4.2.4 Modern Analytical Techniques

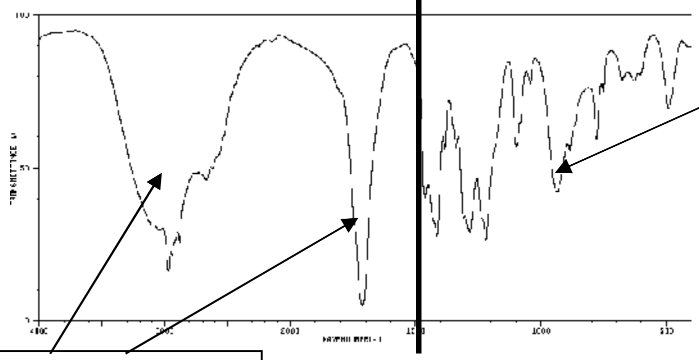
Infrared spectroscopy

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".

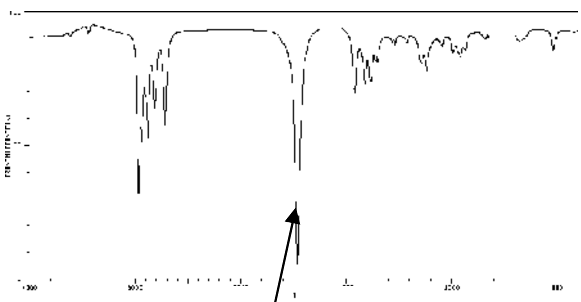
e.g. C=O 1640 - 1750 cm^{-1}
O-H (acid) 2500 - 3300 cm^{-1}

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	Wavenumbe r
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 Alcohols, phenols	3200- 3550 broad

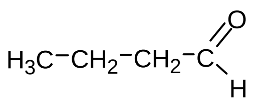
Use spectra to identify particular functional groups limited to data presented in wavenumber form e.g. an alcohol from an absorption peak of the O–H bond.



2000 1500

C=O

Spectra for butanal

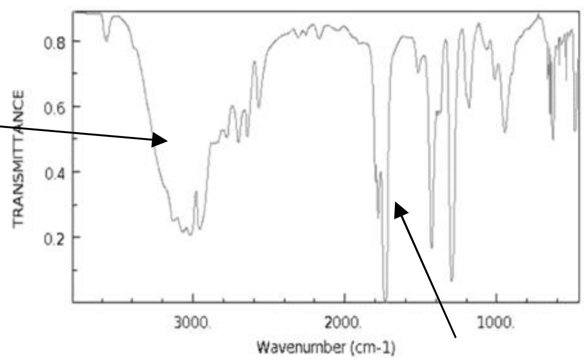


Absorption or trough in between 1640-1750 cm^{-1} range indicates presence of C=O bond.

Always quote the wave number range from the data sheet

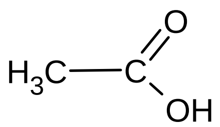
O-H absorptions tend to be broad

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



The 'Greenhouse Effect'

- Carbon dioxide (CO_2), methane (CH_4) and water vapour (H_2O) are all greenhouse gases. (They trap the Earth's radiated infra red energy in the atmosphere).
- Water is the main greenhouse gas (but is natural), followed by carbon dioxide and methane.

Infrared radiation is absorbed by C=O, O–H and C–H bonds in H_2O, CO_2 and CH_4.
These absorptions contribute to global warming

The 'Greenhouse Effect' of a given gas is dependent both on its **atmospheric concentration** and its **ability to absorb infrared radiation** and also its **residence time.** (Time it stays in atmosphere)

Concentrations of carbon dioxide in the atmosphere have risen significantly in recent years due to increasing burning of fossil fuels. Carbon dioxide is a particularly effective greenhouse gas and its increase is thought to be largely responsible for global warming.

The Earth is thought to be getting warmer, and many scientists believe it is due to increasing amounts of greenhouse gases in the atmosphere.

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

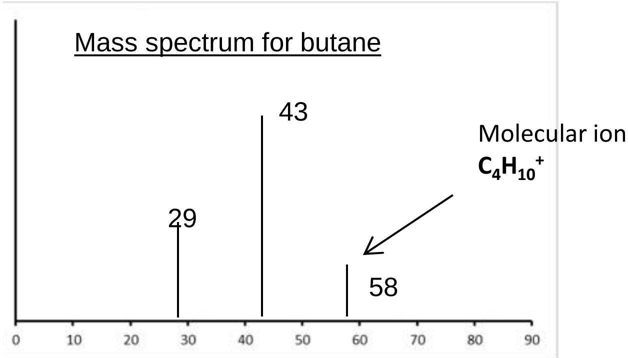
Infrared spectroscopy can be used to monitor gases causing air pollution (e.g. CO and NO from car emissions)

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 → $[M]^{+\cdot}$ + e^-

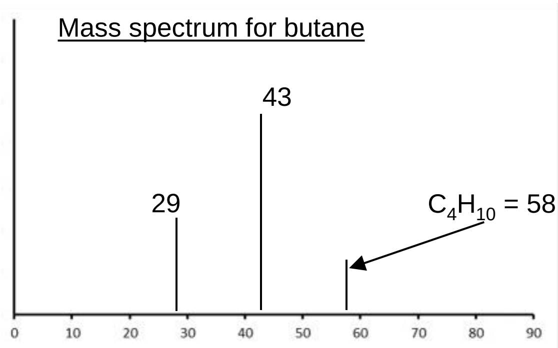
The molecule loses an electron and becomes both an ion and a free radical

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.



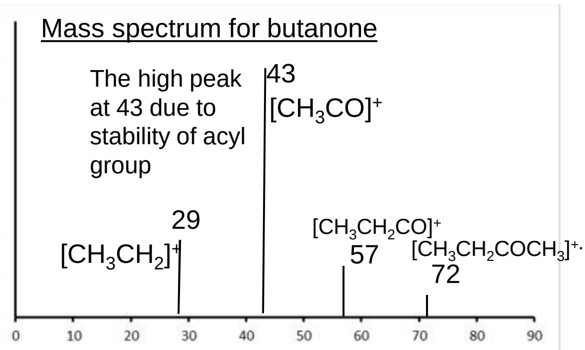
Equation for formation molecular ion

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

A mass spectrum is essentially a fingerprint for the molecule that can be identified by computer using a spectral database.