Topic 3

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Blackman, Bottle, Schmid, Mocerino and Wille,
***Chemistry*, 2012 (John Wiley)**
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Determination of Structure

This Lecture

- Mass spectrometry and molecular mass
- Structural information from mass spectrometry
- IR & UV-visible spectroscopy
- Introduction to nuclear magnetic resonance (NMR) spectroscopy

Determination of structure

There are a number of stages involved with the identification of an unknown compound

- Isolate and purify the compound
- Determine the elements present and the empirical formula
- Determine the molecular formula
- Identify the functional groups present (infrared spectroscopy)
- Assemble the structural formula of the molecule with the correct constitution (bond connectivity) and stereochemistry (shape)

Isolation and purification

By chemical means…

- Acid – base separations

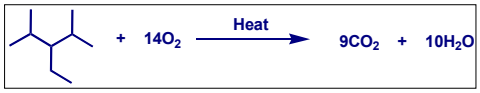
By physical means…

- Precipitation
- Recrystallisation
- Distillation
- Chromatography

Empirical Formula

For organic compounds: combustion analysis

– React with O_2 and measure how much CO_2 & H_2O released



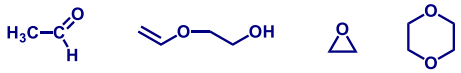
- Carbon and hydrogen always present
- If N, S, P, halogens present, measure other byproducts
- Can't measure O easily, so oxygen assumed to make up the difference to 100%.

⇒ Work out percentage composition

Molecular Formula

- An empirical formula of C_2H_4O means a C:H:O ratio of 2:4:1
- Of limited use: could be many things:

Such as …

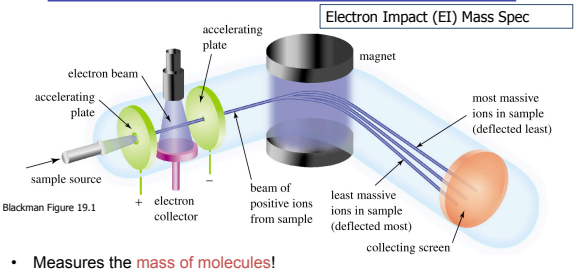


- Their Molecular masses and molecular formulae are different
- To determine molecular formula, we need a molecular mass

Mass spectrometry leads us to the molecular mass

Inside a Mass Spectrometer

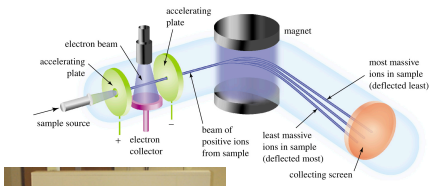
Electron Impact (EI) Mass Spec



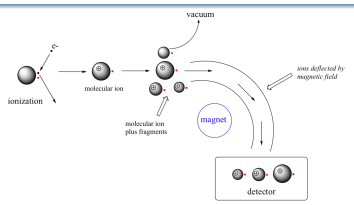
Blackman Figure 19.1

- Measures the mass of molecules!
  - Molecules are ionised by impact with electron in high vacuum (i.e. turned into charged species – ions)
  - Some ions fragment to form smaller ions (*daughter ions*)
  - These ions are then accelerated through an electric field

Inside a Mass Spectrometer



Inside a Mass Spectrometer



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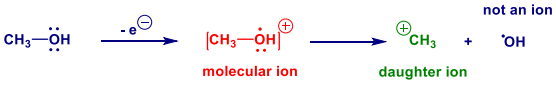
http://bit.ly/1DclQXS

- Ions are separated according to **m/z** (mass/charge)
  - Beam of ions directed into magnetic field, causing ions to bend
  - They trace out circular paths, with radii dependant on **m** and **z** … but charge (z) is almost always 1
  - Detector measures how far ions have bent, so can work out **m**

Mass Spectrometry

- The heaviest ion possible is the **molecular ion**
  - results from loss of one electron from the parent molecule
  - an electron is so light that the mass of the molecular ion is same as parent molecule (CH_3OH)
- Fragmentation may occur to give **daughter ions**
  - these can help us determine the structure of the molecule



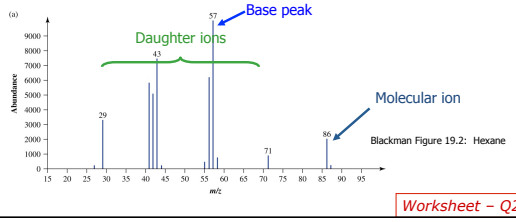
- A typical mass spectrum has a molecular ion and many daughter ions
  - the most intense signal is called the **base peak**, and its intensity is set to 100%

Worksheet – Q1

A typical mass spectrum

Features

- The molecular ion
- Many daughter ions
- The base peak is the most intense signal and is set at 100%



Blackman Figure 19.2: Hexane

Worksheet – Q2

Influence of Isotopes

Each ion recorded in the mass spectrum registers the **specific isotopes** of the elements present

- Many elements have only one isotope of high abundance
- Some elements have more than one abundant isotope

e.g. ^{79}Br 51 % : ^{81}Br 49 %
^{35}Cl 75 % : ^{37}Cl 25 %

- So any sample of bromobenzene contains near equal amounts of $C_6H_5{}^{79}Br$ and $C_6H_5{}^{81}Br$ ⇒ see *two* molecular ion peaks

Remember: isotopes have different numbers of neutrons
… so they have different atomic masses eg ^{13}C vs ^{12}C

Worksheet – Q3

High resolution mass spectrometry

- If we have no empirical formula it is difficult to assign a molecular formula to a molecular ion
  - Eg a molecular ion at m/z = 72 could be C_4H_8O, $C_3H_4O_2$ or $C_3H_8N_2$
- The mass of the major isotopes of each element is known to high accuracy

isotope	atomic mass
^{12}C	12.0000
^{1}H	1.0078
^{14}N	14.0031
^{16}O	15.9949

High resolution mass spectrometry

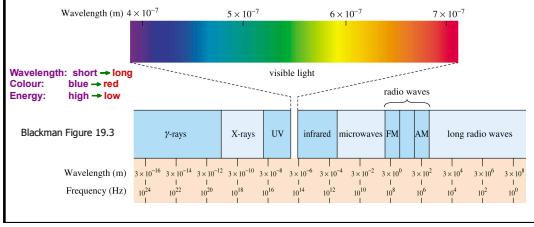
- The different possibilities may be distinguished using high resolution mass spectrometry

Molecular formula	$M^{+\bullet}$ (low resolution)	$M^{+\bullet}$ (high resolution)
C_4H_8O	72	72.0573
$C_3H_4O_2$	72	72.0210
$C_3H_8N_2$	72	72.0686

Worksheet – Q4

Spectroscopy

- Spectroscopy involves absorption of some part of the electromagnetic spectrum
- This is associated with the a change of energy level occupancy within the molecule
- The light absorbed is related to the process involved



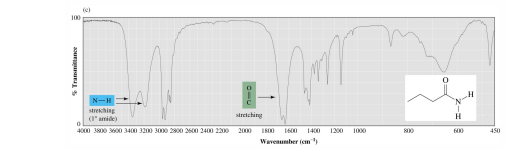
Blackman Figure 19.3

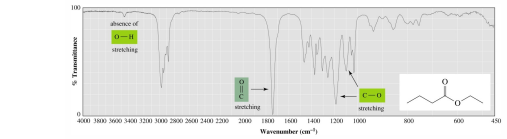
IR spectroscopy

- Absorption of infrared light is associated with excitation of bond vibrations
- An IR spectrum can:
  - Indicate the functional group present
  - 'Fingerprint' the molecule

Bonds	IR absorption (cm^{-1})	
N-H O-H (broad)	~3300	Amines, amides, alcohols, phenols, carboxylic acids
C-H	~3000	
C≡C C≡N	~2200	
C=O	~1700	Ketones, aldehydes, esters, amides, carboxylic acids
C=C	~1600	

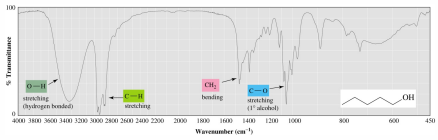
IR

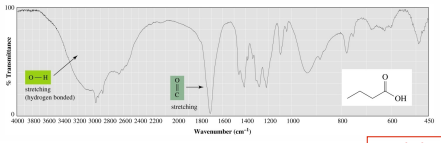




Blackman Figure 19.16 & 19.17

IR



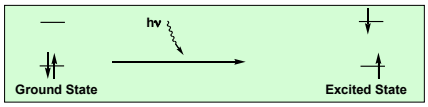


Blackman Figure 19.10 & 19.15

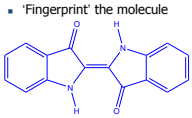
Worksheet – Q5

UV-visible spectroscopy

- Absorption of ultra violet or visible light is associated with excitation of electrons from one molecular orbital to another



- An UV-visible spectrum can:
  - Indicate the presence of conjugation
  - 'Fingerprint' the molecule

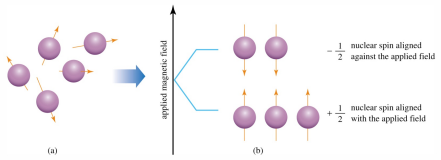


Indigo absorbs light in the visible part of the spectrum and so appears coloured:

Worksheet – Q6

Nuclear Magnetic Resonance (NMR) Spectroscopy

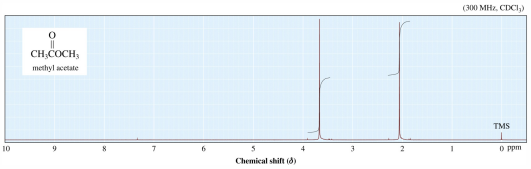
- The nuclei of some isotopes (e.g. ^{1}H, ^{13}C) absorb electromagnetic radiation in the radiofrequency (Rf) region when placed in a strong magnetic field



Blackman Figure 19.18

NMR - No of hydrogen environments

- The number of signals in an NMR spectrum corresponds to the number of distinct types of hydrogen atoms in a molecule

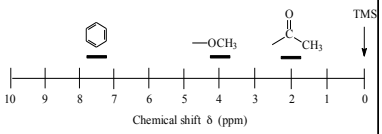


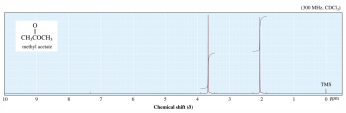
Blackman Figure 19.21

Worksheet – Q7, 8 & 9

NMR - Type of hydrogen environments

- The frequency axis (δ scale) is calibrated in parts per million (ppm)
- A reference compound, TMS, $(CH_3)_4Si$, taken as δ = 0.00 ppm
- The frequency difference between a signal arising from a sample and the TMS signal is called the *chemical shift*



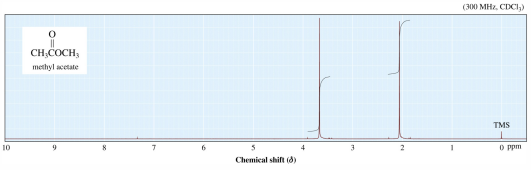


Blackman Figure 19.21

Worksheet – Q10 & 11

NMR - No of Hs of each type

- The *relative intensities* of the signals is proportional to the number of hydrogen atoms which give rise to the signal

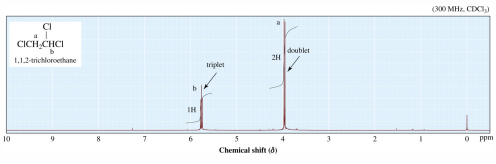


Blackman Figure 19.21

Worksheet – Q12 & 13

NMR - Multiplicity of signal

- Fine structure (*splitting* or *multiplicity*) arises from the hydrogen atoms attached to the neighbouring carbon atoms
- If a hydrogen atom has *"n"* equivalent hydrogen atoms on adjacent carbon atoms, its NMR resonance will appear as a signal which is split into *"n+1"* lines - this is called *the n+1 rule*.



Blackman Figure 19.26

Worksheet – Q14

NMR - Multiplicity of signal

splitting is due to the presence of hydrogen atoms on adjacent carbon atoms

number of neighbouring hydrogen atoms (*n*)	signal multiplicity (no of peaks)	name of signal
0	1	singlet
1	2	doublet
2	3	triplet
3	4	quartet
4	5	quintet

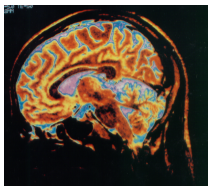
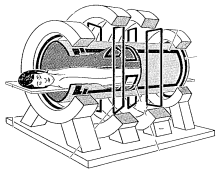
NMR Spectroscopy - Recap

Information	Observation
No. of H environments	No of signals
Type of H environment	Position of signal
No of H of each type	Size of signal
No of adjacent H	Multiplicity of signal

Worksheet – Q15 & 16

NMR (MRI) spectroscopy

- The technique is used in imaging of soft tissue in animals as well as analysis and structure determination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