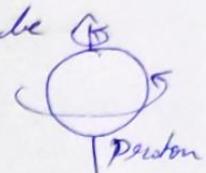


# Unit-1: Nuclear Magnetic Resonance Spectroscopy (NMR) ①

- Interaction b/w matter & EMF observed by subjecting to 2 magnetic fields (1 stationary & other varying at some radio freq).
- At a particular combination of fields, energy is absorbed by sample and this change can be observed as signal developed by RF detector & amplifier. This energy absorption can be related to magnetic dipole nature of spinning nuclei.
- Radio waves are lowest form of EMR. (only sufficient to affect the nuclear spin of atom/molecule)



- Spectra may be described in terms of 3 imp factors.
  - ① Frequency of spectral lines/bands
  - ② Intensity
  - ③ Sp Shape of SL/B.
- ↳ The above properties depend on the molecular parameters
  - ① Shielding constant of nuclei
  - ② Coupling constant
  - ③ Lifetime of energy level.

→ All nuclei carry charge - which creates magnetic dipole along axis.

→ Protons & neutrons (like  $e^-$  - they have property to spin & possess angular momentum  $\frac{1}{2} (h/2\pi)$  in accordance with quantum theory.

The net resultant of angular momentum of all nuclear particles is called nuclear spin.  $I$  = nuclear spin quantum number.

For a nucleus there are  $(2I + 1)$  spin states. 3 principles for  $I$

- ① If the sum of protons & neutrons is even ( $I$  is 0 or integral)
 

Ex:  $^{12}\text{C}$ ,  $^{16}\text{O}$ ,  $^{18}\text{O}$ ,  $^{32}\text{S}$  etc. (equal no. of protons & neutrons)
- ② If the sum of protons & neutrons is odd ( $I$  is half integral)
 

Ex:  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  have  $I = 1/2$  (uniform charge distribution)

"B",  $^{35}\text{Cl}$ ,  $^{79}\text{Br}$ ,  $^{81}\text{Br}$  have  $I = 3/2$
- ③ If protons & neutrons are even numbered ( $I = 0$ ) No NMR signal

Magnetic properties occur with nuclei having

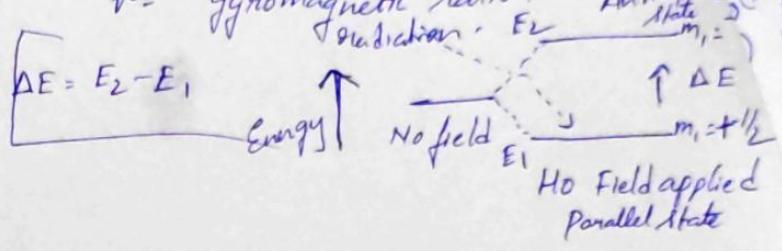
- ① odd atomic no. & odd mass no. Ex:  $^1\text{H}$ ,  $^{15}\text{N}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  -  $I = 1$
- ② odd " " even " " Ex:  $^1\text{H}$ ,  $^{14}\text{N}$  -  $I = 1/2, 3/2$
- ③ Even " " odd " " Ex:  $^{13}\text{C}$  -  $I = 1/2, 3/2$

Spin Angular momentum :  $= \left[ -I(I+1) \right]^{1/2} \frac{h}{2\pi}$   $h = \text{Planck's const}$

$\mu = \gamma \times \text{SAM}$   
 $\mu = \gamma \times \left[ I(I+1) \right]^{1/2} \frac{h}{2\pi}$

$\mu =$  magnetic moment  
 $\gamma =$  gyromagnetic ratio

→ Freq. at which energy is absorbed/emitted given by Bohr's relationship.

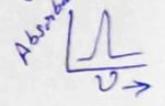


$\nu = \frac{E_2 - E_1}{h}$

$\nu = \frac{\frac{1}{2} \left( \frac{\gamma h}{2\pi} \right) H_0 + \frac{1}{2} \left( \frac{\gamma h}{2\pi} \right) H_0}{h} = \frac{\gamma}{2\pi} H_0$

→ Freq. ( $\nu$ ) abs/emitted by nucleus in moving from one energy level to another  $\propto$  applied magnetic field. In NMR it is absorption of energy is detected.

→ State of resonance - continuous excited & unexcited state of nucleus.  
 → To determine resonance freq. energy absorbed by nuclei is measured as the mag. field  $H_0$ .  $H_0 \uparrow$  to  $\uparrow$  precessional frequency ( $\nu$ ) & when this equals to freq. ( $\nu$ ) of oscillation field transition occurs b/w nuclear energy states.

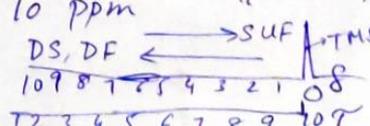


Chemical Shift: The shift in position of NMR signal (compared to standard reference) resulting from the deshielding & shielding by electrons are referred to as chemical shift.

→ The freq. at which nucleus comes into resonance in a mag field may be given by eq.  $\nu = \frac{\gamma}{2\pi} H_0$ .  
 → The position of the peaks in an NMR spectrum relative to the reference peak is expressed in terms of chemical shift 'δ'.

$\delta = \frac{H_0(\text{reference}) - H_0(\text{sample})}{H_0(\text{reference})} \times 10^6 \text{ ppm}$

→ δ is dimensionless & expressed in ppm. In terms of freq.  $\delta = \frac{\nu}{\nu_{\text{ref}}} \times 10^4 \text{ ppm}$ .  
 → Also measured in Tau scale (τ)  $\tau = 10 - \delta$  (reference position at 10)  
 on δ scale TMS signal is at 0.0 ppm & other values from (0-10)  
 on τ " " " " at 10 ppm " " " " (0-10)



Chatwal

= Tetramethyl silane  $(CH_3)_4SiCH_3$  - It gives only one signal. (2)

- a) Chemically inert, magnetically  $CH_3-Si-CH_3$
- a) Volatile & soluble in most org. solvents.  $CH_3$
- b) All H atoms in identical environment & are more strongly shielded than protons in any other organic comp.
- c) Since all 12 methyl H atoms are equiv. a strong signal / sharp absorption peak is obtained.
- d) TMS protons resonate at high field. Low electronegativity of Si & 4  $CH_3$  cause max. electron density & powerful shielding effect.
- e) Does not make any intermolecular association in sample.
- f) When water /  $D_2O$  used as solvent, TMS is used as external reference. (sealed in capillary immersed in the solution)

NMR Spectrum =  
 No. of signals = different kinds of p.  
 Position of signal = what kind of protons

Other reference are :- 2,2-dimethyl-2-silapentane-5-sulphonate (DSS), cyclohexane, dioxane, chloroform.



- Shielding & Deshielding:  
 $e^-$  present close to proton & those in neighbouring bonds
- deshielded / downfield more applied field than induced field by  $e^-$   $\uparrow$  Ho Applied field.
- Shielded / upfield
- peak area  $\propto$  no. of protons; But due to shielding  $\rightarrow$  different absorption position.

B. K. Sharma

Factors Influencing Chemical Shift - Chemical

① Inductive Effect: <sup>Electronegative effect</sup> The shielded protons needs a stronger applied field to produce the absorption signal or absorption takes place upfield. But when  $e^-$  density around the proton is reduced because of inductive effect of neighbouring electronegative atom, the shielding effect is reduced. Deshielding will take place, so that a similar value of applied field will be produced a signal.

- Ex: ①  $e^-$  with drawing groups (EN atoms)  $\rightarrow$  reduce  $e^-$  density  $\rightarrow$  deshielded.
- Ex: ② Proton in  $CH_3OCH_3$  show signal more downfield than  $CH_3-CH_3$  (protons in)

n-Sp  
Nuclei

Ex 3) EN atoms nearness to proton & deshielding.  
 Protons in  $CH_3-F$  deshield more than in  $CH_3-Cl$ .  
 $\rightarrow CH_3 \overset{b}{C}H_2 d$  " " " " labelled 'a' than proton labelled 'b'.

2) Anisotropic Effects :  $\rightarrow$  Space effect

$\rightarrow$  Circulation of  $e^-$ , especially the  $\pi e^-$  about nearby nuclei generates an induced field which can oppose (cause shielding) or reinforce (deshielding) the applied field at the proton, depending upon the location of proton or space occupied by proton.

Ex: - In alkynes - shielding.  
alkenes, benzene, aldehydes - deshielding  
 (In benzene, because of  $\pi e^-$  cloud there is large induced field when in strong magnetic field. The induced field will be in opposite direction to applied field. This is called ring current effect)

$\rightarrow$  Two signals are obtained - 1 from aromatic ring hydrogen (low field/deshielded) other from H atom above the plane (high field/shielded)

Ex 1)

Ex 2)

Ex 3)

3) Hydrogen Bonding :

$\rightarrow$  H atom exhibiting property of HB in a Comp. absorb at low field  
 $\rightarrow$  HB proton attached to a EN atom will have smaller  $e^-$  density around it.  
 $\rightarrow$  As it is deshielded the field felt by such proton will be downfield  
 $\rightarrow$  The downfield shift depends upon strength of HB

Alkene bond rotates plane of  $=$  is at  $90^\circ$  to direction of applied field.  
 $\rightarrow$  Induced circulation of  $\pi e^-$  generates 2<sup>o</sup> mag field which is diamag around C atoms, but paramag in region of alkene protons.  
 $\rightarrow$  Protons come to resonance at higher  $\delta$  values.  
 $\rightarrow$  Any group held above or below the plane will experience shielding effect. Induced field opposes  $H_0$

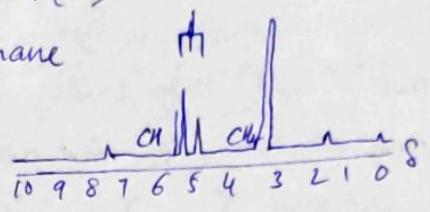
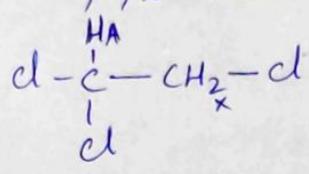
Ex 3) Aromatic ring current

Group	$\delta$ values
① $C=O$	$\rightarrow 9.5 - 10$
② $C=C$	$\rightarrow 4 - 8$
③	$\rightarrow 6 - 9$
④ $-C \equiv C-H$	$\rightarrow 1.5 - 3.5$

### n-Spin Coupling :

- Nuclei can interact with each other to cause mutual splitting of sharp resonance lines into multiplets, called spin-spin coupling.
- The no. of lines, <sup>(multiplicity)</sup> observed in NMR signal is not related to no. of protons in that group, it is related to no. of protons in neighbouring groups.
- (n+1) rule : To find multiplicity of the signal from group of protons, count the no. of neighbours (n) and add 1.

Ex: 1,1,2-Trichloroethane

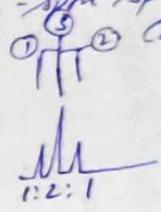


H<sub>X</sub> - Two line signal (doublet) One neighbour  
 H<sub>A</sub> - 3 lines (triplet) Two neighbours

→ Splitting of spectral lines arises because of coupling interaction b/w neighbour protons, and is related to no. of possible spin orientations the neighbour can adopt. This phenomenon is called spin-spin splitting / coupling.

3 possible combinations of neighbour protons gives rise to triplet.

- ① Both Parallel to A (↑↑)
  - ② Both Antiparallel to A (↓↓)
  - ③ one parallel (↑↓) or (↓↑)
- The coupling constant: J



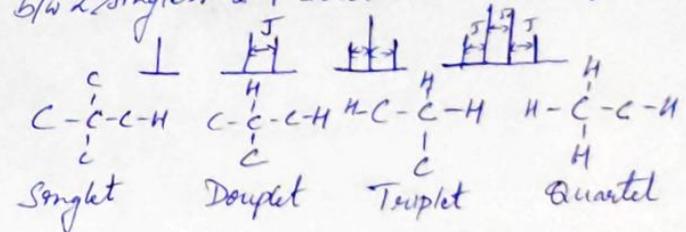
Splitting of one adjacent proton gives 1:1 doublet.

2 adj. protons gives 1:2:1 triplet

### Coupling Constant :-

- The distance b/w centres of two adjacent peaks in a multiplet is constant and is called coupling constant. Denoted by 'J' & measured in Hertz (Hz) or cps
- Value of J is independent of external field.
- Can be distinguished b/w 2 singlets & 1 doublet & also a quartet from 2 doublets.

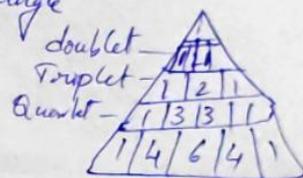
J can be determined by measuring the spectrum at 2 different radiofrequencies.



- If separation b/w lines does not change, the signal indicates doublet.
- " " " increases & ↑ ν then it is 2 singlets.

General Rules to Summarize Imp. requirements and characteristics spin  $1/2$  nuclei.

- 1) Nuclei having same chemical shift (isochronous), do not exhibit spin splitting, they may be spin coupled.
- 2) Nuclei separated by 3 or fewer bonds will be spin coupled, show same  $J$ , & different chemical shift ( $\delta$ )  
Longer range coupling in mol. having rigid configuration of atoms.
- 3) Magnitude of spin-splitting is given by  $J$ ,  $J$  is same for both partners & is independent of ext. mag. field
- 4) Splitting pattern of given nucleus (equivalent nuclei) can be given by  $(n+1)$  rule, with similar  $J$ . Two neighbouring nuclei then  $2+1=3$   
→ Central line of splitting pattern is stronger than those on periphery. which gives triplet...  
The intensity ratio can be given by Pascal's triangle



Relaxation :-

- 1) Spin-lattice / longitudinal relaxation: transfer of energy from <sup>nucleus on</sup> higher energy state to <sup>molecular lattice</sup> spin lattice relaxation time :-  
 $T_1 =$  avg. life time of nuclei on higher energy state.  
Energy = translational, vibrational, rotational. Total energy of system remains same.  
→ In cryst. solids & vis liq  $\neq$  mobility is low,  $T_1$  is large.  
 $T_1$  is largely effected by mobility of the lattice.
- 2) Spin-spin Relation: Mutual exchange of spin by 2 precessing nuclei  $\subset$  are close proximity & each other. Transverse RT  $T_2$ . →  $T_2$  is small for <sup>crystalline</sup> solids / vis liq.

### Width of Absorption Lines in NMR

The width of absorption line (ie, the frequency range over which absorption take place) is affected by no. of factors :-

① The Homogenous field: The  $H_0$  be constant over all parts of the sample which may be 1-2m. long.  
 - If  $H_0$  is not even, the freq( $\nu$ ) of the absorbed radiation will vary in diff. parts of sample, which results in wide absorption line. For qualitative & quant. analysis a WAL is very undesirable, since we may get overlap of neighbouring peaks.

② Retention Time:  
 → The process of losing energy is called relaxation.

→ The time spent in the excited state is the relaxation time.  
 $\Delta E \Delta t = \text{Constant}$   
 $\Delta t = \text{length of time a nucleus spends in the excited state.}$

$\Delta t$  is small.  $\sim \Delta E$  is large.  $h = \text{constant}$   
 $E = h\nu$

$E + \Delta E$ , then  $\nu \neq \Delta \nu$ ,  $E + \Delta E = h(\nu + \Delta \nu)$

When  $\Delta t$  is small,  $\Delta E$  is large &  $\Delta \nu$  is large.

a) Longitudinal Relaxation:  $T_1$

→ When nucleus loses its excitation energy to the surrounding molecules, the system becomes warm as the energy is changed to heat. The process is fast when molecules are able to move quickly (as in liq).  
 → No radiant energy appears, no other nuclei become excited.  
 → As numerous nuclei lose their energy, the temperature of the sample goes up. This process is called LR ( $T_1$ ).

b) Transverse Relaxation:  $T_2$

→ An excited nucleus may transfer its energy to an unexcited nucleus of similar molecule that is nearby.  $E_M \rightarrow U_E$ ,  $U_E \rightarrow E_N$ . There is no net change in energy of the system, but the length of time that

One nucleus stays excited is shortened. This process called  $TR - T_2$ .

→ Liq. samples  $T_2$  is long & narrow absorption lines  
 Solid " " " very short,  $\Delta E$  &  $\Delta V$  are large,  
 due to which wide absorption lines are obtained, &  
 solid samples cannot be examined directly by NMR  
 without prior treatment.

③ Magic Angle NMR: when one rotates a solid sample such that its axis of rotation is  $54.7^\circ$  (the magic angle) to the direction of applied magnetic field, the broadening caused by random nuclear orientations tends to be averaged out resulting in narrower spectra. It is very informative of the functional groups and their positions relative to each other in sample molecules.

### Instrumentation of NMR

① The Magnet: Supply  $H_0$

→ Electromagnet / Permanent magnet  
 → Must have high degree of homogeneity of pole pieces & freq. of 1 part in  $10^8$  within the sample area.

→ Frequency of  $100 \times 10^6$  CPS & fields of 23490 gauss are used.

② The Magnetic field Sweep: An alteration over a small range in the applied field may be made by using a pair of coils (Helmholtz coils) located parallel to magnet face (poles).

③ Radio frequency source: Radio freq. oscillator is used. Perpendicular to applied mag field.

④ Signal detector & Recording system / Radio freq. Receiver → Measure absorption spectrum

⑤ Sample holder — Chemically inert, durable & transparent to  $\gamma$  radiation

⑥ Sample probe — Glass tubes — 8.5 cm long & 0.3 cm diameter  
 holds the sample tube in fixed position in field.  
 & provided with air driven turbine for rotating along long axis at several hundred RPM

