WJEC Chemistry A-level

2.8: Instrumental Analysis

Detailed Notes

Welsh Specification

Mass Spectrometry

This is an **analytical technique** used to identify different **isotopes** and find the overall relative **atomic mass** of an element.

Time of Flight (TOF) Mass Spectrometry

This form of mass spectrometry records the **time** it takes for ions of each isotope to reach a detector. Using this, **spectra** can be produced showing each isotope present. The process of TOF mass spectrometry is as follows:

1. **Ionisation** - A sample of an element is **vapourised** and injected into the mass spectrometer where a **high voltage** is passed over the chamber. This causes electrons to be removed from the atoms (they are **ionised**) leaving **+1 charged ions** in the chamber.

2. **Acceleration** - The positively charged ions are **accelerated** towards a negatively charged **plate**.

3. **Ion Drift** - The ions are **deflected** by a **magnetic field** into a **curved path**. The radius of their path is dependent on the charge and mass of the ion.
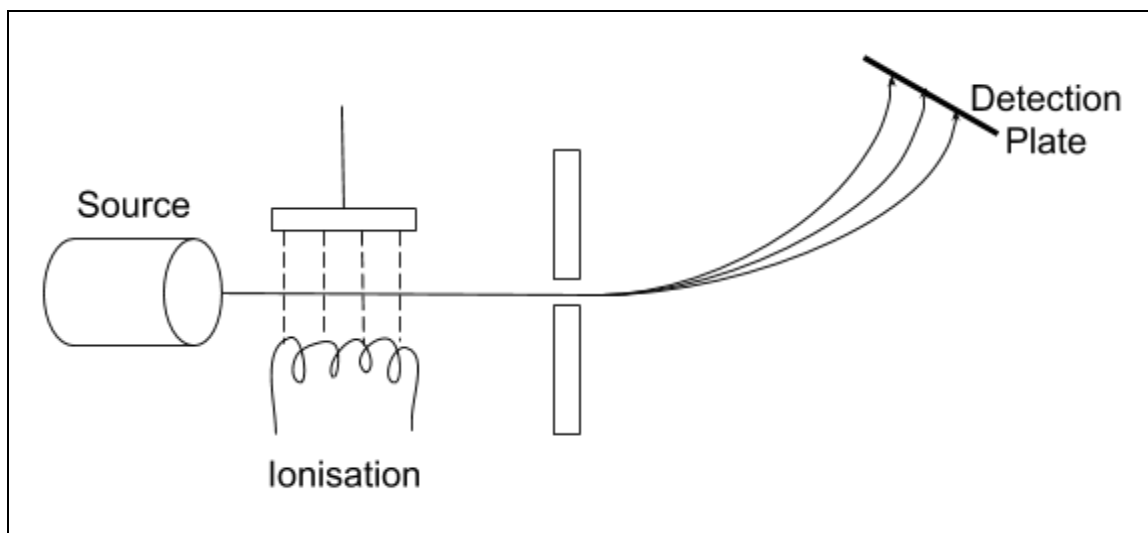

4. **Detection** - When the positive ions hit the detection plate, they **gain an electron** producing a **flow of charge**. The greater the abundance, the greater the current produced.

5. **Analysis** - The **current** values are then used in combination with the **flight times** to produce a **spectra** print-out with the **relative abundance** of each isotope displayed.

During the ionisation process, a **2+ charged ion** may be produced. This means it will be affected more by the magnetic field producing a curved path of **smaller radius**. As a result, its mass to charge ratio (m/z) is **halved** and this can be seen on spectra as a trace at half the expected m/z value.

Example:
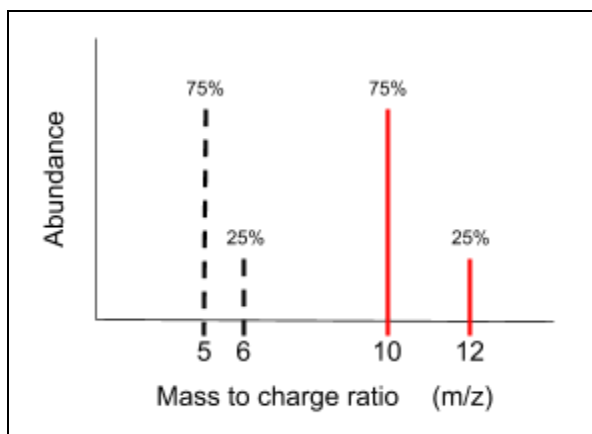
Using this spectra, the **relative atomic mass** can be calculated:

$$Ar = \frac{m/z \times abundance}{Total\ abundance}$$

Example:

$$Ar = \frac{(10 \times 75) + (12 \times 25)}{(75 + 25)} = 10.5$$

High Resolution Mass Spectrometry
This is a much more **sensitive** form of mass spectrometry which allows the Mr of a substance to be determined to **several decimal places**. Precise atomic masses are given which can then be used to calculate the molecular formula of the compound being tested, using the same method as above.

Infrared Spectroscopy
This analytical technique uses **infrared (IR) radiation** to determine the **functional groups** present in organic compounds. The IR radiation is passed through a sample where the different types of bonds **absorb radiation** in different amounts. These varying amounts of absorbance are measured and recorded, allowing certain bonds, and therefore functional groups, to be
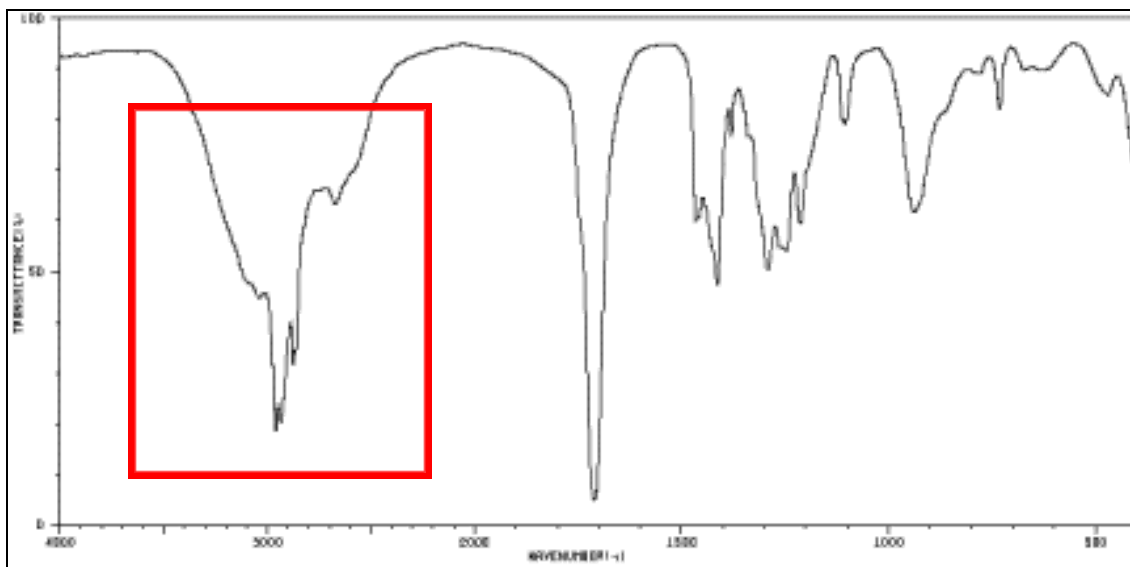
identified. A **spectrum** is produced from the measurements which has **characteristic curves** for the different functional groups:

-OH Alcohol Group - *characteristic peak is in the range 3230 - 3550 cm^{-1}*
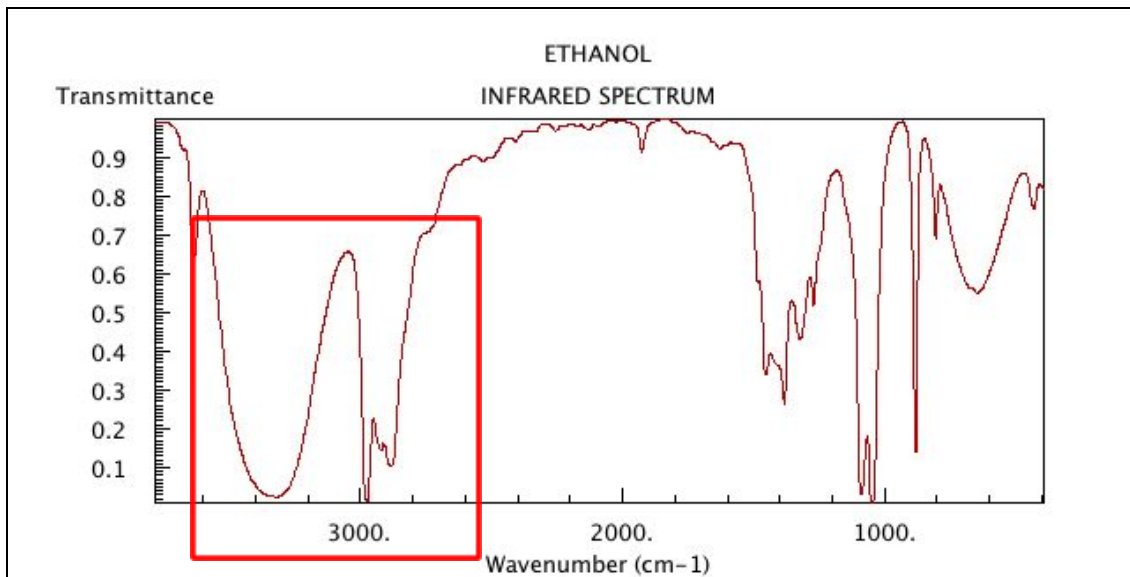
-OH Acid Group - *characteristic peak is in the range 2500 - 3000 cm^{-1}*

C=C Unsaturated Group - *characteristic peak is in the range 1620 - 1680 cm⁻¹*
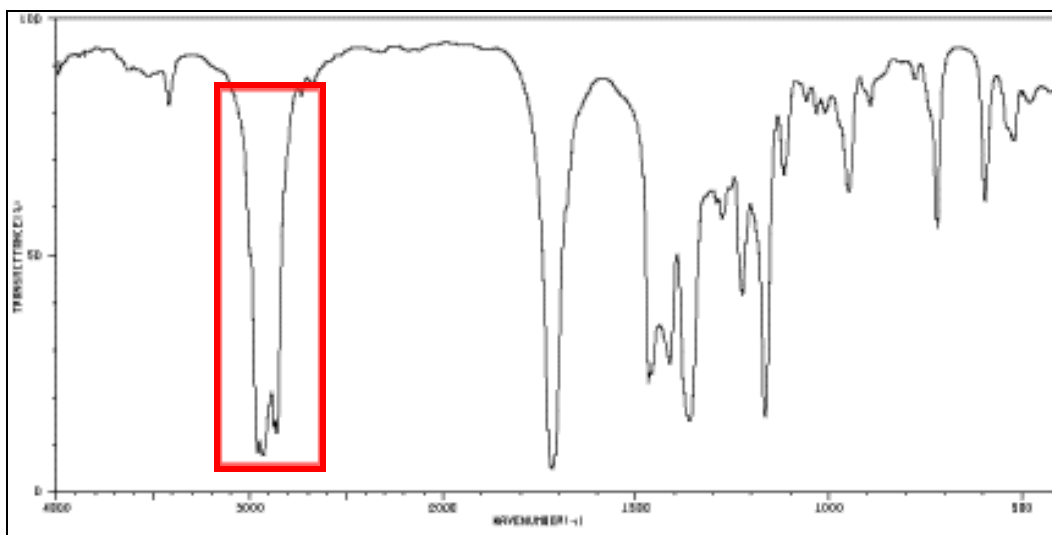
C=O Carbonyl Group - *characteristic peak is in the range 1680 - 1750 cm⁻¹*
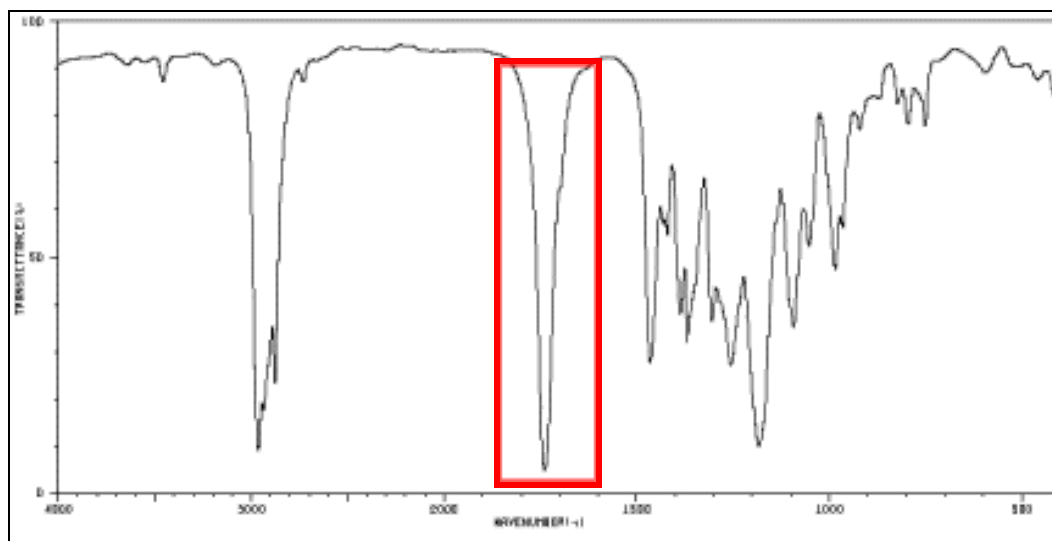
Fingerprint Region

Each IR spectrum has a **fingerprint region** to the far right-hand side (between 500cm^{-1} and 1500cm^{-1}), which appears as an area of lots of peaks very close together. This region appears due to tiny differences in species which act as a molecules' 'fingerprint', allowing it to be **specifically identified**.

Fingerprint regions are **very difficult to interpret** without specialist knowledge. Therefore, at A Level, it is not a requirement to be able to identify compounds from them.

NMR Spectroscopy

This is an **analytical technique** that allows the **structure** of a molecule to be determined by analysing the **energy of bond environments**. Different bond environments within a molecule absorb different amounts of energy, so they show 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 is seen as a peak at ∂=0 ppm on the x-axis. This makes it easy to **distinguish** from the other peaks.
Example:
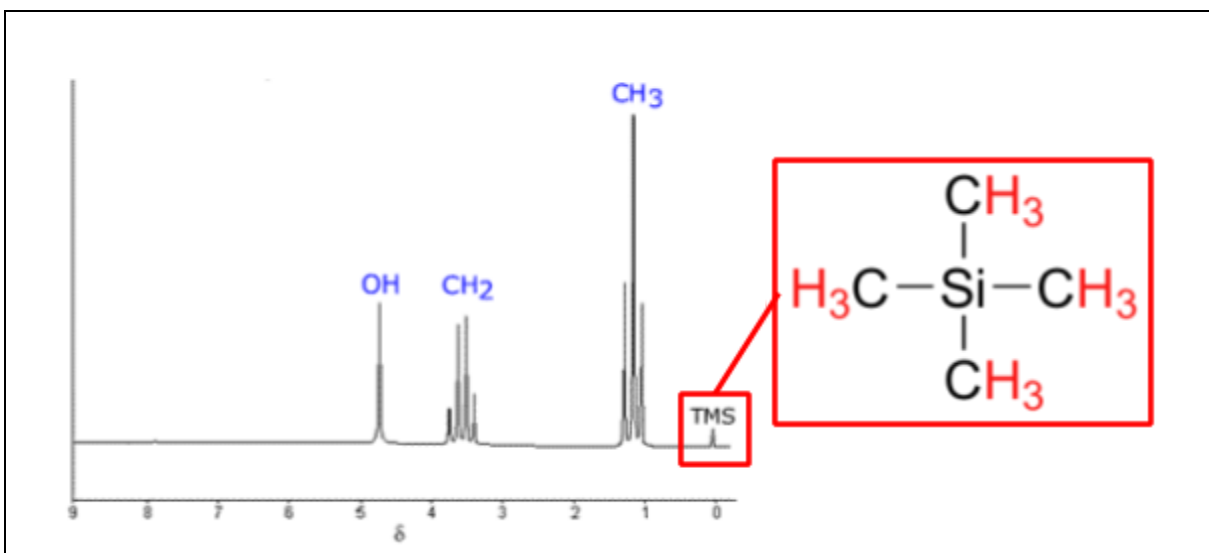
Using the peaks from an NMR spectrum, the structure of a chemical compound can be determined. This is a method of particular use in fields such as **forensics,** as it allows for the analysis and **identification of unknown substances**.
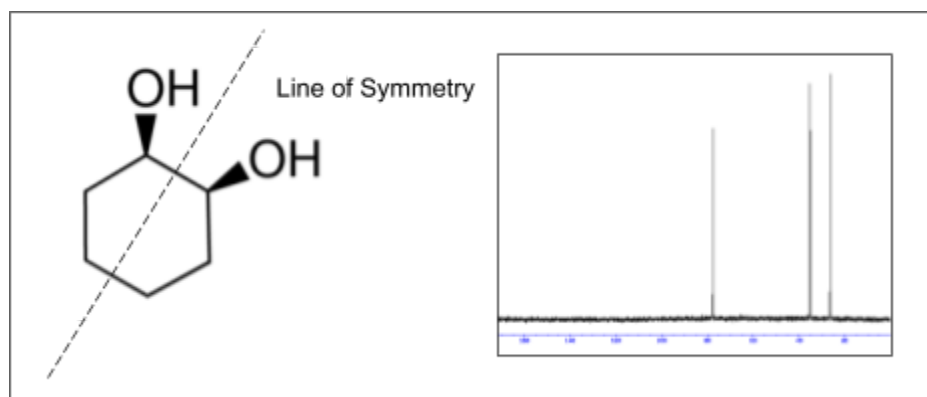
C¹³ NMR

This form of NMR spectroscopy analyses how many different carbon environments are present in the molecule. The different environments are shown as peaks at different ∂ **values**.

Carbon environments that are near to an **oxygen** have ∂ values that are **shifted** to the right. This is because oxygen is **very electronegative** and it acts to pull electrons away from the carbon atom.
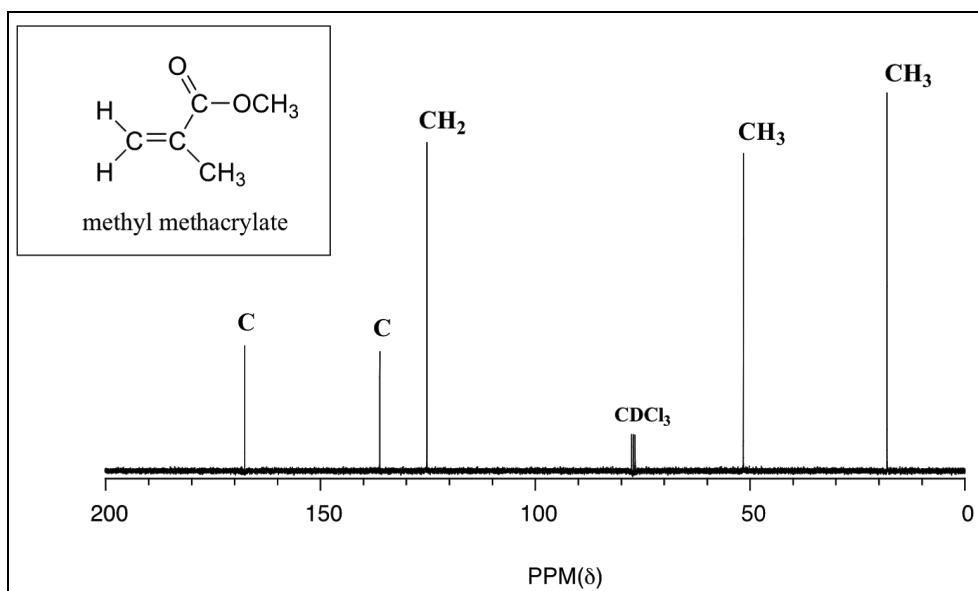
Molecules that have **symmetry**, such as 1,2-cyclohexanediol, may display **fewer ∂ peaks** than the number of carbon atoms in the molecule. Therefore in these cases, it is important to look at the given **molecular formula** of the compound in order to decipher its **displayed structure**:

All C^{13} NMR ∂ shift values can be found in most Chemistry data books and will be provided in the exam.

H^1 NMR (Proton NMR)

In this form of NMR, the different **hydrogen environments** in a molecule are analysed and displayed as peaks on a spectra. These peaks are also measured against the **TMS standard**.

The samples being analysed must be dissolved in a **non-hydrogen-containing solvent** so that it doesn't produce any 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 chemical shift 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:
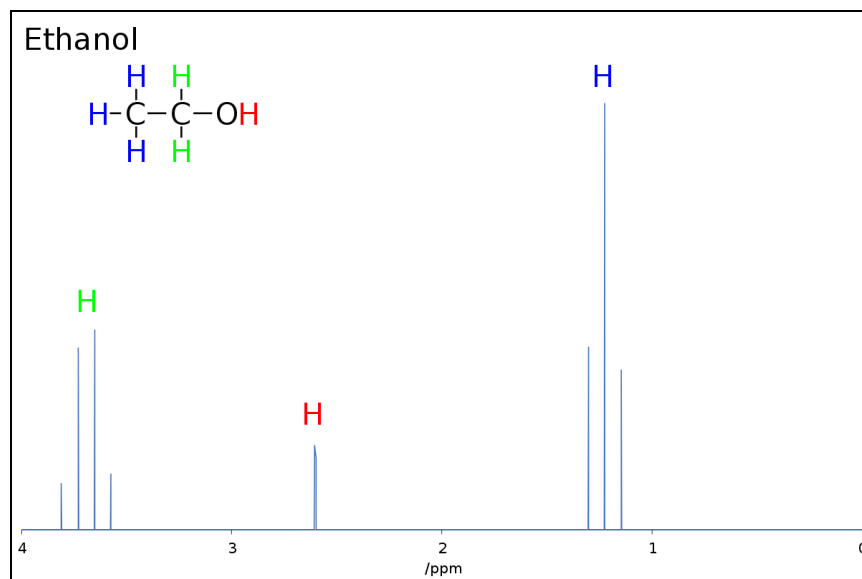
The peaks of a H^1 NMR spectra also inform **where each environment is positioned** within the molecule. Peaks are split into a **small cluster** with smaller peaks indicating how many hydrogens are on the **adjacent carbon** atom within the molecule. These smaller peaks are a **splitting pattern** and follow an **'n+1' rule**, where n is the number of hydrogen on the adjacent carbon.
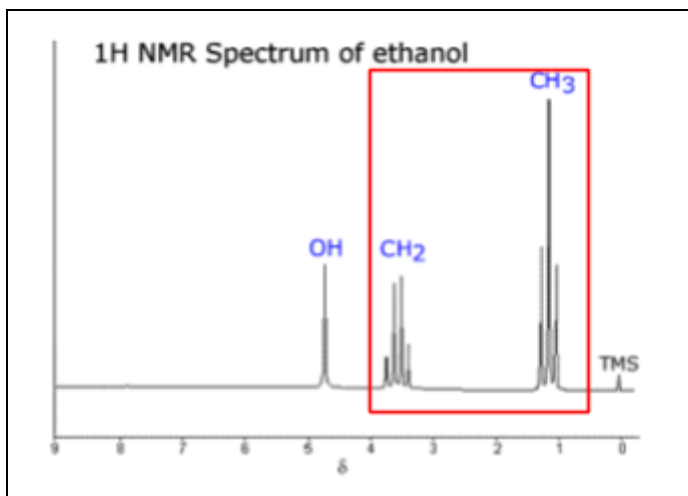
Singlet	=	no H on adjacent carbon
Doublet	=	1 H on adjacent carbon
Triplet	=	2 H on adjacent atom
Quartet	=	3 H on adjacent carbon
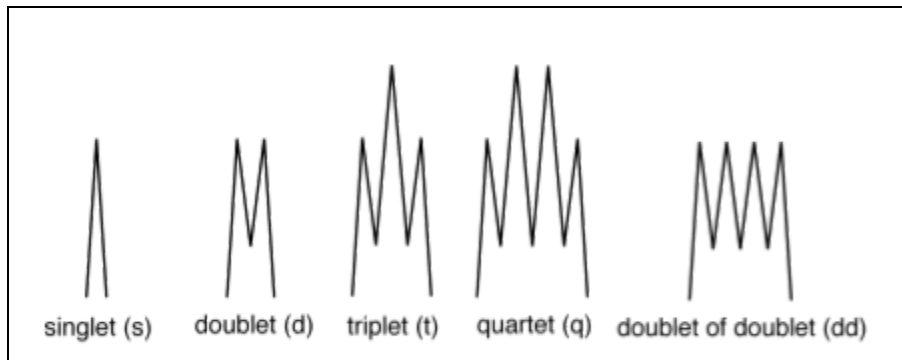
There are some common **combinations of peaks** and splitting patterns that make deciphering the structure of the molecule easier. A **triplet-quartet** splitting pattern is a common combination as it represents a **-CH$_2$-CH$_3$ fragment**.

The boxed peaks are produced by the -CH$_2$-CH$_3$ fragment.

Multiple fragments can be worked out and pieced together to determine the **full molecular structure**.