

A Levels Chemistry:

ANALYTICAL TECHNIQUES

Lesson 37.02

Carbon-13 NMR Spectroscopy

Revision Notes

Cambridge will assess your ability to:

- Analyse and interpret a carbon-13 NMR spectrum of a simple molecule to deduce:
 - The different environments of the carbon atoms present
 - The **possible structures** for the **molecule**
- Predict or explain the number of peaks in a carbon-13 NMR spectrum for a given molecule

Introduction to NMR:

- **NMR spectroscopy** is a powerful technique used in the analysis of **organic compounds.**
- NMR stands for Nuclear Magnetic Resonance Spectroscopy.
- Certain atomic nuclei, like carbon-13 and hydrogen, exhibit magnetic properties.
- Nuclei with an odd number of protons or neutrons have a net nuclear spin and behave like magnets.





- Nuclei with an even number of protons and neutrons have no net nuclear spin and do not behave as magnets.
- NMR spectroscopy utilises the magnetic properties of the carbon-13 and proton nuclei to determine the exact arrangements of carbon atoms and hydrogen atoms in unknown organic compounds.



Types of NMR spectroscopy

- Carbon-13 NMR spectroscopy
 - Provides information about carbon atoms in molecules
- Proton NMR spectroscopy
 - Provides information about hydrogen atoms in molecules

• Principle of NMR:

 When Carbon-13 or proton nuclei are subject to external magnetic fields, the nuclei align with or against an external magnetic field.



 Nucleus are at higher energy states aligned against the external field than one aligned with the external field.



- The energy needed to flip the **nucleus** usually falls in the range of **energy** that lies in the **radio waves region of electromagnetic spectrum.**
- **Radio waves** at specific frequencies are used to **flip nuclei** from one alignment to the other, known as the **resonance condition**.



- Carbon-13 NMR spectroscopy:
 - The main function of this spectroscopy is to give information about carbon atoms in molecules.
 - Carbon-12 and carbon-14 don't have net nuclear spin since they have even numbers of protons and even numbers of neutrons.
 - Peaks in carbon-13 NMR spectra are due to 1% of carbon-13 nuclei present in the sample.
 - Peaks in carbon-13 NMR spectra represent different chemical environments.
 - The number of peaks in carbon-13 NMR spectra indicates the number of carbon environments in the molecule.

- ¹³C nuclei with different chemical environments experience the external magnetic field at different levels.
- Different chemical environments affect the resonance condition of ¹³C nuclei to different extents. That's why peaks are obtained at different chemical shift values.



 Atoms having the same chemical environment are said to be chemically equivalent atoms.

$ \begin{array}{c ccccccc} H & Br & H \\ I & I & I \\ H - C - C - C - H \\ I & I & I \\ H & H & H \end{array} $	D.asia
220 200 180 160 140 120 100 80 60 40 20 0 δ/ppm	
¹³ C NMR spectrum of 2-bromopropane	

 Chemical shift values denote the resonance condition of nuclei in different environments.

Interpretation of NMR Spectra:

- Peaks in NMR spectra correspond to chemically equivalent atoms.
- Different chemical environments lead to peaks at different chemical shift values.

- Interpreting Carbon-13 NMR Spectra for Isomers:
 - Carbon-13 NMR spectra can distinguish between isomers based on the number of peaks.



- **Isomers** with different **chemical environments** for **carbon atoms** yield **different numbers** of **peaks**.
- 2-methylpropanal, with two identical carbon environments, displays three peaks in its spectrum.



¹³C NMR spectrum of methylbenene



- Chemical Shift in Carbon-13 NMR:
 - Chemical shift values denote the position of peaks relative to a reference compound tetramethylsilane.



 Tetramethylsilane (TMS) serves as a standard reference compound due to its unique chemical properties.



• TMS provides a strong peak at the extreme right of the scale, ensuring clear identification of other compound peaks.

• Chemical shift ranges categorise carbon atoms based on their chemical environments and adjacent atoms.

lybridisation of the carbon tom	Environment of carbon atom	Example structures	Chemical shift range (δ)
sp ³	Alkyl	CH3-,-CH2-,-CH4	0-50
sp³	Next to alkene/ arene		10-40
sp³	Next to carbonyl /carboxyl	-CH ₂ -COR, -CH ₂ -CO ₂ R	25-50
sp ³	Next to nitrogen	- CH ₂ - NH ₂ - CH ₂ - NR ₂ - CH ₂ - NHCO	30-65
sp³	Next to chlorine (-CH ₂ -Br and -CH ₂ -I are in the same range as alkyl)	- CH ₂ - CI	30-60
sp ³	Next to oxygen	-CH2-OH,-CH2-O-CO-	50-70
sp ²	Alkene or arene	-x==<, ()	110-160
sp ²	Carboxyl	R-CO,H.R-CO,R	160-185
sp ²	Carbonyl	R-CHO, R-CO-R	190-220
sp	Alkyne	R-C=C-	65-85
sp	Nitrile	R-C=N	100-125

- Effects on Chemical Shift:
 - Chemical shift values are influenced by the type of atoms attached to the carbon atom and its neighbouring atoms.
 - Different neighbouring atoms exert varying effects on the **resonance condition** of **carbon-13 atoms.**

Assigning Chemical Shift Ranges in Carbon-13 NMR Spectra:

- Prediction of chemical shift ranges of carbon-carbon environments involves analysis of the type of bond of the carbon atom and the groups attached to it.
- Attention to bond type and attached groups aids in predicting peak positions.
- Complexity of Proton NMR Spectroscopy:
 - Proton NMR spectra are more intricate compared to carbon-13 NMR spectra.
 - Despite similarities in underlying principles, proton NMR spectra present additional complexities.