NUCLEAR MAGNETIC RESONANCE (NMR)

Dr. Susmita Bajpai
Department of Chemistry
BRAHMANAND College,
Kanpur

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- ☐ **Nuclear magnetic resonance is a powerful tool for identification and structure determination of organic molecules.**
- ☐ **It was discovered by Felix Block and Edward Purcell in 1946.**
- ☐ **The field of NMR spectroscopy has been further divided into number of subfields depending upon the magnetic nucleus being examined.**

For example:

- proton magnetic resonance (C^{13}NMR)
- fluorine magnetic resonance (F^{19}-NMR)
- phosphorus magnetic resonance (P^{31}NMR).

- The most common is the PMR and the basic principles of NMR spectroscopy.

MAGNETIC PROPERTIES OF NUCLEI

- Like electrons, the nuclear particles protons and neutrons are also spin about their axis.
- Each proton and neutrons has a spin quantum number of ½ if the protons and neutrons in a nucleus are not paired, the nucleus as a whole will have a resultant nuclear spin, I.
- The numerical value of this nuclear spin quantum number, I depends upon the number of protons and neutrons having parallel and antiparallel spins.

- It is related to the mass number and atomic number as follows :

Atomic mass	Atomic number	Nuclear spin quantum number (I)
odd	Even or odd	$\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$ etc.
Even	Even	O
Even	odd	1, 2, 3……………..etc.

(i) Nuclei such as ${}_{1}\mathrm{H}^{1}$ (proton), ${}^{3}_{1}\mathrm{H}$, ${}^{13}_{6}\mathrm{C}$, ${}^{15}_{7}\mathrm{N}$, ${}^{19}_{9}\mathrm{F}$, ${}^{31}_{15}\mathrm{P}$, all the I = ½:

(ii) Nuclei such as ${}_{2}\mathrm{HB}^{4}$, ${}_{6}\mathrm{C}^{12}$, ${}_{8}\mathrm{O}^{18}$, ${}_{16}\mathrm{S}^{32}$ all have I = 0 ${}_{5}\mathrm{B}^{10}$

(iii) Nuclei such as ${}_{1}\mathrm{H}^{2}$ and ${}_{7}\mathrm{N}^{14}$ have I = 1 which has I = 3

Atomic nucleus in associated with charge it generates a magnetic field along the axis of its spin. Therefore, such a nucleus behaves as a ting bar magnet and has magnetic moment (m).

PRINCIPLE OF NUCLEAR MAGNETIC RESONANCE

- When a nuclear magnet is placed in an external magnetic field, it well experience a torque which will tends to align it with field. Since the nuclear magnet is spinning, it will not align with the external magnetic field but well process round it, with a certain angular frequency ω called the processional frequency or the armor frequency.
- The frequency at which a proton will process will depend upon the strength of the applied magnetic field.

- Stronger the applied field, higher is the processional frequency.
- Since a proton has two allowed spin states (I = + ½ and I= -½), it can process in two principal orientations- one aligned with the applied field (low energy) and the other opposed to the applied field.
- It is possible to induce transitions between these two orientations by irradiating protons with radiowaves of correct frequency.

- When the processional frequency of the nucleus (proton) is exactly equal to the frequency of the electromagnetic radiations, the absorption occurs and the nuclei in lower energy spin state flip to the higher energy spin state. When this occurs the nucleus and the radiofrequency beam are said to be in resonance and this resonance is due to magnetic properties of the nuclei, it is called nuclear magnetic resonance.

- Radio frequency needed for resonance depends upon the strength of the external magnetic field and on the nucleus being irradiated

$$\Delta E = h\nu = \gamma \frac{h}{\alpha\pi} . H_o$$

ΔE = energy difference between the two spin states

h = Planck's constant

γ = gyromagnetic ratio

For a proton the value of γ = 26, 750

- FT (Fourier transform) instruments which are commonly used these days can be used to observe the resonance of nuclei of several different elements in a single instrument.

PMR spectrum- origin of signals

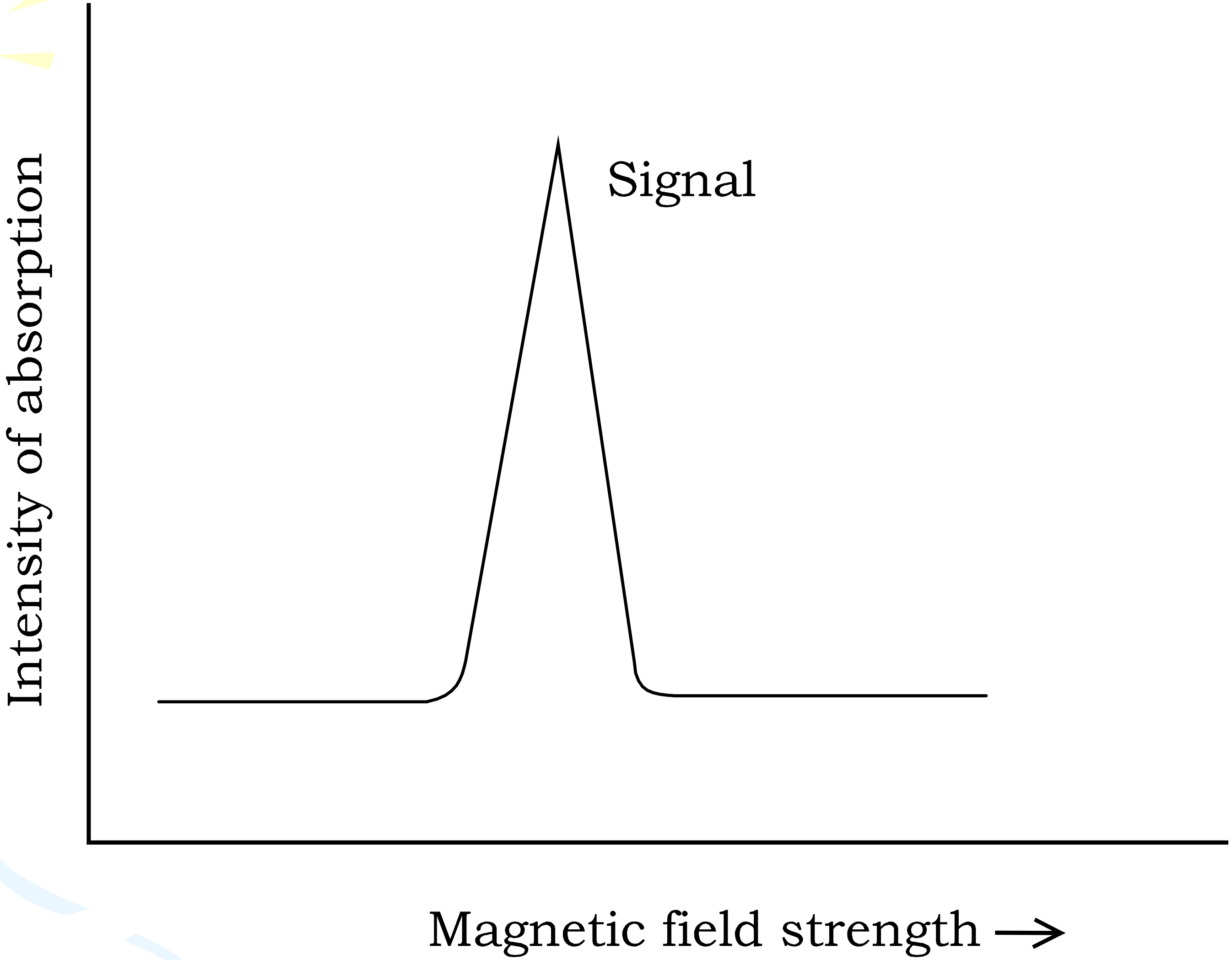
- In principle, a PMR spectrum can be obtained by placing the substance containing hydrogen nuclei or protons in a magnetic field of constant strength and passing electromagnetic radiations of varying frequency through the substance and observe the frequency at which radiation is absorbed.

- In practice, however, it has been found more convenient to keep the frequency of eletromagnetic radiation constant and varying the strength of the magnetic field. At some value of the field strength the energy required to spin the proton matches the energy of the electromagnetic radiations. At this stage absorption occurs and a signal is observed. Such a spectrum is called PMR spectrum.

- In PMR, intensity of absorption is taken along Y-axis and magnetic field strength is taken along X-axis.

$$\upsilon = \frac{\mu H_o}{hI} = \gamma \frac{H_o}{2\pi}$$

This is a relation between magnetic field strength of frequency.



Signals can be expressed in either field or frequency units.

- We know that PMR signal is obtained at some value of the field strength at which the energy required to flip the proton becomes equal to the energy of the electromagnetic radiation. Therefore all protons well absorbs at exactly some field strength, therefore only one signal is obtained it is not true. It has been found that all the protons do not absorb at the same frequency.
- This is due to the reason that the frequency at which a proton absorbs depends upon the magnetic field which proton feels and this effective field strength is not exactly the same as the applied magnetic field.

- This effective field strength depends upon its local environment that is electron density around that proton and the presence of other protons in its neighbourhood.
- Thus it follows that at a given radio frequency, the proton having different environments experience the same effective field strength but absorb at different applied field strength.
- Therefore number of absorption signals are obtained, which is very useful in determining the structure of molecules.

Number of NMR signals-equivalent and non-equivalent protons

- In a given molecule, protons with different environment absorb at different field strength while protons having the same environment absorb at the same applied field strength.
- A set of protons are said to be equivalent if they have the same environment and non-equivalent if they have different environment.
- Therefore the number of signals in an NMR spectrum tells us as to how many different sets of equivalent protons or how many types of protons are present in a given molecule.

- **Examples :**

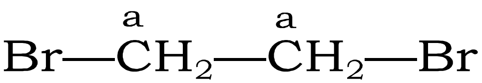
1. CH_3-CH_2-Cl (ethyl chloride). It contains two type of protons and thus gives two signal.

(2)

$\overset{a}{\mathrm{CH_3}}-\overset{b}{\mathrm{CHCl}}-\overset{a}{\mathrm{CH_3}}$

2 Signals

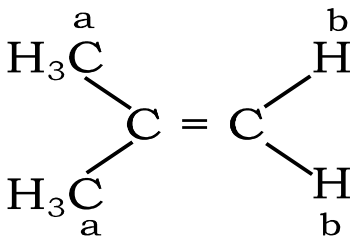
(3)



$\mathrm{Br}-\overset{a}{\mathrm{CH_2}}-\overset{a}{\mathrm{CH_2}}-\mathrm{Br}$

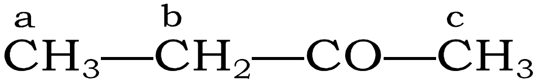
1 Signal

(4)



2 Signals

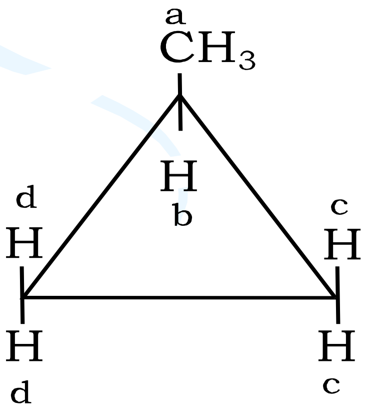
(5)



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

3 Signals

(6)



4 Signals

Position of signals - shielding and deshielding

- The position of signals tells us the actual environments of the various protons and thus indicates the nature of protons, whether the protons are aliphatic (primary, secondary tertiary) aromatic, vinylic, acetylenic or are adjacent to hetero atoms such as oxygen, nitrogen, sulphur, halogens.

- When a molecule is placed in a magnetic field to get its PMR spectrum, the applied magnetic field causes the circulation of electrons surrounding the protons. This circulation of electrons produces a secondary magnetic field called the induced magnetic field. This induced magnetic field may either oppose or reinforce the applied magnetic field.

- Circulation of electrons in σ bonds surrounding the protons generates an induced field which opposes the applied magnetic field on the other hand, circulation of electrons particularly the π electrons generates an induced field which may either oppose or reinforce the applied field acting upon a proton.

For examples:- Circulation of π electron in benzene derivative produces an induced field which reinforce the applied field.

Shielding

- When the induced field opposes the applied field, the actual field acting on the proton decreases and the proton is said to be shielded.
- To get an absorption signal, applied field has to be increased. Thus shielding shifts the absorption upfield.
- **For example** the induced field opposes the applied field at the proton of acetylene.

Deshielding

- When the induced field reinforces the applied field, the actual field acting on proton increases and proton is said to be deshielded.
- To get an absorption signal applied field has to be decreases. Thus deshielding shifts the absorption downfield.
- **For example** it reinforces the applied field at the protons of benzene.

Chemical shift

- The shift in the position of PMR signals resulting through shielding and deshielding by circulation of electrons in chemical bonds is called the chemical shifts.
- Protons in most of the organic compounds absorb over a range of 700 Hz (cps) at a field strength of 14100 Gauss. At this field strength protons absorb at a frequency of about 60 x 10^6Hz.
- The shielding and deshielding of protons by electrons produce very small change in the strength of the applied magnetic field. These small changes in the magnetic field strength cannot be determined accurately. Therefore absolute position of the PMR signal cannot be obtained. Therefore, chemical shifts of protons are expressed in Hz or (cps) with reference to a particular standard.

- The frequency and the strength of the magnetic field are related by the equation

$$\upsilon = \frac{\gamma H_o}{2\pi}$$

- The most commonly used reference for PMR spectroscopy is tetramethylsilane (TMS) $(CH_3)_4Si$. It is chosen as a reference compound for the following reason:-

1. It has 12 equivalent protons, therefore a very small amount of the TMS produces a large single sharp signal.
2. TMS protons absorb at a field much higher than the protons in most of the organic compounds. This is due to the reason that silicon is more electropositive than carbon.
3. It is chemically inert and is also highly volatile (b.p. 300 K). Therefore, after the spectrum has been scanned, the precious sample can be recovered by the removal of TMS by evaporation.
4. It is highly miscible with most of the organic solvents.

Units of Chemical Shift

- The commonly used unit is parts per million (ppm).
- It is dimensionless and are independent of the field strength or oscillator frequency of the instrument.
- It is the function of the chemical environment of the protons in the organic molecule.

Scales of the Chemical Shift

It express in two scales.

(i) The δ (delta) scale

$$\delta = \frac{\Delta\upsilon(\text{Hz})\ \text{x}\, 10^6}{\text{Oscillater frequency (MHz)}}$$

(ii) The τ (tau) scale

$\tau = 10 - \delta$

On the δ scale the position of TMS signal is taken as 0.0 ppm and most of the chemical shifts have δ values between 0-10. Shielded protons have low δ values whereas deshielded protons have large d values.

- On the τ scale, the position of the TMS signal has value 10.0 ppm and most chemical shift have the value between 0-10. Here, a small τ values refers to an adsorption at low field and a high τ value indicates a high field adsorption.

Chemical shifts of different types of protons

- In a given molecule protons with some environment (equivalent protons) have same chemical shifts while protons in different environment (non-equivalent protons) have different chemical shifts.

	Types of proton		Chemical shift δ	ppm τ
1.	Cyclopropane	Δ	0.2	9.8
2.	Primary	$R–CH_3$	0.9	9.1
3.	Secondary	$R_2.CH_2$	1.3	8.7
4.	Tertiary	R_3CH	1.5	8.5
5.	Aromatic	Ar-H	6.0-8.5	1.5-4.0

Factors affecting chemical shifts

- The factors which effect chemical shifts are
    - Inductive effects
    - Hydrogen bonding
    - Anisotropic effects
- **Inductive effects**
- The proton chemical shifts increases as the electronegativity of the atom attached to the carbon atom bearing hydrogen increases. Thus is due to -I effect of the electronegative atom.
- The electron density around the proton decreases which causes deshielding. Thus, higher the electronegativity higher the deshielding and hence higher the d value of the chemical shifts.

For example:

Compound	Element	Electronegativity	Chemical shift
CH_3–C	F	4.0	δ- 4.26 τ- 5.74
CH_3–O	O	3.5	δ- 3.5 τ- 3.40

- Greater the number of halogen atoms, greater in the deshielding

CH_3Cl	CH_2Cl_2	$CHCl_3$
δ 3.0	δ 5.30	δ 7.27

- As the distance of the proton from the halogen increases, the deshielding also decreases.

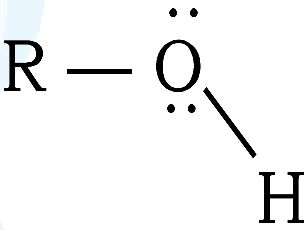
CH_3 — CH_2 — Cl
δ 3.4

CH_3 — CH_2 — Cl
δ 1.7

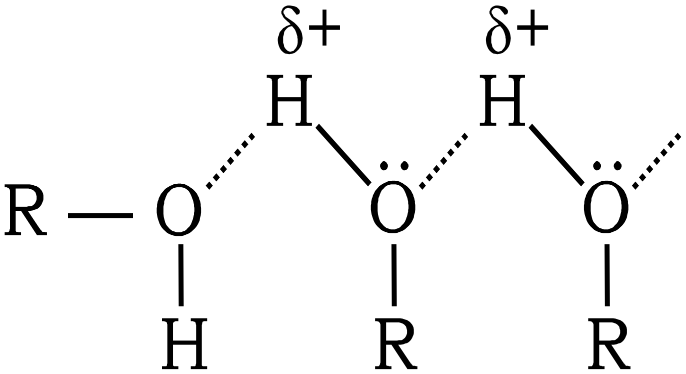
Hydrogen bonding

- Protons which exhibits hydrogen bonding (e.g. —OH and —NH_2 protons) show variable absorption position over a wide range (0.5 - 5.0 ppm) since H– bonding decreases the electron density in the O—H bond, therefore, the proton involved in H–bonding gets deshielding.
- Further stronger the hydrogen bond more deshielded is the proton. The extent of H–bonding depends upon concentration, temperature and nature of the solvent. Thus in concentrated solutions, H– bonding predominates and H– bonded protons appear in the range 4-5 δ.

- But at high dilution H– bonding does not occur and the O–H protons absorb in the range 0.5 - 1.08.



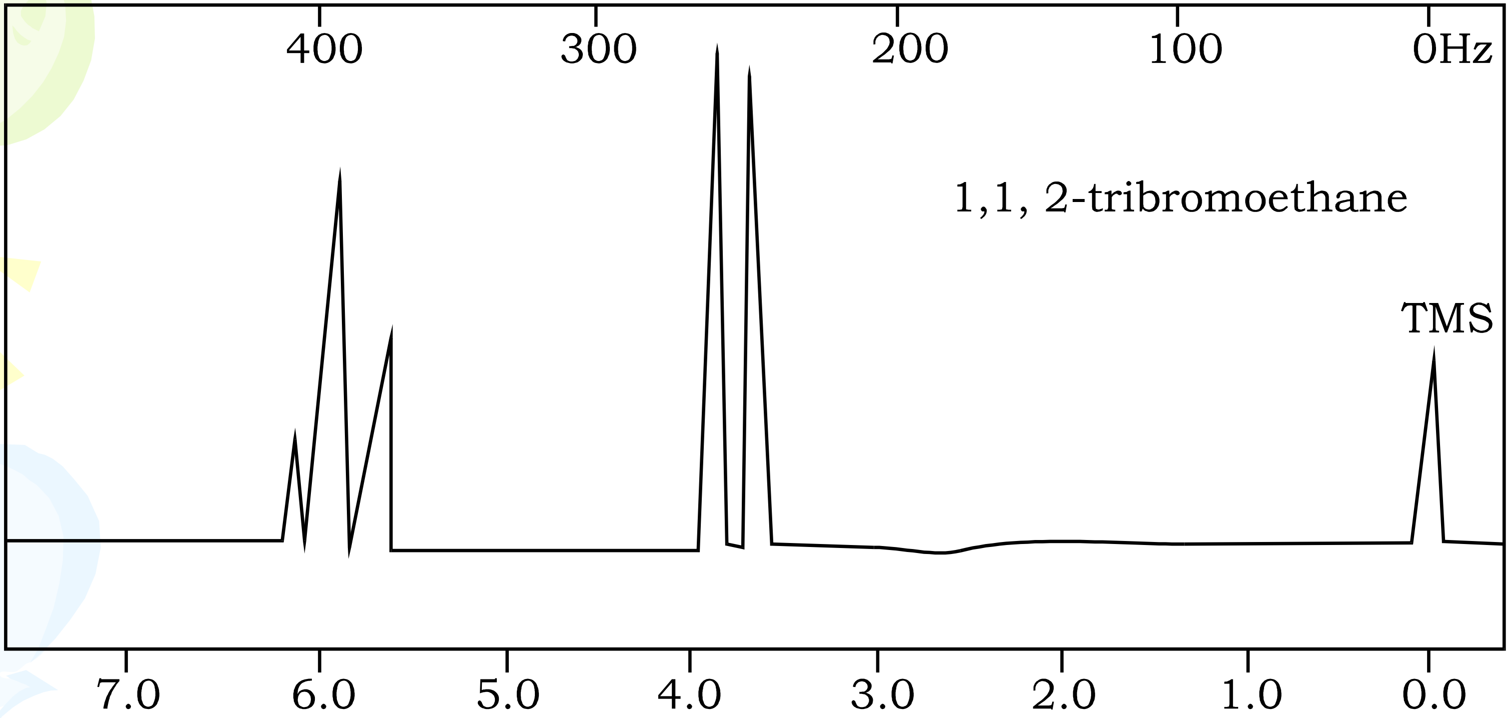
Free (dilue solution)
(0.5-1.0 δ)



Hydrogen bonded (conc. solution)
(4.5 δ)

Splitting of signals - spin-spin coupling

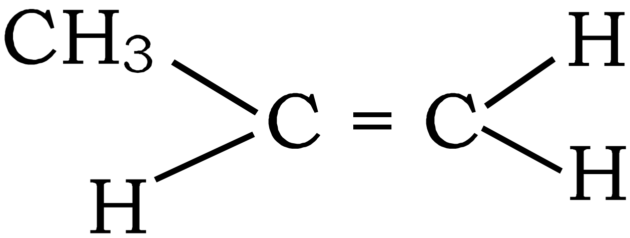
- Every set of equivalent protons gives are PMR signal. But the spectra of most of the organic compounds are much more complicated. **For example :** 1, 1, 2-tribromoethane ($CH_2Br-CHBr_2$).
- This compounds contains two kinds of protons and hence its PMR spectrum to show only two peaks. But spectra of this compound show five peaks.



Thus it follows that the signal from each set of equivalent protons, does not appear as a single peak but appears as a group of peaks. This is commonly known as splitting of PMR signals.

Example:

- In this compound the signal due to methyl proton on C_4 well split into triplet (1:2:1) by the two equivalent protons on C_3. Similarly the due to two equivalent protons on C_3 well be split into quartet by the three equivalent protons on C_4 (1:3:3:1).
- However the signal due to three equivalent methyl protons on C_1 well not be split because there are no protons on the adjacent carbon atom.



- The PMR spectrum of this compound shows three signals. The signals due to the three methyl protons does not split because there are no protons present on the adjacent carbon. Hence it appear as a singlet. However the two vinylic protons although present on the same carbon are magnetically non- equivalent, and hence would split each other signal into a doublet.