COURSE CODE: SC202(CHEMISTRY)
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^{1}H-NMR SPECTROSCOPY
DEPT. OF SCIENCE AND MATHEMATICS
IIITG, GUWAHATI
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Introduction

- Nuclear Magnetic Resonance (NMR) spectroscopy is a spectroscopy technique which is based on the absorption of the electromagnetic radiation in the radiofrequency region by a nucleus of an atom.

- It is used for a wide variety of nuclei, *e.g.*, ^{1}H, ^{13}C, ^{15}N, ^{19}F, etc.

- ^{1}H-NMR Spectroscopy is one of the most useful tools in organic chemistry for structure elucidation.

Relation between Spin quantum number (I) and NMR activity of a nucleus

| I	Atomic Mass	Atomic Number	Examples	
Half-integer	Odd	Odd	^{1}H (1/2)	NMR active
Half-integer	Odd	Even	^{13}C (1/2)	
Integer	Even	Odd	^{2}H (1)	
Zero	Even	Even	^{12}C (0)	Not NMR active

Nucleus with odd mass number or odd atomic number will be NMR active.

- In an external magnetic field, the number of possible orientations is given by (2I+1).
- Hydrogen has I=1/2. So, number of possible orientations for hydrogen is 2.
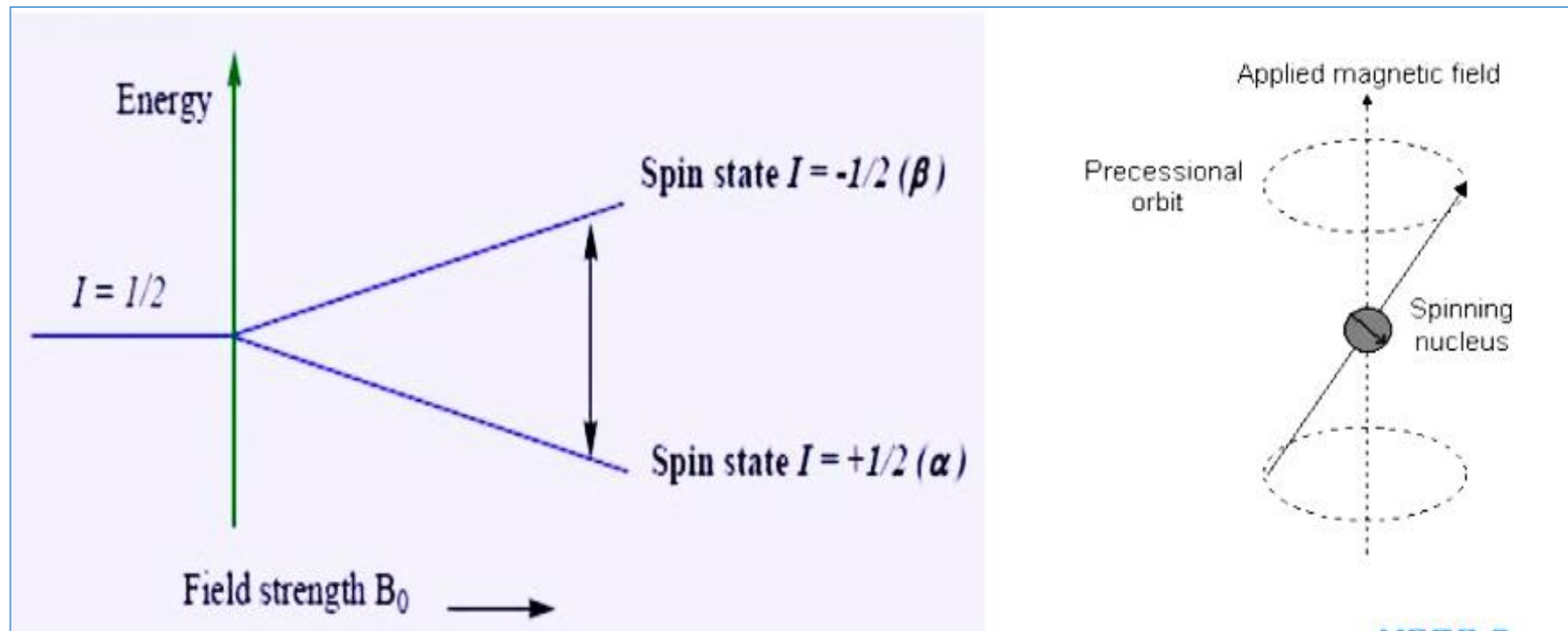
Principle of NMR

- Nucleus of a proton behave like a bar magnet. When no external magnetic field is applied, then the nucleus of proton remains randomly arranged.

- But when an external magnetic field is given, then the nucleus align themselves with or against the external magnetic field.
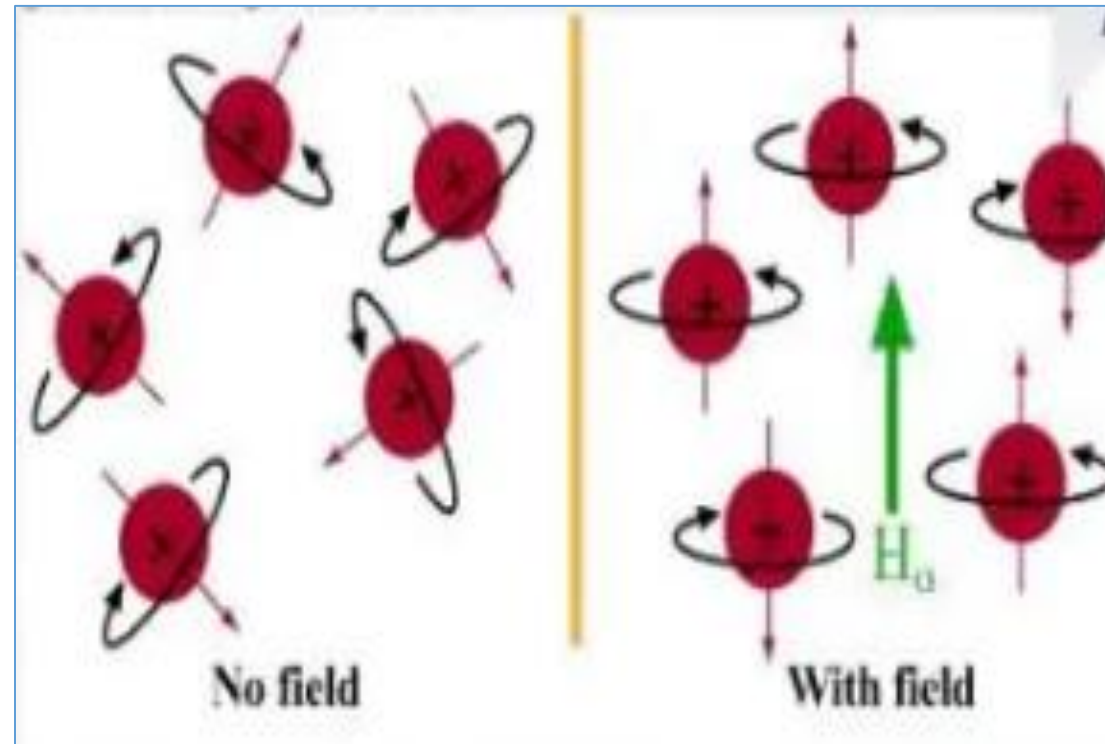
- When an external magnetic field is applied, the nuclei in the ground state absorb the radiofrequency energy and goes to the higher energy state. There is an energy transfer of ΔE.

- When the nuclei from the excited energy state, come back to the ground state, the absorbed radiofrequency energy is emitted.

- The emitted radiofrequency signal gives the NMR spectrum of the concerned nucleus and it is proportional to the strength of the applied magnetic field.
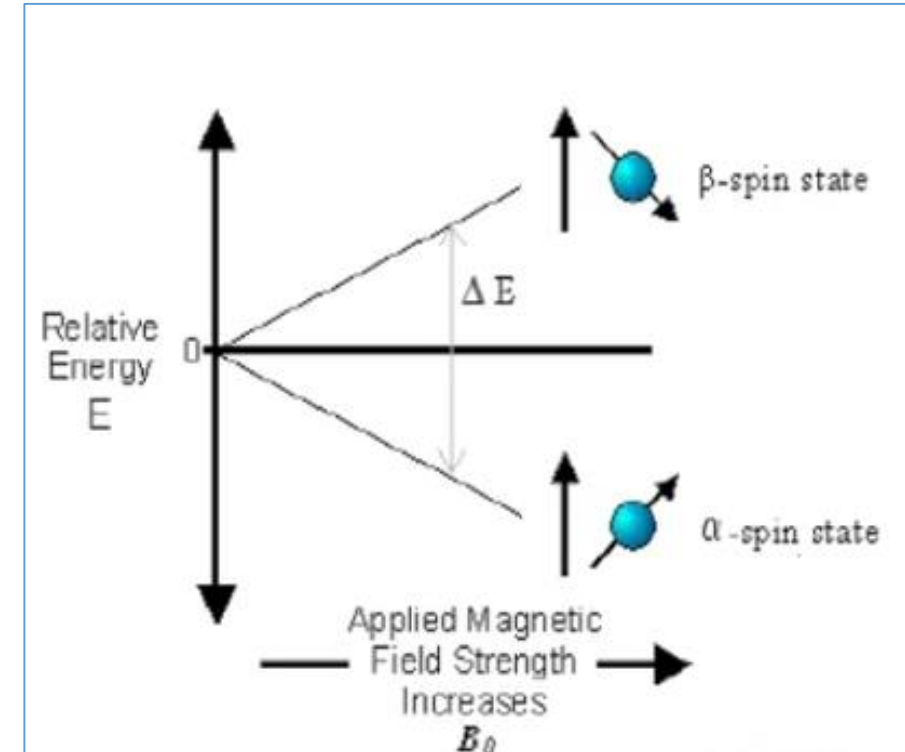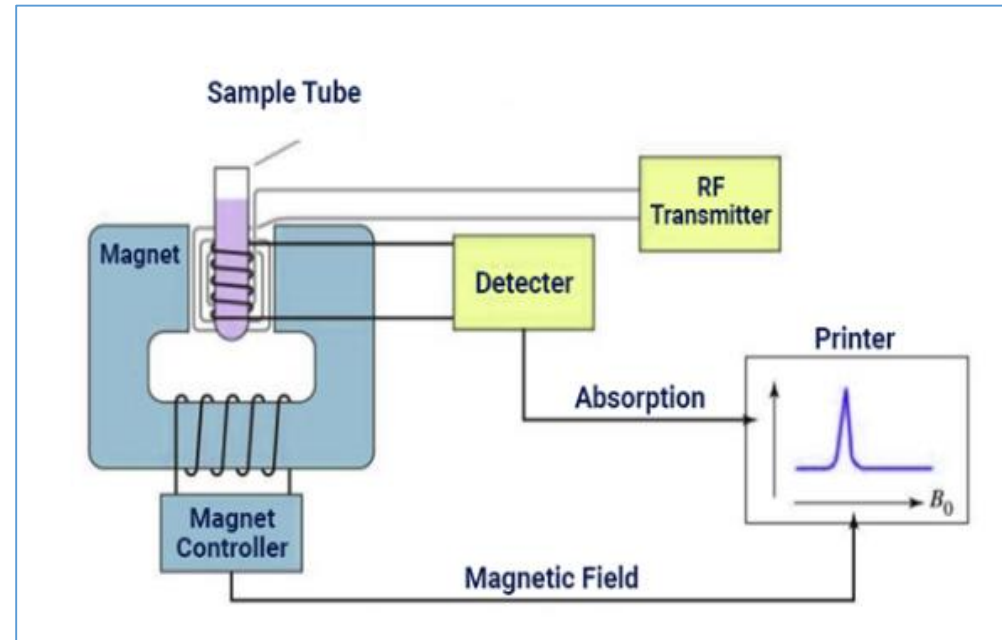
NMR Spectrum
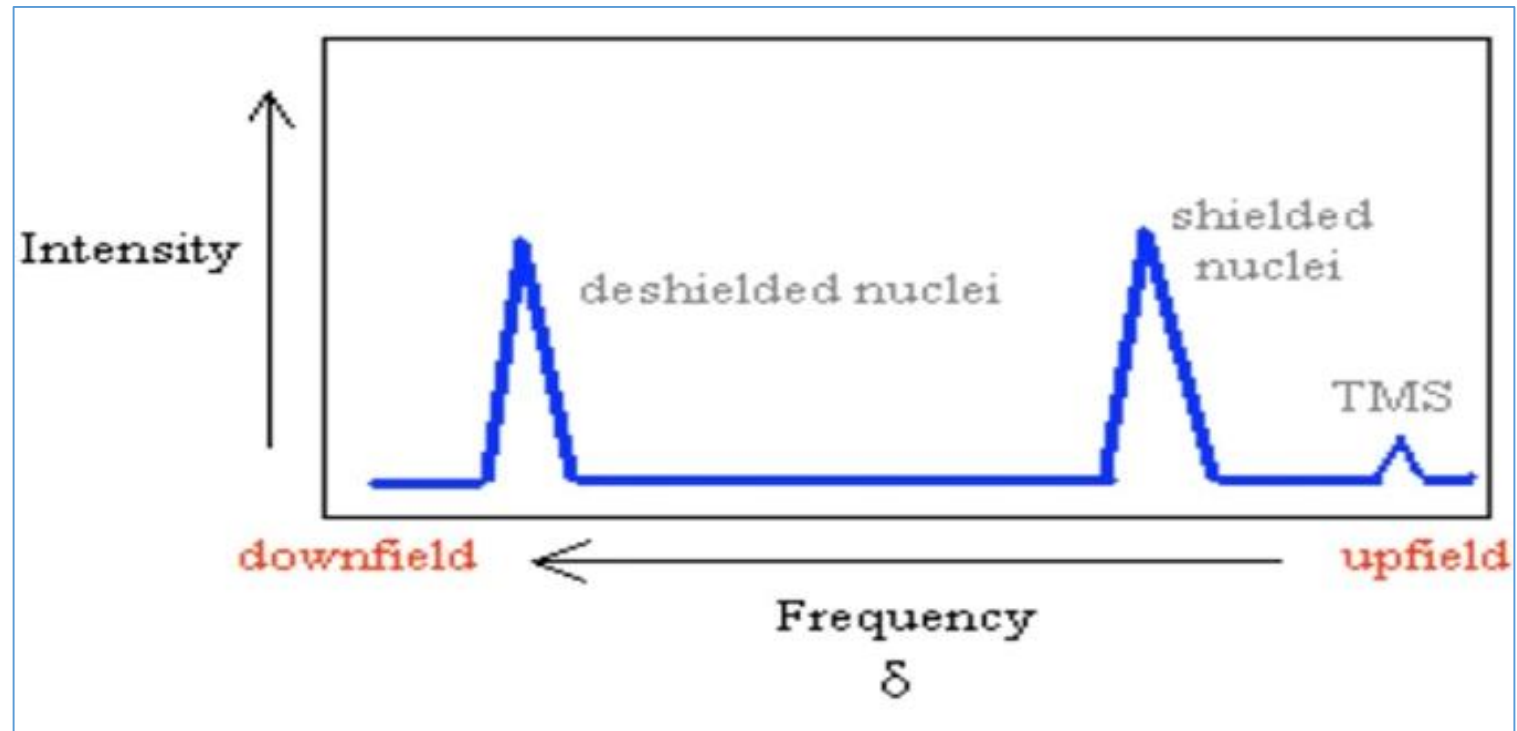
NMR instrumentation

- Sample holder
- Permanent magnet
- Magnetic coils
- Sweep generator
- Radiofrequency transmitter
- Radiofrequency receiver
- Read-out system

Solvents used in NMR

- CCl_4- Carbon tetrachloride
- $CDCl_3$- Deuterated Chloroform
- CS_2- Carbon disulphide
- C_6D_6- Deuterated Benzene
- D_2O- Deuterium oxide or heavy water

Chemical Shift

- Chemical Shift is defined as the difference in parts per million (ppm)between the resonance frequency of the concerned proton and that of the Tetramethyl Silane (TMS) hydrogens.

- TMS is the most common reference compound whose chemical shift is set at δ=0, hence it is known as internal standard.

$$\delta_{sample} = \left(\frac{v_{sample} - v_{reference}}{v_{reference}}\right) \times 10^6$$

Shielding and Deshielding

- Shielding of protons: High electron density around a nucleus shields the nucleus from the external magnetic field, hence the actual field felt by the proton is less and the signals become **upfield** in the spectrum.

- Deshielding of protons: Lower electron density around a nucleus deshields the nucleus from the external magnetic field, hence the actual field felt by the proton is more and the signals become **downfield** in the spectrum.
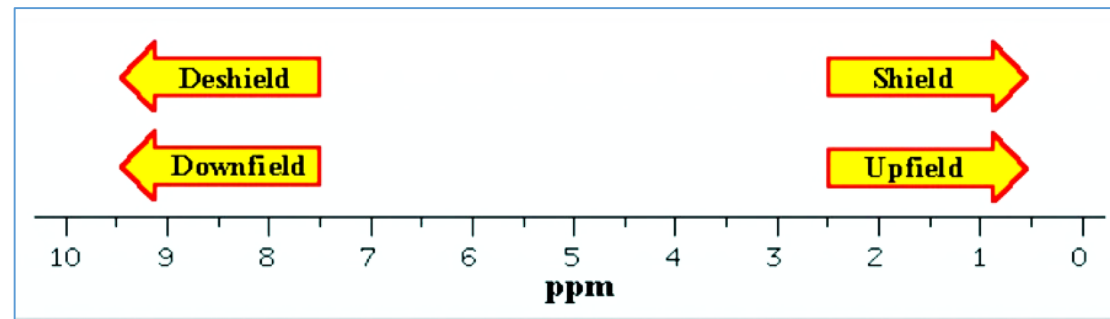
Factors affecting Chemical Shift

- Electronegative groups
- Magnetic anisotropy of π-systems
- Hydrogen bonding

Electronegative groups:- Electronegative groups attached to C-H system decreases the electron density around the protons and thereby causes deshielding. Hence chemical shift value increases.

Magnetic anisotropy of π-systems:-

   The word "anisotropy" means non-uniform. So, magnetic anisotropy leads to non-uniform magnetic field.

 Electrons in π-systems (e.g., aromatic hydrocarbons, alkenes, alkynes, carbonyls, etc.) interact with the applied field that induces a magnetic field that causes anisotropy.

   Anisotropy causes both shielding and deshielding depending on the arrangements of the π-electrons in the molecule.

Example: Benzene, Ethylene, acytelene

applied magnetic field

B_0

Induced magnetic field

Induced magnetic field
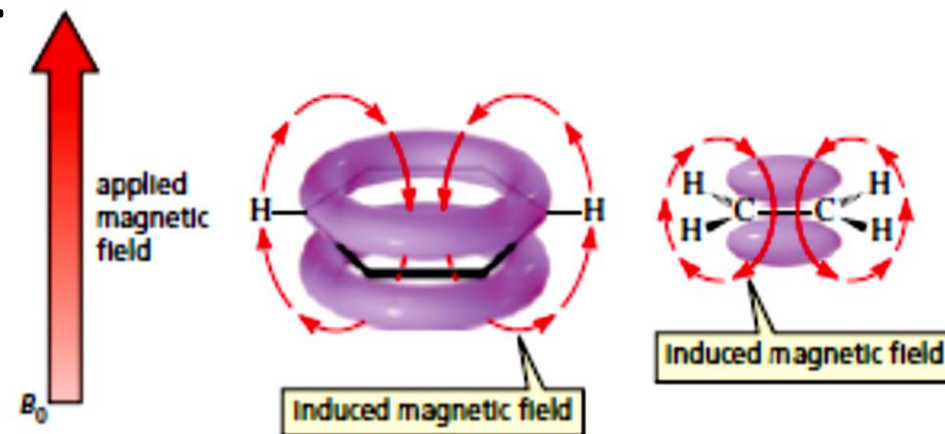
H-bonding:-

 Protons which are involved in H-bonding generally change the chemical shift values.
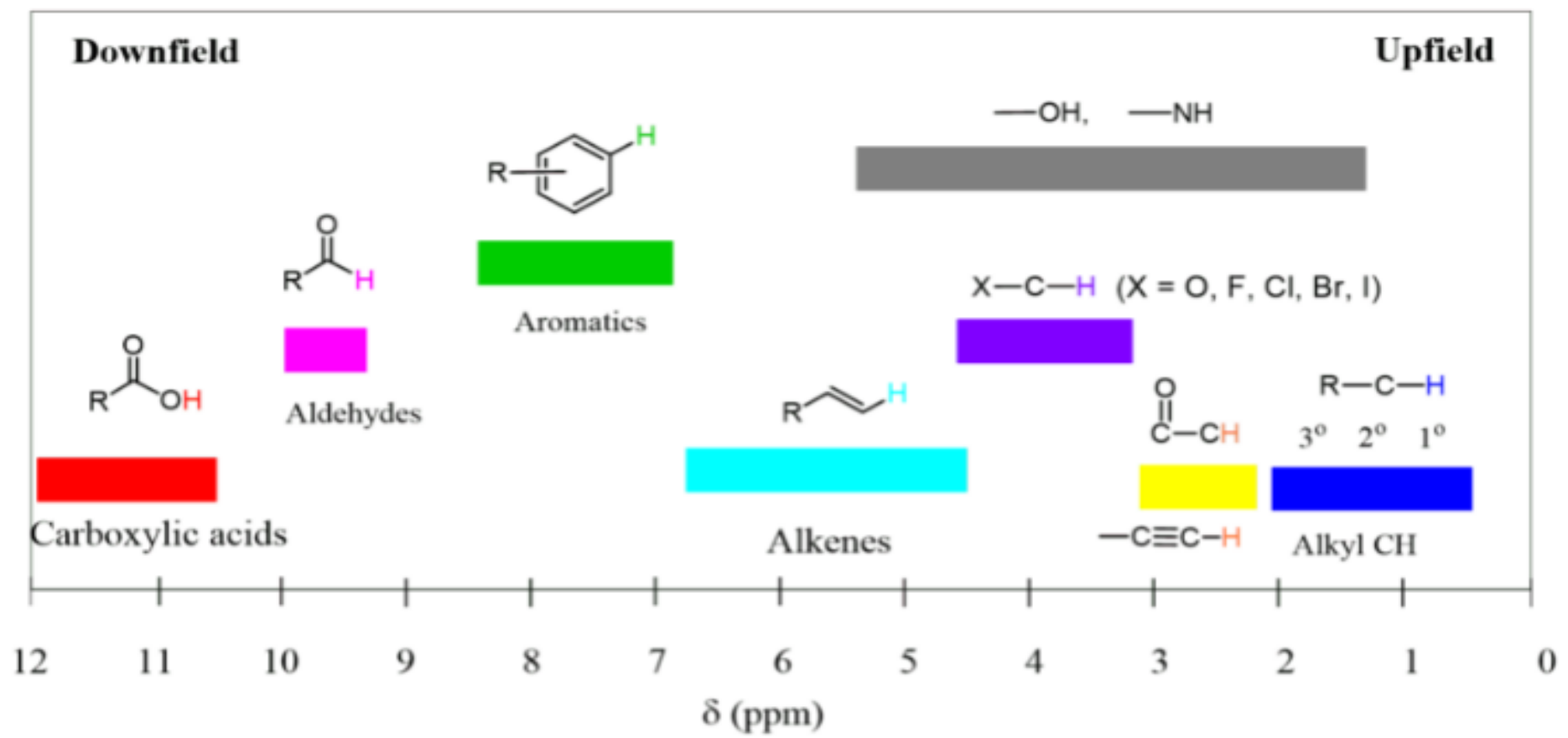

  Higher is the H-bonding, more is the deshielding and higher is the chemical shift value.
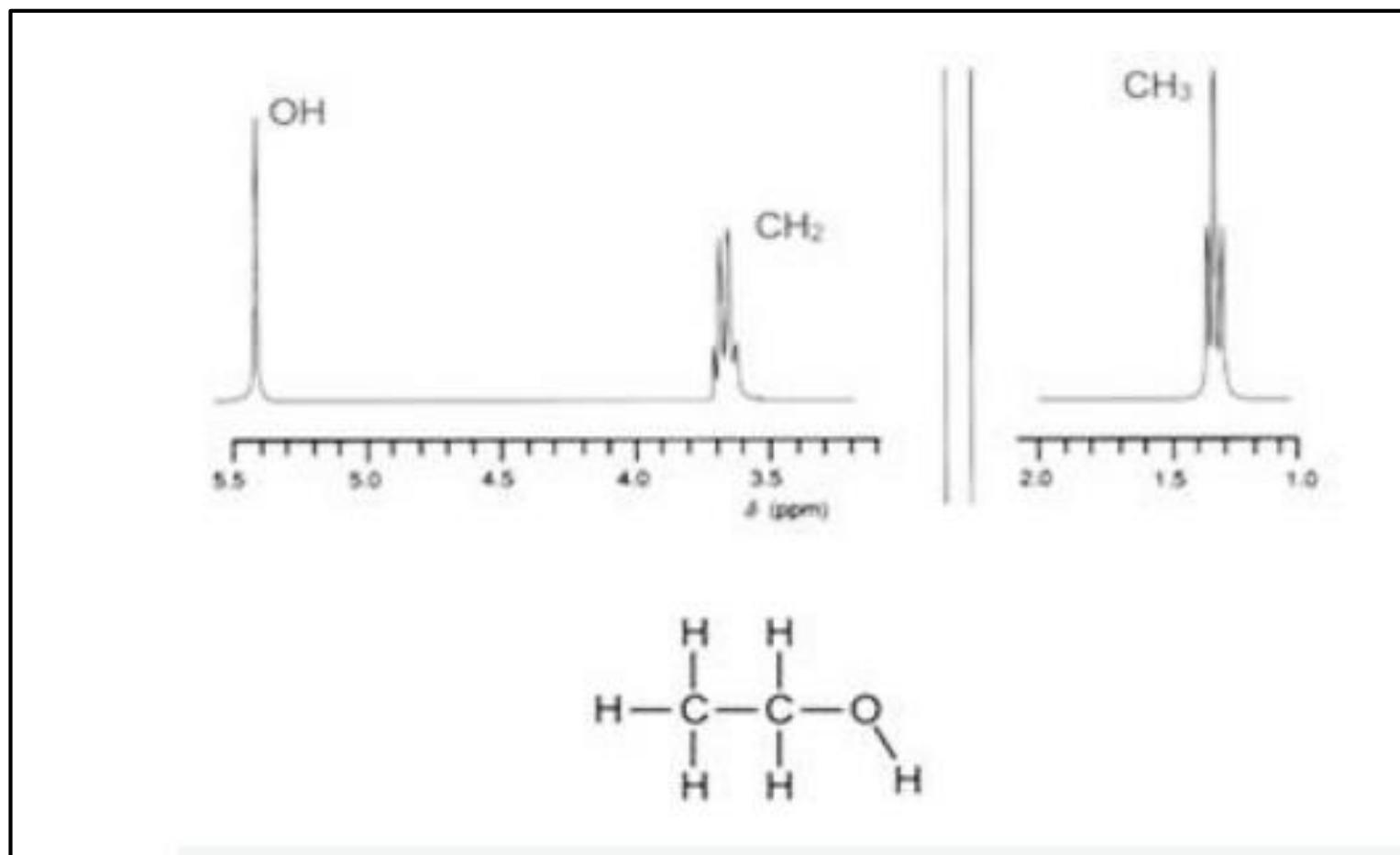
Proton (^{1}H) NMR

- The most common of NMR is the proton NMR which is based on the ^{1}H nucleus.

- From proton NMR, we get different information about the structure of a molecule, number of hydrogens, environment of hydrogens, types of hydrogens.

Chemical shift values of different hydrogens

Type of Proton	Chemical Shift (ppm)	Type of Proton	Chemical Shift (ppm)
$R-CH_3$	0.9 – 1.2	$X-CH_2R$ (X: Cl, Br, I)	3.1 – 3.8
$R-CH_2$ (with R)	1.2 – 1.5	$R-OH$	variable, 1 – 5
$R-CH$ (with R, R)	1.4 – 1.9	$R-NH_2$	variable, 1 – 5
$C=C$ with CHR$_2$	1.5 – 2.5	$C=C$ (with H)	4.5 – 6.0
acyl $R-C(=O)-CH_3$	2.0 – 2.6	$Ar-H$	6.0 – 8.5
$Ar-CH_3$	2.2 – 2.5	aldehyde $R-C(=O)-H$	9.5 – 10.5
$R-C\equiv C-H$	2.5 – 3.0	carboxylic $R-C(=O)-OH$	10 – 13
$(H)R-O-CH_3$	3.3 – 4.0		

Proton NMR spectra of Ethanol
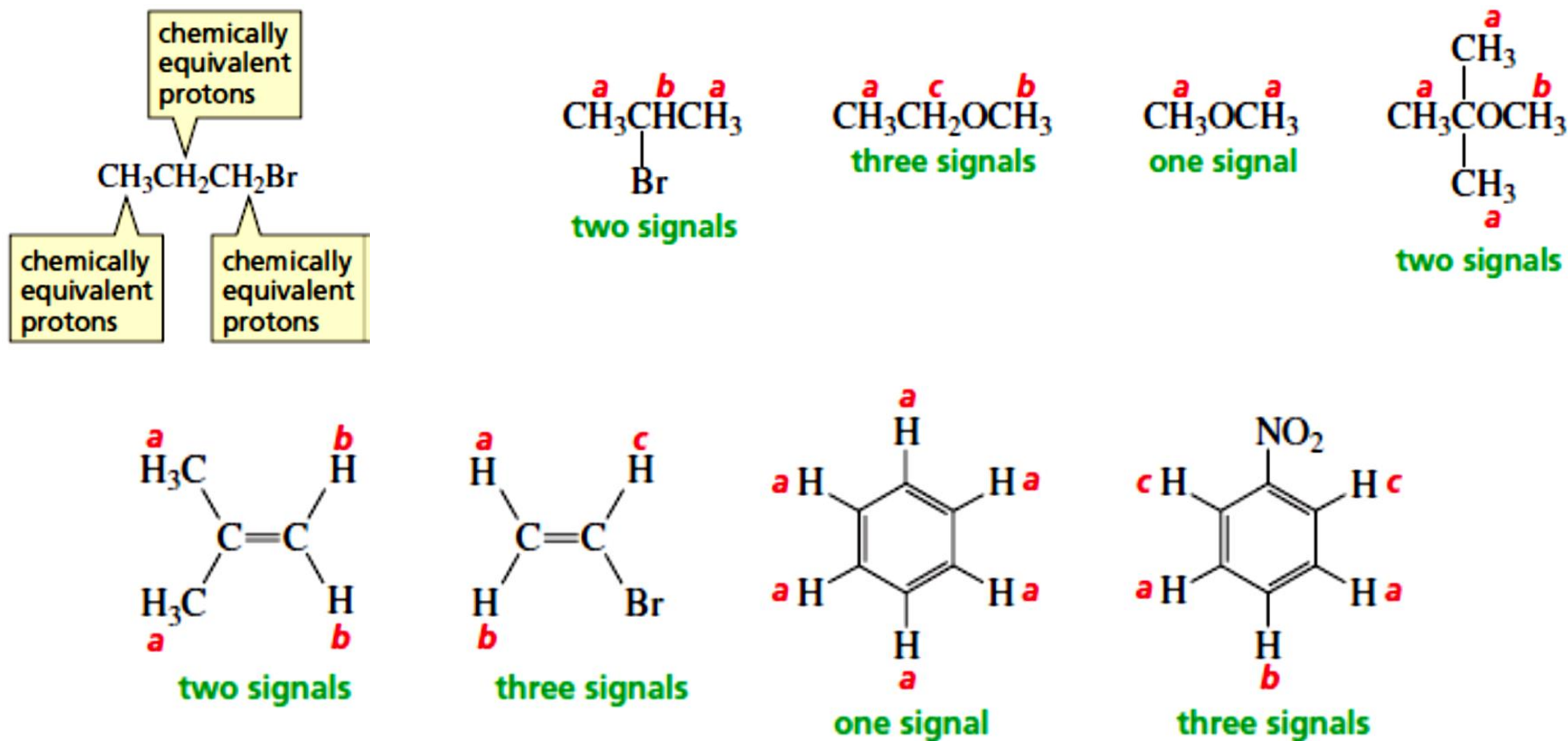
Proton NMR spectra of Benzene
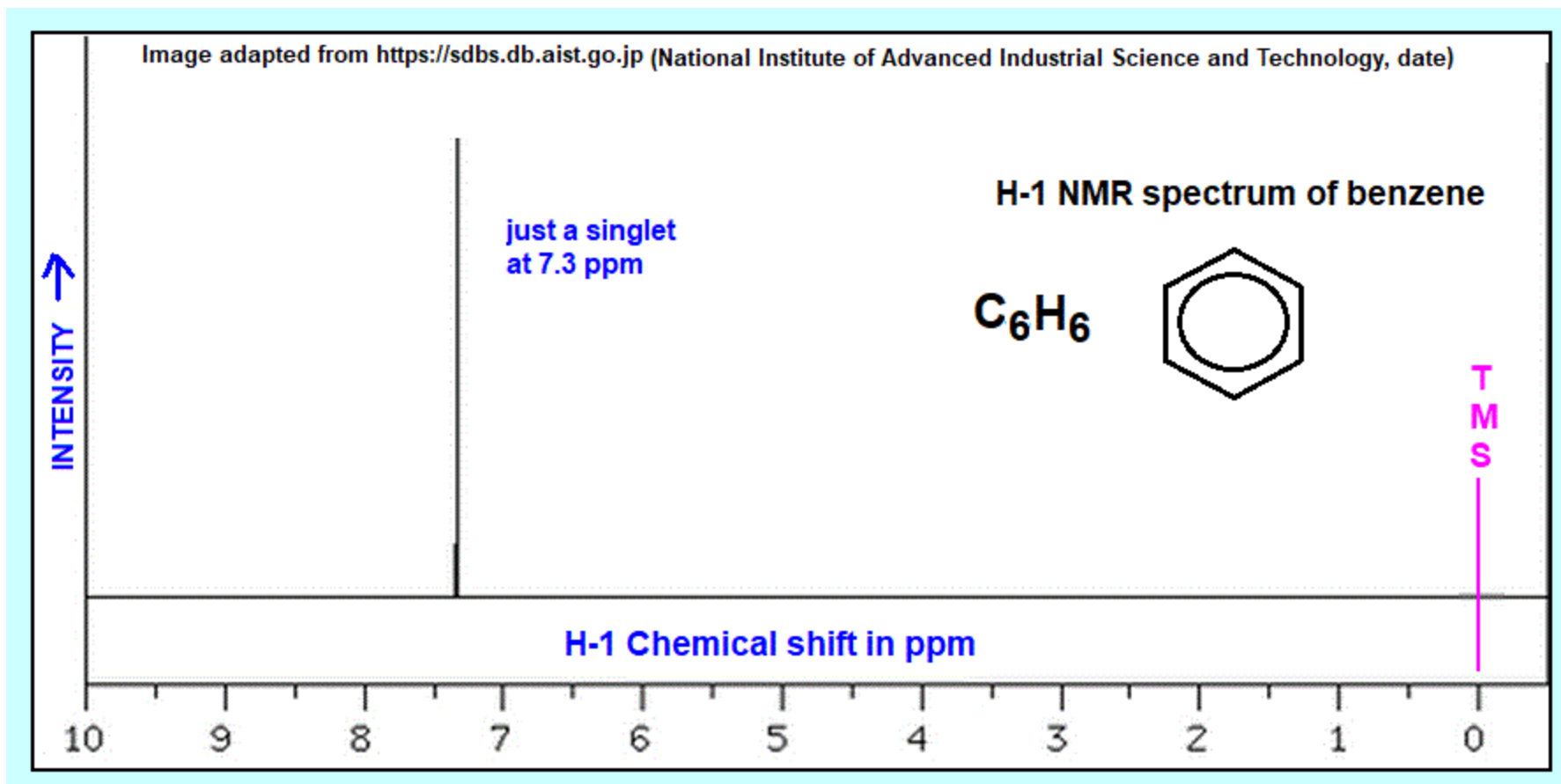
Interpretation of ^{1}H NMR spectra

- Number of signals: Indicates how many different types of H are there

- Position of signals: Indicates about magnetic/electronic environment

- Relative intensity of signals: Gives information about number of hydrogens

- Splitting of signals: Indicates about the number of nearby protons

The Number of Signals in the ¹H NMR Spectrum

Protons in the same environment are called **chemically equivalent protons**.

chemically equivalent protons

$CH_3CH_2CH_2Br$

chemically equivalent protons

chemically equivalent protons

$\overset{a}{C}H_3\overset{b}{C}H\overset{a}{C}H_3$
$|$
Br

two signals

$\overset{a}{C}H_3\overset{c}{C}H_2\overset{b}{O}CH_3$

three signals

$\overset{a}{C}H_3\overset{a}{O}CH_3$

one signal

$\overset{a}{C}H_3$
$|$
$\overset{a}{C}H_3\overset{b}{C}OCH_3$
$|$
CH_3
a

two signals

$\underset{a}{H_3C} \quad \overset{b}{H}$
$\diagdown C=C \diagup$
$\underset{a}{H_3C} \quad \overset{b}{H}$

two signals

$\overset{a}{H} \quad \overset{c}{H}$
$\diagdown C=C \diagup$
$\underset{b}{H} \quad Br$

three signals

$\overset{a}{H}$ ... $a\,H$ ... $H\,a$ ... $a\,H$ ... $H\,a$ ... $\underset{a}{H}$

one signal

NO_2 ... $c\,H$ ... $H\,c$ ... $a\,H$ ... $H\,a$ ... $\underset{b}{H}$
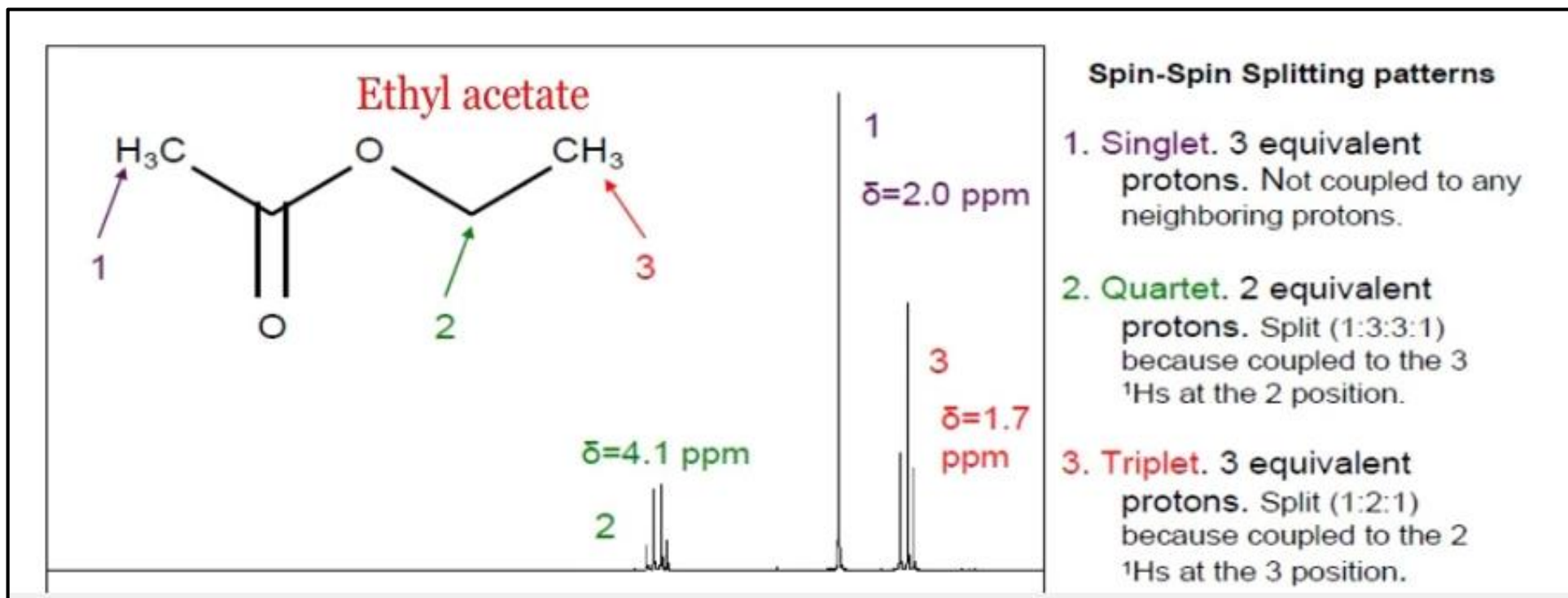
three signals

(n+1) rule

- Splitting of spectral lines arises because of coupling interaction between neighbouring protons and is related to the number of possible spin orientations that these neighbours can adopt. This is known as Spin-spin splitting or **spin coupling**.

- The number of lines (**multiplicity**) observed in the NMR signal for a group of protons is not related to the number of protons in that group, the multiplicity of lines is related to the number of protons in the neighbouring group.

- Multiplicity is given by (n+1), where n is the number of proton in the neighbouring groups.

Pascal's triangle

Number of Equivalent Protons Causing Splitting	Number of Peaks (multiplicity)	Area Ratios (Pascal's triangle)							
0	1 (singlet)				1				
1	2 (doublet)			1		1			
2	3 (triplet)		1		2		1		
3	4 (quartet)	1		3		3		1	
4	5 (quintet)	1	4		6		4		1
5	6 (sextet)	1	5	10		10		5	1
6	7 (septet)	1	6	15	20		15	6	1

Relative Peak Intensities of Symmetric Multiplets

Application of (n+1)rule

Ethyl acetate

Spin-Spin Splitting patterns

1. Singlet. 3 equivalent protons. Not coupled to any neighboring protons.

2. Quartet. 2 equivalent protons. Split (1:3:3:1) because coupled to the 3 ¹Hs at the 2 position.

3. Triplet. 3 equivalent protons. Split (1:2:1) because coupled to the 2 ¹Hs at the 3 position.
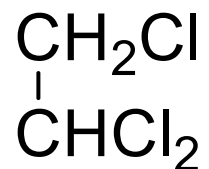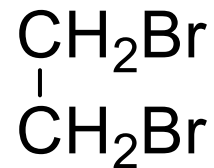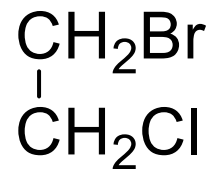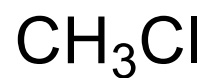
Coupling constant

The distance between the lines in a multiplet is a measure of the effectiveness of the spin-spin coupling and is known as **coupling constant**, denoted by J, expressed in Hz.
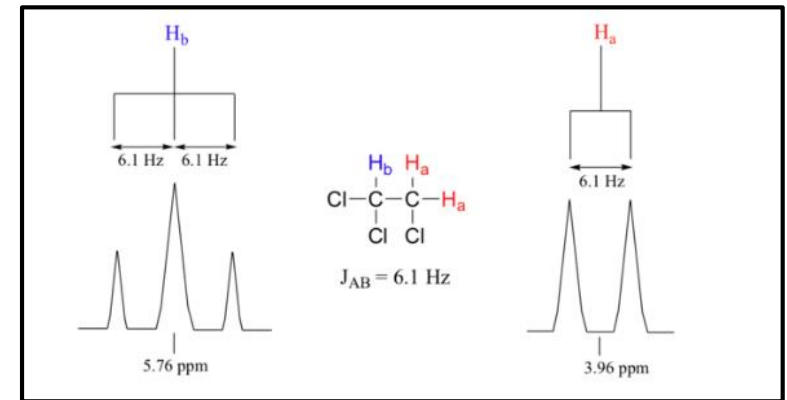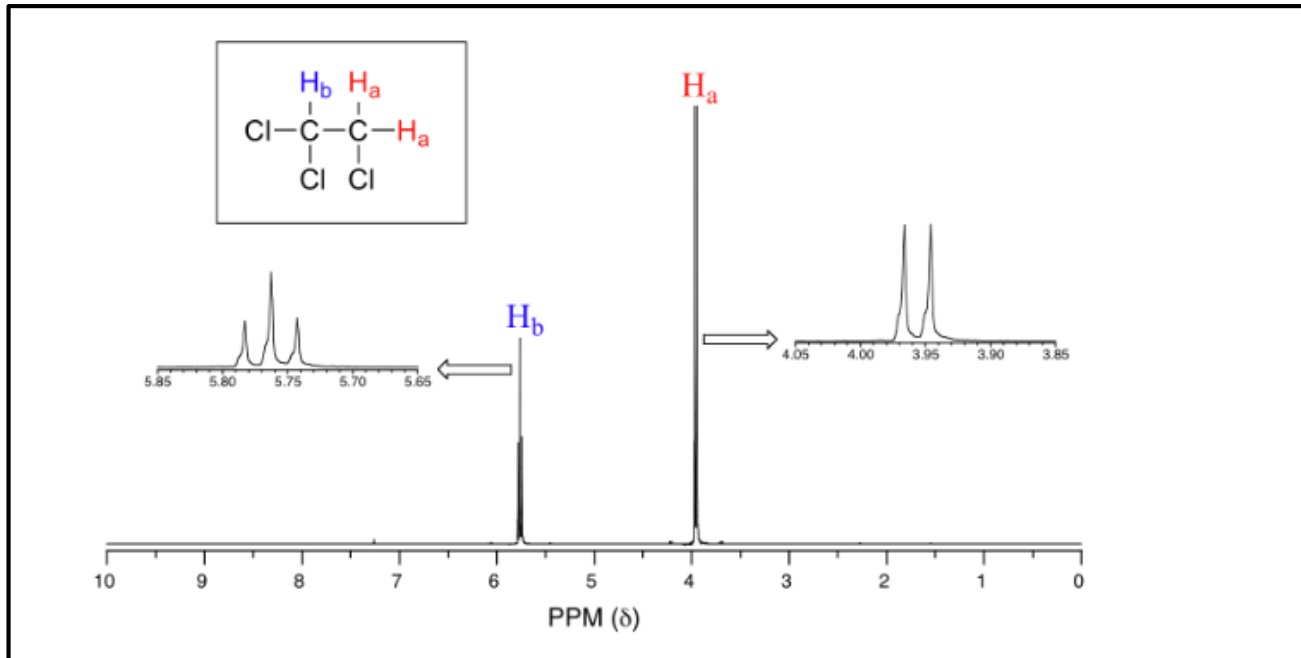
Q. Predict the pattern of proton NMR spectrum for the following molecules.

CH_3Cl

CH_2Br
|
CH_2Cl

CH_2Br
|
CH_2Br

CH_2Cl
|
$CHCl_2$

Application of NMR

- Structure elucidation for organic and inorganic molecules
- Prediction of H-bonding
- Use in peptide and protein chemistry
- Application in medical technology (MRI)
- Exposure in clinical and scientific research

Reference

- **References:**

1. Organic Chemistry, Clayden

2. Organic Spectroscopy, William Kemp

3. Introduction to Spectroscopy, D. Pavia

4. Organic Chemistry, L.G.Wade, Jr.

5. Organic Chemistry, Paula Bruice

6. www.slideshare.net