

Infra-red spectroscopy: reading an IR spectrum (A Level Chemistry notes)

These notes cover infra-red (IR) spectroscopy for Cambridge International AS and A Level Chemistry 9701. They explain why molecules absorb infra-red radiation, how a spectrum is drawn, which absorptions in the Data Booklet you need to recognise, and how to use IR together with mass spectra to identify an unknown compound. The topic also links to the greenhouse effect. Work through the worked interpretations, then try the Quick check at the end.

1. How infra-red absorption works

1.1 Bonds vibrate

The atoms in a covalent bond are not fixed in place. The bond behaves rather like a spring: the atoms move towards and away from each other (stretching) and the angles between bonds open and close (bending). Each bond vibrates at its own natural frequency, which depends on two things:

- **Bond strength.** A stronger bond vibrates at a higher frequency. A C=O double bond absorbs at a higher wavenumber than a C-O single bond.
- **Masses of the atoms.** Lighter atoms vibrate at a higher frequency. Bonds to hydrogen (O-H, N-H, C-H) absorb at high wavenumbers, above about 2500 cm^{-1} .

1.2 Absorbing energy

Infra-red radiation has frequencies in the same range as these vibrations. When the frequency of the radiation exactly matches the natural vibration frequency of a bond, the bond absorbs that radiation and vibrates more strongly. Radiation of other frequencies passes through.

A bond absorbs infra-red radiation when the frequency of the radiation matches the natural frequency of vibration of the bond. The absorbed energy makes the bond stretch or bend more vigorously.

A vibration only absorbs infra-red radiation if it causes a **change in the dipole moment** of the molecule.

Because each type of bond absorbs at its own characteristic frequency, the pattern of absorptions shows which bonds, and therefore which functional groups, are present. Molecules made of two identical atoms, such as N_2 , O_2 and H_2 , have no dipole and stretching them creates none, so they do not absorb infra-red radiation.

1.3 The spectrometer, in outline

A beam of infra-red radiation covering a range of frequencies is passed through the sample. A detector measures how much radiation passes through at each frequency, and the result is plotted as a spectrum. You do not need to know the details of the instrument for 9701.

2. Wavenumber and the shape of a spectrum



2.1 Wavenumber

Wavenumber is the number of waves per centimetre. It equals $1 \div \text{wavelength}$ (with the wavelength in cm), and its unit is cm^{-1} .

Wavenumber is proportional to frequency, so a higher wavenumber means higher frequency and higher energy. IR spectra used in A Level usually run from 4000 cm^{-1} on the left to about 400 or 500 cm^{-1} on the right. Note that the scale gets *smaller* from left to right.

Worked example 1: converting to wavenumber

A bond absorbs radiation of wavelength $5.80 \times 10^{-6} \text{ m}$. Calculate the wavenumber.

Convert to cm: $5.80 \times 10^{-6} \text{ m} = 5.80 \times 10^{-4} \text{ cm}$.

Wavenumber = $1 \div (5.80 \times 10^{-4}) = 1724 \text{ cm}^{-1}$, about 1720 cm^{-1} . This is in the C=O range.

2.2 Reading the axes

The vertical axis is **transmittance**, as a percentage. 100% means all the radiation passed through. An absorption appears as a dip (a "trough") pointing downwards, and chemists usually call these troughs "peaks" or "bands". A deep trough means strong absorption.

When you describe an absorption, note three things:

- **Position:** the wavenumber, which identifies the bond.
- **Intensity:** strong, medium or weak. C=O and C-O are strong because they are very polar.
- **Shape:** sharp or broad. Hydrogen-bonded O-H gives a broad absorption.

3. The Data Booklet absorptions that matter

You are not expected to memorise exact values: the Data Booklet gives a table of characteristic absorptions and you look them up. However, you must know which ones to look for and how to tell similar ones apart. The ranges below are the typical values used at A Level. Always check them against the Data Booklet for your exam year, because the exact figures vary slightly between editions.

Bond	Found in	Typical range / cm^{-1}	Appearance
C-O	alcohols, esters, carboxylic acids, ethers	1040 to 1300	strong, in the fingerprint region
C=C	alkenes	1500 to 1680	medium to weak
C=O	aldehydes, ketones, carboxylic acids, esters, amides	1670 to 1740	strong and sharp
C≡N	nitriles	2200 to 2250	medium and sharp
C-H	alkanes, alkenes, arenes	2850 to 3100	medium to strong
O-H	carboxylic acids (hydrogen bonded)	2500 to 3000	very broad
O-H	alcohols, phenols (hydrogen bonded)	3200 to 3600	broad

N-H	amines, amides	3300 to 3500	medium, sharper than O-H
-----	----------------	--------------	--------------------------

3.1 O-H in alcohols compared with O-H in acids

Both are broad because of hydrogen bonding, which gives the O-H bonds a spread of slightly different strengths and so a spread of absorption frequencies.

- In an **alcohol**, the O-H absorption is broad and centred high, roughly 3200 to 3600 cm^{-1} . It sits to the left of the C-H absorptions.
- In a **carboxylic acid**, the O-H absorption is very broad and lower, roughly 2500 to 3000 cm^{-1} . It is so wide that it often overlaps the C-H absorptions, which appear as small sharp points on top of it.
- A carboxylic acid also shows a strong C=O absorption near 1700 cm^{-1} . An alcohol does not.

3.2 N-H compared with O-H

N-H absorptions fall in a similar region to alcohol O-H, but they are usually less intense and narrower, because N-H is less polar and its hydrogen bonding is weaker. A primary amine ($-\text{NH}_2$) often shows two small points in this region. If the formula contains no nitrogen, there can be no N-H absorption, so use the molecular formula to decide.

3.3 C=O and C-O

A strong, sharp absorption near 1700 cm^{-1} means a carbonyl group. On its own it cannot tell you whether the compound is an aldehyde, ketone, acid or ester, so look at the other absorptions:

- C=O plus very broad O-H at 2500 to 3000 cm^{-1} : **carboxylic acid**.
- C=O plus strong C-O at 1040 to 1300 cm^{-1} , but no O-H: **ester**.
- C=O with no O-H and no strong C-O: **aldehyde or ketone**. You then need a chemical test (for example Tollens' reagent or Fehling's solution) or other data to tell them apart.

3.4 C-H

Almost every organic compound has C-H bonds, so an absorption at 2850 to 3100 cm^{-1} tells you very little. Use it mainly to avoid confusing it with O-H or N-H.

4. The fingerprint region

The **fingerprint region** is the part of an infra-red spectrum below about 1500 cm^{-1} . It contains many overlapping absorptions from the whole molecule and its pattern is unique to each compound.

Bending vibrations and C-C, C-O and C-N stretches all absorb here, and they affect one another, so the pattern depends on the structure of the molecule as a whole. Two different compounds never give exactly the same fingerprint region. This is used in two ways:

- **Identifying a compound**: its spectrum is compared with a database of known spectra. A perfect match in the fingerprint region confirms the identity.
- **Checking purity**: extra absorptions that are not in the reference spectrum show that an impurity is present.

At A Level, do not try to assign individual troughs in the fingerprint region, except for the strong C-O absorption, which is listed in the Data Booklet.

5. Identifying functional groups from a described spectrum

Exam questions often describe a spectrum in words or give a short list of absorptions. Use a fixed order so that you do not miss anything.

Method for interpreting an IR spectrum

1. Look above 2500 cm^{-1} . Is there a broad O-H? Decide whether it is alcohol-type (3200 to 3600) or acid-type (2500 to 3000). Is there an N-H?
2. Look at 1670 to 1740 cm^{-1} . Is there a strong C=O?
3. Look at 1040 to 1300 cm^{-1} . Is there a strong C-O?
4. Check any others: C=C near 1500 to 1680, C≡N near 2200 to 2250.
5. Combine the evidence with the molecular formula, and state each bond with its wavenumber in your answer.

Absence of an absorption is evidence too. "No broad absorption between 3200 and 3600 cm^{-1} , so no alcohol O-H" earns marks.

Worked interpretation 2

Compound A, $\text{C}_3\text{H}_8\text{O}$, has a broad absorption at 3350 cm^{-1} , absorptions at 2880 to 2970 cm^{-1} and a strong absorption at 1050 cm^{-1} . There is no absorption between 1670 and 1740 cm^{-1} . Identify the functional group.

Broad 3350 cm^{-1} : O-H, hydrogen bonded, alcohol range. 2880 to 2970 cm^{-1} : C-H. 1050 cm^{-1} : C-O. No C=O.

A is an **alcohol**. It could be propan-1-ol or propan-2-ol: IR alone cannot separate these two, but their fingerprint regions would differ.

Worked interpretation 3

Compound B, $\text{C}_3\text{H}_6\text{O}_2$, shows a very broad absorption from 2500 to 3200 cm^{-1} with sharp points near 2950 cm^{-1} , a strong sharp absorption at 1715 cm^{-1} and a strong absorption at 1240 cm^{-1} .

Very broad absorption reaching down to 2500 cm^{-1} : O-H of a carboxylic acid. Sharp points on top: C-H. 1715 cm^{-1} : C=O. 1240 cm^{-1} : C-O.

B is a **carboxylic acid**, propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$.

Worked interpretation 4

Compound C, also $\text{C}_3\text{H}_6\text{O}_2$, shows absorptions at 2980 cm^{-1} , 1745 cm^{-1} (strong) and 1200 cm^{-1} (strong), and nothing above 3000 cm^{-1} .

No broad O-H, so not an acid or alcohol. C=O near 1740 cm^{-1} and strong C-O at 1200 cm^{-1} . C is an **ester**: methyl ethanoate, $\text{CH}_3\text{COOCH}_3$, or ethyl methanoate, $\text{HCOOCH}_2\text{CH}_3$.

5.1 Following a reaction with IR

IR is useful for showing that a reaction has happened, because functional groups appear or disappear. For example, when ethanol is heated under reflux with acidified potassium dichromate(VI), the product ethanoic acid shows a new C=O absorption near 1700 cm^{-1} , and the O-H absorption moves from the alcohol range to the broader, lower acid range. If ethanal is formed instead (by distillation), the O-H absorption disappears completely and a C=O absorption appears.

6. Using IR with mass spectra

IR tells you which bonds are present but not how many carbon atoms there are or how they are arranged. Mass spectrometry supplies the missing information:

- The **molecular ion peak**, M^+ , gives the relative molecular mass.
- The **$M+1$ peak** can be used to estimate the number of carbon atoms.
- **Fragment peaks** show pieces of the molecule, for example $m/e = 15$ for CH_3^+ and $m/e = 29$ for C_2H_5^+ or CHO^+ .

Worked interpretation 5: IR with a mass spectrum

Compound D contains only C, H and O. Its mass spectrum has a molecular ion peak at $m/e = 58$ and a large peak at $m/e = 43$. Its IR spectrum has a strong absorption at 1715 cm^{-1} and none between 2500 and 3600 cm^{-1} apart from C-H near 2950 cm^{-1} . Deduce a structure.

IR: C=O present; no O-H, so not an acid or alcohol. Only one oxygen atom is likely, so it is an aldehyde or ketone.

$M_r = 58$. $\text{C}_3\text{H}_6\text{O}$ has $M_r = (3 \times 12) + (6 \times 1) + 16 = 58$, which fits.

Possible structures: propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, or propanone, CH_3COCH_3 . The peak at 43 is CH_3CO^+ , which forms easily from propanone by loss of CH_3 ($58 - 15 = 43$). D is most likely **propanone**. A test with Tollens' reagent (no silver mirror) would confirm a ketone.

7. Infra-red absorption and the greenhouse effect

The Sun's radiation warms the Earth's surface, and the surface then emits energy as infra-red radiation. Some molecules in the atmosphere absorb this infra-red radiation, because their bonds vibrate at matching frequencies. The energy is then re-emitted in all directions, including back towards the surface, which keeps the lower atmosphere warmer than it would otherwise be.

A **greenhouse gas** is a gas whose molecules absorb infra-red radiation emitted from the Earth's surface, because their vibrations change the dipole moment of the molecule. Examples are carbon dioxide, water vapour and methane.

- **CO_2** is a linear, non-polar molecule, but its asymmetric stretch and its bending vibrations do change the dipole moment, so it absorbs infra-red.
- **H_2O** and **CH_4** have polar bonds whose vibrations change the dipole, so they also absorb.
- **N_2** and **O_2** , the main gases of the air, do not absorb infra-red, because stretching a bond between identical atoms produces no change in dipole.

How much a gas contributes to global warming depends on how strongly each molecule absorbs, how concentrated the gas is and how long it stays in the atmosphere.

Exam tips

Always quote the wavenumber or range when you name a bond: "C=O at 1715 cm^{-1} ", not just "C=O".

Use the molecular formula: no oxygen means no O-H, C=O or C-O; no nitrogen means no N-H or C≡N.

Say "broad" for O-H and explain it by hydrogen bonding if asked.

Quick check

1. State what is meant by the term wavenumber and give its unit. [2]
2. Explain why a C-H bond and a C=O bond absorb infra-red radiation at different wavenumbers. [2]
3. State what is meant by the fingerprint region and describe how it is used to identify an organic compound. [3]
4. Explain why nitrogen, N_2 , does not absorb infra-red radiation but carbon dioxide does. [3]
5. A compound shows a strong, sharp absorption at 1720 cm^{-1} . State the bond responsible and list the classes of compound that could give this absorption. [2]
6. Describe two differences you would see between the IR spectra of ethanol and ethanoic acid. [3]
7. Butan-1-ol is oxidised by heating under reflux with excess acidified potassium dichromate(VI). Describe how the IR spectrum of the product would differ from that of butan-1-ol. [3]
8. Compound E, $\text{C}_2\text{H}_7\text{N}$, shows two small, fairly sharp absorptions at 3290 cm^{-1} and 3370 cm^{-1} , absorptions at 2850 to 2960 cm^{-1} , and nothing between 1670 and 1740 cm^{-1} . Identify the functional group and suggest a structure for E. [3]
9. Compound F contains carbon, hydrogen and oxygen only. Its mass spectrum has a molecular ion peak at $m/e = 88$. Its IR spectrum shows a strong absorption at 1740 cm^{-1} , a strong absorption at 1240 cm^{-1} and no absorption between 2500 and 3600 cm^{-1} other than C-H near 2980 cm^{-1} . F contains two oxygen atoms. Deduce the molecular formula of F, identify its functional group and suggest one possible structure. [4]
10. A student says: "Since nitrogen and oxygen make up about 99% of the atmosphere, they must be the most important greenhouse gases." Evaluate this statement. [3]

Answers

1. Wavenumber is the number of waves per centimetre, equal to $1 \div \text{wavelength}$ (wavelength in cm) [1]. Unit: cm^{-1} [1].
2. Each bond has its own natural vibration frequency, which depends on bond strength and on the masses of the atoms [1]. C-H contains the very light hydrogen atom, so it vibrates at a high frequency (about 2850 to 3100 cm^{-1}); C=O involves heavier atoms, so even though it is a strong double bond it absorbs at a lower wavenumber (about 1670 to 1740 cm^{-1}) [1].

3. The fingerprint region is the part of the spectrum below about 1500 cm^{-1} [1]. It contains many overlapping absorptions from the whole molecule, so its pattern is unique to each compound [1]. The spectrum of the unknown is compared with a database of reference spectra, and an exact match in this region identifies the compound [1].
4. A molecule absorbs infra-red radiation only if a vibration changes its dipole moment [1]. N_2 has two identical atoms, so stretching the bond produces no dipole and no absorption [1]. CO_2 has polar $\text{C}=\text{O}$ bonds; although the molecule is linear and has no overall dipole, its asymmetric stretch and bending vibrations produce a changing dipole, so it absorbs infra-red [1].
5. $\text{C}=\text{O}$, the carbonyl group [1]. It could be an aldehyde, a ketone, a carboxylic acid or an ester (also amides) [1]. Further evidence from other absorptions is needed to decide.
6. Any two, with wavenumbers:
Ethanol has a broad $\text{O}-\text{H}$ absorption at about 3200 to 3600 cm^{-1} ; ethanoic acid has a very broad $\text{O}-\text{H}$ absorption at lower wavenumber, about 2500 to 3000 cm^{-1} , overlapping the $\text{C}-\text{H}$ absorptions [1 + 1].
Ethanoic acid has a strong $\text{C}=\text{O}$ absorption at about 1700 cm^{-1} ; ethanol has none [1].
The fingerprint regions differ [1].
7. Heating under reflux with excess oxidising agent forms butanoic acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ [1]. A new strong $\text{C}=\text{O}$ absorption appears at about 1670 to 1740 cm^{-1} [1].
The broad alcohol $\text{O}-\text{H}$ absorption at about 3200 to 3600 cm^{-1} is replaced by a very broad acid $\text{O}-\text{H}$ absorption at about 2500 to 3000 cm^{-1} [1].
8. The absorptions at 3290 and 3370 cm^{-1} are $\text{N}-\text{H}$ (the formula contains no oxygen, so they cannot be $\text{O}-\text{H}$) [1]. Two $\text{N}-\text{H}$ absorptions suggest an $-\text{NH}_2$ group, a primary amine [1]. 2850 to 2960 cm^{-1} is $\text{C}-\text{H}$, and there is no $\text{C}=\text{O}$, so it is not an amide. E is ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$ [1]. (Dimethylamine, $(\text{CH}_3)_2\text{NH}$, has the same formula but only one $\text{N}-\text{H}$ bond, so it would show a single $\text{N}-\text{H}$ absorption.)
9. IR: 1740 cm^{-1} is $\text{C}=\text{O}$; 1240 cm^{-1} is $\text{C}-\text{O}$; no broad $\text{O}-\text{H}$, so it is not an acid or alcohol. F is an **ester** [1].
An ester with two oxygen atoms has the general formula $\text{C}_n\text{H}_{2n}\text{O}_2$. Mass of $\text{O}_2 = 32$, so the C_nH_{2n} part has mass $88 - 32 = 56$. Each CH_2 unit has mass 14, so $n = 56 \div 14 = 4$ [1].
Molecular formula = **$\text{C}_4\text{H}_8\text{O}_2$** . Check: $(4 \times 12) + (8 \times 1) + (2 \times 16) = 48 + 8 + 32 = 88$ [1].
One possible structure: ethyl ethanoate, $\text{CH}_3\text{COOCH}_2\text{CH}_3$ [1]. (Methyl propanoate, $\text{CH}_3\text{CH}_2\text{COOCH}_3$, or propyl methanoate are also correct.)
10. The statement is wrong [1]. N_2 and O_2 are molecules made of two identical atoms, so their vibrations cause no change in dipole moment and they do not absorb infra-red radiation emitted by the Earth [1]. The greenhouse effect depends on gases such as CO_2 , H_2O and CH_4 , whose vibrations do change the dipole; even at low concentrations these absorb infra-red and re-emit it, so what matters is the ability to absorb infra-red, not the amount of gas present [1].