🧪 Cambridge (CIE) A Level Chemistry

Proton (1H) NMR Spectroscopy

Contents

Interpreting & Explaining Proton (1H) NMR Spectra

- **Nuclear Magnetic Resonance (NMR)** spectroscopy is used for analysing organic compounds

- Atoms with odd mass numbers usually show signals on NMR

- In ^{1}H NMR, the magnetic field strengths of protons in organic compounds are measured and recorded on a spectrum

- Protons on different parts of a molecule (in different molecular environments) emit different frequencies when an external magnetic field is applied

- All samples are measured against a reference compound – **Tetramethylsilane (TMS)**

    - TMS shows a single sharp peak on NMR spectra, at a value of zero

    - Sample peaks are then plotted as a 'shift' away from this reference peak

    - This gives rise to 'chemical shift' values for protons on the sample compound

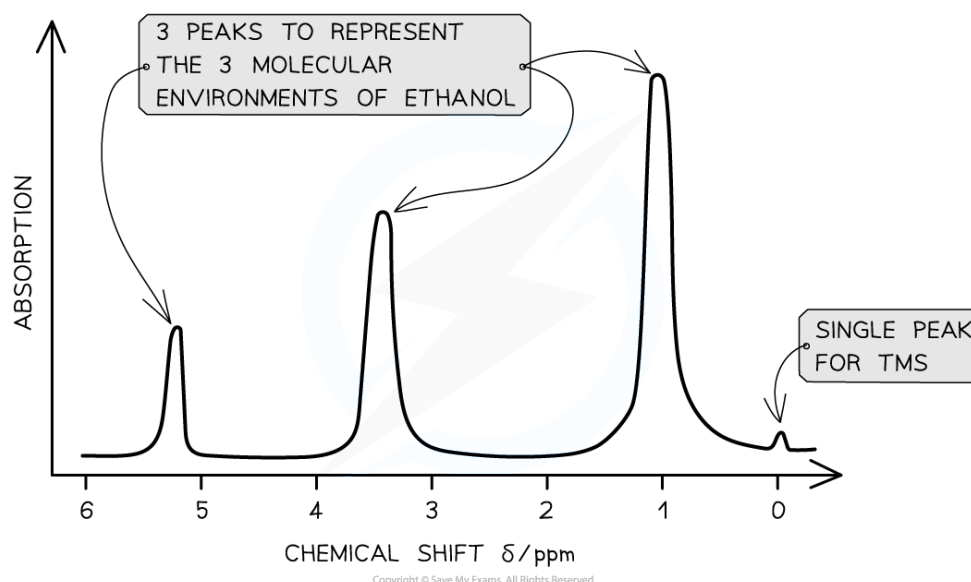   - Chemical shifts are measured in parts per million (ppm)

Features of an NMR spectrum

- NMR spectra show the intensity of each peak against its chemical shift

- The area under each peak gives information about the number of protons in a particular environment

- The height of each peak shows the intensity/absorption from protons

- A single sharp peak is seen to the far right of the spectrum

    - This is the reference peak from TMS

    - Usually at chemical shift 0 ppm

Low resolution ^{1}H NMR for ethanol

> 3 PEAKS TO REPRESENT THE 3 MOLECULAR ENVIRONMENTS OF ETHANOL

> SINGLE PEAK FOR TMS

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The key features of this spectrum are the number and position of the peaks

Molecular environments

- Hydrogen atoms of an organic compound are said to reside in different molecular environments

    - E.g. Methanol has the molecular formula CH_3OH

    - There are 2 molecular environments: $-CH_3$ and $-OH$

- The hydrogen atoms in these environments will appear at 2 different chemical shifts

- Different types of protons are given their own range of chemical shifts
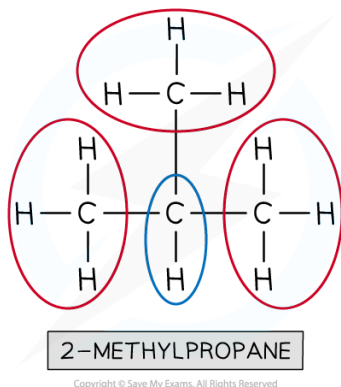
Worked Example

How many different ^{1}H chemical environments occur in 2–methylpropane?

Answer:

- Two different ^{1}H chemical environments occur in 2–methylpropane
- The three methyl groups are in the same ^{1}H environment

    - The lone hydrogen is in its own ^{1}H environment

2–METHYLPROPANE

Chemical shift values for ^{1}H molecular environments table

Environment of proton	Example	Chemical shift range, δ / ppm
alkane	$-CH_3$, $-CH_2-$, $>CH-$	0.9 - 1.7
alkyl next to C=O	$CH_3-C=O$, $-CH_2-C=O$, $>CH-C=O$	2.2 – 3.0
alkyl next to aromatic ring	CH_3-Ar, $-CH_2-Ar$, $>CH_2-Ar$	2.3 – 3.0
alkyl next to electronegative atom	CH_3-O, CH_2-O, CH_2-Cl	3.2 – 4.0
attached to alkene	$=CHR$	4.5 – 6.0
attached to aromatic ring	$H-Ar$	6.0 - 9.0
aldehyde	$HCOR$	9.3 - 10.5
alcohol*	ROH	0.5 – 6.0
phenol*	$Ar-OH$	4.5 – 7.0
carboxylic acid	$RCOOH$	9.0 – 13.0
alkyl amine*	$R-NH-$	1.0 – 5.0
aryl amine*	$Ar-NH_2$	3.0 – 6.0
amide	$RCONHR$	5.0 – 12.0

- Protons in the same chemical environment are chemically equivalent

  - 1,2–dichloroethane, $Cl-CH_2-CH_2-Cl$ has one chemical environment as these four hydrogens are all exactly equivalent

- Each individual peak on a ^1H NMR spectrum relates to protons in the same environment

  - Therefore, 1,2–dichloroethane would produce one single peak on the NMR spectrum as the protons are in the same environment

Identifying molecular environments in 1,2–dichloroethane
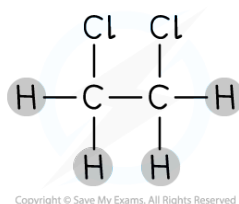
*All four protons in the 1,2–dichloroethane molecule are equivalent*

Low resolution ₁H NMR

- Peaks on a low resolution NMR spectrum refer to molecular environments of an organic compound

  - E.g. Ethanol has the molecular formula CH_3CH_2OH

  - This molecule as 3 separate environments: $-CH_3$, $-CH_2$, $-OH$

  - So 3 peaks would be seen on its spectrum at 1.2 ppm ($-CH_3$), 3.7 ppm ($-CH_2$) and 5.4 ppm (-OH)

Low resolution NMR spectrum of ethanol
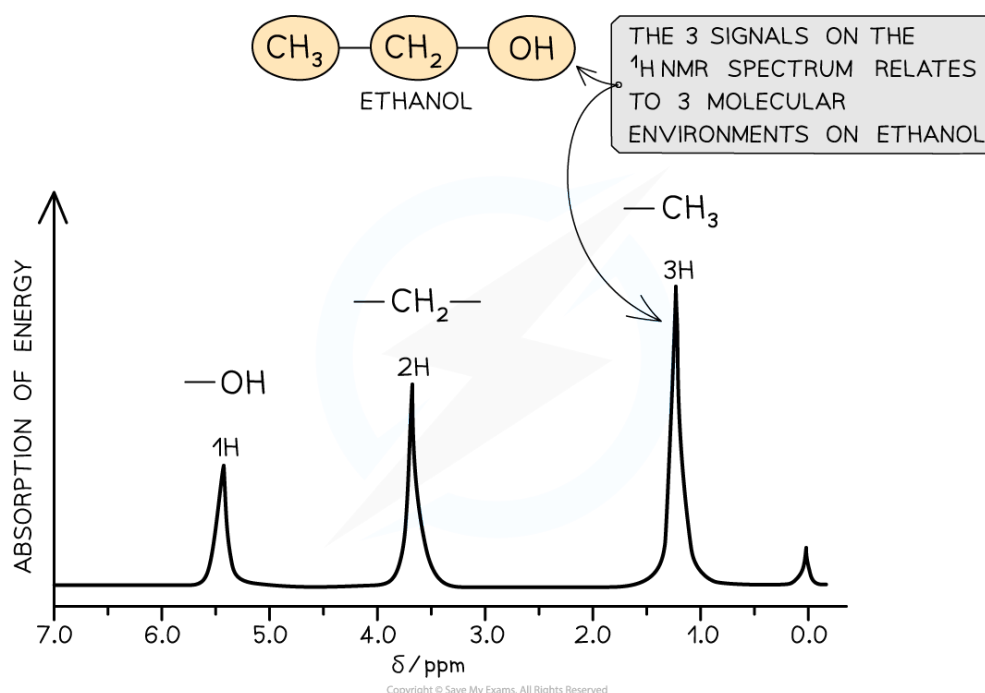
The low resolution NMR spectrum of ethanol shows 3 peaks for the 3 molecular environments

High resolution ¹H NMR

- More structural details can be deduced using high resolution NMR

- The peaks observed on a high resolution NMR may sometimes have smaller peaks clustered together

- The splitting pattern of each peak is determined by the number of protons on neighbouring environments

The number of peaks a signal splits into = n + 1

- (Where n = the number of protons on the adjacent carbon atom)
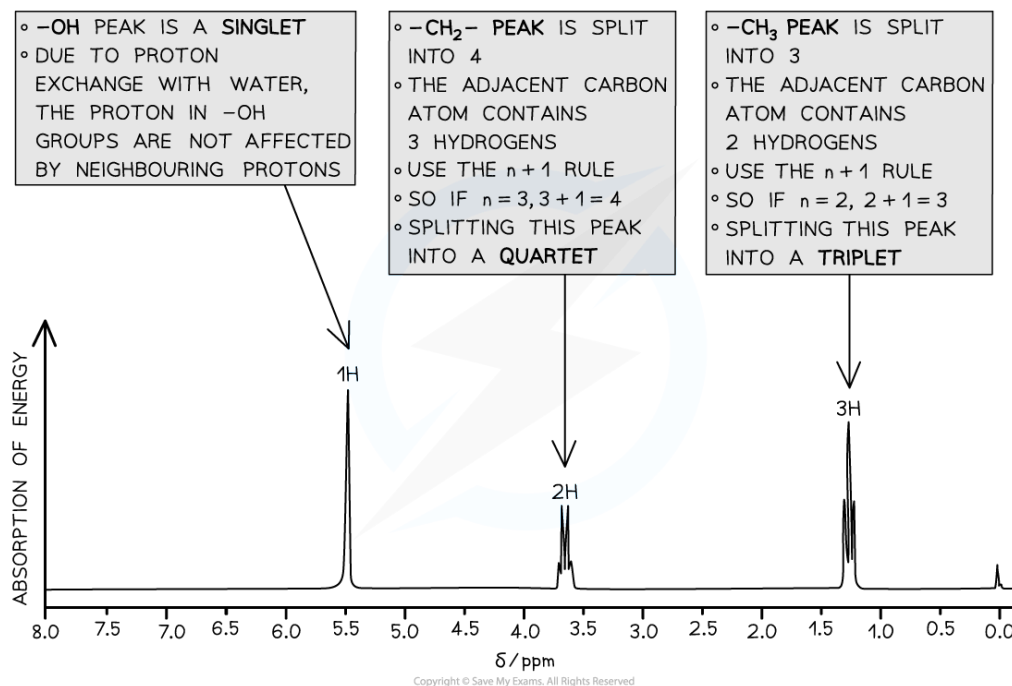
Predicting Shifts & Splitting Patterns

Spin-Spin Splitting

- A high resolution ¹H NMR spectrum can show you the structure of the molecule but also the peaks can be split into sub-peaks or splitting patterns

- These are caused by a proton's spin interacting with the spin states of nearby protons that are in different environments

    - This can provide information about the number of protons bonded to adjacent carbon atoms

    - The splitting of a main peak into sub-peaks is called spin-spin splitting or spin-spin coupling

High resolution ^{1}H NMR spectrum of ethanol

> ○ **–OH** PEAK IS A **SINGLET**
> ○ DUE TO PROTON EXCHANGE WITH WATER, THE PROTON IN –OH GROUPS ARE NOT AFFECTED BY NEIGHBOURING PROTONS

> ○ **–CH$_2$–** PEAK IS SPLIT INTO 4
> ○ THE ADJACENT CARBON ATOM CONTAINS 3 HYDROGENS
> ○ USE THE n + 1 RULE
> ○ SO IF n = 3, 3 + 1 = 4
> ○ SPLITTING THIS PEAK INTO A **QUARTET**

> ○ **–CH$_3$** PEAK IS SPLIT INTO 3
> ○ THE ADJACENT CARBON ATOM CONTAINS 2 HYDROGENS
> ○ USE THE n + 1 RULE
> ○ SO IF n = 2, 2 + 1 = 3
> ○ SPLITTING THIS PEAK INTO A **TRIPLET**

The high resolution ^{1}H NMR spectrum of ethanol showing the splitting patterns of each of the 3 peaks. Using the n+1, it is possible to interpret the splitting pattern

Examiner Tips and Tricks

- It is very rare that the spin-spin splitting of equivalent protons is covered in teaching because it is so rarely asked in exams
- Equivalent protons do **not** cause spin-spin splitting
    - The simplest example of this is benzene
        - In benzene, all of the protons are equivalent
        - This means that they are seen as one singlet in the high resolution ^{1}H NMR spectrum of benzene

The n+1 rule

- The number of sub-peaks is one greater than the number of adjacent protons causing the splitting
    - For a proton with *n* protons attached to an adjacent carbon atom, the number of sub-peaks in a splitting pattern = *n*+1
- When analysing spin-spin splitting, it shows you the number of hydrogen atoms on the adjacent carbon atom
- These are the splitting patterns that you need to be able to recognise from a ^{1}H spectra:

¹H NMR peak splitting patterns table

| Number of adjacent protons (n)	Splitting pattern using the n+1 rule the peak will split into	Relative intensities in splitting pattern	Shape
0	1, singlet	1	
1	2, doublet	1 : 1	
2	3, triplet	1 : 2 : 1	
3	4, quartet	1 : 3 : 3 : 1	

- Splitting patterns must occur in pairs because each proton splits the signal of the other

- There are some common splitting pairs you will see in a spectrum however you don't need to learn these but can be worked out using the *n+1* rule

Your notes

- You will quickly come to recognise the triplet / quartet combination for a CH_3CH_2 because it is so common

Common pair of splitting patterns

- A quartet and a triplet in the same spectrum usually indicate an ethyl group, CH_3CH_2-

- The signal from the CH_3 protons is split as a triplet by having two neighbours

- The signal from the CH_2 protons is split as a quartet by having three neighbours

- Here are some more common pairs of splitting patterns

Common pairs of splitting patterns
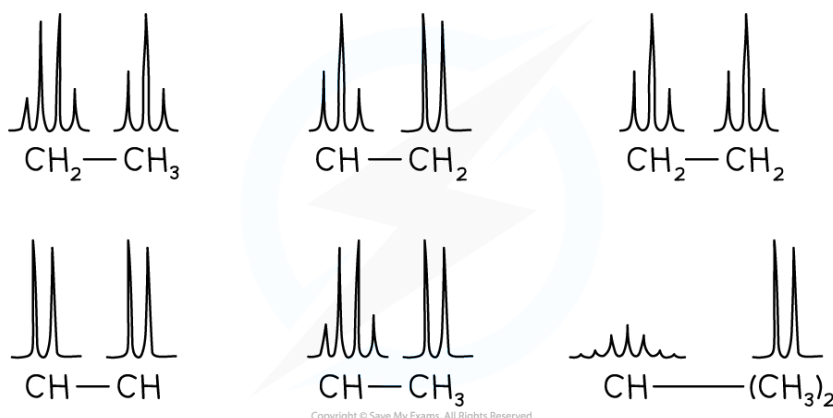
¹H NMR spectrum of propane
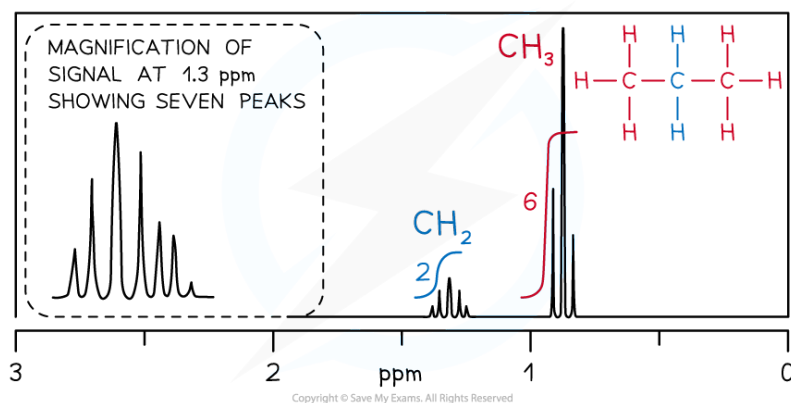
- The CH_2 signal in propane (blue) is observed as a heptet because it has six neighbouring equivalent H atoms (n+1 rule), three on either side in two equivalent CH_3 groups

- The CH_3 groups (red) produce identical triplets by coupling with the CH_2 group

Worked Example

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For the compound $(CH_3)_2CHOH$, predict the following:

1. The number of peaks
2. The type of proton and chemical shift
3. The relative peak areas
4. The splitting pattern

Answers:

1. The number of peaks

   - 3 peaks

2. The type of proton and chemical shift

   - $(\mathbf{CH_3})_2CHOH$ at 0.9 – 1.7 ppm
   - $(CH_3)_2C\mathbf{H}OH$ at 3.2 – 4.0 ppm
   - $(CH_3)_2CHO\mathbf{H}$ at 0.5 – 6.0 ppm

3. The relative peak areas

   - Ratio 6 : 1 : 1

4. The splitting pattern

   - $(\mathbf{CH_3})_2CHOH$ split into a doublet (1+1=2)
   - $(CH_3)_2C\mathbf{H}OH$ split into a heptet (6+1=7)

Use of Tetramethylsilane (TMS)

- In NMR spectroscopy, tetramethylsilane (TMS) is used as a reference compound

- The organic compound is dissolved in TMS before being introduced to the magnetic field of the spectrometer

- It is an ideal chemical to use as a reference

  - TMS is inert and volatile

  - This reduces undesirable chemical reactions with the compound to be analysed

  - It also mixes well with most organic compounds

- TMS gives a single sharp peak on the NMR spectrum and is given a value of zero

- The molecular formula of TMS is $Si(CH_3)_4$

  - There are 12 hydrogens in this molecule

  - All of the protons are in the same molecular environment. Therefore gives rise to just one peak

  - This peak has a very high intensity as it accounts for the absorption of energy from 12 ^1H nuclei
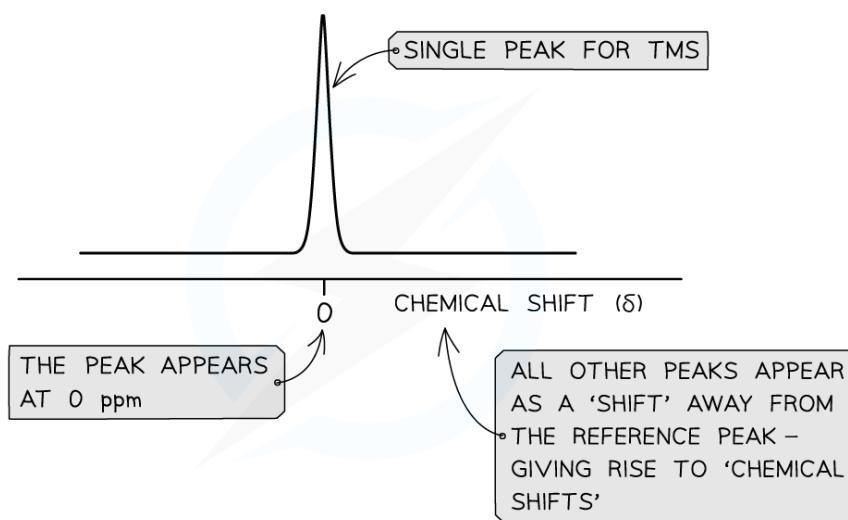
The structure of tetramethylsilane
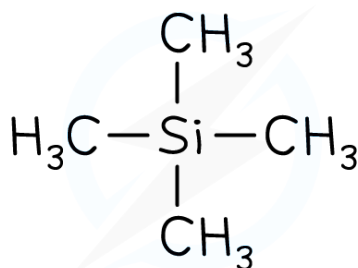
Tetramethylsilane (TMS) – $Si(CH_3)_4$

- When peaks are recorded from the sample compound, they are measured and recorded by their shift away from the sharp TMS peak

- This gives rise to the **chemical shift** values for different ^1H environments in a molecule

The ^1H NMR spectrum for tetramethylsilane

^{1}H NMR spectrum for TMS showing its signal at 0 ppm

Deuterated Solvents in Proton NMR

- When samples are analysed through NMR spectroscopy, they must be dissolved in a solvent

- Tetramethylsilane (TMS) is a commonly used solvent in NMR as it gives one sharp reference peak on NMR spectra

- However, the proton atoms can still interfere with peaks of a sample compound

- To avoid this interference, solvents containing deuterium can be used instead, e.g. $CDCl_3$

    - Deuterium (^{2}H) is an isotope of hydrogen (^{1}H)

- Deuterium nuclei absorb radio waves in a different region to the protons analysed in organic compounds

- Therefore, the reference solvent peak will not interfere with those of the sample

Identifying the –OH or –NH signal in an NMR spectrum

- In ^{1}H NMR, samples are dissolved in a solvent to help separate molecules and prevent them from interacting

- The solvent must:

    - Be a good solvent for organic molecules

    - Not contain any hydrogen (^{1}H) atoms, so it does not interfere with the NMR signals

Deuterated and non-deuterated solvents

- **Carbon tetrachloride, CCl_4:**

- This solvent does not contain hydrogen, so it does not produce ^{1}H NMR signals.

  - It is suitable for ^{1}H NMR but does not dissolve all molecules well.
- Deuterated solvents are often used in ^{1}H NMR spectroscopy because deuterium (^{2}H) is an isotope of hydrogen with no nuclear spin, which does not affect NMR results

- **Deuterochloroform / Chloroform-d, CDCl$_3$:**

  - This is often preferred because it contains **deuterium (^{2}H)** instead of hydrogen, so it does not interfere with the proton NMR spectrum

- **Deuterium oxide / Heavy water, D$_2$O:**

  - The deuterium atoms exchange reversibly with the protons in the –OH and –NH groups, allowing these signals to be identified in the NMR spectrum

Identifying –OH and –NH signals

- Protons in **–OH** (hydroxyl) and **–NH** (amine) groups give **singlet** peaks in ^{1}H NMR, but these signals can be tricky:

  - They are **broad** or sometimes fall outside normal chemical shift ranges

  - The proton in these groups exchanges quickly with protons from water or acids, so only one peak appears

  - Their chemical shift ranges may overlap with other types of protons, making them difficult to interpret

- To identify these groups more clearly, proton exchange with **deuterium oxide (D$_2$O)** is used:

  - The deuterium atoms in D$_2$O exchange reversibly with the protons in the –OH or –NH groups

$$-OH + D_2O \rightleftharpoons -OD + HOD$$

$$-NH-CO- + D_2O \rightleftharpoons -ND-CO + HOD$$
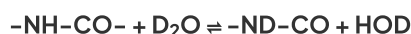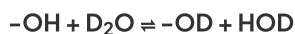
- Since deuterium does not absorb in the same region as protons in the NMR spectrum, the signal for –OH or –NH disappears after D$_2$O is added

- This confirms the presence of –OH or –NH groups in the molecule

  - If a peak disappears after adding D$_2$O, it must have been due to the exchange of a proton from an –OH or –NH group

- This technique is particularly useful because –OH and –NH peaks can be broad and difficult to assign confidently without D$_2$O exchange