

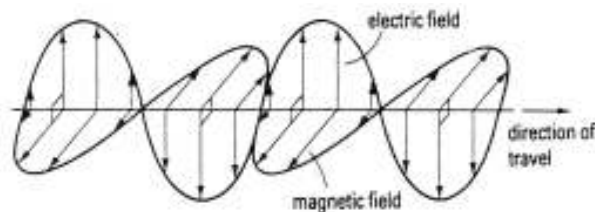


# SPECTROSCOPY

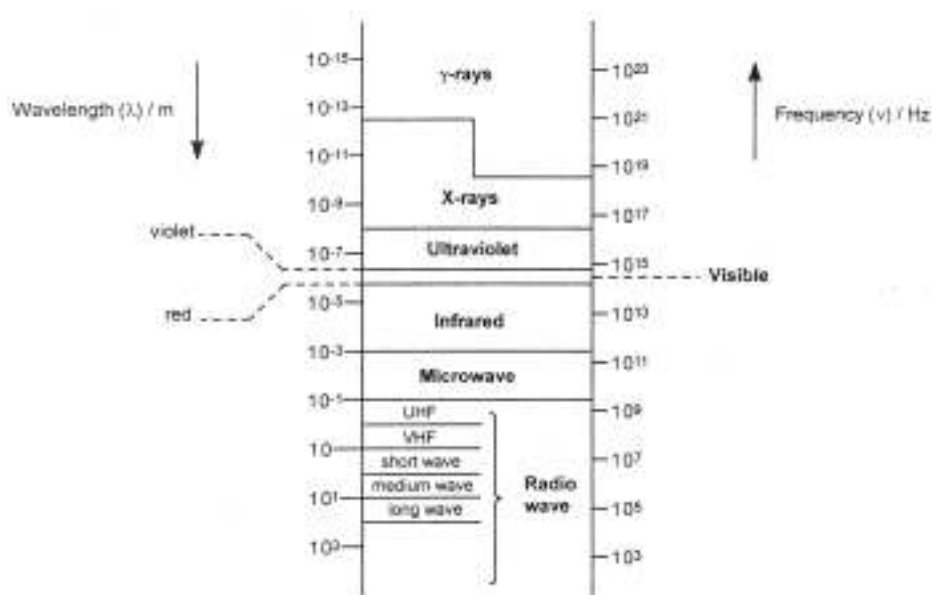


# 1) THE ELECTROMAGNETIC SPECTRUM

- Visible light is the form of light which we can see. It is a form of energy made up of waves known as electromagnetic radiation. What we perceive as light is actually only a very small part of the electromagnetic spectrum.
- Electromagnetic waves consist of electric and magnetic fields which are perpendicular to each other and to the direction of travel of the wave. The electric and magnetic fields vibrate at the same frequency as each other.



- Different electromagnetic waves vibrate at different frequencies. These are shown in the diagram below.



- Atoms, molecules and ions can absorb (or emit) electromagnetic radiation of specific frequencies, and this can be used to identify them. Some examples of the types of electromagnetic radiation absorbed are shown below.

Electromagnetic radiation absorbed	What the energy is used for	Spectroscopy technique
Ultra-violet / visible	Movement of electrons to higher energy levels	Ultra-violet / visible spectroscopy
Infra-red	To vibrate bonds	Infra-red spectroscopy
Microwaves	To rotate molecules	Microwave spectroscopy
Radio waves	To change nuclear spin	NMR spectroscopy

## 2) INFRA-RED (IR) SPECTROSCOPY

- All bonds vibrate at a characteristic frequency (stretching and contracting as well as bending vibrations are the commonest types).



- The frequency depends on the mass of the atoms in the bond, the bond strength, and the type of vibration.
- The frequencies at which they vibrate are in the infra-red region of the electromagnetic spectrum.
- If infra-red light is passed through the compound, it will absorb some or all of the light at the frequencies at which its bonds vibrate.
- Rather than using the actual values of the wavelength or frequency, the IR light is measured in wavenumbers [1/frequency (in cm)] because it gives convenient numbers in the range 4000 – 400  $\text{cm}^{-1}$ .
- There are two main things you need to be able to do with infra-red spectra:
  - 1) know how the "fingerprint" region (below 1500  $\text{cm}^{-1}$ ) can be used to identify compounds
  - 2) be able to identify functional group signals using the region above 1500  $\text{cm}^{-1}$

### 1) Using the "finger-print" region (below 1500 $\text{cm}^{-1}$ )

- This part of the spectrum is more complicated and contains many signals, making picking out functional group signals difficult.
- However, this part of the spectrum is unique for every compound, and so can be used as a "fingerprint". An unknown compound can be identified by an **exact match** of the fingerprint region to that of a known compound.
- This region can also be used to check if a compound is pure. If a comparison of the spectrum of a sample is made to the spectrum of the pure compound, they should be identical. If there are any extra peaks, they must be due to an impurity.

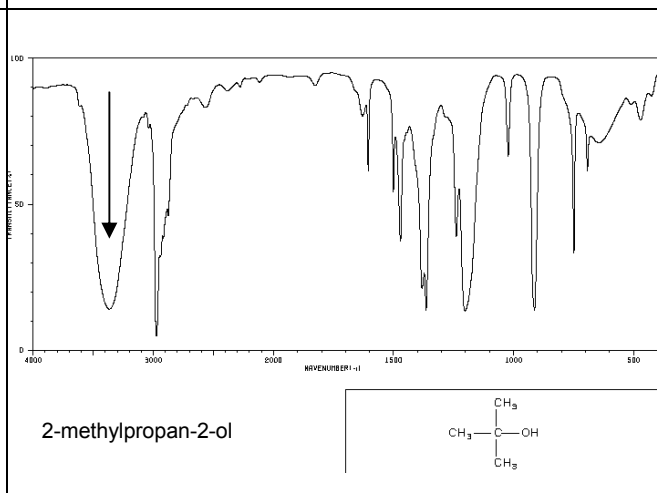
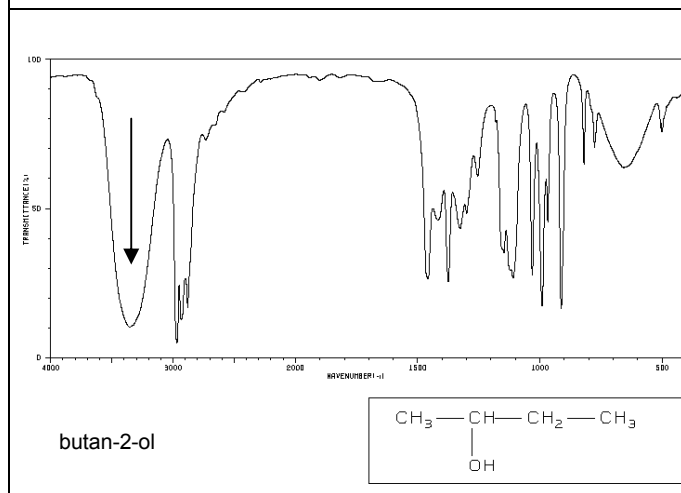
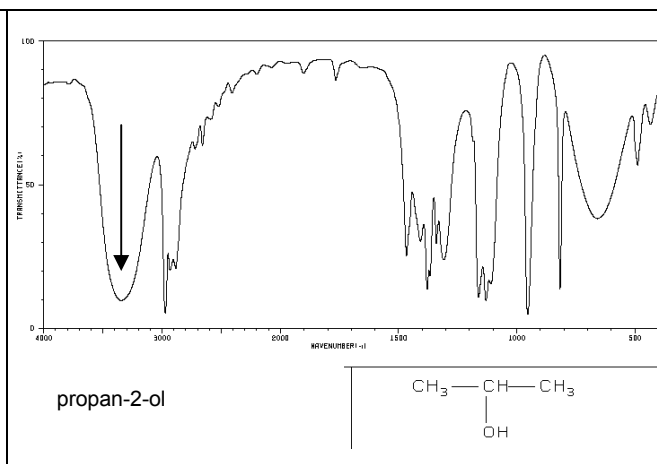
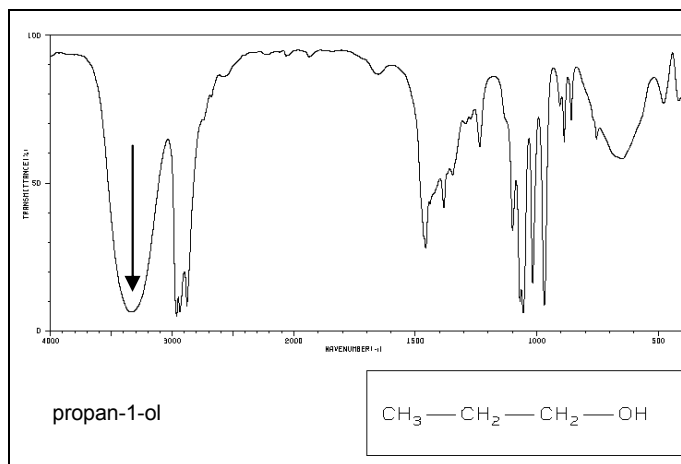
### 2) Identifying functional group signals (above 1500 $\text{cm}^{-1}$ )

- This part of the spectrum is used to spot characteristic signals for functional groups (there are some below 1500  $\text{cm}^{-1}$  but they are usually difficult to identify due to the high number of signals in that region of the spectrum).
- See the data sheet for the frequency of vibration of common bonds (there is a copy on page 3 of this booklet).
- The most important signals (for A level purposes) are: O-H (alcohol), O-H (carboxylic acid), C=O and C=C.

## SERIOUSLY IMPORTANT SIGNALS!

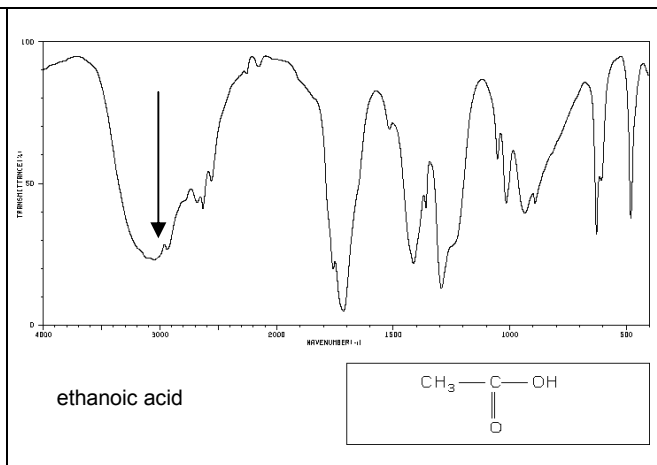
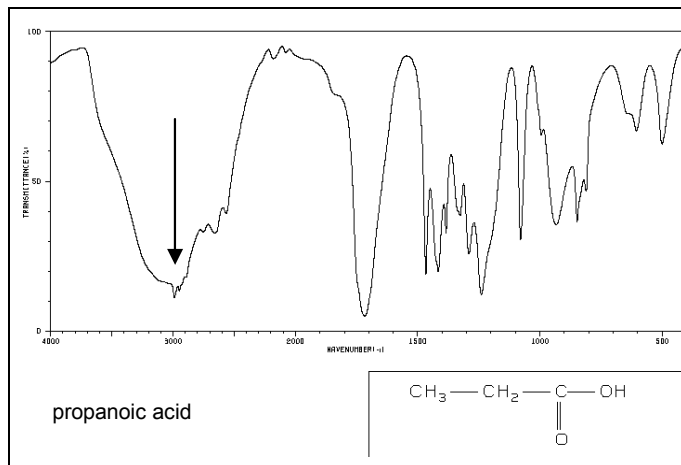
**O-H (alcohol)** - major broad signal  $\sim 3350\text{ cm}^{-1}$

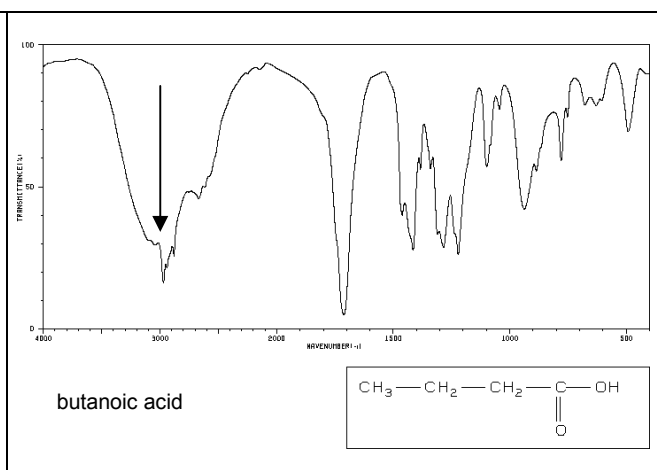
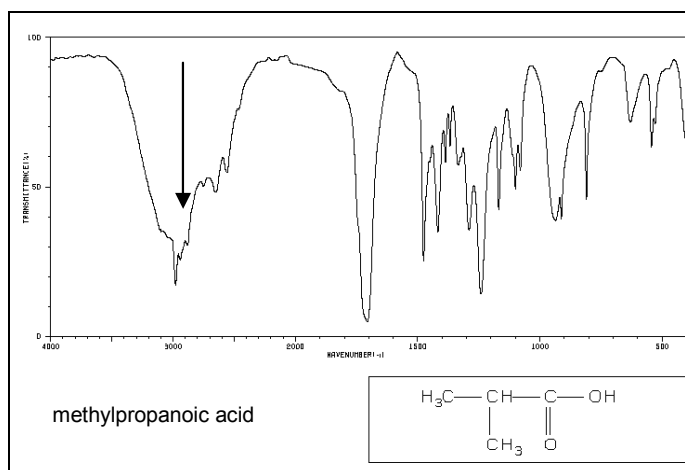
These are centred around  $3350\text{ cm}^{-1}$  (as opposed to carboxylic acids around  $3000\text{ cm}^{-1}$ ) and are very broad.



**O-H (acid)** – major broad signal  $\sim 3000\text{ cm}^{-1}$

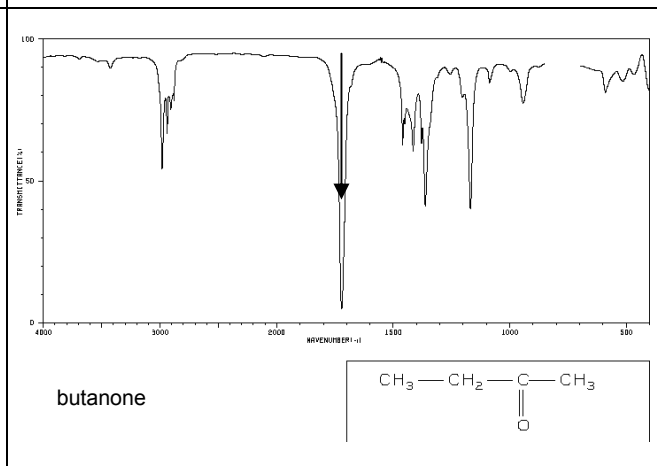
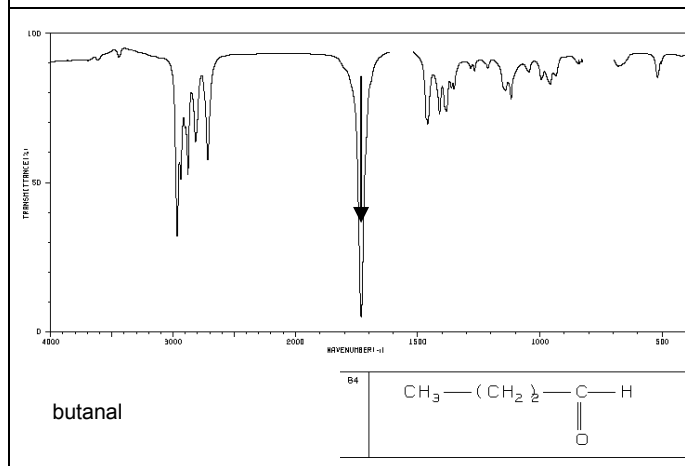
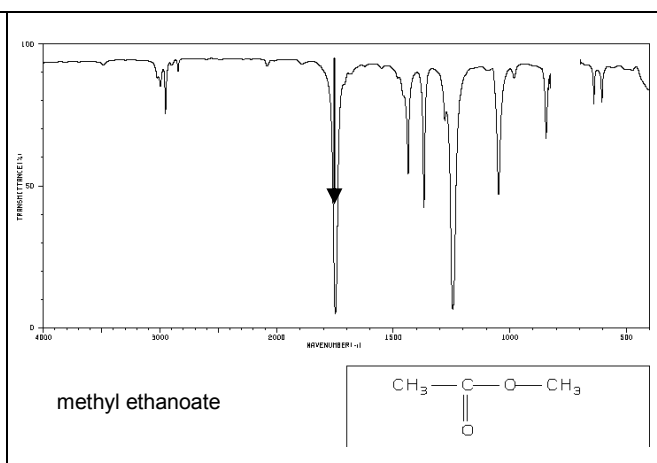
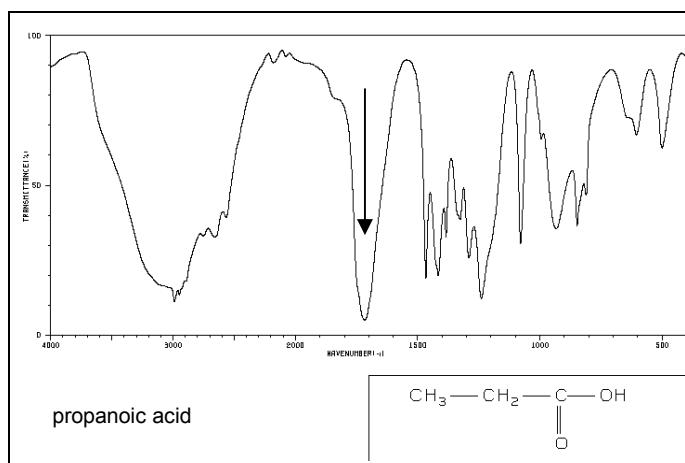
These are centred around  $3000\text{ cm}^{-1}$  (as opposed to alcohols around  $3350\text{ cm}^{-1}$ ) and are very broad. There are signals for C-H bonds in the same area so the signals are not as smooth as alcohol OH signals.





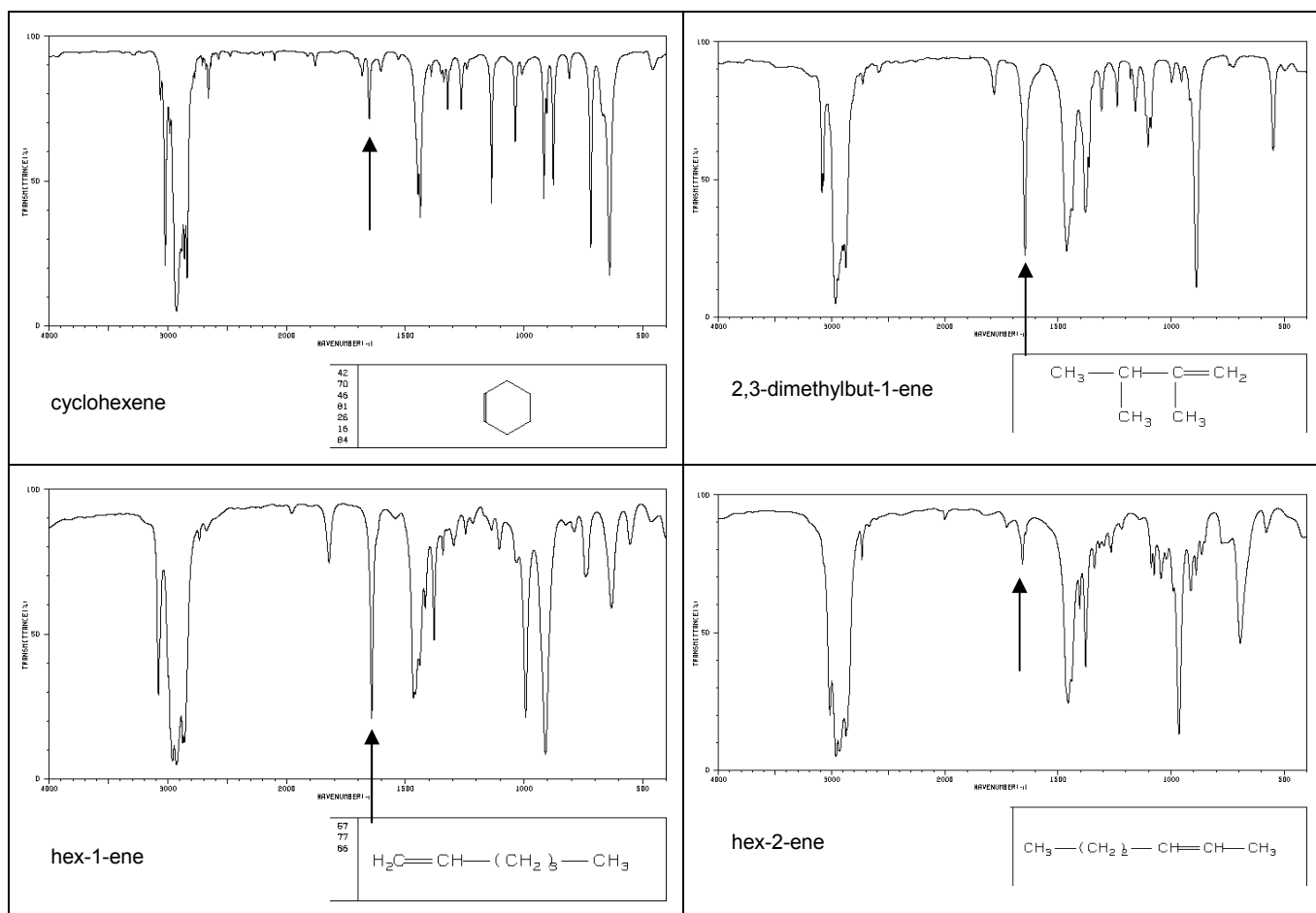
**C=O** - major signal  $\sim 1700 \text{ cm}^{-1}$

This is found in acids, esters, ketones, aldehydes, acyl chlorides and acid anhydrides.



**C=C** - signal  $\sim 1650\text{ cm}^{-1}$  (not always that big a signal)

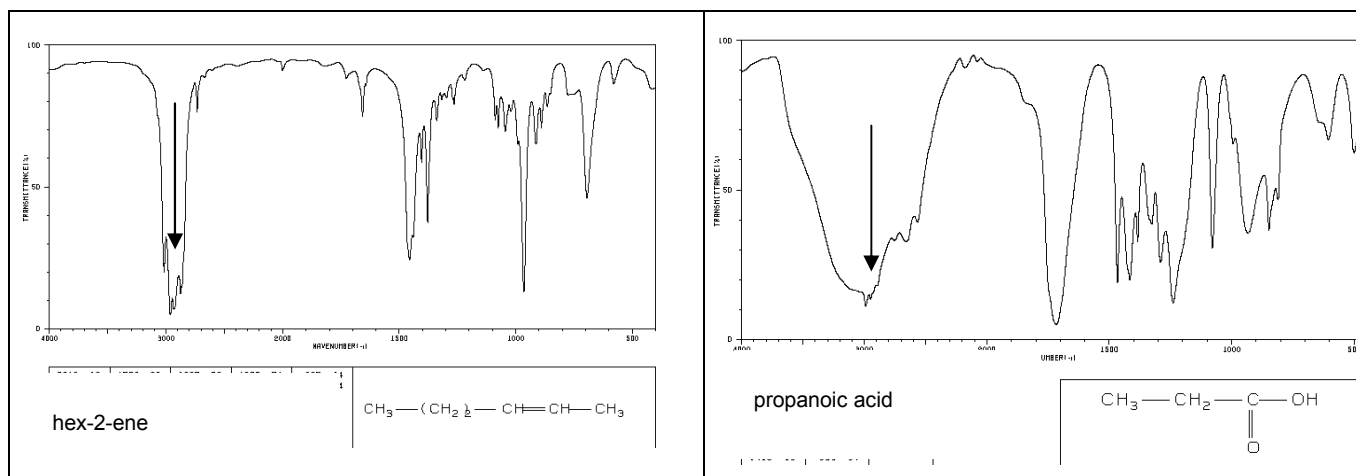
This is found in acids, esters, ketones, aldehydes, acyl chlorides and acid anhydrides.



## OTHER SIGNALS

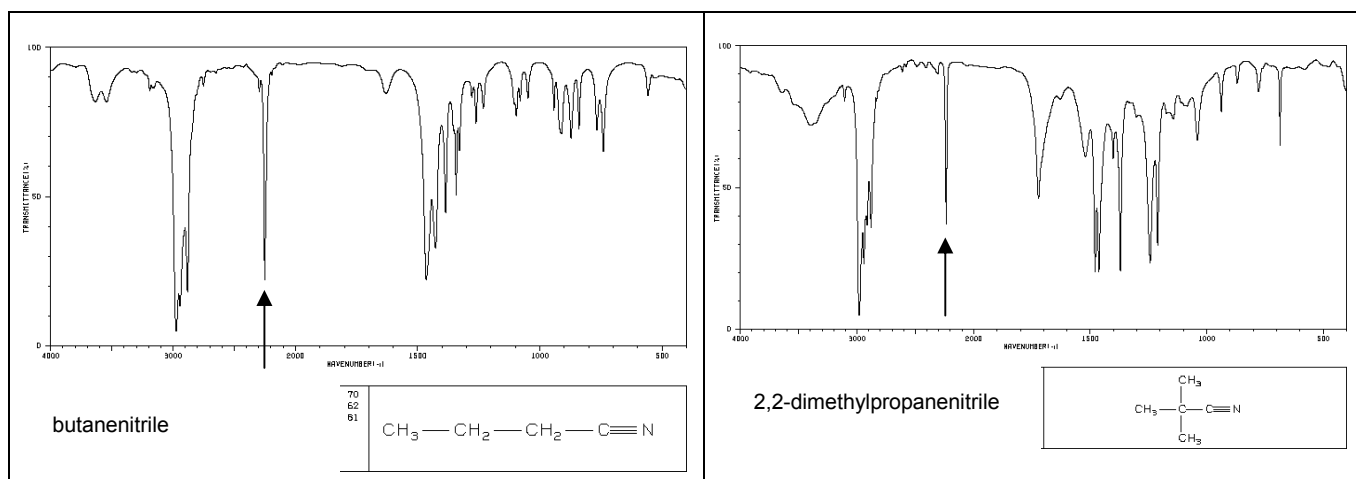
**C-H** - major signals  $\sim 3000\text{ cm}^{-1}$

All organic compounds contain this and at A level you do not need to know about variations in these signals. In other words, just be aware they are there! (and in acids they are in the same place as the acid OH group).



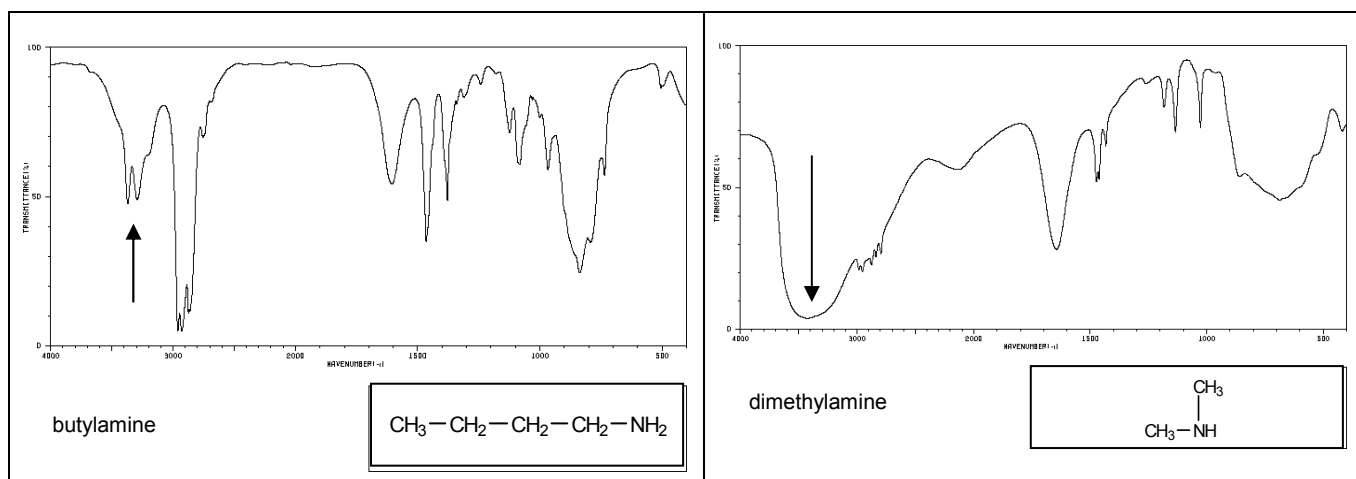
**C≡N** - major signal ~ 2250 cm<sup>-1</sup>

This is a distinctive signal with nothing else appearing in the same region.



**N-H** - major broad signal ~ 3400 cm<sup>-1</sup>

These could be easily confused with alcohol OH being in similar in appearance and position – check to see if the compound contains an N or an O (if it's both – it will be harder for you but unlikely in an A level question!).



# IR TASK 1

The IR spectra of eight compounds are shown. The compounds are:

2,2-dimethylamine

2-methylbut-1-ene

3-methylbutan-1-ol

4-hydroxybutanone

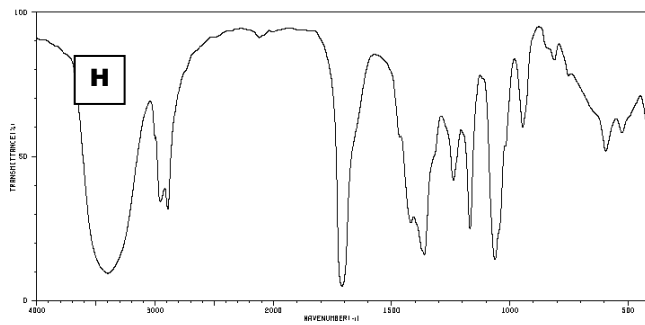
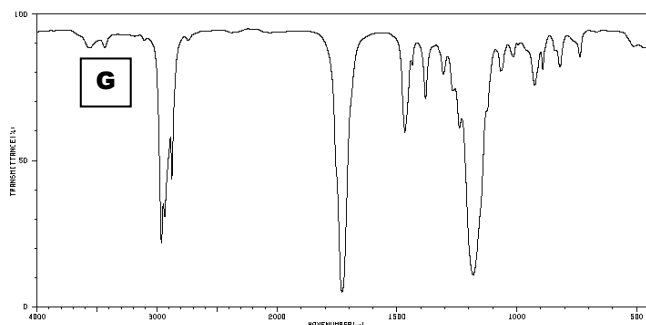
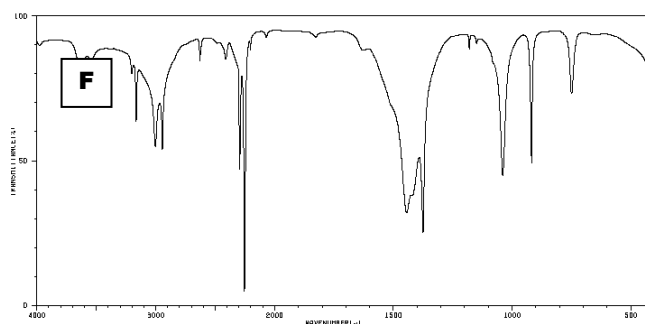
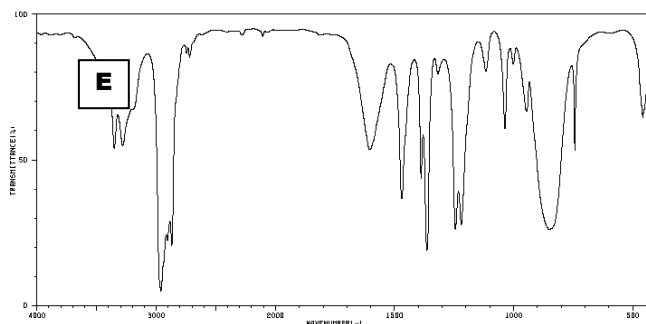
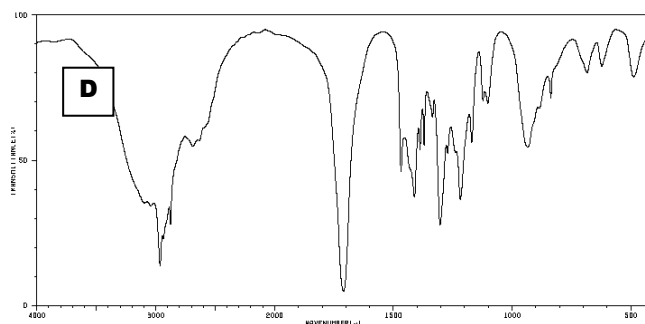
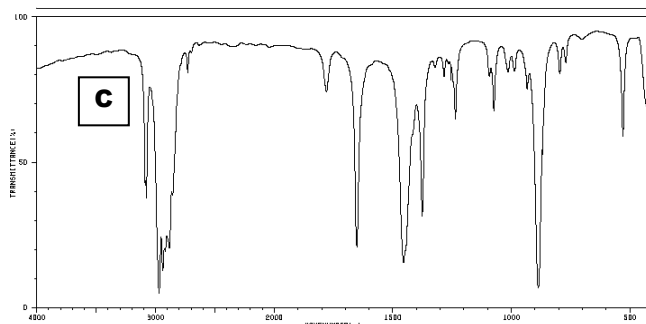
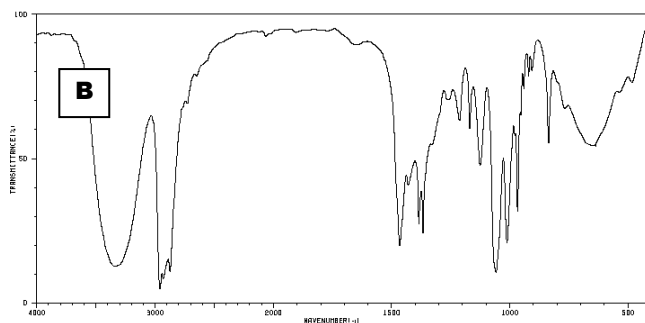
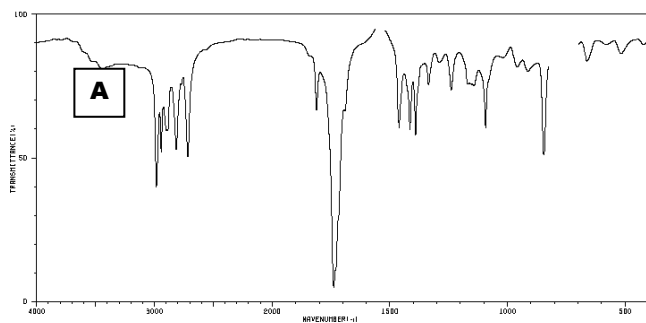
3-methylbutanoic acid

butyl methanoate

ethanenitrile

propanal

Decide which spectrum belongs to which compound and **draw the molecule** next to the spectrum. You may not be able to decide between two of the compounds.





## IR TASK 2

1) The IR spectra of six compounds are shown. The compounds are:

butanoic acid

butanone

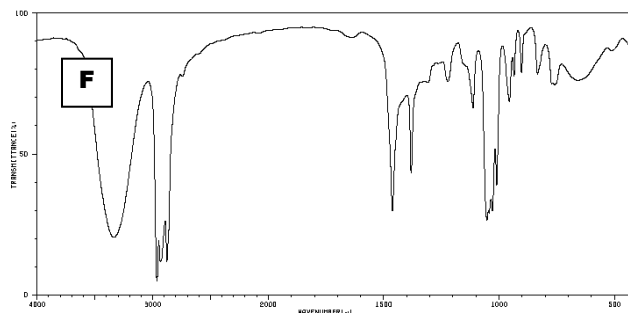
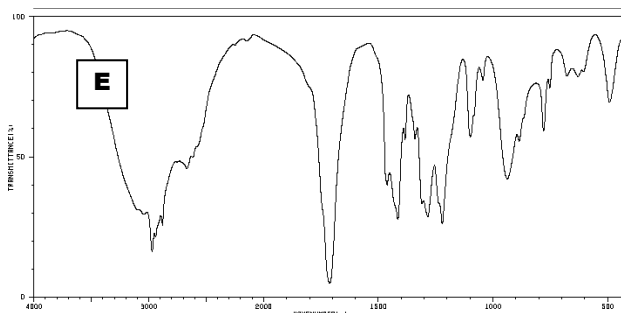
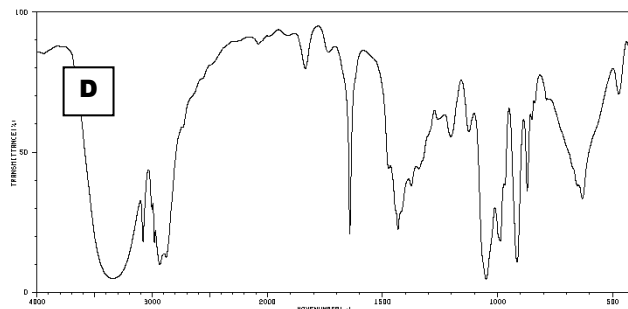
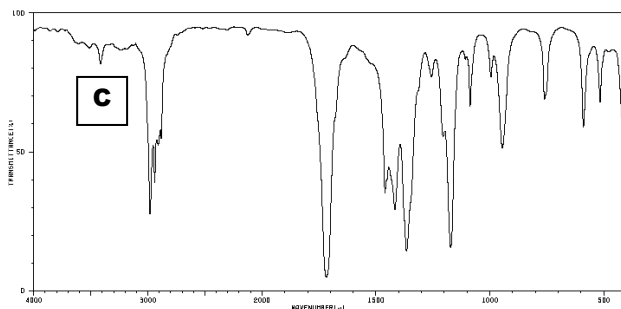
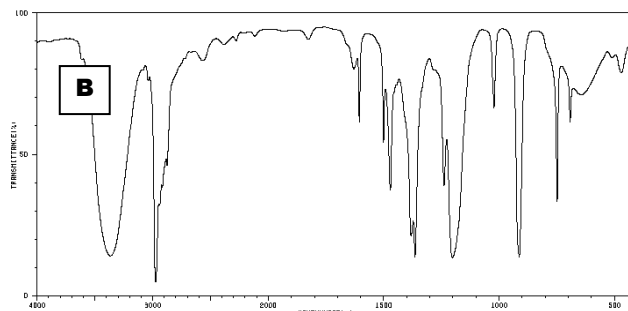
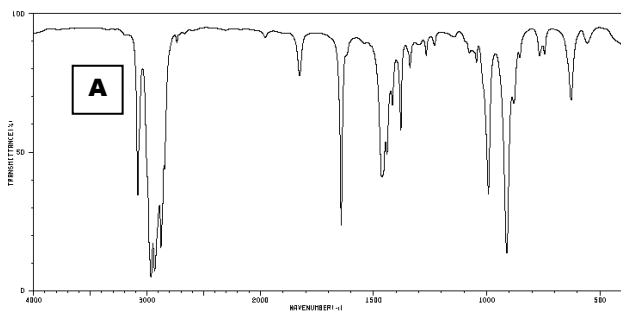
but-3-en-1-ol

2-methylpropan-2-ol

2-ethylbutan-1-ol

pent-1-ene

a) Decide which spectrum belongs to which compound and **draw the molecule** next to the spectrum. You may not be able to decide between two of the compounds.



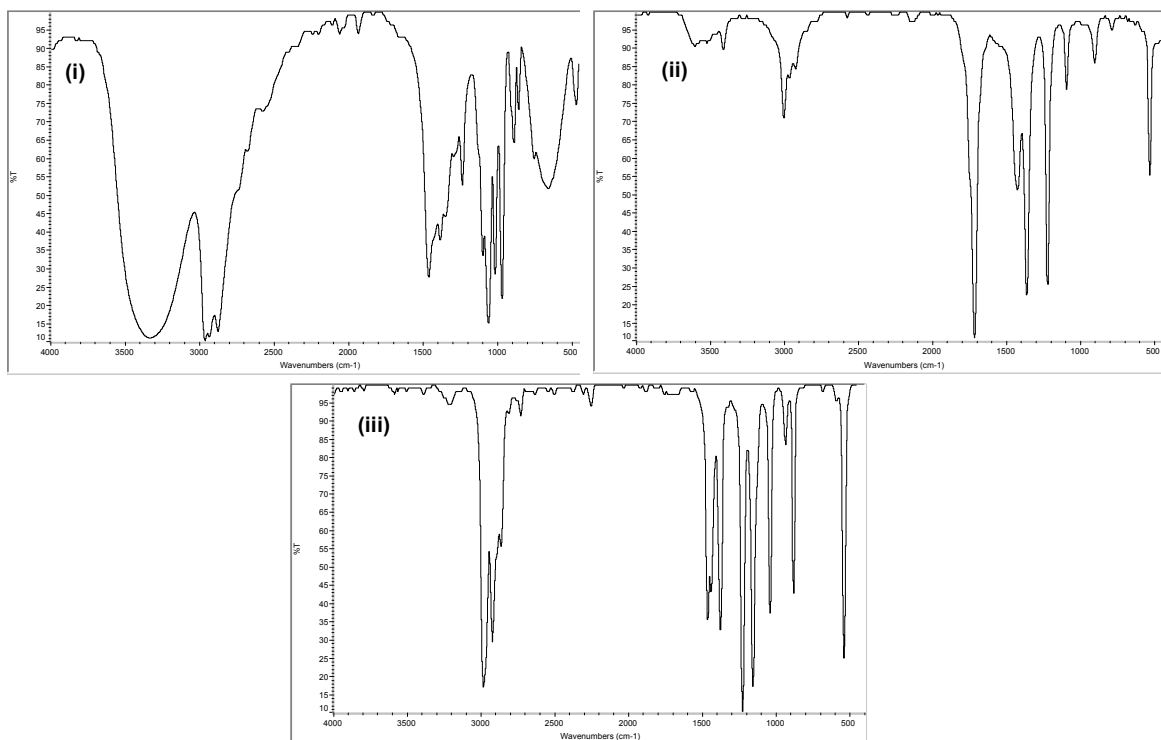
b) For the compounds that cannot be distinguished by use of functional group signals, explain how the infra-red spectra could be used to distinguish the compounds.



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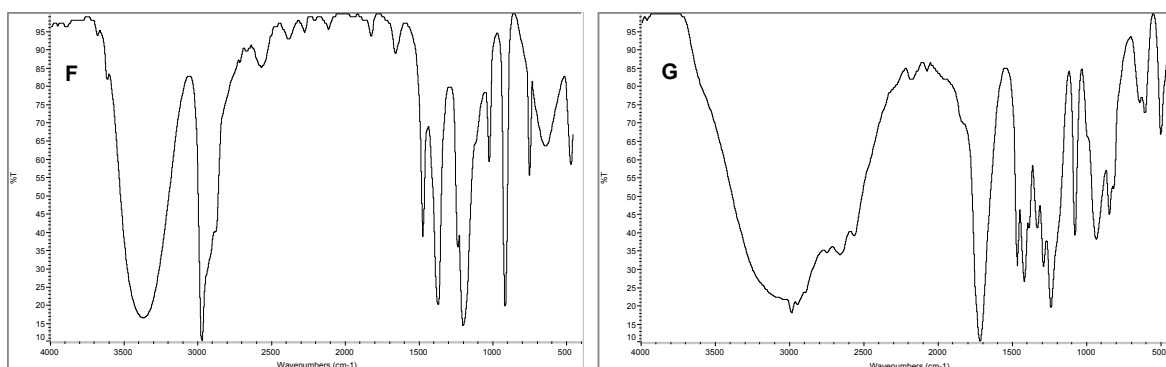
## IR TASK 3

- 1) Propene reacts with HBr to form **H**. **H** reacts with sodium hydroxide to form **I**, and **I** reacts with warm acidified potassium dichromate (VI) to form **J**. The infra-red spectra of **H**, **I** and **J** are given below, but it does indicate which is which. Identify the three compounds **H**, **I** and **J**, using the infra-red spectra below, and decide which spectrum belongs to which compound.



- 2) Compound **E**, which is a branched chain haloalkane, was found to have the composition by mass of 39.8% C, 7.3% H, and 52.9% Br. There were two peaks for the molecular ions in the spectrum at 150 and 152, of approximately equal intensity. **E** reacts with sodium hydroxide to form **F**, whose infra-red spectrum is shown. **F** does not undergo dehydration with concentrated sulphuric acid.

**F** reacts further with acidified potassium dichromate (VI) to form **G**, whose infra red spectrum is also shown. Draw the structures and name **E**, **F** and **G**. Identify the species responsible for the peaks at 150 and 152 in the mass spectrum of **E**.

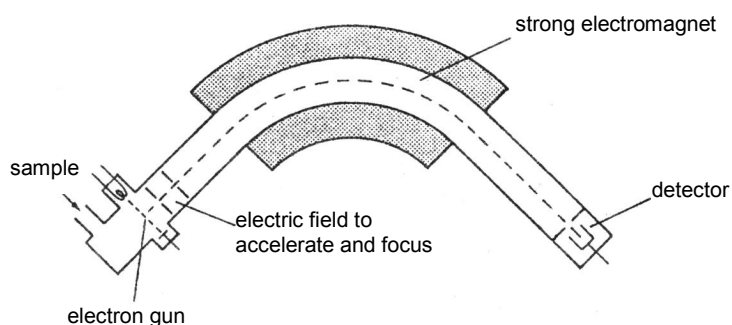




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### 3) MASS SPECTROSCOPY

#### The basics of a mass spectrometer



When the mass spectrum of a compound is run, a sample is vaporised and then the stages are:

- 1) **Ionisation** The sample is bombarded by high velocity electrons, which knock out an electron forming +1 ions (some 2+ ions can be formed as well).



These ions can also fragment into smaller particles when covalent bonds break.

- 2) **Acceleration** The positive ions are accelerated to high velocity and focused into a beam by a strong electric field.
- 3) **Deflection** The ions are deflected by a magnetic field. The amount by which they are deflected depends on the mass/charge ratio ( $m/z$ ) of each ion. Most ions have +1 charge, so amount of deflection depends on  $m$  (the lighter the mass and the greater the charge, the greater the deflection).
- 4) **Detection** The ions hit a detector producing a tiny current – the bigger the current the more ions so it counts how many ions there are of each  $m/z$  ratio (note the magnetic field is scanned through a range, so that each  $m/z$  value is detected one by one, but this scan takes place very quickly).

#### Using mass spectroscopy to find the $M_r$ and molecular formula of compounds

- The first species formed is called the molecular ion,  $[M]^{+}$  (note that this is a radical (has an odd number of electrons) and has a +ve charge).
- The signal for  $[M]^{+}$  gives the  $M_r$  of the compound.
- High resolution mass spectrometers measure the  $m/z$  values to enough accuracy to find the molecular formula. Each molecular formula has a different  $M_r$  if measured to enough precision. For example, the following molecular formulas all have a rough  $M_r$  of 60, but a more precise  $M_r$  can give the molecular formula.

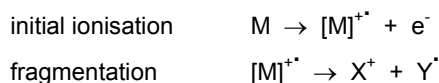
e.g.	molecular formula = $C_2H_4O_2$	$M_r = 60.02112$
	molecular formula = $C_3H_8O$	$M_r = 60.05751$
	molecular formula = $CH_4N_2O$	$M_r = 60.03235$

- However, more than one compound can have the same molecular formula, and so this alone cannot identify a compound (although use of the fragmentation pattern (see below) can).

molecular formula =  $C_3H_8O$        $M_r = 60.05751$   
could be: propan-1-ol, propan-2-ol or methoxyethane

## Fragmentation

- The molecular ion can fragment (split up) into another +ve ion, which is detected, and a neutral radical which is not.
- The fragmentation happens because the covalent bonds have been weakened by the loss of the electron from the molecule.



- For every compound, even those with the same  $M_r$ , the fragmentation pattern is different. Hence every compound has a unique mass spectrum which can be used to "fingerprint" compounds.
- Relatively stable ions such as carbocations (e.g.  $\text{CH}_3^+$ ,  $\text{CH}_3\text{CH}_2^+$ ) and acylium ions (e.g.  $\text{CH}_3\text{CO}^+$ ,  $\text{CH}_3\text{CH}_2\text{CO}^+$ ) are more common fragments in the spectrum.
- The more stable the ion, the greater the intensity of the peak.
- With carbocations, greater peaks are seen  $3^\circ > 2^\circ > 1^\circ$ , due to their stability.
- Acylium ions ( $\text{R-C=O}^+$ ) are more stable than carbocations, so their peaks are much bigger.
- Some common fragments are shown in the table below. Peaks are often seen for these fragments, or for the loss of this fragment from the molecular ion.

m/z	15	29	43	57
fragment	$\text{CH}_3^+$	$\text{CH}_3\text{—CH}_2^+$	$\begin{array}{c} \text{O} \\    \\ \text{CH}_3\text{—C}^+ \end{array}$ $\text{CH}_3\text{—CH}_2\text{—CH}_2^+$ $\begin{array}{c} + \\ \text{CH}_3\text{—CH—CH}_3 \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{CH}_3\text{—CH}_2\text{—C}^+ \end{array}$ $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2^+$ $\begin{array}{c} + \\ \text{CH}_3\text{—CH}_2\text{—CH—CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{—CH—CH}_2^+ \end{array}$ $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{—C}^+\text{—CH}_3 \end{array}$

## Isotopes

- As the mass of individual ions is measured, ions which are otherwise the same but contain different isotopes of the same element appear at different m/z values.
- This is most noticeable with Br and Cl as they contain significant amounts of different isotopes (it only produces tiny peaks for other elements as the amount of other isotopes is small).

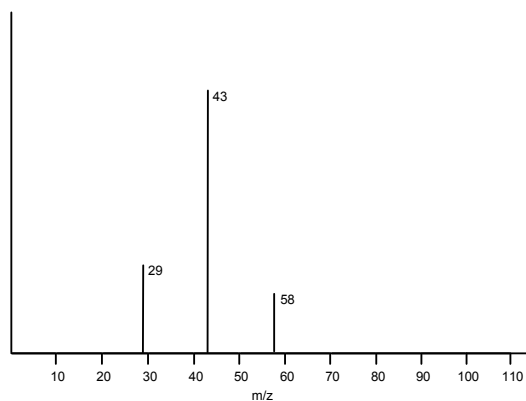
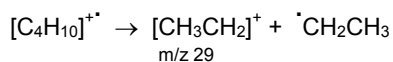
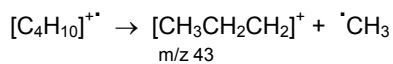
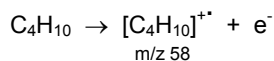
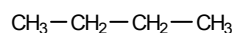
Br - consists of roughly 50%  $^{81}\text{Br}$  and 50%  $^{79}\text{Br}$  (i.e.  $^{81}\text{Br} : ^{79}\text{Br} \sim 1 : 1$ )

Cl - consists of roughly 25%  $^{37}\text{Cl}$  and 75%  $^{35}\text{Cl}$  (i.e.  $^{37}\text{Cl} : ^{35}\text{Cl} \sim 1 : 3$ )

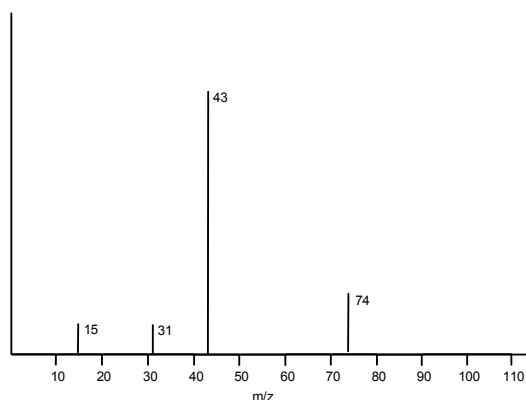
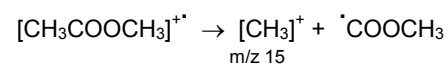
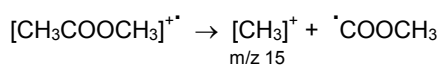
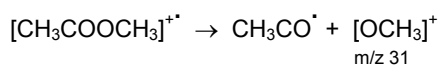
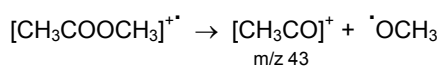
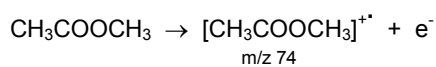
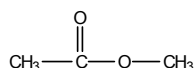
- If a compound contains two or more Cl/Br atoms, then the spectrum is more complicated. For example, chloromethane would have three molecular ion peaks at m/z 88 [ $\text{CH}_2^{37}\text{Cl}_2$ ] $^+$ , m/z 86 [ $\text{CH}_2^{37}\text{Cl}^{35}\text{Cl}$ ] $^+$ , and m/z 84 [ $\text{CH}_2^{35}\text{Cl}_2$ ] $^+$ .
- Small peaks at +1 may also appear due to  $^2\text{H}$  and  $^{13}\text{C}$ .

## Examples

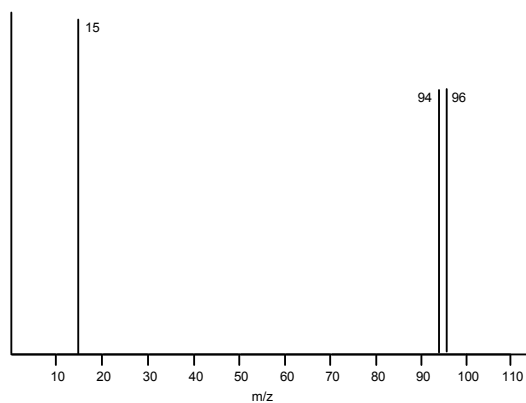
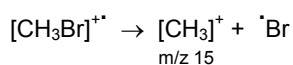
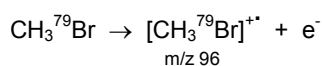
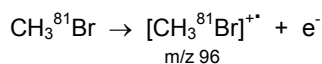
### butane



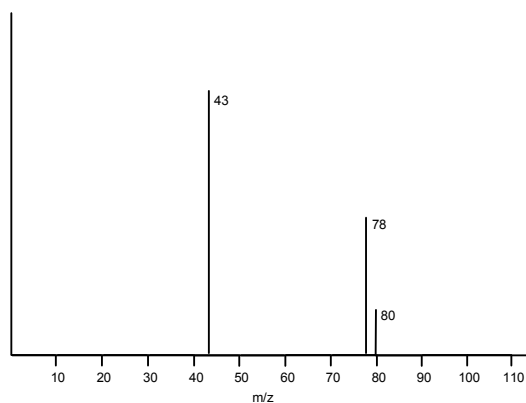
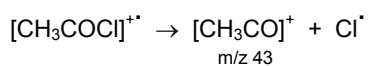
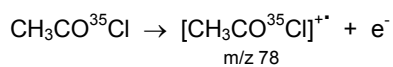
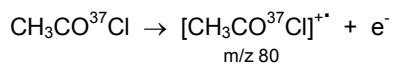
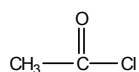
### methyl ethanoate



### bromomethane



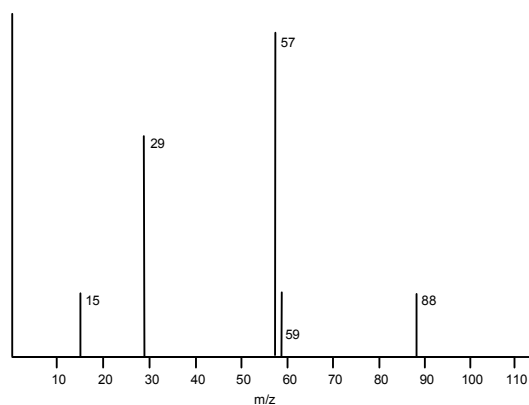
### ethanoyl chloride



# MASS SPECTROSCOPY – TASK 1

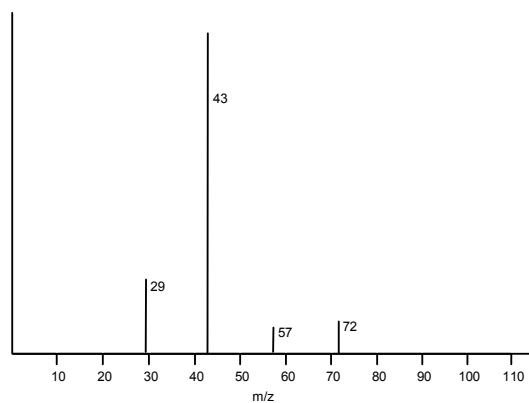
- 1) For each of the following signals:
- identify the species responsible for the signal **and**
  - write an equation to show how that species is formed
- a) the peak at  $m/z$  29 in propane  
b) the peak at  $m/z$  44 in propane  
c) the peak at  $m/z$  122 in 2-bromopropane  
d) the peak at  $m/z$  43 in 2-bromopropane  
e) the peak at  $m/z$  43 in ethyl ethanoate  
f) the peak at  $m/z$  57 in 2-chloro-2-methylpropane  
g) the peak at  $m/z$  57 in methyl propanoate

- 2) Identify the ester with the molecular formula  $C_4H_8O_2$



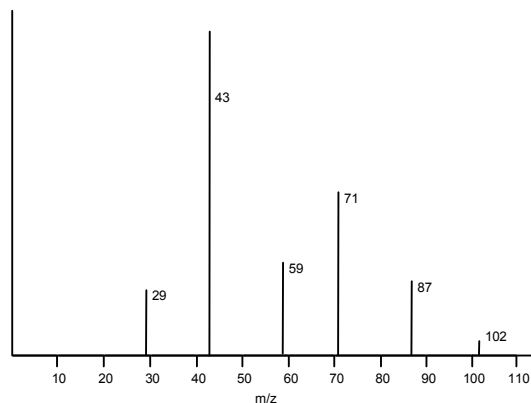
- 3) The mass spectrum of butanone is shown.

- identify the species responsible for all the signals shown
- write an equation for the formation of each species



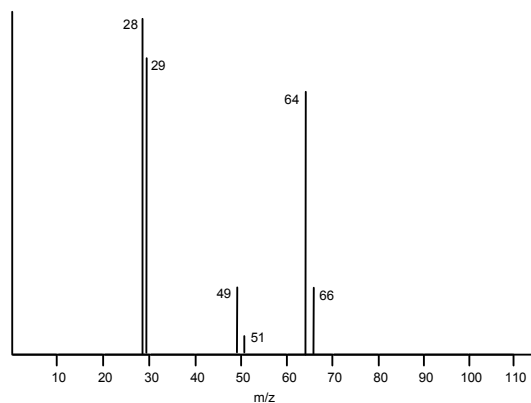
4) The mass spectrum of methyl butanoate is shown.

- identify the species responsible for all the signals shown
- write an equation for the formation of each species



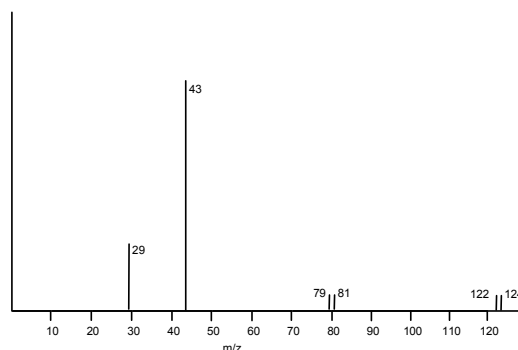
5) The mass spectrum of chloroethane is shown.

- identify the species responsible for signals m/z 66, 64, 51, 49, 29
- write an equation for the formation of each species



6) The mass spectrum of 1-bromopropane is shown.

- identify the species responsible for signals m/z 124, 122, 81, 79, 43 and 29
- write an equation for the formation of each species





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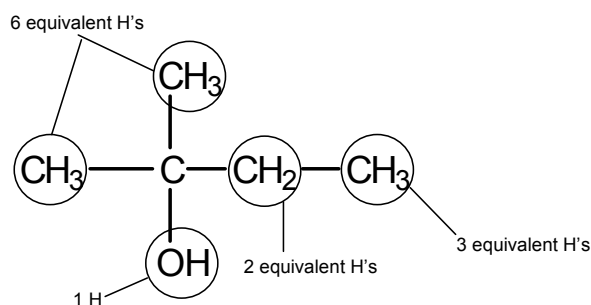
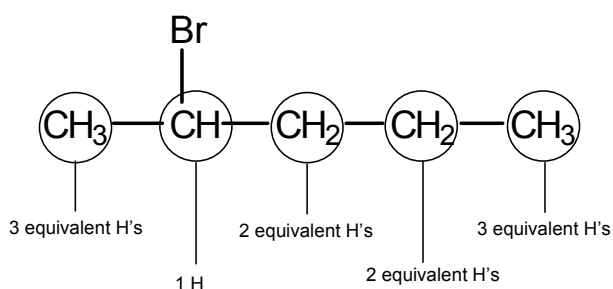
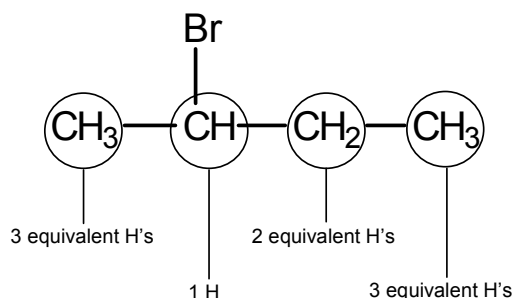
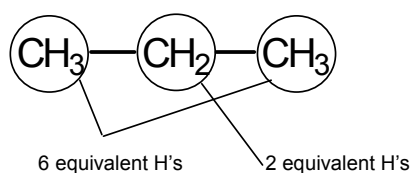
## 4) $^1\text{H}$ NMR SPECTROSCOPY

### Introduction

- NMR is a very powerful tool for identifying compounds.
- The nucleus of some atoms have nuclear spin (e.g.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ), although many atoms do not (e.g.  $^{12}\text{C}$ ).
- A nucleus with spin generates a small magnetic field.
- When a nucleus with spin is placed in a magnetic field, the small magnetic field generated by the nuclear spin can be aligned with or against the main magnetic field.
- There is a small difference in energy between these two alignments that corresponds to the energy of radiowaves. Consequently, if radiowaves are passed through the substance, some frequencies of radiowaves will be absorbed.
- this radiowaves to flip from one spin direction to the other.
- The resulting spectrum gives invaluable information about the compound.
- NMR is especially useful to organic chemists as they can find out about the H atoms (through  $^1\text{H}$  NMR) and the C atoms (through  $^{13}\text{C}$  NMR).

### 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.



### $^1\text{H}$ NMR TASK 1

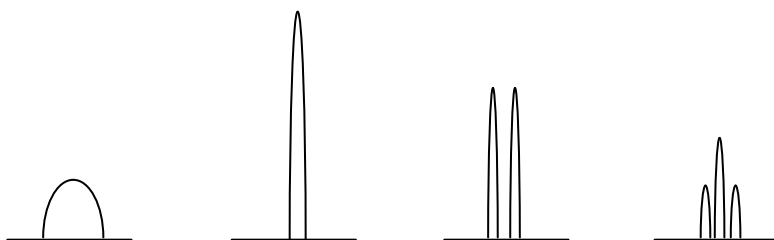
For each of the following compounds indicate the number of signals in its NMR spectrum. In each case, draw the compound and clearly show equivalent H atoms.

- |                    |                     |                             |
|--------------------|---------------------|-----------------------------|
| a) methylpropene   | d) propanone        | g) 1,2-dibromopropane       |
| b) propene         | e) methylamine      | h) dimethylethyl propanoate |
| c) 2-chloropropane | f) ethyl propanoate | i) but-2-ene                |



## Relative intensity of signals – number of equivalent H atoms

- In  $^1\text{H}$  NMR (but not  $^{13}\text{C}$  NMR) the area of the signal is proportional to the number of H 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 H atoms, even though the signals have different heights and in some cases are made of a number of signals (in a specific pattern – see splitting).

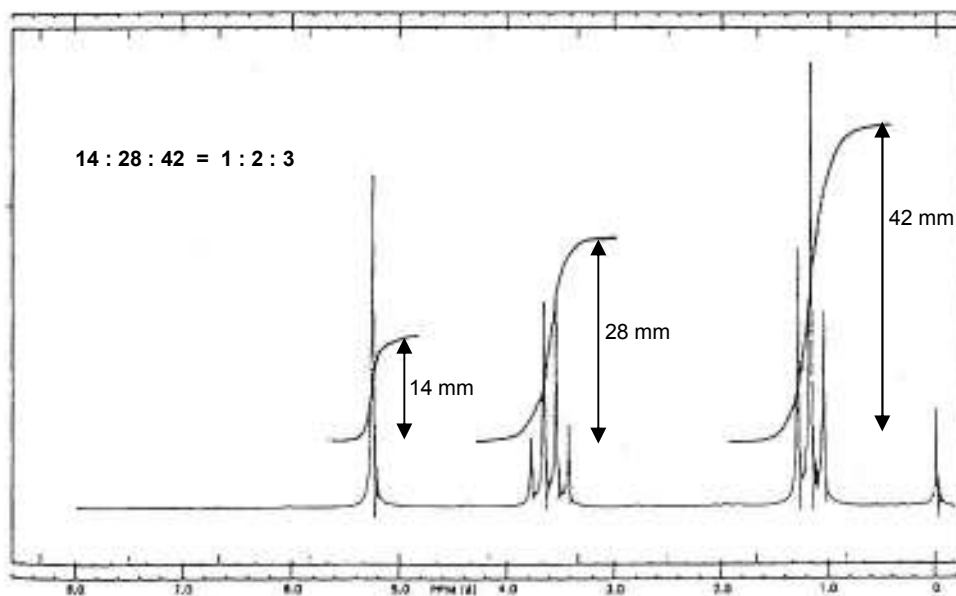


There are four signals here – each has the same area and so represents the same number of H atoms

### $^1\text{H}$ NMR TASK 2

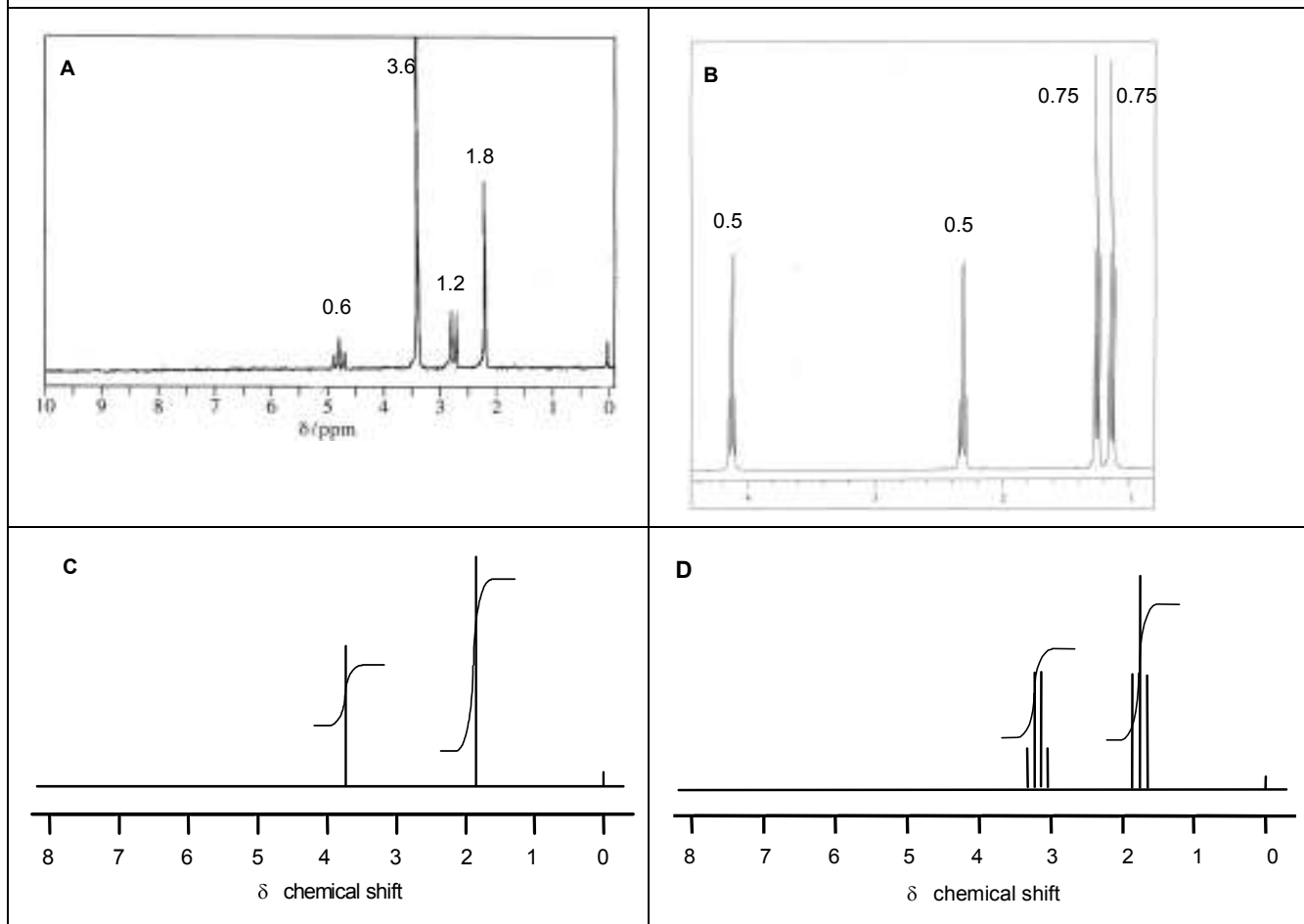
For each of the compounds in TASK 1, indicate the relative intensity of each signal in its NMR spectrum.

- There are a number of ways in which the relative size (area) of the signals can be shown. The most common one at A level is to indicate the relative intensity of the signals from which the simplest whole number ratio can be calculated.
  - 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 : 6
- Sometimes an “integration trace” drawn on the spectrum. The relative height of these traces gives the relative number of hydrogen atoms represented by each signal.



### <sup>1</sup>H NMR TASK 3

For each of the NMR spectra below, calculate the relative number of H atoms associated with each signal. Either the integration trace or measurements already taken from the integration traces are shown in each case.

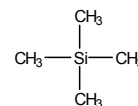


### Solvents

- <sup>1</sup>H NMR spectra are nearly always recorded using a solution of the sample.
- If the solvent contains any <sup>1</sup>H atoms, then these will appear in the spectrum (and may hide signals due to H atoms in the sample).
- Consequently solvents are used that contain no <sup>1</sup>H atoms. Often these solvents contain deuterium (D or <sup>2</sup>H) atoms instead of <sup>1</sup>H atoms as D atoms have no nuclear spin.
- Examples of commonly used solvents include: CCl<sub>4</sub> and deuterated solvents such as CDCl<sub>3</sub>, C<sub>6</sub>D<sub>6</sub>, etc.

### Calibration

- To calibrate the spectrum, a small quantity of tetramethylsilane (TMS) is added to samples as this produces a single peak providing an internal standard to which other peaks are compared.



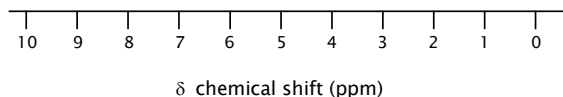
- This is used because:
  - it gives a signal that is further right than most of the signals from organic compounds (due to the low electronegativity of Si);
  - it only gives one signal as all twelve H atoms are chemically equivalent;
  - it is non-toxic;
  - it is inert;
  - it has a low boiling point (26°C) and so can be easily removed from the sample afterwards.

## Chemical shift

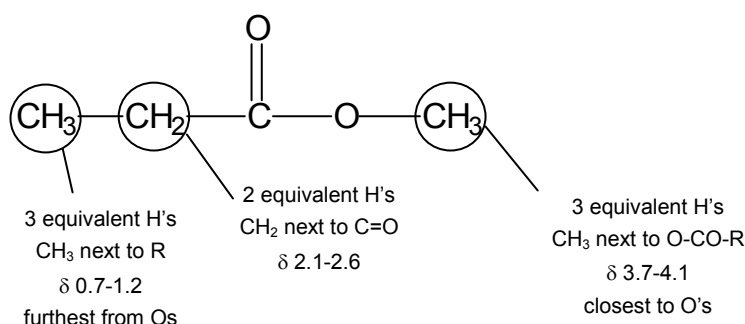
- The spectra are recorded on a scale known as the chemical shift ( $\delta$ ), which is how far the signal is away from the signal for TMS in parts per million.

$$\delta = \frac{\text{Field for TMS} - \text{Field measured}}{\text{Field for TMS}} \times 10^6$$

- Most signals are between 0 and 10 ppm away from the signal for TMS, and the scale is usually shown as below on the final spectrum.



- The chemical shift depends on what other atoms/groups are near the H. The closer the H is to electronegative atoms (e.g. O, Cl), the greater the shift. Also the more electronegative atoms near, the greater the shift. In the example below, it can be seen that the closer the Hs to any O's, the greater the chemical shift.



- The data sheet can be used to find approximate values for chemical shifts. It is not always straightforward using the limited data in this table, but the best match is taken. The example above shows how this can be done.

### <sup>1</sup>H NMR TASK 4

For each of the following compounds,

- draw the molecule
- predict the number of signals
- predict the relative intensity of each signal
- predict the approximate chemical shift ( $\delta$ ) of each signal

a) propanoic acid

c) 2-chloropropane

e) methylpropene

b) propanal

d) 2-methylbutane

f) methyl propanoate

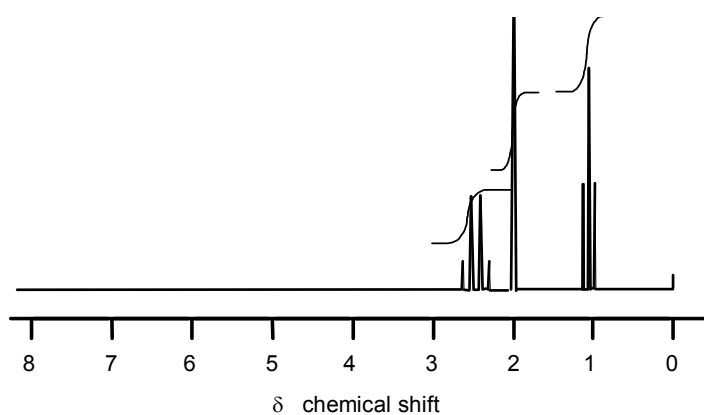
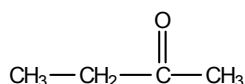
## Spin-spin splitting (also known as coupling or multiplicity)

- The number of lines a signal is split into gives information about neighbouring H atoms - whether they are inequivalent, and if they are, how many H atoms there are.
- Usually only H atoms on the neighbouring C atom cause splittings (couplings).
- The signal for H atoms is only split by inequivalent Hs - so if the H atoms on the next atom are equivalent they do not cause splittings.
- The number of lines = 1 + the number of inequivalent H atoms on adjacent C atoms** (the "n+1" rule)
- 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).

signal	singlet	doublet	triplet	quartet
appearance				
number of lines	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

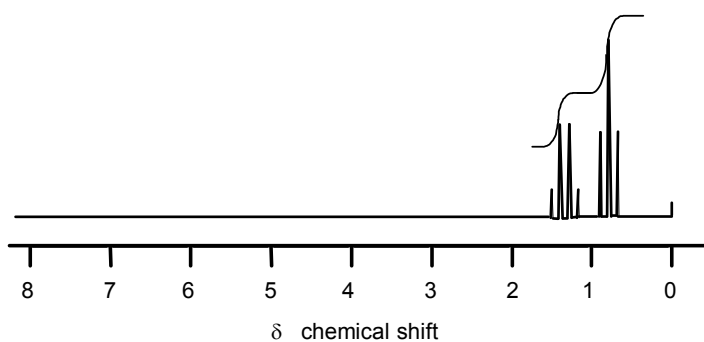
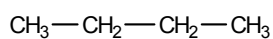
- It should be noted that the H atom of the OH group in alcohols rarely causes splittings (couplings), or is split (coupled) itself. Sometimes the H atom of an OH group appears as a broad hump.

### Example 1 - butanone



shift ( $\delta$ )	assignment	relative intensity	coupling	coupled to
1.0	$\text{CH}_3\text{CH}_2$	3	triplet	$\text{CH}_2$
2.0	$\text{CH}_3\text{CO}$	3	singlet	
2.4	$\text{CH}_2$	2	quartet	$\text{CH}_3$

### Example 2 - butane

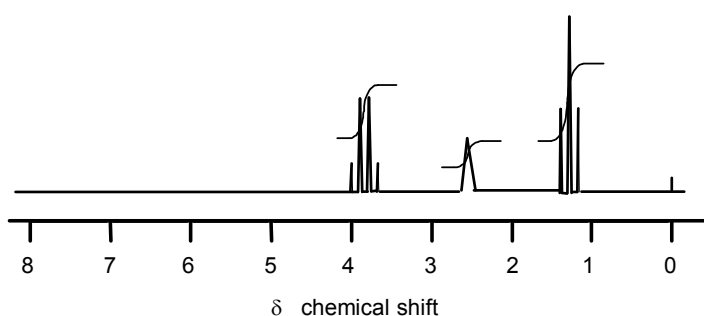
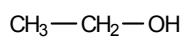


shift ( $\delta$ )	assignment	relative intensity	coupling	coupled to
1.3	$\text{CH}_2$	2	quartet	$\text{CH}_3$
0.8	$\text{CH}_3$	3	triplet	$\text{CH}_2$

**Note:**

The  $\text{CH}_2$  only couples to the  $\text{CH}_3$  and not the other  $\text{CH}_2$  as the  $\text{CH}_2$  is equivalent.

### Example 3 - ethanol



shift ( $\delta$ )	assignment	relative intensity	coupling	coupled to
1.3	$\text{CH}_3$	3	triplet	$\text{CH}_2$
2.6	OH	1	singlet	
3.8	$\text{CH}_2$	2	quartet	$\text{CH}_3$

**Note:**

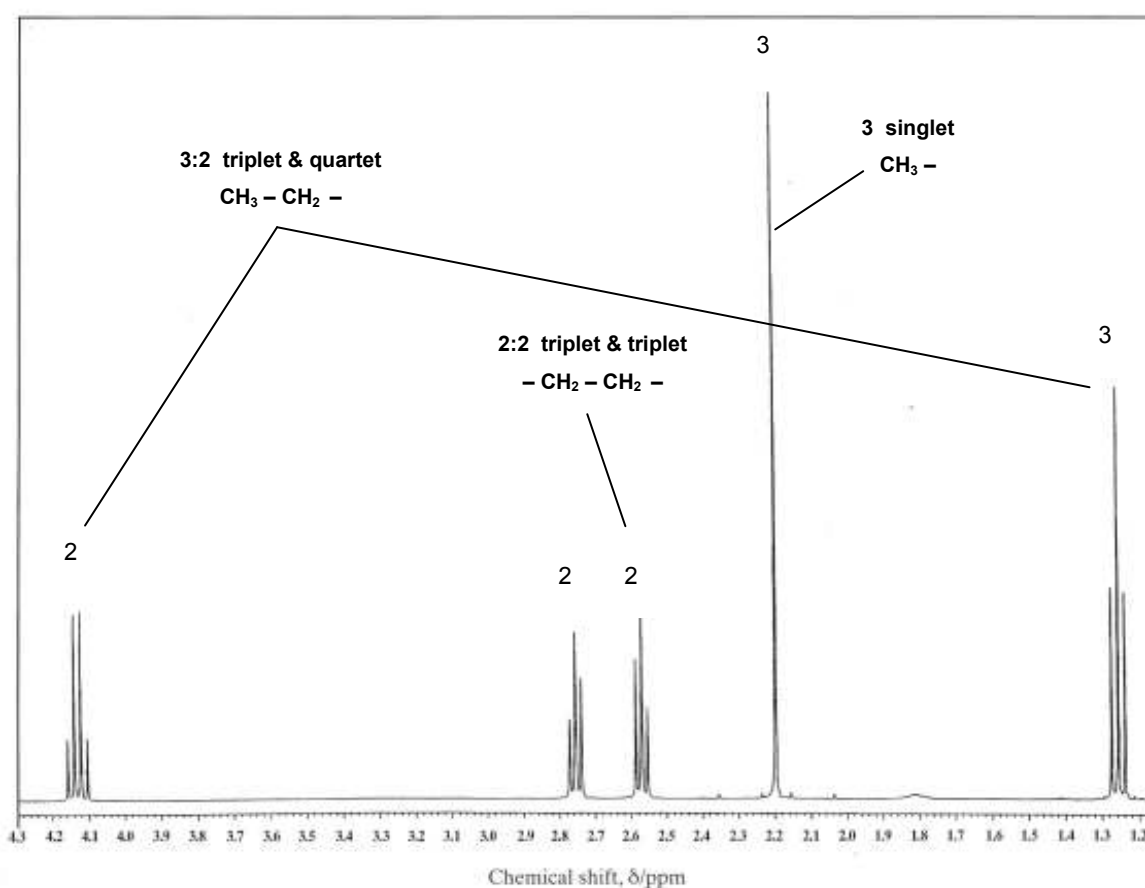
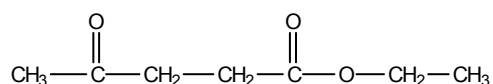
The  $\text{CH}_2$  and OH do not couple to each other (alcohol OHs rarely get involved in coupling)

### Some common signals to look out for in exam questions:

The following three signals seem to crop up over and over again in exam questions and it is very handy if you can spot them as you work towards the answer.

Triplet & quartet	3:2	CH <sub>3</sub> -CH <sub>2</sub> - (ethyl group)	<ul style="list-style-type: none"><li>The triplet and quartet do not have to be next to each other in the spectrum.</li><li>The atom joined to the other side of the CH<sub>2</sub> cannot have an H's on (unless they do not do not couple, e.g. OH group or an equivalent CH<sub>2</sub> as in butane).</li></ul>
Triplet & triplet	2:2	-CH <sub>2</sub> -CH <sub>2</sub> -	<ul style="list-style-type: none"><li>The two triplets do not have to be next to each other in the spectrum.</li><li>The two CH<sub>2</sub> groups must be inequivalent (otherwise they would produce one signal not two!).</li><li>The atoms joined either side of the CH<sub>2</sub>s cannot have any H's on them.</li></ul>
Singlet	3	CH <sub>3</sub> - (methyl group)	<ul style="list-style-type: none"><li>The atom joined to the CH<sub>3</sub> cannot have any H's on it.</li></ul>

This example spectrum contains all three of these signals. The spectrum is of this compound:



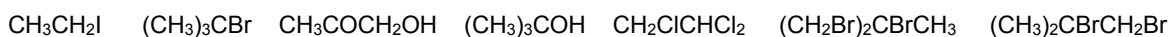
## **<sup>1</sup>H NMR TASK 5**

For each of the compounds from task 1, indicate the splitting pattern (multiplicity) of each signal.

- |                    |                     |                             |
|--------------------|---------------------|-----------------------------|
| a) methylpropene   | d) propanone        | g) 1,2-dibromopropane       |
| b) propene         | e) methylamine      | h) dimethylethyl propanoate |
| c) 2-chloropropane | f) ethyl propanoate | i) but-2-ene                |

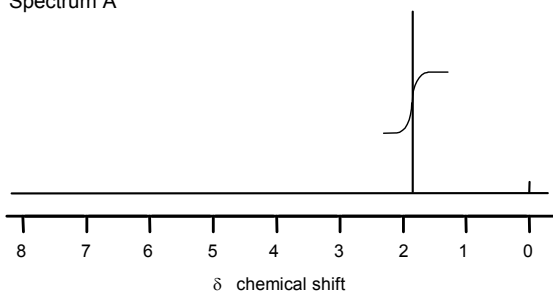
## **<sup>1</sup>H NMR TASK 6**

For each of the following compounds:

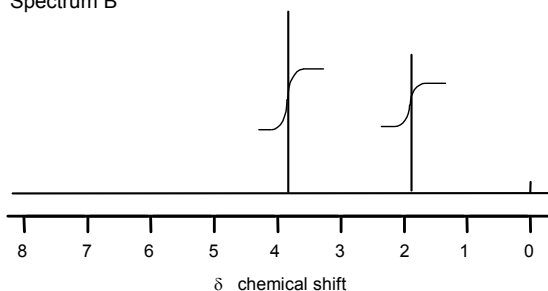


- a) For each compound, predict the number of signals, and relative intensity and multiplicity of each signal.  
b) Work out which spectrum belongs to which compound.

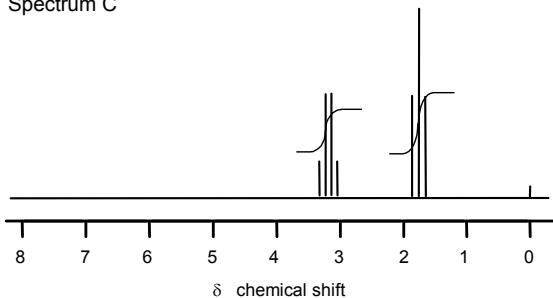
Spectrum A



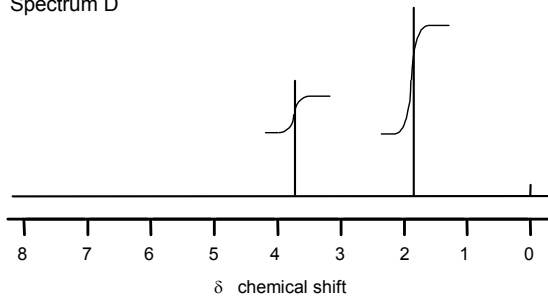
Spectrum B



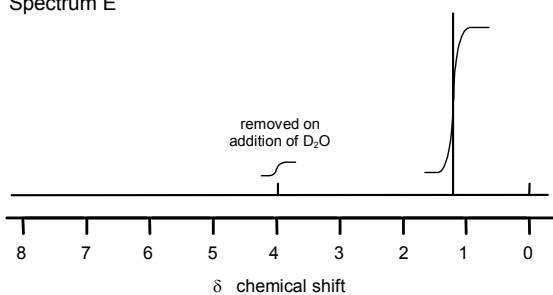
Spectrum C



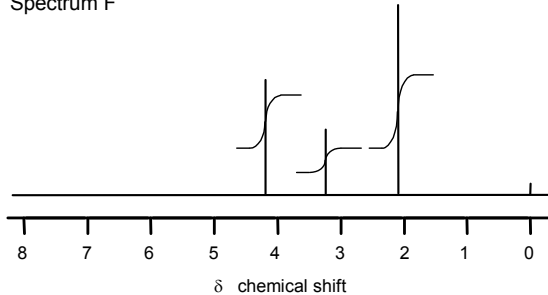
Spectrum D



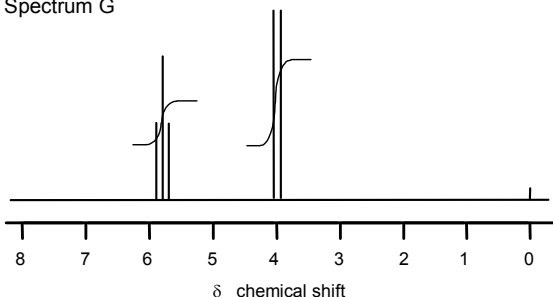
Spectrum E



Spectrum F



Spectrum G

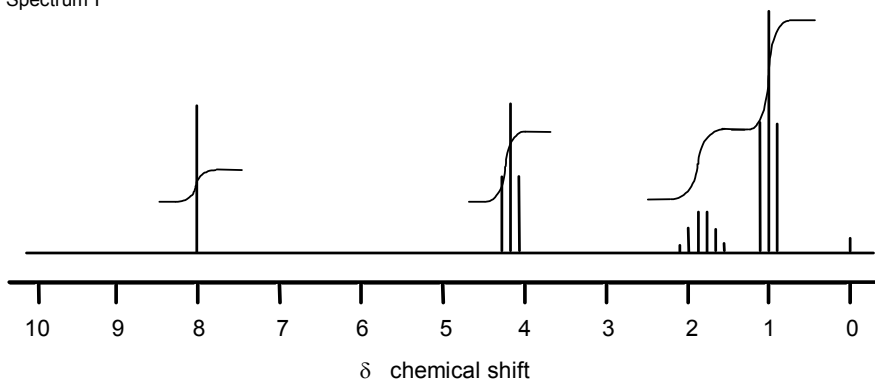


## <sup>1</sup>H NMR TASK 7

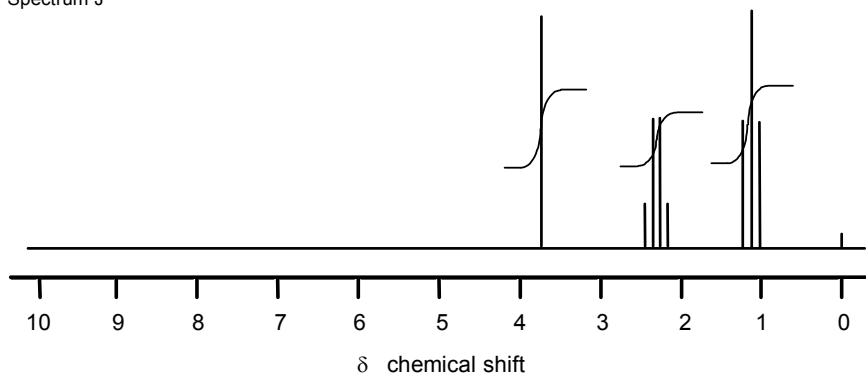
The spectra of three isomers of C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> are shown.

- Draw the structural formulae of all the isomers of C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> 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. You will need to use the chemical shift data to work it out.

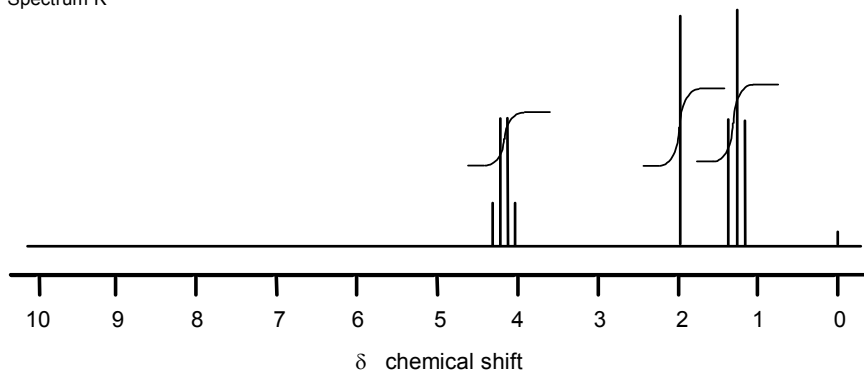
Spectrum I



Spectrum J



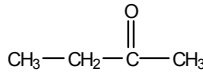
Spectrum K



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# <sup>1</sup>H NMR – TASK 8

Complete the table about each compound.

1) butanone					
protons	CH <sub>3</sub> -CH <sub>2</sub>	CH <sub>2</sub>	COCH <sub>3</sub>		
relative intensity	3	2	3		
δ / ppm	0.7 – 1.2	2.1 – 2.6	2.1 – 2.6		
multiplicity	triplet	quartet	singlet		
coupled to	CH <sub>2</sub>	CH <sub>3</sub>			

4) 2,2-dimethyl pentan-3-one					
protons					
relative intensity					
δ / ppm					
multiplicity					
coupled to					

2) methyl ethanoate					
protons					
relative intensity					
δ / ppm					
multiplicity					
coupled to					

5) ethyl ethanoate					
protons					
relative intensity					
δ / ppm					
multiplicity					
coupled to					

3) methylpropane					
protons					
relative intensity					
δ / ppm					
multiplicity					
coupled to					

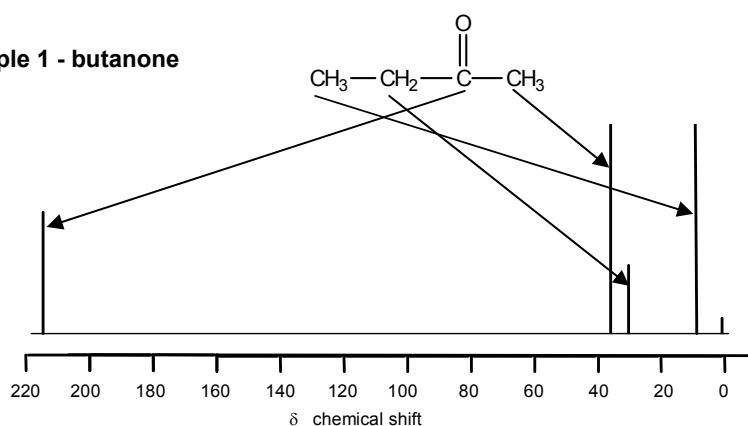
6) butane					
protons					
relative intensity					
δ / ppm					
multiplicity					
coupled to					



## 5) <sup>13</sup>C NMR SPECTROSCOPY

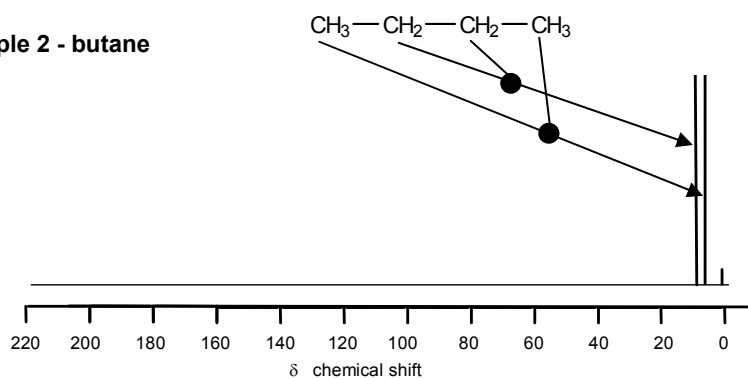
- <sup>12</sup>C atoms do not have nuclear spin, but 1.1% of C atoms are <sup>13</sup>C and these do have nuclear spin and so produce NMR spectra.
- <sup>13</sup>C NMR spectra are often simpler than <sup>1</sup>H NMR spectra.
- They give a lot of valuable information about the chemical environment of C atoms (e.g. the difference between C atoms in C=O, C-N, C≡N, C-C, C=C, etc.). This comes from the chemical shift (δ). As in <sup>1</sup>H NMR, the closer the atom to electronegative atoms (like O and Cl), and the more of those electronegative atoms, the greater the chemical shift.
- There is one signal for each set of equivalent C atoms.
- There is no coupling (unlike <sup>1</sup>H NMR).
- The size of signal is not relative to the number of equivalent C atoms (unlike H atoms in <sup>1</sup>H NMR).
- As in <sup>1</sup>H NMR, the chemical shift (δ) is measured relative to TMS.
- Although deuterated solvents are usually used, there will be a signal for any C atoms in the solvent.

Example 1 - butanone



shift (δ)	assignment
8	<u>C</u> H <sub>3</sub> CH <sub>2</sub>
32	<u>C</u> H <sub>3</sub> CO
37	CH <sub>2</sub>
215	CO

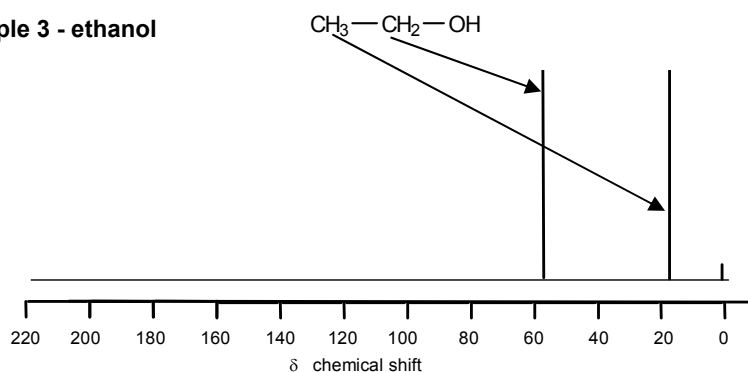
Example 2 - butane



shift (δ)	assignment
8	CH <sub>3</sub>
10	CH <sub>2</sub>

- There are only 2 signals as each signal represents 2 C atoms that are equivalent.

Example 3 - ethanol



shift (δ)	assignment
18	CH <sub>3</sub>
58	CH <sub>2</sub>

### <sup>13</sup>C NMR TASK 1

For each of these compounds

- indicate the number of signals in the <sup>13</sup>C NMR spectrum
- predict the approximate chemical shift of each signal using the data sheet

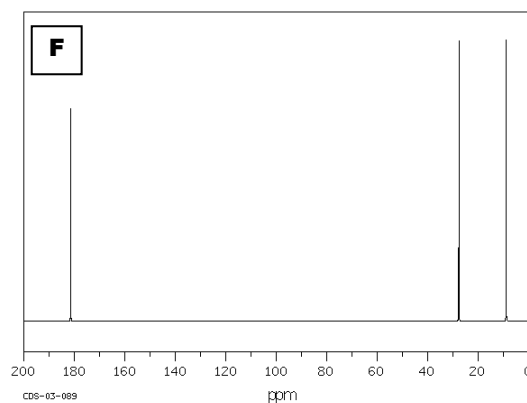
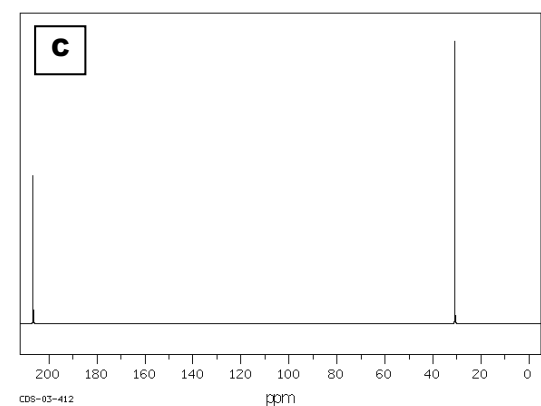
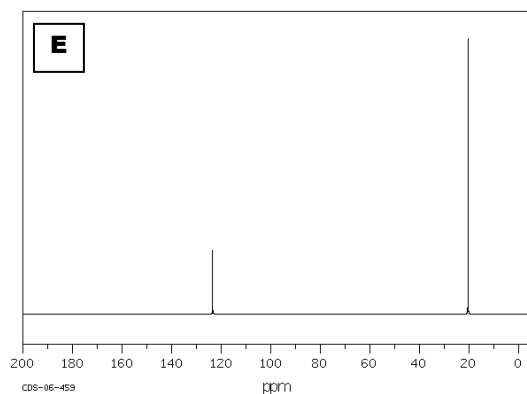
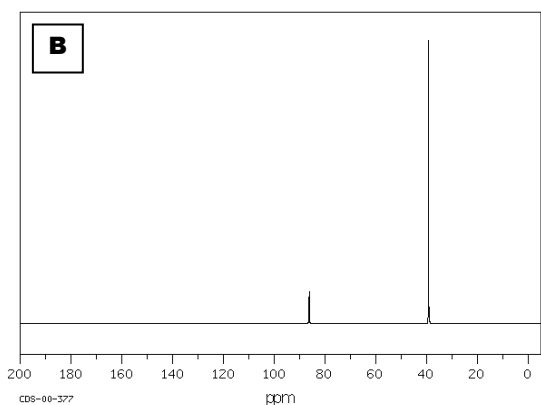
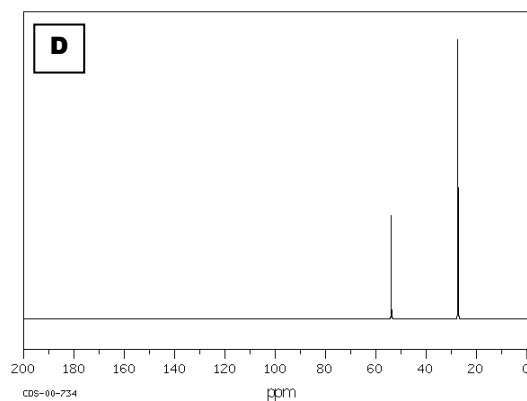
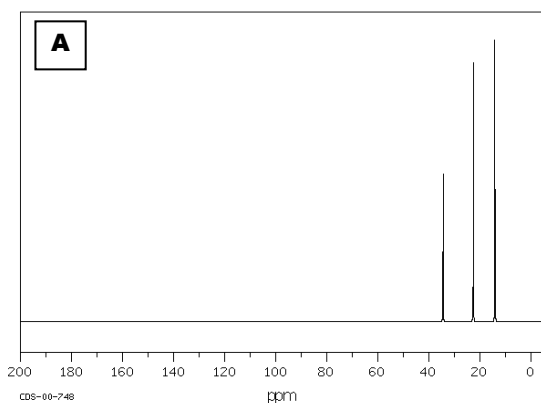
- |                    |                     |                             |
|--------------------|---------------------|-----------------------------|
| a) methylpropene   | d) propanone        | g) 1,2-dibromopropane       |
| b) propene         | e) methylamine      | h) dimethylethyl propanoate |
| c) 2-chloropropane | f) ethyl propanoate | i) but-2-ene                |

### <sup>13</sup>C NMR TASK 2

For each of the following compounds:

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

- For each compound, predict the number of signals, and position of each signal.
- Work out which spectrum belongs to which compound.

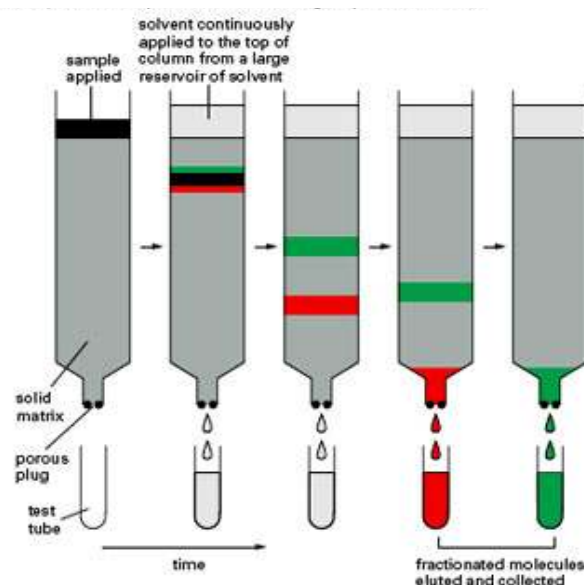


## 6) CHROMATOGRAPHY

- There are many different types of chromatography.
- All forms involve a fixed stationary phase (a solid or a liquid supported on a solid, e.g. paper in paper chromatography) and a mobile phase (a liquid or a gas, e.g. a solvent such as water in paper chromatography).
- The mobile phase flows through the stationary phase and carries the substances being separated.
- Separation takes place because the substances in a mixture have a different affinity for the stationary phase and mobile phase. Put in *over-simplistic* terms, the more a substance “sticks” to the stationary phase (e.g. through H-bonds or other attractions) the less distance / slower it travels.
- The *retention time* is the time it takes a substance to pass through the column.

### Column chromatography

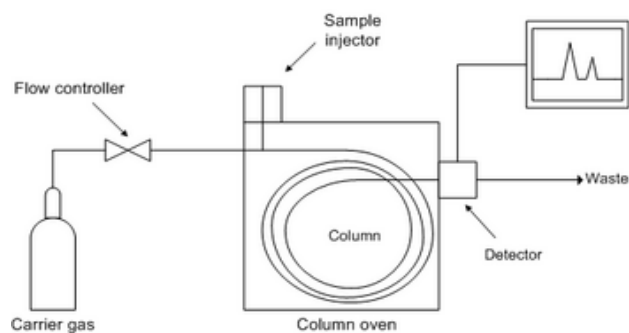
- This method is very useful for separating large quantities of soluble substances.
- The stationary phase is a powder (such as silicon dioxide or aluminium oxide) often packed into a glass column.
- The mobile phase is a solvent.
- The mixture is dissolved in the solvent and placed at the top of the column.
- As the solvent (eluent) moves down through the powder in the column, the substances in the mixture move through the column at different rates allowing them to be collected separately at the bottom.
- The time it takes to move down the column depends on the balance between the solubility of each substance in the mobile phase (the solvent) and its retention in the stationary phase (the powder).
- It is easiest to separate coloured substances using column chromatography, but colourless ones are routinely separated this way.



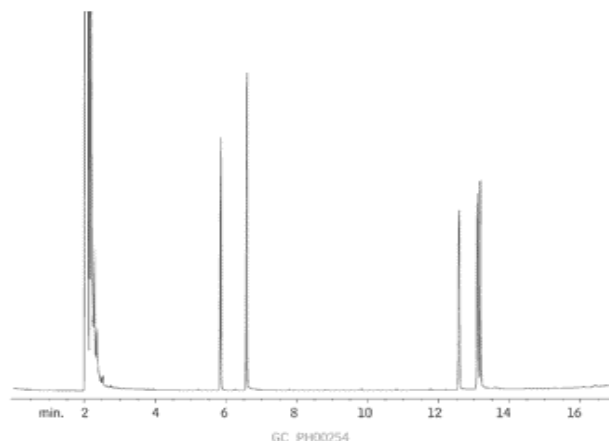
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### Gas-liquid chromatography

- This method is used to separate mixtures of volatile liquids.
- The stationary phase is a powder coated with a film of a non-volatile liquid. This coated powder is packed into a long, narrow, steel tube. The tube is coiled so that it takes up less space.
- The tube is kept inside an oven to heat it up (so vaporising the volatile liquids).
- The mobile phase is a unreactive gas such as nitrogen (a carrier gas).
- The sample is injected into the column and a continuous flow of the carrier gas passes through the column.
- The substances are separated as they travel through the column depending on their affinity (attraction) for the stationary and mobile phases.
- The chromatogram shows the time it takes for each substance to pass through the column. The size of the signal is proportional to the amount of that substance in the mixture.
- It is very common for a mass spectroscopy machine to be connected to a GLC machine. As each separated substance reaches the end of the column, it can be analysed by mass spectroscopy.

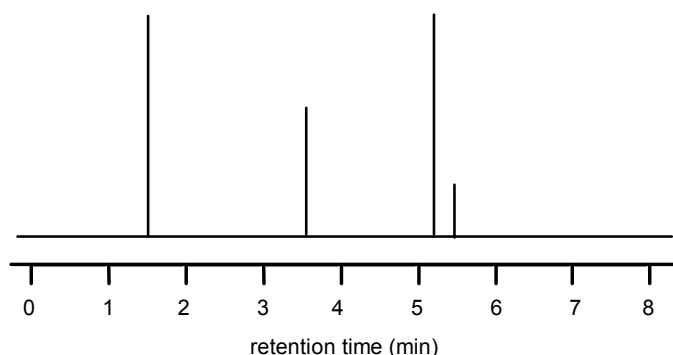


From: [http://en.wikipedia.org/wiki/File:Gas\\_chromatograph.png](http://en.wikipedia.org/wiki/File:Gas_chromatograph.png)

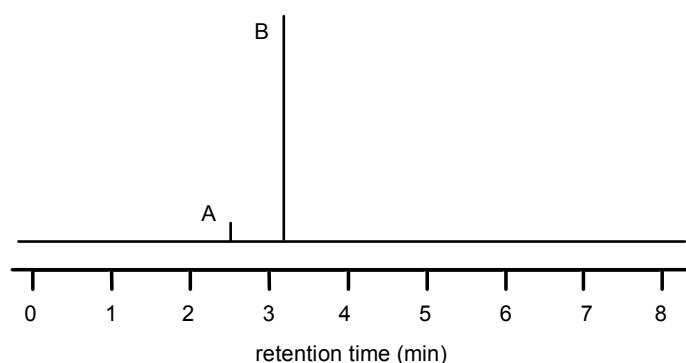


## CHROMATOGRAPHY TASK 1

1) A mixture of volatile liquids was analysed by gas chromatography. The chromatogram is shown.



- How many substances were in the mixture?
  - What is meant by the term *retention time*?
  - What is the stationary phase in gas chromatography?
  - What is the mobile phase in gas chromatography?
  - Why are substances separated by gas chromatography?
- 2) Propene was reacted with hydrogen bromide forming a mixture of products. This mixture was analysed by gas chromatography. The chromatogram is shown. Give the structure of both **A** and **B** and explain the relative abundance of the two compounds in the mixture.



- 3) Column chromatography is a very useful of separating substances for analysis.
- What type of mixtures are separated by column chromatography?
  - What is the stationary phase in column chromatography?
  - What is the mobile phase in column chromatography?
  - Why are substances separated by column chromatography?



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