Nuclear Magnetic Resonance

Theory :- Nucleus is spinning about an axis like top, in which the spinning axis of the top moves slowly around the vertical. This is precessional motion and the top is said to be precessing around the vertical axis of earth's graviterational field.

All nuclei carry a charge, so they ~~po~~ will possess spin angular momentum. Only those nuclei which have a finite value of spin quantum number ($I \neq 0$) will precess along the axis of rotation.

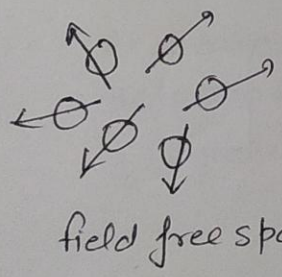
Mass No	Atomic No	Spin quantum No. (I)
odd	odd or even	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ ---
even	even	0
even	odd.	1, 2, 3 ---

$^{31}_{15}P$ & $^{13}_{6}C$ $-\frac{1}{2}$, $^{14}_{7}N \rightarrow 1$.

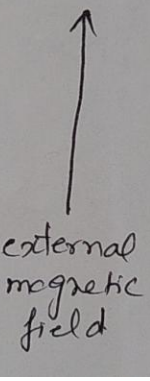
The circulation of nuclear charge generates a magnetic field (magnetic moment). The magnetic moments are in random manner.

If the proton is placed in external magnetic field, then ~~it~~ it starts processing at a certain frequency and capable of taking any two orientations.

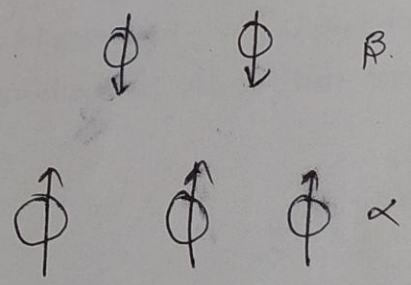
(a) Alignment with the field (α)
(b) " against " " (β)



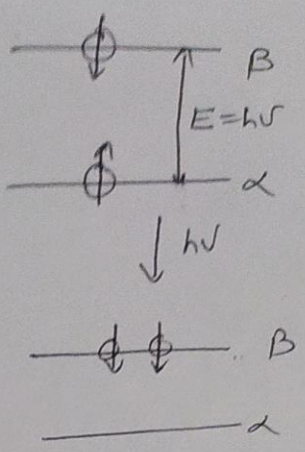
field free space



external magnetic field

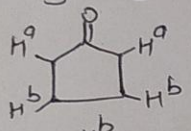
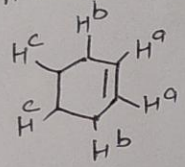
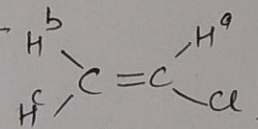
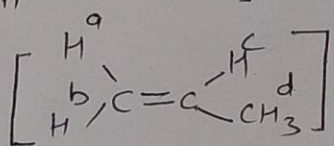


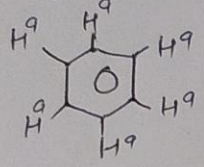
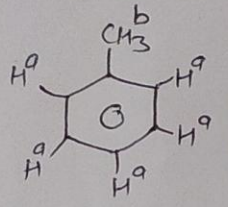
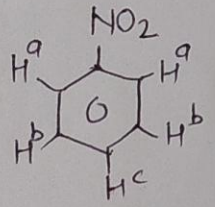
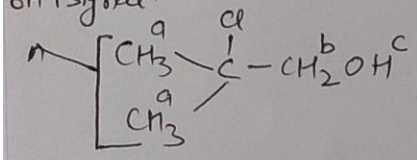
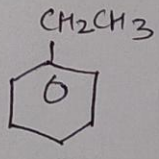
Energy is needed to flip the proton from its lower energy state to the higher energy state. In the NMR this energy is provided by electromagnetic radiation in the radio frequency region. The transition from one energy level to other is called flipping of spin.



* It is generally more convenient to keep the radio-frequency constant and the strength of the magnetic field is constantly varied. At some value of field strength, the energy required to flip the proton matches the energy of radiation. Absorption occurs and a signal is observed.

NMR

Compound	Type of H	Theoritical No of nmr Signals
CH_4^a	1	1
$CH_3^aOCH_3^a$	1	1
$CH_3^aC(=O)-CH_3^a$	1	1
$ClCH_2^aCH_2^aCl$	1	1
	1	1
$CH_2^a=CH_2^a$	1	1
$CH_3^aCH_2^bCl$	2	2
$CH_3^aOCH_2^bCH_3^c$	3	3
	2	2
	3	3
$ClCH_2^aCH_2^bCH_2^cBr$	3	3
$CH_3^bC(=O)OCH_3^a$	2	2
$CH_3^aCH_2^bOH^c$	3	3
$CH_2=CHCl$ 	3	3
$CH_2=CH-CH_3$ 	4	4
$CH_2=CHCHO$	4	4

Compound	Types of H	No of Signals
$CH_3^a CH_2^b CH_3^a$	2	2
$CH_3^a CH_2^b NH_2^c$	3	3
$CH_3^a-CH_2^b(OH^d)-CH_3^c$	4	4
$CH_3^c CH_2^b CH_2^a Cl$	3	3
	1	1
 [If one H of benzene is replaced by +I group. then its rest five H are equivalent]	2	2
 [If one H of benzene is replaced by -I group, then it will give 3 signals]	3	3
$CH_3^a-C(CH_3^a)(CH_3^a)-Br$ [9 H one signal]	1	1
6H 1 signal. 	3	3
	3	3
$CH_3^a O-C(=O)-CH_2^b-CH_3^c$	3	3

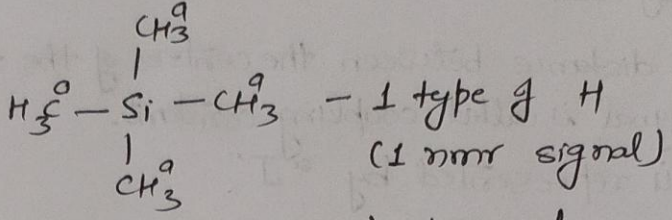
Types of protons and chemical shift values :

Type of Proton	chemical shift (δ)
$R-CH_3$	0.9
$C=C-H$	4.6 – 5.9
$C\equiv C-H$	2 – 3.
$Ar-H$	6 – 8.5
$Ar-CH$	2.2 – 3.
$-\overset{O}{\overset{\|\|}{C}}-C-H$	2 – 2.7
$R-\overset{O}{\overset{\|\|}{C}}-H$	9 – 10
$H-C-OH$	3 – 3 – 4.
$R-\overset{O}{\overset{\|\|}{C}}-O-H$	10.5 – 12.

Internal Standard in NMR :-

Tetra methyl silane is used as internal standard.

[TMS]



– 1 type of H (1 nmr signal)

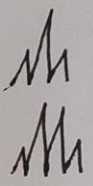
(a) ~~One only~~ only one peak for TMS is observed.
(b) Highly volative – can be easily removed.
(c) Misible with most of organic compounds.
[d] Inert to most compound.

[n+1 Rule] – taking example of CH_3CH_2Cl

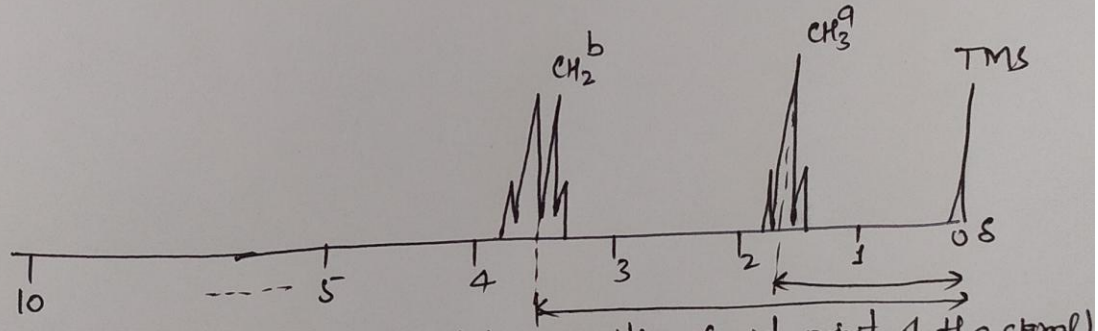
$CH_3^a CH_2^b - Cl$ 2 type of H – 2 nmr signals

Pattern of signal for CH_3^a (Proton) = 2+1 = 3 (Triplet)

" " " " CH_2^b (") ⇒ 3+1 = 4 (Quarted)



Chemical shift (δ) :-



The difference in the absorption position (mid point of the signal) of the proton w.r.t TMS signal on δ scale is called chemical shift.

Coupling constant :- (J)

The distance between the centres of the two adjacent peak in a signal is called coupling constant.

* It is represented by "J".
* It is measured in hertz.
* It is independent to the applied magnetic field.