

(d)

Radiowaves are considered to be the lowest form of energy. The amount of energy is not sufficient to excite, vibrate or rotate an atom or molecule. The amount of energy available is just sufficient to affect the nuclear spin of the atom in a molecule & hence constitute the most fundamental part of NMR spectroscopy.

Radiofrequency radiation by nuclei is called NMR. It was first developed by E M Purcell & Felix Bloch (1946).

All the nuclei carry a charge. This charge spins on the nuclear axis & this circulation of nuclear charge generates a magnetic dipole along the axis.

A rotating charged sphere has associated magnetic moment with it & hence all the charged particles in the nucleus will make the nucleus to behave like a bar magnet with its magnetic moment along the axis of rotation.

like as these particles have the property to spin on their own axis & each of them has the angular momentum $I = \frac{1}{2} (\hbar/2\pi)$ in accordance with the quantum theory.

Like all bar magnets, the proton will respond to the influence of external magnetic field & will tend to align with that of the field. Because of quantum restrictions, the proton can adopt 2 orientations with respect to the external magnetic field - either aligned with the field (lower energy state) or opposed to the field (higher energy state). These 2 orientations are called parallel to antiparallel.

The precessing proton will only absorb energy from the RF region source. If the precessing frequency ω_{RF} is the same as the frequency of the RF beam, the nucleus & the RF beam is said to be in resonance. Hence the name NMR.

THEORY OF NMR:

The only nuclei that exhibit NMR phenomenon are those for which the spin quantum no I is greater than zero. The spin quantum no I is associated with mass number & atomic number of the nuclei as follows.

<u>Mass no</u>	<u>Atomic no</u>	<u>Spin quantum no</u>
ODD	ODD OR EVEN	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$
EVEN	EVEN	0
EVEN	ODD	1, 2, 3, ...

The nucleus of 1H , the proton has $I=\frac{1}{2}$ whereas ^{12}C & ^{16}O have $I=0$ & therefore non-magnetic. Other important magnetic nuclei that have been studied extensively by NMR is ^{11}B , ^{13}C , ^{14}N & ^{15}N , ^{17}O , ^{19}F & ^{31}P .

Under the influence of an external magnetic field, a magnetic nucleus can take up different orientations with respect to that field, the no. of possible orientations is given by $[2I+1]$ so that for nuclei with spin 1H , ^{13}C , ^{19}F ($I=\frac{1}{2}$) only 2 orientations are allowed. Deuterium & ^{14}N have $I=1$ so that they can take up three orientations.

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For a proton $I=\frac{1}{2}$ there are 2 possible orientations parallel & antiparallel field, characterized by energies

$$E_1 = +\frac{1}{2} \mu B_0 \quad E_2 = -\frac{1}{2} \mu B_0$$

Energy difference between them

$$\boxed{\Delta E = E_1 - E_2 = \mu B_0}$$

$\mu \rightarrow$ mag. moment of spinning nuclei

$B_0 \rightarrow$ strength of the external field.

Applying Bohr frequency relation $\Delta E = h\nu$ we have

$$\nu = \frac{\mu B_0}{h}$$

Energy will be absorbed from the radio frequency field at frequency ν , if condition $E=h\nu$ is fulfilled.

This equation is the basic NMR equation & would imply that all protons would resonate at the same field & frequency.

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The fundamental equation for NMR correlating electro-magnetic frequency with magnetic field strength can be expressed as

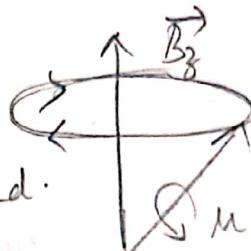
$$\nu = \frac{\gamma B_0}{2\pi} ; \quad \gamma = \frac{2\pi \mu}{hI}$$

The constant γ is called gyro-magnetic ratio or magnetogyric ratio & is characteristic of any nuclear species that has a finite value of I .

It is a fundamental nuclear constant.

LARMOR PRECESSION

Larmor precession of a nucleus in a mag. field.



It is a term used in honour of the mathematician Sir J. Larmor.

A nucleus having a magnetic moment $\underline{\mu}$ can behave as a bar magnet which spins on its axis. In the presence of the mag. field, B_0 the interaction of $\underline{\mu}$ with B_0 produces a torque. This torque causes $\underline{\mu}$ to precess about B_0 as shown in Fig. This phenomenon is called Larmor precession & the angular frequency is called Larmor precessional frequency, ω expressed in radians per second.

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- Mathematically Larmor frequency is given by

$$\boxed{\omega = \gamma B_0}$$

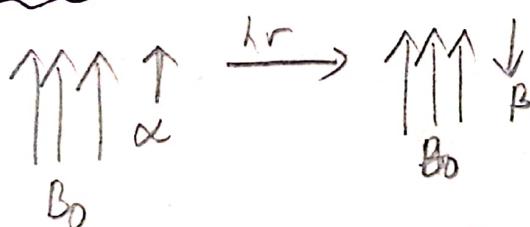
\rightarrow ~~ge~~ magnetic ratio of the nucleus.

It is defined as the ratio of the nuclear magnetic moment μ & the nuclear spin angular momentum $I(h/2\pi)$

$$\gamma = \frac{\mu}{I(h/2\pi)}$$

It is expressed in terms of radians T^{-1}, s^{-1}

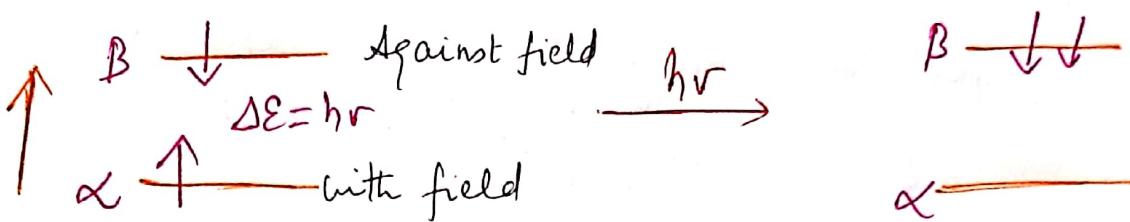
FLIPPING - THE ORIGIN OF NMR SIGNAL



When the compound in the applied field is irradiated with electromagnetic radiation of proper frequency, a nucleus with α -spin can absorb a photon & gets converted to β -spin state. This process is called flipping.

The energy required to bring about the transition or to flip the proton depends on the strength of the applied external field. Since,

$$\nu = \frac{\gamma B_0}{2\pi}$$



Energy required to flip a proton from its lower energy state (ie with the field) to its higher energy state (ie against the field) is supplied by electromagnetic radiation in the radio frequency region.

When the absorption of energy occurs at a frequency that causes flips, the nuclei is said to be in resonance with the electromagnetic radiation. This terminology is the origin of the name Nuclear magnetic resonance.

ΔE is the energy difference b/w the 2 states & is prop. to the strength of the applied field.

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Greater the applied field, the greater the energy gap b/w the possible states of the proton.

A proton in the lower energy state can be promoted to the higher energy state by applying the energy ΔE . When expressed in terms of frequency

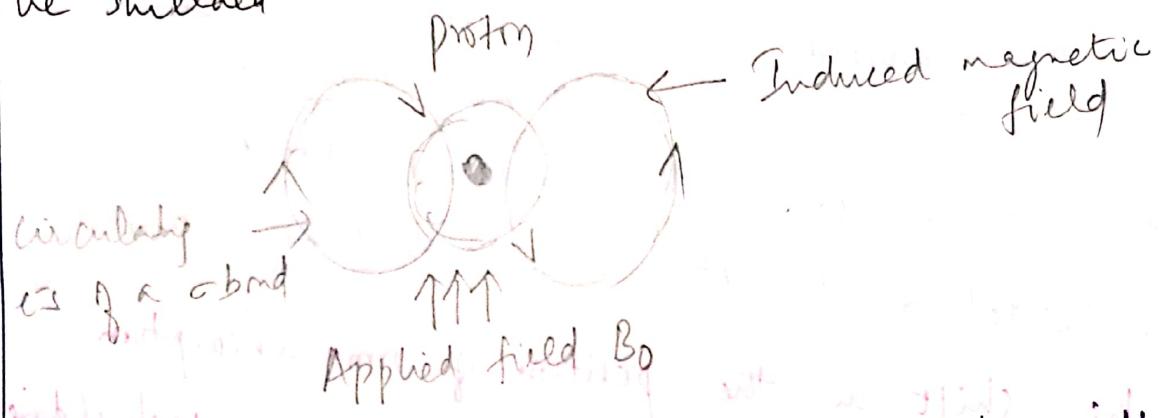
$$\Delta E = h\nu = 2\mu B_0$$



In the NMR technique, radiofrequency is kept constant. Ex. at 60MHz & strength of the mag. field is varied. At certain value of applied field strength, depending on the nature of the proton or nucleus, the energy required to flip the proton matches the energy of radiation. As a result, absorption takes place & a signal is observed in the spectrum. Such a signal or peak is called NMR Spectrum.

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Electrons circulate under the influence of a magnetic field & in doing so, generate their own magnetic field (called the secondary mag. field or Induced mag. field) opposing the applied mag. field; Circulation of e^- about the proton itself generates a field aligned in such a manner that at the proton it opposes the applied field. Hence the field actually experienced by the proton is diminished & the proton is said to be shielded.



If circulation of e^- of a C-H bond under the influence of an external mag. field, the e^- circulation generate a magnetic field (an Induced field) that shields the proton from external field.

(W)

In order for NMR to occur the proton has to flip its spin from lower energy level to higher energy level. In other words, it has to change its spin from \uparrow to \downarrow . If the induced mag. field reinforces the applied mag. field, a small external field will be needed for flipping the spin of the proton. Such a proton is said to be deshielded & the absorption is said to be downfield.

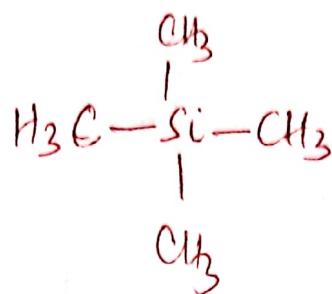
If the induced mag. field, opposes the external mag. field, the stronger mag. field will be required to flip the proton. The proton is said to be shielded & absorption is said to be upfield.

The shift in the position of nmr absorption which arises due to shielding or deshielding of protons by the es are called chemical shifts.

The chemical shift is used for the identification of functional groups & aid in determining structural arrangement of groups.

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These chemical shifts are measured with reference to a standard TMS (Tetramethyl silane)



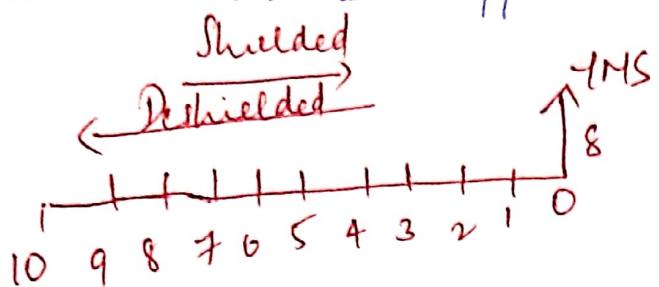
- a) It is chemically inert & soluble in most organic solvents.
- b) All of its hydrogen atoms remain in identical environment & they are more strongly shielded than the protons in any purely organic compound.
- c) TMS is highly volatile & therefore easily removed, removed, if sample has to be recovered.

G. E. H. Lieb introduced the τ or (t) scale, to define the chemical shift from internal TMS. The (t) scale is used for recording the chemical shifts in a variety of solvents. The position of TMS on the chemical shift scale is arbitrarily assigned the δ value of 0.

The two scales are related by the expression

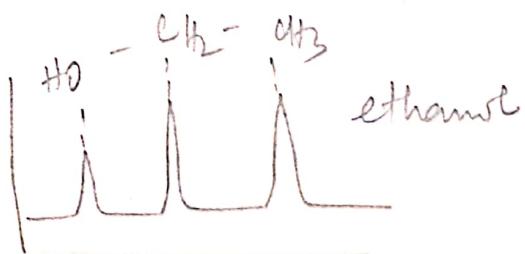
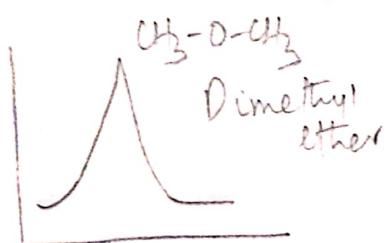
$$\boxed{\tau = 10 - \delta}$$

In the τ scale, signal for the standard reference is taken as 10 ppm.



NMR Signal is usually plotted with magnetic field strength increasing to the right. Signal for TMS appears to the extreme right of the spectrum with $\delta = 0$ ppm. Greater the deshielding of the protons, larger will be value of δ .

Position of signals in NMR Spectrum.



All protons in an organic molecule, at a given radio frequency may give NMR signals at diff. applied field strengths. It is this applied field strength that is measured against which absorption is plotted. As a result an NMR

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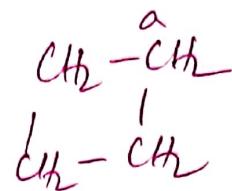
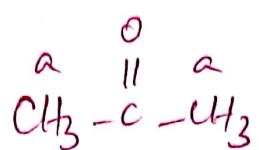
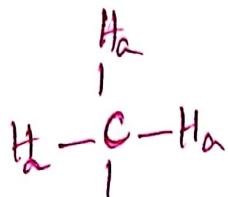
Spectrum is obtained which shows many absorption signals or peaks whose relative positions give vital information regarding the molecular structure.

The no. of signals or peaks signify how many diff. kinds of protons (equivalent & non-equivalent) are present in the molecule. The position of the signals tells us about the electronic environment of the diff. types of protons present. The shift in position is known as chemical shift. The intensity of signals tells us about the diff. kinds of protons present.

The splitting of a signal into several peaks or hyperfine structure tells us the no. of protons in the adjacent positions. The $n+1$ rule operates for proton-proton influence where the presence of n protons in the neighbouring position splits the main peak into $n+1$ components.

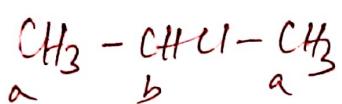
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A set of protons with the same environment is said to be equivalent protons.



One NMR signal.

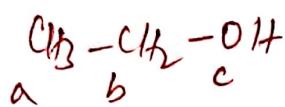
In CH_4 all the four hydrogens are equivalent because all bond distances & bond angles are equal & all four hydrogens are in equal & identical environment. This is true in the case of ethane. But in propane, there are six equivalent 1° (primary) hydrogens & 2° (secondary) equivalent hydrogens.



(2 NMR signals)

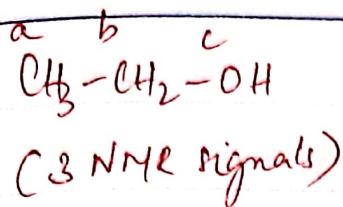


3 NMR signals



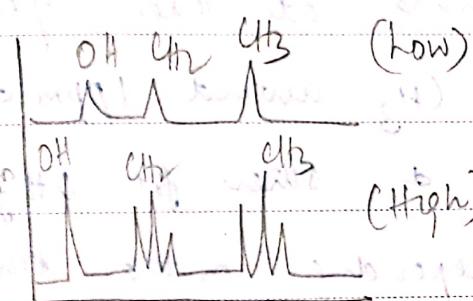
(3 NMR signals).

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(Benzene)
 1NMR signal

In ethyl alcohol $\text{CH}_3-\text{CH}_2-\text{OH}$, the nuclei of carbon & oxygen atoms have zero nuclear spin & will not produce any nuclear magnetic spectra. However hydrogen atom has spin quantum no. of $\frac{1}{2}$ & hence it would give a single absorption frequency.



At low resolution as many as three absorption peaks are actually obtained.

This is due to the fact that diff. hydrogen nuclei exist in the molecule in diff. environments. As a consequence each type of hydrogen atom interacts differently with the applied magnetic field.

At high resolution, a fine structure is obtained. In the case of CH_3 group produces four closely packed absorption lines & CH_2 group three.

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These fine structures are due to interaction b/w the various protons. The CH_3 group is adj. to CH_2 group.

NMR Spectrum of Ethanol.

The chemical shift provides information about the structure of the molecule.

In the ^1H NMR spectrum of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$). One would expect signals at three specific chemical shifts. one for CH_3 around 1 ppm & one for CH_2 around 4 ppm & other for OH group anywhere b/w 2-6 ppm depending on the solvent used & amount of hydrogen bonding.

Pascal's triangle gives the relative intensity of multiplets.

A triplet has relative intensity

$\begin{array}{ccccccc} & & 1 & & 1 & & \\ & 1 & & 1 & & 1 & \\ 1 & & 1 & 2 & 1 & & \end{array}$ A doublet has 1:1

$\begin{array}{ccccccc} & & 1 & & 2 & & 1 \\ & 1 & & 3 & & 8 & \\ 1 & & 1 & 3 & 6 & 4 & 1 \end{array}$ A triplet has $\rightarrow 1:2:1$

$\begin{array}{ccccccc} & & 1 & & 4 & & 1 \\ & 1 & & 4 & & 6 & \\ 1 & & 5 & 10 & 10 & 5 & 1 \end{array}$ quartet $\rightarrow 1:3:3:1$

quintet $\rightarrow 1:4:6:4:1$

Coupling to n equivalent nuclei splits the signal to $(n+1)$ multiplet with intensity ratios following Pascal's triangle.

The CH_3 group is split into a triplet with an intensity ratio of 1:2:1 by two neighbouring CH_2 protons. The CH_2 is split into a quartet with an intensity ratio of 1:3:3:1 by three neighbouring CH_3 protons.

In principle, the 2 CH_2 protons would also be split up into a doublet by the hydroxyl proton, but intermolecular exchange of the andri hydroxy proton results in a loss of coupling information.