

Example 1.39. Methane is IR inactive. Why?

Solution: The four hydrogen atoms in methane vibrate symmetrically. Since there is no change in dipole moment during vibration, so methane does not absorb IR radiation. Hence, methane is IR inactive.

Example 1.40. What is the importance of IR spectroscopy in finger print region?
(P.T.U. Dec 2006, Dec 2007)

Solution: The region below 1500 cm^{-1} is called finger print region. In the I.R. spectrum of a molecule, a number of absorption bands are obtained in the finger print region due to bending vibrations of the different bonds of molecule. The pattern of peaks obtained in finger print region is very complex but these peaks are characteristic feature of a compound. The finger print region can be used for comparing spectra of unknown compounds with known compounds to establish the identity of the unknown compound.

1.14 NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

Nuclear magnetic resonance (NMR) spectroscopy is the study of transition of a nucleus from one spin state to another on the absorption of radio frequency waves when the nucleus is placed in a magnetic field.

The NMR spectroscopy is different from other kinds of spectroscopy as an external magnetic field is used to provide the energy levels required for nuclear transitions. The transitions between the energy levels produced by external magnetic field are obtained by radio frequency waves.

NMR spectroscopy is the most important spectroscopic method for the determination of structure of organic, inorganic and bio-molecules. NMR spectroscopy provides information about the chemical environment around an atom in a molecule. The applications of NMR spectroscopy include the detection of electronegative groups, distinction between cis and trans isomers, detection of aromaticity and the detection of hydrogen bonding. NMR spectroscopy is also being used in determining the electron distribution in molecules and to study the kinetics of chemical transformations.

1.14.1 Principles of NMR Spectroscopy

Nuclear Spin Quantum Number (I) Nucleus of any atom consists of protons and neutrons. Like electrons, the protons and neutrons spin about their own axis in the nucleus. Each proton and neutron have spin quantum value of $\pm \frac{1}{2}$. If the proton or neutron spins clockwise the spin is $+\frac{1}{2}$, and if it spins anticlockwise the spin is $-\frac{1}{2}$.

The spin quantum number (I) of a nucleus can be $0, \frac{1}{2}, 1, \frac{3}{2}, 2$ etc. depending upon the number of protons and neutrons with parallel spins ($\uparrow\uparrow$) or antiparallel spins ($\uparrow\downarrow$).

Consider the example of deuterium (${}_1\text{H}^2$ or ${}_1\text{D}^2$), an isotope of hydrogen. The nucleus of deuterium consists of one proton and one neutron. If the proton and neutron have antiparallel spin i.e.

$$\text{spin of proton} = +\frac{1}{2}$$

$$\text{spin of neutron} = -\frac{1}{2}$$

$$\text{Then, spin quantum number } I = +\frac{1}{2} - \frac{1}{2} = 0.$$

However, if the proton and neutron have parallel spin i.e.,

$$\text{spin of proton} = +\frac{1}{2}$$

$$\text{spin of neutron} = +\frac{1}{2}$$

$$\text{Then, spin quantum number } I = +\frac{1}{2} + \frac{1}{2} = 1$$

It has been found experimentally that spin quantum number of deuterium is 1 (i.e. $I = 1$). So, in the nucleus of deuterium, the proton and neutron have parallel spin.

The spin quantum number (I) of a nucleus is a fixed characteristic property of a nucleus.

The spin quantum number, I , of an atom depends on its atomic number and mass number, and can be found using the following general rules :

(a) When atomic number and mass number are even, then $I = 0$.

For example, ${}^4_2\text{He}^4$, ${}^{12}_6\text{C}^{12}$, ${}^{16}_8\text{O}^{16}$ etc.

(b) When atomic number is odd and mass number is even, then ' I ' is a non-zero whole number i.e. $I = 1, 2, 3, \dots$ etc.

For example ${}^{14}_7\text{N}^{14}$, ${}^{10}_5\text{B}^{10}$, ${}^2_1\text{D}^2$ etc.

(c) When atomic number is odd or even and mass number is odd, then ' I ' is non-zero fraction i.e. $I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ etc.

For example ${}^1_1\text{H}^1$, ${}^{19}_9\text{F}^{19}$, ${}^{23}_{11}\text{Na}^{23}$.

This information is summarised in Table (1.5).

Table 1.5. Spin quantum number (I) of different elements

Atomic Number	Mass Number	Spin quantum number (I)	Examples
Even	Even	0	${}^4_2\text{He}^4$, ${}^{12}_6\text{C}^{12}$, ${}^{16}_8\text{O}^{16}$
Odd	Even	1, 2, 3,	${}^{14}_7\text{N}^{14}$, ${}^{10}_5\text{B}^{10}$, ${}^2_1\text{D}^2$
Odd or Even	Odd	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$	${}^1_1\text{H}^1$, ${}^{19}_9\text{F}^{19}$, ${}^{23}_{11}\text{Na}^{23}$

It is important to note that only those nuclei can show NMR spectrum which have non-zero value of spin quantum number i.e. $I > 0$.

The nuclei having $I > 0$ are called spin active nuclei or magnetic nuclei. The nuclei such as ${}^{12}_6\text{C}^{12}$, ${}^{16}_8\text{O}^{16}$ which have $I = 0$ are called non-magnetic nuclei.

Nuclear Magnetic Moment

The nucleus of any atom behaves as a tiny spinning bar magnet due to its electric charge and spin. The spin of nucleus gives rise to a magnetic field whose axis coincides with the axis of spin. So, each nucleus can be considered to be equivalent to a magnet having a magnetic moment μ . The magnetic moment associated with a nucleus having nuclear spin quantum number I ($I > 0$) is given by

$$\vec{\mu} = g\mu_N \vec{I} \quad \dots(1.14)$$

where

g = nuclear g -factor

μ_N = nuclear magneton

Also,

$$\mu_N = \frac{e\hbar}{4\pi m_p}$$

where

e = electronic charge

m_p = mass of proton

The magnitude of nuclear magnetic moment is given by

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

Magnetic Nuclei in External Magnetic Field

A nucleus with nuclear spin ' I ' can take $(2I + 1)$ orientations in space.

For example, in case of ${}_1H^1$, $I = \frac{1}{2}$

So, number of orientations = $2I + 1 = 2 \times \frac{1}{2} + 1 = 2$

Hence, ${}_1H^1$ can take two orientations in space. In the absence of an external magnetic field, these two orientations are of equal energy.

When the external magnetic field 'B' is applied, then the energy levels split. The following two energy levels corresponding to two different orientations are obtained :

- (a) Alpha orientation where the direction of magnetic moment of nucleus is in the direction of 'B' i.e. nucleus is orienting along B.
- (b) Beta orientation where the direction of magnetic moment of nucleus is in the opposite direction to 'B' i.e. nucleus is orienting against B (Fig. 1.19.).

These two orientations, alpha and beta, do not have same energy. The orientation which is orienting along applied field B i.e. alpha orientation, has lower energy while the orientation which is against the applied field B i.e. beta orientation, has high energy (Fig. 1.20).

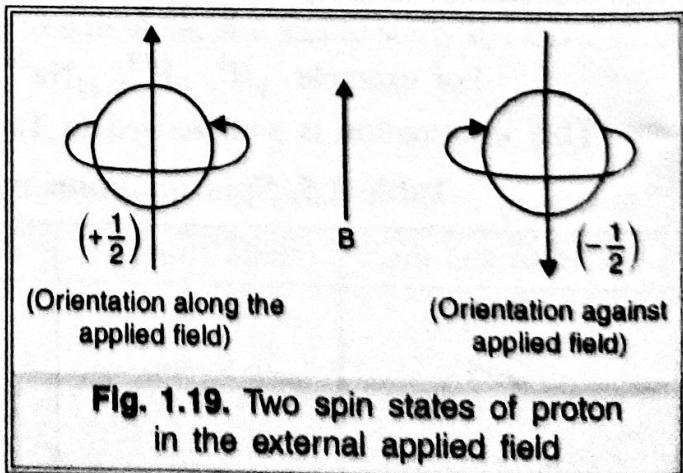


Fig. 1.19. Two spin states of proton in the external applied field

The energy associated with each orientation is given in terms of magnetic quantum number, m_I . For nuclear spin quantum number I, m_I can have the following values

$$m_I = +I, I-1, I-2 \dots 0 \dots -I$$

For ${}^1\text{H}^1, I = \frac{1}{2}$

Hence $m_I = +\frac{1}{2}, -\frac{1}{2}$

Further, the energy of interaction of nuclear magnetic moment μ with an external magnetic field B is given by

$$E = -\vec{\mu} \cdot \vec{B} \quad \dots(1.15)$$

Substituting $\vec{\mu}$ from eq. (1.14) in (1.15)

$$E = -g\mu_N B I \quad \dots(1.16)$$

As the energy of a nuclear spin orientation is given in terms of magnetic quantum number, m_I , so, from eq. (1.16), we may write

$$E_{m_I} = -g\mu_N B m_I \quad \dots(1.17)$$

The energy of alpha orientation corresponds to $m_I = +\frac{1}{2}$ and energy of beta-orientation

corresponds to $m_I = -\frac{1}{2}$.

So, from eq. (1.17)

$$\text{Energy of alpha orientation } E_{m_I} = E_{\frac{1}{2}} = -\frac{1}{2} g\mu_N B$$

$$\text{Energy of Beta orientation } E_{m_I} = E_{-\frac{1}{2}} = \frac{1}{2} g\mu_N B$$

In the absence of external magnetic field, these two orientations have same energy. But in the presence of magnetic field these two orientations have different energy (Fig. 1.21).

Now, when radio frequency is incident on the nucleus, the proton undergoes transition from lower energy level to high energy level, thereby producing the electromagnetic spectrum. The transition of a proton from one energy level to another is called flipping of proton.

The energy required for this transition is given by

$$\Delta E = E_2 - E_1$$

$$= \frac{1}{2} g\mu_N B - \left(-\frac{1}{2} g\mu_N B \right) = g\mu_N B$$

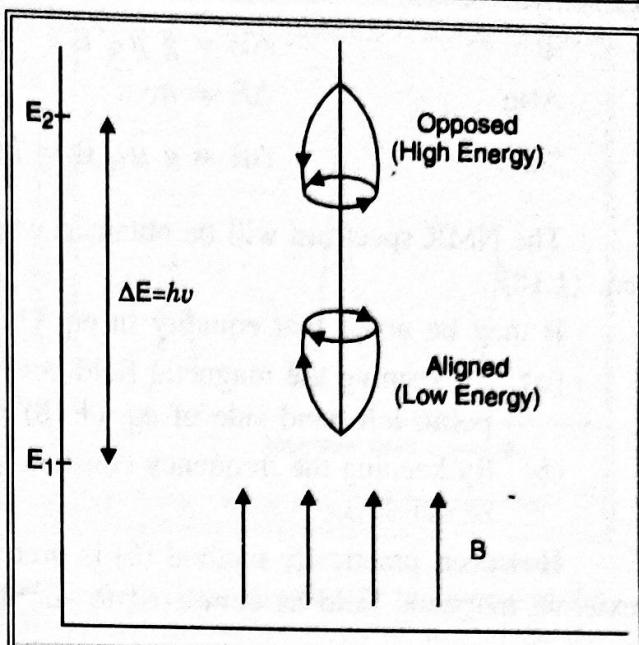


Fig. 1.20. Energy level of a proton

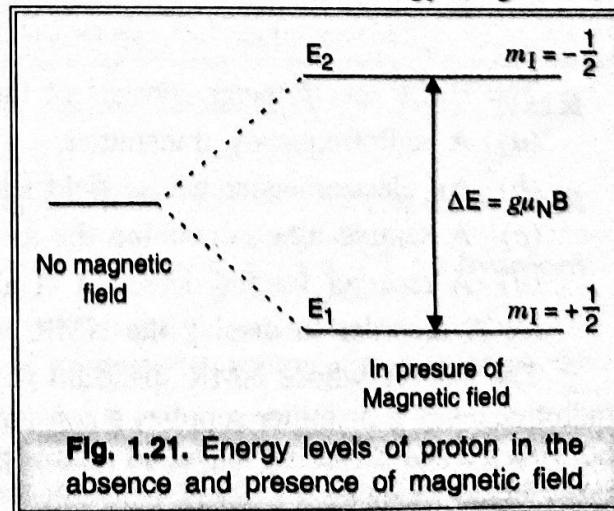


Fig. 1.21. Energy levels of proton in the absence and presence of magnetic field

$$\Rightarrow \Delta E = g \mu_N B$$

Also $\Delta E = h\nu$

So, $\Delta E = g \mu_N B = h\nu \Rightarrow \nu = \frac{g \mu_N B}{h}$... (1.18)

The NMR spectrum will be obtained when the frequency ' ν ' of radiowaves satisfies the eq. (1.18).

It may be noted that equality in eq. (1.18) can be achieved by two methods :

- (a) By keeping the magnetic field constant and varying the frequency so that at some point, left hand side of eq. (1.18) will become equal to right hand side.
- (b) By keeping the frequency constant and varying the magnetic field till the eq. (1.18) is satisfied.

However, practically method (b) is preferred as it is easy to supply a variable value of external magnetic field as compared to supply of variable frequency.

1.14.2 Instrumentation

The NMR spectrum of a compound is noted with NMR spectrometer. The block diagram of an NMR spectrometer is depicted in Fig. 1.22.

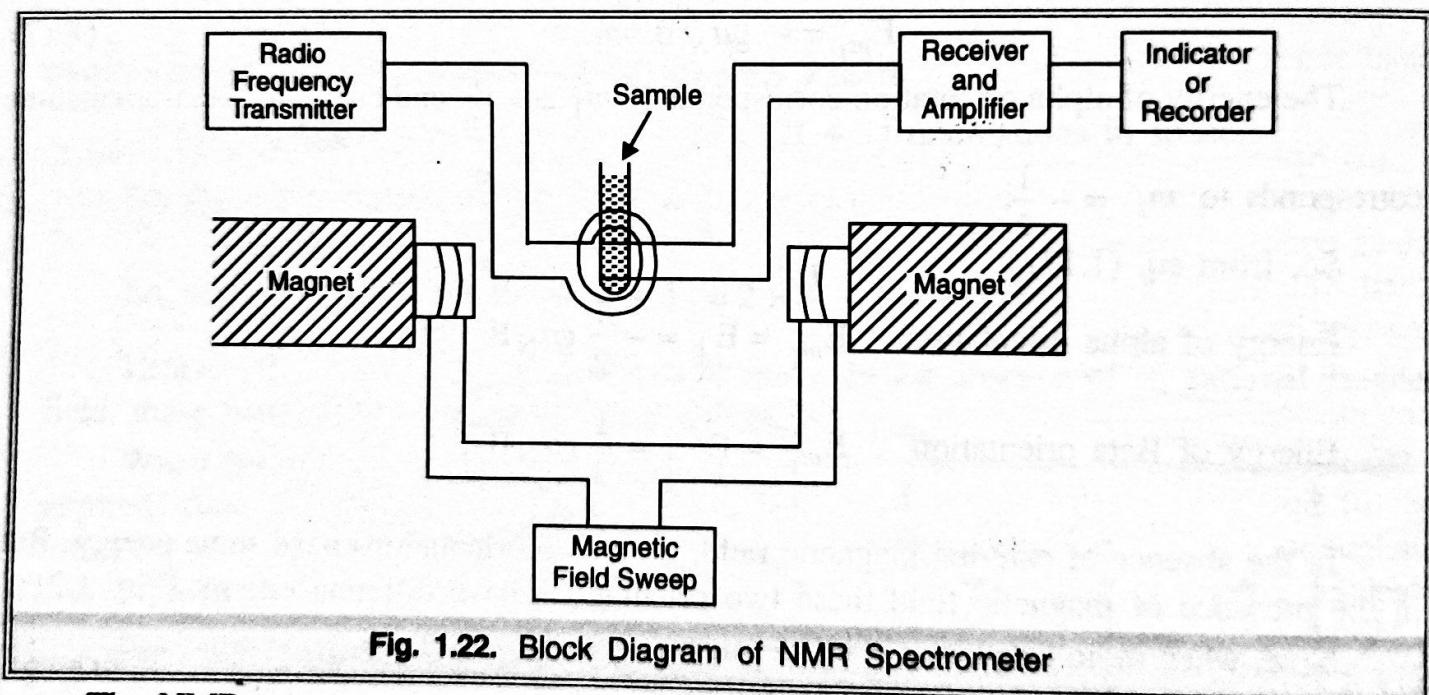


Fig. 1.22. Block Diagram of NMR Spectrometer

The NMR spectrometer consists of the following parts :

- (a) A radiofrequency transmitter.
- (b) An electromagnet whose field strength can be changed by varying the voltage.
- (c) A sample tube containing the sample whose NMR spectrum is to be studied.
- (d) A receiver for the detection of absorption of energy.
- (e) A recorder to display the NMR spectrum.

The sample whose NMR spectrum is to be studied is placed in the sample tube. The radiofrequency transmitter supplies a constant radiofrequency usually 60 megacycles/sec. (i.e. 60 MHz). Then a varying magnetic field is supplied. The absorption of energy by the sample takes place when eq. (1.18) is satisfied.

$$\nu = \frac{g \mu_N B}{h} \quad \dots(1.18)$$

When this energy is absorbed, the corresponding nuclei undergo transition to excited state i.e. undergo spin flipping. This absorption of energy is detected by the receiver and displayed by recorder.

The different nuclei undergo absorption at different values of external magnetic field. So, different nuclei show signals or peaks at different positions in NMR spectrum (Fig. 1.23).

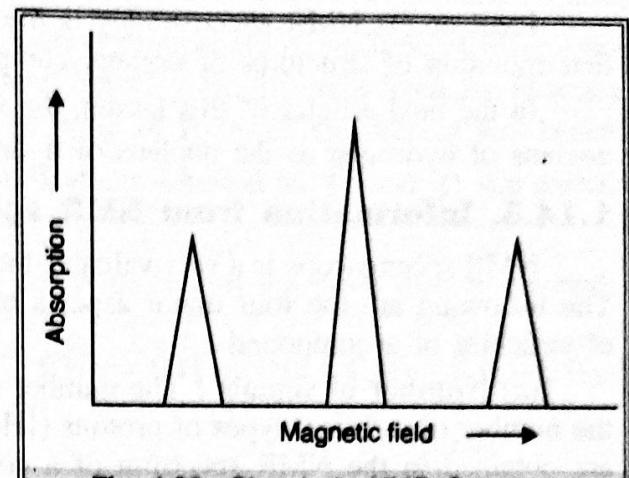


Fig. 1.23. Signals in NMR Spectrum

1.14.3 Relaxation Processes

The absorption of radiofrequency by a nucleus results in spin flipping of nucleus and the nucleus undergoes transition to excited state. It increases the population of nuclei in the excited state. After some time, the population of nuclei in upper and lower energy state become equal. In such case, no further nuclei will be excited to higher state and absorption of radiation would stop.

However, in reality, the nuclei in the upper state continuously lose energy and return to ground state by different processes called relaxation process.

The relaxation processes are of two types :

(a) **Spin-spin relaxation** : Spin-spin relaxation refers to the transfer of energy by a nucleus in the upper state to a neighbouring nucleus in the ground state. Hence, the excited nucleus comes down to a lower state and the neighbouring nucleus in the ground state is excited. The spin-spin relaxation process can take place only if the nuclei undergoing exchange of energy have same precessional frequency. Spin-spin relaxation does not produce any net change in the population of energy levels, but it decreases the average life time of a nucleus in the excited state. It also results in broadening of NMR spectral lines. Spin-Spin relaxation is also called transverse relaxation.

(b) **Spin-lattice relaxation** : Spin-lattice relaxation refers to the transfer of energy by a nucleus in the upper state to the surrounding lattice i.e. to the neighbouring frame work of molecules. This energy is transferred to lattice in the form of additional translational, rotational and vibrational energy. This energy is ultimately passed on to the walls of sample tube from where it is dissipated. Spin-lattice relaxation is also called longitudinal relaxation.

1.14.4. Proton Magnetic Resonance Spectroscopy : ^1H NMR Spectroscopy

All the nuclei having non-zero nuclear spin quantum number ($I > 0$) can show NMR spectrum. For Hydrogen (^1H) the nuclear spin quantum number is $\frac{1}{2}$ ($I = \frac{1}{2}$). So hydrogen can show NMR spectrum.

^1H NMR spectroscopy refers to the nuclear magnetic resonance spectroscopy of nucleus of hydrogen.

The nucleus of hydrogen contains only one proton and no neutron. Hence, ^1H NMR spectroscopy is also called Proton NMR spectroscopy or PMR spectroscopy.

PMR or ^1H NMR spectroscopy is the most widely studied spectroscopy technique for determination of structures of organic compounds.

In the next articles of this lesson, the word 'proton' will be often used to represent the nucleus of hydrogen as the nucleus of hydrogen contains one proton only.

1.14.5. Information from NMR spectra

NMR spectroscopy is a very valuable tool for the identification of structure of a compound. The following are the four major aspects of an NMR spectrum that leads to determination of structure of a compound :

(a) **Number of signals** : The number of signals (peaks) in an NMR spectrum indicate the number of different types of protons (^1H nucleus) present in a compound. If three signals are obtained in the NMR spectrum of a compound, then there are three different types of hydrogen atoms present in that compound.

(b) **Position of signals** : The position of signals (peaks) in the NMR spectrum indicates about the electronic environment about each type of hydrogen atom. If a hydrogen atom is attached to an electronegative element, then the NMR signal of that hydrogen will be obtained at low magnetic field.

(c) **Intensity of signals** : The intensity of signals or relative heights of signals indicates about the number of protons (or ^1H atoms) of different type. If the NMR spectrum of a compound shows two peaks and the ratio of heights of those peaks is $2 : 3$, then it indicates that there are 2 protons of one type and 3 protons of other type.

(d) **Splitting of signals** : The splitting of a signal into two peaks (doublet) or three peaks (triplet) is called multiplicity of a signal. The splitting of a signal of a proton gives information about the number of protons present on the neighbouring carbon atoms in the compound.

1.14.6. Number of Signals : (Equivalent and Non-Equivalent protons)

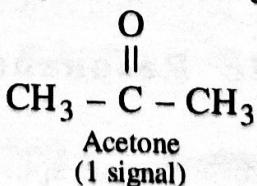
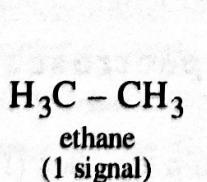
The protons with different electronic environment absorb radio frequency radiation at different field strength in NMR spectrum. So, the number of signals obtained in NMR spectrum tells about the number of different types of protons present in a molecule.

Protons which have the same type of electronic environment are called equivalent protons.

Protons with different type of electronic environment are called non-equivalent protons.

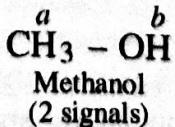
For example in methane (CH_4) all the four hydrogen atoms are equivalent as they are present in the same electronic environment. So methane shows one signal in its NMR spectrum.

The following are other examples of compounds showing only one signal in NMR spectrum:



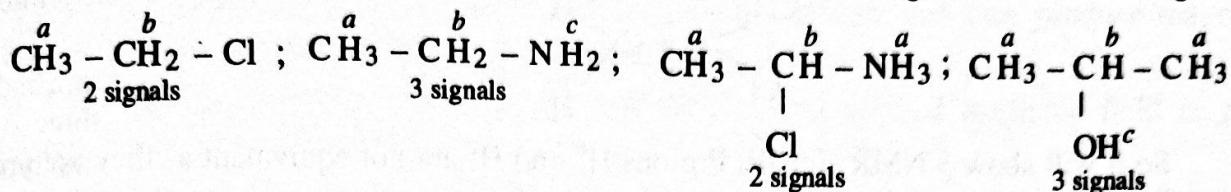
As shown above, acetone has 6H atoms. But as all these 6H atoms are present in same electronic environment, so they are equivalent. Hence, acetone will show only one signal in its NMR spectrum. Similarly, ethane and benzene show only one signal.

Consider the example of methanol :



In methanol, the three H atoms present in methyl group have same type of electronic environment. Hence, these 3H atoms are equivalent, but they are different from the H atom attached to oxygen. So, in methanol two different types of H-atoms are present and hence it will show 2 signals in its NMR spectrum. The H atoms labelled as $\overset{a}{\text{H}}$ and $\overset{b}{\text{H}}$ are called non-equivalent protons.

The following are some other examples of compounds showing more than one signal:



Some typical examples of compounds having different types of H-atoms are shown in Table 1.6.

Table 1.6. Number of NMR signals of some compounds

Compound	Number of NMR Signals
$\text{CH}_3 - \underset{\substack{a \\ }}{\text{CH}_2} - \underset{\substack{b \\ }}{\text{CH}_2} - \underset{\substack{c \\ }}{\text{CH}_2 - \text{Cl}}$	3
$\text{CH}_2 - \underset{\substack{a \\ }}{\text{CH}_2} - \underset{\substack{a \\ }}{\text{CH}_2}$	1
$\text{Br} \quad \text{Br}$	
$\text{CH}_3 - \underset{\substack{a \\ }}{\text{CH}_2} - \underset{\substack{b \\ }}{\text{C}} - \underset{\substack{c \\ }}{\text{CH}_3}$	3
$\text{CH}_3 - \underset{\substack{a \\ }}{\text{CH}_2} - \underset{\substack{b \\ }}{\text{CH}_2} - \underset{\substack{b \\ }}{\text{CH}_2} - \underset{\substack{a \\ }}{\text{CH}_3}$	2
$\text{CH}_3 - \underset{\substack{a \\ \\ O \\ }}{\text{C}} - \underset{\substack{b \\ }}{\text{OH}}$	2
$\text{CH}_3 - \underset{\substack{a \\ }}{\text{CH}} - \underset{\substack{b \\ }}{\text{CH}_2} - \underset{\substack{c \\ \\ \text{Cl} \\ }}{\text{CH}_2 - \text{Cl}}$	3
$\text{CH}_3 - \underset{\substack{a \\ }}{\text{O}} - \underset{\substack{a \\ }}{\text{CH}_3}$	1
$\text{CH}_3 - \underset{\substack{a \\ }}{\text{CH}_2} - \underset{\substack{b \\ }}{\text{O}} - \underset{\substack{b \\ }}{\text{CH}_2} - \underset{\substack{a \\ }}{\text{CH}_3}$	2
$\text{CH}_3 - \underset{\substack{a \\ }}{\text{CH}_2} - \underset{\substack{b \\ }}{\text{OH}} - \underset{\substack{c \\ }}{\text{H}}$	3
$\text{CH}_3 > \text{C} = \text{C} < \begin{matrix} \text{H} \\ \text{H} \\ \text{H} \end{matrix}$	3
$\text{CH}_3 > \text{C} = \text{C} < \begin{matrix} \text{H} \\ \text{H} \\ \text{H} \end{matrix}$	2

Thus, chemical shift is measured in terms of δ scale (Delta Scale) defined as :

$$\delta = \frac{B_{\text{sample}} - B_{\text{reference}}}{B_{\text{applied}}} \times 10^6 \quad \dots(1.19)$$

where B_{sample} = Magnetic field at which sample shows resonance.

$B_{\text{reference}}$ = Magnetic field at which reference compound shows resonance

B_{applied} = External applied magnetic field.

Further, As $v \propto B$ (From 1.18)

$$\text{So, } \delta = \frac{v_{\text{sample}} - v_{\text{reference}}}{v_0} \times 10^6 \quad \dots(1.20)$$

where v_{sample} = frequency at which sample shows resonance.

$v_{\text{reference}}$ = frequency at which reference compound shows resonance

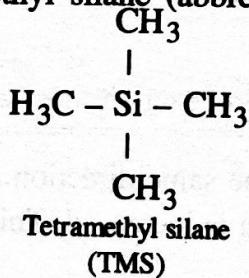
v_0 = operational frequency in megacycles (in MHz).

The δ -value for most of the compounds is in the range 0 – 10.

It may be noted that in eq. (7.7), v_{sample} and $v_{\text{reference}}$, have units of cycles/sec (i.e., Hz), and v_0 has units of megacycles/sec. i.e. Mega Hz (or MHz).

Tetramethyl Silane : Standard reference

The chemical shifts of protons in different compounds are measured relative to a standard reference compound. The universally accepted standard reference compound in NMR spectroscopy is tetramethyl silane (abbreviated as TMS).



The shielding effect produced by induced magnetic field is proportional to the electron density circulating the nuclei. So, if the electron density around a proton (or H atom) is more, then that proton will undergo more shielding effect.

In tetramethyl silane (TMS), carbon has more electronegativity than silicon. Carbon has more tendency to attract the shared pair of electron of Si – C bond towards it. So, Si – C bond may be polarised as $\text{Si}^{\delta+} - \text{C}^{\delta-}$.

Thus, more electron density is generated around carbon. Hence, in other words, more electron density is generated in the vicinity of proton (or H atom). So, the proton undergoes strong shielding effect.

It may be stated that in all the organic compounds, carbon acquires more electron density only when it is attached to silicon as in Si – C bond. On the other hand when carbon is attached to more electronegative elements like oxygen, nitrogen, chlorine etc., carbon acquires partial positive charge (e.g., $\text{C}^{\delta+} - \text{O}^{\delta-}$) i.e. low electron density.

So, it may be concluded that the protons of TMS undergo the highest shielding effect as carbon in TMS is acquiring high electron density.

Greater the electron density around a proton, more will be shielding effect.

Hence, the protons of TMS, being strongly shielded will require the maximum value of external magnetic field to show NMR spectrum.

The protons present in other compounds will require less external magnetic field to show NMR spectrum. So, the NMR signal shown by all other compounds will be on left side of the TMS signal. No compound can show NMR signal to the right side of TMS signal.

Hence, for convenience the position of NMR signal of TMS is given the reference value of $\delta = 0$. The signals for protons in other compounds are measured with reference to this $\delta = 0$ value towards the left side (Fig. 1.25).

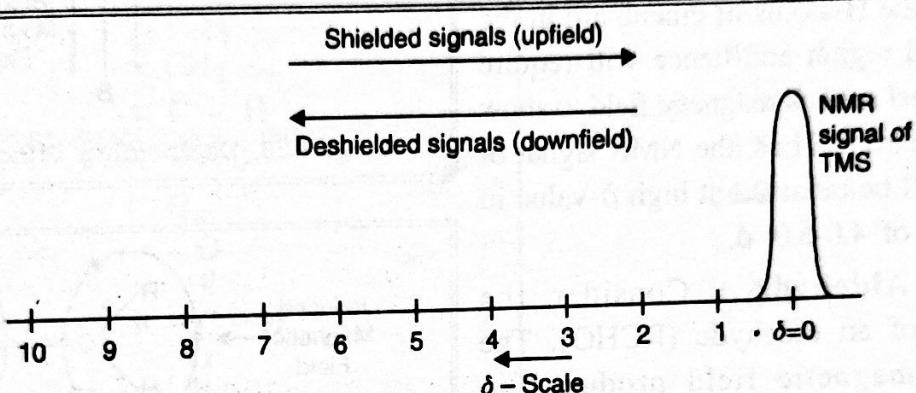


Fig. 1.25. NMR Signal of TMS and δ -scale

The more shielded protons show NMR signal at high field i.e. upfield. The deshielded protons show NMR signals at low field i.e. downfield.

Tetramethyl silane is added to the compound whose NMR spectrum is to be measured. The NMR spectrum thus obtained will show signals due to compound and also a signal corresponding to TMS. Then the δ -values to the signals of compound are assigned by giving $\delta = 0$ value to TMS.

Tetramethyl silane is used as a standard reference compound due to following factors :

- (a) TMS contains 12 H atoms which are equivalent, so a very intense sharp signal is shown by TMS even at low concentrations.
- (b) Due to less electronegativity of silicon, more electron density is created around methyl (CH_3) group. It results in shielding and TMS gives NMR signal at very high field i.e. upfield ($\delta = 0$).
- (c) TMS is chemically inert and miscible with almost all organic solvents.
- (d) TMS has low boiling point (27°C), so it can be removed from a compound easily after taking the NMR spectrum.

Chemical shift of some functional groups

The different functional groups give NMR signal at different δ -values. The chemical shift of some functional groups is explained on next page.

(a) **Alkene** : Consider the example of ethene ($\text{CH}_2 = \text{CH}_2$). When ethene is placed in external magnetic field (B), the electronic circulations produce induced magnetic field in ethene (Fig. 1.26).

The induced magnetic field near the H-atoms of ethene is in the same direction as the direction of external magnetic field. Whereas the induced magnetic field is opposing the external magnetic field near the $\text{C} = \text{C}$ region.

So, the H-atoms of ethene are in the deshielded region and hence will require less external applied magnetic field to show NMR spectrum. Thus, the NMR signal of ethene will be obtained at high δ -value in the range of 4.0-6.0 δ .

(b) **Aldehyde** : Consider the example of an aldehyde (RCHO). The induced magnetic field produced in aldehyde on the application of external magnetic field is shown in Fig. 1.27.

The induced magnetic field near the H-atom of aldehyde is in the same direction as the applied magnetic field. So, H-atom is in the deshielded region and hence will require less external applied magnetic field to show NMR spectrum. Thus NMR signal of aldehydes will be obtained at high δ -value.

Further, due to high electronegativity of oxygen, the electron density around carbon is decreased. The $\text{C} = \text{O}$ bond is polarised as $\delta_+ \text{C} = \delta_- \text{O}$. In turn, the electron density around H-atom is also decreased. Hence, H-atom undergoes further deshielding. The NMR signal of aldehydes is obtained in the range of 8.0 – 9.5 δ .

(c) **Alkyne** : Consider the example of acetylene ($\text{HC} \equiv \text{CH}$). The induced magnetic field produced in acetylene on the application of external magnetic field is shown in Fig. 1.28.

The induced magnetic field near the H-atoms of acetylene is in the opposite direction to the external applied magnetic field. So these

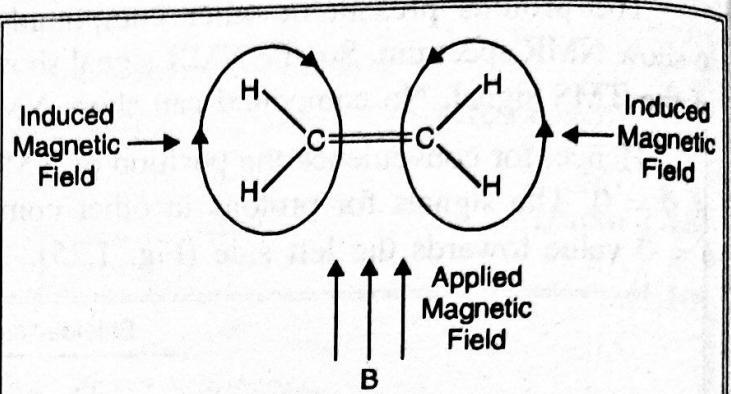


Fig. 1.26. Deshielding Effect in Ethene

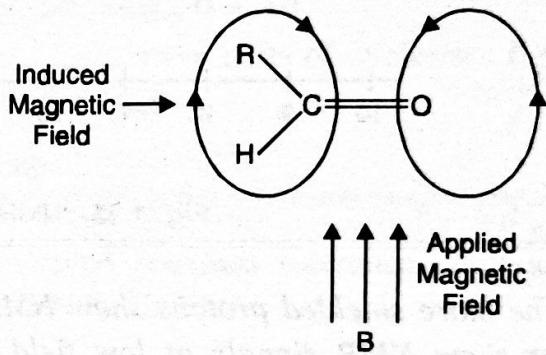


Fig. 1.27. Deshielding Effect in Aldehyde

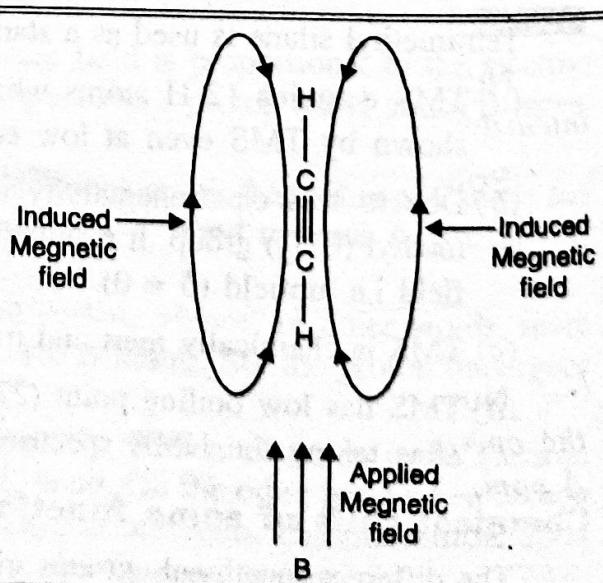


Fig. 1.28. Shielding Effect in Acetylene

H-atoms are lying in the shielded region. Hence, acetylene will require more external applied magnetic field to show its NMR spectrum. Acetylene gives NMR signal in the range 2.0–3.0 δ .

The chemical shift of protons in important functional groups is shown in Table 1.7.

Table 1.7. Chemical Shift δ -values of some protons

Type of protons	δ -value
TMS	0
Alkane	$\begin{array}{c} \\ - \text{C} - \text{H} \\ \end{array}$ 0.1 – 1.6
Alkene	$= \text{CH}_2$ 4.5 – 6.0
Alkyne	$\equiv \text{C} - \text{H}$ 2.0 – 3.0
Alcohol	$\text{R} - \text{OH}$ 3.5 – 4.5
Aromatic	$\begin{array}{c} \text{C}_6\text{H}_6 \\ \\ \text{O} \\ \end{array}$ 6.0 – 8.5
Aldehyde	$\begin{array}{c} \text{R} - \text{C} - \text{H} \\ \\ \text{O} \\ \end{array}$ 9.0 – 10.0
Carboxylic Acid	$\text{R} - \text{C} - \text{OH}$ 10.5 – 12.0
Amine	$\text{R} - \text{NH}_2$ 1.5 – 5.0
Alkyl Halides	CH_3X ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{F}$) 2.0 – 4.5
Phenol	$\text{C}_6\text{H}_5 - \text{OH}$ 4.5 – 6.5
Aniline	$\text{C}_6\text{H}_5 - \text{NH}_2$ 3.0 – 6.0

Solved Numericals

Numerical 1.4. Calculate the NMR frequency of the proton in a magnetic field of intensity 1.4092 tesla. Given $g = 5.585$ and $\mu_N = 5.05 \times 10^{-27} \text{ J T}^{-1}$.

Solution. From eq. (1.18)

$$\nu = \frac{g \mu_N B}{h} = \frac{(5.585) \times (5.05 \times 10^{-27}) \times (1.4092)}{6.626 \times 10^{-34}} \\ = 60 \times 10^6 \text{ sec}^{-1} = 60 \times 10^6 \text{ Hz} = 60 \text{ MHz}$$

Numerical 1.5. The observed chemical shift of a proton is 300 Hz from TMS and the operative frequency of spectrometer is 100 MHz. Calculate the chemical shift in δ ppm.

Solution. From eq. (1.20)

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\nu_0} \times 10^6$$

Given :

$$\nu_0 = 100 \text{ MHz} = 100 \times 10^6 \text{ Hz}$$

$$\nu_{\text{sample}} - \nu_{\text{TMS}} = 300 \text{ Hz}$$

So,

$$\delta = \frac{300}{100 \times 10^6} \times 10^6 = 3$$

Numerical 1.6. A compound shows ^1H NMR signal at 480 Hz downfield from TMS signal in a spectrometer operating at 60MHz. Find the Chemical shift in δ ppm.

Solution.

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\nu_0} \times 10^6$$

Given :

$$\nu_0 = 60 \text{ MHz} = 60 \times 10^6 \text{ Hz}$$

$$\nu_{\text{sample}} - \nu_{\text{TMS}} = 480 \text{ Hz}$$

So,

$$\delta = \frac{480}{60 \times 10^6} \times 10^6 = 8 \text{ ppm}$$

Numerical 1.7. The OH signal of benzyl alcohol is obtained at 144 Hz higher frequency than TMS in a 60 MHz instrument. How many δ -units does this correspond to? (P.T.U., Dec. 2004)

Solution.

$$\nu_0 = 60 \text{ MHz} = 60 \times 10^6 \text{ Hz}$$

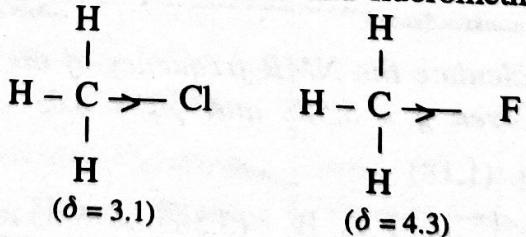
$$\nu_{\text{sample}} - \nu_{\text{TMS}} = 144 \text{ Hz}$$

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\nu_0} \times 10^6 = \frac{144}{60 \times 10^6} = 2.4 \text{ ppm}$$

Factors influencing Chemical Shift

The chemical shift of protons in different compounds is influenced by the extent of shielding and deshielding caused by induced magnetic field. The main factors affecting chemical shift are :

(a) **Inductive effect** : A proton attached to an electronegative atom feels more deshielding. Consider the example of chloroethane and fluoromethane :



Due to high electronegativity of F, it pulls the electrons towards it more strongly as compared to Cl. So, the electron density around H-atoms in fluoromethane gets decreased. Hence, H-atom in fluoromethane undergo more deshielding. This, δ -value of protons in CH_3F is 4.3 and in CH_3Cl it is 3.1.

Greater the electronegativity of atom or group, greater will be deshielding of proton.

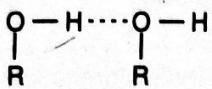
(b) **Anisotropic effect** : Anisotropic effect refers to the different extent of shielding and deshielding in different directions in a compound.

Acetylene shown NMR signal at 2.0 – 3.0 δ because the protons of acetylene lie in the shielding region (Fig. 1.28). Whereas the protons of ethene lie in the deshielding region and

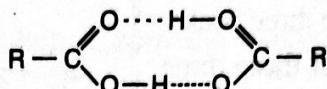
give NMR spectrum at 4.5–6.0 (Fig. 1.26). Similarly, aldehyde group gives NMR signal at 9–10 δ due to strong deshielding (Fig. 1.27).

(c) **Hydrogen bonding** : If a H-atom in a molecule is involved in hydrogen bonding, then it is strongly deshielded and gives NMR signal at high δ -value. The extent of deshielding depends on the strength of hydrogen bond. Stronger the hydrogen bond, greater is deshielding.

For example, – OH group in alcohol gives NMR signal at 3.5–4.5 δ . But – OH group in carboxylic acid gives NMR signal at 10–11 δ due to more strong hydrogen bonding in carboxylic acid :



Hydrogen bonding
in alcohol



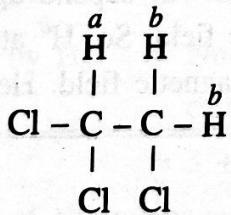
Hydrogen bonding
in carboxylic acid

1.14.8 Splitting of signals : Spin-spin coupling

The number of NMR signals shown by a compound is equal to the number of different types of protons present in that compound. However, in practice, the NMR signals of a compound undergo splitting and give rise to a complex NMR spectrum.

The magnetic field of chemically non-equivalent nuclei interact with each other and split the NMR signal into a number of closely spaced peaks. This phenomenon is called spin-spin coupling.

Consider the example of 1, 1, 2-trichloro ethane :

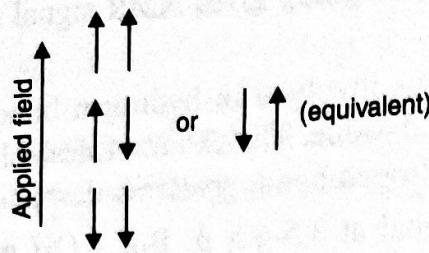


It contains three H-atoms. Two H-atoms are chemically equivalent (labelled as H^b) and they are chemically different from third H-atom (labelled as H^a).

The effective magnetic field felt by H^b is modified by the spin of H^a . If the spin of H^a is aligned with the applied magnetic field (*i.e.* $\uparrow\uparrow$) then H^b will feel more magnetic field and if the spin of H^a is aligned against the applied magnetic field (*i.e.* $\uparrow\downarrow$) then H^b will feel less magnetic field. So, H^b will show NMR signal at two different values of magnetic field and hence H^b will show two peaks (called doublet).

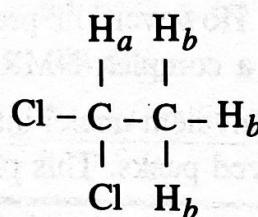
Further, as the probability of H^a to align with or against the applied magnetic field is equal, hence, the intensity (or height) of two peaks shown by H^b will be equal. (Fig. 1.29).

Similarly, the magnetic field felt by H^a is modified by the spin of two H^b atoms. The spin of both H^b atoms may align with or against the applied magnetic field, or spin of one of H^b atom may align with field and spin of other H^b may align against the field. So, total four combinations of spin of H^b are possible out of which two are equivalent:



Due to these three different combinations of spin of H^b , the NMR signal of H^a will be split into three peaks, (called triplet). The height of these three peaks is in the ratio 1 : 2 : 1. (Fig. 1.29).

Example of 1, 1-dichloroethane : 1, 1-dichloro ethane contains 4 H-atoms ; three H^b atoms and one H^a atom :



The effective magnetic field of H^b atoms will depend upon whether the spin of H^a is aligned with or against the external magnetic field. So, H^b atoms will give NMR spectrum at two different values of external applied magnetic field. Hence, H^b will show two peaks (doublet) (Fig. 1.30).

Similarly, the effective magnetic field of H^a will depend upon the spin of H^b atoms. The different possibilities of spin of H^b are :

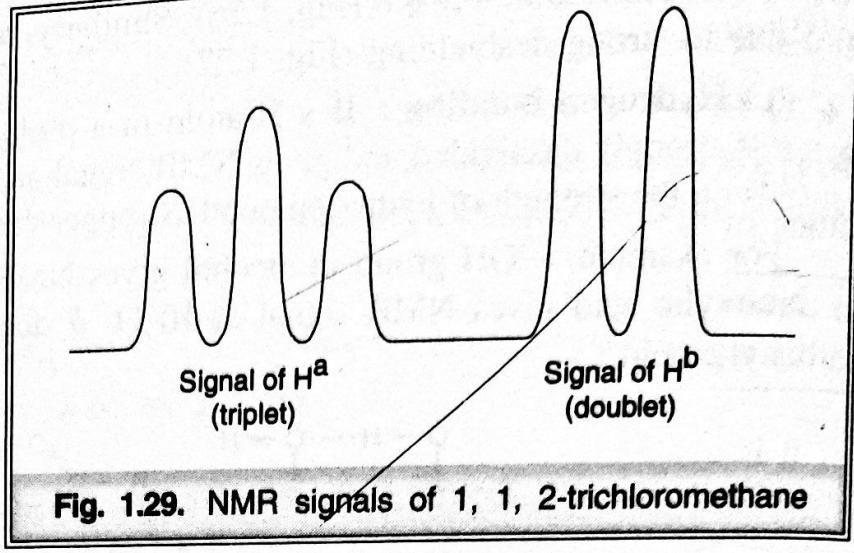
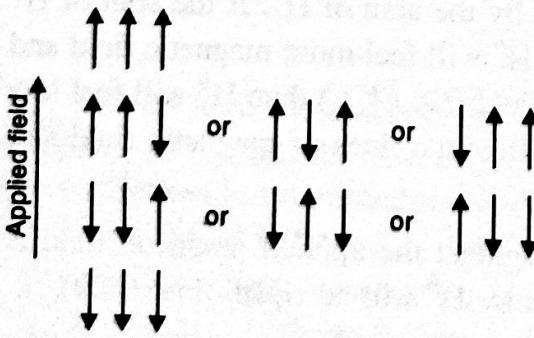


Fig. 1.29. NMR signals of 1, 1, 2-trichloromethane

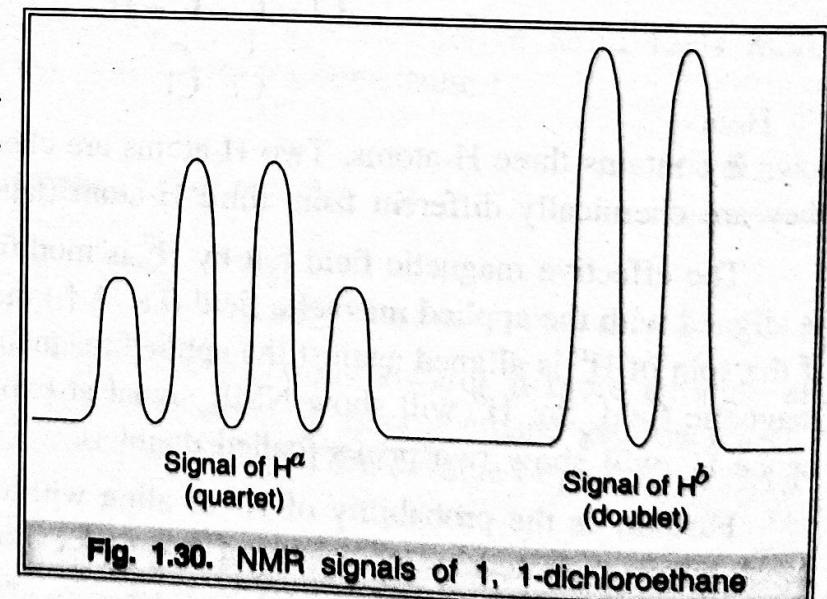


Fig. 1.30. NMR signals of 1, 1-dichloroethane

So, total four different combinations of spin of H^b atoms are possible. Thus, H^a will give four NMR signals (called quartet). The height of those four peaks is in the ratio 1 : 3 : 3 : 1 (Fig. 1.30).

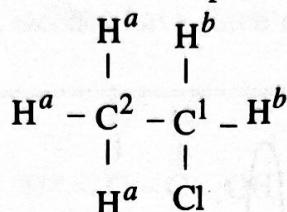
The intensity (height) of H^b signal is more than that of H^a as in 1, 1-dichloroethane, there are 3 H-atoms of 'b' type and only one H-atom of 'a' type.

(n + 1) RULE:

The NMR signals of different compounds get split as doublet, triplet, quartet etc. The splitting of a NMR signal can be found using the following general rule :

Number of signals shown = Number of H-atoms on the
by a proton (H-atom) neighbouring carbon atom +1

It is also called $(n + 1)$ rule. Let us explain it with the example of chloroethane:



For H^a - atoms, the neighbouring carbon atom is C^1 and for H^b -atoms, the neighbouring carbon atom is C^2 .

For H^a

Number of signals shown by H_a = Number of H-atoms on neighbouring carbon atom i.e. C¹
 $= 2 + 1 = 3$ peaks (i.e. triplet) +1

For H^b

$$\begin{aligned} \text{Number of signals shown by } H_b &= \text{Number of H-atoms on neighbouring} \\ &\quad \text{carbon atom i.e. } C^2 \\ &= 3 + 1 = 4 \text{ peaks (i.e. quartet)} \end{aligned}$$

Hence, in NMR spectrum of chloroethane, a triplet is shown by H^a and a quartet is shown by H^b (Fig. 1.31).

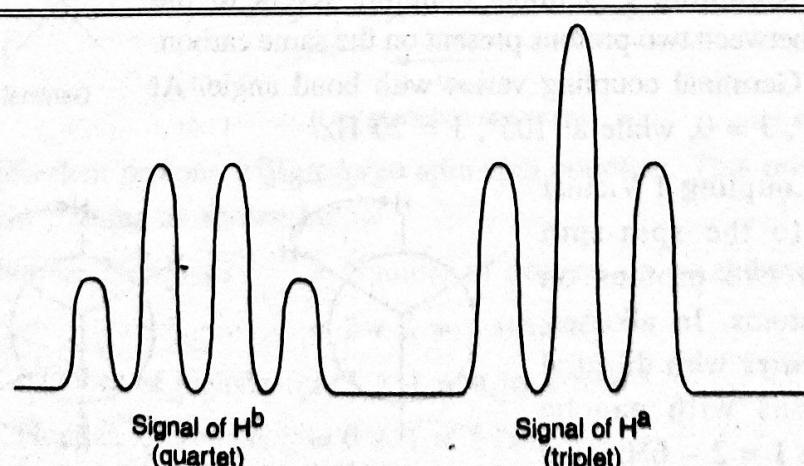


Fig. 1.31. NMR signals of chloroethane

The height of different peaks of triplet, quartet etc. can be found using the Pascal's triangle:

		1		
	1	1		
1		2	1	
	1	3	3	1
1	4	6	4	1
1	5	10	10	5
				1

Pascal's triangle

Signal	Ratio of heights
Singlet	-
doublet	1 : 1
triplet	1 : 2 : 1
quartet	1 : 3 : 3 : 1
quintet	1 : 4 : 6 : 4 : 1
hextet	1 : 5 : 10 : 10 : 5 : 1

1.14.9. Coupling Constant

The distance between two adjacent peaks of a multiplet is called coupling constant.

Coupling constant is denoted by symbol 'J' and measured in the units of cycles per second or Hertz (Hz). Coupling constant does not depend on the applied magnetic field. The magnitude of coupling constant depends on the structural relationship between the coupled protons. The coupling constant for a triple and quartet is shown in Fig. 1.32.

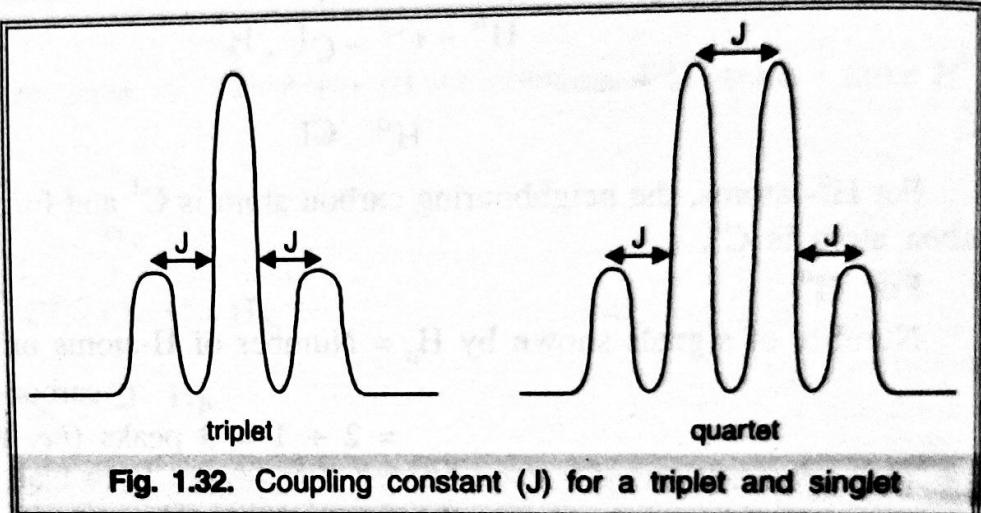
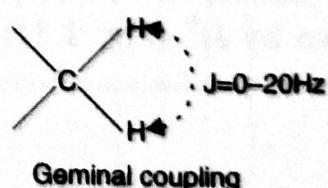


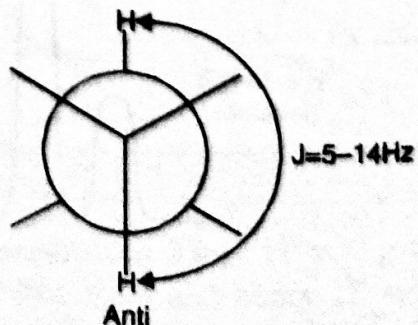
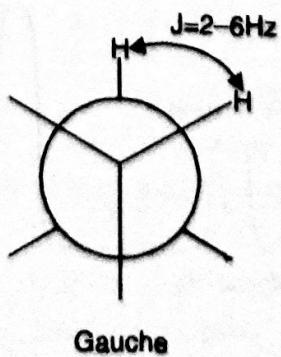
Fig. 1.32. Coupling constant (J) for a triplet and singlet

Depending upon nature and geometry of compound the following types of spin-spin coupling is observed between the protons :

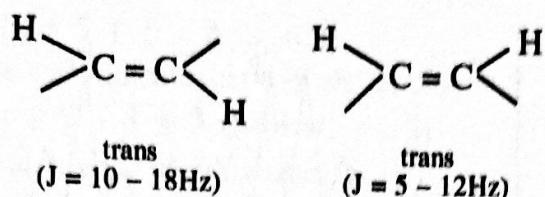
(a) **Geminal Coupling** : Geminal coupling refers to the spin-spin coupling between two protons present on the same carbon. The magnitude of Germinal coupling varies with bond angle. At bond angle of 125° , $J = 0$, while at 105° , $J = 20$ Hz.



(b) **Vicinal Coupling** : Vicinal coupling refers to the spin-spin coupling between two protons on adjacent carbon atoms. In alkanes, vicinal coupling varies with dihedral angle. The protons with gauche conformation have $J = 2 - 6$ Hz, and protons with anti conformation have $J = 5 - 14$ Hz.



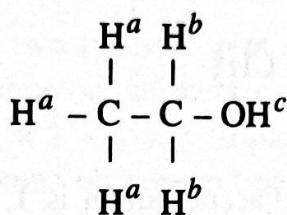
In alkenes, the trans isomer has $J = 10\text{--}18 \text{ Hz}$, whereas cis isomer has $J = 5\text{--}12 \text{ Hz}$.



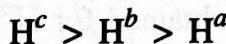
1.14.10 NMR spectrum of some Compounds

The NMR spectrum of some compounds is being discussed here for better understanding of concepts :

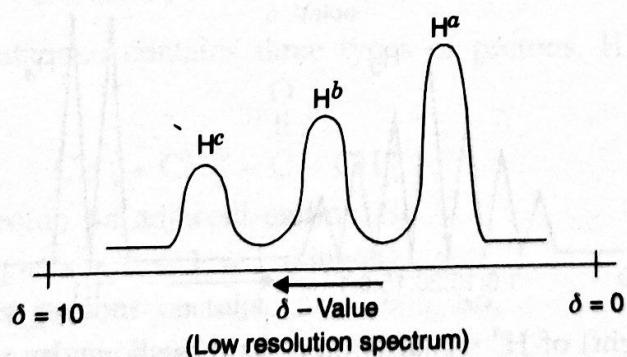
1. Ethyl alcohol : Ethyl alcohol have three different types of protons labelled as H^a , H^b , H^c .



The NMR signal for H^c will be obtained at highest δ -value as H^c is directly attached to electronegative oxygen. The signal for H^a will be at lowest δ -value as it is not near to oxygen and signal for H^b will be at intermediate δ -value. So, the order of δ -value for different protons is :



These three non-equivalent protons will give three peaks in the low resolution spectra as shown below :



The non-equivalent protons will undergo spin-spin coupling. This results in splitting of signals of different protons as shown below :

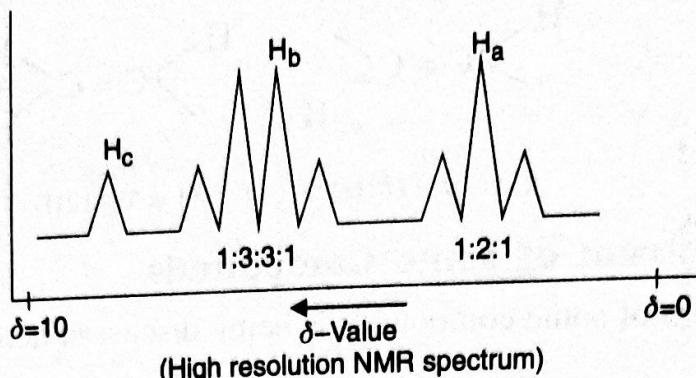
$$\begin{array}{ll} \text{For } \text{H}^a : \text{Number of signals} & = \text{Number of protons on neighbouring carbon} + 1 \\ & = 2 + 1 = 3 \text{ (triplet)} \end{array}$$

$$\text{For } \text{H}^b : \text{Number of signals} = 3 + 1 = 4 \text{ (quartet)}$$

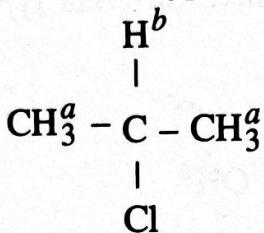
$$\text{For } \text{H}^c : \text{Number of signals} = 0 + 1 = 1 \text{ (singlet)}$$

The four peaks in quartet of H^b are in the ratio $1 : 3 : 3 : 1$ and three peaks in triplet of H^a are in the ratio $1 : 2 : 1$.

This splitting of signals obtained in high resolution spectrum is shown below :



2. 2-Chloropropane : It has two types of protons i.e. H^a and H^b



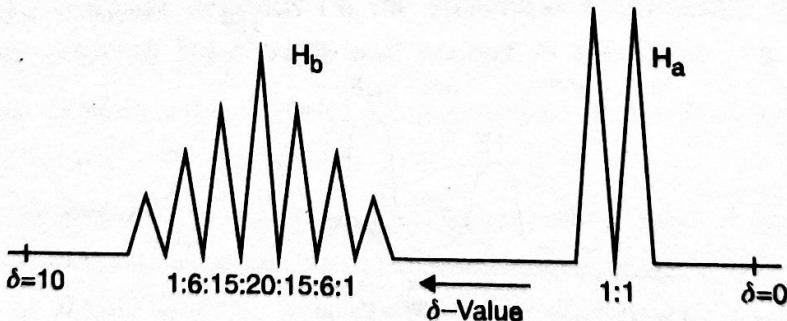
For H^a, the number of protons on adjacent carbon is 1, so applying (n + 1) rule :

For H^a, Number of signals = 1 + 1 = 2 (doublet)

Similarly, For H^b number of protons present on adjacent carbon are 6 (3 on each carbon), So,

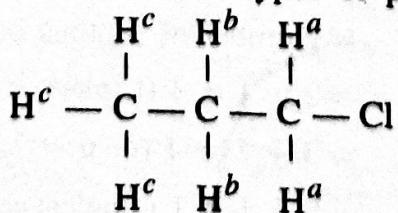
For H^b, Number of signals = 6 + 1 = 7 (septet)

So, in 2-chloropropane, a doublet will be obtained for H^a and septet for H^b. The ratio of height of peaks of septet is 1 : 6 : 15 : 20 : 15 : 6 : 1 and for doublet it is 1 : 1. The δ-value of H^b is more than H^a.



The intensity (height) of H^a signal is more as it is shown by six H^a- atoms whereas H^b signal is shown by one H^b- atom.

3. 1-Chloropropane : It contains three types of protons i.e. H^a, H^b, H^c



For H^a, number of protons on adjacent carbon are two, So

For H^a, Number of signals = 2 + 1 = 3 (triplet)

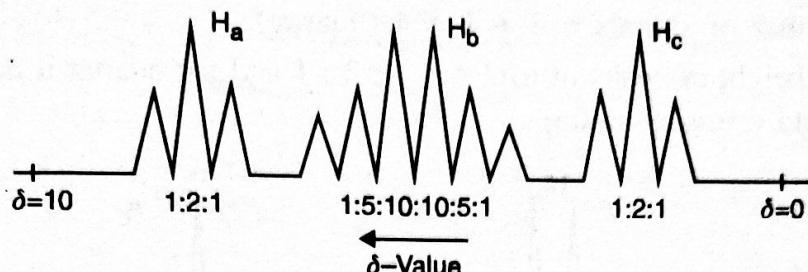
For H^b , number of protons on the adjacent carbons are 5 (2 on one carbon and 3 on other carbon), So,

For H^b Number of signals = $5 + 1 = 6$ (sextet)

For H^c , number of protons on adjacent carbon are 2, So

For H^c , Number of signals = $2 + 1 = 3$ (triplet)

The signal for H^a will be at highest δ (downfield).



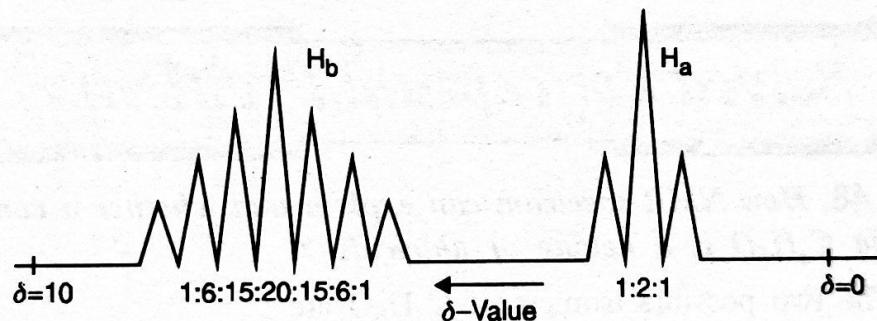
4. Propane : Propane has two types of protons H^a and H^b $CH_3^a - CH_2^b - CH_3^a$

For H^a , the number of protons on adjacent carbon are 2, So

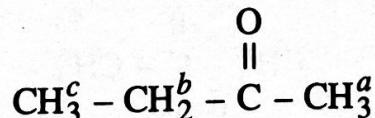
For H^a , Number of signals = $2 + 1 = 3$ (triplet)

For H^b , the number of protons on adjacent carbons are 6 (3 on each carbon), So,

For H^b , Number of signals = $6 + 1 = 7$ (septet)



5. 2-Butanone : 2-Butanone contains three types of protons, H^a , H^b , H^c



For H^a , there is no proton on adjacent carbon, So

For H^a , Number of signals = $0 + 1 = 1$ (singlet)

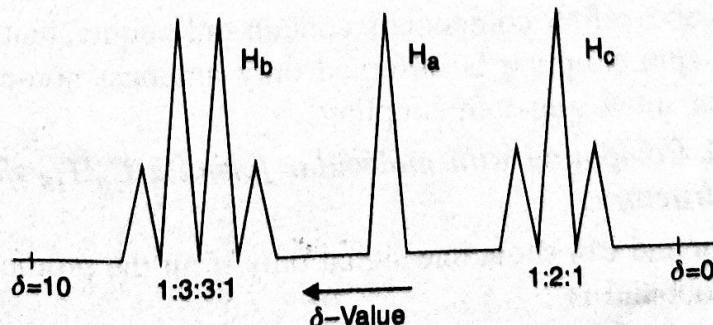
For H^b , there are three protons on adjacent carbon, So,

For H^b , Number of signals = $3 + 1 = 4$ (quartet)

For H^c , there are two protons on adjacent carbon, So,

For H^c , Number of signals = $2 + 1 = 3$ (triplet)

The order of δ -value is $H^b > H^a > H^c$



6. Diethyl ether : In diethyl ether there are two types of protons, i.e. H^a and H^b

$$CH_3^a - CH_2^b - O - CH_2^b - CH_3^a$$

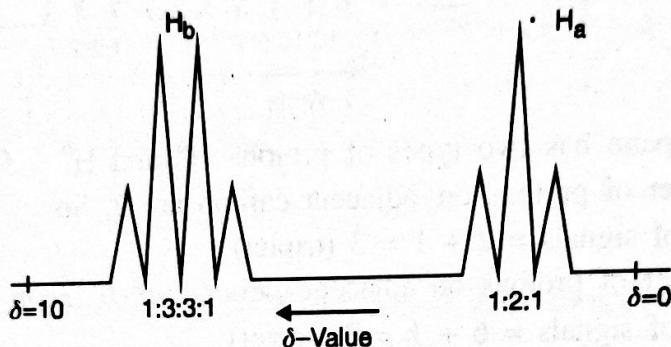
For H^a , there are two protons on the adjacent carbon, So,

For H^a Number of signals = $2 + 1 = 3$ (triplet)

For H^b , there are three protons on the adjacent carbon, So,

For H^b Number of signals = $3 + 1 = 4$ (quartet)

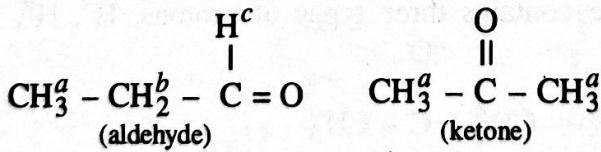
The ratio of height of peaks of triplet is $1 : 2 : 1$ and for quartet it is $1 : 3 : 3 : 1$. Signal for H^b is downfield (more δ -value)



Solved Conceptual Problems

Example 1.46. How NMR spectrum can explain that whether a compound having molecular formula C_3H_6O is a ketone or aldehyde ?

Solution. The two possible isomers of C_3H_6O are :

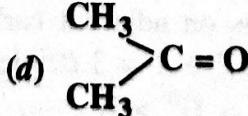
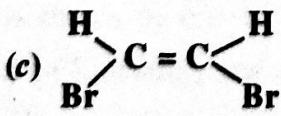


The aldehyde will show 3 NMR signals whereas ketone will show only one NMR signal.

Example 1.47. Which of the following compounds will show spin-spin coupling ?

(a) $ClCH_2CH_2Cl$

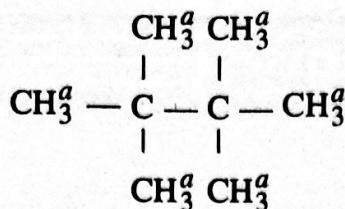
(b) $CH_3 - C(Cl_2) - CH_3$



Solution. All the above four compounds contain only equivalent protons i.e. one type of protons. As the spin-spin coupling is observed only amongst non-equivalent protons, so above compounds do not show spin-spin coupling.

Example 1.48. A Compound with molecular formula C_8H_{18} shows only one signal in NMR. Predict its structure.

Solution. A compound can show one signal only if all the protons in it are equivalent. So the structure of compound is :



Example 1.49. How will you verify that a particular signal in NMR spectrum arises from – OH, – NH or – SH groups ? (P.T.U., Dec. 2006, 2007)

Solution. H-atom attached with more electronegative element experiences more deshielding. So H-atom in – OH group will have more deshielding as electronegativity of O is more than that of N and S. The δ -value is in the order : – OH > – NH > – SH

Example 1.50. How many NMR signals are observed in spectrum of following compounds

- (a) $\text{CH}_3\text{COOCH}_3$ (b) CH_3OCH_3 (c) $\text{CH}_3\text{CH}_2\text{CH}_3$

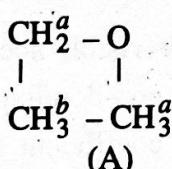
(P.T.U., Dec. 2005)



- Solution.** (a) $\text{CH}_3^a - \text{C} - \text{OCH}_3^b$ 2 signals
 (b) $\text{CH}_3^a - \text{O} - \text{CH}_3^a$ 1 signal
 (c) $\text{CH}_3^a - \text{CH}_2^b - \text{CH}_3^a$ 2 signals

Example 1.51. How many NMR signals are shown by following compound ‘A’ ?

Solution. This compound contains two types of protons, so two signals will be shown by it in its NMR spectrum.



Example 1.52. What type of nuclei can show NMR spectrum ? (P.T.U., May, 2005)

Solution. The nuclei having spin quantum number I greater than zero exhibit NMR spectrum. For example ^1H , ^2H , ^{13}C , ^{15}N , ^{19}F , ^{31}P

Example 1.53. What type of solvents can be used in NMR spectroscopy ?

Solution. The solvents which are free of protons can be used in NMR spectrum because these solvents can not show NMR absorption. Commonly used solvents in NMR are carbon tetra chloride (CCl_4), carbon disulphide (CS_2), deutero-chloroform (CDCl_3), hexachloroacetone (Cl_3COCl_3)).

Example 1.54. How NMR spectroscopy can distinguish between cis and trans isomers of a compound ?

Solution. The coupling constant (J) of trans isomer is more than that of cis isomer

