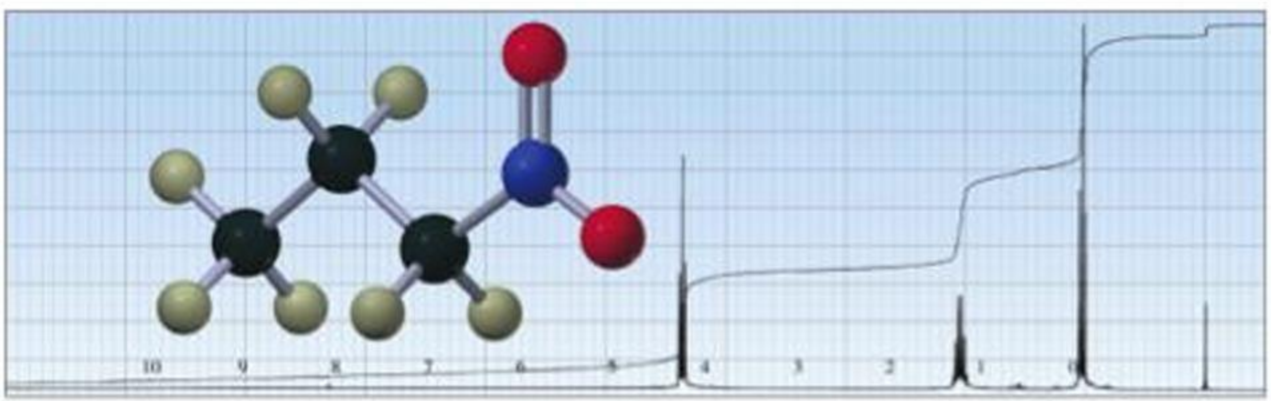
NUCLEAR MAGNETIC RESONANCE (NMR)



1-Nitropropane

Introduction:-

Nuclear Magnetic Resonance (NMR) is a spectroscopy technique which is based on the absorption of electromagnetic radiation in the **radio frequency region 4 to 900 MHz** by nuclei of the atoms.

Proton Nuclear magnetic resonance spectroscopy is one of the most powerful tools for elucidating the number of hydrogen or proton in the compound.

It is used to study a wide variety of nuclei:

- ^{1}H ^{15}N
- ^{19}F
- ^{13}C ^{31}P

Theory of NMR:-

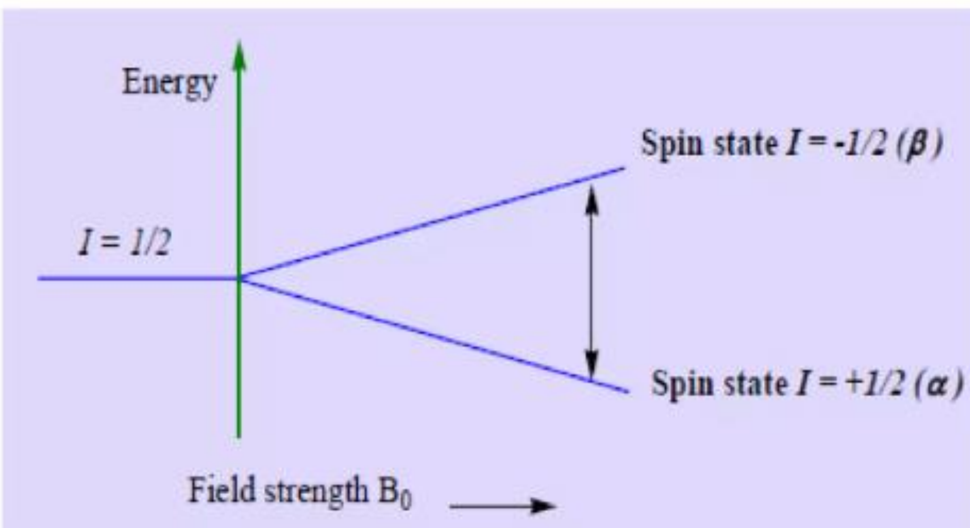
Spin quantum number (I) is related to the atomic and mass number of the nucleus.

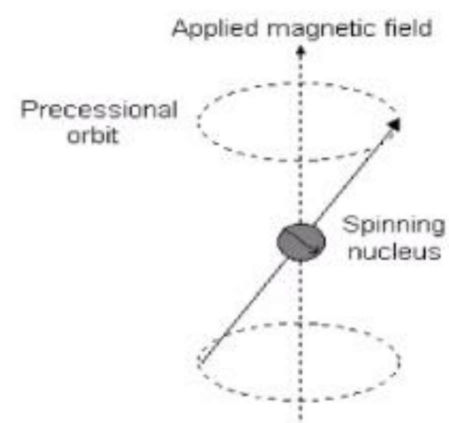
I	Atomic Mass	Atomic Number	Examples	
Half-integer	Odd	Odd	^{1}H (1/2)	NMR active
Half-integer	Odd	Even	^{13}C (1/2)	
Integer	Even	Odd	^{2}H (1)	
Zero	Even	Even	^{12}C (0)	Not NMR active

Elements with either odd mass or odd atomic number have the property of nuclear "spin".

If an external magnetic field is applied, the number of possible orientations calculated by **(2I+1).**

Hydrogen has spin quantum number **I=1/2** and possible orientation is (2*1/2+1=2) two **+1/2** and **-1/2.**

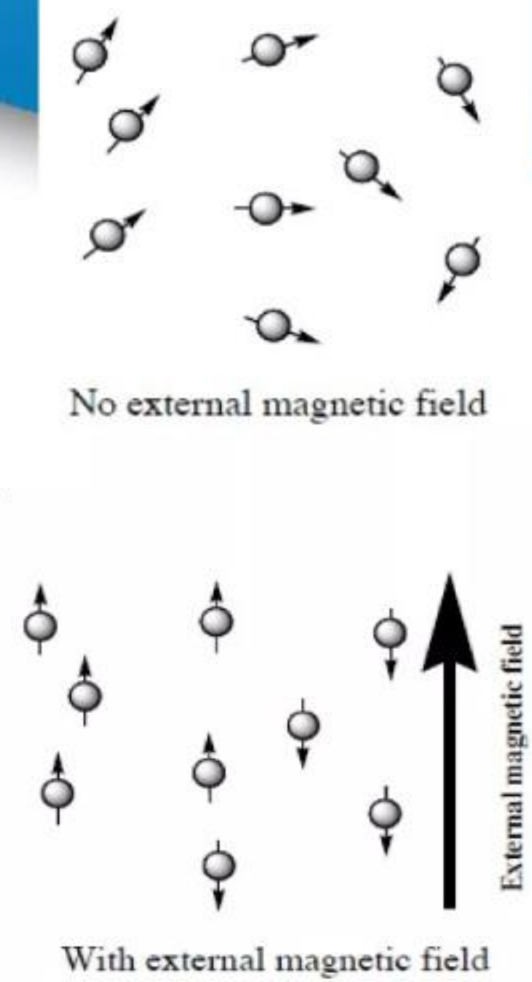




Principles of NMR

The theory behind NMR comes from the spin of a nucleus and it generates a magnetic field. Without an external applied magnetic field, the nuclear spins are random in directions.

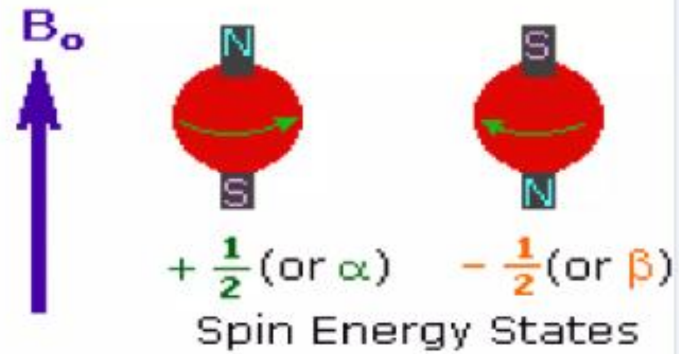
But when an external magnetic field(B_o), is present the nuclei align themselves either with or against the field of the external magnet.

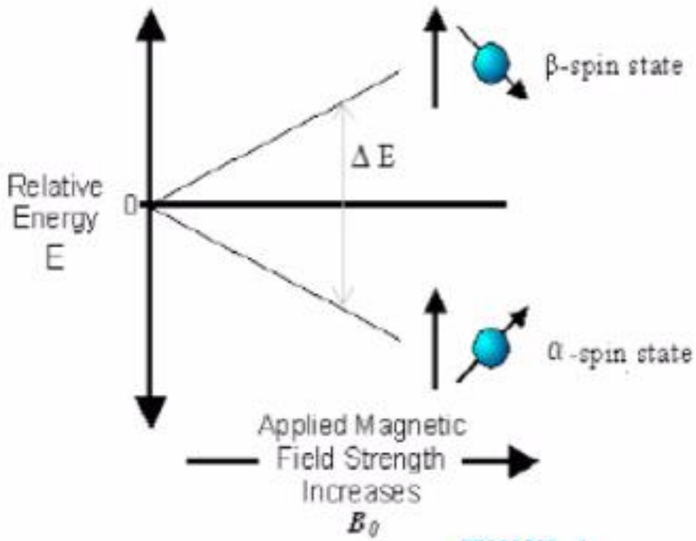


If an external magnetic field is applied, an energy transfer (ΔE) is possible between ground state to excited state.

when the spin returns to its ground state level, the absorbed radiofrequency energy is emitted at the same frequency level.

The emitted radiofrequency signal that give the NMR spectrum of the concerned nucleus.





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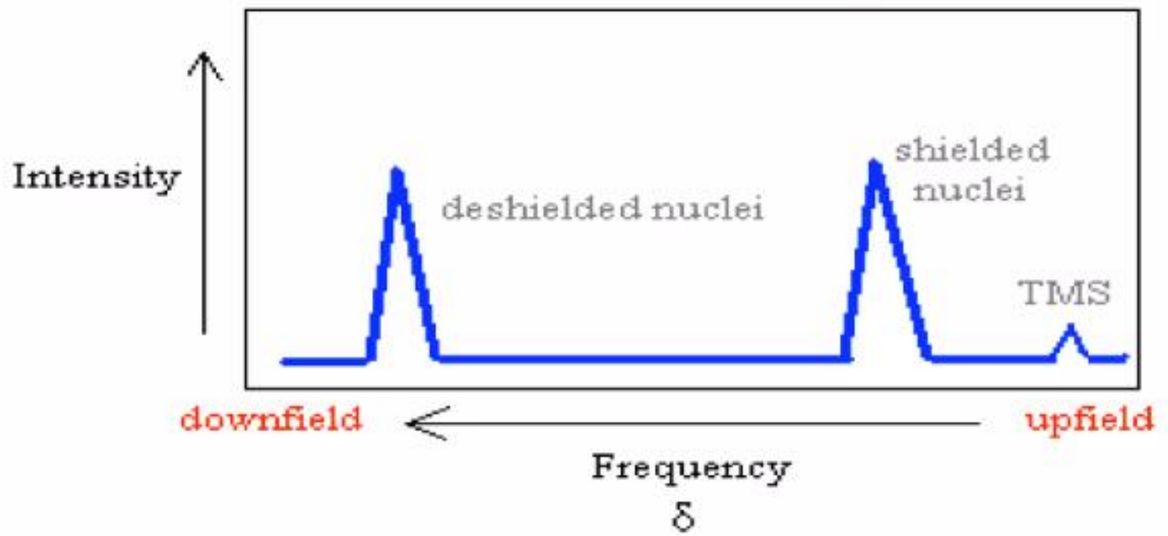
The emitted radio frequency is directly proportional to the strength of the applied field.

$$\nu = \frac{\gamma B_o}{2\Pi}$$

B_o = External magnetic field experienced by proton

γ = Magnetogyric ratio (The ratio between the nuclear magnetic moment and angular moment)

NMR spectrum

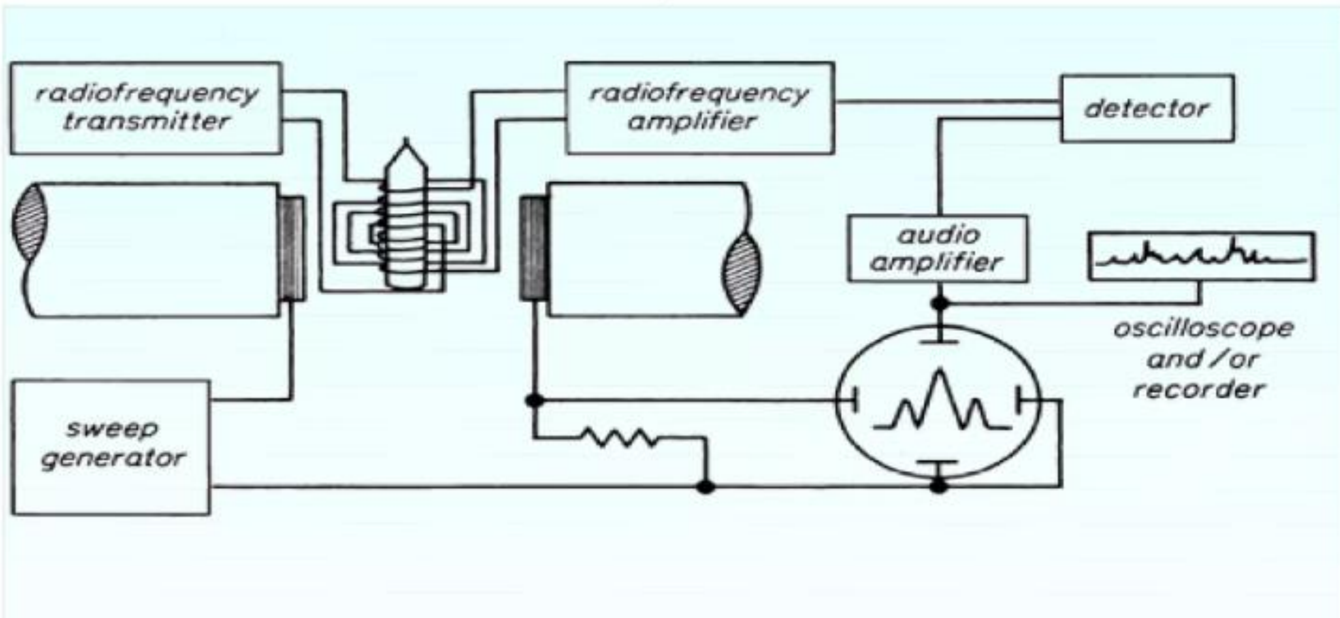


The NMR spectrum is a plot of intensity of NMR signals VS magnetic field (frequency) in reference to TMS

NMR instrumentation

1. Sample holder
2. Permanent magnet
3. Magnetic coils
4. Sweep generator
5. Radio frequency transmitter
6. Radio frequency receiver

7.Read out systems



1.Sample holder :- Glass tube with 8.5 cm long,0.3 cm in diameter

2.Permanent magnet :- It provides homogeneous magnetic field at 60-100 MHZ

3.Magnetic coils :- These coils induce magnetic field when current flows through them.

4.Sweep generator :- To produce the equal amount of magnetic field pass through the sample

5.Radio frequency transmitter :- A radio transmitter coil that produces a short powerful pulse of radio waves

6.Radiofrequency Receiver :- A radio receiver coil that detects radio frequencies emitted as nuclei relax to a lower energy level

7.Readout system :- A computer that analyses and record the data

Solvents used in NMR

The following solvents are normally used in which hydrogen replaced by deuterium.

CCl_4 - carbon tetrachloride

CS_2 - carbon disulfide

$CDCl_3$ - Deuteriochloroform

C_6D_6 - Hexa deuteriobenzene

D_2O - Deuterium oxide

Chemical shift

A **chemical shift** is defined as the difference in parts per million (ppm) between the resonance frequency of the observed proton and tetramethylsilane (TMS) hydrogens.

TMS is the most common reference compound in NMR, it is set at $\delta=0$ ppm

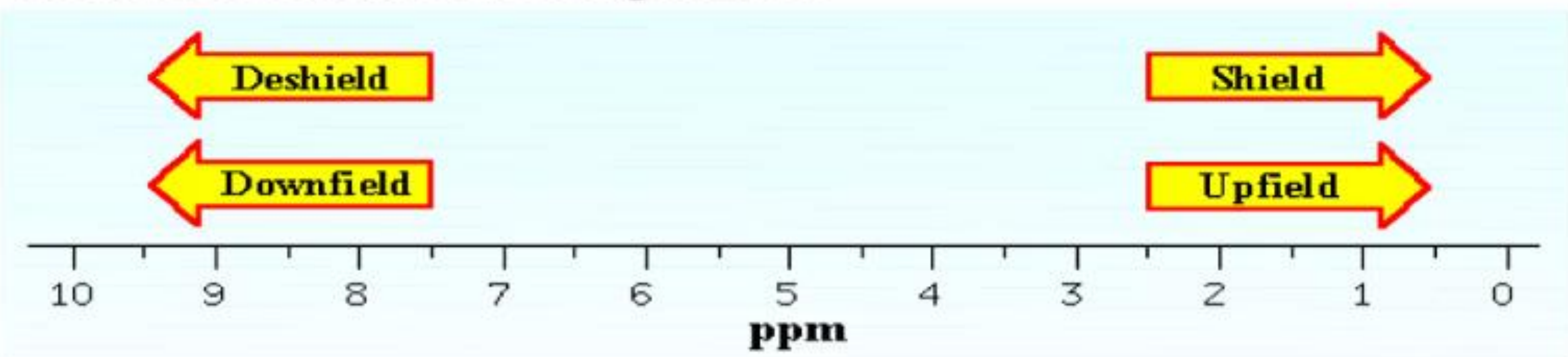
$$\text{Chemical shift, } \delta = \frac{\text{frequency of signal} - \text{frequency of reference}}{\text{spectrometer frequency}} \times 10^{6}$$

Shielding of protons:-

High electron density around a nucleus **shields** the nucleus from the external magnetic field and the signals are **upfield** in the NMR spectrum

Deshielding of protons:-

Lower electron density around a nucleus **deshields** the nucleus from the external magnetic field and the signals are **downfield** in the NMR spectrum



Factors affecting chemical shift:-

- Electronegative groups
- Magnetic anisotropy of π-systems
- Hydrogen bonding

Electronegative groups:-

Electronegative groups attached to the C-H system decrease the electron density around the protons, and there is less shielding (*i.e.*deshielding) and chemical shift increases

Compound	Chemical shift
CH_3I	2.16
CH_3Br	2.65
CH_3Cl	3.10
CH_3F	4.26