

(ii) For nuclei in which the sum of protons and neutrons is even but number of protons and neutrons is odd, $I = 1, 2, 3$.

For example, $I = 1$ for 2_1D and ${}^{14}_7N$.

(iii) For nuclei in which sum of protons and neutrons is odd, I is always odd integral multiple of $\frac{1}{2}$ i.e. $I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ etc.

For example, $I = \frac{1}{2}$ for 1_1H and ${}^{19}_9F$, $I = \frac{3}{2}$ for ${}^{23}_{11}Na$ and $I = \frac{5}{2}$ for ${}^{35}_{17}Cl$.

(In this case number of protons can be even and number of neutrons can be odd or vice-versa)

The above discussion can be summarised in a Table 1.2.

Table 1.2: Nuclear constitution and the Nuclear Spin Quantum Number

Number of protons	Number of neutrons	I
Even	Even	0 (e.g. ${}^2_2He^4, {}^6_6C^{12}$)
Odd	Odd	integer (1, 2, 3... e.g. ${}^7_7N^{14}, {}^5_5B^{10}$)
Even	Odd	half integer ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$, e.g. ${}^6_6C^{13}$)
Odd	Even	half integer ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$, e.g. ${}^1_1H^1, {}^9_9F^{19}$)

Spinning of various particles in the nucleus leads to net spinning of the nucleus about an axis. Now the nucleus is a charged particle. When this charged particle spins about its axis (when $I \neq 0$ i.e. $I > 0$), it acts as a small magnet (nuclear magnet) and hence must have some magnetic moment.

1.13 PRECESSIONAL MOTION

To understand precessional motion of nucleus, let's take the example of a top. Spinning top shows the precessional motion. If we see the spinning top carefully it can be observed that top shows spinning around its axis and simultaneous **rotation around the vertical axis**. This vertical axis is actually of earth's gravitational field. This motion is called precessional motion and the top is said to be precessing around the vertical axis of earth's gravitational field. This results because of interaction between spin and earth's gravity acting vertically downwards. It is called gyroscopic motion. Now let's consider a magnetic nucleus ($I > 0$) e.g. proton (nucleus of H atom), spinning in an externally applied magnetic field. It can be observed that proton precesses about the axis of external magnetic field in the same manner in which a spinning top precesses under the influence of gravity.

It is known that

$$w = \gamma H_0$$

w = angular precessional frequency

H_0 = applied field in gauss

$$\gamma = \text{gyroscopic ratio} = \frac{2\pi\mu}{hI}$$

μ = magnetic moment of spin

I = spin of quantum number of spinning magnet

h = Planck constant

As

$$w = 2\pi\nu$$

So,

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

ν = precessional frequency which may be defined as number of revolutions per second made by magnetic moment vector of the nucleus around the external field H_0 .

Or It may be defined as equal to the frequency of electromagnetic radiation in megacycles/sec. necessary to induce a transition in nucleus from one spin state to another.

The discussion so far has resulted that NMR spectroscopy is shown by magnetically

active nucleus i.e. If $I = 1, 2, 3, \dots$ or If $I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ etc. For nuclei, $I = 0$, NMR

spectroscopy is not observed because these are non-magnetic nuclei i.e. nuclei having only charge (positive) but no spin. So magnetically active nuclei are those nuclei which

have charge as well as spin i.e. either $I = 1, 2, 3$ or $I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ etc.

There may be many magnetically active nuclei but for the sake of simplicity, we will be discussing nucleus of H atom, called proton to understand the concept of NMR.

1.14 BASIC PRINCIPLE OF NMR AND INSTRUMENTATION

1.14.1 Basic Principle

If a proton is placed in a magnetic field, then it starts precessing (at a certain frequency) [Frequencies of nuclei at the fields normally applied, lie in radio frequency region of the electromagnetic spectrum. So, NMR is a radio frequency technique e.g. at 12T, protons show frequency about 500 MHz (radio frequency)]

It is capable of taking up one of the two orientation w.r.t. axis of external magnetic field.

(i) alignment with the field and (ii) alignment against the field.

(i) means magnetic field of proton aligns with applied magnetic field.

(ii) means magnetic field of proton aligns against the applied magnetic field.

The first state is of lower energy and second state is of higher energy.

If the proton is in lower state, it can pass to the higher state by absorbing energy, from the source of **radiowaves** ($3 \times 10^6 - 3 \times 10^{10}$ Hz).

From the **higher energy state**, the proton can come down to lower energy state by releasing energy. The transition from one energy state to other is called **flipping of proton**.

This transition (from lower energy state to higher energy state) can be brought about by the absorption of a quantum of electromagnetic radiation in the radiowave region with energy $h\nu$.

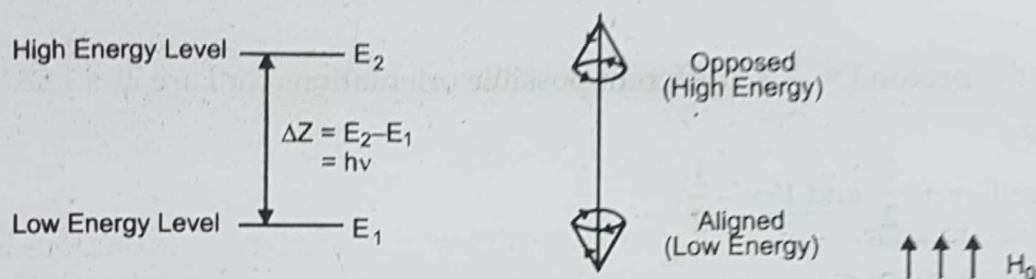


Fig. 1.28 Energy level of proton (more details of Fig. 1.28 are given in fig. 1.29)

The energy (ΔE) required for the flipping of proton depends on strength of **external field**. Stronger the field, greater the tendency of proton to remain aligned with it and higher will be frequency or energy of radiation required to flip the proton to higher energy. (The precessional frequency of the proton is directly proportional to strength of external magnetic field)

Nuclear spin is the characteristic of nucleus and is represented by spin quantum no. of the nucleus i.e. I. For a given magnetic nucleus, there are $(2I + 1)$ orientations possible in the presence of externally applied magnetic field, which are represented by I'.

As nucleus behaves as a magnet, its magnetic moment μ can be represented as

$$\mu = g_n \mu_n I'$$

or

$$\mu = K I'$$

where

$$K = g_n \mu_n$$

as

g_n = Lande splitting factor and

μ_n = nuclear magnetic factor

I' can have $(2I + 1)$, orientations or values because for a given value of I, I' can have values from I to $-I$ i.e. total $2I + 1$ values. This means that keeping H_0 constant a nucleus with a spin (I) has $2I + 1$ energy levels in presence of external magnetic field.

In the absence of the external magnetic field, all these orientations have same energy. But when a magnetic field of strength H is applied, each orientation corresponds to different value of energy E.

$$E = -\mu H_0$$

where μ is magnetic moment of the nucleus

$$E = -g_n \mu_n I' H_0$$

$$E = -KI' H_0$$

When $I = 0$, $I' = 0$, hence $E = 0$ and $2I + 1 = 1$

This means that nuclei with 0 spin, show no splitting in magnetic field, means one energy level. Hence no flipping of spin is possible.

When $I = \frac{3}{2}$, then values of $I' = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ ($2I + 1 = 2 \times \frac{3}{2} + 1 = 4$) Orientations

\Rightarrow hence for energy levels of energies $-\frac{3}{2} KH_0, -\frac{1}{2} KH_0, \frac{1}{2} KH_0, \frac{3}{2} KH_0$.

For the proton $I = \frac{1}{2}$ so different possible orientations for I are $2I + 1$ i.e. $2 \times \frac{1}{2} + 1 = 2$

these are $I' = +\frac{1}{2}$ and $I' = -\frac{1}{2}$.

Energy for state $I' = +\frac{1}{2}$, $E_1 = -\frac{1}{2} KH_0$.

and

Energy for state, $I' = -\frac{1}{2}$,

$$E_2 = \frac{1}{2} KH_0$$

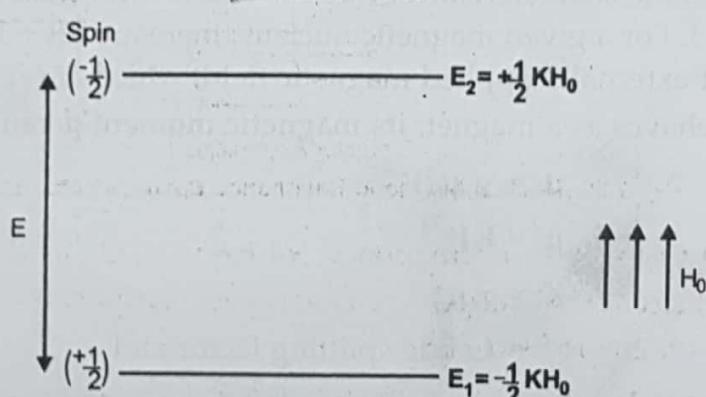


Fig. 1.29 Lower and higher energy levels of the proton along with corresponding Spin of nucleus and energy of the states in presence of external magnetic field H_0

$$\Delta E = E_2 - E_1$$

i.e.

$$= \frac{1}{2} KH_0 - \left(-\frac{1}{2} KH_0 \right)$$

$$\Delta E = \pm KH_0$$

Now we know that $\Delta E = h\nu$

$$h\nu = \pm KH_0$$

$$\nu = \frac{\pm KH_0}{h}$$

$$= \pm \frac{KH_0}{h}; K \text{ is constant} = g_n \mu_n$$

here ν is precessional frequency of nucleus.

1.14.2 Instrumentation

A sample under investigation is taken in a glass tube placed between two magnets. A radiofrequency radiation (60 MHz) is made to fall on the sample. It can be done by feeding energy into coil wound around the sample. The spectrophotometer can work in either two ways.

- (i) Keeping magnetic field constant and radiofrequency may be varied gradually.
- (ii) Keeping radiofrequency constant and varying the magnetic field.

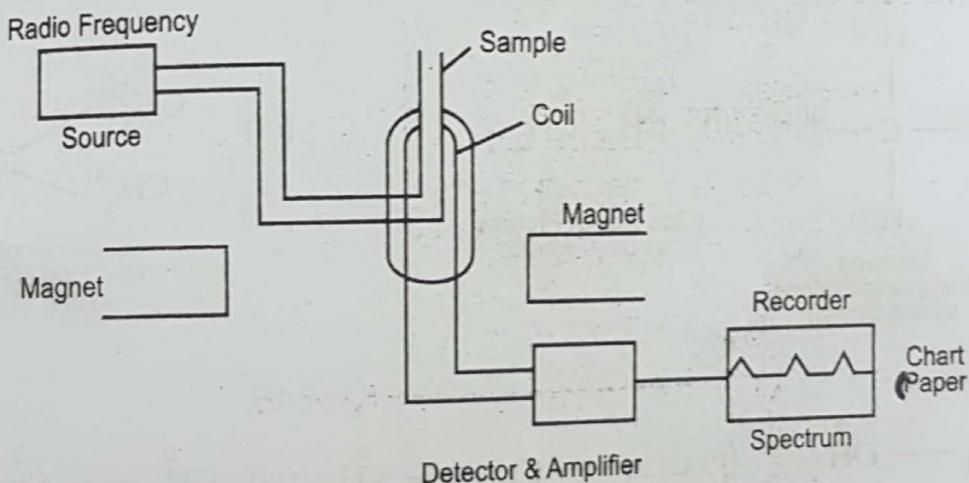


Fig. 1.30 Nuclear Magnetic Resonance Spectrophotometer.

For practical purposes, radiofrequency source is held steady at a said frequency (60 MHz) and field strength is varied (Two energy levels appear for the proton when it is placed in external magnetic field H_0).

Permanent magnets are not preferred in NMR. But temporary magnets are used, because it is easy to change the field strength of a temporary magnet.

As the field strength increases, the precessional frequency of each set of protons increases. Now the precessing proton will absorb energy from the radiofrequency source only if the precessing frequency is the same as frequency of radiofrequency beam i.e. when quantum energy $h\nu$ of electromagnetic radiation is equal to the energy difference between two energy states at the field strength H_0 when this occurs nucleus and radiofrequency beam are said to be in resonance. Hence the technique is known as nuclear magnetic resonance. (In simple words, condition of strong effective coupling when the frequencies of two oscillators are identical is called Resonance).

Absorption of energy results into signal. Such spectrum is called nuclear magnetic resonance spectrum.

A precessional frequency of the other sets of protons is different from the frequency of the radiofrequency source. Magnetic field is increased further and at resonance other sets of protons also show signal at different values of H_0 . Hence signals for other sets of protons are also obtained on the spectrum.

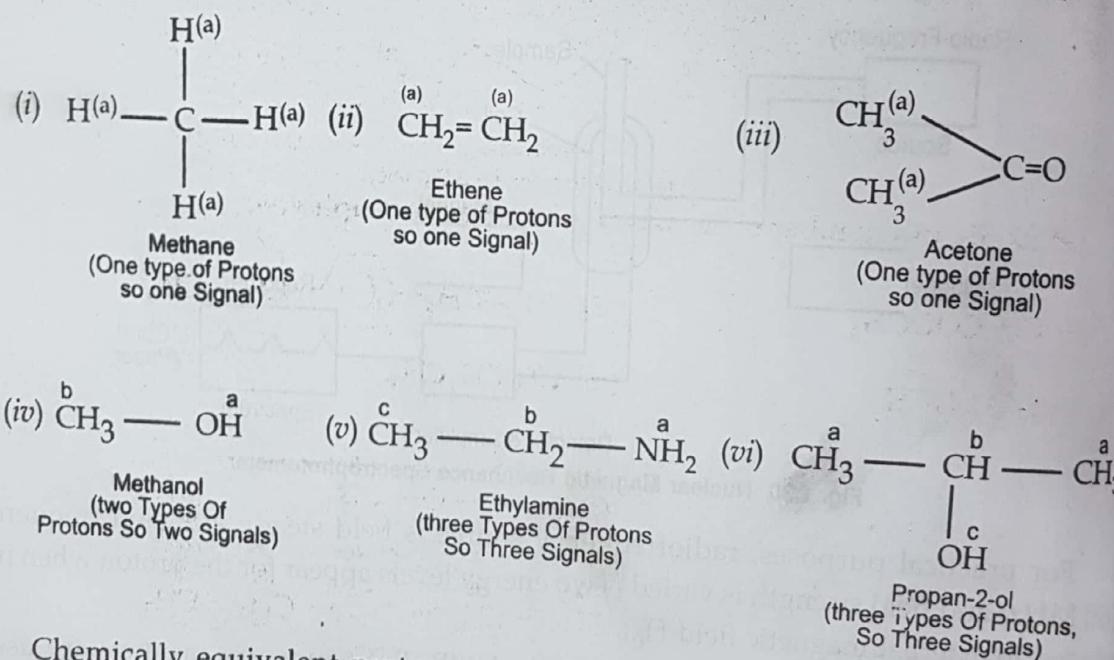
1.15 NUMBER OF SIGNALS

Each signal in NMR spectrum corresponds to set of equivalent protons.

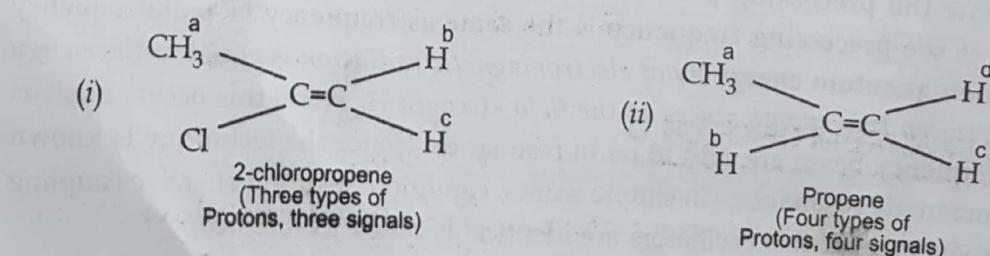
A set of protons with the same environment are said to be **equivalent protons**.

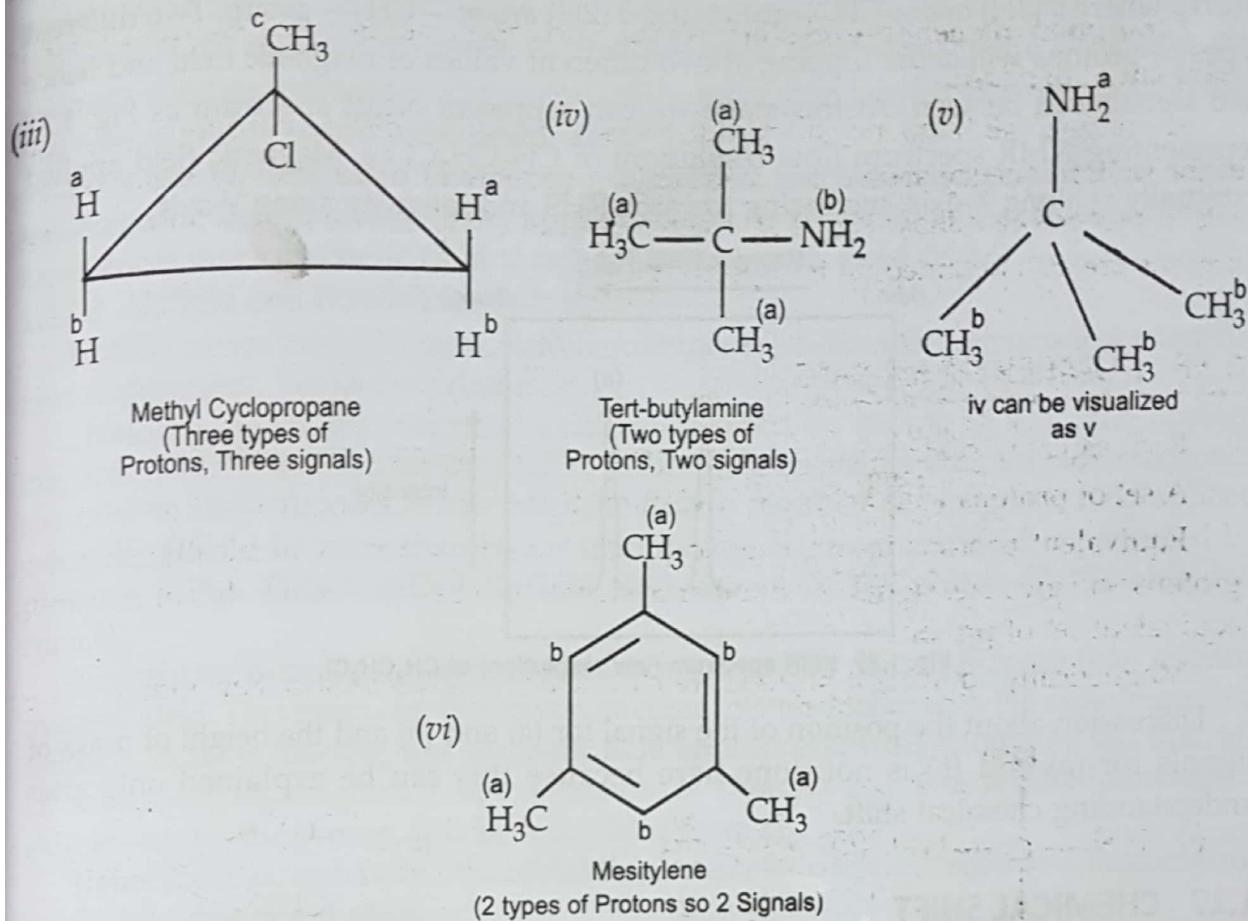
Equivalent protons means chemically equivalent protons. Chemically equivalent protons will give one signal. So, number of signals will be equal to number of chemically equivalent set of protons.

Magnetically equivalent protons are chemically equivalent also. Few examples are

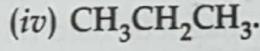
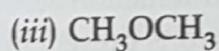
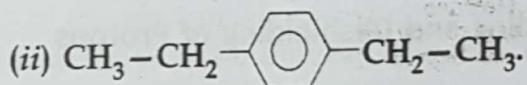
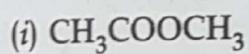


Chemically equivalent protons must also be stereochemically equivalent i.e. a particular set of protons are chemically equivalent only if they remain exactly in similar environment when the stereochemical formulae of the molecule under consideration is written.

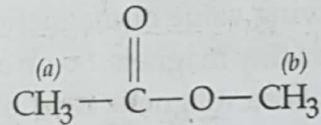




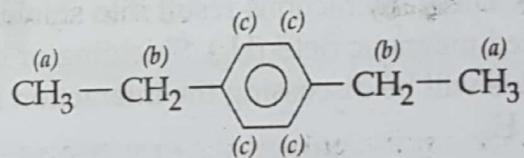
Let us discuss number of signals in some more examples :-



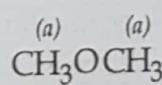
(i) Two signals



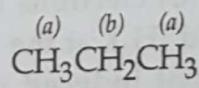
(ii) Three signals



(iii) One signal



(iv) Two signals



1.16 NMR SPECTRUM OF $\text{CH}_3\text{CH}_2\text{Cl}$

In $\text{CH}_3\text{CH}_2\text{Cl}$ two types of protons are present. These are represented as *a* (3H) and

b (2H), where a (3H) are of CH_3 -group and b (2H) are of $-\text{CH}_2-$ group. Two different types of protons will show flipping at two different values of magnetic field and hence two signals can be seen. At this stage we can represent NMR spectrum as Fig. 1.31 representing NMR spectrum (low resolution) of $\text{CH}_3\text{CH}_2\text{Cl}$ i.e. Magnetic field applied externally is along X-axis, increasing towards RHS and intensity along Y-axis.

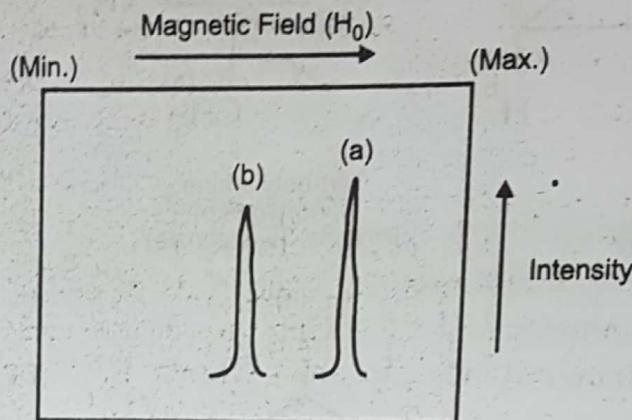


Fig. 1.31 NMR spectrum (low resolution) of $\text{CH}_3\text{CH}_2\text{Cl}$

Discussion about the position of the signal for (a) and (b) and the height of peaks of signals for (a) and (b) is not done here because this can be explained only after understanding chemical shift.

1.17 CHEMICAL SHIFT

1.17.1 Shielding and Deshielding of Protons

When the sample molecule is placed in the magnetic field, there is interaction between the magnetic nuclei and external magnetic field (H_0). But the (σ) electrons present in the sample molecule are also having value of magnetic moment i.e. electrons have spin and charge so these also behave as tiny magnets. So on applying magnetic field to the sample, there will be interaction between magnetic field of (σ) electrons and external magnetic field (H_0) also. These interactions result into shielding or deshielding of the nuclei from external applied magnetic field (H_0). Shielding or deshielding result into chemical shift. In this topic, we will be discussing the interaction between magnetic field induced by σ electrons and H_0 .

1.17.2 Explanation

In the sample molecule, sigma (σ) electrons rotate around the nuclei. When it is placed in the external magnetic field (H_0), at the proton secondary/induced magnetic field is produced in such a way, that induced magnetic field opposes the applied magnetic field. Thus net magnetic field experienced by proton (nucleus) is diminished. Hence proton is said to be shielded. That means more the electron density around the nucleus, more is shielding of nucleus from external magnetic field (H_0).

But, the rotation of electrons around the neighbouring nuclei generates a magnetic field (Induced Magnetic field) that can either oppose or align with applied field at

proton. If the induced magnetic field opposes the applied field, then proton is said to be shielded. If the induced magnetic field aligns with applied magnetic field, then net magnetic field experienced by the proton will be more than applied magnetic field. Hence this type of proton is said to be deshielded.

So it can be concluded from above discussion that shielded proton experiences less magnetic field than externally applied magnetic field (H_0) and deshielded proton experiences more magnetic field than applied magnetic field (H_0).

1.17.3 Upfield and Downfield Shift

Upfield means more magnetic field requirement and downfield means less magnetic field requirement. Let us now discuss it.

Shielding means net magnetic field experienced by proton is less than applied magnetic field. That means for the proton, to come into resonance with the radiofrequency source or to show flipping, more magnetic field is required i.e., magnetic field applied externally should be more than H_0 (as on applying H_0 , magnetic field experienced by proton is $< H_0$). This is called **Upfield shift shown by the proton if it is shielded from H_0** .

Deshielding means net magnetic field experienced by proton is more than applied magnetic field. That means for the proton, to come into resonance with the radiofrequency source or to show flipping, less magnetic field applied externally should be less than H_0 (as on applying H_0 , magnetic field experienced by proton $> H_0$). This is called **downfield shift shown by the proton, if it is deshielded from H_0** .

Hence it can be concluded that shielding results into upfield shift and deshielding results into downfield shift.

The shift (up field or down field) in the magnetic field (required to cause flipping) caused by the induced magnetic field of the electrons is called **chemical shift**. All the equivalent protons give NMR signal at same position but the different nonequivalent protons give NMR signal at different positions. The position of NMR signal in spectrum gives information about the type of protons present in a compound i.e. aliphatic protons, aromatic protons, acetylenic protons etc. can be shown in table 1.3.

Chemical shift is represented as δ (delta). After discussing the above concept now we are in the position to discuss NMR spectrum.

1.17.4 NMR Spectrum

It is a graph plotted between chemical shift/magnetic field along X-axis and intensity along Y-axis.

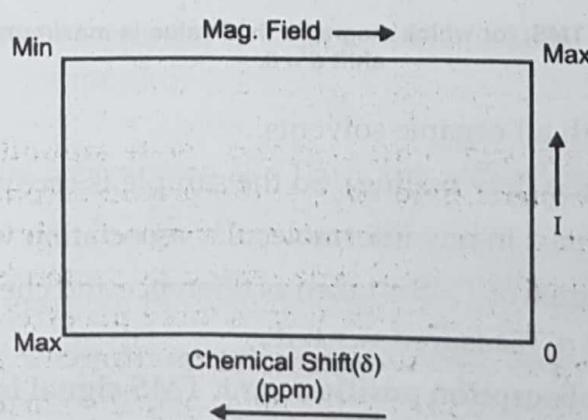
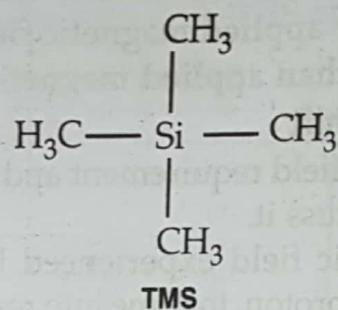


Fig. 1.32 Different scales selected along X and Y-axis in NMR spectrum.

Chemical shift of a particular proton (nucleus) is always w.r.t. standard reference. NMR technique TMS (Tetramethyl silane) is taken as standard reference. To see the chemical shift of a proton in a sample, TMS is added as a reference. This is selected as reference because :



- (i) All the twelve protons are equivalent.
- (ii) Due to low value of electronegativity of Si, the shielding effect is maximum. So maximum value of magnetic field is required to bring the absorption of energy of the proton of TMS.

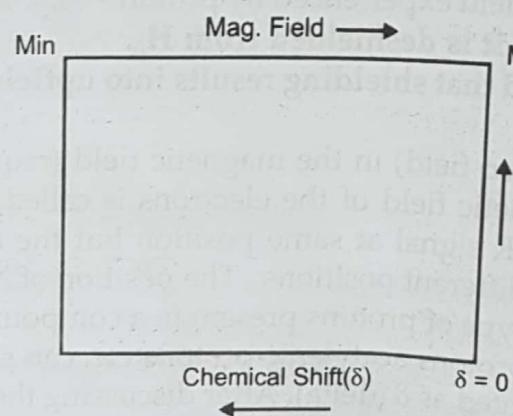


Fig. 1.33

Fig. 1.33 signal for TMS, for which magnetic field value is maximum and chemical shift $\delta = 0$.

- (iii) It is miscible with all organic solvents.
- (iv) It is highly volatile (low boiling). So the sample is recovered easily.
- (v) It does not take part in any intermolecular association with the sample.

That's why the NMR signal of TMS is taken as reference and chemical shift for different set of equivalent protons are measured w.r.t. it.
The difference in the absorption position w.r.t. TMS signal is called chemical shift.

Let us now discuss the NMR of CH_4 (methane). TMS is added to the sample and is placed in spectrophotometer. Its NMR may be represented as shown in Fig. 1.34.

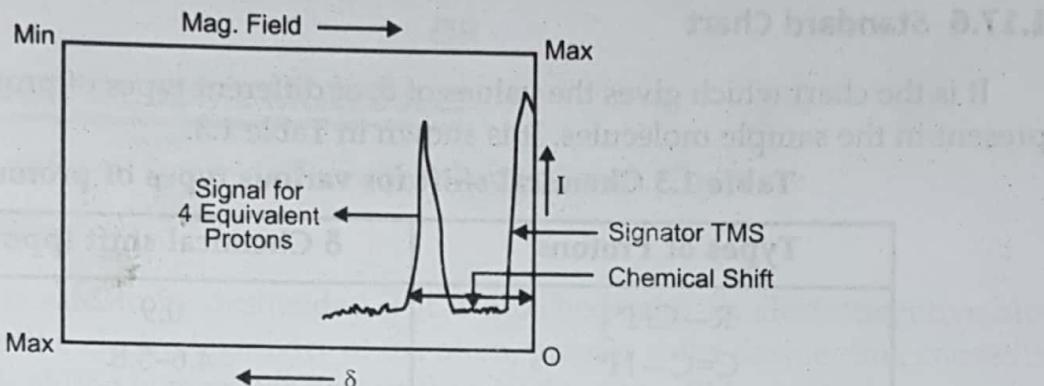


Fig. 1.34 NMR of methane

1.17.5 Chemical Shift

Chemical shift (δ) can be represented as :

$$\delta = \frac{\Delta H}{H_0} \times 10^6$$

ΔH = Magnetic field difference between H sample and H_{reference}

where

H_{sample} = Magnetic field at which sample shows resonance

$H_{\text{reference}}$ = Magnetic field at which reference or standard shows resonance.

H_0 = External magnetic field applied.

As $\nu \propto H_0$ so,

$$\delta = \frac{\Delta v \text{ in Hz or Cps}}{\text{Operating frequency in Mega cycles or MHz}}$$

Units of δ are ppm.

where Δv = difference in frequency in Cps between the absorption frequency of sample and TMS (the reference compound)

For TMS, $\delta = 0$ ppm

Chemical shift can be represented as τ (tau). It is related to δ .

$$\tau = 10 - \delta$$

Let us discuss the example of ethanol $\text{CH}_3\overset{\text{a}}{\text{C}}\text{H}_2\overset{\text{b}}{\text{C}}\text{H}_2\overset{\text{c}}{\text{O}}\text{H}$. In this case, three kinds of protons are present as these are chemically different because of different chemical environment.

Hence there will be three signals (in the NMR spectrum) with three different values of chemical shift/magnetic field.

1.17.6 Standard Chart

It is the chart which gives the values of δ , of different types of protons which may be present in the sample molecules. It is shown in Table 1.3.

Table 1.3 Chemical shift for various types of protons

Types of Protons	δ Chemical shift (ppm)
$R-CH_3^*$	0.9
$C=C-H^*$	4.6-5.8
$C\equiv C-H^*$	2-3.5
$Ar-H^*$	6-9.0
$*H-C-F$	4-4.5
$*H-C-Cl$	3-4
$*H-C-OH$	3.4-4
$*H-C-OR$	3.3-4
$*H-C-COOR$	2-2.2
$*H-C-COOH$	2-2.5
 $\begin{array}{c} O \\ \\ *H-C-R \end{array}$	 9-10
$*H-O-R$	1-5.5
$*H-O-Ar$	4-12
$*H-O-C=C$	15-17
 $\begin{array}{c} O \\ \\ *H-O-C-H \end{array}$	 10.5-12

1.18 SOLVENT USED

The sample to be studied by NMR technique is first dissolved in a solvent. The solvent used should have the following properties :

- (i) A solvent free of protons should be used.
- (ii) It should be capable of dissolving atleast 10% of sample.
- (iii) It should be chemically inert.

Few examples, CCl_4 (Carbon tetrachloride), CS_2 (Carbon disulphide), $CDCl_3$ (deuterochloroform), $Cl_3-C-C-CCl_3$ (hexachloroacetone) etc.

1.19 FACTORS INFLUENCING CHEMICAL SHIFT

OR

CHEMICAL SHIFT OF SOME MOLECULES

There are different factors influencing chemical shift. These are :

(i) Inductive Effect

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

e.g. $\text{CH}_3\text{CH}_2\text{F}$, two signals are expected for this sample molecule. One for (a) 2H and one for (b) 3H protons. Now we are in a position to comment on the value of δ for (a) and (b). As (a) type of protons are more near to $-\text{F}$, an electronegative atom having $-I$ effect. So it will withdraw the e density around (a) type of protons towards itself. Hence (a) will undergo deshielding more as compare to (b) type of protons. The later is more distant from $-\text{F}$. (As we know the inductive effect decreases with increase in distance).

(ii) Anisotropic Effect

Anisotropic effect is resulted from π electrons. As in NMR, nuclei of sample as well as σ electrons, interact with external magnetic field when applied to sample. If the sample has π electrons also, then π electrons being tiny magnets, will also interact with externally applied magnetic field. This results into anisotropic effect so discussed.

The value of δ is aldehydic and aromatic protons are much higher. Alkyne protons appear at relatively low value of δ as compare to alkene. The values in these cases can be justified by explaining the manner in which π electrons circulate under the influence of applied field.

Let us take the example of alkene first.

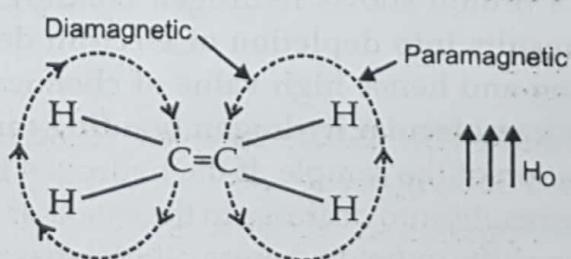
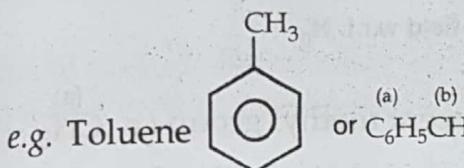


Fig. 1.35 Direction of magnetic field induced by π electrons in the alkene.

When an alkene is placed in the external magnetic field H_0 , molecule orients itself in the space in such a way that its plane is perpendicular to the axis of applied magnetic field (H_0). π electrons induce magnetic field which is diamagnetic around carbon atoms and paramagnetic in the region of alkene protons. The protons will feel greater field

1.20 PEAK AREA AND PROTON COUNTING

Size or area of each peak tells the number of protons responsible for it because for flipping, protons absorb energy. Greater the number of equivalent protons, greater is the amount of energy absorbed for flipping and greater is the area under peak. Squares under each peak are counted and **ratio** between various kinds of protons is found out. The ratio is converted into whole numbers. And these **whole numbers** give us the number of protons representing various signals.



1.21 SPLITTING OF THE SIGNALS

Each signal or peak in an NMR spectrum represents one kind or one set of protons in molecule. It is found that in certain molecules, a single peak or signal (called singlet) is not observed for each set of protons, but instead a group of peaks (called multiplet) are

observed for one set/type of protons. Let us now consider one example of $\text{Cl}_2\text{CH}-\text{CH}_2\text{Cl}$. Whatever we have discussed so far, accordingly the sample has two set of protons *a* (1H) and *b* (2H). Hence two signals or two peaks are expected. But actually the peaks/signals are not singlet but multiplets i.e., for *a* type of protons, a **triplet** is observed and for *b* type of protons, a **doublet** is observed.

Let us take another example of $\text{CH}_3-\text{CH}_2\text{Cl}$. In this case for (*a*) type of protons a triplet is observed and for (*b*) type of protons a **quartet** is observed.

Now we are to study the origin of multiplets for particular kind of protons. The splitting of the signal/peak i.e. appearance of multiplets is due to **spin-spin coupling**/spin-spin interaction. e.g. $\text{CH}_3\text{CH}_2\text{CH}_3$.

1.22 SPIN-SPIN INTERACTION OR SPIN-SPIN COUPLING

Spectra in which spin-spin interactions are considered, are called **high Resolution NMR spectra**.

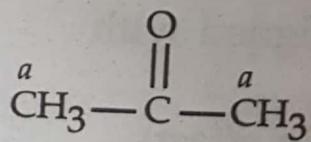
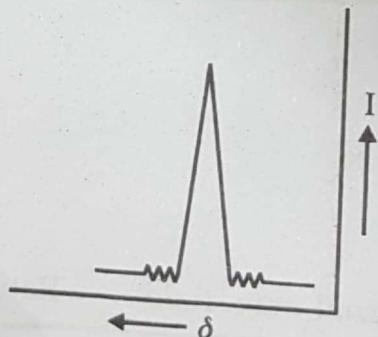
To explain this concept. Let us take the example of $\overset{\text{a}}{\text{CH}_3}\overset{\text{b}}{\text{CH}_2}\text{Cl}$, when this sample molecule is placed in external magnetic field, in presence of radiofrequency source. Then for $-\text{CH}_2-$ group i.e. (*b*) type of proton the possible orientation of induced magnetic field of two protons w.r.t. external magnetic field is represented in Fig. 1.38.

The peak intensities of various multiplets are shown in Table.

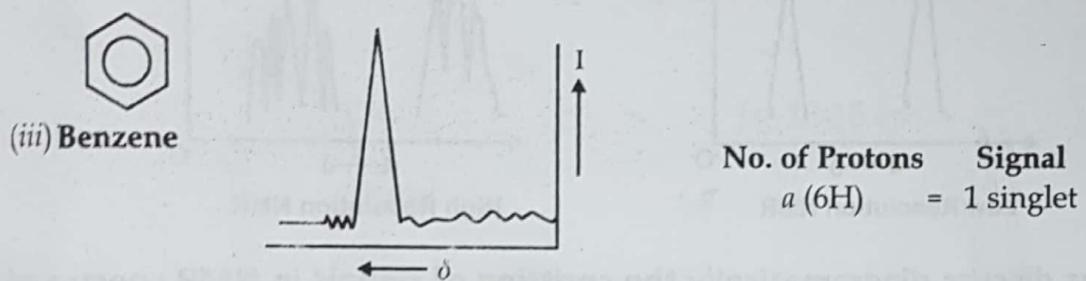
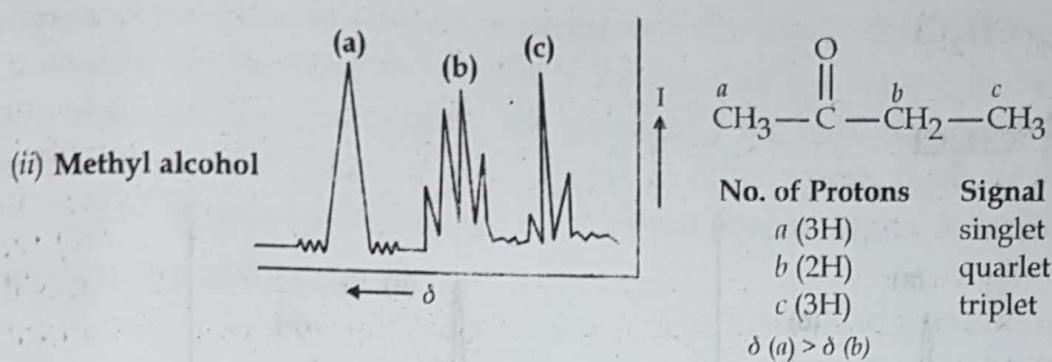
Peak Area Ratio	Kind of Signal
1	Singlet
1 : 1	Doublet
1 : 2 : 1	Triplet
1 : 3 : 3 : 1	Quartet
1 : 4 : 6 : 4 : 1	Quintet
1 : 5 : 10 : 10 : 5 : 1	Sextet

1.22.1 Let us discuss High resolution NMR of few examples :

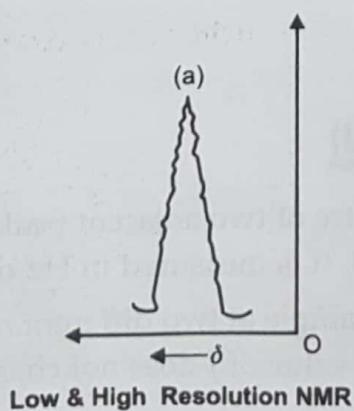
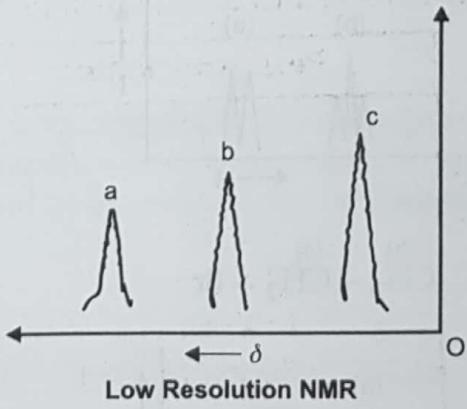
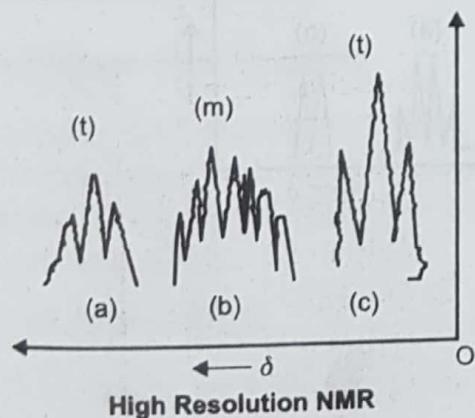
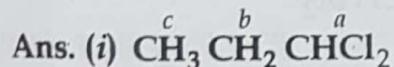
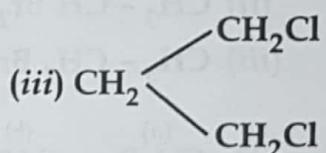
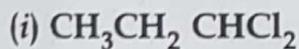
(i) Acetone

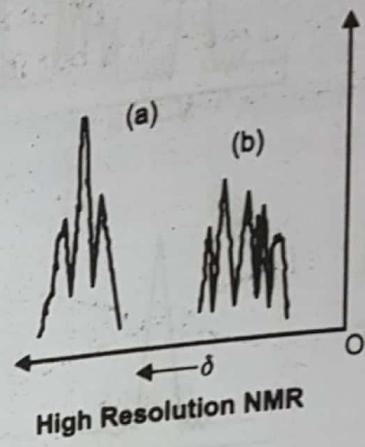
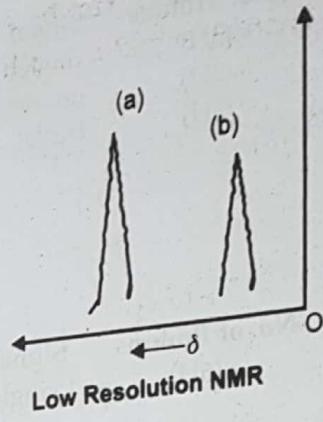
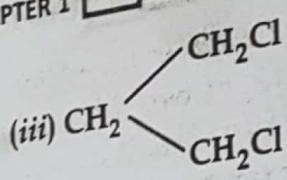


No. of Protons Signal
 α (6H) = singlet

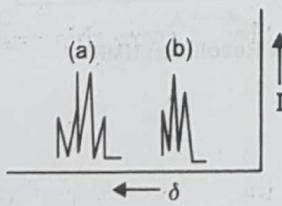
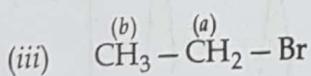
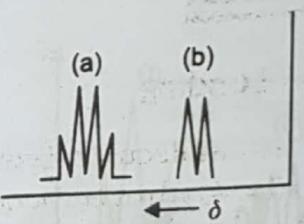
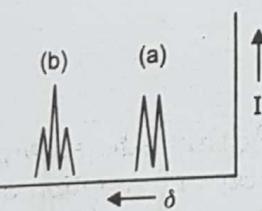
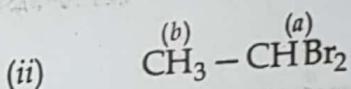
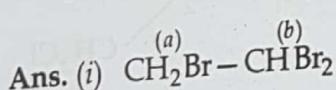
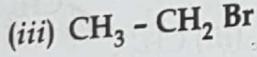
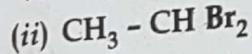
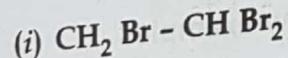


1.22.2 Let us draw low and high resolution NMR of few examples





1.22.3 Let us discuss diagrammatically the splitting of signals in NMR spectra of



1.23 COUPLING CONSTANT (J)

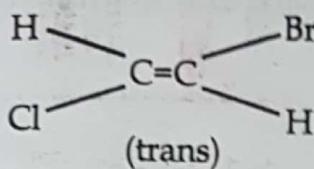
The distance between the centre of two adjacent peaks in a multiplet is constant and is known as coupling constant (J). It is measured in Hz or Cps.

If we take the spectrum of a sample at two different radiofrequencies, then the value of chemical shift changes but the value of J does not change.

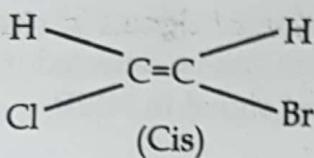
By comparing the value of J between peaks, one can assure that whether the given signal is a doublet or two singlets. Similarly by running the sample at two different radiofrequencies, and then comparing the value of J for both the spectra, it can be concluded that what is the nature of given signal. In other words, it can be said that if J changes, the signal is not a multiplet, but if J does not change, signal is multiplet.

In case of geometrical isomers :

$$J_{\text{trans}} > J_{\text{cis}}$$



$$J = 13-18 \text{ cps}$$



$$J = 7-12 \text{ cps}$$

Fig. 1.44 Different J values for cis and trans isomers.

1.24 APPLICATIONS OF NMR

1. Detection of Hydrogen bonding

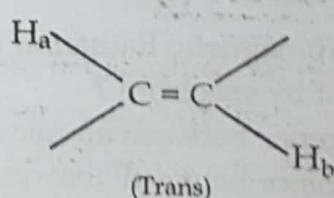
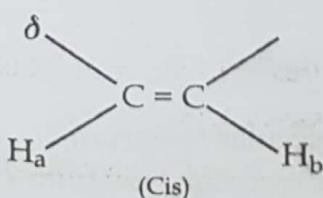
Intermolecular and intramolecular hydrogen bonding shifts the absorption for concerned proton downfield. Hydrogen bonding depends on concentration of sample and temperature. The type of hydrogen bond present in the sample can be detected by varying the concentration.

2. Detection of Aromaticity

Signal for aromatic protons appear at a very low field. Hence from this aromatic character of sample can be detected.

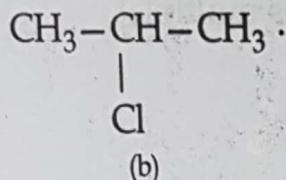
3. Detection between Cis and Trans isomers

The cis and trans isomers can be easily distinguished as the protons have different values of δ and J .



4. Identification of Structural Isomers

The structural isomers can be easily identified from its NMR spectrum e.g. a sample with molecular formulae C_3H_7Cl can have structural formula (a) or (b).



Their NMR spectra will be different. So from NMR spectrum it can be detected if sample is (a) or (b).

5. Detection of Electronegative atom

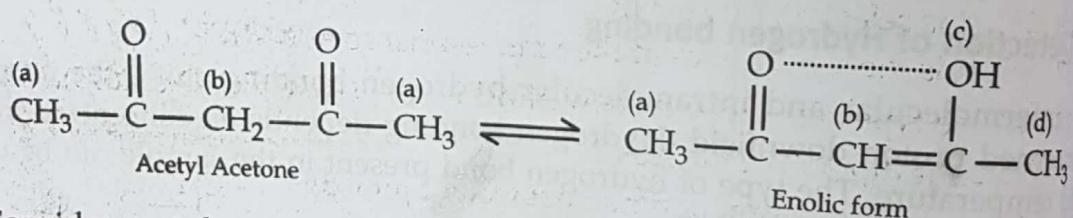
Presence of electronegative atom causes deshielding of proton if attached to the same C or in neighbourhood.

Hence the presence of electronegative atom can be detected if present in the sample with downfield shift from expected position of signal in NMR.

6. In quantitative Analysis

(A) NMR technique is very useful in knowing the ratio of water and alcohol in the alcohol sample because in pure ethanol, a triplet is observed for $-OH$ but due to presence of water, triplet changes into singlet.

(B) It is very useful technique in studying Keto-enol tautomerism



Consider acetyl acetone in equilibrium with its enolic form. In the NMR spectrum of keto form, there will be 2 signals highlighting 2 types of protons whereas in case of enolic form, four signals highlights four types of proton.

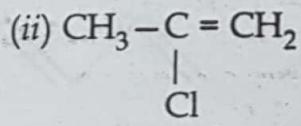
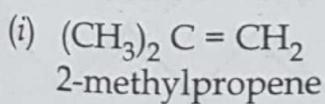


Exercise

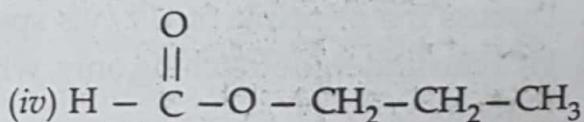
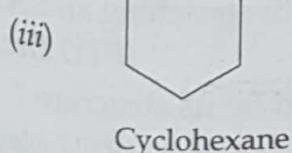
Short Answer Type Questions

- What is electromagnetic Radiation ?
- What is meant by spectrum ?
- What is difference between atomic and molecular spectrum ?
- What is difference between absorption and emission Spectrum ?
- What are the main components of a spectrophotometer ?

6. What is dispersing element in spectrophotometer ?
7. What is difference between single beam and double beam spectrophotometer ?
8. What do you understand by U.V. spectroscopy ? (PTU May 2005)
9. What do you understand by IR spectra ? (PTU Dec. 2004)
10. What is line width of a spectrum ? (PTU Dec. 2004)
11. What is selection scale for absorption spectroscopy ?
12. What is effect of size of halogen atom on $n \rightarrow \sigma^*$ transitions of alkyl halides ?
13. What is the effect of H-Bonding (in alcohols/ amines) on the λ absorbed ?
14. Define chromophore quote one example. (PTU May 2014)
15. What is an auxochrome ? (PTU May 2014)
16. Define Franck Condon Principle.
17. What are Isobestic points ?
18. Define Hooke's law ?
19. What is selection rule for SHO in IR spectroscopy ?
20. What is zero point energy of SHO.
21. Why vibrational energy levels in anharmonic oscillator are more closely spaced as compare to harmonic oscillator ?
22. What are overtones ?
23. What is UV spectrum ? Give various regions associated with UV spectrum. (PTU May 2007)
24. What is importance of IR spectroscopy in finger print region ? (PTU May 2007)
25. What is coupling constant ? (PTU Dec. 2008)
26. What is selection rule for IR ? (PTU May 2009)
27. What is the significance of the term resonance in NMR ?
28. Which type of nuclei can show NMR ? (GNDEC, Dec. 2015)(PTU May 2013)
29. What is flipping of nucleus ?
30. What are equivalent and non-equivalent protons ?
31. What is chemical shift ? What are its units ?
32. Why usually TMS is used as reference standard ? (PTU May 2010)
33. Why $\delta = 0$ for TMS ?
34. Which of the following compounds will have multiplets in their spectra ?

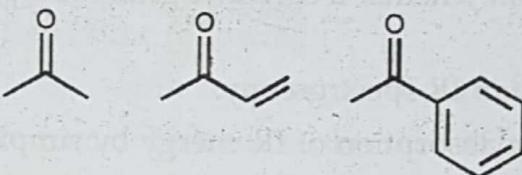


2-Chloropropene

*n*-propyl formate

35. What is 'J' ?
36. How NMR is useful in identification of structural isomers ?
37. How NMR is useful in distinguishing between geometrical isomers ?
38. Why alkenes show high value of δ while alkynes show low value ?
39. What is meant by shielding and deshielding of protons in 'HNMR' ?
- (PTU May 2005)
40. Give the high resolution HNMR spectrum of ethanol.
41. Indicate the number and type of 'HNMR signals expected in $\text{CH}_3 - \text{CH} = \text{CH}_2$
42. How many kinds of signal are obtained in NMR spectrum of $\text{CH}_3\text{CH}_2\text{OH}$?
- (PTU Dec. 2005)
43. How many 'HNMR signals are expected for ethyl acetate molecule ? Show the splitting pattern.
- (PTU May 2005 (Reappear))
44. How will you verify that a particular signal in NMR spectrum arises from $-\text{NH}$ or $-\text{SH}$ groups ?
- (PTU May 2005)
45. What is coupling constant ?
- (PTU Dec. 2005)
46. What is cause of chemical shift in NMR ?
- (PTU Dec. 2005)
47. What do you understand by bathochromic and hypsochromic shift ?
- (PTU Dec. 2015)(PTU May 2015)
48. Match each absorption bond with the following groups :
- | | | | | |
|-------------------------|-----------------------|--------------|--------------|-------------------------------|
| Functional group = | $\text{C} = \text{O}$ | $-\text{NH}$ | $-\text{OH}$ | $-\text{C} \equiv \text{C} -$ |
| $\nu \text{ cm}^{-1} =$ | 3400 | 2050 | 1700 | 3350 |
- (PTU May 2015)
49. The absorption band in UV - Vis spectroscopy is broad. Explain.
- (PTU Dec. 2015)
50. What is range of peak identification region in IR spectrum ?
- (PTU May 2015)
51. How ^1H NMR can be used to distinguish $p - \text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$ from $\text{C}_2\text{H}_5\text{C}_6\text{H}_5$?
- (PTU Dec. 2015)
52. Arrange the following in increasing order of UV absorption maxima ?
-
53. Give one example in each case of $\sigma \leftrightarrow \sigma^*$, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$.
- (PTU Dec. 2015)
54. Discuss the principle of UV/vis spectroscopy.
- (PTU Dec. 2015)
55. HCl can undergo stretching only, while CO_2 can show both stretching and bending. Explain.
- (PTU Dec. 2015)
56. The ^1H NMR of $\text{C}_2\text{H}_4\text{Br}_2$ has only one signal. What could be its structure ?
- (PTU Dec. 2015)

57. Why permanent magnets are not used in NMR ? (PTU Dec. 2015)
58. Calculate the number of vibrational degree of freedom in CO_2 and SO_2 . (PTU May 2015)
59. Which of the following exhibit IR spectra ? Why ? N_2 , HCl , O_2 , CO_2 . (PTU May 2015)
60. Explain the Selection Rules of UV-V is spectroscopy. (PTU Dec. 2014)
61. Which of the following will absorb at higher wave number for C = O Stretching ? (PTU Dec. 2014)



62. Methanol is a good solvent for UV but not for IR studies. Why ? (PTU May 2016)
63. What is finger print Region in IR spectroscopy. (GNDEC, Dec. 2014, Dec. 2015)
64. A compound having molecular formula $\text{C}_3\text{H}_6\text{O}$ show only one singlet in its NMR. Comment on its structure. (GNDEC, Reappear 2015)
65. How can the vibrations of C-C and O-H groups be differentiated by using principles of IR ? (GNDEC, Dec. 2015 Reappear)
66. What is internal standard used in NMR ? Why ? (GNDEC, May 2016)
67. How can the C = O group be differentiated among the following molecules by using IR spectroscopy : HCHO , CH_3CHO and CH_3COCH_3 . (GNDEC, May 2016)

Long Answer Type Questions

1. Write a short note on experimental technique of the absorption spectroscopy.
2. What do you understand by term line width ? Explain different factors responsible for line width. (PTU May 2010, 2012)
3. Explain the principle of UV-visible spectroscopy.
4. Write a short note on different possible transitions which are affected by absorption of UV-visible spectroscopy. (PTU May 2010)
5. Explain the following : (PTU May 2005)
 - (i) Franck-Condon principle (ii) Chromophore and auxochrome.
6. Explain the following w.r.t. UV-visible spectroscopy.
 - (i) Bathochromic shift (ii) Blue shift
 - (iii) Hyperchromic shift (PTU) (GNDEC Dec. 2013)
7. Which of the following will show high value of λ_{abs} and why ?
 - (a) $\text{CH}_2 = \text{CH}_2$
 - (b) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$

8. Out of benzene and aniline, which is expected to show high value of λ_{abs} and Why ?
 (PTU May 2012)
9. Write a short note on auxochrome.
10. What is the effect of extension of conjugation on the λ_{abs} value ? Explain.
 (PTU May 2012)
11. Explain the factors responsible for the blue and red shift.
12. Write a short note on application of UV-visible spectroscopy.
13. On the basis of IR spectroscopy, how can you distinguish among 1-hexyne, 1-hexene and hexane.
 (GNDEC May 2013)
14. How can one establish whether a carbonyl group is a part of an aldehyde, ester or ketone ?
 (PTU May 2006)
15. Explain the principle of IR spectroscopy.
 (PTU May 2013)
16. Write a short note on absorption of IR energy by simple harmonic oscillators.
17. Define and explain Hooke's law. What are its applications ?
18. Write a short note on vibrations shown by a polyatomic molecule.
19. Write a short note on factors affecting \bar{v} of a molecule.
20. Explain application of IR spectroscopy.
 (PTU May 2012)
21. How the following can be explained in context of IR spectroscopy ?
 (a) H- bonding (b) Keto-enol Tautomerism.
22. What modes of vibrations are active in IR absorption spectrum and why ? Taking nitro group as an example show various types of vibration which will be observed in IR spectra.
 (PTU May 2009)
23. What type of molecules give vibrational-rotational spectra and why ?
 (PTU May 2009)
24. Using IR spectroscopy, how will you determine whether the oxygen in an organic compound is present as a carbonyl or hydroxyl group.
 (PTU May 2007)
25. (a) Give examples of $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions.
 (b) What is effect of α, β unsaturation on carbonyl absorption in UV spectrum.
 (c) What are different modes of vibrations in IR spectroscopy ?
 (d) Which type of molecules show vibrational-rotational spectra ? Why ?
 (GNDEC May 2014)(PTU Dec. 2013, May 2007)
26. Describe briefly the theory of NMR spectrometry. What information can be obtained from NMR absorption peaks ?
 (PTU Dec. 2008)
27. What do you understand by the positions of the signals in an NMR spectrum ? How many signals are expected in each of the following compounds ?
 (a) Propane (b) Isobutane (c) Ethanol (d) Cyclobutane
 (e) Ethylmethylether (f) Ethyl acetate (g) Butanal.

28. (a) What is meant by chemical shift ? (PTU May 2013)
 (b) Write with examples, the shielding and deshielding effects involved in NMR. (GNDEC Dec. 2013)

29. Explain different factors which affect the magnitude of chemical shift ?
30. What do you understand by term splitting of signals ? Explain by taking an example.

(PTU Dec. 2012)

31. Write a short note on use of solvents in NMR.

32. Write a short note on chemical exchange as observed in NMR.

33. Write a short note on two of the following :

(a) Chemical shift (b) Spin-spin coupling (c) Coupling constant.

34. Explain why NMR spectrum of benzene is observed at high δ value whereas that of acetylene is at low δ value ?

35. Describe briefly the various applications of NMR.

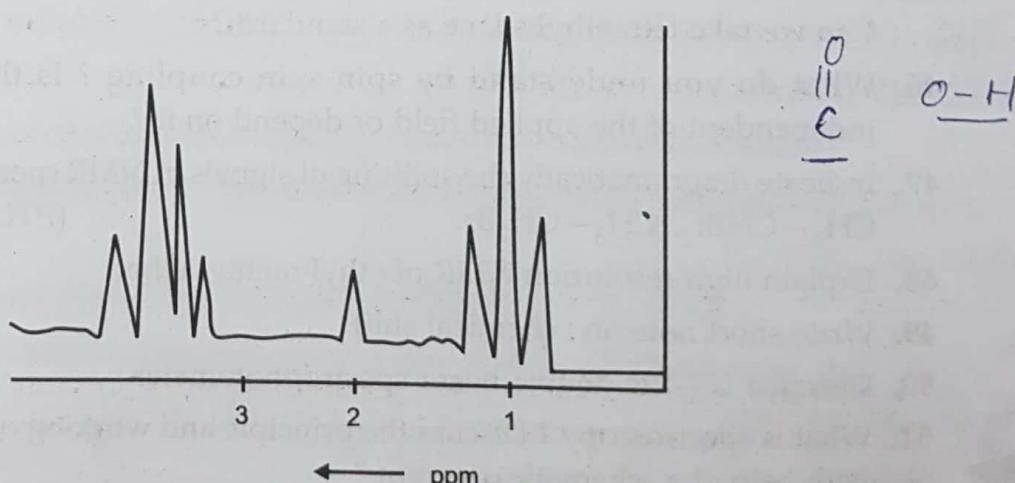
36. (a) Which of the following atoms do not exhibit NMR
 $C^{12}, O^{16}, N^{14}, N^{15}, H^2, F^{19}, C^{13}, P^{31}$

(b) How many types of 'H' are there in :
(i) $CH_3 - CH_2 - CH_3$ (ii) $CH_2 = CH_2$
(iii) $CH_3 - CH = CH_2$ (iv) $C_6H_5 - CH_3$

37. Draw the NMR of following :

- (a) $\text{CH}_3\text{CH}_2\text{Cl}$ (b) $\text{CH}_2\text{Br}-\dot{\text{C}}\text{H}_2\text{Br}$ (c) $(\text{CH}_3)_2\text{CH}-\text{CH}_3$
 (d) $\text{CH}_3-\underset{\substack{| \\ \text{Cl}}}{\text{C}}\text{H}-\text{COCH}_3$

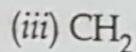
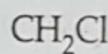
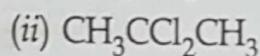
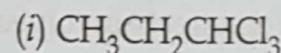
38. A compound on analysis has found to have molecular formula C_2H_6O . Write down the possible structure of the compound. The proton NMR spectrum of the molecule is as :



Identify the molecule.

(PTU May 2005 Reappear)

39. (a) Draw a low and high resolution NMR spectra of :



(b) Explain the application of NMR to any one of the following :

(i) Hydrogen Bonding

(ii) Structural Diagnosis.

40. (a) State and explain principle of NMR.

(PTU 2005)

(b) Explain the term J with examples.

(PTU 2005 Reappearing)

41. (a) Predict NMR of $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_2\text{Cl}-\text{CHCl}_2$, $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$.

(b) In relation to NMR. Explain any one of the following :

(i) Chemical shift and TMS

(ii) Shielding and Deshielding.

42. (a) What is principle behind NMR ?

(PTU May 2005)

(b) Write short note on :

(i) Spin-Spin splitting

(ii) Chemical shift

43. How will you differentiate between primary, secondary and tertiary alcohol.

44. Give brief account of significance of chemical shift in NMR. (PTU May 2007)

45. Why TMS is taken as standard for measuring chemical shift ?

(PTU May 2009)

Can we take tetraethyl silane as a standard ?

(PTU Dec. 2008)

46. What do you understand by spin-spin coupling ? Is the coupling constant independent of the applied field or depend on it ? (PTU May 2009)

47. Indicate diagrammatically the splitting of signals in NMR spectra of $\text{CH}_2\text{Br}-\text{CHBr}_2$, $\text{CH}_3-\text{CHBr}_2$, $\text{CH}_3-\text{CH}_2\text{Br}$. (PTU Dec. 2009)

48. Explain high resolution NMR of ethyl methyl ether. (PTU Dec. 2009, Dec. 2008)

49. Write short note on : chemical shift. (PTU May 2010)

50. Describe UV-Vis double beam spectrophotometer. (PTU May 2010)

51. What is spectroscopy ? Discuss the principle and working of a spectrophotometer with help of a schematic diagram ? (PTU Dec. 2013)

(PTU Dec. 2012)

52. Draw and explain ^1H NMR for $\text{Cl}_2\text{CH} - \text{CHCl} - \text{CHCl}_2$. (PTU Dec. 2011)
53. (a) Define auxochrome. Explain the effect of addition of auxochrome to a chemophore by taking one example.
 (b) Explain high resolution NMR of $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$. (GNDEC Dec. 2012)
54. (a) Define Bathochromic shift. How is it caused by presence of an auxochrome ? Explain.
 (b) Draw and Explain high resolution NMR of $\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{CH}_3$. (GNDEC May 2014)
55. (a) Explain Principle of NMR.
 (b) What information can be obtained from UV vis spectrum ? (PTU May 2014)
56. What are different kinds of electronic transitions ? Explain each type with suitable examples. (PTU May 2016)
57. (a) Explain the selection Rules of UV-Vis spectroscopy.
 (b) "Butadiene shows absorption at higher wavelength than ethene". Explain with respect to MO diagram and wave function. (PTU Dec. 2015)
58. (a) State and explain Franck-Condon principle.
 (b) Why butadiene shows absorption at higher wavelength than ethene ? Give suitable energy level diagram. (PTU May 2015)
59. (a) "IR spectra is often characterized as molecular finger prints". Justify this statement.
 (b) Calculate the number of vibrational degree of freedom in following compounds.
 (i) CO_2 (ii) SO_2 (iii) CH_4
 (c) Which of the following molecules will show IR spectra and why :
 $\text{H}_2, \text{HCl}, \text{CH}_4, \text{CO}_2, \text{H}_2\text{O}$ (PTU Dec. 2014)
60. (a) What do you understand by shielding and deshielding of protons in NMR ?
 (b) Describe bathochromic shift and hypsochromic shift by using suitable example. (GNDEC, Dec. 2014)
61. (a) How IR can distinguish between 1-hexyne, 1-hexene and hexane.
 (b) Explain Bathochromic shift and Hypsochromic shift with suitable examples. (GNDEC, Dec. 2015)
62. (a) Explain and draw high resolution NMR of $\text{CH}_3\text{CH}_2\text{COCH}_3$.
 (b) Define an auxochrome and discuss how it causes Bathochromic shift. (GNDEC, May 2016)