

# UNIT-1: NMR Spectroscopy

## Principles of Nuclear Magnetic Resonance (NMR)

### 1. Introduction

- **NMR spectroscopy** is one of the most powerful analytical tools used for the **structural elucidation of organic compounds**.
- It provides information about the **number and type of hydrogen atoms ( $^1\text{H}$  NMR)** or **carbon atoms ( $^{13}\text{C}$  NMR)** present in a molecule, and their environments.
- Discovered by **Bloch and Purcell in 1946** (Nobel Prize, 1952).

### 2. Basic Principle

- Certain atomic nuclei (like  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ) possess **nuclear spin ( $I \neq 0$ )**.
- A spinning nucleus behaves like a **tiny magnet** with a magnetic moment ( $\mu$ ).
- When such nuclei are placed in a strong external magnetic field ( $B_0$ ), they can align either:
  - **With the field** (low energy state,  $\alpha$ -spin), or
  - **Against the field** (high energy state,  $\beta$ -spin).

- The energy difference ( $\Delta E$ ) between these two states is given by:

$$\Delta E = h\nu = \gamma \hbar B_0$$

where

$h$  = Planck's constant

$\nu$  = frequency of absorbed radiation

$\gamma$  = gyromagnetic ratio of the nucleus

$B_0$  = applied magnetic field

- When a sample is irradiated with **radiofrequency (RF) radiation** of energy equal to  $\Delta E$ , nuclei undergo **resonance transition** ( $\alpha \rightarrow \beta$ ). This is called **Nuclear Magnetic Resonance**.

### 3. Essential Conditions for NMR

- The nucleus must have a **non-zero spin quantum number ( $I \neq 0$ )**.
- Example:  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  ( $I = 1/2$ ).
- Nuclei with even mass number and even atomic number (like  $^{12}\text{C}$ ,  $^{16}\text{O}$ ) do not show NMR ( $I = 0$ ).

- A **strong external magnetic field ( $B_0$ )** is applied.
- Sample is irradiated with **RF radiation (typically 60–900 MHz range)**.

#### 4. Shielding and Chemical Shift

The magnetic field experienced by a nucleus is affected by the **electron cloud around it**.

Electrons create a small opposing magnetic field (shielding effect).

Thus, nuclei in different chemical environments absorb at slightly different frequencies.

This difference is expressed as **chemical shift ( $\delta$ )**:

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{ref}}}{\nu_{\text{ref}}} 10^6 \quad (\text{in ppm})$$

The reference used is **Tetramethylsilane (TMS)**,  $\delta = 0$  ppm.

#### 5. Spin-Spin Coupling

- Nearby nuclei influence each other's magnetic environment, causing **splitting of NMR signals**
- into multiplets (doublet, triplet, quartet, etc.).
- This gives information about the **number of adjacent protons (n+1 rule)**.

#### 6. Information Obtained from NMR

**Number of signals** → types of chemically distinct protons or carbons.

**Position of signals ( $\delta$ )** → type of proton environment (alkyl, aromatic, aldehydic, etc.).

**Splitting pattern** → number of neighbouring protons.

**Intensity of signals** → relative number of protons.

#### 7. Examples

**CH<sub>3</sub>-CH<sub>2</sub>-Br** (ethyl bromide):

CH<sub>3</sub> group shows a **triplet** (due to 2 protons of CH<sub>2</sub>).

CH<sub>2</sub> group shows a **quartet** (due to 3 protons of CH<sub>3</sub>).

**Benzene**: shows a **single peak** at  $\delta \sim 7.2$  ppm (all 6 protons equivalent).

#### 8. Applications of NMR

- Determination of **molecular structure**.
- Identification of **functional groups**.
- Analysis of **complex mixtures**.
- In medicine: **MRI (Magnetic Resonance Imaging)** is based on NMR principles.

Equivalent and non-equivalent protons

Position of signals.

Chemical shift

NMR splitting of signals

Spin-spin coupling, coupling constants.

Applications of NMR with suitable examples

Ethyl bromide,

Ethanol

Acetaldehyde

1,1,2tribromo ethane

Ethyl acetate

Toluene

Acetophenone.