

## NMR-Nuclear Magnetic spectroscopy

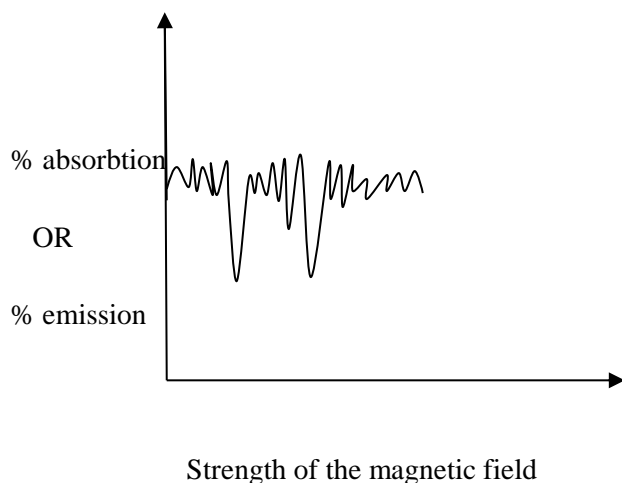
NMR is the study of properties of molecules containing magnetic nuclei by the application of a magnetic field and the observation of the frequency at which they come into resonance with a radiofrequency electromagnetic field.

This is a tool for investigating nuclear structure. In this, radio waves induce transitions between magnetic energy levels of nuclei in molecules. Magnetic energy levels arise when the nuclei is kept in a strong external magnetic field. In the absence of this magnetic field, the nuclei possess the same energy and no transition is possible. In presence of magnetic field, energy levels gets separate and radio frequency cause transition between different energy levels.

Radio waves are the lowest energy form of Electromagnetic radiations. The frequency of radio waves lies between  $10^7$ - $10^8$  cps. This much amount of energy is too small to cause vibration, rotation and excitation of electron to higher energy levels. But this is enough to influence the nuclear spin of atom or molecules.

When a nucleus is placed in a system it absorbs energy and becomes excited. Thereafter it loses energy and returns to the un-excited ground state. It will be repeated (ie excitation & de-excitation) and said to be in a state of resonance.

To determine the resonant frequency, measure the energy absorbed by the nucleus as the strength of the magnetic field ( $H_0$ ) is varied. The energy absorbed in the process produces a signal, which is amplified and recorded as a band in the spectrum. NMR spectrum is a plot of absorption signal in the detector vs the strength of the magnetic field ( $H_0$ ).



## CHEMICAL SHIFT

Chemical shift is dimensionless and is expressed in ppm. All protons in a given molecule do not possess the same frequency. Absorption depends upon the radiofrequency which a particular proton feels. This in turn depends upon the chemical environment of the proton. Thus at a given magnetic field, different protons require different frequency to cause absorption. This shift in frequency of absorption is chemical shift which depends upon the chemical environment of the molecule.

In NMR, the accurate determination of the value of magnetic field corresponding to a peak is difficult. The resonance frequency of nucleus in a sample is measured relative to the resonance frequency of a nucleus in the reference compound. The position of the peak in NMR spectrum relative to the reference peak is expressed in terms of chemical shift.

$$\text{Chemical shift} = \frac{H_0(\text{reference}) - H_0(\text{sample})}{H_0(\text{reference})} \times 10^6 \text{ ppm}$$

In terms of frequency:

$$\text{Chemical shift} = \frac{\text{Frequency (sample)} - \text{Frequency (reference)}}{\text{Frequency (reference)}} \times 10^6 \text{ ppm}$$

The normal reference compound is TMS (Tetra Methyl Silane). It is chemically inert & volatile & soluble in most of the organic solvents. All protons in TMS are equivalent and exhibit a single resonance line at high applied field and this will not make confusion with the lines due to other protons in the compound. TMS is insoluble in water. So for water soluble substances, DSS (2,2-Dimethyl-2-silapentane-5-sulphonate) can be used.

$C^{12}$  is 99% abundant. But it is not having magnetic spin. It is having even no. of neutrons and even no. of protons. So it is not detected by NMR.  $C^{13}$  is less abundant but it has odd no. of protons & neutrons. It gives a magnetic spin of  $\frac{1}{2}$ . The magnetic resonance of  $C^{13}$  is much weaker.  $C^{13}$ -based NMR analysis is known as

CMR. Another important NMR analysis is PMR (Proton NMR). This is hydrogen NMR i.e. hydrogen nucleus. Both  $C^{13}$  & hydrogen nucleus are magnetic isotopes.

## **Shielding**

Different nuclei in a molecule experience different magnetic field as a result of the sec-field associated with the molecules. The sec-field is due to the spinning electrons and this can effect the chemical shift also.

Positive shielding –

When sec- field produced by the circulating electrons oppose the applied field, the effective field experienced by the nucleus will be less than the applied field. This is positive shielding. The resonance position moves upfield in the spectrum because the value of applied field necessary to bring the nucleus into resonance will be greater than when there is no sec opposing field.

Negative shielding-

If the sec field due to the circulating electrons will reinforce the applied field, the position of resonance moves downfield in the spectrum. This is negative shielding.

## **Uses**

1. Characterisation & Identification of compounds.
2. Study of Hydrogen bonding.
3. Quantitative analysis.