Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear magnetic resonance (NMR) is a spectroscopic technique that detects the energy absorbed due to changes in the nuclear spin state. Physical chemists originally developed NMR spectroscopy to study the different properties of atomic nuclei in the late 1940's. It was however, used for structure elucidation of organic compounds 1951 onwards based on the property of nuclear spin.

NMR spectroscopy reveals information about the number and types of protons and carbons (and also other elements like nitrogen, fluorine etc.) present in the molecule. The phenomenon of NMR spectroscopy is similar to that of visible spectroscopy. In visible spectroscopy the absorption of a photon by an electron causes the electron to move from its ground state orbital to a higher energy level orbital in the excited state while in NMR, the absorption of radio-frequency photon promotes a nuclear spin from its ground state to its excited state.

Inspite of having some similarity of NMR spectroscopy with other form of spectroscopy, it differs from other form of spectroscopy in some respect as well. Firstly, an external magnetic field is required for the generation of the ground and excited NMR states while in case of other spectroscopic phenomenon no such magnetic field is required. This requirement is a very important distinction of NMR spectroscopy in sense that it allows the change in characteristic frequencies of the transitions by simply changing the applied magnetic field strength. Secondly, the lifetime of excited state in NMR is about 10^9 times longer than the lifetime of the excited electronic states.

Nuclear Spin Transitions

In all forms of spectroscopy it is necessary to have two or more different states of the system that differ in energy. In a system with two energy levels, the one of lower energy is often referred to as the ground state and the higher energy state is the excited state. In the case of nuclear magnetic resonance spectroscopy, the energies of the states arise from the interaction of a nuclear magnetic dipole moment with an intense external magnetic field. Excitation of transitions between these states is stimulated using radio-frequency (rf) electromagnetic radiation.

Nucleus of hydrogen (proton) behaves as a tiny spinning magnet bar. It possesses both electric charge and mechanical spin. As any spinning charged body will generate a magnetic field, so the nucleus of hydrogen also generates it own magnetic field.

In presence of an external magnetic field, protons respond to the influence of the external magnetic field and tend to align itself with that field.

Proton adopts two orientations with respect to an external field:

Aligned with field or parallel (lower energy state),

Opposed to the field or anti-parallel (higher energy state).

The number of allowed orientations is given by (2*I* + 1), where I is spin quantum number of the nucleus.

In the absence of magnetic field, the two spin states are of equal energy or degenerate. When placed in an external magnetic field, a proton’s spin, and the associated magnetic field can align either with or against the external field. The splitting of the spin states in presence of magnetic field is shown in **figure 4.1**.

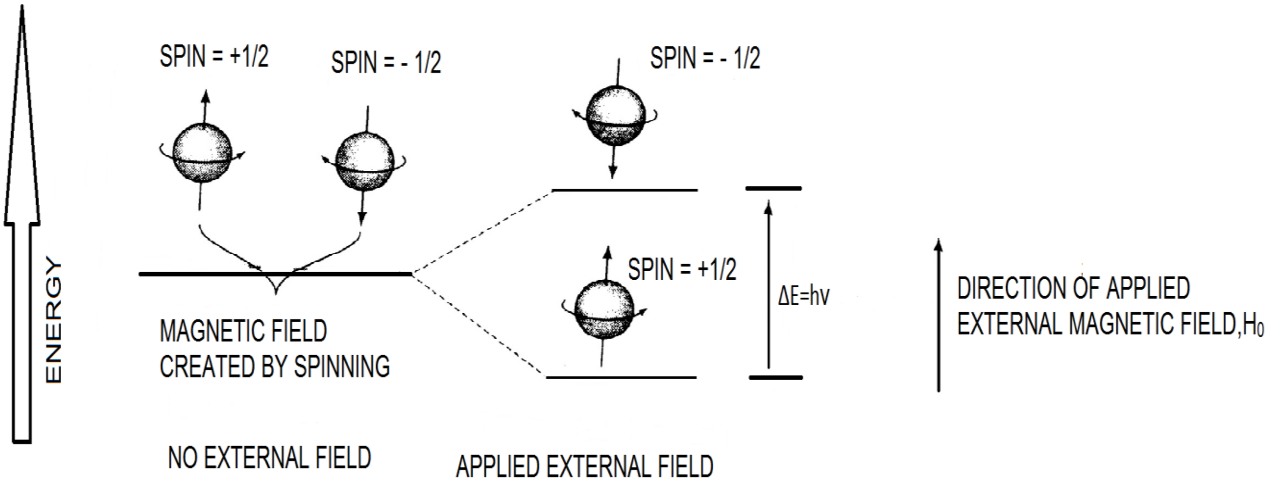
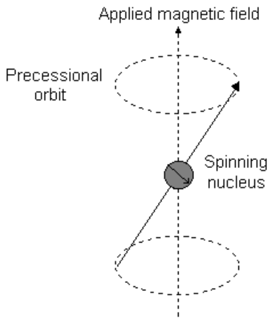


Fig 4.1 The splitting of the spin states in presence of magnetic field

If a proton is precessing in the *aligned* orientation, It can absorb the energy and pass into the *opposed* orientation which subsequently losses the energy and relax back to aligned position. If we irradiate the precessing nuclei with a beam of rf energy of the correct frequency, the low energy nuclei may absorb energy and move to a higher energy state. The precessing nuclei will only absorb energy if the frequency of the Rf beam matches the precessional frequency; when this occurs, the nucleus and the Rf beam are said to be in *resonance*; hence the term ***Nuclear Magnetic resonance.***

Theory

When a magnetic field is applied, the nucleus (proton) begins to precess about its own axis of spin with angular frequency ω (which is sometimes called its **Larmor frequency)**. As the nucleus has a charge it behaves as a tiny spinning magnet bar and its precession generates an oscillating electric field of the same frequency. If radiofrequency waves of this frequency are supplied to the precessing proton, the energy can be absorbed. That is, when the frequency of the supplied radiofrequency waves just matches the frequency of the electric field generated by the precessing nucleus, the two fields may couple and energy may be transferred from the supplied radiofrequency waves to the nucleus, thus causing a spin change. If a proton is precessing in the *aligned* orientation (lower energy state), it can absorb the energy and pass into the *opposed* orientation (higher energy state) which subsequently losses the energy and relax back to aligned position. The emitted energy in this region produces an NMR signal.



This condition at which the frequency of the supplied radiofrequency waves just matches the frequency of the magnetic field generated by the precessing nucleus is called resonance, and the nucleus is said to be in resonance with the incoming electromagnetic wave.

Expression for precessional frequency

Nuclear spin magnetic moment for simplest nucleus can be expressed as

$$\mu_N = \text{nuclear angular momentum} \times g_N\, e/\,2m_p \quad \ldots\ldots\ldots (4.1)$$

Here g_N is the magnetogyric ratio for nuclear spin (also called nuclear g-factor) and m_p is the mass of the proton. For protons the value of g_N is **5.585**.

Again, the nuclear angular momentum can be given as $[I(I+1)]^{1/2}\,h/2\pi$.

Thus, equation (4.1) can be written as

$$\mu_N = [I(I+1)]^{1/2}\,h/2\pi \times g_N\,e/2m_p \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(4.2)$$

If we put $\beta_N = eh/4\pi m_p$

where β_N is a constant, known as the nuclear magneton and for protons, its value in SI units is **5.051 X 10^{-27} JT^{-1}**.

Equation (4.2) can be written as

$$\mu_N = [I(I+1)]^{1/2}\,g_N\,\beta_N$$

The components of the nuclear magnetic moment in the direction of the field (z-direction) are given by

$$\mu_{mI} = g_N\,\beta_N\,m_I \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.3)$$

which will have (2I+1) orientations in space, ranging the values of m_I from –I - - - - 0 - - - - - +I.

Here m_I is spin quantum number.

If we consider that the nucleus is placed in a homogeneous external magnetic field of flux density B_0 , then there will be an interaction between the nuclear magnetic moment and the applied field strength.

The potential energy V due to the interaction of the nucleus with the magnetic field (B_0) is given as

$$V = -\mu_{mI}\,B_0 \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.4)$$

Combining (4.3) and (4.4), we get

$$V = -g_N\,\beta_N\,m_I\,B_0 \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.5)$$

Thus from equation (4.5), it is evident that

V will increase with increase of B_0 for a negative value of m_I

V will decrease with increase of B_0 for a positive value of m_I

V will remain unchanged for $m_I = 0$

For protons, we have $m_I = \pm ½$

For $m_I = + ½$, $V_{1/2} = - ½ g_N \beta_N B_0$

For $m_I = - ½$, $V_{-1/2} = ½ g_N \beta_N B_0$

The energy difference between the two levels is given by

$$\Delta E = V_{-1/2} - V_{1/2} = g_N \beta_N B_0$$

or, $$hv_0 = g_N \beta_N B_0$$

or, $$v_0 = g_N \beta_N B_0 / h \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.6)$$

Equation (4.6) can be used determine the precessional frequency of radiation required for the transition between two levels.

In terms of angular frequency, the energy difference between two levels can be expressed as

$$\omega_0 = 2\pi v_0$$
$$= 2\pi g_N \beta_N B_0 / h$$
$$= \gamma B_0$$

Here $\gamma = 2\pi g_N \beta_N / h$, is called the magnetogyric ratio.

Problem 4.1: Find the energy difference between the two spin states of a proton.

Problem 4.2: A proton NMR spectrometer operates with a radiation of frequency 100 MHz. Find at what magnetic field, a free proton will show resonance given that the values of nuclear magneton and nuclear g factor are 5.05×10^{-27} JT^{-1} and 5.585 respectively. [**GU 2016**]

Solution

Here, frequency, $v_0 = 100 \times 10^6 \ s^{-1}$

$g_N = 5.585$

$\beta_N = 5.051 \times 10^{-27}\ JT^{-1}$

$B_0 = ?$

We know, $B_0 = h\ v_0 / g_N\ \beta_N$

$= 6.627 \times 10^{-34}\ Js \times 100 \times 10^{6}\ s^{-1} / 5.585 \times 5.051 \times 10^{-27}\ JT^{-1}$

$= 2.349\ T$

Problem 4.3: Calculate the precessional frequency of a proton in a magnetic field strength of 2.349 T.

Solution

Here, $g_N = 5.585$

$\beta_N = 5.051 \times 10^{-27}\ JT^{-1}$

$B_0 = 2.349\ T$

Frequency, $v_0 = ?$

We know, $v_0 = g_N\ \beta_N B_0 / h$

$= 2.349\ T \times 5.585 \times 5.051 \times 10^{-27}\ JT^{-1} / 6.627 \times 10^{-34}\ Js$

$= 99.9 \times 10^{6}\ s^{-1}$

Problem 4.4: Calculate the magnetogyric ratio of a proton.

Solution

Here, $g_N = 5.585$

$\beta_N = 5.051 \times 10^{-27}\ JT^{-1}$

We know, $\gamma = 2\pi\ g_N\ \beta_N / h$

$$= 2 \times 3.14 \times 5.585 \times 5.051 \times 10^{-27}\ JT^{-1} / 6.627 \times 10^{-34}\ Js$$

$$= 2.673 \times 10^{8}\ T^{-1}\ s^{-1}$$

NMR Active and Inactive Nuclei

Nucleus for which the nuclear spin quantum number, I = 0 are NMR inactive, while other nuclei are NMR active.

The following rules may be used to find the nuclear spin of nuclei:

(i) **Zero nuclear spin:**

For the nuclei having both numbers of protons (p) and neutrons (n) even. Even number of p and n gives even charge and mass. eg ^{4}He,^{12}C,^{16}O etc.

(ii) **Intregral nuclear spin:**

For the nuclei having both numbers of protons (p) and neutrons (n) odd. Odd number of p and n gives odd charge but even mass (p+n). eg ^{2}H (I = 1),^{14}N (I = 1), ^{10}B (I = 3) etc.

(iii) **Half Intregral nuclear spin:**

For the nuclei having odd mass. eg ^{1}H (I = ½),^{15}N (I = ½), ^{17}O (I = 5/2) etc.

Problem 4.5: Predict which of the following nuclei are NMR active: ^{1}H, ^{2}H, ^{12}C, ^{14}N, ^{16}O and ^{19}F.

Solution

I = 0 for ^{12}C and ^{16}O, so they are NMR inactive, except ^{12}C and ^{16}O, all are NMR active.

Instrumentation

The instrument contains a radio frequency transmitter to transmit the radio frequency. The sample under study is placed in a spinning tube, which is placed between two magnet poles. Two sweep coils are placed between the spinning tube and the magnets. The sweep coils are fitted with a sweep generator. The radio frequency transmitter transmits radio frequency which passes through the sample under observation and is then received in radio frequency receiver and amplifier. Finally, it is recorded in the control console and recorder. The block diagram of NMR spectrometer is shown in **figure 4.2**.

The basic requirements of a typical NMR spectrometer are:

i. **Electromagnet**: A powerful electromagnet provides a homogeneous and stable magnetic field. It should be constant over the area of the sample and during the period of the experiment.

ii. **Sweep Generator** : It supplies variable current to a secondary magnet. As a result the total applied magnetic field can be varied over a small range.

iii. **Sample Tube**: A sample tube is usually made of glass. It is the tube which contains the sample under investigation. The sample tube is rotated by an air-driven turbine which provides homogeneous magnetic field to the sample under investigation.

iv. **Radio-frequency Transmitter**: A radio frequency transmitter transmits desired energy to the sample.

v. **Radio-frequency Receiver & Amplifier**: A radio frequency receiver receives the signals coming from the sample. It also amplifies the signal.

vi. **Control Console and Recorder**: It is a read out system. It records the signal coming from the receiver. It also increases the sensitivity and resolution. It plots the output results in the form of spectrum.

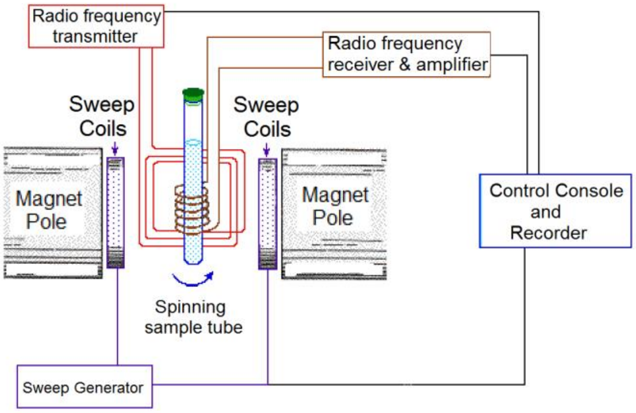


Fig 4.2. Block diagram of NMR Spectrometer

Solvents in NMR

For ^1H NMR spectroscopy, the solvent must be free from Proton (H). Common solvent for ^1H NMR spectroscopy is CCl_4,$CDCl_3$ etc.

Generally, deuterated solvents are used in NMR spectroscopy. The main reasons for using deuterated solvents are

i) During analysis much more solvent is used than the substance of interest in the sample to be investigated, if proton (H) is present in the solvent then its absorption will be more than the sample itself, so, NMR spectra will not give much information about the sample.

ii) Modern NMR spectrometers measure the deuterium absorption of the solvent to stabilize the magnetic field strength. As the observation frequency is field dependent, the deuterium receiver notices a field fluctuation through a change of the observation frequency and can correct the field strength correspondingly.

Shielding and Deshielding

Shielding effects

Under an applied magnetic field, circulating electrons in the electron cloud produce a small opposing magnetic field, ultimately decreasing the effective magnetic field felt by the proton, shifting the signal to the right (or *upfield*). This effect, in which the electron cloud "shields" the proton from the applied magnetic field is called *shielding effect.* The shielding and deshielding effects are shown in **figure 4.3**.

The higher the electron density around the nucleus, the higher the opposing magnetic field to B_0 from the electrons, the greater the shielding. Because the proton experiences lower external magnetic field, it needs a lower frequency to achieve resonance, and therefore, the chemical shift shifts **upfield (lower ppms)** .

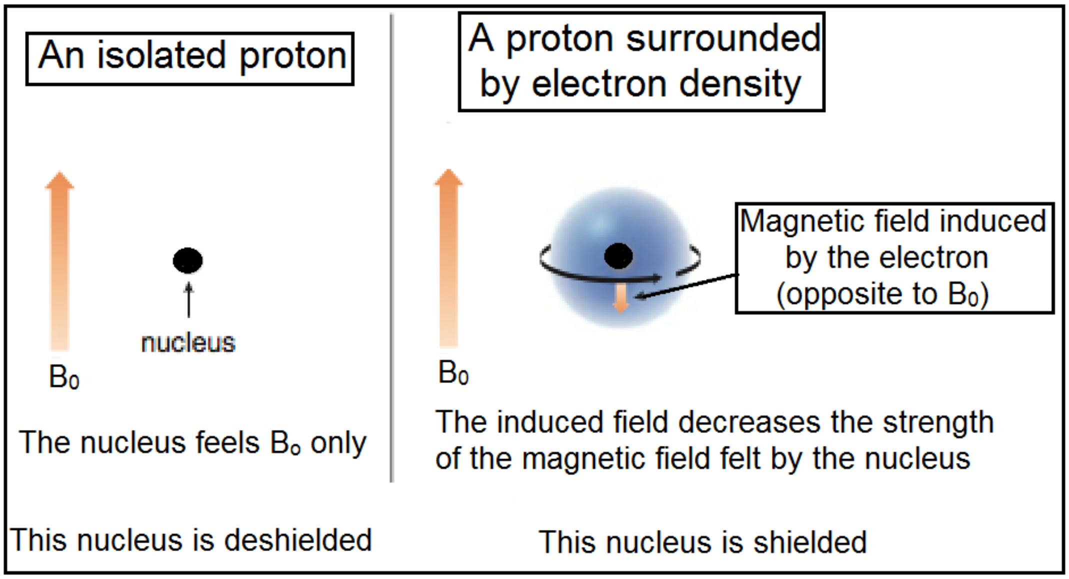


Fig.4.3 Shielding and deshielding effects

Deshielding Effect

If the electron density around a proton decreases, the opposing magnetic field becomes small and therefore, the proton feels more external magnetic field B_0, such type of proton is known as deshielded and the effect is known as *deshielding effect*. As the proton experiences higher external magnetic field, it needs a higher frequency to achieve resonance, and therefore, the chemical shift, shifts **downfield (higher ppms)**.

Protons (H's) that are attached to more electronegative atoms experience higher chemical shifts. Electronegative atoms also remove electrons from the electron cloud, which decreases their density and results in less shielding; hence electronegative atoms are said to *deshield* the proton and cause it to have a higher chemical shift, moving it to the left (or *downfield*). The *magnitude of the deshielding* effect, however, rapidly decreases as the distance between the proton and electronegative atom increases.

If we compare the chemical shift of CH_4 protons and CH_3Cl protons, it is seen that the peak for CH_3Cl protons appear downfield in comparison to CH_4 protons. In case of CH_3Cl, Cl atom being an electronegative atom pull the electron density toward it (**electron withdrawing**), resulting in a deshielding of the hydrogen nucleus; as a result the H atom feel higher external magnetic field B_0, which increases the resonance frequency and therefore shifting the peak to higher ppms. Chemical shift due to deshielding effect is shown in **figure 4.4**. Hydrogen nucleus is shielded in the case of CH_4 and therefore, the peak appears on the lower ppm side.

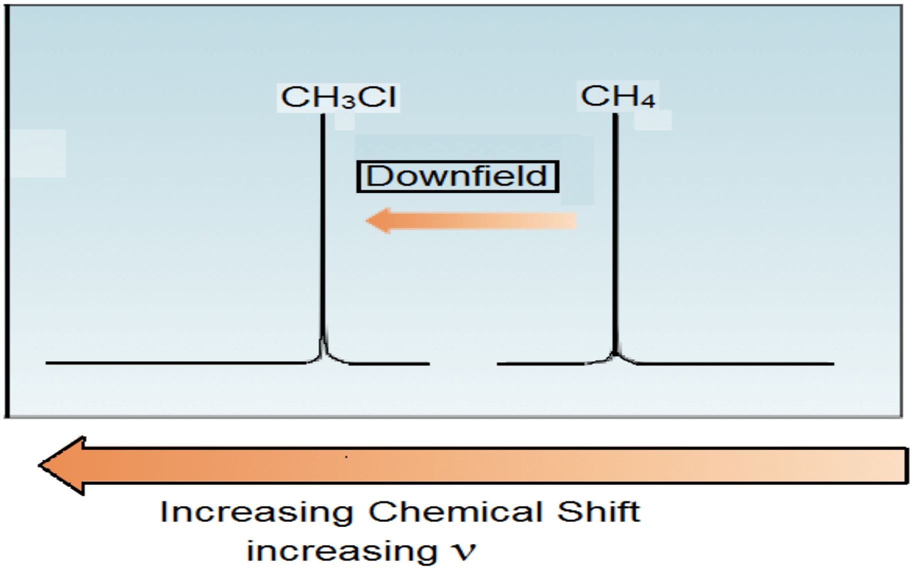


Fig. 4.4 Chemical shift due to deshielding effect

NMR signal

The NMR Spectrum is a plot of the intensity of NMR signals versus the magnetic field (frequency) in reference to Tetra Methyl Silane (TMS) (shown in **figure 4.5**). The intensity is measured by the integration of the area under the triangles.

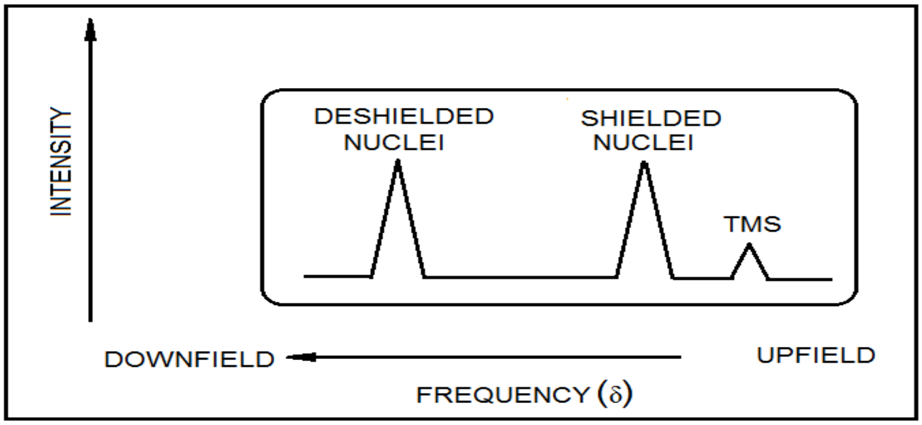


Fig.4.5 Representation of NMR spectrum

Reference compound

Tetra Methyl Silane (TMS) {$(CH_3)_4Si$} is usually used as the reference compound in NMR spectroscopy because

(i) It can easily be removed from the sample by evaporation due to its volatile properties.

(ii) Its resonance peak occurs at a higher field than almost all organic protons because its methyl protons are in a more electron dense environment than most other protons. This is so because silicon is less electronegative than carbon.

(iii) It dissolves without reaction in most organic solvents and hence can be readily recovered from most samples after use.

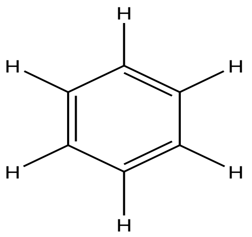
(iv) It gives single sharp absorption peak as its 12 protons are in the same chemical environment.

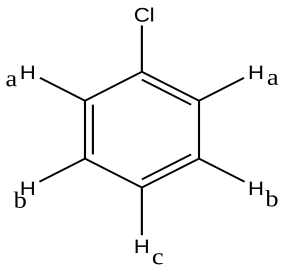
Problem 4.6: Explain why tetra methyl silane is used as reference in ^{1}H-NMR spectroscopy. [**GU 2016**]

Equivalent and Non-Equivalent Protons

Chemically equivalent protons are those protons which reside in the same magnetic environment. This type of protons absorb in the same δ value at a certain applied field strength i.e they give only one signal.

On the other hand, chemically non-equivalent protons are those protons which reside in different magnetic environment. This type of protons absorb in different δ value at a certain applied field strength i.e they give more than one signal, depending on the number of protons.

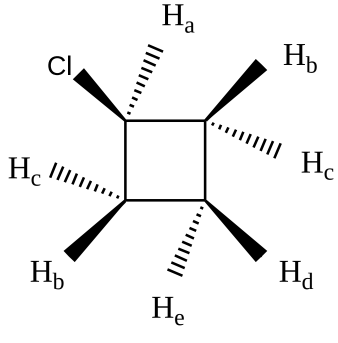




In benzene all the protons (H s) are in same chemical environment, so, they are termed as equivalent protons and they show only one signal in NMR spectra.

On the other hand, in chlorobenzene, there are three different sets of protons, a, b and c. Here, the two protons H_a are equivalent. Similarly the two protons H_b are also equivalent. But H_a, H_b and H_c are non-equivalent. So, it will give three signals in NMR spectra.

One question always comes to our mind, whether the protons on the same carbon are always equivalent. The answer of this question is simply no. Usually, protons on the



same carbon are equivalent. But, sometimes, they may not be equivalent because they are not in the same environment. One proton may be trans and the other proton may be cis. Under that condition, they will create two different signals.

Although in chlorocyclobutane, it seems to give three signals, but the NMR study of this compound actually shows five signals. Here ,H_b and H_c are not equivalent because H_b is cis to Cl while H_c is trans to Cl. Again, H_d and H_e are not equivalent because H_e is trans to Cl while H_d is cis to Cl. So, in chlorocyclobutane , there are five different types of protons, H_a, H_b, H_c, H_d and H_e, which will show five signals.

Following some simple rules, we can determine the sets of equivalent protons in a molecule. For example,

Firstly, protons that are aligned on a line of symmetry are equivalent.

Secondly, if the two molecules formed by replacing two protons with deuterium are same, then the two protons are equivalent.

Thirdly, if the environment around two sets of proton are same, then they are said to be equivalent and if the environment around two sets of proton are not same i.e some heteroatom is present, then they are said to be non-equivalent.

Splitting of the NMR signal at high resolution (n+1 rule)

In the high resolution the splitting of the NMR signal for a particular proton depends on the number of neighboring H atoms present. If there is no any H atom near the H atom under consideration, the NMR signal will be a single line, known as singlet. If there is one H atom near the H atom under consideration, the NMR signal will split into two lines in the ratio 1:1, known as doublet. So, as a general rule, we can say that if there are n numbers of H atom near the H atom under consideration, the NMR signal will split into (n+1) lines. So, this rule is often known as *(n+1) rule*.

Splitting of the NMR signals in high resolution is given by Pascal's triangle (shown in **table 4.1**).

Table 4.1 Pascal’s triangle showing the splitting of the NMR signals in high resolution

PASCAL’S TRIANGLE		
Number of Neighboring H’s	Relative Intensities of splitted peaks	Name of Multiplet
0	1	Singlet
1	1 1	Doublet
2	1 2 1	Triplet
3	1 3 3 1	Quartet
4	1 4 6 4 1	Quintet
5	1 5 10 10 5 1	Sextet
6	1 6 15 20 15 6 1	Septet

Chemical Shift

Chemical shift may be defined as the shift in the position of NMR absorptions of a particular proton in a molecule with respect to the signal of reference compound (TMS).

The knowledge of chemical shift helps one to know about the electron density around a proton. When a H nucleus is surrounded by high electron density, the proton experiences a lower magnetic field due to shielding effect. So, in order to bring the proton to resonance, the magnetic flux density must overcome this shielding effect and as a result a lesser δ value (upfield) results.

There are several factors on which chemical shifts depends

(i) Electronegativity

Greater the electronegativity of the atom (X) near the proton to be investigated, greater is the chemical shift for the proton.

Thus, for the following molecules the δ values are

Molecule:	CH_3I	CH_3Br	CH_3Cl	CH_3F
δ value:	2.16	2.68	3.05	4.26

Since the electronegativity of the halogens is in the order I < Br < Cl < F, so, shielding effect of the protons in the compounds follows the order $CH_3I > CH_3Br > CH_3Cl > CH_3F$, hence the order of δ values follows.

As these effects are transmitted through a chain, so, chemical shift decreases with increase in chain length.

(ii) Hydrogen Bonding

The hydrogen bonded proton being attached to a highly electronegative atom, is less shielded and the field felt by such a proton is more. As a result, resonance occur downfield (higher δ value). Downfield shift depends upon the strength of H-bonding.

Intermolecular H-bonding show a downfield shift of absorption, while intramolecular H-bonding does not show any shift in absorption.

(iii) Anisotropic effect

When a magnetic is applied to a molecule containing π electrons, then these electrons begin to circulate perpendicularly to the direction of the applied field, which results in the production of induced magnetic field. The effect of this induced magnetic field on nearby proton depends upon the orientation of the proton with respect to the π electrons that produces the induced magnetic field.

The induced magnetic field opposes the applied field (shielding), in case of C_2H_2 and hence resonance occurs upfield (lower δ value). On the other hand, in case of alkenes and aromatic hydrocarbons, the induced magnetic field reinforces the applied field (deshielding) and hence resonance occurs downfield (higher δ value).

Problem 4.7: The order of electronegativity in halogens is I < Br < Cl < F and proton NMR signals in CH_3X (X= I,Br,Cl, F) are

CH_3F	CH_3Cl	CH_3Br	CH_3I
4.26 δ	3.0 δ	2.82 δ	2.16 δ

Explain the trend in NMR signals. [**GU 2015**]

NMR Scale

Chemical shifts of NMR spectra are expressed in two scales –

δ – scale: In this scale the signal for TMS is taken at δ value 0 (zero) and it increases downfield.

ζ – scale: In this scale the signal for TMS is taken at ζ value 10 and it decreases downfield.

The relation between the two scales can be given as

$$\zeta = 10 - \delta$$

Expression for chemical Shift

The expression for the precessional frequency of radiation, when shielding effects are included may be given as

$$v = g_N \beta_N (1-\delta) B_0 / h \quad \text{--------------------------} \quad (4.7)$$

where δ is the shielding constant

Again the magnetogyric ratio can be given as

$$\gamma = 2\pi g_N \beta_N / h \quad \text{--------------------------------} \; (4.8)$$

Combining (4.7) and (4.8), we can write

$v = (1-\delta)\ \gamma\ B_0 / 2\pi$ ------------------------- (4.9)

Since the above expression for frequency contains the shielding constant (δ), so different nuclei will come into resonance at different frequencies. If we consider, two different proton in different chemical environments with their shielding constants δ_1 and $\delta_{2,}$ then their frequencies can be given as

For proton 1, $v_1 = (1-\delta_1)\ \gamma\ B_0 / 2\pi$

And for proton 2, $v_2 = (1-\delta_2)\ \gamma\ B_0 / 2\pi$

Thus,

$v_2 - v_1 = (\delta_1-\delta_2)\ \gamma\ B_0 / 2\pi$ -------------------------------- (4.10)

If v_0 is the frequency of the operating spectrometer, then dividing the equation (4.10) by v_0, we get,

$v_2 - v_1/ v_0 = (\delta_1-\delta_2)\ \gamma\ B_0 / 2\pi\ v_0$ --------- (4.11)

since v_0 is measured in MHz and v_1 and v_2 are measured in Hz, so, a conversion factor of 10^6 will have to be introduced in equation (4.11). Hence, the equation can be written as

$(v_2 - v_1) X\ 10^6/ v_0 = (\delta_1-\delta_2)\ \gamma\ B_0\ X\ 10^6 /2\pi\ v_0$ --------- (4.12)

The quantity on the left hand side of equation (4.12) i.e. $(v_2 - v_1) X\ 10^6/ v_0$, is also called the chemical shift of proton 1 (δ_H) with respect to proton 2 and can be written as

$\delta_H = (v_2 - v_1) X\ 10^6/ v_0$ ----------------------- (4.13)

Thus, equation (4.12) can also be written as

$$\delta_H = (\delta_1 - \delta_2)\ \gamma\ B_0 \times 10^6 / 2\pi\ v_0$$

If v_2 is the resonance frequency of the sample under investigation i.e. $v_2 = v_s$ and v_1 is the frequency of the reference compound i.e. $v_1 = v_{TMS}$, then equation (4.13) can be written as

$$\delta_H = (v_s - v_{TMS}) \times 10^6 / v_0 \quad \text{ppm}$$

Thus chemical shift for a proton can be calculated by using the above equation.

Problem 4.8: The protons of benzene give a signal at frequency 510.5 Hz, when analyzed in a spectrometer having magnetic field 1.65 T. Calculate the chemical shift.

(Given $g_N = 5.585$, $\beta_N = 5.0508 \times 10^{-27}\ JT^{-1}$)

Solution

Here, $g_N = 5.585$

$\beta_N = 5.0508 \times 10^{-27}\ JT^{-1}$

$B_0 = 1.65\ T$

$v_s = 510.5\ Hz$

$v_{TMS} = 0\ Hz$

We know,

$$v_0 = g_N\ \beta_N\ B_0 / h$$

$$= 5.585 \times 5.0508 \times 10^{-27}\ JT^{-1} \times 1.65\ T / 6.626 \times 10^{-34}\ Js$$

$= 7.02 \text{ X } 10^7$ Hz

Again,

$\delta_H = (v_s - v_{TMS}) \text{X } 10^6 / v_0$ ppm

$= (510.5 \text{ Hz} - 0 \text{ Hz}) \text{ X } 10^6 / 7.02 \text{ X } 10^7 \text{ Hz}$ ppm

$= 7.27$ ppm

Thus, the chemical shift of the proton is 7.27 ppm.

Unit of Chemical Shift

Chemical shift (δ) is calculated using the relation

$$\delta = (v_s - v_{TMS}) \text{X } 10^6 / v_0$$

Here, v_s is the absolute resonance frequency of the sample and

v_{TMS} is the absolute resonance frequency of Tetra Methyl Silane (TMS) (reference compound).

Chemical shift (δ) is usually expressed in **parts per million** (ppm).

Coupling Constant

If there is no any neighbouring proton, near a proton under consideration, then NMR signals will be a single peak. But it is not seen usually because in organic compounds, there are protons around a proton under consideration that can couple with it, resulting in the splitting of the peak. Depending on the number of neighbouring protons, a peak splits into a doublets (2 peaks), triplets (3 peaks), quartets (4 peaks), etc.

The distance between the splitted peaks are called coupling constants. It is usually denoted by J_{ab} (shown in **figure 4.6**). Here, a and b denotes the type of proton (H_a and H_b) that are coupled.

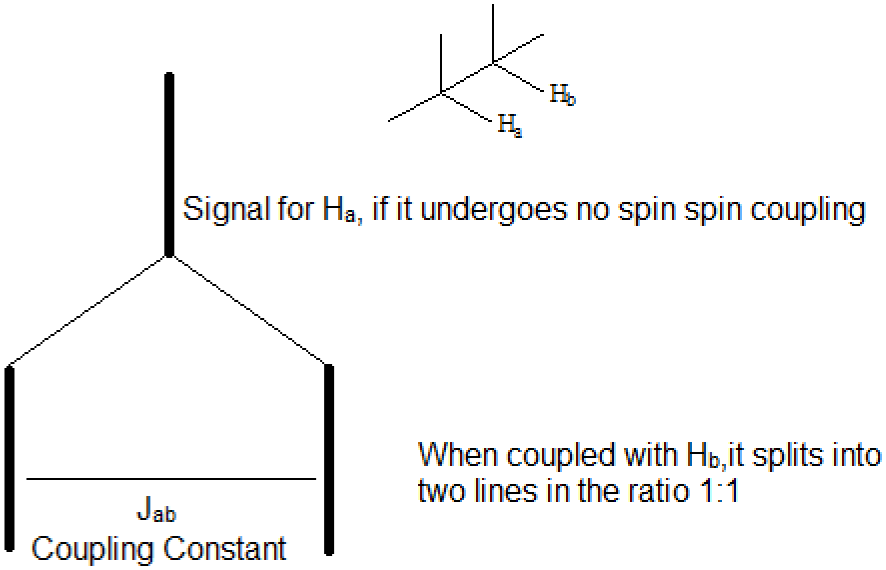


Fig. 4.6 Splitting of peaks due to spin-spin coupling

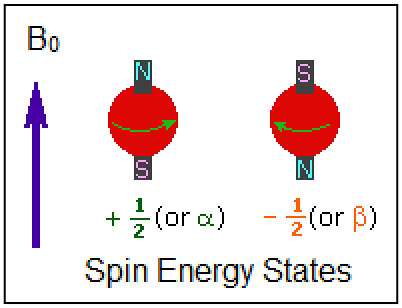
The magnitude of the coupling constant depends on the number and type of bonds that connect the coupled protons, as well as the geometric relationship among the protons. On the other hand it is independent of the operating frequency of the spectrometer i.e the coupling constant value for a set of protons will be same whether, it is obtained from a 200 MHz or 300 MHz spectrometer.

Splitting is always reciprocated between the protons i.e. if a proton H_a splits other proton H_b, then H_b must split H_a. Moreover, the splitting effect is same for both the protons within the molecule i.e the coupling constant J_{ab} will be equal to J_{ba}.

Problem 4.9: Define and explain what do you mean by equivalent hydrogens, coupling constant and up field and down field in NMR spectroscopy. [**GU 2015**]

Splitting of the spin states

The number of allowed orientations is given by (2*I* + 1), since a proton has I=1/2, so, it adopts two orientations with respect to an external field.



One orientation is aligned with the applied field, it is known as α-spin state (anticlockwise). It is assigned +1/2 value and remains in lower energy state.

Other orientation is opposed to the applied field, it is known as β-spin state (clockwise). It is assigned -1/2 value and remains in higher energy state.

The energy difference between the two spin states is dependent on the external magnetic field strength. The two spin states have the same energy when the external field is zero, but diverge as shown in the **figure 4.7**, with the increase of field strength.

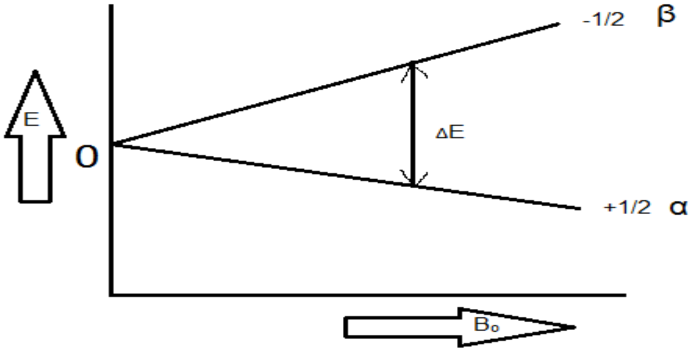


Fig. 4.7 Splitting of the spin states in magnetic field

Problem 4.10: Show schematically the splitting of the spin states of the protons of CH_3OH in continuously increasing magnetic field. If a radiation with a definite frequency is applied, explain which will show resonance at down field compared to the other protons. [**GU 2016**]

Spin-Spin Coupling

The actual field experienced by a proton, besides depending on the surrounding electron density, is also influenced by the neighbouring magnetically active nuclei. Spin-spin coupling arises because the magnetic field of adjacent protons influences the field that the proton experiences. If the field generated by an adjacent proton is aligned to the applied magnetic field then it deshields the neighbouring protons and as a result resonance occurs at higher frequency. On the other hand, if the field generated by an adjacent proton is opposed to the applied magnetic field then it effectively shields the neighbouring protons and as a result resonance occurs at lower frequency.

The phenomenon, where the spin of the nucleus of one proton is close enough to affect the spin of another, is called *spin-spin coupling.*

To explain this phenomenon let us take 1,1-dichloroethane as an example. The signal due to –CH_3 (methyl) group, will depend on its adjacent –CH (methine) group. As the –CH proton can adopt two alignments with respect to the applied field as shown in the **figure 4.8 (a)**, so, the signal for –CH_3 protons split into two lines of equal intensity, called a doublet.

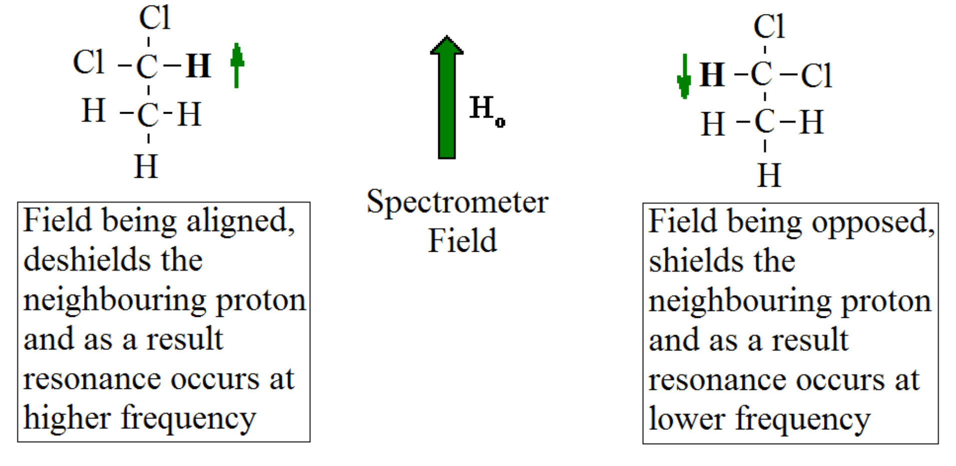


Fig. 4.8 (a) Spin-spin coupling of - CH_3 proton with -CH proton in 1,1-dichloroethane

Again, the signal due to –CH (methine) group, will depend on its adjacent –CH_3 (methyl) group. The –CH_3 protons can adopt eight different alignments with respect to the applied field as shown in the **figure 4.8(b)**.

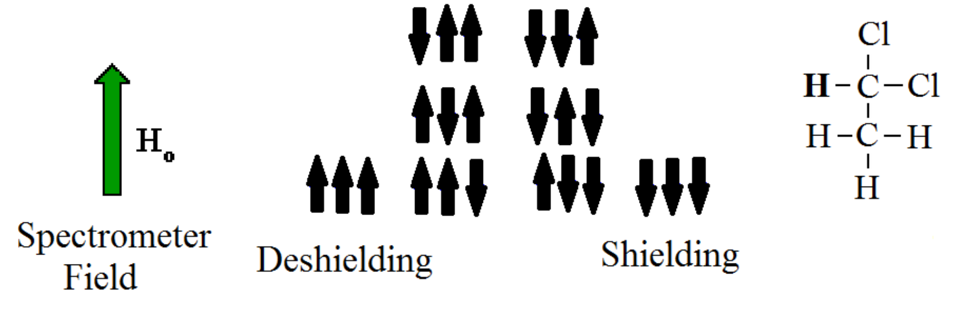


Fig. 4.8 (b) Spin-spin coupling of - CH proton with -CH_3 proton in 1,1-dichloroethane

Out of 8 combinations, 6 combinations give two equivalent set of combinations i.e. out of 8 combinations 4 magnetically different sets can be obtained and as a result the signal for –CH proton, splits into four lines with intensity 1:3:3:1, called a quartet.

To know about the spin-spin coupling of the protons, we should remember the following simple rules -

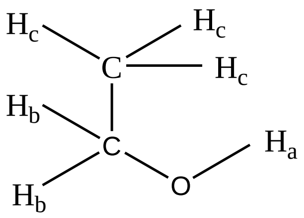
- Equivalent protons are in the same environment, so, their signals overlap and hence cannot couple. Only non equivalent protons can split signals.

- Protons that are separated by more than three single bonds usually do not couple as they are not close enough to each other to be influenced by the magnetic fields of each other. However, π bonds do not count toward this, so, in such cases coupling may occur but the coupling constants may be too small to distinguish.

Problem 4.11: How many proton NMR signals will be shown by 2-chloropropane? Discuss the effect of spin-spin coupling on the signals. [**GU 2016**]

High Resolution NMR Spectra of Ethanol

In ethanol, there are three different sets of protons H_a,H_b and H_c. The peak due to O-H proton i.e H_a will appear as single peak and it is attached to a highly electronegative atom O, so being deshielded, it appears downfield i.e at higher δ value. The peak due to $–CH_2$ protons couple with its nearby protons - CH_3 and appears as a quartet (n+1 rule). The peak due to $–CH_3$ protons couple with its nearby protons - CH_2 and appears as a triplet (n+1 rule).



The NMR spectrum of ethanol is shown in **figure 4.9**.

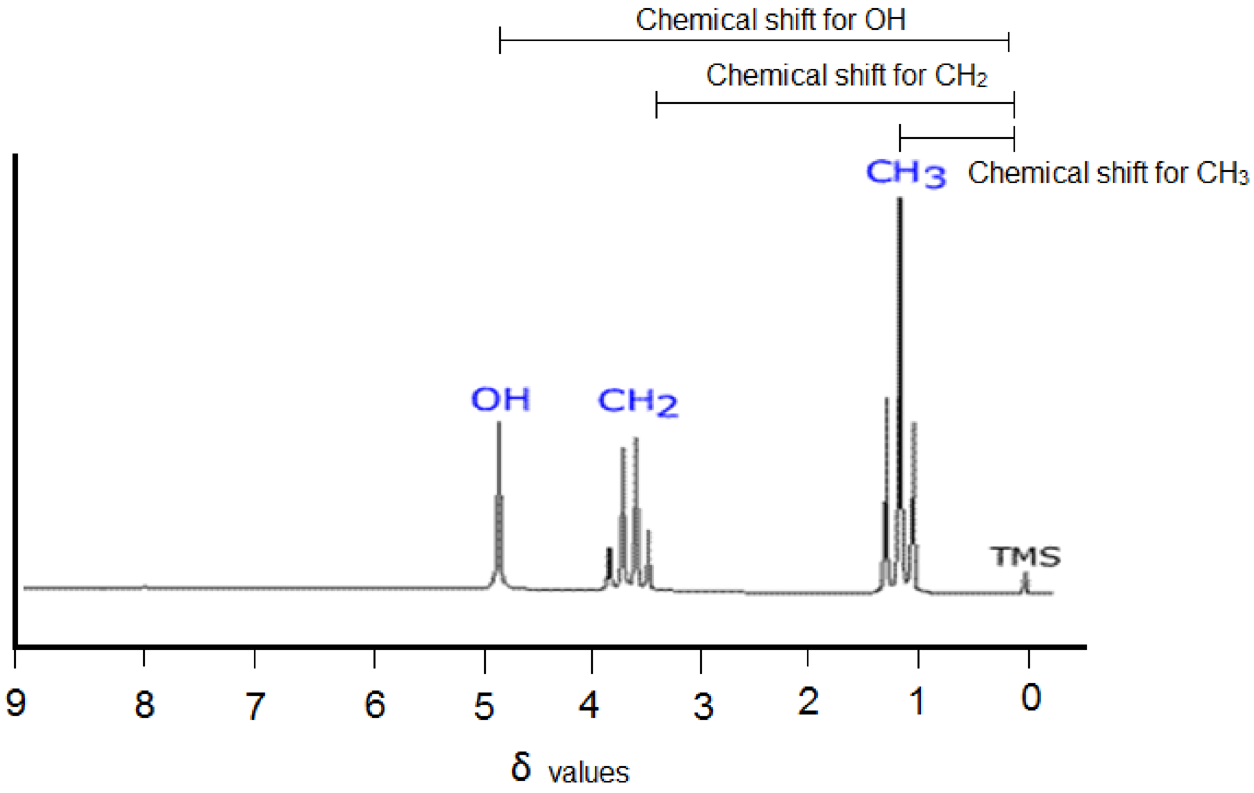
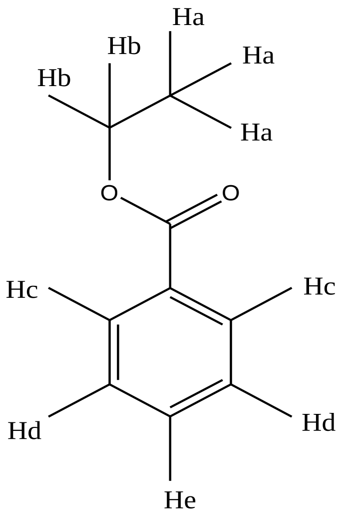


Fig.4.9 High resolution ^{1}H-NMR spectrum of ethanol

High Resolution NMR Spectra of Ethyl Benzoate

In ethyl benzoate, there are five different sets of protons H_a,H_b ,H_c ,H_d and H_e. The peak due to $–CH_2$ protons (H_b) couple with its nearby protons - CH_3 (H_a) and appears as a quartet (n+1 rule). This peak being attached to a highly electronegative O atom appears downfield (deshielded proton). The peak due to $–CH_3$ protons (H_a) couple with its nearby protons - CH_2 (H_b) and appears as a triplet (n+1 rule). This peak being shielded appears upfield.

The aromatic π electrons are delocalized cylindrically over the aromatic ring. The aromatic protons experience a magnetic field greater in magnitude than the applied field. Such protons are deshielded and hence appears downfield. As there are three types of protons, so, it gives three signals. The NMR spectrum of ethyl benzoate is shown in **figure 4.10**.



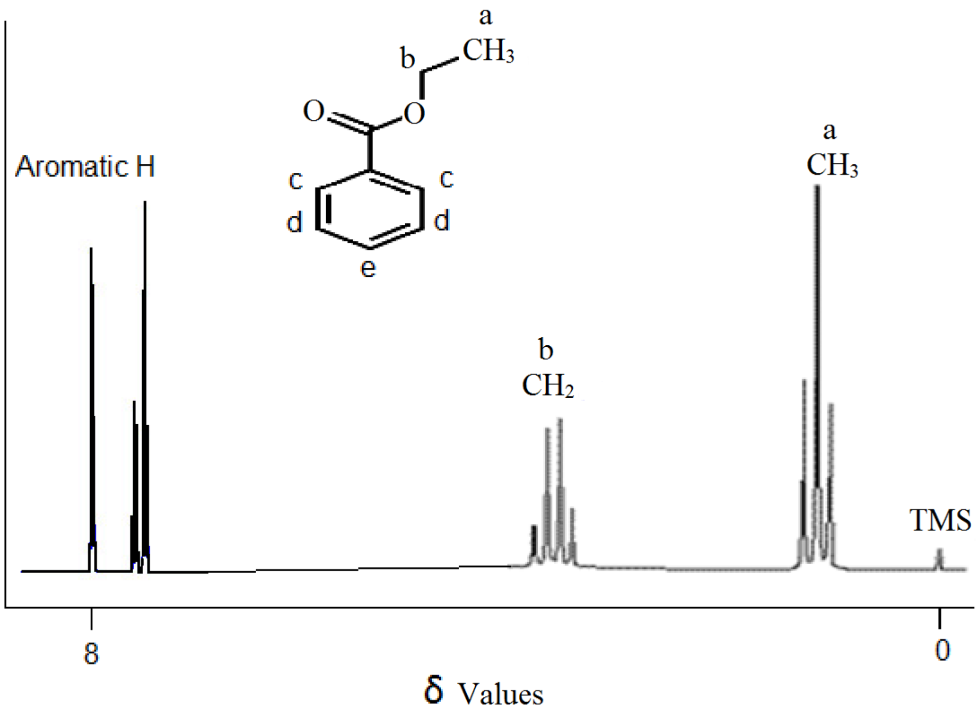


Fig. 4.10 High resolution ^1H- NMR spectrum of ethylbenzoate

High Resolution NMR Spectra of 2-Iodopropane

In 2-Iodopropane, there are two types of protons- a and b. Proton a has 6 neighbors while proton b has only 1 neighbor. So, signal for b will be a doublet while signal for a will be a septet. The NMR spectrum of 2-iodopropane is shown in **figure 4.11**.

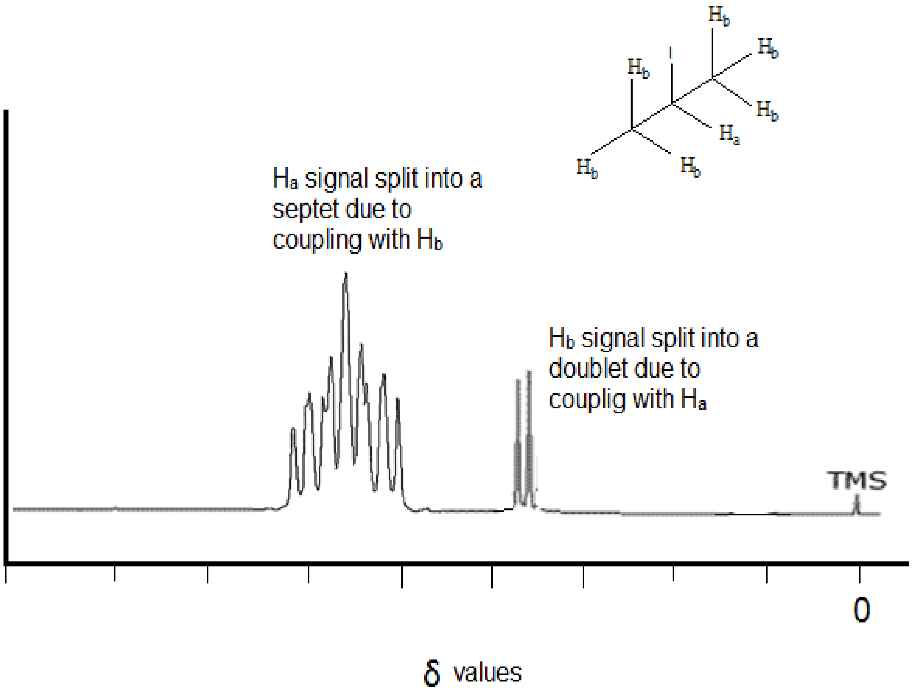


Fig. 4.11 High resolution ^{1}H-NMR spectrum of 2-iodopropane

Problem 4.12: Predict how the high resolution 1H-NMR spectrum of each of the following compounds will appear 2-iodopropane and ethanol. [**GU 2015**]

Problem 4.13: Draw the proton NMR spectra of CH_3CH_2Br and $CH_3CHBrCH_3$. Indicate the approximate chemical shift, fine structure due to spin-spin coupling and the relative intensities of the lines. [**GU 2014**]

Solution

In ethylbromide there are two types of protons $–CH_3$ (indicated as a) and $–CH_2$ (indicated as b). As the $– CH_2$ protons are attached to an electronegative atom (Br), so, these protons are deshielded and appear downfield. On the other hand $–CH_3$ protons appear upfield being shielded. Due to spin-spin coupling of $–CH_3$ protons with $–CH_2$

protons, the line due –CH_3 protons split into a triplet (n+1 rule) with the relative intensity of the lines 1:2:1. On the other hand due to spin-spin coupling of –CH_2 protons with –CH_3 protons, the line due –CH_2 protons split into a quartet with the relative intensity of the lines 1:3:3:1. The NMR spectrum of ethylbromide is shown in **figure 4.12**. The chemical shift of the protons are shown in the figure.

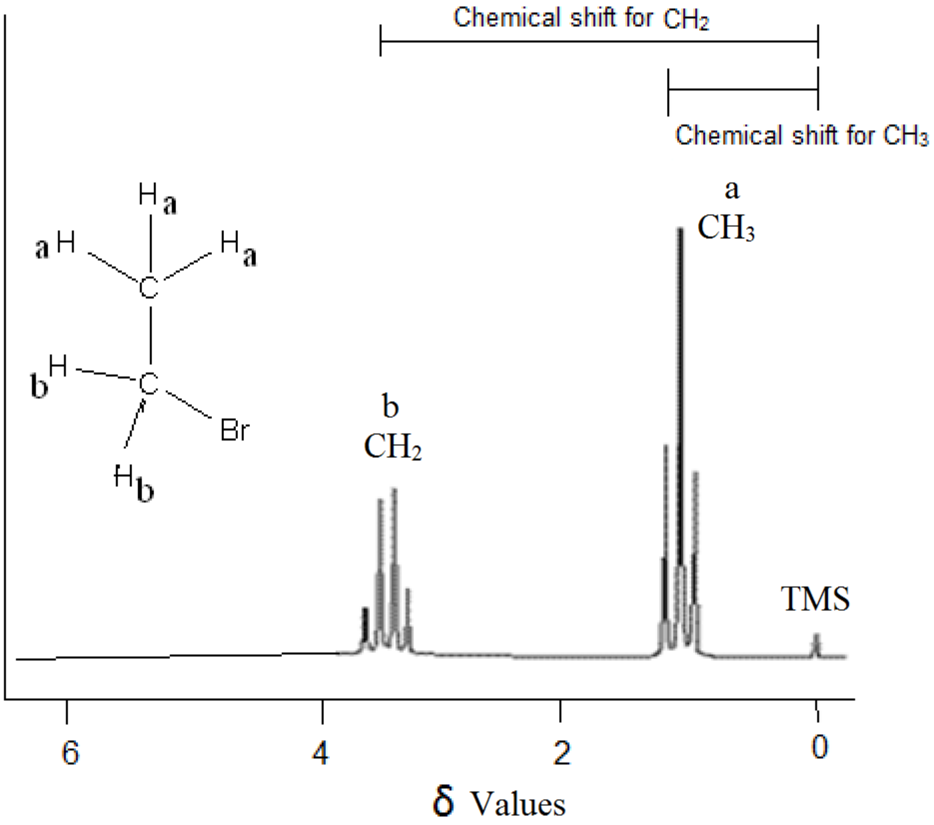


Fig. 4.12 NMR spectrum of ethylbromide

In 2-bromopropane, there are two types of protons –CH_3 (indicated as b) and –CH (indicated as a). As the – CH proton is attached to an electronegative atom (Br), so, this proton is deshielded and appear downfield. On the other hand –CH_3 protons appear upfield. Due to spin-spin coupling of –CH_3 protons with –CH proton, the line due –CH_3 protons split into a doublet with the relative intensity of the lines 1:1. On the other hand due to spin-spin coupling of –CH protons with two group of –CH_3 protons, the line due –CH proton split into a septet with the relative intensity of the lines 1:6:15:20:15:6:1. The NMR spectrum of 2-bromopropane is shown in **figure 4.13**. The chemical shift of the protons are shown in the figure.

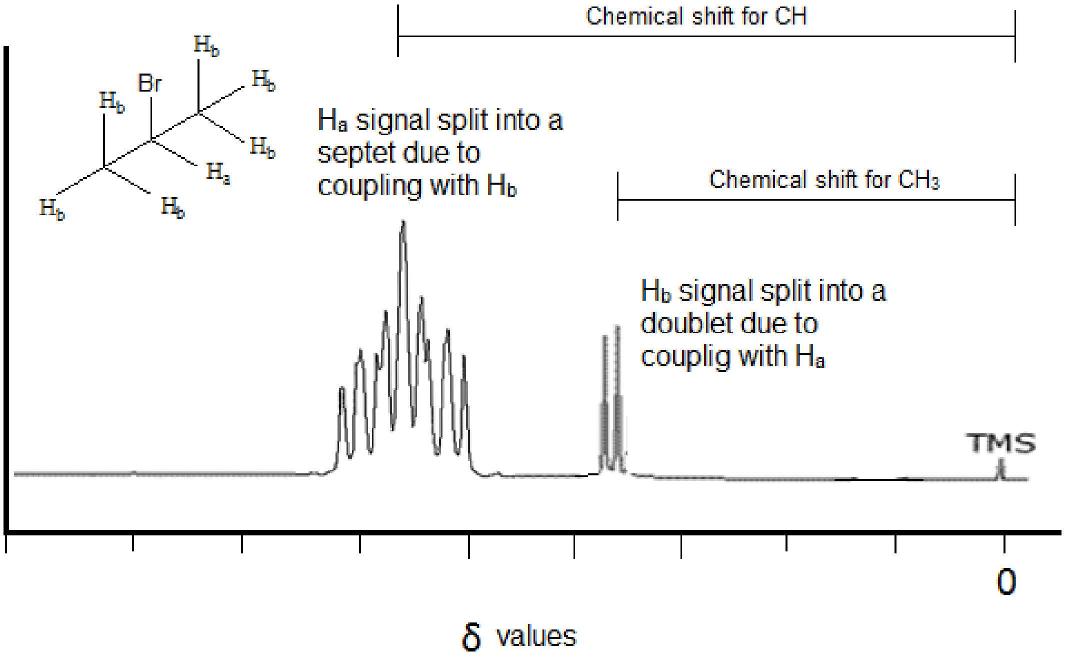


Fig. 4.13 High resolution ^{1}H NMR spectrum of 2-bromopropane

EXERCISE

4.1 Show that the precessional frequency of radiation required for the transition between two levels is proportional to the magnetic field.

4.2 Is it possible to differentiate between intermolecular and intramolecular hydrogen bonding using NMR spectroscopy, if so, explain how?

4.3 Explain how the magnetic field of an adjacent proton influences the resonance frequency of a proton under consideration?

4.4 What do you mean by equivalent protons in NMR spectroscopy? How many types of equivalent protons are there in 1,4-dichlorobenzene?

4.5 Show the high resolution ^{1}H-NMR spectra of propan-1-ol and propan-2-ol.

4.6 Mention the factors on which the magnitude of coupling constant depends.

4.7 The protons of benzene give a signal at frequency 255.25 Hz, when analyzed in a spectrometer having magnetic field 33 T. Calculate the chemical shift.

(Given g_N= 5.585, β_N = 5.0508 X 10 $^{-27}$ JT^{-1})

4.8 What do you mean by shielding and deshielding protons in NMR spectroscopy? Which of the following two types of protons are more shielded CH_3F and CH_3I.

4.9 Calculate the precessional frequency of a proton in a magnetic field strength of 4.78 T.