# 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 $^{1}H$ or $^{13}C$) respond to a magnetic field and radiofrequency energy.

### Key Concepts:

- **Chemical Shift (δ):** 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:

- **$^{1}H$ NMR:** Focuses on hydrogen atoms.
- **$^{13}C$ 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) = α state
    - Opposed (higher energy) = β state
- The difference in energy between these two states is proportional to the magnetic field strength and a property called the gyromagnetic ratio (γ).
- 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:**

- γ = gyromagnetic ratio
- $B_0$ = magnetic field strength
- ν = resonance frequency

## $^{1}$H-NMR (Proton NMR) Principles:

1. **Nuclear Spin:** Hydrogen nuclei ($^{1}$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.

## $^{13}$C-NMR (Carbon-13 NMR) Principles:

1. **Low Natural Abundance:** Only ~1.1% of carbon atoms are $^{13}$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:

- $^{1}$H NMR: 0 – 12 ppm
- $^{13}$C NMR: 0 – 220 ppm

## Reference Standards

### 1. TMS (Tetramethylsilane)

- Resonates at 0 ppm due to strong shielding.
- Used as an internal standard for $^{1}H$, $^{13}C$, $^{29}Si$ 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 $D_2O$ 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 δ).

### 2. Hybridization of Carbon Atoms:

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

### 3. Anisotropy (Magnetic Anisotropy):

- π 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 –OH, –NH).

### 5. Solvent Effects:

- Polar solvents can alter electron density and shift δ values slightly.

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