



# **SPECTROSCOPY**

**Programme Code- MSCCH-17/18/19**

**Course Code-CHE- 504**

**Block – 2 : Introduction to NMR Spectroscopy**

**Lecture-3**

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## ❖ LEARNING OUTCOMES

After studying this Chapter, you shall be able to:

- To understand the basic concept of NMR.
- To know about NMR active and inactive nuclei.
- To know about the conditions of a nuclei to be called an NMR active nuclei.
- To know the types of relaxation processes a nuclei undergoes.
- To know when a nuclei is called shielded and deshielded.

## ❖ INTRODUCTION:

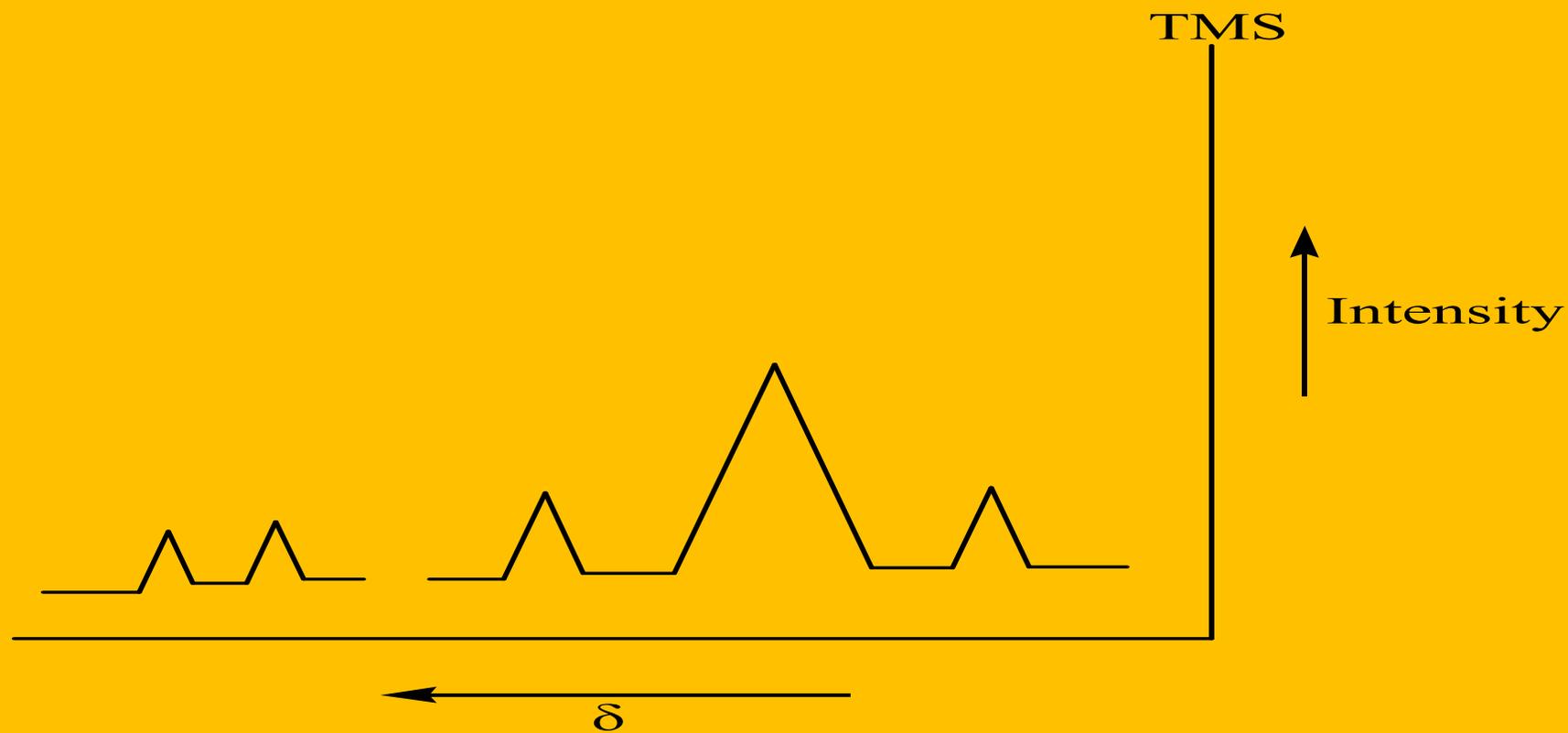
The concept of NMR was represented at first in 1946 by two groups of eminent physicist; Black Hensen and Packard at Stanford University detected a signal from the Protons of water and Parcell, Torrey and pound at Havard University observed a signal from the photons in Paraffin wax. Black and Parcell were jointly awarded a Nobel Prize for Physics in 1952 for this discovery.

NMR spectroscopy involvers transition of a nucleus from one spin state to other with the resultant absorption of electromagnetic radiation by spin active nuclei (having nuclei spin not equal to zero) when they are placed in magnetic field. Nuclear magnetic resonance spectroscopy related to the nuclei and only one type of nucleus at a particular timeline.

$^1\text{H}$  or  $\text{C}^{13}$ ,  $\text{F}^{19}$  when the frequency of the rotating magnetic field and that of the processing nucleus (Lamar Frequency) become equal, they are said to be in resonance absorption or emission of energy by the nucleus can be obtained. Plot of the peak intensities versus the frequencies of objection (represented by  $\delta$  or  $\tau$ ) establish an NMR spectrum.

The  $^1\text{H}$  nucleus is most commonly studied by NMR spectroscopy because of its high natural abundance (99.98%) and the fact that it is present in the majority of organic compounds, the PMR or  $^1\text{H}$  NMR spectrum provides information about the number of different types of protons and also the chemical environment of each of them.

• *A simple representation of NMR spectrum can be given as:*



## ❖ *PROTON MAGNETIC RESONANCE ( $^1\text{H}$ NMR) SPECTROSCOPY*

$^1\text{H}$ NMR or PMR spectroscopy is the most widely applicable Nuclear Magnetic Resonance spectroscopy for the structural determination of various organic compounds but the other NMR spectroscopic methods like  $\text{C}^{13}$  and  $\text{P}^{31}$  NMR spectroscopy;  $\text{F}^{19}$  spectroscopy can also be helpful in the structural determination of the compounds.

### ➤ Spin active nuclei:

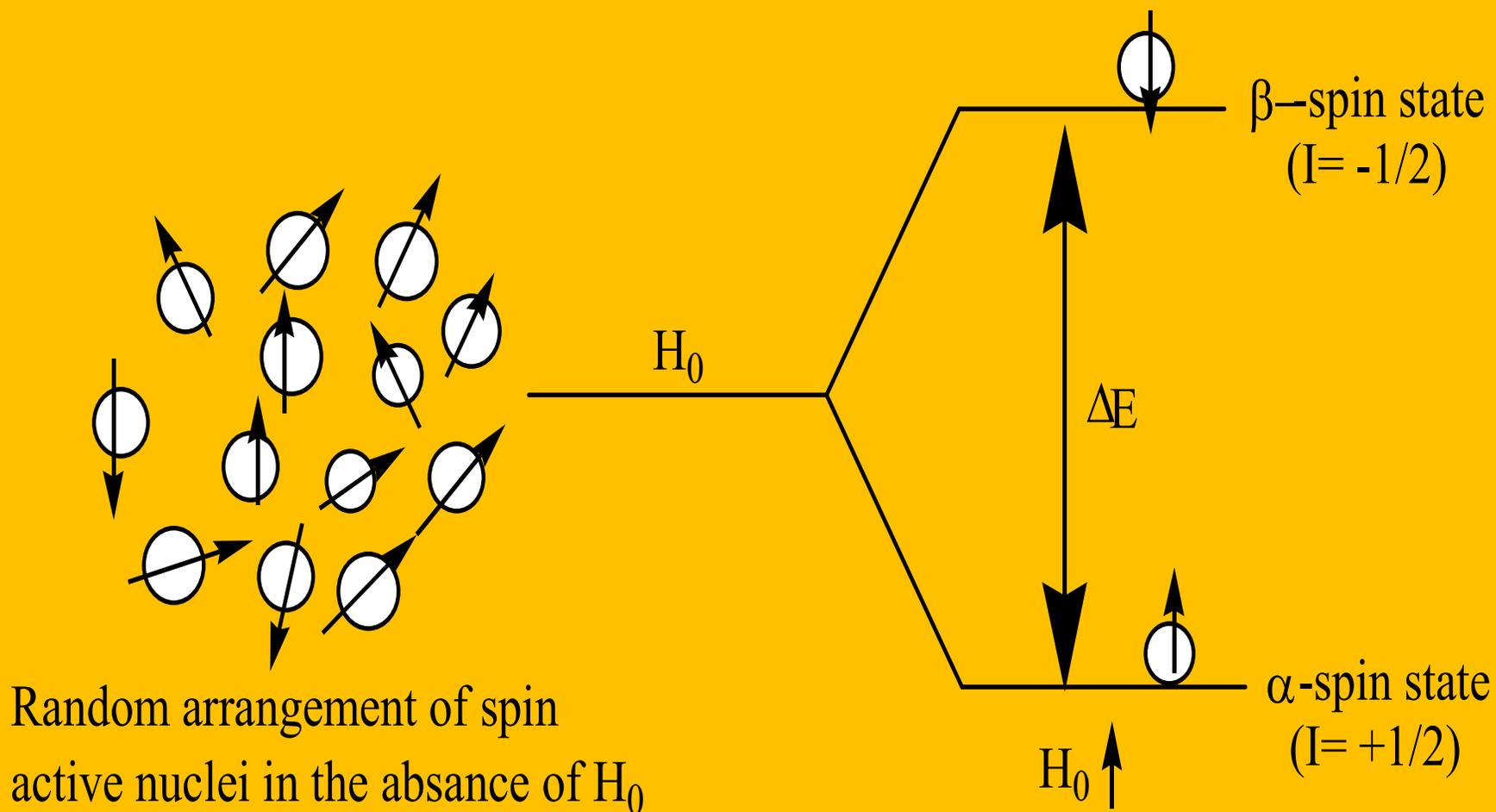
All those nuclei which having the full integer or half integer nuclear spin value are known as spin active nuclei. With the help of the number of the electron/proton and neutron in the various nuclei, the spin active or inactive nature for them can be defined as:

e <sup>-</sup> /p	Neutron (n)	Nuclear spin (I)	Nuclei	Examples
Even	Even	0	Inactive	${}^8\text{O}^{16}$
Odd	Odd	Full integer	Active	${}^7\text{N}^{14}$ , ${}^6\text{C}^{12}$
Even	Odd	Full integer	Active	${}^6\text{C}^{13}$
Odd	Even	Half integer	Active	${}^{15}\text{P}^{31}$ , ${}^1\text{H}^1$

➤ **Phenomena of energy absorption (Resonance & relaxation phenomena):**

In the absence of external magnetic field  $H_0$  the nuclear spin are randomly oriented, However when the sample is placed in an external magnetic field then the nuclei (proton) with the spin +half (1/2) are aligned with the applied field in that lower energy  $\alpha$ - spin stagehand the

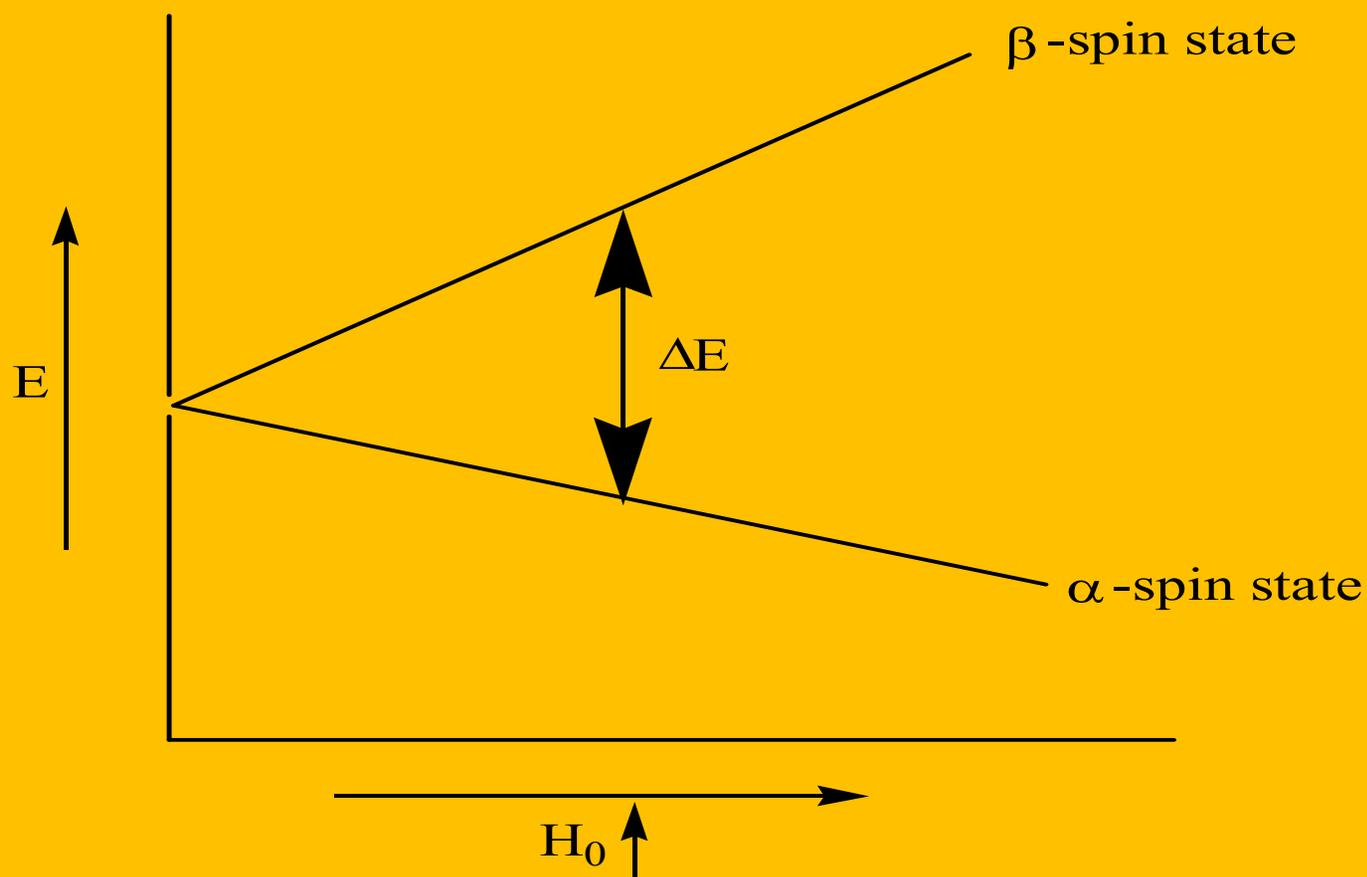
nuclei with the spin  $-1/2$  are aligned against to the external magnetic field in the higher energy  $\beta$ - spin state that can be represented as:



Random arrangement of spin active nuclei in the absence of  $H_0$

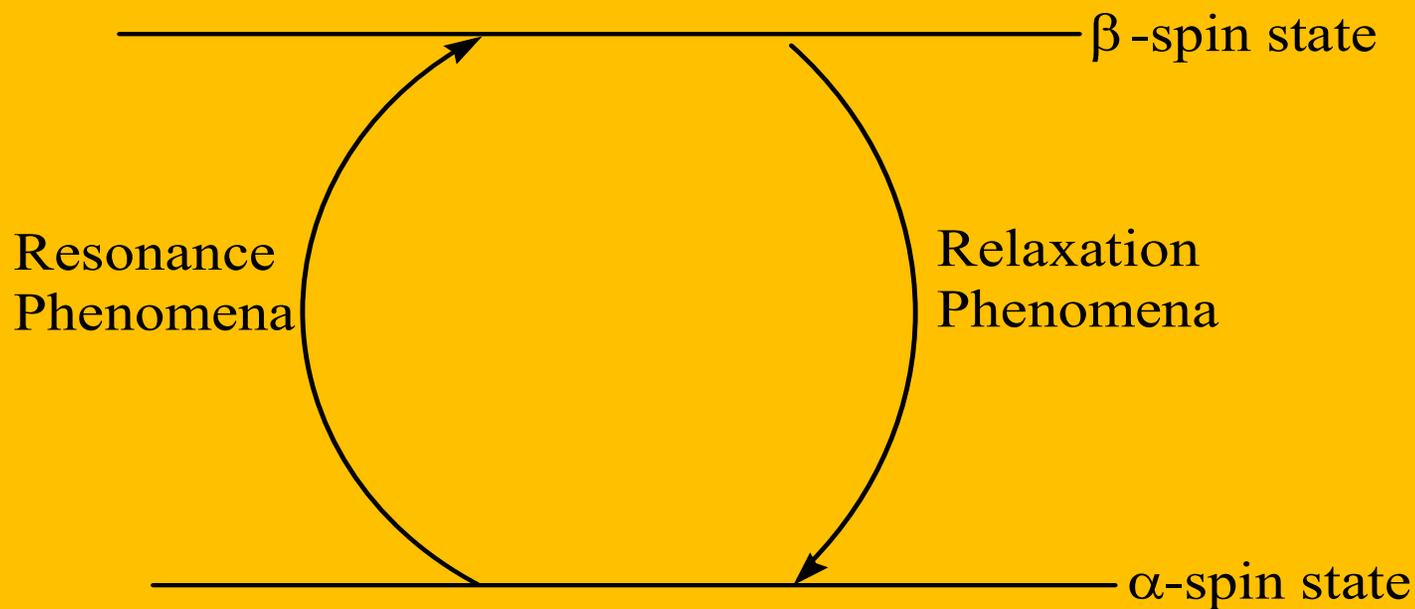
***Orientation of spinning nuclei in absence and presence of external magnetic field***

The value of energy difference b/w  $\alpha$  and  $\beta$  spin state depends on the strength of external magnetic field  $H_0$  according to the equation  $\Delta E = 2\mu h_0$  during the PMR spectroscopy, and then it can be represented as:



*Energy states of nuclear spin*

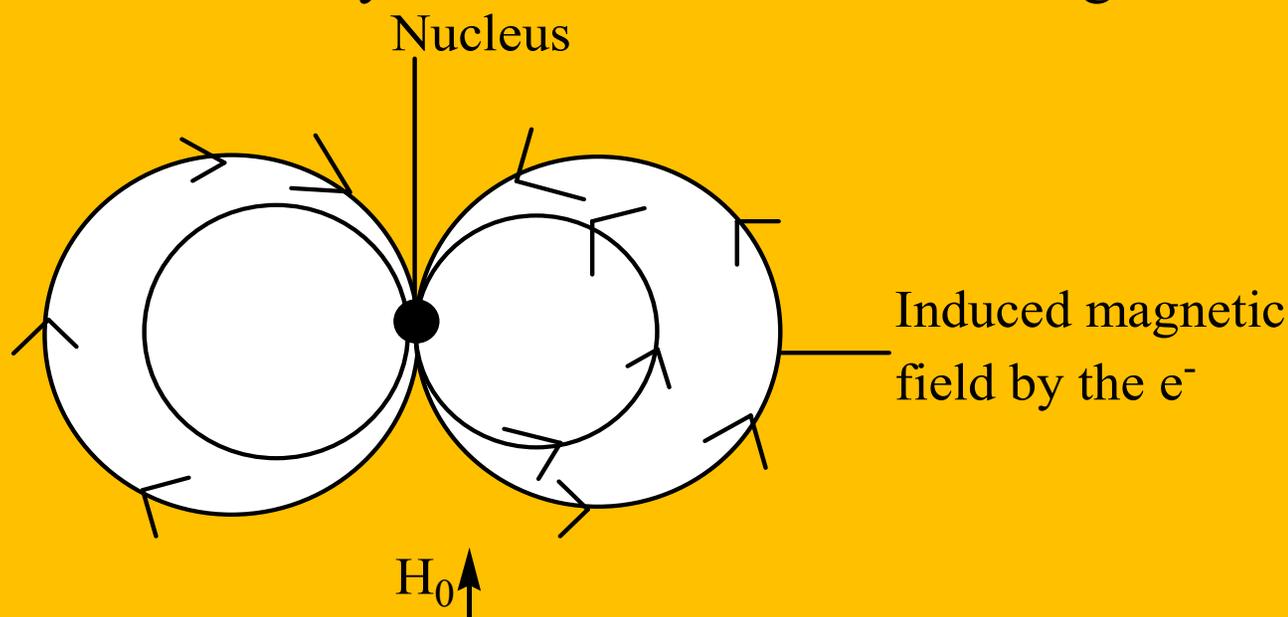
Thus according to above spin states **resonance phenomena** may be defined as the transition of spin active nuclei from  $\alpha$ -spin state to the  $\beta$ -spin state by the absorption of Rf radiation while the phenomena of returning the spin active nuclei from high energy  $\beta$ - spin state to the low energy  $\alpha$ -spin state is known as **relaxation phenomena**. Both the resonance and relaxation phenomena can be represented as:



*Resonance and Relaxation phenomenon*

## ❖ ***NUCLEAR SHIELDING AND DESHIELDING:***

Electron surrounding the spin active nuclei can also generate their own magnetic field which is called as induced magnetic field, that oppose the applied magnetic field in the region of the nucleus and these  $e^-$  which generate their induced magnetic field are known as diamagnetic  $e^-$  and this effect on the nucleus by these  $e^-$  is known as diamagnetic shielding



*Shielding and deshielding of a nucleus*

The external magnetic field is uniform over the entire molecule and therefore cannot differentiate to the different types of the proton. However the induced magnetic field generated by the e<sup>-</sup> around the nucleus is not uniform, this situation makes the different spin active nuclei (proton) to be non-equivalent. Thus each proton in the different electronic environment show slightly different magnetic field due to the circulation of e<sup>-</sup> in the neighboring bond.

Thus the effective magnetic field for the different spin active nuclei can be calculated through the following equations:

$$\mathbf{H}_{\text{effect}} = \mathbf{H}_0 - \mathbf{H}_{\text{induced}}$$

Form the above equation the shielded and deshielded proton concept can be given as:

**•For shielding:**



**•For deshielding:**

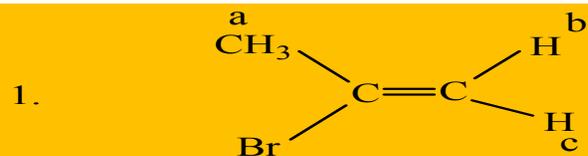


## ❖CHEMICALLY EQUIVALENT & NON-EQUIVALENT PROTONS:

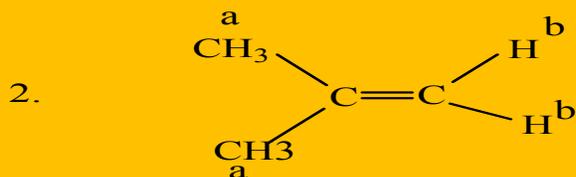
Those protons present in the sample of spin active nuclei which having same chemical environment are known as chemically equivalent protons.

The entire chemically equivalent protons appear as a single signal in the PMR spectrum.

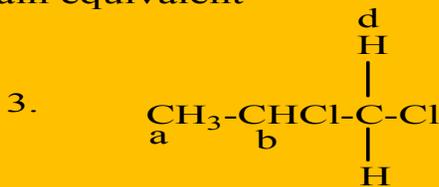
On the other hand those protons present in the sample of spin active nuclei which having different chemical environment are known as chemically non-equivalent proton. Chemically non-equivalent proton represents the different signal in the PMR spectrum.



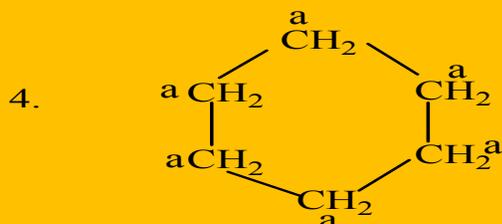
In a molecule reveals that three different types of protons, indicated by the letters a,b,c.



There are two types of protons. Six methyl protons on the LHS are equivalent. The protons on RHS are again equivalent



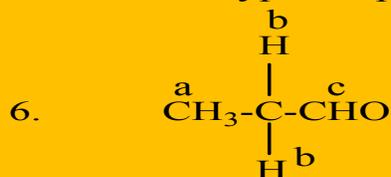
Protons marked c and d appear to be equivalent, but they are not actually so. Thus it has four types of protons.



In this case all the protons are equivalent giving rise to only one PMR signals



There are two types of protons, benzene ring protons and the methyl protons. Two signals will be observed.



There are three kind of protons giving rise to three signals.

## ❖ *CHEMICAL SHIFT :*

Chemical shift it expresses the difference in the resonance frequency of a given proton compared to that of the methyl protons of TMS, under the experimental conditions. In practice, this difference is divided by the operating radio-frequency of the instrument and the chemical shift  $\delta$  is expressed, downfield from TMS, as per the given equation.

$$\text{chemical shift } \delta = \frac{V_s - V_{\text{TMS}}(\text{H}_\beta)}{V_0(\text{MHz})} \times 10^6$$

For example, if the observed shift from TMS is 200 Hz and the operating frequency of the instrument is 100 MHz, then the chemical shift  $\delta$  is given by the following expression:

$$\delta \frac{200\text{Hz}}{100 \times 10^6 \text{ Hz}} = 2.0 \times 10^{-6}$$

This frequency ratio ( $2.0 \times 10^{-6}$ ) is multiplied by  $10^6$  in order to obtain an easily handled number ( $2.0 \times 10^{-6} \times 10^6$  ppm) and consequently the chemical shift  $\delta$  is expressed as part per million ( $10^6$ ) of the operating frequency.

Thus,

$$\text{Chemical shift} = \frac{\nu_s - \nu_{\text{TMS}} (\text{Hz})}{\text{Operating frequency}} \times 10^6$$

TMS



←  
Chemical shift  
 $\delta$  ppm

*Chemical shift region*

## ❖ **Internal standard for NMR spectroscopy:**

That compound which is used as a reference standard to represent the NMR/PMR signal of the compounds is known as internal standard for the NMR or PMR spectroscopy.

In case of PMR spectroscopy Tetramethylsilane (TMS) used as a internal standard due to the following reasons:

1. Due to the more shielded nature of the proton of TMS in compare to the protons of most of the organic compound.
2. It is chemically inert and miscible with large range of solvent.
3. It does not take part in intermolecular association with the sample.
4. Due to the volatile nature of TMS.

The internal standard for some other type of the NMR spectroscopic methods can be given as:

$F^{19}$  NMR –  $CFCI_3$

$N^{15}$  NMR –  $NH_4NO_3$

$C^{13}$  NMR – TMS

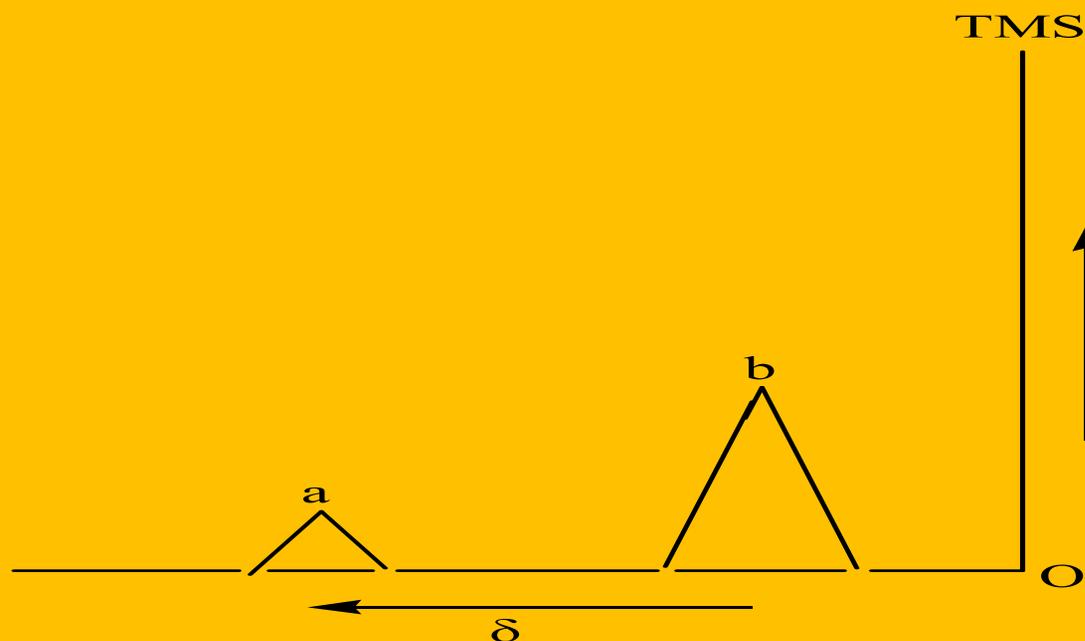
**❖ *SPIN-SPIN SPLITTING AND COUPLING CONSTANTS:***

The coupling interaction between two or more protons, most often through the bond, results in splitting of the spectral lines. This is called spin-spin coupling. It is related to the possible combinations of the spin orientations of the neighboring protons. The phenomena of splitting the signal of any particular type of proton by the spin orientation of the non-equivalent proton present adjacent to it is known as spin-spin coupling phenomena.

**Example:**

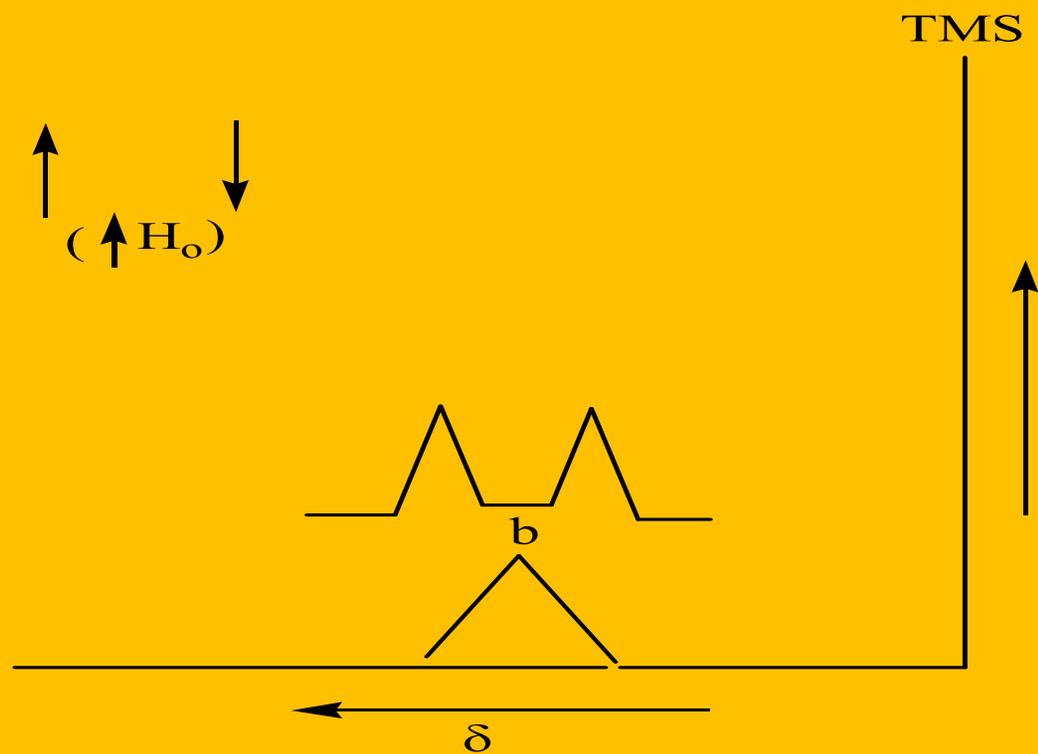


According to the NMR spectroscopy the signal of two different type of the proton present in this compound can be give as:

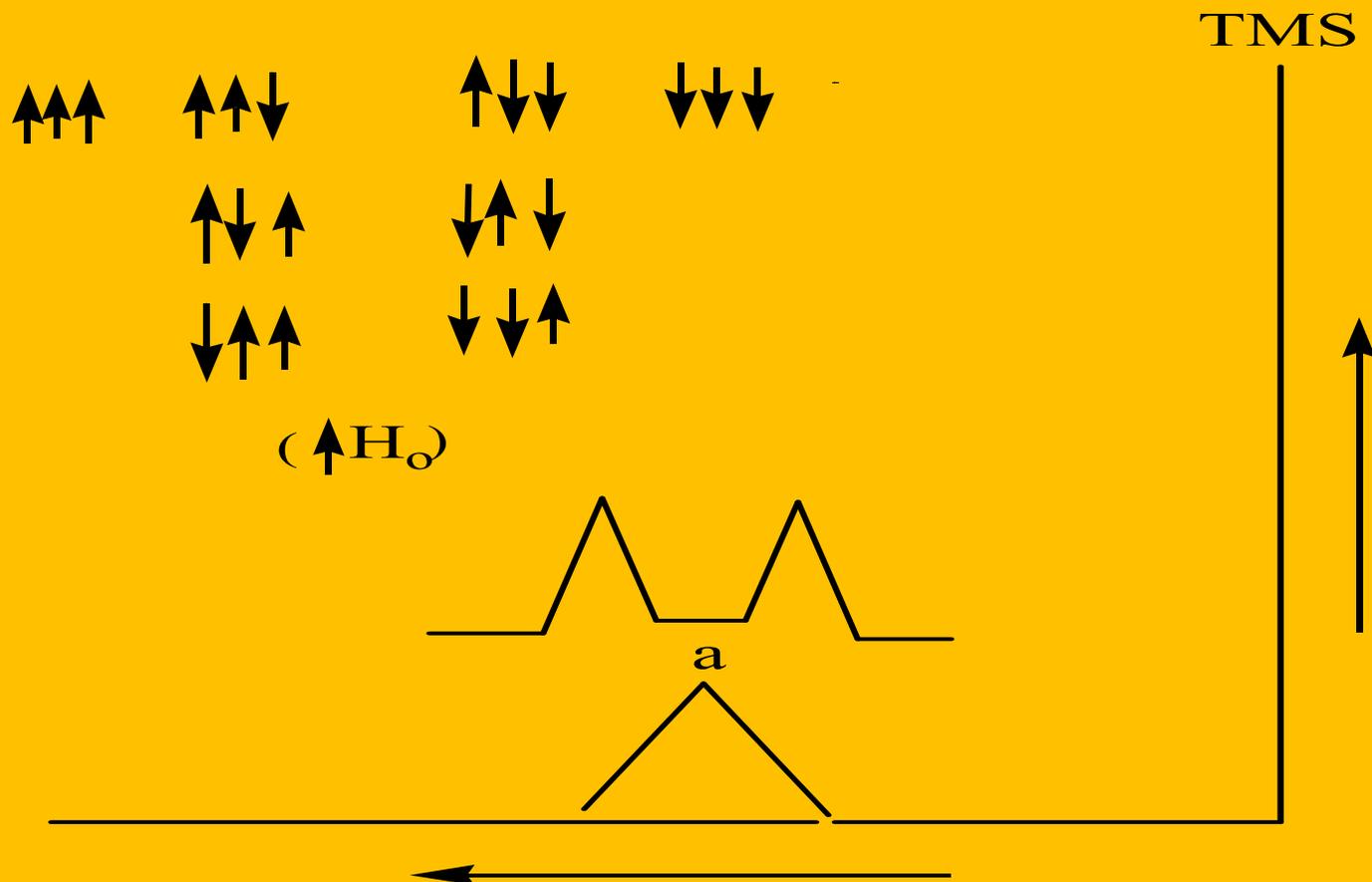


According to the spin-spin coupling phenomena the splitting of the signal of  $H_b$  proton &  $H_a$  proton according to the spin orientation of non-equivalent adjacent proton can be given as:

# 1. Spin orientation of $H_a$ for the splitting of the signal of $H_b$ :



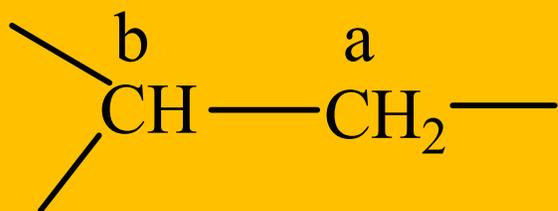
## 2. Spin orientation of $H_b$ for the splitting of the signal of $H_a$



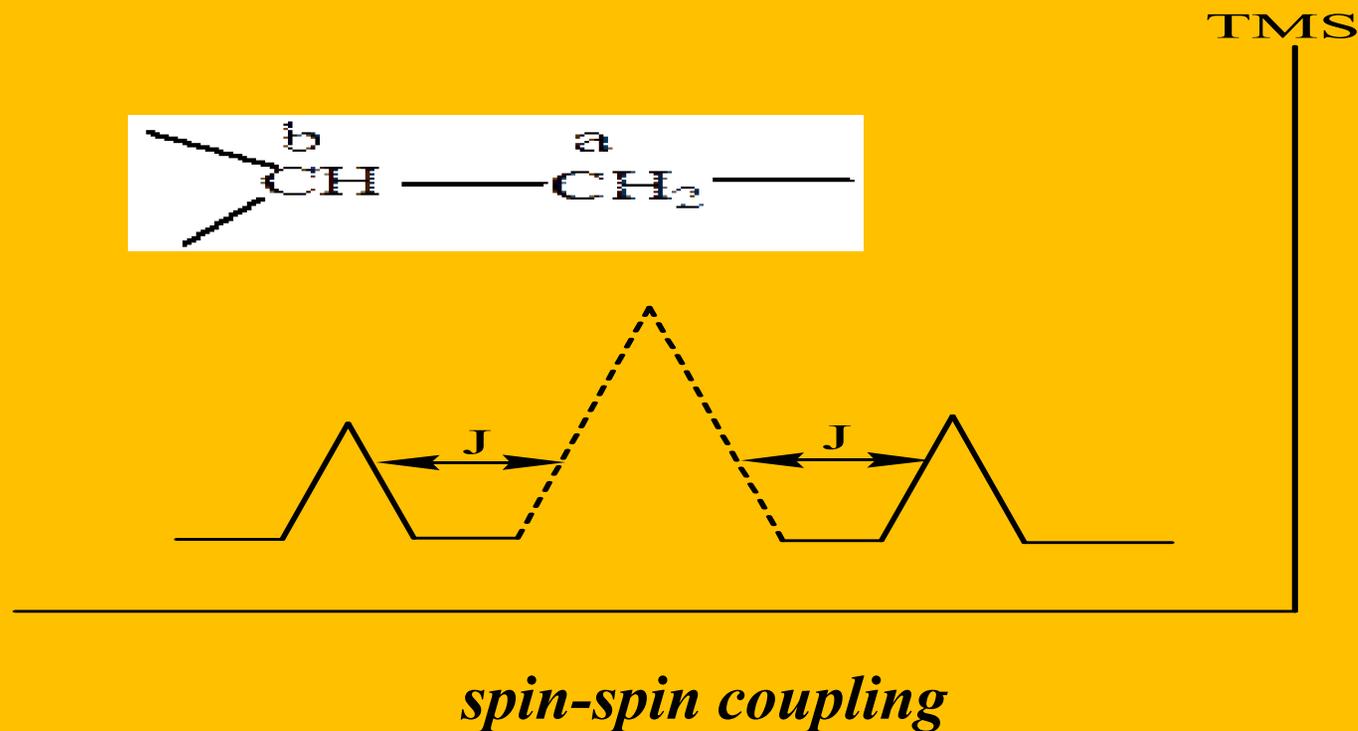
## Coupling constant (J):

The distance between the centers of the two adjacent peaks in a multiplet is usually constant and is called the coupling constant. The value of coupling constant is independent of the external field. It is measured Hertz (Hz) or in cps (cycle per second). It is denoted by the letter J. In other words, we can say the value of J remains the same whatever the applied field. The value of J generally lies between 0 and 20 Hertz (Hz). Always the value of coupling constant being same for the protons which causing the splitting each other signal.

Now, let us consider a compound:



In this compound two signals are expected in the NMR spectrum. Under the influence of two equivalent proton a, the signal for proton b will appear as a triplet. The distance between any two adjacent peaks in a multiplet will be exactly the same. The spin-spin coupling is given below:

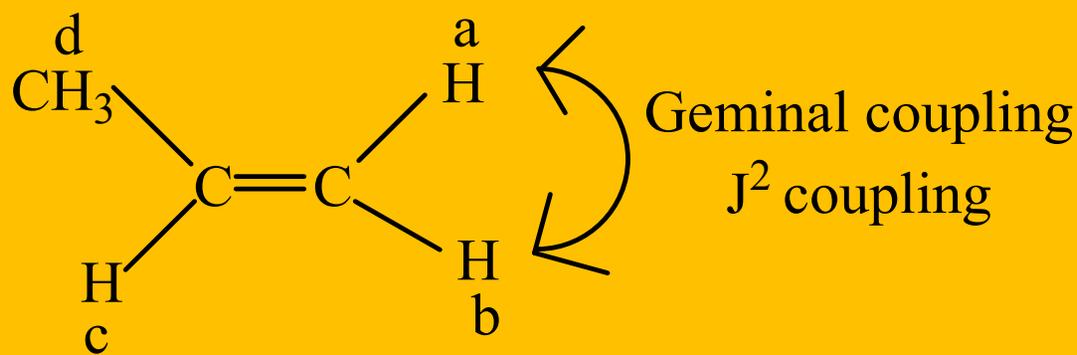


It may be clearly noted that the value of coupling constant depends on the number of covalent bonds through which protons may interact and also upon the structural relationship between the coupled protons.

Various types of the coupling may be given as:

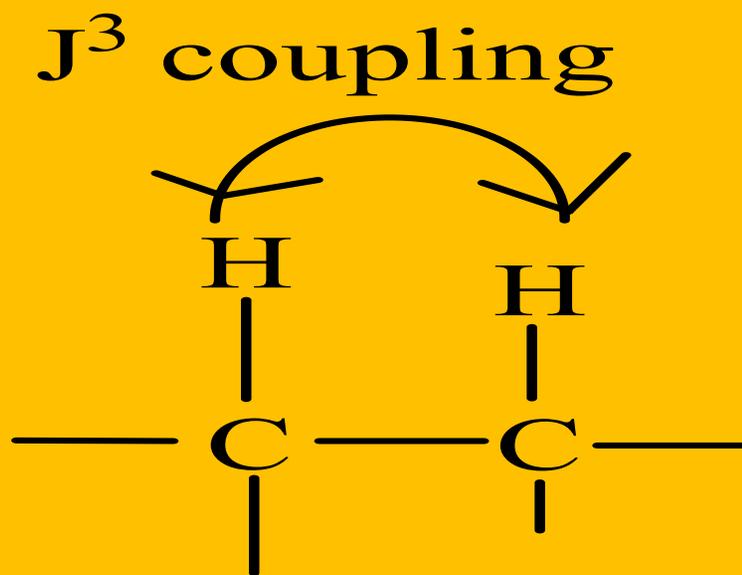
➤ **Geminal coupling:**

Such type of the spin-spin coupling phenomena in which two chemically non-equivalent protons present at the same c atom causing the splitting of each other signal will be called as Geminal coupling or  $J^2$  coupling.



## ➤ Vicinal coupling-

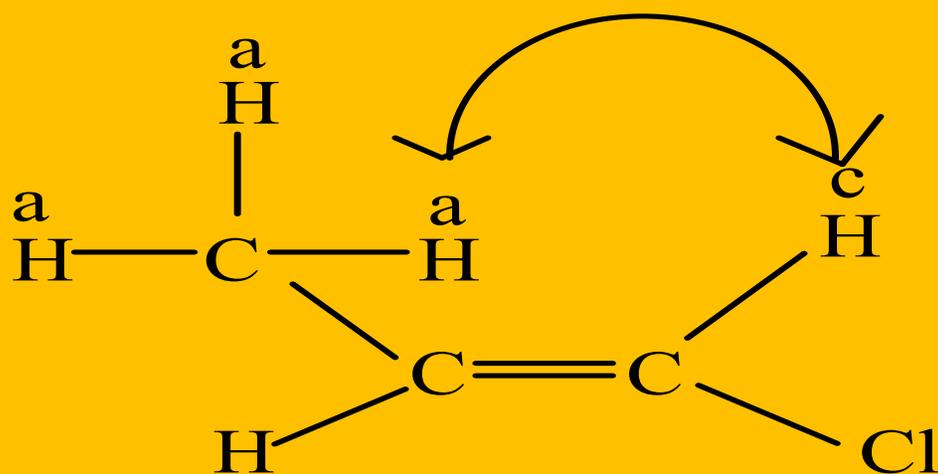
Such type of the coupling phenomena in which two chemically non-equivalent protons present at the adjacent carbon atom causing the splitting of each other signal are known as vicinal coupling or  $J^3$  coupling.



## ➤ Long range coupling:

Such type of the coupling phenomena in which two chemically non-equivalent protons causing the splitting of each other signal being separated by more than three covalent bonds are known as multi range/long range coupling. The probability of this type of the coupling phenomena in the organic compounds being very low.

### Long range coupling



## ❖ *APPLICATIONS OF NMR SPECTROSCOPY:*

The NMR spectroscopy is very widely used for the identification of an unknown compound.

### **1. Identification of structural isomers:**

The distinction between the following isomers can be easily made from their NMR spectra:



In the isomer 'a' three signals are observed whereas we see only two signals in the spectrum for 'b' which is a clear distinction between the above isomers. The three signals for isomer 'a' in order of decreasing tau values are:

1. A three proton triplet
2. A two proton sextet and
3. A two proton triplet For isomer (b), two signals have their multiplicities as:
4. Doublet (6H)-up field and
5. Septet (1H)-downfield

## **2. Detection of hydrogen bonding:**

Intermolecular hydrogen bonding shifts the absorption for a concerned proton downfield. The extent of hydrogen bonding varies with the nature of solvent, concentration of the solution and the temperature. The intramolecular hydrogen bonding also shifts the absorption downfield. The two types of hydrogen bonding can be distinguished as the intramolecular hydrogen bonding is not concentration dependant.

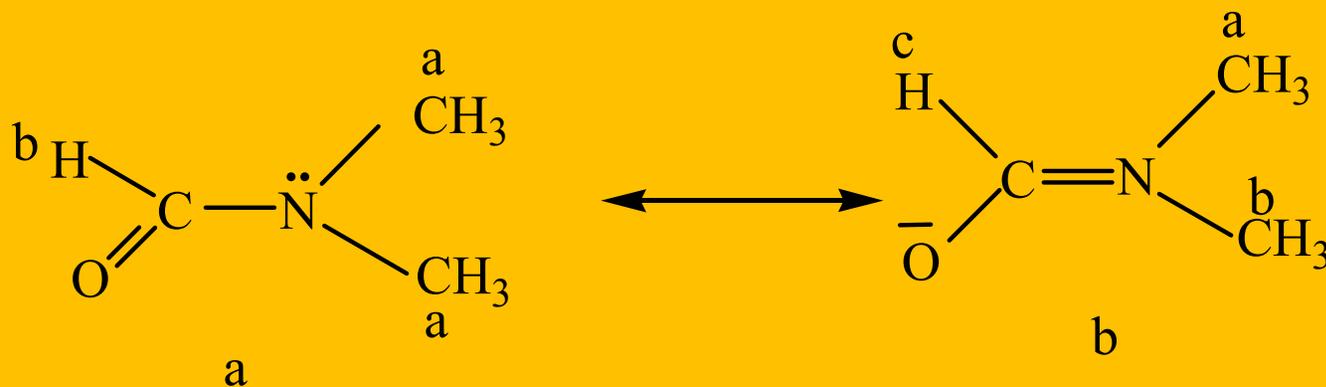
### **3. Distinction between Cis-Trans Isomers and conformers:**

The cis and trans isomers of a compound can be easily distinguished as the concerned protons have different values of the chemical shift as well as the coupling constants. Similarly, the various conformation of a compound, the axial and equatorial positions of the proton or group carrying a proton can be distinguished from their different values of the coupling.

### **4. Detection of some double bond character due to resonance:**

In some compounds, the molecule acquires a little double bond character due to resonance. Due to this, two signals can be expected for apparently equivalent protons, It is due to the hindered rotation which changes the geometry of the molecules. Consider N, N- dimethyl formamide.

It can be written in the following resonating structures:



For structure (a), two signals (singlets) should be expected with peak areas 6:1 as the two methyls are exactly equivalent.

In structure (b), the presence of double bond restricts rotation and now the two methyl groups remain no longer equivalent (Geometrical isomers). For this structure, two signals, appear for two methyl groups.

## ❖ *INTERPRETATION OF PMR SPECTRA OF SIMPLE ORGANIC MOLECULES:*

NMR interpretation plays an important role in molecular identifications.

As interpreting NMR spectra, the structure of an unknown compound, as well as known structures, can be assigned by several factors such as chemical shift, spin multiplicity, coupling constants, and integration. For the interpreting of the NMR spectra, the following points may be noted:

1. Molecular formula is determined by chemical analysis such as elementary analysis.

2. **Double-bond equivalent or Degree of Unsaturation:** It is calculated by a simple equation to estimate the number of the multiple bonds and rings. It assumes that oxygen (O) and sulfur (S) are ignored and halogen

(Cl, Br) and nitrogen is replaced by CH. The resulting empirical formula is  $C_xH_y$

$$\text{Double Bond Equivalent (DBE)} = \frac{(2x + 2) - y}{2}$$

3. Structure fragmentation is determined by chemical shift, spin multiplicity, integral (peak area), and coupling constant ( $1J$ ,  $2J$ )

4. Molecular skeleton is built up using 2-dimensional NMR spectroscopy.

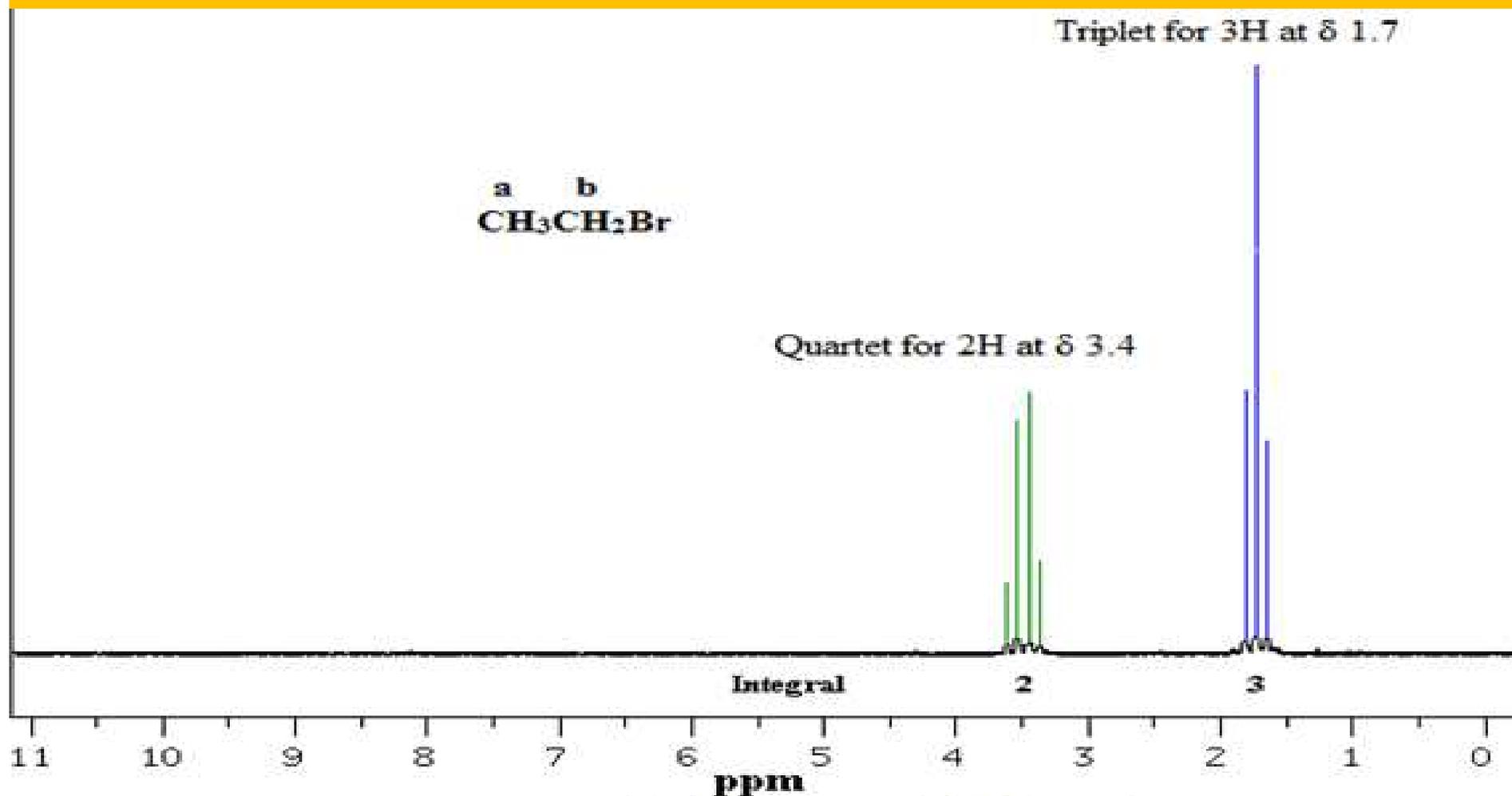
5. Relative configuration is predicted by coupling constant ( $^3J$ ).

### ➤EXAMPLES:

#### 1. Ethyl bromide ( $CH_3CH_2Br$ ):

In this compound (Ethyl bromide) containing two set of equivalent protons 'a' and 'b' types. The signal due to equivalent protons a will be under the influence of neighboring proton b.

Similarly, the signal for proton b will be under the influence of three equivalent proton a whose spin possibilities with respect to the applied field can be given as-



*NMR Spectra of ethyl bromide*

The following peaks can be identified in the spectrum

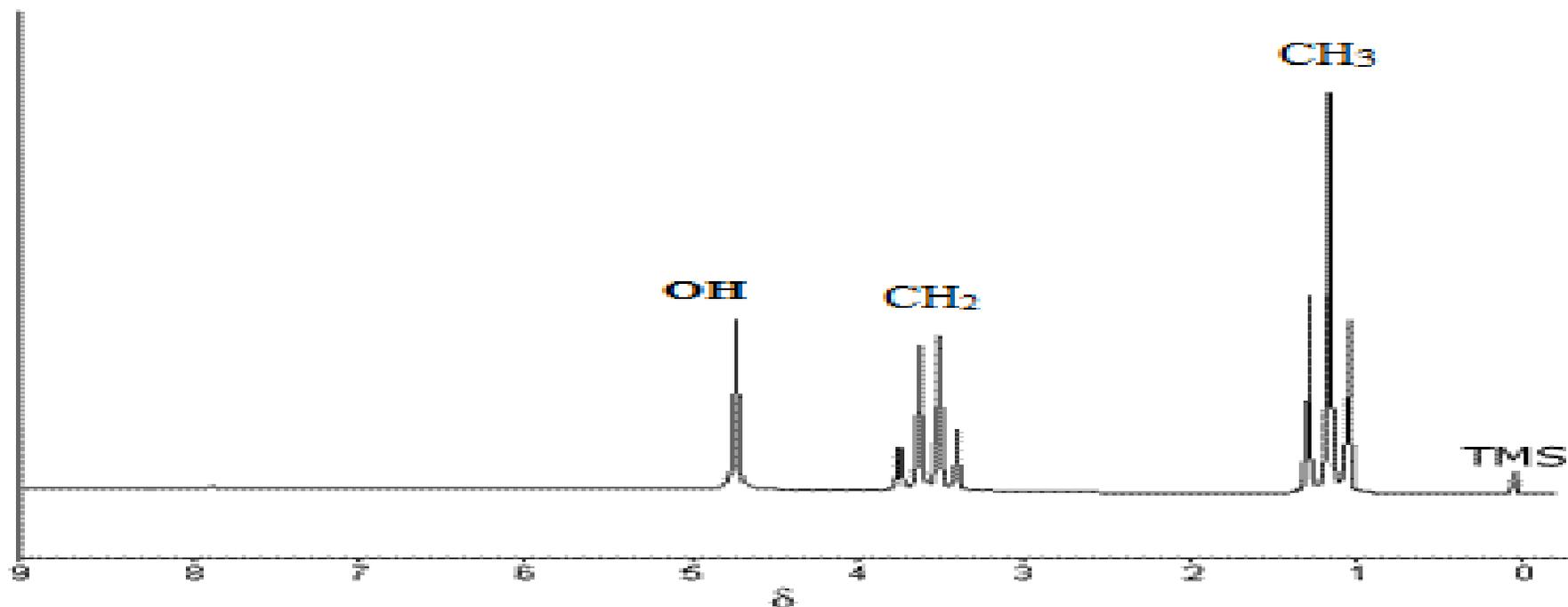
(a) Triplet,  $\delta$  1.7, 3H

(b) Quartet,  $\delta$  3.4, 2H

The proton at  $\delta$  1.7 is given by the three methyl protons which are magnetically equivalent and are coupled with the two methylene protons to give a shielding. While the quartet at  $\delta$  3.4 is from the two equivalent methylene protons which are coupled with the three methylene protons to produce a downfield quartet as a result of deshielding influence of bromine.

## 2. Interpretation of PMR spectra of ethanol:

The  $^1\text{H}$  NMR spectrum of ethanol (Figure 1.9) shows the methyl peak has been split into three peaks (triplet) and the methylene peak has been split into four peaks (quartet). This occurs because there is a small interaction between the two groups of protons. The space between the peaks of the methyl triplet is equal to the space between the peaks of the methylene quartet. This spacing is measured in Hertz and is called the coupling constant,  $J$ .



### *PMR Spectrum of Ethyl alcohol*

In the above PMR spectrum of ethyl alcohol the following observation takes place:

- A triplet centered at 1.18  $\delta$ , equivalent to 3H, represents the CH<sub>3</sub> (a) proton.
- A singlet at 4.51  $\delta$ , equivalent to 1H, exhibit the OH (c) proton.
- A quartet centered at 3.63  $\delta$ , equivalent to 2H indicates the CH<sub>2</sub> (b) proton.

THANK YOU