

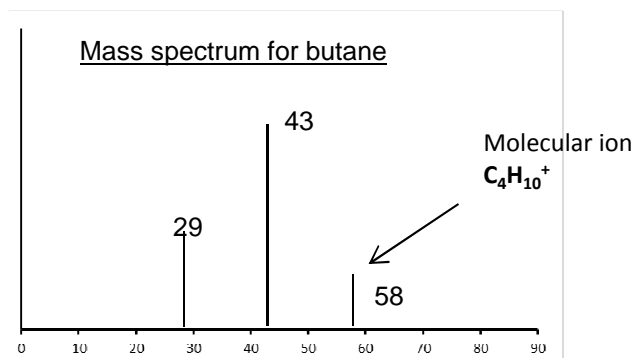
8. Mass spectra and IR

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.



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

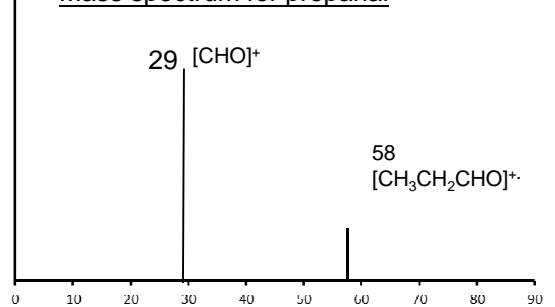
Several peaks in the mass spectrum occur due to fragmentation. The Molecular ion fragments due to covalent bonds breaking: $[M]^+ \rightarrow X^+ + Y\cdot$

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

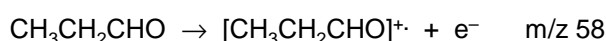
Relatively stable ions such as carbocations R^+ such as $CH_3CH_2^+$ and acylium ions $[R-C=O]^+$ are common. The more stable the ion, the greater the peak intensity.

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 .

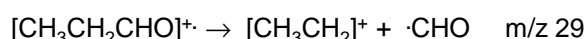
Mass spectrum for propanal



Equation for formation molecular ion



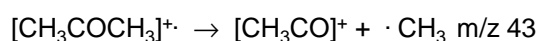
Equations for formation of fragment ions from molecular ions



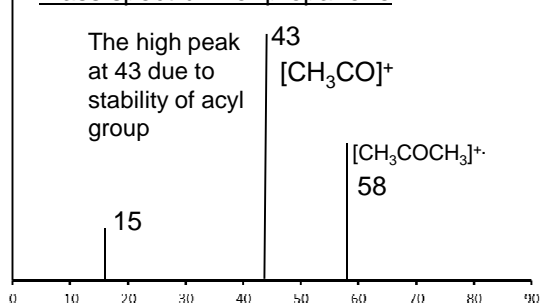
Equation for formation molecular ion



Equations for formation of fragment ions from molecular ions



Mass spectrum for propanone



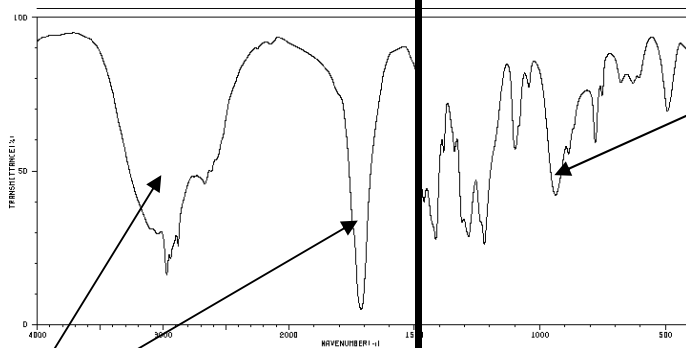
It is not possible for propanone to fragment to give a peak at 29 so the fragmentation patterns can distinguish between the structural isomers of propanone and propanal

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”.

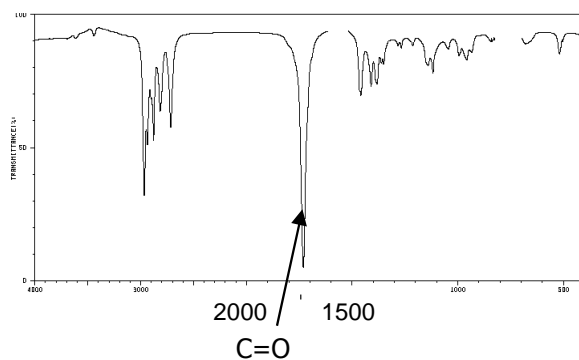
e.g. C=O 1640 – 1750 cm^{-1}
O-H (acid) 2500- 3300 cm^{-1}

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

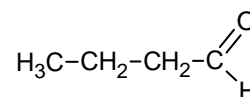
Use an IR absorption table provided in exam to deduce presence or absence of particular bonds or functional groups

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

Use spectra to identify particular functional groups e.g. an alcohol from an absorption peak of the O–H bond, or C=O stretching absorption in aldehydes and ketones

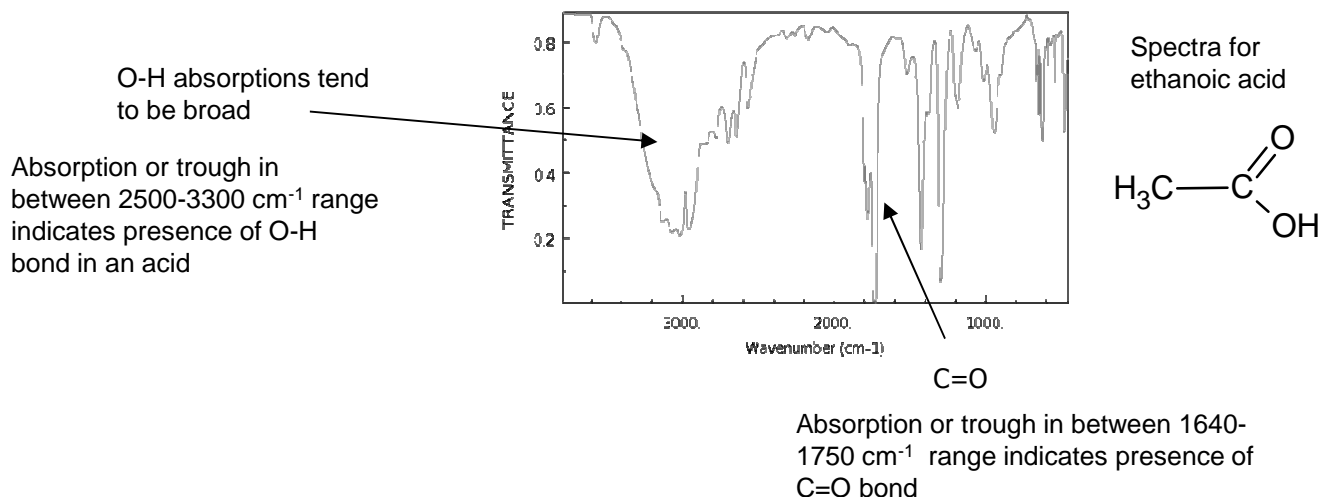


Spectra for butanal



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



Molecules which change their polarity as they vibrate can absorb infrared radiation. E.g. C-H, C=O, O-H

Molecules such as H_2 , O_2 and N_2 cannot change their polarity as they vibrate so can absorb infrared radiation and don't register on an infra red spectrum

The absorption of infra-red radiation by bonds in this type of spectroscopy is the same absorption that bonds in CO_2 , methane and water vapour in the atmosphere do that cause them to be greenhouse gases.

H_2O , CO_2 , CH_4 and NO molecules absorb IR radiation and are greenhouse gases, whilst O_2 and N_2 are not.