- **Spin resonance** is a physical phenomenon resulting from the intrinsic angular momentum associated with the spin of the nucleus or electron of an atom.
- Spectroscopy is the study of interaction between electromagnetic radiations and matter.
- NMR is the study of magnetic properties of nuclei under the influence of a strong magnetic field and radiofrequency.

γ rays	X-rays	UV Vis	IR	μ-wave	radio
10^{-10}	10^{-8}	10^{-6}	10^{-4}	10^{-2}	10^{0}

Introduction:

Over the past fifty years nuclear magnetic resonance spectroscopy, commonly referred to as NMR, has become the preeminent technique for determining the structure of organic compounds. Of all the spectroscopic methods, it is the only one for which a complete analysis and interpretation of the entire spectrum is normally expected. Although larger amounts of sample are needed than for mass spectroscopy, NMR is non-destructive, and with modern instruments good data may be obtained from samples weighing less than a milligram. To be successful in using NMR as an analytical tool, it is necessary to understand the physical principles on which the methods are based.

Nuclear magnetic resonance (NMR) spectroscopy involves the change of the spin sate of a nuclear magnetic moment when the nucleus absorbs electromagnetic radiation in a strong magnetic field[1]. Today two types of NMR spectroscopy are used

(i) ^{1}H NMR(i.e. proton NMR)
(ii) ^{13}CNMR (Carbon-13 NMR).

Proton nuclear magnetic resonance spectroscopy

By the study of PMR spectroscopy of a compound we can know-

- The number of signals in the spectrum shows the number of different kinds of hydrogen atom in the molecule.
- The relative areas under the signals are proportional to the numbers of equivalent protons giving rise to the signals.
- The signals may get split into smaller peaks the type of splitting pattern observed depends on the number of neighboring protons.
- The spacing between the peaks is labeled as 'J' is coupling constant between 2 protons & J value give further information on molecular structure.

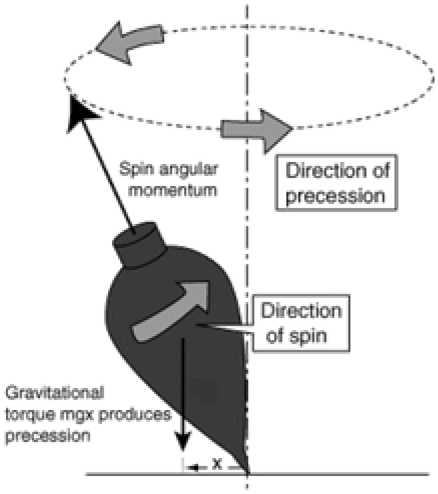
Theory of proton nuclear magnetic resonance spectroscopy

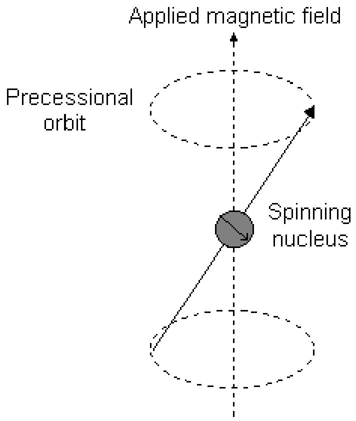
Spinning nuclei:

Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axes. In many atoms (such as ^{1}H, ^{12}C) these spins are paired against each other, such that the nucleus of the atom has no overall spin.

However, in some atoms (such as ^{1}H and ^{13}C) the nucleus does possess an overall spin. The rules for determining the net spin of a nucleus are as follows;

1. If the number of neutrons and the number of protons are both even, then the nucleus has NO spin.
2. If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
3. If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)





The atomic nuclei spin about their axis. Since rotating the charge nucleus generates a magnetic field whose magnitude and direction can be described by magnetic moment. So all the charged particles in a nucleus will cause to behave like a small bar magnet with its magnetic moment along the axis of rotation. The nucleus is composed of protons & neutrons. Proton carry unit positive charge and the neutron are electrically neutral. Magnetic properties occur with those nuclei which have-

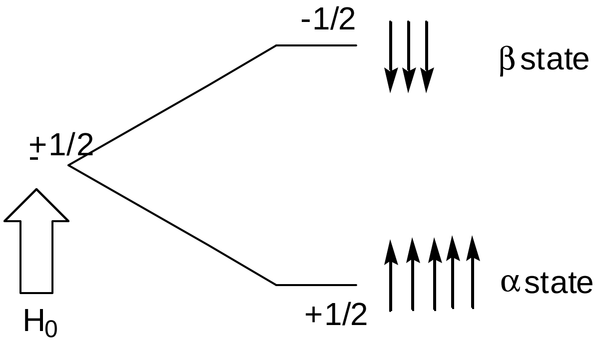
(a) Odd atomic and odd mass numbers
(b) Odd atomic numbers and even mass number
(c) Even atomic number and odd mass number

The overall spin, *I*, is important. Quantum mechanics tells us that a nucleus of spin *I* will have 2*I* + 1 possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. 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 a *magnetic quantum number, m*.

Nuclei which have no magnetic moment are those with even atomic number and even mass number e.g. = $^{6}C_{12}$, $^{8}O_{16}$, $^{16}S_{32}$. It has been assumed that the particles in such nuclei are paired i.e. spinning in opposite directions, as a result of this, there is no resultant spin and consequently no magnetic moment. The nuclear spin can have only two alternative value associated with the quantum number +1/2(alpha) and -1/2(Beta) when these nuclei are placed in a magnetic field which is designated as H0, their magnetic moments tend either to align with the field (corresponding to Beta-spin). The energy difference between the proton alpha and beta spin states is very small.®

Flipping the spin:

When a magnet is aligned against the magnetic field it is in a higher energy state than one aligned with the field. So the beta spin state with the magnetic moment aligned against the field corresponds to a higher energy state and alpha-spin state aligned with the field is corresponds to a lower energy state. When the compound in the applied field is irradiated with electromagnetic radiation of the proper frequency, a nucleus with alpha-spin can absorb a light quantum & converted to the higher energy Beta-spin state, this process is called "Flipping in spin"



This electromagnetic radiation is supplied by an oscillator.(with its magnetic field at right angles to the applied field) and since the position of the absorption peak i.e. where resonance occur, depends on the frequency of the oscillator or the strength of the applied field. It is possible to change from the lower to the higher energy level by using a variable frequency with a fixed applied magnetic field or vice versa. The difference between the two energy level , ⊕, for a proton is given by this expressions-

$$\Delta E = 2\mu H_O \text{ and } E = h\nu$$

$$\nu = \frac{2\mu H_O}{h}$$

Where h = Planck's constant

ν = frequency of radiation

H_0 = Nuclear magnetic moment.

Chemical shift and Resonance frequency

All protons have the same gyromagnetic ratio and therefore are expected to exhibit the same type of magnetic behavior. Had this been the case, all the protons would give only one signal and the purpose of NMR would have been defeated. The thing that makes the protons behave differently is the electronic environment around it. The electrons are charged particles, which are moving in their orbits. This circular motion of electrons generates its own magnetic field, which is always opposing the applied magnetic field. The proton therefore experiences the magnetic field of the electrons in addition to the externally applied magnetic field. Thus if the electron density around a proton is high, the magnetic field generated by the electrons will be quite strong and will oppose the external magnetic field more. In fact it will shield the proton from the external magnetic field and the signal will appear upfield that is at a higher frequency. Thus the electronic environment makes the proton signals resonate within a range of 1000 Hz at a magnetic field of 2.3 tesla (100 MHz). *Chemical shift is defined as the difference in the resonance position of a signal with respect to a reference signal*. *The resonance frequency is defined as the frequency difference between the reference signal and a proton signal.*

The chemical shift is determined by dividing the total range of proton resonance which is 1000 Hz on a 100 MHz spectrometer, into 10 equal parts. Then each part is numbered starting from zero at the extreme right of the spectra. Each part therefore comprises of a frequency of 100 Hz on a 100 MHz spectrometer. The relationship between the resonance frequency and chemical shift is given by the following expression:

$$\delta = \frac{\text{Resonance Frequency (in Hz)}}{\text{Spectrometer Frequency (in Hz)}} \quad \text{X } 10^{6}$$

The electronegativity and inductive effect of groups attached to the vicinity of the proton effects the chemical shift. An electron-attracting group decreases the electron density around the proton thereby reducing the intensity of the electronic magnetic field. Such a proton experiences an enhanced amount of the external magnetic field. Such groups or atoms, which decrease the electron density around the proton, are said to be deshielding the proton from the applied magnetic field. Such groups make the proton signal appear at a lower frequency or in the downfield direction (high δ). Similarly an electron-repelling group enhances the electronic magnetic field thereby shielding the proton causing the proton to resonate at a higher frequency and the signal to move in the upfield direction (low δ).

Equivalent and non equivalent protons:

Protons which are in identical molecular fields in a compound are termed magnetically equivalent. If protons are magnetically equivalent, they have the same chemical shift & spin-spin splitting is not observed for equivalent protons i.e. their absorption occur at the same location in a PMR spectrum. All four hydrogen of CH4 are equivalent because all 4 H are in identical environments. In CH3CH2CH3 there are 6 H of methyl group are equivalent & 2H of CH2 group are equivalent but both 6H of CH3 & 2H of CH2 group are non equivalent to each other.

Spin-spin coupling and coupling constant

The spin of a proton, which acquires two energy states when exposed to a strong magnetic field, is also influenced by the spin of neighboring magnetically active protons. Let us consider two protons H_a and H_b, which are present on adjacent carbon atoms in a molecule. The spin of H_a is affected by the spin of H_b. the interaction of the spins of H_a and H_b is through the intervening bonding electrons. The spin of H_b will have two orientations in the applied magnetic field.

The two spin states of H_b effect the signal by partially shielding and deshielding the spin of H_a. The lower energy levels of the spin of H_b which is aligned in the direction of the applied magnetic field will cause deshielding of the signal of H_a and will result in a slight downfield shift while the higher energy level of the spin of H_b which is aligned against the direction of the applied magnetic field will cause shielding of the signal of H_a and will result in a slight upfield shift of the signal. This shifting of the signal of H_a in the upfield and downfield direction makes the signal to appear as a doublet. The signal of H_b will be affected in the same way by the spin states of H_a. This interaction of spins through bonds resulting in the splitting of the signals is called Spin-Spin Coupling. This is also called Scalar Coupling as the interaction takes place through the intervening bonding electrons and is limited to three bond distances only.

The general formula for splitting is given as 2nI+1 where n is the number of chemically and magnetically similar nuclei interacting with the proton under consideration, I is the spin number of the interacting nuclei. If there are more than one type of nuclei interacting, the formula becomes (2nI+1)(2mI+1)(2oI+1)… where n, m, o, etc are the number of chemically and magnetically similar nuclei in one set. Since we are studying the interactions between protons, which have I as ½, the formula could be written as (n+1)(m+1)…. . e.g. in case of a molecule like CH_3-CH_2-CH_3 the methylene protons interact with six methyl protons. Since the methyl groups are identical, they belong to one set and therefore will split the methylene protons onto a septet. The signal for the methyl group will be split into a triplet due to interaction with the two-methylene protons. If we replace one of the methyl protons with chlorine atom, then the two-methyl groups no longer remain identical and this results in the methylene protons interacting with two sets of protons, one set containing three protons and the second set containing two protons. The signal of methylene will now be split into twelve lines [(3+1)(2+1)].

The spacing between the component peaks of a signal depends upon its interaction with the neighboring nuclei. This spacing is called the Coupling Constant