ANALYTICAL METHODS IN CHEMISTRY

COMBUSTION ANALYSIS

The organic compound is burned in Oxygen and the product gases separated. The gases produced depend on the elements present in the original compound e.g.

Element	**Product of combustion**
C	CO_2
H	H_2O
S	SO_2
N	N_2

PROBLEM

When a sample of an unknown hydrocarbon was burned in Oxygen the following gases were obtained:

Carbon dioxide	5.5440g
Water	0.8100g

Calculate the empirical formula of the hydrocarbon.

ANSWER:

Number of moles of CO_2 = $\frac{5.5440}{44}$

= 0.1260 moles

=> Number of moles of C = $\underline{0.1260 \text{ moles}}$

Number of moles of H_2O = $\frac{0.8100}{18}$

= 0.0450 moles

=> Number of moles of H = $\underline{0.0900 \text{ moles}}$

=> Ratio C : H = 0.1260 : 0.0900

= 1.4 : 1

= 14 : 10

=> Empirical formula is $C_{14}H_{10}$

Combustion analysis has certain limitations:

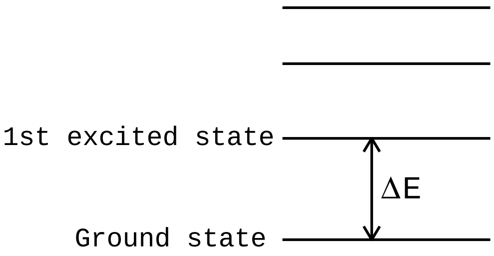
- It produces empirical, rather than molecular, formulae
- It cannot detect Oxygen

Combustion analysis is therefore usually used alongside other methods of analysis.

Infra Red Spectroscopy

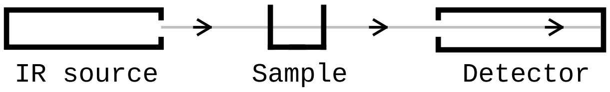
The vibrational energy of a chemical bond is quantised - it can have only certain values of energy. Most vibrating bonds are in the ground state.

Infra Red radiation contains photons of the correct energy to promote a ground state vibrating bond into its first excited state. The energy required, ΔE, depends on the type of bond and groups attached to it.



In H-Cl this energy is 5.73×10^{-20} Joules per molecule.
IR radiation of this energy would therefore promote a ground state vibrating H-Cl bond into its first excited state. We can calculate the wavenumber of this radiation - it is 2883 cm^{-1} (Check this!)

In the Infra Red spectrometer, IR radiation of varying wavenumber (dropping from 4000 to 700 cm^{-1}) is passed into the sample. The intensity of the radiation passing through the sample is measured using an infra red detector:

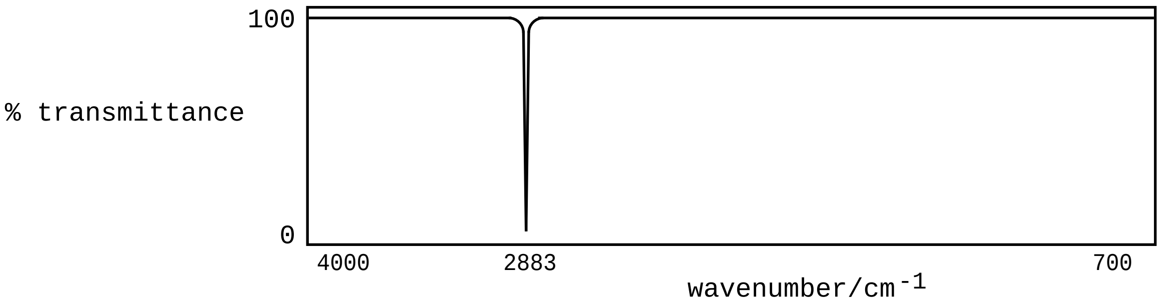


Let us suppose that the sample contains H-Cl gas.

When the wavenumber reaches 2883 cm^{-1}, it contains photons of exactly the right energy to promote a ground state vibrating H-Cl bond into its first excited state. The radiation is used up and does not pass through the sample. The detector records a drop in the radiation transmitted.

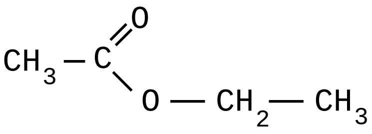
Wavenumbers above and below 2883 cm^{-1} contain photons of the wrong energy to excite the vibration and this radiation is not absorbed by the sample. The detector records 100% transmittance.

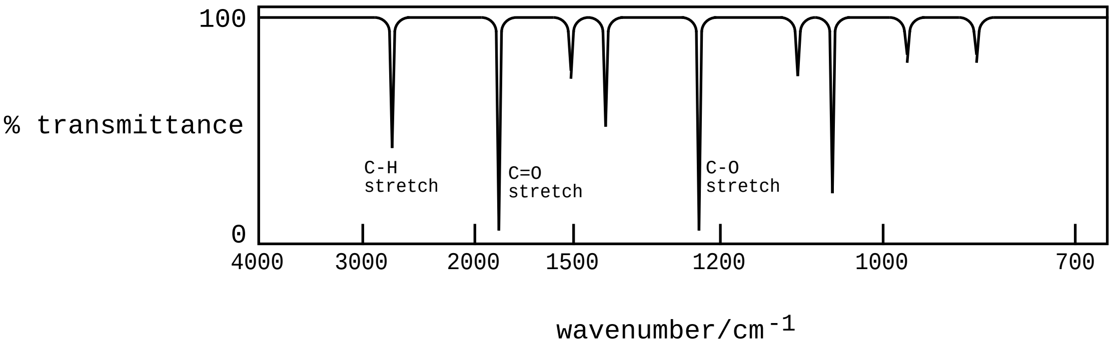
The spectrometer presents this result as a graph called an 'Infra Red Spectrum':



As each bond has its own characteristic absorption wavenumber (see SQA Data Booklet), Infra Red spectroscopy can be used to identify certain functional groups in an organic molecule.

Example: Infra Red spectrum of Ethyl ethanoate





MASS SPECTROSCOPY

The mass spectrometer is an instrument which can be used to determine the accurate formula mass and structural features of an organic compound.

Before considering the analysis of molecules we shall investigate how the instrument works by analysing a mixture of gaseous Chlorine atoms. This consists of 75% ^{35}Cl and 25% ^{37}Cl.

- The gaseous sample is injected into an ionisation chamber. (Solid or liquid samples are vaporised first).

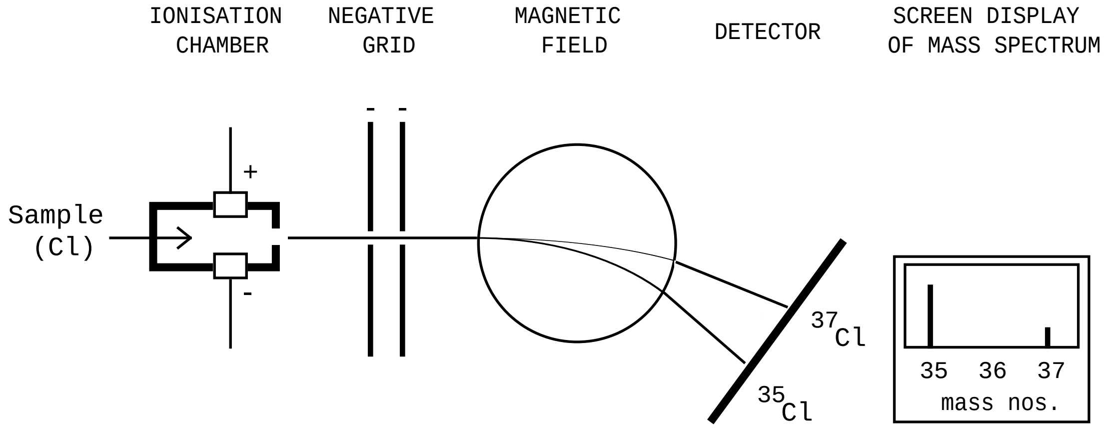
- In the ionisation chamber the sample is bombarded with electrons. Positive ions are formed:

  $Cl + e \rightarrow Cl^{+} + 2e$

  $Cl^{+} + e \rightarrow Cl^{2+} + 2e$

  etc

- The positive ions are accelerated through a series of negative slits.



- The positive ions are then deflected by a magnetic field.

  The lower the mass (m) the greater the deflection.
  The ^{35}Cl isotope in our sample will be deflected more than the ^{37}Cl isotope.

  The greater the charge (e) the greater the deflection.
  A Cl^{2+} ion would be deflected more than a Cl^{+} ion.

  The degree of deflection is thus proportional to e/m.

  Most of the ions created are 1+ so we will not consider multiply-charged ions any further.

- The mass of each ion is drawn as a peak on the mass spectrum produced.

  The area under the peak is proportional to the quantity of each ion present so the peaks in our Chlorine sample are in the ratio 75% ^{35}Cl : 25% ^{37}Cl or 3:1.

MASS SPECTROSCOPY OF MOLECULES

Mass spectroscopic analysis of molecules differs from single atoms in one respect only: **fragmentation** occurs in the ionisation chamber.

Usually the energy available in the ionisation chamber is more than sufficient to ionise the molecules. The excess energy breaks the molecules down into a complex mixture of ions including the parent ion.

Mass spectrum of Chloromethane CH_3Cl

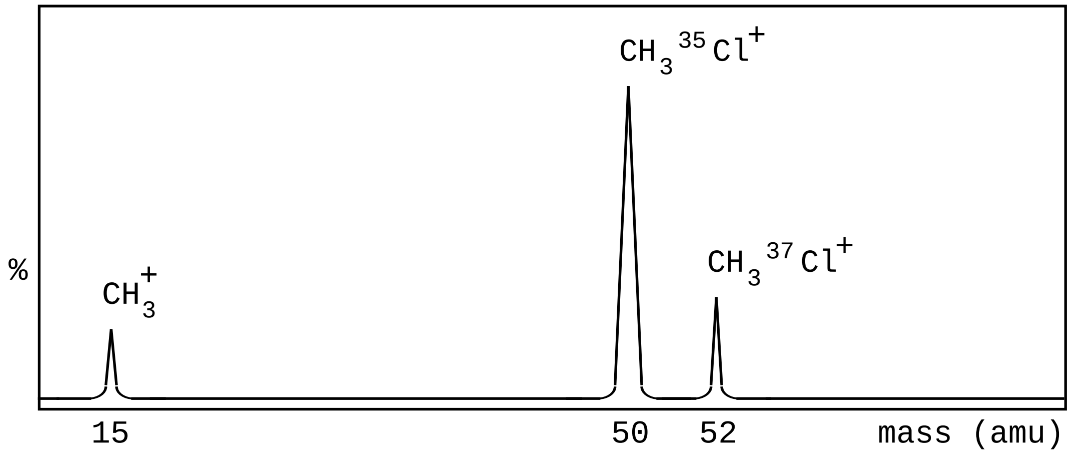
Ionisation of the CH_3Cl occurs in the ionisation chamber:

$CH_3Cl + e \rightarrow CH_3Cl^+ + 2e$

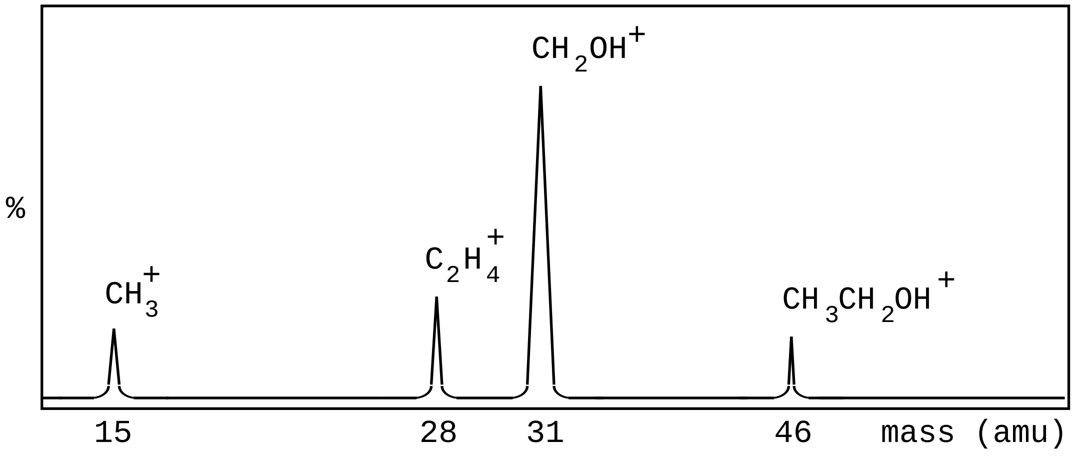
The ion then fragments in the ionisation chamber:

$CH_3Cl^+ \rightarrow CH_3^+ + Cl$

The mass spectrum therefore contains peaks due to CH_3Cl^+ and CH_3^+. Notice that the mass spectrum is further complicated by peaks due to the presence of isotopes in the molecule.



Mass spectrum of Ethanol C_2H_5OH



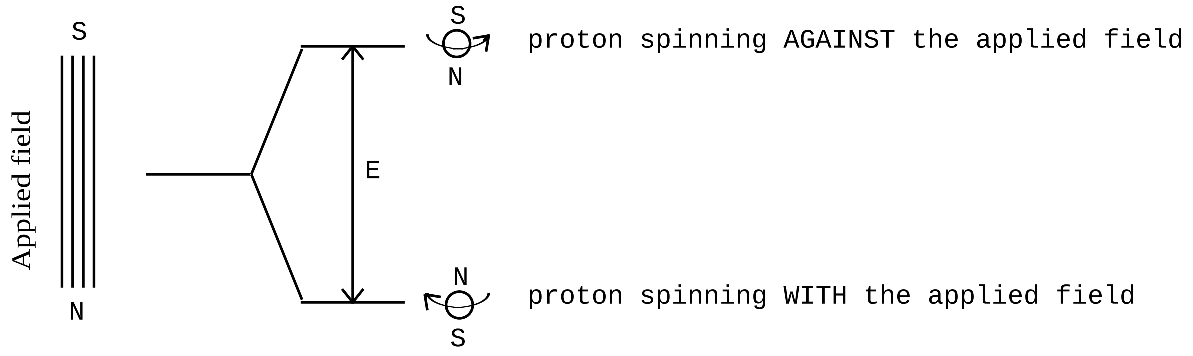
Note the appearance of $C_2H_4^+$ fragment at mass 28.
This is due to dehydration of $C_2H_5OH^+$ in the ionisation chamber:

$C_2H_5OH^+ \rightarrow C_2H_4^+ + H_2O$

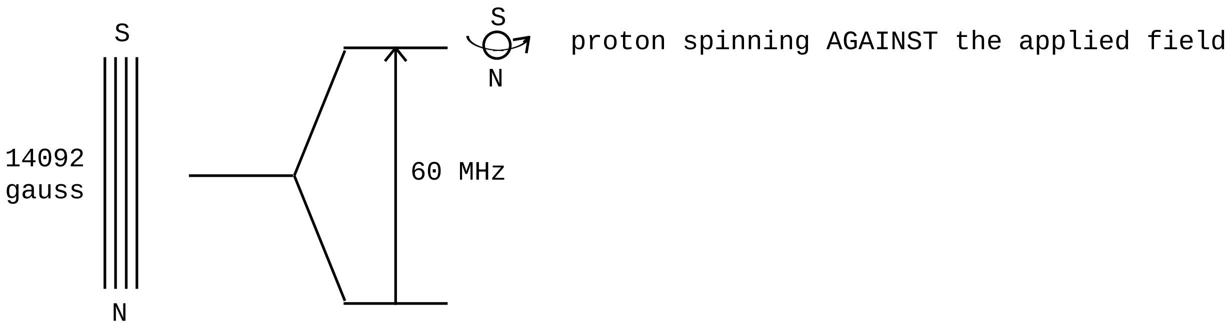
NUCLEAR MAGNETIC RESONANCE

The Hydrogen nucleus, a proton, can have a spin of + 1/2 or - 1/2 just like an electron. The spinning positive charge generates a magnetic field so the proton behaves like a tiny magnet.

If the proton is placed in an applied magnetic field its magnetic field will align itself with the field (low energy) or against the field (high energy). The energy difference E is so low that the protons distribute themselves almost equally between the two levels:



The energy difference E depends on the intensity of the applied field. For a field strength of 14092 gauss the value of E is 3.975 x 10^{-26} J. This corresponds to a radio frequency of 60 MHz (work this out yourself!). Hence, if we irradiate these protons with 60 MHz radiation they will absorb energy, flip their spins and jump to the higher energy state:



This is the principle behind the NMR spectrometer. The radio frequency is held constant at 60 MHz and the applied magnetic field is varied. When E reaches the energy corresponding to 60 MHz the proton flips its spin and jumps into the higher energy level. The radiation emitted when it returns to the lower level is detected and used to mark the exact value of the applied field at which the transition took place. The intensity of the radiation emitted depends on the number of protons.

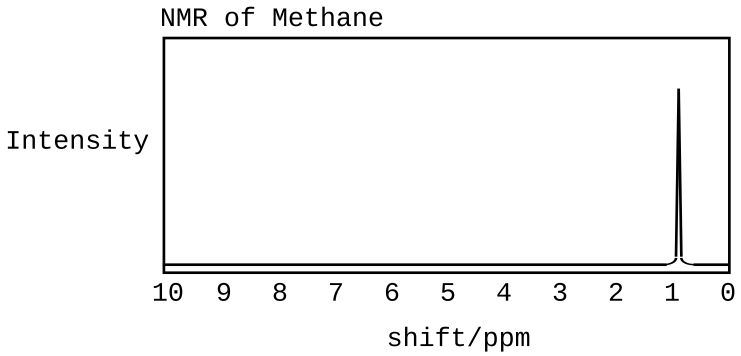
Surely transitions will always occur at 14092 gauss if the applied field is 60 MHz! Not so!! The environment of the proton can affect the strength of the applied field it actually experiences.

The applied field induces weak electric currents in the electrons in the bonds surrounding the proton. These currents produce a local magnetic field which opposes the applied field. The proton therefore will always experience a slightly reduced total field. This reduction, or shift (δ), is measured in parts per million of the applied field e.g. for a proton experiencing a shift of 1 ppm the applied field will need to be raised to 14092.014 gauss for the proton to experience a true field of 14092 gauss.

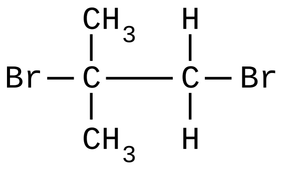
Example 1: Methane

The protons in CH_4 are all equivalent. The shift is 0.9 ppm.

The NMR spectrometer plots a graph of shift vs. intensity:



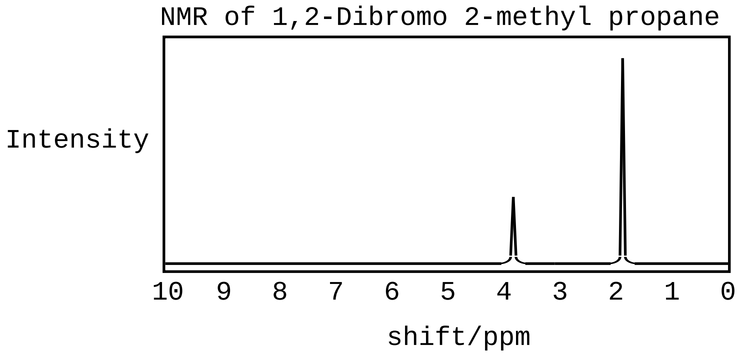
Example 2: 1,2-Dibromo 2-methyl propane



$Br-C(CH_3)_2-CH_2-Br$

The $-CH_2-Br$ protons have a shift of 3.9 ppm.

The CH_3- protons have a shift of 1.9 ppm.



Notice that the areas under the 1.9 ppm and 3.9 ppm peaks are in the ratio 1:3 reflecting the ratio of the $-CH_2-Br$ and the CH_3- protons in the molecule.

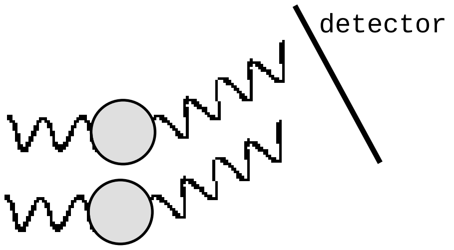
X-Ray Crystallography

X-ray crystallography can be used to determine the precise three-dimensional structure of organic compounds.

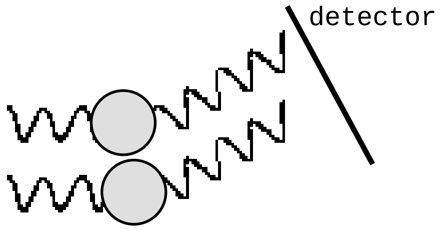
When a crystal of an organic compound is exposed to X-rays of a single wavelength (e.g. 0.154 nm) the atoms of the crystal act as a diffraction grating. The electrons of each atom bend or 'diffract' the X-rays.

The more electrons, the more the X-rays are deflected. Large atoms like Oxygen (8 electrons) bend the X-rays more than smaller atoms like Hydrogen (1 electron).

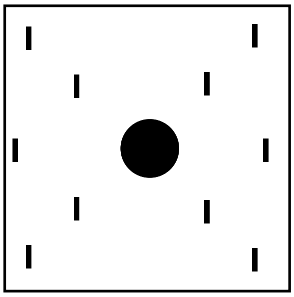
When individual diffracted waves are in-phase, the peaks and troughs add together and <u>constructive</u> interference occurs. This increases the intensity of the beam and produces a bright spot on an electronic detector placed in front of the beam.



When individual diffracted waves are out-of-phase, the peaks and troughs subtract and <u>destructive</u> interference occurs. This reduces the intensity of the beam and produces only faint spots on the detector.



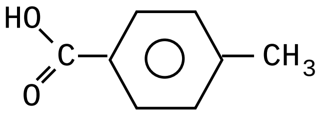
The size and distance between the atoms determines whether the diffracted beam is in-phase or out-of-phase and thus the pattern of bright spots produced on the detector can be used to determine the three-dimensional shape of the molecule.

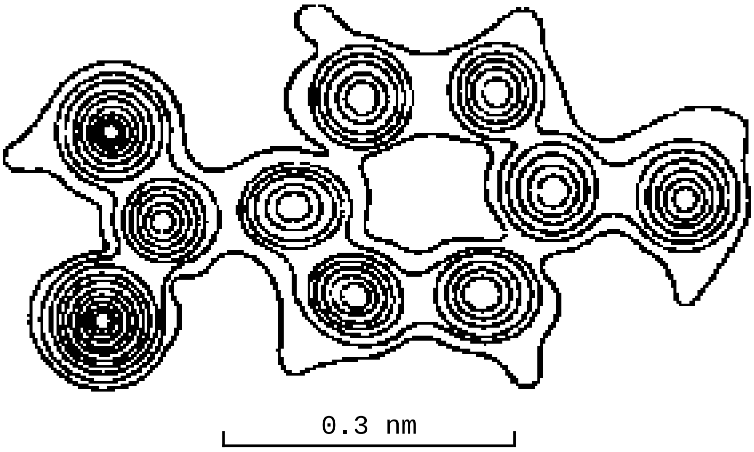


X-ray diffraction pattern produced on photographic film.

Computer analysis of the X-ray diffraction patterns can produce electron density maps of the molecule

e.g. 4-Methyl benzoic acid





From the electron density map the precise location of each atom in the molecule can be determined. Heavier atoms like Oxygen can be identified by the greater intensity of the contours. Hydrogen atoms, with low electron densities, are not easily detected.