SEM IV STUDY MATERIAL

UV Spectroscopy

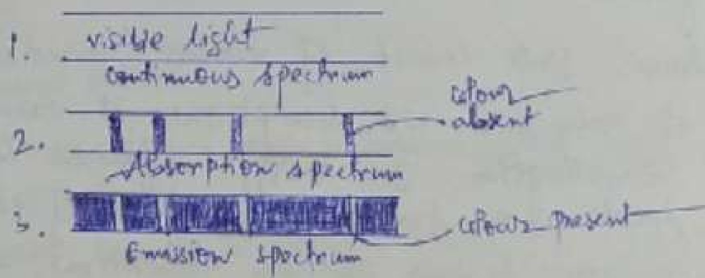
ULTRAVIOLET SPECTROSCOPY

- Spectroscopy is the study of the interaction between matter and electromagnetic radiation.

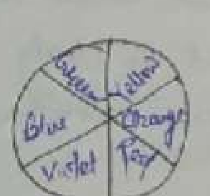
- Electromagnetic radiation refers to the waves of the electromagnetic field, propagating through space, carrying electromagnetic radiant energy.

=) Electromagnetic spectrum:

Radiation type:	Radio	Microwave	Infrared	Visible	Ultraviolet	X-ray	Gamma-ray
Wavelength (m):	10^{3}	10^{-2}	10^{-5}	0.5×10^{-6}	10^{-8}	10^{-10}	10^{-12}
Approximate scale of wavelength:	Buildings	Humans	Needle point	Protozoans	molecules	Atoms	Atomic nuclei



- Complementary Colour:



VIBGYOR

Violet: 380 - 450 nm
Blue: 450 - 495 nm
Green: 495 - 570 nm
Yellow: 570 - 590 nm
Orange: 590 - 620 nm
Red: 620 - 750 nm

- Compounds that absorb light in the visible region of the spectrum do not possess the colour corresponding to the wavelength of the absorbed light. Rather, there is an inverse relationship between the observed colour and the color absorbed.

- Basic of UV: Range of UV is from 190 nm to 800 nm.

=) UV light can be absorbed by molecules to excite higher energy (most loosely bound) electrons from lower energy states to higher states. The energy difference between electronic levels in most molecules vary from 125 to 650 KJ/mole

=) Such transitions can be studied extensively to understand the binding energy of the corresponding electrons undergoing transition.

=) Since π electrons are most loosely bound in an organic molecule. UV spectroscopy yields a lot of information about the degree of unsaturation in a molecule.

[P.T.O]

⇒ When the wavelength of the transition exceeds the UV range, based on the same principle, even the colours of molecules can be explained on the basis of absorption of visible light.

β-carotene

$\lambda_{max} = 452\ nm$

⇒ 452 nm lies in the blue range so its complementary colour orange is seen by us.

Origin of UV spectroscopy:

Basically origin of UV spectroscopy is the electronic transition from electronic ground state to electronic excited state.

⇒ Every electronic state consist of various vibrational and rotational state so instead of only one UV absorption, it occurs over a wide range of wavelengths. The energy difference between vibrational and rotational levels are smaller than those of electronic levels. Thus Because there are so many possible transitions, each differing from the others by only a slight amount, each electronic transition consists of a vast number of lines spaced so closely that the spectrophotometer cannot resolve them. Thus it traces an "envelope" over the entire pattern.

Principles of Absorption Spectroscopy:

Lambert-Beer's Law

$$A = \log_{10}\frac{I_0}{I} = \varepsilon c l$$

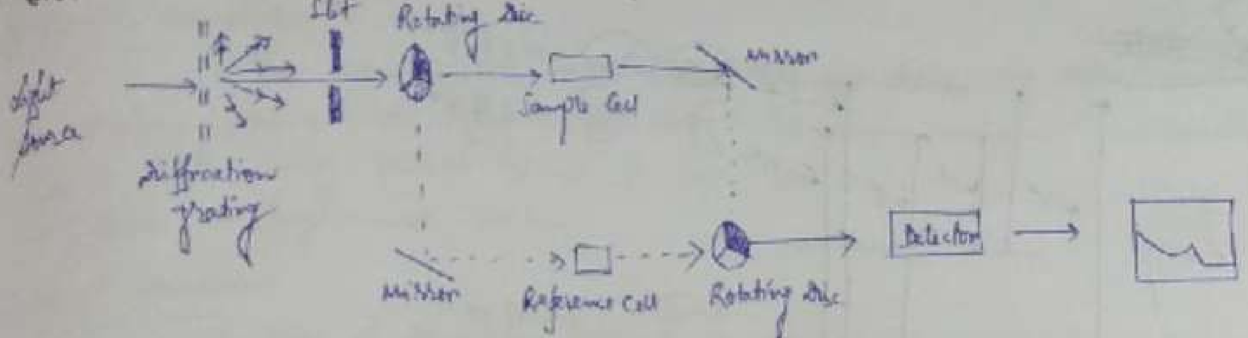
A = Absorbance
ε = molar absorptivity / molar extinction coefficient
c = molar concentration of solute
l = length of sample cell (cm)

⇒ Molar absorptivity = Absorbance of 1 mol dm^{-3} solution if cell length is 1 cm.

⇒ The intensity of an absorption band in UV is expressed as the "molar absorptivity" at maximum absorption ε_{max}.

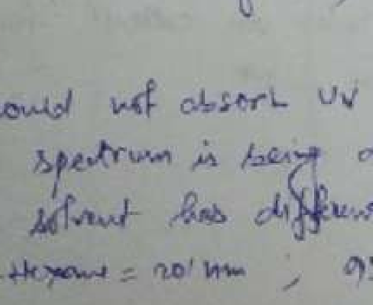
With increasing the concentration of solution or chromophore, ε increases. Thus more conjugation; more ε value.

- Instrumentation: (Double Beam UV Spectrometer)



- Light source: Deuterium lamp for UV range
  Tungsten/halogen for visible range
- Diffraction grating splits lights to its component colour like prism
- Slit allows to pass only a narrow range of wavelengths to the rotating disk
- 

- Reference cells is designed in such a manner that light has to travel 1 cm through the contents.
  - ⇒ Glass or plastic cannot be used because they absorb UV light radiation. Thus cells made of quartz is used as it does not absorb radiation in this range.
- Detector convert light to current. The greater is the intensity of light, the higher is the current.
- An absorbance (A) could be written as -



$A = \log_{10} \frac{I_0}{I}$

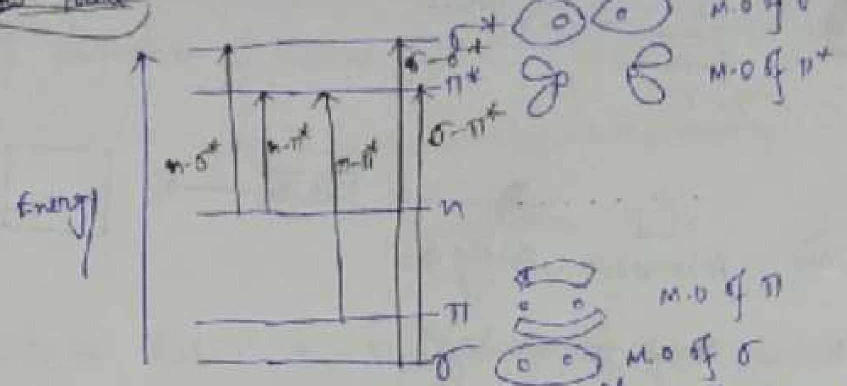
Intensity of light passing through reference cell = I_0

Intensity of light passing through sample = I

- Solvents:
  - ⇒ It should not absorb UV radiation in the same region as the substance whose spectrum is being determined.
  - ⇒ Every solvent has different cut-off points or minimum regions of transparency
    eg n-Hexane = 201 nm, 95% Ethanol = 205 nm
  - ⇒ A nonpolar solvent does not hydrogen bond with the solute, and the spectrum of the solute closely approximates the spectrum that would be produced in the gaseous state ie a fine structure is often observed.
- Vacuum Ultraviolet: Below 200 nm, O_2 begins to absorb UV. Thus to study the higher energy transition below 200 nm. the entire path length must be evacuated and for this reason the region below 200 nm is usually referred to as vacuum ultraviolet.

Nature of electronic transition:

~~Selection rule~~



⇒ These energy gaps are different in different compounds.

⇒ The difference in energy between two orbitals $= \Delta E = h\nu = h\frac{c}{\lambda} = h\bar{\nu}c$

⇒ When light passes through a compound, some of its energy promotes an electron from one of the bonding or non-bonding orbitals to one of the antibonding orbitals.

⇒ The frequency (or wavelength) of absorption depends on the energy gaps between those two energy levels.

- The higher the energy gaps, the lower is the wavelength of the light absorbed.
- Thus

↑ Increasing energy

$\sigma-\sigma^*$ [Alkanes]

$\sigma-\pi^*$ [carbonyl compound]

$\pi-\pi^*$ [Alkenes, $\overset{O}{\overset{\|}{C}}-$, ≡, azo compounds etc]

$n-\sigma^*$ [-O, N, S, X compounds]

$n-\pi^*$ [Carbonyl compounds]

Selection rule:

⇒ Not all electronic transitions are allowed. Certain restrictions should be considered for electronic transitions, called "Selection rules".

① The spin quantum number of an electron should not change during the electronic transition.

② The transition between two orbitals should be symmetry allowed.

⇒ Any transition that violates these rules are called "forbidden transition". Most common "forbidden transition" is $n-\pi^*$.

- Various types of transitions:

① $\sigma-\sigma^*$ transition:

In alkanes the only transition available is the promotion of an electron from a low lying σ orbital to a higher energy σ^* antibonding orbital. This is high energy process since σ bond are in general very strong and requires very short wavelength near 150 nm.

(ii) $n-\sigma^*$ transition:

This type of transition takes place in saturated compounds containing one hetero atom with unshared pair of electrons. Eg, H_2O absorbs at 167 nm, CH_3OH at 174 nm, CH_3Cl at 172-175 nm, CH_3I at 258 nm, as nonbonding electrons of chlorine atom are comparatively difficult to excite and nonbonding electrons of iodine are loosely bound.

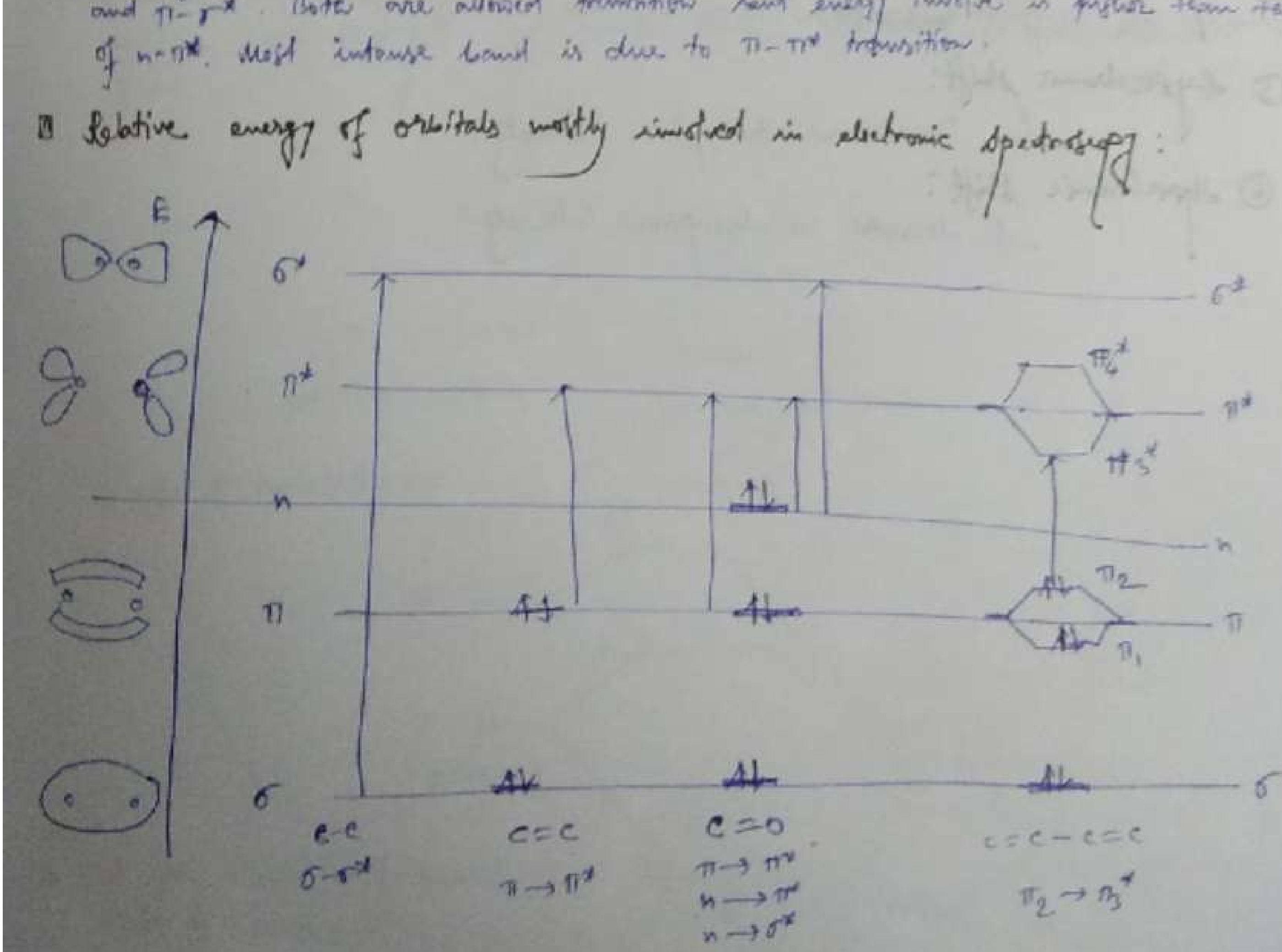
(iii) $\pi-\pi^*$ transitions:

This type of transition occurs in the unsaturated molecules i.e in simple alkene, aromatic compound, alkyne, carbonyl, cyanide etc. This transition requires lesser energy and therefore absorption occurs at longer wavelength. In non-conjugated alkene absorption band appears around 170-190 nm.

(iv) $n-\pi^*$ transitions:

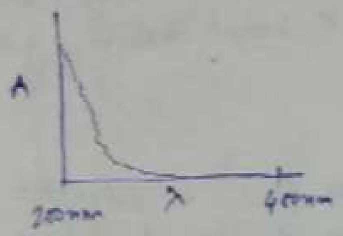
This type of transitions requires least amount of energy and occurs at longer wave-length. In saturated aliphatic ketones, the lowest energy transition involves one of the non-bonding electron on oxygen to the relatively low lying π^* orbital at around 280 nm and higher energy $\pi-\pi^*$ transition occurring around 180 nm. This $n-\pi^*$ transition is forbidden in symmetry terms and therefore intensity is low although wavelength is high. Two other transition available in carbonyl compound are $n-\sigma^*$ and $\pi-\sigma^*$. Both are allowed transition but energy involve is higher than that of $n-\pi^*$. Most intense band is due to $\pi-\pi^*$ transition.

- Relative energy of orbitals mostly involved in electronic spectroscopy:



11 End absorption:

It is special phenomenon of increase in absorption intensity as the λ decreases towards 200nm (End of UV range), which is due to $n-\sigma^*$



Significance: End absorption is possible due to only compound having n electrons and having σ bonds. Eg. n electrons present in most of the solvent like water and alcohol. N electrons have higher E and lower λ value.

12 Convention & terminology:

① Chromophore:

A covalently unsaturated group responsible for electronic absorption.

(Eg, C=C, C=O, esters, amides NO_2 etc)

② Auxochrome:

A saturated group with non-bonded electrons which when attached to a chromophore alters both the wavelength and the intensity of the absorption.

(Eg, –OH, $-NH_2$, $-NR_2$, –SH etc)

③ Bathochromic Shift:

The shift of absorption to a longer wavelength. (also known as red shift)

④ Hypsochromic Shift:

The shift of absorption to a shorter wavelength (also known as blue shift

⑤ Hyperchromic shift:

An increase in absorption intensity.

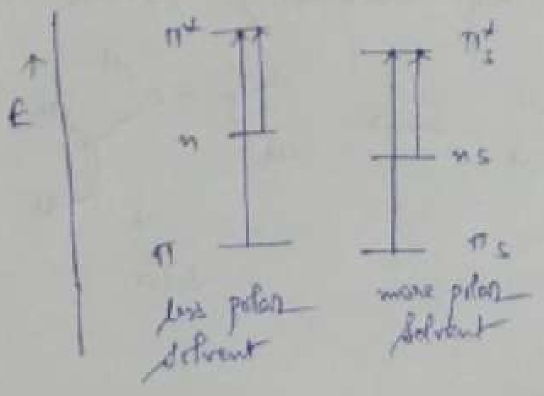
⑥ Hypochromic shift:

A decrease in absorption intensity.

Effects of various factor on λ max.

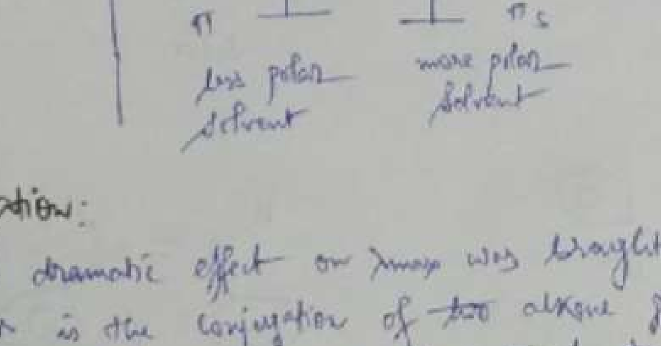
① Solvent:

Solvation by a polar solvent stabilises π, π* and n orbitals. The stabilization of non-bonding orbitals is particularly pronounced with hydrogen bonding solvents and π* orbitals are more stabilized by solvation than are π orbitals because π* orbitals are more polar. The net result is that the energy of transition π-π* becomes less with solvation which leads to red shift while the energy of transition n-π* becomes larger which leads to hypsochromic shift.

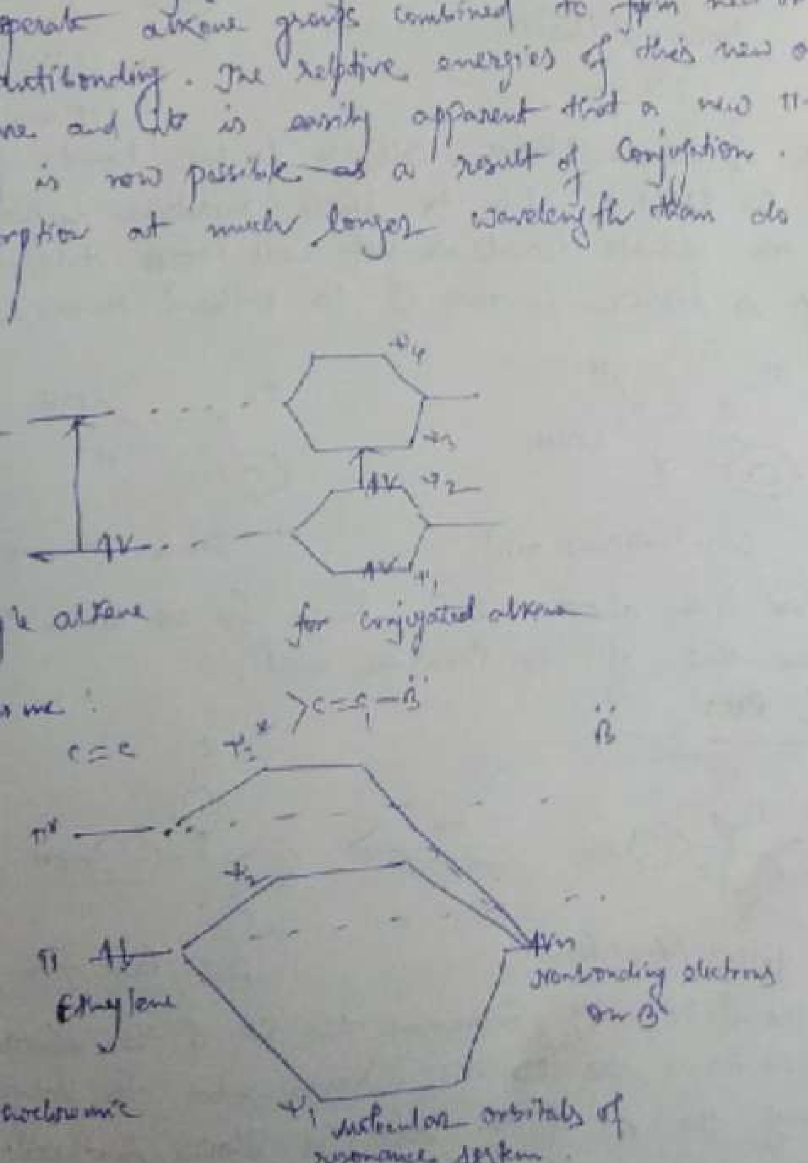


② Effect of conjugation:

The most dramatic effect on λmax was brought about by conjugation. The simplest case is the conjugation of ~~two~~ alkene groups. In conjugated diene, the π orbitals of separate alkene groups combined to form new orbitals, two bonding and ~~the~~ antibonding. The relative energies of this new orbital are shown in the following figure and it is easily apparent that a new π-π* transition of very low energy is now possible as a result of conjugation. Conjugated diene therefore show absorption at much longer wavelength than do isolated alkene groups.



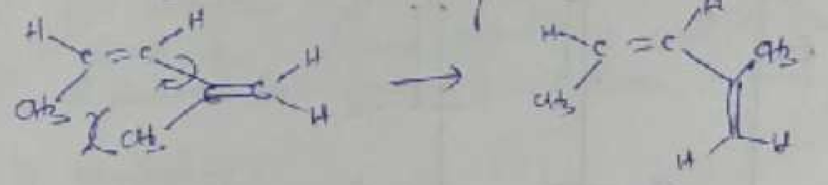
③ effect of auxochrome:



B Just like above, bathochromic shift is observe.

S-cis & S-trans conformation:

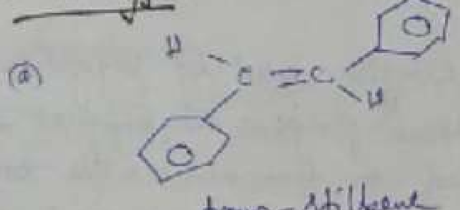
Butadiene and many simple conjugated diene exist in a planar s-trans conformation, as noted. Generally, alkyl substitution produces bathochromic shifts and hyperchromic ~~shift~~ effects. However, with certain patterns of alkyl substitution the wavelength increases but the intensity decreases. The 1,3-dialkylpentadienes possess too much crowding between alkyl groups to permit them to exist in the s-trans conformation. They convert, by rotation around the single bond, to an s-cis conformation, which absorbs at longer wavelengths but with lower intensity than the corresponding s-trans conformation.

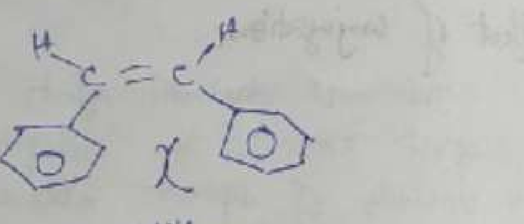

S-trans

S-cis

③ Steric effect:

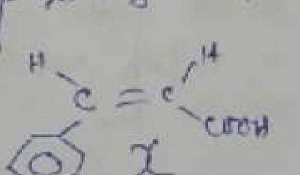
(a)

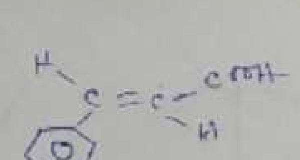

trans-Stilbene
230 nm


cis-Stilbene
225 nm

In case of trans-Stilbene, all the double bonds are well delocalized ~~conjugated~~. But in case of cis-Stilbene due to steric repulsion between the ~~two~~ phenyl group, all the double bonds are not well ~~conj~~ delocalized. Thus π-π* energy gap is higher in case of cis-stilbene than that of trans-stilbene.

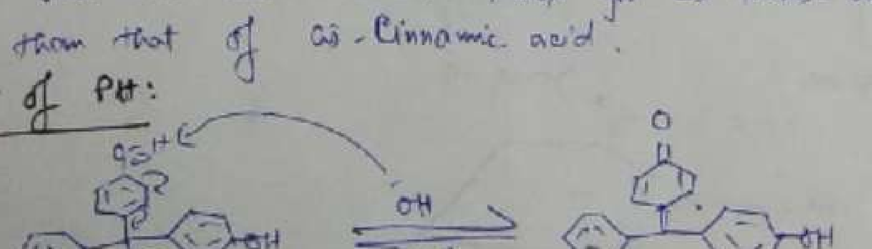
(b)


cis-Cinnamic acid


Trans-Cinnamic acid

- Just like above case, λmax for ~~cis~~ trans-Cinnamic acid is higher than that of cis-Cinnamic acid.

④ Effect of PH:


Yellow / Acid form

Red / Base form

- For phenol-red, with increasing the pH of the solution, conjugation increases which in terms ~~changes~~ shifts the λmax value to longer region. Thus with increasing the pH of the ~~soln~~ it shows bathochromic shift.

The woodward - Fieser rules for dienes:

Parent :

Heteroannular (transoid) λ = 214 nm

Increments for:

1. Cisoid Conformation = 39 nm; Thus for Homoannular (cisoid) = (214+39) nm = 253 nm
2. Double bond extending Conjugation = 30 nm
3. Alkyl Substituent on ring residue = 5 nm
4. Exocyclic double bond = 5 nm
5. polar groupings:
   - $-OCOCH_3$: 0 nm
   - $-OR$; 6 nm
   - $-Cl/Br$; 5 nm
   - $-NR_2$; 60 nm.

eg;

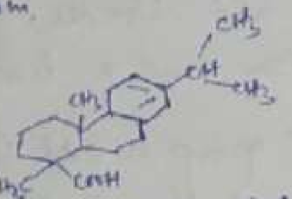
Transoid = 214 nm

Ring residue = (3×5) = 15 nm

Exocyclic double bond = 5 nm

Total = 234 nm

observed = 235 nm



Cisoid = 253 nm

Alkyl substituent = 5 nm

Ring residue = (3×5) nm = 15 nm

Exocyclic double bond = 5 nm

278 nm

observed = 275 nm

Woodward's rule for enones:

Parent: Six-membered ring or acyclic parent enone = 215 nm $\left[\beta-\overset{\beta}{C}=\overset{\alpha}{C}-C=O\right]$

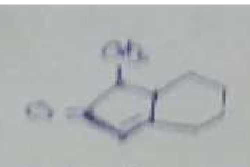
Five-membered ring parent enone = 202 nm

For Aldehyde = 207 nm $\left[\beta-\overset{\beta}{C}=\overset{\alpha}{C}-\overset{4}{C}=O\right]$

Increaments for:

1. Double bond extending conjugation = 30 nm
2. Alkyl group on ring residue α = 10 nm ; β = 12 nm ; γ and higher = 18 nm
3. Polar groupings:
   - $-OH$; α = 35 nm ; β = 30 nm ; γ = 30 nm ; δ = 50 nm
   - $-OCOCH_3$; $\alpha, \beta, \gamma, \delta$ = 6 nm
   - $-OCH_3$; α = 35 nm ; β = 30 nm, γ = 17 nm ; δ = 31 nm
   - $-Cl$; α = 15 nm ; β, γ, δ = 12 nm
   - $-Br$; α = 25 nm ; β = 30 nm , γ, δ = 25 nm
   - $-NR_2$; β = 95 nm
   - $-SR$; β = 80 nm
4. exocyclic double bond = 5 nm
5. Homocyclic diene component = 39 nm
   - Solvent Correction = variable.

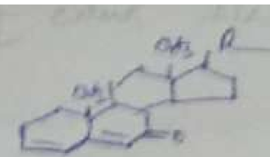
eg:



Five membered enone = 202 nm
β-ring residue = 2×12 nm = 24 nm
exocyclic double bond = 5 nm

Total = 231 nm

Observed = 226 nm



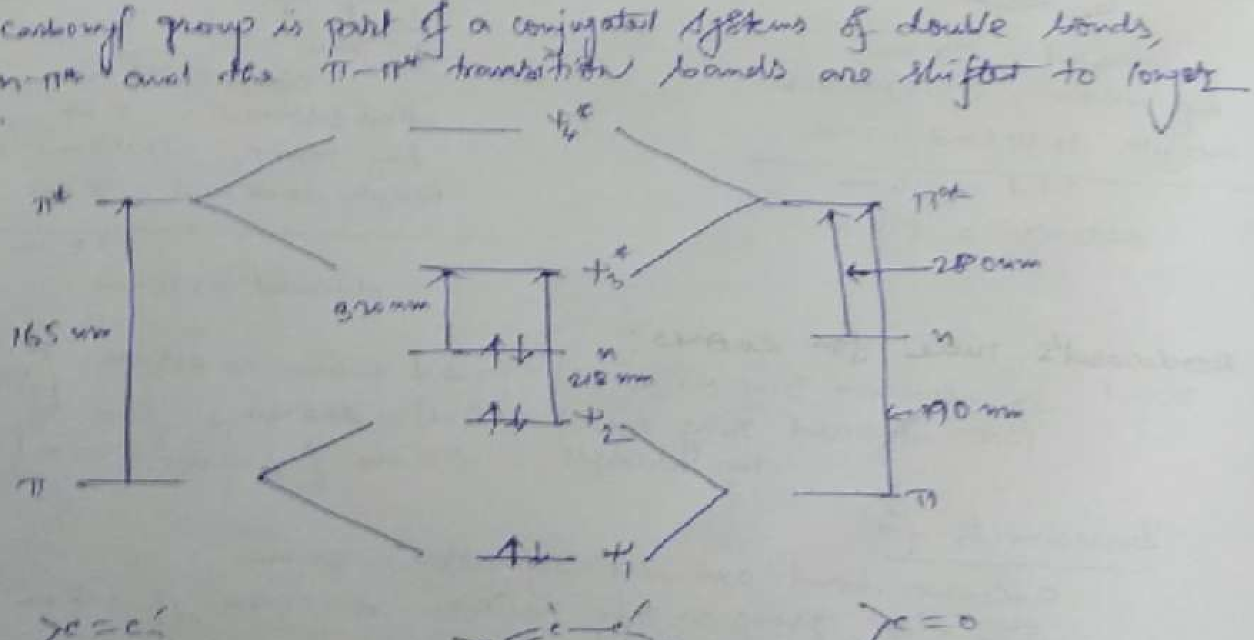
Six-membered enone = 215 nm
Double bond extending conjugation = 30 nm
β ring residue = 12 nm
δ ring residue = 18 nm
exocyclic double bond = 5 nm

Total = 280 nm

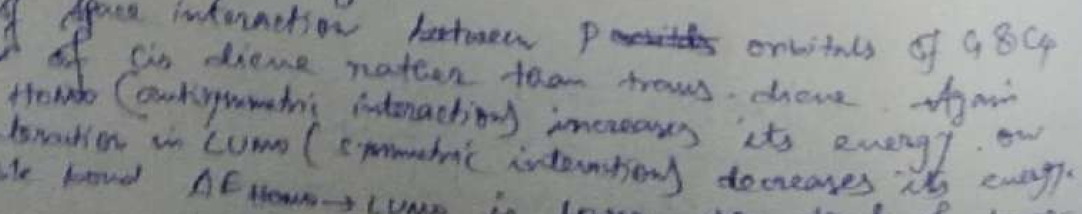
observed = 280 nm

- Substitution on the carbonyl group by an auxochrome with a lone pair of electrons, such as $-NR_2$, $-OH$, $-OR$, $-NH_2$ or $-X$ as in amides, acids, esters, or acid chlorides, gives a pronounced hypsochromic effect on the n–π* transition and a lesser bathochromic effect on the π–π* transition.

- If the carbonyl group is part of a conjugated systems of double bonds, both the n–π* and the π–π* transition bands are shifted to longer wavelengths.



- Why 29 nm is added for cis-double bond?



The probability of space interaction between p ~~orbitals~~ orbitals of C_1 & C_4 is higher in case of cis diene rather than trans-diene. Again interaction in HOMO (antisymmetric interaction) increases its energy. On the other hand interaction in LUMO (symmetric interaction) decreases its energy. Thus for cis double bond $\Delta E_{HOMO \rightarrow LUMO}$ is lower than that of trans-double bond.

Violation of woodward rule:

i)

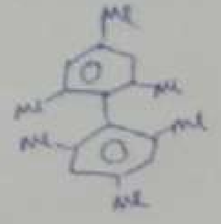
I

II

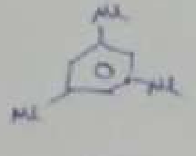
λ_{max} 250 (ϵ 19000) : λ_{max} 237 (ϵ 10250)

According to woodward rule, with increasing alkyl substituent λ_{max} must increase. But in case of II addition of one -Me group removes the coplanar of the molecule, leading to hypsochromic shift.

Removal of coplanarity for compound III is such extent that it behaves like IV under UV. ii/



III [λ_{max} = 266 nm]



IV

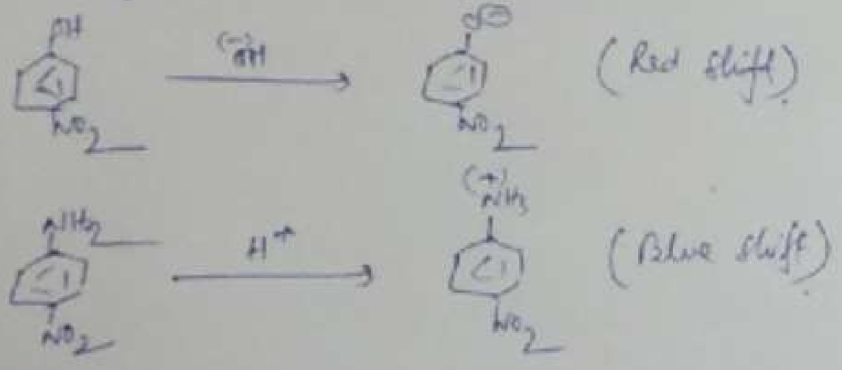
For benzene ring:

(i) When -M group para to +M group then the shift in λ_{max} is greater than the sum of individual effects that may be because of the extended conjugation.
(examples are p-nitroaniline & p-nitrophenol.)

(ii) usually a -M group ortho or meta to a +M group produces merely a small shift from that of the isolated chromophores.

(iii) Non bonding pair availability may alter the position of λ_{max}.

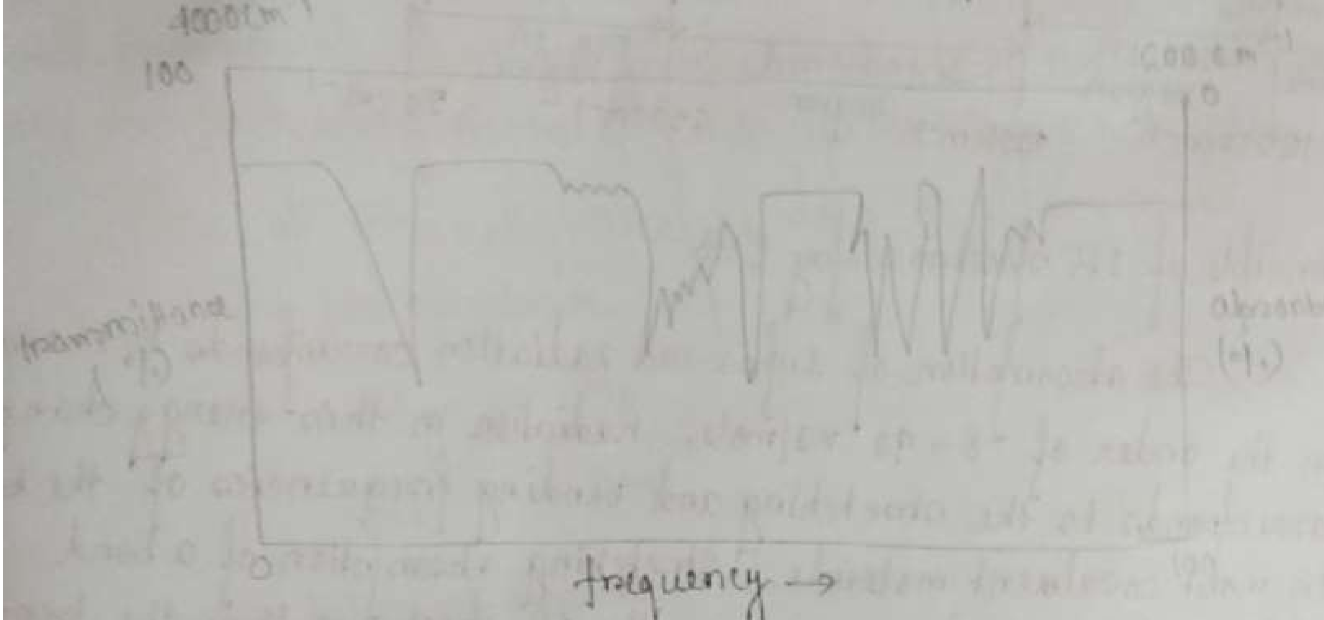
Eg



[Due to change in conjugation]

IR Spectroscopy

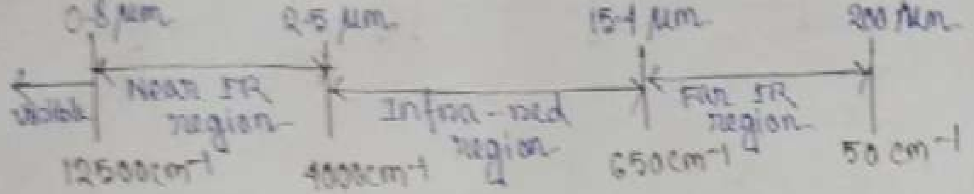
Infra-red Spectroscopy



When Infra-red light is passed through a sample of an organic compound, some of these frequencies are absorbed while other frequencies are transimitted to the sample without being absorbed If we plot absorbance of or transmittance against frequency, the result is an Infra-red spectrum. Molecule will absorb Infra-red light of particular frequency (such that $\Delta E = h\nu$) if there is an energy transition within the molecule such that $\Delta E = h\nu$. The transition involved in infra red absorption are associated with vibrational changes within the molecule. eg. Band near 3000 cm^{-1} has exactly the same frequency as a C–H bond undergoing stretching vibrations. Therefore, band near 3000 cm^{-1} is called C–H (stretch) absorption represented as C–H str. Band near 1400 cm^{-1} corresponds to the frequency of the bending vibration of C–H bonds and are called C–H bend absorption represented as C–H deformation (C–H def) Infra-red spectroscopy is therefore basically a vibrational spectroscopy. Different bonds (C–C, C=C, C≡C, C=O, –OH) have different vibrational frequencies and we can detect the presence of these bonds in an organic molecule by identifying this characteristic frequency as an absorption band in the Infra-red spectrum.

eg. $\nu_{C=O\ str} \Rightarrow 1700\ cm^{-1}$

$\nu_{C\equiv N\ str} \Rightarrow 2250\ cm^{-1}$



☐ Principle of IR spectroscopy :⇒

The absorption of Infra-red radiation corresponds to changes on the order of ~8 – 40 KJ/mole. Radiation in this energy change corresponds to the stretching and bending frequencies of the bond in most covalent molecule. Stretching absorption of a bond appear at higher frequencies in the IR spectrum than the bending absorption of the same bond.

☐ Calculation of vibrational frequencies :⇒

$$\text{frequency } (\nu) \propto \sqrt{\frac{\text{Bond strength}}{\text{Mass (reduced)}}}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{K}{\frac{m_1 m_2}{m_1+m_2}}}$$

K = force constant of the bond

μ = reduced mass. $= \frac{m_1 m_2}{m_1+m_2}$

The vibrational frequency of a bond is expected to increase when the bond strength increases also when the reduced mass of the system decreases.

☐, Modes of vibration :⇒

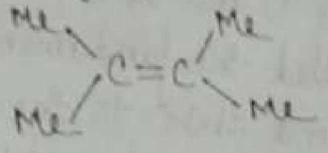
Molecules with large no of atoms possesses many vibrational frequencies. For a non-linear molecule, with n atoms, no. of vibrational mode is $(3n-6)$. So that, CH_4 theoretically have 9 and C_2H_6 has 18 vibrational modes. But theoretical no. of fundamental vibrations are seldom observed, Because—

I. Some fundamental vibration fall outside the range of investigation (4000cm^{-1} – 650 cm^{-1}):

II. Some vibrations may have the same frequency i.e they are degenerates and their absorption band will overlap.

■ In order to see an absorption band, the particular vibration should produce of fluctuating dipole, otherwise it cannot interact with the fluctuating electric fields of the Infra red light.

$\bar{\nu}$str. of tetramethyl ethelene does not appear in the Infra-red spectrum.



There are two types of molecular vibrations—

1. Stretching
2. Bending

A stretching vibration is a rythmical movement along the bond axis such that interatomic distance is increasing or decreasing. A bending vibration may consist of change in bond angle.

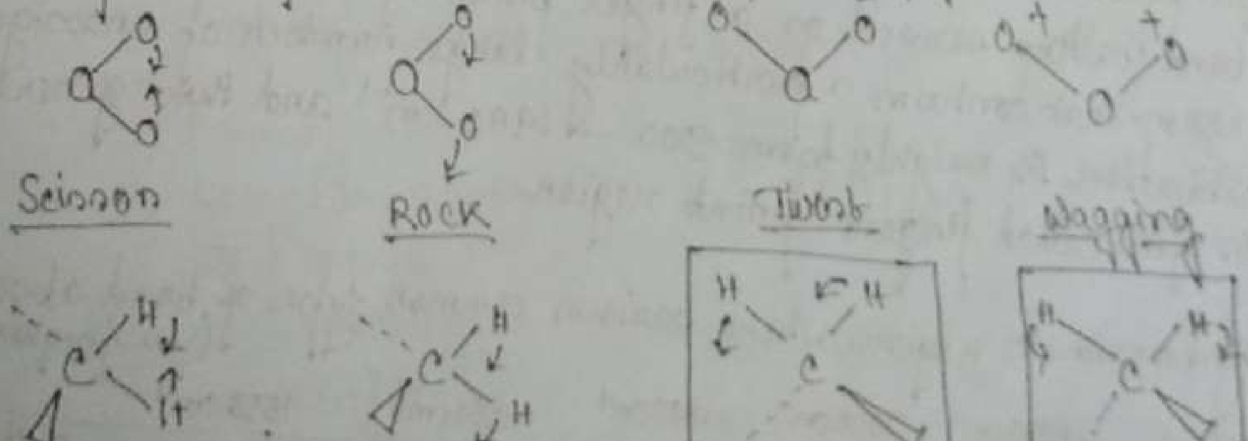
Stretching mode of CH_2 :

I. Symmetric stretching

II. Anti symmetric stretching

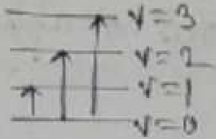
Bending mode of CH_2 :

In plane deformation — out of plane deformation



'+' and '−' indicates movement perpendicular to the plane of molecule i.e plane of page.

The vibration we have been discussing are called fundamental absorption. They arise from excitation from the ground state



(V=0) to the 1st excited state (V=1) and absorbed light strongly give rise to intensed band called the fundamental bands.

Transition from ground state to the 2nd excited state (V=2) or higher excited state with the absorption of Infra-red radiation give rise to weak bands called overtones and it arises at integral multiples of the frequency of the fundamental. For a fundamental band at $\bar{\nu}$, weak overtone band at $2\bar{\nu}$ and $3\bar{\nu}$ may be observed.

☐ Uses of IR spectroscopy :⇒

No two molecules of different structure have exactly the same Infra red absorption pattern or Infra-red spectrum as every type of bond has a different natural frequency of vibration and two of the same type of bond in two different compound are in two slight different environment. Thus, the Infra-red spectrum can be used for molecules such as a finger print can be used for humans. If IR spectrum of two substances coincide peak for peak in most cases the two substance will be identical. This band pattern served as a finger print of the molecule, the region that contain a particularly large number of unassigned vibration is roughly from 900 → 1400 cm^{-1} and this general area is often called fingers print region.

Approximate region where various common type of bond absorbed — (Str. frequency)

4000 cm^{-1} 2800 cm^{-1} 2000 cm^{-1} 1800 cm^{-1} 1650 cm^{-1} 1550 cm^{-1} 600 cm^{-1}

O-H C-H N-H	C≡C C≡N	very few band	C=O	C=N ←C=C	C-Cl C-O C-N C-C

A simplified co-relation chart —

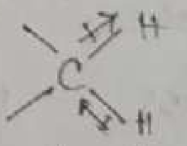
		frequency(cm^{-1})	Intensity
C–H	alkanes	2850 – 3000	S
=C–H	alkenes	3000 – 3100	S–m
	aromatic	3050 – 3650	S
	alkyne	3300	S
	*aldehyde	2800 – 2900	w
C=C	alkene	1600 – 1680	m-w
	Aromatic	1475 – 1600	m-w
*C≡C	alkyne	2100 – 2250	m-w
C=O	aldehyde	1720 – 1740	S
	Ketone	1705 – 1725	S
	Carboxylic acid	1700 – 1725	S
	ester	1730 – 1750	S
	Amide	1600 – 1680	S
	Anhydride	1760 & 1710	S
	Acid chloride	1800	S
O–H	Alcohol & phenol		
	free —	3600 – 3650	S
	H-bonded —	3200 – 3400	m–s (broad)
	carboxylic acid	2400 – 3400	m–s "
N–H	Primary and secondary amine and amide	3400 – 3500	m "
	Stretching	3100 – 3500	m-S
	Bending	1550 – 1650	m-S
C–O	Alcohol, Acid, ether, ester,	1000 – 1300	S
C–N	Amine	1000 – 1350	m-S
C=N	Imines and Oximes	1640 – 1690	w-S

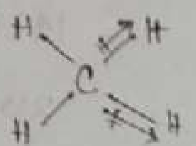
		frequency (cm^{-1})	Intensity
C≡N	nitriles	2240 - 2260	m-s

Factors influencing vibrational frequency :⇒

(I) Inductive effect
(II) Mesomeric effect
(III) Coupling

Vibrational coupling and Fermi Resonance :


Asymmetry Str.


Symmetric Str.

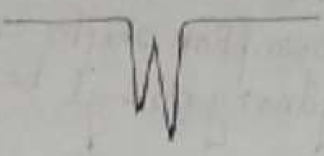
An isolated C-H bond has only one stretching frequency but in case of methelene group two absorption occurs due to symmetric and asymmetric vibrations. In such cases asymmetric vibrations occur at higher wave number compared with the symmetric vibrations. These are called coupled vibrations as these vibrations occur at different frequencies than that required for an isolated C-H stretching.

Vibrational coupling takes place between two bonds vibrating with similar frequency provided that the bonds are resonably closed in the molecule. The coupling vibration may both be fundamental or a fundamental vibration may couple with overtone of some other vibration. This coupling is called Fermi resonance.

eg. In aldehydes the C-H stretching absorption usually appears as a doublet because of interaction between the C-H stretching fundamental and overtone of C-H deformation. It appear at around 2820 cm^{-1} and 2720 cm^{-1}.

In Carboxylic acid anhydrides give rise to two C-O stretching absorption, $\bar{\nu}_{asi}$ and $\bar{\nu}$ symmetric (between 1850-1800 cm^{-1} and 1790 - 1745 cm^{-1}) with a seperation of about 65 cm^{-1}, coupling occurs between the two carbonyl groups which is indirectly linked to oxygen. The interaction is enhanced due to slight double bond character in the carbonyl oxygen bond. Higher frequency band in this case is due to symmetric as stretching.

In amides, two absorption band appears around 1600–1700 cm^{-1}, corresponding mainly to C=O stretching and –N-H deformation. Because of vibrational coupling the original characters of the vibration are modified.



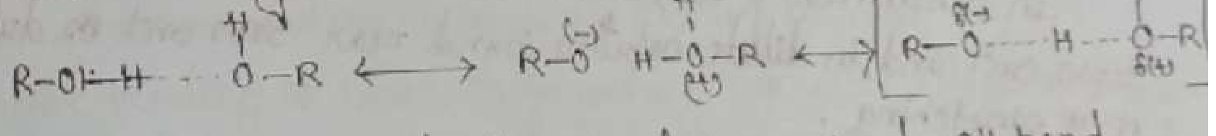
☒ Hydrogen bonding :⇒

☐ Alcohols and Phenols :

In aliphatic alcohols, a sharp band appears at around 3650 cm^{-1} in dilute solution due to free –OH group while a broad band is isolated at around 3350 cm^{-1} due to hydrogen bonded –OH group. Alcohols and phenols in the condensed phases (bulk liquid or KBr disc). are strongly H-bonded usually in the form of dynamic polymeric association and this lead to a wide envelop of absorption and hence to a broadening of the absorption band.

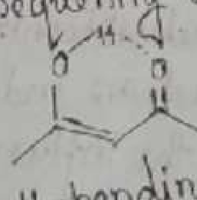
In dilute solution or in the vapour phase, the proportion of free molecules increases and give rise to the 3650 cm^{-1} band.

Bonded O-H stretching should appear at lower frequency than free -O-H str. The hydrogen bond can be regarded as a following resonance hybrid.



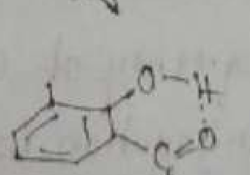
$$R{-}O{-}H\cdots\overset{H}{\overset{|}{O}}{-}R \longleftrightarrow R{-}\overset{(-)}{O}\quad H{-}\underset{(+)}{\overset{H}{\overset{|}{O}}}{-}R \longleftrightarrow \left[R{-}\overset{\delta(-)}{O}\cdots H\cdots\underset{\delta(+)}{\overset{H}{\overset{|}{O}}}{-}R\right]$$

So that H-bonding involves a lengthening of the original –OH bond. This bond is consequently weak. So, str. frequency is lower.

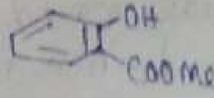
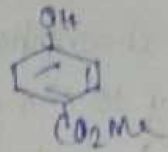


(down to 2800 cm^{-1})

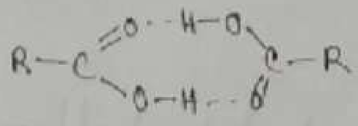
Intramolecular H-bonding present in ortho carbonyl substituted phenols or enols usually shifts the broad –OH band to a lower frequency.



down to 3000 cm^{-1}

Q. Distinguish  and 

The intramolecular H-bonded band does not change its position significantly even at high dilution as the internal bonding is not altered by a change in concentration. But intermolecular H-bonding changes by dilution. So, -OH str. absorption shifts towards higher value by dilution, in case of p-hydroxy methyl benzoate.



A broad band reaching from 2500 cm^{-1} – 3500 cm^{-1} in H-bonded -OH stretching. It is -OH stretching band for carboxylic acid dimer structure. In very dilute solution in hexane, it is just possible to distinguish free-OH stretching. But this is extreme dilution.

π-cloud interaction :

Frequency of -OH stretching can be lowered by 40-100 cm^{-1} when the spectra is recorded in benzene solution compared with CCl_4 solution. It is due to π bonds (behave as lewis base) can form H-bonds to acidic hydrogen.

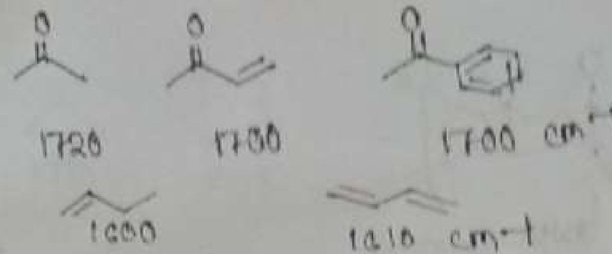
II, Amines :

In condensed phase, amine show bonded N-H stretching around 3300 cm^{-1} and in dilute solution band near 3400 cm^{-1} is due to free N-H stretching.

II Electronic effect :⇒

Changes in the absorption frequencies for a particular band can take place for change in the neighbouring substituents. The frequency shifts are due to electronic effects such as inductive effect and mesomeric effect and field effect. Under the influence of these effect the force constant or bond strength changes and its absorption frequency changes from the normal value.

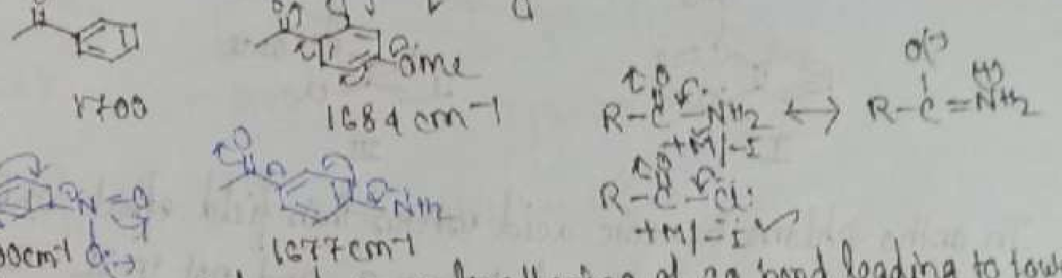
Conjugation lowers the frequency of C=O stretching and C=C stretching wheather the conjugation is brought about by α,β-unsaturation or aromatic ring.

eg. 

$\bar{\nu}_{C=O}$ 1720 1700 1700 cm^{-1}

$\bar{\nu}_{C=C}$ 1600 1610 cm^{-1}

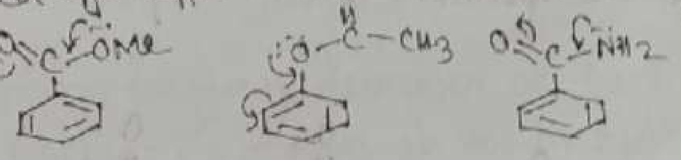
delocalisation of π electron between C=O and the ring increases the double bond character of the bond joining the -CO to the ring. This leads to lower bond order in the C=O bond which is consequently weaken. Also any substituent that enchances the mesomeric shift will decreases the bond order of the C=O bond and lead to lower C=O stretching frequency.

eg. 

$\bar{\nu}_{CO}$ ≈ 1700 1684 cm^{-1}

$\bar{\nu}_{CO}$ ≈ 1700cm^{-1} 1677cm^{-1}

In amide +M effect produces a lengthening of CO bond leading to lower frequency than in the corresponding ketone. -I effect of N is here dominated by +M effect. In acid chloride -I effect of chlorine is more influential than +M effect and higher vibrational frequency occurs.



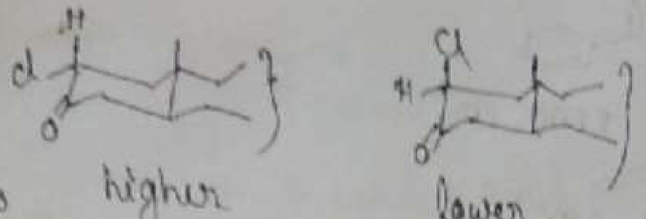
$\bar{\nu}_{C=O}$ ~1730cm^{-1} 1770cm^{-1} 1693cm^{-1}

In ester also, their is a confliction between I and M effect. In alkyl ester, the nonbonding electron on oxygen increase the +M conjugation tending to lower CO frequency. Here -I effect of oxygen is being dominated by +M effect. In phenyl ester, the non bonding electrons are partly drawn into the ring and their conjugation with CO is consequently diminished and then -I effect of oxygen become dominant and CO moves to higher frequency.

Field effect :⇒

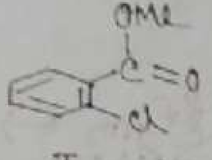
Two groups of an influence each others vibrational frequency by a through space interaction which may be electrostatic or steric in nature.

eg. In α-chloro ketone derivative of steroids C=O stretching frequency is higher when -Cl is equatorial then when it is axial.

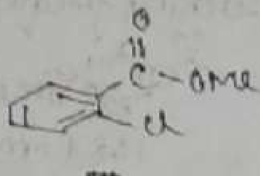


$\bar{\nu}_{C=O}$ higher lower

Non bonding electron of oxygen and chlorine undergo repulsion when they are closed together in the molecule. This result in change in hybridisation state of oxygen and shift the C=O stretching frequency.



I



II

In ortho chloro benzoic acid esters this field effect shift the C=O frequency in the rotational isomer I and not in II. Both isomer are normally present. so that, two C=O stretching absorptions are ~~abs~~ observed in the spectrum of this compound.

24 Bond angle :⇒

$\bar{\nu}_{C=O}$ = 1815 1780 1745 1715 cm⁻¹ 1705 cm⁻¹

(Normal value)

$>C=C=O$ ← sp hybridized

$\bar{\nu}_{C=O}$ ⇒ 2140 cm⁻¹

6 membered rings with carbonyl groups are unstrained and absorbed at about the values same as acyclic molecule. Decreasing the ring size increases frequency of C=O absorption. Smaller rings required the use of more p character to make C–C bonds to form the requisite small angle ($sp = 180°$, $sp^2 = 120°$, $sp^3 - 109°28'$, $sp^{>3} \leq 109°28'$). This removes p character from the σ bond of the double bond with oxygen and gives it more s character. Thus strenthening the double ~~do~~ bond. The force constant K is then increased and the absorption frequency increases.

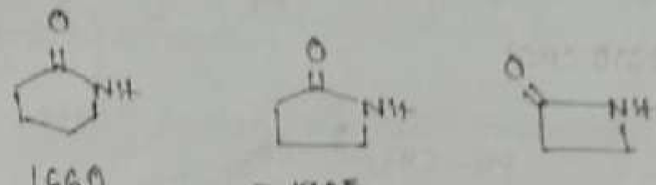
$\bar{\nu}_{C=C}$ 1780 1778 1657 1651 cm^{-1}

Normal value ⇒ 1655 cm^{-1}

sp hybridised

$CH_2=C=CH_2$

$\bar{\nu}_{C=C}$ ⇒ 1940 cm^{-1}



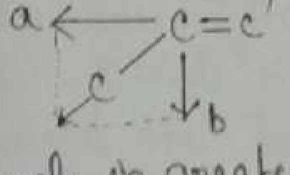
(Lactum)

$\bar{\nu}_{CO}$ 1660 ~1705 1745 cm^{-1}

☐ Ring size effect with internal double bond :⇒

$\bar{\nu}_{C=C}$ 1650 1646 1611 1566 1656 cm^{-1}

Absorption frequency decreases as the internal angle decreases untill it reaches a minimum at 90° in cyclobutene. The frequency increases again in cyclopropene when angle drops to 60°. It is because C=C vibration in cyclopropene is strongly coupled to the attached C–C vibration. When the attached C–C bonds are perpendicu to the C=C axis as in cyclobutane their vibrational modes is orthogonal to that of C=C bond and does not couple.



When the angle is greater than 90°, C–C single bond stretching vibration can be resolved into two components. One of which is coincident with the direction of the C=C stretch. Since the component a is in line with the C=C stretching vector the C–C and C=C bond are coupled leading to a higher frequency of absorption. A similar pattern exist for cyclopropene which has bond angle less than 90°.

NMR Spectroscopy

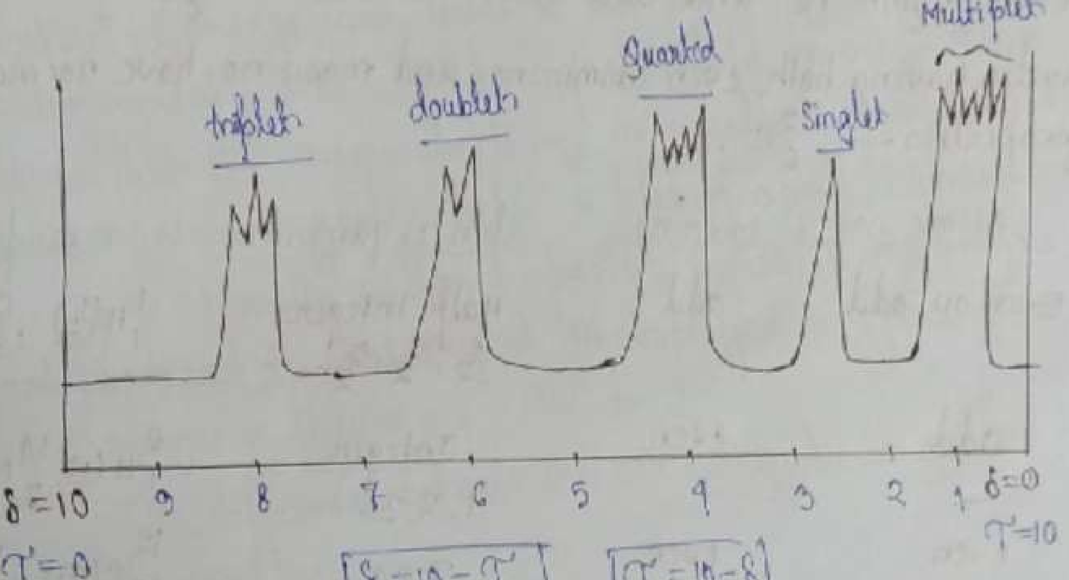
Nuclear Magnetic Resonance Spectroscopy
(NMR)

Discovered by Felix Bloch and M. Purcell

Under appropriate condition in a magnetic field a sample can absorbed electromagnetic radiation in the radiofrequency region, at frequency governed by the characteristic of the sample. Absorption is a function of certain atomic nuclei in the molecule. A plot of the frequency of the absorption peak versus peak intensity constitute a NMR spectrum.

PMR : Proton Magnetic resonance (^1H-NMR)

CMR ⇒ ^{13}C - NMR



$\boxed{\delta = 10 - \tau,}$ $\boxed{\tau = 10 - \delta}$

These signals are produced by protons present in the molecule. The position of the signal depends upon the natures of the proton, nature means their chemical environment. The position of a signal in δ scale is termed as chemical shift position of the signal. chemical shift position is a relative with respect to a standard signal.

NMR - signal :⇒

1. <u>No. of signal</u> ⇒ How many different types of protons are there.
2. <u>Positions of the signal</u> ⇒ Electronic environment of each type of proton.
3. <u>Intensity of signal</u> ⇒ How many protons of each kind are present in the molecule

4. Splitting of signal : Environment of proton of each with respect to other nearby protons.

NMR is a branch of spectroscopy in which radio frequency waves are used to induce transition between magnetic energy levels of atomic nuclei of a molecule. This magnetic energy levels are created by keeping the nuclei in a magnetic field.

Atomic nuclei are composed of protons and neutrons. Magnetic properties occurs with those nuclei which has —

I. Odd atomic no. and odd mass number — $^{1}_{1}H$, $^{19}_{9}F$

II. odd atomic no. and even mass number — $^{2}_{1}H$, $^{14}_{7}N$

III. even atomic no. and odd mass number — $^{13}_{6}C$

Nuclei having both even atomic no. and mass no. have no magnetic properties — $^{12}_{6}C$.

	Atomic no.	Mass no	Spin (I) quantum no.	Example
(i)	Even or odd	odd	Half integer $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ . . .	$^{1}_{1}H(\frac{1}{2})$, $^{17}_{8}O(\frac{5}{2})$
(ii)	odd	even	Integer 1, 2, 3 . . .	$^{2}_{1}H(1)$, $^{14}_{7}N(1)$
(iii)	even	even	zero	$^{12}_{6}C(0)$, $^{16}_{8}O(0)$

Thus, nucleus of ^{1}H has $I = \frac{1}{2}$ whereas ^{12}C and ^{16}O have $I = 0$ and are therefore non-magnetic. Atomic nuclei having magnetic spin which have values $\frac{1}{2}$, 1, $\frac{3}{2}$, 2 will therefore behave as spining magnets and will tend to orient themselves in an applied magnetic field. The no. possible orientation i.e energy level with respect to the applied field is given by the expression $2I+1$.

The simplest of a spinning nucleus is that of proton with $I = \frac{1}{2}$, only two orientations are possible. ^{2}H and ^{14}N have $I = 1$ and so can take up three orientations.

Thus, under the influence of an external magnetic field, the spining nucleus of proton can take up only two orientation — lined up with or against the direction of the applied field (aligned orientation and oppose orientation). Since work must be done to turn a magnet against a magnetic field, each orientation corresponds to a definite energy state of the nucleus. These levels are quantised and therefore it should be possible to find out electromagnetic radiation of a definite frequency which will be absorbed, thereby changing the orientation of the proton from the aligned orientation to oppose orientation and change its from lower to higher energy level. The energy, electromagnetic radiation is supplied by an oscillator and since the position of the absorption peak i.e where resonance occurs depends on the frequency of the oscillator or strength of the applied field, it is possible to change from lower to higher energy by using a beam of radiofrequency with a fixed magnetic field or vice-versa. The result is that the NMR-spectrum is usually a graph of signal intensity against magnetic field. A plot of signal intensity versus frequency is normally called a spectra in which the unique signal produced by each signal is displayed as a peak at a specific resonance frequency. ~~The di~~

The difference between the two energy levels ΔE is given by the equation —

$$\Delta E = \frac{h\gamma H}{2\pi}$$

where H = strength of applied magnetic field experienced by the proton.

γ = Gyromagnetic ratio (const) for a proton.

h = Planck constant.

Again, $\Delta E = h\nu$

$$\therefore h\nu = \frac{h\gamma H}{2\pi}$$

$$\Rightarrow \nu = \frac{\gamma H}{2\pi}$$

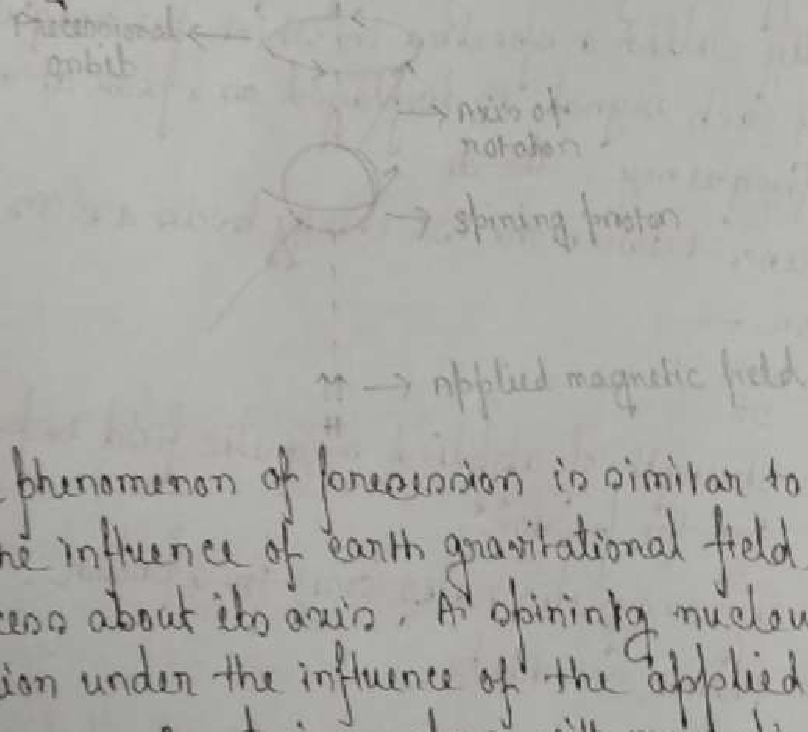
$$\boxed{\nu \propto H}$$

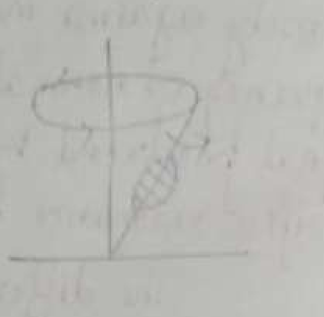
ν = frequency of the oscillator expressed in Hz or cycles/sec and called precessional frequency.

The precessional frequency is directly proportional to the strength of the applied magnetic field experiented by the proton. For example following precessional energy in MHz as a function of increasing field strength are observed.

H / Tesla	→	1.4	2.3	14.1	
$^{1}_{1}H$	→	60	100	600	MHz
$^{2}_{1}H$	→	9.2	153	92	MHz

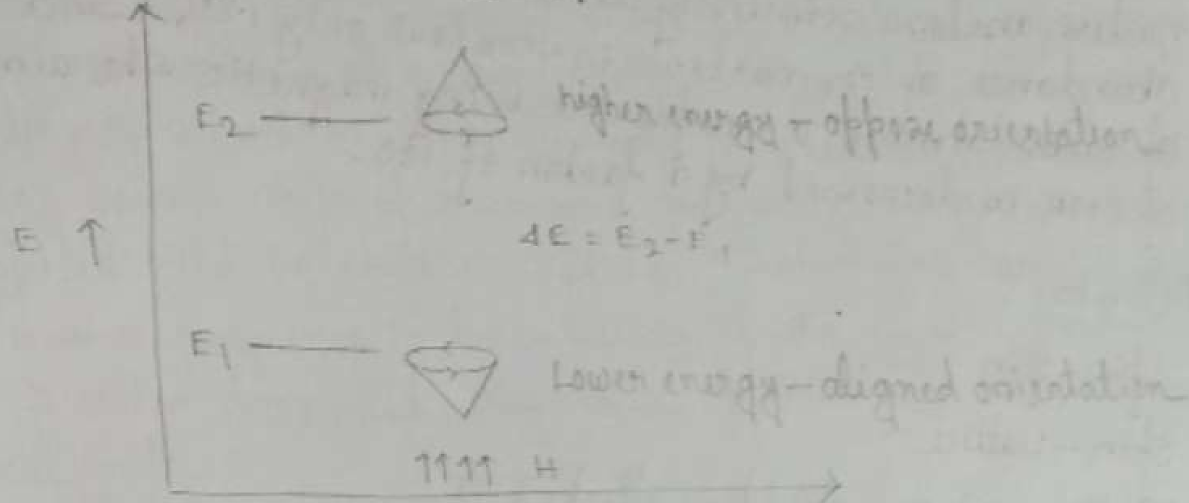
The precessional frequency is defined as equal to the frequency of electromagnetic radiation necessary to induce a transition of a spining atomic nucleus from one spin state to another. It is normally expressed as MHz or M-cycles/sec. Proton absorb energy because they begin to precess in an applied magnetic field.
~~Owing to the influence of the earth gravitational field~~





The phenomenon of precession is similar to a spining top. Owing to the influence of earth gravitational field, the top begins to precess about its axis. A spining nucleus behaves in a similar fashion under the influence of the applied magnetic field.

An atomic nucleus with magnetic properties perform slower waltz-like motion (rapid circular movements), in which the spining axis of the top moves slowly around the vertical. This is precessional motion and the top is said to be precessing around the vertical axis of the earth gravitational field. The precession arises from interaction of spin with earth gravity acting vertically downwards, it is called gyroscopic motion. Since the nucleus has a charge, the precession generates an oscillating electric field of the same frequency. If the radiofrequency waves of this frequency are supplied to the precessing, the energy can be absorbed and energy can be transferred from incoming radiation to the nucleus. Thus causing a spin change from lower energy aligned orientation to higher energy oppose orientation.



From the higher energy-oppose orientation, it comes back to the lower energy aligned orientation by losing energy. The transition from one energy state to other is called flipping of the proton. The energy required to bring about this transition ($E = h\nu$) or to flip the proton depends upon the external magnetic field. It has been calculated that in a magnetic field of 14092 gauss or 1.41 Tesla the energy required to cause flipping of a bare proton correspond to electromagnetic radiation of frequency 60 million cycles/sec or 60MHz. Stronger the applied field, greater will be the tendency to remain lined up with it and higher will be the frequency of radiation needed to flip the proton from lower to higher energy state. When precessing nucleus is irridiate with an electromagnetic radiation of suitable energy, then low energy nuclei will absorb this energy and moved to higher energy state. The precessing proton will only absorb that frequency which is identical with its precessional frequency under the given applied magnetic field. When this occurs, the nucleus and the radiofrequency beam are said to be in resonance, hence the term Nuclear Magnetic Resonance is used.

The strength of signal and hence the sensitivity of the NMR experiment for a particular nucleus are related to the magnitude of the particular magnetic moment (μ). The magnetic moment of ^1H and ^{19}F are relatively high and detection of NMR with these nuclei is fairly sensitive. The magnetic moment of ^{13}C is one forth of ^1H. This nucleus are less sensitively detected in NMR. Further natural abundance of ^{13}C nucleus is very low only 1.1%. Since only 1.1% of carbon atom in a sample are being magnetic the sensitivity of CMR is decreased by a factor of 100.

Relaxation :

1. Spin - spin
2. Spin - Lattice

Shielding and De-shielding effect :⇒

It might be expected that the resonance frequency for a given field depend only on the nature of the atomic nucleus concerned and hence all proton in a compound will absorb at the same energy for flipping and a single absorption spectrum is observed in the NMR spectrum but this is not the case. Hydrogen or any nuclei in a molecule are surrounded by an electronic charge and this shields the nucleus slightly from the influence of the ~~electric~~ applied field. The applied field causes electrons round the nucleus to circulate and this circulation produces a small secondary magnetic field which opposes the applied magnetic field. Hence, the effective magnetic field (H) experienced by a nucleus is less than the applied magnetic field (H_0) and the relationship between them is given by –

$$H = H_0(1-\sigma)$$

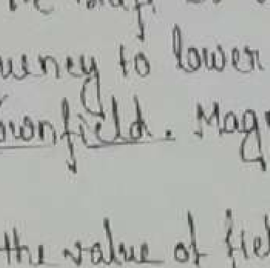
σ ⇒ shielding or spining const and has a positive value.

Hence to bring a proton to resonance, the applying field must be increased to overcome the shielding effect. clearly, greater the electron density around the proton, greater will be induced secondary magnetic field which will oppose the applied magnetic field. This effect is called local diamagnetic effect. Hence, greater external field will be necessary to cause proton resonance. In certain circumstances, σ becomes negative i.e effective becomes larger than applied field. Presence of electron attracting or withdrawing atom or group cause reduction in electron density around the nucleus. In this case proton is said to be deshielding. The numerical value of σ depends upon the chemical environment of a given nucleus. Hence, shielding and deshielding of a nucleus depends upon its chemical environment. Shielding causes shift of resonance frequency to higher value of the applied field i.e shift is upfield. Deshielding causes a shift of resonance frequency to lower values of the applied field. The shift is called downfield. Magnitude of this shift is known as chemical shift.

Since the value of field experienced by the sample cannot be determined accurately, chemical shift are measured relative to some standard which contains the nucleus under consideration.

Measurement of chemical shift- Internal standard :→

Various reference compounds are used in NMR technique but for PMR and ^{13}C NMR, the universally accepted reference is Tetra methyl silane (TMS).



$$\mathrm{Me{-}\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{Si}}{-}Me}$$

TMS is choosen in PMR because —

1. It contains twelve equivalent proton. The PMR spectrum of this compound shows a single sharp line.
2. 12 protons in TMS are shielded than the protons in the most available organic compounds due to low electronegativity of Si. As a result of which PMR spectrum of TMS occurs at higher field than any proton in almost all of the organic compounds i.e most PMR signal of organic compounds occurs downfield with respect to TMS.
3. TMS is chemically inert.

4. TMS is high volatile., low boiling point (b.p 27°c). So that it is easily removed from a recoverable sample of a valuable organic compound.

5. It is soluble in most organic solvent.

The chemical shift may be reported in various way since the resonance frequency is dependent on the strength of the applied field, the shift may be reported in field unit. Again, the field can also be expressed in term of frequency ($\nu = \frac{\gamma H}{2\pi}$). Hence, shift may be expressed in terms of Hz or cycles/sec. The separation in Hz is also proportional to the frequency of the oscillator. If the separation between a proton signal and TMS is 60 Hz at 40 MHz oscillator frequency, the separation at 60 MHz will become 90 Hz. Hence, it is desirable to report chemical shift which are independent of operating frequency or oscillator frequency of the instrument. This has been done by defining chemical shift δ by the expression —

$$\delta = \frac{\nu_{sample} - \nu_{reference}}{\text{Oscillator frequency}} \times 10^6$$

$$= \frac{\text{Separation between signal in Hz}}{\text{Oscillator frequency in MHz}} \times 10^6$$

The factor 10^6 is introduced to record chemical shift in a convenient value. This is usually in the range 1–10 ~~quoted~~ coated in parts per million (ppm). The value of δ remain unchanged can be visualised as follows —

At an oscillator frequency of 40 MHz, let us consider the separation between two signal is 60 Hz,

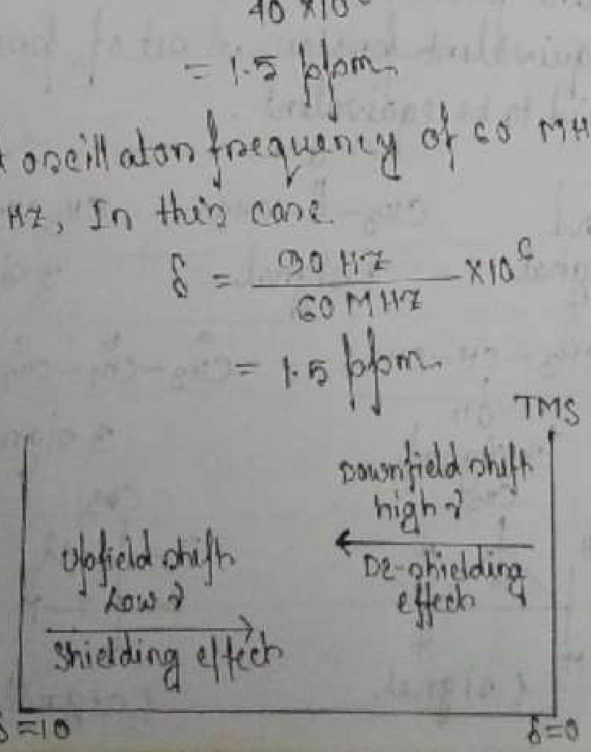
$$\delta = \frac{60}{40 \times 10^6} \times 10^6$$

$$= 1.5 \text{ ppm}$$

Now at oscillator frequency of 60 MHz, the separation will become 90 Hz, In this case

$$\delta = \frac{90 \text{ Hz}}{60 \text{ MHz}} \times 10^6$$

$$= 1.5 \text{ ppm}$$



$\delta_H \Rightarrow CH_3I$ – 2.17 ppm,
CH_3Br – 2.65 ppm, CH_3F – 430 ppm

	$C-CH_3$	$N-CH_3$	$O-CH_3$
$\delta_H \Rightarrow$	0.88 ppm	2.15 ppm	3.30 ppm

☒ Chemical shift :

In NMR spectroscopy the position of various signal are defined as chemical shift. Such position are always with reference to a standard signal. The difference in position of two sharp single peak is called the difference in chemical shift. Since, all signal position are relative, the position of a signal with respect to a standard is often called a chemical shift.

☒ Solvent used in NMR :

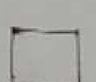
A substance free from proton should be suitable for its used as a solvent in NMR. This means that would not give a signal of its own. Moreover, solvent must be capable to dissolve the sample. The most frequently used organic solvent are $CDCl_3$ (deuterio chloroform), CCl_4, CS_2, $F_3C-\overset{O}{\overset{\|}{C}}-CF_3$ (Hexafluoro acetone), C_6D_6 (Hexadeuterio benzene), $D_3C-\overset{O}{\overset{\|}{S}}-CD_3$ (Hexadeuterio dimethyl sulfoxide).

No. of signal : Equivalent and non-equivalent proton :⇒

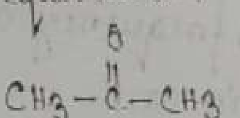
The no. of signal in the PMR spectra describes the the no. of different sets of equivalent proton in a molecule. Each signal corresponds to a set of equivalent proton. A set of proton with same environment are said to be equivalent.

$CH_3-CH_2-CH_2-Cl$

3 signal



1 signal

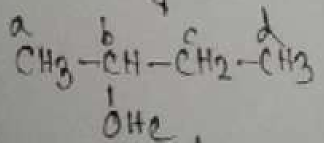


$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

1 signal

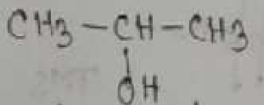
CH_3CH_2OH

3 signal



$\overset{a}{CH_3}-\overset{b}{\underset{\underset{OH_e}{|}}{CH}}-\overset{c}{CH_2}-\overset{d}{CH_3}$

5 signal

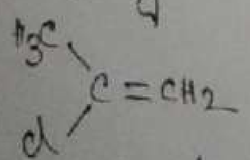


$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

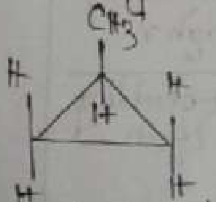
3 signal

$\overset{a}{CH_3}-\overset{b}{CH_2}-\overset{c}{CH_2}-\overset{b}{CH_2}-\overset{a}{CH_3}$

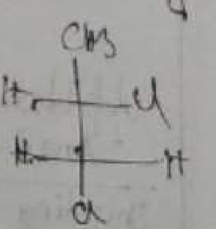
3 signal



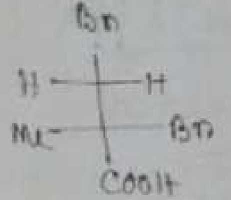
3 signal



1 signal



4 signal



(4 signal)

(2 signal)

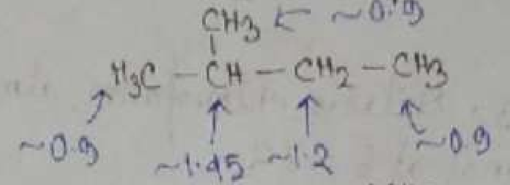
Due to impurity of hydrogen in $CDCl_3$, deuterio chloroform, almost invariably exhibit a small PMR signal at $\delta = 7.2$

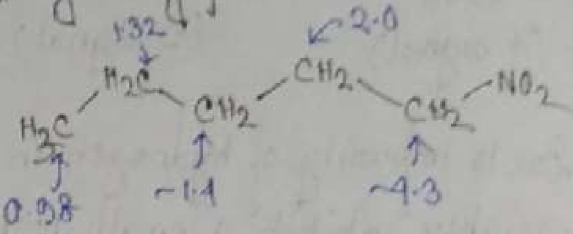
Types of proton	Approximate chemical shift value
$-CH_3$	0.7-1.3
$-CH_2-$	1.2-1.4
$-\underset{\vert}{CH}-$	1.4-1.7
$>C=C<_{CH_3}$	1.3-2.5
$>\overset{O}{\overset{\Vert}{C}}-CH_3$	2.1-2.6
$Ar-CH_3$	2.2-2.7
$>C=C<_{H}$	4.5-6.5
$Ar-H$	6-9
$-C\equiv C-H$	2.5-3.5
$-\overset{O}{\overset{\Vert}{C}}-H$	9.5-10.5
$>\overset{O}{\overset{\Vert}{C}}-O-H$	10-12
$-\underset{\vert}{\overset{\vert}{C}}-O-H$	1-6 (change with solvent polarity)
$-O-CH_3$	3.3-4.0
$-N-CH_3$	2-3
$Cl-\underset{\vert}{\overset{\vert}{C}}-H$	3-4
$Br-\underset{\vert}{\overset{\vert}{C}}-H$	2.5-4
? $I-\underset{\vert}{\overset{\vert}{C}}-H$	2-4
$>C=C<_{O-H}$	13-17

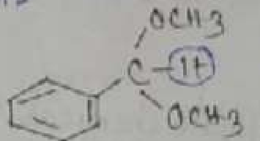
Type of proton ——— Approximate chemical shift value (δ ppm)

Ar—O—H ————→ 11–14

Basic resonance frequency are modified by many factors —







δ = 5.3 ppm.

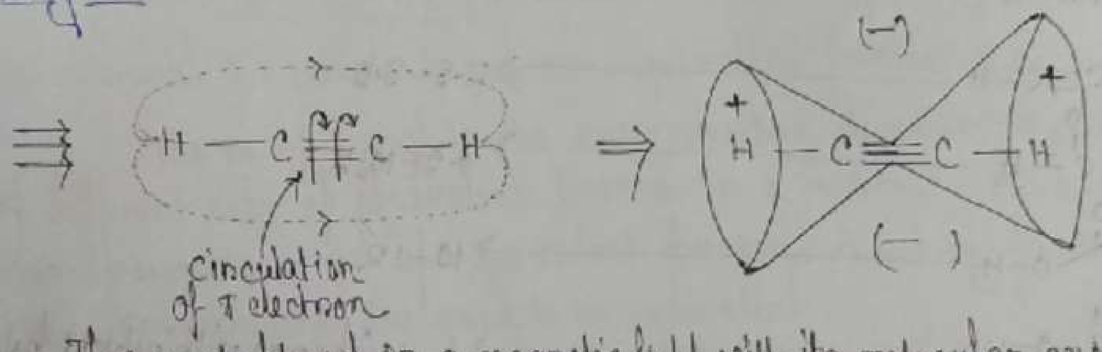
Effect on molecules containing π electron system :⇒

$H-C\equiv C-H$ > $H_2C=CH_2$ > CH_3-CH_3

δ = ~2.5 ppm ~5 ppm ~0.9 ppm

In molecules containing π electron system, it has been found that the absorption position depends upon the manner in which the π electrons circulate under the influence of the applied magnetic field. Such circulation of π electrons under the influence of the applied magnetic field causes additional shielding or deshielding to the neighbouring protons.

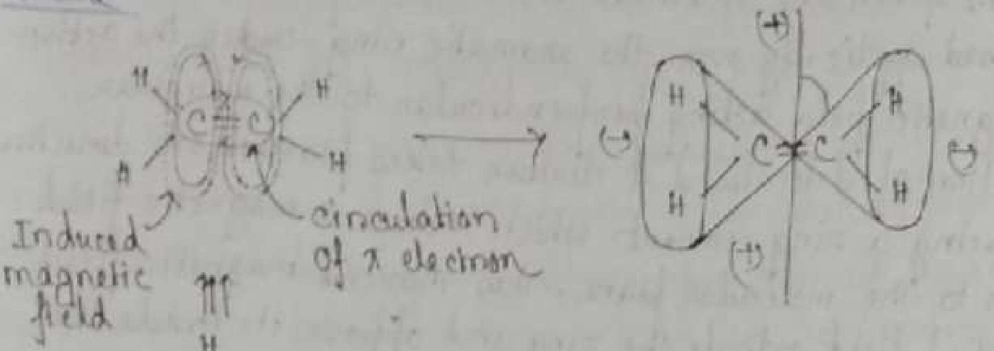
Alkyne



If C_2H_2 is placed in a magnetic field with its molecular axis parallel to the field the π electron of the triple bond can circulate at right angles to the applied field. Thus, producing an induced magnetic field which oppose the applied magnetic field. Since the proton lies along the molecular axis, the magnetic lines of force induced by the circulating electrons act to shield the protons. Thus, the protons in lying with the triple bond is shielded resulting in a decreased chemical shift (low δ value). The protons which lie above and below the bonding line, however, are deshielded. The result is that there are formation of zone within which shielding is experienced indicated by + sign) and outside the zone deshielding is experienced (indicated by – sign) by the protons.

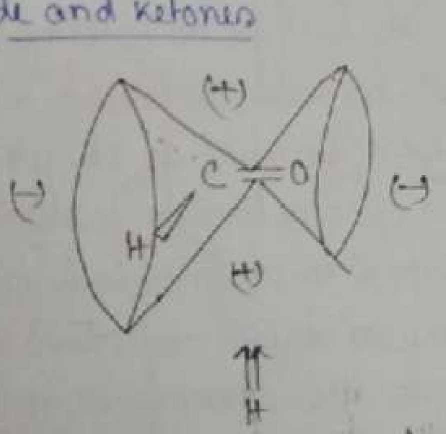
If the molecular axis of C_2H_2 is perpendicular to the direction of applied no extra π electron circulation occurs and hence there is no additional shielding or deshielding effect. The effect of π electron circulation averaged out over all possible orientations with respect to the applied field, obviously produces some shielding effect in the line of the acetylenic bond resulting in a relatively low δ value of proton (acetylenic).

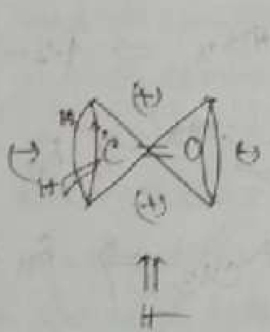
Alkene



A double bond is also associated with shielding and deshielding effects like triple bond. In this case the induced current is produced only when the molecular axis lies perpendicular to the applied field. The ethelenic proton lies deshielding zone of the cone and their absorption is downfield. The shielding and deshielding is however weaker for a double bond than for a triple bond.

Aldehyde and ketones

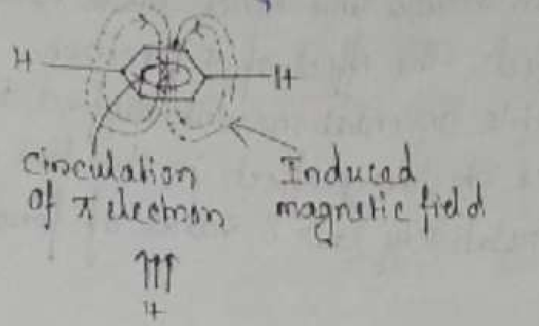


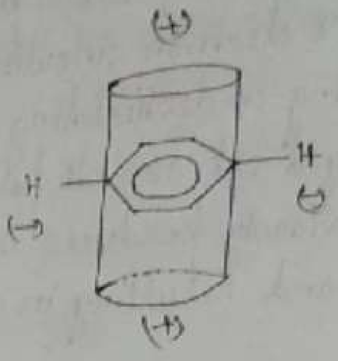


In aldehyde, the aldehydic protons lie in the deshielding zone showing absorption around 9.5 - 10.5 ppm. The deshielding effect obviously is greater than those of olefining protons arising due to both π electron circulation of C=O bond and also –I effect of the carbonyl group.

In ketones the protons attached to the alkyl group lie outside the negative zone and deshielding occurs due to inducting effect.

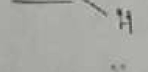
The aromatic ring



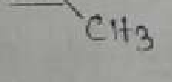


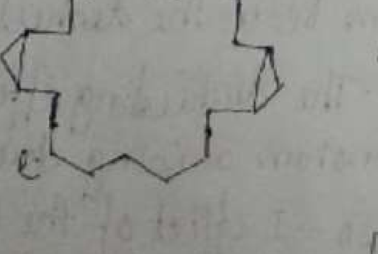
In the molecules of benzene and other aromatic compounds, π electrons are ~~ey~~ delocalised cyclically over the aromatic ring. Under the action of applied magnetic field acting perpendicular to the molecular plane, circulation of delocalised π electron takes place in one direction. Thereby, producing a ring current which induce a magnetic field perpendicular to the molecular plane. This induced magnetic field assist the applied field outside the ring and oppose it inside the ring also above and below the ring. Hence there are volumes in which deshielding ~~sh~~ and shielding occurs. Since, Hydrogen atom of benzene lie in the plane of the ring, they become deshielded and their chemical shift occurs at much lower field. Thus in aromatic compounds the induced field is diamagnetic in the centre and above and below the ring and is paramagnetic outside the ring.

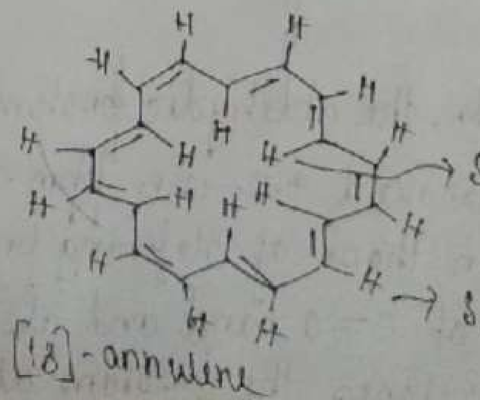

⇒ 6-9 ppm


⇒ 4.5 – 6.5 ppm


⇒ $\delta_H \sim 2.3$ ppm


⇒ $\delta_H \sim 1.95$ ppm

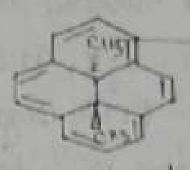

$18\pi / (4n+2)\pi\ e^-$
$n=4$



→ $\delta_H = -1.8$ ppm

→ $\delta_H = 8.9$ ppm

[18]-annulene



$\rightarrow \delta_H = -4.2$ ppm

$\frac{14\pi, e}{(4n+2)\pi}$, n=3

Di-hydro dimethyl pyrene.

[18]- annulene has 18 electrons delocalised inside the aromatic ring. According to Huckel's rule it is aromatic (n= 4). Here, 6 protons lie inside the ring which are shielded and remaining 12 proton lie outside the ring which are deshielded. The PMR spectrum of 18 annulene shows two sharp signals at δ_H - 8.9 ppm and -1.8 ppm with intensity ratio 2:1 accountable for 12 and 6 protons respectively.

The induced magnetic field formed by the circulation of π electron under the influence of the magnetic field, when opposes the field, the effect is called diamagnetic effect. When induced magnetic field reinforces the applied magnetic field, i.e, act in direction of the field, proton feel more magnetic field and become deshielded and the effect is called paramagnetic effect.

In C_2H_2 : the proton experience a diamagnetic shielding effect. In C_2H_4. the olifinic proton experience paramagnetic effect. Hence, we see compounds containing multiple bond when placed in a magnetic field, the π electron circulate under the influence of the field. The effect of such circulation is quite complex and can lead to downfield (paramagnetic) or upfield (diamagnetic) shift. The effects are paramagnetic in certain direction around the π cloud and diamagnetic in other. The magnitude of induced magnetic field in such compounds depends on the angle of molecular axis with respect to the applied field. The effects are described as anisotropic effect ~~[illegible]~~ opposite to the term isotropic which means operation equally to the space. Due to this reason, compounds with multiple bonds are said to be magnetically anisotropic.

Relaxation : (Saturation of signal)

1. spin-spin relaxation (Time - t_2)
2. spin-lattice relaxation (Time - t_1)

If t_1 and t_2 are small then the life of excited nucleus are short and give rise to broad spectra line in NMR spectra. If t_1 and t_2 are large sharp spectra line are arises. In order that PMR signal be observed, the proton must be in the excited state for 10^{-2} to 10^{-1} sec. The spectra line width is inversely proportional to the time that the proton spend in the higher energy state. Hence larger the time spend in this state, the sharper the line and conversely shorter the time spend, the broader the line. The relationship between relaxation time and peak broadening can be qualitatively understand from the Uncertainty principle. According to principle —

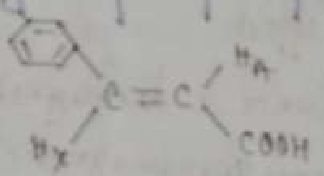
$$\Delta E . \Delta t \simeq \frac{h}{2\pi} \quad , \quad \Delta t = t_1 + t_2$$

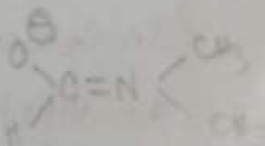
$$\Rightarrow h\Delta\nu \, (t_1 + t_2) \simeq \frac{h}{2\pi}$$

$$\Rightarrow \Delta\nu \, (t_1 + t_2) \simeq \frac{1}{2\pi}$$

$$\boxed{\Delta\nu \, \Delta t \simeq \frac{1}{2\pi} = \text{constant}}$$

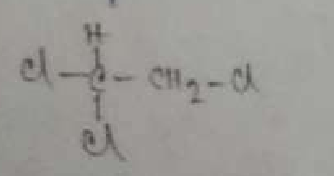
Ex Spin-spin coupling or spin-spin splitting :⇒





Aromatic proton 5 in numbers appears as multiplet around $\delta_H = 7.1$ The carboxyl proton is off scale at $\delta_H = 13$, the proton H_A appears as two lines (doublet) at $\delta_H = 6.5$ and proton H_x also appears at two lines at around $\delta_H = 7.8$.

PMR spectrum of 1,1,2-trichloro ethane :⇒



$$Cl-\overset{H}{\underset{Cl}{C}}-CH_2-Cl$$

In the above spectrum, the signal for $-CH$ proton appears as a triplet while signal for $-CH_2$ proton appears as a doublet.

Thus, we see that no of lines (multiplicity) observed-in the PMR signal for a group of proton is not related to the number of proton in that group. The multiplicity depends on the no of proton in the neighbouring carbon..

(n+1) rule :

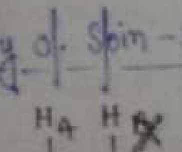
It states that the PMR signal of a group of equivalent proton will be splitted into (n+1) lines if the neighbouring carbon contains n number of equivalent proton.

Thus, in 1,2- dichloro ethane, the methelene proton have one neighbouring proton and is appeared as doublet and while $-CH$ has two neighbouring proton and is appeared as triplet.

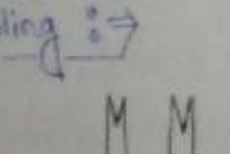
The splitting of PMR signal arises due to coupling interaction between neighbouring protons and is related to the no. of possible spin orientation that this neighbour can adopt. This phenomenon is called spin-spin coupling and spin-spin splitting.

The spacing between signal in a multiplet is called coupling constant. It is represented by J (expressed in Hz) and is actually a mag measure of effectiveness of spin-spin coupling.

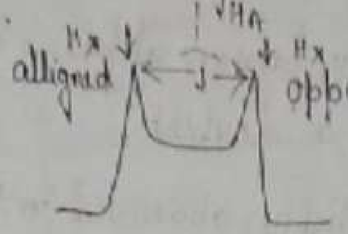
Theory of spin-spin coupling :→



$$-\overset{H_A}{\underset{|}{\overset{|}{C}}}-\overset{H_X}{\underset{|}{\overset{|}{C}}}-$$



A simple explanation of this is that the resonance position of H_A depends upon its total magnetic environment. Its nearby proton H_X is also magnetic and H_X can either have its nuclear magnet alligned with the magnetic field of H_A or oppose to H_A. Hence H_x can either increased the net magnetic field experienced by H_A or decrease it when H_x oppose. Infact, it does the both. The spin orientation of H_x create two different magnetic field around H_A. Therefore, A comes to resonate not once but twice and give rise to doublet. In a similar way magnetic behaviour of H_x is also effected by H_A and H_x also exhibit a doublet.



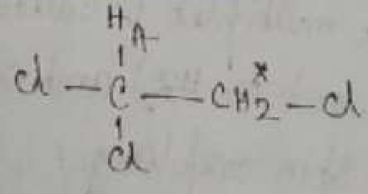
proton appear as a doublet.

The H_A and H_x proton of cinnamic acid gives rise to this characteristic doublet caused by two protons undergoing coupling and such a spectrum is called an AX spectrum.

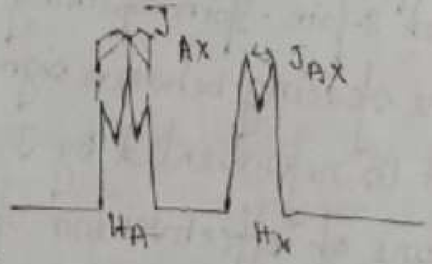
This mutual magnetic influence between H_x and H_A is not transmitted through space but via the electrons in the intervaining bond.

The nuclear spin of H_A couples with the electron spin of C–H_A bonding electron. This in turn couple with C–C bonding electron and then with the C–H_x bonding electron. This coupling is transmitted to the spin of H_x nucleus. This electron coupled spin interaction operates strongly through 1 or two bond and less strongly through three bond and very weakly through four or more bonds.

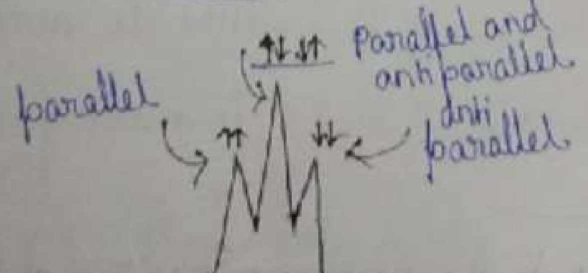
▨ 1,1,2- trichloro ethane



$Cl-\overset{H_A}{\underset{Cl}{C}}-\overset{x}{CH_2}-Cl$



Effect of H_2^x on H_A



H_A does not give a singlet but each signal is splitted into triplet with 1:2:1 intensity ratio.

Thus, the spectrum of 1,1,2- trichloro ethane consist of characteristic doublet and triplet of two protons coupling with one proton can be called AX_2 spectrum.

Spin-spin coupling is a reciprocal affairs and the effect of H_A proton on the H_X must be identical with effect of H_X proton on the H_A proton. In the above example the coupling constant J i.e seperation between lines of triplet is exactly the same as a seperation between lines in the doublet.

In a complicated spectrum contains many peak, the peak with identical seperation (equal J value) will tell us that this peak has been produced by protons attached to adjacent carbon atoms. Hence, peak intensity reflects the no. of absorbing proton and multiplicity reflects the no. of neighbouring protons.

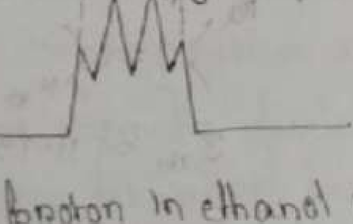
Ex PMR spectrum of ethanol :⇒

CH_3CH_2OH

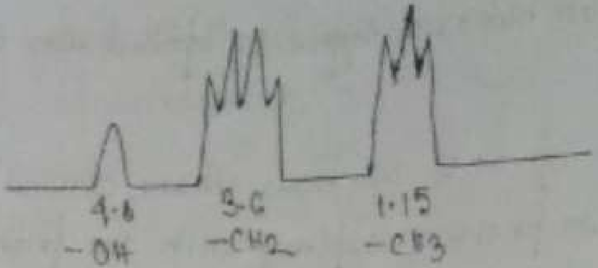
Effect of CH_3 proton on $-CH_2$:⇒

↑↑↑   ↑↓↓ ↓↓↑ ↑↓↑   ↑↑↓ ↑↓↑ ↓↑↑   ↓↓↓

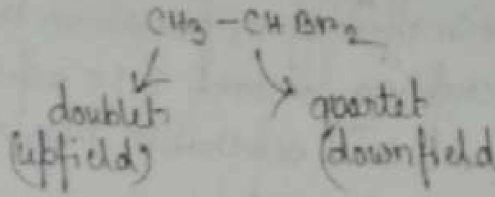
1:3:3:1



The signal of $-CH_2$ proton in ethanol will be splitted into quartet with 1:3:3:1 intensity ratio and appear at $\delta_H = 3.6$ ppm. Thus 3 equivalent on adjacent carbon can split a proton into quartet. The signal of $-CH_3$ proton splits into a triplet with 1:2:1 intensity ratio and appear at $\delta_H = 1.15$ ppm.

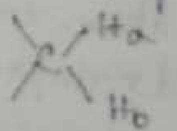


PMR spectrum of $CH_3-CH\cdot Br_2$:→



Types of coupling and coupling constant values :→

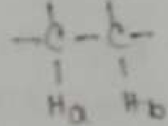
Geminal coupling



: $J_{ab} \approx 10-18$ Hz

It involves protons separated by only two bonds. Here the coupling effect is strong and it is observed only when these geminal protons have different chemical shift position.

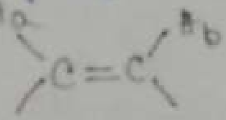
Viscinal coupling



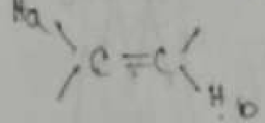
$$\underset{H_a}{-\overset{|}{C}}-\underset{H_b}{\overset{|}{C}}-$$

$J_{ab} \simeq 8$ Hz.

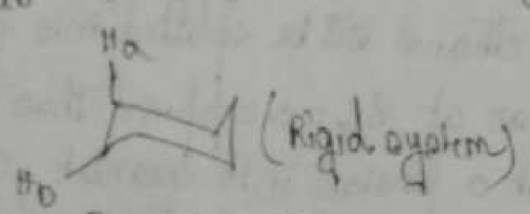
Trans coupling in alkene is stronger than cis coupling



$J_{ab} \simeq 5-14$ Hz

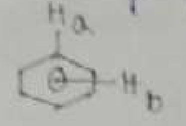


$J_{ab} \simeq 11-19$Hz



$J_{ab} \simeq 0-12$Hz

Aromatic coupling

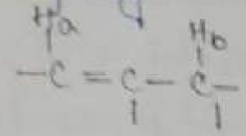


J_{ab} (ortho) ≃ 7–10 HZ

J_{ab} (meta) ≃ 2–3 HZ

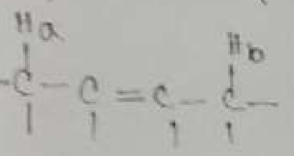
J_{ab} (para) ≃ 0–1 HZ

Allylic coupling



For both cis and trans orientation $J_{ab} \simeq 0-2$ HZ. In many cases it is characteristically 1.2 Hz. In allyl chloride such type of 4 bond coupling is observed. But the effect is very small.

$J_{ab} \simeq 10-13$ HZ



$J_{ab} \simeq 0-2$ HZ

Coupling and chemical shift of ~~double bond~~ aromatic protons :⇒

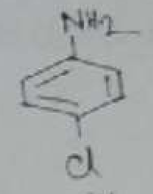
Due to magnetic anisotropy, the aromatic protons are always deshielded than simple proton and absorbed at higher δ values. PMR spectra in which the seperation between multiplates (i.e. the chemical shift difference between signals expressed in HZ is much larger than the coupling constant J, $\Delta\delta \gg J$; generally $\Delta\delta \gg 6J$), then unperturbed spectra will arise are called 1st order spectra. The majority of aromatic coupling system are non 1st order

Single line aromatic spectra are produced by several monosubstituted benzene derivatives provided that the substituent has no strong shielding or deshielding effect. As per example toluene. Compounds with identical para substituents whatever their electronegativity gives single line spectra because of molecular symmetry. All protons in the ring are magnetically equivalent

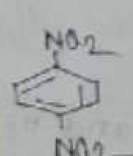
eg.

Unsymmetrical para substitution with the two substituent having different shielding influence gives rise to AB type spectra for aromatic proton.

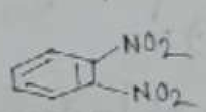
eg.



A single substituent i.e either strongly shielding or deshielding (eg $-COCH_3$ in acetophenone or $-CO_2H$ in benzoic acid) usually causes the ortho proton to move to lower or higher δ values with respect to meta or para proton. We usually observe a two proton complex multiplet separated from a three proton complex multiplet.



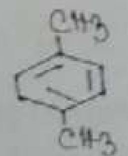
1-signal



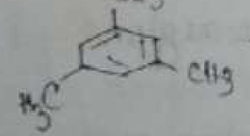
2 strong signal

→ singlet, $\delta_H = 7.37$ ppm.

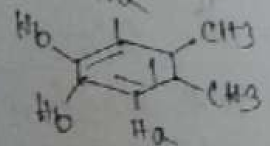
→ ~~doublet~~, $\delta_{CH_3} = 2.34$; 5 aromatic proton appears as singlet at $\delta_H = 7.17$ ppm.



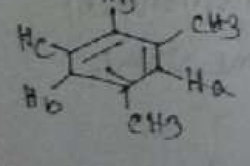
→ 2 signal, (δ_{CH_3} →) 2-CH_3 appears as singlet at $\delta_H = 2.3$ and 4 aromatic proton appears as singlet $\delta_H = 7.05$ ppm.



→ 2 signal, 3-CH_3 identical.
For 3-CH_3 $\delta_H = 2.3$, singlet
For 3-aromatic protons $\delta_H = 6.78$ ppm.

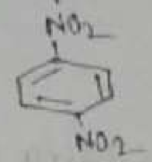


→ 3 signal. 2-CH_3 group are identical, give singlet at $\delta_H = 2.3$. Two types of aromatic protons give pair of doublet.

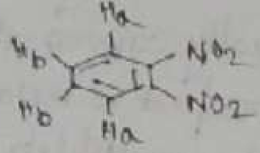


→ Two types of methyl groups are identical and a singlet will produce. Three types of aromatic protons. They will couple with each other. Hence, there will be a multiplet in the aromatic region.
(3 signals)

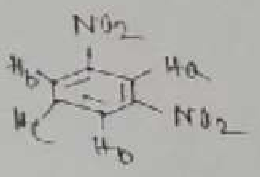
Hence, all three isomer could be distinguished from their respective NMR spectrum considering the signal for aromatic proton.



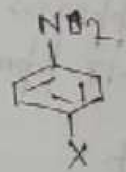
⇒ 1 signal



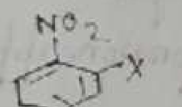
⇒ 2 signal. 2 types of protons Ha and Hb. Ha, ortho to nitro group, so highly deshielded than the other two Hb protons. Hence there will be a pair of doublet in the aromatic region. (AB types).



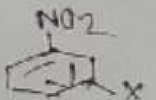
⇒ 3 types of protons Ha, Hb and Hc. Ha and Hb is ortho to nitro group and Hc is meta to nitro group. Ortho protons are more deshielded in comparison to meta proton. The net result will be a complex multiplet in the aromatic region.

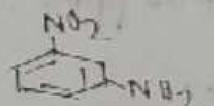


⇒ pair of doublet.



⇒ multiplet in aromatic region





⇒ complex multiplet in aromatic region

In all the three cases protons attached to nitrogen atom are exchangable and produce a broad singlet in the usual region 3-4.

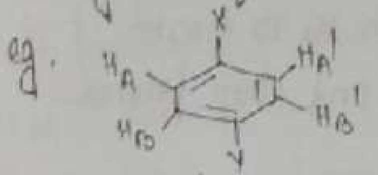
▨ chemical and Magnetic equivalence in NMR :→

Two protons are defined as chemically equivalent if by virtue of symmetry within the molecule, their electronic environment are indistinguishable and therefore they possesses same value of chemical shift.

Two protons are defined as magnetically equivalent if they couple equally to a third neighbouring proton. Otherwise they are magnetically non equivalent.

chemical equivalence means simply chemical shift equivalence and magnetic equivalence means coupling equivalence.

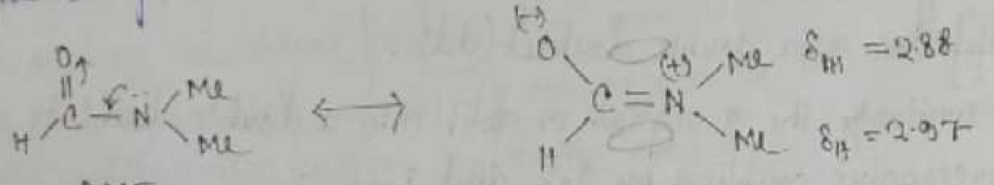
eg.



Because of symmetry H_A and H_A' will have the same chemical shift value. Also H_B and H_B' have the same chemical shift value. Now H_A will undergo spin-spin coupling to H_B but this will be different from the coupling of H_A' to H_B. Hence, H_A and H_A' are chemically equivalent but magnetically non equivalent.

Protons which cannot be distinguished by PMR spectroscopy are called isochronous.

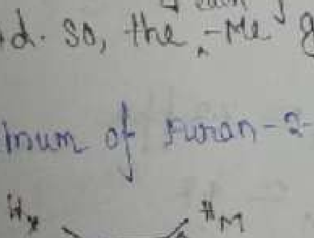
Influence of restricted rotation :⇒



DMF

The PMR spectrum of N, N-dimethylformamide recorded at room temperature show two signals for the -Me proton. It may be predicted that the two -Me group in DMF are magnetically equivalent but its PMR data opposes this prediction. DMF could be represented by two resonance form and due to resonance C-N bond acquires some double bond character, which is sufficient to restrict the C-N bond rotation and one methyl group is cis to oxygen and other becomes trans. When the spectra is recorded at high temperature (>120°C), the spectrum shows only one signal for -me groups which indicate that at high temperature rotation around C-N bond is very rapid. So, the each -Me group experiences same type of experience

NMR spectrum of Furan-2-aldehyde :⇒



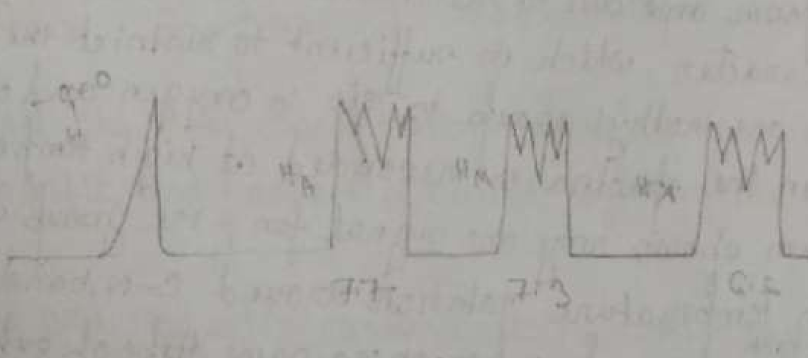
In the case of Furan-2-aldehyde, four signals are observed. Three for three aromatic protons (H_A, H_M and H_X) and one for aldehydic proton. Peak position for aldehydic proton is around 9.7, most deshielded. Among the three aromatic protons H_A is most deshielded and appears at around $\delta_{H_A} = 7.7$ and other proton $\delta_{H_M} = 7.3$ ppm and $\delta_{H_X} = 6.6$ ppm.

Proton H_A couple with H_X which split the A signal into doublet but A also couples with M, so that each line of A is further split into two giving four lines in all. The signal for proton A shows two splitting. So, two coupling constant value. J_{AX} and J_{AM} and is therefore a double doublet (dd).

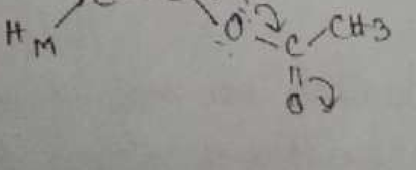
Similarly, the M signal is split into two by coupling with X and each line is further split into two by coupling with A. Two coupling constant value are again observed. J_{AM} and J_{MX} and M appears as a double doublet (dd).

Similarly, the X signal is split into a double doublet by two successive coupling by J_{AX} and J_{MX}

This type of NMR spectrum is called AMX system where the coupling pattern involves interaction between the protons separated by four bonds and all three J values have been identified.



Vinyl system



$\delta_{H_X} \simeq 7.2$ ppm

$\delta_{H_M} \simeq 4.8$

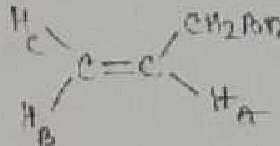
$\delta_{H_A} \simeq 4.5$

$\delta_{H\,CH_3} \simeq 2.1$

The vinyl system (substituent is an oxygen function) give rise to AMX coupling. Here, H_A and H_M are trans and cis respectively with respect to the substituent. So, they have different chemical shift position. All three protons H_A, H_M and H_X appears as dd with three J values (J_{AM}, J_{AX}, J_{MX}).

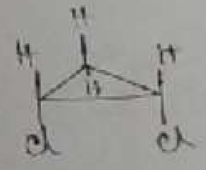
In absence of any strongly electronegative substituent, vinyl spectra will have ABC type spectra and only approximate chemical shift data should be extracted.

Allyl system

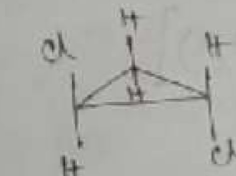


A very large 3 proton multiplet may extend from δ = 5.0 to δ = 6.1 generated by the alkene protons. The methelene protons appears at δ = 4.0 as a doublet because of coupling to H_A but the smalle allylic coupling two protons H_B as H_C may also be observed under closer examination.

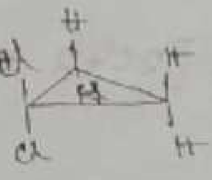
Q. Dichloro cyclopropane has three structural isomer. One isomer yield 1 signal, 2nd isomer give 2 signal and 3nd isomer give 3 signal. Identify them.



3 signal



2 signal



1 signal

2D-NMR

MALDI-MASS

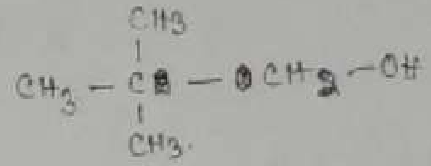
$C_5H_{12}O$ (i) δ = 0.93 (9H)

(ii) δ 7.19 = 1H (brs)

(iii) δ 3.3H (2H)

DBE = $\frac{1}{2}$(10+2−12)

= 0.



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-OH$

$C_{15}H_{24}O$ (i) δ = 1.47 (18H)

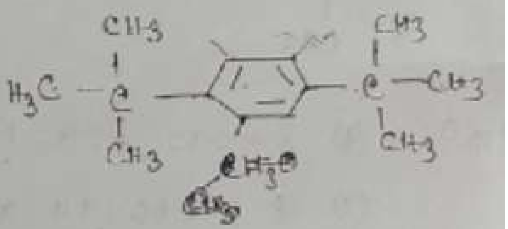
(ii) δ = 2.29 (3H)

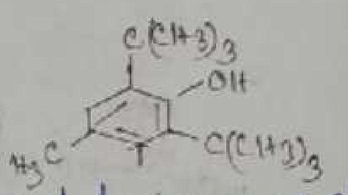
(iii) δ = 4.99 (1H, brs)

(iv) δ 7.0 (2H)

DBE = $\frac{1}{2}$(30+2−24)

= 4.





Summary chart of proton NMR shifts ⇒

Start with

CH	CH_2	CH_3
1.7	1.3	0.9

1. shift 1 ppm ←

alkene $-C=C$

alkyne $-C\equiv CR$

nitrile $-C\equiv N$

carbonyl $-C=O$

$-CHO$
$-COR$
$-CO_2H$
$-CO_2R$
$-CONH_2$

thiol $-SH$

sulfide $-SR$

2. shift 1.5 ppm ←

Aryl ring — Ar

Benzene hetero cycles

amine $-NH_2$

sulfoxide $-\underset{O}{S}-R$

3. shift 2 ppm ←

alcohol $-OH$

ether $-OR$

amide $-NHCOR$

halide — Hal

$-I$
$-Br$
$-Cl$

Sulfone — SO_2R

4. shift 2.5 ppm ←

aryl ether $-OAr$

5. Shift 3 ppm ←

Nitro — NO_2

ester → $-OCOR$

fluoro $-F$