Instrumental Analysis

Bonds and Infrared Energy

Covalent bonds can absorb infrared energy, which causes the bonds to vibrate. Depending on the masses of the bonded atoms, different frequencies of radiation are absorbed. Each specific bond has a characteristic frequency at which it absorbs infrared radiation.

Global warming is a result of molecules in the atmosphere absorbing the infrared emitted by the earth after it has been heated by the sun. Bonds that absorb infrared radiation include C=O, O-H and C-H bonds, so CO_2, H_2O and CH_4 are all greenhouse gases, but so are lots of other trace gases.

How significantly a greenhouse gas contributes to Global Warming depends on
- how strongly the bonds in it absorb infrared
- how much of that gas is present in the atmosphere

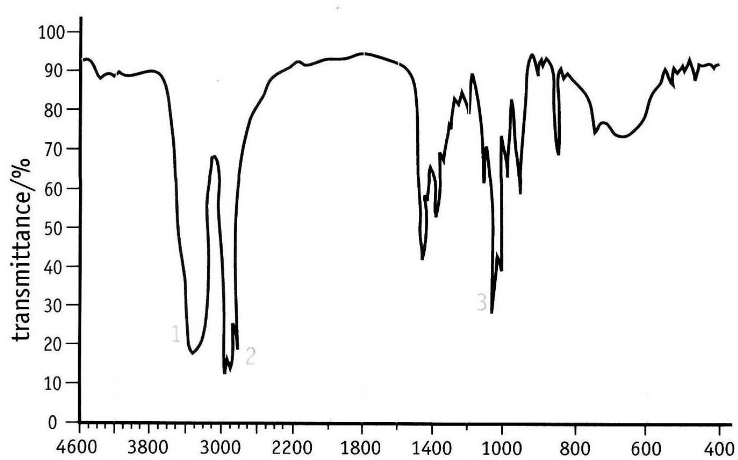
- H_2O from the evaporation of oceans and lakes is most abundant greenhouse gas
- CO_2 is the 2nd most abundant; from volcanic eruptions, respiration, burning and decay of organic matter (including fossil fuels)
- CH_4 is 3rd most abundant, but makes a greater contribution to global warming than the same amount of CO_2 because of the strong absorption of its four C-H bonds. It arises from rotting organic waste (in forests, landfill etc., as a by-product of digestion released from e.g. cows, emitted during the processing of fossil fuels.

How large the man-made contribution to global warming is as a result of burning fossil fuels is still a matter of scientific debate, but governments have accepted scientific evidence that the consequences of global warming in terms of climate change require policies towards the use of renewable energy resources and a reduction in the use of non-renewable energy.

Infrared Spectroscopy

Used to identify the bonds present in a compound rapidly and non-destructively. This allows the functional groups to be identified.

Principle:



The infrared spectrum is therefore a plot of absorbance (y-axis) vs. frequency of the infrared absorbed. Chemists use the units **wavenumbers** (cm^{-1}) for this axis. This is the number of wavelengths per centimetre, so high wavenumbers correspond to high frequencies of vibration.

Characteristic absorptions:

O-H	in alcohols	3230 – 3550 cm^{-1}	strong and broad (due to H-bonding)
O-H	in carboxylic acids	2500 – 3300 cm^{-1}	strong and broad (due to H-bonding)

C-H Most organic compounds show sharp strong absorptions around 2900 – 3100cm^{-1} due to C-H vibrations, these peaks tend to look "hairy", and should not be confused with the broad O-H peaks which can occur in the same region

C=O in ketones, aldehydes, esters, carboxylic acids 1680 – 1750cm^{-1} very strong

C-O (in alcohols, esters and carboxylic acids) is often found as a medium-strong sharp absorption between 1000cm^{-1} and 1300cm^{-1}, but beware as there are other bonds which absorb in this region too, so this can only be a "possibly C-O" assignment.

Note: The region from 1500cm^{-1} to 500cm^{-1} (the fingerprint region) contains a wealth of fine detail and is difficult to interpret other than by using a computer with a spectral matching database.

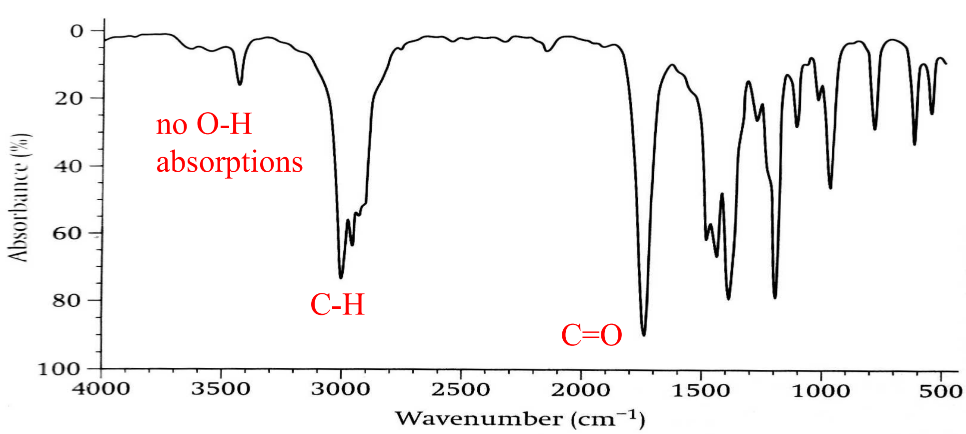
N.B. Datasheets in the exam give these wavenumbers, so they don't need to be learned, but you must be able to use them correctly !

Interpreting an infrared spectrum

Using the data sheet provided in the exam, identify the main absorptions present in the spectrum and label which bonds they represent. Also note where significant absorptions such as O-H are *not* present, as evidence that the molecule being analysed does not have these bonds.

Then use the information list the functional group(s) present in the molecule, given the context information in the question.

Example: The infrared spectrum shows what was produced when butanol was oxidised by refluxing with excess acidified potassium dichromate. Identify the product, and hence decide whether the butanol was butan-1-ol or butan-2-ol.



Interpretation:
Having identified that there is C=O present, but not O-H the product is either an aldehyde or a ketone, but not a carboxylic acid. Butanal could be produced by oxidising butan-1-ol, but the conditions for this are wrong - heat, reflux and an excess of the oxidising agent indicate that any butanal formed would be further oxidised to butanoic acid. Butanone could be produced by oxidising butan-2-ol, and would not oxidise further, so it is likely that this is the product shown, and that the alcohol was butan-2-ol.

Uses of infrared spectroscopy:

i) atmospheric monitoring

The main gases we are concerned about in the lower atmosphere that we breathe are carbon monoxide, oxides of nitrogen, and hydrocarbons.

We monitor the concentration of gases such as these using infrared spectrometers. The pollutants are identified by matching their infrared spectra with reference spectra in databases. The concentrations of these gases are monitored by measuring the amount of absorption of infrared at specific wavelengths where their bonds absorb. A network of monitoring stations across the country, and in other countries, allows monitoring and modelling to predict future trends and impacts.

Carbon monoxide

Origin: incomplete combustion of hydrocarbons/fossil fuels with limited oxygen in internal combustion engines, heat and power generation
e.g. C_8H_{18} (main alkane in petrol) + 8½ O_2 → 8CO + $9H_2O$

Problem: Toxic, odourless, colourless

Hydrocarbons

Origin: unburnt or partially-burnt fossil fuels. Longer-chain molecules in diesel engines don't always burn completely, but produce **particulates**: tiny particles of carbon coated with unburnt hydrocarbons

Problem: Unburnt benzene (C_6H_6) is particularly dangerous because it is carcinogenic.

Nitrogen Oxides (NOx):

Source: At the high temperatures inside internal combustion engines, N_2 in the air burns, reacting with O_2 to form a variety of oxides of nitrogen, the main ones being NO and NO_2.

Problems: NOx can be oxidized and react with atmospheric moisture to produce acid rain.

ii) Motor vehicle exhaust emissions

Fitting cars with exhaust catalyst systems is a legislative requirement for all newly built cars. The catalytic converter contains a honeycomb structure of aluminium or ceramic (large surface area) coated with a thin layer of alloy of Pt, Pd and Rh (expensive) on the surface of which a number of important reactions are catalysed as the exhaust gas flows over them. The catalyst is heated by the hot gases from the engine, and catalysts only work at high temperature, so that catalyst systems in cars are only effective on longer journeys after they have warmed up.

Heterogeneous catalysis takes place on the catalyst surface:
i) Unburnt hydrocarbons removed by fully burning them in the remaining oxygen in the gas stream

$$C_8H_{18(g)} + 12½\ O_2 \rightarrow 8CO_2 + 9H_2O$$

ii) NO, NO_2 and CO are removed by using the NOx to oxidize the CO:

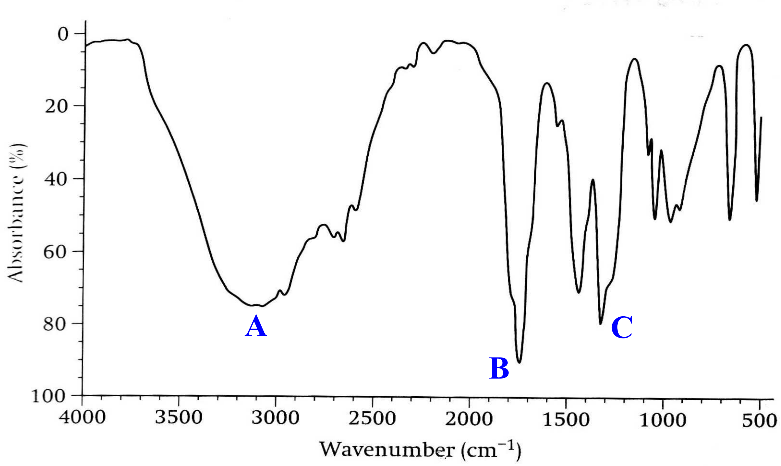
$$2\ NO + 2\ CO \rightarrow N_2 + 2\ CO_2$$
$$2\ NO_2 + 4CO \rightarrow N_2 + 4\ CO_2$$

At an MOT test, exhaust gases from the engine are drawn through an infrared spectrometer so that the concentrations of the pollutant gases can be measured and the functioning of the engine and catalyst system checked. To pass, these must be below the legislative limits for the type of vehicle.

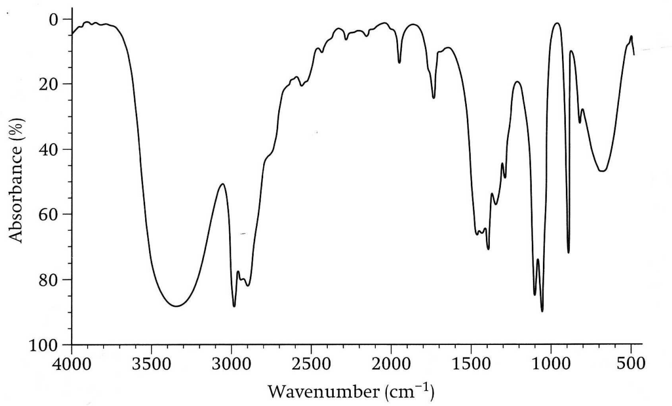
iii) Breathalysers
Breathalysers can use infrared spectroscopy to estimate the blood alcohol content (BAC) from the ethanol content in a breath sample. These are used as preliminary tests to decide whether samples should be taken at a police station for a BAC measurement that could be used for prosecution.

The first generation of breathalysers were based on acidified permanganate or dichromate ions, which oxidised the alcohol to a carboxylic acid and showed a colour change. Subsequent breath alcohol analysers used infrared sensors to monitor the strength of infrared absorptions due to ethanol molecules, although the current generation of breathalysers are based on an ethanol fuel cell which generates an electrical current by oxidising ethanol to ethanoic acid: the size of the current indicates the concentration of ethanol in the breath.

Check your understanding:
i) Identify the main bonds which cause the labelled absorptions in the following infrared spectrum:



ii) Decide whether this molecule is i) an alcohol; ii) a carboxylic acid or iii) a ketone, giving reasons.



Mass Spectrometry

A variety of analytical methods, including mass spectrometry, are capable of telling us what elements are present in a compound, and in what quantity. With this we can determine the empirical formula of the compound.

Example: e.g. "44g of a gas is analysed and found to contain 18g of carbon and 48g of oxygen. Calculate the empirical formula."

	C	O	
Mass (g)	18	48	
A_r	12	16	
Moles	1.5	3.0	
Ratio	1	2	Empirical CO_2

This elemental analysis of CO_2 example could have been written as:
"A gas was analysed and found to contain 27.27% by mass of carbon and 72.73% of oxygen… calculate its empirical formula."

We can use the same layout, with the % in place of the mass (this works because we can pretend the total mass of sample is 100g so each % is also a mass in g)

	C	O	
Mass	27.27	72.73	
RAM	12	16	
Moles	2.2725	4.5456	
Ratio	1	2.00027	Empirical formula: CO_2

Sometimes we get fractions in the ratio to deal with:
e.g. A 14.2g sample containing P and O is found to contain 6.2g of P.

	P	O

Mass (g)	6.2	14.2 – 6.2 = 8.0	
A_r	31.0	16.0	
Moles	0.2	0.5	
Ratio	1	2.5	x 2 to clear fractions…
	2	5	Empirical P_2O_5

Check your understanding:

iii) 8.00g of Na is burnt in excess oxygen to produce 10.78g of a yellow solid. Find its empirical formula.

iv) 10.00g of an oxide of lead, when reduced, produced 9.07g of lead. What was the empirical formula of the oxide ?

v) Compound F contains 39.74% C, 7.28% H and 52.98% Br. Show that its empirical formula is $C_5H_{11}Br$.

vi) A compound contains 29.1% Na, 40.5% S and 30.4% O Calculate its empirical formula.

The empirical formula only gives us the simplest whole number ratio of the atoms present. All alkenes, for example, would have the empirical formula CH_2. To determine the molecular formula, we need to know the mass of a molecule. Mass spectrometry also allows us to measure the relative molecular mass of substances.

Molecular ion peak

The mass spectrometer is able to remove an electron from sample molecules, turning them into molecular ions, which the mass spectrometer can then measure the mass of. These show up as the peak furthest to the right (at highest m/z). This is usually not the strongest peak. It is called the **molecular ion peak**, and tells you M_r for the molecule.

N.B. You may well see a very small peak at m/z = M_r+ 1. This is due the presence of carbon-13 atoms in all natural organic materials at about 1.1% abundance. Do not mistake this for the molecular ion peak !

Once you know the M_r and the empirical formula, you can work out how many times the empirical formula must be multiplied up to get to the molecular formula:

e.g. A hydrocarbon is found to have empirical formula CH and its mass spectrum shows a molecular ion peak at m/z = 78. What is its molecular formula ?

M_r	= 78
Mass of atoms in empirical formiula	= 12.0 + 1.0 = 13.0
Multiplying factor	= 78 / 13 = 6
Molecular formula = 6 x CH	= C_6H_6

Check your understanding:

vii) An alkene has empirical formula CH_2 and the mass spectrum of the alkene shows a molecular ion peak at m/z = 42. What's its molecular formula ?

viii) A salt of silver comprises silver, carbon and oxygen only. It contains 7.89% C and 21.06% O by mass and has Mr = 304. What's its molecular formula ?

Fragment ions

The mass spectrometer also breaks the molecules into fragments, and ionizes each of these by removing an electron. This allows the structure to be worked out by identifying the fragments from which the molecule is built up:

e.g.	$[CH_3]^+$	m/z = 15	$[(CH_3)_2CH]^+$	m/z = 43
	$[CH_3CH_2]^+$	m/z = 29	$[OH]^+$	m/z = 17
	$[CH_3CH_2CH_2]^+$	m/z = 43	$[CH_2OH]^+$	m/z = 31

Note that the fragment ions should be drawn in square brackets, and given a positive charge (either that or the positive charge must be shown on the correct atom – the one where the bond to the rest of the molecule was broken).

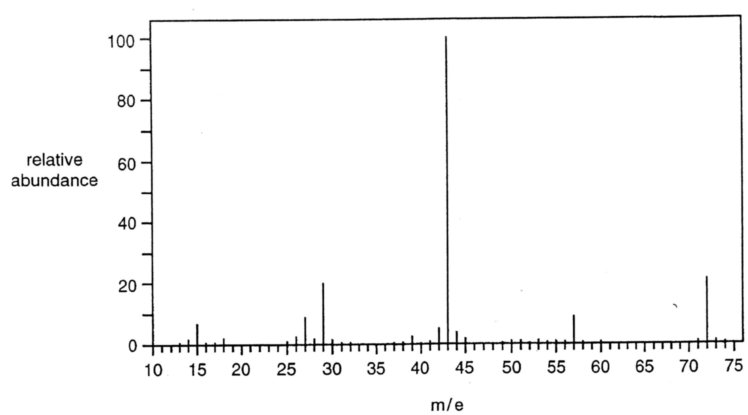
- List the m/z values of the main fragment ion peaks in the mass spectrum
- Use the m/z values to suggest structural or displayed formulae for the fragments, bearing in mind the contextual information about the sample being analysed
- Look to see if fragment ions are present in the spectrum at the m/z values you would expect for your proposed molecule

The peaks all taken together constitute a fingerprint for the molecule, and are usually matched to mass spectral databases using a computer. This technique is used e.g. for identifying traces of drugs or explosives in forensics and security work.

Check your understanding:

ix) Suggest identities for the fragments giving rise to the following peaks in this mass spectrum of butanone

m/e = 15
m/e = 29
m/e = 43
m/e = 57
m/e = 72

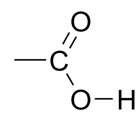


Answers to Check your Understanding questions:

i) Identify the main bonds which cause the labelled absorptions in the following infrared spectrum:

A - strong broad absorption at 3100cm^{-1} is O-H in an carboxylic acid
(if it were O-H in an alcohol it would be at higher wavenumbers)
B – strong sharp absorption at 1720cm^{-1} is C=O
C – the medium absorption at 1300cm^{-1} may possibly be a C-O

ii) Decide whether this molecule is i) an alcohol; ii) a carboxylic acid or iii) a ketone, giving reasons.

The evidence suggests a carboxylic acid functional group: 

Empirical formula calculations

iii) 8.00g of Na is burnt in excess oxygen to produce 10.78g of a yellow solid. Find the empirical formula:

	Na		O	
Mass (g)	8.00		10.78 – 8.00 = 2.78	
RAM	23.0		16.0	
Moles	0.3478		0.I7375	** watch rounding !
Ratio	2	:	1	Empirical Na_2O

iv) 10.00g of an oxide of lead, when reduced, produced 9.07g of lead. What was the empirical formula of the oxide ?

	Pb	O	
Mass(g)	9.07	10.00 – 9.07 = 0.93	
RAM	207.2	16	
Moles	0.04377	0.058125	
Ratio	1.0	1.33	Recognise 1/3 so x all by 3
Ratio	3	4	Empirical Pb_3O_4

v) Compound F contains 39.74% C, 7.28%H and 52.98%Br. Show its empirical formula is $C_5H_{11}Br$.

	C	H	Br	
%	39.74	7.28	52.98	
RAM	12.0	1.0	79.9	
Moles	3.31167	7.28	0.66308	
Ratio	4.994	10.979	1	
	5	11	1	$C_5H_{11}Br$

vi) A compound contains 29.1% Na, 40.5% S and 30.4% O
Calculate its empirical formula.

	Na	S	O	
%	29.1	40.5	30.4	
RAM	23.0	32.1	16.0	
Moles	1.2652	1.2616	1.9	
Ratio	1	1	1.5	recognise ½ so x2
Ratio	2	2	3	Empirical: $Na_2S_2O_3$

Molecular formulae from composition data and M_r

vii) An alkene has empirical formula CH_2 and molecular ion peak at = 42
What's its molecular formula ?

Mr	42
EFM = 12 + 2	14
Mr/EFM	3
Molecular formula = 3 x CH_2	= C_3H_6

viii) A salt of silver comprises silver, carbon and oxygen only. It contains 7.89% C and 21.06% O by mass and has Mr = 304. What's its molecular formula ?

	Ag	C	O	
%	71.05 (calc)	7.89	21.06	
RAM	107.9	12.0	16.0	
Moles	0.6585	0.6575	1.316	
Ratio	1	1	2	$AgCO_2$ empirical

Mr	304		
Empirical formula mass	151.9	(107.9 + 12 + 16 + 16)	
Mr/EFM	2.00		
Molecular formula:	2 x $AgCO_2$		Molecular formula: $Ag_2C_2O_4$

ix) Suggest identities for the fragments giving rise to the following peaks in this mass spectrum of butanone.

m/e = 15 this is likely to be $[CH_3]^+$
m/e = 29 this is likely to be $[CH_3CH_2]^+$
m/e = 43 this is likely to be $[CH_3CO]^+$ (since butanone doesn't have $CH_3CH_2CH_2$- in it)
m/e = 57 this is likely to be $[CH_3CH_2CO]^+$
m/e = 72 this is the molecular ion $[CH_3CH_2COCH_3]^+$