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

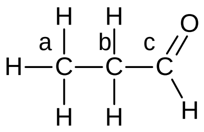
There are two main types of NMR

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

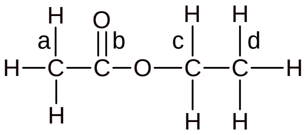
There is only around 1% C^{13} in organic molecules but modern NMR machines are sensitive enough to give a full spectra for C^{13}
The C^{13} spectra is a simpler spectrum than the H NMR

Equivalent Carbon atoms.

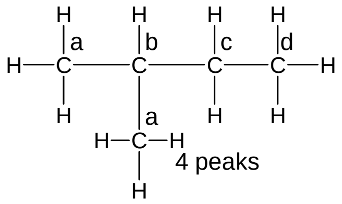
In a C^{13} NMR spectrum, there is one signal (peak) for each **set of equivalent C atoms.**



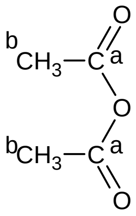
3 peaks



4 peaks

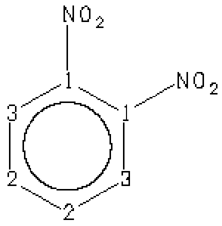


4 peaks



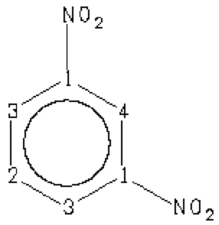
2 peaks

1,2 dinitrobenzene



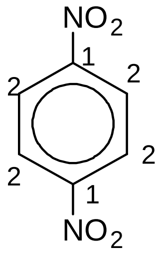
3 peaks

1,3 dinitrobenzene

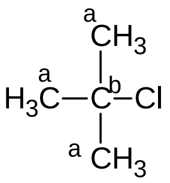


4 peaks

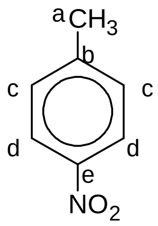
1,4 dinitrobenzene



2 peaks



2 peaks

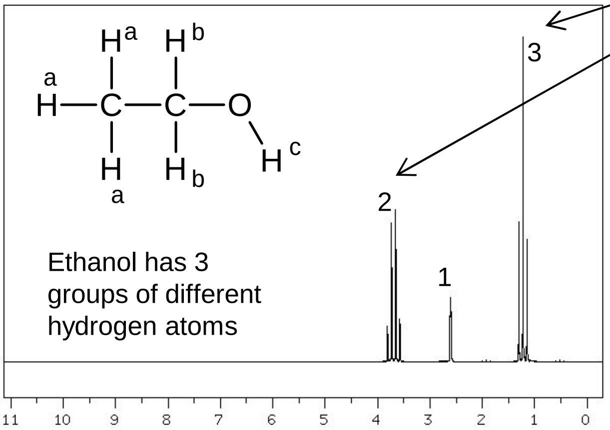


5 peaks

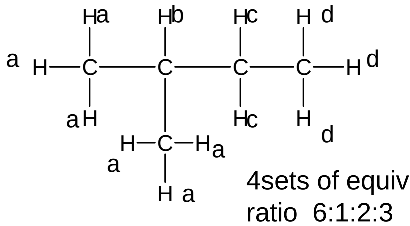
Equivalent Hydrogen atoms.

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

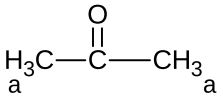
In addition the **intensity (integration value)** of each signal is proportional to the **number of equivalent H atoms** it represents.



Ethanol has 3 groups of different hydrogen atoms

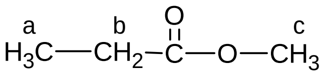


4sets of equivalent H's: ratio 6:1:2:3



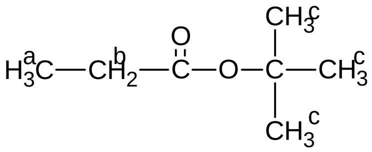
$\underset{a}{H_3C}-\overset{\overset{O}{\|}}{C}-\underset{a}{CH_3}$

1 signal



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

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

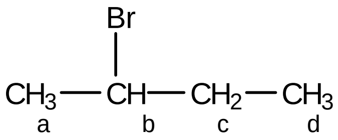


$\overset{a}{H_3C}-\overset{b}{CH_2}-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{c}{CH_3}}{\underset{\underset{c}{CH_3}}{C}}-\overset{c}{CH_3}$

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

$\overset{a}{H_3C}-\overset{b}{CH}=\overset{c}{CH_2}$

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



$\underset{a}{CH_3}-\overset{Br}{\underset{b}{CH}}-\underset{c}{CH_2}-\underset{d}{CH_3}$

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, $CDCl_3$.

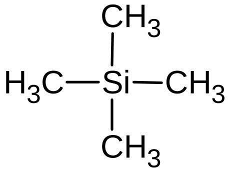
This means that in the H NMR the solvent will not give any peaks

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.

Calibration and shift

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

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



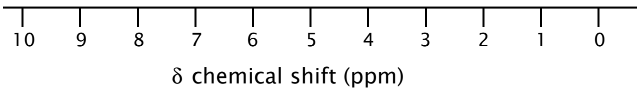
$H_3C-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$

tetramethylsilane

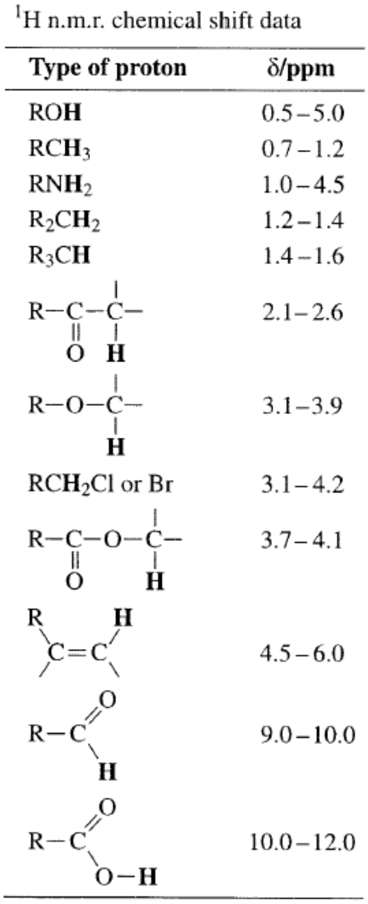
The same calibration compound is used for both H and C NMR

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

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.



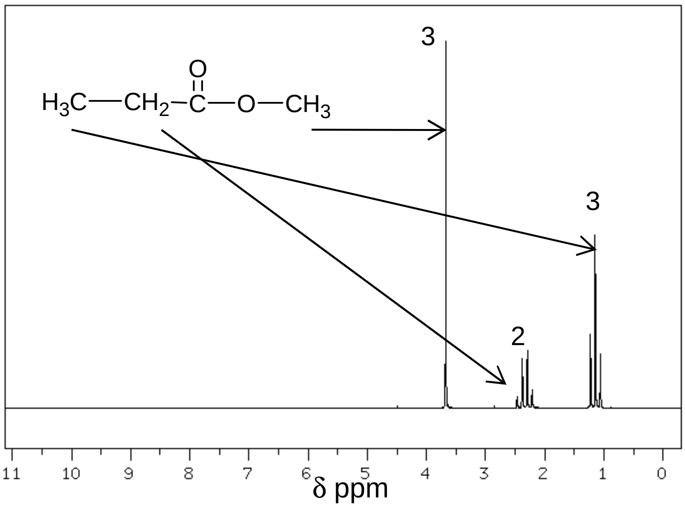
H NMR shift

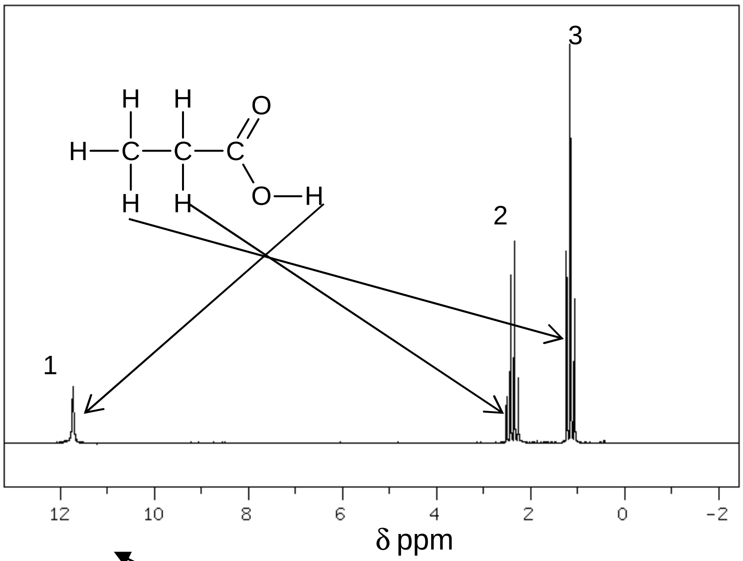


^{1}H n.m.r. chemical shift data

Type of proton	δ/ppm
ROH	0.5–5.0
RCH_3	0.7–1.2
RNH_2	1.0–4.5
R_2CH_2	1.2–1.4
R_3CH	1.4–1.6
$R-\underset{\displaystyle O}{\underset{\Vert}{C}}-\underset{\displaystyle H}{\underset{\vert}{\overset{\vert}{C}}}-$	2.1–2.6
$R-O-\underset{\displaystyle H}{\underset{\vert}{\overset{\vert}{C}}}-$	3.1–3.9
RCH_2Cl or Br	3.1–4.2
$R-\underset{\displaystyle O}{\underset{\Vert}{C}}-O-\underset{\displaystyle H}{\underset{\vert}{\overset{\vert}{C}}}-$	3.7–4.1
$R(\,)C=C(\,)H$	4.5–6.0
$R-C(=O)H$	9.0–10.0
$R-C(=O)O-H$	10.0–12.0

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



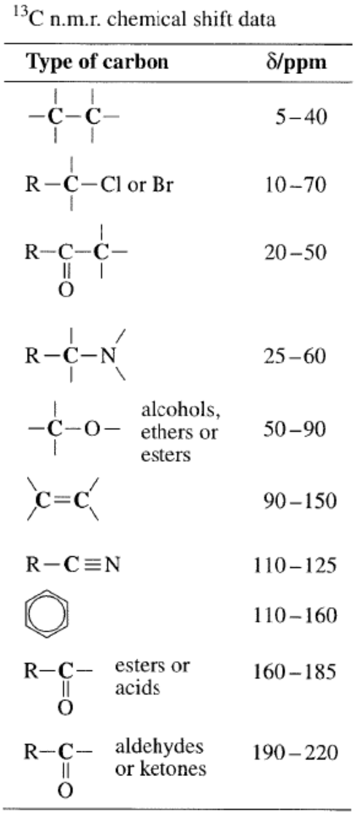


Proton exchange using D_2O

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.

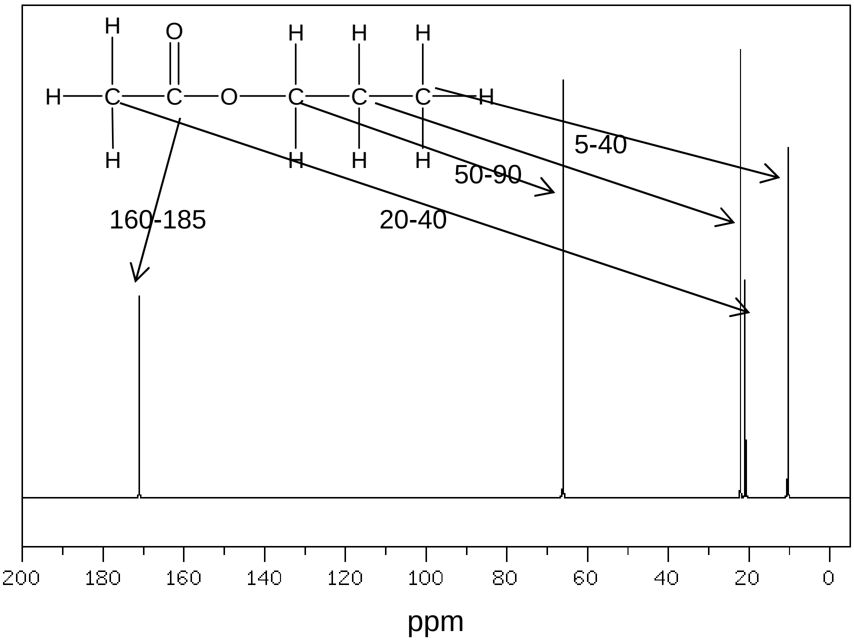
Addition of D_2O to the sample of Propanoic acid would make the peak at δ = 11.7 (ppm) in the above spectrum disappear

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



Type of carbon	δ/ppm
—C—C—	5–40
R—C—Cl or Br	10–70
R—C(=O)—C—	20–50
R—C—N	25–60
—C—O— alcohols, ethers or esters	50–90
C=C	90–150
R—C≡N	110–125
benzene ring	110–160
R—C(=O)— esters or acids	160–185
R—C(=O)— aldehydes or ketones	190–220

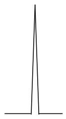
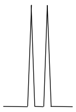
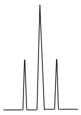
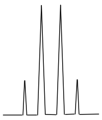
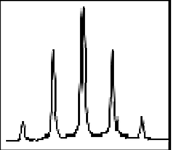
C^{13} NMR shift



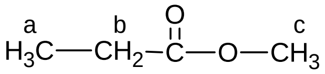
Spin-Spin coupling in H NMR

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!



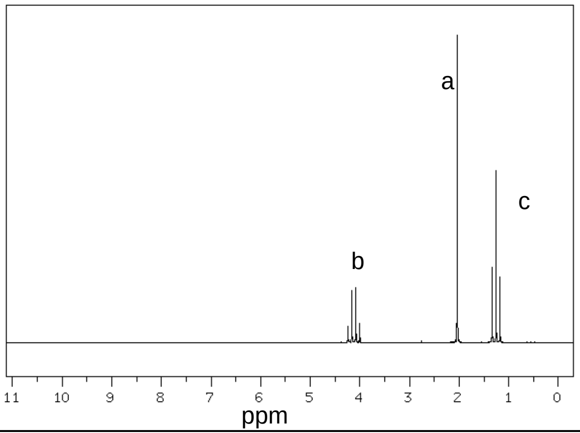
$\overset{a}{H_3C}-\overset{b}{CH_2}-\overset{O}{\overset{||}{C}}-O-\overset{c}{CH_3}$

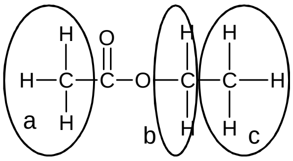
The peak due to group **a** will be a **triplet** as it is next to **b** (a carbon with 2 H's)

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

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

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

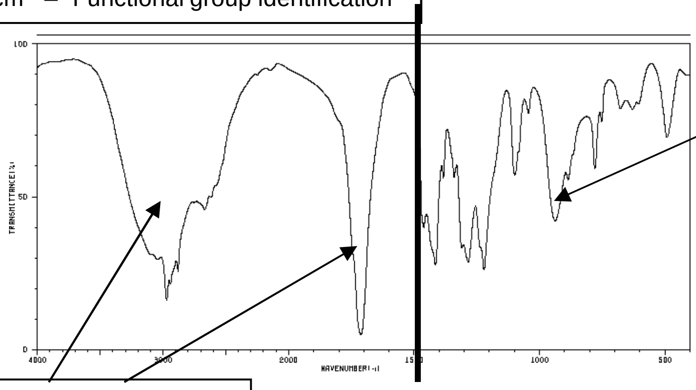
Infrared spectroscopy

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".

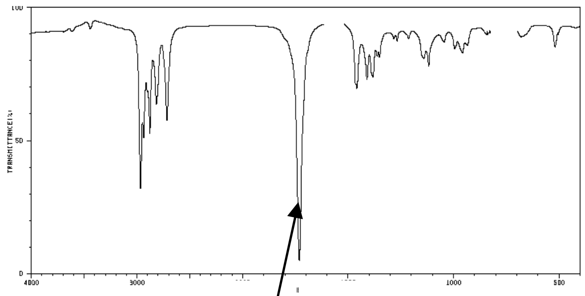
e.g. C=O 1640 – 1750 cm^{-1}
O-H (acid) 2500- 3300 cm^{-1}

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 <u>or</u> absence of particular bonds or functional groups

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

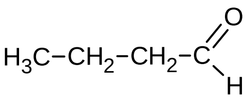
use spectra to identify particular functional groups limited to data presented in wavenumber form e.g. an alcohol from an absorption peak of the O–H bond,



2000 1500

C=O

Spectra for butanal

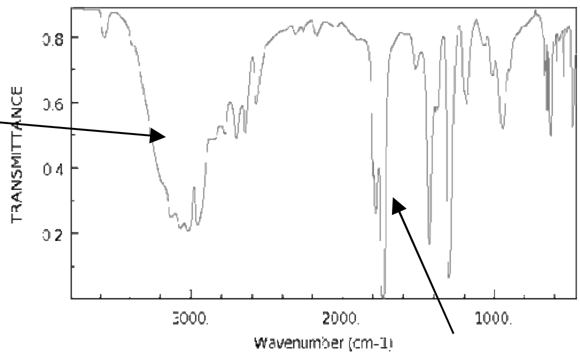


Absorption or trough in between 1640-1750 cm^{-1} range indicates presence of C=O bond

Always quote the wave number range from the data sheet

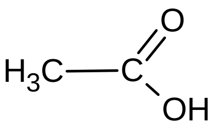
O-H absorptions tend to be broad

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



C=O

Spectra for ethanoic acid



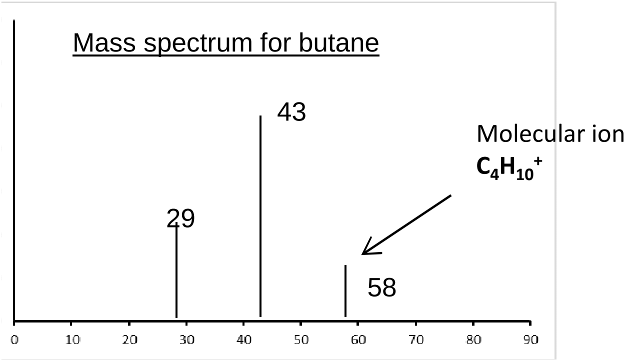
Modern breathalysers measure ethanol in the breath by analysis using infrared spectroscopy

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

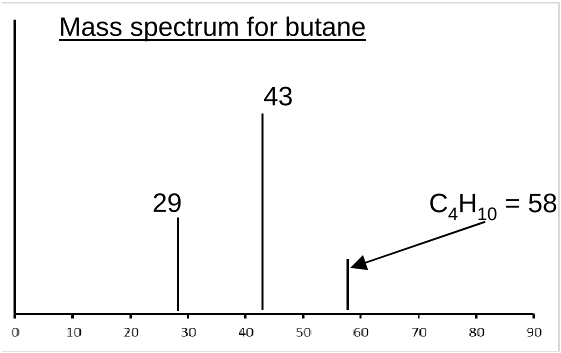
The molecule loses an electron and becomes both an ion and a free radical

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 Mr.



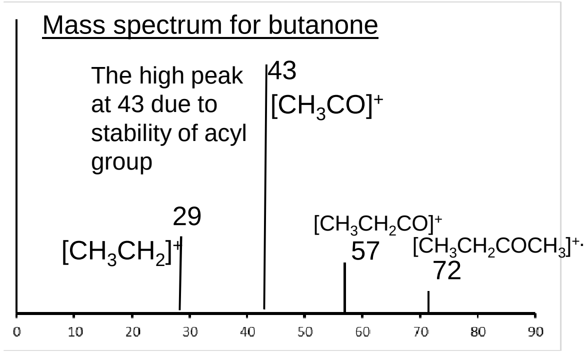
Equation for formation molecular ion

$C_4H_{10} \rightarrow [C_4H_{10}]^{+\cdot} + e^-$ 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

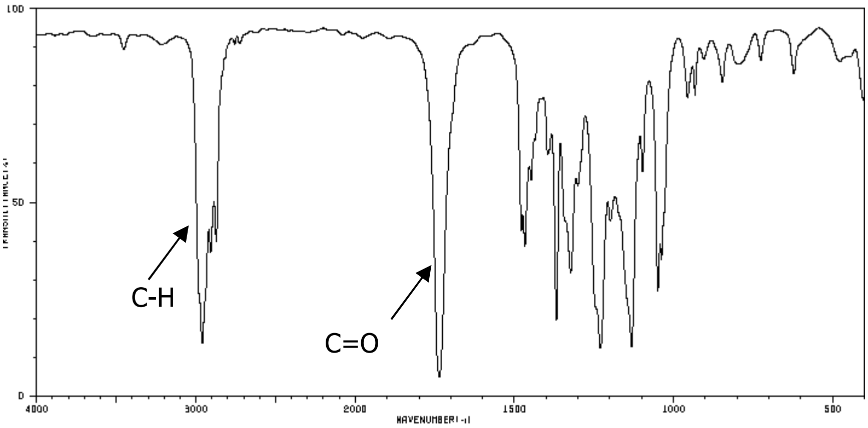
molecular ion peak m/z value= 144

Mr empirical formula C_4H_8O = 72

If Mr 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

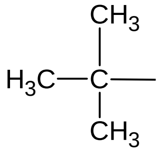


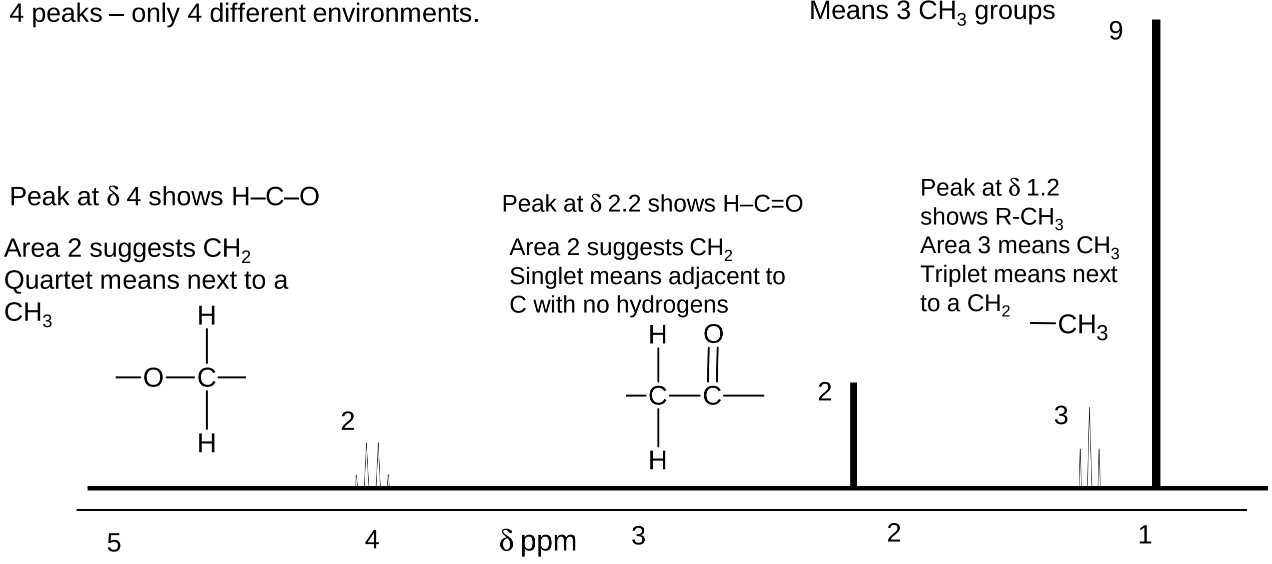
There is a C=O but no O-H absorptions, so must be an ester.

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





Peak at δ 4 shows H–C–O

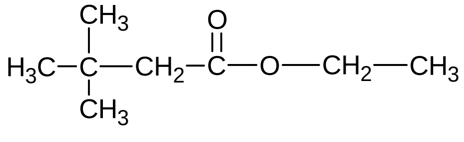
Area 2 suggests CH_2
Quartet means next to a CH_3

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



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