

① Spin Resonance Spectroscopy.

Nuclear magnetic resonance spectroscopy (NMR)

In presence of an external magnetic field, a nucleus can have different orientations and what is the effect of the magnetic field on the nuclei is studied in the NMR Spectroscopy.

Basic principle

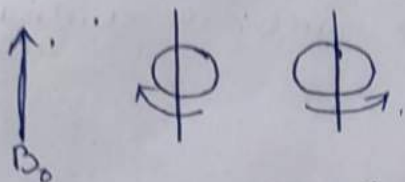
~~Like electrons~~ In an atom like the electrons nucleus also spin (both protons and neutrons spin) along its own axis. As a result a magnetic moment is generated, and the nucleus behave as a tiny magnet. In case of a nucleus, the angular momentum is given by $\sqrt{I(I+1)} \frac{h}{2\pi}$, where I is the spin quantum number of the nucleus. It may have value $0, \frac{1}{2}, 1, \frac{3}{2}, \frac{5}{2}$ etc.

~~To give an NMR~~ For a nucleus to give NMR spectra I must not be equal to zero ($I \neq 0$). The nuclei which have $I=0$ will be NMR inactive.

- (i) Nuclei with both p and n even (charge and mass even) have zero spin (e.g. ${}^4_2\text{He}$, ${}^{12}_6\text{C}$, ${}^{16}_8\text{O}$ etc)
- (ii) Nuclei with both p and n odd (hence charge odd but mass = $p+n$, even) have integral spin (eg ${}^2_1\text{H}$, ${}^{14}_7\text{N}$, ${}^{10}_5\text{B}$ etc).
- (iii) Nuclei with odd mass have half integral spin [eg ${}^{15}_7\text{N}$, ${}^{17}_8\text{O}$ etc]

(2)

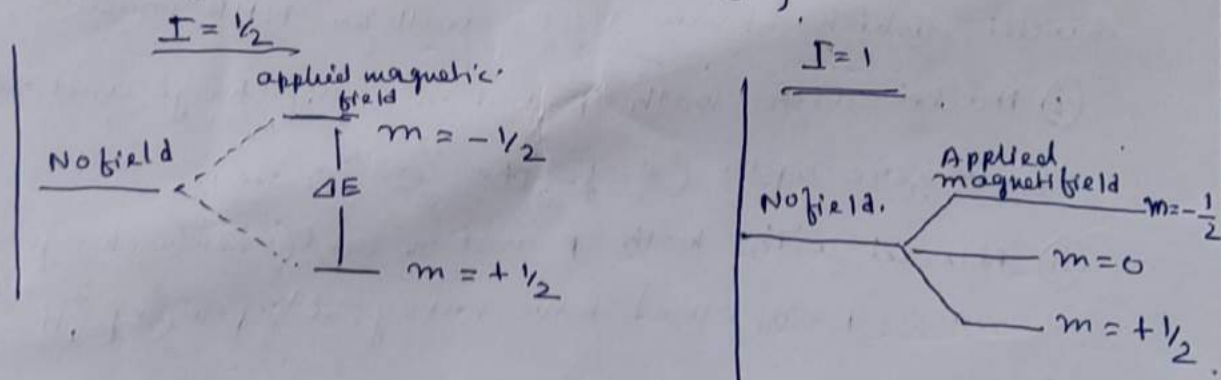
When an magnetic field is applied a nucleus can have one of the two orientations, one in the direction parallel to the applied magnetic field and the other in the opposite direction of the applied magnetic field.



$I = +\frac{1}{2}$ (called the ground state or α -orientation)

$I = -\frac{1}{2}$ (excited state or β orientation)

In presence of a magnetic field, a nucleus of spin I will have $(2I+1)$ possible orientations, e.g. a nucleus with $I = \frac{1}{2}$, will have $(2 \cdot \frac{1}{2} + 1) = 2$ two orientations. with $I = 1$, the nucleus will have 3 ($2 \cdot 1 + 1 = 3$) orientations and so on. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given by a magnetic quantum number (m).



When we apply a electro-magnetic radiation equivalent to the energy difference ΔE , the electron can jump from one state to another state. It is called flipping of electrons, and we get a signal spet in the NMR spectra.

(3).

Now, if a fixed magnetic field is applied on the sample and the frequency of radiation is varied, the absorption of radiation can occur, when,

$$2 \mu_B B_0 = h\nu.$$

Where μ_B is the magnetic moment of the proton.

B_0 is the applied external magnetic field.

$\mu_B B_0$ is the energy of the proton.

$$\Delta E = [\mu_B B_0 - (-\mu_B B_0)] \\ = 2 \mu_B B_0.$$

We can adjust both the field strength or radio frequency to get a flipping (when resonance is ~~observed~~ ^{obtained}).

In practice, however, it has been found more convenient to keep the radiation frequency constant and to vary the strength of the magnetic field. 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. Such a spectrum is called, a nuclear magnetic resonance spectrum.

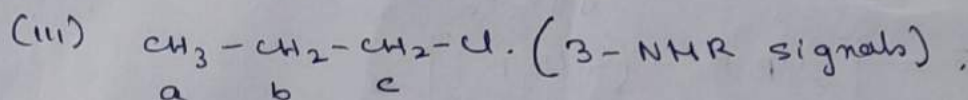
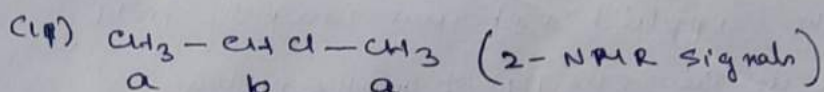
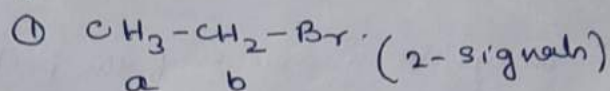
Interpretation of NMR spectra.

① Number of signals (equivalent and non equivalent protons). In a given molecule, protons with the same chemical environment, absorb at the same applied field and the protons with different environments absorb at different applied field strength. A set ⁿ of protons with the same environment are said to be equivalent and the protons with different environment

(4)

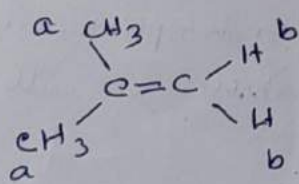
are said to be non equivalent. The number of signals in an NMR spectrum tells us, therefore how many sets of equivalent protons i.e. how many kinds of proton the molecule contains,

e.g.

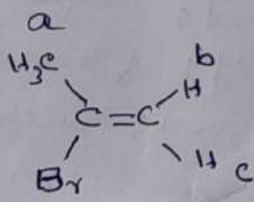


Equivalent protons are designated with the same letter in a given structural formula.

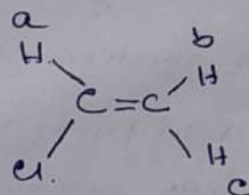
In the above examples, magnetically equivalent protons are simply chemically equivalent protons. ~~Protons~~ To be chemically ~~active~~ equivalent, protons must also be stereo chemically equivalent. The following structural formulae can be analysed from stereo-chemical equivalence point of view.



2 NMR signals
(isobutylene)



3 NMR signals
(2-bromopropene)



3 NMR signals
(vinyl chloride)

(2) Multiplicity of signals (n+1) rule and the intensity of the signals.

The number of peaks into which a proton signal (nmr signal) splits are equal to one more than the number of equivalent protons in the neighbouring group.