# 6.3.2 Spectroscopy

## NMR spectroscopy

### Different types of NMR

NMR spectroscopy involves interaction of materials with the low-energy radiowave region of the electromagnetic spectrum

NMR spectroscopy is the same technology as that used in ‘magnetic resonance imaging’ (MRI) to obtain diagnostic information about internal structures in body scanners

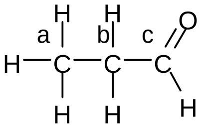
There are two main types of NMR

1. $C^{13}$ NMR
2. H (proton) NMR

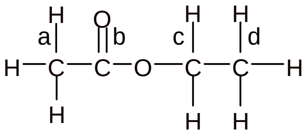
There is only around 1% $C^{13}$ in organic molecules but modern NMR machines are sensitive enough to give a full spectra for $C^{13}$
The $C^{13}$ spectra is a simpler spectrum than the H NMR

**Equivalent Carbon atoms.**

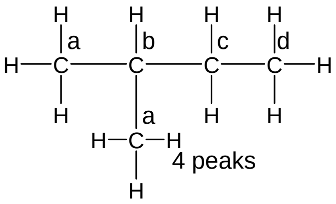
In a $C^{13}$ NMR spectrum, there is one signal (peak) for each **set of equivalent C atoms.**



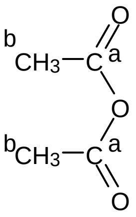
3 peaks



4 peaks

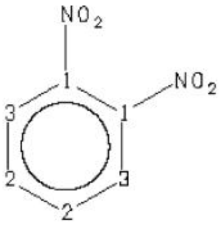


4 peaks



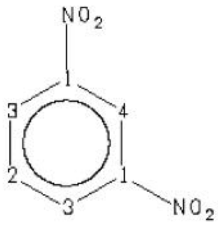
2 peaks

1,2 dinitrobenzene



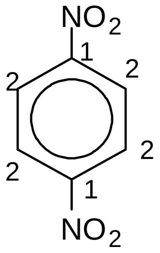
3 peaks

1,3 dinitrobenzene

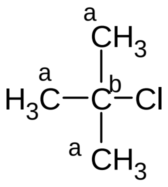


4 peaks

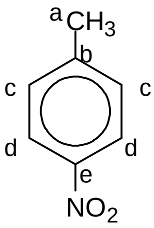
1,4 dinitrobenzene



2 peaks



2 peaks

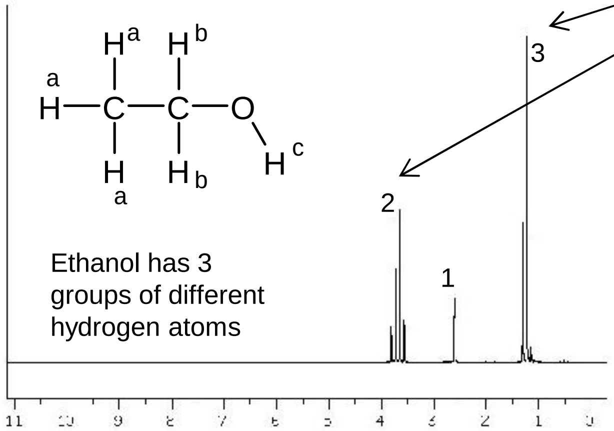


5 peaks

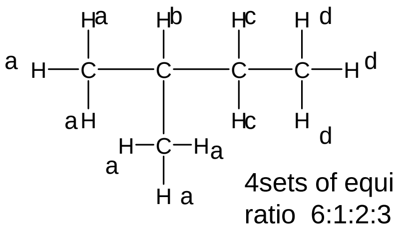
## Equivalent Hydrogen atoms.

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

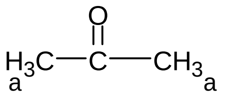
In addition the **intensity (integration value)** of each signal is proportional to the **number of equivalent H atoms** it represents.



Ethanol has 3 groups of different hydrogen atoms

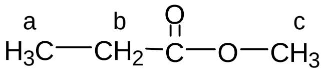


4sets of equivalent H's: ratio 6:1:2:3



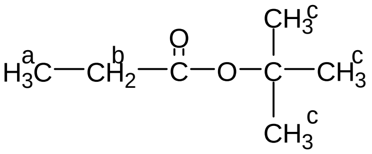
$H_3C-C(=O)-CH_3$

1 signal



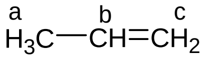
$H_3C-CH_2-C(=O)-O-CH_3$

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



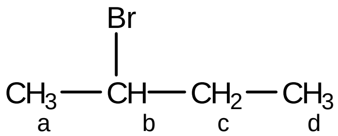
$H_3C-CH_2-C(=O)-O-C(CH_3)_3$

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



$H_3C-CH=CH_2$

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



$CH_3-CH(Br)-CH_2-CH_3$

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

### Solvents

Samples are dissolved in solvents without any $^1H$ atoms, e.g. $CCl_4$, $CDCl_3$.

This means that in the H NMR the solvent will not give any peaks

The same solvent is used in $C^{13}$ 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.

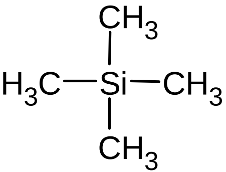
$CCl_4$ is a non-polar compound that is a good solvent for non-polar organic molecules
$CDCl_3$ is a polar covalent molecule that is a good solvent for polar organic molecules

### Calibration and shift

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

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

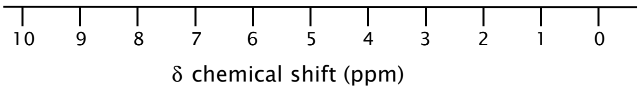
TMS is used because:
- its signal is away from all the others
- it only gives one signal
- gives strong signal so only a small amount needed
- it is non-toxic
- it is inert
- it has a low boiling point and so can be removed from sample easily



$Si(CH_3)_4$

tetramethylsilane

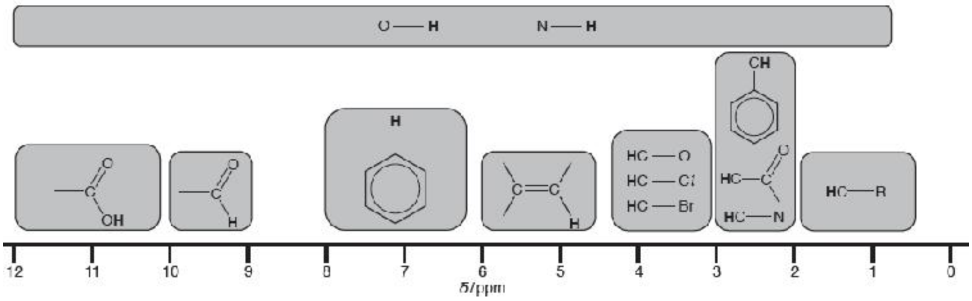
The spectra are recorded on a scale known as the chemical shift (δ), which is how much the field has shifted away from the field for TMS..

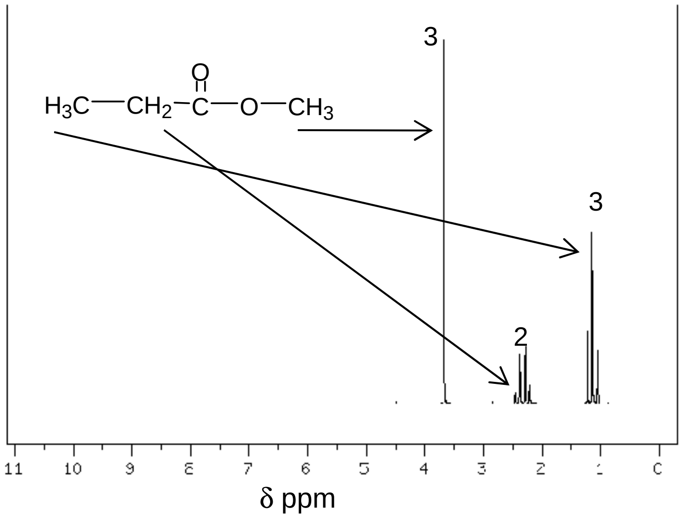


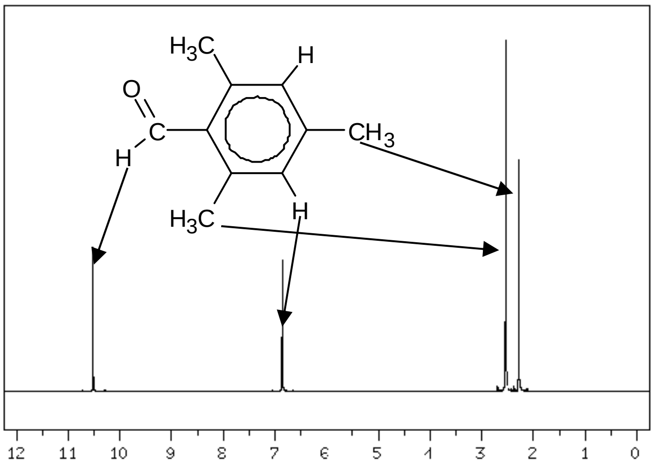
The δ is a measure in parts per million (ppm) is a relative scale of how far the frequency of the proton signal has shifted away from that for TMS.

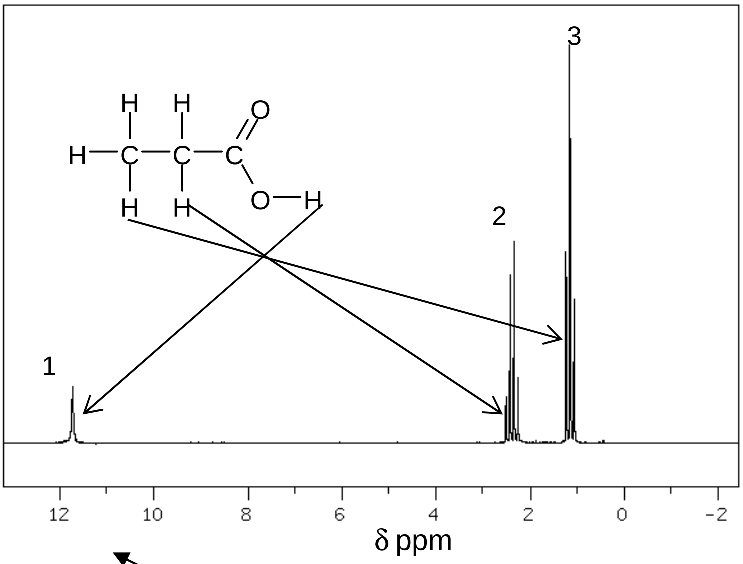
### H NMR shift

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







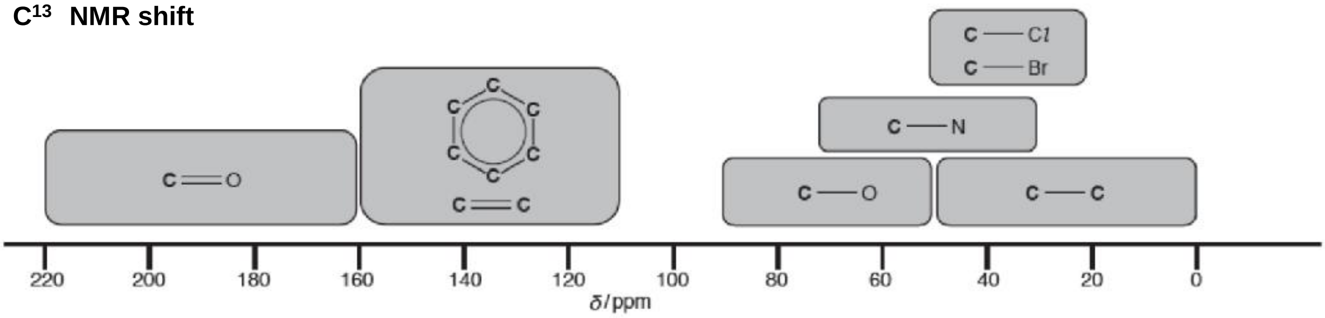


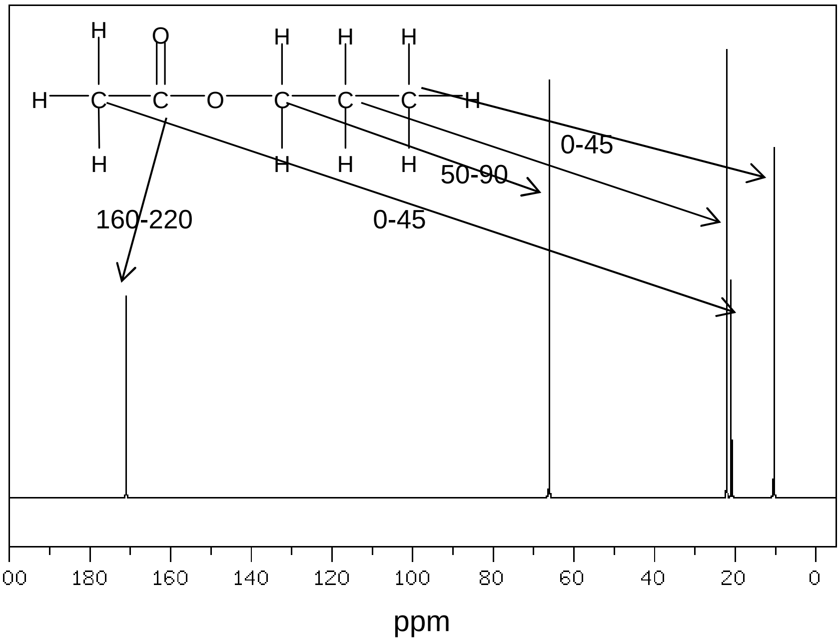
### Proton exchange using $D_2O$

If $D_2O$ is added to a sample then a process of proton exchange happens with the H in any O-H and N-H bonds. This has the effect of removing the peaks from the H-NMR spectra. This can help with the identification of O–H and N–H peaks on the spectra.

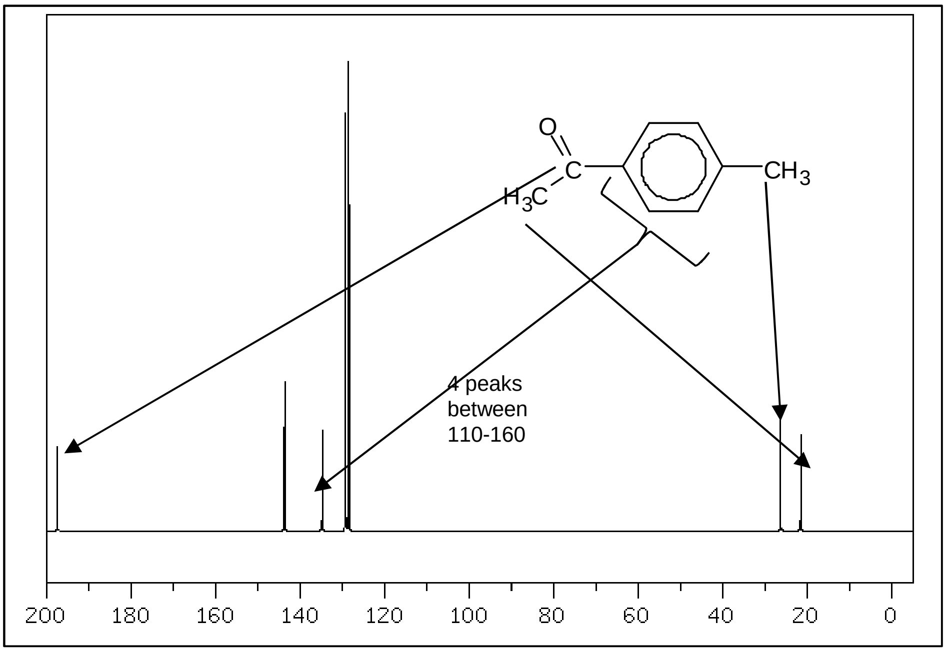
Addition of $D_2O$ to the sample of propanoic acid would make the peak at δ = 11.7 (ppm) in the above spectrum disappear

**$C^{13}$ NMR shift**





It will not be possible to identify the exact carbon corresponding to each peak if several carbons are in the same range

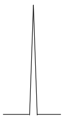
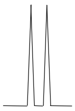
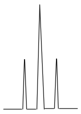
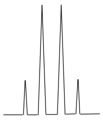


It is not possible to distinguish between similar shifts for each carbon in a benzene ring. In this example it should be possible to work out there are four different carbons in the benzene ring and these correspond to the four peaks between 120-145

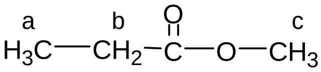
## Spin-Spin coupling in H NMR

In high resolution H 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 | quintet |
|---|---|---|---|---|---|
| appearance |  |  |  |  |  |
| Split number of peaks | 1 | 2 | 3 | 4 | 5 |
| number of neighbouring inequivalent H atoms | 0 | 1 | 2 | 3 | 4 |
| relative size | | 1:1 | 1:2:1 | 1:3:3:1 | 1:4:6:4:1 |

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



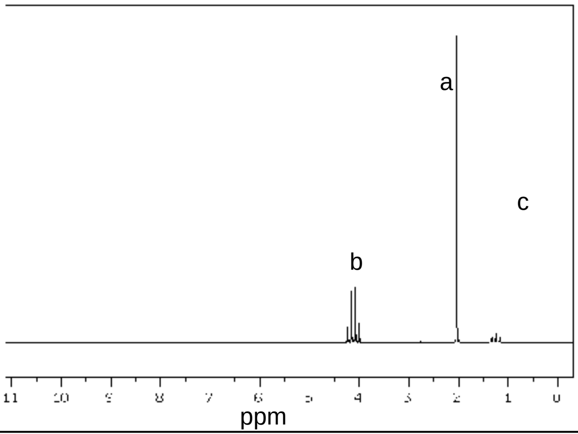
$H_3C-CH_2-\overset{O}{\overset{||}{C}}-O-CH_3$

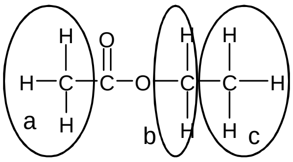
The peak due to group **a** will be a **triplet** as it is next to **b** (a carbon with 2 H's)

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)

For 6 split peaks use the term hextet or multiplet





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

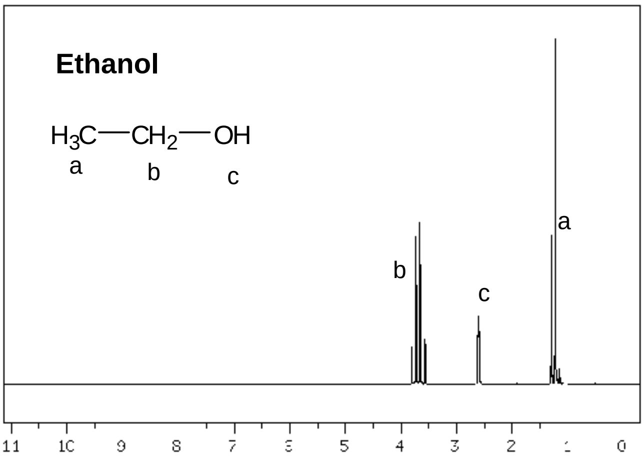
The peak due to group **b** will be a **quartet** as it is next to a carbon with 3 H's
Shift 3.7 -4.1
Integration trace 2

Hydrogens bonded to a nitrogen or oxygen usually do not couple with other protons and appear as singlets on the 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



You will not be asked to interpret splitting patterns for the protons attached to a benzene ring

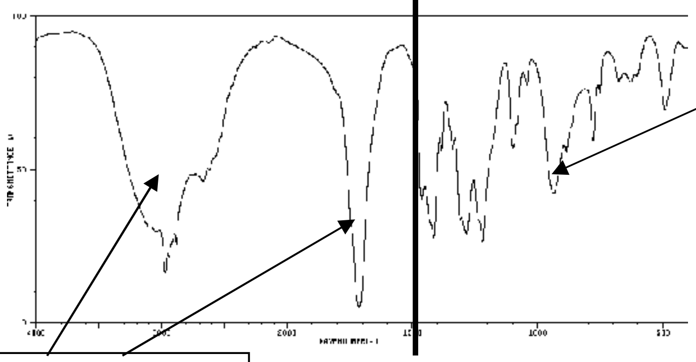
## Infrared spectroscopy

Certain bonds in a molecule absorb infra-red radiation at characteristic frequencies causing the covalent bonds to vibrate

Complicated spectra can be obtained than provide information about the types of bonds present in a molecule

ABOVE 1500 $cm^{-1}$ – "Functional group identification"

BELOW 1500 $cm^{-1}$ – "Fingerprinting"



Complicated and contains many signals – picking out functional group signals difficult.

This part of the spectrum is unique for every compound, and so can be used as a "fingerprint".

e.g. C=O 1640 – 1750 $cm^{-1}$

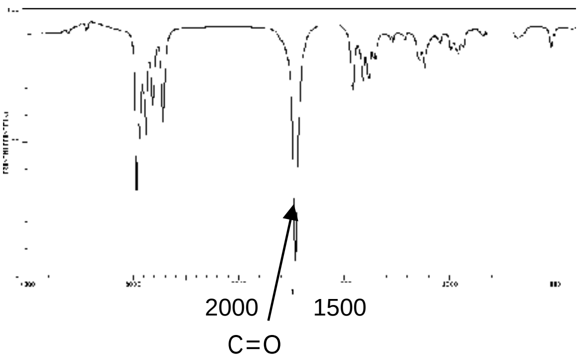
O-H (acid) 2500- 3300 $cm^{-1}$

A computer will compare the IR spectra against a database of known pure compounds to identify the compound

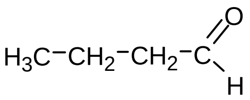
Use an IR absorption table provided in exam to deduce presence or absence of particular bonds or functional groups

| Bond | Wavenumber |
|---|---|
| C-O | 1000-1300 |
| C=O | 1640-1750 |
| C-H | 2850 -3100 |
| O-H<br>Carboxylic acids | 2500-3300<br>Very broad |
| N-H | 3200-3500 |
| O-H<br>Acohols, phenols | 3200- 3550<br>broad |

Use spectra to identify particular functional groups limited to data presented in wavenumber form e.g. an alcohol from an absorption peak of the O–H bond.



Spectra for butanal



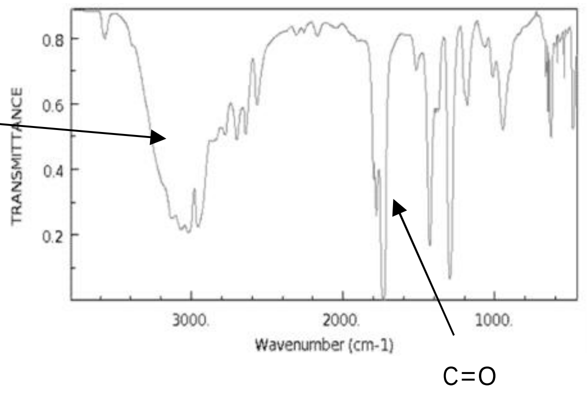
$H_3C-CH_2-CH_2-CHO$

Absorption or trough in between 1640-1750 $cm^{-1}$ range indicates presence of C=O bond

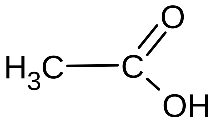
Always quote the wave number range from the data sheet

O-H absorptions tend to be broad

Absorption or trough in between 2500-3300 $cm^{-1}$ range indicates presence of O-H bond in an acid



Spectra for ethanoic acid



$H_3C-COOH$

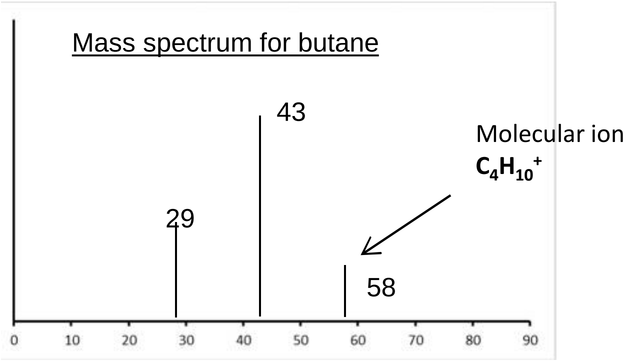
Modern breathalysers measure ethanol in the breath by analysis using infrared spectroscopy

## Mass spectrometry

### Measuring the $M_r$ of an organic molecule

If a molecule is put through a mass spectrometer it will often break up and give a series of peaks caused by the fragments. The peak with the largest m/z, however, will be due to the complete molecule and will be equal to the $M_r$ of the molecule. This peak is called the parent ion or **molecular ion.**

**Spectra for $C_4H_{10}$**



### Fragmentation

When organic molecules are passed through a mass spectrometer, it detects both the whole molecule and fragments of the molecule.

Molecular ion formed: $M \rightarrow [M]^{+\cdot} + e^-$

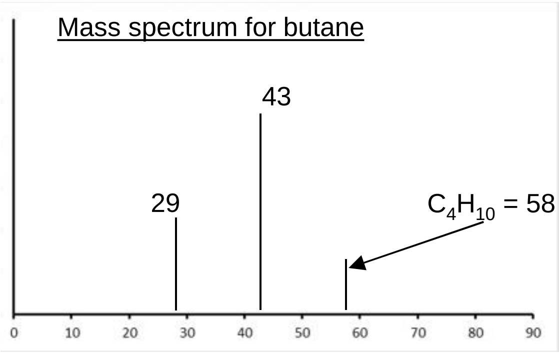
The molecule loses an electron and becomes both an ion and a free radical

Several peaks in the mass spectrum occur due to fragmentation.
The molecular ion fragments due to covalent bonds breaking: $[M]^{+\cdot} \rightarrow X^+ + Y^\cdot$

This process produces an ion and a free radical. The ion is responsible for the peak

Relatively stable ions such as carbocations $R^+$ such as $CH_3CH_2^+$ and acylium ions $[R\text{-}C{=}O]^+$ are common. The more stable the ion, the greater the peak intensity.

The peak with the highest mass/charge ratio will be normally due to the original molecule that hasn't fragmented (called the molecular ion) . As the charge of the ion is +1 the mass/ charge ratio is equal to $M$r.



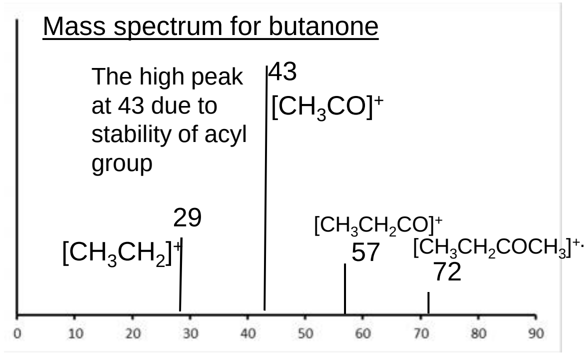
Equation for formation molecular ion

$C_4H_{10} \rightarrow [C_4H_{10}]^{+\cdot} + e^-$ m/z 58

Equations for formation of fragment ions from molecular ions

$[C_4H_{10}]^{+\cdot} \rightarrow [CH_3CH_2CH_2]^+ + \cdot CH_3$ m/z 43

$[C_4H_{10}]^{+\cdot} \rightarrow [CH_3CH_2]^+ + \cdot CH_2CH_3$ m/z 29



Equation for formation molecular ion

$CH_3CH_2COCH_3 \rightarrow [CH_3CH_2COCH_3]^{+\cdot} + e^-$ m/z 72

Equations for formation of fragment ions from molecular ions

$[CH_3CH_2COCH_3]^{+\cdot} \rightarrow [CH_3CH_2CO]^+ + \cdot CH_3$ m/z 57

$[CH_3CH_2COCH_3]^{+\cdot} \rightarrow [CH_3CO]^+ + \cdot CH_2CH_3$ m/z 43

$[CH_3CH_2COCH_3]^{+\cdot} \rightarrow [CH_3CH_2]^+ + \cdot COCH_3$ m/z 29

## 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 calculate molecular formula

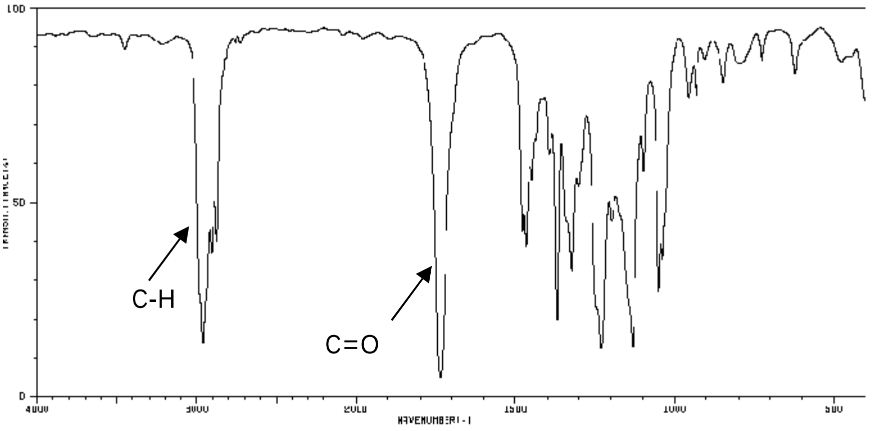
molecular ion peak m/z value= 144

*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

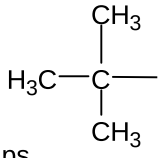


There is a C=O but no O-H absorptions, so must be an ester.

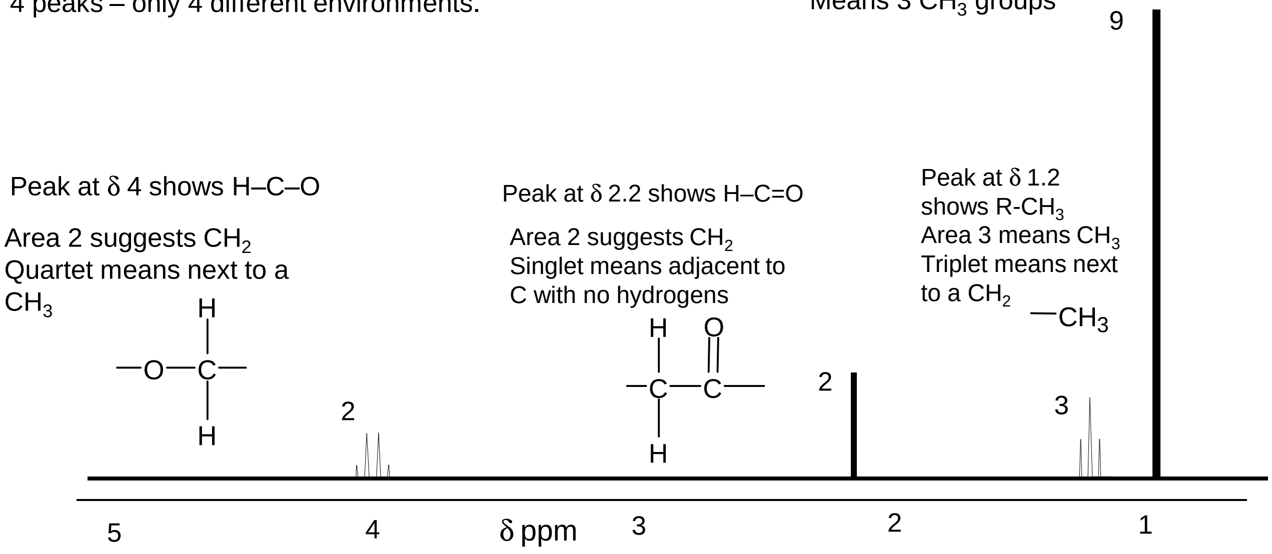
4. Use NMR spectra to give details of carbon chain

4 peaks – only 4 different environments.

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



$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-$



Peak at δ 4 shows H–C–O

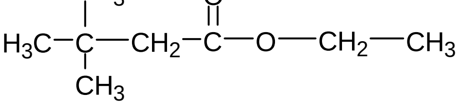
Area 2 suggests $CH_2$
Quartet means next to a $CH_3$

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 final structure



$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$