

Nuclear Magnetic Resonance

Introduction:

Nuclear magnetic resonance (NMR) spectrometry is basically another form of absorption spectrometry. Under appropriate conditions in a magnetic field, a sample can absorb electromagnetic radiation in the radio frequency (rf) region at frequencies governed by the characteristics of the sample. Absorption is a function of certain nuclei in the molecule. A plot of the frequencies of the absorption peaks versus peak intensities constitutes an NMR spectrum. This chapter covers proton magnetic resonance (^1H NMR) spectrometry.

With some mastery of basic theory, interpretation of NMR spectra merely by inspection is usually feasible in greater detail than is the case for IR or mass spectra. The present account will suffice for the immediate limited objective, identification of organic compounds in conjunction with other spectrometric information. References are given at the end of this chapter.

We begin by describing some magnetic properties of nuclei. All nuclei carry a charge. In some nuclei this charge “spins” on the nuclear axis, and this circulation of nuclear charge generates a magnetic dipole along the axis (Fig-1). The angular momentum of the spinning charge can be described in terms of quantum spin

numbers I ; these numbers have values of 0 , $\frac{1}{2}$, 1 , $\frac{3}{2}$, and so on ($I = 0$ denotes no spin). The intrinsic magnitude of the generated dipole is expressed in terms of nuclear magnetic moment, μ .

Relevant properties, including the spin number I , of several nuclei are given in Appendix H. The spin number I can be determined from the atomic mass and the atomic number as shown in the next column.

Spectra of several nuclei can be readily obtained (e.g., ^1_1H , ^3_1H , $^{13}_6\text{C}$, $^{15}_7\text{N}$, $^{19}_9\text{F}$, $^{31}_{15}\text{P}$) since they have spin numbers I of $\frac{1}{2}$ and a uniform spherical charge distribution (Fig. 1).

I	Atomic Mass	Atomic Number	Example (I)
Half-integer	Odd	Odd or even	$^1_1\text{H}\left(\frac{1}{2}\right)$, $^{17}_8\text{O}\left(\frac{5}{2}\right)$, $^{15}_7\text{N}\left(\frac{1}{2}\right)$
Integer	Even	Odd	$^2_1\text{H}(1)$, $^{14}_7\text{N}(1)$, $^{10}_5\text{B}(3)$
Zero	Even	Even	$^{12}_6\text{C}(0)$, $^{16}_8\text{O}(0)$, $^{36}_{16}\text{S}(0)$

Nuclei with a spin number I of 1 or higher have a non-spherical charge distribution. This asymmetry is described by an electrical quadrupole moment which, as we shall see later, affects the relaxation time and, consequently, the line width of the signal and the coupling with neighboring nuclei. In quantum mechanical terms, the spin number I determines the number of orientations a nucleus may assume in an external uniform magnetic field in accordance with the formulas $2I + 1$. We are concerned with the proton whose spin number I is $\frac{1}{2}$.

Thus in Fig.2, these are two energy levels and a slight excess of proton population in the lower energy state ($N_\alpha > N_\beta$) in accordance with the Boltzmann distribution. The states are labelled α and β or $\frac{1}{2}$ and $-\frac{1}{2}$; ΔE is given by

$$\Delta E = \frac{h\gamma}{2\pi} B_0$$

where h is Planck's constant, which simply states that ΔE is proportional to B_0 (as shown in Fig. 4.2) since h , γ and π are constants. B_0 represents the magnetic field strength.

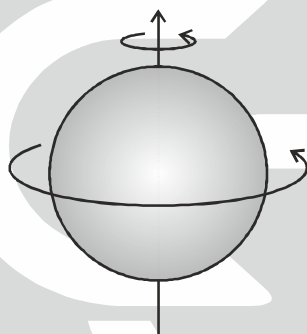


Fig. 1. Spinning charge on proton generates magnetic dipole

Once two energy levels for the proton have been established, it is possible to introduce energy in the form of radio frequency radiation (ν_1) to effect a transition between these energy levels in a stationary magnetic field of given strength B_0 . The fundamental NMR equation correlating the applied radio frequency ν_1 with the magnetic field strength is

$$\nu_1 = \frac{\gamma}{2\pi} B_0$$

since $\Delta E = h\nu$

The introduced radio frequency ν_1 is given in megahertz (MHz). A frequency of 100 MHz is needed at a magnetic field strength B_0 of 2.35 tesla (T) for the proton (or any other desired combination of ν_1 and B_0 at the same ratio). At this ratio, the system is in resonance; energy is absorbed by the proton, raising it to the higher energy state, and a spectrum results. hence the name nuclear magnetic resonance spectrometry. The constant γ is called the magnetogyric ratio, a fundamental nuclear constant; it is the proportionality constant between the magnetic moment μ and the spin number I .

$$\gamma = \frac{2\pi\mu}{hI}$$

The radio frequency ν_1 can be introduced either by continuous-wave (CW) scanning or by a radio frequency pulse.

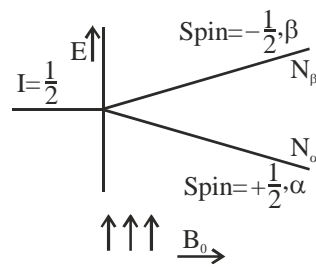


Fig. 2. Two proton energy levels, from quantum mechanics, in a magnetic field of magnitude B_0 . N is population. The direction of the magnetic field ($\uparrow\uparrow\uparrow$) is up, parallel to the ordinate, and B_0 increases to the right.

Physical Significance:

If a nucleus has a spin angular momentum I , the magnetic moment is given by

$$\mu_I = g_N \frac{e}{2m_p c} \frac{h}{2\pi} \sqrt{I(I+1)} \quad \dots (1)$$

where g_N is a nuclear g-factor, m_p is the mass of a proton and $\sqrt{I(I+1)} \frac{h}{2\pi}$, is the magnitude of the spin angular momentum vector.

When a proton is placed into a uniform magnetic field strength B , the nuclear magnetic dipole will precess about the axis of the field. This precession occurs because there is a tendency for the magnetic field to turn the nuclear magnetic moment around into the field direction. But this effort is opposed by the rotational inertia due to the revolution of the proton and the consequent motion is analogous to the precession of a spinning mechanical under the influence of gravity. The angular precession frequency, ω , which is called the *Lamor Frequency* (the precession frequencies) is given by

$$\omega = \gamma\beta \quad \dots (2)$$

where γ the gyromagnetic ratio, is defined as

$$\gamma = \frac{\text{magnetic moment}}{\text{angular momentum}} = \frac{\mu_I}{\sqrt{I(I+1)} \frac{h}{2\pi}} \quad \dots (3)$$

The energy due to this interaction is given by

$$E = -\mu_I B \cos \theta \quad \dots (4)$$

where θ is the angle between the axis of the dipole and the field direction. Classically, θ can take any value, so that energy varies continuously. Quantum mechanically, the angular momentum is quantized in space, so there are only certain allowed values of θ . Figure shows the vector representation of the relation between the angular momentum and its component along the axis of quantization, that is, the external field and direction of precession of axis.

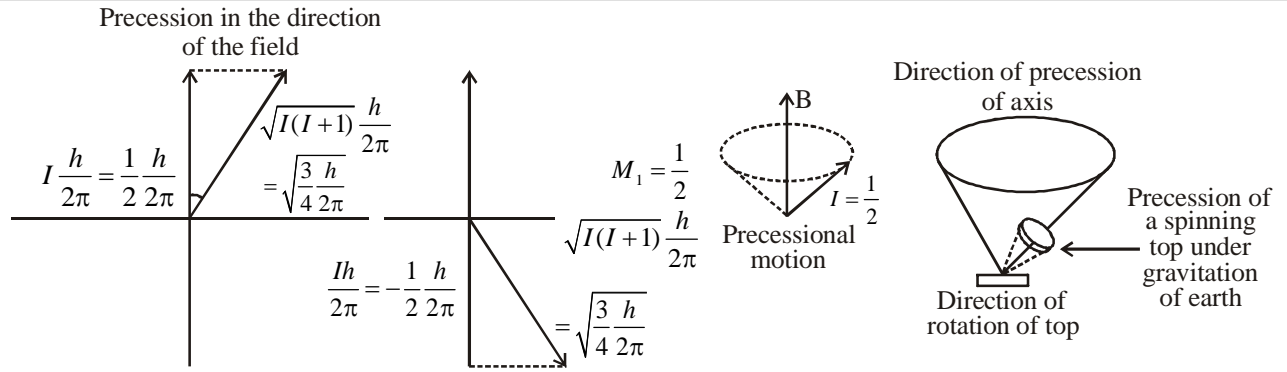


Fig. Nuclear spin angular momentum vector and its component along the external field strength B

For a proton spin I is $\frac{1}{2}$ and there are only two possible values of M_I . The projection of the spin angular momentum vector on to axis of quantization gives $\frac{1}{2}\hbar$, and $-\frac{1}{2}\hbar$, this can be written as $M_I\hbar$, where M_I

is the magnetic spin angular momentum which has values $\pm \frac{1}{2}$. It can be shown that θ in this case is either $35^\circ 15'$ or $144^\circ 45'$. If μ_B is the component of μ_I in the direction of the field, then

$$\cos \theta = \frac{\mu_B}{\mu_I} \quad \dots (5)$$

Eq. (4) now becomes

$$E = -\hat{\mu}_B \cdot \hat{B} \quad \dots (6)$$

where $\mu_B = g_N \beta_N M_I$... (7)

where β_N is the nuclear magneton equal to $(e/2m_p c) \frac{h}{2\pi}$. Substituting (7) into (6) we obtain.

$$E = -g_N \beta_N B \cdot M_I \quad \dots (8)$$

The negative sign in energy expression (8), as compared to the energy of an electron spin ($Em_s = \mu_B m_s B$) reflects the opposite charge of nucleus and electron. Thus, the energy, E, depends on the applied magnetic field strength and M_I . Thus for a spin $I = \frac{1}{2}$, $M_I = \pm \frac{1}{2}$ and it has a lower energy level of $-\frac{1}{2} g_N \beta_N B$, which corresponds to parallel alignment of the magnetic moment to the applied field and higher energy level of $\frac{1}{2} g_N \beta_N B$, corresponds to antiparallel situation. In the absence of the field, these two levels are said to be degenerate. The degeneracy is removed when an external field is applied. It is possible to measure splitting of these levels in an applied external field. This form of spectroscopy is called the Nuclear Magnetic Resonance Spectroscopy (NMR). Since much NMR is done on proton, one also uses the term proton magnetic resonance or PMR.

The energy of magnetic moment is expressed by equation (8) and depends on M_I . For any nucleus of spin I , there are $2I + 1$ values of M_I , which are $I, I - 1, I - 2, \dots, 0, \dots, -(I - 3), (I - 1), -I$. For example, for proton, $I = \frac{1}{2}$, $M_I = \pm \frac{1}{2}$, the energy levels will split into two levels under magnetic field; when $I = 1$, $M_I = 0, \pm 1$; the energy levels will split into 3 and when $I = \frac{3}{2}$, $M_I = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$, there will be four energy levels under the influence of an external applied magnetic field. However, when $I = 0$, $M_I = 0$ and the energy, $E = 0$, the energy level will not split. The energy of the nuclear spin levels is given by (8), hence.

$$\text{For } I = \frac{1}{2}, M_I = \pm \frac{1}{2}$$

$$E_{1/2} = -\frac{1}{2} g_N \beta_N B \text{ and } E_{-1/2} = g_N \beta_N B \left(\frac{1}{2} \right)$$

When $I = \frac{3}{2}, M_I = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$, the energy of levels will be

$$E_{3/2} = -\frac{3}{2} g_N \beta_N B; E_{1/2} = -\frac{1}{2} g_N \beta_N B; E_{-1/2} = \frac{1}{2} g_N \beta_N B$$

$$\text{and } E_{-3/2} = \frac{3}{2} g_N \beta_N B$$

and when $I = 1, M_I = 0, \pm 1$ the energies will be

$$E_1 = -g_N \beta_N B, E_0 = 0 \text{ and } E_{-1} = g_N \beta_N B$$

The energy levels and their splitting under applied magnetic field is shown in figure.

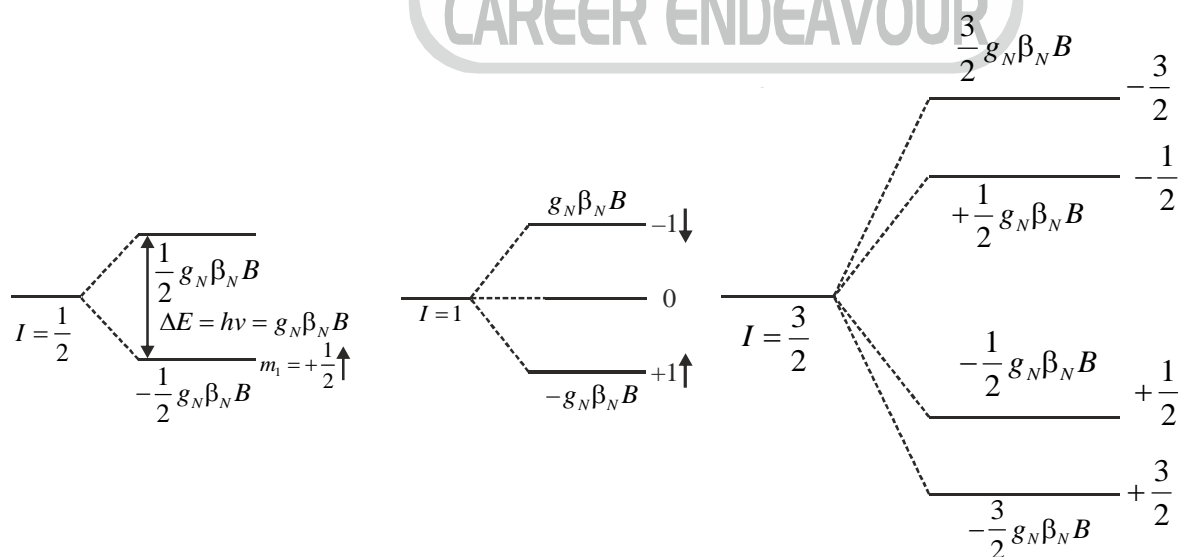


Fig. Splitting of nuclear spin energy levels in a magnetic field of strength B

It may be noted that β_N , the nuclear magneton is about 1836 times smaller than Bohr magneton. Therefore, nuclear magnetic moments are much smaller than electron spin magnetic moment (since nucleus is regarded as rotating much slower than electron due to its mass). The energy difference between two states is

$$\begin{aligned}\Delta E = E_{1/2} - E_{-1/2} &= -\left[-\frac{1}{2}g_N\beta_N B - \frac{1}{2}g_N\beta_N B\right] \text{ when } I = \frac{1}{2} \text{ and } M_I = \pm \frac{1}{2} \\ &= g_N\beta_N B\end{aligned}$$

Therefore, when a sample consisting of a nucleus of spin $\frac{1}{2}$, is placed in a magnetic field, the degeneracy

of the spin states is removed and split into a doublet whose energy difference is, $\Delta E = g_N\beta_N B$

If electromagnetic radiation of frequency ν is present, it induces transition between energy levels by resonance condition.

$$\Delta E = h\nu = g_N\beta_N B \quad \dots (9)$$

NMR is only applicable to the nuclei which have non-zero nuclear spin. For a system containing as assembly

of non-interacting protons, the ratio of the proton population in the $M_I = -\frac{1}{2}$ state $n_{-1/2}$, to that in the

$M_I = \frac{1}{2}$ state, $n_{1/2}$, is given by the Boltzmann equation (Boltzmann distribution) that is

$$\frac{n_{-1/2}}{n_{1/2}} = e^{-\Delta E/RT} = e^{-g_N\beta_N B/k_B T} \quad \dots (10)$$

Problem: The g_N value for F^{19} nucleus is 5.256. Calculate the resonance frequency when it is placed in a magnetic field of strength 1.0 T (tesla) and β_N is $5.0504 \times 10^{-27} \text{ JT}^{-1}$. Also calculate relative population in two spin state at 300K.

Soln. The resonance condition from (9); $h\nu = g_N\beta_N B$, hence,

$$\nu = \frac{g_N\beta_N B}{h} = \frac{5.256 \times 5.0504 \times 10^{-27} \text{ JT}^{-1} \times 1.0 \text{ T}}{6.626 \times 10^{-34} \text{ Js}}$$

$$= 4.006 \times 10^7 \text{ s}^{-1} = 40 \text{ MHz}$$

The relative population in $M_I = -\frac{1}{2}$ and $M_I = \frac{1}{2}$ spin states from (10)

$$\frac{n_{-1/2}}{n_{1/2}} = e^{-g_N\beta_N B/k_B T} = \exp\left(-\frac{5.256 \times 5.0504 \times 10^{-27} \text{ JT}^{-1} \times 1.0 \text{ T}}{1.38 \times 10^{-23} \text{ JK}^{-1} \times 300 \text{ K}}\right)$$

Problem: A NMR spectrometer operating at a 60 MHz frequency gives proton spectra at a field of 1.4092T. At what field would the ^{11}B spectrum be observed at 60 MHz. (For ^{11}B , $I = \frac{3}{2}$ and $g = 1.7920$).

Soln. $\nu =$ Operating frequency $= 60 \times 10^6$ hz

$$\text{and } \frac{\Delta E}{h} = \frac{g_N \mu_N B}{h} = \frac{1.7920 \times 5.0504 \times 10^{-27} \text{ JT}^{-1}}{6.626 \times 10^{-34} \text{ Js}^{-1}} \times B$$

$$B = \frac{60 \times 10^6 \times 6.626 \times 10^{-37} \text{ Js}^{-1}}{1.7920 \times 5.0504 \times 10^{-27} \text{ JT}^{-1}} = 43.93 \times 10^{-1} = 4.393 \text{ T}$$

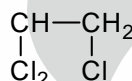
Problem: Find the frequency at which a proton NMR spectrometer should be operating under a magnetic field 1.8. T ($g = 2.7245 \times 2$ and $\mu_N = 5.0504 \times 10^{-27} \text{ JT}^{-1}$)

Soln. $\Delta E = g_N \mu_N B$ for transition for $M_I = \frac{1}{2} \rightarrow -\frac{1}{2}$ in proton

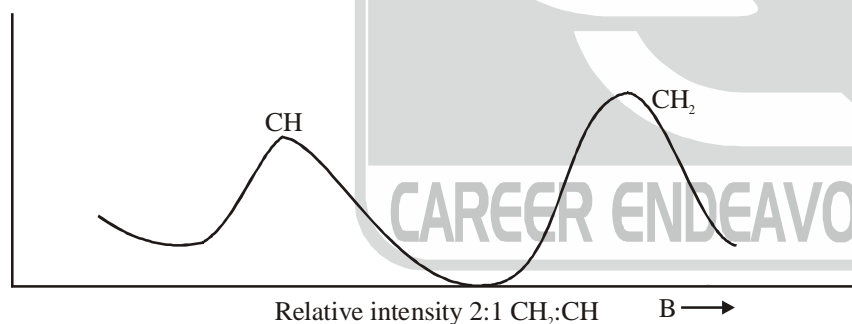
$$\nu = \frac{\Delta E}{h} = \frac{2 \times 2.7245 \times 5.0504 \times 10^{-27} \text{ JT}^{-1} \times 1.8 \text{ T}}{6.626 \times 10^{-34} \text{ Js}^{-1}}$$

$$= 7.48 \times 10^7 \text{ Hz} = 74.8 \text{ MHz}$$

Problem: Sketch the NMR spectra of



Soln.



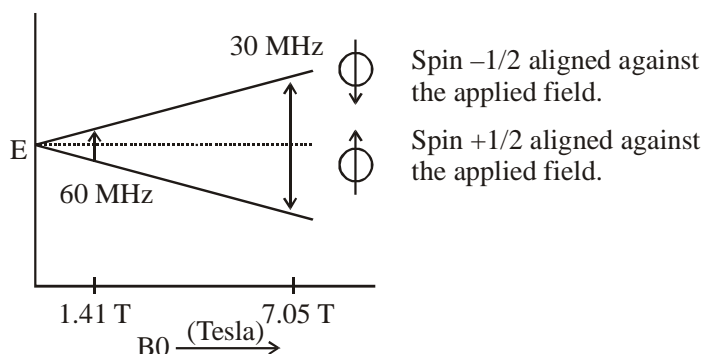
A spectroscopic technique that gives us information about the number and types of atoms in a molecules.

- Hydrogen using ^1H -NMR spectroscopy
- Carbon using ^{13}C -NMR spectroscopy
- Phosphorus using ^{31}P -NMR spectroscopy
- Silicon using ^{29}Si -NMR spectroscopy
- ^{19}F NMR, ^{119}Sn NMR and ^{195}Pt NMR.

NMR SPECTROMETER

- Essentials of an NMR spectrometer are a powerful magnet a radio-frequency generator, and a radio frequency detector.
- The sample is dissolved in a solvent, most commonly CDCl_3 or D_2O and placed in a sample tube which is then suspended in the magnetic field and set spinning.
- Deuterated solvents are used to eliminate ^1H signals from the solvent.

NUCLEAR SPIN IN B_0 : Energy difference between allowed nuclear spin states for ^1H nuclei.



- In an applied field strength of 1.41 T , which is the strength of the electromagnet in our NMR spectrometer, the difference in energy between nuclear spin states for ^1H is approximately 0.00572 cal/mol , which corresponds to electromagnetic radiation of 60 MHz , ^{13}C is approximately 0.00143 cal/mol , which corresponds to electromagnetic radiation of 15 MHz .
- In an applied field strength of 7.05 T , which is readily available with present day, superconducting electromagnets, the difference in energy between nuclear spin states for ^1H is approximately 0.0286 cal/mol , which corresponds to electromagnetic radiation of 300 MHz , ^{13}C is approximately 0.00715 cal/mol , which corresponds to electromagnetic radiation of 75 MHz .

Properties of nucleus to give NMR

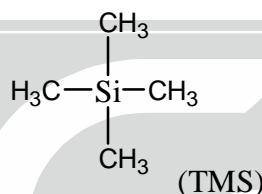
Chemical Shift:

Table of characteristic proton NMR chemical shifts

Type of proton	Type of compound	Chemical shift range, ppm
RCH_3	1° aliphatic	0.9
R_2CH_2	2° aliphatic	1.3
R_3CH	3° aliphatic	1.5
$\text{C}=\text{C}-\text{H}$	vinyllic	4.6–5.9
$\text{C}=\text{C}-\text{H}$	vinyllic, conjugated	5.5–7.5
$\text{C}\equiv\text{C}-\text{H}$	acetylenic	2–3
$\text{Ar}-\text{H}$	aromatic	6–8.5
$\text{Ar}-\text{C}-\text{H}$	benzylic	2.2–3
$\text{C}=\text{C}-\text{CH}_3$	allylic	1.7
$\text{HC}-\text{F}$	fluorides	4–4.5
$\text{HC}-\text{Cl}$	chlorides	3–4
$\text{HC}-\text{Br}$	bromides	2.5–4
$\text{HC}-\text{I}$	iodides	2–4
$\text{HC}-\text{OH}$	alcohols	3.4–4
$\text{HC}-\text{OR}$	ethers	3.3–4
$\text{RCOO}-\text{CH}$	esters	3.7–4.1
$\text{HC}-\text{COOR}$	esters	2–2.2
$\text{HC}-\text{COOH}$	acids	2–2.6
$\text{HC}-\text{C}=\text{O}$	carbonyl compounds	2–2.7

RCHO	aldehydic	9–10
ROH	hydroxylic	2–4
ArOH	phenolic	4–12
C=C–OH	enolic	15–17
RCOOH	carboxylic	10–13.2
HC–NHR	amine	1.5–2.0
RNH ₂	amino	1–5
RNHC(=O)R'	amides	5–8.5

- If we were dealing with nuclei isolated from other atoms and electrons, any combination of applied field and radiation that produces a signal for one nucleus would produce a signal for all identical nuclei.
- Hydrogen or carbon nuclei in organic molecules are not isolated from other atoms, they are surrounded by electrons which are caused to circulate by the presence of the applied field.
- The circulation of electrons around a nucleus in an applied field is called diamagnetic current and the nuclear shielding resulting from it is called diamagnetic shielding.
- The difference in resonance frequencies among the various hydrogen or carbon nuclei within a molecule due to shielding or deshielding is generally very small.
- It is customary to measure the resonance frequency (signal) of a reference compound.
- The reference compound now universally accepted is tetramethylsilane (TMS).



Chemical shift (s): The shift of an NMR signal from the signal of TMS. Normally given in parts per million (PPM).

$$\delta = \frac{\text{Shift in frequency from TMS (Hz)}}{\text{Frequency of spectrometer (Hz)}}$$

SOLVED PROBLEMS

1. The uncertainty in the NMR frequency of a compound in liquid state (relaxation time = 1 s) is 0.1 Hz. The uncertainty in the frequency (in Hz) of same compound in solid state (relaxation time = 10^{-4} s) is
- (a) 10^{-4} (b) 100 (c) 1000 (d) 10^{-3}

Soln. (c) From Heisenberg uncertainty principle,

$$\Rightarrow \Delta E \cdot \Delta t \geq \frac{h}{4\pi} \quad \Rightarrow h \Delta \nu \cdot \Delta t \geq \frac{h}{4\pi} \quad \Rightarrow \Delta \nu \cdot \Delta t \geq \frac{1}{4\pi}$$

$$\text{Or } \Delta \nu \cdot \Delta t \geq \text{constant} \quad \dots(\text{i})$$

(where t = life time or Relaxation time and $\Delta \nu$ = uncertainty in frequency)

$$\therefore (0.1 \text{ Hz})(1 \text{ sec}) \geq \text{constant} \quad \dots(\text{ii})$$

$$\text{And } (\Delta \nu \text{ Hz})(10^{-4}) \geq \text{constant} \quad \dots(\text{iii})$$

From equation (ii) and (iii)

$$0.1 \times 1 = \Delta \nu \times 10^{-4} \quad \therefore \Delta \nu = 10^3 = 1000$$

2. What magnetic field strength is required for proton magnetic resonance at 220 MHz, Given: The factor 'g' for proton is 5.585.

Soln. Since, $\Delta V = \mu_N g B$

$$\text{We have, } B = \frac{\Delta V}{\mu_N g} = \frac{(220 \times 10^6 \text{ s}^{-1})(6.626 \times 10^{-34} \text{ J s})}{(5.047 \times 10^{-27} \text{ J T}^{-1})(5.585)} = 5.1715 \text{ T}$$

3. Calculate the precessional frequency of a proton in a field of 1.5 T.

Soln. The precessional frequency is given by $\nu = \frac{\mu_N g B}{h}$

$$\text{Hence, } \nu = \frac{(5.047 \times 10^{-27} \text{ J T}^{-1})(5.85)(1.5 \text{ T})}{(6.626 \times 10^{-34} \text{ J s})} = 6.38 \times 10^7 \text{ s}^{-1}$$

4. Calculate the value of gyromagnetic ratio γ .

Soln. Since, $\gamma = \frac{2\pi \mu_N g}{h}$

$$\text{We have, } \gamma = \frac{2(3.14)(5.047 \times 10^{-27} \text{ J T}^{-1})(5.584)}{(6.626 \times 10^{-34} \text{ J s})}$$

5. Calculate the angular momentum and magnetic moment values for a proton. Given: $g = 5.585$

Soln. We have, $L = \sqrt{I(I+1)} \left(\frac{h}{2\pi} \right)$

And $\mu_m = g \mu_N \sqrt{I(I+1)}$

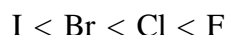
For proton, $I = 1/2$. Thus, we have

$$L = \sqrt{\frac{1}{2} \left(\frac{1}{2} + 1 \right)} \cdot \left(\frac{h}{2\pi} \right) = 0.866 \left(\frac{h}{2\pi} \right) = 0.866 \left(\frac{6.626 \times 10^{-34} \text{ J s}}{2 \times 3.14} \right) = 0.9137 \times 10^{-34} \text{ J s}$$

$$\begin{aligned} \text{And } \mu_m &= (5.585)(\mu_N) \sqrt{\frac{1}{2} \left(\frac{1}{2} + 1 \right)} = 4.837 \mu_N \\ &= 4.837 (5.047 \times 10^{-27} \text{ J T}^{-1}) = 2.441 \times 10^{-26} \text{ J T}^{-1} \end{aligned}$$

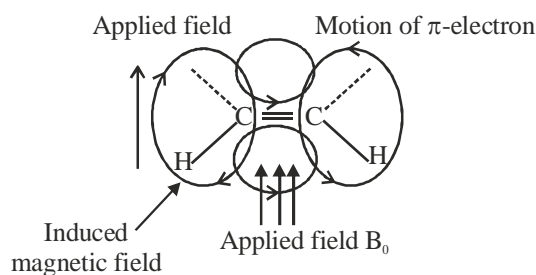
Factors Affecting Chemical Shift:

(a) Electronegativity: In an organic compound, the proton is covalently bonded to carbon, nitrogen, oxygen or other atoms by a σ -bond. When it is placed in a strong magnetic field, the electron of the σ -bond produces a small magnetic field which opposes the applied field. A nearby electronegative atom pulls electron charge density from neighbouring proton, so that a smaller field is needed for a resonance. The signal of the deshielded proton is observed downfield than the signal from the proton which is not deshielded. For example, halogens, the order of electronegativity of these is

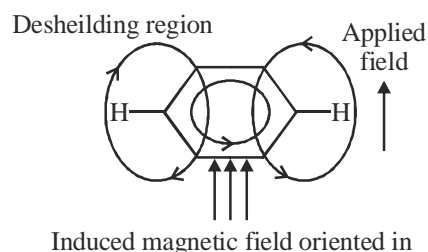


Thus, proton on fluoromethane is most deshielded and in iodomethane it is least shielded. Therefore, the proton signal in fluoromethane will be for these downfield and in iodomethane least downfield. The values are:

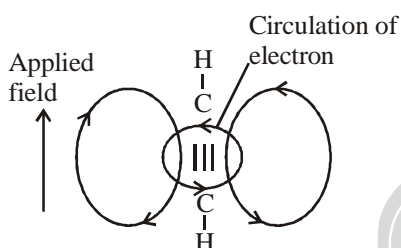
$\text{CH}_3 - \text{F}$	$\text{CH}_3 - \text{Cl}$	$\text{CH}_3 - \text{Br}$	$\text{CH}_3 - \text{I}$
4.26 δ	3.0 δ	2.82 δ	2.16 δ



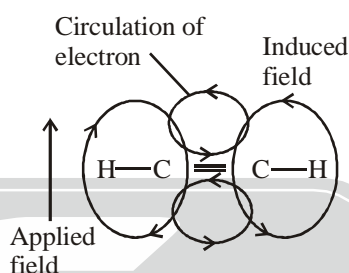
(a) Induced field and applied field are in the same direction (protons are deshielded)



(b) Induced magnetic field oriented in the same direction as around H's (proton are deshielded)



(c) Triple bond Parallel to applied field
Shielding of protons Resonance on field

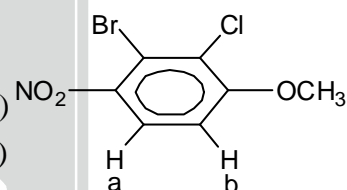


(d) Triple bond perpendicular to applied field
Protons are deshielded Resonance down field

Fig. Induced field effects due to π -electron is organic compounds

$C = C - H$	$C \equiv C - H$	$Ar - H$	$Ar - C - H$
4.6 – 5.9 δ	2 – 3 δ	6 – 8.5 δ	2.7 – 3 δ

- (a) One vicinal non-equivalent proton H(b) splits into $1 + 1 = 2$ (doublet)
 (b) One vicinal non-equivalent proton H(a) splits into $1 + 1 = 2$ (doublet)
 (c) For CH_3 protons no vicinal protons No splitting



- (d) The number of peaks in to which a proton signal splits equals one more than number of equivalent protons, n , or $(n + 1)$ peaks.
 (e) The peak areas are into ratio of similar to the coefficient of binomial expansion and Pascals Triangle.
 (f) The chemical shift of a multiplet (split peak) is at its entire.
 (g) The spacing between the peaks in a NMR multiplet is called the coupling constant between two protons. It is labelled as J . The value of J value, with the environment of the protons and independent of B . The J values are reported in Hz and not in δ value. For example, in case of pair of vicinal and non-equivalent proton J is around 7 Hz.

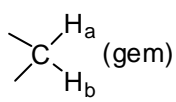
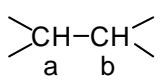
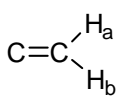
Therefore, the proton NMR spectral peaks are usually, reported as:

4.7	$\delta(2H)$	d	$J = 7$
Chemical shift in δ	No. of proton	doublet	coupling constant

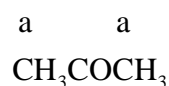
The distance between the centres of two adjacent signal in a particular multiplet is given by J -value which is called *coupling constant* between nucleus y and neighbour x . It is hertz (Hz) or cps (cycles per second) and measures the extent to which the electrons are liable to influences of x on y . J -value is independent of

the field applied. For example, for CH_4 $J_{\text{HH}'}$ cycle s^{-1} . 12.4 *cis*; $J_{\text{CH}'}$ C_6H_6 is 159 cycle s^{-1} . It helps in differentiating between two singlets and one doublet or a quartet from two doublets by recording spectrum at two different radiofrequencies. If the separation between lines does not change it is a doublet on the other hand if the separation between lines increases with frequency, the signal consists of two singlets. The magnitude of J varies with structure. Some J values are given in table. At a given ratio frequency, all protons in an organic compound give NMR signals at different B_0 . The NMR spectra give the following information.

Table : Some J values of organic groups.

	J_{ab}, Hz 10-18 depending upon the electronegativity of attached groups
	8 (depending upon dihedral angle)
	2 (simple Alkenes)
<i>cis</i> -isomers	5-14
<i>trans</i> -isomers	11-19
<i>o</i> -disubstitute ring compounds	7-10
<i>m</i> -disubstitute ring compounds	2-3
<i>p</i> -disubstitute ring compounds	0-1

(a) Number of Signals in NMR Spectrum: The number of signals in an NMR spectrum tell the number of different sets of equivalent protons in a molecule. Each signal corresponds to a set of equivalent protons. Magnetically, equivalent protons. For example,



acetone

(all 6 protons are in similar environment and equivalent)

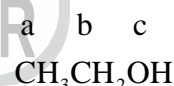
(1 signal)



methanol

(CH_3 and OH protons are in different environment)

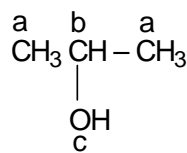
(2 signals)



ethanol

(Three different 3 non-equivalent protons)

(3 signals)

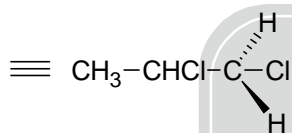
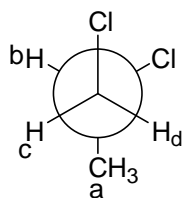


2-propanol

(Two CH_3 protons are equivalent, CH proton and OH proton
Thus three non-equivalent protons (3 signals))

Problem: Give the number of NMR signals in the following compounds:

Compound	No. of non-equivalent	No. of signals proton
$\text{CH}_3\text{CH}_2\text{Cl}$	$\text{CH}_3 - \text{CH} - \text{Cl}$ a b	2
$\text{CH}_3\text{CHCl}-\text{CH}_3$	$\text{CH}_3 - \text{CHCl} - \text{CH}_3$ a b a	2
$\text{CH}_3\text{CH}_2\text{CH}_2-\text{Cl}$	a b c $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$	3
$\text{CH}_3\text{CHCl} - \text{C} \begin{array}{l} \text{H} \\ \text{Cl} \\ \text{H} \end{array}$	a b $\text{CH}_3 - \text{CHCl} - \text{C} \begin{array}{l} \text{H}_c \\ \text{Cl} \\ \text{H}_d \end{array}$	4



(b) Position of Signals (Chemical shift) : The screening constant σ depends on the electron density around it. Higher σ (shielding) higher field, higher τ and lower δ .

CH_4	$\text{CH}_3 - \text{I}$	$\text{CH}_3 - \text{Br}$	$\text{CH}_3 - \text{Cl}$	$\text{CH}_3 - \text{F}$
$\tau = 9.77$	$\tau = 7.34$	$\tau = 7.32$	$\tau = 6.65$	$\tau = 5.74$
$\delta = 0.23$	$\delta = 2.16$	$\delta = 0.268$	$\delta = 3.05$	$\delta = 4.26$

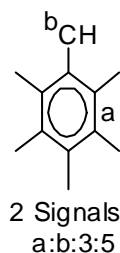
the shift is due to electronegativity of Halogen and shielding decreases for higher electronegativity, lower shielding and low τ .

$\text{C} - \text{H}$	$\text{N} - \text{H}$	$\text{O} - \text{H}$	$\text{Ar} - \text{H}$
$\tau = 9.1$	$\tau = 7.8$	$\tau = 6.5$	$\tau = 1.5 - 4$
$\delta = 0.9$	$\delta = 2.2$	$\delta = 3.5$	$\delta = 8.5 - 6$

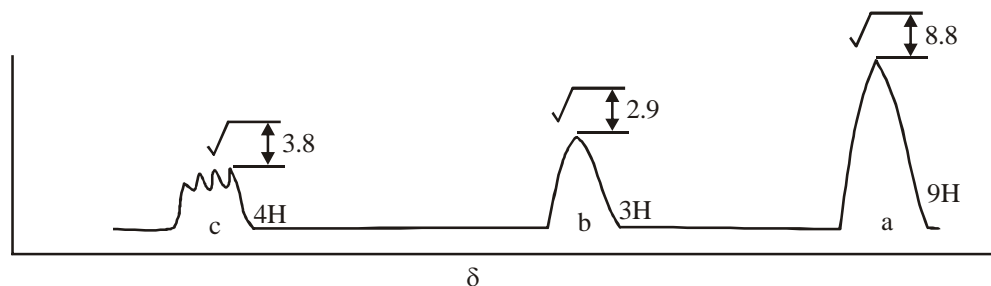
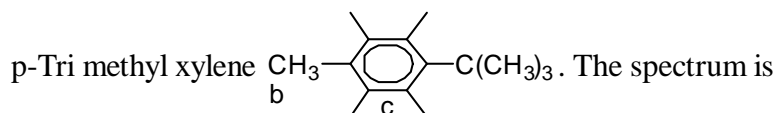
Thus, the position of signals in NMR spectra provides information about the environment in which proton in the compound is present.

(c) Peak Area and Proton Counting: The area under the NMR peak is proportional to the number of H or protons.

$\text{CH}_3 - \text{OH}$	a b c
a b	$\text{CH}_3 - \text{CH}_2 - \text{OH}$
2 signals peak area 3:1	3 signals 3:2:1

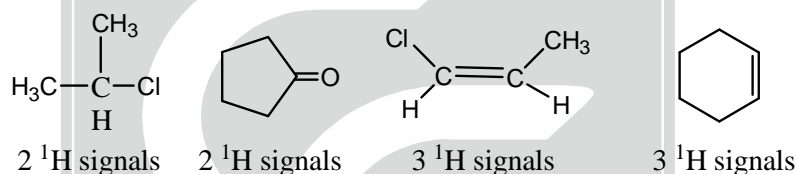


Area is found by integration method. The integrated curve is always given at top of the peaks. For example NMR spectrum of



Equivalent atoms:

- Equivalent atoms have the same chemical environment and may be related by symmetry.
- Molecules with one set of equivalent atoms give one NMR signal.
- Two or more sets of equivalent atoms give a different NMR signal for each set.



Chemical shift depends on:

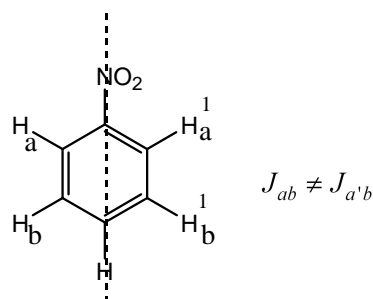
- Electron density \rightarrow Induced magnetic field \rightarrow shielding and deshielding.
- Electron density depends on electronegativity of near by atoms hybridization of nearby atoms magnetic induction within an adjacent π bond.

Notes:

- The number of signals shows how many different kinds of protons are present.
- The location of the signals shows how shielded or deshielded proton
- The intensity of the signal shows the number of protons of that type.
- Signal splitting shows the number of proton on adjacent atoms.

Magnetic equivalence: Magnetically equivalent nuclei are isochronous have identical chemical shift and have equal coupling (J) to every other nuclei in the molecule.

Similarly, if two nuclei are magnetically equivalent, they give a single signal and do not split one another.



Chemically identical nuclei (H_a and H_a') is different to H_b .

Table - Properties of some nuclei with non-zero spin

Nucleus	Spin	Resonance frequency (MHz) in field of 2.3487 T	g value
¹ H	1/2	100.00	5.585
¹⁰ B	3	10.75	0.6002
¹¹ B	3/2	32.08	1.792
¹³ C	1/2	25.14	1.404
¹⁴ N	1	7.22	0.4036
¹⁵ N	1/2	10.13	-0.5660
¹⁷ O	5/2	13.56	-0.7572
¹⁹ F	1/2	94.07	5.255
²⁹ Si	1/2	19.87	-1.110
³¹ P	1/2	40.48	2.261
³⁵ Cl	3/2	9.80	0.5472
³⁷ Cl	3/2	8.16	0.4555
¹⁰⁷ Ag	1/2	4.05	-0.2260
¹¹⁹ Sn	1/2	37.27	-2.082
¹²⁷ I	5/2	20.00	1.118
¹⁹⁹ Hg	1/2	17.83	0.996

Population of Energy Levels: When first confronted with nuclear and electron spin spectroscopy the student (who has experimented earlier with bar magnetics in the earth's field) usually asks: why don't the nuclear (or electronic) magnetic moments immediately line themselves up in an applied field so that they all occupy the lowest energy state?

There are several facets to this question and its answer. Firstly, if we take 'immediately' to refer to a period of some seconds, then spin magnetic moments do immediately orientate themselves in a magnetic field, although they do not all occupy the lowest available energy state. This is a simple consequence of thermal motion and the Boltzmann distribution. We have seen that spin energy levels are split in an applied field, and

their energy separation is ΔE joules. Let us confine our attention to particles with spin $\frac{1}{2}$ (and hence just two energy levels) for simplicity - our remarks, however, are easily extended to cover the general case. Classical theory states that at a temperature T K the ratio of the populations of such levels will be given by:

$$\frac{N_{upper}}{N_{lower}} = \exp\left(-\frac{\Delta E}{kT}\right)$$

where k is the Boltzmann constant. Thus at all temperatures above absolute zero the upper level will always be populated to some extent, although for large ΔE the population may be insignificant. In the case of nuclear and electron spins, however, ΔE is extremely small.

$$\Delta E \text{ nuclei} \approx 7 \times 10^{-26} \text{ J in a 2.3487 T field}$$

$$\Delta E \text{ electrons} \approx 6 \times 10^{-24} \text{ J in a 0.34 T field}$$

and since $k = 1.38 \times 10^{-23} \text{ JK}^{-1}$, we have at room temperature ($T = 300\text{K}$)

$$\frac{N_{upper}}{N_{lower}} \approx \exp\left(-\frac{7 \times 10^{-26}}{4.2 \times 10^{-21}}\right) \approx \exp(-1 \times 10^{-5})$$

$$\approx 1 - (1 \times 10^{-5}) \text{ for nuclei}$$

$$\text{and } \frac{N_{upper}}{N_{lower}} \approx \exp\left(-\frac{6 \times 10^{-24}}{4.2 \times 10^{-21}}\right) \approx \exp(-1 \times 10^{-3})$$

In both cases the ratio is very nearly equal to unity and we see that the spins are almost equally distributed between the two (or, in general, $2I + 1$) energy levels.

We need to discuss now the nature of the interaction between radiation and the particle spins which can give rise to transitions between these levels.

No. of Neighbouring Proton

0	Singlet	1
1	Doublet	1:1
2	Triplet	1:2:1
3	Quar	1:3:3:1
4	Quentet	1:4:6:4:1
5	Sixtet	1:5:10:10:5:1

(Ranker triangle)

Neighbour proton behave as a magnet splitting always by neighbouring proton.

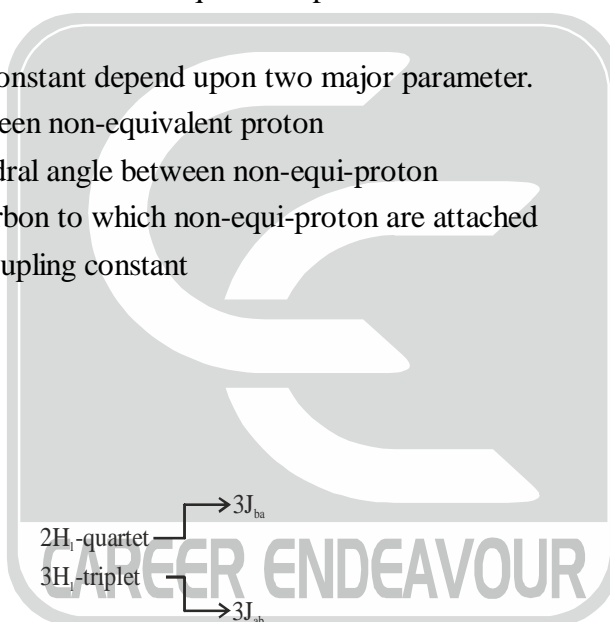
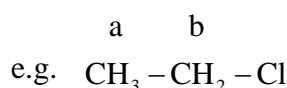
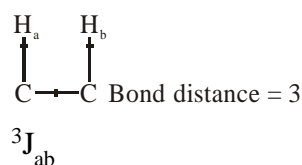
Coupling constant: [Interaction or pairing \rightarrow coupling]

The extent of coupling between non-equivalent proton can be measured in terms of value of coupling constant.

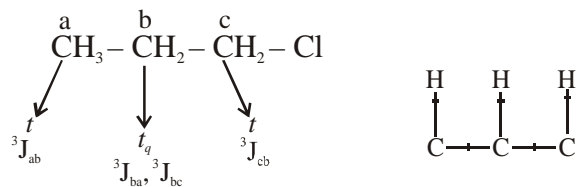
The value of coupling constant depend upon two major parameter.

- Bond distance between non-equivalent proton
- Bond angle or dihedral angle between non-equi-proton
- Hybridization of carbon to which non-equi-proton are attached

The representation of coupling constant



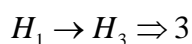
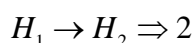
the coupling constant value of mutually interacting proton will be identical



$[ab = ba, bc = ca]$ (Mutually interacting)

In the most of the molecule the value of coupling constant will be inelible after three bond distance.

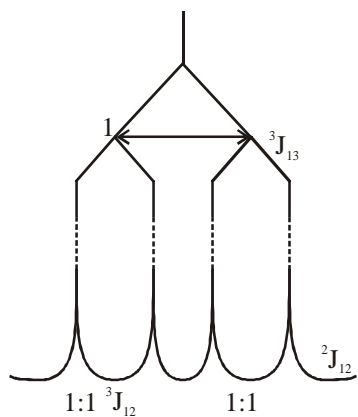
In some special example we can absorb the coupling constant at more than three bond distance which is known as long range coupling.



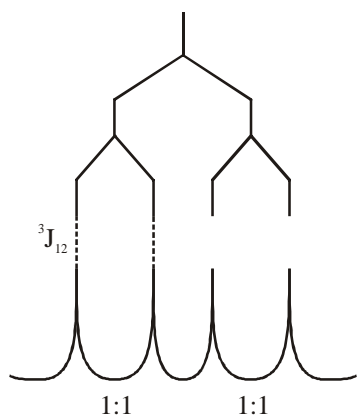
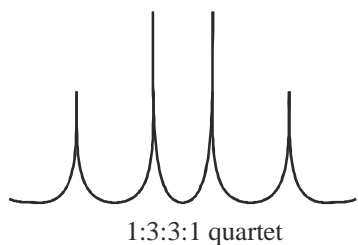
$$H_2 \rightarrow H_3 \Rightarrow 3$$

$$H_1 \rightarrow H_3 \Rightarrow 4$$

$$^1H = d, d[{}^2J_{12} \quad {}^3J_{13}]$$

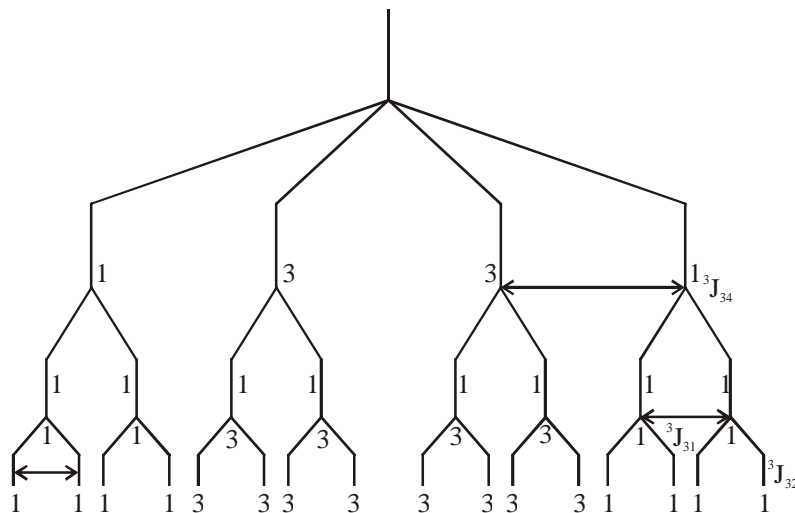


but in quartet

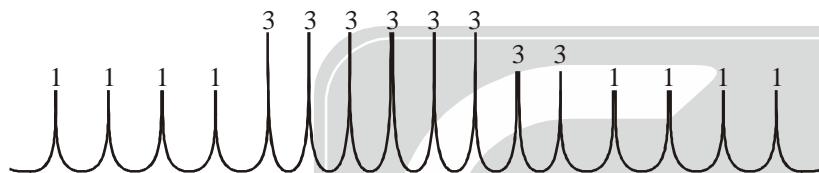


$$^2H \rightarrow d.d.[{}^2J_{21}, \quad {}^3J_{23}]$$

$$^3H \rightarrow d.d.q[{}^3J_{32}, \quad {}^3J_{31}, \quad {}^3J_{34}]$$



$= 2 \times 2 \times 4 = 16$ line

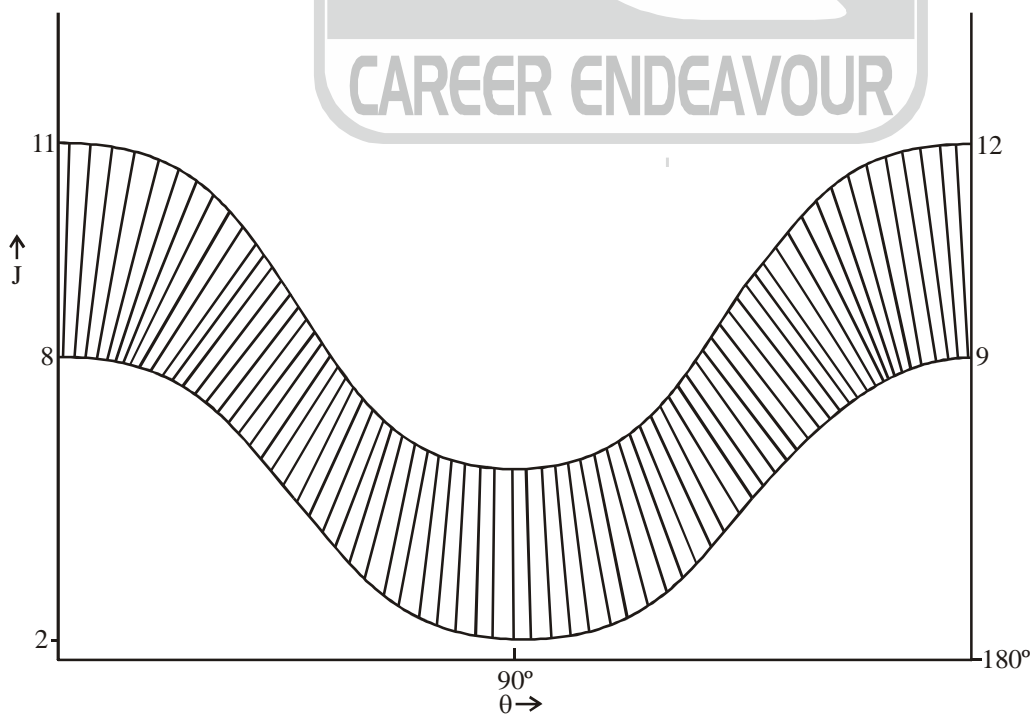


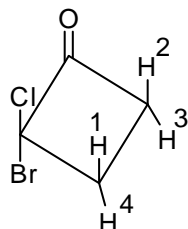
$H^4 \rightarrow$ doublet ${}^3J_{43}$

* If rotation is restricted for vicinal protons and sp^3 carbon then J-value will be dependent on dihedral angle and can be calculated by KARPLUS EQUATION:

${}^3J = 8.5 \cos^2 \theta - 0.28 \quad [\theta = 0^\circ - 90^\circ]$

${}^3J = 9.5 \cos^2 \theta - 0.28 \quad [\theta = 90^\circ - 180^\circ]$




 $^1\text{H} = \text{d.d.d}$

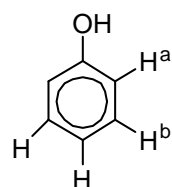
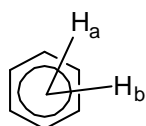
$$^2J_{14} = 10 - 12 \text{ Hz}$$

$$^3J_{12} = 8 - 11 \text{ Hz}$$

$$^3J_{13} = 5 - 7 \text{ Hz}$$

\therefore [Dihedral angle \cong K 120]

In case of Benzene ring some long range coupling can also be observed at high frequency.

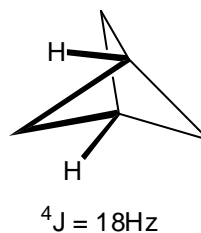
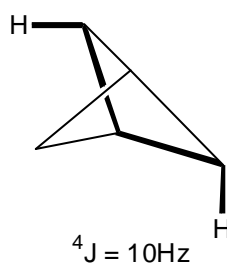
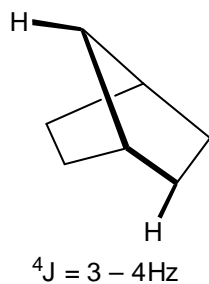
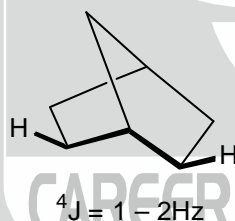
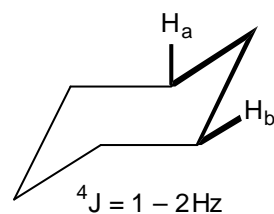


$$J_{\text{ortho}} = ^3J = 7 - 8 \text{ Hz}$$

$$J_{\text{meta}} = ^4J = 2 - 3 \text{ Hz}$$

$$J_{\text{para}} = ^5J = 0 - 1 \text{ Hz}$$

Long range coupling can also be observed in some specific examples when the Non-equivalent proton are oriented making W, which is also known as W-coupling.



* **Non-first order NMR or Second order NMR** * : When value of $\frac{\Delta\nu}{J}$ for the multiplet in NMR spectrum is less than 10 the intensity ratio of multiplet starts to distort from accepted Pascal intensity pattern. In this situation the spectrum is known as NON-FIRST ORDER NMR SPECTRUM.