NMR Spectroscopy (Nuclear Magnetic Resonance Spectroscopy)

1. Introduction to NMR Spectroscopy

Nuclear Magnetic Resonance (NMR) is one of the most powerful analytical techniques used in organic chemistry for determining molecular structure.

It allows chemists to identify:

- number of chemically different atoms
- molecular skeleton
- neighboring atoms
- stereochemistry
- purity of compounds

NMR is mainly used for nuclei possessing **spin quantum number I ≠ 0**, such as:

- **^{1}H (proton NMR)**
- **^{13}C (carbon NMR)**
- **^{19}F**
- **^{31}P**

2. Conditions for Nuclear Absorption in NMR

Only nuclei with a **spin quantum number (I) different from zero** can absorb or emit electromagnetic radiation and are therefore active in **Nuclear magnetic resonance**.

A nucleus can be observed in NMR only if it possesses a non-zero nuclear spin.

Classification of Nuclei According to Mass Number (A) and Atomic Number (Z)

1. Even Mass Number (A) and Even Atomic Number (Z)

When both the mass number **A** and the atomic number **Z** are even:

I = 0

These nuclei are **NMR inactive**, because they do not possess a magnetic moment.

Examples:

- Carbon ($^{12}_{6}C$)
- Oxygen ($^{16}_{8}O$)
-

2. Even Mass Number (A) and Odd Atomic Number (Z)

When the mass number is **even** and the atomic number is **odd**, the spin quantum number is generally an integer:

I = 1, 2, 3...

These nuclei are **NMR active**.

Examples:

- Nitrogen ($^{14}_{7}N$)

- Boron ($^{10}_{5}B$)
- Deuterium ($^{2}_{1}H$)

3. Odd Mass Number (A) and Even Atomic Number (Z)

When the mass number is **odd** and the atomic number is **even**:

$$\boldsymbol{I = \frac{1}{2}}$$

These nuclei are **NMR active**.

Examples:

- Carbon-13 ($^{13}_{6}C$)
- Oxygen-15 ($^{15}_{8}O$)

4. Odd Mass Number (A) and Odd Atomic Number (Z)

When both A and Z are **odd**, nuclei are also **NMR active**.

Example:

- Hydrogen-1 ($^{1}_{1}H$)

Nuclear Spin States

The spin states of a nucleus are quantized and defined by the magnetic quantum number:

$$\mathbf{m = I, I-1, I-2, ..., -I}$$

Thus, a nucleus with spin **I** has:

$$\mathbf{2I + 1}$$

Possible spin orientations.

Examples for Common NMR Nuclei

For nuclei such as:

- Hydrogen-1
- Carbon-13
- Nitrogen-15

The nuclear spin is:

$$\boldsymbol{I = \frac{1}{2}}$$

and the two possible spin states are:

$$\boldsymbol{m = +\frac{1}{2}, -\frac{1}{2}}$$

2. Physical Principle of NMR

Certain nuclei behave like tiny magnets because they possess nuclear spin.

When placed in an external magnetic field ($\mathbf{B_0}$):

- nuclei align either:

- parallel (low energy)
- antiparallel (high energy)

Energy absorption occurs when radiofrequency matches the energy gap.

The resonance condition is:

$$\mathbf{\Delta E = h\nu = \gamma \hbar B_0}$$

Where:

- ΔE = energy difference
- h = Planck constant
- ν = frequency
- γ = gyromagnetic ratio

3. Instrumentation of NMR Spectrometer

Main components:

a) Magnet

Produces strong magnetic field.

Modern spectrometers:

- 300 MHz
- 400 MHz
- 500 MHz
- 600 MHz

b) Radiofrequency transmitter

Sends RF pulse.

c) Sample tube

Contains sample dissolved in deuterated solvent.

d) Detector

Records signal.

e) Computer

Transforms signal into spectrum by Fourier Transform.

4. Deuterated Solvents

Used because ordinary solvents contain protons.

Common solvents:

- Deuterated chloroform
- Dimethyl sulfoxide-d6
- Deuterium oxide

Reasons:

- avoid solvent proton interference
- provide lock signal

5. Principle of the NMR Spectrometer

The following elements are essential for constructing an NMR spectrometer:

5.1. NMR Signals

An NMR signal results from the absorption of electromagnetic radiation by nuclei possessing non-zero spin.

The detected signal depends on:

- the type of nucleus
- its chemical environment
- neighboring atoms

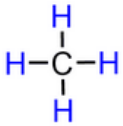
Each signal corresponds to nuclei in a specific electronic environment.

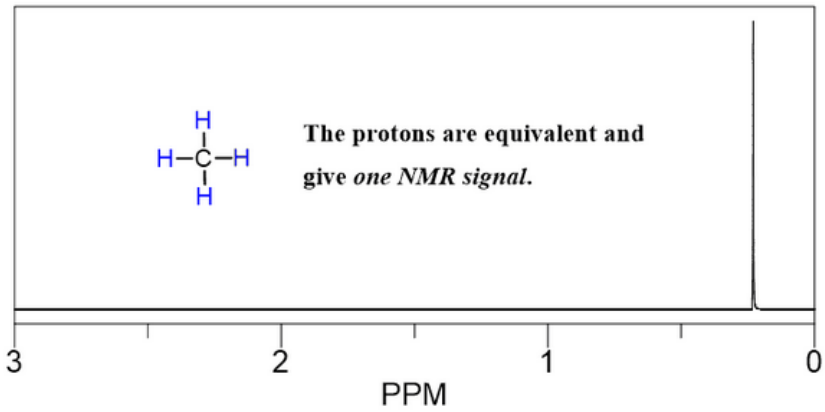
For example:

- equivalent nuclei give one signal
- non-equivalent nuclei give different signals

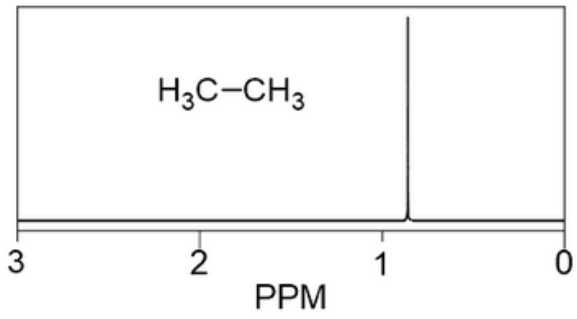
Example

Ex 1: methane (one type of proton, therefore one signal on the spectrum)

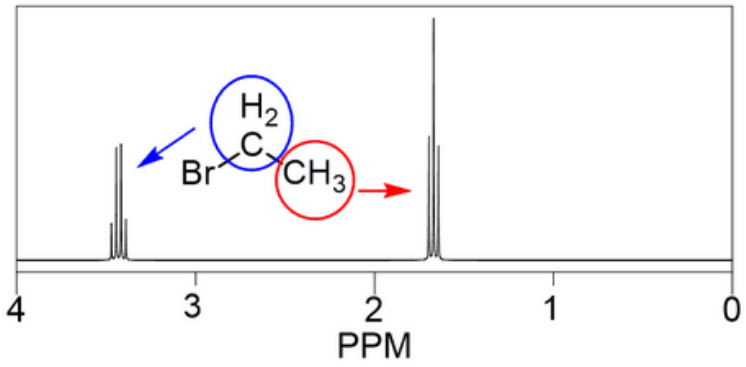




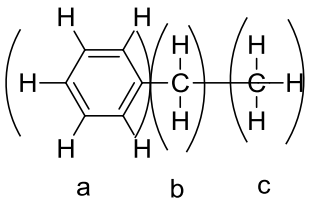
Ex 2: ethane

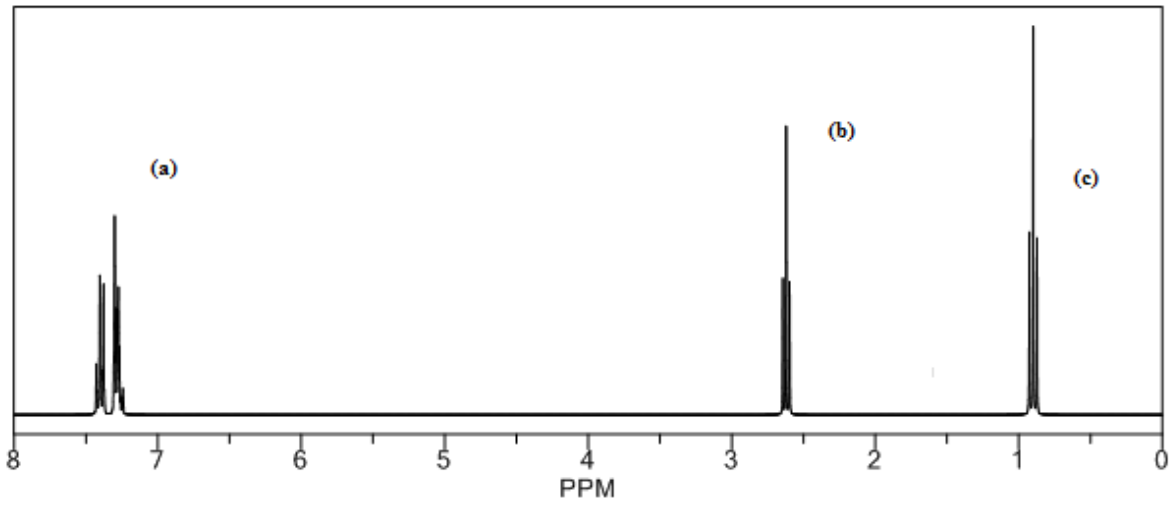


Ex 3: example, **Bromoethane gives two NMR signals** because the protons of the CH_2 groups, being closer to the bromine, are different from those in the CH_3 group (Two different types of protons, therefore two signals on the spectrum):

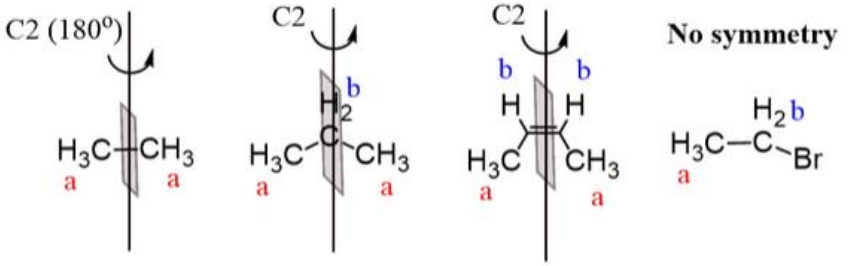


Ex 5: three different types of protons, therefore three signals on the spectrum

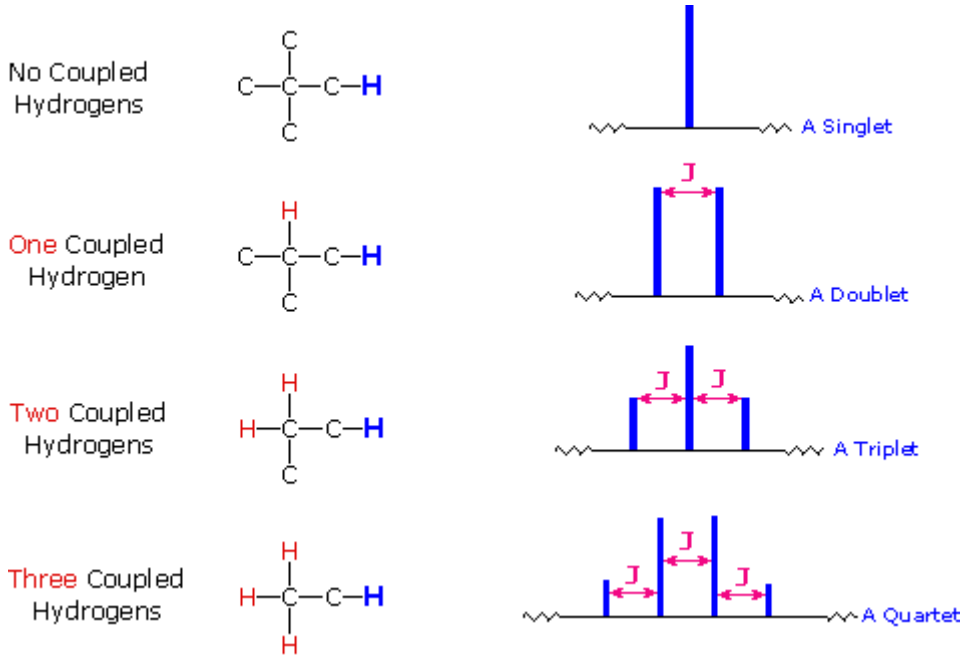




Ex 4: From these examples, you might have noticed that the **number of NMR signals** is somehow **related to the symmetry** of the molecule.



6 protons but only 1 type	8 protons but 2 types	8 protons but 2 types	5 protons but 2 types
1 signal	**2 signals**	**2 signals**	**2 signals**



Summary of Signal Splitting Patterns in ^{1}H NMR Spectroscopy

The pattern is that n protons split the signal into n+1 peaks, which is known as the **n+1 rule**.

Multiplicity	N +1	H_a	Signal	H_b	N +1	Multiplicity
Doublet	1+1 = 2				1+1 = 2	Doublet
Triplet	2+1 = 3				1+1 = 2	Doublet
Triplet	2+1 = 3				2+1 = 3	Triplet
Quartet	3+1 = 4				1+1 = 2	Doublet

5.2. Chemical Shift (δ)

Chemical shift indicates electronic environment of nuclei.

Formula:

$$\delta = \frac{\nu_{Sample} - \nu_{Reference}}{\nu_{Spectrometer}} \times 10^6$$

Unit:

- **ppm**

Reference:

- Tetramethylsilane = 0 ppm

6. Multiplicity and Spin–Spin Coupling in ^{1}H NMR

In **^{1}H NMR spectroscopy**, each set of equivalent protons produces a signal. However, this signal is often **split into multiple peaks** due to interactions with neighboring protons.

*This splitting is called **multiplicity** or **spin–spin coupling**.*

6.1. Origin of Spin–Spin Coupling

Multiplicity arises from the interaction between **non-equivalent neighboring protons** through chemical bonds (usually 2–3 bonds).

- A proton can have two spin states:
  - α (aligned with magnetic field)
  - β (opposite)

Neighboring protons create slightly different magnetic environments → signal splitting.

6.2. The (n + 1) Rule

The number of peaks in a signal is given by:

$$2\,n\,I\ +\ 1 => I = \frac{1}{2}$$

$$2\,n\,\frac{1}{2} + 1 => n + 1$$

Number of peaks = n + 1

Where:

- **n = number of equivalent neighboring protons**

Examples:

Neighbors (n)	Multiplicity	Pattern

Neighbors (n)	Multiplicity	Pattern
0	Singlet	S
1	Doublet	D
2	Triplet	T
3	Quartet	Q
4	Quintet	quint

6.3. Common Splitting Patterns

- **Singlet (s)**
- No neighboring protons
- Example: CH_3–C (no adjacent H) => **One peak**

- **Doublet (d)**
- 1 neighboring proton => **Two peaks** (1:1)

- **Triplet (t)**
- 2 neighboring protons => **Three peaks** (1:2:1)

- **Quartet (q)**
- 3 neighboring protons => Four peaks (1:3:3:1)

6.4. Pascal's Triangle (Peak Intensity)

The intensity of peaks follows **Pascal's triangle**:

Multiplicity	Ratio
Doublet	1:1
Triplet	1:2:1
Quartet	1:3:3:1
Quintuplet	1:4:6;4:1
Sextuplet	1:5:10:10:5:1

This helps confirm the number of neighboring protons.

6.5. Coupling Constant (*J*)

The **coupling constant (*J*)** measures the distance between split peaks:

$$J = \Delta\nu \text{ (Hz)}$$

- Unit: **Hertz (Hz)**
- Same *J* value → signals are coupled

Typical values:

- Vicinal coupling (3 bonds): **6–8 Hz**
- Geminal coupling (2 bonds): **10–15 Hz**
- Aromatic: **6–9 Hz**

6.6. Types of Coupling

- **Vicinal Coupling (^3J)**
- Between protons on adjacent carbons
- Most common
- **Geminal Coupling (^2J)**
- Between protons on same carbon (CH_2)
- **Long-range Coupling (^4J, ^5J)**
- Weak coupling over 4–5 bonds
- Seen in conjugated or aromatic systems

6.7. Complex Splitting (Non-equivalent Neighbors)

If a proton is coupled to **different sets of protons**, splitting becomes more complex:

Example:

- Coupled to 2H and 1H → **doublet of triplets (dt)**

Rule: Split step-by-step for each neighboring group.

6.8. First-Order vs Second-Order Spectra

First-order (simple):

- Follows (n+1) rule
- Peaks symmetric

Second-order (complex):

- Occurs when $\Delta\delta \approx J$
- Peaks distorted (roofing effect)

6.9. Practical Interpretation Strategy

When analyzing multiplicity:

1. Identify number of peaks
2. Determine multiplicity
3. Use (n+1) → find neighbors
4. Check *J* values → confirm coupling
5. Combine with integration + chemical shift

6.10. Example

Ethyl group (CH_3–CH_2–):

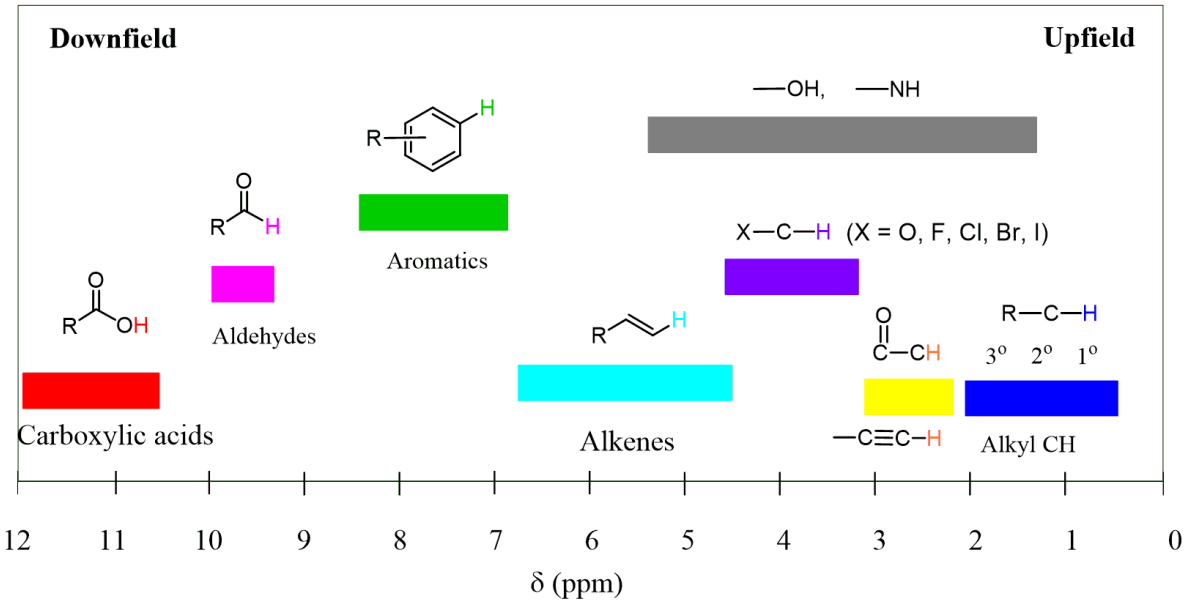
- CH_3 → triplet (n=2)
- CH_2 → quartet (n=3)

❖ **Classic pattern**:

- Triplet + Quartet → confirms ethyl group

7. Typical ^1H Chemical Shift Regions

Proton Type	δ (ppm)
Alkane	0.8 – 1.5
Alkene	4.5 – 6.5
Aromatic	6.5 – 8.5
Aldehyde	9 – 10
Carboxylic acid	10 – 13



R-CH_3	**0.7 - 1.3**
R-CH_2-R	**1.2 - 1.4**
R_3CH	**1.4 - 1.7**
R–C=C–CH_3	**1.6 - 2.6**
R–C(=O)–CH_3	2.1 - **2.5**
RO–C(=O)–CH_3	**2.1 - 2.6**
N≡C–CH_3	**2.1 - 3.0**
Ar–C–H	**2.3 - 2.7**
R–C≡C–H	**1.7 - 2.7**
R–N–C–H	**2.2 - 2.9**
R–S–C–H	**2.0 - 3.0**

R= H or alkyl

I–C–H	**2.0 - 4.0**
Br–C–H	**2.7 - 4.1**
Cl–C–H	**3.1 - 4.1**
RO–C–H	**3.2 - 3.8**

R= H or alkyl

R–C(=O)–O–C–H	**3.5 - 4.8**
O_2N–C–H	**4.1 - 4.3**
F–C–H	**4.2 - 4.8**
R–C=C–H	4.5 - **6.5**
Ar–H	**6.5 - 8.0**
R–C(=O)–H	9.0 - **10**

NH and OH peaks are most often broad or may as well be missing completely unless the sample is very dry.

This is also true for any proton capable of making hydrogen bonding:

R—SH R = alkyl or aryl	1.0 - **5.0**
$R—NH_2$ 1°, 2°	1.0 - **5.0**
R—OH 1°, 2°, 3°	1.0 - **5.0**
Ar—OH	**4.0 - 7.0**
R–C(=O)–N(R)–H 1°, 2°	**5.0 - 9.0**
R–C(=O)–OH	11 - **12**

Downfield shifts more common

8. Shielding and Deshielding

Shielded proton

High electron density:

→ signal appears upfield

Deshielded proton

Near electronegative atom:

→ signal appears downfield

Electronegative atoms causing deshielding:

- O
- N
- Cl

9. Proton Exchange Signals

Signals often broad:

- OH
- NH
- COOH

Disappear with Deuterium oxide

10. Factors Affecting Chemical Shift

- electronegativity
- hybridization
- anisotropy
- hydrogen bonding

11. Steps for Interpreting ^{1}H NMR

Step 1

Count signals

Step 2

Check chemical shifts

Step 3

Analyze integration

Step 4

Analyze splitting

Step 5

Assemble structure

12. ^{13}C NMR Spectroscopy

^{13}C NMR spectroscopy is used to study the carbon skeleton of organic molecules.

- ✓ Detects the isotope ^{13}C (≈1.1% natural abundance)
- ✓ Less sensitive than ^{1}H NMR
- ✓ Provides number and type of carbon environments

Characteristics:

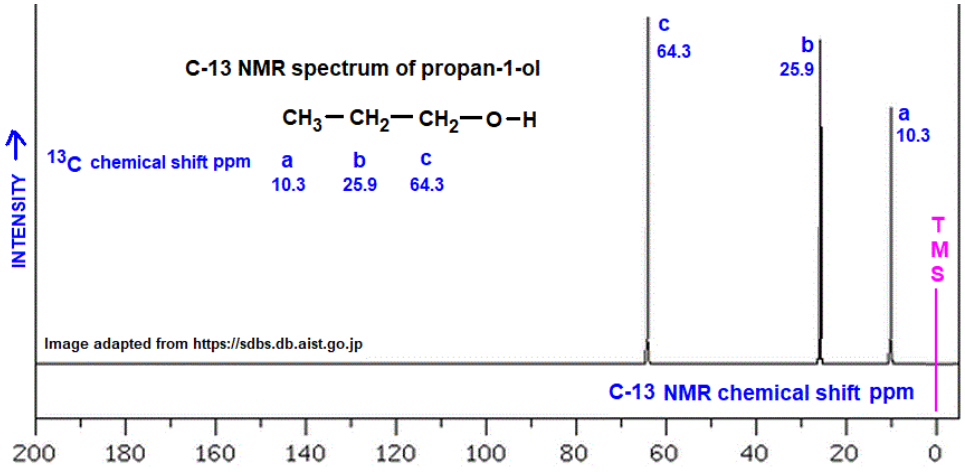
- no integration usually
- wider chemical shift range

Typical range: **0–250 ppm (practically between 0-220 ppm)**

12.1. Proton Decoupling

- ➢ **Broadband Decoupling**
- Removes C–H coupling
- Each carbon appears as a **single peak (singlet)**

This simplifies the spectrum



12.2. Number of Signals

- Each **unique carbon environment → one signal**
- Symmetry reduces number of signals

Example:

- Ethanol → 2 signals (CH_3 and CH_2)

12.3. Signal Intensity

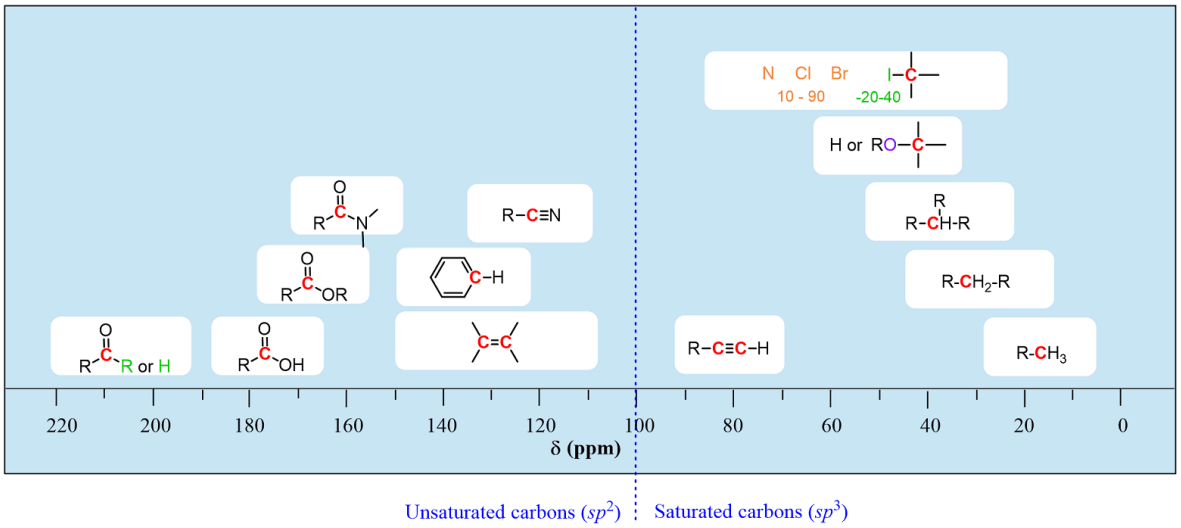
- Not directly proportional to number of carbons
- Affected by:

- Relaxation time
- NOE (Nuclear Overhauser Effect)

So integration is** not reliable **in ^{13}C NMR.

13. Typical ^{13}C Chemical Shifts

^{13}C NMR Chemical Shift Values



Approximate Values of Chemical Shifts for ^{13}C NMR

$(CH_3)_4Si$	0	* I–C	-20 - 40	C=C	100 - 150		155 - 185
R-CH_3	8 - 30	Br–C	25 - 65	C–H	110 - 170		
R-CH_2-R	15 - 55	Cl–C	35 - 80	C=N	150 - 170		165 - 185
R_3CH	20 - 60	O–C	40 - 80	C≡N	110 - 140		
R_4C	30 - 50	N–C	30 - 65				190 - 220

14. DEPT Technique

Distinguishes carbons:

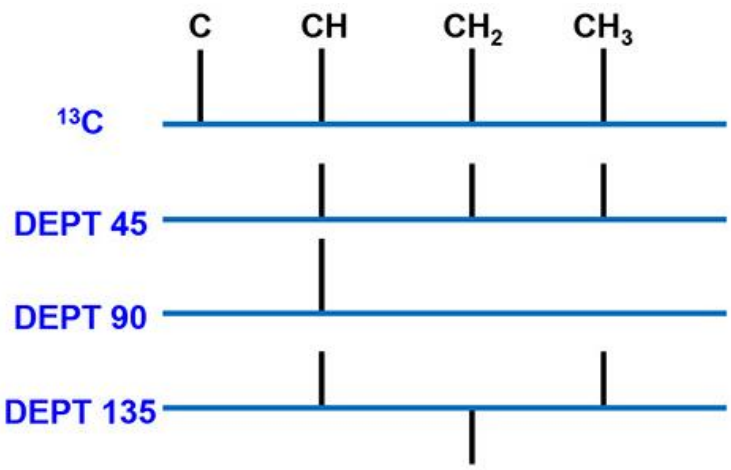
- CH_3
- CH_2
- CH
- quaternary carbon

Types:

- DEPT-45
- DEPT-90

- DEPT-135

Ex:



15. Applications of NMR

Used in:

- organic synthesis
- pharmaceutical analysis
- natural product identification
- purity control
- biomolecular studies

23. Comparison with Other Techniques

Technique	Gives
IR	functional groups
UV	Conjugation
MS	molecular mass
NMR	full structure

24. Important Modern NMR Methods

2D NMR

Examples:

- COSY
- HSQC
- HMBC

These give proton-carbon correlations.