UNIT 10 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Structure

10.1 INTRODUCTION

Upto now we have described various spectroscopic techniques in which we measured the energy levels of electronic, vibrational and rotational states of atoms and molecules. In the above cases we simply subjected the system to electromagnetic radiations of appropriate energy (or wavelength) and looked for absorption at specific regions. There is an intetesting new branch of spectroscopy, known as *magnetic resonance spectroscopy* where we subject the system to an external magnetic field and examine the **energy levels created in these systems by the magnetic field.** If a system is to produce a number of new energy levels under the influence of a magnetic field, it is obvious that the system itself should have some magnetic properties. For example, systems which have unpaired electrons or 'free' electrons (examples are free radicals and systems containing incompletely filled electron shells) and also systems which have some specific atomic nuclei possessing a permanent magnetic dipole moment, have magnetic properties. The former systems are termed **electron paramagnetic systems,** while the latter are called **nuclear paramagnetic systems.** We shall in this unit address ourselves to the spectroscopic study of paramagnetic nuclei, called Nuclear Magnetic Resonance or NMR and in the next unit describe the electron paramagnetic resonance spectroscopy. In essence, magnetic resonance spectroscopy deals with energy levels of atoms or molecules when these are placed in an external magnetic field.

Objectives

After studying this unit, you should be able to:

- predict whether a nucleus will show magnetic properties or not?
- describe the magnetic moment,
- discuss Larmor precession,
- explain the principle of nuclear magnetic resonance,
- give the schematic representation of the NMR spectrometer,
- describe relaxation phenomenon and its mechanism,
- define chemical shift,
- discuss spin-spin splitting,
- explain time domain NMR,
- describe uses of NMR spectroscopy in structure elucidation, and
- correlate the NMR spectrum of simple molecules with their structure.

10.2 MAGNETIC AND NON-MAGNETIC NUCLEI

10.2.1 Magnetic Moments

Before we describe the Nuclear Magnetic Resonance phenomenon, let us first ask ourselves why some nuclei are magnetic and why some others are not. We know from our previous background, all atomic systems as well as atoms in molecules have a nucleus at the centre with electrons occupying the extranuclear space. We also know that (in order that atoms and molecules are neutral) the nuclei are positively charged. Although **ALL** nuclei are positively charged, only some of them have, in addition, the property of "spinning". This is shown in Fig. 10.1.

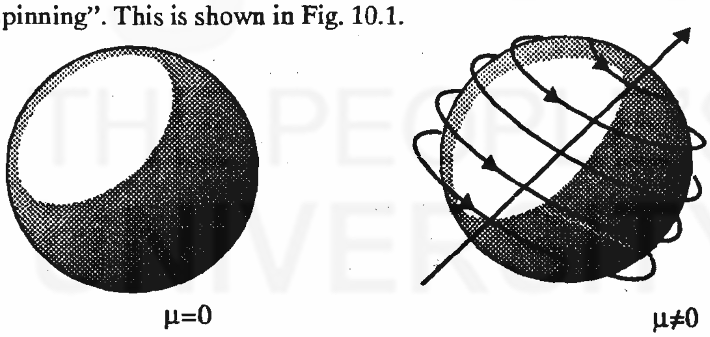
Nuclear spin is described by the spin angular momentum quantum number, I. The nuclei which exhibit NMR spectra have $I > 0$.

Given below are some generalisations for the spin quantum number of different nuclei:

(i) Nuclei having **even** number of protons and neutrons have $I = 0$. The examples of such nuclei are ^{4}He, ^{12}C and ^{16}O.

(ii) Nuclei having **odd** number of protons and neutrons have integral value of I. For example, ^{2}H and ^{14}N have $I = 1$.

(iii) Nuclei having **odd** value for the sum of protons and neutrons have half integral value of I. Thus ^{1}H and ^{15}N have $I = \frac{1}{2}$ and ^{17}O have $I = \frac{5}{2}$.



Spherical nonspinning nucleus

Spherical spinning nucleus

Fig. 10.1 : A nonspinning and a spinning nucleus.

The spin characteristics of nuclei are defined by a ***spin angular momentum quantum number,*** I. The magnitude of the spin angular momentum $|\mathbf{I}|$ is related to the spin angular momentum quantum number I in the following way.

$$|\mathbf{I}| = \sqrt{I(I+1)}\,\hbar \qquad \text{...(10.1)}$$

Remember that we expressed the spin angular momentum of an electron by a similar expression, (Eq. 1.14b) in Unit 1, Block 1. This spin angular momentum is a vector sum of the individual spin angular momentum of the component particles of the nucleus, namely neutrons and protons. The exact way in which the neutrons and protons are vectorially coupled can be understood from nuclear shell models but this is not important for us now. If the nucleus has a spin angular momentum $\mathbf{I} \neq 0$, then this corresponds to a spinning positive charge and any spinning charge will generate a magnetic moment (μ). The magnetic moment, μ, of any nucleus is proportional to its spin angular momentum ($\mathbf{I}$) and is given by the following expression.

$$\mu = \frac{g_N e}{2m} \mathbf{I}$$

where g_N is called the **nuclear g-factor** which is characteristic of the particular nucleus, e is the charge on a proton and m is the mass of the proton. Similarly, the magnitudes of magnetic moment and spin angular momentum are thus related as follows:

$$|\mu| = \frac{g_N e}{2m} \sqrt{I(I+1)}\,\hbar \qquad \text{(Using I from Eq. 10.1)}$$
$$= g_N \beta_N \sqrt{I(I+1)} \qquad \text{...(10.2)}$$

where $\beta_N = \frac{e\hbar}{2m}$ and is called **nuclear magneton.**

Note that the quantity $\frac{g_N e}{2m}$ is called the gyromagnetic ratio, γ. Hence, we can say that

$$\mu = \gamma \mathbf{I}$$
$$= \gamma \sqrt{I(I+1)}\,\hbar$$

When the charge of the particle is positive, the magnetic moment vector ($\vec{\mu}$) and the angular momentum vector ($\vec{I}$) point in the **same** direction. But when the particle is negatively charged (e.g. electron), these two vectors point in the **opposite** direction.

SAQ 1

Calculate the value of nuclear magneton for proton.
(Given $e = 1.602 \times 10^{-19}$ C, $h = 6.626 \times 10^{-34}$ J s, mass of proton $= 1.672 \times 10^{-27}$ kg)

....

....

....

....

The following table (Table 10.1) lists some of the magnetic nuclei with their spin angular magnetic quantum number I, magnetic moment μ and nuclear g_N factors. The nuclei such as ^{12}C (6 protons + 6 neutrons) and ^{16}O (8 protons + 8 neutrons) have $I = 0$ and are non-magnetic, i.e. they are not affected by a magnetic field.

Table 10.1: Properties of Some Magnetic Nuclei

Name	(% abundance)	Z	M	I	μ (in nuclear magnetons)	g_N
^1H	Proton (99.99)	1	1	1/2	2.7928	5.585
^2H	Deutron (0.01)	1	2	1	0.8574	0.857
^{13}C	Carbon (1.1)	6	13	1/2	0.7024	1.405
^{19}F	Fluorine (100)	9	19	1/2	2.6288	5.257
^{31}P	Phosphorus (100)	15	31	1/2	1.1317	2.263
^{14}N	Nitrogen (99.63)	7	14	1	+0.4038	0.403
^{15}N	Nitrogen (0.37)	7	15	1/2	−0.2831	−0.567

10.2.2 Quantization

Those nuclei which have a spin angular momentum, are therefore, associated with a magnetic moment, and can be looked at as a small bar magnet. There is, however, a very clear distinction between an ordinary laboratory bar magnet and a "nuclear spin magnet" since the latter is a quantum particle. In other words, while a bar magnet can take up any orientation when placed in an external field corresponding to a continuous variation of the potential energy (Fig. 10.2 a), the nuclear magnetic "quantum bar magnet" is allowed to take **only certain allowed** orientations. Thus, a nucleus with spin quantum number I, can take $(2I + 1)$ orientations in the external magnetic field. If the spin quantum number $I = \frac{1}{2}$, then it can take two $(2I + 1 = 2 \times \frac{1}{2} + 1 = 1 + 1 = 2)$ **orientations only in an external field.** We can easily understand the orientation of spin $\frac{1}{2}$ nuclei, in that they can either align parallel or antiparallel to the external field. No other orientation is permitted. This is schematically illustrated in the Fig. 10.2(b).

It should be noted that although the spins can be classified as parallel or antiparallel to the magnetic field, the magnetic moment vector is not completely aligned or non-aligned to the magnetic field because of the relation

$$\cos\theta = \frac{I_z}{|I|} = \frac{m_I \hbar}{\sqrt{I(I+1)}\,\hbar} = \frac{m_I}{\sqrt{I(I+1)}}$$

where θ is the angle between the magnetic moment vector and the direction of the magnetic field. For a proton $I = \frac{1}{2}$ and $m_I = \pm\frac{1}{2}$.

Thus,

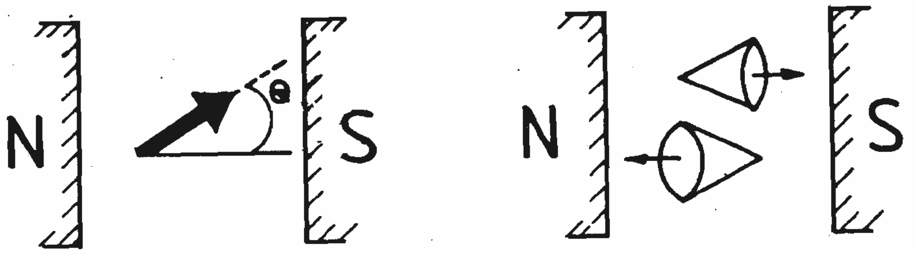
$$\cos\theta = \frac{+\frac{1}{2}}{\sqrt{\frac{1}{2}(\frac{1}{2}+1)}} = \frac{\frac{1}{2}}{\frac{\sqrt{3}}{2}} = \frac{1}{\sqrt{3}}$$

and $\theta = 35°15'$

and

$$\cos\theta = \frac{-\frac{1}{2}}{\sqrt{\frac{1}{2}(\frac{1}{2}+1)}} = \frac{-\frac{1}{2}}{\frac{\sqrt{3}}{2}} = -\frac{1}{\sqrt{3}}$$

$\therefore\ \theta = 144°45'$



$E \,\alpha\, (3\cos^2\theta - 1)$ $\qquad$ $E = \pm\, g_n \beta_n B_z m_I$

(a) $\qquad$ (b)

Fig. 10.2: (a) The orientation of a macroscopic magnet in a field, where it can take any orientation (θ) and the energy is proportional to ($3\cos^2\theta - 1$).
(b) The nuclear magnetic moments being quantum mechanical entities are either aligned parallel or antiparallel to the external field.

The component of the magnetic moment of the nucleus in the direction of the applied magnetic field, μ_z is given as follows:

$$\mu_z = \frac{|g_N|\, e}{2m} I_z \qquad \text{...(10.3)}$$

where I_z is the component of spin angular momentum in the direction of the applied magnetic field.

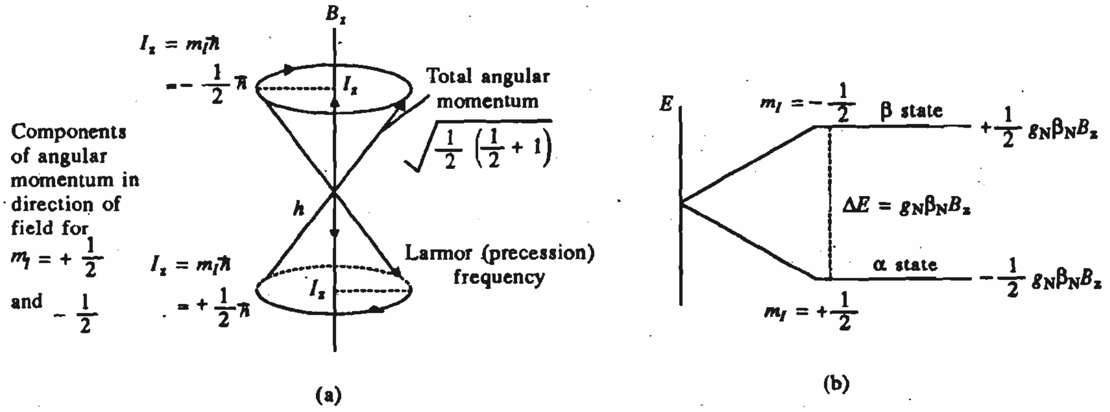
Eq. 10.3 can also be written as $\mu_z = \gamma I_z$

Also I_z can be expressed as follows:

$$I_z = m_I \hbar \qquad \text{...(10.4)}$$

where m_I is the quantum number for z-component and can take values $-I$, ..., $+I$. This is illustrated in Fig. 10.3 (a).

Remember that you studied similar expressions for the case of electron in Unit 1, Block 1.



(a) $\qquad$ (b)

Fig. 10.3: (a) Total angular momentum $I = \sqrt{I(I+1)}\,\hbar$ for $I = \frac{1}{2}$ and its components I_z ($= m_I\hbar$ for $m_I = +\frac{1}{2}$ and $-\frac{1}{2}$) in the direction of applied magnetic field.
(b) Two energy levels corresponding to $m_I = +\frac{1}{2}$ (lower level) and $m_I = -\frac{1}{2}$ (upper level).

The different values of m_I yield different values of I_z and μ_z in turn.

Thus, we can say for $I = \frac{1}{2}, m_I = -\frac{1}{2}$ and $+\frac{1}{2}$

and $I_z = -\frac{1}{2}\hbar$ and $+\frac{1}{2}\hbar$ (from Eq. 10.4)

$$\mu_z = \gamma I_z$$
$$= \gamma m_I \hbar$$

Hence,

$$E = -\gamma m_I \hbar \ B_z$$

For

$$m_I = \frac{1}{2}, E\alpha = \frac{-\gamma}{2}\hbar B_z$$

$$m_I = -\frac{1}{2}, E_\beta = \frac{\gamma}{2}\hbar B_z$$

And

$$\Delta E = E_\beta - E\alpha = \frac{\gamma}{2}\hbar B_z - \left(\frac{-\gamma}{2}\hbar B_z\right)$$
$$= \gamma \hbar B_z$$

Therefore

$$\nu = \frac{\Delta E}{h} = \frac{\gamma h B_z}{h\, 2\pi}$$
$$= \frac{\gamma B_z}{2\pi}$$

Substituting these values of I_z in Eq. 10.3, we can say that

$$\mu_z = \frac{|g_N|\,e}{2m} \times -\frac{1}{2}\hbar \text{ and } \frac{|g_N|\,e}{2m} \times \frac{1}{2}\hbar$$

$$= \frac{-|g_N|\,e\hbar}{4m} \text{ and } \frac{|g_N|\,e\hbar}{4m}$$

Using β_N for $\frac{e\hbar}{2m}$

$$\mu_z = -\frac{1}{2}\,|g_N|\,\beta_N \text{ and } \frac{1}{2}\,|g_N|\,\beta_N$$

Since the energy of the magnetic dipole in a magnetic field of strength B_z is given as

$$E = -\mu_z B_z \qquad \text{...(10.5)}$$

we get, $E = +\frac{1}{2}\,|g_N|\,\beta_N B_z$ and $E = -\frac{1}{2}\,|g_N|\,\beta_N B_z$

These energy levels are shown in Fig. 10.3 (b).

In the absence of magnetic field, these two levels have the same energy and are called *degenerate*.

Note that for a proton ($I = \frac{1}{2}$), the lower spin level corresponds to $m_I = +\frac{1}{2}$ and is known as α state. The upper spin state having $m_I = -\frac{1}{2}$, is known as β state. The energy difference between these two spin states is thus given as

$$\Delta E = E_\beta - E_\alpha = \frac{1}{2}|g_N|\,\beta_N B_z - \left(-\frac{1}{2}|g_N|\,\beta_N B_z\right) = |g_N|\beta_N B_z$$

and $$\nu = \frac{\Delta E}{h} = \frac{|g_N|\,\beta_N B_z}{h} \qquad \text{...(10.6)}$$

The splitting of the nuclear energy into $(2I + 1)$ levels for a nucleus of spin I is known as the **nuclear Zeeman effect** and is the primary phenomenon in NMR spectroscopy.

10.3 LARMOR PRECESSION AND RESONANCE PHENOMENON

10.3.1 Magnetic Torque and Gyration

Apart from the above understanding that the nuclear magnetic energy levels are split in a magnetic field, it is also important to understand the phenomenological description of the motion of the spins. Thus, the spin of a nucleus (proton) under the influence of an external magnetic field can either align with the field or oppose an external field. In addition to this, it shows **precessional motion**. The precessional motion of a spinning top is shown in Fig. 10.4. The top is spinning about the axis A. In addition the spinning axis A moves slowly around the vertical axis O which is the precessional motion.

Just as a spinning top experiences a gravitational torque and undergoes a precessional motion (gyroscopic motion), the spinning atomic nucleus also undergoes a precessional motion under the influence of the magnetic torque from the external magnetic field.

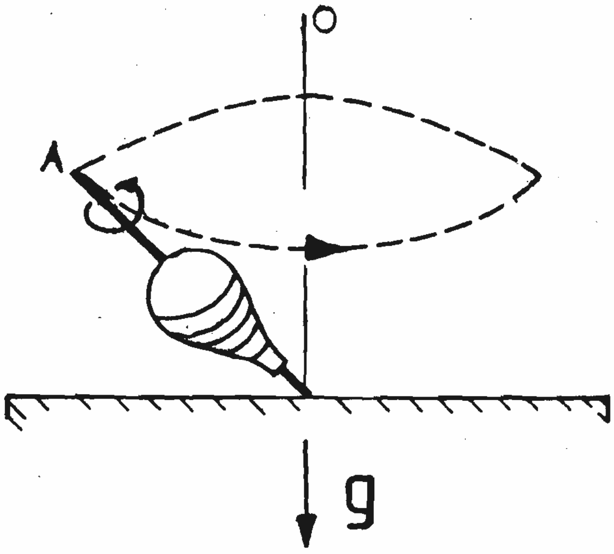


Fig. 10.4: The gyroscopic motion of a spinning top under the influence of the gravitational torque, g.

The precessional motion of a proton can take two orientations as shown in Fig. 10.5. The lower energy orientation shows the alignment with the field and the higher energy orientation is opposed to the field.

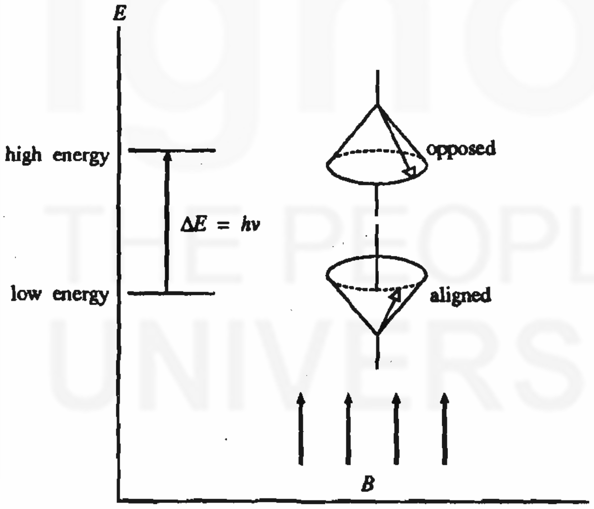


Fig. 10.5: Precession of a nucleus (proton).

The phenomenon of precession is known as *Larmor precession* and the precessional frequency is known as *Larmor frequency*.

Now we have two kinds of motion and frequencies. One, the **spinning frequency** (around axis A) and the second **precessional frequency** (around axis O). The spinning frequency does not change but the precessional frequency is proportional to the strength of the applied field. The expression for precessional frequency, ω is given below:

$$\nu = \frac{\gamma B_z}{2\pi} \text{ or } 2\pi\nu = \omega = \gamma B_z \qquad ...(10.7)$$

where γ is the gyromagnetic ratio and B_z is the strength of the applied magnetic field felt by the proton.
You may remember from unit 1, Sec 1.10 that we called ω as Larmor frequency.

If we replace γ in the above equation by $\frac{\mu}{I}$, we get

$$\nu = \frac{\mu B_z}{2\pi I}$$

Substituting the values for μ and I we can write

$$\nu = \frac{g_N \beta_N \sqrt{I(I+1)}.B_z}{2\pi \sqrt{I(I+1)}\hbar}$$

$$= \frac{g_N \beta_N B_z}{2\pi \frac{h}{2\pi}}$$

$$= \frac{g_N \beta_N B_z}{h} \qquad \text{...(10.8)}$$

The precessional frequencies for some of the nuclei at selected field strengths are given in Table 10.2.

Table 10.2: Precessional frequencies for some nuclei at various field strengths

B_z/T Nucleus	1.4	1.9	2.3	4.7	7.1	11.7	14.1
^1H	60	80	100	200	300	500	600
^2H	9.2	12.3	15.3	30.6	46.0	76.8	92
^{11}B	19.2	25.6	32.0	64.2	96.9	159.8	192
^{13}C	15.1	20.1	25.1	50.3	75.5	125.7	151
^{14}N	4.3	5.7	7.2	14.5	21.7	36.1	43
^{15}N	6.1	8.1	10.1	20.3	30.4	50.7	61
^{17}O	8.1	10.8	13.6	27.1	40.7	67.8	81
^{19}F	56.5	75.3	94.1	188.2	288.2	470.5	565
^{31}P	24.3	32.4	40.5	81.0	121.5	202.4	243

If you compare Eq. 10.8 with Eq. 10.6, you will note that the precessional frequency is the *same* as the frequency of separation between the two energy levels.

Let us now study the phenomenon of resonance.

10.3.2 Resonance and Nuclear Induction

The Larmor precession which you read above, provides a mechanism by which an electromagnetic radiation can interact with the spinning nucleus. If an electromagnetic radiation of frequency ν as given by Eq. 10.6 (and is same as in Eq. 10.8) is allowed to interact with the nuclei, then the nuclei from lower energy level may absorb energy and go to the higher energy level.

In an ensemble of nuclei, they distribute themselves between the two energy levels according to the Boltzmann distribution as given below:

$$\frac{N_2}{N_1} = e^{-\frac{\Delta E}{kT}}$$

When

$\Delta E = 7 \times 10^{-26}$ J

$k = 1.38 \times 10^{-23}$ J K^{-1}

$T = 300$ K

$$\frac{N_2}{N_1} \approx e^{-\frac{7 \times 10^{-26}\,\text{J}}{1.38 \times 10^{-23}\,\text{J K}^{-1} \times 300\,\text{K}}}$$

$$\approx e^{-1 \times 10^{-5}}$$

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

Since the energies of the upper and lower levels do not differ very much, the number of nuclei occupying these levels *is also not* very different. For example, in case of protons studied using a 200 MHz instrument, the difference in the number of nuclei is of the order of 1 in 10^5. Because of this small difference in population, the sample has a net magnetisation M is the direction of the applied field, Fig. 10.6(a).

The magnetic dipole moment per unit volume is known as **magnetisation.**

When the radiofrequency is applied at the right angle to magnetic field, it produces a rotating magnetic field having a component in the (*x*–*y*) plane. It is necessary that the frequency of rotation of the rotating magnetic field be exactly **the same** as the Larmor frequency (Fig. 10.6b). Only when such a condition is met, i.e. the two

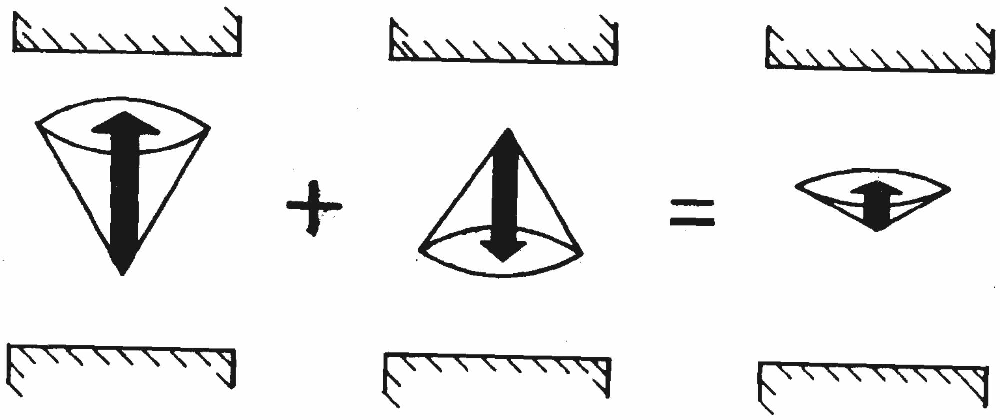


Fig. 10.6: (a) The vector sum of nuclear magnetic moments which are precessing about an axis parallel or antiparallel to the external field, leads, due to Boltzmann distribution, a net excess population in the lower energy state.

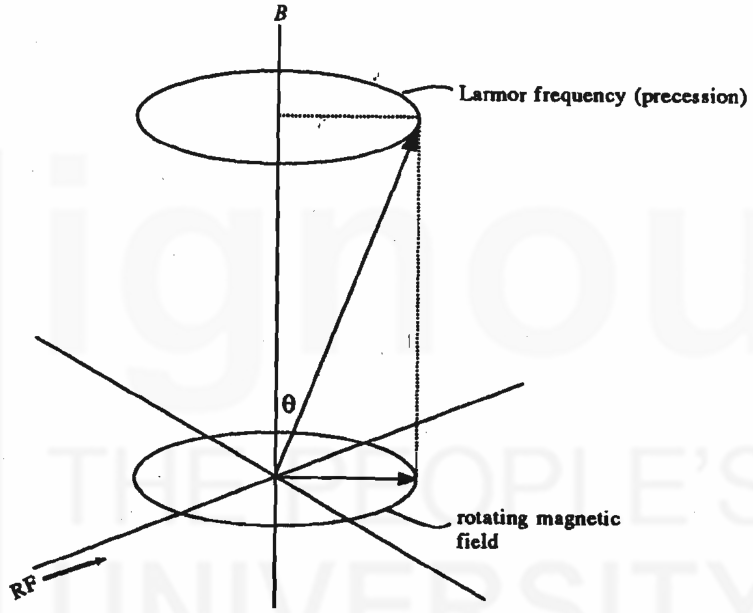
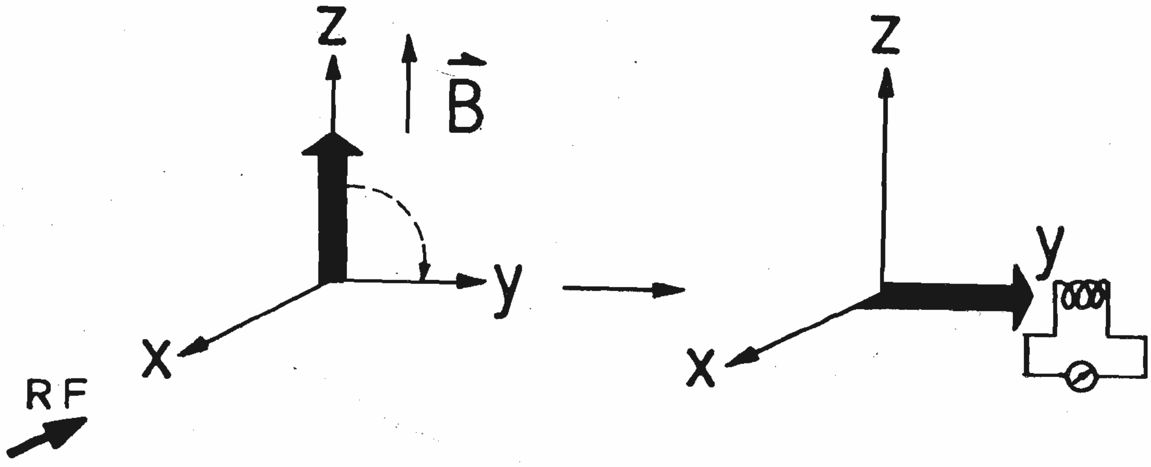


Fig 10.6 (b)

(b) Resonance will be observed when the frequency of rotating magnetic field matches with that of Larmor frequency.



(c) An rf field applied perpendicular to the magnetic field produces a torque rotating the net magnetisation from the z-axis to the transverse plane ($x-y$) where it can produce a nuclear magnetic induction signal in a tuned coil.

frequencies are in **resonance,** the nuclei will absorb energy. This is the reason why this phenomenon is called **nuclear magnetic resonance.** Hence, the condition for resonance is

$$h\nu = g_N \beta_N B_z \qquad \ldots(10.9)$$

The application of the radiofrequency rotates the net magnetisation into the (x–y) plane as is shown in Fig. 10.6(c). This induces a current in the tuned coil. The details of this are given in Sec. 10.4 under instrumentation. Before you study the details of instrumentation of NMR spectroscopy, it is worthwhile to understand the phenomenon of relaxation as given below.

10.3.3 Relaxation Phenomenon

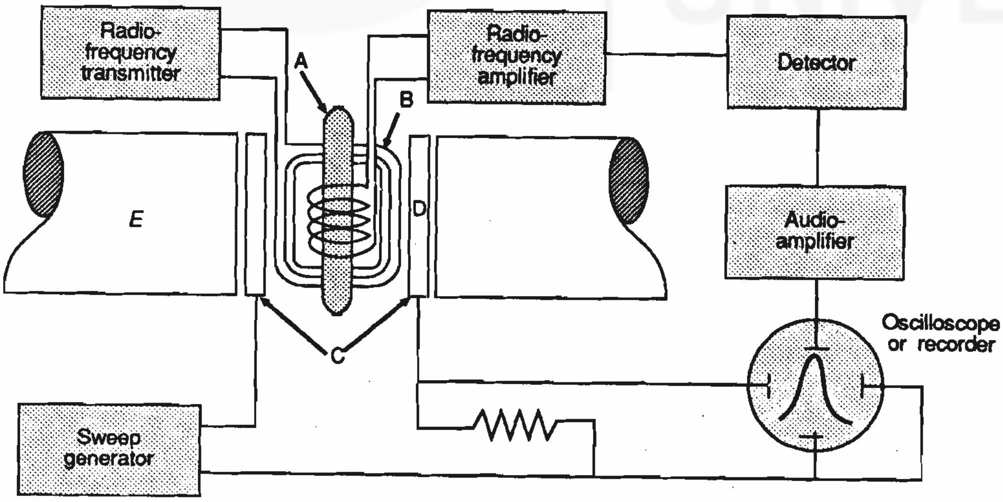
You have studied above that the population of various energy levels is governed by Boltzmann distribution. Absorption of radiofrequency radiation will disturb this distribution. Hence, after some time, the population of lower and higher levels will become equal. When this happens, no more energy will be absorbed. This situation is referred to as the **saturation** of the resonance signal. To record the NMR spectrum, it is necessary that the original equilibrium is restored. This is done by the dissipation of excess energy through **relaxation process.** Two types of relaxation processes are **spin-lattice relaxations** and **spin-spin relaxations.**

The name spin-lattice relaxation originated from the fact that earlier studies were made on solid samples where the relaxation of spin excitation energy occurs due to lattice vibrations. The random motions of the adjacent nuclei set up fluctuating magnetic fields at the nucleus leading to its interaction with the magnetic dipole of the excited nucleus. The result of this overall process is the transfer of energy from the excited nucleus to the neighbouring atoms.

The spin-spin relaxations involve the interaction of spin of one nucleus with the spins of neighbouring nuclei. For example, if there are two nuclei, then one nucleus can flip up and the other can flip down by mutual exchange of spins.

10.4 RECORDING OF NMR SPECTRUM

The schematic representation of an NMR spectrometer is shown in Fig. 10.7.



A, sample tube; *B*, transmitter coil; *C*, sweep magnet; *D*, receiver coil; *E*, main magnet

Fig. 10.7 : Schematic representation of an NMR spectrometer.

A very small amount of sample is required for recording the NMR spectrum.

The components of an NMR spectrometer include a magnet, a radiofrequency source and a detection system in addition to the recording device. The sample whose NMR spectrum is to be recorded is dissolved in a suitable solvent and placed in a glass tube having 15 cms length and 0.5 cm diameter. The sample tube is placed between the poles of a magnet. The sample tube is spun to ensure that a uniform magnetic field is experienced by all the nuclei of the sample. When the radiofrequency is applied, the nuclei absorb energy which is detected and recorded. Two alternatives are available here. We can either keep the frequency constant and vary the magnetic field to know the position of resonance or we can keep the magnetic field strength constant and vary the frequency and record the resonance position.

The solvents used for recording NMR spectrum are CCl_4, $CDCl_3$, C_6D_6, d_6 –DMSO, D_2O, $(CD_3)_2SO$.

In most NMR spectrometers, the frequency is kept fixed and the magnetic field is varied till the resonance condition is reached.

Modern NMR spectrometers are of Fourier transform type. They are very sensitive and can be used to record the NMR spectra of a variety of nuclei. You will study more about this technique in Sec. 10.11.

Till now you were studying the principle behind NMR spectroscopy and its instrumentation. Let us now study the reason why this technique is so important to the chemists.

10.5 THE CHEMICAL SHIFT

So far what we have talked about nuclei holds good only when they are bare. For bare nuclei the resonance condition is as given by Eq. 10.9, i.e. $h\nu = g_N \beta_N B_z$.

It implies that all the nuclei of a given type (for example, hydrogen atoms) in a sample should absorb the energy corresponding to the above ν value. If such had been the case, the NMR spectroscopy would have been of no use to the chemists. In real systems, however, the nuclei are surrounded by extranuclear electrons and these can modify the external field by either shielding or deshielding the nucleus.

The circulating electrons produce an induced magnetic field which opposes the applied field (B_z). Hence, the magnetic field experienced by the nucleus (B_{eff}) is given by the following equation:

$$B_{eff} = B_z - B_{induced} \qquad ...(10.10)$$

The induced field is proportional to the applied field and is given by the following expression:

$$B_{induced} = \sigma B_z \qquad ...(10.11)$$

where σ is the shielding constant.

Substituting the value of $B_{induced}$ from Eq. 10.11 into Eq. 10.10, we get

$$\begin{aligned} B_{eff} &= B_z - \sigma B_z \\ &= B_z(1-\sigma) \qquad ...(10.12) \end{aligned}$$

Note that for an unshielded proton

$\Delta E = h\nu = g_N \beta_N B_z$

Hence $\nu = \dfrac{g_N \beta_N B_z}{h}$

Similarly, for a shielded proton

$\Delta E' = h\nu' = g_N \beta_N B_z(1-\sigma)$

Hence, $\nu' = \dfrac{g_N \beta_N B_z(1-\sigma)}{h}$

Thus, $\nu' = \nu(1-\sigma)$

Thus, in presence of the extranuclear electronic environment, the resonance condition has to be modified as:

$$h\nu = g_N \beta_N B_z(1-\sigma) \qquad ...(10.13)$$

This is shown in Fig. 10.8.

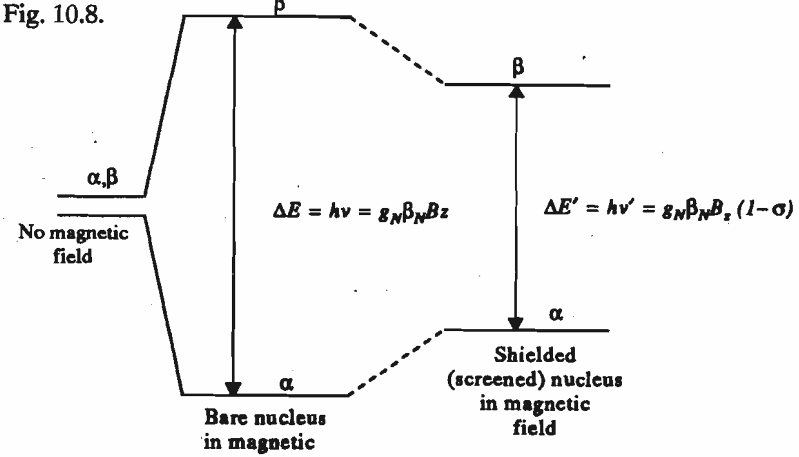


Fig. 10.8 :

Fig. 10.8: Modification of nuclear Zeeman level splitting as a result of electronic shielding.

Positive value of σ means that the nuclei are *shielded* by the electronic environment, while negative σ corresponds to *deshielding* of the nucleus. When shielding occurs, the B_{eff} is **less than** B_z, hence B_z **must be increased** to bring the nucleus in resonance. On the other hand when deshielding occurs, B_{eff} is more than B_z, resulting in the resonance at **lower** field. Thus, due to shielding (or deshielding) identical nuclei (e.g. H) which have different chemical environment (in other words, different electron density) resonate at **different** values of the applied field. These values being characteristic can be used to identify various types of environment in which the nucleus is present. Since the shift in the position of resonance is due to difference in **chemical** environment, it is called **chemical shift.** Since we cannot measure the NMR of bare nuclei we have to use some reference standard with respect to which we can measure the extent of shielding or deshielding of the external field in various chemical environments. (This is very similar to the choice of the standard hydrogen electrode as the reference for defining electrode potentials of various half-cells in Electrochemistry).

The reference chosen is the molecule Tetramethyl silane, $(CH_3)_4Si$ (TMS). The choice of TMS as reference is due to the fact that it contains 12 protons per molecule, all of which are chemically equivalent. With the consequent high specific proton concentration TMS will give strong NMR absorption even in dilute solutions. Secondly the protons in TMS are highly shielded and hence occur at "higher fields" compared to protons of most organic compounds. This will make the TMS resonance non-interfering with test spectra.

Since the protons of TMS are more shielded as compared to those of most organic compounds, the chemical shift for most organic compounds is a positive number.

Unit of Chemical Shift

Suppose we measure a test sample and TMS using the same magnetic field B_z, the resonance conditions are given by

$$h\nu_{Test} = g_N \beta_N B_z (1 - \sigma_{Test}) \quad \ldots(10.14)$$

$$h\nu_{TMS} = g_N \beta_N B_z (1 - \sigma_{TMS}) \quad \ldots(10.15)$$

Thus

$$h\nu_{Test} - h\nu_{TMS} = g_N \beta_N B_z (1 - \sigma_{Test}) - g_N \beta_N B_z (1 - \sigma_{TMS})$$

$$h(\nu_{Test} - \nu_{TMS}) = g_N \beta_N B_z [1 - \sigma_{Test} - (1 - \sigma_{TMS})]$$

$$h(\nu_{Test} - \nu_{TMS}) = g_N \beta_N B_z [-\sigma_{Test}] \quad \ldots(10.16)$$

By definition $\sigma_{TMS} = 0$ (Reference)

If we measure the same two samples (Test and TMS) by doubling the field then,

$$2h(\nu_{Test} - \nu_{TMS}) = 2g_N \beta_N B_z (-\sigma_{Test}) \quad \ldots(10.17)$$

Now the frequency difference between test and reference gets *doubled.* In order to represent shifts in a universal manner we have to quote these shifts **independent** of the strength of the field. This is achieved by dividing the shift in field (constant frequency measurement) or shift in frequency (constant field measurement) by the respective spectrometer field or frequency and represent it by δ. This makes the shift dimensionless, but makes it a very small value since the shift in field or frequency is nearly 10^6 times smaller than the measuring field or frequency. Therefore, we multiply this dimensionless constant by 10^6 and express it in terms of parts per million (ppm). Thus the chemical shift, δ can be given as

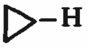
Note that there is a change of signs when we use field (B) instead of frequency (ν) in Eq. 10.18.

$$\delta = \frac{\nu_{Test} - \nu_{TMS}}{\text{Spectrometer frequency}} \times 10^6 \text{ ppm}$$

$$= \frac{B_{z_{TMS}} - B_{z_{Test}}}{\text{Spectrometer field}} \times 10^6 \text{ ppm} \quad \ldots(10.18)$$

Table 10.3 shows the chemical shifts for protons in some classes of organic compounds.

Table 10.3: Chemical Shifts of Common Proton Groups.

Functional Group		δ
Organometallic	RCH_2M	−1.2–0.1
Cyclopropyl		0.2
Methyl	$-CH_3$	0.9
Methylene	$-CH_2-$	1.3
Tertiary	R_3C-H	1.5
Allylic	$-C=C-CH_2-$	1.7
Alkyne	$-C\equiv C-H$	2-3
Benzylic	$Ar-CH_2-$	2.3-3
Vinyl	$-C=C-H$	4.5-6.0
Aromatic	$Ar-H$	6-8.5
Amino	$RC\underline{H_2}NH_2$ $R-NH_2$	2.0-2.8 1-5
Alkyl halides	$R-CH_2-X$	2-4
Ketones	$R-CH_2-CO-R$	2-2.7
Alcohols	$RC\underline{H_2}-OH$ $R-OH$	3.4-4 1-5
Ethers	$R-O-CH_2-R$	3.3-4
Esters	$R-CO-OCH_2-R$ RCH_2-COOR	3.7-4.1 2-2.2
Aldehydic	$RCO-H$	9-10
Carboxylic acids	$R-COOH$	10-12
Enolic	$-C=C-OH$	15-17

Remember that the chemical shift values for protons are related to the electron density around the atom to which they are bonded. If the electron density is high, then the protons are shielded from the magnetic field and hence higher magnetic field is to be applied to achieve resonance. Protons having smaller values of chemical shift are said to appear at **upfield** as compared to those which have higher chemical shift values and are said to appear **downfield.** But you should not forget that both these types of protons are still appearing downfield with respect to TMS.

SAQ 2

The chemical shift of protons in a test sample occurs at 2 ppm. What is the difference in Hz between TMS and test proton resonances when measured in a 100 MHz spectrometer and in a 200 MHz spectrometer?

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From here onwards, we will focus our discussion mainly on the ^1H – NMR, or proton NMR as hydrogen is present in most of the organic molecules and hence a study of ^1H–NMR helps in their structure elucidation. Before that let us see how does an NMR spectrum look like?

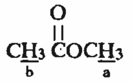
10.6 PRESENTATION OF THE NMR SPECTRUM

Remember that chemically equivalent protons absorb at the same δ value.

The NMR spectrum is recorded on a chart paper. It has at its botton δ scale (in ppm) with δ values increasing from right to left. The 0 (zero) δ value corresponds to TMS. TMS when added as an internal standard to the solution of the sample whose NMR spectrum is to be recorded, shows a signal (peak) at 0 δ as shown in Fig. 10.9. The *lower δ* value means an *upfield chemical shift* and indicates that the proton whose signal appears in this region has high electron density around it. Similarly the *higher* the value of δ for a particular signal, the *higher* the dishielding and *lower* the electron density around the proton giving that signal. Thus, as said earlier, chemically (or magnetically) different protons will show signals at different δ values. Hence, by counting the number of signals, you can say how many chemically different protons are present in the molecule of the sample.

Besides showing the **number** of different kinds of protons, the ^1H – NMR spectrum also tells **how many** protons of each kind are present in a molecule. This is shown by the intensity of the signal. The intensity of a signal is measured in terms of the **area** under that peak. The area under an NMR signal is directly proportional to the number of protons giving rise to that signal. This area is measured by an electronic integrator and is recorded by the instrument on the spectrum as a stepped curve. The height of each step can be counted by counting the number of squares on the graph.

In the light of the above discussion, let us go through Fig. 10.9. It shows *two signals* indicating that *two kinds of hydrogens* are present in methyl acetate.



$\underset{b}{\underline{CH_3}}\overset{\overset{O}{\|}}{C}O\underset{a}{\underline{CH_3}}$

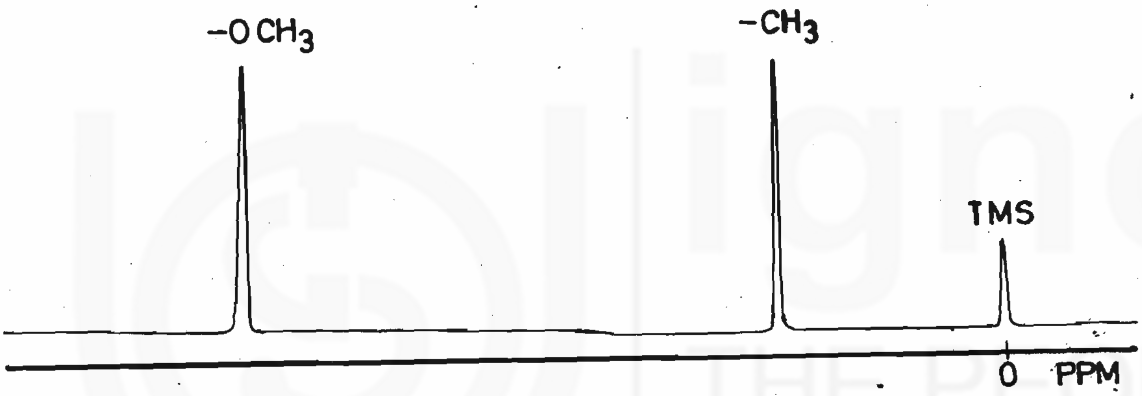


Fig. 10.9: The NMR spectrum of methyl acetate (not drawn to scale) showing two peaks from the two chemically different methyl groups and the TMS at 0 ppm.

One signal is due to the hydrogen atoms of the methyl group attached to the oxygen and the other signal is due to the methyl group attached to the carbonyl group. These two sets of hydrogens are non-equivalent and can be represented by a,b,c..... etc.

The two signals are of equal intensity because the number of protons responsible for them is equal (3 in this case).

Besides giving the above information, the NMR spectrum of a compound can tell how many different protons are present on the neighbouring carbon atom of a particular proton. This is explained in the next section.

Before that attempt the following SAQ to check your understanding of the above concepts.

SAQ 3

Identify the chemically different set of protons in $(CH_3)_2$ CHCHO and label them using letters, a,b,c .... etc.

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10.7 SPIN-SPIN COUPLING

Apart from the phenomenon of chemical shift, protons which are on adjacent atoms can also indirectly interact with each other depending upon the nature and number of the bonds between them. This can be illustrated by studying a portion of the NMR spectrum of a compound having two protons on adjacent carbons as shown in Fig. 10.10.

Protons on adjacent carbons are known as *vicinal* protons.

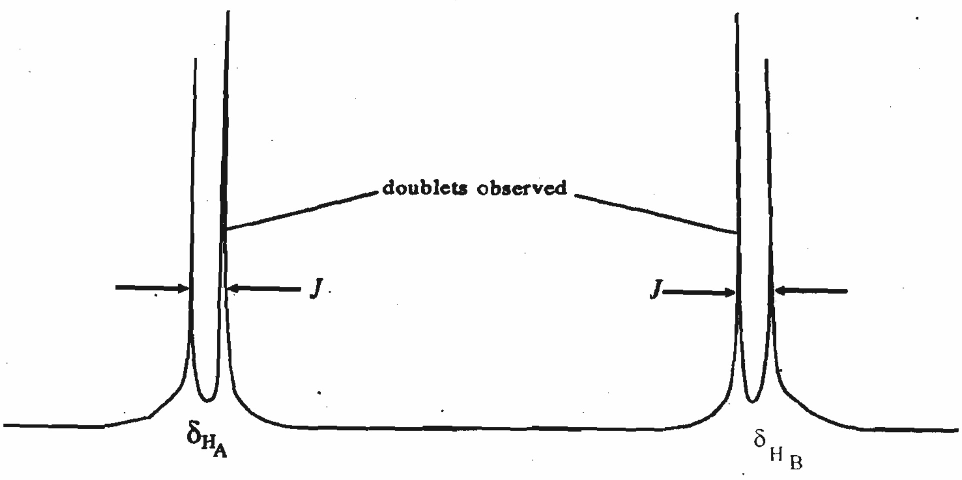


Fig. 10.10 Splitting in the signals of two vicinal protons.

Let the two protons present on the adjacent carbon atoms be represented as H_A and H_B. These two protons when present in different magnetic environments resonate at different position and hence show different values of chemical shifts. The signal due to each proton is split into a *doublet*. This can be explained as follows. For H_A, there are two possibilities of spin orientations of H_B. The spin of H_B can be either aligned (parallel) to H_A or opposed to H_A. In roughly half of the molecules, the spin of H_B is parallel to H_A and in rest half, it is opposed to H_A. In one case H_A proton is deshielded and in other it is shielded. Thus, H_A experiences two different magnetic fields and resonates at two different positions resulting in a doublet in the NMR spectrum. Similarly, H_B also yields a doublet.

Let us consider one more example, i.e. the NMR spectrum of ethanal as shown in Fig.10.11.

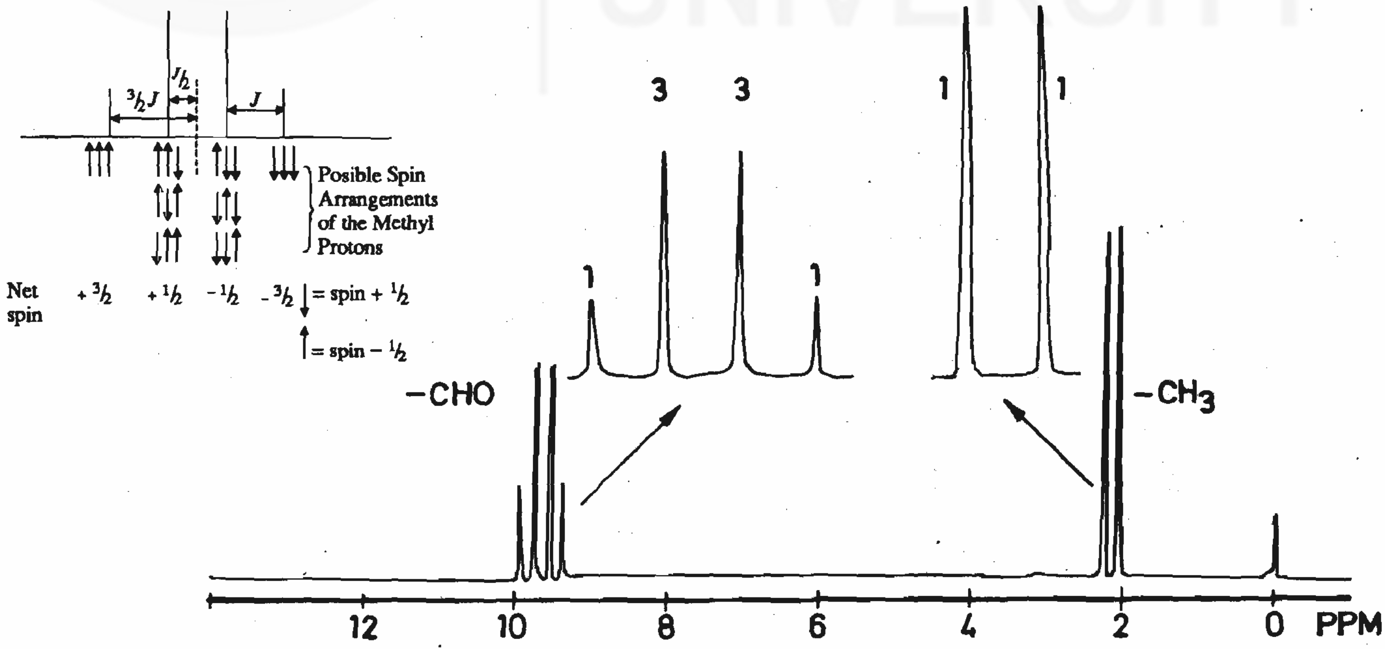


Fig. 10.11: NMR spectrum of ethanal. The spectrum shows a signal at δ 2.12 ppm due to the CH_3 group being split into a doublet due to spin-spin coupling to the aldehyde proton and a quartet at δ 9.9 ppm from the aldehyde proton due to coupling to methyl protons; inset shows the multiplets in expanded scale.

The spectrum consists of two groups of lines. The group occurring at δ 9.9 ppm comes from the aldehyde proton while the lines occurring at δ 2.12 ppm are from the methyl group. The relative intensities of these lines are in the ratio 1:3. However, the aldehyde resonance(lines)occur as an equally spaced quartet (four lines) with relative intensity 1:3:3:1 with a spacing of 3 Hz in between them.

This fine structure or splitting of lines is due to the indirect coupling between aldehyde proton and the methyl protons. This is called *spin-spin coupling* and can be understood as due to a small magnetic field produced at the site of the aldehyde proton by various statistical distributions of the *spin* orientation of the methyl protons. There are three methyl protons and their spins can be aligned parallel or antiparallel to the field as is shown in Fig. 10.12.

STATISTICAL DISTRIBUTION OF ORIENTATIONS

TOTAL SPIN QUANTUM NO. (M_I)	**METHYL PROTONS (as seen by CHO proton)**	**RELATIVE WEIGHTAGE**
3/2	$\uparrow\ \uparrow\ \uparrow$ ($\alpha\alpha\alpha$)	1
1/2	$\uparrow\ \uparrow\ \downarrow$ ($\alpha\alpha\beta$) $\uparrow\ \downarrow\ \uparrow$ ($\alpha\beta\alpha$) $\downarrow\ \uparrow\ \uparrow$ ($\beta\alpha\alpha$)	3
–1/2	$\downarrow\ \downarrow\ \uparrow$ ($\beta\beta\alpha$) $\downarrow\ \uparrow\ \downarrow$ ($\beta\alpha\beta$) $\uparrow\ \downarrow\ \downarrow$ ($\alpha\beta\beta$)	3
–3/2	$\downarrow\ \downarrow\ \downarrow$ ($\beta\beta\beta$)	1
	ALDEHYDE PROTON (as seen by CH$_3$ protons)	
1/2	$\uparrow$ α	1
–1/2	$\downarrow$ β	1

Fig. 10.12: The origin of spin-spin coupling multiplets and their relative intensities. The eight possible orientations of the spin of three methyl protons leads to total spin quantum numbers of 3/2, 1/2, –1/2 and –3/2 with a statistical weight ratio of 1:3:3:1 leading to a quartet splitting of the aldehyde resonance in this ratio. Similar arguments will lead to a 1:1 doublet of the methyl protons by aldehyde proton. If we denote spins with $m_I = +\frac{1}{2}$ by α and those with $m_I = -\frac{1}{2}$ with β, we get notations for the spin orientations a s given in brackets.

The statistical distribution of the methyl proton orientations leading to net m_I (total) of 3/2, 1/2, –1/2, –3/2 has the weightage 1:3:3:1. While the $m_I = 3/2$ configuration can provide a local field, say, of $3/2\,J$, the others will provide $\pm\,1/2\,J$ and $-3/2\,J$, so that the aldehyde proton will give now four resonances relative to the position of chemical shift (in the absence of coupling) at $\pm 3/2\,J$ and $\pm 1/2\,J$ with intensities 1:3:3:1 and separation J. Thus the aldehyde resonance occurs as a quartet of intensity 1:3:3:1. Here J is known as the **coupling constant** and is measured in Hz.

We now look at the effect of aldehyde proton on the methyl resonance; the former can be either parallel or antiparallel ($m_I = +\frac{1}{2}$ or $-\frac{1}{2}$) giving rise to local field of $\pm\,J/2$. Thus the methyl resonance is split into a doublet of separation J = 3 Hz with equal intensities. Spin-spin coupling can range between few Hz to tens of Hz depending on the hybridization of the bonds involved and the number of bonds intervening the two coupled nuclei under consideration.

On similar grounds, an ethyl group will give a quartet (1:3:3:1) for the methylene resonance and a triplet (1:2:1) for the methyl resonance. This is shown in the NMR spectrum of ethanol in Fig. 10.13.

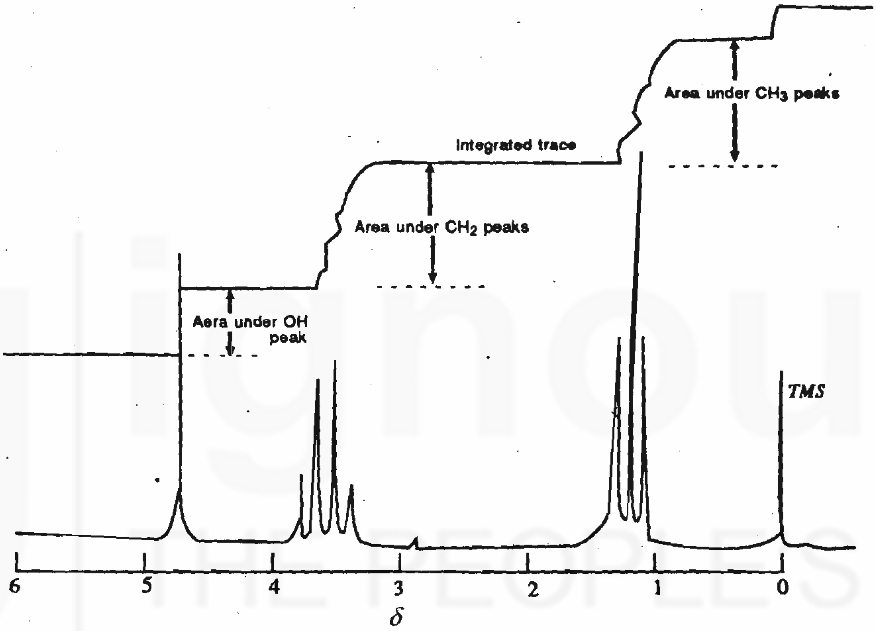
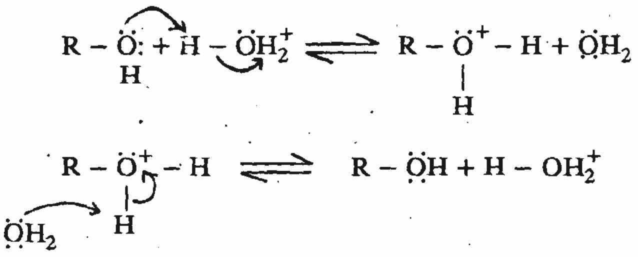


Fig. 10.13 : **The NMR spectrum of a solution of ethanol. The methyl and methylene groups are mutually coupled giving a triplet (1:2:1) and quartet (1:3:3:1) respectively, while the OH group, due to rapid exchange does not show any spin-spin coupling with neighbouring protons and no splitting of the signals is observed due to the –OH proton.**

The ^1H – NMR spectrum of ethanol was discussed in unit 4 of CHE -05 (Organic chemistry) course also..

If any atom in the molecule undergoes rapid exchange in the intra-or intermolecular way (exchange between solutes or between solvent and solute), then the coupling between the exchanging and rest of the nuclei is averaged to zero. Thus an aqueous solution of alcohol will give spin-spin coupling pattern for the methyl and methylene protons by mutual coupling, while the OH group which undergoes rapid exchange with the solvent water molecules will appear as a single line.

Chemical Exchange



$$\mathrm{R-\underset{H}{\ddot{O}}\colon + H-\ddot{O}H_2^+ \rightleftharpoons R-\underset{\stackrel{|}{H}}{\dot{O}^+}-H+\ddot{O}H_2}$$

$$\mathrm{R-\underset{\stackrel{|}{H}}{\dot{O}^+}-H \rightleftharpoons R-\ddot{O}H + H-OH_2^+}$$

$$\mathrm{\ddot{O}H_2}$$

In general, we can say that for n equivalent protons coupled to a particular set of protons, spin-spin coupling leads to splitting of the signal of this set into $(2nI + 1)$

lines with the intensities given by the coefficients of the bionominal expansion of $(x+1)^n$. For ^1H – NMR, I for a proton $= \frac{1}{2}$ leading to $2nI + 1 = 2 \times n \times \frac{1}{2} + 1 = n + 1$. Thus, in ^1H – NMR spectrum, n equivalent protons will split a signal into $n + 1$ lines. This is shown below in the form of Pascal triangle in Fig.10.14.

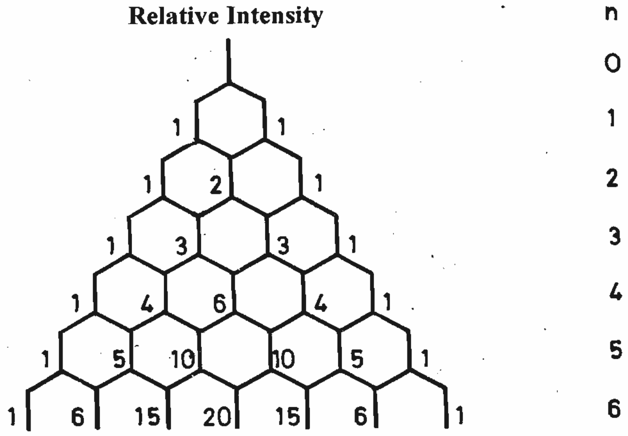
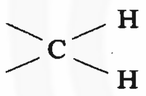
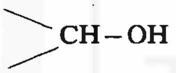
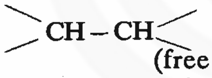
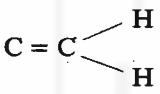
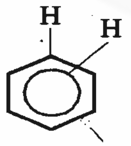
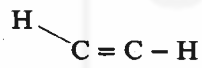
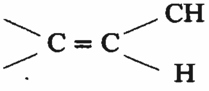
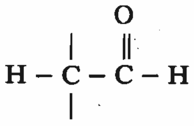
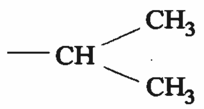
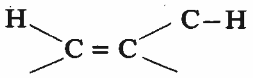


Fig. 10.14: The relative intensities of the spin-spin splitting multiplets for n coupled equivalent protons.

Spin-spin coupling patterns are also transferable between molecules. Thus whenever a molecule contains an ethyl group, the quartet-triplet pattern (as shown for ethyl alcohol) will appear in the NMR spectrum. Table 10.4 lists some characteristic spin- spin coupling constants.

Table 10.4 : Spin-spin coupling constants

Type of compound	J, (Hz)	Type of compound	J, (Hz)
	12-15		5
 (free rotation)	6-8		0-3
	(o) 8 (m) 2-3 (p) 0-1		(cis) 6-14 (trans) 11-18
	4-10	 $H-\underset{\mid}{\overset{\mid}{C}}-\overset{O}{\overset{\|}{C}}-H$	1-3
	10-13	Cyclohexane	(a-a)8-9 (a-e) 2-3 (e-e) 2-3
H–C–C≡C–H	2-3		6–7
$-CH_2-CH_3$	7		–2

SAQ 4

How many resonances will occur in the proton NMR of isopropyl chloride and what will be the nature of the spin-spin coupling ?

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$CH_3\overset{\overset{Cl}{|}}{C}HCH_3$

Isopropyl chloride

SAQ 5

An organic compound with molecular formula C_8H_{10} gives three NMR signals at 7 ppm (singlet), 2.4 ppm (quartet) and 1.2 ppm (triplet) with relative intensities 5:2:3. Identify the compound.

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10.8 FACTORS AFFECTING CHEMICAL SHIFT

(i) Electronegativity of the groups present

Let us study the NMR spectrum of 1,1,2-trichloroethane (Cl_2CHCH_2Cl) as shown in Fig. 10.15.

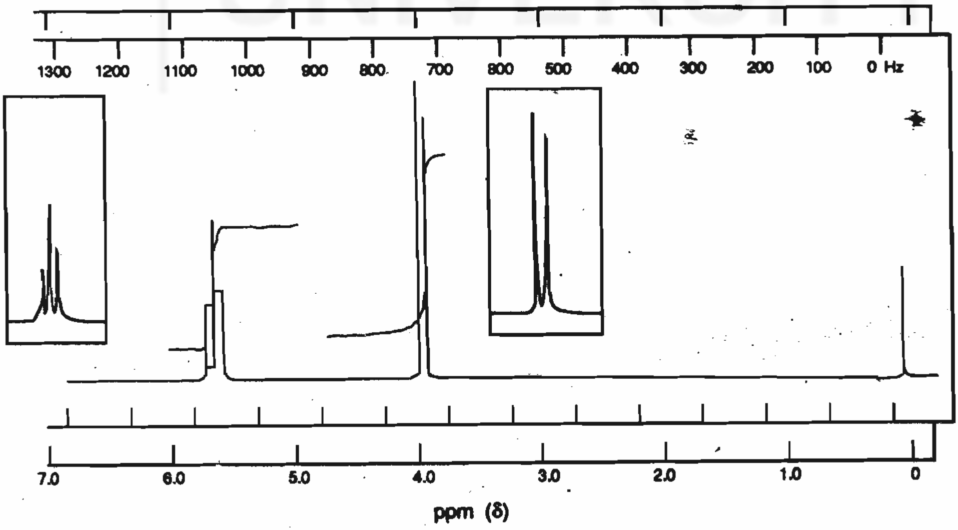


Fig. 10.15 : NMR spectrum of 1,1,2-trichloroethane.

The spectrum shows two groups of signals. The signal due to $C\underline{H}_2$ protons is of double intensity as compared to that for $C\underline{H}$ protons. The signal due to $-C\underline{H}_2$ protons is split due to the adjacent $-C\underline{H}$ proton into a doublet as per the $n + 1$ rule. Similarly, the signal due to $-C\underline{H}$ proton is split into a **triplet** due to two protons of the adjacent

$-C\underline{H}_2$ group. Also the signal due to $-C\underline{H}$ protons appears downfield as compared to the signal due to $-C\underline{H}_2$ proton because the two chlorine atoms attached to the carbon bearing this hydrogen withdraw electrons due to their inductive effect and deshield the proton to a larger extent as compared to the single chlorine atom present on the other carbon atom.

Similarly, the NMR spectrum of ethyl bromide as shown in Fig. 10.16. shows **one triplet** due to methyl protons and one **quartet** due to methylene ($-C\underline{H}_2$) protons.

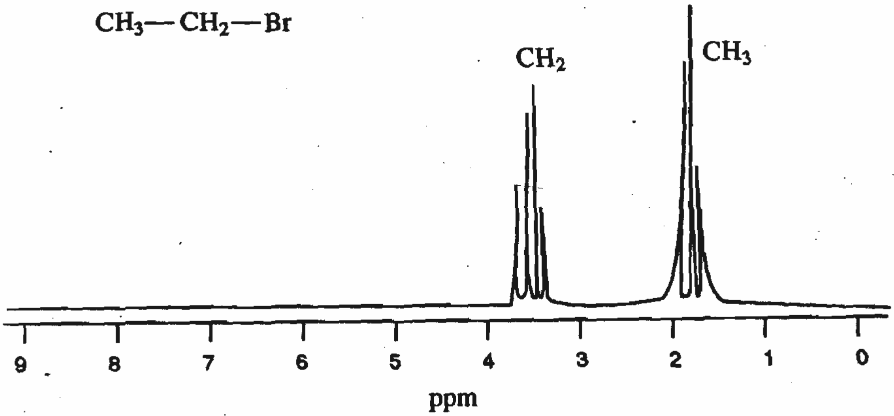


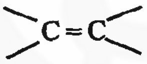
Fig. 10.16 : NMR spectrum of ethyl bromide.

In addition to the *electronegativity* of the groups, the other factor which influences the position of the chemical shift is **magnetic anisotropy.**

(ii) **Magnetic Anisotropy**

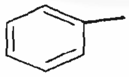
Anisotropy means difference in a property depending upon the direction. Thus, anisotropic properties have unequal value in different directions. Various functional groups present in organic molecules containing multiple bonds show this behaviour.

Various classes of organic compounds having multiple bonds are given below:

(i)  alkenes

(ii) $-C{\equiv}C-$ alkynes

(iii) $C{=}O$ carbonyl compounds

(iv)  aromatic compounds

In these molecules, the circular motion of π electrons in the presence of applied magnetic field, generates an induced magnetic field. The induced magnetic field **opposes** the applied magnetic field in the **centre** of the molecule. But it reinforces the applied magnetic field outside the region of π electrons. This is shown in Fig. 10.17.

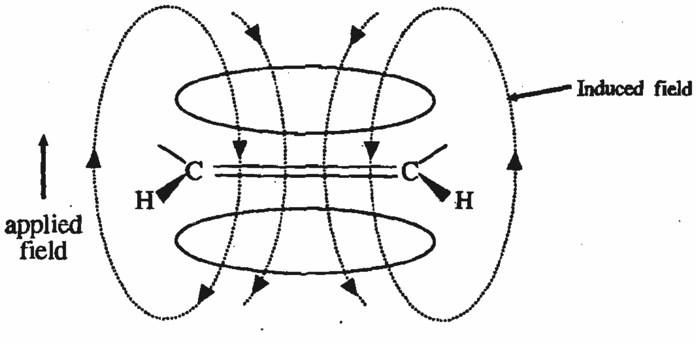
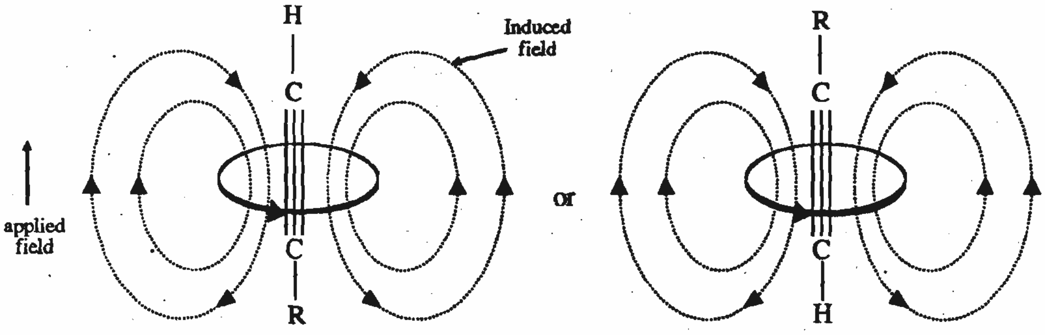


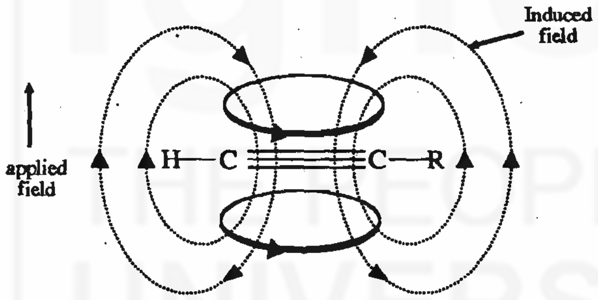
Fig. 10.17 : Direction of induced magnetic field

Thus the H atoms attached to the double bond are **deshielded** and appear downfield in the NMR spectrum at δ 4-8 ppm.

But in case of alkynes, the protons appear *upfield* because the region in which they lie has induced field **opposite** to the magnetic field, see Fig. 10.18 given below. They appear in the range δ 1.5-3.5.



Shielding of acetylenic protons by a triple bond in parallel orientation to the applied field



Shielding of acetylenic protons by a triple bond perpendicular to the applied field

Fig. 10.18: Direction of induced magnetic field in alkynes.

The aromatic protons of benzene are similar to the protons of the double bond. The direction of the induced magnetic field is shown in Fig. 10.19 for aromatic ring. The aromatic protons are deshielded and appear in the region δ 6-9.

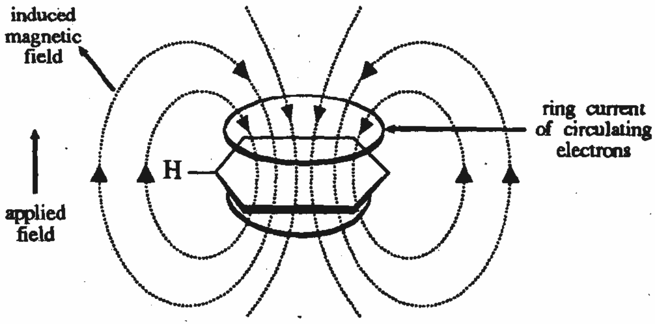


Fig. 10.19 : Effect of ring current in benzene π-system increases effective magnatic field at the proton.

10.9 SPIN DECOUPLING

It is also possible to decouple the spin-spin coupling between two groups of resonances (signals) by sweeping the spectrum while simultaneously applying a second constant frequency at the resonance position of one of the groups. This irradiation scrambles the population of various orientations leading to a net zero magnetization from this group and the spin-spin coupling to this group is decoupled. Spin decoupling can be used to identify the connectivities between groups of spins. This is shown below in Fig.10.20.

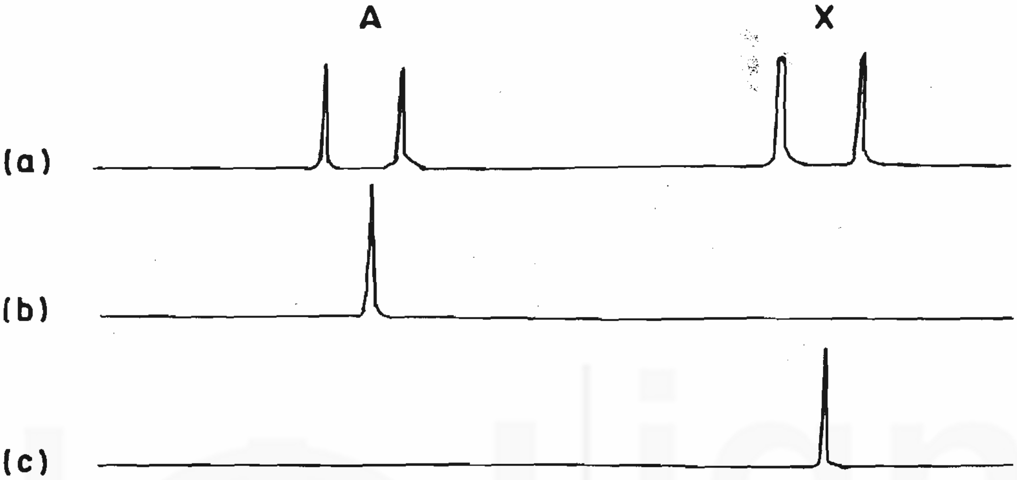


Fig. 10.20: (a) NMR spectrum of a two spin (A and X) system: both A and X showing a doublet coupling pattern. (b) When X nucleus is irradiated and the spectrum measured, resonance of A appears as a singlet since coherent irradiation at X frequency decouples it from the A nucleus. (c) When A nucleus is irradiated and the spectrum measured, X appears as a singlet.

10.10 NMR OF NUCLEI OTHER THAN PROTONS

Other nuclei such as ^{31}P, ^{19}F and ^{13}C can also be studied by NMR. Both ^{31}P and ^{19}F have $I = \frac{1}{2}$ and are 100% abundant in this state. Their spectra can be measured in the same ways as for protons. ^{31}P and ^{19}F compounds can be analysed in terms of their characteristic chemical shifts and spin-spin coupling to neighbouring nuclei.

However as far as ^{13}C is concerned, it is very difficult to obtain good spectra due to the following reasons. The natural abundance of ^{13}C is only 1.1% and the remaining ^{12}C isotope is non-magnetic. Besides, the magnetic moment is $\frac{1}{4}$ of that of a proton. It can be shown that in a given magnetic field, the sensitivity of NMR detection is proportional to the (Resonance frequency)^3 × abundance. ^{13}C spectra are approximately 1/6400 times weaker than proton spectra for identical molar concentrations, so that normal detection by field sweep or frequency sweep gives practically no spectrum. One can measure isotopically enriched ^{13}C compounds, but these are prohibitively expensive. The way to circumvent this difficulty is to resort to the practice of time domain NMR and Fourier transform techniques, which we shall very briefly and in a qualitative manner describe below.

10.11 TIME DOMAIN NMR

Normally we let the ensemble of molecules in a strong magnetic field and sweep the radio-frequency slowly, so that sequentially different chemically shifted protons are brought to resonance and we obtain the spectrum as a function of frequency. This sequential way of obtaining spectrum subjects the system to a single monochromatic radiation at a time and searching for NMR absorption. In order to obtain well resolved spectrum, we have to sweep the frequency slowly giving sufficient time for the recorder to react. Typically several minutes or even hours will be required to record one spectrum, even when the concentration of the spins are high.

However, if we subject the system to a radiofrequency "pulse" (i.e., a high power radiofrequency source is electronically pulsed-switched on and off-within a time interval of a few microseconds), it can be shown mathematically as well as in reality that this sudden "gating" of the radiofrequency can produce a wide range of spectral distribution in a single shot. By pulsing the radiofrequency transmitter, we produce and subject all nuclei, irrespective of their chemical shifts, simultaneously to a broad spectrum of frequencies leading to the so called "multichannel excitation". It is possible, therefore, to simultaneously "tip" all different chemically shifted nuclei into the x-y plane in a very short time (much less compared to spin-lattice and spin-spin relaxation). The resulting magnetization vectors will induce current simultaneously in the receiver coil which will produce a time varying signal from each and every different type of nuclei at their characteristic frequencies. The resulting induced signal known as *free induction decay* (FID) will gradually decay in a sinusoidal fashion depending on chemical shift, spin-spin coupling and spin- spin relaxation. This time-domain signal when mathematically Fourier transformed will produce the full NMR spectrum that would otherwise be obtained by the conventional way of slowly sweeping the frequency through the entire spectrum. Schematically this is shown in Fig. 10.21.

Fig. 10.21: **Schematic representation of the pulse NMR method. An intense RF pulse applied close to resonance will bring all nuclei into resonance irrespective of their chemical shifts. All these precessing magnetic moments will produce a free induction decay signal (FID) which upon Fourier transformation will produce the full spectrum which would otherwise be obtained by a slow scan of the spectrum.**

The whole process which corresponds to multichannel excitation followed by multichannel detection can be accomplished in a few seconds. This process can be repeated several hundred times and spectra coherently added to produce a good signal to noise ratio even from ^{13}C or ^{1}H at micromolar concentrations. In the pulsed Fourier transform method it can be shown that while the signal from nuclear resonances will add linearly proportional to the number of co- added spectra, the noise being a random process will only add proportional to the square root of the number of co-added spectra.

Thus if a ^{13}C spectrum has a signal to noise ratio of 1:1 (i.e., the signal cannot be distinguished from noise) after co-adding one hundred spectra we get a meaningful spectrum, of signal to noise ratio of 10. This is illustrated in Fig. 10.22.

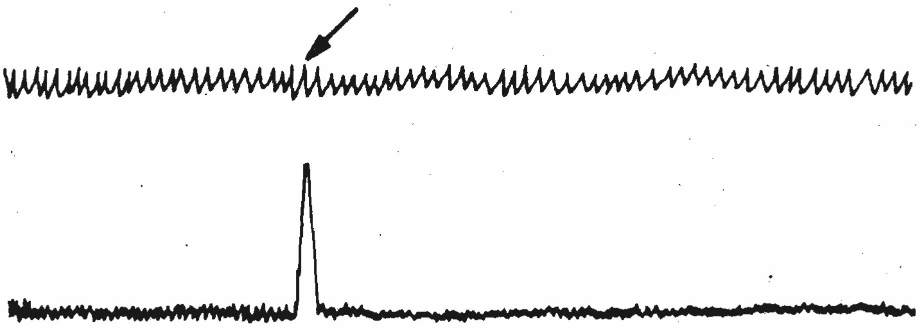


Fig.10.22: Schematic representation of the dramatic improvement in the signal to noise ratio from 1:1 (top spectrum) to nearly (10:1 when 100 spectra are co-added).

With the advent of commercially available pulse– FT spectrometers, almost all magnetic nuclei in the periodic table, irrespective of their magnetic moment and low natural abundance, are now accessible for NMR study.

Let us now study some analytical applications of NMR study.

10.12 REPRESENTATIVE EXAMPLES WITH ANALYTICAL APPLICATIONS

The NMR spectrum of B_2H_6, diborane, gives two groups of resonances for protons. The two possible structures for diborane are shown in Fig. 10.23.

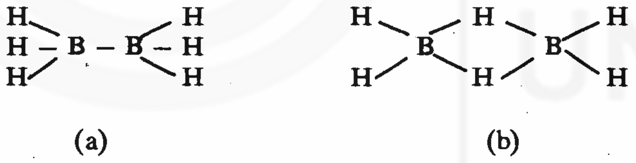


Fig. 10.23 : Two possible structures for diborane, B_2H_6. The NMR results will show that structure (b) is correct.

Structure (a) contains two equivalent BH_3 units and is expected to give a single resonance (all protons are equivalent), while structure (b) has two bridged protons and four terminal protons and is expected to give two different resonances, as observed. Hence structure (b) is supported by NMR.

The spectrum of *N, N*-dimethylnitrosoamine shows two different methyl resonances at room temperature and at high temperatures it shows only one resonance corresponding to the middle point of the room temperature spectrum. This can be understood as follows. At room temperature, there is only restricted rotation about the *N–N* bond so that statistically 50% of methyl groups are *trans* to N = O bond. Therefore, the methyl groups (a) and (b) have different chemical shifts. When free rotation sets in at high temperatures, the two methyl groups interchange rapidly between *cis* and *trans* configurations, so that on a "time average" they are identical and neither is *cis* or *trans* leading to an equivalence and a single transition, (see Fig. 10.24).

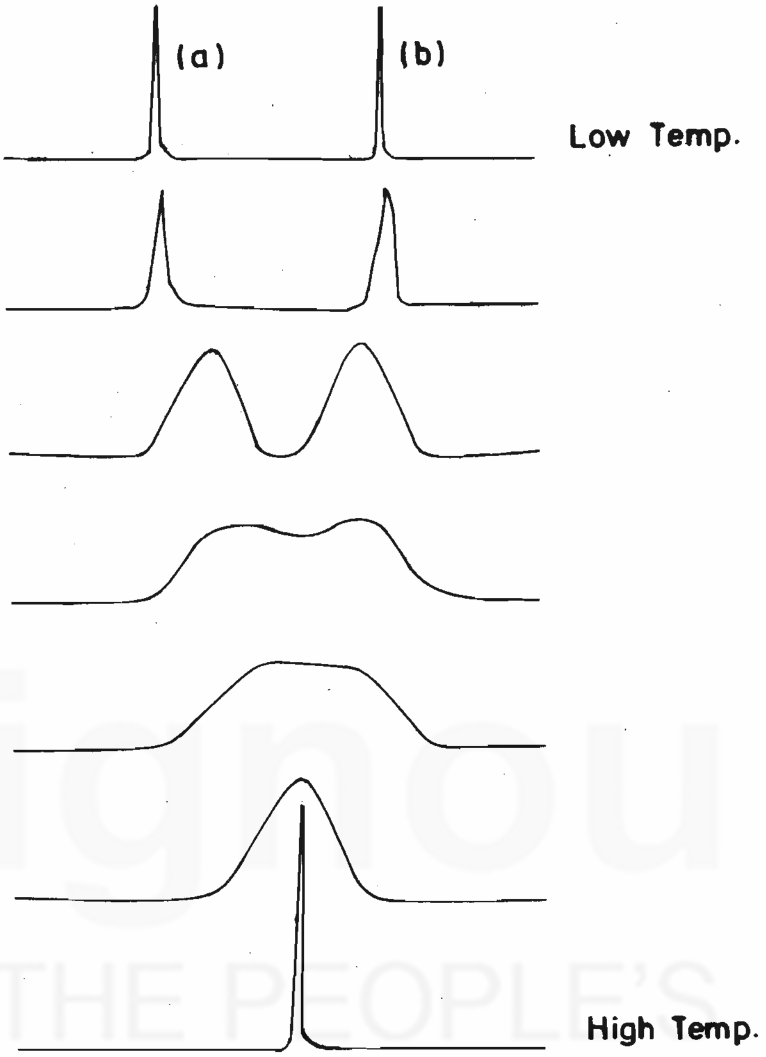
The rate of rotation of C-N bond, k is given as

$$k = \frac{1}{2\tau}$$

where τ is the mean lifetime of a particular configuration and can be measured at any temperature. The activation energy ΔE for rotation can then be calculated using the Arrhenius equation

$$\ln k = \ln A - \frac{\Delta E}{RT}$$

where A is a constant characteristic of the reaction.



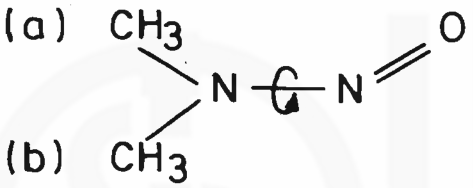


Fig. 10.24: The effect of hindered internal rotation and subsequent free rotation about the N-N bond in N, N-dimethylnitrosoamine as a function of temperature. At low temperature, the two methyl groups appear as two distinct peaks. As the rotation sets in, they undergo slow exchange leading to broadening of the lines, and when the exchange frequency is higher than the shift difference (in the static spectrum) they are no longer distinguishable.

10.13 SUMMARY

In this unit, you studied about the magnetic behaviour of common nuclei. Then the principle of NMR spectroscopy was discussed. The details of instrumentation were described followed by relaxation phenomenon. A detailed account of chemical shift and spin-spin interactions was presented. The NMR spectrum of nuclei other than hydrogen was briefly introduced. Due emphasis was given on the time domain NMR keeping in view its importance in the recent times. Finally, some examples illustrating the use of NMR spectroscopy were taken.

10.14 TERMINAL QUESTIONS

1. Predict qualitatively the NMR of propargyl bromide, $HC \equiv CH - CH_2 - Br$ if the spin-spin coupling is 2.7 Hz.
2. Predict the nature of the ^{31}P and ^{1}H spectrum of trimethyl phosphine, $(CH_3)_3P$, if the coupling between ^{31}P and ^{1}H is 8 Hz.

3. Predict the nature of the NMR spectrum for the isomers of butyl chloride, assuming coupling only between protons on adjacent carbons.

10.15 ANSWERS

Self Assessment Questions

1. $$\beta_N = \frac{e\hbar}{2m} = \frac{(1.602 \times 10^{-19}\ \text{C})\ (6.626 \times 10^{-34}\ \text{J s})}{2 \times 2\pi \times 1.672 \times 10^{-27}\ \text{kg}}$$

$$= 5.050 \times 10^{-27}\ \text{J T}^{-1}$$

2. The chemical shift $\delta = 2$ ppm

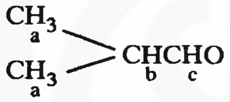
By definition

$$2 = \frac{\nu_{\text{TEST}} - \nu_{\text{TMS}}}{\text{spectrometer frequency}} \times 10^6$$

At 100 MHz

$$\Delta\nu = \frac{2 \times 100 \times 10^6}{10^6} = 200\ \text{Hz}$$

Similarly, for 200 MHz, $\Delta\nu = 400$ Hz

3. 

$$(\underset{a}{CH_3})_2\underset{b}{CH}\underset{c}{CHO}$$

4. Isopropyl chloride has the formula $(CH_3)_2\ CHCl$. The two methyl groups are identical, while the CH group is different. Therefore, there are two groups of resonances. The resonance from the two methyl groups will give a 1:1 doublet through coupling with the CH proton. The resonance of CH proton will be split into a seven line pattern (septet) whose relative intensities are 1:6:15:20:15:6:1 (refer to Fig. 10.14).

5. The peaks at δ 2.4 and δ 1.2 ppm consisting of a quartet and triplet are from an ethyl group. The peak at δ 7 ppm corresponds to protons attached to a benzene ring. From the relative intensities, if there is one ethyl group, then there is one C_6H_5 group. Together the molecule is likely to be ethyl benzene. If it is so, the molecular formula is $C_6H_5CH_2CH_3 = C_8H_{10}$. Hence, the compound is ethyl benzene.

Terminal Questions

1. Propargyl bromide contains two types of protons. The $\equiv C\underline{H}$ protons are like in acetylene and will occur at δ 2.2 ppm and the $-C\underline{H_2}\,Br$ protons will occur around δ 3.68 ppm. The $C\underline{H_2}$ resonance will occur as a doublet (1:1) and the CH resonance as a triplet (1:2:1). The splitting between the doublet and triplet is 2.7 Hz.

2. The ^1H–NMR spectrum will give a resonance corresponding to a single chemical shift due to all three equivalent methyl groups, split into a doublet with a spacing of 8 Hz due to P, with intensities 1:1.

The ^{31}P spectrum will give a resonance corresponding to chemical shift of ^{31}P split into 10 lines from 9 equivalent protons of methyls with intensity distribution given by 1:9:36:84:126:126:84:36:9:1.

3. Normal butyl chloride, $CH_3 - CH_2 - CH_2 - CH_2 - Cl$ will give four resonances. The methyl group will give triplet (from adjacent $-CH_2$, the next methylene will be a triplet of quartet (4 × 3), the next methylene will be a triplet of triplet (3× 3), and the last methylene adjacent to Cl will give a triplet.

Isobutyl chloride will give a single resonance from two equivalent methyls, split into a doublet (CH), the CH group will give a resonance split into a septet of triplets (7 × 3) and the last CH_2 group will give a doublet.

Tertiary butyl chloride, $(CH_3)_3 - C - Cl$, will give a single line from three equivalent methyls and there will be no spin-spin coupling.