

3.15 NMR spectroscopy

Different types of NMR

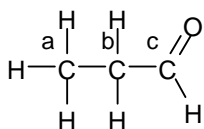
There are two main types of NMR

- ^{13}C NMR
- ^1H (proton) NMR

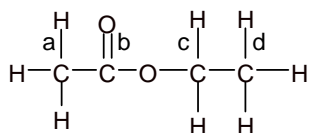
There is only around 1% C^{13} in organic molecules but modern NMR machines are sensitive enough to give a full spectra for C^{13}
The C^{13} spectra is a simpler spectrum than the H NMR.

Equivalent carbon atoms.

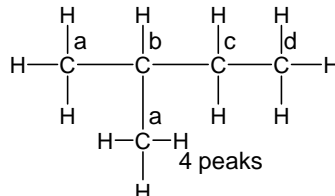
In a C^{13} NMR spectrum, there is one signal (peak) for each **set of equivalent C atoms**.



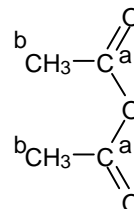
3 peaks



4 peaks

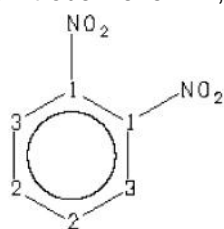


4 peaks

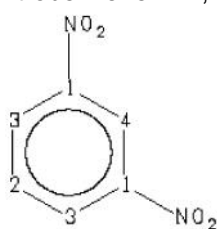


2 peaks

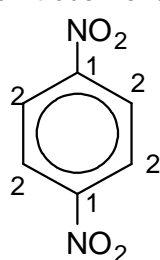
1,2 dinitrobenzene 1,3 dinitrobenzene 1,4 dinitrobenzene



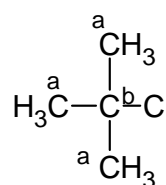
3 peaks



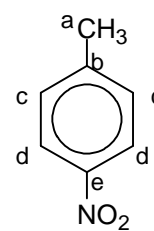
4 peaks



2 peaks



2 peaks

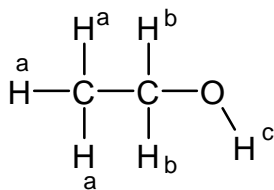


5 peaks

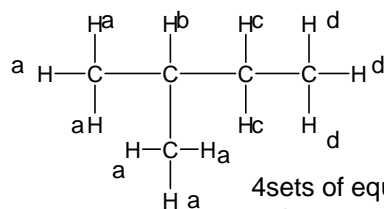
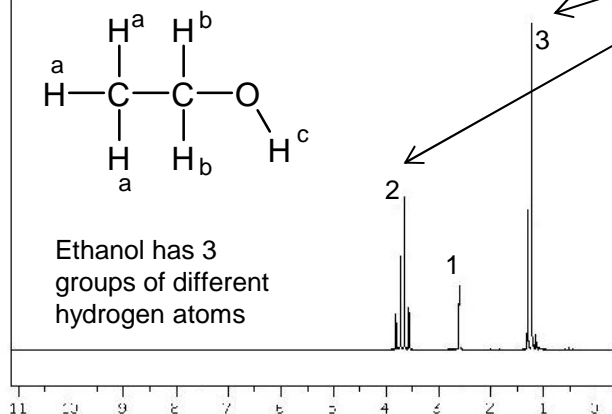
Equivalent hydrogen atoms.

In an ^1H NMR spectrum, there is one signal for each set of equivalent H atoms.

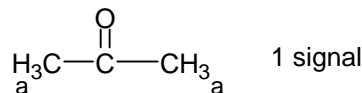
In addition the **intensity (integration value)** of each signal is proportional to the **number of equivalent H atoms** it represents.



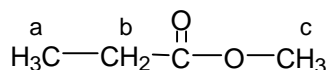
Ethanol has 3 groups of different hydrogen atoms



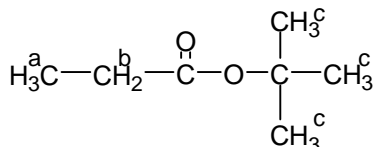
4 sets of equivalent H's:
ratio 6:1:2:3



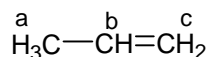
1 signal



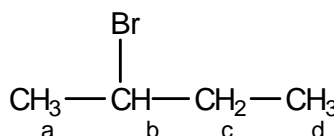
3 sets of equivalent H's: ratio 3:2:3



3 sets of equivalent H's: ratio 3:2:9



3 sets of equivalent H's: ratio 3:1:2



4 sets of equivalent H's: ratio 3:1:2:3

Solvents

Samples are dissolved in **inert** solvents with **no ^1H atoms**, e.g. CCl_4 , CDCl_3 .

These solvents have no H atoms so will not give any peaks in the ^1H NMR spectrum.

The same solvents are used in ^{13}C NMR and in this case there will be one peak due to the solvent that will appear on the spectrum. However, it is known where this peak is so it can be ignored. In the exam it is likely this peak will not occur on the spectra.

CCl_4 is a non-polar compound that is a good solvent for non-polar organic molecules.

CDCl_3 is a polar covalent molecule that is a good solvent for polar organic molecules.

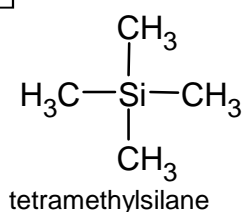
Calibration and shift

A small amount of TMS (tetramethylsilane) is added to the sample to calibrate the spectrum.

TMS is used because:

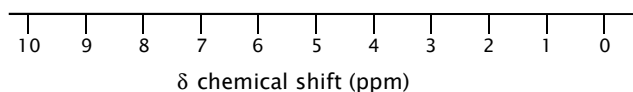
- it only gives **one signal**
- its signal is **away from all the other H signals**
- gives strong signal so only a small amount needed
- it is non-toxic
- it is inert
- it has a **low boiling point** and so **can be removed from sample easily**

The δ is a measure in parts per million (ppm) is a relative scale of how far the frequency of the proton signal has shifted away from that for TMS.



The same calibration compound is used for both H and C NMR

The spectra are recorded on a scale known as the chemical shift (δ), which is how much the field has shifted away from the field for TMS.

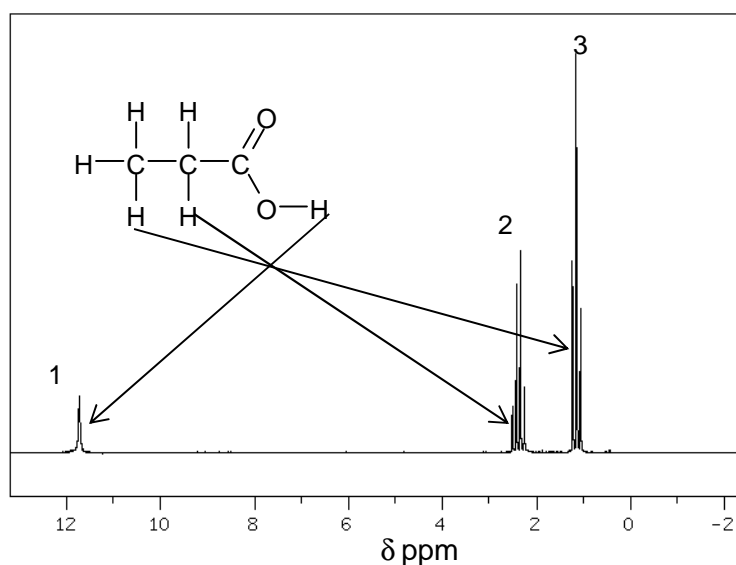
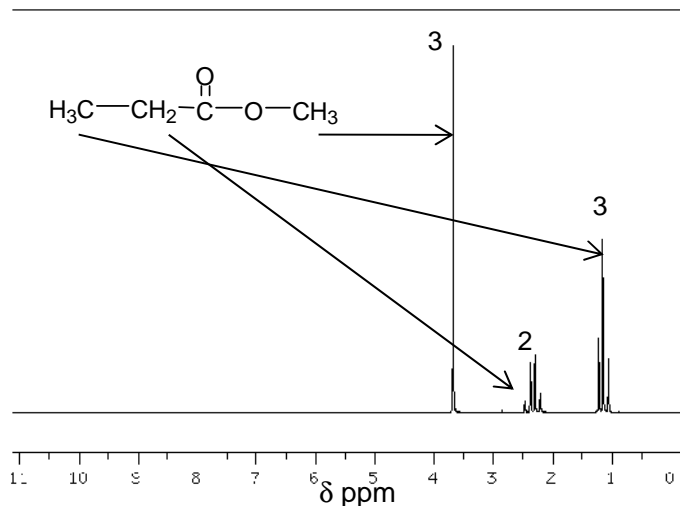


^1H NMR shift


^1H n.m.r. chemical shift data

Type of proton	δ/ppm
ROH	0.5–5.0
RCH ₃	0.7–1.2
RNH ₂	1.0–4.5
R ₂ CH ₂	1.2–1.4
R ₃ CH	1.4–1.6
$\begin{array}{c} \\ \text{R}-\text{C}-\text{C}- \\ \quad \\ \text{O} \quad \text{H} \end{array}$	2.1–2.6
$\begin{array}{c} \\ \text{R}-\text{O}-\text{C}- \\ \\ \text{H} \end{array}$	3.1–3.9
RCH ₂ Cl or Br	3.1–4.2
$\begin{array}{c} \\ \text{R}-\text{C}-\text{O}-\text{C}- \\ \quad \\ \text{O} \quad \text{H} \end{array}$	3.7–4.1
$\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{C} \\ / \\ \text{H} \end{array}$	4.5–6.0
$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C} \\ \\ \text{H} \end{array}$	9.0–10.0
$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C} \\ \\ \text{O}-\text{H} \end{array}$	10.0–12.0

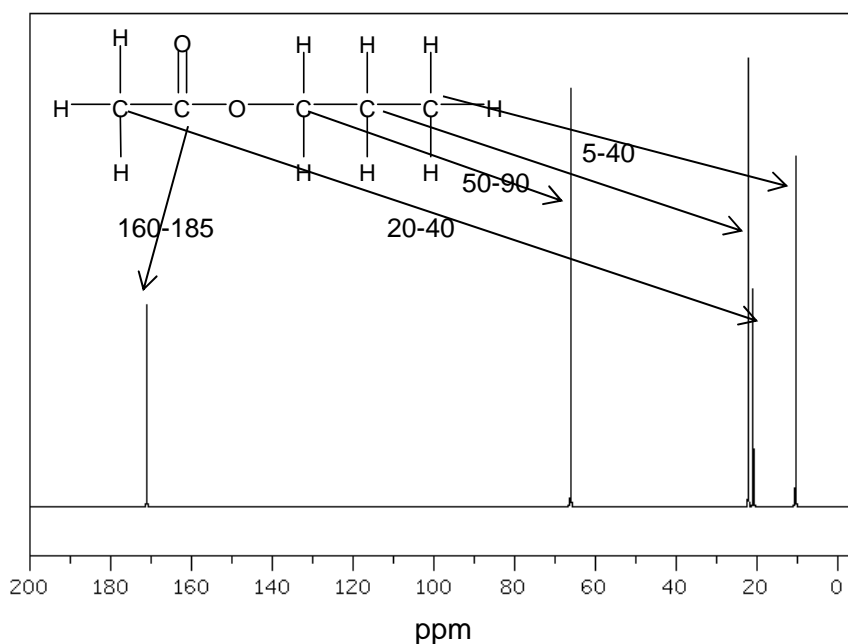
The δ depends on what other atoms/groups are near the H – more electronegative groups gives a greater shift.



^{13}C n.m.r. chemical shift data

Type of carbon	δ/ppm
$\begin{array}{c} \\ -\text{C}-\text{C}- \\ \quad \end{array}$	5–40
R- $\begin{array}{c} \\ \text{C}-\text{Cl} \text{ or } \text{Br} \\ \end{array}$	10–70
$\begin{array}{c} \\ \text{R}-\text{C}-\text{C}- \\ \quad \\ \text{O} \end{array}$	20–50
R- $\begin{array}{c} \diagup \\ \text{C}-\text{N} \\ \diagdown \end{array}$	25–60
$\begin{array}{c} \\ -\text{C}-\text{O}- \\ \end{array}$ alcohols, ethers or esters	50–90
$\begin{array}{c} \diagdown \\ \text{C}=\text{C} \\ / \end{array}$	90–150
R-C \equiv N	110–125
	110–160
R- $\begin{array}{c} \text{O} \\ \\ \text{C}- \end{array}$ esters or acids	160–185
R- $\begin{array}{c} \text{O} \\ \\ \text{C}- \end{array}$ aldehydes or ketones	190–220

^{13}C NMR shift



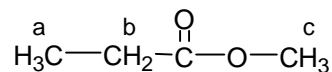
Spin-Spin coupling in ^1H NMR

In high resolution ^1H NMR, each signal in the spectrum can be split into further lines due to inequivalent H's on neighbouring C atoms.

Splitting of peak = number of inequivalent H's on neighbouring C atoms + 1

signal	singlet	doublet	triplet	quartet
appearance				
Split number of peaks	1	2	3	4
number of neighbouring inequivalent H atoms	0	1	2	3
relative size		1:1	1:2:1	1:3:3:1

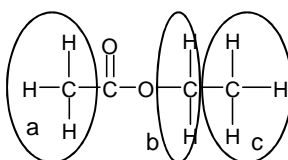
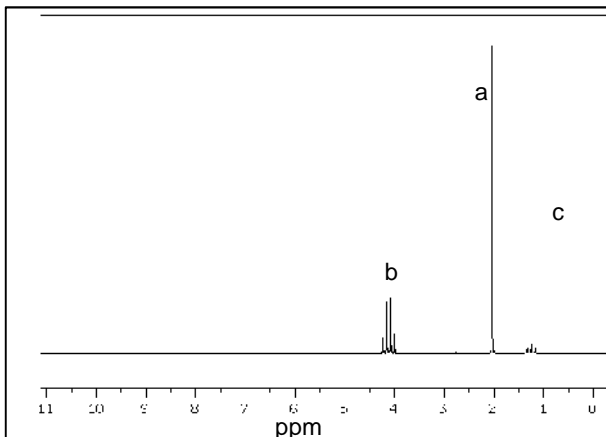
Nuclei in identical chemical environments do not show coupling amongst themselves.



The peak due to group **a** will be a **triplet** as it is next to **b** (a carbon with 2 H's)

The peak due to group **b** will be a **quartet** as it is next to **a** (a carbon with 3H's)

The peak due to group **c** will be a **singlet** as it is next to a carbon with no H's)



The peak due to group **a** will be a **singlet** as it is next to a carbon with 0 H's
Shift 2.1-2.6
Integration trace 3

The peak due to group **c** will be a **triplet** as it is next to a carbon with 2 H's
Shift 0.7-1.2
Integration trace 3

The peak due to group **b** will be a **quartet** as it is next to a carbon with 3 H's
Shift 3.7 -4.1
Integration trace 2

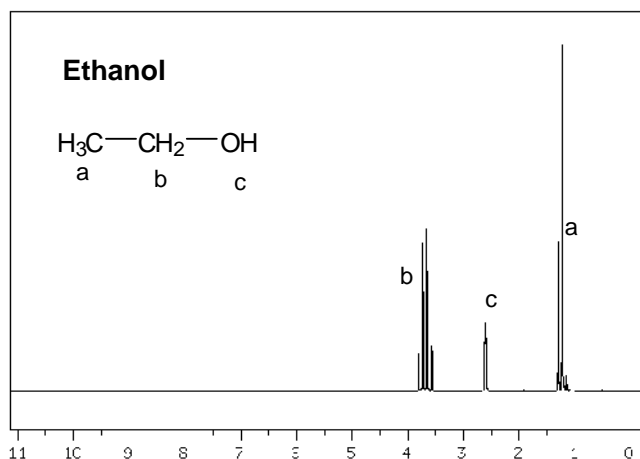
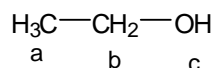
A hydrogen bonded to a nitrogen or an oxygen usually do not couple with other protons and appear as singlets on the ^1H NMR spectra.

The peak due to group **a** will be a **triplet** as it is next to a carbon with 2 H's
Shift 0.7-1.2
Integration trace 3

The peak due to group **b** will be a **quartet** as it is next to a carbon with 3 H's
Shift 3.7 -4.1
Integration trace 2

The peak due to group **c** will be a **singlet** as the hydrogen is bonded to an oxygen and this does not split
Shift 0.5-5.0
Integration trace 1

Ethanol



Bringing it all together

1. Work out empirical formula

Elemental analysis C 66.63% H 11.18% O 22.19%

C	H	O
66.63/12	11.18/1	22.19/16
=5.5525	=11.18	=1.386875
=4	=8	=1

2. Using molecular ion peak m/z value from mass spectrum to determine the molecular formula

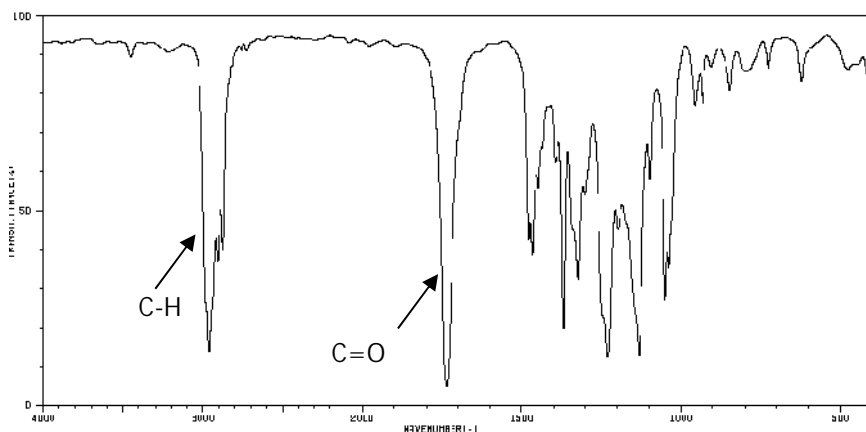
molecular ion peak m/z value= 144

M_r empirical formula $C_4H_8O = 72$

If M_r molecular formula 144 then compound is $C_8H_{16}O_2$

3. Use IR spectra to identify main bonds/functional group

$C_8H_{16}O_2$ could be an ester, carboxylic acid or combination of alcohol and carbonyl. Look for IR spectra for C=O and O-H bonds

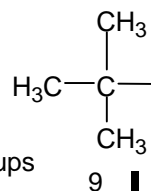


There is a C=O but no O-H absorptions, so must be an ester.

4. Use NMR spectra to give details of carbon chain

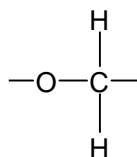
4 peaks – only 4 different environments.

singlet of area 9
At $\delta = 0.9$
Means 3 CH_3 groups



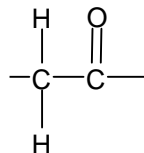
Peak at δ 4 shows H-C-O

Area 2 suggests CH_2
Quartet means next to a CH_3



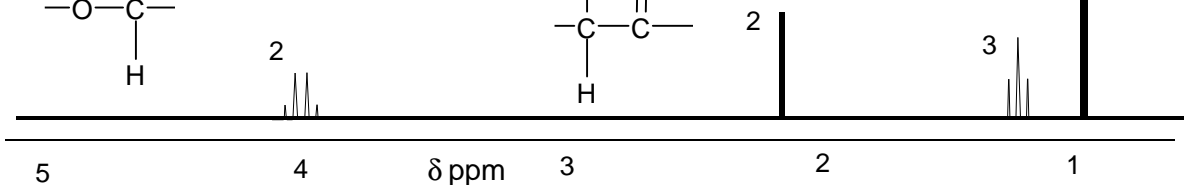
Peak at δ 2.2 shows H-C=O

Area 2 suggests CH_2
Singlet means adjacent to C with no hydrogens



Peak at δ 1.2 shows R- CH_3

Area 3 means CH_3
Triplet means next to a CH_2



Put all together to give the final structure

