

NUCLEAR MAGNETIC RESONANCE SPECTROMETRY (NMR)

PRINCIPLE:

“Absorption of electromagnetic radiation in the radio-frequency region of the spectrum resulting in changes in orientation of spin nuclei in a magnetic field”

NMR spectroscopy provides a rapid, accurate and nondestructive method for determining the structure of simple inorganic to complexed biochemical compounds. Unlike ultraviolet visible and/or infrared spectroscopy, NMR does not involve electron or bonds but the nuclei of the compound.

The nuclei of all atoms possess a **charge** and **spin** about an axis; this creates a magnetic field that is analogous to a field produced when an electric current (electron) passes through a coil of wire. So the absorption of radiation in the radio-frequency (rf) region of the electromagnetic spectrum can be observed for those nuclei which are considered to spin about their own axis.

The energy changes are associated with the orientation of the nuclear axis in space relative to an external applied magnetic field and are of the order of 10-100 MHz (100 cm to 10 m).

The nuclei of all atoms possess a charge and spin about axis. The spin number for both electron and proton is $\frac{1}{2}$; however, not all nuclei possess a magnetic moment. Only nuclei with odd sum of protons and neutrons have magnetic moments; ^1H and ^{13}C are the most often studied. An instrument designed to study the magnetic resonance of ^1H nuclei or proton, is referred to as **proton magnetic resonance (PMR) spectrometer**.

Spectral and magnetic properties of some common nuclei

Nucleus	Spin number	Absorption frequency MHz
^1H	$\frac{1}{2}$	60.0
^2H (deuterium)	1	9.2
^{12}C	0	--
^{13}C	$\frac{1}{2}$	15.1
^{19}F	$\frac{1}{2}$	56.6
^{31}P	$\frac{1}{2}$	24.3

—

All nuclei can be assigned a spin quantum number “I”, which may be zero, Integral or half integral. Only those with a non-zero value can give rise to an NMR spectrum. The charge on the nucleus and spinning about axis (its axis) produces a magnetic moment or dipole (μ) along the

axis. When a substance containing hydrogen nuclei (almost any organic compound) is placed in a powerful magnetic field, the tiny magnetic moment of each proton will orient itself either in alignment with this external magnetic field or against the external field.

Thus the applied external magnetic field causes all the sample protons to be in either a low energy state (aligned with the magnetic field) or a high energy state (aligned against the magnetic field). The nuclei in the lower energy state can be caused to absorb electromagnetic radiation (in the radio-frequency range) to make the transition from the lower to higher energy state.

When a radio-frequency field is super- imposed over a stationary magnetic field containing specific nuclei, the energy transition (ΔE) from the lower energy state to higher state can be calculated from plank's equation

$$\Delta E = \frac{\gamma H_0}{2\pi}$$

Where,

ΔE = frequency

γ = gyro-magnetic ratio

H_0 = magnetic field strength

π = 3.142

Calculation with plank's equation yield a frequency of $60.00 \times 10^6 \text{ S}^{-1}$ (or 60 MHz) for ^1H .

The quantity 1 MHz represents a million hertz (Hz) or cycles per second.

NMR studies are now a day's used for structural studies of all major type of organic compounds. The utility of NMR in the study of dynamic chemical system and in conformational analysis has also been clear.

The development of powerful super conducting magnets and the introduction of pulsed Fourier transform (FT) technique vastly increased the sensitivity and resolving power of the method. Thus now NMR can be extended to nearly all elements in the periodic table.

Like the spectroscopy (U.V / Visible or IR), NMR spectroscopy deals with:

Measurements of energy gaps between states of different energy but in contrast to other technique, it requires the presence of an external magnet field and concern nuclei rather than electron or bonds. This is the origin of terms nuclear and magnetic in nuclear magnetic resonance spectroscopy. As the nuclei resonate between lower energy state and higher energy state, the

term resonance is used. Atomic nuclei have charge (they contain proton) and some also behave as if they spin.

A spinning charge is equivalent to a current in a conductor loop, So nuclei with nonzero spin will generate a magnetic field, it mean may have a magnetic moment or dipole spin quantum No. I, it can be 0, $\frac{1}{2}$, 1, $\frac{3}{2}$ etc.

If,

1) $I = 0$ (non spinning nuclei). These have no magnetic moment and are composed of even numbers of proton and neutron e.g. ${}^6\text{C}^{12}$, ${}^8\text{O}^{16}$.

2) $I = \frac{1}{2}$ (spherical spinning charge).
e.g. ${}^1\text{H}$, ${}^{13}\text{C}$, ${}^{19}\text{F}$, ${}^{15}\text{N}$ → from these over 95 % observations in NMR account for ${}^1\text{H}$, ${}^{13}\text{C}$.

3) $I > \frac{1}{2}$ (non-spherical spinning)

e.g. $I = 1$ → ${}^2\text{H}_1$, ${}^{14}\text{N}_7$

$I = \frac{3}{2}$ → ${}^{11}\text{B}_5$, ${}^{35}\text{Cl}_{17}$, ${}^{37}\text{Cl}_{17}$

$I = 2$ → ${}^{36}\text{Cl}_{17}$,

RADIOFREQUENCY 40 - 600 MHz

Fundamental quantum law is that: In a uniform magnetic field, a nucleus of spin I may assume $2I+1$ orientation.

e.g. for a nucleus $I = \frac{1}{2}$, two possible orientations

$$2I + 1$$

$$2(\frac{1}{2}) + 1 = 2$$

So, nucleus is $I = \frac{1}{2}$

Is analogous to magnet bar in magnetic field

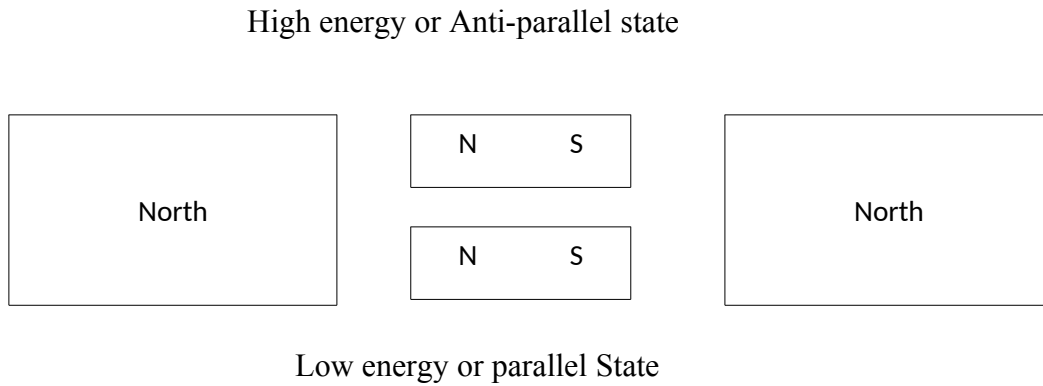


Fig: Bar magnet analogue for nuclei with $I = \frac{1}{2}$

As magnet bar has two (different energy state) orientations in a magnetic field, it is possible to induce a nuclear transition analogous to the flipping of the bar magnet, by applying electromagnetic radiation of an appropriate frequency (ν) given by

$$\nu = \gamma H_0 / 2\pi$$

γ = fundamental constant called magnetogyric or gyro-magnetic ratio, which is different for each atomic nucleus (H, C, N, etc)

The above equation can be reduced to

$$\nu = \text{constant} \times H_0$$

It is known as “Larmor equation”

Above equation shows that one could observe a molecular transition by keeping the magnetic field constant and varying the applied frequency (or vice versa) until the combination of field strength and irradiated frequency characteristic of nucleus concerned reached. This condition is often describe as resonance and is, of course, the origin of the term resonance in nuclear magnetic resonance.

RELAXATION PROCESS:

Relaxation process involves some non-radiative (irradiative) transitions by which a nucleus in an upper transition state returns to the lower spin state.

Two kinds of relaxation processes are:

- i. Spin-spin relaxation
- ii. Spin-lattice relaxation

(i) Spin-spin relaxation: (Transverse relaxation)

It is due to mutual exchange of spins by two precessing nuclei which are in close proximity to each other. We know that each precessing nucleus is associated with a magnetic vector component rotating in a plane perpendicular to the field. If this small rotating magnetic field is the same as required to induce a transition in the neighboring proton, then mutual exchange of spin takes place.

In other words, it involves the transfer of energy from one nucleus to the other. There is no net loss of energy. The spread of energy among the nuclei concerned results in broadening which makes NMR spectra of solids comparatively more interesting.

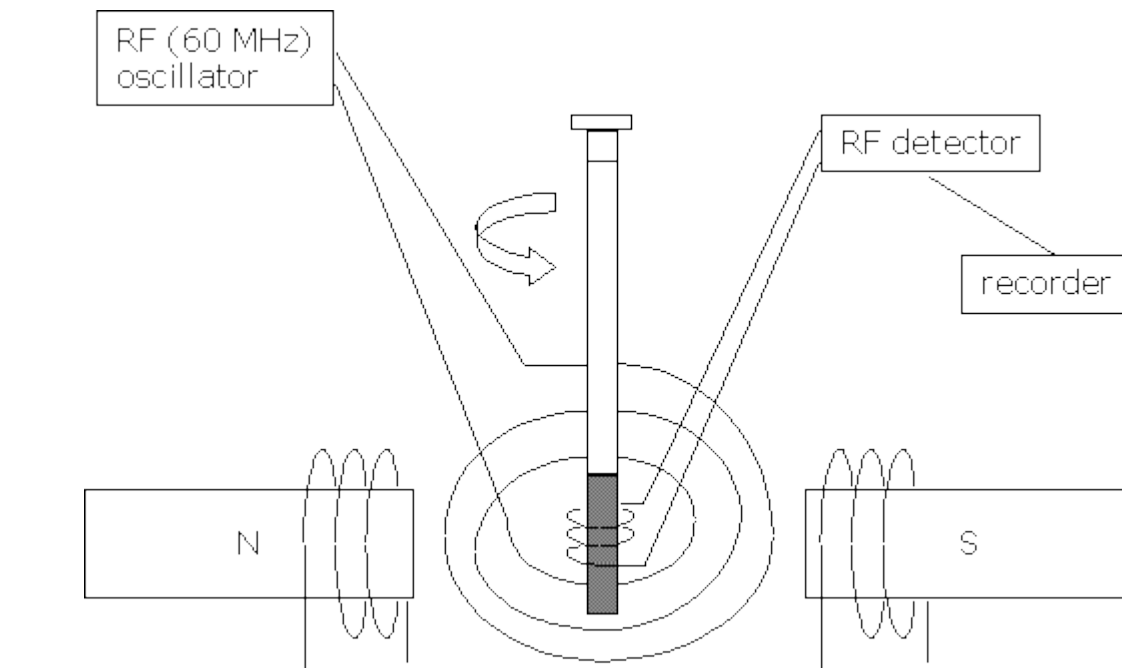
(ii) Spin-lattice relaxation: (Longitudinal relaxation)

It involves the transfer of energy from the nucleus in its higher energy state to the molecular lattice. The energy is transferred to the components of the lattice as the additional translational, vibrational and rotational energy. The total energy of the system remains the same. An efficient relaxation process involves a short time and results in the broadening of absorption peaks. Smaller the time of excited state, greater is the line width. This mechanism is not effective in solids. The process keeps the excess of nuclei in the lower energy state which is a necessary condition of nuclear magnetic resonance phenomenon.

INSTRUMENTATION:

Following are the major parts of nuclear magnetic resonance spectrophotometer.

1. A magnet
2. Field sweep generator
3. A radio frequency source
4. Detector (radio frequency receiver)
5. Signal recorder
6. An integrator
7. NMR cells (sample tube)



Schematic diagram of NMR spectrometer.

1. A permanent magnet:

Which produce field in the range of 10,000 G and electromagnets of approximately 25000 G are most often used. These permanent magnets tend to be found in cheaper instruments and are very temperature sensitive. Electromagnets and superconductive magnets are found in the more expensive NMR instruments.

2. A field sweep generator:

It consists of a pair of coils located parallel to the permanent magnets faces is used to alter the applied magnetic field over a very small range. e.g. a PMR instrument fixed at 60 MHz radio frequency might have a magnetic sweep range maximum of 6.7 ppm (1000 Hz) or it is equivalent of 235 mG.

These sweep ranges are normally expressed in parts per million (ppm), which is not a concentration expression. It simply indicates the proportion change in the fixed magnetic field strength.

3. A radio frequency source:

Generates a signal from a transmitter fed into a pair of coils mounted perpendicular to the magnetic field path. In a PMR instrument this frequency is fixed at 60 MHz and must be constant to 1 ppb for high resolution work.

4. A radio frequency receiver (detector):

A radio frequency receiver detects the transmitted signal after it passes through the sample.

5. A signal recorder:

A signal recorder is used to trace the absorption of energy verses the abscissa drive which is connected to a radio-frequency receiver coil and is synchronized to the magnetic sweep expressed in ppm.

6. An integrator:

An integrator is also available on the NMR. It provides a relative area under each absorption peak.

7. NMR cells:

NMR cells are usually 5-mm glass tubes designed to contain 0.5 ml of sample (a column approximately 2.5 cm high). These tubes are usually fitted with a simple turbine with a spinning turbine which is set at the proper depth by a depth gauge supplied with instrument.

Caution or note:

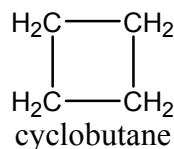
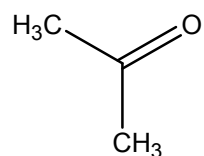
Always wipe a tube with a lint free cloth or material before inserting into the instrument. Microtubules are also available for smaller volumes of samples. These NMR tubes should never be cleaned dichromate cleaning solution. Dirty tubes are best cleaned with a moderately hot soap solution introduced by a suitable pipette. Rinse the soap solution away with water, rinse with acetone and blow dry.

NUMBER OF SIG NALS:

The numbers of signals in the NMR spectrum will tell the number of different sets of equivalent protons in a molecule. Each signal corresponds to a set of equivalent proton.

It may be noted that magnetically equivalent protons are chemically equivalent protons.

Let us find the various sets of equivalent protons (signals) in the following types of compounds.



In acetone all six protons are in exactly similar environment i.e. one signal obtained. Similar is in the case of cyclobutane.

(b) some compounds show more than one signal one as follows

- | | |
|-------|--------------|
| (i) | 2 NMR signal |
| (ii) | 3 NMR signal |
| (iii) | 3 NMR signal |
| (iv) | 3 NMR signal |

(c) Strictly, chemically equivalent protons must also be stereo-chemically equivalent i.e. a particular set of protons are said to be chemically equivalent only if they remain in exactly similar environment when the stereo chemical formula of the molecule under consideration is written. e.g. 2-chloropropene

In general one can expect two sets of equivalent protons. But stereo-chemical formula reveals three sets of protons in it. H^b and H^c are not exactly in similar environment.

Now consider methyl cyclo-propane one can expect 3-NMR signals but in actual 4 NMR signals.

Position of signals (chemical shifts):

The number of signals in an NMR spectrum tells the number of the sets of equivalent protons in a molecule.

The position of signals in the spectrum help us to know the nature of proton, aromatic, aliphatic, acetylenic, vinylic, adjacent to some electron attracting or electron releasing group etc. Each of these types of protons will have different electronic environments and thus, they absorb at different applied field strengths. It is important to note that it is the electronic environment which tells where a proton shows absorption in the spectrum.

When a molecule is placed in a magnetic field, its electrons are caused to circulate and thus, they produce secondary magnetic field i.e. induced magnetic field. Rotation of electrons about the proton itself generates a field in such a way that at the proton, it opposes the applied field. Thus the field felt by the proton is diminished and the proton is said to be “shielded”.

Rotation of electrons (especially π electrons) about the nearby nuclei generates a field that can either oppose or reinforce the applied field at the proton. If the induced field opposes the applied field, then proton is said to be “shielded”.

But if the induced field reinforces the applied field, the proton feels higher field strength and thus, such a proton is said to be deshielded.

Shielding shifts the absorption up-field and de-shielding shifts the absorption downfield to get effective field strength necessary for absorption.

Such shifts (compared with a standard with a standard reference) in the position of NMR absorption which arise due to shielding or de-shielding of protons by the electrons are called **chemical shifts**.

For measuring chemical shifts of various protons in a molecule, the signal for tetra-methyl silane (TMS) is taken as a reference. Due to low electro negativity of silicon; the shielding of equivalent protons in tetra-methyl silane is greater than most of the organic compounds. Therefore, NMR signal for tetra-methyl silane is taken as a reference and chemical shifts for different kinds of protons are measured relative to it.

The difference in the absorption position of the protons with respect to TMS signal is called chemical shifts (δ -value called delta). It is not measured in gauss (G) but is measured in equivalent frequency unit which is then divided by the frequency of the spectrometer used. This gives the value of δ (delta), δ (delta) or tau scales are commonly used.

In majority of organic compounds, protons resonate at a lower field than the protons of TMS. Thus assigning delta (δ) value for TMS equal to zero a scale can be defined in which most proton resonances are of the same sign. Any proton or set protons which absorbs at a field higher than TMS is given a positive value for δ .

TMS is the most convenient reference and has the following characteristics.

- (i) It is miscible with almost all organic substances.
- (ii) It is highly volatile (low boiling) and is readily removed from the system.
- (iii) It does not take part in intermolecular association with the sample.

The values of δ for a substance with respect to TMS can be obtained by measuring $V_s - V_{TMS}$

Where

V_s = Resonance frequency of the sample

V_{TMS} = Resonance frequency of TMS

Keeping the radio frequency constant, an NMR signal for a particular set of proton in the sample will appear at different field strength than the signal obtained from TMS.

Thus, the value for $V_s - V_{TMS}$ can be expressed in the corresponding field strength in gauss.

Since the operating frequency of the instrument is directly proportional to the strength of magnetic field, we can define δ as

$$\delta = \frac{V_{\text{sample}} - V_{\text{reference}}}{\text{Operating frequency in megacycles}}$$
$$= \frac{\Delta V}{\text{Operating frequency in megacycles}}$$

Where ΔV is frequency shift.

The value of delta (δ) is expressed in parts per million (ppm). Most chemical shifts have delta values between zero and 10. In the tau scale signal for the standard reference, TMS is taken as 10 ppm.

It has been found that signals for fluorine resonance (absorption due to fluorine nuclei) don't appear in this range but are observed down field by about 50 ppm or even more.

Two scales are related by the expression

$$\text{Tau} = 10 - \delta$$

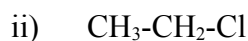
Factors influencing chemical shift:

Following are the factors which influence the chemical shift.

- a) Inductive effect
- b) Vander waal's deshielding
- c) Anisotropic effects
- d) Hydrogen bonding

a) Inductive effect:

A proton is said to be deshielded if it is attached with an electronegative atom or group. Greater the electronegativity of the atom, greater is the de-shielding caused to the proton. If the de-shielding is more for the proton, then its δ value will also be more, consider the following compounds.



Two signals are expected for each of the two compounds. De-shielding for proton "a" in compound (i) is more than that for similar proton in compound (ii).

As the distance from the electronegative atom increase the de-shielding effect due to it diminishes. Protons b are comparatively less deshielded and hence will be resonate at comparatively lower value of δ

Electronegative atoms or groups withdraw electron density around the proton and thus, causes de-shielding. Due to de-shielding smaller value of applied field will be needed to bring the proton to resonance.

Greater the electronegativity of the atom or group, greater will be de-shielding effect on a proton.

Greater the distance of electronegative atom from a particular proton, smaller is the de-shielding effect on it.

b) Van der waal's deshielding:

In overcrowded molecules, it is possible that some protons may be occupying sterically hindered position. Clearly, electron cloud of a bulky group (hindering group) will tend to repel the electron cloud surrounding the protons. Thus, such a proton will be deshielded and will resonate at slightly higher value of δ than expected in the absence of this effect.

c) Anisotropic effects: (space effects)

The deshielding effect on protons attached to C=C is higher than can be accounted for by the inductive effect alone. Aldehydic and aromatic protons are much more deshielded. Alkyne protons appear at relatively low value of δ . The value of δ (chemical shift) in each case can be justified by explaining the manner in which the π electrons circulate under the influence of the applied field.

Consider an alkene: It is so oriented that the plane of the double bond is at right angles to the applied field. Induces circulation of π electrons generates induced magnetic field which is diamagnetic around carbon atom and paramagnetic in the region of alkene protons. Thus the protons will feel greater field strength and hence resonance occurs at lower applied field

Alkynes: In alkynes, electronic circulation around triple bond takes place in such a way that the protons experience diamagnetic shielding effect, when the axis of alkyne group lies parallel to the direction of the applied field, the π electrons are induced to circulate around the axis in such a way that the induced field opposes the applied field. Thus, protons feel smaller field strength (shielding) and hence resonance occurs at higher applied field (low tau value).

Benzene: In case of benzene loops of π electrons are delocalized cylindrically over the aromatic ring. These loops of electrons are induced to circulate in the presence of the applied field producing ring current.

The induced current is diamagnetic (opposing the applied field) in the centre of the ring and paramagnetic outside the ring. Thus the aromatic protons (around the periphery of the

ring) experience a magnetic field greater in magnitude than the applied field. Such protons are said to be deshielded and hence, smaller applied field (higher value of tau) will be required to bring them to resonance.

d) Hydrogen bonding:

It has been found that a hydrogen atom exhibiting property of hydrogen bonding in a compound absorbs at a low field in comparison to the one do not. The hydrogen bonded proton being attached to the highly electronegative atom will have smaller electron density around it. Being less shielded, the field felt by such a proton will be more and hence resonance will occur downfield. The downfield shift depends upon the strength of H-bonding.

Intermolecular and intramolecular H-bonding can easily be distinguished as the latter does not show any shift in absorption due to change in concentration. In case of phenol absorption occur between -2 to 6 -- but if the concentration is decreased, that is, if the volume of solvent, say CCl_4 is increased, then the absorption for OH protons occur up-field. In case of OH group on benzene, is intra-molecularly bonded with some other group in the ortho position, the absorption for OH proton may occur even at the negative tau. e.g. the OH proton in salicylic acid absorbs at -0.6 I.

Solvent used:

A substance free of proton should be used as solvent, that is, which does not given absorption of its own in NMR spectrum. Moreover, the solvent should be capable of dissolving at least 10 % of the substance (sample) under investigation.

Following solvents are commonly used in NMR spectroscopy.

1. Carbon tetra chloride - CCl_4
2. Carbon disulfide - CS_2
3. Deuteriochloroform - CDCl_3
4. Hexa-chloroacetone - $(\text{CCl}_3)_2 \text{C}=\text{O}$ etc.

These solvents differ considerably as regards their polarity. Clearly, NMR spectrum of a compound measured in one solvent may be slightly different from that measured in another solvent of different polarity.

Dimethyl sulphoxide, (DMSO) (highly polar solvent) can be used in NMR spectroscopy.

Some important characteristics of solvents used in this technique are:

1. It should be chemically inert and magnetically isotropic.
2. It should be devoid of H atom.
3. It should dissolve the sample to a reasonable extent.

Splitting of signals:

It is already pointed out that each signal in NMR spectrum represents one kind or set of protons in a molecule. It is found that in certain molecules, a single (singlet) peak is not observed, but instead a multiple (group of peaks) is observed. Consider a molecule of ethyl bromide.



This molecule has two kinds of proton in it and thus two signals are suspected in its NMR spectrum. It has been observed that for each kind of protons, we do not get singlets but a group of peaks are observed.

For 'a' kind of protons (CH_3), a triplet i.e. a group of peaks is observed and a quarter (group of 4 peaks) is noticed for 'b' kind of protons ($-\text{CH}_2-$)

NMR Spectra of ethyl bromide

Signals and their absorption positions

- i) A three proton triplet 8.35 I
- ii) A two proton quarter 6.6 I

The splitting of an NMR signal is due to spin-spin coupling.

Spin-spin coupling:

Consider a molecule of ethyl bromide ($\text{CH}_3\text{CH}_2\text{Br}$).

The spin of two protons (-CH₂-) can couple with the adjacent methyl group (-CH₃) in three different ways relative to the external field. The three different ways of alignment are

- | | | | |
|-------|---------|-----------------|---------------------|
| (i) | ↑ ↑ | (reinforcing) | ↑
external field |
| (ii) | ↓ ↑ ↑ ↓ | (not effecting) | |
| (iii) | ↓ ↓ | (opposing) | |

Thus a triplet peaks results with the intensity ratio of 1:2:1 which corresponds to the distribution ratio of alignment.

Similarly, the spin of three protons (CH₃-) can couple with the adjacent methylene group (-CH₂-) in four different ways relative to the external field.

- | | | | |
|-------|---------------------|----------------------|---------------------|
| (i) | ↑ ↑ ↑ | strongly reinforcing | ↑
external field |
| (ii) | ↑ ↑ ↓ ↑ ↓ ↑ ↓ ↑ ↑ ↓ | weakly reinforcing | |
| (iii) | ↓ ↓ ↑ ↓ ↓ ↑ ↑ ↓ ↓ ↓ | weakly opposing | |
| (iv) | ↓ ↓ ↓ | strongly opposing | |

Thus quarter of peaks results with an intensity ratio of 1:3:3:1 which correspond to the distribution ratio of all the alignments.

The relative intensities of the individual lines of a multiplet correspond to the numerical coefficient of the line in the binomial expression

$$(1+x)^n = 1+x \quad \text{if; } n=1$$

If n=2, then

$$(1+x)^2 = 1 + 2x + x^2$$

Thus, the lines of the triplet have relative intensities 1:2:1

If n=3, then

$$(1+x)^3 = 1 + 3x^2 + 3x + x^3$$

Lines of quarter have intensities 1:3:3:1

Hence, the splitting of a signal is due to the different environment of the absorbing proton not with respect to electrons but with respect to the nearby protons (protons attached to the adjacent carbon atom). Spin-spin coupling takes place between non-equivalent neighboring (an adjacent carbon atom) protons. Non equivalent protons are those which have different chemical shifts.

Coupling constant (J):

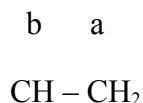
The distance between the centers of the two adjacent peaks in a multiplet is usually constant and is called the coupling constant. The value of the coupling constant is independent of the external field. It is measured in hertz (Hz) or in cycles per second (cps). It is denoted by the letter J.

If we work the spectrum of a particular compound at different radio frequencies, the separation of signal due to different chemical shift change but the separation of two adjacent peaks in a multiplet remain always constant. In other words, we say that the value of J remains the same whatever the applied field.

From the value of coupling constant, one can distinguish between the two singlets and one doublet and also a quarter from two doublets. It can be done by simply recording the spectrum at two different radiofrequencies.

If the separation (in Hz) between the lines (value of J) does not change, then the singlet is a doublet. On the other hand, if the separation between the lines increases with increasing frequency, then the single infect, will be two singlets. The value of J generally lies between zero and 20 Hz. Same explanation can be given to distinguish a quarter from the doublets.

Now let us consider a compound,



In this compound two signals are expected in NMR spectrum. Under the influence of two equivalent proton 'a' the signal for proton 'b' will appear as a triplet. The distance between any two adjacent peaks, in a multiplet will be exactly the same. The triplet formed due to spin-spin coupling is shown as, splitting of proton 'b' signal

With respect to equivalent proton 'a'

Consider a compound $\text{CH} - \text{CH}_3$

In the NMR spectrum of this compound, proton 'b' is under the influence of the equivalent proton 'a'. Thus due to spin-spin coupling, the signal for proton 'b' will appear as quarter with intensity ratio 1:3:3:1

Important TIPS for interpreting an NMR spectrum:

A) Following points regarding the value of chemical shift may be useful.

i. Tau value of methyl, methylene and methane protons have the order:

Methyl > methylene > methane

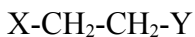
- ii.** Tau value depends upon the nature of the substituent on the carbon atom bearing the proton. Greater the electronegativity of the substituent, lower is the value of tau.
- iii.** The value of tau depends upon the type of hybrid orbital holding the proton.
 $Sp^3 > sp > sp^2$
- iv.** The tau value for aromatic proton is always less than 4 ppm. The value depends upon the degree and nature of substitution.
- v.** The tau values for the aldehydic protons are generally lower, that is, 0.8 ppm or lower.
- vi.** Tau value of compounds in a cyclic compound is always higher than that of any other proton. The set of protons in cyclo-propane has the maximum tau value.
- vii.** The chemical shift of the protons in $-OH$ group and also in $-NH_2$ group depend upon temperature, solvent, concentration and the neighbouring group. e.g. the alcoholic ($-OH$) proton gives a singlet at 4.5-9.0 tau, the phenolic OH absorbs at -2 to 6 tau. If $c=O$ group is present in the ortho position in phenol, then due to intramolecular hydrogen bonding, absorption occurs even at negative values of tau. The OH proton in the enolic form absorbs at -4 to -5 tau.
- viii.** The absorption due to $-COOH$ group appears at -0.5 to -2 tau.

B) The number of signals in an NMR spectrum tells the number of sets of protons in different chemical environments.

C) It also tells the number of equivalent protons causing the splitting of a signal.

Let us consider a few cases:

- i.** In a spectrum, two signals, say, singlets are observed. This spectrum can be interpreted by saying that there are two kinds of protons and the two carbon atoms carrying the two sets of protons are not the adjacent carbon atoms otherwise splitting of signals would have taken place.
- ii.** The spectrum consisting of one doublet and one triplet must be due to the molecule having $-CH_2-CH-$ as its part.
- iii.** Formation of two triplets must be due to methylene groups whose protons are in different environments.



NMR spectroscopy is an important tool in the hands of an organic chemist for getting structural information from the spectrum of an unknown component. It also helps in studying the stereochemical details within the molecule. Although important, it cannot replace other techniques such as U.V, IR, Mass etc.

Applications of NMR spectroscopy:

The NMR spectroscopy is very widely used for the detailed investigation of any unknown compound.

1. Identification of structural isomers:

The identification between the following isomers can be easily made from their NMR spectra



(a)

(b)

In isomer (a) three singlets are observed whereas we see only two signals in the spectrum for (b) which is a clear distinction between the above isomers. The three signals for isomer (a) in order of decreasing tau values are

- i. A three proton triplet (CH_3)
- ii. A two proton ? ($-\text{CH}_2-$)
- iii. A two proton triplet ($-\text{CH}_2\text{Cl}$)

For isomer (b) two singlets have their multiplicities as

- i. Doublet (6H) -upfield and
- ii. ? (1H) - downfield

Similarly distinction between the position isomers like propanol -1 and propanol -2 can be made.

2. Detection of hydrogen bonding:

Intermolecular hydrogen bonding shifts the absorption for a concerned proton downfield. The extent of hydrogen bonding varies with the solvent, concentration of the solutions and the temperature. Intra molecular hydrogen bonding also shifts the absorption down field. The two types of hydrogen bonding can be distinguished as the intra molecular hydrogen bonding is not concentration dependant.

3. Detection of aromaticity:

Protons attached to the benzene, polynuclear and heterocyclic compounds where π electrons follow ? rule {i.e. (? =2) π electrons where $n=1,2,3$ (whole number)} are extremely deshielded due to the circulating ? (ring current) of π electrons.

As a result of this, the signal for the aromatic protons appear at a very low field than that observed even for benzene. From this, the aromatic character of the compound under investigation can be predicted.

4. Distinction between cis-trans isomers and compounds:

The cis and trans isomer of a compound can be easily distinguished as the concerned protons have different values of the chemical shifts as well as the coupling constant.



(cis)

?=7-12 CPS

(trans)

?=13-18 CPS

Similarly, the various conformation of a compound, the axial and equatorial, positions of the proton or group carrying a proton can be distinguished from their different values of the coupling constants.

5. Detection of electronegative atom or group:

It is known that the presence of an electronegative atom or group in the neighborhood of the protons cause deshielding and the signal is shifted downfield. greater the electronegativity of the adjacent atom, smaller is the tau.

.....?
