NMR Spectroscopy - II

Dr. M. Ganapathi,
Assistant Professor,
Department of Chemistry,
Govt. Arts College, Tiruvannamalai.

CONTENT

Theory of NMR spectroscopy

Chemical Shift

Theory of NMR Spectroscopy

A) Spinning Nuclei Magnetic Moments:

- Some elements have isotopes with nuclei that behave as through they were spinning about an axis, (Fig.) much like the earth or child's top.
- The spinning of a charged particle generates a magnetic field. Isotopes with nuclear sin, therefore have small magnetic fields whose magnitude and direction can be described by a vector called a magnetic moment.
- Consequently, the spinning nuclei behave as though they were tiny bar magnets with a north pole and a south pole.

Theory of NMR Spectroscopy

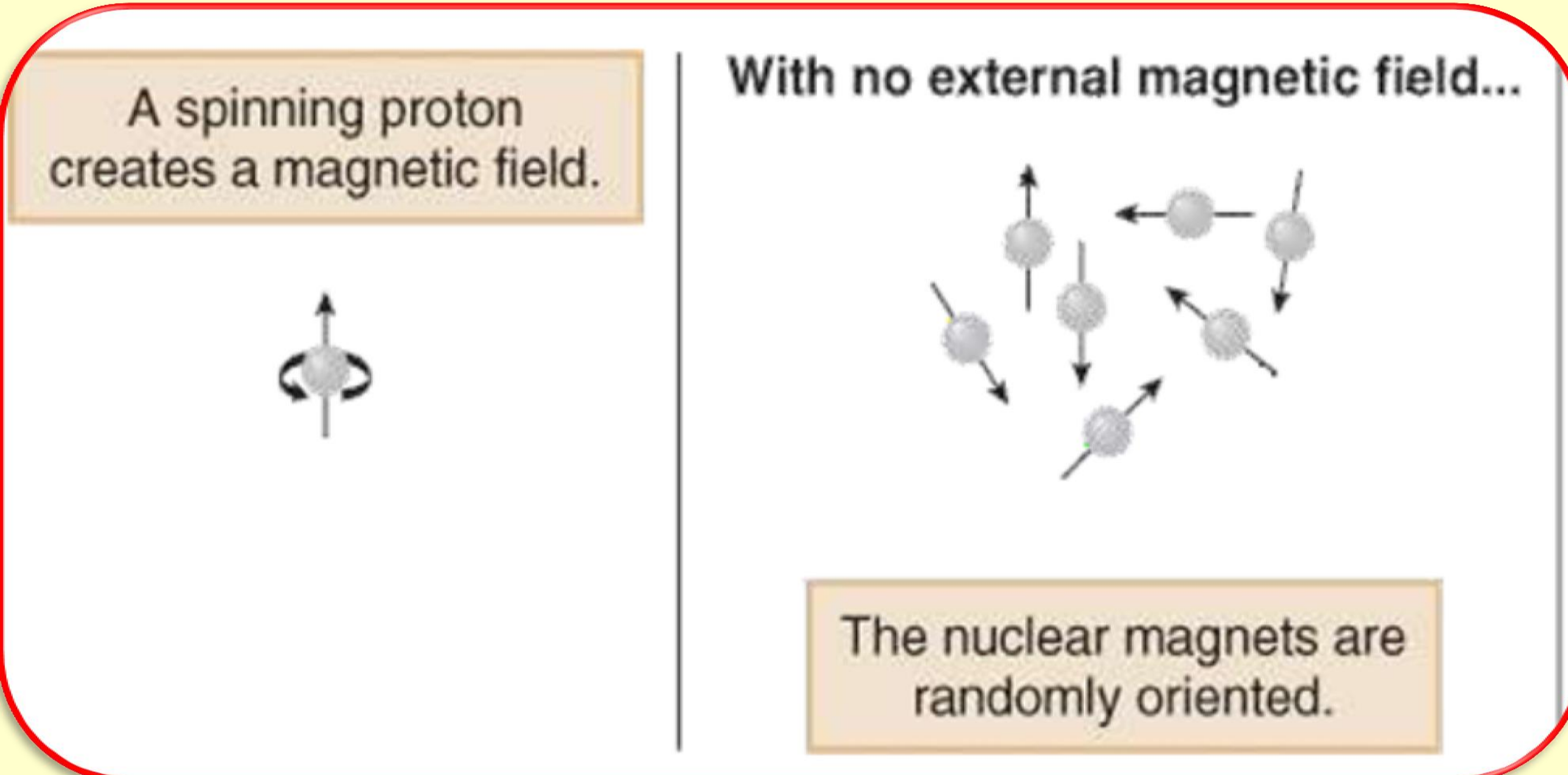


Fig.

Theory of NMR Spectroscopy

B) Magnetic moment and Magnetic field:

- A particle that possess magnetic moment, when it is kept external field, it may becomes oriented to the magnetic field.

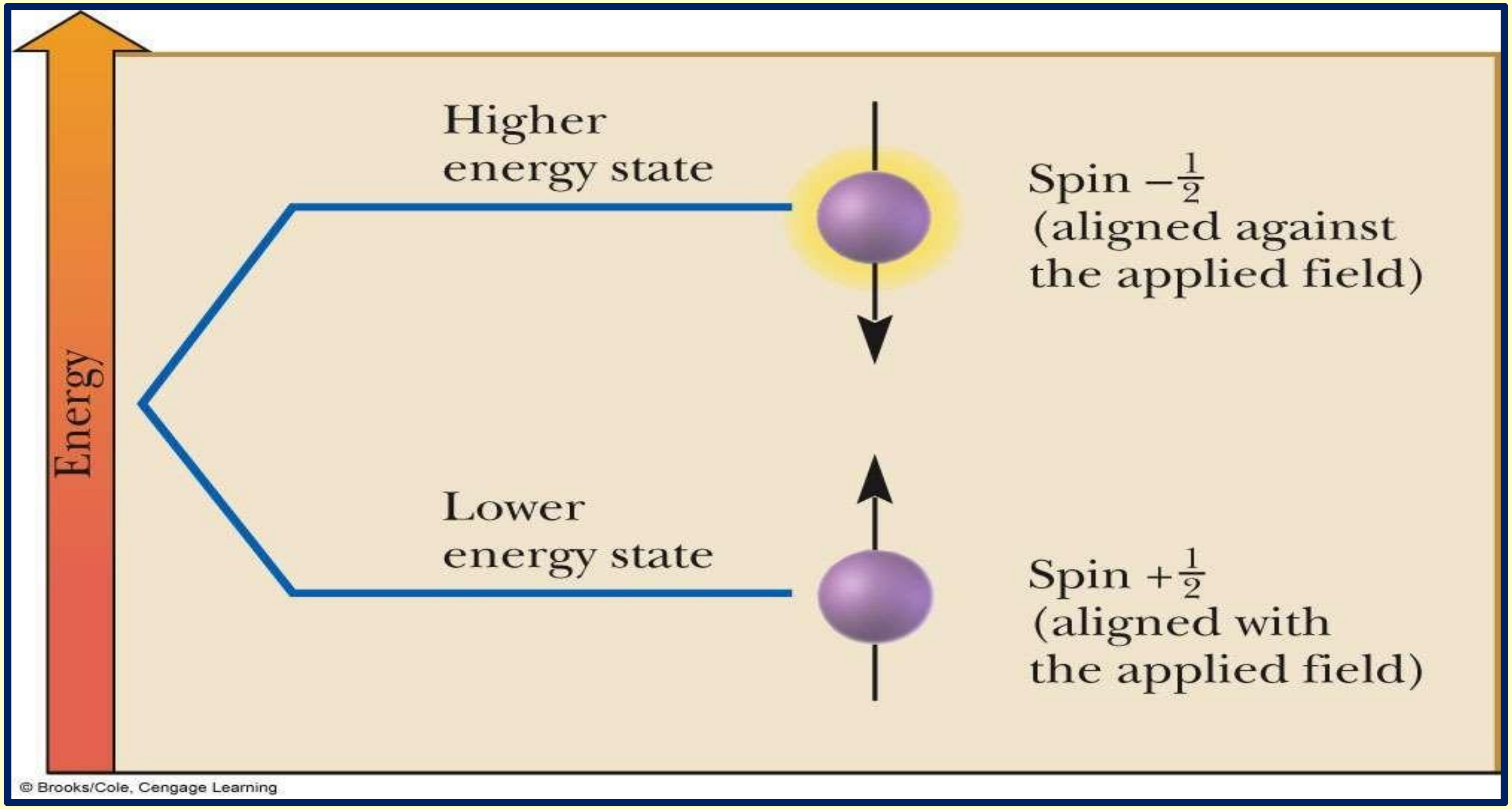
$$E = -\mu_H H_o$$

Where H_o – Strength of external field

μ_H - the component of magnetic moment in the direction of the field.

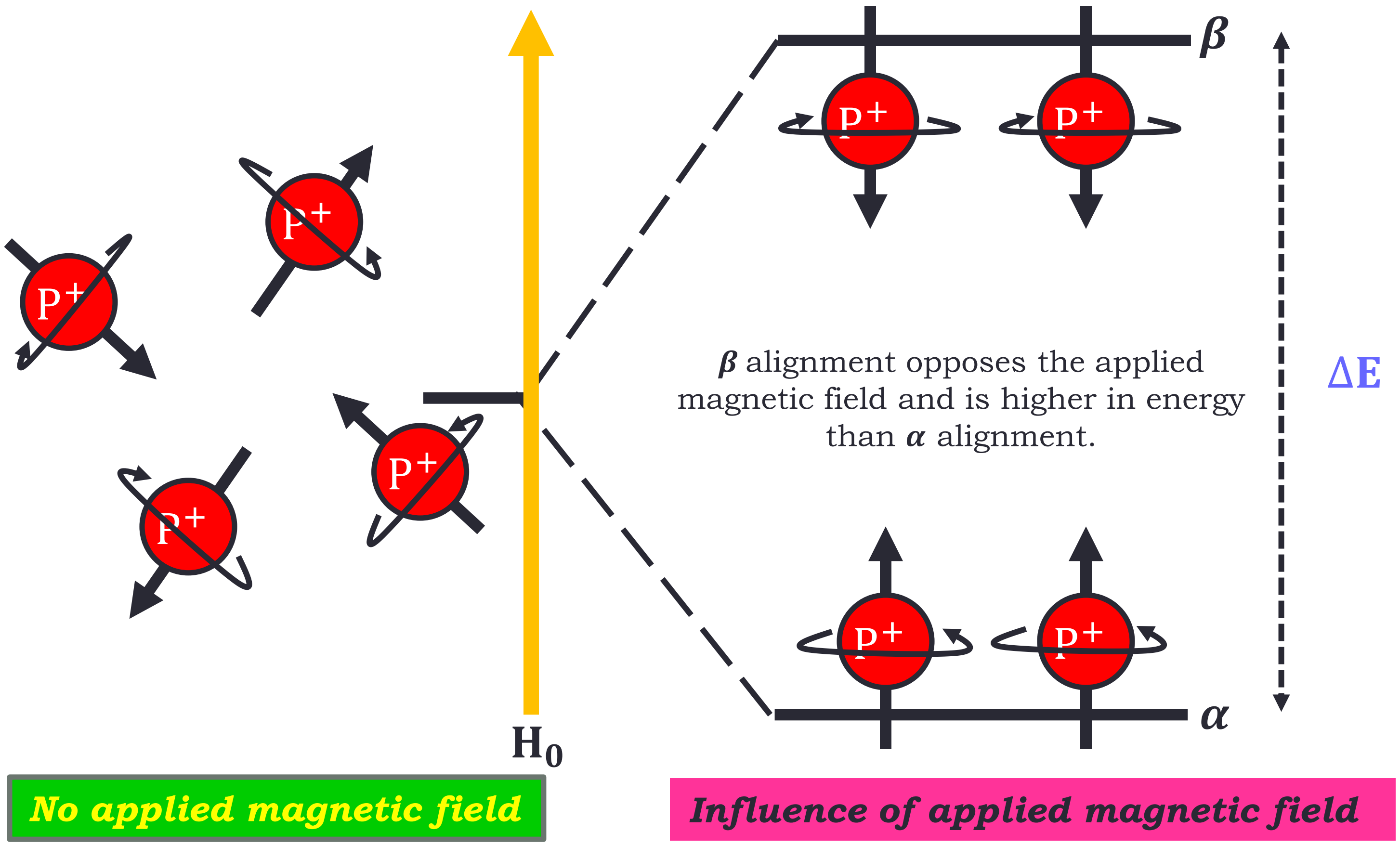
Their magnetic moments tend either to align with the field (corresponding to α–spin) or against the field (corresponding to β–spin)

Theory of NMR Spectroscopy



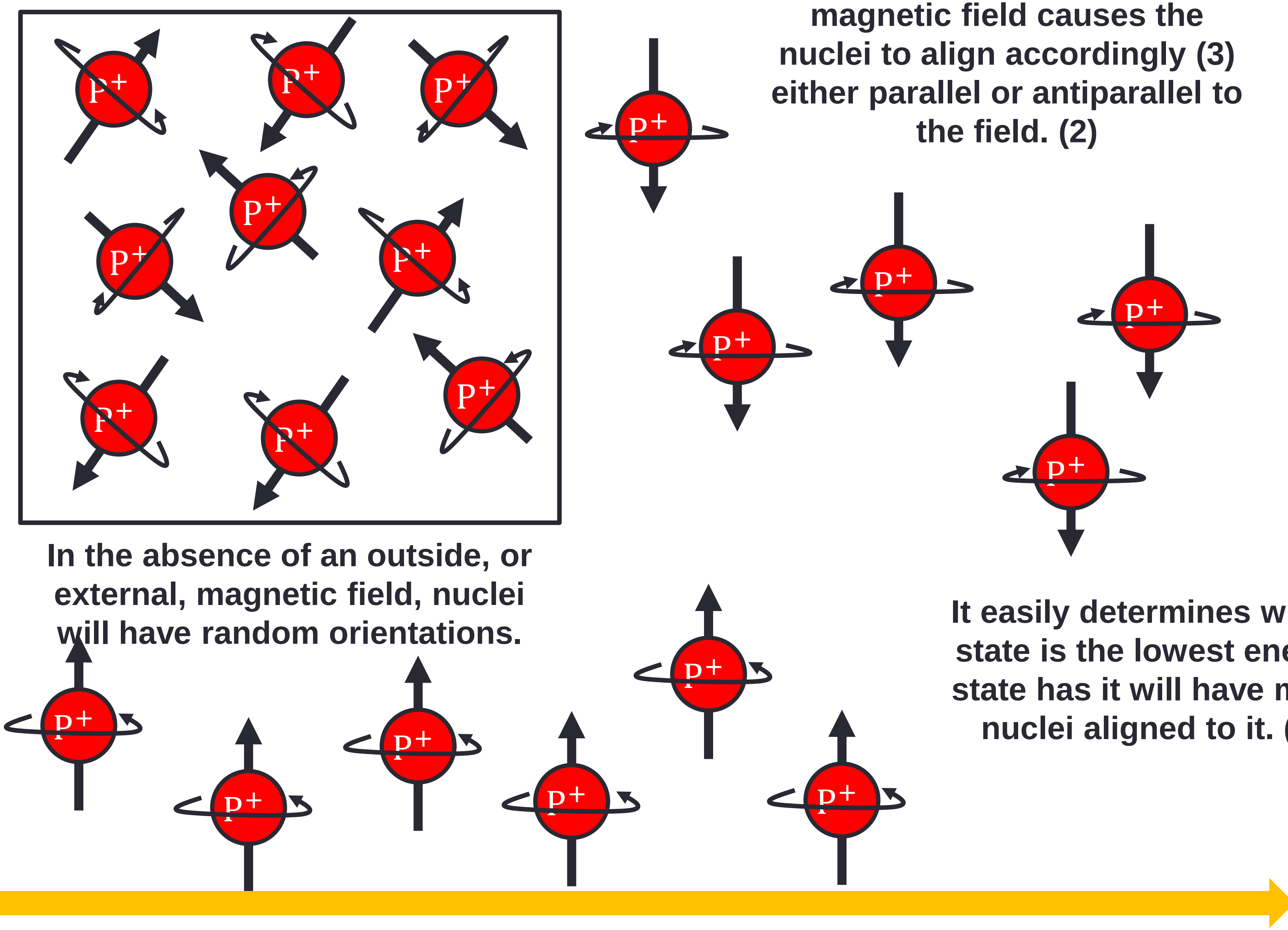
Change in spin state energy separation with increase by applied magnetic field ,B_0

Theory of NMR Spectroscopy



Manipulation of nuclei is through the application of an applied magnetic field, H_0. In the example, the nucleus, such as ^{1}H, has a nuclear spin of ½.

The presence of an external magnetic field causes the nuclei to align accordingly (3) either parallel or antiparallel to the field. (2)



In the absence of an outside, or external, magnetic field, nuclei will have random orientations.

It easily determines which state is the lowest energy state has it will have more nuclei aligned to it. (2)

Theory of NMR Spectroscopy

C) Nuclear Resonance:

When the applied frequency from the radiofrequency source become equal to the larmor frequency or angular frequency of precession, the two are said to in resonance

Chemical Shift

"The difference between the magnitudes of the magnetic field at which free nuclei and molecular nuclei resonate is called Chemical shift"

- **The utility of NMR is that all protons do not show resonance at same frequency because, it is surrounded by particular no. of valence electrons which vary from atom to atom so, they exist in slightly different electronic environment from one another.**

Chemical Shift

- **Position of signals in spectrum help us to know nature of protons i.e. aromatic, aliphatic, acetylinic, vinylic, adjacent to electron releasing or withdrawing group. Thus they absorb at different field strength.**

- **The relative energy of resonance of a particular nucleus resulting from its local environment is called chemical shift.**

Chemical Shift

- For Measuring chemical shifts it is not possible to use a free nucleus as a reference. Instead chemists use those compounds that exhibit only a single sharp resonance line as a reference for measuring chemical shifts.

- The most frequently employed reference compound is tetramethylsilane (TMS) having formula $Si(CH_3)_4$.

Chemical Shift

- The local magnetic field B_{local} experienced by a nucleus in a molecule is related to the external magnetic field B_o by,

$$B_{local} = B_o (1 - \sigma)$$

Where σ, a dimensionless quantity, is called the screening constant [or shielding constant]

For two nuclei A and B in a molecule , the local fields are,

$$B_A = B_o (1 - \sigma_A)$$

$$B_B = B_o (1 - \sigma_B)$$

Where, σ_A and σ_B are the respective screening constants

Chemical Shift

$$B_B - B_A = B_o (1 - \sigma_B) - B_o(1 - \sigma_A)$$

$$= B_o [\sigma_A - \sigma_B]$$

$$= B_o \, \delta_{AB}$$

Where, δ_{AB} (or simply, δ) is the chemical shift of nucleus A with respect to nucleus B. In practice we define chemical shift of a sample as,

$$\delta = \frac{B_{sample} - B_{ref}}{B_o} \times 10^6 \text{ ppm}$$

Chemical Shift

Since, B ∞ ν

Hence, $$\delta = \frac{\nu_{sample} - \nu_{ref}}{\nu_o} \text{ X } 10^6 \text{ ppm}$$

Chemical Shift $$\delta = \frac{\nu_s - \nu_{TMS}}{\nu_o} \text{ X } 10^6 \text{ ppm}$$

Chemical Shift

- **The Chemical shift (δ) values expressed in terms of ppm (parts per million)**

- **The Chemical shift value expressed as δ (Telta) and τ (Tau) scale.**

  i) For TMS, in a δ scale is equal to zero [δ = 0]

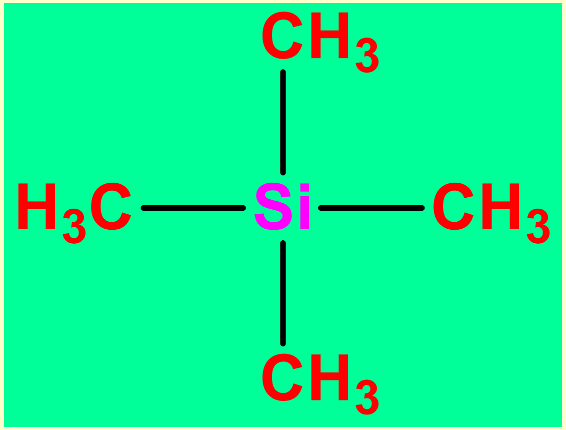
  ii) For TMS, In a τ scale is equal to 10 [τ= 10]

$$\tau = 10 - \delta$$

ie., TMS protons are resonates at upfield signal.

Internal Standards (Reference)

TMS (Tetramethylsilane) is most commonly used as *Internal standard* in NMR spectroscopy.



Due to following reasons:

- **It is chemically inert and miscible with a large range of solvents.**

Internal Standards (Reference)

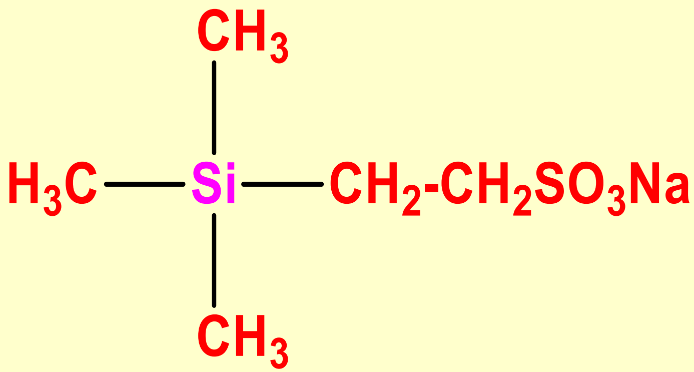
- **Its twelve protons are all magnetically equivalent.**
- **Its protons are highly shielded and gives a strong peak even small quantity.**
- **It is less electronegative than carbon.**
- **It is highly volatile and can be easily removed to get back sample**

Note:

TMS generally employed as internal standard for measuring the position of ^{1}H, ^{13}C and ^{29}Si in the NMR spectrum.

Internal Standards (Reference)

DSS(Sodium salt of 3-(trimethyl silyl)propanesulphonate)



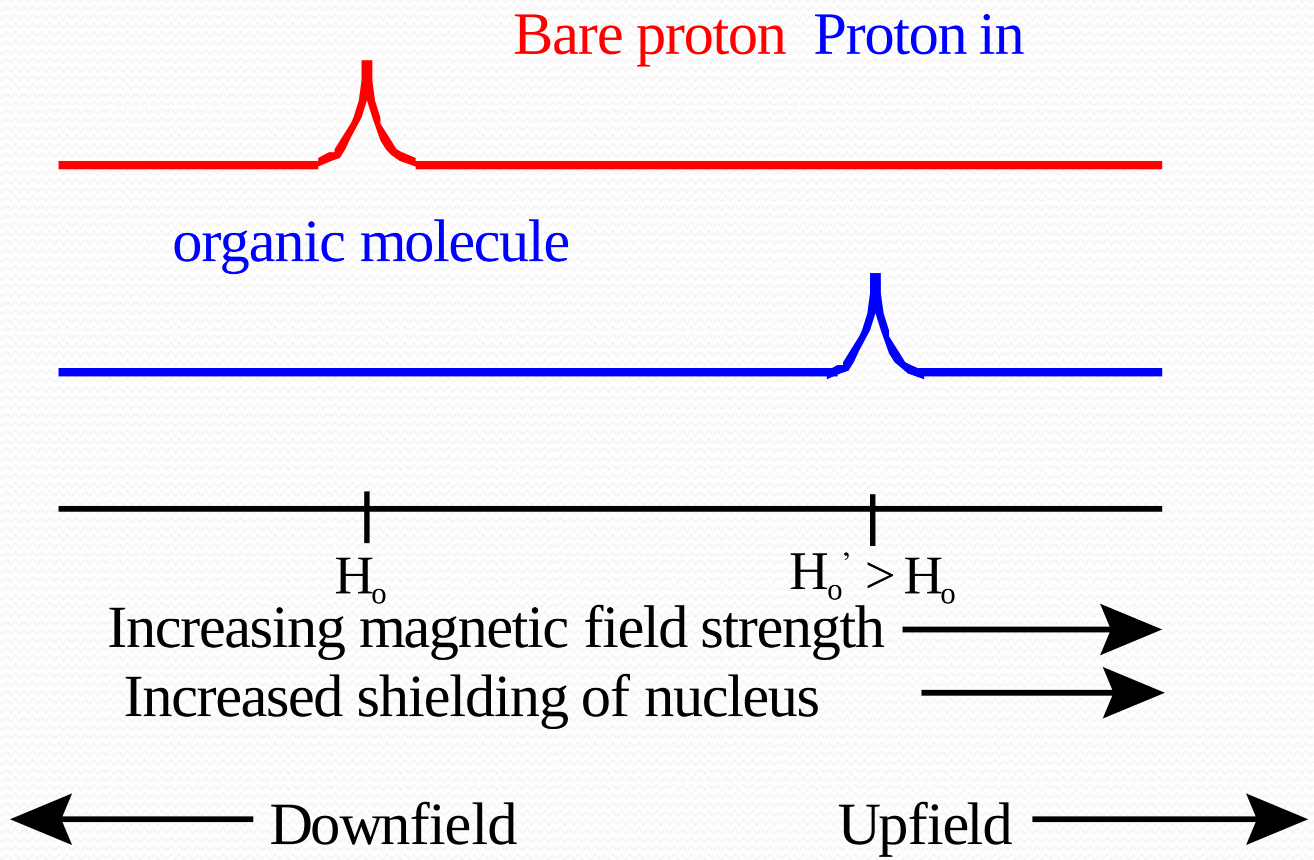
DSS is a water soluble compound. It is used as internal Standard for running PMR spectra of water soluble substances in D_2O solvent.

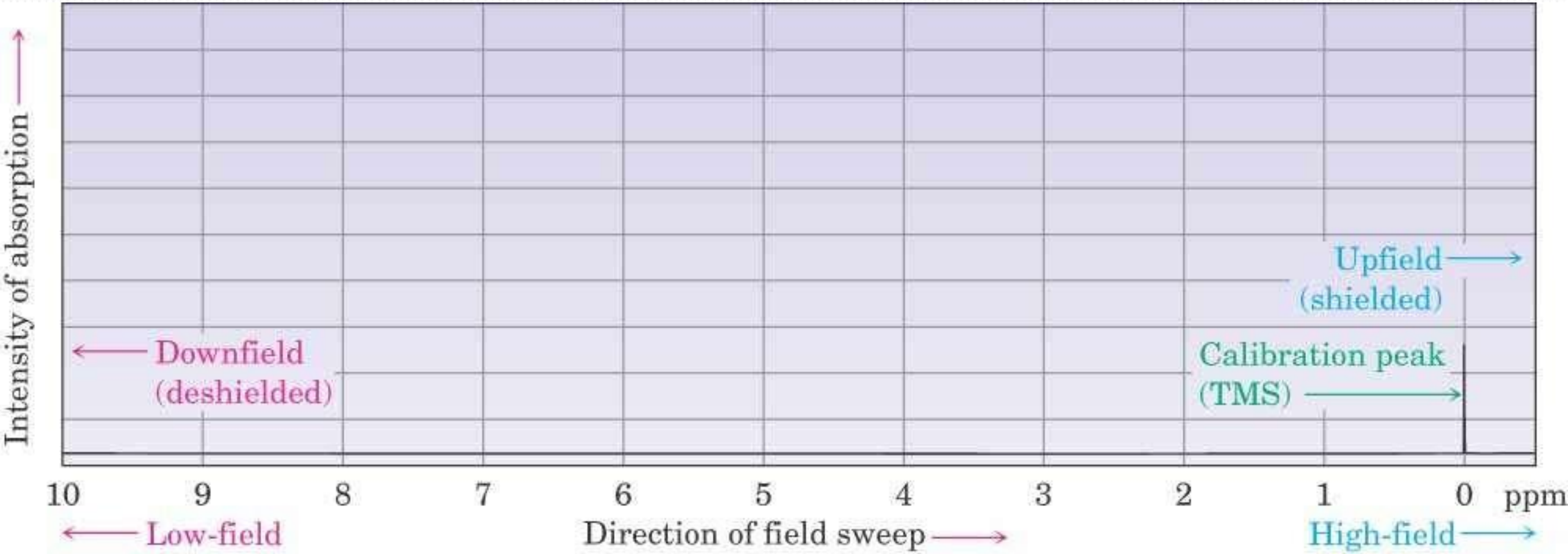
Measuring Chemical Shift

Numeric value of chemical shift: difference between strength of magnetic field at which the observed nucleus resonates and field strength for resonance of a reference.

- **The relative energy of resonance of a particular nucleus resulting from its local environment is called chemical shift.**
- **NMR spectra show applied field strength increasing from left to right**
- **Left part is down field right part is up field.**
- **Nuclei that absorb on up field side are strongly shielded.**

- **Let’s consider the just the proton (^{1}H) NMR**




Intensity of absorption
Downfield
(deshielded)
Upfield
(shielded)
Calibration peak
(TMS)
10
9
8
7
6
5
4
3
2
1
0
ppm
Low-field
Direction of field sweep
High-field