CIE A Level Chemistry

Your notes

37.4 Proton (1H) NMR Spectroscopy

Contents

Proton (1H) NMR Spectroscopy

Your notes

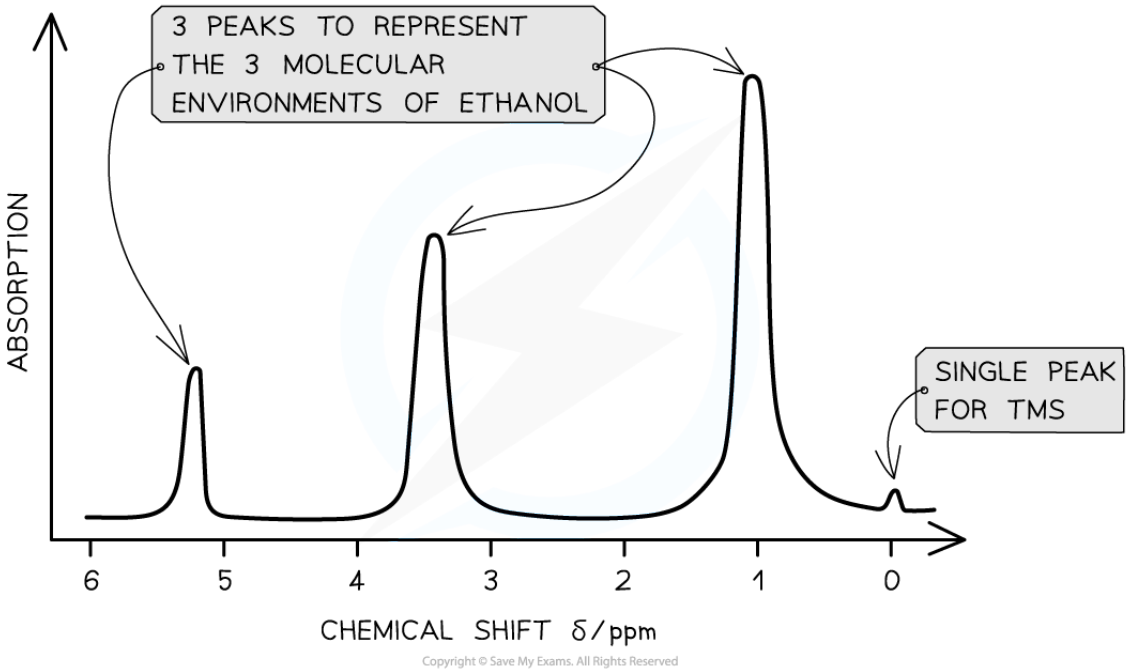
Interpreting & Explaining Proton (1H) NMR Spectra

- **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



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

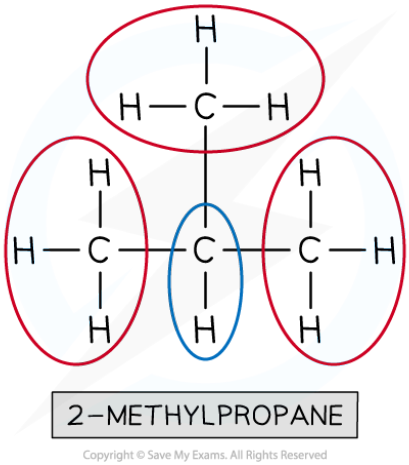
Your notes

Worked example

How many different ^1H chemical environments occur in 2-methylpropane?

Answer:

- Two different ^1H chemical environments occur in 2-methylpropane
  - The three methyl groups are in the same ^1H environment
  - The lone hydrogen is in its own ^1H environment



Your notes

Chemical shift values for ^1H molecular environments table

Environment of proton	Example	Chemical shift range, δ / ppm
alkane	$-C\mathbf{H}_3$, $-C\mathbf{H}_2-$, $>C\mathbf{H}-$	0.9 - 1.7
alkyl next to C=O	$C\mathbf{H}_3-C=O$, $-C\mathbf{H}_2-C=O$, $>C\mathbf{H}-C=O$	2.2 - 3.0
alkyl next to aromatic ring	$C\mathbf{H}_3-Ar$, $-C\mathbf{H}_2-Ar$, $>C\mathbf{H}_2-Ar$	2.3 - 3.0
alkyl next to electronegative atom	$C\mathbf{H}_3-O$, $C\mathbf{H}_2-O$, $C\mathbf{H}_2-Cl$	3.2 - 4.0
attached to alkene	$=C\mathbf{H}R$	4.5 - 6.0
attached to aromatic ring	$\mathbf{H}-Ar$	6.0 - 9.0
aldehyde	$\mathbf{H}COR$	9.3 - 10.5

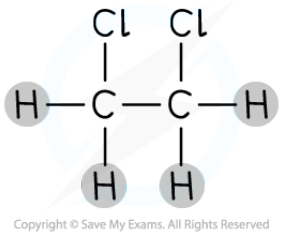
alcohol*	RO**H**	0.5 - 6.0
phenol*	Ar–OH	4.5 - 7.0
carboxylic acid	RCOO**H**	9.0 - 13.0
alkyl amine*	R–N**H**–	1.0 - 5.0
aryl amine*	Ar–N$\mathbf{H_2}$	3.0 - 6.0
amide	RCON**H**R	5.0 - 12.0

* δ values for O-H protons and N-H protons vary depending on the solvent and concentration

Your notes

- 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 ^{1}H 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

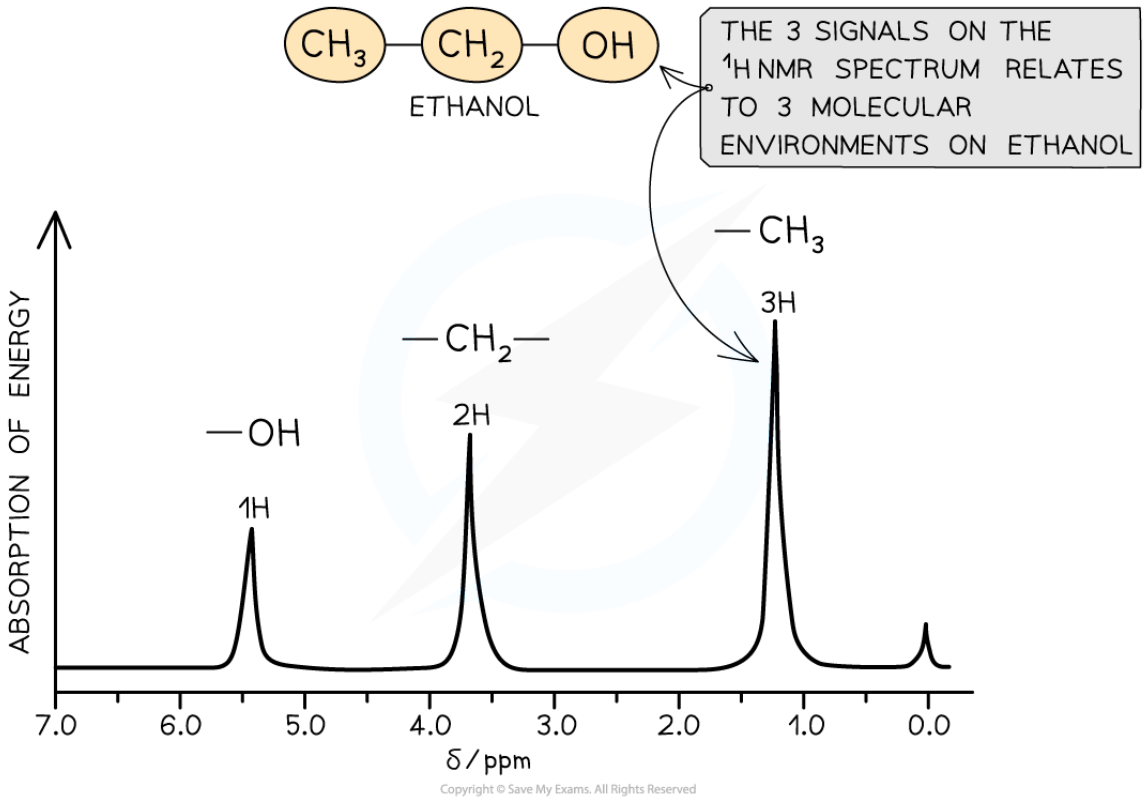


All four protons in the 1,2–dichloroethane molecule are equivalent

Low resolution ^{1}H 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 ^{1}H 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)

Your notes

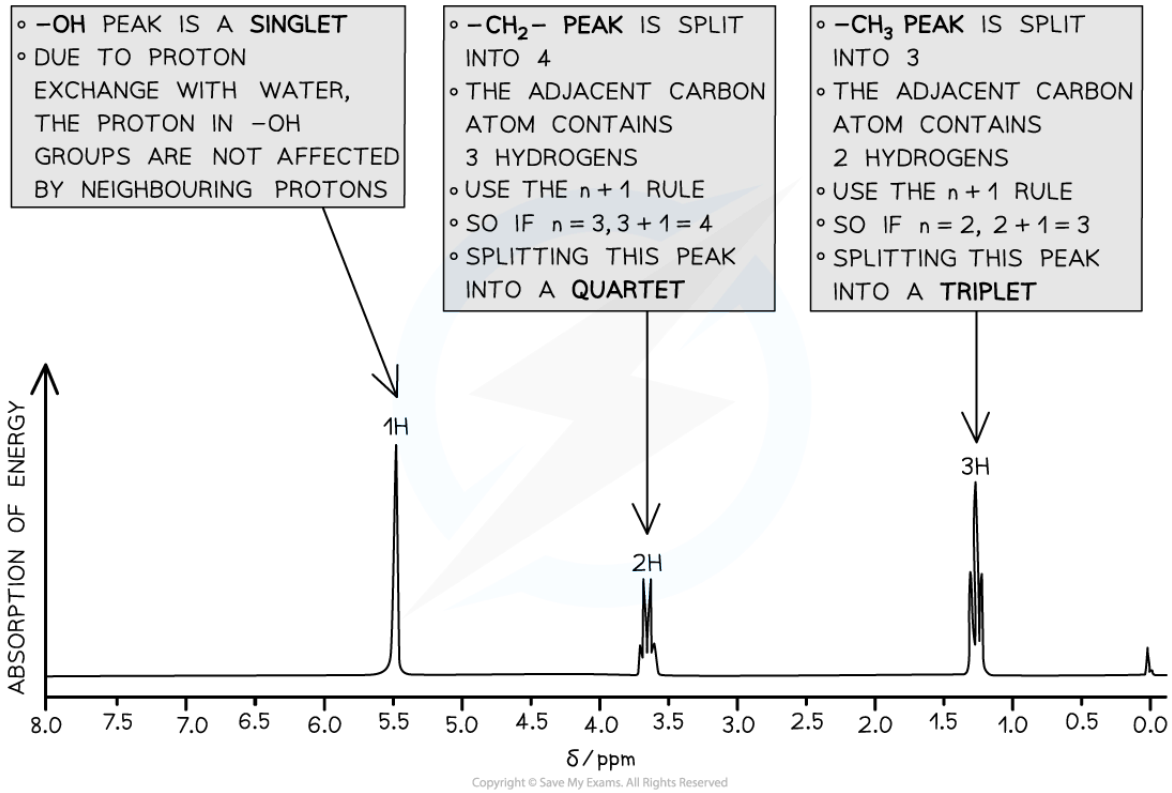
Predicting Shifts & Splitting Patterns

Your notes

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 ^1H NMR spectrum of ethanol



The high resolution ^1H 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 Tip

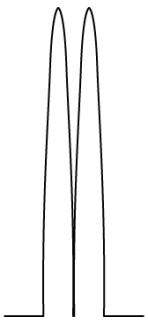
- It is very rare that the spin-spin splitting of equivalent protons is covered in teaching because it is so rarely asked in exams
- Equivalent protons do **not** cause spin-spin splitting
  - The simplest example of this is benzene
    - In benzene, all of the protons are equivalent
    - This means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

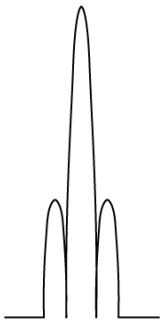
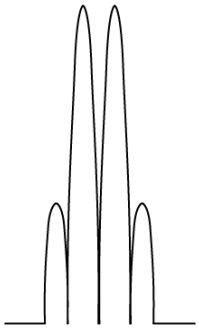
Your notes

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:

^{1}H 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	

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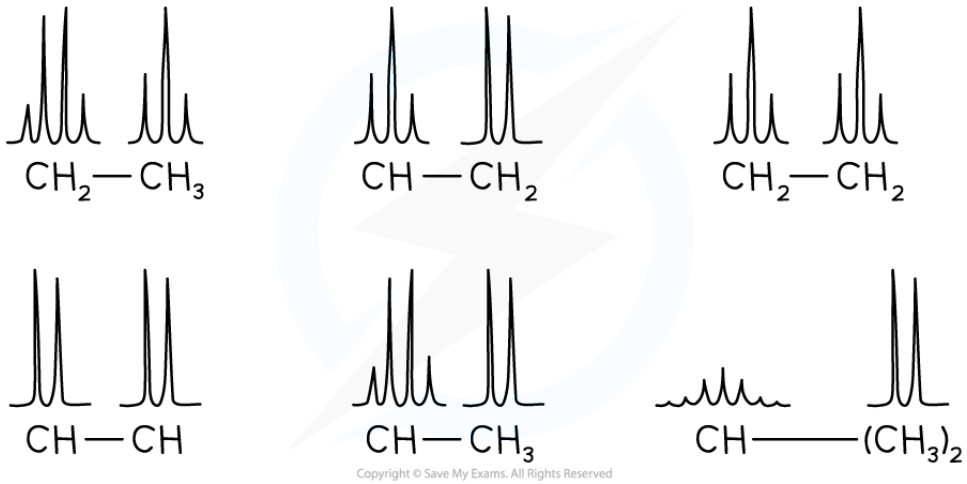
- Splitting patterns must occur in pairs because each proton splits the signal of the other
- There are some common splitting pairs you will see in a spectrum however you don't need to learn these but can be worked out using the *n*+1 rule
  - You will quickly come to recognise the triplet / quartet combination for a CH_3CH_2 because it is so common

Common pair of splitting patterns

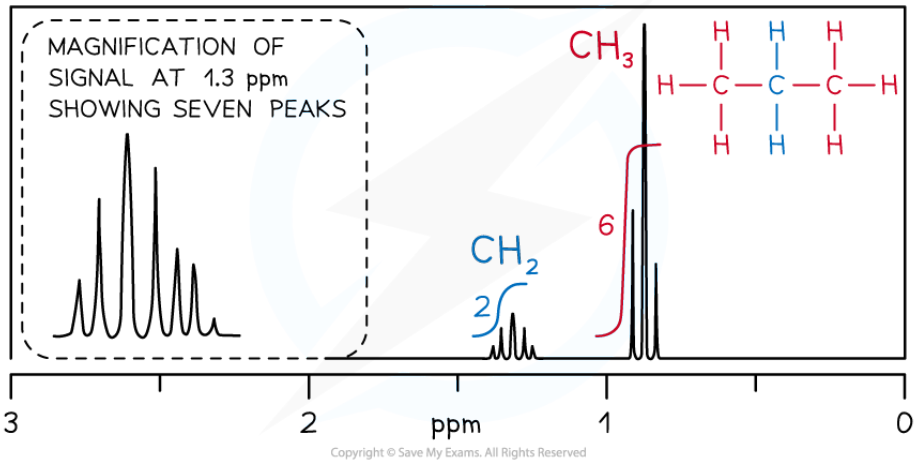
- A quartet and a triplet in the same spectrum usually indicate an ethyl group, CH_3CH_2-
- The signal from the CH_3 protons is split as a triplet by having two neighbours
- The signal from the CH_2 protons is split as a quartet by having three neighbours
- Here are some more common pairs of splitting patterns

Common pairs of splitting patterns

Your notes



^{1}H 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

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
   - $(C\mathbf{H_3})_2CHOH$ 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
   - $(C\mathbf{H_3})_2CHOH$ split into a doublet (1+1=2)
   - $(CH_3)_2C\mathbf{H}OH$ split into a heptet (6+1=7)

Your notes

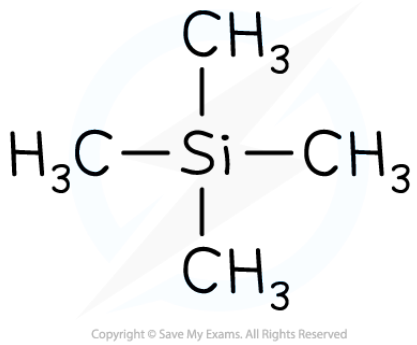
Tetramethylsilane (TMS) & Deuterated Solvents

Your notes

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

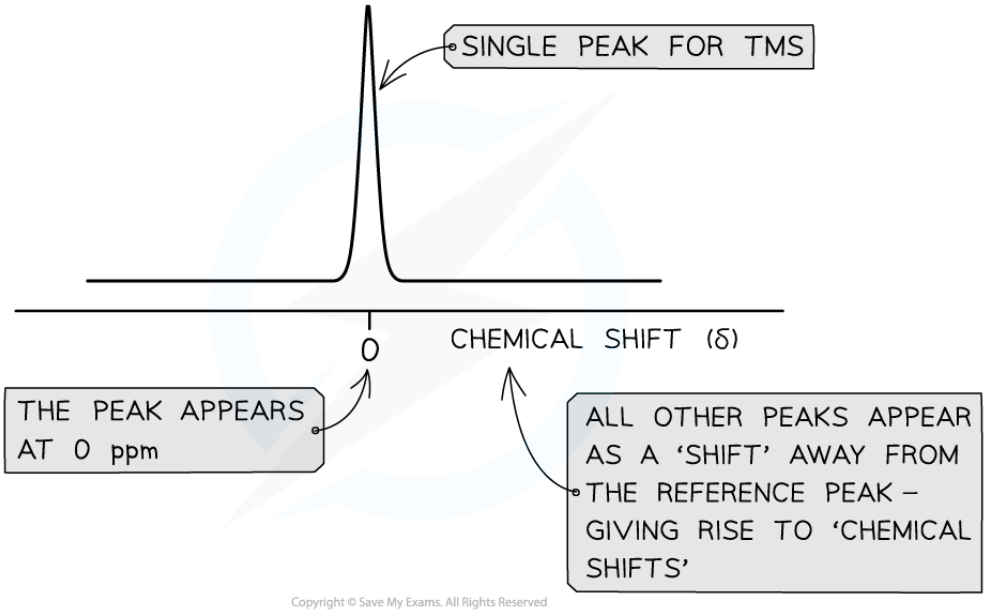


***Tetramethylsilane (TMS)* – $Si(CH_3)_4$**

- 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

Your notes



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

Deuterated Solvents in Proton NMR

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
- Despite TMS showing one sharp reference peak on NMR spectra, the proton atoms can still interfere with peaks of a sample compound
- To avoid this interference, solvents containing deuterium can be used instead
  - For example $CDCl_3$
  - Deuterium (^2H) is an isotope of hydrogen (^1H)
- 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