

4.2 Alcohols, haloalkanes and analysis

4.2.1 Alcohols

- Definitions

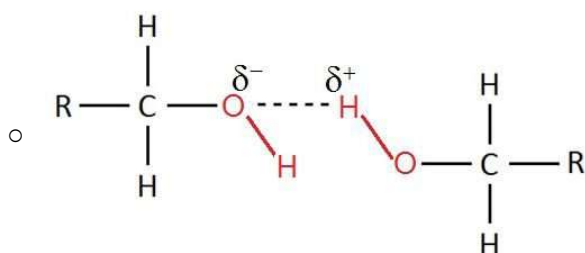
Term	Definition
Dehydration	A water molecule is removed from the starting material

- Alcohol structure

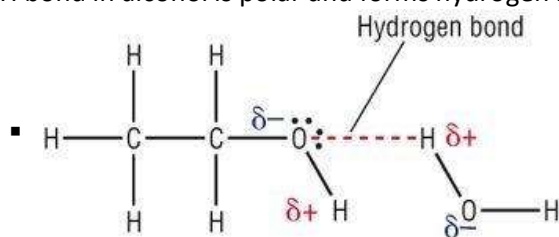
- Functional group = -OH (hydroxyl group)
- Has **polar and non-polar** parts
 - The O-H bond is **polar** (oxygen is more electronegative than hydrogen)
 - The side chain is **non-polar**
 - so alcohol can mix with both polar and non-polar liquids

- Alcohol properties

- Less volatile + higher melting point than alkanes
 - Induced dipole-dipole interactions between the non-polar side chains
 - Strong hydrogen bonds** + permanent dipole-dipole interactions between alcohol molecules hold them together (stronger than London forces)
 - Extra heat energy is required to break the strong hydrogen bonds



- Greater water solubility than alkenes
 - Alkanes are non-polar so they cannot form hydrogen bonds with water
 - O-H bond in alcohol is polar and forms hydrogen bond with water



- Longer carbon chain = less miscible in water
- More -OH groups = more miscible in water

- Classifying alcohols

- Primary: -OH group attached to a carbon atom attached to **2 hydrogen atoms + 1 alkyl group**
- Secondary: -OH group attached to a carbon atom attached to **1 hydrogen atom + 2 alkyl groups**
- Tertiary: -OH group attached to a carbon atom attached to **no hydrogen atoms + 3 alkyl groups**

- (Complete) combustion of alcohols

- Alcohol + oxygen → carbon dioxide + water
- Exothermic reaction
 - A large quantity of energy released in the form of heat
 - Burn with a clear blue flame
- More carbon atoms in the alcohol chain = more heat energy released per mole
- Alcohols undergo complete combustion more often due to the oxygen atom in the molecule

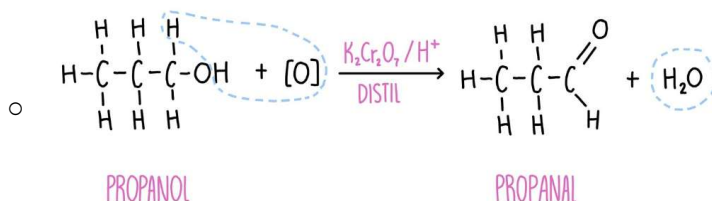
- Oxidation of alcohols

- Heat with an oxidising agent ([O])

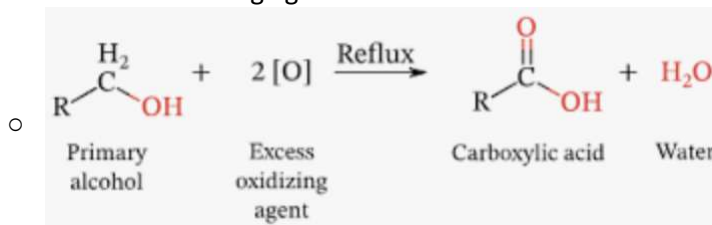
- Normally acidified dichromate (VI) ($\text{Cr}_2\text{O}_7^{2-} / \text{H}^+$)
- e.g. acidified potassium dichromate (VI) ($\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4$)
- Observations
 - Cr will be reduced
 - Reaction mixture turn from orange (Cr^{6+} in $\text{Cr}_2\text{O}_7^{2-}$) to green (Cr^{3+})

- Oxidation of primary alcohols

- Gentle heating + **distil** = aldehyde formed
 - Aldehyde distilled out of the reaction mixture as it forms to prevent any further reaction (distil)
 - Acidified dichromate (VI) ions change colour from orange to green

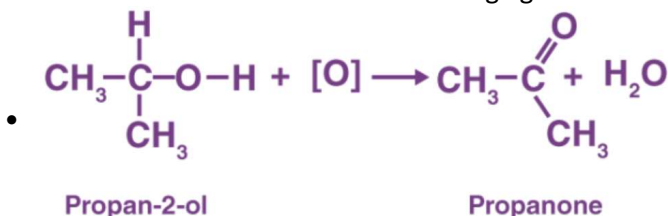


- Heated strongly + **reflux** + **excess of acidified potassium dichromate (VI)** = carboxylic acid
 - Reflux = ensure that all aldehyde formed initially also oxidised to carboxylic acid
 - Excess of oxidising agent = ensure that all alcohol is oxidised



- Oxidation of secondary alcohols

- Oxidised to ketones with an oxidising agent (acidified dichromate (VI) ions)
- Ketones cannot be further oxidised
- Heated under **reflux** with the oxidising agent to ensure that the reaction goes to completion

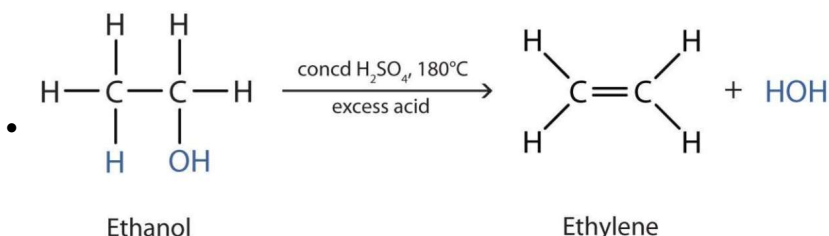


- Oxidation of tertiary alcohols

- Do not undergo oxidation reactions
- Acidified dichromate (VI) ions remain orange when added to a tertiary alcohol

- Dehydration of alcohols

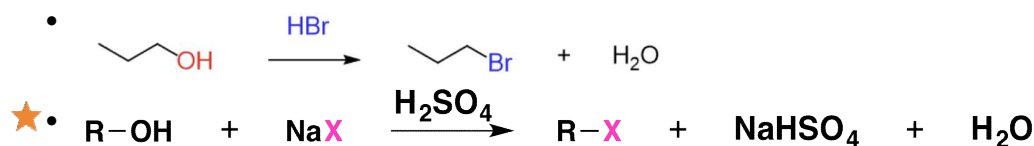
- Heated under **reflux** with **acid catalyst** (e.g. concentrated H_2SO_4 / H_3PO_4)
- Product = an alkene
- Type = elimination reaction



- Substitution reaction of alcohols

- Alcohols react with halide ions to form haloalkanes
- Heated under **reflux** with **concentrated acid catalyst** & halide ion e.g. $\text{H}_2\text{SO}_4 + \text{NaBr}$
 - Acid need to be concentrated to minimise back reactions
- Used to produce hydrogen halide in situ when carrying out chemical reactions

Alcohols can be converted to Alkyl Halides with HX acids



4.2.2 Haloalkanes

Definitions

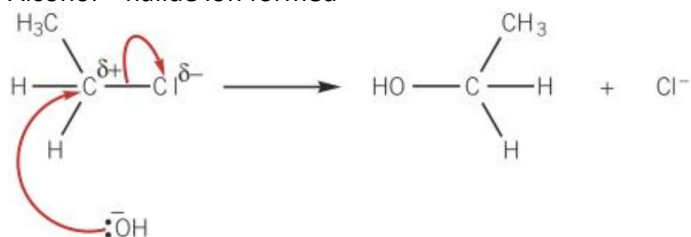
Term	Definition
Nucleophile	An atom or group of atoms which is attracted to an electron-deficient centre or atom, where it donates a pair of electrons to form a new covalent bond
Nucleophilic substitution	A reaction in which a nucleophile is attracted to an electron-deficient centre or atom, where it donates a pair of electrons to form a new covalent bond
Hydrolysis	A reaction with water that breaks a chemical compound into two compounds, the H and OH in a water molecule becomes incorporated into the two compounds

Reactivity of haloalkanes

- Reactivity: alkenes > haloalkanes > alkanes
- Halogen atoms are more electronegative than carbon atoms so the carbon-halogen bond is polar
- $\delta+$ on carbon can attract nucleophiles (contain a lone pair of electrons)
- The nucleophile replaces the halogen atom
- A new compound with a different functional group is formed

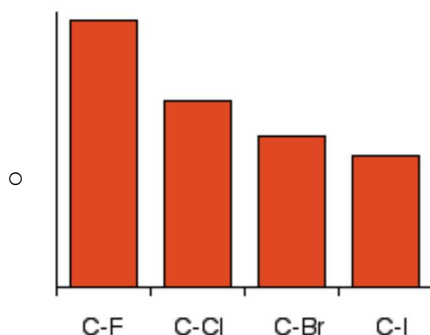
Hydrolysis mechanism

- Nucleophilic substitution**
- OH^- normally from NaOH
- OH^- (nucleophile) approaches the carbon atom attached to the halogen from the opposite side of halogen to minimise repulsion
- A lone pair on OH attracted & donated to $\delta+$ carbon atom
- New bond formed between oxygen atom of OH and the carbon atom
- Carbon-halogen bond breaks by heterolytic fission**
- Alcohol + halide ion formed



Trend in reaction rates of hydrolysis of primary haloalkanes

- C-F has the greatest bond enthalpy (strongest), C-I has the lowest bond enthalpy (weakest)
 - Going down the table = larger halogen atom = longer bond = bond becomes weaker
- Rate: iodoalkanes > bromoalkanes > chloroalkanes > fluoroalkanes
 - Increases as strength of carbon-halogen bond decreases
 - Less energy is needed to break the carbon-halogen bond to start the reaction so the activation energy is lower



- Measuring rate of hydrolysis
 - Set up 3 test tubes of 1 cm³ ethanol and couple drops of 1-chlorobutane / bromobutane / iodobutane
 - Put the test tubes + a test tube with silver nitrate in water bath at 60°C
 - Allow them to reach constant temperature (60°C)
 - Add 1 cm³ of silver nitrate to each test tube quickly + start stop watch
 - Observe time taken for precipitate to form
 - Chlorine = white, bromine = cream, iodine = yellow
 - Speed: iodobutane > bromobutane > chlorobutane
- CFCs
 - Shorthand for chlorofluorocarbons
 - Compounds containing carbon with chlorine and fluorine atoms attached
- Uses of CFCs
 - CFCs are non-flammable and not very toxic so they have a lot of uses
 - Refrigerants
 - Propellants for aerosols
 - Generating foamed plastics
 - Solvents for dry cleaning and for general degreasing purposes
- Problems associated with CFCs
 - Global warming
 - Breakdown of ozone layers in the atmosphere
- Ozone layer
 - Ozone continually formed and broken down by the action of UV radiation
 - Initially very high energy UV breaks oxygen molecules into oxygen radicals: $O_2 \rightarrow 2O$
 - A steady state then set up where rate of ozone formation is the same as the rate of ozone being broken down: $O_2 + O \rightleftharpoons O_3$
 - Equilibrium disturbed by human activities e.g. production and use of CFCs
- How CFCs break down ozone
 - CFCs remain stable until they reach the stratosphere
 - In the stratosphere UV breaks carbon-halogen bond by homolytic fission to form radicals (initiates the breakdown of ozone)
 - Photodissociation (Initiation): e.g. $CF_2Cl_2 \rightarrow CF_2Cl\cdot + Cl\cdot$
 - Chlorine radical formed is a very reactive intermediate and can react with an ozone molecule
 - Propagation step 1: $Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$
 - Propagation step 2: $ClO\cdot + O \rightarrow Cl\cdot + O_2$
 - (Overall: $O_3 + O \rightarrow 2O_2$)
 - There is a significant amount of O_3 and free oxygen atoms in the upper atmosphere for reaction
 - Chlorine radical can go on in chain reaction to break down other ozone molecules
- How nitrogen oxide break down ozone
 - Reaction with NO
 - Initiation: $NO \rightarrow N\cdot + O\cdot$
 - Propagation step 1: $N\cdot + O_3 \rightarrow \cdot NO + O_2$
 - Propagation step 2: $\cdot NO + O \rightarrow N\cdot + O_2$
 - Overall: $O_3 + O \rightarrow 2O_2$
 - Reaction with NO_2

- Initiation: $\text{NO}_2 \rightarrow \text{NO}\cdot + \text{O}\cdot$
- Propagation step 1: $\text{NO}\cdot + \text{O}_3 \rightarrow \text{NO}_2\cdot + \text{O}_2$
- Propagation step 2: $\text{NO}_2\cdot + \text{O} \rightarrow \text{NO}\cdot + \text{O}_2$
- Overall: $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$
- Alternatives for CFCs
 - Replace the C-Cl bond with stronger C-F bond
 - Hydrochlorofluorocarbons (HCFCs) or hydrofluorocarbons (HFCs) can be used
 - Still volatile, non-toxic and non-flammable
 - Still damage the ozone layer
 - Replace the C-Cl bond with a C-H bond
 - Use hydrocarbons
 - The C-H bond is much weaker and the molecules don't persist until they reach the upper atmosphere
 - They are very flammable

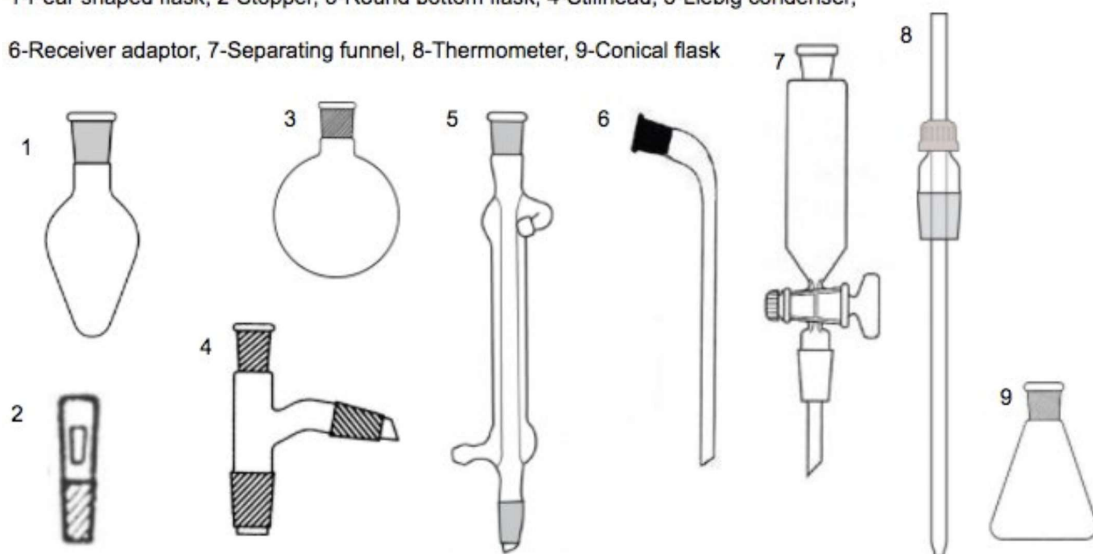
4.2.3 Organic synthesis

- Definitions

Term	Definition
Fractional distillation	The separation of components in a liquid mixture by their different boiling points into fractions with different compositions
Drying agent	An anhydrous solid that readily absorbs water from the mixture to become hydrated

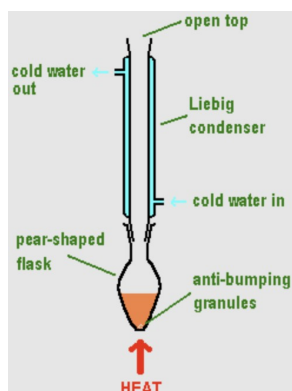
- Quickfit apparatus set

1-Pear shaped flask, 2-Stopper, 3-Round bottom flask, 4-Stillhead, 5-Liebig condenser, 6-Receiver adaptor, 7-Separating funnel, 8-Thermometer, 9-Conical flask

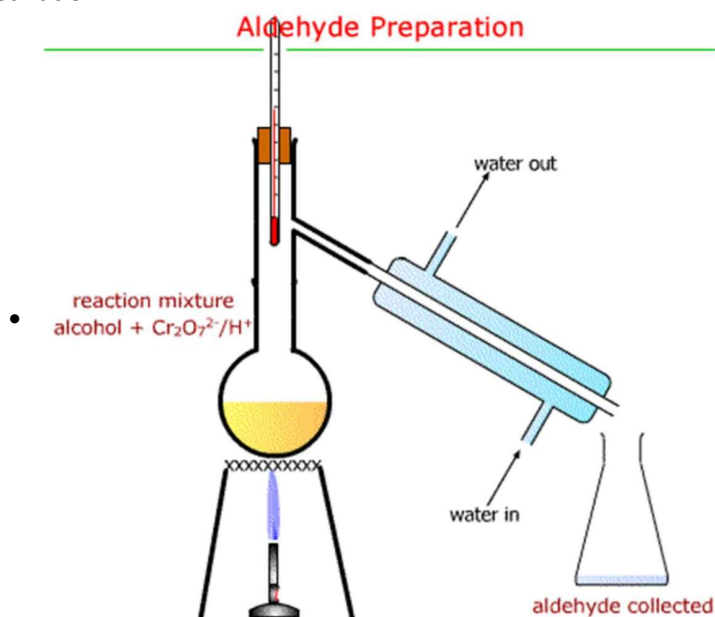


- Heating under reflux

- To prepare organic solid without boiling off solvent, reactants or products
- Water bath can be used rather than Bunsen if can be carried out below 100°C
- Heating mantle can be used for flammable liquids
- Anti-bumping granules added to liquid so it boils smoothly
 - Otherwise large bubbles will form at bottom so the glassware vibrate / jump
- Glass joints greased lightly so apparatus comes apart easily after experiment
- Condensers should be clamped loosely as the outer jacket is very fragile + kept in upright position
- Never put stopper in top-closed system or pressure would build up and the apparatus would explode
- Rubber tubing used to connect the inlet of condenser to tap and outlet to the sink (water always enters the condenser at the bottom and leaves at the top)

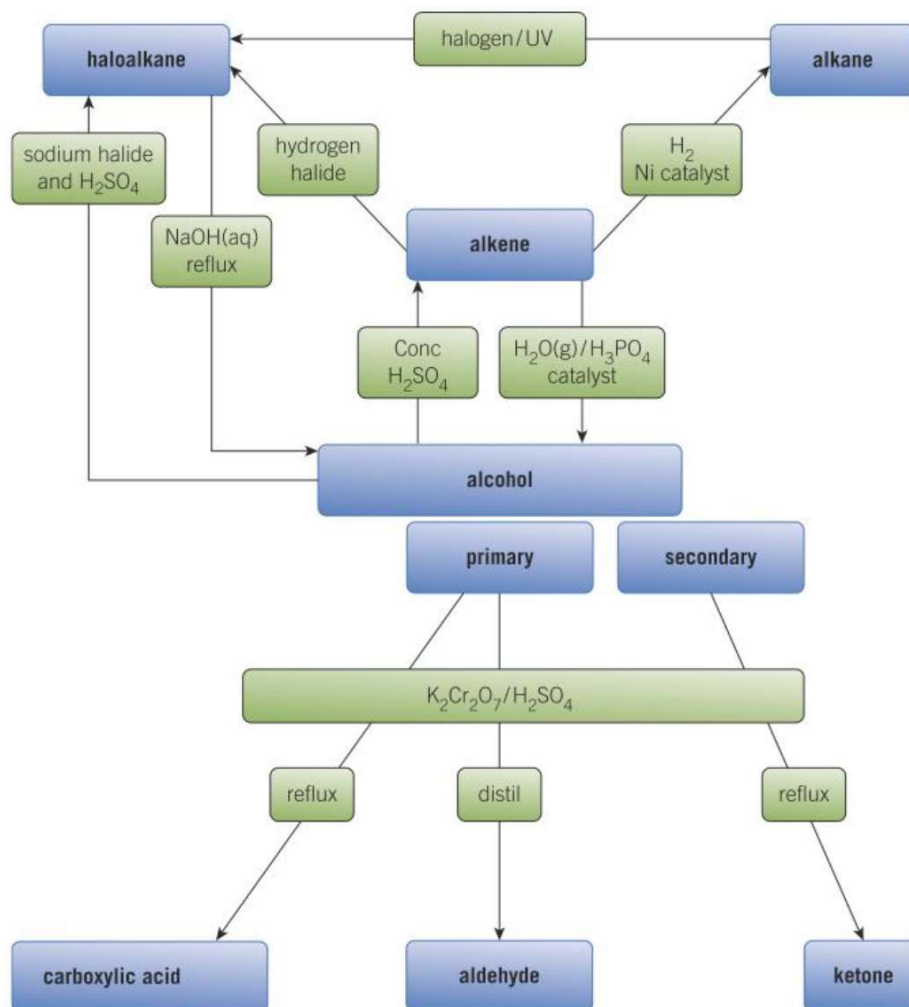


- Distillation



- Separates a pure liquid from impurities
- Flask clamped by neck
- Still head connected to the flask
- Condenser connected to rubber tubing for water (**water enters at the bottom**)
- Flask used to collect the distillate so the apparatus is not airtight
- Heat the mixture gently (make sure the temperature doesn't reach the boiling point of the less volatile compound)
- Purifying organic products using a separating funnel
 - When there are two layers inside the collection flask: one organic layer, one aqueous / water layer
 - Ensure tap of the separating funnel is closed
 - Pour in mixture and place a stopper in the top of the funnel + invert to mix the contents
 - Allow layers to settle
 - Can't tell the layers: add water to the mixture, the layer that increase in volume is the aqueous layer
 - Place conical flask under the separating funnel
 - Remove stopper + open the tap until whole lower layer has left the funnel
 - If the top layer is accidentally poured then pour the content in the first conical flask back into the separating funnel and restart
 - Repeat this several times until the bottom layer is almost completely removed
- Redistillation
 - Organic compounds may have relatively close boiling points so the sample may still have some impurities left over
 - Carry out a second distillation (or more)
 - Only collect product with the exact boiling point of the target compound
 - Try to not overheat the mixture
 - Narrower boiling point range = purer product
- Drying an organic product

- There may be water left in the organic product
- Add organic liquid to conical flask
- Add some drying agent with spatula + swirl the contents
 - e.g. CaCl_2 for drying hydrocarbons, CaSO_4 / MgSO_4 for general drying
- Put a stopper on to prevent product from evaporating away
- Leave for about 10 minutes
- If the solid stuck in a lump water is still present so add more drying agent until it becomes a fine powder
- After all the water is absorbed the organic mixture can be separated by filtration / simply decanting the liquid
- Synthetic routes



- Predicting properties of organic compounds
 - Find all functional groups
 - Find the properties and reactions for each functional group

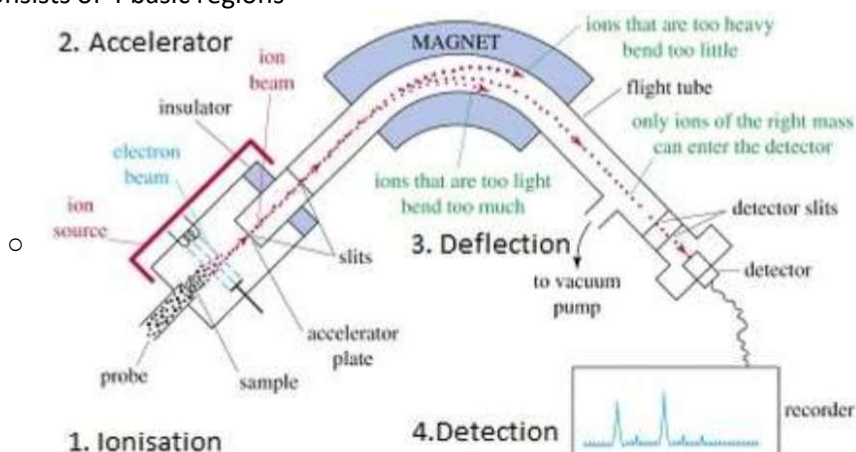
4.2.4 Analytical technique

- Definitions

Term	Definition
Fragmentation	The process in mass spectrometry that causes a positive ion to split into smaller pieces, one of which is a positive fragment ion
Fragment ions	Ions formed from the breakdown of the molecular ion in a mass spectrometer

- Vibrations in bonds
 - Bonds vibrate at a particular frequency
 - Stretch: moving along the line between atoms so the distance between them changes
 - Bend: results in change in bond angle
 - Bonds only absorb radiation with the same frequency as the natural frequency of the bond

- The frequency of the light depends on bond strength, bond length and atomic masses at both ends of the bond
 - Most bonds absorb at a frequency of $300 - 4000 \text{ cm}^{-1}$, i.e. IR radiation
- Absorbing IR radiation causes covalent bonds to absorb energy and vibrate more
- Greenhouse effect
 - Most of the Sun's radiation is **short wave** and is relatively unaffected by atmospheric gases
 - They pass through the atmosphere to the Earth's surface and some is reflected as **long wave** radiation
 - C=O, O-H and C-H bonds absorb radiation in the IR range which causes bond in gas molecules to vibrate
 - e.g. CO_2 , H_2O and CH_4 molecules
 - The vibrating bonds eventually re-emit the energy as radiation that increases the temperature of the atmosphere close to the Earth's surface
 - This creates incentives to reduce CO_2 emission to reduce global warming
- Infrared spectroscopy
 - Determine the functional groups present
 - Sample placed in IR spectrometer
 - IR radiation beams with wavenumber $200\text{-}4000 \text{ cm}^{-1}$ is passed through the sample
 - Molecules absorb some IR + emerging beam is analysed to identify frequencies absorbed
 - IR spectroscopy is usually connected to a computer that plots a graph of transmittance against wavenumber
 - The computer uses the fingerprint region to identify the compound
 - Fingerprint region: region **below 1500 cm^{-1}** with **unique peaks to identify particular molecule**
 - All organic compounds produce a peak $2850\text{-}3100$ from C-H bond
 - Look at other peaks to identify other bonds present
- Uses of IR spectroscopy in real life
 - Remote sensors analyse IR spectra of vehicle emissions to detect pollutants
 - IR-based breathalysers pass beams of IR through breathed out gas + detect IR absorbance
 - Detecting C-O bonds in alcohol molecules
 - O-H bond is present in water vapour breathed out so it is not used
 - Blood test taken if the result suggests that the person is too drunk to drive safely
- Mass spectroscopy
 - Used to analyse **gaseous** samples
 - Consists of 4 basic regions



- Some molecular ions break down into smaller fragments by fragmentation
- Analysing the structure from a mass spectrum
 - M_r = the m/z value of the **rightmost peak**
 - There might be a small peak after M^+ peak called the $M+1$ peak due to the presence of carbon-13 isotope
 - Other peaks are due to fragment ions
- Common m/z values for fragment ions

m/z value	Ion (remember to include the + charge)
-------------	----------------------------------------

15	CH_3^+
29	CH_3CH_2^+
31	CH_2OH^+
41	$\text{C}_3\text{H}_5, \text{C}_2\text{H}_3\text{N}$
43	$\text{CH}_3\text{CH}_2\text{CH}_2^+ / \text{CH}_3\text{CO} / \text{C}_3\text{H}_7$
45	$\text{CH}_3\text{CH}_2\text{O}^+$
49	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+$

- Identifying the organic compound
 - Elemental analysis: empirical formula
 - Mass spectrometry: determine molecular mass + identify sections of the molecule
 - IR spectrometry: identify bonds + functional groups present