

# WJEC Chemistry A-Level

## C3.5: Instrumental Analysis

Detailed Notes

English Specification

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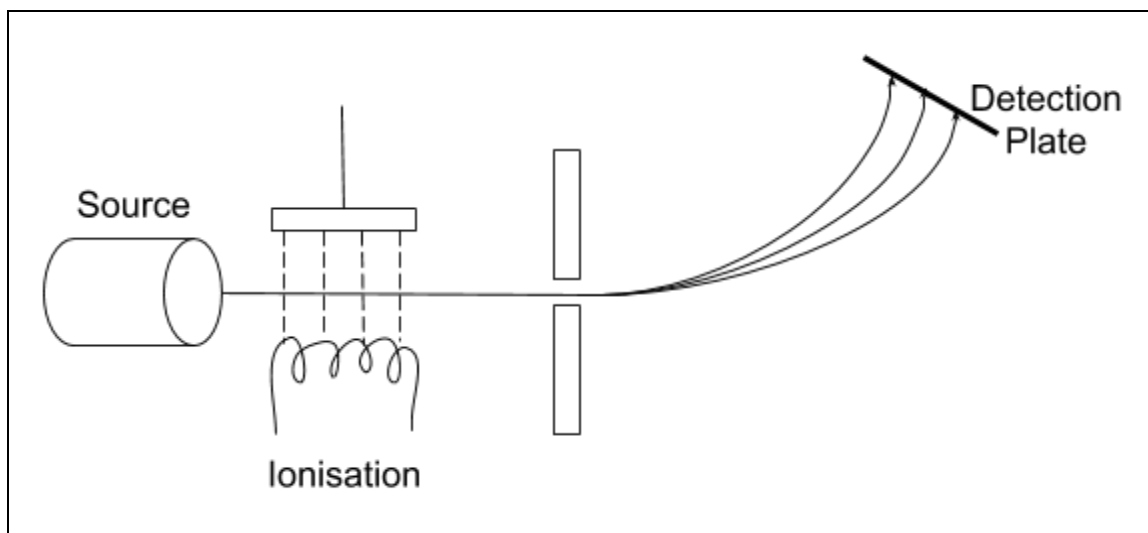
## Mass Spectrometry

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.



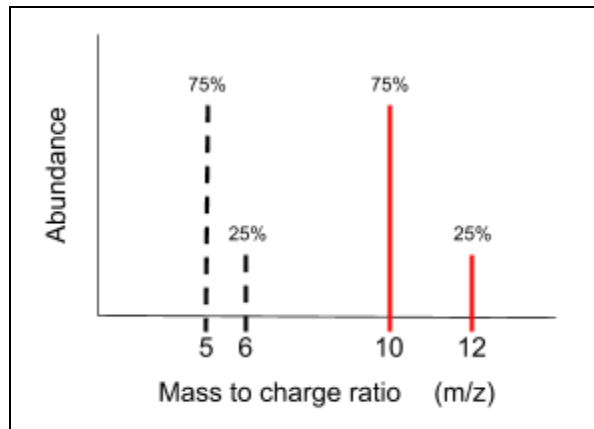
4. **Detection** - When the positive ions hit the detection plate, they **gain an electron** producing a **flow of charge**. The greater the abundance, the greater the current produced.
5. **Analysis** - The **current** values are then used in combination with the **flight times** to produce a **spectra** 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:

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

Example:

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

## High Resolution Mass Spectrometry

This is a much more **sensitive** form of mass spectrometry which allows the  $M_r$  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

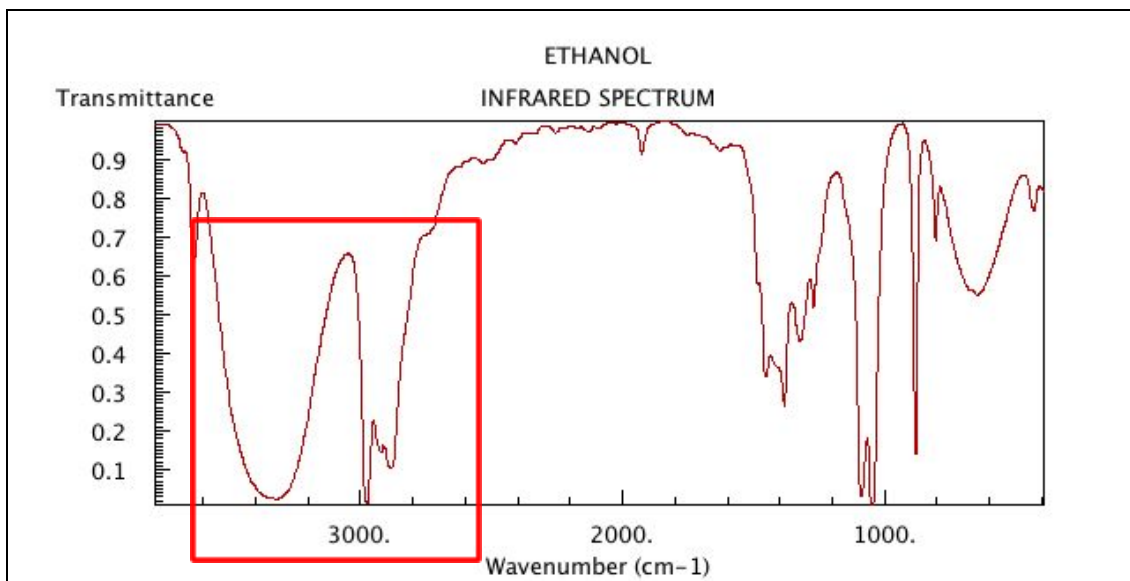
This analytical technique uses **infrared (IR) radiation** to determine the **functional groups** present in organic compounds. The IR radiation is passed through a sample where the different types of bonds **absorb radiation** in different amounts. These varying amounts of absorbance





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:

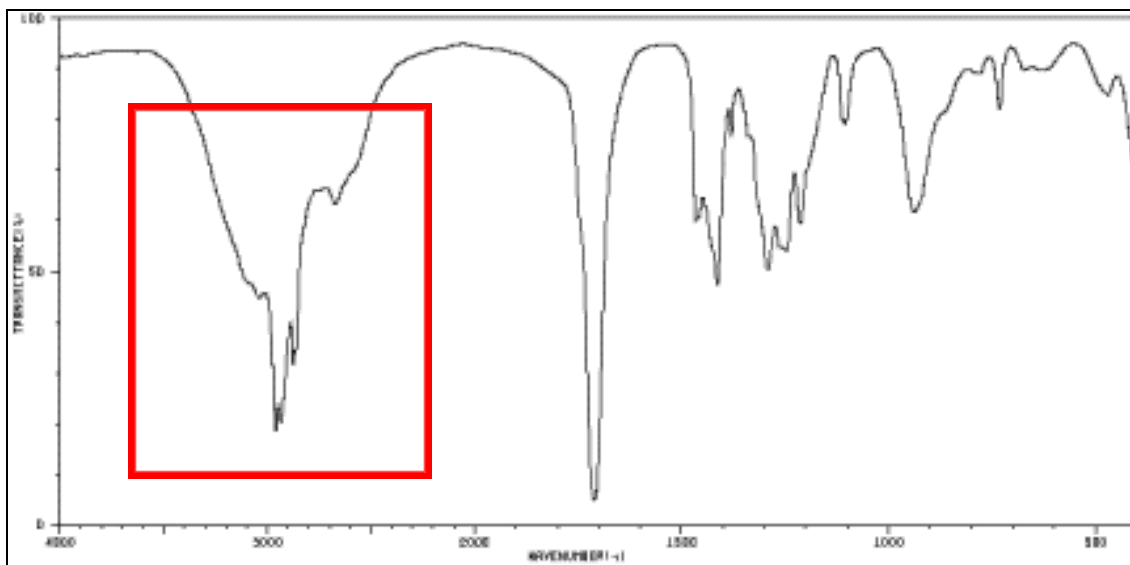
**-OH Alcohol Group - characteristic peak is in the range  $3230 - 3550\text{ cm}^{-1}$**



[https://commons.wikimedia.org/wiki/File:EtOH\\_Spectra.png](https://commons.wikimedia.org/wiki/File:EtOH_Spectra.png)

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**-OH Acid Group - characteristic peak is in the range  $2500 - 3000\text{ cm}^{-1}$**



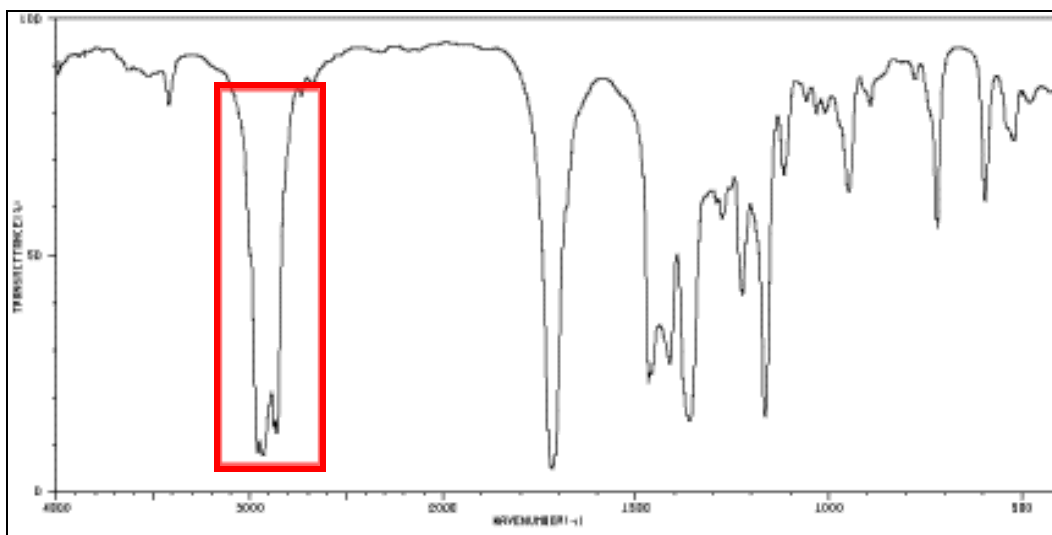
(Modified from [https://chem.libretexts.org/Bookshelves/Physical\\_and\\_Theoretical\\_Chemistry\\_Textbook\\_Maps/Supplemental\\_Modules\\_\(Physical\\_and\\_Theoretical\\_Chemistry\)/Spectroscopy/Vibrational\\_Spectroscopy/Infrared\\_Spectroscopy/Interpreting\\_Infrared\\_Spectra/IR8.\\_More\\_Complicated\\_IR\\_Spectra](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Vibrational_Spectroscopy/Infrared_Spectroscopy/Interpreting_Infrared_Spectra/IR8._More_Complicated_IR_Spectra))

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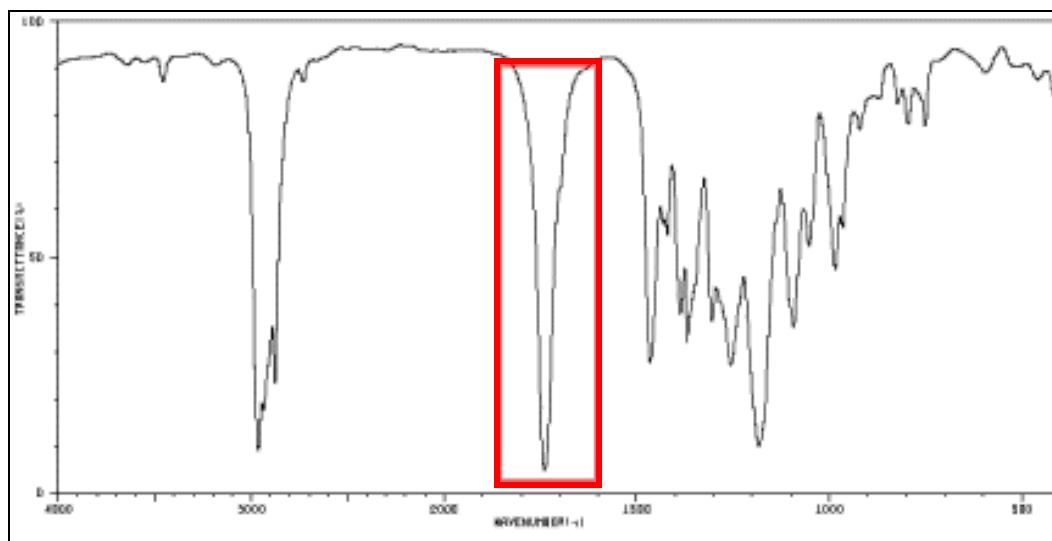


**C=C Unsaturated Group - characteristic peak is in the range  $1620 - 1680\text{ cm}^{-1}$**



(Modified from <https://employees.csbsju.edu/cschaller/Principles%20Chem/structure%20determination/IRHydrocarbon.htm>)  
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**C=O Carbonyl Group - characteristic peak is in the range  $1680 - 1750\text{ cm}^{-1}$**



(Modified from <https://employees.csbsju.edu/cschaller/Principles%20Chem/structure%20determination/IRHydrocarbon.htm>)  
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## Fingerprint Region

Each IR spectrum has a **fingerprint region** to the far right-hand side (between  $500\text{cm}^{-1}$  and  $1500\text{cm}^{-1}$ ), 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 molecule's 'fingerprint', allowing it to be **specifically identified**.

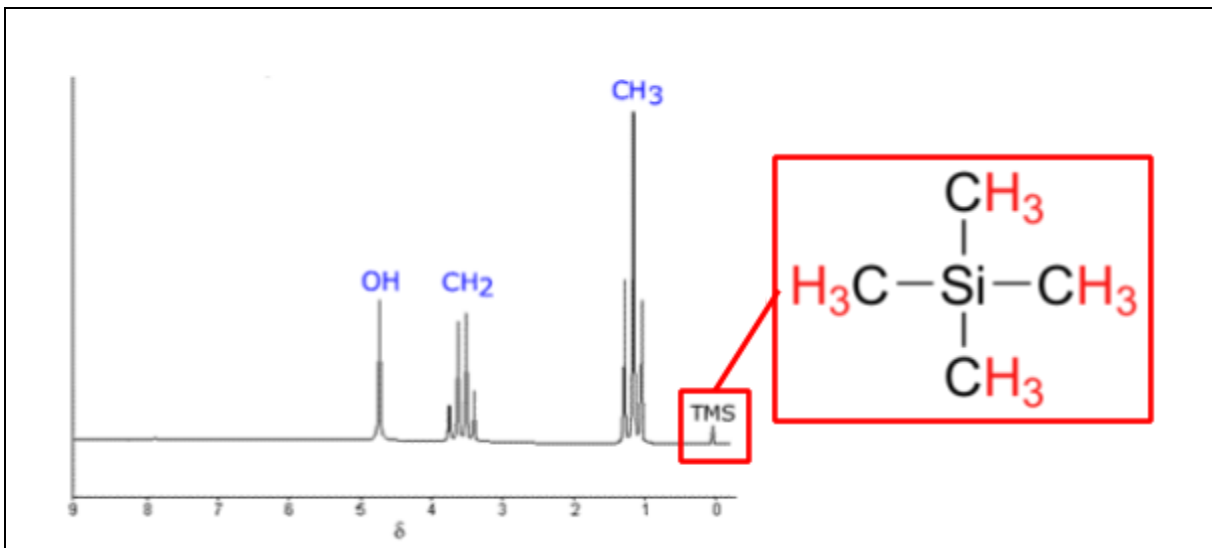
Fingerprint regions are **very difficult to interpret** without specialist knowledge. Therefore, at A Level, it is not a requirement to be able to identify compounds from them.

## 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** ( $\text{Si}(\text{CH}_3)_4$ ), known as TMS. This is a standard molecule as it contains four **identical** carbon and hydrogen environments. It is seen as a peak at  $\delta=0$  ppm on the x-axis. This makes it easy to **distinguish** from the other peaks.

*Example:*



(Modified from <https://chemistry.stackexchange.com/questions/42757/why-only-one-peak-is-observed-in-nmr-spectrum-of-h2>)

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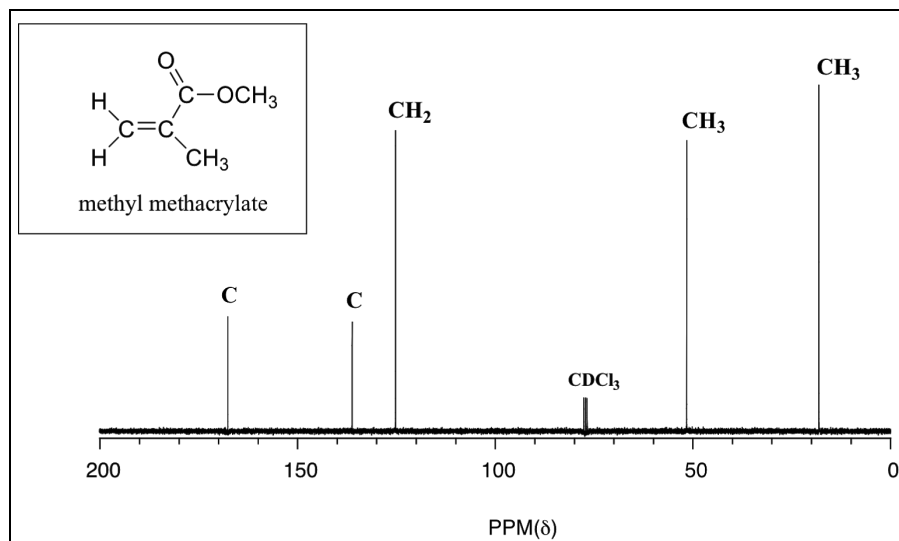


Using the peaks from an NMR spectrum, the structure of a chemical compound can be determined. This is a method of particular use in fields such as **forensics**, as it allows for the analysis and **identification of unknown substances**.

### $C^{13}$ NMR

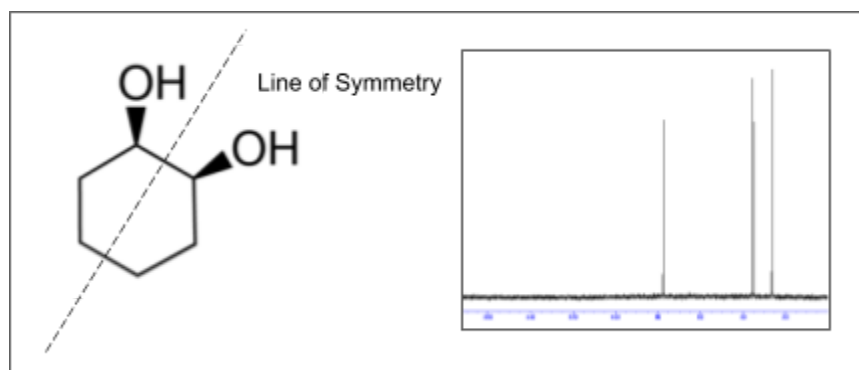
This form of NMR spectroscopy analyses how many different carbon environments are present in the molecule. The different environments are shown as peaks at different  $\delta$  values.

Carbon environments that are near to an **oxygen** have  $\delta$  values which are **shifted** to the right. This is because oxygen is **very electronegative** and it acts to pull electrons away from the carbon atom.



[https://chem.libretexts.org/Under\\_Construction/Purgatory/Book%3A\\_Organic\\_Chemistry\\_with\\_a\\_Biological\\_Emphasis\\_\(Soderberg\)/Chapter\\_05%3A\\_Structure\\_Determination\\_II/5.6%3A\\_13C-NMR\\_spectroscopy](https://chem.libretexts.org/Under_Construction/Purgatory/Book%3A_Organic_Chemistry_with_a_Biological_Emphasis_(Soderberg)/Chapter_05%3A_Structure_Determination_II/5.6%3A_13C-NMR_spectroscopy)  
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Molecules that have **symmetry**, such as 1,2-cyclohexanediol, may display **fewer  $\delta$  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**:



(Modified from [https://chem.libretexts.org/Bookshelves/Physical\\_and\\_Theoretical\\_Chemistry\\_Textbook\\_Maps/Supplemental\\_Modules\\_\(Physical\\_and\\_Theoretical\\_Chemistry\)/Spectroscopy/Magnetic\\_Resonance\\_Spectroscopies/Nuclear\\_Magnetic\\_Resonance/NMR%3A\\_Structural\\_Assignment/NMR3.\\_Symmetry\\_in\\_NMR](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Magnetic_Resonance_Spectroscopies/Nuclear_Magnetic_Resonance/NMR%3A_Structural_Assignment/NMR3._Symmetry_in_NMR))  
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All  $C^{13}$  NMR  $\delta$  shift values can be found in most Chemistry data books and will be provided in the exam.

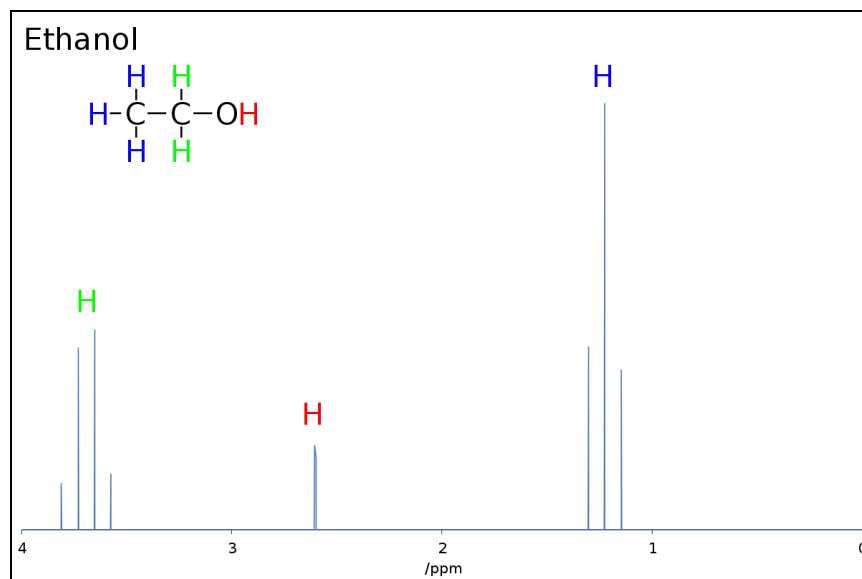
## $H^1$ NMR (Proton NMR)

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:*



(<https://nl.wikipedia.org/wiki/Ethanol>)

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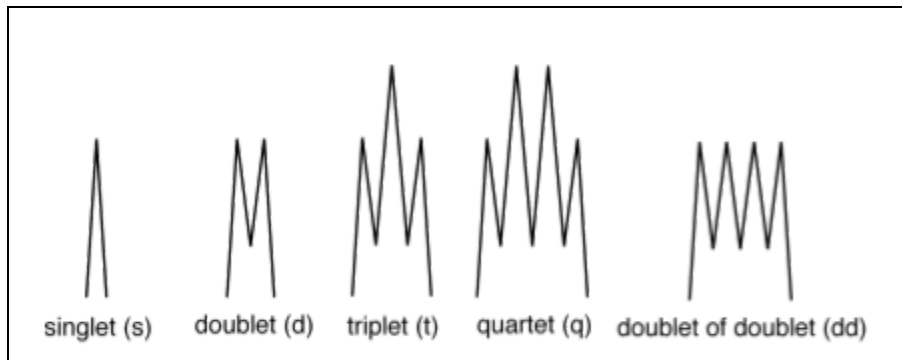
The peaks of a  $H^1$  NMR spectra also inform **where each environment is positioned** within the molecule. Peaks are split into a **small cluster** with smaller peaks indicating how many hydrogens are on the **adjacent carbon** atom within the molecule. These smaller peaks are a **splitting pattern**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





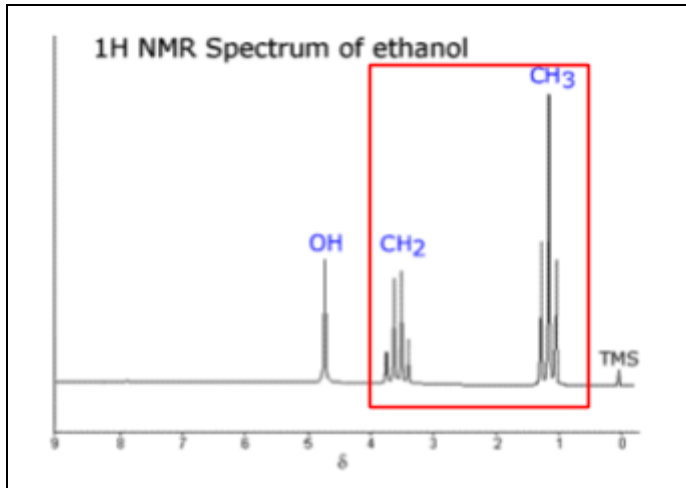


Singlet	=	no H on adjacent carbon
Doublet	=	1 H on adjacent carbon
Triplet	=	2 H on adjacent atom
Quartet	=	3 H on adjacent carbon



(Modified from [https://chem.libretexts.org/Ancillary\\_Materials/Reference/Organic\\_Chemistry\\_Glossary/Splitting\\_Pattern](https://chem.libretexts.org/Ancillary_Materials/Reference/Organic_Chemistry_Glossary/Splitting_Pattern)  
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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<sub>2</sub>-CH<sub>3</sub> fragment**.



**The boxed peaks are produced by the -CH<sub>2</sub>-CH<sub>3</sub> fragment.**

(Modified from <https://chemistry.stackexchange.com/questions/42757/why-only-one-peak-is-observed-in-nmr-spectrum-of-h2>  
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Multiple fragments can be worked out and pieced together to determine the **full molecular structure**.

