Determination of Structure: Modern Analytical Techniques

Once an organic compound is isolated it must be characterized and identified. The similarity between organic compounds poses difficulties when they have to be separated. In many cases two or more compounds are so alike, in solubility, boiling point and chemical reactions, that separating them from one another on the basis becomes a difficult and a lengthy process. The first step in identifying an organic compound is to obtain it in as pure a state as possible. **See notes on Purification Techniques.**

Chemical analysis may be divided into: **structural analysis, qualitative analysis and quantitative analysis.**

In **structural analysis** the object is to determine the chemical structure of a pure substance, i.e. the way in which the atoms present are joined together, in the case of large molecules, the way in which the molecule is arranged in three-dimensions. Example: the determination of the structure of a protein molecule.

Qualitative analysis is designed to find out what components are present in a complex mixture of substances.

In **quantitative analysis** the amount of a particular substance in a mixture is determined, example: the percentage of a particular metal in an alloy.

Nowadays, most analysis is carried out by "**physical methods**." Many physical techniques involve **spectroscopy: the absorption or emission of electromagnetic radiation by substances**.

Def. Spectroscopy : techniques that measure the response of a molecule to the input of energy.

The four main techniques used are : ultraviolet and visible spectroscopy, infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and mass spectrometry.

Spectroscopy is useful because only a small quantity of sample is needed, and the sample may be reused after an IR, NMR, or UV spectrum is obtained.

There are many kinds of electromagnetic radiation ranging from X-rays through to radio waves and beyond, that vary only in the frequency of the radiation.

Just like atoms are the smallest particles of elements with a specific atomic number, so *quanta are the smallest packets of energy of a particular frequency*.
The amount of energy, E, corresponding to one quanta is related to its frequency according to the equation: $\mathbf{E = h \bullet f = hc \backslash \lambda}$
(where E = energy, h = Planck's constant, f = frequency of the energy, λ = wavelength and c = speed of light (2.9979×10^8 m/s)).
The frequency is related to the wavelength of the radiation by: $\mathbf{f = c / \lambda}$

The energy carried by each quantum of radiation also increases with its frequency, and so the type of changes that it can bring about in a substance also vary. Different parts of the molecule interact with different wavelengths of radiation, but each can provide structural information.

The quantities of energy required for excitation are approximately: electronic energy 100 kJ mol^{-1}, vibrational energy 1 kJ mol^{-1}, and rotational energy 0.01 kJ mol^{-1}. Ultraviolet, visible, infrared and microwave radiation are all part of the **electromagnetic spectrum**.

The table below shows how different wavelengths of radiation cause different changes in a particle:

The Electromagnetic Spectrum

Radiation Type	X-ray	UV light	Visible light	IR light	Micro-wave	Radio wave
Trends	**Decreasing frequency (Hz), Decreasing Energy, Increasing Wavelength (cm)**					
Changes	Inner electrons may be removed	Outer electrons excited to higher orbitals		Vibrations	Rotations	Magnetic state

A particle (atom, molecule or ion) can absorb a quantum of light and this will affect its state, this being affected upon the amount of energy carried by the quanta. In **emission spectroscopy** the frequency of the radiation emitted by excited particles is studied. For example the colour from a neon lamp is an emission process. In **absorption spectroscopy** radiation of a wide range of frequencies is passed through the sample and the way in which the absorption of radiation varies with its frequency is studied.

The energy absorbed causes atoms, molecules, ions or electrons to move into a higher energy state. The red colour from red paint is the result of an absorption process because of the wide range of frequencies in the white light shining on it, the paint absorbs the blue, green, and yellow colours, but reflects the red light.

For high energy **X-ray** (high frequency), this energy **is sufficient to remove electrons from the inner shells** of the particle.
With the **lower frequency, UV and visible quanta, the energy is sufficient to excite an electron to a higher energy orbital**. This is useful in working out the electronic structures of atoms and molecules, and for quantitative analysis in both inorganic and organic chemistry.
With **IR radiation the energy is sufficient to affect the vibrations** (i.e. stretching and bending motions) of a molecule. Used in **detecting the presence of functional groups** in organic chemistry.
Microwaves affect the rotational state of the molecule.
The energy in a quantum of a **radio wave is only sufficient to alter the magnetic state** of the particle.

Effect of Different Types of Radiation on Chemicals

Type of radiation	Frequency range (Hz)	Effect on molecule	Type of spectroscopy
ultraviolet	$10^{15} - 10^{17}$	excites the electrons	UV/visible
visible light	$10^{14} - 10^{15}$	excites the electrons	UV/visible
infrared	$10^{11} - 10^{12}$	makes bonds vibrate	IR
microwaves	$10^{9} - 10^{11}$	makes molecules rotate	microwave
Radio waves	$10^{6} - 10^{8}$	changes the magnetic alignment of the nuclei of some atoms	NMR

The effect of different types of radiation on the water molecule:

O
/ \
H **H**

Visible or UV ⟶ electrons excited
IR ⟶ bonds vibrate
Microwave ⟶ molecules rotate
radio waves ⟶ magnetic alignment of hydrogen nucleus changes (NMR)

Visible and Ultraviolet Spectroscopy

(Nature of a conjugated π electron system)

Ultraviolet and visible spectroscopy are concerned with the movement os electrons between energy levels as the result of the absorption of energy in the ultraviolet and visible regions of the electromagnetic spectrum.

Explaining Emission Spectra

The UV region of the electromagnetic spectrum extends from the low-wavelength end of the visible region (400 nm) to 10 nm. The range of interest for chemists is from 200 nm to 400 nm.

The energy carried by a *quantum of light in the UV and visible regions of the spectrum corresponds to the amount necessary to promote an electron from one orbital to another*.

When a sample is excited, (absorption of energy occurs) by either moving faster or moving out, away from the nucleus. The outer electrons move to a higher energy level. Sometime later the energy is given out as radiation as the electrons slow down or move back in.

Transition between electronic energy levels gives rise to lines in the absorption spectrum, because the energy is *quantized*. This means that only certain energy levels are allowed in the atom and the electrons can only move between these levels. So each line in an emission spectrum is the result of electrons moving from one quantized energy level to a lower one. The difference in energy between the two levels is related to the frequency of radiation by Planck's constant: $\Delta E = h \bullet f = hc / \lambda$

The spectrum

The spectrum produced differs from the normal spectrum of white light in two ways:

- i) it is **made up of separate lines** (it is discontinuous).
- ii) the **lines are in a converging pattern**, getting closer as the frequency or energy of the lines increases.

A simple *saturated hydrocarbon does not absorb in the UV region*. Compounds with π-electrons, since these are less strongly held than σ-electrons, absorb light intensely. **The presence of carbon - carbon multiple bonds, conjugated bonds, aromatic systems, or of functional groups containing multiple bonds - that is, the presence of π electrons and π orbitals is required for UV absorption.**

UV spectra show a single peak or few peaks for each isolated functional group or carbon - carbon multiple bond present in the molecule. The ultraviolet spectrum of a compound is like a fingerprint. If it can be matched up with the spectrum of a known compound, it can be used as a means of identification.

The hydrogen spectrum

In the visible part of the hydrogen spectrum four lines can be seen. Each of these lines represents electrons falling back to the *second energy level from one of the levels above*
(n = 6 —> n = 2 : violet, n = 3 —> n = 2 : red). The visible part of the hydrogen spectrum is called the *Balmer Series*.

Flame Tests

The emission spectrum of each element is unique to that element and can be used to identify the element. Flame tests, in which a sample of the element or its compound is heated on a wire in a Bunsen flame can be used to identify some elements in the s-block.

Flame colour	orange	pale purple	brick red	crimson	apple green
Element	sodium	potassium	calcium	strontium	barium

Infra-Red Spectroscopy
(What functional groups are present)

This is a very useful technique for determining the presence of functional groups in a molecule or for confirming the identity of a compound by comparing its infra-red spectrum with that of a known compound. All organic compounds absorb infrared (IR) radiation. Books of recorded spectra are available for comparison. If the unknown compound is a new substance, its spectrum will not match with any recorded IR spectrum; yet it is still possible to infer a great deal about the structure of a compound. Functional groups can be identified from their IR spectra, and the IR spectrum is the most rapid method of detecting the series to which a compound belongs.

The atoms in a molecule are in constant motion relative to each other, as the bonds between them bend and stretch. The energy needed for this motion is in the infrared region of the elect4omagnetic spectrum. Infra-red radiation is of a wavelength just greater than that of visible light (8×10^{-5} cm (800 nm) to 3×10^{-2} cm (300 μm)). Each bond vibrates at a particular frequency that depends on the strength of the bond and the masses of the atoms bonded together. The frequency of vibration for a particular bond is similar, but not identical.

The **energy of infrared radiation can also be expressed in frequency**, ($E = hf$), where the **unit is cm^{-1} (reciprocal centimetres or wavenumbers, $E = hc / \lambda$,** wavenumber = 1 / wavelength**)**. The frequency range for infrared radiation is 12821 cm^{-1} to 100 cm^{-1} (however in most spectrophotometers, the infrared radiation is measured between 4000 cm^{-1} — 625 cm^{-1}, since most organic molecules absorb infrared radiation in this energy range).

A quantum of infrared radiation does not have sufficient energy to excite an electron to a higher energy level, but it *does have sufficient energy to excite a molecule to a higher vibrational level.*

See Data, Table 18

Why does an organic molecule absorb some wavelengths or IR radiation but not others?
The atoms in a molecule are never motionless, but vibrate about their equilibrium positions at constant frequencies. All molecules have a certain amount of energy distributed throughout their structure that causes bonds to stretch and bend, atoms to wag and rock, and other molecular vibrations to occur. The amount of energy a molecule contains is not continuously variable but is **quantized**. That is, a molecule can stretch, bend, or vibrate only at specific frequencies corresponding to specific energy levels.
When a molecule absorbs IR radiation, then the molecular vibration with a frequency matching that of the radiation increases in amplitude. In other words, the 'spring' connecting the two atoms stretches and compresses a bit further. Since, each frequency absorbed by a molecule corresponds to a specific molecular motion, we can see what kinds of motion a molecule has by measuring its IR spectrum. Hence, by interpreting these motions, we can find out what kinds of bonds (∴ functional groups) are present in the molecule.

IR spectrum ⟶ What molecular motions? ⟶ What functional groups?

Why do different functional groups absorb at different frequencies?
Like a *stretched spring between masses,* the **energy absorbed by a bond depends on the masses of the atoms and the bond strength**.
Spring, similar to a bond connected to small weights vibrate faster than springs connecting large weights. Thus, C - H, O - H, and N - H bonds vibrate at a higher frequency than bonds between heavier C, O, and N atoms.

Short, strong bonds vibrate at a higher frequency than do long, weak bonds, cf. to a short, strong spring vibrates faster than a long, weak spring. Thus, triple bonds absorb at a higher frequency than double bonds, which in turn absorb at a higher frequency than single bonds.

In order for absorption to be recorded, the motion must result in a change in a dipole moment. Molecules comprised of atoms with the same electronegativity, as well as symmetrical molecules, do not experience a change in dipole moment and therefore do not exhibit absorption. For example, O_2 and Br_2 do not absorb, but HCl and CO do.

The Infrared Spectrum

An infrared spectrum is the plot of either absorbance or % transmittance (the percentage of radiation transmitted) as a function of wavelength (in µm) and/or frequency or the wavenumber(cm $^{-1}$).

When an organic molecule absorbs infrared energy of a particular wavelength, then the wavelengths of the energy absorbed, often expressed in wavenumbers, appears as a '**dip**' or as a strong absorption (i.e. weak % transmittance) and if little energy is absorbed the peak will show a small absorption (large % transmittance).

Most infrared spectrophotometers are calibrated in % transmittance with the linear scale in frequency (cm^{-1}). The wavelength scale (measured in microns, µm = 10^{-4} cm or 10^{-6} m) is also shown on the spectrum.

Some of these peaks indicate the presence of particular functional groups and others are characteristic of the whole molecule. The wavelength at which absorption occurs is a characteristic of a particular bond and can be used to identify it.

Bonds with significant dipole moments will give strong signals in the infrared, (the larger the change in dipole moment during a bending or stretching vibration, the stronger the absorption). Intensity of light absorbed is directly related to the magnitude of the dipole moment, the stronger the dipole moment, the stronger the absorption.
Bonds with significant dipole moments (∴ strong signals), are O - H, C - O, N - H, C - X, C = O.

The more complicated a molecule is, the more possibilities there are for relative motions of the atoms. Therefore, infrared spectra can be quite complex, and the larger the molecule, the larger the number of peaks that appear in the spectrum.

The Functional Group Region of the Infrared

Most common functional groups (OH, NH, CHO, C=O, COOH, C = O, C≡N) appear at the high energy region of the infrared spectrum, usually between 4000 - 1400 cm^{-1}. This region is called the ***functional group region***. Most functional groups have characteristic IR absorption bands that don't change from one compound to another.
The C = C absorption of an alkene is almost always in the range 1680 - 1750 cm^{-1}; an O-H absorption of an alcohol is in the range of 3400 - 3650 cm^{-1} and a C = O absorption of a ketone is in the range of 1680 - 1750 cm^{-1}.
By learning where characteristic functional-group absorptions occur, it is possible to get structural information from IR spectra.

The Fingerprint Region of the Infrared

The low energy portion of the spectrum below 1500 cm^{-1} *contains a few functional group absorptions*, but is usually the region where low energy bending and stretching vibrations absorb; corresponds to vibrations of many single bonds. *Each individual molecule will have its own peculiar set of bending and stretching, this leads to a 'fingerprint' of the molecule* that can often be used *to identify a specific molecule by 'matching fingerprints'* if a library of known compounds is available. This region of the spectrum is generally known as the ***fingerprint region***.

If there is an unknown organic molecule and you have a 'library' of pre-recorded infrared spectra, the fingerprint region can be used to find the proper 'match'. Fingerprinting the molecule in the library allows its identification. Obviously, if your molecule is not in the library, you cannot use this technique to identify it.

Infrared spectra are most useful in two ways:

(1) It depends upon the fact that the same functional groups can cause absorption at the same wavelength in the spectra of all molecules in which they occur.

(2) Secondly, IR spectra are also used as fingerprints, i.e. in the identification of a compound.

Use the Data Book, Table 18, to answer the following:

1. Give the Infrared Absorptions for the following major functional groups:
   a) alcohols
   b) alkanones (ketones)
   c) alkanals (aldehydes)
   d) alkanoic acids
   e) amines
   f) esters
   g) benzene derivatives

2. Refer to Table 18 in the Data Book, and make educated guesses about which functional groups the following molecules might contain:

a) A compound with a strong IR absorption at 1710 cm^{-1}
b) A compound with a strong IR absorption at 1540 cm^{-1}
c) A compound with a strong IR absorption at 1720 cm^{-1} and at 2500 - 3100 cm^{-1}

3. How could you use IR spectroscopy to distinguish between the following pairs of isomers?

a) CH_3CH_2OH and CH_3OCH_3
b) cyclohexane and 1-hexane
c) CH_3CH_3COOH and $HOCH_2CH_2CHO$

4. Propose structures for compounds that meet the following descriptions ...

a) C_5H_8, with IR absorptions at 3300 and 2150 cm^{-1}
b) C_4H_8O, with a strong IR absorption at 3400 cm^{-1}
c) C_4H_8O, with a strong IR absorption at 1715 cm^{-1}
d) C_8H_{10}, with a strong IR absorption at 1600 cm^{-1} and 1500 cm^{-1}

5. How could you use IR spectroscopy to distinguish between the following pairs of isomers?

a) $HC = CCH_2NH_2$ and $CH_3CH_2C\equiv N$
b) CH_3COCH_3 and CH_3CH_2CHO

6. At what approximate positions might the following compounds show IR absorptions?

a) $CH_3CH_2C = O$ CH3 b) $CH_3CH_2CH_2COOCH_3$

7. Assume that you are carrying out the dehydration of 1-methylcyclohexanol to yield 1-methylcyclohexene. How could you use infrared spectroscopy to determine when the reaction is complete?

8. Which of the following compounds will show a strong absorption in the region 1600 – 1800 cm^{-1} of the infrared spectrum?
   A. Chloroethane B. Ethylbenzene C. Propanone D. Butan-1-ol

9. Work through the exercises that follow at the end of these notes.

Nuclear Magnetic Resonance Spectroscopy (NMR)
(Carbon - Hydrogen framework)

Hospitals possess an instrument called a body scanner, this is an NMR spectrometer in which a patient can be placed so as to lie inside a large magnet. NMR spectrometer obtains images called magnetic resonance images of soft tissues.

Protons in water, carbohydrates, proteins and lipids give different signals. Different parts of the body possess protons in different environments and therefore give different signals. These enable different organs in the body to be differentiated in the magnetic resonance image. The technique of NMR has been used to diagnose cancer, multiple sclerosis, hydrocephalus (water on the brain) and other diseases.

NMR spectra give information concerning the structure of hydrogen-containing groups within a molecule. NMR filled a 'gap' evident in X-ray diffraction results which did not show up hydrogen atoms at all well.

Like electrons, both protons and neutrons have spin, this induces a weak magnetic field which can interact with an external magnetic field. Normally, there is an equal number of atoms in a sample with each direction of spin and so they cancel each other out. When a strong external magnetic field is applied, the magnetic field induced by the nuclear spin can align in the same direction as the external field or in the opposite direction. This gives two possible energy levels.

/\
| ____↓_____ - ½ against the external field (↑)
|
| $\Delta E = hf$ (corresponds to radio frequencies, ΔE is the basis for the technique NMR)
| ____↑_____ + ½ With the external field (↑)
|

Nuclei with spins that are aligned with the applied field can absorb energy and change their orientation from with the field to against the field, (i.e to the high energy alignment, this corresponds to radio frequencies). They are described as '**flipping**'. The absorption of energy that makes the nuclear spin **flip** is called nuclear magnetic resonance. The quantity of energy absorbed depends on the identity of the nucleus and the magnitude of the applied field. However the hydrogen nucleus is protected from the external field to some extent by the electrons, this is called **shielding**,, less shielding for hydrogen bonded to electronegative atoms, ∵these pull electrons away.

If a sample of a compound is irradiated with radiation from the radio region of the electromagnetic spectrum then at some frequency, f, absorption of energy results in transitions from the lower-energy spin state to the higher-energy spin state. The absorption of this energy, ΔE, is called nuclear magnetic resonance. In reality, spectra are usually measured by keeping the frequency of the radiation constant and varying the strength of the external magnetic field.

The amount of energy absorbed depends on other atoms or groups which are bonded. Hydrogen atoms in different chemical environments will absorb radio waves at different frequencies. The scale is not in frequency units, as might be expected, but is measured as the amount of shielding by the **chemical shift, represented by the symbol δ**, from a standard compound, measured in units of **parts per million (ppm); (where 1 δ equals 1 ppm**) of spectrometer frequency is plotted on the x-axis. The greater the chemical shift, the less the shielding. The standard compound called **tetramethylsilane, TMS, $(CH_3)_4Si$**, which is arbitrarily given a chemical shift value, δ , of zero. 0.00. The field required to bring protons into resonance is compared with that required for TMS, the standard. The instrument is adjusted so that the **TMS signal is set on zero**, and is chosen, because it gives a strong signal as there are 12 protons in an identical chemical environment; and the signal from its hydrogen atoms is well away from those of most other compounds. TMS is chemically inert and miscible with most organic solvents. The greater the chemical shift, the less the shielding.

The spin due to protons, ^{1}H,, the **proton NMR spectrum**, is often used to provide an NMR spectrum of an organic compound. Most ^{1}H nuclei come into resonance between **0 and 10 δ** downfield from TMS, the further to the left of the TMS peak is the peak of the compound the smaller is the shielding. Each distinct set of nuclei gives rise to a separate peak. The relative area of each peak reflects the ratio of the number of protons of each type producing each peak.

Atoms containing an odd number of protons and even number of neutrons in the presence of a strong magnetic field absorbs radio frequency energy. A nucleus that contains an odd number of protons and (or both) has spin and is magnetically active, (i.e. any nucleus with an odd atomic number or odd mass number can be studied). The smallest nucleus that meets this requirement is ^{1}H but so do ^{13}C, ^{17}O, ^{19}F, ^{14}N and ^{31}P. These nuclei behave as if they were spinning about an axis, i.e. as if they were a magnet. Two very common nuclei ^{12}C and ^{16}O have zero spin and zero magnetic moment and are invisible in NMR spectrometry. NMR is most commonly used to identify ^{1}H nuclei.

The NMR spectrum gives four important pieces of information about the chemical structure of a compound:

- The number of absorptions indicates the number of different 'types of protons. These are more correctly described as protons in different chemical environments.
- The position of each absorption gives information about the environment of the protons involved (See Table 19 of the Data Book).
- The intensities of the absorptions, indicated by the areas under the peaks, give the ratio of protons in each environment.
- Different protons on adjacent carbon atoms cause each other's signal to split. The signal of protons on a carbon atom adjacent to another carbon atom having **n hydrogen atoms will be split into n +1 peaks**. This is called **spin - spin coupling** and gives additional information about the compound.

Examples

1) 1,1-dibromo-2,2-dichloroethane will produce two peaks of equal intensity, a doublet. However, 1,1-dibromo-2-chloroethane results in three peaks, with an area ratio of 1:2:1

2) Ethoxyethane, $CH_3 – CH_2 – O – CH_2 – CH_3$, there will be two peaks in the ratio 2 : 3. There are 10 protons so they will form a set of 4 and a set of 6. These are 4 protons in two – CH_2 – groups and 6 protons in 2 – CH_3 – groups.

3) In propanol, there are CH_3 -, - CH_2 -, and - OH groups and the hydrogen in each of these groups will come into resonance at different frequencies. The NMR spectrum of propanol will show three absorption peaks.

4) dichloromethyl methyl ether, $CH_3 - O - CCl_2H$: has two distinct sets of ^{1}H nuclei, thus two separate peaks are expected. Each peak represents a single proton or a group of equivalent protons. (The number of peaks represents the number of groups of non-equivalent protons.)

5) C_6H_6 1 peak observed since all the H's are the same
6) $CH_3 - O - CH_3$ 2 methyl groups in identical environments
7) $CH_3 - CH_2 - CH_2 - O-H$ 3 H's are in 3 different environments

A table such as **Table 19 of the Data Book** gives typical chemical shift values, δ, relative to TMS = 0 for different types of proton (hydrogen). **This table gives the common bonding situations of hydrogen atoms in organic molecules**. This can be used to identify different types of proton. Knowing the way in which all the hydrogen atoms are bonded, along with the relative numbers of these, will frequently identify the structure of the molecule. Information obtained is important for hydrogen atoms in a molecule, $^{1}_{0}H$.

Summary

This technique is ***used to show the number of hydrogen atoms attached*** to their atoms or groups of atoms, also this technique can be ***used to show the bonding of all the hydrogen atoms*** in the molecule, i.e. the presence of hydrogen atoms in different functional groups.

Assignment

1.(a) Explain why the proton, ^{1}H, NMR spectrum of cyclohexane, C_6H_{12} , and that of dichloromethane, CH_2Cl_2 , each contain only one peak. (b) the proton NMR spectrum of a mixture of equal numbers of moles of cyclohexane and dichloromethane shows two peaks. Explain why the areas under the two peaks are in the ratio 6 :1.

Mass Spectrometry

We have already studied the mass spectrometer in the Atomic Structure Unit, where we considered its use in determining relative atomic masses. In the same way, the mass spectrometer can be used to determine by relative molecular mass of a compound but, in addition, the structure can be determined by identifying the fragments formed when the molecule is ionized.

A mass spectrometer is an instrument that bombards an organic gaseous molecule (or any other molecule) with high-energy electrons. When a high energy electron strikes an organic molecule, it dislodges a valence electron from the molecule, producing a cation radical (because the molecule now has an odd number of electrons) or a **molecular ion**, M^{+1}:

$$\text{compound} + \text{fast electron} \longrightarrow \text{Molecular ion, } M^{+1} + \text{two slow electrons}$$

Electron bombardment transfers such a large amount of energy to the molecules that most of the **molecular ions fragment** after formation, i.e. to say the beam of electrons ruptures chemical bonds resulting in the formation of positively charged fragments. The molecule '**fragments**' into a number of particles, some of which will be free radicals, other free cations, and some will remain as neutral molecules. The initially formed ion is the molecular cation-radical (M^{+1}) resulting from a single electron being removed from a molecule of the sample. This unstable species usually decomposes rapidly into a cationic fragments and radical fragments.

For example, propane forms the ions: $C_3H_8^{+1}$, $C_3H_8^{+2}$, $C_2H_5^{+1}$, and CH_3^{+1}.
The last two are produced when C_3H_8 molecules split and then ionize:

$$C_3H_8 + \text{fast electron} \longrightarrow C_3H_8^{+1} + 2 \text{ slow electrons}$$

The various ions have different mass / charge ratios, (written as m/e or m/z) and also have different speeds.

An electric field accelerates and focuses the cations, i.e. puts the charged particles in flight; (only the ions will be affected by the electric potential on the plates, and only they will move, neutral fragments are lost on the walls of the spectrometer) towards a large magnet, which separates the cations that are produced according to their mass and charge. Ions with the same mass/charge ratio come to one focus on a detector. The detector records the number of particles of each mass exiting the deflector area.

The lower the mass of the ion, the greater the deflection and so, by varying the strength of the magnetic field, the ions of differing mass can be brought to focus on a detector, where they are recorded.
The mass spectrum records the relative abundances of the fragments of different mass reaching the detector.

Since there are many molecules in the sample and usually more than one way for the initially-formed molecular ion to decompose into fragments, a typical mass spectrum is composed of many lines, each corresponding to a specific mass/charge ratio, (m/z). If the charge is 1, then this ratio is equal to the relative molecular mass of the ion.

A mass spectrum is the plot of mass/charge ratio, (m/z), on the horizontal axis and relative abundance of the various cationic fragments, on the vertical axis.

[In studying the spectrum for elements, a different peak for each isotope is observed. The height of the peak indicates the amount of each isotope. **]**

However, the spectrum for compounds will show peaks. The highest peak, representing **the whole compound particle, this will have the largest mass**, it corresponds to the most stable fragment, and is called the **base peak** and is allocated a relative abundance of 100 %.

The spectrum will also show 'fragments' of the molecular ion which broke up when they were ionized in the electron beam. The peak with the highest m/z ratio is generally the molecular ion peak, (**parent ion peak**), M^{+1}, its mass gives the molecular mass, M, of the compound. Since the numbers of charges, z, on each ion is usually 1, the value of m / z for each ion is simply its mass, m. Other peak heights are expressed as percentages of the base peak (or the parent ion peak).

(In some spectra there is a very small peak at M + 1, where M is the molar mass of the compound, due to the presence of molecules containing the ^{13}C isotope. This isotopic peak is relatively small because the ^{13}C isotope has a natural abundance of only 1 %, i.e. one ^{13}C atom for every 99 ^{12}C atoms.)

The **molecular ion will often break down, or 'fragment'**, inside the mass spectrometer giving rise to a '**fragmentation pattern**' of lower molecular mass ions. This fragmentation pattern can be used for '**fingerprint**' purposes, and the mass of the units that have broken off will also give **clues to the structure of the molecule**. Mass spectrometry can be used to indicate the structure of a parent organic compound.

The way in which a molecular ion fragments depends on the relative stabilities of the species that can be formed. The CH_3^{+1} ion less stable than the ion R_3C^{+1} in which the positive charge is less localised.

Example1: the spectrum of butane will show peaks at 58 due to the molecular ion, $C_4H_{10}^{+1}$, the peak at 15 corresponds to the CH_3^{+1} ion, that at 29 to the $C_2H_5^{+1}$ ion and that at 43 to the $C_3H_7^{+1}$ ion. The molecule has fragmented: $CH_3 — CH_2 — CH_2 — CH_3$
| | |
15 29 43

Example 2: The mass spectrum of ethanal shows a peak at 44 corresponding to the molecular ion, the peak at 15 corresponds to CH_3^{+1} and that at 29 to the CHO^{+1}. The molecule has fragmented:
$CH_3 — CHO$ (Propanone: $CH_3 - CO - CH_3$)
15 | 29 15 | |

The peak at **77** is very common in aromatic compounds corresponding to the $\mathbf{C_6H_5^{+1}}$ ion. Certain fragments are very common in mass spectra: **15 : $\mathbf{CH_3^{+1}}$, 28 : $\mathbf{CO^{+1}}$ or $\mathbf{C_2H_4^{+1}}$, 29 : $\mathbf{CH_3CH_2^{+1}}$**

The molecular ion and the fragmentation pattern can often identify an organic compound. Isomers have the same molecular ion but different fragmentation patterns.

Compounds containing element that have two (or more) isotopes present in significant proportions, for example chlorine and bromine, show more than one molecular ion.
Example: 2-bromopropane has two molecular ions at m/z = 122 and 124, corresponding to molecular ions containing bromine – 79 and bromine – 81, respectively. The size of the peaks in the mass spectrum is similar, since the two isotopes are present in similar amounts.
Example: In chloroalkanes the peak sizes in the mass spectrum reflect the relative abundance of the chlorine isotopes chlorine – 35 (75.77 %) and chlorine – 37 (25.23 %). For chloroethane, the molecular ion peaks appear at m/z = 64 and m/z = 66 in the approximate ratio of 3 :1, corresponding to the ions $C_2H_5{}^{35}Cl^{+1}$ and $C_2H_5{}^{37}Cl^{+1}$ respectively.

The mass spectrometer depends on the fact that a charged particle travelling in an electric field will be deflected and the amount of deflection depends on:
(a) the mass of the particle (b) the speed of the particle
(c) the strength of the field (d) the charge of the particle

Review Questions

1.(a) When 0.200 g of a compound **A**, which contains only carbon and hydrogen, was burned completely in a stream of dry oxygen, 0.629 g of carbon dioxide and 0.257 g of water were formed. Find the empirical formula of the compound.
(b) When 0.200 g of **A** is vaporised, the volume which it occupies, at STP is 53.3 cm^3. Find the molar mass of **A**
(c) Use the molar mass of **A** to convert the empirical formula from (a) into a molecular formula.
[Answer: (a) CH_2 (b) 84.0 g mol^{-1} (c) C_6H_{12}]

2. 0.23 g of a compound **X** containing carbon, hydrogen and oxygen only, gave 0.44g of CO_2 and 0.27 g of H_2O on complete combustion in oxygen.
a. What is its formula?
b. What would be the relative molecular mass of **X** be if its formula were $C_6H_{18}O_3$?
c. The IR spectrum of **X** shows peaks at 3300 cm^{-1} and at 1100 cm^{-1}. Deduce the structure of **X**. If you suspected that compound **X** was an aldehyde, what peak would you look for in the IR spectrum to confirm or deny this?
d. The low resolution NMR spectrum shows three peaks at δ : 4.7, 3.8, and 1.5, in the ratio of 1:2:3. Deduce the environment of the hydrogens
e. Use the information given above to deduce the structure of **X**
[Answer: (a) C_2H_6O (b) 138 g mol^{-1} (c) IR peaks are caused by an O–H and a C–O , a C=O stretching peak at ~ 1700 cm^{-1} (d) O– H, – CH_2 – , – CH_3 (e) X is ethanol, CH_3CH_2OH]

3. 0.44 g of a compound **Y** containing carbon, hydrogen and oxygen only gave 0.88 g of $CO_{2\,(g)}$ and $H_2O_{(l)}$ on complete combustion in oxygen. Compound **Y** gave a orange -red precipitate with 2,4-dinitrophenylhydrazine. The mass spectrum shows the highest peak at 44, and fragments at 29 and at 15. The IR spectrum shows a broad band at ~ 1750 cm^{-1}. The NMR spectrum shows δ values at 2.1 and at 9.7 in the ratio of 3:1. Deduce the structure of **Y**
[Answer: ethanal, CH_3 — CHO]

4. A test on a compound **X** was shown to contain sulphur and chlorine. From 0.1000 g of **X** was obtained 0.1322 g of $BaSO_4$. Another 0.1000 g sample of **X** gave 0.0813 g of AgCl. The combustion of 0.2000 g of X gave 0.2992 g of CO_2 and 0.0510 g of H_2O. Find the empirical formula of **X**. (Remember that if the percentages of C, H, S and Cl do not total 100 %, the difference is due to oxygen.)
[Answer: empirical formula: $C_6H_5SO_2Cl$]

5. (a) Explain what is meant by the term fragmentation as used in mass spectrometry. Include in your answer a general equation for the fragmentation os a molecular ion into two new species.
(b) An aromatic hydrocarbon **D**, C_7H_8, is converted into compound **E,** $C_9H_{10}O$, on treatment with ethanoyl chloride, CH_3COCl, in the presence of $AlCl_3$. When **E** is treated with $NaBH_4$, it is converted into **F**, $C_9H_{12}O$. Compound **G** is formed when **F** is warmed with concentrated H_2SO_4 .
Note that compound **E** is formed as a mixture of three isomers.

Compound **E** has a strong absorption band in the infrared at 1685 cm^{-1}, compound **F** has a broad absorption at 3340 cm^{-1} and compound **G** has an absorption band close to 1630 cm^{-1}.
(i) Show how the information provided in the question and the Data Book can be used to deduce structures of for compounds **D, E, F**, and **G**, respectively. Choose one of the isomers of compound **E** to show the formation of compounds **F** and **G**.
(ii) Name the types of reaction taking place and outline a mechanism for the formation of **G**.
[Answer: D = $C_6H_5CH_3$, D — > E substitution of CH_3CO – , E = $CH_3C_6H_4COCH_3$ with isomers 1,2– , 1,3– and 1,4 – , E — > F adds 2 H ; F = $CH_3C_6H_4CHOHCH_3$. Dehydration of F — > G, G = $CH_3C_6H_4CH = CH_2$. The IR peak at 1685 cm^{-1} shows the presence of a C = O, the band at 3340 cm^{-1} shows the presence of — OH in an alcohol; the band at 1630 cm^{-1} indicates a C = C bond. (ii) acylation, reduction, dehydration.]