

# NMR [Nuclear Magnetic Resonance] Spectroscopy

Topics :- [Complete hand Made Notes]

1. Basic Introduction
2. Principle of NMR
3. Spin Quantum Number
4. Instrumentation and working
5. Solvent used in  $^1\text{H}$ NMR
6. Chemical shift
7. Factors affecting chemical shift
8. Numerical problem on chemical shift.
9. Number of signal
10. Splitting of signals.
11. Spin - Spin Coupling
12. Coupling Constant.
13. Types of Coupling Constant.
14. Spin Decoupling [Double Resonance]
15. Carbon -  $^{13}\text{C}$  NMR Spectroscopy
16. Different between  $^{13}\text{C}$ NMR and  $^1\text{H}$ NMR
17. Chemical shift of  $^{13}\text{C}$ NMR
18. No. of signals in  $^{13}\text{C}$ NMR
19. DEPT Spectrum
20. Application of NMR Spectroscopy

# NMR (Nuclear Magnetic Resonance Spectroscopy)

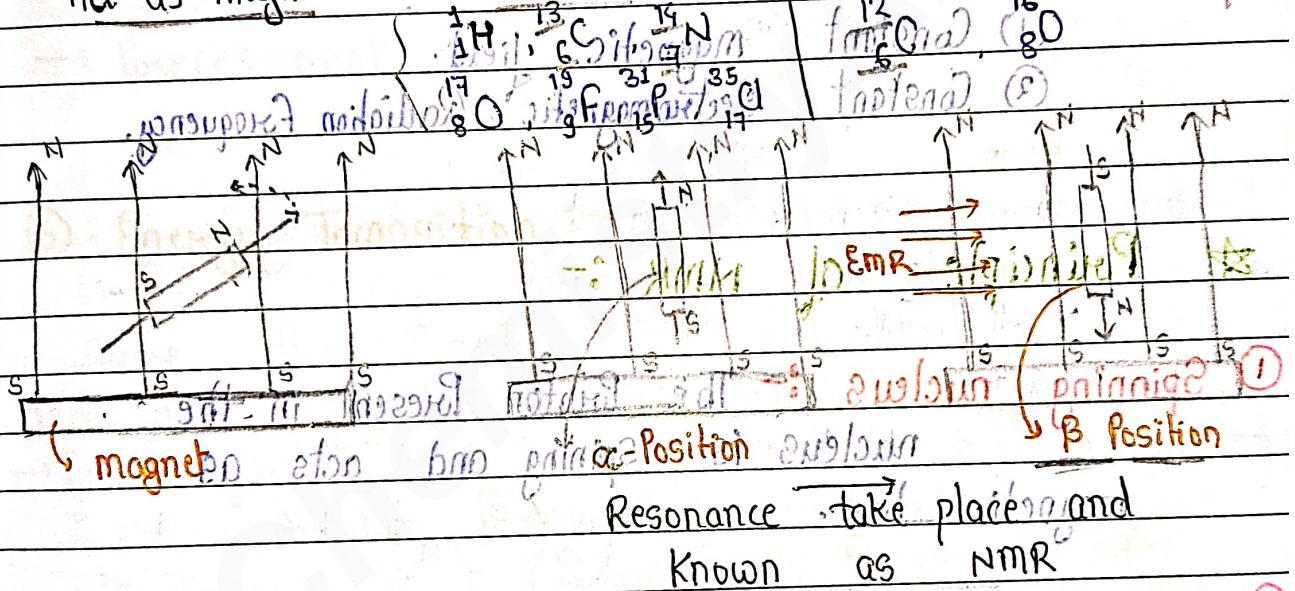
**Introduction** :- Proton is present in the nuclei and proton shows spin moment, due to this spin, proton acts as a small magnet. → Due to electromagnetic radiation, resonance in this small magnet take place and process in NMR Spectroscopy.

Spin quantum no. should be more than 1/2, then NMR active.

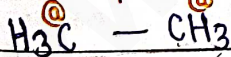
Act as magnet

NMR active

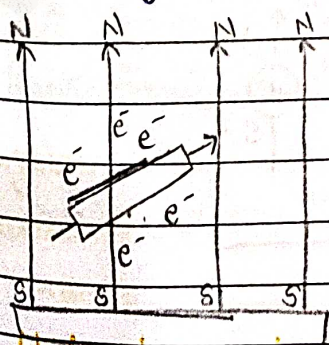
NMR Inactive



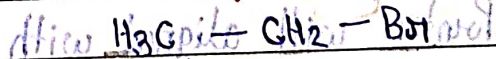
Example - 1.



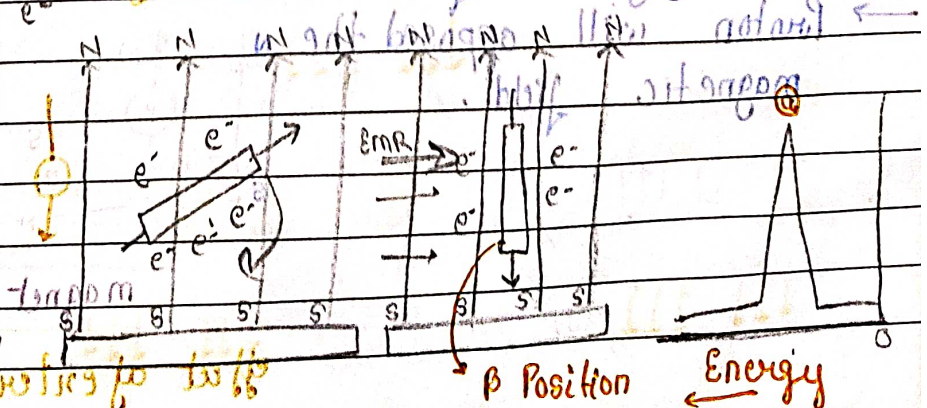
shielding

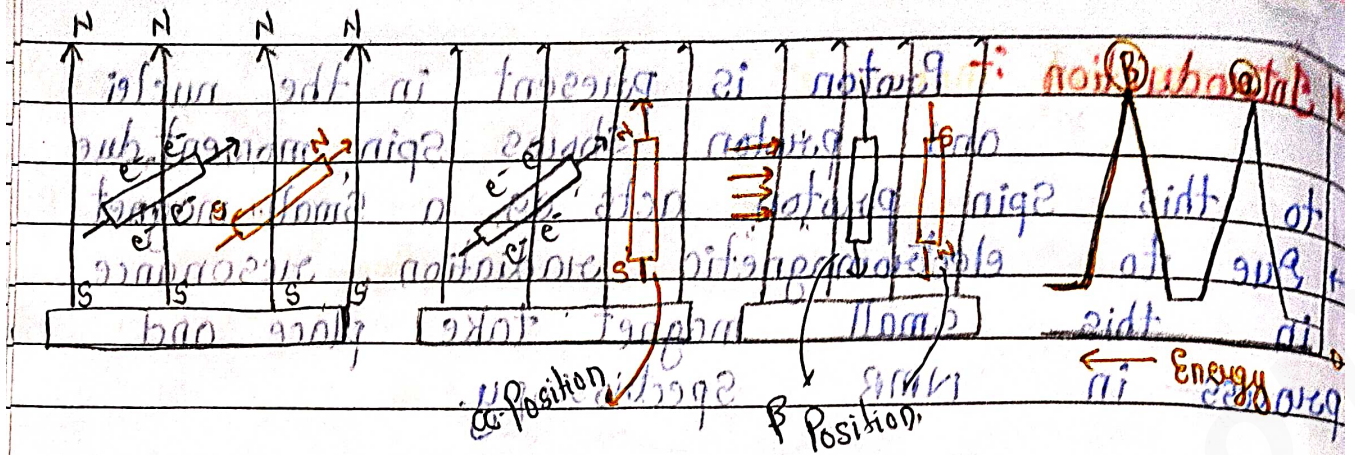


Example - 2.



deshielding





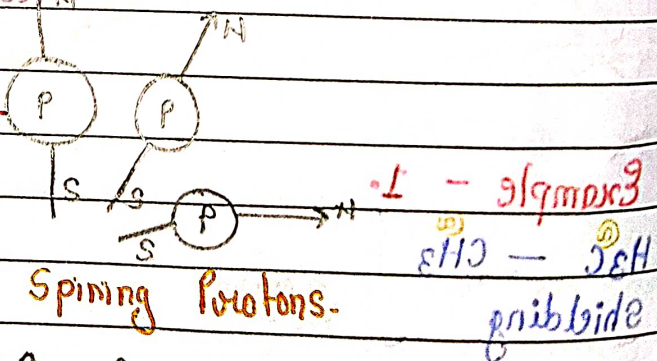
Resonant frequency is the frequency required to convert spin from up position to down position.

- operation condition :-
- ① Constant magnetic field.
  - ② Constant electromagnetic radiation frequency.

### \* Principle of NMR :-

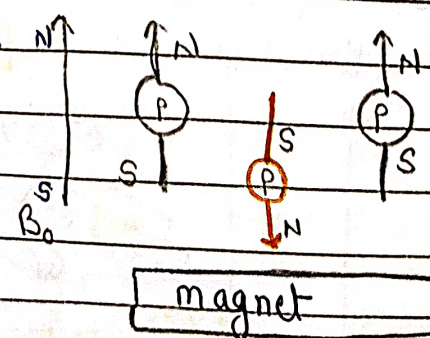
① Spinning nucleus :- The Proton Present in the nucleus is spinning and acts as a magnetic bar.

② effect of external magnetic field :-



→ Proton will aligned with the magnetic field.

→ Proton will opposed the magnetic field.

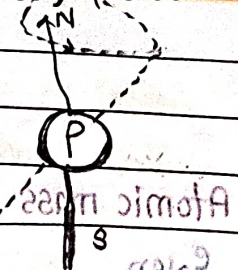


magnet

effect of external magnetic field.

③ Precessional motion :- Proton will be showing

Precessional motion due to interaction of spin and gravitational forces [Gyroscopic motion]



Energy of orientation of magnetic dipoles  
 $\Delta E = h\nu$   
 Planck Const.  $\rightarrow$  Frequency of radiation.

④ Precessional frequency :- Spinning frequency of Proton will be same.

$\rightarrow$  Precessional frequency  $\propto$  External magnetic field.  
 $\nu \propto B_0$

⑤ Energy transition :- If Proton's Precessional frequency will be exactly same then only it will absorb radiation and resonance takes place which is known as NMR.

$\rightarrow$  Proton goes to low energy level to high energy level.

Angular Precessional velocity :-  
 $\omega = \gamma B_0$  — (1)  $\gamma =$  Gyromagnetic ratio  
 $B_0 =$  External magnetic field.

⑥ Larmor equ. for NMR :-

$$\gamma = \frac{2\pi u}{hI}$$

$h =$  plank constant  
 $u =$  magnetic moment of Proton  
 $I =$  Spin quantum no.

$$\nu = \lambda B_0$$

$$2\pi \nu = \lambda B_0$$
 — (2)

Substituting equ<sup>n</sup> (2) in equ<sup>n</sup> (1) we get:

$$\omega = 2\pi \nu$$
 — (3)

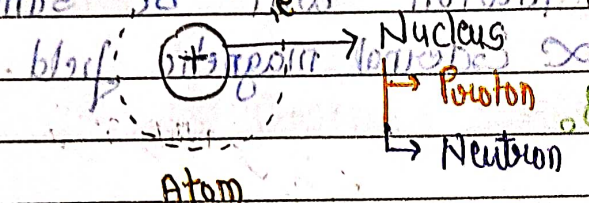
Angular Precessional velocity

$$\omega = \frac{I}{s} = \gamma B_0$$

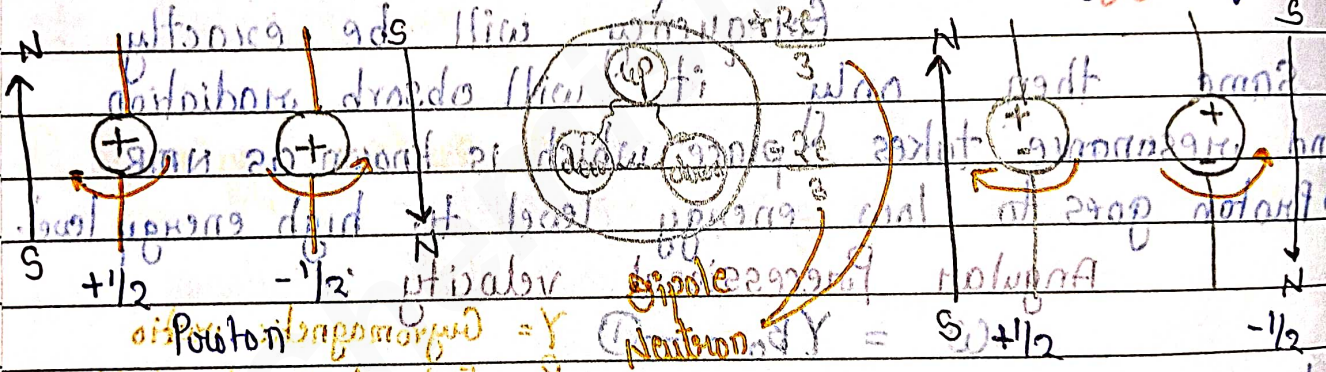
## \* Spin Quantum Number

Atomic mass	Proton	Neutron	Spin Quan. Num.	Example
Even	Even	Even	$1/2, 3/2, 5/2$	$^{12}_6\text{C}, ^{16}_8\text{O}, ^{16}_8\text{S}$
Odd	Odd	Even	$1/2, 3/2, 5/2$	$^{11}_5\text{B}, ^{19}_9\text{F}, ^{14}_7\text{N}$
Odd	Even	Odd	$1/2, 3/2, 5/2$	$^{13}_6\text{C}$
Even	Odd	Odd	$1/2, 3/2, 5/2$	$^2_1\text{H}, ^{14}_7\text{N}$

The total angular momentum of a nucleus in its ground state is known as nuclear spin.

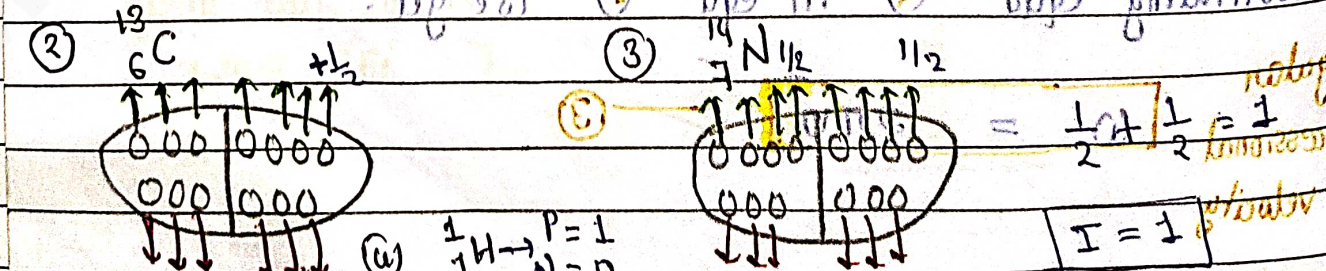


Protons and Neutrons are able to create magnetic field.



Proton spin =  $Y$ , Neutron spin =  $S$

Example:  $^{12}_6\text{C}$  (6 protons, 6 neutrons). In this, green colour arrow will denote by  $+1/2$  and red colour arrow is  $-1/2$  and all are cancel each other.  $I = 0$

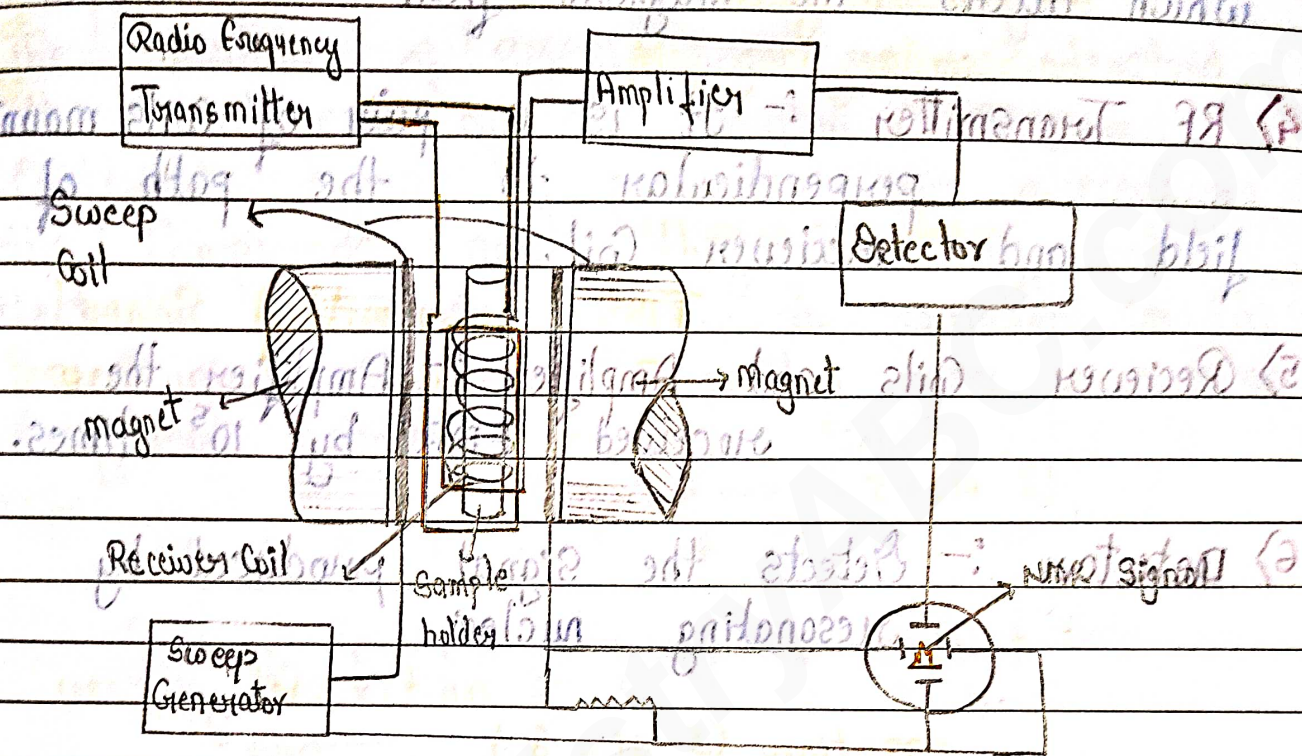


$I = 1$

$^1_1\text{H} \rightarrow P = 1, N = 0$

By: Anjali Singh

## ★ Instrumentation and Working



1) Sample Holder :- 5mm glass tube is used which can hold 0.4 ml liquid sample. microtubes are used for low volume.

2) Magnet :- Accuracy and quality of the Instrument is dependent on its strength.

→ Resolution  $\uparrow$  increases with increase in the field strength

→ Three types of magnets can be used.

1. Conventional magnet [30-60 MHz]

2. Permanent or Electromagnet [60, 90, 100 MHz]

3. Superconducting solenoids [60-70 MHz]

- 3) Sweep Generator :- A set of Helmholtz Coil is located parallel to the magnet which alters the magnetic field.
- 4) RF Transmitter :- It is a pair of coils mounted perpendicular to the path of field and receiver coil.
- 5) Receiver Coils and Amplifier :- Amplifier the received EMR by  $10^5$  times.
- 6) Detector :- Detects the signal produced by resonating nuclei.

### ★ Solvent used in $^1\text{H NMR}$

Characteristics of Solvents :-

- Chemically inert solvent is used.
- Solvents should be magnetically isotropic in nature.
- Free from any hydrogen ( $^1\text{H}$ ) atom.

Isotopes of Hydrogen :- Proton, Neutron

$^1\text{H}$  Hydrogen       $^2\text{H}$  Deuterium



- Solvent should be able to dissolve the molecule/sample in a reasonable quantity (App. 10% or more)

Commonly used solvents :-

① Carbon tetrachloride ( $\text{CCl}_4$ )

② Carbon disulphide ( $\text{CS}_2$ )

③ Deuterio benzene ( $\text{C}_6\text{D}_6$ ) etc.

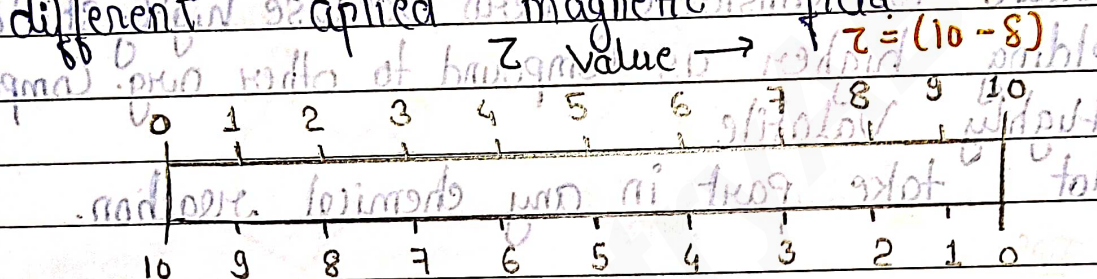
# Chemical Shift [Position of Signal]

→ No. of signal and position of signal plays very important role in NMR Spectroscopy.

→ The position of signal helps us to understand the nature of the proton in compounds.

→ Different type of protons are present in the compounds and they have different electronic environment; due to variation in

electronic environment proton gets absorb at different applied magnetic field.



$\delta$  value  $\leftarrow (\delta = 10 - \tau)$  unit = ppm.

$\leftarrow$  Deshielding

shielding  $\rightarrow$

$\leftarrow$  Down field

upfield  $\rightarrow$

$\leftarrow$  High frequency

low frequency  $\rightarrow$

$\leftarrow$  High chemical shift value.

low chemical shift value.  $\rightarrow$

## Type of Protons

1. Aliphatic Alicyclic

$\delta = 0$  to  $2$

2.  $\beta$ -Substituted Aliphatic

$\delta = 1$  to  $2$

3. Alkyne

$\delta = 2$  to  $3$

4.  $\alpha$ -monosubstituted Aliphatic

$\delta = 2$  to  $5$

5.  $\alpha$ -Disubstituted Aliphatic

$\delta = 2.5$  to  $7$

6. Alkene

$\delta = 4.5$  to  $7.5$

7. Aromatic and Heteroaromatic

$\delta = 6$  to  $9$

8. Aldehydic

$\delta = 9$  to  $10$



→ [moleculer] placed into external magnetic field

will produce secondary magnetic field

Secondary magnetic field → opposed → shielded → up field

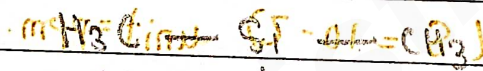
Secondary mag field → Reinforced → deshielded → down field

up field / down field is known as chemical shift.

Reference Compound: TMS [Tetra methyl Silane]

- δ value is considered zero because highly shielded.
- Shielding higher as compound to other org. compound.
- Highly Volatile
- Not take part in any chemical reaction.

TMS



Calculation of TMS:-

Formula :- 
$$\text{Chemical shift } (\delta) = \frac{V_{\text{Sample}} - V_{\text{TMS}}}{V_{\text{TMS}}} \times 10^6$$

Operating frequency (in MHz)

$\delta = 0$

$\delta = 1$

$V_{\text{Sample}}$  → Resonance frequency of Sample

$V_{\text{TMS}}$  → Resonance frequency of TMS

$\delta = 2$

$\delta = 3$

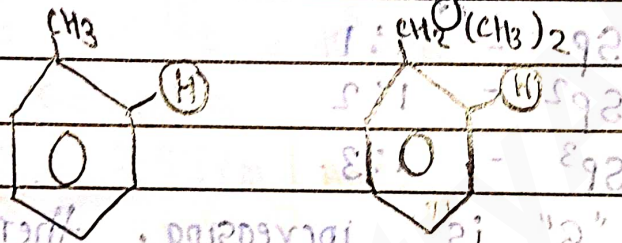
$\delta = 4$

# \* Factors affecting Chemical shift :-

① Inductive Effect :- when proton is attached with any electronegative group/atom, then proton will be deshielded and  $\delta$  value will be high.

	$\text{CH}_3\text{F}$	$\text{CH}_3\text{Cl}$	$\text{CH}_3\text{Br}$	$\text{CH}_3\text{I}$	$\text{CH}_4$
$\delta$ value	4.26	3.05	2.68	2.16	0.23

② Van der Waals Deshielding :- [steric effect]

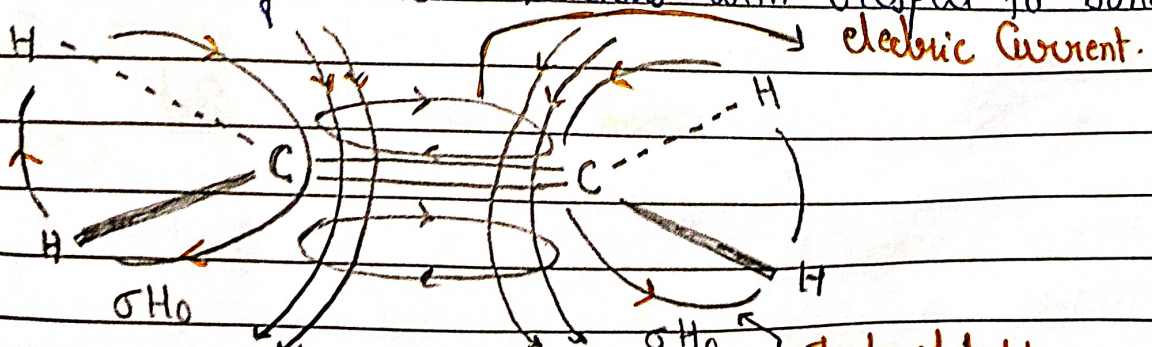


→  $e^-$  clouds of bulky group will repel the  $e^-$  cloud of proton due to electrostatic repulsion → Deshielding →  $\delta$  value is increase.

③ Anisotropic effect :- chemical bonds of the molecules are also high  $e^-$  density region and sets magnetic field.

→ These fields are stronger in one direction than others and known as anisotropic.

→ Chemical shift of nearby nuclei is dependent on the orientation of the nucleus with respect to bond.



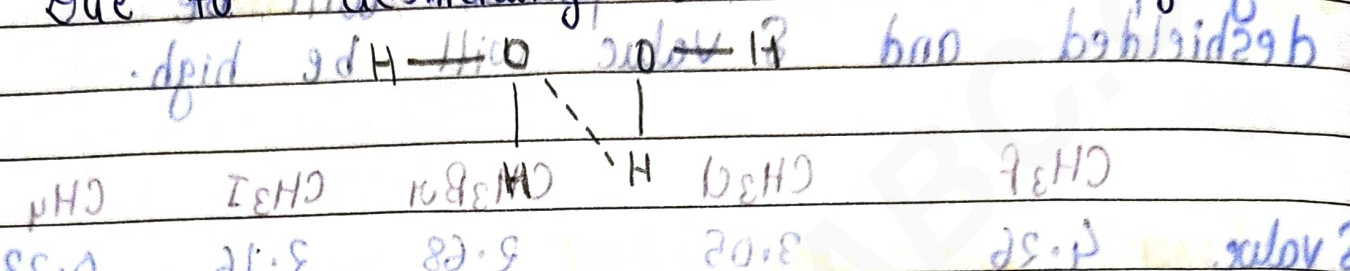
Deshielding of ethylenic protons

www.ChemistryABC.com

Induced field.

By: Anjali Singh

④ Hydrogen Bonding :- Hydrogen atom goes for hydrogen bonding with two electronegative atoms and they will take the  $e^-$  cloud from "H" and it will be deshielding.  
 → Due to deshielding  $\delta$  value will be higher



⑤ Hybridization of "C" attached with "H" atom :-  
 → Hybridized "C" affects the  $e^-$  density of "H" atoms

- $sp$  - 1:1
- $sp^2$  - 1:2
- $sp^3$  - 1:3

Proportion of "s" is increasing. then bonding  $e^-$  will be more closer to carbon and away from hydrogen.  
 → Deshielding (High  $\delta$  value).

⑥ Anisotropic effect :- Chemical bonds of the molecules are also dipole density region. These fields are stronger in one direction than others and known as anisotropic. (Chemical shift in nucleus is dependent on the magnetic field.)

## Numerical Problems On Chemical Shift

Que:-① Calculate the chemical shift in ppm ( $\delta$ ) for a proton that has resonance at 150 Hz downfield from TMS on NMR Spectrophotometer that operate at 60 MHz.

Solve:-

$$\text{Chemical shift } \delta = \frac{V_{\text{sample}} - V_{\text{TMS}}}{\text{Operating frequency (in MHz)}}$$

Formula:-

$$\delta = \frac{\Delta V}{60 \text{ MHz}} \times 10^6 \text{ ppm}$$

$$\delta = \frac{150 \text{ Hz}}{60 \times 10^6 \text{ Hz}} \times 10^6 \text{ ppm}$$

$$\delta = 2.5 \text{ ppm} \quad \text{Ans.}$$

Que:-② If the observed shift from TMS is 300 Hz and operating frequency of the instrument is 100 MHz calculate the chemical shift value ( $\delta$ ).

Solve:-

$$\text{Formula } (\delta) = \frac{V_{\text{sample}} - V_{\text{TMS}}}{\text{Operating frequency (in MHz)}}$$

$$\delta = \Delta V \times 10^6 \text{ ppm.}$$

$$\delta = \frac{300 \text{ Hz}}{100 \times 10^6 \text{ Hz}} \times 10^6 \text{ ppm}$$

$$\delta = 3 \text{ ppm.} \quad \text{Ans.}$$

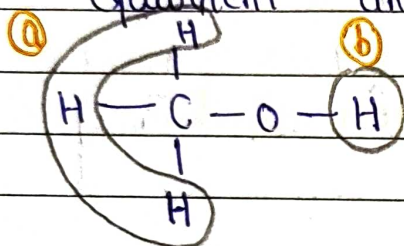
Numerical problems on chemical shift

★ Number of Signals

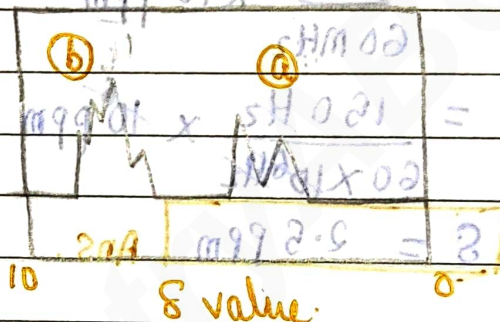
→ The number of signals in the NMR Spectrum gives the information about different sets of equivalent proton in a molecules.

→ Each signal in the NMR spectrum represents a set of equivalent proton.

→ magnetically equivalent protons are known as chemically equivalent and gives a single signal in NMR.

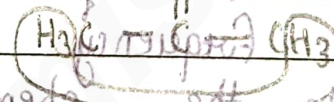


methanol.



Examples:-

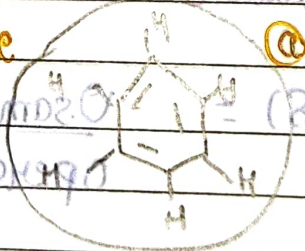
★ molecules giving single signal.



1 NMR Signal

② Tetramethyl methane

② Benzene



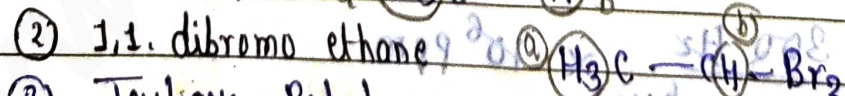
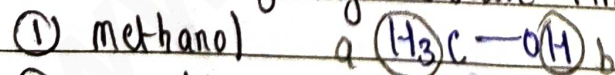
1 NMR Signal.

③ 1,2-dibromo ethane

④ Cyclobutane.

1 NMR Signal.

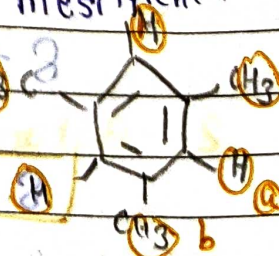
→ molecule giving double NMR signal



④ mesitylene.

③ Tertiary Butyl amine

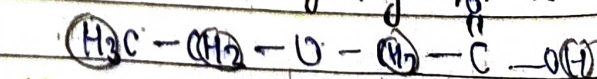
④ Diethyl ether.



→ molecule giving three signals



→ molecule giving 4 NMR

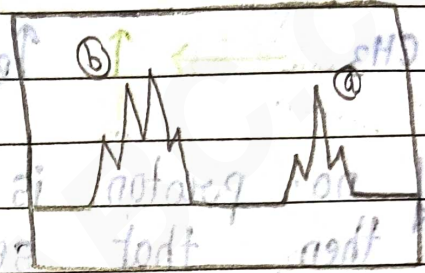
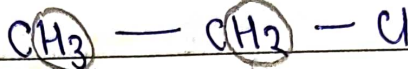


4 NMR Signal  
By: Anjali Sirgh

## ★ Splitting of Signals

- In NMR spectrum, each signal represents one kind or one set of protons in a molecule.
- In certain molecule singlet of signal will not be observed. it occurs may be multiplet
- doublet, triplet or quartet etc.

eg. Ethyl chloride.

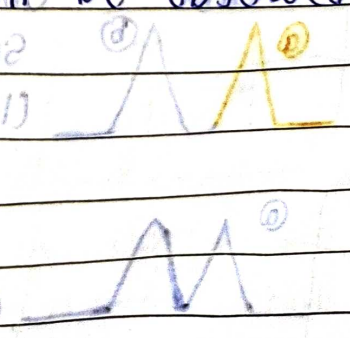
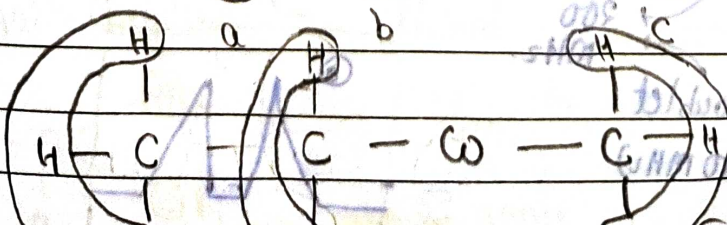
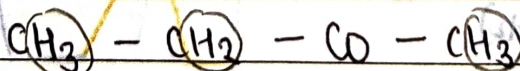


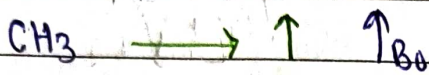
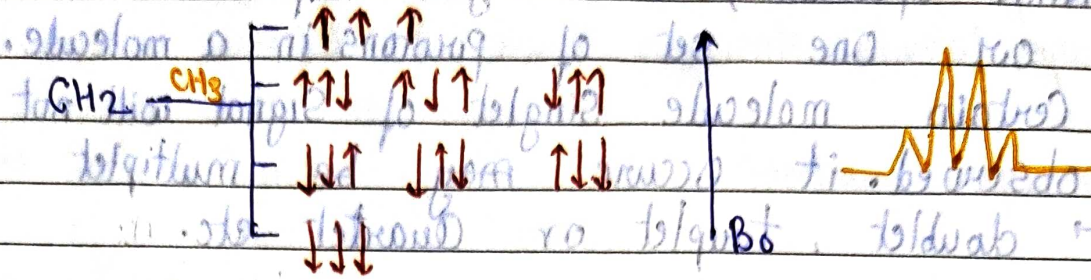
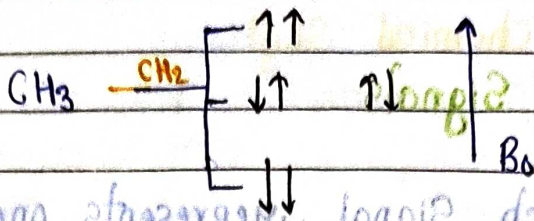
- The interaction between the spins of neighbouring magnetic nuclei in a molecule may cause the splitting of the signal in NMR spectrum.

## ★ Spin-Spin Coupling

- when spin of two protons are coupled, then it is known as spin-spin coupling.
- For spin-spin coupling minimum two sets of protons are required.
- Due to spin-spin coupling between the nearby protons, splitting of signal will be observed.

eg:- 2-Butanone.



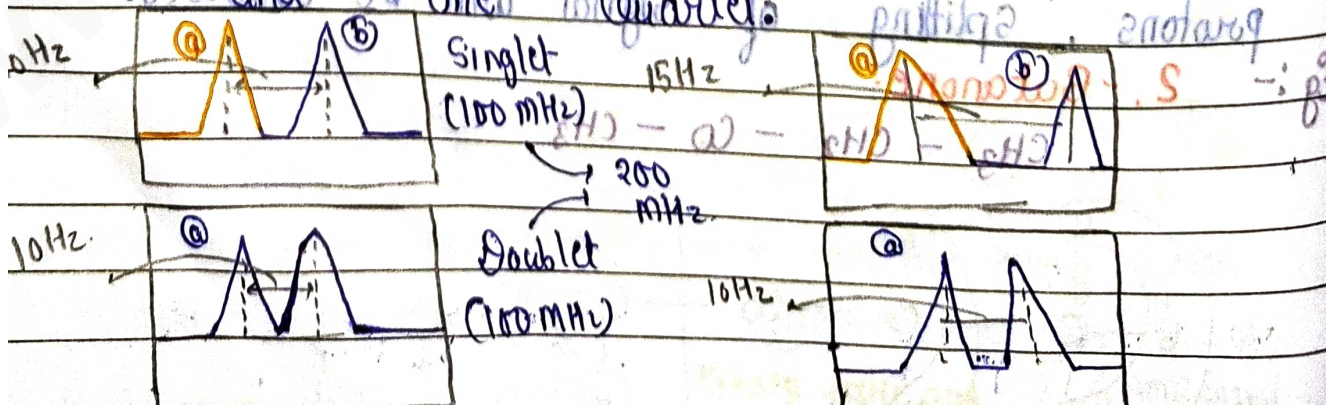


→ If no. proton is present in the adjacent carbon then that set of proton will give singlet.

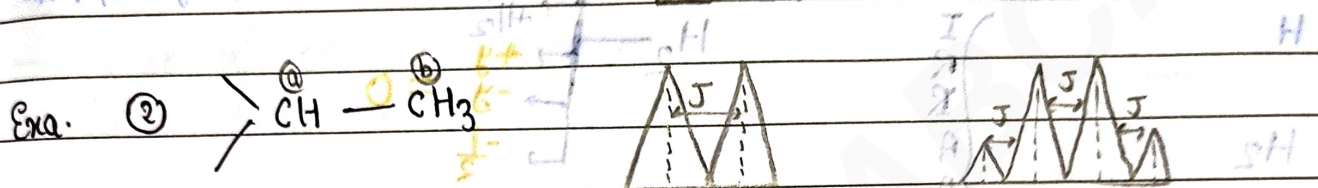
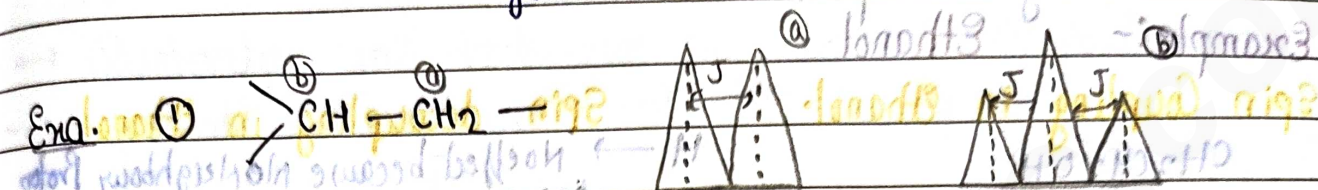
### ★ Coupling Constant

[Spin-Spin Splitting with NMR]

- The distance between the centres of the two adjacent peaks in a multiplet is constant and it is known as Coupling Constant.
- It is denoted by "J"
- The value of the Coupling Constant is independent because there is no effect of external applied magnetic field.
- It is mainly used to differentiate between two singlet and one doublet, two doublet and one quartet.

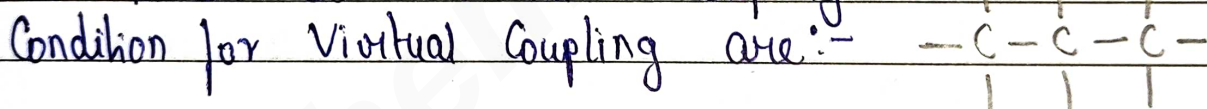


- Unit of Coupling Constant is Hz, Cycles per Second (CPS)
- is also the Unit for Coupling Constant
- Generally value of Coupling Constant is upto 20 Hz
- It can be [ Positive / Negative.

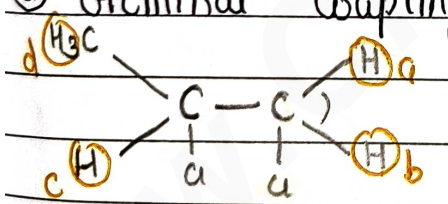


### Types of Coupling Constant :-

① Virtual Coupling :- Protons A and M are said to be virtually coupled and such an interaction is known as virtual coupling.



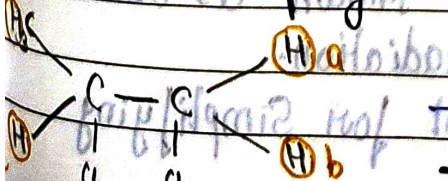
② Geminal Coupling :- Proton attached with same Carbon but environment are diff. is known as Geminal Proton.



$J_{AB} > \Delta\delta_{A,B}$   
 $J_{AM} = 0$

- value of  $J_{gem}$  depends upon the bond angle between the geminal protons of saturated protons.
- $J_{gem}$  will increase with increase in the bond angle.

③ Vicinal Coupling :- Vicinal protons are protons which are separated by three bonds.



Value of  $J_{vic}$  varies with dihedral angle.  $\rightarrow$  if angle is  $90^\circ$  then it will show -ve  $J_{vic}$ .



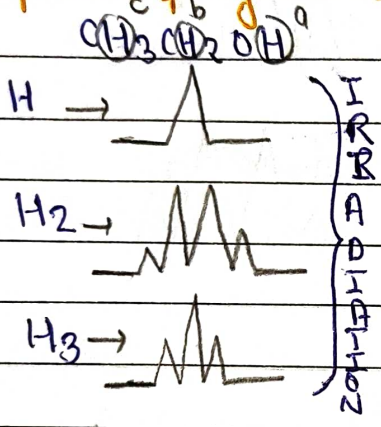
# \* Spin Decoupling (Double Resonance)

→ It is a technique which involves irradiation of a set of protons. This irradiation is done by intense radio frequency energy.

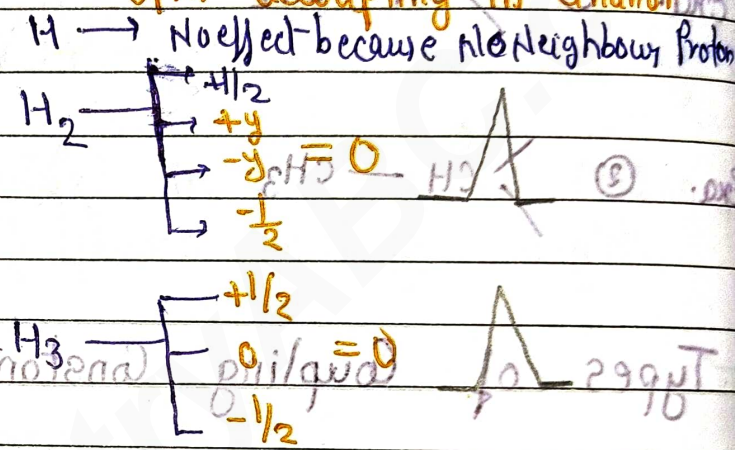
→ This energy eliminates Spin-Spin Coupling amongst protons.

Example:- Ethanol.

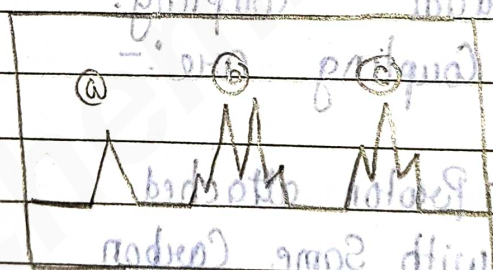
## Spin Coupling in Ethanol.



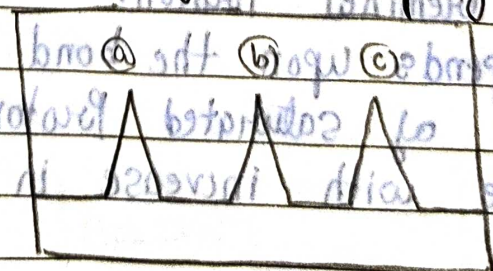
## Spin decoupling in Ethanol



Before decoupling.



After decoupling.



→ Two radio frequency is used, so known as double resonance or double irradiation.

This technique is a powerful tool for simplifying the spectrum.

# Carbon-13 NMR Spectroscopy

Basic :- mass no. is odd no. in  $^{13}\text{C}$ , but it is even no. in  $^{12}\text{C}$  So it is NMR active.

$^{12}\text{C}$  :- Proton - 6 Neutron - 6

$^{13}\text{C}$  :- Proton - 6 Neutron - 7

→ Relatively new technique as compare to proton NMR.

→ natural abundance of  $^{13}\text{C}$  is 1.11% and  $^{12}\text{C}$  is 98.89%.

→ Due to less % age of  $^{13}\text{C}$ , it is less sensitive and quantity of sample required is higher.

★ Principle :- Proton is present in the nucleus of the atom and acts as a magnetic bar. → when external magnetic field will be applied protons will be parallel.

→ Electromagnetic radiation will be applied & resonance takes place  $^{13}\text{C}$  NMR signal occurs.

→  $^{13}\text{C}$  has lower gyromagnetic ratio as compared to  $^1\text{H}$  NMR, which  $\frac{1}{4}$ th of  $^1\text{H}$

$$^1\text{H} \Rightarrow \gamma = 267.53 \text{ radians/sec-Tesla}$$

$$^{13}\text{C} \Rightarrow \gamma = 67.28 \text{ radians/sec-Tesla}$$

$$\nu = \left( \frac{\gamma}{2\pi} \right) B_0$$

$\nu$  = radio frequency

$B_0$  = Applied magnetic field

$\gamma$  = gyromagnetic ratio.

Exa:-  $B_0 = 10.41 \text{ T} / 14100 \text{ G} \Rightarrow \nu = \frac{67.18}{2 \times 3.14} \times 10.41 = 111.1 \text{ MHz}$

**Difference between  $^{13}\text{C}$ NMR and  $^1\text{H}$ NMR :-**

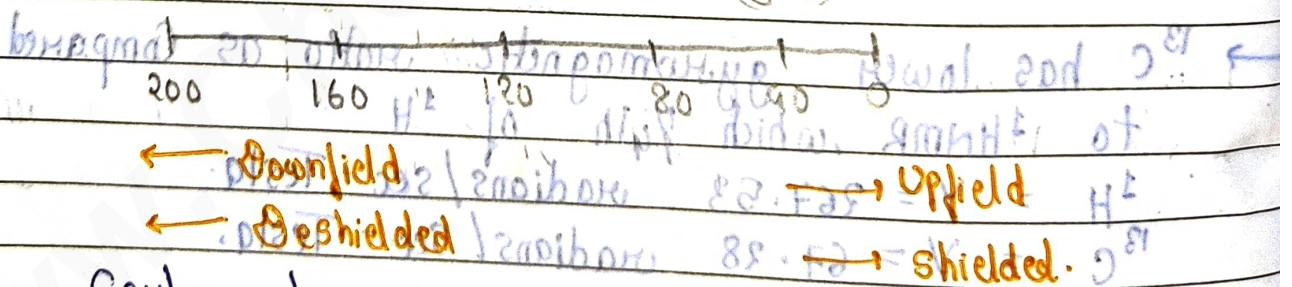
**$^{13}\text{C}$ -NMR**

**$^1\text{H}$ NMR**

- |   |  |
|---|--|
| ① Study of spin changes of Carbon nuclei            | ① Study of spin changes of Proton nuclei       |
| ② Chemical shift ranges between 0-240 ppm           | ② Chemical shift range 0-14 ppm                |
| ③ Very fast process                                 | ③ Very slow process                            |
| ④ Pulse FT technique is used                        | ④ Continuous wave method is used               |
| ⑤ Value of Coupling Constant ranges from 125-250 Hz | ⑤ Range from 0-15 Hz                           |
| ⑥ it work on Frequency Sweep                        | ⑥ It work on either Field Sweep or Freq. Sweep |

**★ chemical shift of  $^{13}\text{C}$ NMR**

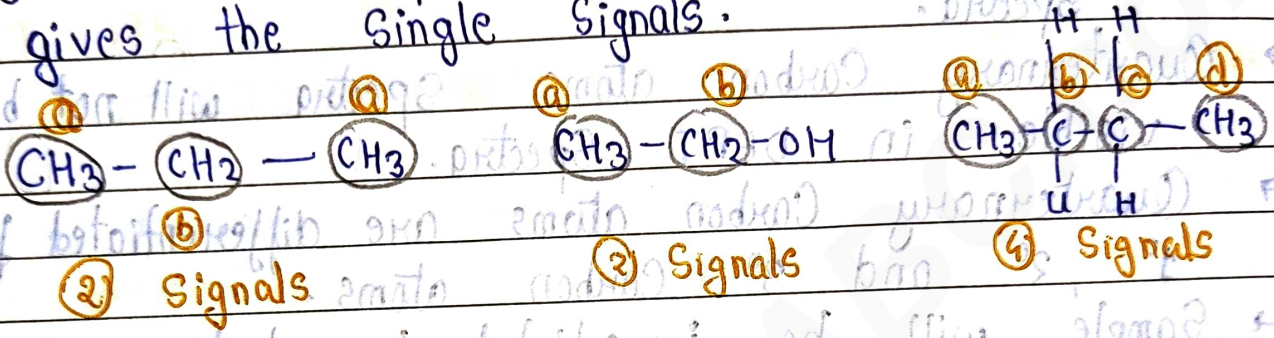
- chemical shift ( $\delta$ ) value ranges from 0 to 200 ppm
- It is approximately 20 times greater than  $^1\text{H}$ NMR ( $\delta=0$ ) TMS



Carbon type	$\delta$ value (ppm)
$\text{R}-\text{CH}_3$	0-30
$\text{R}_2-\text{CH}_2$	15-55
$\text{R}_3-\text{CH}$	20-60
$\text{C}=\text{O}$	0-40
$\text{C}-\text{Br}$	25-65

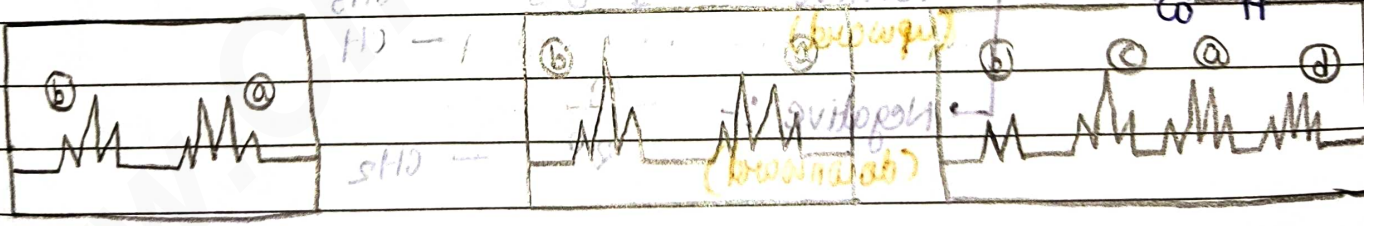
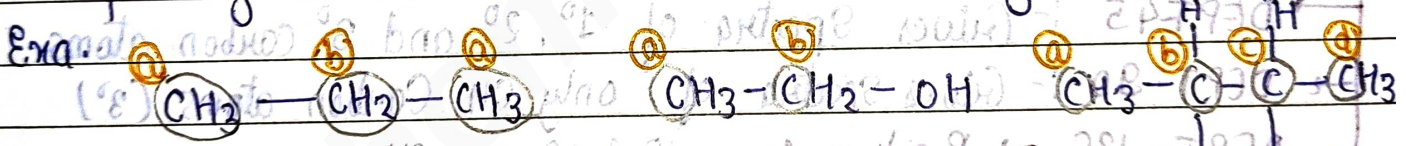
**No. of Signals in  $^{13}\text{C}$  NMR**

- No. of equivalent set of Carbons present in the Sample.
- Each signal is  $^{13}\text{C}$  NMR represents the equivalent set of Carbon atoms.
- Carbon atoms present in the same environment gives the single signals.



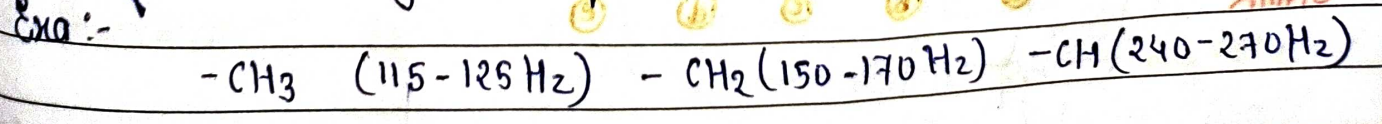
**Spin-Spin Coupling in  $^{13}\text{C}$  NMR & Splitting.**

- when spin of  $^{13}\text{C}$  NMR is coupled with  $^1\text{H}$ , then it is known as proton coupled spectra.
- Splitting occurs due to directly bonded proton.



**Coupling Constant (J) in  $^{13}\text{C}$  NMR**

- Coupling Constant value (J) will be more than 115 Hz if directly coupled with proton.



# ★ DEPT Spectrum [Distortionless Enhancement by Polarization Transfer]

- used to differentiate between primary, secondary, tertiary and quaternary Carbon atoms.
- In DEPT, Sequence of pulses with various delay times is used to create the DEPT Spectra.
- Quaternary Carbon atoms Spectra will not be visible in DEPT Spectra.
- Quaternary Carbon atoms are differentiated from  $1^{\circ}$ ,  $2^{\circ}$  and  $3^{\circ}$  Carbon atoms.
- Sample will be irradiated by electromagnetic radiation of different angle of pulses  
i.e :-  $45^{\circ}$ ,  $90^{\circ}$  and  $135^{\circ}$

$^{13}\text{C}$  NMR : All Spectra of Carbons will be visible.

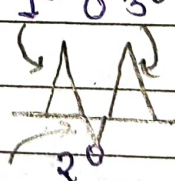
DEPT :-

DEPT-45 :- Gives Spectra of  $1^{\circ}$ ,  $2^{\circ}$  and  $3^{\circ}$  carbon atoms.

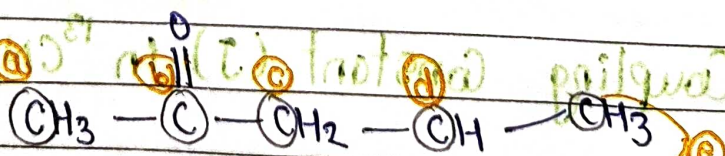
DEPT-90 :- Gives Spectra of only CH Carbon atoms ( $3^{\circ}$ )

DEPT-135

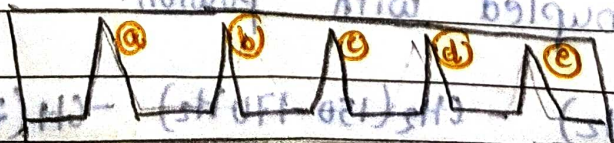
- Positive :-  $1^{\circ}$  &  $3^{\circ}$  - CH<sub>3</sub>
- (upward)
- Negative :-  $2^{\circ}$  - CH<sub>2</sub>
- (downward)



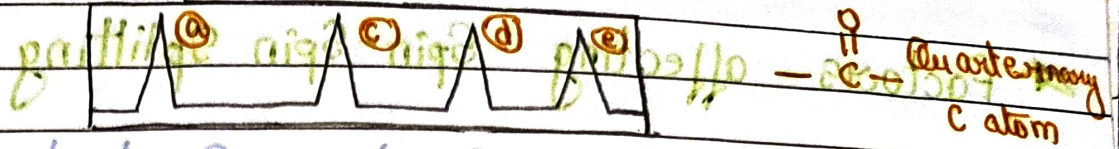
Example :-



$^{13}\text{C}$  NMR



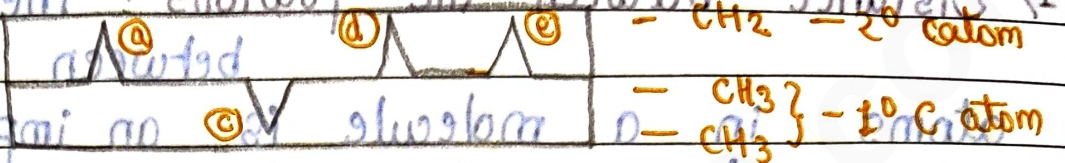
DEPT-45



DEPT-90



DEPT-135



★ Application of <sup>13</sup>C NMR

→ <sup>13</sup>C-NMR helps to elucidate organic and biochemical structures. It provides information about the backbone to molecules rather than periphery. It is often possible to observe individual resonance peaks for each carbon atom in a compound having molecular weight from 200 to 400.

★ Biological Application of NMR Spectroscopy.

→ 1. Structure of Protein and peptides: Biomolecular NMR Spectroscopy can be used to determine the structure of proteins upto a mass of ~50 kDa.

2. Assessment of Protein Conformational Exchange by NMR: Apart from providing the 3D structure of molecules, NMR method also help to identify Protein-Protein interaction for molecular recognition by mapping.

## ★ Factors - affecting Spin-Spin Splitting in NMR :-

The value of the Coupling Constant depends on the following factors:-

1) Distance between the protons :- The distance between the hydrogen atoms in a molecule is an important determinant in the value of J Constant.

If the Hydrogen atoms involved in the coupling are closer to each other, these give rise to a greater value of J Constant than if these atoms are further apart.

2) The Orientation of the Coupled protons :-

The orientation of the Coupled protons and the orientation of the protons with respect to each other is equally important. The value of J Constant is greater in molecules where the H atoms are in the cis Conformation. Conversely it is less when the H atoms are in the trans Conformations.