Edexcel Chemistry A-level

Topic 19: Modern Analytical Techniques II

Detailed Notes

Topic 19A: Mass Spectrometry

High Resolution Mass Spectrometry

High resolution mass spectrometry is a much **more sensitive** form of mass spectrometry (seen in Topic 7) which allows the Mr of a substance to be determined to **several decimal places**. Precise atomic masses can then be used to calculate the molecular formula of the compound being tested.

Once a molecular formula has been determined, you can predict **possible structures** of the compound. Knowledge of **general formulas** and **functional groups** aids this prediction.

Topic 19B: Nuclear Magnetic Resonance (NMR)

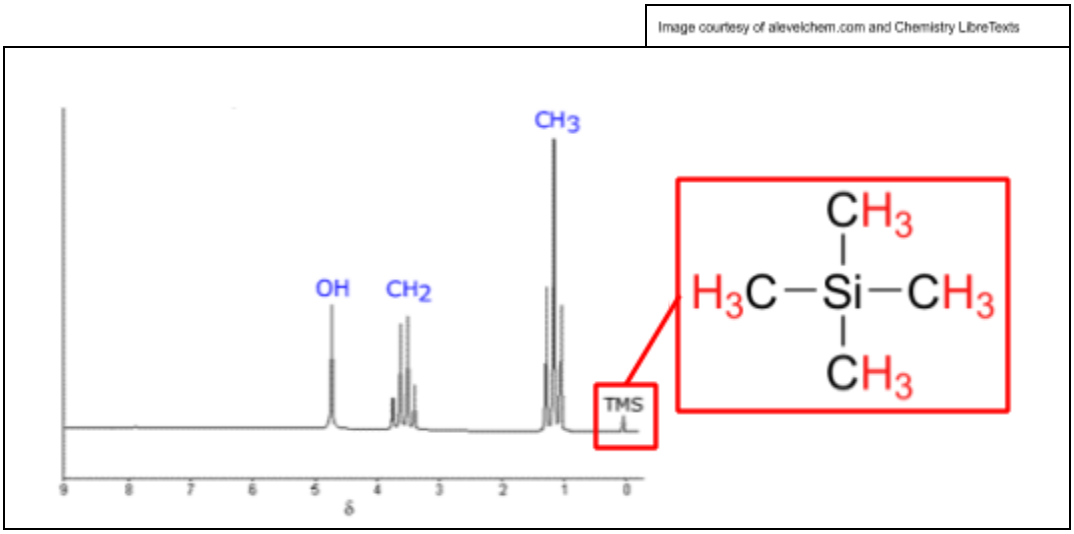
Introduction to NMR

NMR is an **analytical technique** that allows the structure of a molecule to be determined by analysing the energy of each bond environment. Different bond environments within a molecule **absorb different amounts of energy** so they are displayed as **different peaks** on a spectra print out.

The bond environment peaks are measured against a standard molecule, **tetramethylsilane ($Si(CH_3)_4$)**, known as TMS. This is a standard molecule as it contains four **identical** carbon and hydrogen environments. It can be easily identified as it is seen as a peak at **δ=0 ppm** on the x-axis.

Example:

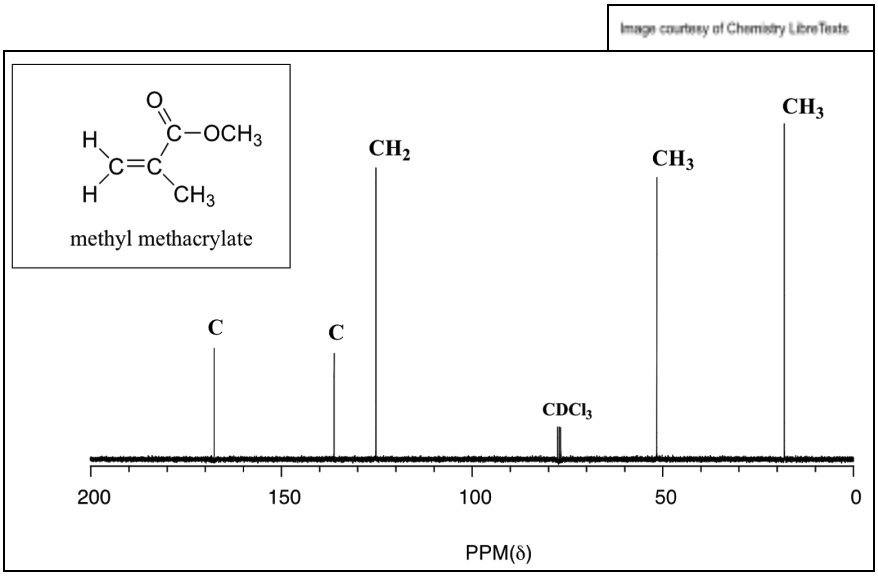
Image courtesy of alevelchem.com and Chemistry LibreTexts



C^{13} NMR

C^{13} NMR spectroscopy analyses the different **carbon environments** in a molecule. The different environments are shown as peaks at different δ values.

Example:

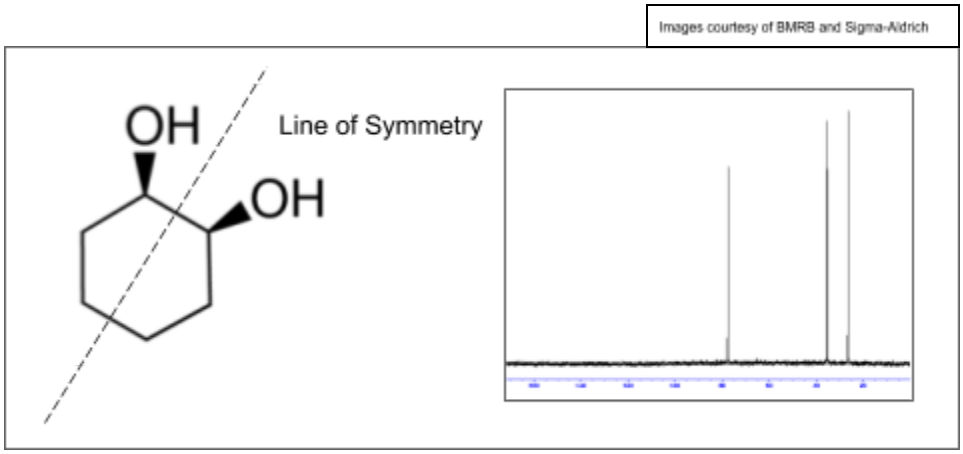


Carbon environments that are **near to oxygen atoms** have δ values that are **shifted to the right**. This is because oxygen is very **electronegative** and changes the bond environment and affects how it absorbs energy.

Molecule Symmetry

Molecules that have **symmetry** may display fewer δ peaks than the number of carbon atoms in the molecule. Therefore in these cases, it is important to look at the given molecular formula of the compound in order to decipher its displayed structure.

Example:



This molecule, 1,2-cyclohexanediol, contains six carbon atoms but the NMR spectrum only has three peaks due to the symmetry of the molecule.

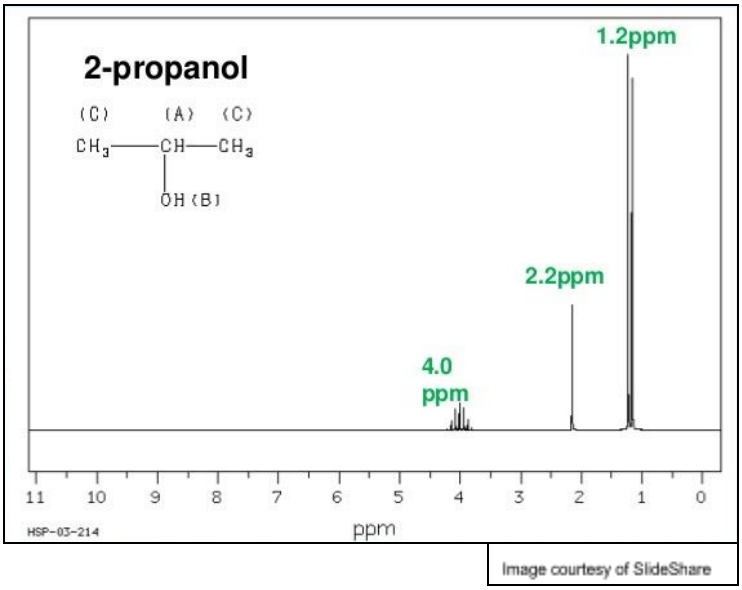
H^1 NMR (Proton NMR)

In H^1 NMR, the different **hydrogen environments** in a molecule are analysed and displayed as peaks on a spectrum. These peaks are also measured against the TMS standard.

The samples being analysed must be dissolved in a **non-hydrogen-containing solvent** so that the solvent doesn't produce any δ peaks on the spectrum. **CCl_4** is therefore a common solvent used along with **deuterated solvents** containing deuterium, an isotope of hydrogen.

H^1 NMR spectra are more complex than C^{13} spectra as the heights of the peaks show the **relative intensity** of each δ value. These relative intensities correspond to the number of hydrogens in that certain environment within a molecule, shown as a number above the peak.

Example:

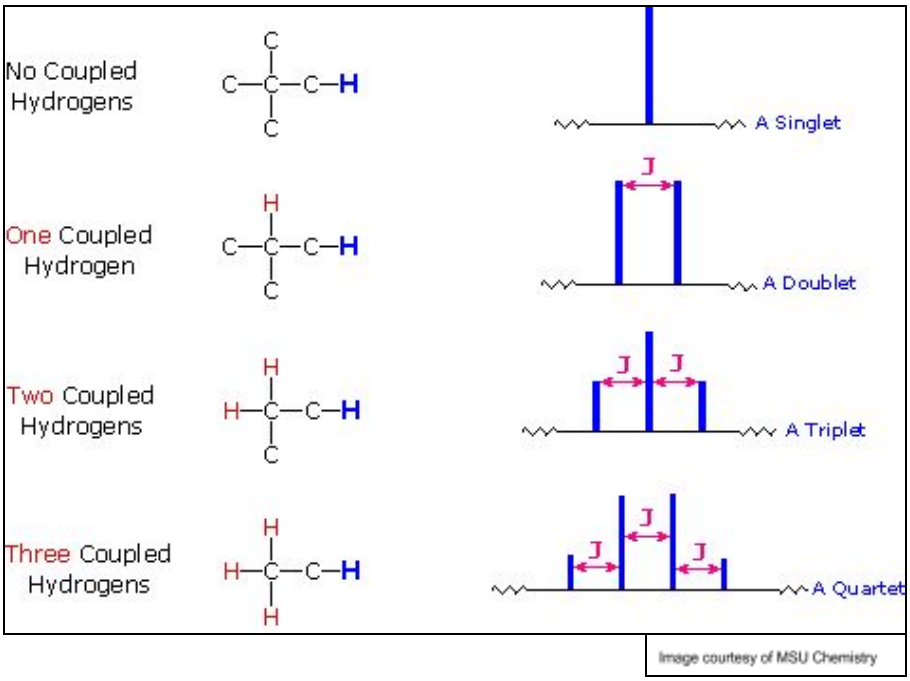


Splitting Patterns

The peaks of a H^1 NMR spectra also inform **where each environment is positioned** within the molecule. Peaks are split into a **small cluster,** with smaller peaks indicating how many hydrogens are on the **adjacent carbon atom** within the molecule. These smaller peaks are a **splitting pattern** and follow an **'n+1' rule**, where n is the number of hydrogen on the adjacent carbon:

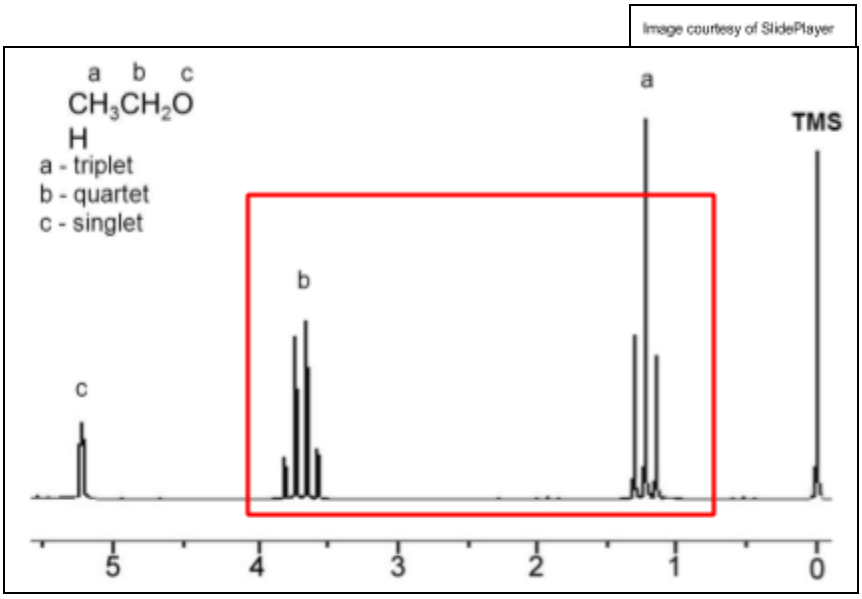
- **Singlet** = 0 H on adjacent carbon
- **Doublet** = 1 H on adjacent carbon
- **Triplet** = 2 H on adjacent atom
- **Quartet** = 3 H on adjacent carbon

Example:



There are some common **combinations of peaks and splitting patterns** that make deciphering the structure of the molecule easier. A **triplet-quartet** splitting pattern is a common combination as it represents a **-CH_2-CH_3** fragment.

Example:



The boxed peaks are produced by the -CH_2-CH_3 fragment.

Multiple fragments can be worked out from these peaks and **pieced together** to determine the **full molecule structure**.

Topic 19C: Chromatography Methods

Introduction

Chromatography is an **analytical technique** used to separate and identify component molecules of a mixture. It involves a **mobile phase** and a **stationary phase**.

Mobile and Stationary Phases

The mobile phase is a substance that allows molecules to **move over or through** the stationary phase. It can be in the form of a **liquid or a gas** depending on the type of chromatography being carried out. Species that are more soluble in the mobile phase **move further and/or faster** within the mobile phase.

The stationary phase is a substance that has **affinity** to molecules in the mixture being analysed. The **greater the affinity** of a molecule to the stationary phase, the **shorter the distance and/or the slower** it moves within the mobile phase.

Rf Values

An Rf value is a value that is **unique** to each different component molecule in the mixture being analysed. This is because different molecules within the mixture will have **different affinities** for the mobile and stationary phase and so will move at different rates within the mobile phase. It is calculated by comparing the **distance moved by the component molecule to the distance moved by the mobile phase.**

Example:

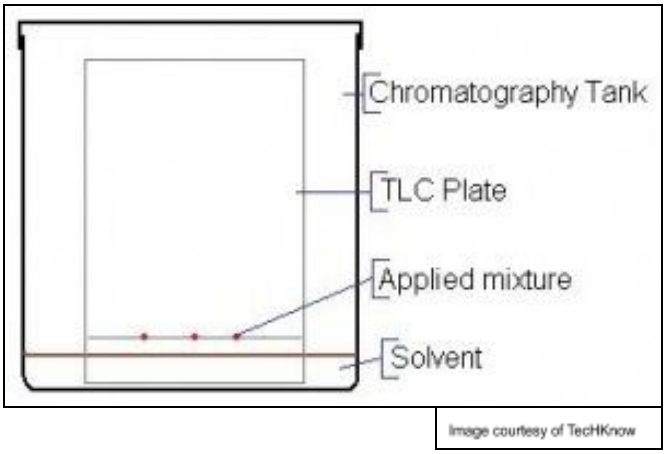
$$Rf = \frac{\text{Distance moved by molecule}}{\text{Distance moved by solvent}}$$

There are different types of chromatography that use different mobile and stationary phases. This will lead to **different Rf values** for the molecules present. A particular component molecule will have a different Rf value in different solvents.

Thin-Layer Chromatography (TLC)

In TLC chromatography, a **metal plate** is coated with a **thin layer of silica** and the sample being analysed is dotted on the plate. The **solvent** is then allowed to move up the plate, separating the substances within the sample. The plate is then dried in a fume cupboard to reduce toxic fumes. The chemical traces can then be viewed using a **UV lamp** and the distances travelled can be measured. Alternatively, a **developing agent** can be added, such as **iodine**, to allow the traces to be seen by the naked eye.

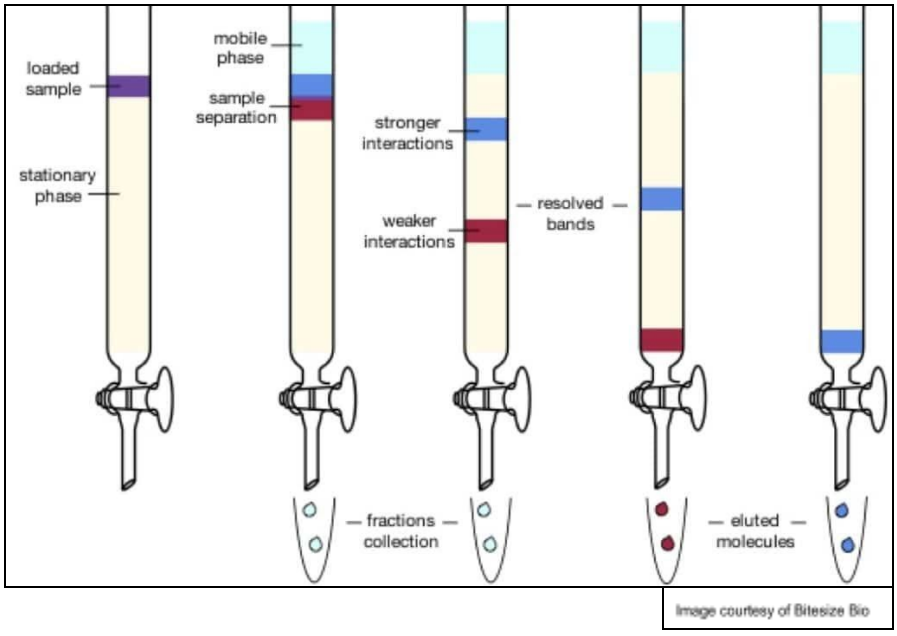
Example: TLC setup



Column and HPL Chromatography

For column and HPL chromatography, a **vertical column** is packed with a **solid, powdered substance** which acts as the stationary phase. A **solvent** containing the mixture being analysed is then added and moves down the column as the mobile phase.

Example:



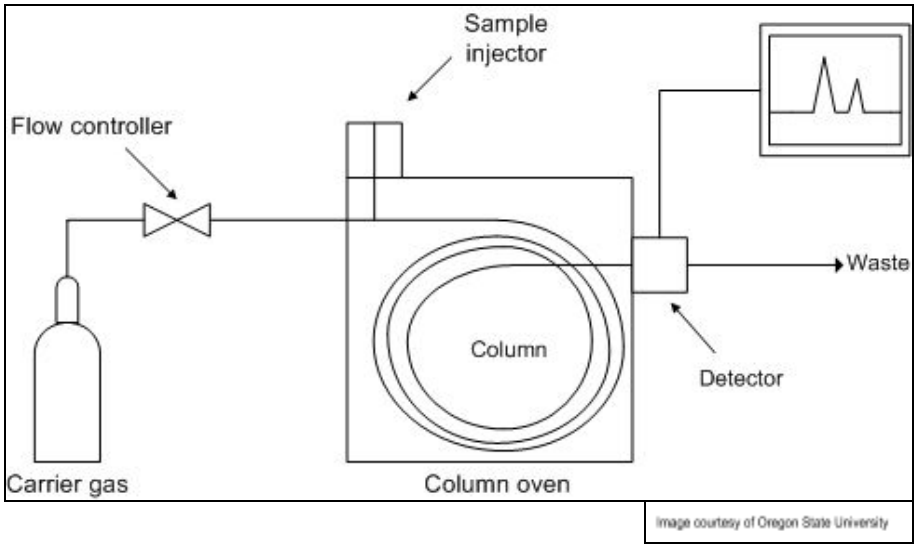
The varying affinities of the molecules present means that they **drain out of the column at different times**, allowing them to be collected as **separate samples**. The time taken for a substance to travel down the column is measured as the **retention time**. Similar to Rf values, retention times allow the individual molecules in the mixture to be identified.

High Performance Liquid Chromatography (HPLC) is an improved form of column chromatography which uses **high pressures** to force the mobile phase through the column. It allows much **smaller** samples to be analysed in a much **shorter time**.

Gas Chromatography (GC)

In gas chromatography, a **thin tube** is packed with a **solid, powdered substance** that acts as the stationary phase. Instead of a solvent, a **high pressure gas** is passed through this tube and acts as the **mobile phase**. This method is used to separate mixtures of **volatile liquids** which are fed into the gas chromatography machine as vapours.

Example:



The analysis machine **records a retention time** for each component molecule in the mixture, allowing them to be identified.

Applications of Chromatography

Chromatography can be used to determine the identity of compounds within a mixture. This makes it useful for **drug testing** in sports and in **forensics**, where specific compounds may be screened for.