Nuclear Magnetic Resonance [NMR]

NMR is a branch of spectroscopy, in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule. The magnetic energy levels are created by keeping the nuclei in a magnetic field.

Without the magnetic field the spin states of nuclei are degenerate, i.e. posses the same energy, and energy level transition is not possible.

When a magnetic field is applied, the separate levels and radio frequency radiation can cause transitions between these energy levels.

NMR spectroscopy is most often concerned with nuclei with $I = 1/2$.

Ex – ^{1}H, ^{31}P and ^{19}F.

NMR Spectra cannot be obtained from nuclei with $I = 0$.

In Special cases, spectra can be obtained from nuclei where $I \geq 1$.

NMR spectroscopy is a powerful tool for investigating nuclear structure.

The first observations of NMR Signals were observed independently by Purcell at Harvard and Bloch at Stanford in 1945. The first application to study the structure of ethyl alcohol was made in 1951. In 1952 Purcell and Bloch won the Noble Prize in Physics.

Radio Waves:-

Radio waves are the lowest-energy form of electromagnetic radiation. The freq. of radio waves lies between 10^7 and 10^8 cps.

The energy of radio frequency (rf) radiation can be calculated by using the equation:

$$E = h\nu \quad \text{———} \quad ①$$

Where,

h is the Planck's constant
ν is the frequency.

Here is h is 6.6×10^{-7} erg sec and ν is between 10^7 and 10^8 cps.

$$E = 6.6 \times 10^{-27} \ (\text{or } 10^8 \text{ ergs}).$$
$$= 6.6 \times 10^{-20} \ (\text{or } 6.6 \times 10^{-19} \text{ ergs}).$$

It is seen that the quantity of energy involved in rf radiation is very small, too small to vibrate, rotate or excite an atom or molecule.

But this energy is sufficient to affect the nuclear spin of the atoms of a molecule. Therefore, the nuclei of atoms in a molecule on absorbing rf radiation may change their direction of spin.

Quantum Description of Nuclear Magnetic Resonance

According to the quantum theory, a spining nucleus can only have values for the spin angular momentum given by

Spin angular momentum $= [I(I+1)]^{1/2} h/2\pi$ —— ①

where,

I is the spin quantum number of the nucleus

h is the Planck's constant.

But, $\mu = \gamma \times$ spin angular momentum

$\therefore \mu = \gamma \times [I(I+1)]^{1/2} h/2\pi$ —— ②

where,

μ = magnetic moment of the nucleus

γ = gyromagnetic ratio.

If a nucleus having a magnetic moment is introduced into a magnetic field, H_0 the two ~~magnet~~ energy levels become separate corresponding to $m_I = -1/2$ (antiparallel to the direction of magnetic field) and to $m_I = +1/2$ (parallel to the direction of magnetic field).

A nucleus with $I = 1/2$, the energies E_1 and E_2 for the two states with $m_I = +1/2$ and $m_I = -1/2$, respectively are.

$E_1 = -1/2 \left(\frac{\gamma h}{2\pi}\right) H_0$ —— ③

Expt. No.

and $E_2 = +\frac{1}{2}\left(\frac{\gamma h}{2\pi}\right) H_2$ ———— ④

The energy of two states are represented in figure 1.

Energy level of a nucleus with $I = \frac{1}{2}$ in absences and in presence of mag. field.

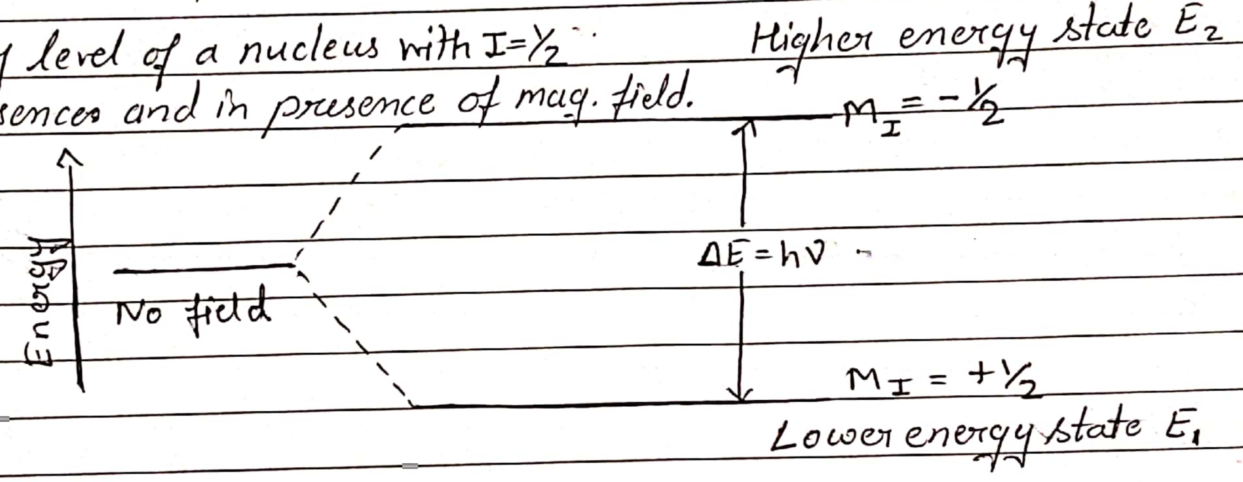

Figure-1.

When the nucleus absorbs energy, the nucleus will be promoted from the lower energy state E_1 to the higher energy state E_2 by absorption of energy, ΔE, equal to the energy difference, $E_2 - E_1$. It means that the absorption of energy changes the magnetic moment from the parallel state $M_I = +\frac{1}{2}$ to the antiparallel state $M_I = -\frac{1}{2}$.

If the nucleus lies in the upper energy state, E_2 and radiation of energy ΔE is incident upon the system, the nucleus will come to lower energy level E_1, emitting energy corresponding to ΔE.

The frequency ν at which energy is absorbed or emitted is given by Bohr's relationship.

$$\nu = \frac{E_2 - E_1}{h} \quad \text{———} \quad ⑤$$

On substituting equation ③, ④ in eq^n ⑤, we get.

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

$$\Rightarrow \quad \nu = \frac{\gamma}{2\pi} H_0 \quad \text{———} \quad ⑥$$

From eq^n ⑦ it follows that the frequency absorbed or emitted by a nucleus is moving from one energy level to another is directly proportional to the applied magnetic field. In NMR it is the absorption of energy which is detected.

When a nucleus is placed in a system where it absorbs energy, it becomes excited. It then losses energy to return to the unexcited state. It absorbs energy and again enters an excited state. This nucleus which alternately becomes excited and unexcited is said to be in a state of resonance.

To determine the resonance frequency, the energy absorbed by nuclei is measured as the magnetic field H_0 is varied. As the field H_0 is increased so that precessional frequency of the nucleus increases and when this frequency becomes equal to the frequency of oscillation field, transitions occur between nuclear energy states. The energy absorbed in this process produces a signal at the detector and this signal is amplified and recorded as a band in the spectrum.

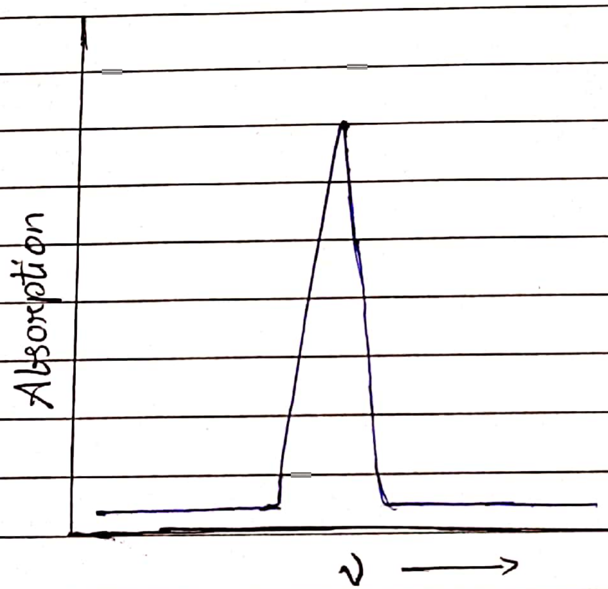

Figure-2. Absorption versus the frequency ν of rf radiation.

An NMR spectrum is plotted between absorption signal at the detector and the strength of the magnetic field H_0. It is important to mention here that the NMR spectrum is generally calibrated in units of frequency rather than in units of magnetic field strength as shown in figure. 2.