Topic 6 – Structure Determination
Revision Notes

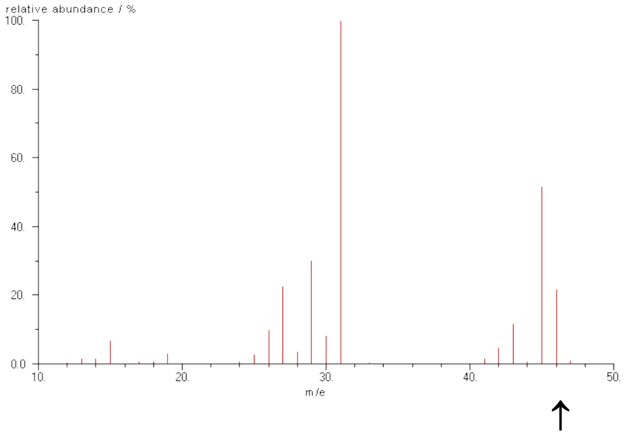
1) Introduction

- Mass spectrometry, infrared spectroscopy and NMR spectroscopy can be used to determine the structure of unknown compounds

2) Mass spectrometry

- In a mass spectrometer an electron is knocked off an organic molecule to create a molecular ion
- A molecular ion has a positive charge and a lone electron (it is a radical cation) and is represented as $M^{+\bullet}$
- The molecular ion produces the peak furthest to the right (or highest m/z) in the spectrum
- The mass of the molecular ion can be used to determine the molecular formula of an unknown compound

a) Example spectrum – ethanol



- The molar mass of ethanol is 46. The molecular ion peak is indicated by the arrow
- Compounds containing Cl or Br will produce two molecular ion peaks because of the two different isotopes of Cl and Br

b) Fragmentation

- The molecular ion is unstable and fragments to give a characteristic spectrum. One fragment will have a positive charge and the other fragment will have a lone electron. Only the positive ion will produce a peak in the spectrum
- Fragmentation equations have the general form

$$\mathbf{M^{+\bullet} \rightarrow X^{+} + Y^{\bullet}} \qquad (X^{+} \text{ will produce a peak but } Y^{\bullet} \text{ won't})$$

- More stable fragments give taller peaks e.g. CH_3^+ at m/z 15, CH_3CO^+ at m/z 43

c) Example question

The reaction of but-1-ene with chlorine produces 1,2-dichlorobutane, $C_4H_8Cl_2$

a) Given that chlorine exists as a mixture of two isotopes, ^{35}Cl and ^{37}Cl, predict the number of molecular ion peaks and their m/z values in the mass spectrum of $C_4H_8Cl_2$

Answer:
C_4H_8 has a mass of 56. Possible combinations of Cl are:
^{35}Cl and ^{35}Cl giving an m/z of 126
^{35}Cl and ^{37}Cl giving an m/z of 128
^{37}Cl and ^{37}Cl giving an m/z of 130

b) The mass spectrum of 1,2-dichlorobutane contains peaks at m/z = 77 and 79. Draw the structure of fragment ion which produces the peak at m/z = 77 and write an equation showing its formation from the molecular ion

Answer:
As these fragments differ in m/z by 2, it suggests the fragment contains one Cl atom. From the structure of the molecule, $CH_3CH_2CHClCH_2Cl$, if we lose the CH_2Cl from the end we get a fragment $CH_3CH_2CHCl^+$, which has a mass of 77 if it contains ^{35}Cl and a mass of 79 if it contains ^{37}Cl

The fragmentation equation is

$$[\mathbf{C_4H_8Cl_2}]^{+\bullet} \rightarrow [\mathbf{CH_3CH_2CHCl}]^{+} + [\mathbf{CH_2Cl}]^{\bullet}$$

Source: AQA Paper January 2006

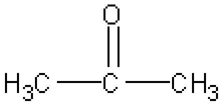
3) Infrared spectroscopy

- The bonds in organic molecules absorb certain frequencies of infrared radiation.
- The frequencies that are absorbed can be used to identify the presence of certain bonds.
- The absorptions you need to know are:

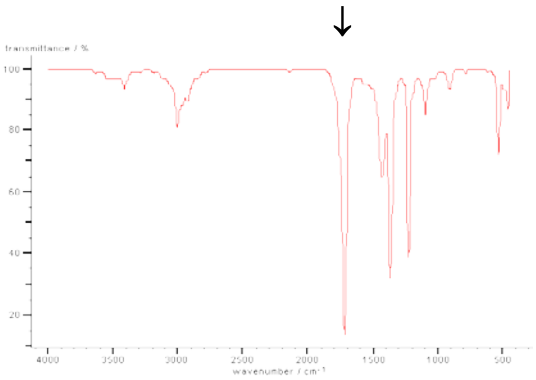
a)	C=O	1680 - 1750 cm^{-1}
b)	-OH in alcohols	3230 - 3550 cm^{-1}
c)	-OH in carboxylic acids	2500 - 3000 cm^{-1} (broad peak)
d)	C=C	1000 - 1300 cm^{-1}

- The region below 1500 cm^{-1} is called the fingerprint region. A molecule can be identified by finding an exact match in a database of spectra of known compounds

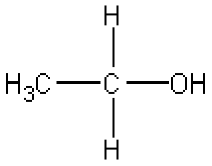
a) Example spectrum 1 – propanone



Of the absorptions mentioned above, only the C=O peak will be present in propanone's IR spectrum:

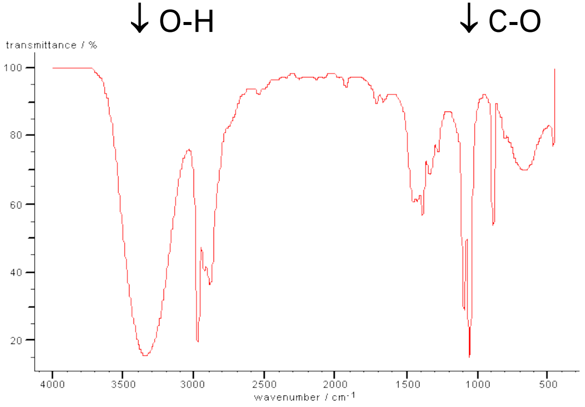


b) Example spectrum 2 – ethanol

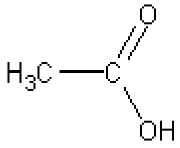


$$H_3C-\overset{H}{\underset{H}{C}}-OH$$

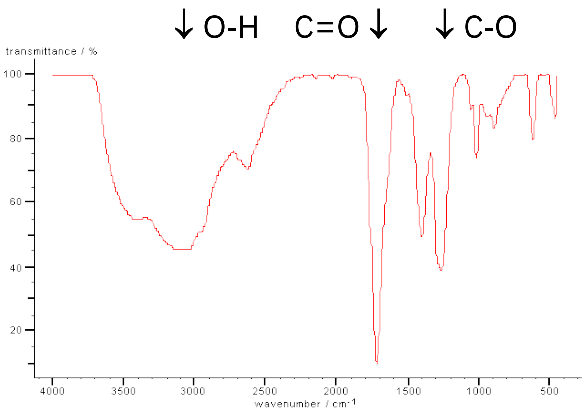
Of the absorptions mentioned above, the –OH in alcohols and the C-O peaks will be present in ethanol's IR spectrum:



c) Example spectrum 3 – Ethanoic acid



Of the peaks mentioned above, the –OH in acids, the C=O and the C-O peaks will be present in ethanol's IR spectrum:



3) NMR spectroscopy

- NMR spectroscopy provides information about carbons and hydrogens in organic molecules
- It only works on nuclei where the total of protons and neutrons is an odd number. The nuclei of relevance to us are ^{13}C and ^{1}H
- NMR spectra are obtained by dissolving a sample in a proton-free solvent, such as CCl_4 or $CDCl_3$
- A small amount of tetramethylsilane (TMS), $(CH_3)_4Si$, is added to each sample to act as a standard. TMS produces a single, intense peak that is upfield (to the right) of most other peaks. TMS is also inert, non-toxic and volatile

a) ^{13}C NMR

- The peaks in a ^{13}C NMR spectrum give the following information above the carbon atoms in an organic compound:
  - The number of peaks shows the number of different types of carbon atom
  - The ratio of the areas under the peaks gives the number of carbons of each type
  - The distance along the axis (chemical shift, δ) shows the environment of each type of carbon (see data sheet)
  - There is no splitting of peaks in ^{13}C NMR because of the low abundance of ^{13}C

b) ^{1}H NMR

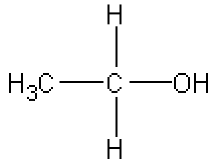
- The peaks in a ^{1}H NMR spectrum give the following information above the hydrogen atoms in an organic compound:
  - The number of peaks shows the number of different types of hydrogen atom
  - The ratio of the areas under the peaks gives the number of hydrogens of each type (shown by an integration trace)
  - The distance along the axis (chemical shift, δ) shows the environment of each type of proton (see data sheet)
  - The splitting pattern shows how many neighbouring protons there are

c) Peak splitting

1) A peak will be split if there are H's on the next C or O.
2) Splitting follows the 'n+1' rule
3) 1H splits an adjacent peak into two (a doublet), 2H's split an adjacent peak into three (a triplet) and 3H's split an adjacent peak into four (a quartet)
4) If splitting occurs from both sides a more complicated pattern is produced (a multiplet)

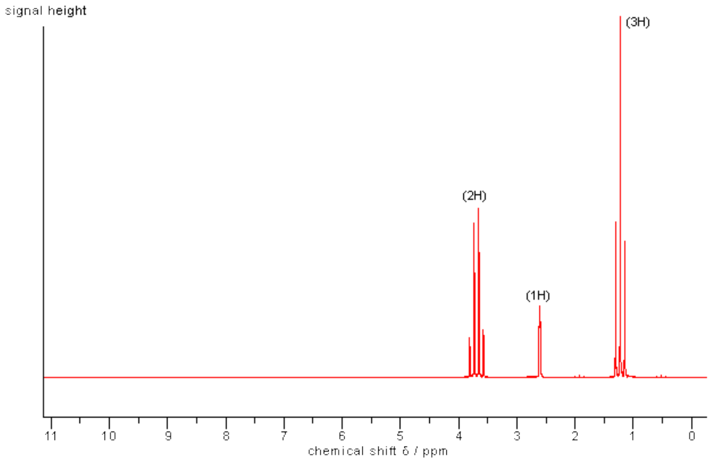
5) In a doublet, the ratio of the areas under the peaks is 1:1. In a triplet, the ratio of the areas under the peaks is 1:2:1. In a quartet, the ratio of the areas under the peaks is 1:3:3:1

d) Example spectrum – ethanol



H_3C-CH_2-OH

- Three different types of H so three peaks
- Size of peaks in ratio 3:2:1
- RCH_3 at δ 0.7-1.2, $ROCH_3$ at δ 3.1-3.9 and ROH at δ 0.5-5.0
- CH_3 peak split into triplet by 2Hs on next C
- CH_2 split into quartet by 3Hs on next C
- The OH peak is not split and does not split other peaks. Technically, this H is decoupled by fast proton exchange



e) Example question

Compound W is one of the isomers of $C_5H_{10}O_2$. The proton NMR spectrum of W shows 4 peaks. The table below gives the chemical shifts (δ values), for each of these peaks, together with their splitting patterns and integration values.

δ/ppm	2.18	2.59	3.33	3.64
Splitting pattern	singlet	triplet	singlet	triplet
Integration value	3	2	3	2

State what can be deduced about the structure of W from the presence of the following in its NMR spectrum.

(i) The singlet peak at δ = 2.18

Answer: From δ value must be $RCOCH_3$ and this fits with integration value and lack of splitting

(ii) The singlet peak at $\delta = 3.33$

Answer: From δ value must be $ROCH_3$ and this fits with integration value and lack of splitting

(iii) Two triplet peaks

Answer: For two triplets need $–CH_2CH_2–$ with no other splitting

(iv) Hence, deduce the structure of W

Answer: Putting the answers together gives $CH_3COCH_2CH_2OCH_3$

Source: AQA Paper June 2005