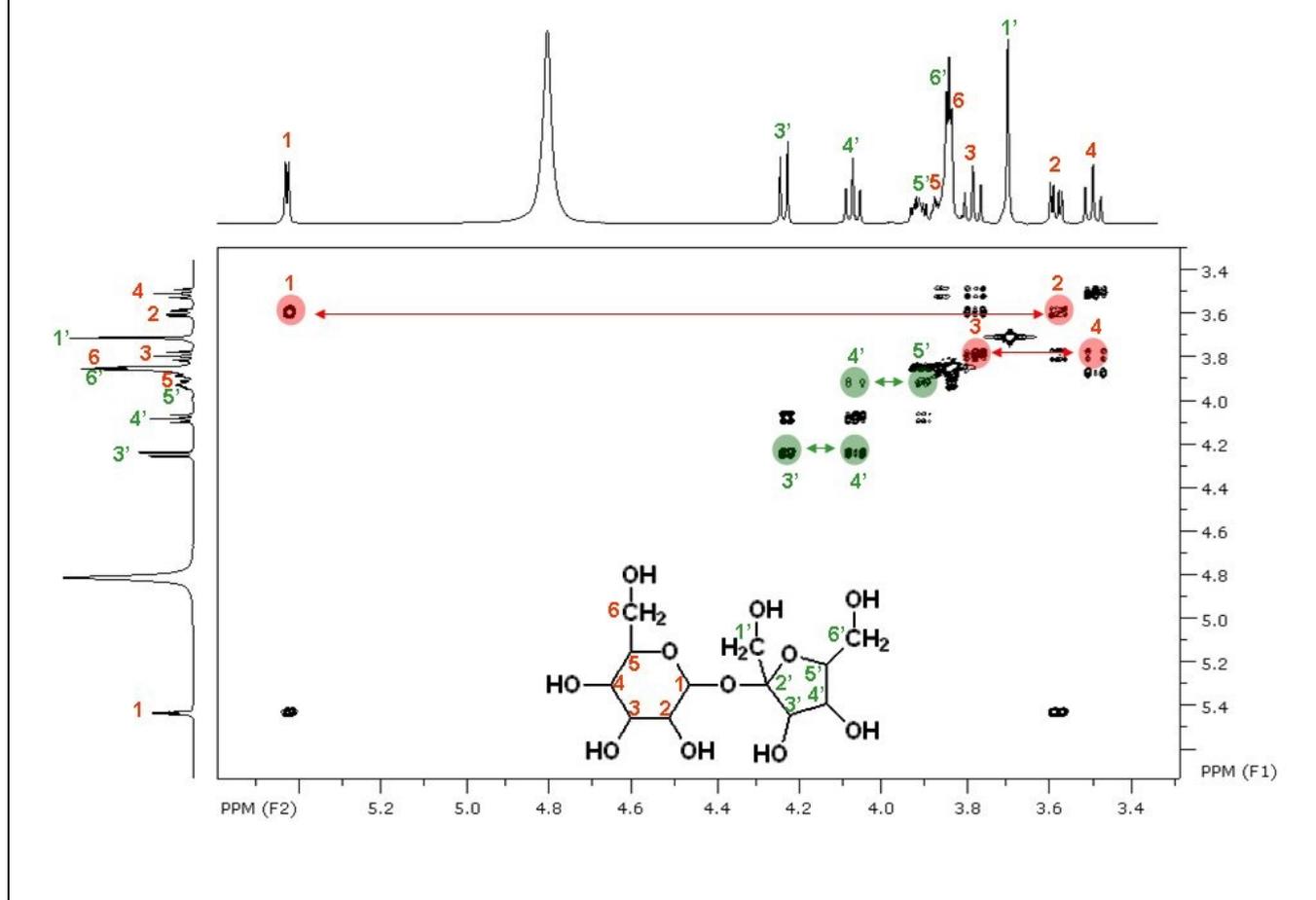


NMR

SPECTROSCOPY



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SECTION 1 – INTRODUCTION

What is NMR?

- NMR (nuclear magnetic resonance) spectroscopy is a very powerful form of analysis used by organic chemists.
- ^1H NMR (known as “proton NMR”) gives information about the hydrogen atoms in organic molecules.
- ^{13}C NMR (known as “carbon-13 NMR”) gives information about the carbon atoms in organic molecules.

Solvent

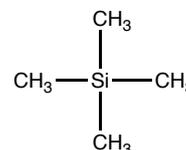
- The compound is usually dissolved in a solvent (although sometimes it is done in the solid state).
- The solvents used should not contain any ^1H atoms as these might hide the signals due to ^1H atoms in the compound.
- Some common solvents used are:
 - CCl_4
 - CDCl_3 (where D = deuterium = ^2H)

What happens?

- The compound being analysed is put into a very strong magnetic field.
- Radio-waves are passed through the compound.
- The compound absorbs some the radio-waves to change the “spin” direction of the nuclei of the ^1H or ^{13}C atoms.

Standard used for calibration

- The signals show the frequency at which the compound absorbs radio waves relative to the standard compound tetramethylsilane (TMS)
- TMS is used because it
 - only produces one signal
 - is inert
 - is non-toxic
 - gives a signal in an area that does not overlap with those from most organic compounds



Chemical shift (δ)

- The signals in the spectrum have a **chemical shift (δ)** – this represents the difference between the frequencies at which the compound and TMS absorb in parts per million (ppm).
- The closer a C atom is to a very electronegative atom (e.g. O, Cl), or to a double bond, the greater the chemical shift.

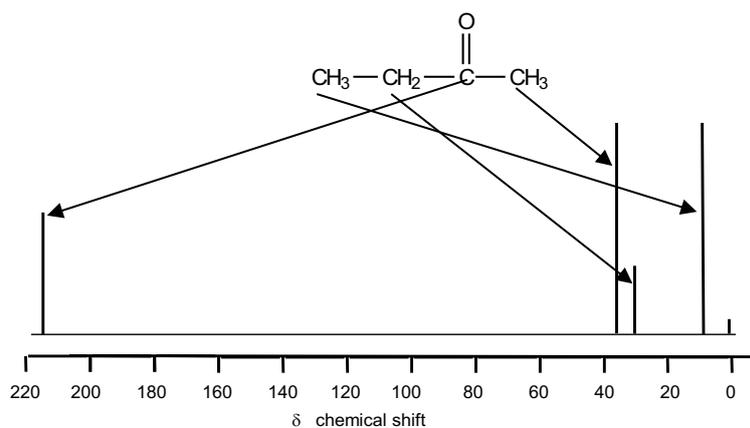
SECTION 2 – ¹³C NMR

- The table shows some data for chemical shifts in ¹³C NMR spectra.

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

Examples of ¹³C NMR spectra

Example 1 - butanone

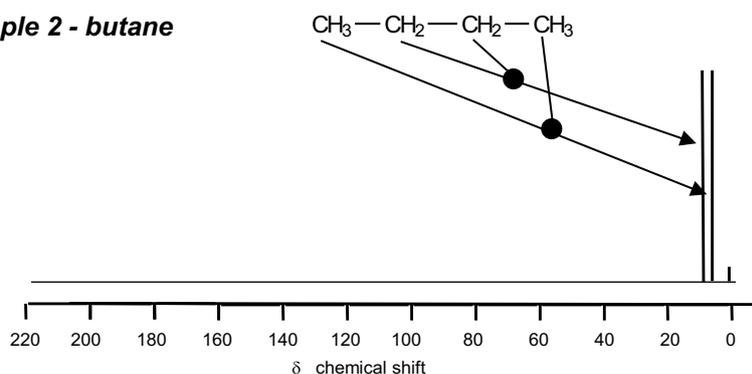


- There are 4 signals – one for each C atom as each C atom is in a unique chemical environment.

shift (δ)	assignment
8	$\underline{\text{C}}\text{H}_3\text{CH}_2$
32	$\underline{\text{C}}\text{H}_3\text{CO}$
37	CH_2
215	CO

- Note how the C of the C=O group directly next to the O has the biggest chemical shift.
- Note how the C furthest from the O has the smallest chemical shift.

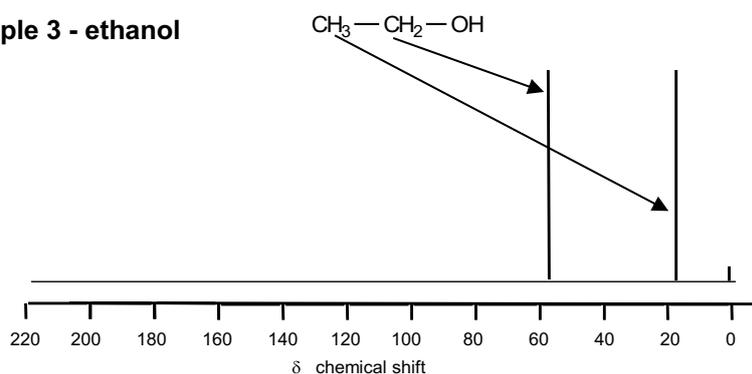
Example 2 - butane



shift (δ)	assignment
8	CH_3
10	CH_2

- There are only 2 signals as each signal represents 2 C atoms that are chemically equivalent.
- You would not be expected to know which signal was for which C atom.

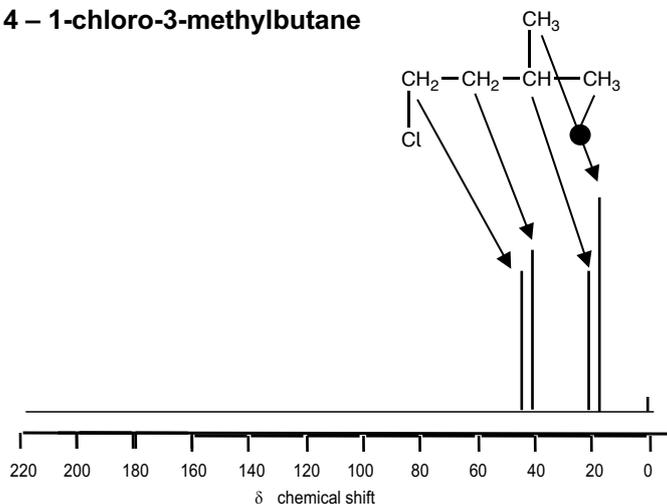
Example 3 - ethanol



shift (δ)	assignment
18	CH_3
58	CH_2

- Note how the C closest to the O has the biggest chemical shift.

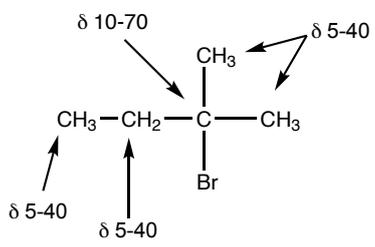
Example 4 - 1-chloro-3-methylbutane



shift (δ)	assignment
18	CH_3
22	CH
40	CH_2
46	CH_2Cl

- Note how the closer the C atom to the Cl, the bigger the chemical shift

TASK 1 – Predicting ^{13}C NMR spectra

Compound	Structure and chemical shift (δ)	Number of signals
2-bromo-2-methylbutane	 <p style="text-align: center;"> δ 10-70 δ 5-40 δ 5-40 δ 5-40 </p>	4
methylpropene		
propene		
2-chloropropane		
propanone		

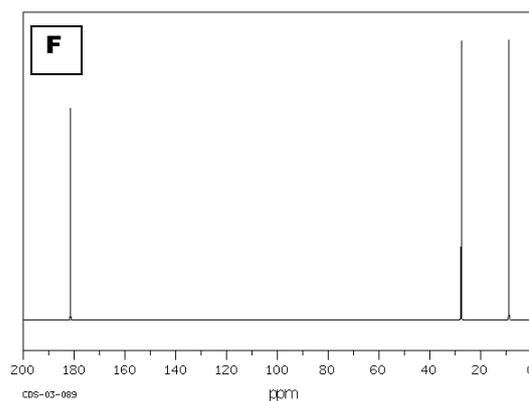
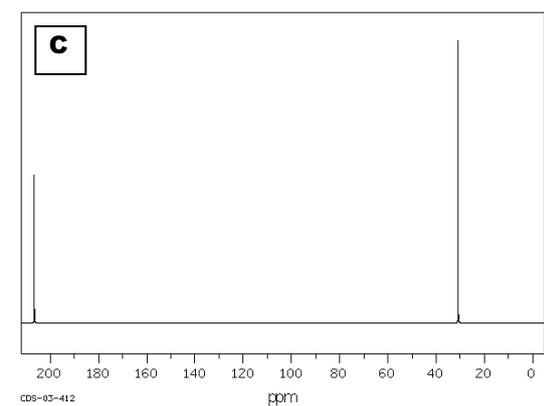
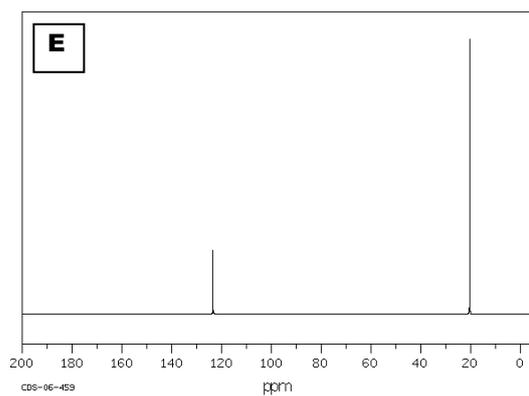
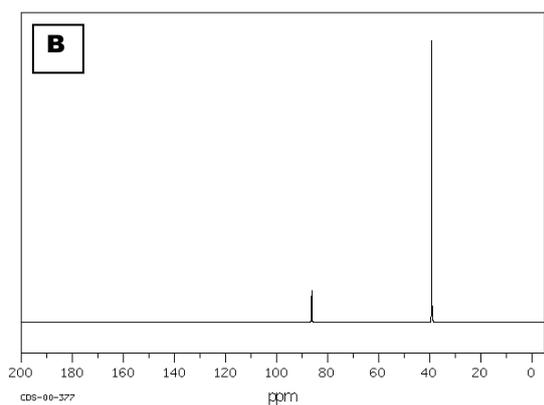
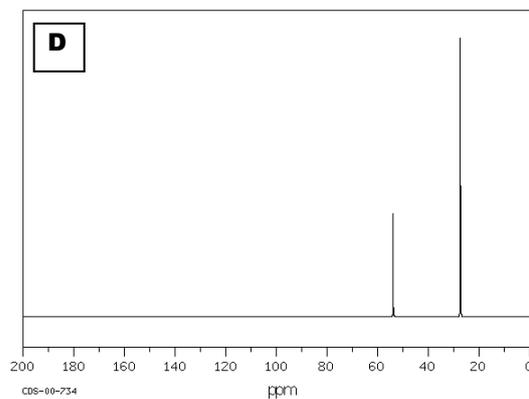
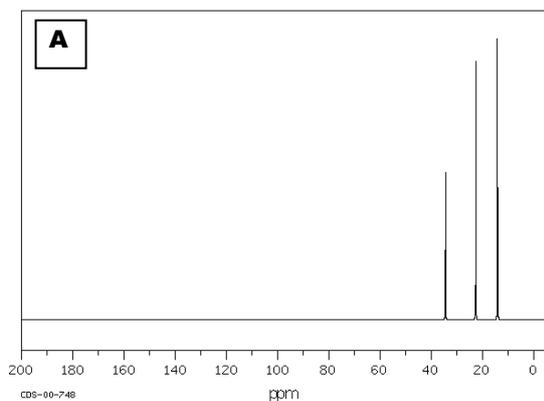
Compound	Structure and chemical shift (δ)	Number of signals
methylamine		
ethyl propanoate		
1,2-dibromopropane		
dimethylethyl propanoate		
but-2-ene		

TASK 2 – Which ^{13}C NMR spectrum is which?

For each of the following compounds:

propanoic acid pentane 2-chloropropane propanone 2,2-dichloropropane 2,3-dimethylbut-2-ene

Work out which spectrum belongs to which compound.



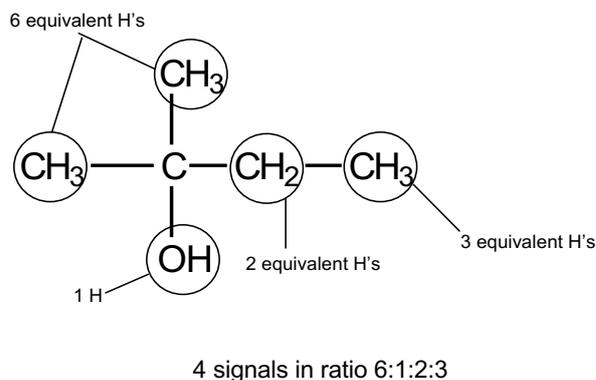
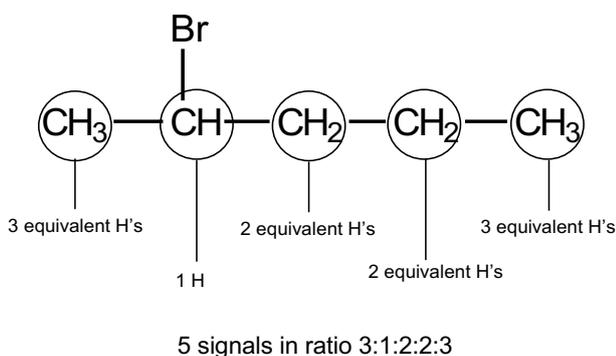
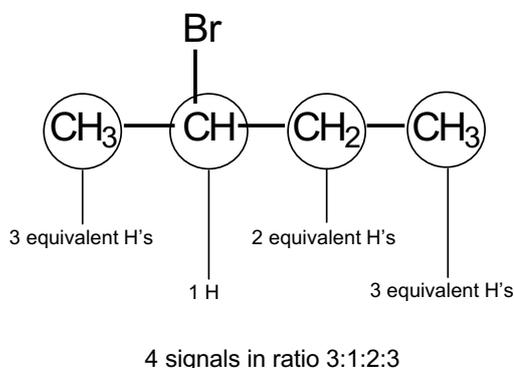
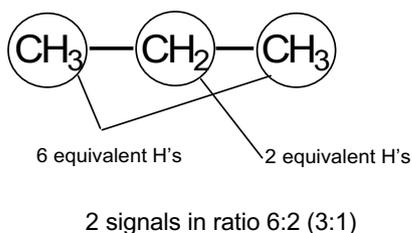
SECTION 3 – ¹H NMR

- ¹H NMR is similar to ¹³C NMR but looks at ¹H rather than ¹³C atoms.
- There are some very useful extra features in ¹H NMR spectra compared to ¹³C NMR spectra.
- The table shows some key similarities and differences between ¹H and ¹³C NMR spectra.

	Similar or different	¹ H NMR	¹³ C NMR
Number of signals	similar	One signal for each set of equivalent ¹ H or ¹³ C atoms	
Position of signal	similar	The closer the atom to a very electronegative atom and/or double bond, the greater the chemical shift	
Relative size of signals	different	Relative area of signals related to relative number of ¹ H atoms	No link between area of signal to number of ¹³ C atoms
Splitting of signals	different	Signal split by ¹ H atoms on adjacent atom (into doublets, triplets, etc)	No splitting

Number of signals - equivalent H atoms

- In a spectrum, there is one signal for each set of equivalent H atoms, with the area of each signal being proportional to the number of equivalent H atoms it represents.
- Here are some examples.



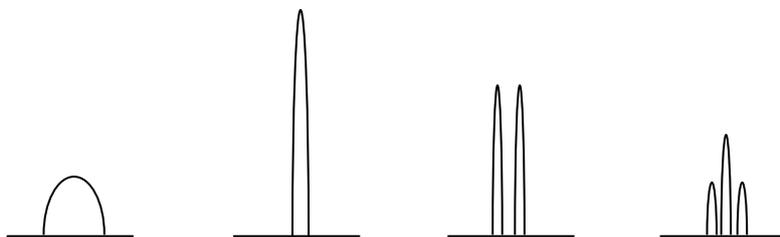
TASK 3a – Predicting ¹H NMR spectra 1

Complete the second, third and fourth columns in this table.

Compound	Structure	Number of signals	Relative intensity of signals	Splitting patterns of signals
2-bromo-2-methylbutane	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{CH}_3 \\ \\ \text{Br} \end{array}$	3	3 : 2 : 6	t, q, s
methylpropene				
propene				
2-chloropropane				
propanone				
methylamine				
ethyl propanoate				
1,2-dibromopropane				
dimethylethyl propanoate				
but-2-ene				

Relative intensity of signals – number of equivalent H atoms

- In ^1H NMR (but **not** ^{13}C NMR) the area of the signal is proportional to the number of ^1H atoms it represents.
- It is not the height of the signal that matters but the overall area that the signal covers. For example, the following four signals have the same area and so represent the same number of ^1H atoms, even though they have different heights and in some cases are made of a number of individual peaks



There are four signals here – each has the same area and so represents the same number of H atoms

Splitting patterns (also known as coupling or multiplicity)

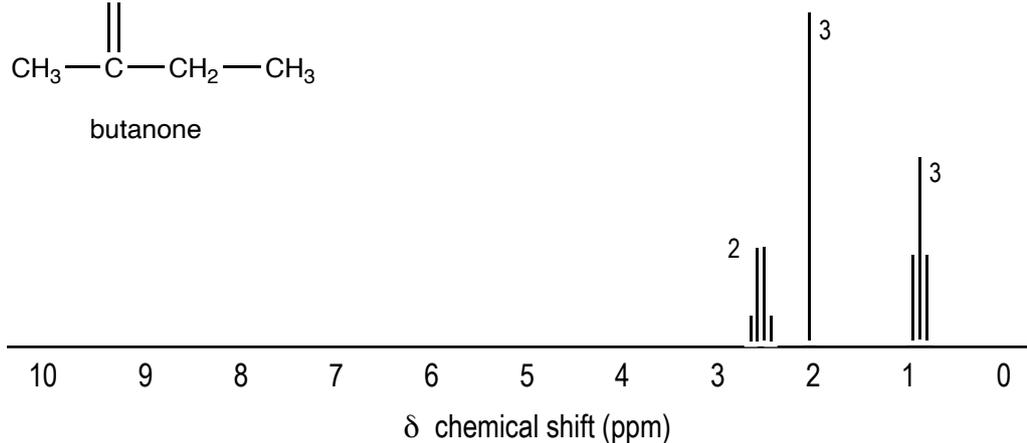
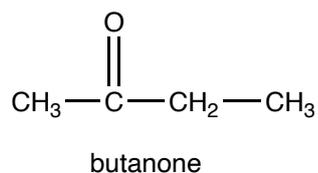
- In ^1H NMR the signals are split into a series of lines due to **coupling** between ^1H atoms.
- Coupling happens between ^1H atoms that are not equivalent to each other on neighbouring C atoms. Coupling does not happen between equivalent ^1H atoms.
- The number of lines the signal is split into is given by the **n+1 rule**

number of lines = 1 + the number of inequivalent H atoms on adjacent C atoms

splitting pattern	singlet (s)	doublet (d)	triplet (t)	quartet (q)
number of neighbouring inequivalent H atoms (n)	0	1	2	3
number of lines (n+1)	1	2	3	4
appearance				
relative size of lines		1:1	1:2:1	1:3:3:1

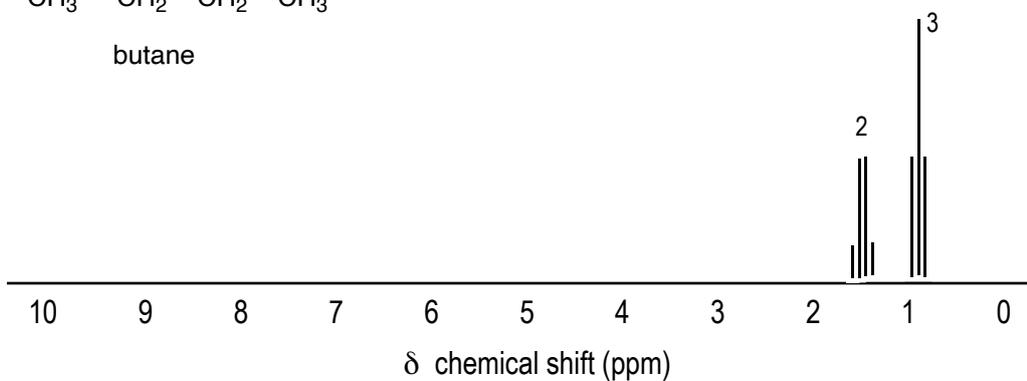
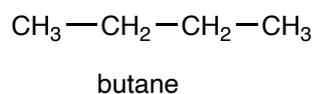
- If there are more than 3 neighbouring inequivalent H atoms, then it can be classed as a multiplet (though exam questions are unlikely to involve these).
- It should be noted that the following H atoms do not couple to each other:
 - equivalent H atoms
(e.g. in $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ – the H atoms in the two CH_2 groups do not couple to each other)
 - H atoms to H atoms of an OH group
(e.g. in $\text{CH}_3\text{CH}_2\text{OH}$ – the H atoms in CH_2 do not couple with the H in OH)
 - H atoms to H atoms of an NH_2 group
(e.g. in $\text{CH}_3\text{CH}_2\text{NH}_2$ – the H atoms in CH_2 do not couple with the H atoms in NH_2)

Example 1



	assignment	relative intensity	splitting pattern	coupled to
1.0	CH ₃ CH ₂	3	triplet	CH ₂
2.0	CH ₃ CO	3	singlet	
2.4	CH ₂	2	quartet	CH ₃

Example 2



	assignment	relative intensity	splitting pattern	coupled to
1.3	CH ₂	2	quartet	CH ₃
0.8	CH ₃	3	triplet	CH ₂

Note:

The two CH₂ groups do not couple to each other as they are equivalent. Therefore each CH₂ group only couples to one CH₃

- There are a number of ways in which information about the relative intensity of the signals can be given. Often a series of values is given and you will need to convert it to the simplest whole number ratio.

e.g. relative intensity = 1.2 : 1.2 : 1.8 = 2 : 2 : 3

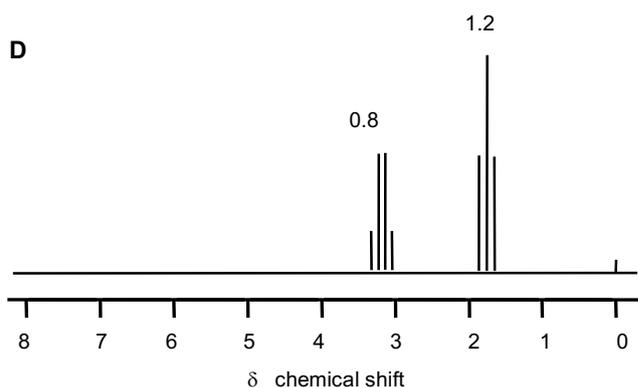
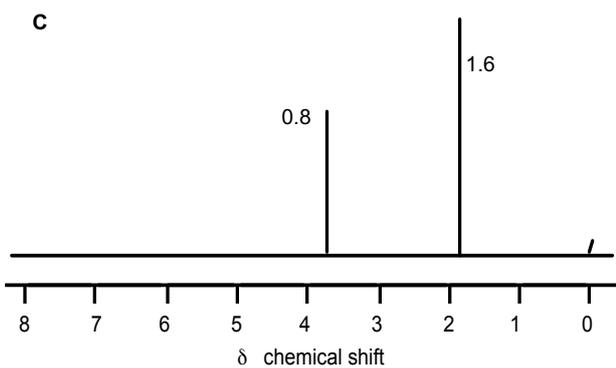
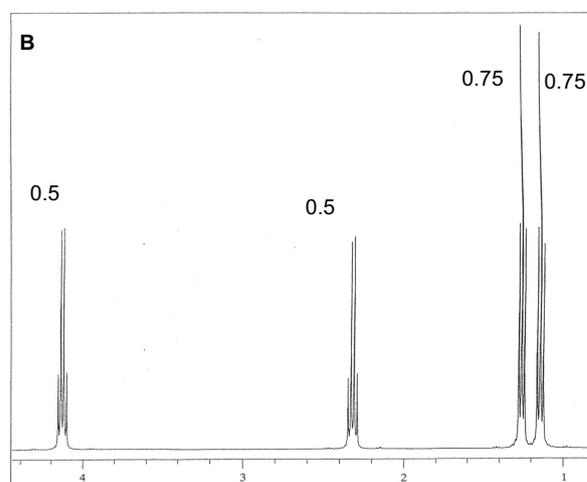
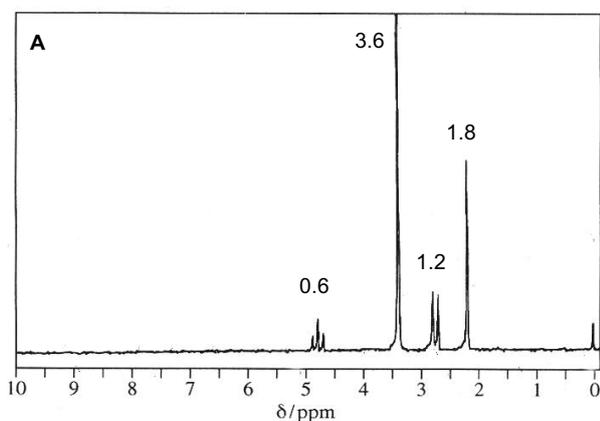
relative intensity = 2.1 : 2.8 = 3 : 4

relative intensity = 1.5 : 0.5 : 2.0 = 3 : 1 : 4

relative intensity = 0.3 : 0.15 : 0.3 : 0.6 = 2 : 1 : 2 : 4

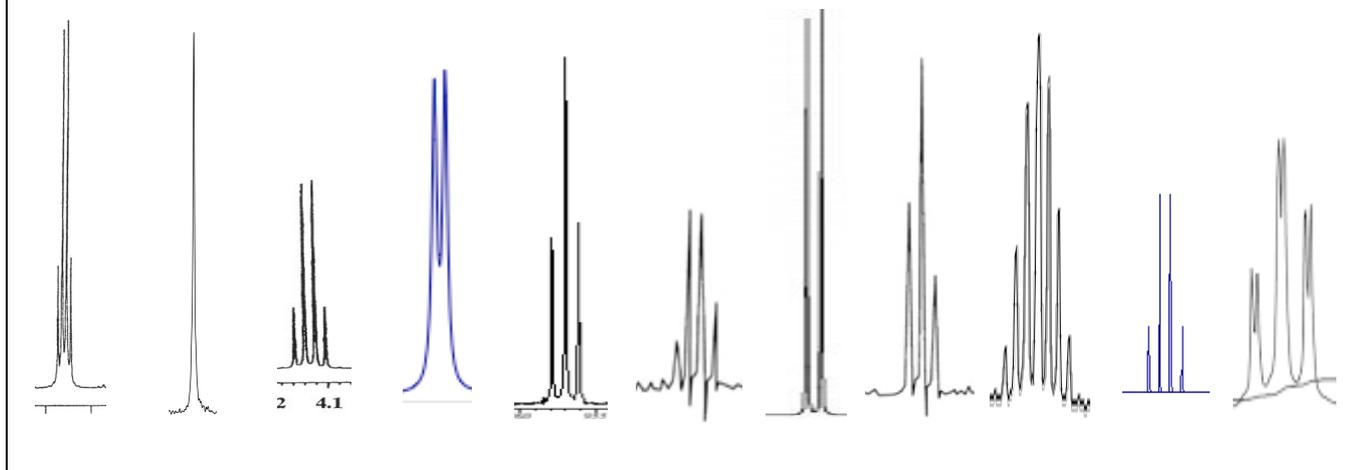
TASK 4 – Finding the relative intensity of signals from a spectrum

For each of the NMR spectra below, calculate the relative number of H atoms associated with each signal.



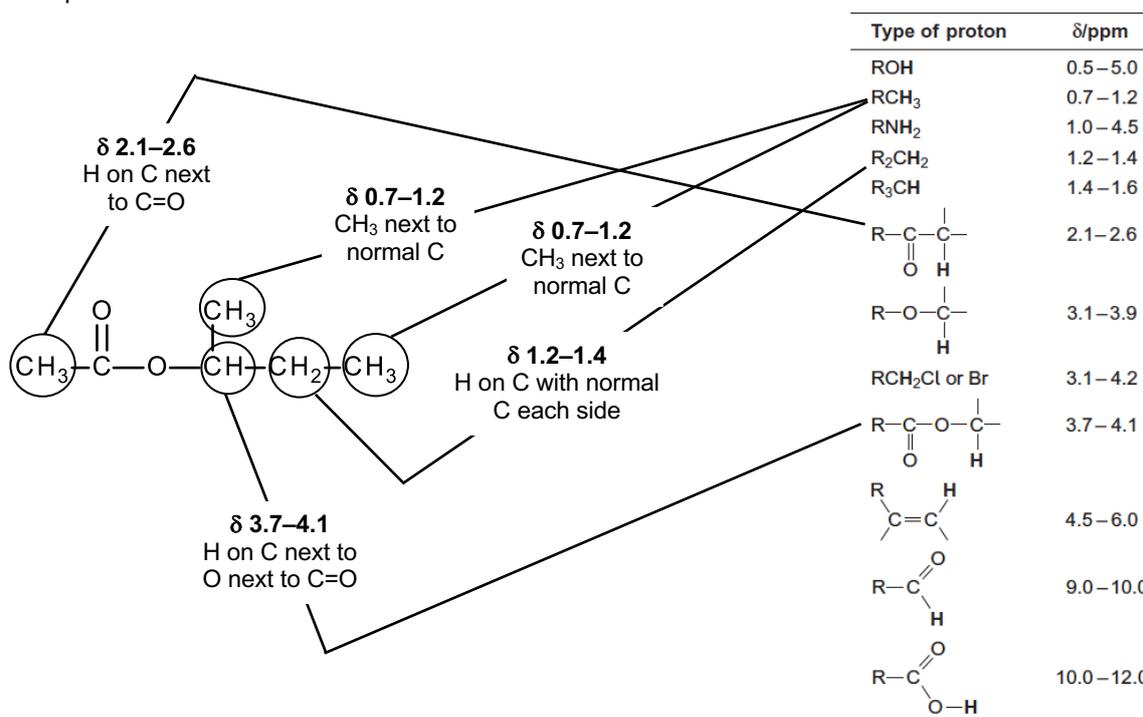
TASK 5 – Identifying splitting patterns

Look at each of the following signals and decide whether it is a singlet (s), doublet (d), triplet (t), quartet (q) or multiplet (m).

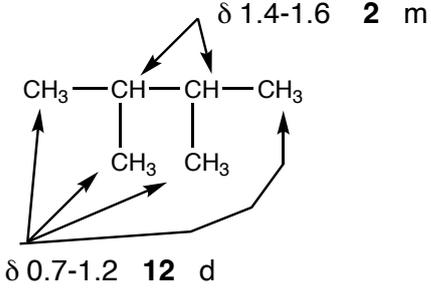


The position of signals

- The chemical shift (δ) of each signal gives us information about the chemical environment of the ^1H atoms in the molecule.
- The closer the ^1H atoms are to very electronegative atoms (e.g. O, Cl) and/or double bonds, the greater the chemical shift.
- Table of data can give us guidance as to what the chemical shift will be. Often, the exact environment of the H atom will not be in the data table, but we should look for the closest match.
- An example is shown below:



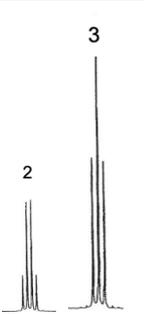
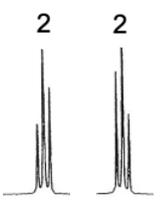
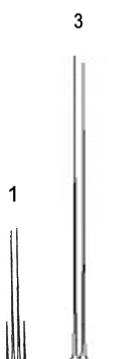
TASK 6 – Predicting ¹H NMR spectra

Compound	Structure, δ , relative intensity & splitting	Number of signals
2,3-dimethylbutane	 <p style="text-align: center;">δ 1.4-1.6 2 m</p> <p style="text-align: center;">CH₃—CH—CH—CH₃ CH₃ CH₃</p> <p style="text-align: center;">δ 0.7-1.2 12 d</p>	2
3,4-dimethylheptane		
cyclohexane		
methylcyclohexane		
2-bromo-3-chlorobutane		

Compound	Structure, δ , relative intensity & splitting	Number of signals
pentan-3-one		
2-methylpropan-2-ol		
propanoic acid		
methyl propanoate		
methylpropanal		

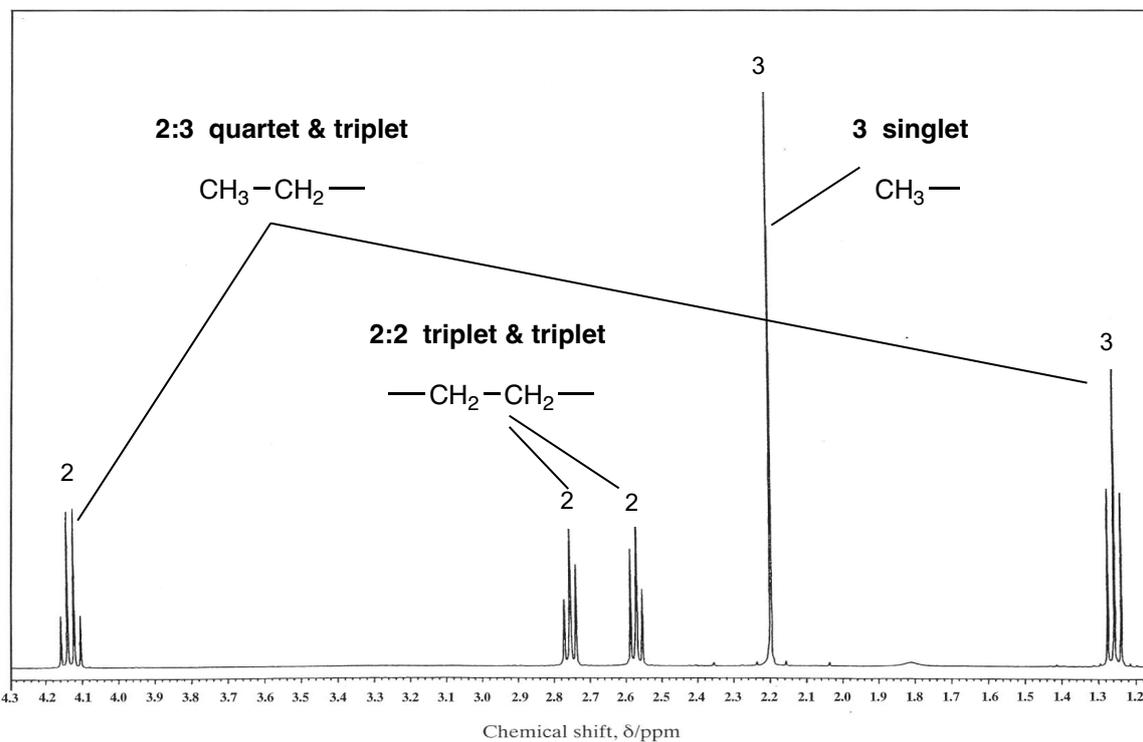
Deducing the structure of a compound from its ¹H NMR spectrum

- The structure of an organic compound can often be deduced from the ¹H (and ¹³C) NMR spectrum. One way to approach this is to
 - look at each signal to work out what group it represents in a molecule (gathering the pieces of a jigsaw)
 - look for the ends of the molecule (like finding the corner pieces of a jigsaw)
 - and then work out where the non-end groups fit in (finishing off the jigsaw)
- The table shows some common "jigsaw pieces":

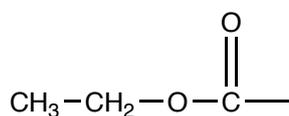
	quartet & triplet 2 : 3	CH ₃ —CH ₂ —	<ul style="list-style-type: none"> The triplet and quartet do not have to be next to each other in the spectrum. The atom joined to the other side of the CH₂ cannot have any H's on (unless they do not couple, e.g. OH group or an equivalent CH₂ as in butane).
	triplet & triplet 2 : 2	—CH ₂ —CH ₂ —	<ul style="list-style-type: none"> The two triplets do not have to be next to each other in the spectrum. The two CH₂ groups must be inequivalent (otherwise they would produce one signal not two!). The atoms joined either side of the CH₂ groups cannot have any H's on them.
	singlet 3	CH ₃ —	<ul style="list-style-type: none"> The atom joined to the CH₃ cannot have any H's on it.
	singlet 6	$\begin{array}{c} \text{CH}_3 \\ \\ \text{—C—} \\ \\ \text{CH}_3 \end{array}$	<ul style="list-style-type: none"> The atom joined to the CH₃ cannot have any H's on it.
	singlet 9	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—C—} \\ \\ \text{CH}_3 \end{array}$	<ul style="list-style-type: none"> The atom joined to the CH₃ cannot have any H's on it.
	singlet 1	—OH	<ul style="list-style-type: none"> A singlet for one H is usually an OH on either an alcohol or a carboxylic acid. This H does not usually couple to other H atoms.
	quartet & doublet 1 : 3	$\begin{array}{c} \\ \text{CH}_3\text{—CH—} \end{array}$	<ul style="list-style-type: none"> The doublet and quartet do not have to be next to each other in the spectrum. The atoms joined to the other side of the CH cannot have any H's on (unless they do not couple, e.g. OH group or an equivalent CH).

Example

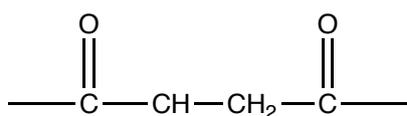
The ^1H NMR spectrum of a compound with molecular formula $\text{C}_7\text{H}_{12}\text{O}_3$ is shown. Deduce the structure of the compound.



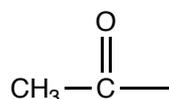
Jigsaw pieces:



- 2:3 quartet-triplet
- indicates CH_3CH_2
- δ 4.1 suggests the CH_2 is next to O-CO-
- **this MUST be an end group**

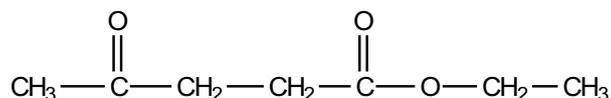


- 2:2 triplet-triplet
- indicates CH_2CH_2
- δ 2.5-2.8 suggest the CH_2 groups are both next to CO groups



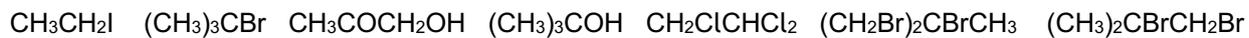
- 3 singlet
- Indicates CH_3
- δ 2.2 suggest the CH_3 group is next to CO groups
- **this MUST be an end group**

Structure of compound:



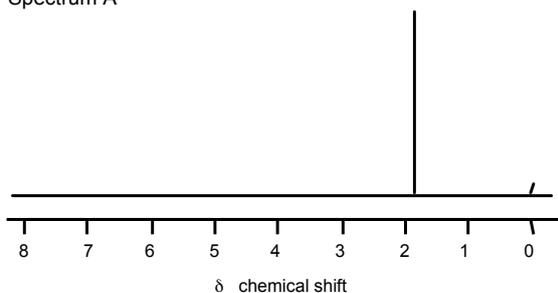
TASK 7 – Which ^1H NMR spectrum is which?

For each of the following compounds:

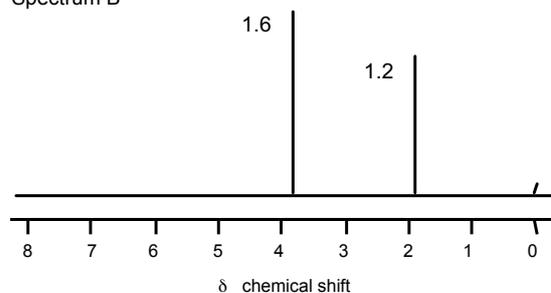


Work out which spectrum belongs to which compound.

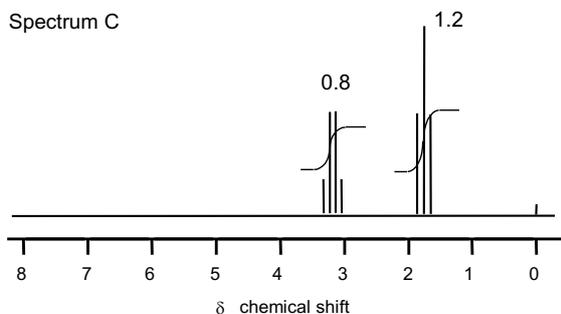
Spectrum A



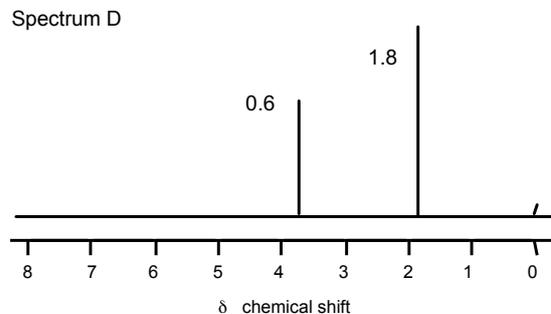
Spectrum B



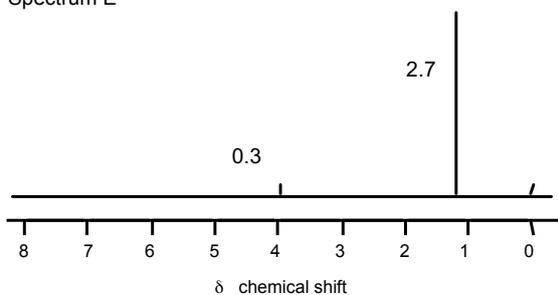
Spectrum C



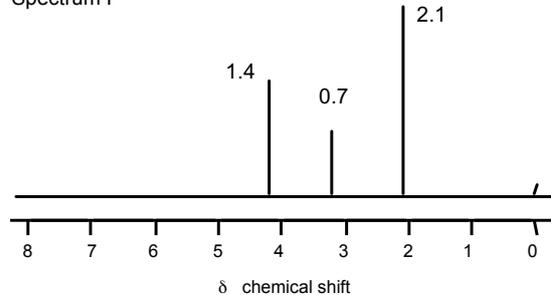
Spectrum D



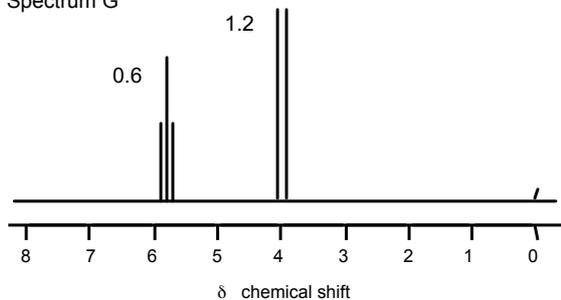
Spectrum E



Spectrum F



Spectrum G

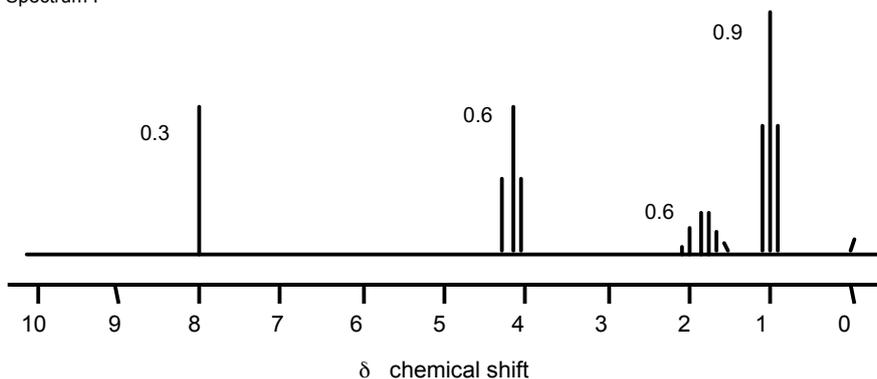


TASK 8 – Identifying compounds

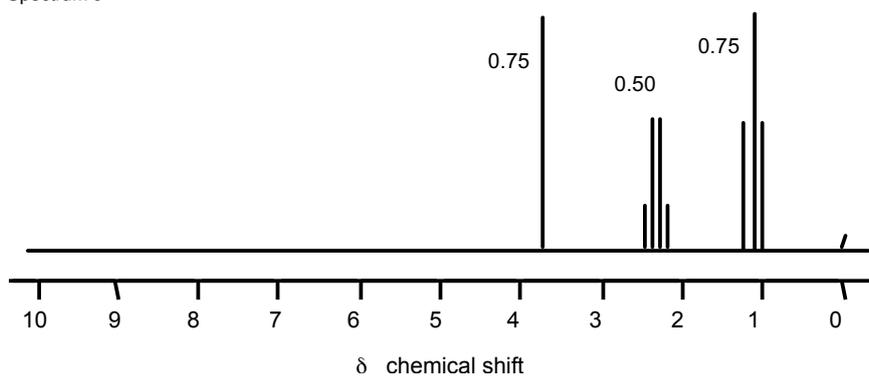
The ^1H NMR spectra of three isomers of $\text{C}_4\text{H}_8\text{O}_2$ are shown.

- Draw the structural formulae of all the isomers of $\text{C}_4\text{H}_8\text{O}_2$ that are carboxylic acids or esters.
- Indicate the number of signals, and relative intensity and multiplicity of each signal for each isomer.
- Deduce which spectrum belongs to which isomer.

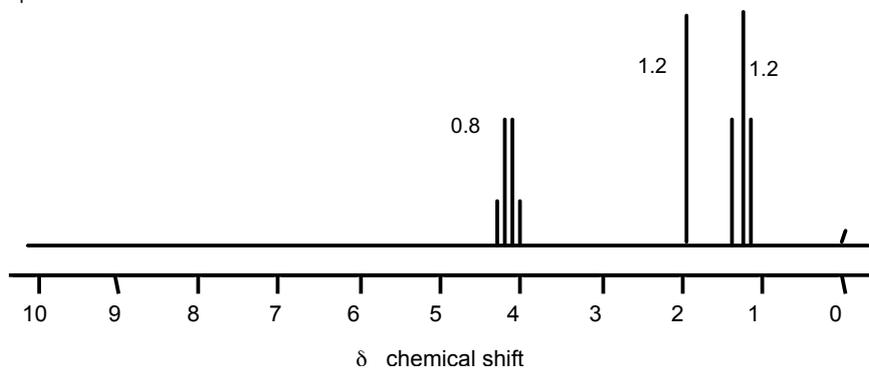
Spectrum I



Spectrum J

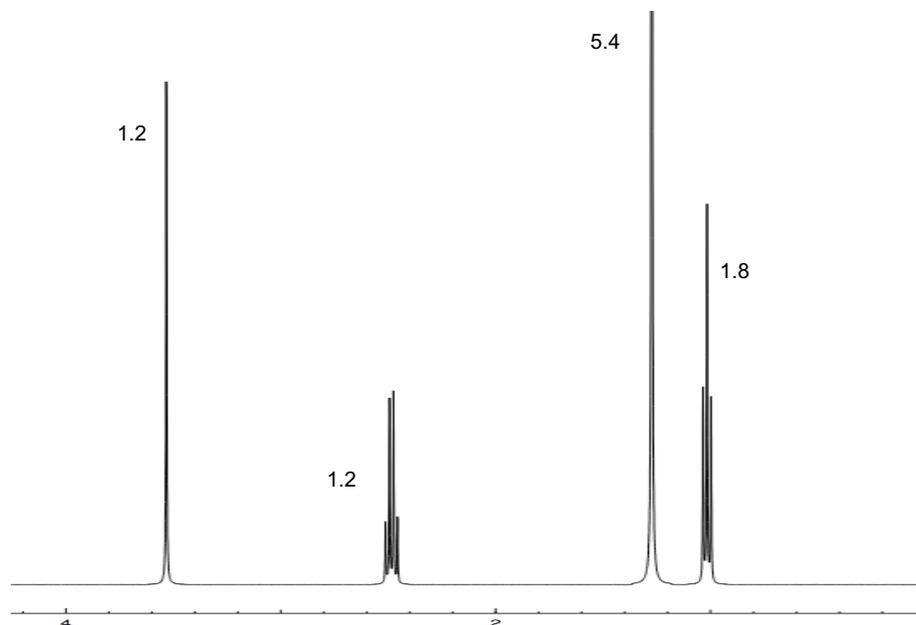


Spectrum K

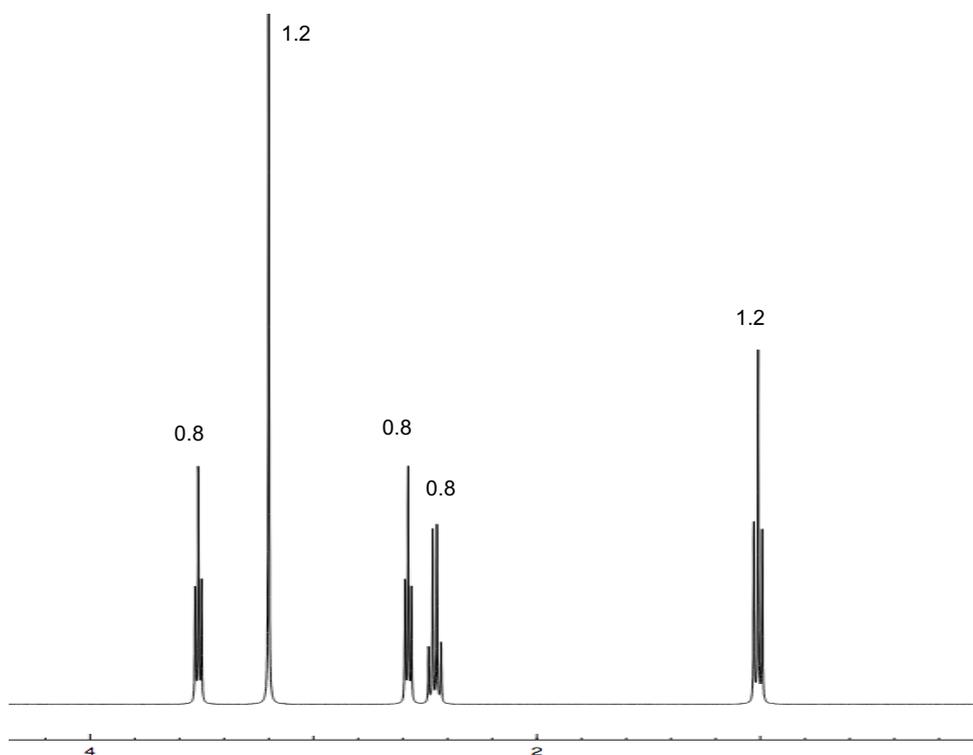


TASK 9 – Identifying compounds using ^1H NMR

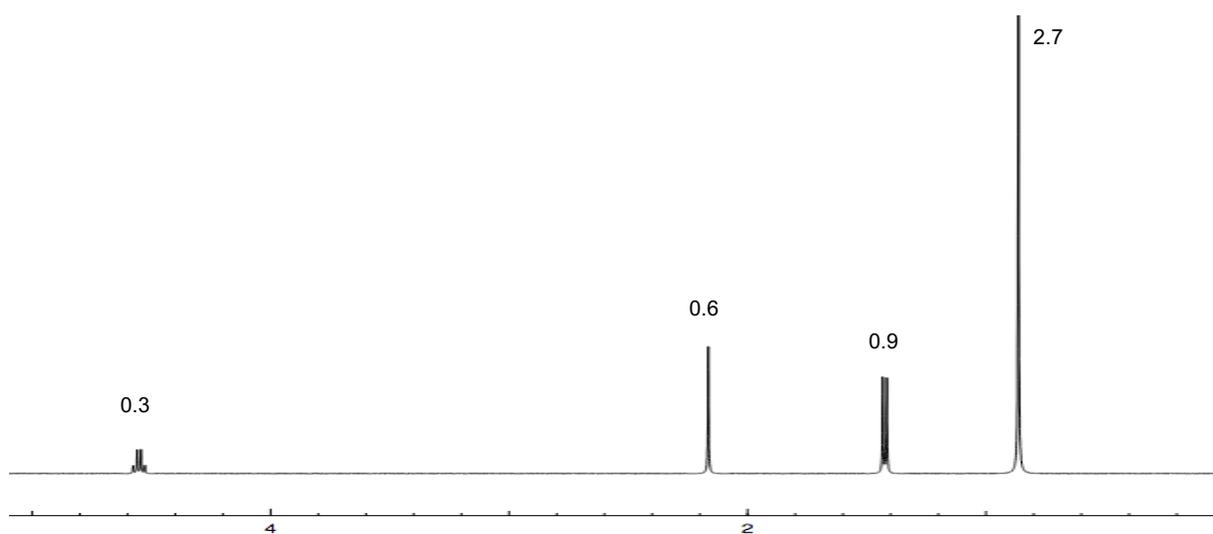
- 1 The ^1H NMR spectrum of $\text{C}_9\text{H}_{16}\text{O}_2$ is shown. The compound has a large peak at 1705 cm^{-1} in its IR spectrum. It does not react with sodium hydrogencarbonate or Tollen's reagent. Deduce the structure of the compound.



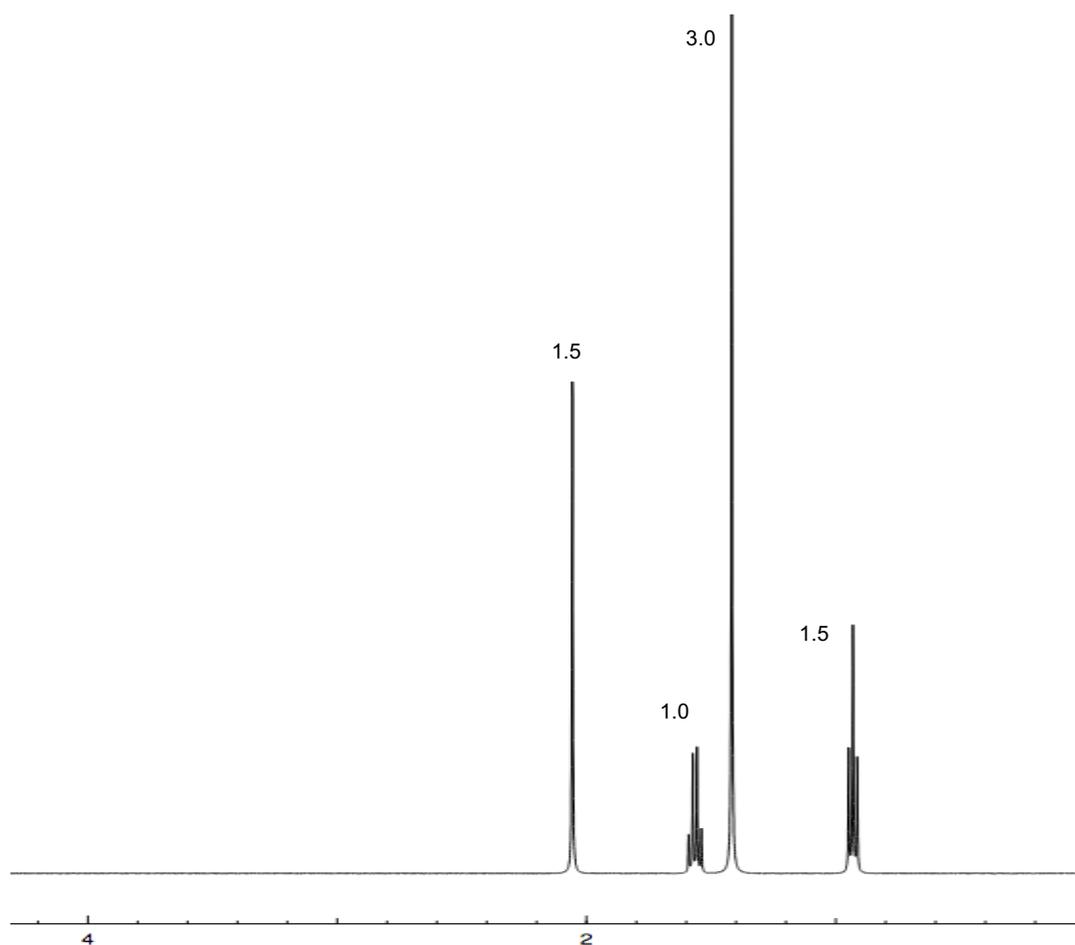
- 2 The ^1H NMR spectrum of $\text{C}_6\text{H}_{12}\text{O}_2$ is shown. Deduce the structure of the compound.



3 The ^1H NMR spectrum of $\text{C}_8\text{H}_{15}\text{OCl}$ is shown. Deduce the structure of the compound.

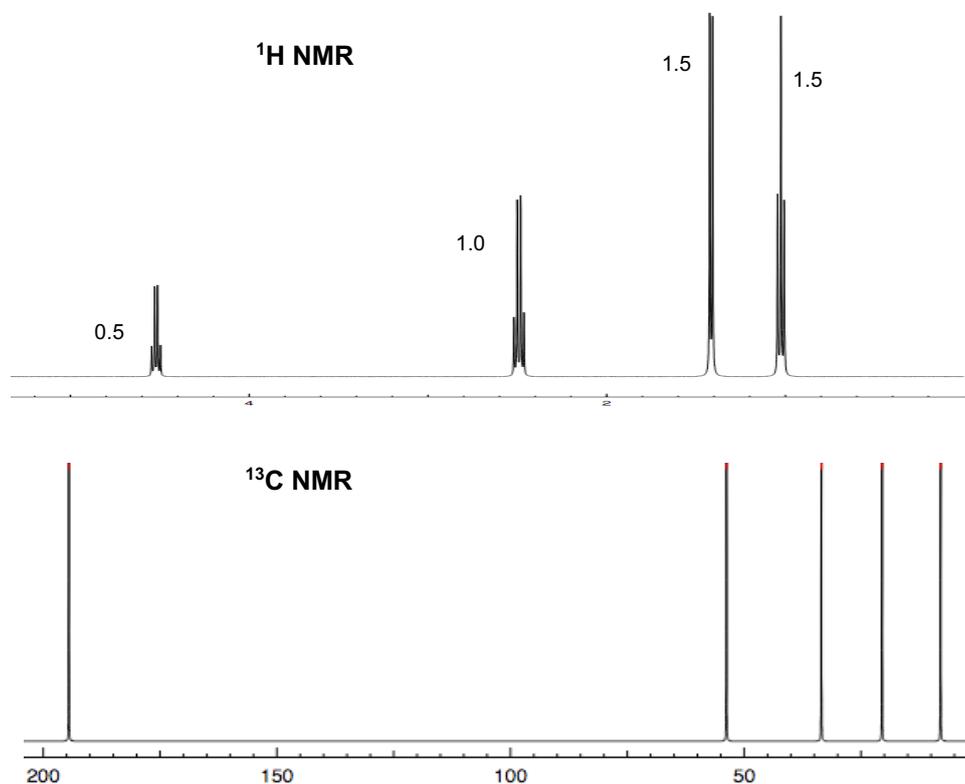


4 The ^1H NMR spectrum of $\text{C}_7\text{H}_{14}\text{O}_2$ is shown which is an ester. Deduce the structure of the compound.

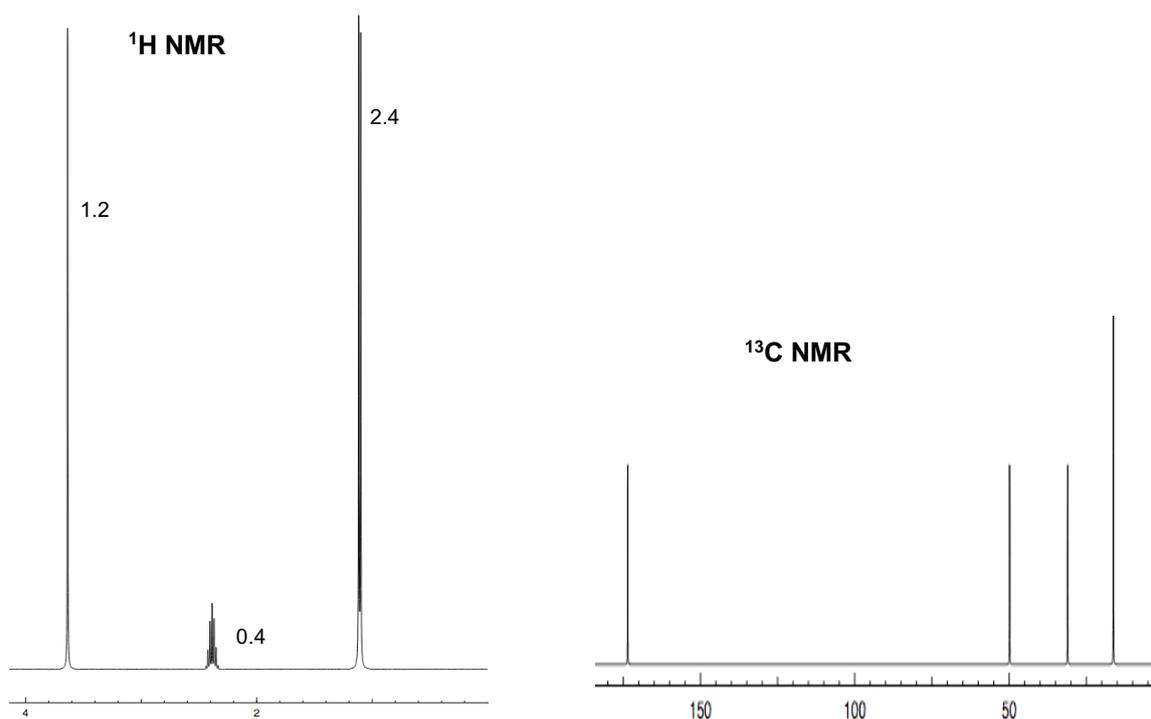


TASK 10 – Using ^1H and ^{13}C NMR together to identify compounds

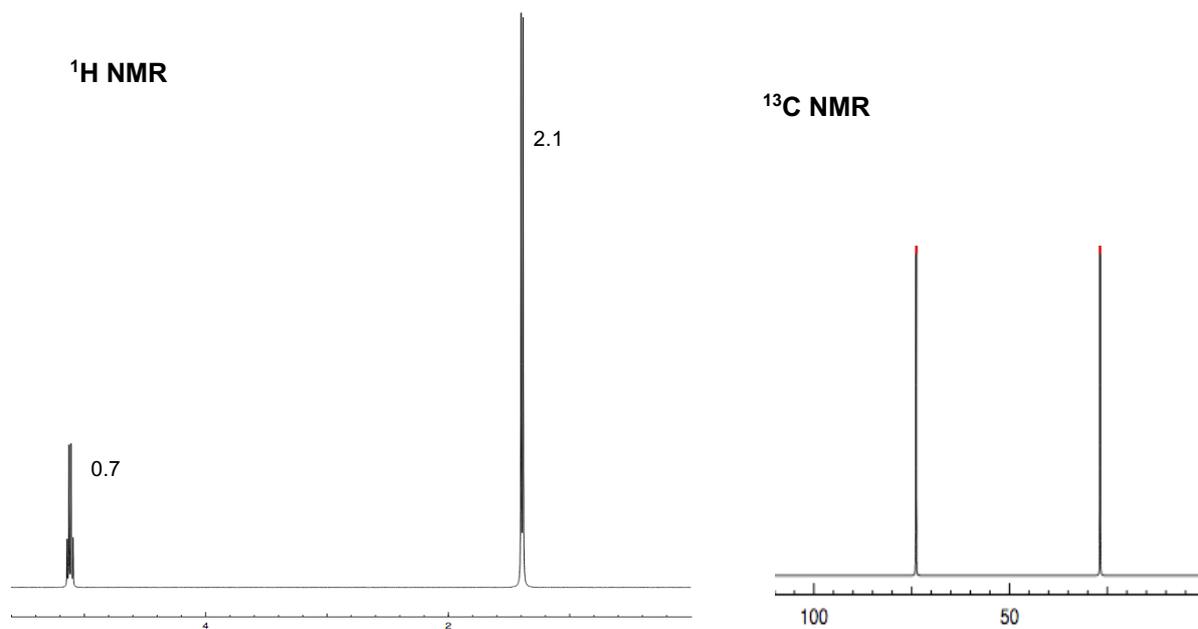
- 1 The ^1H and ^{13}C NMR spectra of $\text{C}_5\text{H}_9\text{OCl}$ are shown. Deduce the structure of the compound and then identify which signal represents which atom(s).



- 2 The ^1H and ^{13}C NMR spectra of $\text{C}_5\text{H}_{10}\text{O}_2$ are shown. Deduce the structure of the compound and then identify which signal represents which atom(s).



- 3** The ^1H and ^{13}C NMR spectra of $\text{C}_4\text{H}_8\text{OBr}_2$ are shown. Deduce the structure of the compound and then identify which signal represents which atom(s).



- 4** The ^1H and ^{13}C NMR spectra of $\text{C}_6\text{H}_{10}\text{O}_3$ are shown. Deduce the structure of the compound and then identify which signal represents which atom(s).

