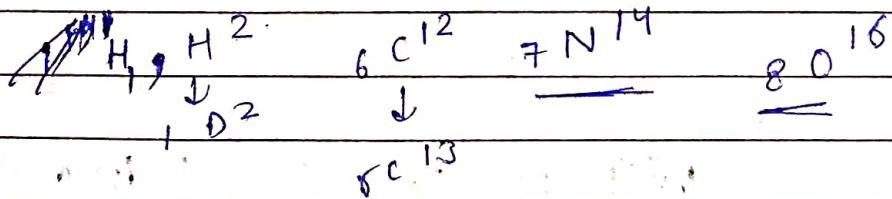


NMR spectroscopy

 {Nuclear Magnetic Resonance Spectroscopy}

- Spectroscopy is the study of interaction b/w the EMR with matter
- NMR spectroscopy is the study of molecules by recording the radiation interaction of EMR form radio wave region with the nuclei of molecules which are placed in strong MF.

Theory:-

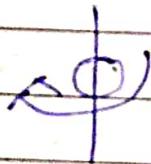
- The nuclei of some atoms have spinning property. These atoms have either odd atomic no. or odd atomic mass or both. For them Nuclear spin quantum no. $I > 0$. Such atom are NMR active.

Ex- ^1H , ^{13}C , ^{15}N , ^{19}F , etc.

- The nuclei of hydrogen atom is a proton. ^1H atoms are present in most organic compounds. Therefore ^1H NMR is a useful way to study their structure.
- The atomic nuclei are spinning charged particle, and they generate RF.
- Thus, they behave like tiny bar magnet & respond to MF.

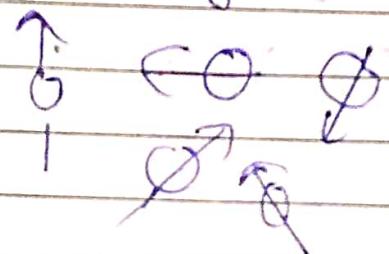
But when external MF is present, the nuclei align themselves either with or against the field of the external MF.

A spinning proton creates a MF



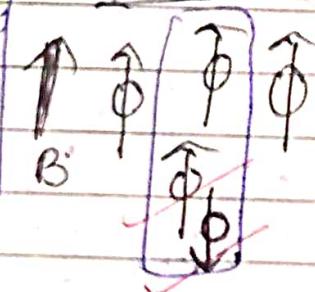
With no external MF

Nuclear magnets are randomly oriented



In a MF external

Nuclear magnets are oriented with or against B



In a MF, there are 2 energy states for a proton.

- ↳ A lower energy state with the nucleus aligned in the same direction as B_0 .
- ↳ A higher energy state in which the nucleus aligned against B_0 .

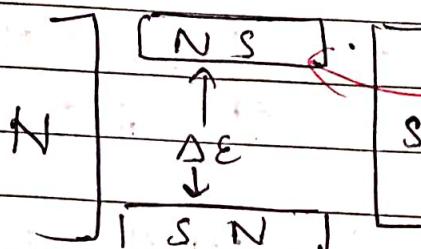
(No. of orientation of spin state = $2J+2$
(for $H = 1/2$)

Energy $\downarrow \downarrow \uparrow$ $I = -1/2$ (β spin state)
 B_0 $\epsilon = h\nu$ (High energy)

(field energy B_0) $\downarrow \downarrow \uparrow$ $I = 1/2$ (α spin state)
 $\epsilon_{\text{Evergreen}}$ (Low energy)

For proton $I = 1/2$

$$2I+1 = 2 \times 1 + 1 = 2 \quad \begin{matrix} \nearrow -1/2 \\ \text{ways} \\ \searrow +1/2 \end{matrix}$$



High energy state (B or $-1/2$)

ΔE = from radiowave region.

Lower energy state (α or $+1/2$)

Thus, there is two type of alignment of the Magnetic moment of proton in MF.

- When an external energy source ($h\nu$) that matches the energy difference (ΔE) b/w the two state is supplied, energy is absorbed, causing the nucleus to 'spin flip' from one orientation to another.
- This transition from one energy state to other → flipping of a nuclei (proton)
- This energy can be supplied by electromagnetic radiation (from radiowave region). → $h\nu$
- Frequency is Rept constant, MF is varied
- Wavelength of radiowave used are $0.3 \times 10^{-6} \text{ m}$
R frequency absorbed is $60 - 600 \text{ MHz}$.
- In NMR spectroscopy, the frequency is Rept constl and the magnitude of the applied MF is varied till the absorption of the radiation by proton (flipping of proton) occurs

Sr. No. _____

Date: _____

for resonance condition, $\tau = \frac{QH_0}{B_0}$

$H_0 / B_0 = \text{External M.F.}$

Generally, 14.092.0 gauss, at this field strength, EMR of 60 MHz bring ^1H nuclei into resonance.

Information from ^1H - NMR spectra.

1.) Number of signals

How many different type of hydrogen in the molecule

2.) Position of signals (chemical shift).

What types of Hydrogen in that molecule

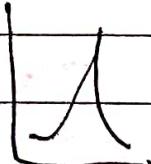
3.) Splitting Pattern of a signal

How many neighbouring hydrogen (protons)

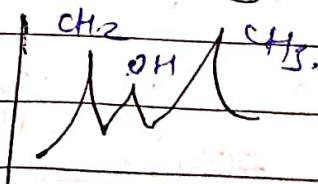
Relative areas under signal.

How many Hydrogen of each type present in molecule

Ex - CH_3OH_3 - (2) type



$\text{HO}-\text{CH}_2-\text{CH}_3$ - (2) type

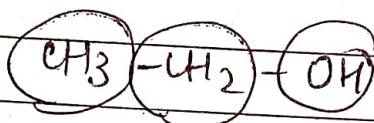


Number of signal and splitting of proton signals

The number of NMR signals represent the number of different types of protons in a molecule.

Equivalent Proton

In a molecule, protons in the same magnetic environment absorb at the same applied MF strength, B_0 are known as equivalent proton.



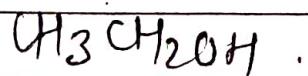
Non equivalent

In a molecule, proton in the diff magnetic environment absorb at the diff applied MF strength, B_0 .

Spin-Spin Coupling

The magnetic interaction b/w the spins of neighbouring, non equivalent NMR-active nuclei may cause splitting of NMR spectrum which is known as spin spin coupling.

The splitting pattern of a given nucleus (for set of equivalent nuclei) can be predicted by $n+1$ rule; where n is the no. of proton present on the adjacent carbon(s).



→ no. of signal = 3

{ No. of splitting pattern = $n+1$ } = 3

→ no. of neighbouring atoms

NMR Spectroscopy

Information from ^1H NMR spectrum

- ① Number of signal - gives how many types of proton (H_s) are present in that molecule.
- ② Position of signal (chemical shift) - gives types of proton

~~Imp~~ 9/10/24 Equivalent & Non-Equivalent Proton
 A set of protons with identical environment absorb the radio frequency energy at the same strength and are called as field equivalent proton.
 They give only 1 PMR signal.

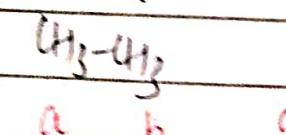
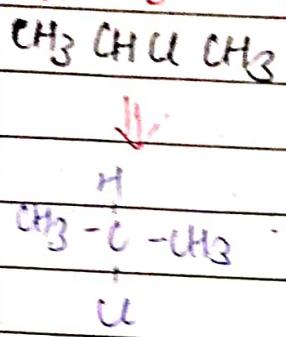
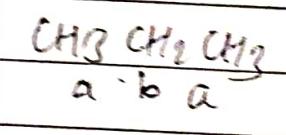
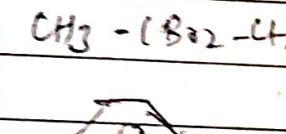
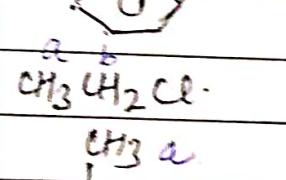
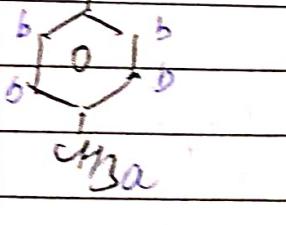
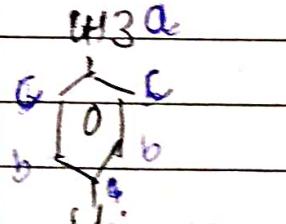
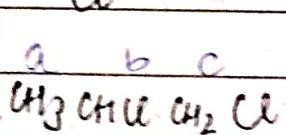
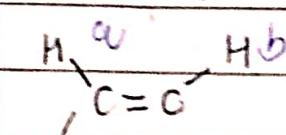
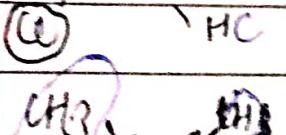
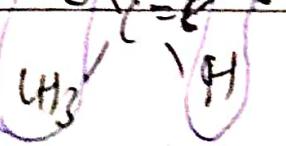
While protons with different environment are referred as non-equivalent. Each one of these give different PMR signals equal to the number of non-equivalent protons.

Note! PMR = NMR both are same.

Compound	a b c	Nature of protons	Total No. of PMR signals
1.) $\text{CH}_3\text{CH}_2\text{OH}$		a - CH_3- , 3H b - CH_2- , 2H c - $\text{OH}-$, 1H	(3)
2.) CH_3OCH_3	a a	a - $2(\text{CH}_3-)$, 6H b - $2(\text{OCH}_3-)$, 2H	(1)

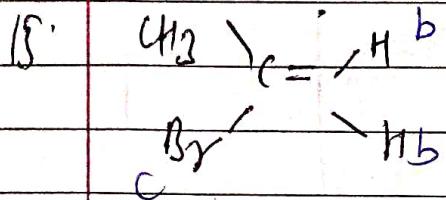
Sr. No. 8th Effect on CH_2

Date: _____

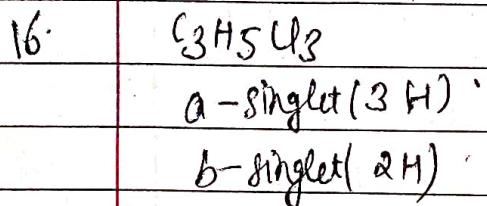
3.) 	a - $(-\text{CH}_3) = 3\text{H}$ b - $(-\text{CH}_2) = 2\text{H}$ c - $(\text{CH}_2) = 2\text{H}$	3
4.) 	a - $2(\text{CH}_3) = 6\text{H}$	1
5.) 	a - $2(\text{CH}_3) = 6\text{H}$ b - $(\text{CH}_2) = 1\text{H}$	2
6.) 	a - $2(\text{CH}_3) = 6\text{H}$ b - $(\text{CH}_2) = 2\text{H}$	2
7.) 	a - $2(\text{CH}_3) = 6\text{H}$	1
8.) 	b (=C-H) = 6H	1
9.) 	a - $\text{CH}_3 = 3\text{H}$ b - $\text{CH}_2 = 2\text{H}$	2
10.) 	a - $2\text{CH}_3 = 6\text{H}$ b (=C-H) = 4H	2
11.) 	a - $2(\text{CH}_3) = 6\text{H}$ b (=C-H) = 4H c (=C-H) = 1H	3
12.) 		3
13.) 	=3	3
14.) 		2

Sr. No.

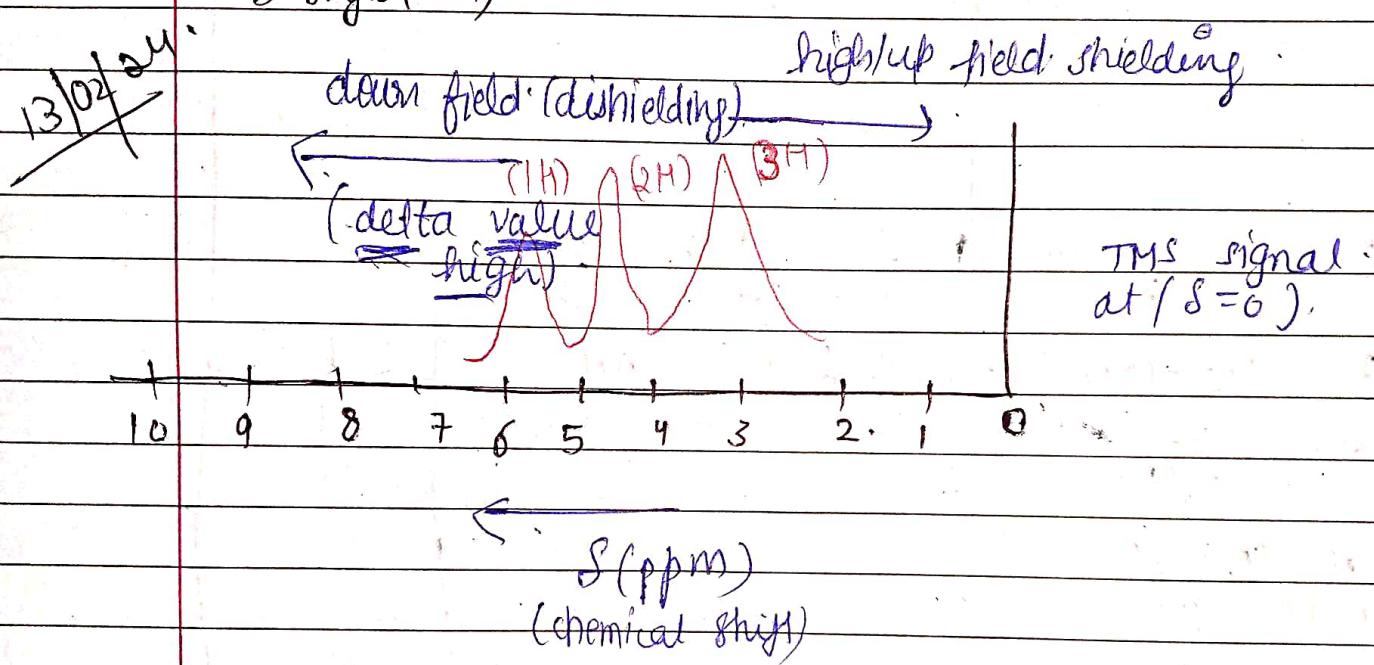
Date:



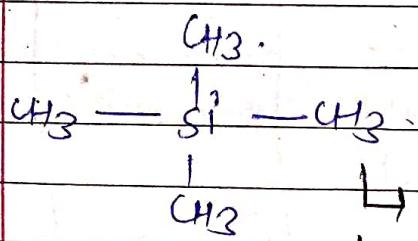
3



Structure: $\text{CH}_3-\text{C}(\text{CH}_3)-\text{CH}_2\text{Cl}_2$



* Reference used in ^1H NMR Tetramethyl silane (TMS)



CH_3

CH_3 \rightarrow ^1H NMR signal.

\rightarrow 12 Hs or 4H equivalent

\rightarrow highly shielded by nearly electron

\rightarrow High amount of external MF is required to flip

~~Q.~~ Why TMS is used as refer?

TMS is used as reference as it is —

(1) Volatile

(2) Inert

& Non toxic

(3) Easily soluble

(4) Boiling point

26.5 °C

(5) All the 12 Hydrogen are equivalent

(6) SP atom is electron releasing. Thus, high shielding of proton causes resonance at high field having $\delta = 0$

Chemical shift

- It is the measure of delta value (δ) from TMS signal to a particular signal.
- TMS signal is the signal of a standard compound at ($\delta = 0$).
- When a molecule is placed in a MF, the electron of the nearby chemical bonds circulate & generate a MF known as induced MF which may either inforce or oppose the applied MF.

• If the induced field, opposes the applied field, proton requires a more strong applied MF, to give a signal and such proton is said to be shielded. Thus, it arises at high field or upfield.

The phenomena is called as dimagnetic shielding.



↳ When the induced field reinforces the applied MF, the effective field strength on proton increases and the proton is deshielded.

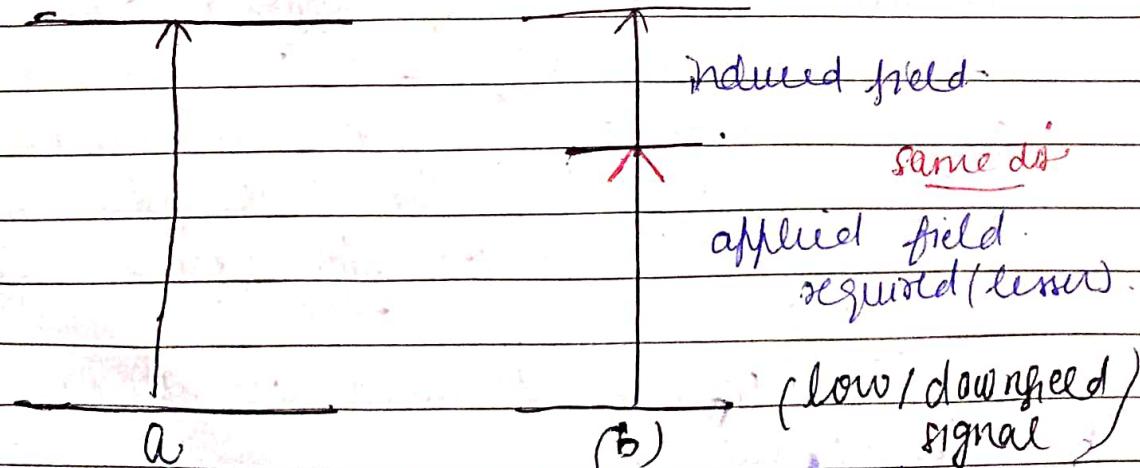
Therefore, only a smaller ~~force~~ applied MF is required for the resonance of proton i.e. to give a signal.

• It absorbs at down field.

• Thus, the shift in the position of NMR absorptions compared with a standard reference (TMS) resulting from shielding or deshielding of proton by ϵ (present in chemical bonds) referred as chemical shift denote by δ

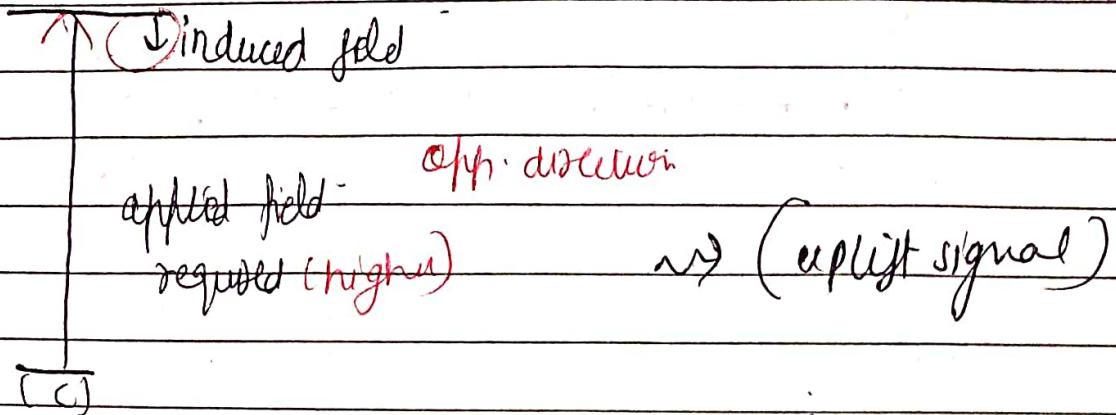
$$\delta (\text{ppm}) = \frac{\gamma_{\text{sample}} - \gamma_{\text{TMS}}}{\nu_0} \times 10^{-6}$$

ν_0 (frequency of instrument or operational frequency)



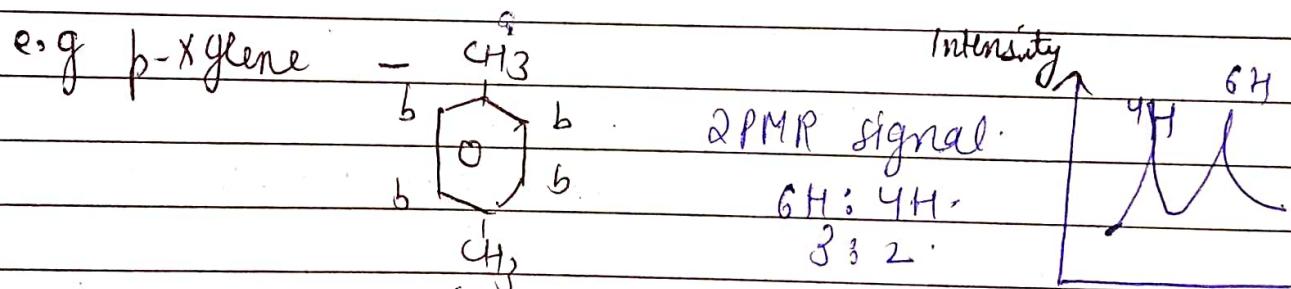
$a = \text{No. shielding/deshielding}$

Evergreen



Peak Area & proton Counting

- 1.) No. of signal = No. of types of eq. proton.
- 2.) Intensity of signal \propto No. of eq. proton giving that signal.



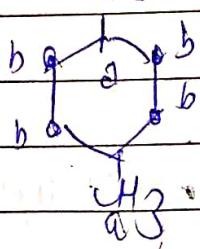
Splitting of signal / spin-spin Coupling ← 8

The splitting of signal occurs due to the spin-spin coupling of the absorbing & neighbouring proton & occurs only when the non equivalent protons are present in the neighbourhood

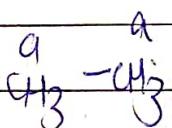
Eg: In p -xylene no splitting occurs as both the signals are in the form of singlets.

ST. NO. n

CH₃



Pylyene



* The no. of peak ~~into~~ into which a signal split = $n+1$.

$4n$ = no. of equivalent neighbouring proton.

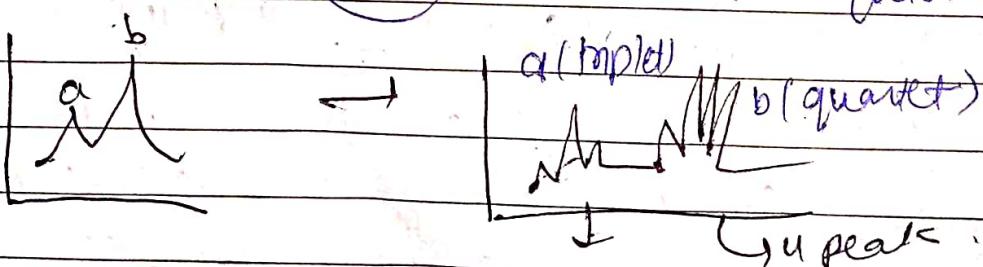
e.g. CH₃CH₂Cl \rightarrow 2 PMR signal

For a proton b and a
proton b is non equivalent

(n=2) $n+1 = 2+1 = 3$ triplet

For b proton, a proton are non equivalent

(n=3) $n+1 = 4$ = quartet



Pascal's Δ

Multiplet
singlet
doublet

Relative Intensity
1
1:1

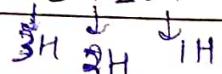
triplet	1:2:1
quartet	1:3:3:1
quintet	1:4:6:4:1
sextet	1:5:10:10:5:1
septet/heptet	1:6:15:20:15:6:1

14/02/2024

Topic (7)

Peak Area & Photon Counting

Ques

Eg: $\text{CH}_3\text{CH}_2\text{OH}$ → 3 PMR signals

OH ~~one~~
OH ke par c niche hai

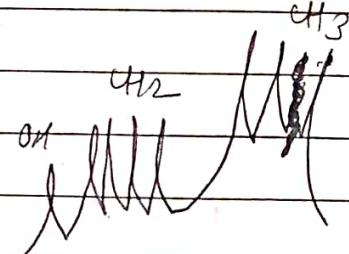
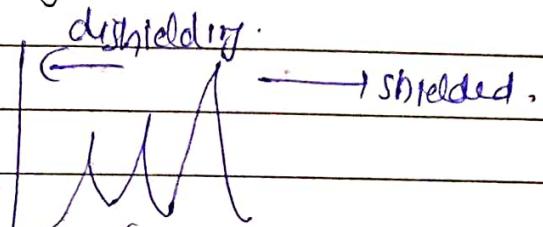
For OH ⇒ $n=0$ in basal line carbon $n+1=1$ singlet ~~one~~ ^{mai} white haiCH₂ ⇒ $n=3$ [CH₃]

⇒ 3+1=4. quartet = 1:3:3:1

CH₃ ⇒ $n=2$ [CH₂]

⇒ 2+1

= 3. triplet = 1:2:1

ques: $\text{CH}_3\text{CH}_2\text{CH}_3$ → 2 PMR signals

a b a

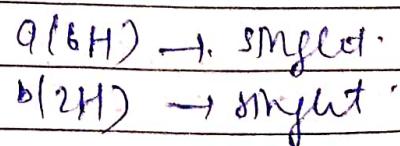
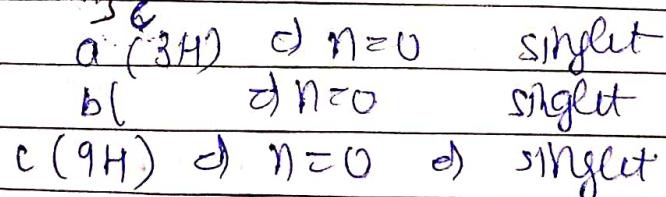
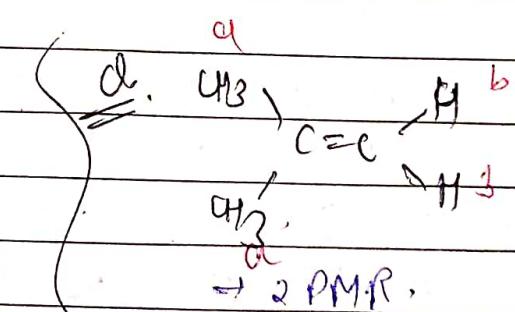
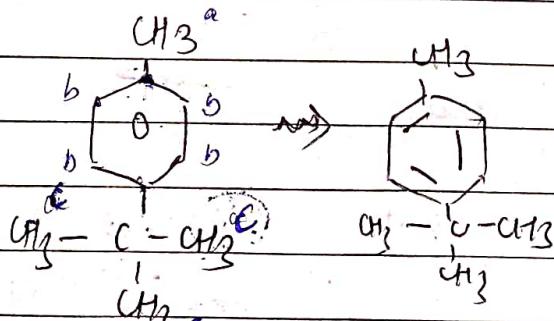
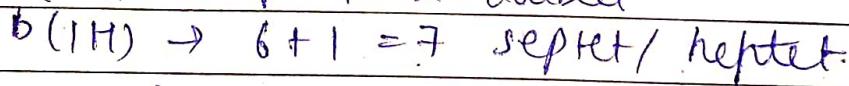
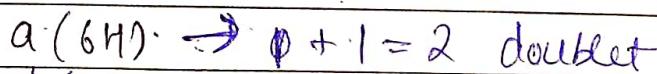
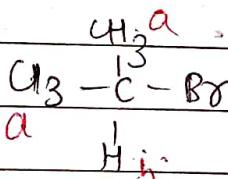
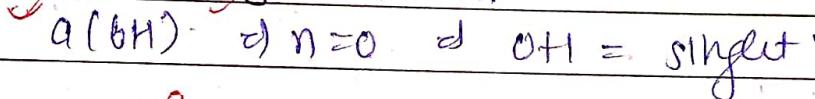
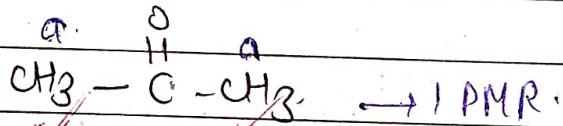
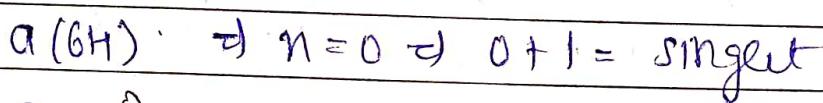
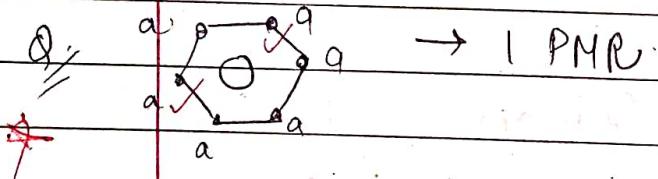
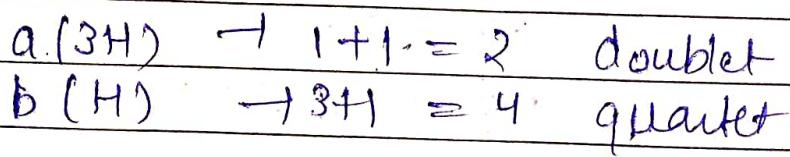
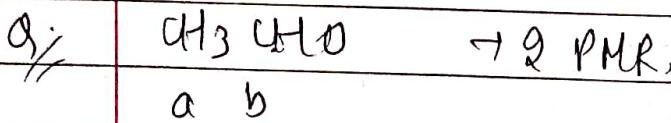
CH₃ ⇒ a=6H ⇒ n=2 ⇒ n+1 ⇒ 2+1=3 tripletCH₂ ⇒ b=2H ⇒ n=6 ⇒ 6+1 ⇒ 7 = Septet

a b c

CH₃ CH₂ CO CH₃O (CH₃ (a) → 3) → 2+1 ⇒ 3 tripletCH₂ (b) → 2 → 3+1 ⇒ 4 quartetCH₃ (c) → 3 → 0+1 ⇒ 1 singlet

Sr. No. _____

Date: _____

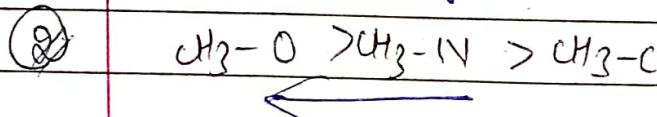
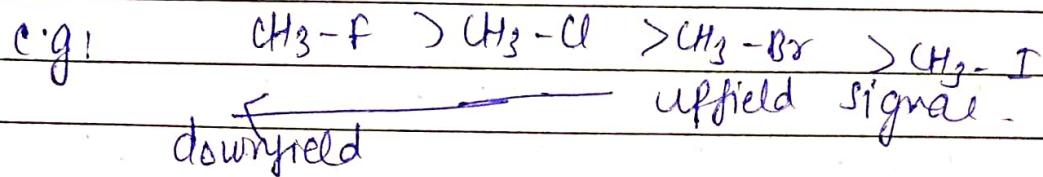


Sr. No. _____

Date: _____

Factors affecting chemical shift (δ).

① Electronegativity



③ More the H no. of atoms \rightarrow Higher \rightarrow lower δ

Unsaturation: [shielding]

Li cause deshield \rightarrow high δ

④ Aldehyde & aromatic proton \rightarrow deshield \rightarrow high δ

δ (ppm)

①	1° RCH_3	-0.9
②	$2^\circ \text{ R}_2\text{CH}_2$	-1.3
③	$3^\circ \text{ R}_3\text{CH}$	-1.5
④	$-\text{C}=\text{C}-\text{H}$	4.0 - 5.6
	$-\text{C}\equiv\text{C}-\text{H}$	2-3
	$\text{H}-\text{C}=\text{O}$	2-3
	$\text{R}-\text{C}\equiv\text{O}$	9-10
	H	

$\text{H}-\text{C}-\text{OH}$ 3.5 - 4.0

$\text{HC}-\text{OR}$ 3-4

$\text{R}-\text{COOH}$ 10.5 - 12

$\text{HC}-\text{COOH}$ 2-2.5

$\text{Ar}-\text{H}$ 6-8.5

$\rightsquigarrow \text{sp}^2 > \text{sp} > \text{sp}^3$

Sr. No. _____

Date: _____

Two scales are employed to express chemical shift in terms of ppm:

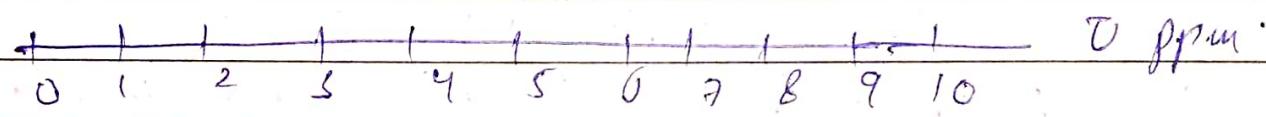
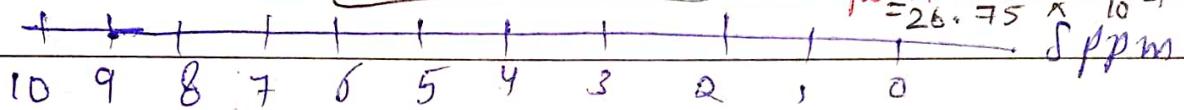
1.) δ scale where $\delta = \gamma_{\text{sample}} - \gamma_{\text{ref}} \times 10^6$

2.) τ scale where $\tau = 10 - \delta$

3.) In δ scale, TMS signal at $\delta = 0.0$ ppm

In τ scale $\tau = 10.0$ ppm

~~(4.)~~ $\gamma = \gamma_0 B_0 / 2\pi$ $\Rightarrow \gamma = \text{giantomagnetic ratio}$
 ~~$\gamma_0 = 26.75 \times 10^7$~~ H- nucleus



$\tau_{\text{sample}} - \tau_{\text{ref}} = \gamma_s$ (shift of resonance).

Ques.

What is the shift of the resonance from PMS of a group of nuclei with $\delta = 3.5$ & operating frequency of 350 MHz.

$\gamma_0 = 350$
 $\gamma_0 = 350 \times 10^6$ Hz

$\gamma_0 = 350; \delta = 3.5; \gamma_0 = 350 \times 10^6$ Hz

Ques.

$\delta = \gamma_{\text{sample}} - \gamma_{\text{ref}} \times 10^6$

γ_0

$\delta = \frac{\gamma_s \times 10^6}{\gamma_0} \quad \delta = 3.5 = \frac{\gamma_s}{350 \times 10^6} \times 10^6$

$\gamma_s = 1225$ Hz

Ques. In a 12 T magnetic field calculate the frequency at which radiation comes into resonance with proton spins.

$B_0 = 12$ T.

$\nu = \frac{12 \times 26.75 \times 10^7}{2\pi} = 51.11 \times 10^7$ Hz

ANSWER