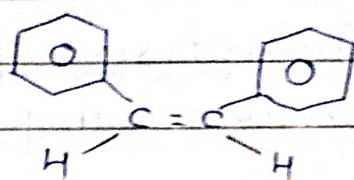
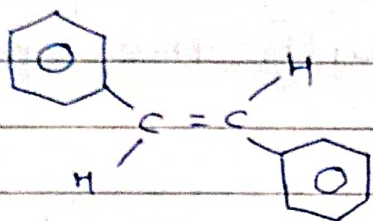
- A weak absorption ($\epsilon = 10$ to 100) suggest $n \rightarrow \pi^*$ transition of an isolated carbonyl group.

- Absorption ~~form~~ in form in region of 270-350 nm on aldehyde or ketone is probable.

③ Detection of Geometrical Isomer -
- Compare to cis-isomer the trans-isomer shows higher absorption.

eg. -

①



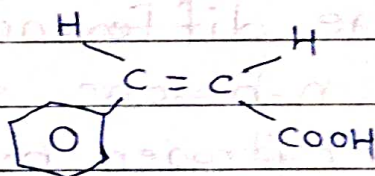
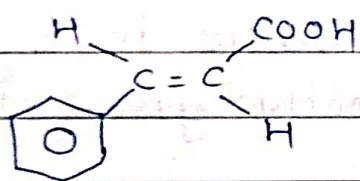
trans-stilbene

Cis-stilbene

($\lambda_{max} = 294 \text{ nm}$) (E isomer)

($\lambda_{max} = 278 \text{ nm}$) (Z-isomer)

②



trans-cinnamic acid

cis-cinnamic acid.

④ Structure of Organic Compound.

- UV-spectroscopy is one of the methods used for structure analysis of organic compounds (molecules). From the location of peaks & combination of peaks it can be calculated that compound is saturated & un-saturated heteroatom is present or not.

⑤ Quantitative Analysis -

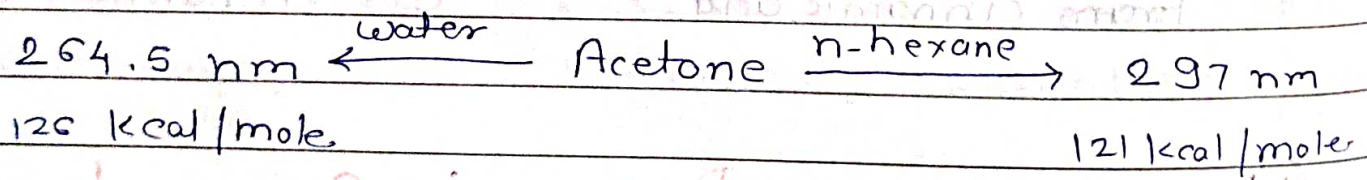
- UV-spectroscopy is used for conjugative determination of compound that absorbs UV-radiation.
- This determination is based on Beer's law.

⑥ Qualitative Analysis -

- UV-spectroscopy is specially used of characterising aromatic compound & aromatic olefins.
- Identification is done by comparing the absorption spectrum with the spectra of known compound.

⑦ The strength of Hydrogen Bond -

- The strength of hydrogen bond can be calculated by taking UV-spectrum in polar (water) & non-polar (n-hexane) solvent.
- The difference in λ_{max} value in water & n-hexane should directly gives strength of Hydrogen bond.



★ Calculation of λ_{max} by Woodward Fisher Rule

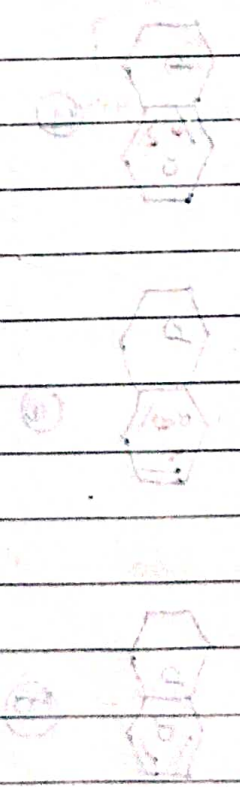
1) Conjugated diene & triene -

- Acyclic diene - 214 nm
- Heterocyclic diene - 214 nm
- Homoannular diene - 253 nm

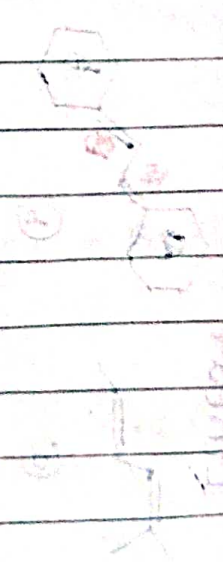
Nature of substituent

Add Increment

- 1) -R-alkyl (include ring residue) 5
- 2) OR alkoxy 6
- 3) -Cl, -Br 5
- 4) -O, COR 0
- 5) double bond (extended conjugation) 30
- 6) One double bond exocyclic 5
- 7) two double bond exocyclic 10

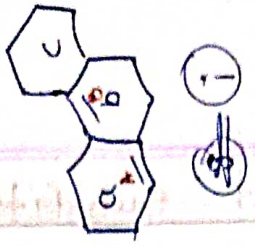
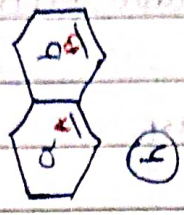
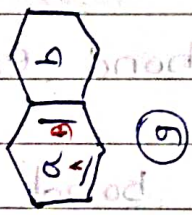
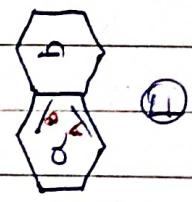
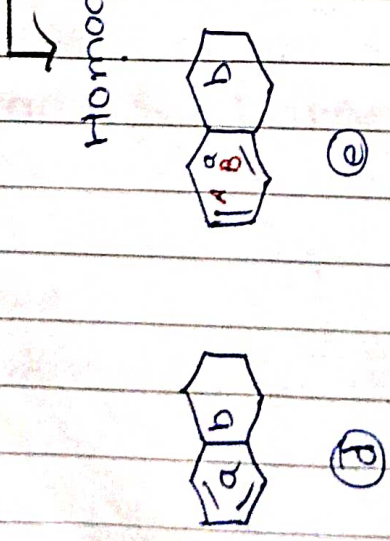
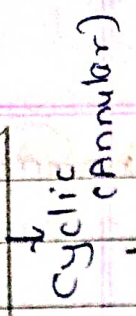
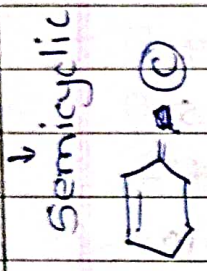
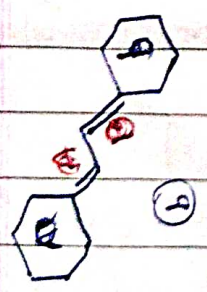
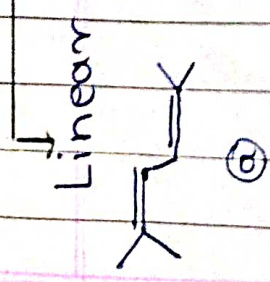


Alkyl substituent



Diene

Dienes

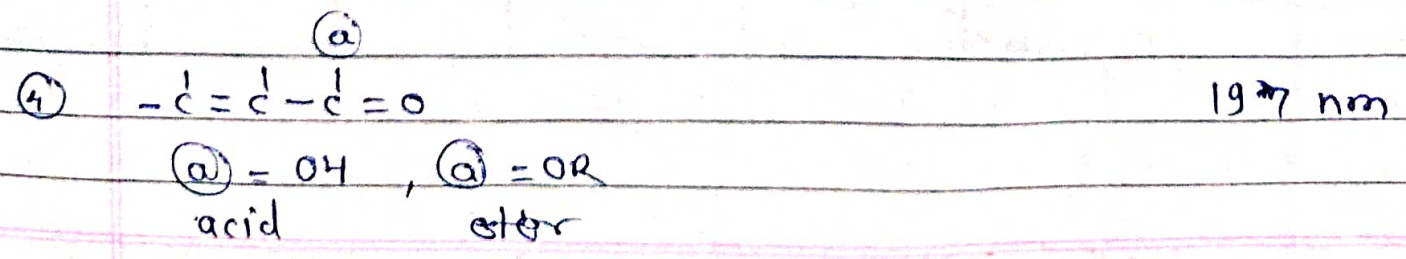
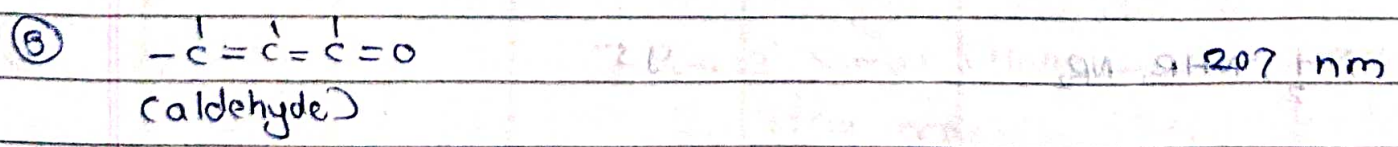
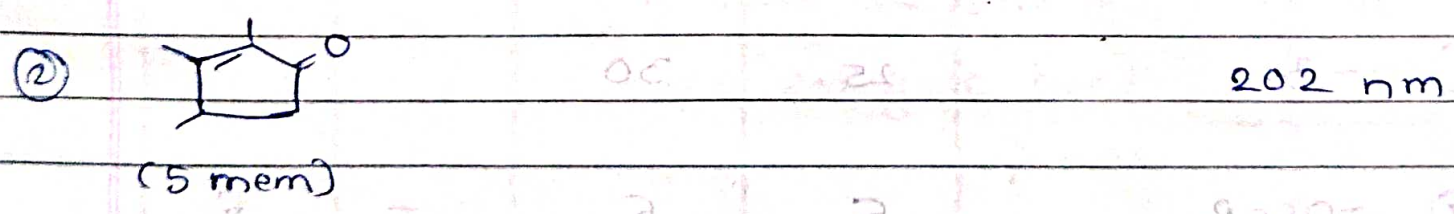
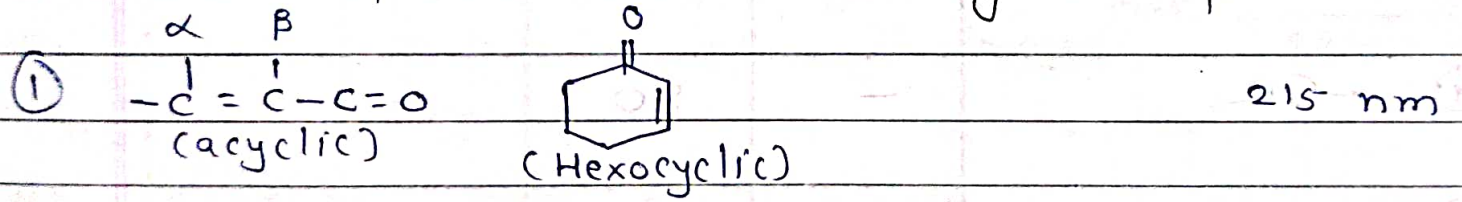


Heteroannular

- (a) Simple conjugated diene.
- (b) Double bond (A) exocyclic to ring (a) }
Double bond (B) exocyclic to ring (b) }
- (c) One double bond is exocyclic.
- (d) Both double bond are endocyclic.
- (e) Double bond (B) is exocyclic to ring (b).
- (f) Both double bonds are exocyclic to ring (b).
- (g) Double bond (B) is exocyclic to ring (b)
- (h) Double bond (A) is exocyclic to ring (b)
- (i) Double bond (A) is exocyclic to ring (b) }
double bond (B) is exocyclic to ring (a) }

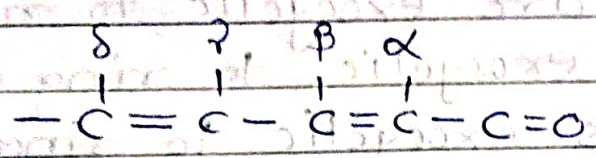
*** Enone System -**

(α , β unsaturated Carbonyl Compound)



③ Extended conjugation add 30 nm

④ Homodiene component add 39 nm
 one exocyclic = bond add 5 nm
 two exocyclic = bond add 10 nm



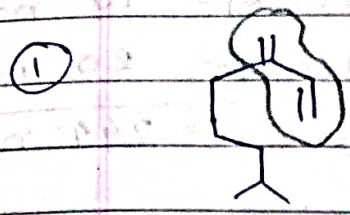
①	Group	Increment for each group				above 18
		α	β	γ	δ	
①	-R alkyl	10	12	18	18	18
②	-OR	35	30	17	31	-
③	-OH	35	30	17	50	-
④	-SR	-	80	-	-	-
⑤	-Cl	15	12	-	-	-
⑥	-Br	25	30	-	6	-
⑦	-OCOR	6	6	-	6	-
⑧	-NH ₂ , -NHR, -NR ₂	-	95	-	-	-



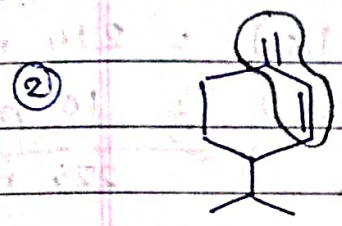
310 - (a) 110 - (b)

ratio 1100

* Examples —



Base value (acyclic) = 214
 One alkyl substituent = 05
 $\lambda_{max} = 219 \text{ nm}$



Base value (semicyclic) = 214
 two ring residue (2x5) = 10
 one '=' exocyclic = 05
 $\lambda_{max} = 229 \text{ nm}$



Base value (acyclic) = 214
 2 alkyl substituent (2x5) = 10
 $\lambda_{max} = 224 \text{ nm}$



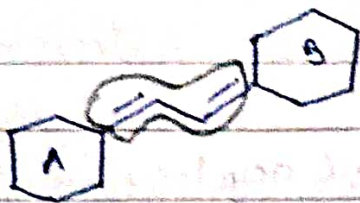
Base value (heteroannular) = 214
 2 ring residue (2x5) = 15
 one exocyclic bond = 5
 $\lambda_{max} = 234 \text{ nm}$



Base value (homoannular) = 253
 2 ring residue (2x5) = 10
 $\lambda_{max} = 263 \text{ nm}$

Handwritten notes and scribbles at the bottom right of the page.

8)



Base value (cyclic) = 214 nm
 two e'=' exocyclic (2x5) = 10 nm
 four ring residue (4x5) = 20 nm
 $\lambda_{max} = 244 \text{ nm}$

9)



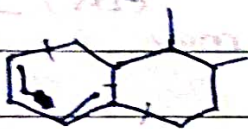
Base value (cyclic) = 214 nm
 two allyl sub. (2x5) = 10 nm
 $\lambda_{max} = 224 \text{ nm}$

10)



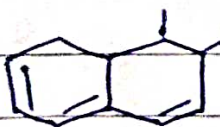
Base value (heterocyclic) = 214 nm
 One '=' bond exocyclic = 05 nm
 three ring residue (3x5) = 15 nm
 $\lambda_{max} = 234 \text{ nm}$

11)

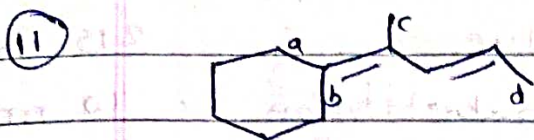


Base value (homoannular) = 253 nm
 one '=' exocyclic = 05 nm
 three ring residue (3x5) = 15 nm
~~263 nm~~
 $\lambda_{max} = 273 \text{ nm}$

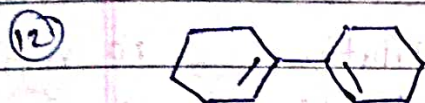
12)



Base value (homoannular) = 253 nm
 three ring residue (3x5) = 15 nm
 Extended conjugation = 30 nm
 One '=' exocyclic = 05 nm
 $\lambda_{max} = 303 \text{ nm}$



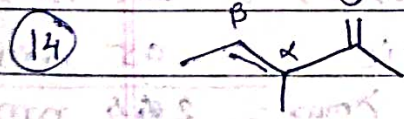
Base value (acyclic) = 214 nm
 two alkyl substitution (c-d): 10 nm
 (2x5)
 two ring residue (2x5) (ab) = 10 nm
 one '=' exocyclic = 05 nm
 $\lambda_{max} = \underline{239 \text{ nm}}$



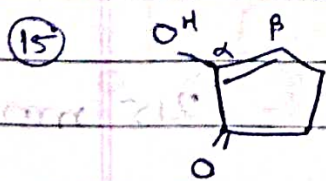
Base value (heterocyclic) = 214 nm
 four ring residue (4x5) = 20 nm
 $\lambda_{max} = \underline{234 \text{ nm}}$



Base value (semicyclic) = 214 nm
 four ring residue (4x5) = 20 nm
 one '=' bond exocyclic = 10 nm
 $\lambda_{max} = \underline{244 \text{ nm}}$

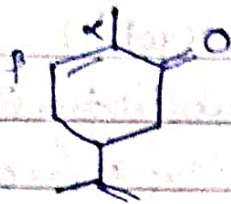


Base Value (acyclic) = 215 nm
 one alkyl substitution = 10 nm
 one β -substitution = 12 nm
 $\lambda_{max} = \underline{237 \text{ nm}}$



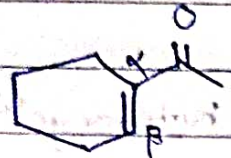
Base value (5 mem) = 202 nm
 one α -hydroxy sub. = 35 nm
 one β -alkyl sub. = 12 nm
 $\lambda_{max} = \underline{249 \text{ nm}}$

16



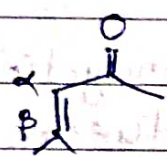
Base value = 215 nm
 One α -substitution = 10 nm
 one β -substitution = 12 nm
 $\lambda_{max} = 237$ nm

17



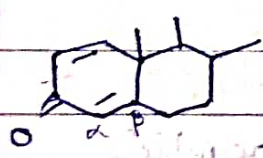
Base value = 215 nm
 One α -substitution = 10 nm
 one β -substitution = 12 nm
 $\lambda_{max} = 237$ nm

18



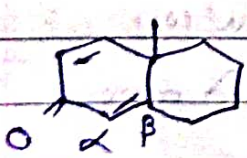
Base value = 215 nm
 two β -substitution (2x12) = 24 nm
 $\lambda_{max} = 239$ nm

19



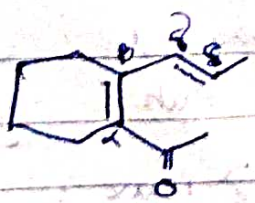
Base value = 215 nm
 two β -Subst (2x12) = 24 nm
 One '=' exocyclic = 05 nm
 $\lambda_{max} = 244$ nm

20



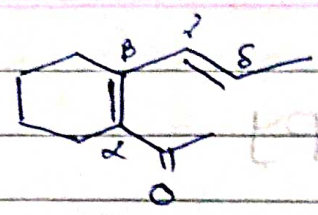
Base value = 215 nm
 two β -substitution (2x12) = 24 nm
 One '=' exocyclic = 05 nm
 $\lambda_{max} = 244$ nm

21



Base value = 215 nm

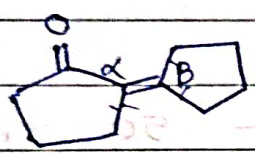
22



Base value = 215 nm
 one α -sub = 10 nm
 One β -sub = 12 nm
 one δ sub = 18 nm
 one extended conjugation = 30 nm

$\lambda_{max} = 285 \text{ nm}$

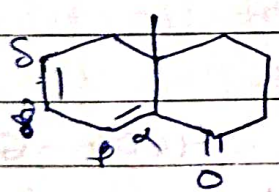
23



Base value = 202 nm
 one α -sub = 10 nm
 two β -substitution (2x12) = 24 nm
 one '=' exocyclic bond (2x5) = 10 nm

$\lambda_{max} = 246 \text{ nm}$

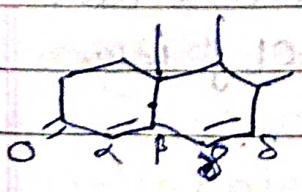
24



Base Value = 215 nm
 One α -substitution = 10 nm
 one δ -substitution = 18 nm
 One '=' exocyclic = 05 nm
 One homodiene component = 39 nm
 one extended conjugation = 30 nm

$\lambda_{max} = 317 \text{ nm}$

25



Base value = 215 nm
 One β -sub. = 12 nm
 one δ sub = 18 nm
 one extended conjugation = 30 nm
 one '=' exocyclic bond = 05 nm

$\lambda_{max} = 280 \text{ nm}$

IR Spectroscopy

- Infra red spectroscopy which important record which gives sufficient information about structure of compound.

12500 — 4000 — 650 — 50 cm^{-1}

near IR Mid IR

Far IR

- It divided into three region.

① Near IR

② Mid IR

③ Far IR

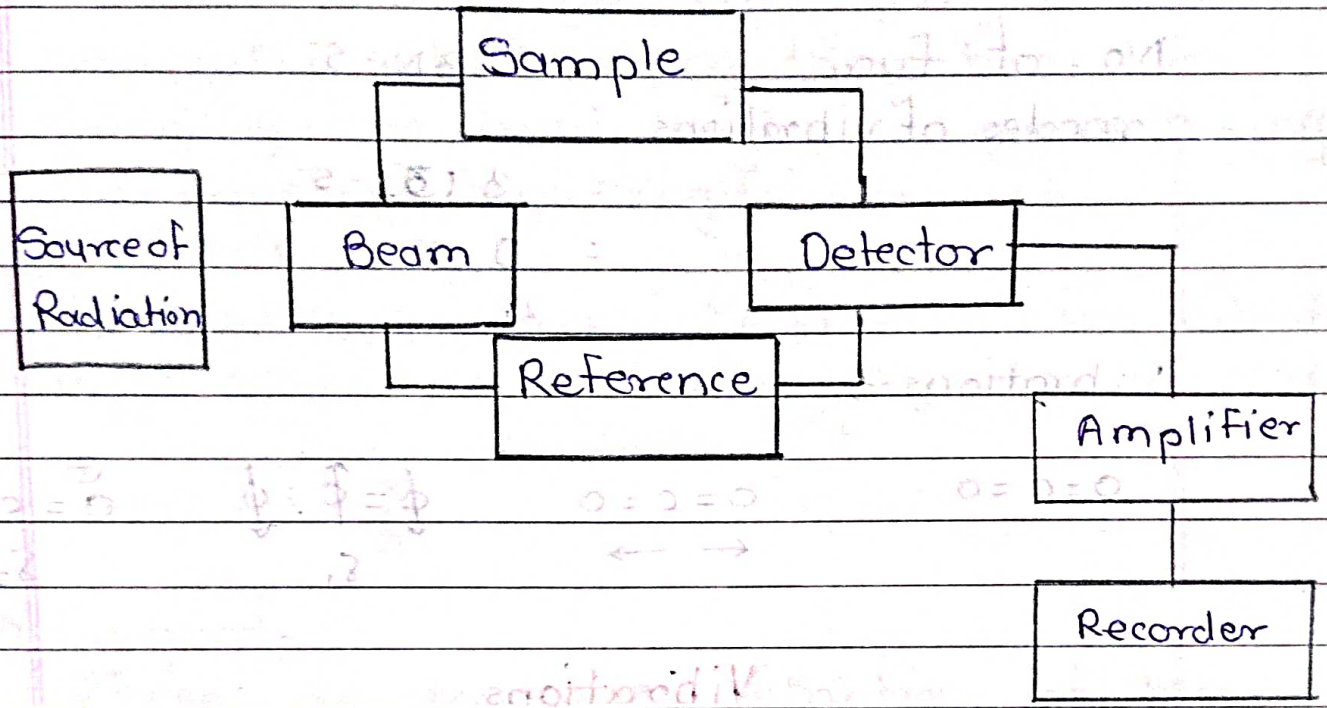
- So for practical purpose 4000 - 667 cm^{-1} region of radiation is simply called IR region.

- The IR radiations are obtained by heating a rod of earth oxide.

- The IR radiation absorbed by glass & quartz.

- So in IR spectrophotometer the sample cell prism & other accessories are made from alkyl metal halides like NaCl & KBr.

o) Instrumentation -



* Fundamental modes of vibrations -

- At all temperature atoms of molecule vibrate and rotating variety of base the motion leading to change in bond distance (stretching) and bond angle are called vibrational motions.
- The stretching & bending vibrations are known as fundamental modes of vibrations.
- Number of fundamental modes for poly atom i.e., molecule can be calculated from number of atoms (N) present in molecule & their degree of freedom.
- For non-linear molecule number of fundamental modes of vibrations calculated by formula $(3n-6)$ where n = no. of atoms.
- For linear molecule formula will be $(3n-5)$

e.g., CO_2 linear triatomic molecule.

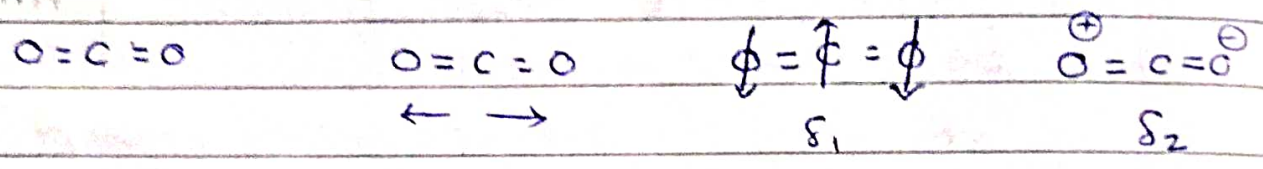
No. of fun. modes of vibrations = $3N - 5$

$$= 3(3) - 5$$

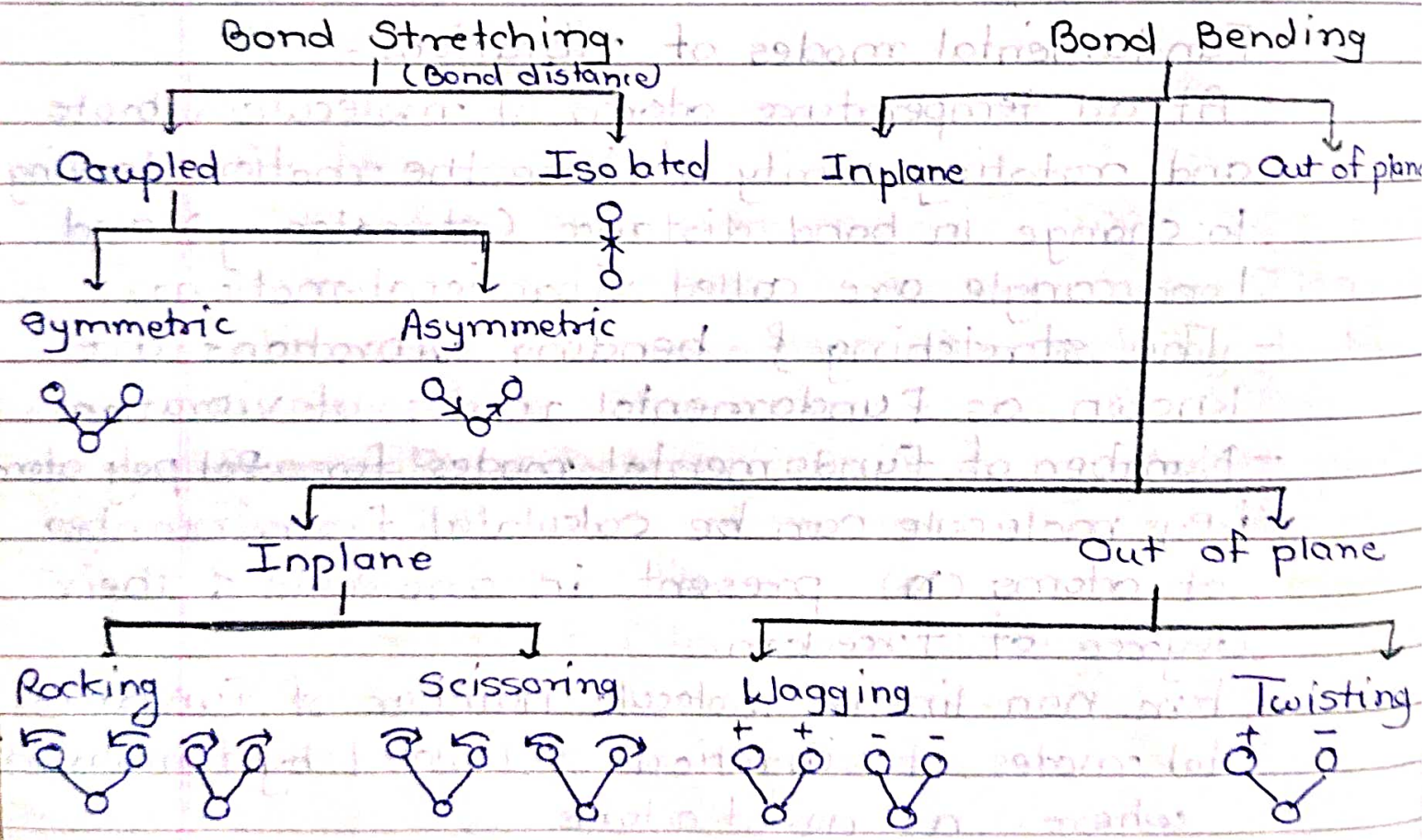
$$= 9 - 5$$

$$= 4$$

Vibrations =>



Vibrations



→ Bond stretching -
 - These vibrations in which pair of atoms constantly vibrate along their bond axis changing the bond length but maintaining the constant bond angle.

① Isolated -

- Two atoms undergo bond stretching vibrations with respect to each other e.g., C=O or O-H

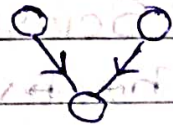


② Coupled -

- These are stretching vibrations of two atoms w.r.t. common central atoms.

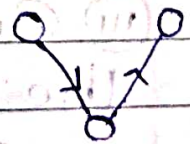
① Coupled symmetric -

Both atoms simultaneously move towards the (move away) from central atom.



② Coupled asymmetric -

- When (one atoms) move towards, the other atom moves away from central atom.



- Stretching vibration required higher energy than bending vibrations.

So give absorption band at higher frequency
 4000 - 1400 cm^{-1}

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→ Bond Bending - vibrations -

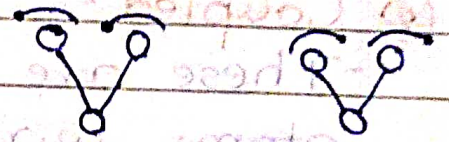
The central atom remain fix to a point on fix plane but two atoms bound to it vibrate in to change the bond angle keeping the bond length constant so the shape of molecule changes hence it is also known as deforming vibrations.

① Inplane Bending vibrations -

The vibrating atom remain in same plane along with common atom.

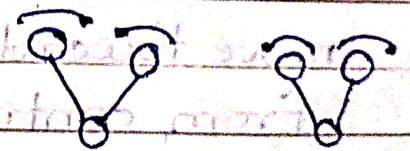
(i) Rocking vibrations -

The vibrating atom move simultaneously back (←) or forth (→)



(ii) Scissoring -

The vibrating atom move back & forth towards each other.

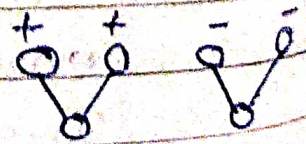


(iii) Out of plane bending vibrations -

The vibrating atom move out of the plane of central atom.

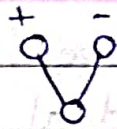
(a) Wagging vibrations -

The vibrating atoms simultaneously move back or forth of common



(b) Twisting vibrations -

The vibrating atom move in opposite direction to the common plane.



* Selection Rule

Selection rule for IR spectrum says that only those vibrations are effective in causing IR absorption which are not centric symmetric about centre of molecule so we have,

(I) IR active transitions.

The vibration that generate oscillating dipole moment absorb in IR & are known as IR active transitions.

e.g., H-Cl, I-Cl, ~~CH₃Cl~~ CHCl₃, C=O.

(II) IR inactive transitions -

The vibrations that does not generate an oscillating dipole moment do not absorb in IR are known as IR inactive transitions.

e.g., Symmetrical stretching of C=C in ethylene (Centrosymmetric molecule will not produce change in dipole moment therefore these mode of vibrations is IR inactive.

e.g., H₂, N₂, Cl₂, CCl₄.

(III) Allowed & forbidden transition -

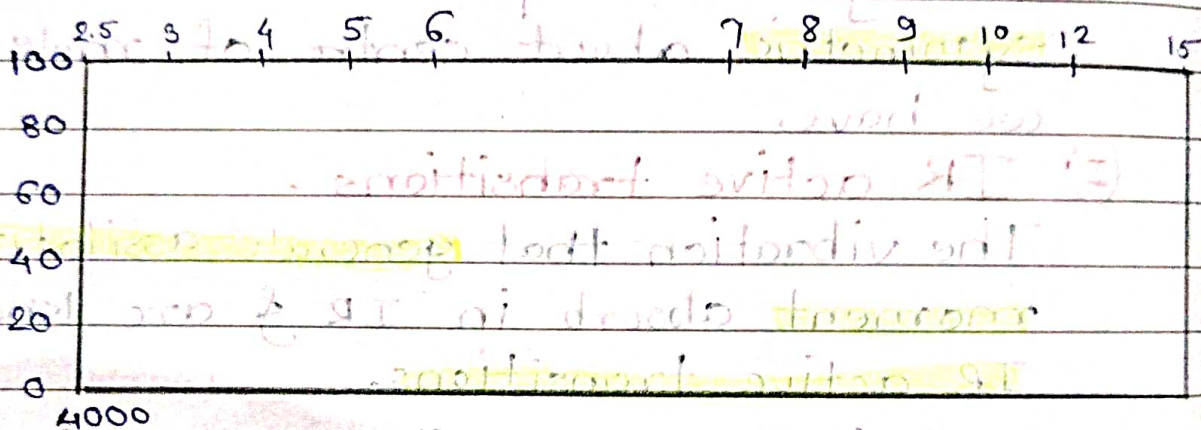
Only transition from ψ_0 to next higher

level i.e., ν_1 ($\nu_0 - \nu_1$) or ν_1 to ν_2 are allowed to ideal system such as perfectly harmonic oscillator.

★ Region of IR spectrum -

IR range of IR spectrum divided into -

- ① Functional group region ($4000 - 1400 \text{ cm}^{-1}$)
- ② Fingerprint region ($1400 - 665 \text{ cm}^{-1}$)



① Functional group region -

- It is high energy or high frequency region lies between $4000 - 1400 \text{ cm}^{-1}$ is called functional group region. The absorption band seen in this region of IR spectra are due to stretching mode of vibration of diatomic group of molecule like $\text{C}-\text{O}$, $\text{C}-\text{N}$, $\text{C}-\text{H}$, $\text{N}-\text{H}$, $\text{C}=\text{O}$, $\text{C}=\text{N}$, $\text{C}=\text{S}$, $\text{C}=\text{C}$, $\text{C}\equiv\text{N}$.

- It is also known as group frequency.
- The group frequency region is subdivided into four smaller frequency ranges corresponding to bond of hydrogen single bond, double bond & triple bond.

Frequency cm^{-1}	Vibration due to bond	Type of compound
① Bond of Hydrogen (H) atom region		
i) 3600 - 3650	-O-H free	alcohol, phenol.
ii) 3200 - 3500	-O-H bonded	H-bonded alcohol & phenol
iii) 3405 - 3600	Sharp	Intermolecular H bond
iv) 3200 - 3500	Broad	Intermolecular H bond.
v) 3300 - 3350	-N-H	Amines, Amides.
vi) 3200 - 3310	$\equiv\text{C}-\text{H}$	Acetylene, Acetylene.
vii) 3000 - 3100	$=\text{C}-\text{H}$	Ethylenic, Aromatic
viii) 2850 - 2950	$-\text{C}-\text{H}$	Saturated alkane
ix) 2700 - 2900	$-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	Aldehyde.
x) 2500 - 3600	$-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	Carboxylic acid

(ii) = Bond hydrogen (H) atom region.

(i) 1740 - 1850	$R-\overset{\overset{O}{\parallel}}{C}-O-\overset{\overset{O}{\parallel}}{C}-R$	Unhydried
(ii) 1770 - 1815	$R-\overset{\overset{O}{\parallel}}{C}-X$	acylhalide
(iii) 1780 - 1750	$R-\overset{\overset{O}{\parallel}}{C}-OR$	Ester
(iv) 1730 - 1740	$R-\overset{\overset{O}{\parallel}}{C}-H$	Aldehyde
(v) 1705 - 1720	$R-\overset{\overset{O}{\parallel}}{C}-R$	Ketone
(vi) 1700 - 1725	$R-\overset{\overset{O}{\parallel}}{C}-OH$	Carboxylic acid
(vii) 1370 - 1540	$-N-\overset{\overset{O}{\parallel}}{O}$	Nitrogroup
(viii) 1680 - 1700	$R-\overset{\overset{O}{\parallel}}{C}-N$	Amide
(ix) 1590 - 1690	$-C=N$	imine
(x) 1620 - 1680	$-C=C-$	Alkene
(xi) 1600 - 1600	>C=C<	Aromatic

(iii) \equiv Bond.

(i) 2240 - 2260	$-C \equiv N$	Non-conjugated nitriles
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(ii)	2215 - 2240	$-C \equiv N$	Conjugated nitriles
(iii)	2100 - 2140	$-C \equiv C-H$	Terminal alkene
(iv)	Single bond region -		
(i)	1000 - 1300	$\begin{array}{c} \\ -C-O- \\ \end{array}$	Alcohol, Phenol, Ester, Ether
(ii)	1100 - 1120	$\begin{array}{c} \quad \\ -C-C- \\ \quad \end{array}$	Saturated alkane
(iii)	500 - 750	$\begin{array}{c} \\ -C-X \\ \end{array}$	Haloalkanes.

* II Fingerprint Region :-

It lies between $1400 - 665 \text{ cm}^{-1}$. It

is low frequency or low energy region the absorption bands in this region are due to both stretching & bending mode of vibration.

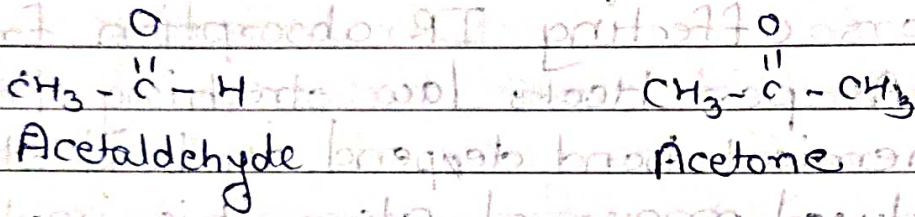
- Most single bonds give absorption bands in this region.

* Hooke's law -

- The vibration of diatomic species or molecule in which two atoms having mass M_1 & M_2 joined by covalent bond form a simple harmonic oscillator like two balls joined by spring.

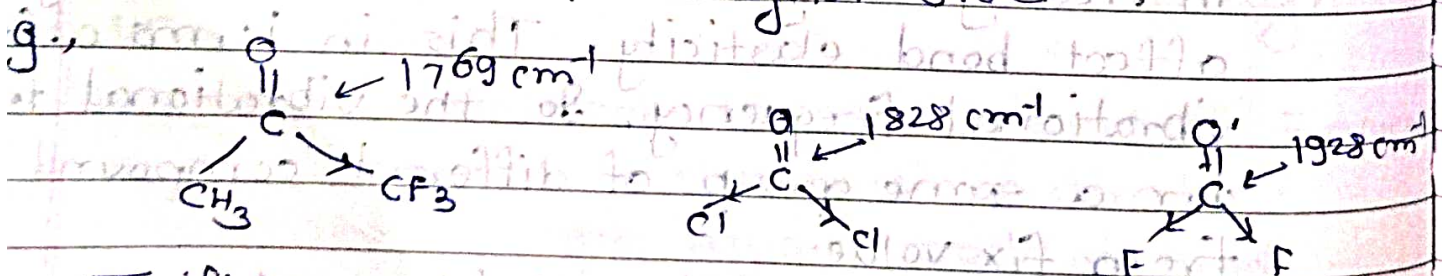
① Inductive effect -

① The electron releasing or donating (+I effect) attach. the functional group decreases the stretching frequency and shift IR bond to a lower side.



An extra methyl group (exerts +I) in acetone decrease bond strength the double bond character of (C=O) group. the decrease bond strength rises vibrational frequency & push IR absorption to a lower side.

② The electron withdrawing effect stabilise the double bond character of C=O group & increases stretching frequency to shift IR band to the higher side.



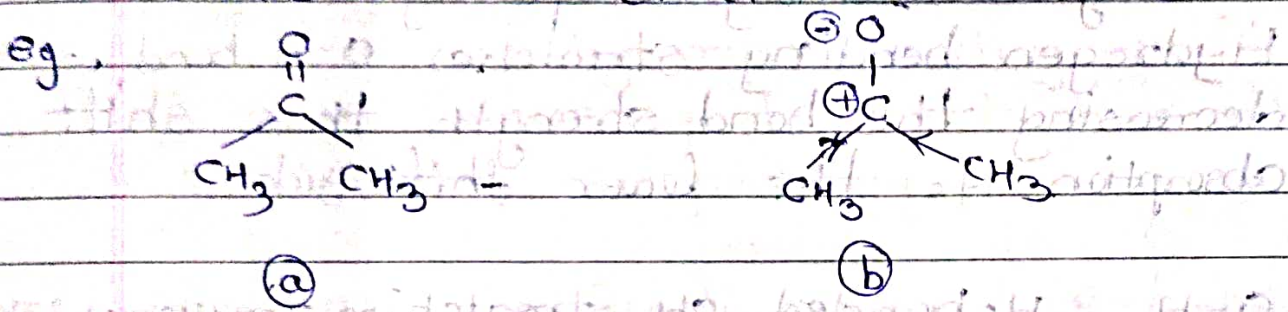
Trifluoroacetone

Carbonyl chloride

Carbonyl fluoride

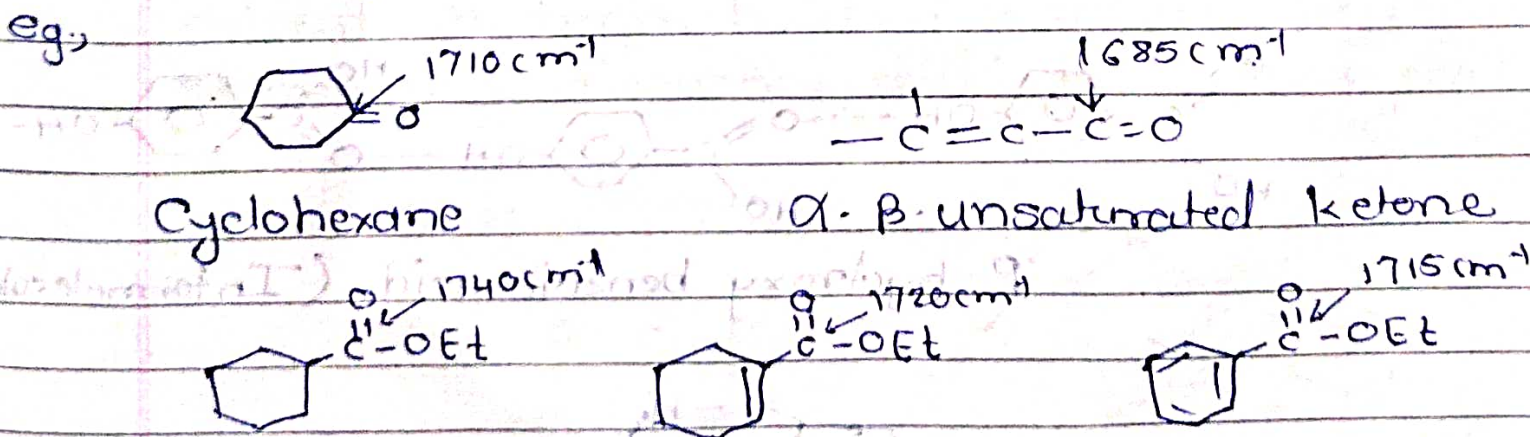
② Resonance Effect —

① The stretching frequency of functional group is decrease by electron donating resonance (+R) effect & increase by electron withdrawing resonance (-R) effect.



② The (+I) effect of two methyl group help to stabilise the single bonded resonance form (b). As single bond energy is less than for double bond energy the stretching frequency decreases from 1720 cm^{-1} (Acetaldehyde) to 1710 cm^{-1} (Acetone).

- Conjugated aldehydes & ketones shows electron donating resonance (+R effect).



- Conjugation of carbonyl group to a double bond exerts +R effect.

- This decrease double bond character of $C=O$ group decreases stretching frequency. (Hydrogen-bonding) The involvement of $C=O$ in hydrogen bonding weakens the $C=O$ & lowering the carbonyl stretching frequency.
- Hydrogen bonding stretches $O-H$ bond decreasing the bond strength this shift absorption to the lower shift side.

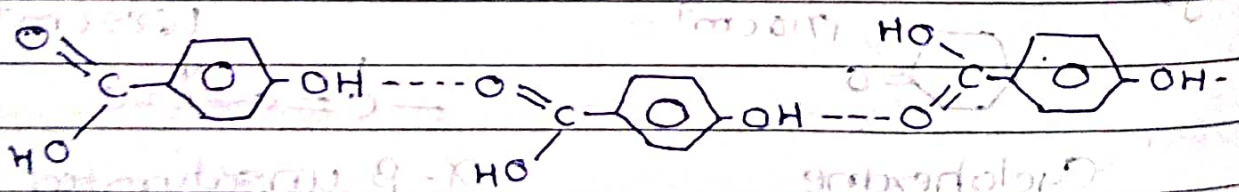
$O-H$ H-bonded OH stretching frequency 2700 cm^{-1}

$O-H$ Free $O-H$ stretching frequency 3500 cm^{-1}

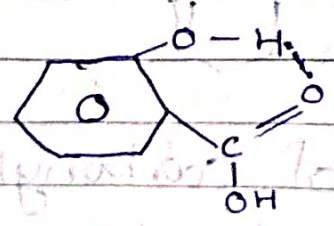
③ Intramolecular hydrogen bonding -

- It shows greater effect on $C=O$, $O-H$, stretching than intermolecular hydrogen bonding.

e.g, Parahydroxy benzoic acid.



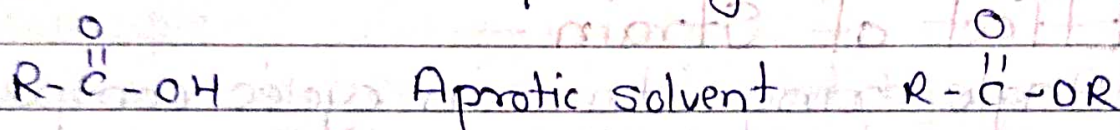
p-hydroxy benzoic acid (Intermolecular)



o-Hydroxy benzoic acid (Intramolecular)

(A) Effect on dilution on hydrogen bonding -

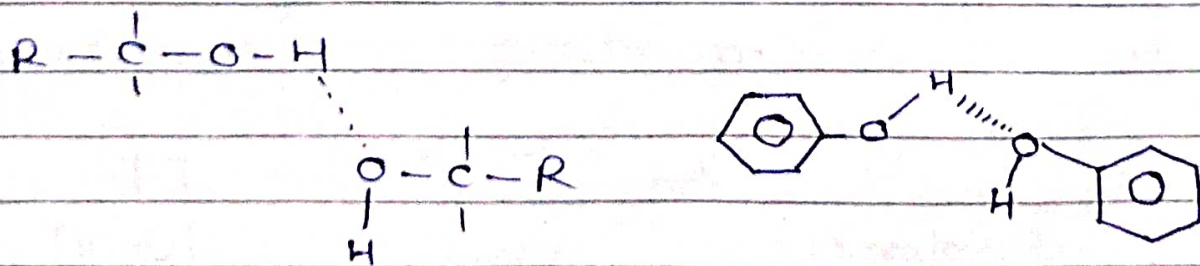
- Dilution with aprotic solvent prevent inter-molecular hydrogen bonding this stabilises -OH bond & shifts the IR absorption to the higher side, so it is called dilution effect
- e.g., Lack of hydrogen bonding shift $C=O$ & $O-H$ frequency to the higher side 1780 cm^{-1} & 3550 cm^{-1} respectively.



$C=O$ & $O-H$ both are free from H-bonding.

(B) Alcohol & Phenols -

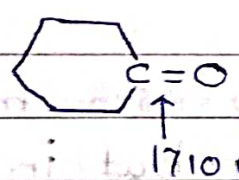
- Strong H-bonding effect are also observe in alcohol & phenols.
- Alcohol shows peak in $3200-3500\text{ cm}^{-1}$ range due to H-banded -OH group but in gas phase or in extreme dilution with aprotic solvent Hydrogen bonding is missing and stretching frequency shift to the 3550 cm^{-1} .



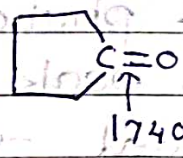
- ③ Amines & Amides -
- Strong H-bonding effects are observed in 1°/2° amine & 1°/2° amide.
 - The hydrogen bonding effect is not shown by 3° amine & amide because of absence of N-H bond.

④ Effect of Strain -

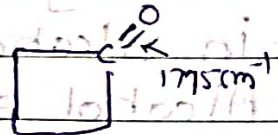
- Angle ring strain in cyclic compound causes long shift in frequency.
- As the ring size decreases angle strain increases this causes increase in carbonyl stretching frequency.



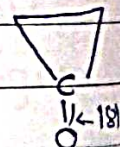
Cyclohexanone



Cyclopentanone



Cyclobutanone



Cyclopropanone

