

# Nuclear Magnetic Resonance spectroscopy

## Introduction: Nuclear Magnetic Resonance spectroscopy

- Nuclear Magnetic Resonance (NMR) Spectroscopy is a technique used to determine the structure of organic molecules by analyzing how certain atomic nuclei (like  $^1\text{H}$  or  $^{13}\text{C}$ ) respond to a magnetic field and radiofrequency energy.

### Key Concepts:

- **Chemical Shift ( $\delta$ ):** Indicates the electronic environment of nuclei.
- **Multiplicity:** Splitting of peaks shows nearby hydrogen atoms (n+1 rule).
- **Integration:** Reflects the number of equivalent nuclei in a signal.
- **Coupling Constant (J):** Distance between split peaks, showing connectivity.

### Common Types:

- $^1\text{H}$  NMR: Focuses on hydrogen atoms.
- $^{13}\text{C}$  NMR: Analyzes carbon atoms.

## Principles of H-NMR and C-NMR

### Basic Principle:

- Nuclei with a non-zero spin ( $I \neq 0$ ) possess a magnetic moment.
- When placed in an external magnetic field ( $B_0$ ), these nuclei align with or against the field.
  - Aligned (lower energy) =  $\alpha$  state
  - Opposed (higher energy) =  $\beta$  state
- The difference in energy between these two states is proportional to the magnetic field strength and a property called the gyromagnetic ratio ( $\gamma$ ).
- Applying radiofrequency (RF) radiation at the correct resonance frequency causes the nucleus to absorb energy and move from the lower to the higher energy state.
- When the RF is turned off, the nucleus relaxes back and emits energy, which is detected and analyzed as the NMR signal.
- The resonance condition is:

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

#### Where:

- $\gamma$  = gyromagnetic ratio
- $B_0$  = magnetic field strength
- $\nu$  = resonance frequency

## <sup>1</sup>H-NMR (Proton NMR) Principles:

1. **Nuclear Spin:** Hydrogen nuclei (<sup>1</sup>H) have spin and act like tiny magnets in a magnetic field.
2. **Chemical Shift (δ):** Protons in different chemical environments absorb at different frequencies (measured in ppm).
3. **Spin-Spin Coupling:** Nearby non-equivalent protons split signals into multiplets, following the **n+1 rule**.
4. **Integration:** The area under each signal is proportional to the number of protons contributing to it.

## <sup>13</sup>C-NMR (Carbon-13 NMR) Principles:

1. **Low Natural Abundance:** Only ~1.1% of carbon atoms are <sup>13</sup>C, so signals are weaker.
2. **Chemical Shift (δ):** Each carbon gives a signal based on its electronic environment, typically from 0–220 ppm.
3. **No Integration:** Peaks usually aren't integrated due to low sensitivity and decoupling.
4. **Proton Decoupling:** Spectra are often simplified by removing proton-carbon splitting, so each carbon appears as a singlet.

## Chemical Shift (δ)

- When a proton is placed in a magnetic field, circulating electrons create a secondary (induced) magnetic field.
- This induced field can oppose (shielded) or align with (deshielded) the applied field.
- Shielding moves the absorption upfield (right), while deshielding shifts it downfield (left).

## Key Points

- Chemical shift (δ) is the difference in absorption position, measured in ppm relative to a reference (usually TMS).
- It is dimensionless and independent of field strength.
- Formula:

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\text{Operating Frequency (MHz)}}$$

- δ values typically range from 0 to 10 ppm.
- T scale increases right to left (low to high field), while δ scale increases left to right.

## Typical δ ranges:

- <sup>1</sup>H NMR: 0 – 12 ppm
- <sup>13</sup>C NMR: 0 – 220 ppm

## Reference Standards

### 1. TMS (Tetramethylsilane)

- Resonates at 0 ppm due to strong shielding.
- Used as an internal standard for  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR.
- Advantages:
  - Chemically inert, volatile, and soluble.
  - All protons are magnetically equivalent.
  - Doesn't interact with samples.
  - Resonance is far from most organic protons.

### 2. Sodium salt of 3-(Trimethylsilyl) Propane Sulphonate

- Water-soluble alternative to TMS.
- Commonly used with  $\text{D}_2\text{O}$  for water-soluble compounds.

## Factors Affecting Chemical Shift

### 1. Electronegativity of Nearby Atoms:

- Electronegative atoms (e.g., O, F, Cl) withdraw electron density.
- This deshields nearby protons, shifting signals downfield (higher  $\delta$ ).

### 2. Hybridization of Carbon Atoms:

- Protons attached to  $\text{sp}^2$  carbons (alkenes, aromatics) appear downfield due to less shielding.
- $\text{sp}^3$  carbons provide more shielding  $\rightarrow$  upfield shift.

### 3. Anisotropy (Magnetic Anisotropy):

- $\pi$  systems (aromatics, alkenes, alkynes) generate local magnetic fields.
- These influence nearby proton environments significantly:
  - Aromatic protons: downfield
  - Alkyne protons: upfield

### 4. Hydrogen Bonding:

- Involves partial deshielding due to electron withdrawal.
- Causes variable and often downfield shifts (especially in  $-\text{OH}$ ,  $-\text{NH}$ ).

### 5. Solvent Effects:

- Polar solvents can alter electron density and shift  $\delta$  values slightly.



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