Nuclear Magnetic Resonance (NMR) Spectroscopy

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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 ^{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	^1H (1/2)	NMR active
Half-integer	Odd	Even	^{13}C (1/2)	
Integer	Even	Odd	^2H (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.**
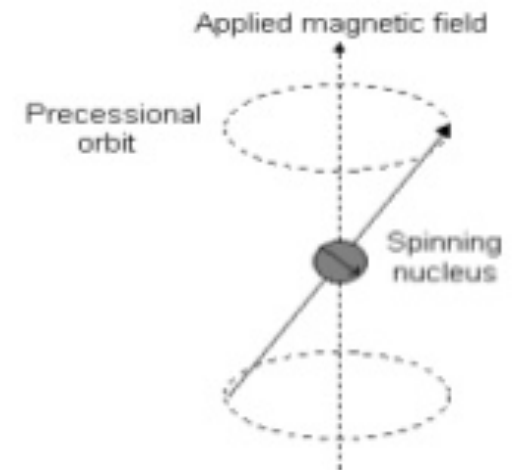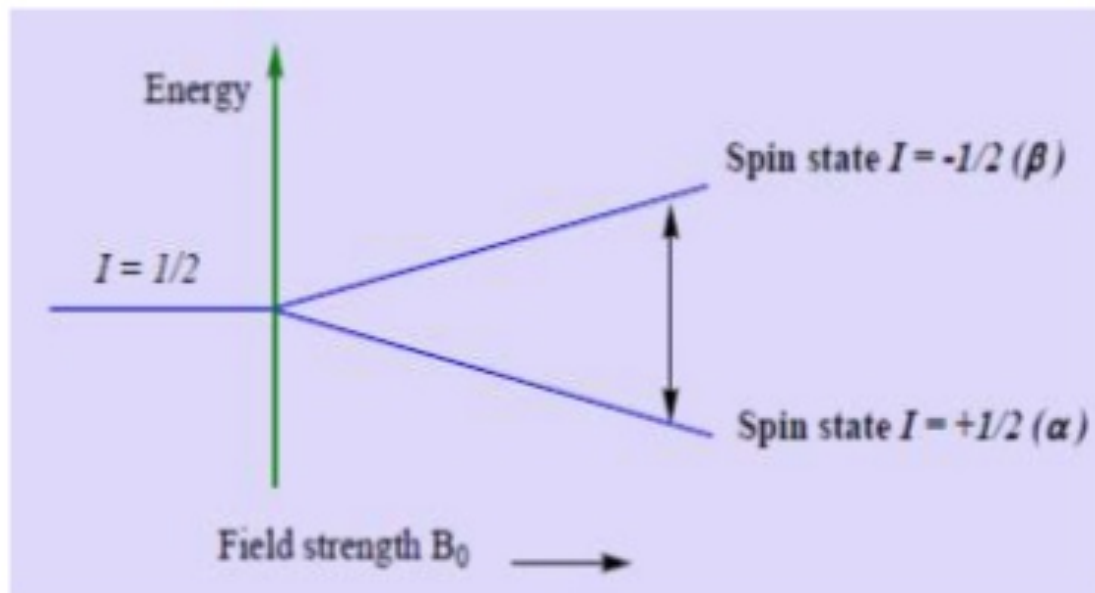
Principles of NMR

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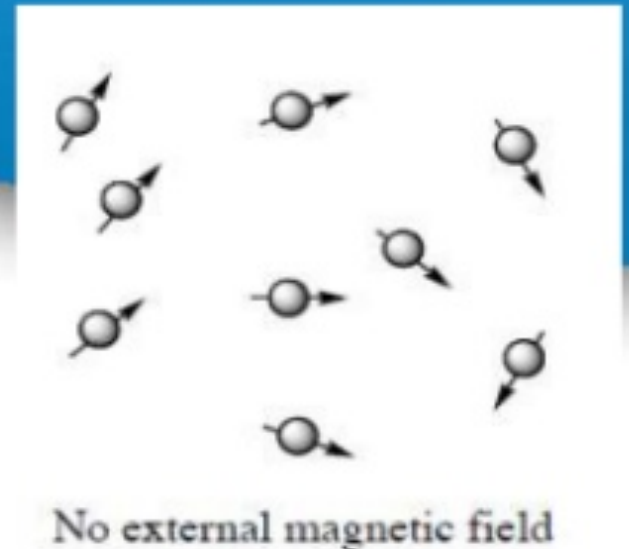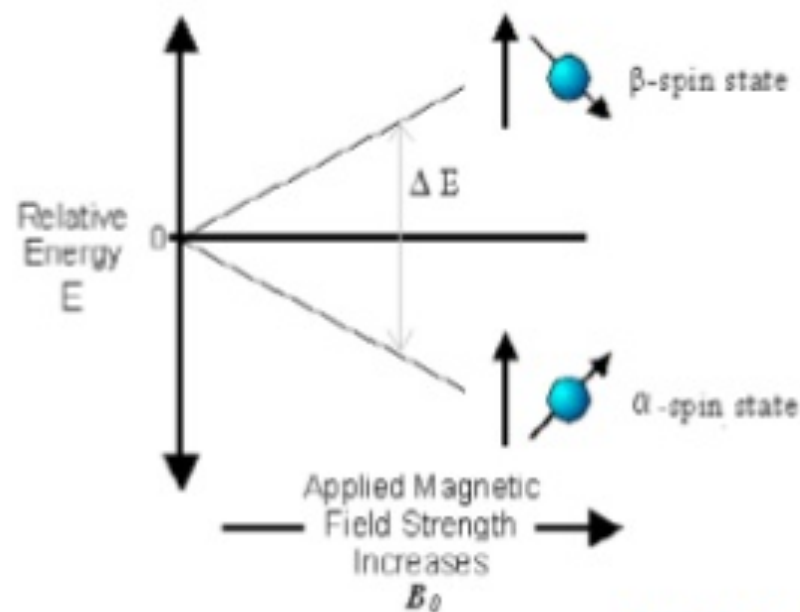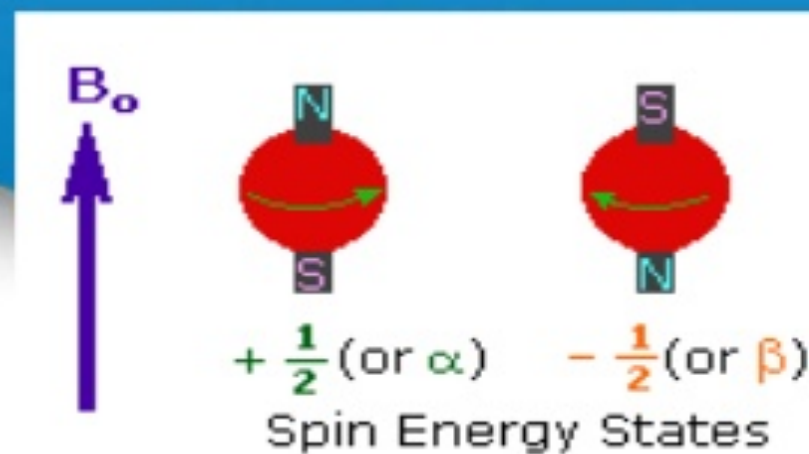
But when an external magnetic field(B_o), is present the nuclei align themselves either with or against the field of the external magnet.

No external magnetic field

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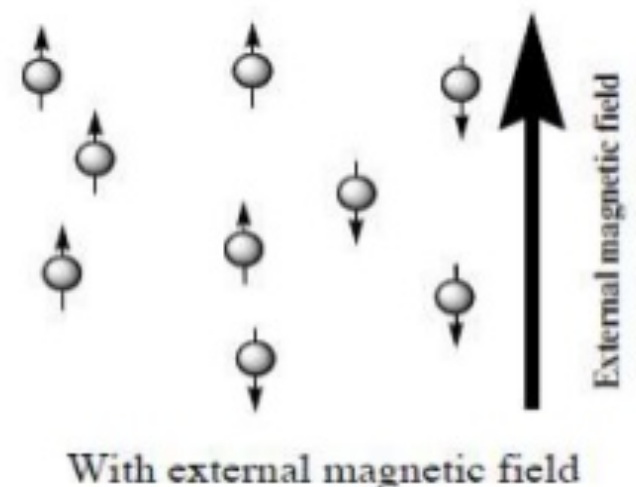
If an external magnetic field is applied, an energy transfer (ΔE) is possible between ground state to excited state.

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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B_o

$+\frac{1}{2}$ (or α) $-\frac{1}{2}$ (or β)

Spin Energy States

ΔE

Relative Energy E

β-spin state

α-spin state

Applied Magnetic Field Strength Increases
B_0

Let us consider a bare proton with **I=1/2** so that $m_I = \pm \frac{1}{2}$

$$E_{mI} = -g_N \mu_N B_z m_I$$

For $m_I = +1/2$, $E_{1/2} = (-1/2)\, g_N \mu_N B_z$

For $m_I = -1/2$, $E_{-1/2} = (1/2)\, g_N \mu_N B_z$

The energy difference is,

$$\mathbf{\Delta E} = E_{-1/2} - E_{1/2} = g_N \mu_N B_z$$

As $\Delta E = h\upsilon = g_N \mu_N B_z$,

The NMR frequency of a bare proton is given by,

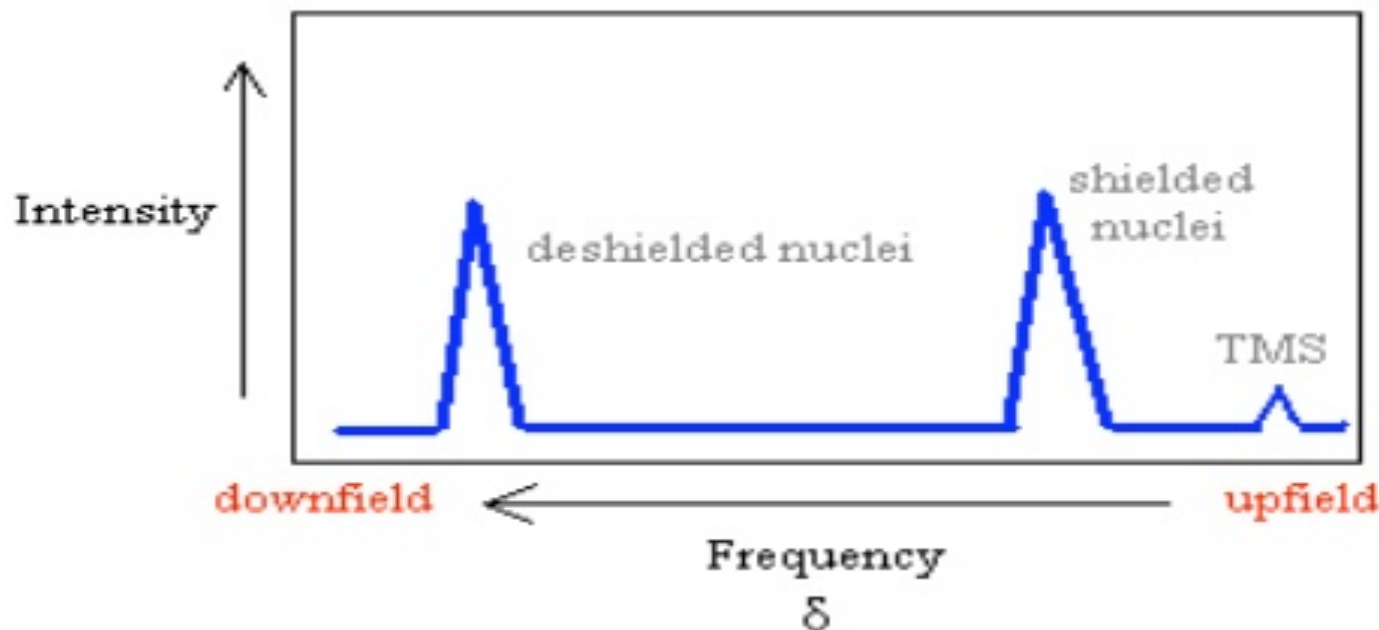$$\mathbf{\upsilon = g_N \mu_N B_z / h}$$

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

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

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 <u>intensity of NMR signals</u> VS <u>magnetic field (frequency)</u> in reference to TMS

Qn-1: Which of the following nuclei do not show nuclear magnetic resonance?

^{1}H, ^{2}H, ^{12}C, ^{13}C, ^{14}N, ^{15}N, ^{16}O, ^{19}F, ^{31}P, ^{32}S

Ans: ^{12}C, ^{16}O, ^{32}S (having both even atomic number and mass number)

Qn-2: How many kinds of protons are there?

(a) CH_3CH_3 (b) $CH_3CH_2CH_3$, (c) $(CH_3)_2CHCH_2CH_3$, (d) $C_6H_5CH_3$

Ans: (a) 1, (b) 2, (c) 4, (d) 2

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

Deshield		Shield
Downfield		Upfield

10   9   8   7   6   5   4   3   2   1   0

ppm
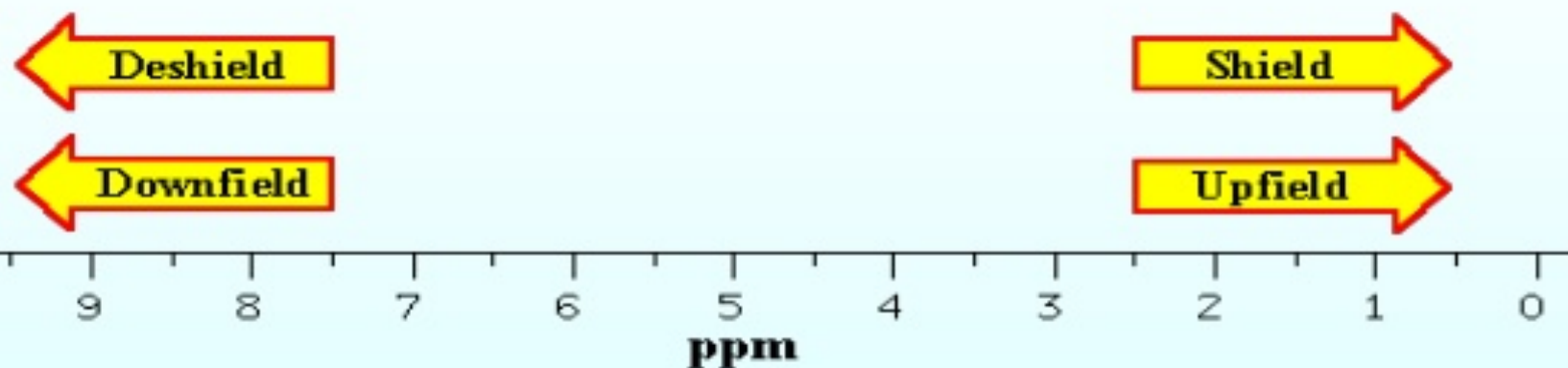
Factors affecting chemical shift:-

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

<u>Electronegative groups:-</u>

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

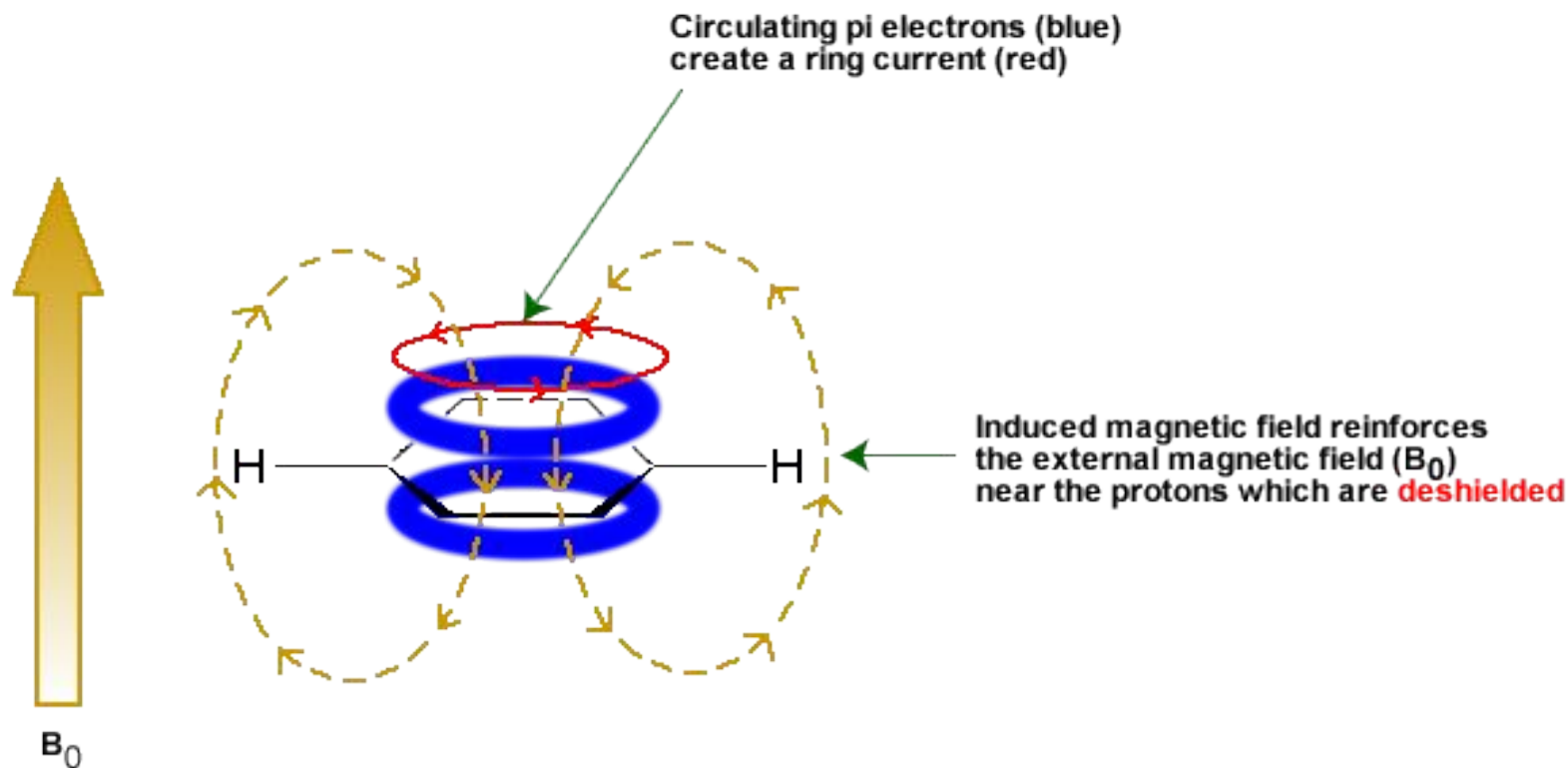## Magnetic anisotropy of π-systems:-

➢ The word "anisotropic" means "non-uniform". So magnetic anisotropy means that there is a "non-uniform magnetic field".

➢ Electrons in π systems (e.g. aromatics, alkenes, alkynes, carbonyls etc.) interact with the applied field which induces a magnetic field that causes the anisotropy.

➢ It causes both shielding and deshielding of protons.

➢ Example:-Benzene

Hydrogen bonding:-

➢ Protons that are involved in hydrogen bonding are typically change the chemical shift values.

➢ The more hydrogen bonding, the more proton is deshielded and chemical shift value is higher.

Deshielding of benzylic protons in Benzene

Circulating pi electrons (blue) create a ring current (red)

Induced magnetic field reinforces the external magnetic field (B_0) near the protons which are deshielded

B_0

Benzylic protons, due to the anisotropy of the induced field, generated by the ring current, appear to be highly deshielded. Thus, their chemical shift is far downfield in 6.5-8 ppm region.

Proton NMR

The most common for of NMR is based on the hydrogen-1 (^1H), nucleus or proton.

It can give information about the structure of any molecule containing hydrogen atoms.
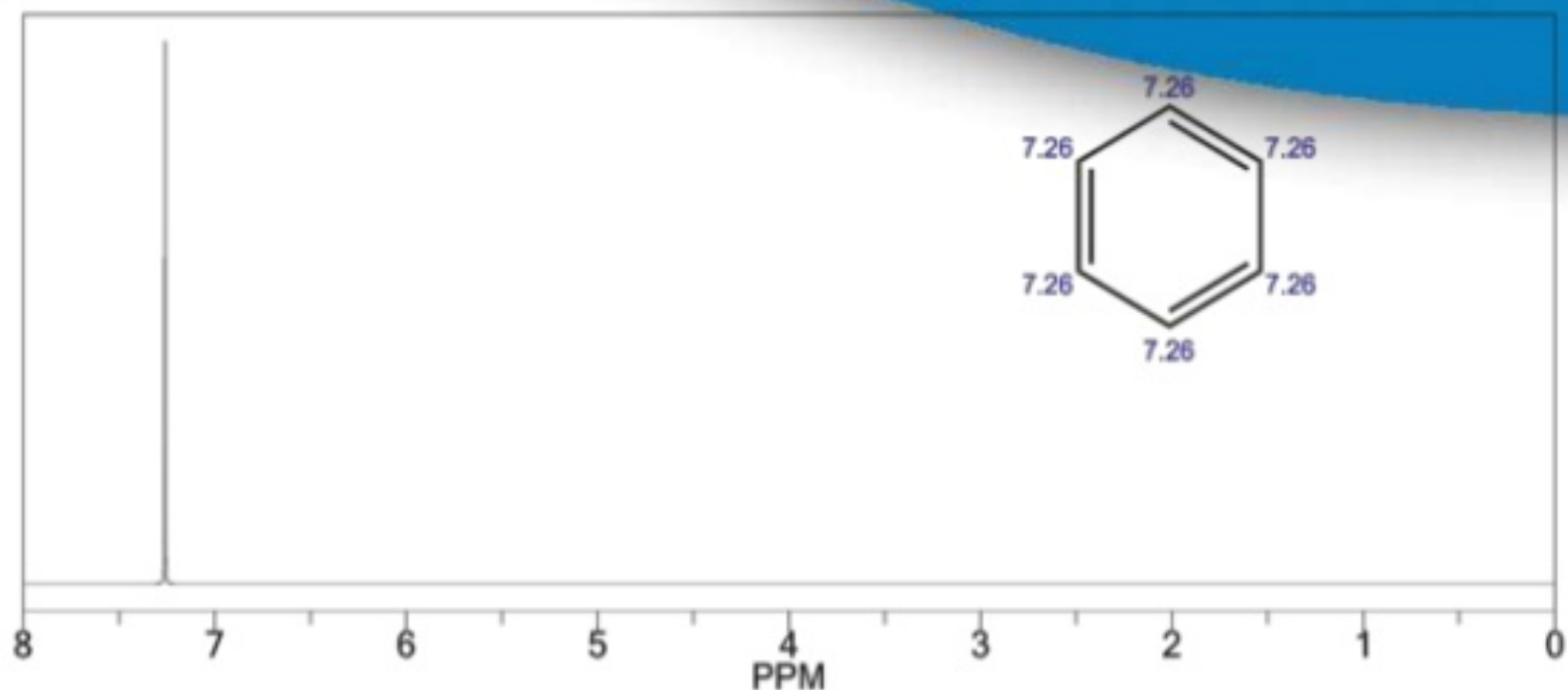
Proton NMR spectra of Ethanol:-
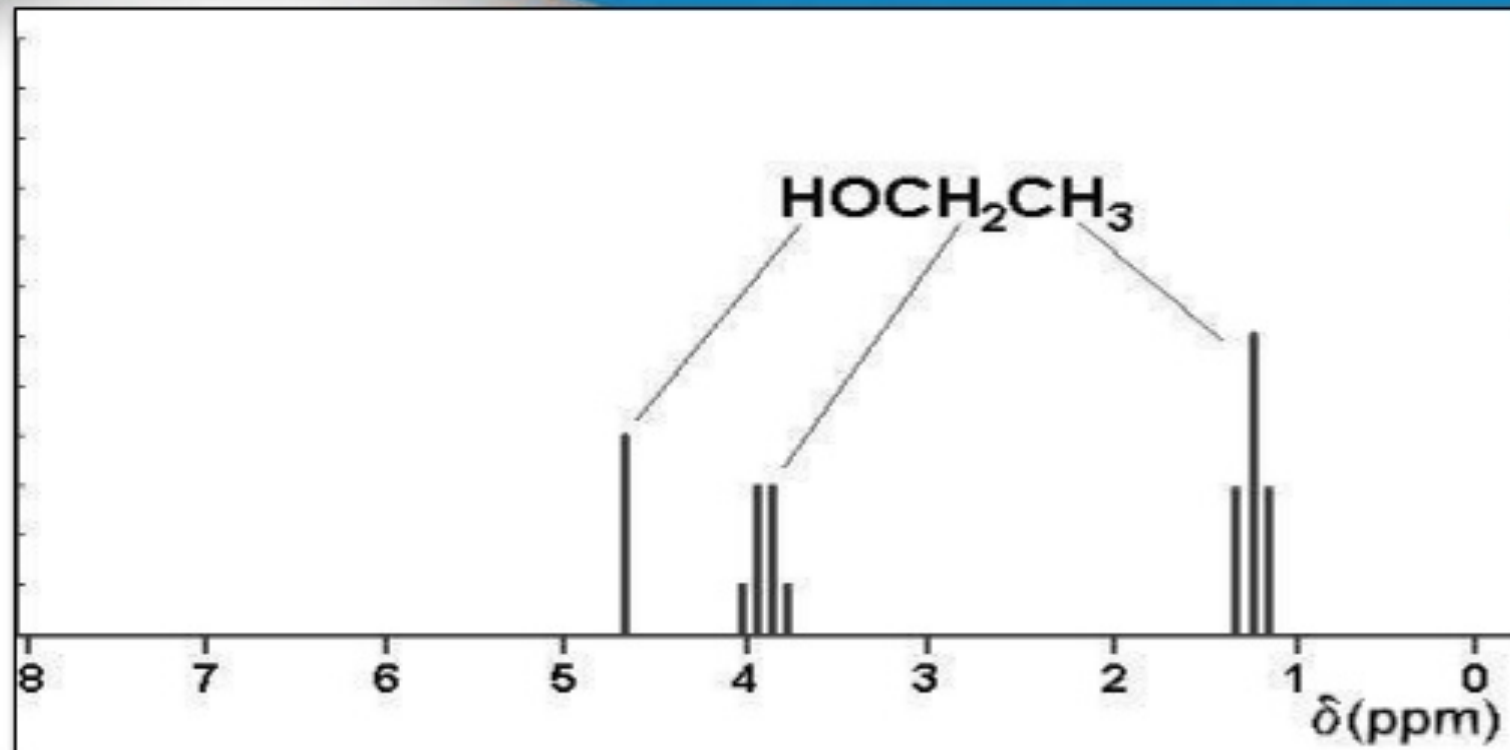
^{1}H spectrum of Ethanol:-

3 types of proton

CH_3, CH_2, OH

^{1}H NMR spectra of Benzene

- Aromatic Hydrogen shows peak in the chemical shift scale 6.5-8.0 ppm.
- From the above spectrum Benzene has same type of protons and it shows single peak at 7.26

Interpretation of ^{1}HNMR spectra:-

Number of signals — Indicates how many "different kinds" of protons are present.

Position of signals — Indicates something about (chemicalshift) magnetic (electronic) environment of protons

Relative intensity of signals — Proportional to number of protons present

Splitting of signals (spin spin coupling) — Indicates the number of nearby nuclei usually protons

n+1 rule:-

❖ The multiplicity of signal is calculated by using n+1 rule.

❖ This is one of the rule to predict the splitting of proton signals. This is considered by the nearby hydrogen nuclei.

Therefore, n= Number of protons in nearby nuclei

➢ Zero H atom as neighbour n+1=0+1=1(singlet)

➢ One H atom as neighbour   n+1=1+1 = 2(doublet)

➢ Two H atom as neighbour   n+1=2+1 =3(triplet)

Spin-spin coupling (splitting)

The interaction between the spins of neighbouring nuclei in a molecule may cause the splitting of NMR spectrum.This is known as spin-spin coupling or splitting.

The splitting pattern is related to the number of equivalent H-atom at the nearby nuclei.

Ethyl acetate
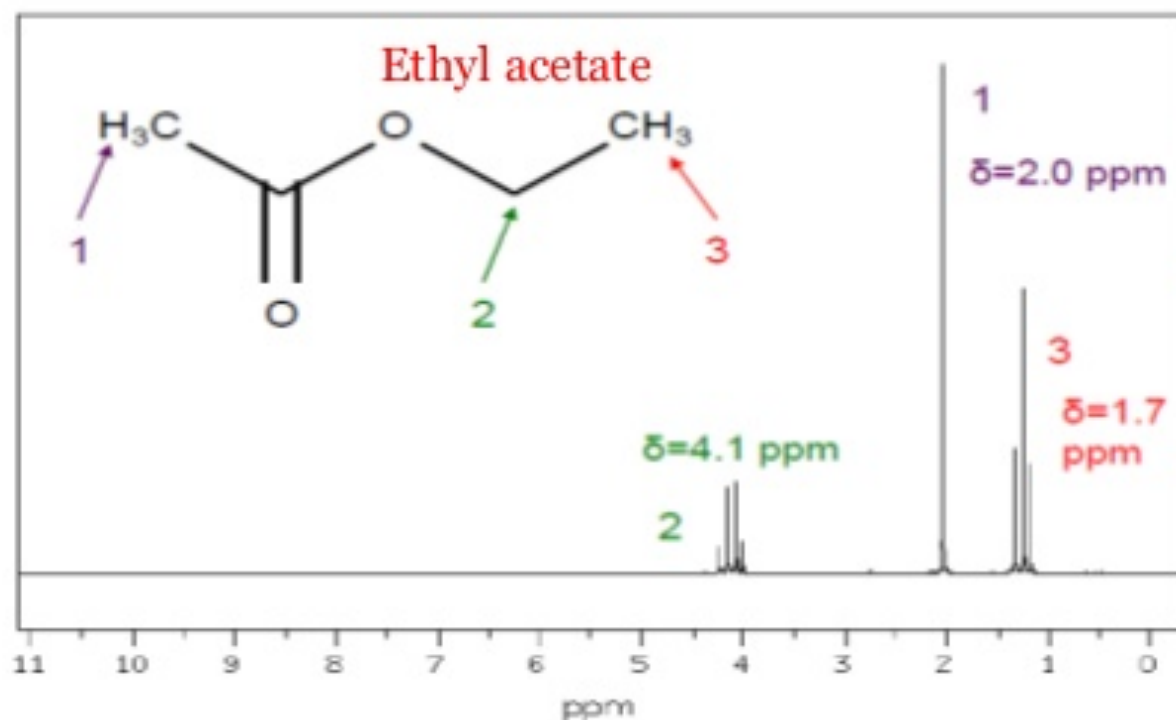
Spin-Spin Splitting patterns

1. Singlet. 3 equivalent protons. Not coupled to any neighboring protons.

2. Quartet. 2 equivalent protons. Split (1:3:3:1) because coupled to the 3 ^{1}Hs at the 2 position.

3. Triplet. 3 equivalent protons. Split (1:2:1) because coupled to the 2 ^{1}Hs at the 3 position.

Rules for spin-spin coupling:-

* Chemically equivalent protons do not show spin-spin coupling.
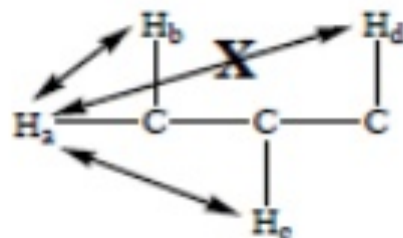
* Only nonequivalent protons couple.
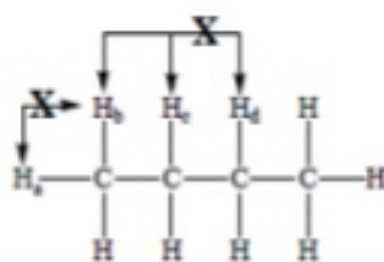
H_b couples with H_c.
H_b and H_a do not couple because they are equivalent.
H_c and H_d do not couple because they are equivalent.

* Protons on adjacent carbons normally will couple.

* Protons separated by four or more bonds will not couple.

H_a can couple with H_b
H_a can couple with H_c
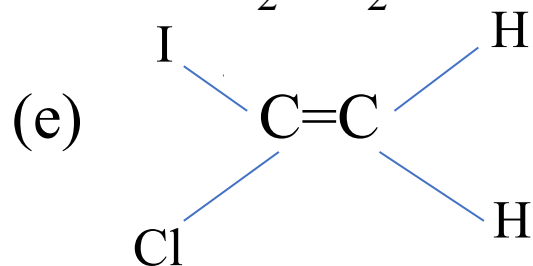H_a cannot couple with H_d

Coupling Constant

- The distance between the peaks in a given multiplet is a measure of the splitting effect known as <u>coupling constant</u>.

- It is denoted by symbol J, expressed in Hz.

- Coupling constants are a measure of the effectiveness of <u>spin-spin coupling</u> and very useful in ^{1}H NMR of complex structures.
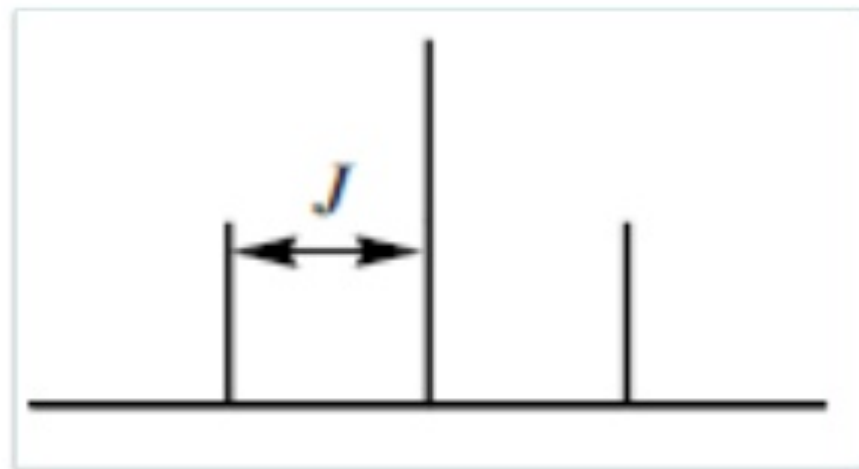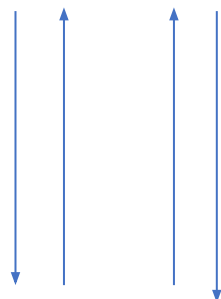
Qn: Which will show spin-spin coupling in their NMR spectra?

(a) $ClCH_2CH_2Cl$, (b) $ClCH2CH2I$, (c) $CH3-CH=O$, (d) $(CH3)_2C=O$

(e)

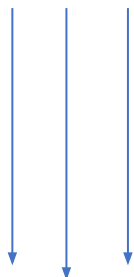$$\underset{Cl}{\overset{I}{\diagdown}}C=C\underset{H}{\overset{H}{\diagup}}$$

n=1, n+1 =2

If n=2, n+1 =3

If n=3, n+1 =4