

SPECTROSCOPY

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INTRODUCTION

- During the last six decades or so, spectroscopic methods have emerged as powerful tools for identification and structure determination of organic molecules.
- The first NMR signals were observed independently by Purcell at Harvard and Bloch at Stanford in 1945, and the first application to study the structure of ethyl alcohol was made in 1951.
- Purcell and Bloch won the Noble Prize in Physics for their discovery.

MAGNETIC PROPERTIES OF NUCLEI

Like electrons, the nuclear particles, i.e., protons and neutrons are also considered to spin about their axes. Further like electrons, each proton and neutron has a spin quantum number of $\frac{1}{2}$. If the protons and neutrons in a nucleus are not paired, the nucleus as a whole will have a resultant nuclear spin I . The numerical value of this nuclear spin quantum number, I , depends upon the number of protons and neutrons having parallel and anti parallel spins. It is related to the mass number and atomic number as follows:

<u>Atomic mass</u>	<u>Atomic Number</u>	<u>Nuclear spin, I</u>
Odd	Even or odd	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ etc.
Even	Even	0
Even	Odd	1, 2, 3, ... etc.

- i) Nuclei such as ^1H , (proton), ^{13}C , ^{15}N , ^{19}F , ^{31}P etc. all have $I = \frac{1}{2}$;
- ii) Nuclei such as ^4He , ^{12}C , ^{18}O , ^{32}S all have $I=0$. It is fortunate for organic chemists that ^{12}C and ^{18}O are non-magnetic.

Thus atomic nucleus is associated with charge therefore, like any other rotating charge, it generates a magnetic field along the axis of its spin. Therefore, such a nucleus behaves as a tiny bar magnet and has a characteristic magnetic moment, μ .

For a nucleus with spin quantum number $I > 0$ has $(2I + 1)$ allowed spin states which differ from one another by unity

The variable spin states are $-I, (-I+1), \dots, (I-1), +I$.

For ^1H $I = \frac{1}{2}$, ^{35}Cl $I = \frac{3}{2}$, ^{17}O $I = \frac{5}{2}$

Without the magnetic field the spin states of nuclei are degenerate, i.e., possess the same energy, and energy level transitions is not possible. When the magnetic field is applied, the separate levels and radio frequency radiation can cause transition between these energy levels.

The field of NMR (Nuclear magnetic resonance) spectroscopy further divided into number of subfields, depending upon the magnetic nucleus being examined.

For example:

- Proton magnetic resonance
(PMR or ^1H NMR)
- Carbon magnetic resonance (^{13}C NMR)
- Fluorine magnetic resonance (^{19}F NMR)
- Phosphorous magnetic resonance
(^{31}P NMR) etc.

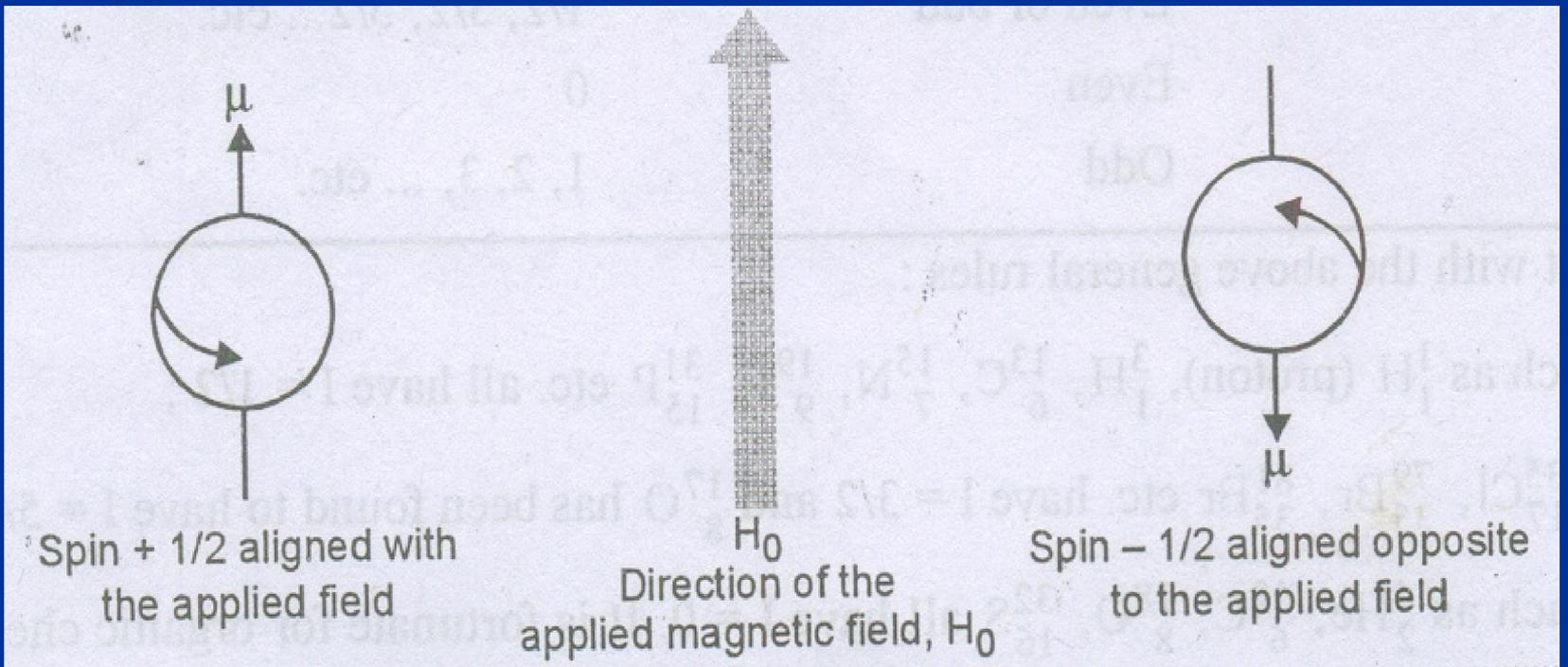
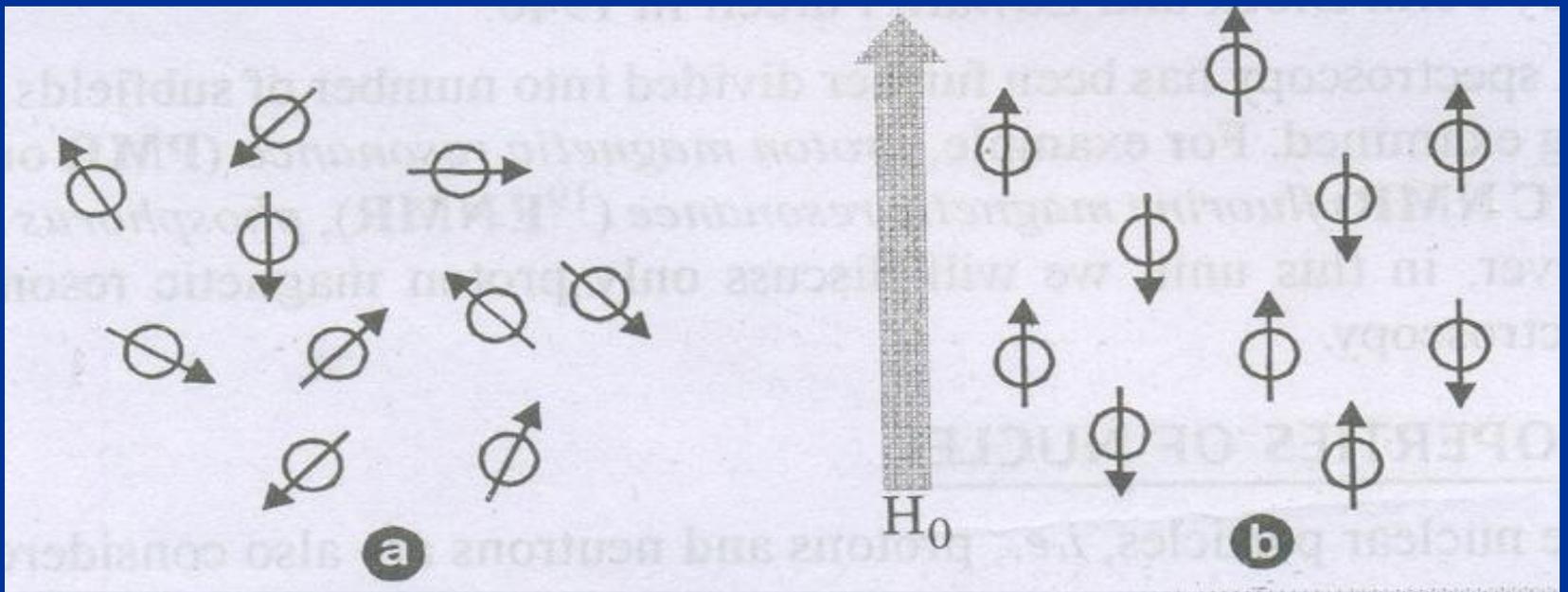
In this unit we discuss only proton magnetic resonance.

PMR OR ^1H -NMR SPECTROSCOPY:

The simplest nucleus having magnetic properties is the hydrogen nucleus consisting of a single proton and we shall be concerned with the NMR spectra of only those molecules which contain protons (^1H) as nuclei with magnetic properties. The field of spectroscopy dealing with the NMR spectra of only hydrogen nuclei or protons is often referred to as

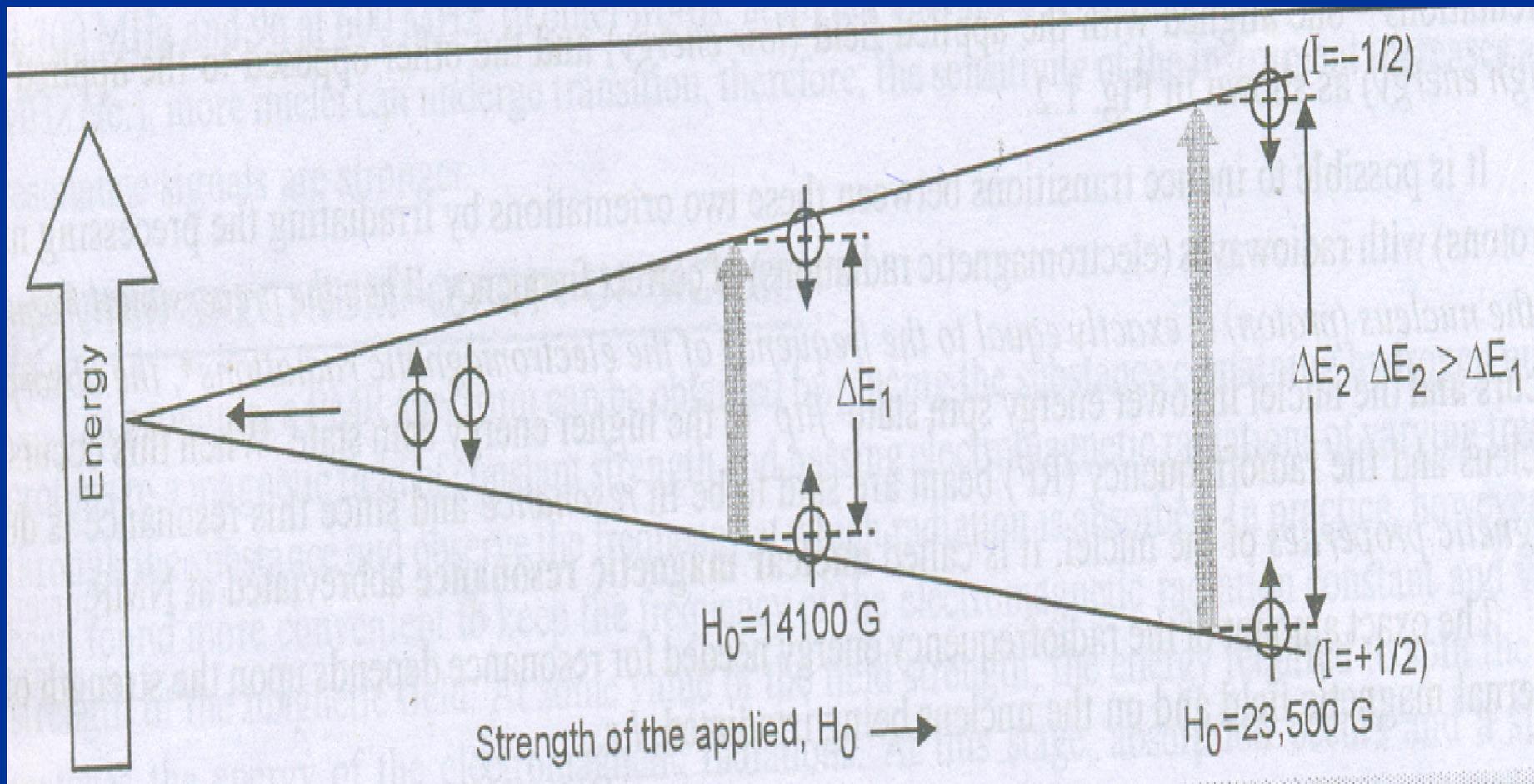
**proton magnetic resonance
(PMR or ^1H -NMR spectroscopy.)**

The nuclear spin of the protons of a given sample are normally oriented randomly. But when a compound containing hydrogen (a protons) is placed in an external magnetic field (H_0), the protons may adopt one of the two possible orientations with respect to the external magnetic field. Either the proton can orient so that its magnetic moment (H') is aligned with (i.e. parallel) to the applied field or it may orient so that its magnetic moment is aligned against (i.e antiparallel) to the applied field.

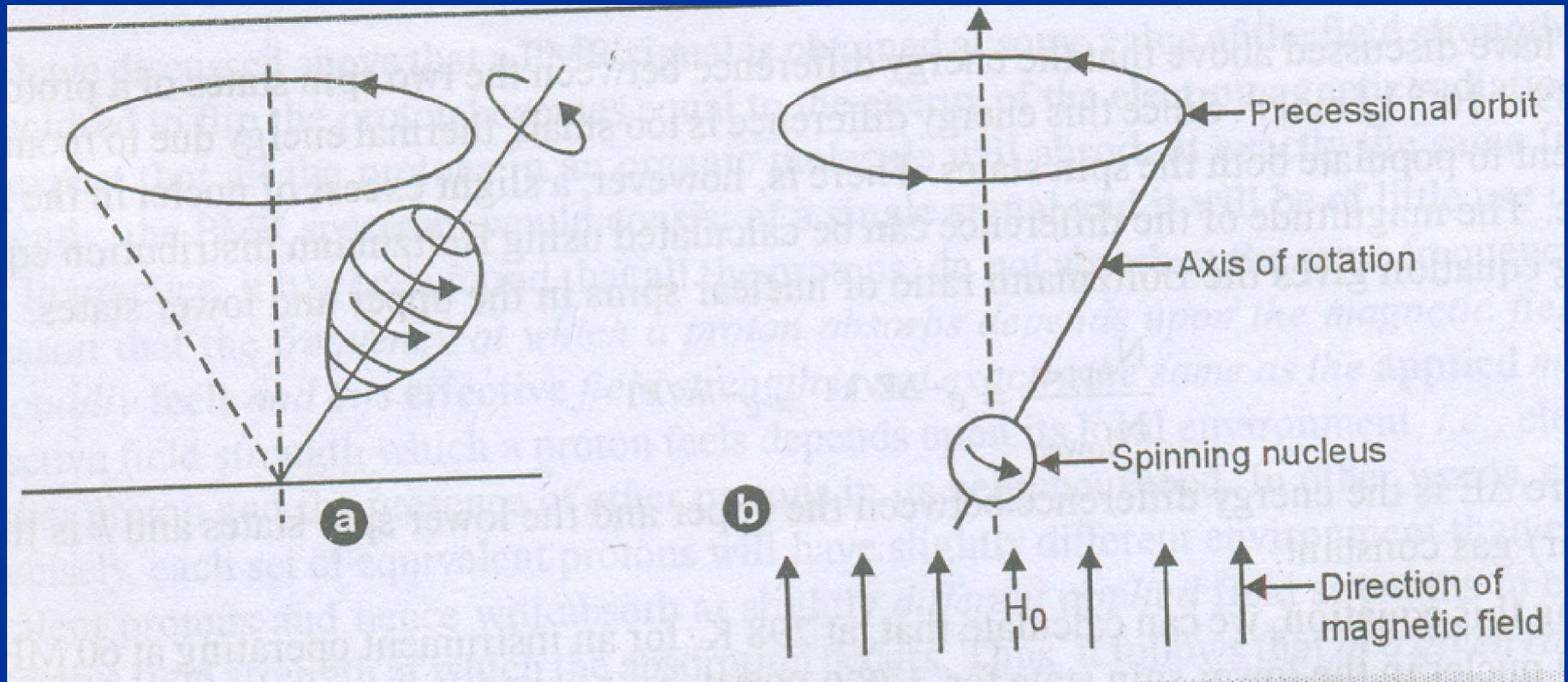


By convention protons with spin state $+ \frac{1}{2}$ are said to be aligned with the applied field, associated with lower energy and more stable.

While protons with spin state $- \frac{1}{2}$ are said to be aligned against the magnetic field, associated with more energy and less stable. The difference between the two states is designated as ΔE . In general, the value of ΔE is very small but its magnitude varies directly with the applied field strength.



Consider the motion of a common spinning top.
When the spinning top is disturbed a little, its spinning axis will trace out a circle perpendicular to the earth's gravitational field as shown in the fig. Such a motion is called **Precession**



In a similar way, when a nuclear magnet is placed in an external magnetic field, it will experience a torque which will tend to align it with field. Since the nuclear magnet is spinning, it will not align with the external magnetic field but will precess around it with a certain frequency ω , called **Precessional Frequency** or the **Larmor Frequency**.

The frequency at which a proton will precess, depend upon the strength of the applied magnetic field. Stronger the applied field, higher the Precessional frequency.

For a proton if the applied magnetic field is **14100 Gauss**, the Precessional frequency will be **60 MHz**.

It is possible to induce transitions between two orientations of proton i.e. one aligned with the applied Field (low energy) $I = +1/2$ and other opposed to the applied field (high energy) $I = -1/2$. The transition between the two orientations of nuclei (proton) can exist, when it is placed in the external applied magnetic field.

When the precessional frequency of the proton is exactly equal to the frequency of the applied magnetic field, the absorption occurs and the proton in the lower energy spin state flip to the higher energy spin state. When this occurs, the nucleus and the radiofrequency beam are said to be in resonance due to the magnetic properties of the nuclei thus it is called

Nuclear Magnetic Resonance (NMR)

The exact amount of radiofrequency energy required for the flipping of the proton spin state will depend upon the strength of the external magnetic field.

The fundamental relational between the magnitude of ΔE , frequency (ν) of radiation absorbed and the strength of the applied field H_0 are as shown below:

$$\Delta E = h \times \nu = h \times \gamma H_0 / 2\pi. \quad (\nu = \gamma H_0 / 2\pi.)$$

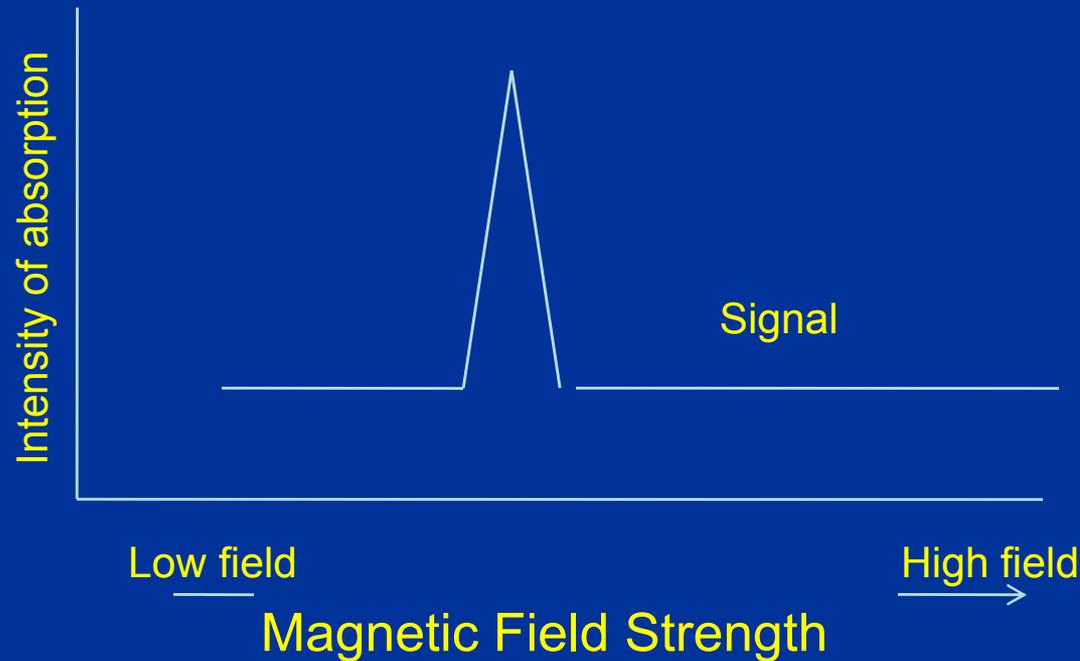
where h is Planck's constant and γ is a nuclear constant, known as Gyromagnetic ratio.

For a proton, value of $\gamma = 26750$.

PMR OR ^1H -NMR SPECTRUM : ORIGIN OF SIGNALS

In principle, a PMR spectrum could be obtained by placing the substance containing hydrogen nuclei or protons in a magnetic field of constant strength and passing a radiation of varying frequency through the substance. At a certain frequency of the radiation, energy of the radiation would match the energy required to flip the proton. This radiation would be absorbed by the proton and its frequency could be recorded.

The PMR spectrum is a plot of intensity of absorption along Y-axis against magnetic field strength along x-axis. The position of absorption signal along x-axis can be expressed in either field strength or frequency units.



In actual practice, NMR spectrometers usually operate by keeping the applied radio-frequency constant (generally maintained at 40, 60, 100.... MHz) and varying the strength of applied magnetic field. At some value of the field strength, the energy of radiation is just sufficient to flip over the proton and absorption of radiation takes place. This gives rise to an absorption band, commonly called a signal.

PMR spectra are recorded on charts. If all the Protons in a molecule were to absorb the radiation at exactly the same applied magnetic field strength, the PMR spectrum would consist of a single signal and PMR spectroscopy would have little utility. Fortunately, however, it is not so in actual practice. This is because the field strength at which absorption by a particular proton takes place is strongly influenced by the local environments of the proton such as electron density around it and the presence of other protons in its neighbourhood.

As a result, the magnetic field strength which a proton actually experiences is not the same as the applied field strength, rather it is the applied field strength modified by the local environments of that proton. A proton having different environments than another will require somewhat different applied field strength to experience the same effective field strength at which absorption takes place.

It follows that at a given radio-frequency, the protons having different environments absorb at the same effective field strength but they absorb at different applied field strengths. Since the absorption is plotted against the applied field strength, the PMR spectrum consists of many signals which give very useful information about molecular structure.

NUMBER OF SIGNALS : EQUIVALENT AND NON-EQUIVALENT PROTONS:

In a given molecule the protons with different environments absorb at different applied field strengths while the protons with identical environments absorb at the same field strength. A set of protons having identical environments are referred to as equivalent protons and all of them give rise to one signal. The protons with different environments are termed as non-equivalent protons and they give rise to different signals.

Therefore, the number of signals in a PMR spectrum tells us how many kinds of protons are present in a given molecule.

Prediction of different kinds of protons.

Let us now try to analyse theoretically the different kinds of protons that a molecule contains. For this purpose it may be noted that in general simply means chemically equivalent protons.

As such, the equivalence of protons can be judged quite easily by following the method of isomer number as illustrated below :

Imagine each hydrogen or proton in the molecule to be substituted by some other atom Z. If the substitution of either of two protons by Z is expected to furnish the same product or enantiomeric products (i.e. mirror images), the two protons are chemically and magnetically equivalent, otherwise not.

For instance, let us consider the case of ethyl chloride $\text{CH}_3 - \text{CH}_2 - \text{Cl}$.

(i) The substitution of a methyl proton by Z would yield $\text{CH}_2\text{Z} - \text{CH}_2 - \text{Cl}$.

(ii) Substitution of a methylene proton would give $\text{CH}_3 - \text{CHZ} - \text{Cl}$.

Since the products of (i) and (ii) are different products, methyl protons are not equivalent to methylene protons.

(iii) The three methyl protons are equivalent amongst themselves as the replacement of any one of three would furnish the same product. Such protons are also known as homotopic.

(iv) In case of methylene protons, however, replacement of either of two would yield one of a pair of enantiomeric products.

But such pair of protons called enantiotopic protons are also magnetically equivalent to each other. This is because the environments of enantiomeric products are just mirror images of each other and PMR spectrum does not distinguish between mirror images.

Hence ethyl chloride contains only two kinds of protons and this is confirmed by PMR spectrum of the molecule which gives two signals.

2) Proceeding along the same lines we can judge the number of types of protons in a given molecules as shown below. Equivalent protons are indicated here by the same letter.



All protons equivalent; only 1 PMR signal



Two kinds of protons; two PMR signals.



Three kinds of protons; three PMR signals

Let us now extend our study to some molecules in which the protons may be treated as non-equivalent on stereo-chemical considerations. It may be pointed out in this connection that in order to be chemically equivalent, protons must also be stereochemically equivalent.

- How many proton signals would be expected in the following molecules.



iv) $\text{ClCH}_2\text{CH}_2\text{Br}$

v) Cyclopentane

vi) Cyclohexane

vii) Benzene

- Propose the structural formula for each of the following compounds in accordance with the number of signals obtained.

i) C_2H_6O (one signal)

ii) C_2H_6O (three signals)

iii) $\text{C}_2\text{H}_4\text{Cl}_2$ (one signal)

iv) $\text{C}_2\text{H}_4\text{Cl}_2$ (two signals)

v) C_6H_{12} (one signal)

How will you distinguish between the following pair of organic compound on the basis of PMR spectroscopy?



POSITIONS OF SIGNALS AND CHEMICAL SHIFT

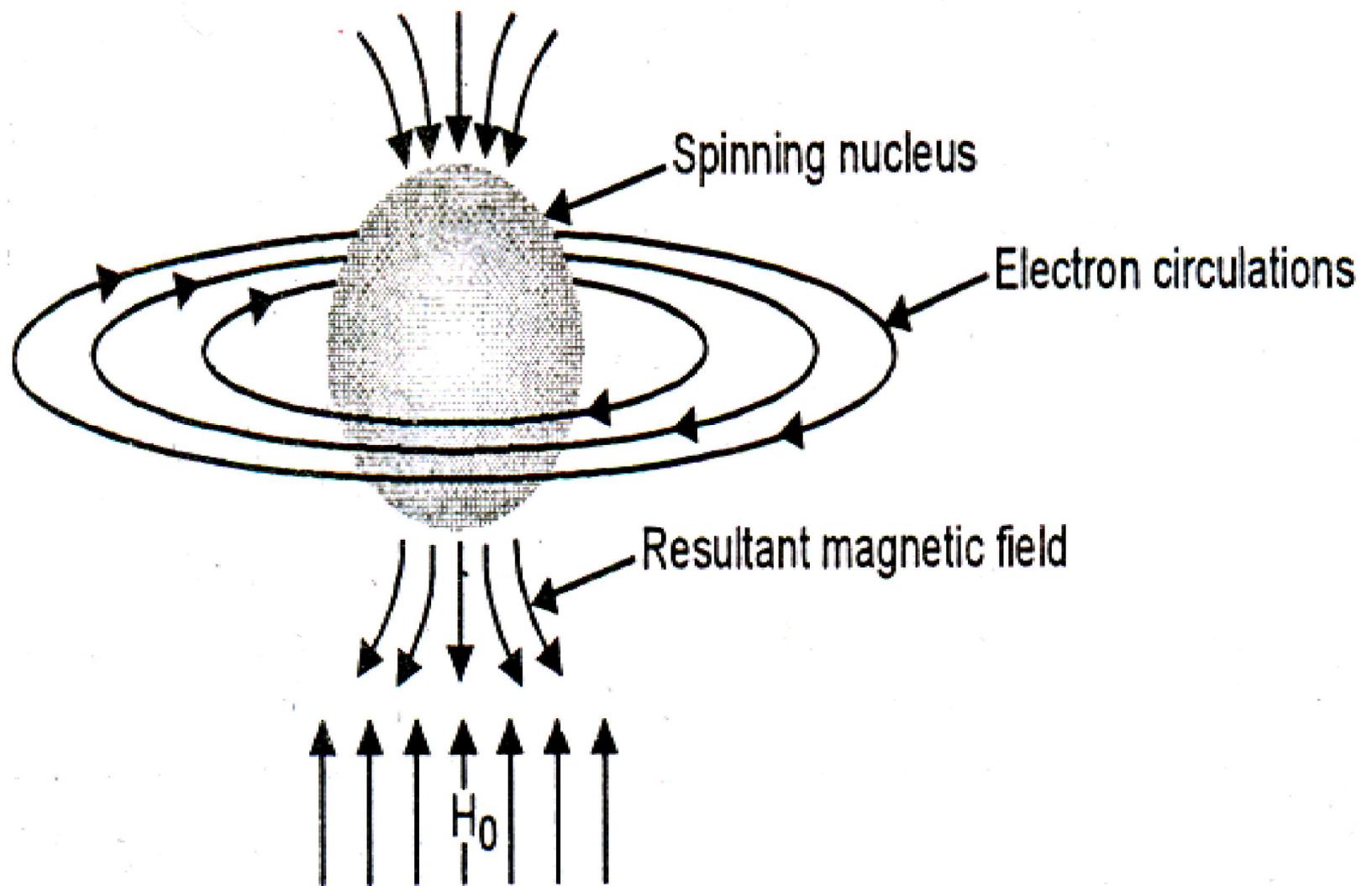
- The number of signals in a PMR spectrum tells us about the number of types of protons that a molecule has. At the same time, the position of the signals reveals the actual nature of protons, i.e., whether the protons are aliphatic, aromatic, vinylic, acetylenic, hydroxyl, etc. as discussed below.

SHIELDING AND DESHIELDING OF PROTONS.

- For determining its PMR spectrum, a molecule is placed in a magnetic field. This causes the electrons of the molecule to circulate and in doing so they generate secondary magnetic fields called induced magnetic fields. The induced magnetic field may either oppose or reinforce the applied field. For example, circulation of σ -electrons about a given proton itself generates a magnetic field which opposes the applied field.

On the other hand, circulation of electrons particularly the π electrons about the neighboring nuclei generates a field which may either oppose or reinforce the applied field.

If the induced field opposes the applied field, the effective field strength experienced by the proton decreases. This is called shielding of the proton. Compared to a naked proton, a shielded proton required stronger magnetic field to produce an absorption signal or in other words it absorbs up field.

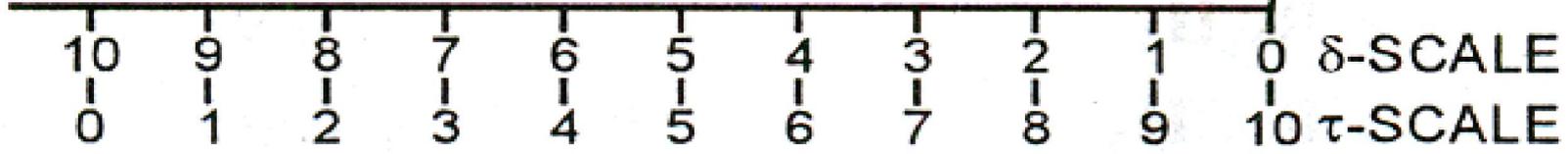


TMS SIGNAL

SHIELDED PROTONS, UPFIELD SIGNAL



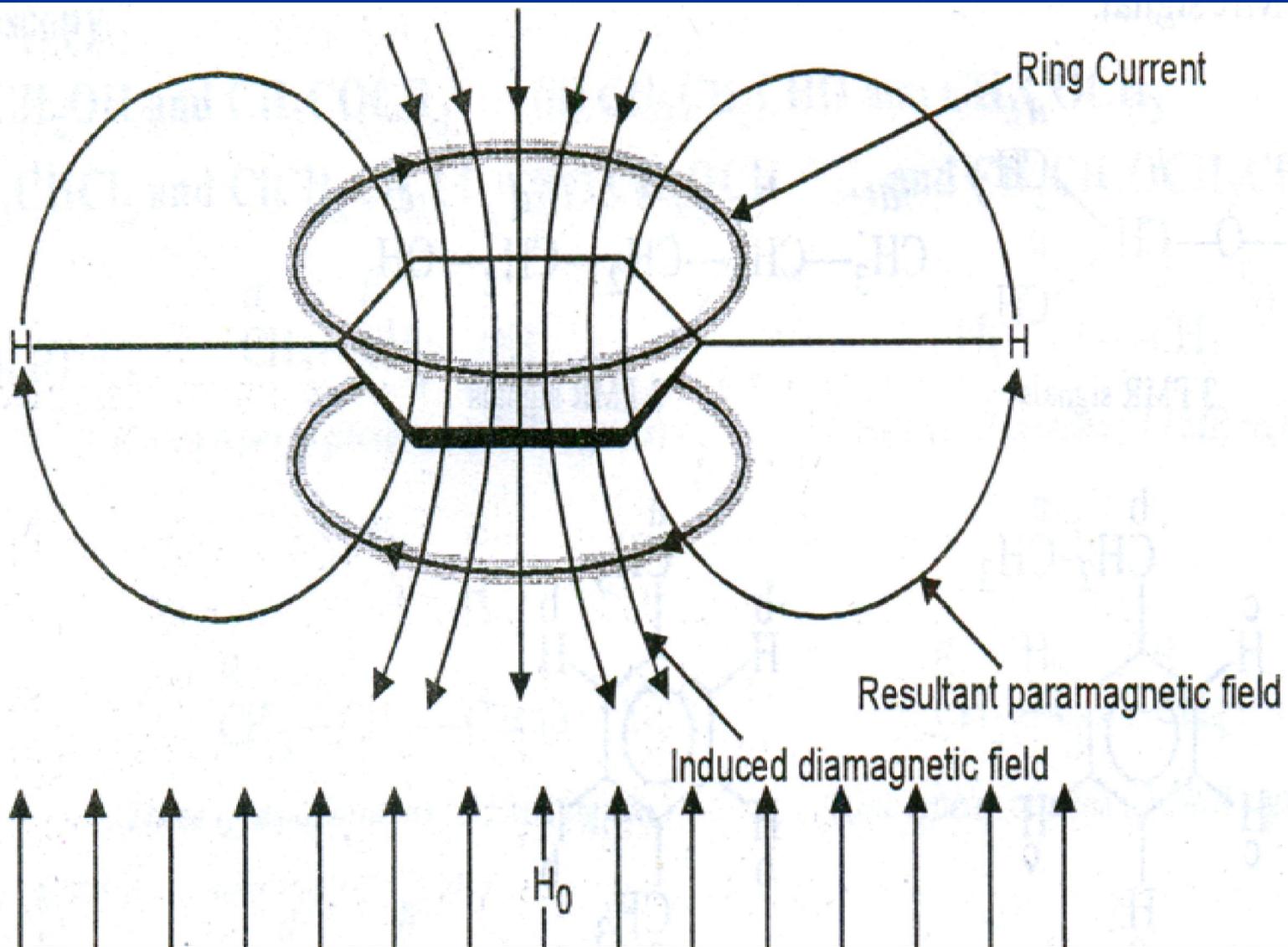
DESHIELDED PROTONS, DOWNFIELD SIGNAL



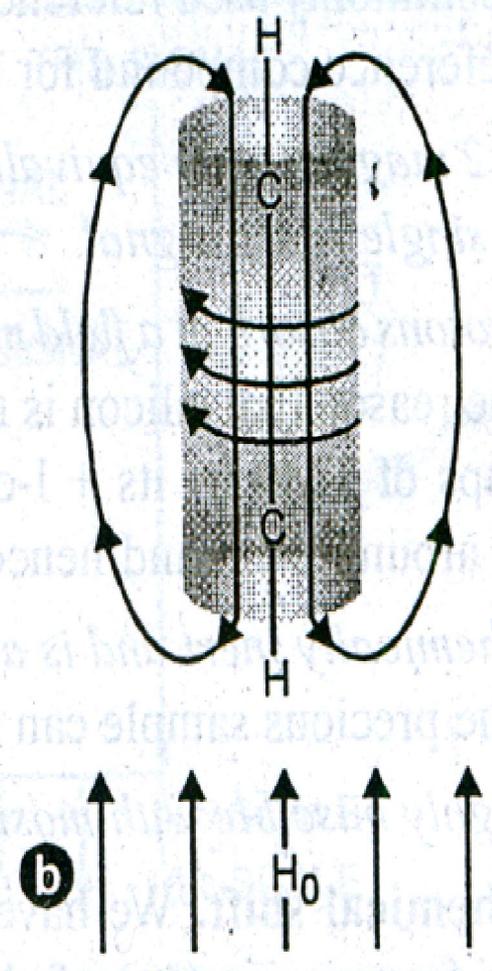
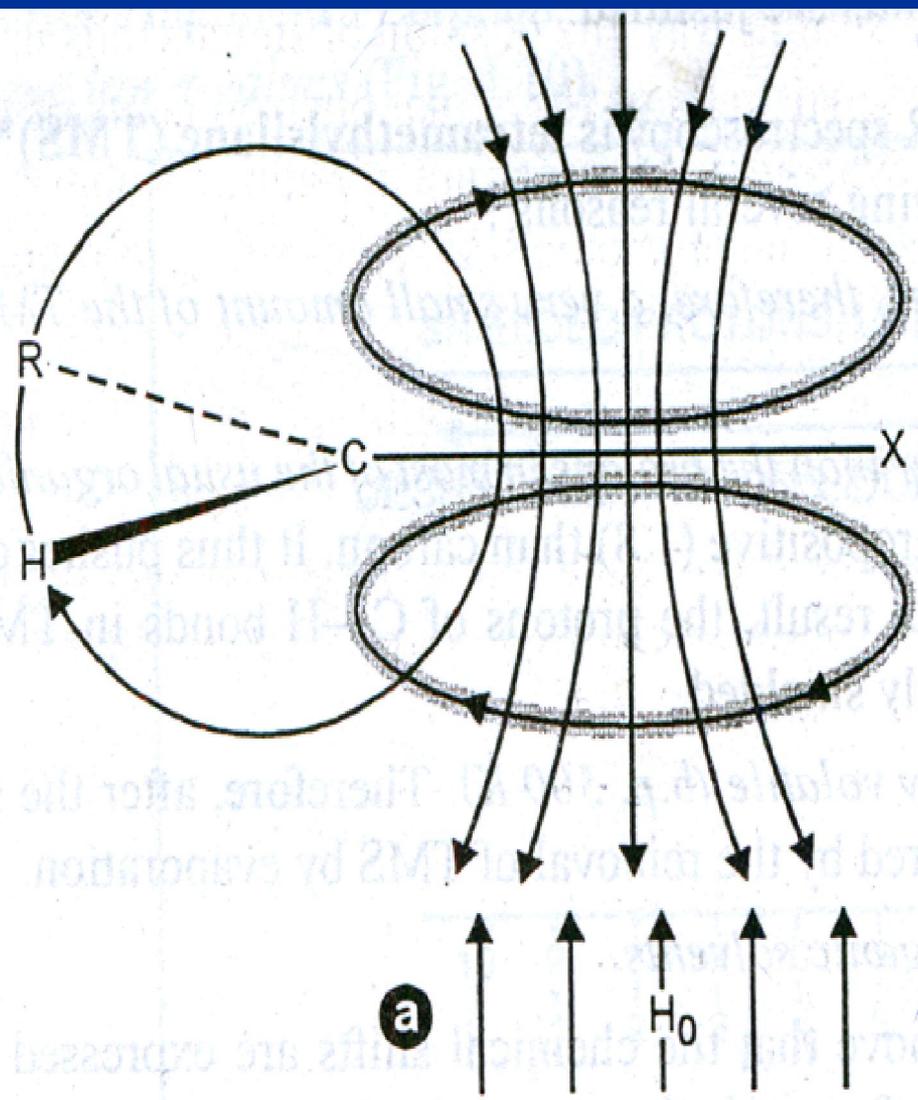
If the induced field reinforces the applied field, the effective field strength experienced by the proton increases. This is called deshielded of the proton. A deshielded proton naturally requires only smaller applied field to give signal, i.e., its signal appears downfield.

Whether the induced field opposes or reinforces the applied field depends upon the manner in which π -electrons circulate under the influence of applied field.

For example, when a benzene derivative is placed in a magnetic field, the delocalised π -electrons of benzene ring are induced to circulate in such a way that induced magnetic field reinforces the applied field at the aromatic protons. As a result, aromatic protons experience a greater magnetic field strength or, in other words, they get deshielded.



On the other hand, when acetylene is placed in a magnetic field, the π -electrons are induced circulate around the axis of the molecule in such a way that the induced field opposes the applied field at the acetylenic protons. As a result, acetylenic protons experience lesser magnetic field strength and thus get shielded.



CHEMICAL SHIFTS AND THEIR MEASUREMENT

The protons in different environments in a molecule would give absorption signals at different field strengths due to the difference in the extent of shielding or deshielding experienced by them. In order to identify the chemical environments of different kinds of protons a sample, the phenomena of shielding and deshielding have been put on a quantitative basis.

For this purpose, the field strengths at which different kinds of protons give their respective signals and recorded with reference to a standard signal. The standard or reference chosen is a sharp signal from tetramethylsilane [TMS, $(\text{CH}_3)_4\text{Si}$].

TMS gives a sharp signal in a position quite removed from the signals of most other protons in organic molecules.

A small quantity of TMS is added to the sample under examination while recording its PMR spectrum. The shifts in the positions of PMR signals of different protons in a given sample relative to the signal of TMS are referred to as chemical shifts.

Thus in simple words the shift in the position of PMR signals resulting through shielding and deshielding by circulation of electrons in the chemical bonds is called Chemical Shift.

The shielding and deshielding of protons by electrons produce a very small changes in the strength of the applied magnetic field. These small changes in the applied magnetic field strength cannot be determined accurately. However, relative proton frequencies can be readily determined with an accuracy of about ± 1 Hz. Therefore, chemical shifts of protons are expressed in Hz or cps with reference to a particular standard.

Reasons for taking TMS as the reference compound.

The choice of TMS as the reference compound is based upon the following facts:

- i) TMS has 12 equivalent protons and gives an intense single signal.
- ii) The electronegativity of silicon is very low (1.8) as compared to carbon (2.5). As a result of this, the shielding of equivalent protons in TMS is more than that of almost all the organic compounds.

Consequently, with reference to TMS signal, almost all other signals appear in the downfield direction.

- iii) TMS is chemically very inert and has a very low boiling point (300 K) so that it can be easily removed by evaporation after the spectrum has been recorded. In this way, the sample of the compound under study can be easily recovered.
- iv) Highly miscible with most of the organic solvent.

Expressing the chemical shifts.

The chemical shifts are expressed in Hz as the frequency difference ($\Delta\nu$) in Hz between the absorption frequencies of the sample and the reference compound i.e., TMS.

But we know the chemical shift is directly proportional to the magnetic field strength applied or the radio frequency used in the instrument.

Since different NMR Spectrometers have different oscillator frequency such as 60, 90, 100,200 MHz.

However, the chemical shift expressed in Hz is directly proportional to the strength of the applied field or, what is equivalent, proportional to the radiofrequency used in the spectrometer.

For instance, signals 100 Hz apart when radiofrequency used is 60 MHz, would appear at 166.6 Hz apart when the radiofrequency is 100 M Hz.

It is desirable to express the chemical shift in some unit which is independent of the field strength.

The most commonly employed unit is parts per million (ppm) of the oscillator frequency.

This is done by multiplying the shifts in Hz by a factor 10^6 and dividing by the radiofrequency employed so that the shifts are reported parts per million (ppm) as illustrated below.

If a signal comes at 100 Hz downfield with reference to TMS in an instrument using 60 MHz, it can be reported as

$$100 \times 10^6 / 60 \times 10^6 = 1.66 \text{ ppm.}$$

In an instrument of 100 MHz, the same signal would be 166.6 Hz downfield. But in terms of ppm it would still be reported as 1.66 ppm.

$$166.6 \times 10^6 / 100 \times 10^6 = 1.66 \text{ ppm.}$$

Thus ppm units are dimensionless and independent of the radiofrequency and the magnetic field used in the spectrometer.

They are a function of only the proton in the molecule. It may be noted that the factor 10^6 is included simply for convenience to avoid fractional values.

In terms of ppm, the chemical shifts are expressed in either of the following two scales

(i) The delta scale δ , (ii) The tau scale,

On the δ scale, the position of the TMS signal is taken as 0.0 ppm and most chemical shifts have values between 0 and 10.

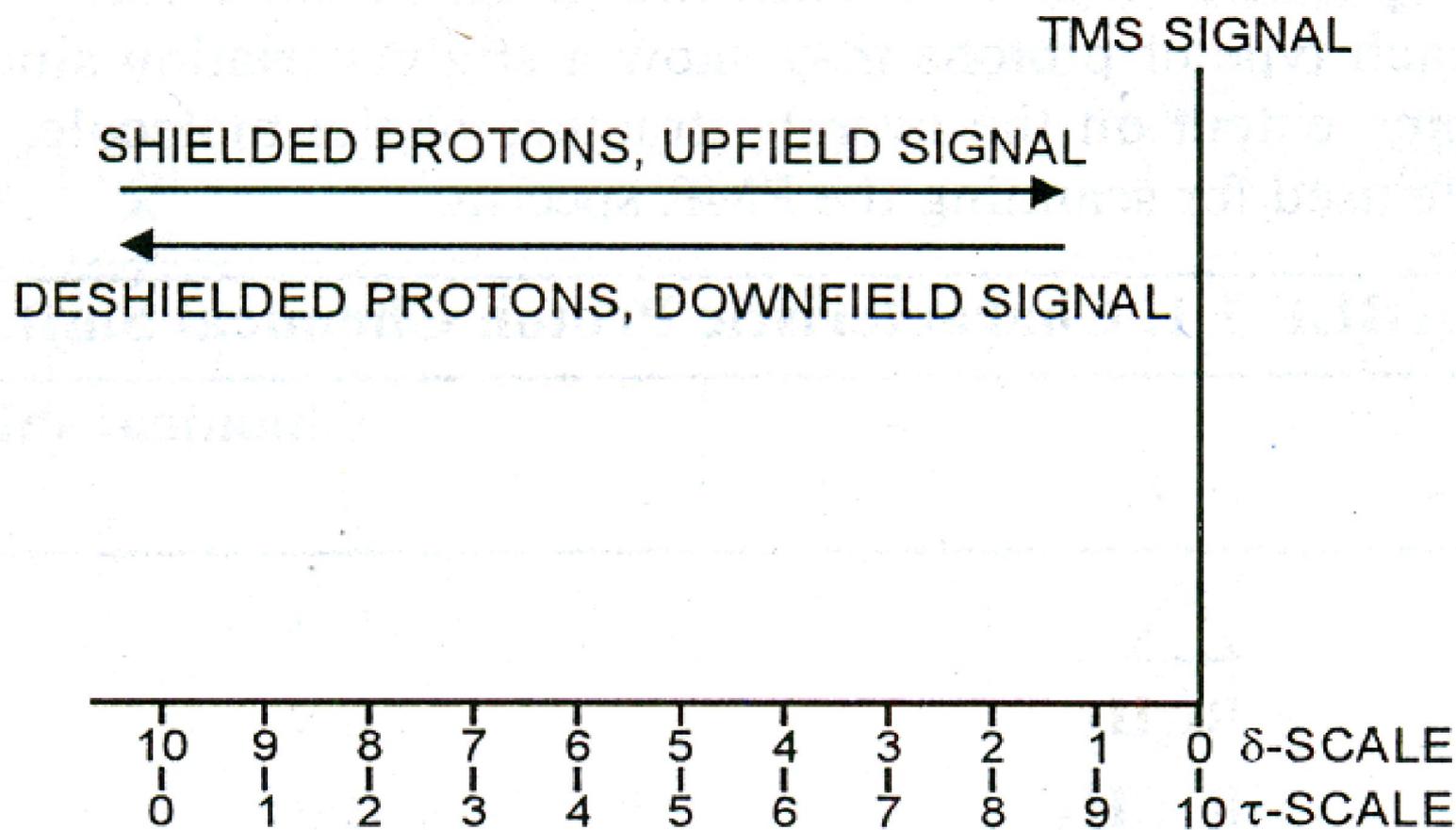
The relationship between TMS signal, δ and τ values and the effect of shielding and deshielding chemical shifts has been summed up in the figure given below:

It may be remembered that greater the deshielding of protons, larger the values of δ or smaller value of τ .

$$\tau = 10 - \delta$$

A small numerical value of δ indicates a small downfield shift while large value indicates a large downfield shift.

On the τ -scale, the position of TMS signal is assigned a value of 10.0 ppm and most chemical shifts have values between 10 and 0. A small value of τ represents a low-field absorption and a high value indicates a high field absorption.



Q.

In a given organic compound two kind of protons exhibit signals at 50Hz and 200Hz using 60 M Hz NMR instrument. What would be their equivalent positions using 90 M Hz instrument?

And also convert these signals into δ scale and τ -scale.

Answer:

75, 300 Hz and 0.83, 3.33 δ

&

9.17 6.67 τ

- Q. In a given organic compound two kind of protons exhibit signals at 139.2Hz and 430.2Hz using 60 M Hz NMR instrument. What would be their equivalent positions using 100 M Hz instrument?

And also convert these signals into δ scale and τ -scale.

Answer:

232, 717 Hz and 2.32, 7.17 δ

&

7.68, 2.83 τ

Thank you

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