NMR Overview

- NMR only works for nuclei that have the quantum mechanical property of **SPIN!**
- The spin properties of nuclei characterize each nucleus according to a physical parameter called the chemical shift.
- For a given molecule, coupling constants and relaxation times give information about the connectivity between atoms.
- NMR can be used to follow chemical reactions.
- NMR samples can be solid, liquid, or gas.
- NMR can be used to analyze mixtures.
- Sample quantities should be in the micro- to milligram range.

CONCEPT OF SPIN

The necessary condition for nuclei to exhibit the magnetic resonance phenomenon is that it should have a nett free spin. The nuclei which have the necessary features to exhibit NMR lines can be classified as follows:

a) Nuclei with odd mass number but odd or even charge number have half integral spin and will exhibit magnetic resonance phenomenon e.g. ^{1}H, ^{17}O, ^{15}N.
b) Nuclei with an even mass number and even charge number have zero spin and do not exhibit magnetic resonance phenomenon, e.g. ^{12}C, ^{16}O, ^{32}S.
c) Nuclei with an even mass number but an odd charge have integral spin and do not exhibit magnetic resonance phenomenon, e.g. ^{2}H, ^{14}N.

The nuclei are charged particles, which are spinning. These spinning charges make the nuclei to behave as dipoles, and a magnetization is generated along the axis of spin of these dipoles. The angular momentum of this spin is the spin quantum number or spin number and is represented as **I**. The spin number I could have two values, +½ and -½. The number of orientations the dipole could have, when placed in a strong magnetic field depends on the spin number. The general formula for this is 2nI+1, where n is the number of nuclei, e.g. in case of protons the spin number is ½ and therefore it can have two orientations.

In the ground state or the state in which the sample has not been influenced by the strong external magnetic field, these two values of spin exist as degenerate energy levels. As soon as magnetic field is applied the degeneracy is removed and these spins form two distinct energy levels, the +½ spin being of lower energy (α state) is aligned in the direction of the applied magnetic field (with the field) and the -½ spin being of higher energy (β state) is aligned in the opposite direction (against the field). There is a slight excess of population in the lower energy level according to the Boltzmann's distribution law. Thus the nett magnetization in the lower energy level is slightly more in the lower energy level. This difference in the magnetization between the two energy levels is known as **Macroscopic Magnetization**. This macroscopic magnetization is responsible for giving the NMR signals.

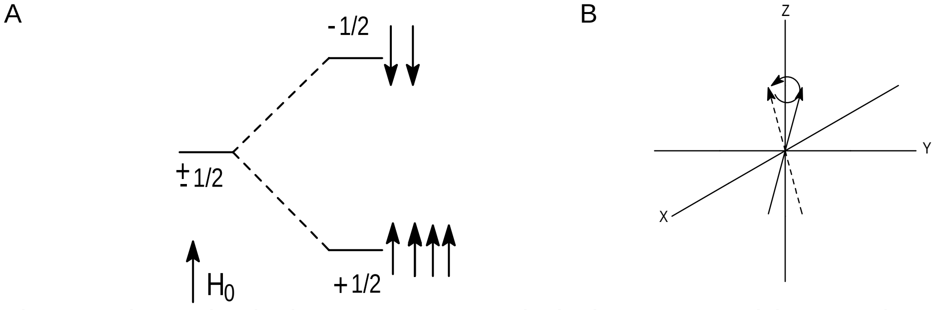


Fig.1 A Spins under the influence of magnetic field. B Precisional Motion

Apart from spinning on their own axis, the nuclei also have a precisional motion in which the axis of spin moves about the axis of the applied magnetic field. The frequency with which nuclei precess is known as the Precisional Frequency or Larmor Frequency. It is this precisional frequency of nuclei, which is in the range of radio frequency.

Precession: The circular movement of the magnetic moment in the presence of the applied field.

Larmor Frequency: The angular frequency (ω_o) for the precessional motion of the magnetic moment around B_0.

Absorption of Energy	Emission of Energy
+ ½ → - ½	- ½ → + ½

RESONANCE: The net absorption of energy caused by an electromagnetic wave hitting a nucleus at the Larmor frequency (spin flip).

SHIELDING: The electronic modulation of the B_0 field caused by the electrons surrounding a given nucleus.

DIAMAGNETIC SHIELDING: The magnetic field generated by the valence electrons surrounding a nucleus that opposes the applied magnetic field. The greater the strength of the electronic environment, the lower the frequency of precession of the nucleus.

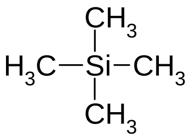
The electronegativity and inductive effect of groups attached to the vicinity of the proton effects the chemical shift. An electron-attracting group decreases the electron density around the proton thereby reducing the intensity of the electronic magnetic field. Such a proton experiences an enhanced 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 (highδ). 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 (lowδ). To remember this, it is best to keep in mind that Deshielding starts with **D** and it moves the signal in the downfield Direction which also starts with **D**.

CHEMICAL SHIFT: The variation of the resonance frequency with shielding.
Shielding = opposing magnetic field
= electrons around a nucleus
= low frequency precession
= small chemical shift value (ppm)
= upfield shift
Deshielding = decreasing the magnitude of the electron cloud
= neighboring an electron withdrawing group
= high frequency precession
= large chemical shift value (ppm)
= downfield shift

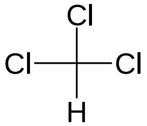
The impact of shielding (or deshielding) causes a difference in chemical shift of nuclei that is very small.

Thus to observe the chemical shift, a reference compound is used as an internal standard. TMS is the standard! The solvent is often used as a standard in research situations.

The chemical shift (δ) equals the shift (Hz) divided by the spectrometer frequency (MHz). Thus 1 over one million = 1 ppm.



$Si(CH_3)_4$



$CHCl_3$

The higher the magnetic field, the greater the shift of the nuclei subjected to that magnetic field.