DP IB Chemistry : HL

## 11.1 Spectroscopic Identification

Contents

Your notes

11.1.1 Index of Hydrogen Deficiency

Index of Hydrogen Deficiency

- The **degree of unsaturation** or **index of hydrogen deficiency** provides information about the number of double or triple bonds in a molecule
- The **IHD** is the number of hydrogen molecules, H_2, needed to convert the molecule to the corresponding saturated, non-cyclic molecule
- There are two ways to solve **IHD** problems. One way is to draw the structure and identify rings and double and triple bonds, counting each one as an **IHD** value of 1.
- The second way is to use a formula,
  - For a compound containing C_xH_y, **IHD= (2x+2−y)/2**
  - This is a little complicated, since for the formula to work you need to:
    - ignore O and S
    - count halogens as hydrogen
    - add one C and one H for every nitrogen in the formula

C_5H_{12}
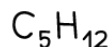
$$IHD = (2x + 2 - y)/2$$
$$= (10 + 2 - 12)/2$$
$$= 0$$

ALKANE
- SATURATED
- NO RINGS
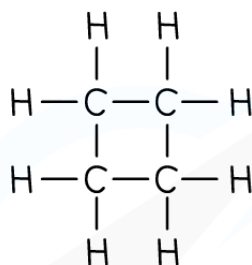
$$IHD = (2x + 2 - y)/2$$
$$= (8 + 2 - 8)/2$$
$$= 1$$

CYCLOALKANE
- 1 RING
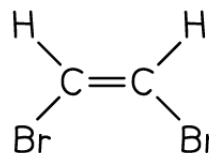
$$IHD = (2x + 2 - y)/2$$
$$= (4 + 2 - 4)/2$$
$$= 1$$

SUBSTITUTED ALKENE
- 1 DOUBLE BOND

$$IHD = (2x + 2 - y)/2$$
$$= (10 + 2 - 8)/2$$
$$= 2$$

DIENE
- 2 DOUBLE BONDS

$$IHD = (2x + 2 - y)/2$$
$$= (8 + 2 - 4)/2$$
$$= 3$$

CYCLIC DIENE
- 1 RING
- 2 DOUBLE BONDS

C_6H_5OH

$$IHD = (2x + 2 - y)/2$$
$$= (12 + 2 - 6)/2$$
$$= 4$$

PHENOL
- AROMATIC RING
- 3 DOUBLE BONDS

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Index of Hydrogen Deficiency Examples

✏ Worked example

Deduce the Index of Hydrogen Deficiency in ethyne, C_2H_2, methyl benzene, $C_6H_5CH_3$, and propanone, CH_3COCH_3

Answer:

Answer 1: Ethyne, C_2H_2 **IHD= 2**

TRIPLE BOND
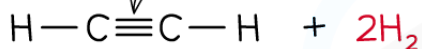
$$H-C\equiv C-H \ + \ 2H_2 \longrightarrow$$

H—C—C—H (FULLY SATURATED)

$$IHD = (2x + 2 - y)/2$$
$$= (4 + 2 - 2)/2$$
$$= 2$$
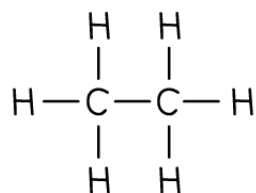
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Answer 2: Methylbenzene, $C_6H_5CH_3$, **IHD= 4**

1 RING
3 DOUBLE BONDS

$+ \ 4H_2 \longrightarrow$

FULLY SATURATED

$IHD = (2x + 2 - y)/2$
$= (14 + 2 - 8)/2$
$= 4$
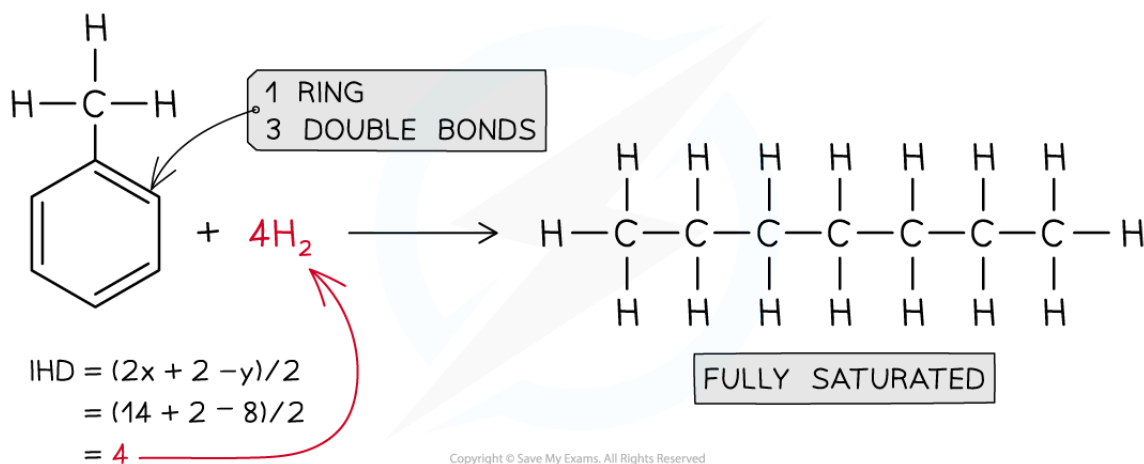
Answer 3: Propanone, CH_3COCH_3 **IHD = 1**

$+ \ H_2 \longrightarrow$

FULLY SATURATED

$IHF = (2x + 2 - y)/2$
$= (6 + 2 - 6)/2$
$= 1$
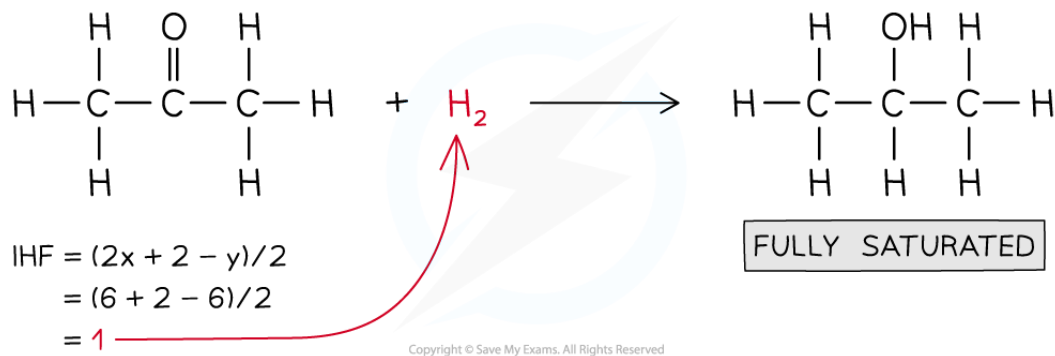
💡 Exam Tip

Drawing out the structure is a much faster way to solve IHD problems, but using the formula is helpful when you are struggling to draw the structure

11.1.2 Mass Spectrometry

Determining Molecular Mass

- When a compound is analysed in a mass spectrometer, vaporised molecules are bombarded with a beam of high-speed electrons
- These knock off an electron from some of the molecules, creating **molecular ions**:

Electron bombardment

MOLECULE ⟶ MOLECULE$^+$• + e$^-$

Molecular ion

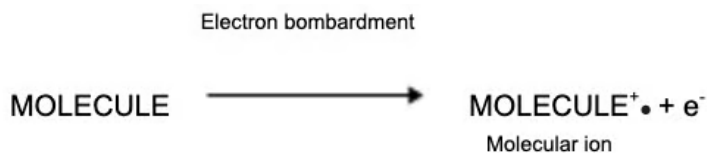- The relative abundances of the detected ions form a **mass spectrum**: a kind of molecular fingerprint that can be identified by computer using a spectral database
- The peak with the highest *m/e* value is the molecular ion (**M$^+$**) peak which gives information about the **molecular mass** of the compound
- This value of m/z is equal to the **relative molecular mass** of the compound

The M+1 peak

- The [**M+1**] peak is a smaller peak which is due to the natural abundance of the isotope **carbon-13**
- The height of the [**M+1**] peak for a particular ion depends on how many carbon atoms are present in that molecule; The more carbon atoms, the larger the [**M+1**] peak is
  - For example, the height of the [**M+1**] peak for an hexane (containing six carbon atoms) ion will be greater than the height of the [**M+1**] peak of an ethane (containing two carbon atoms) ion

Your notes

✏️ Worked example

Determine whether the following mass spectrum belongs to propanal or butanal
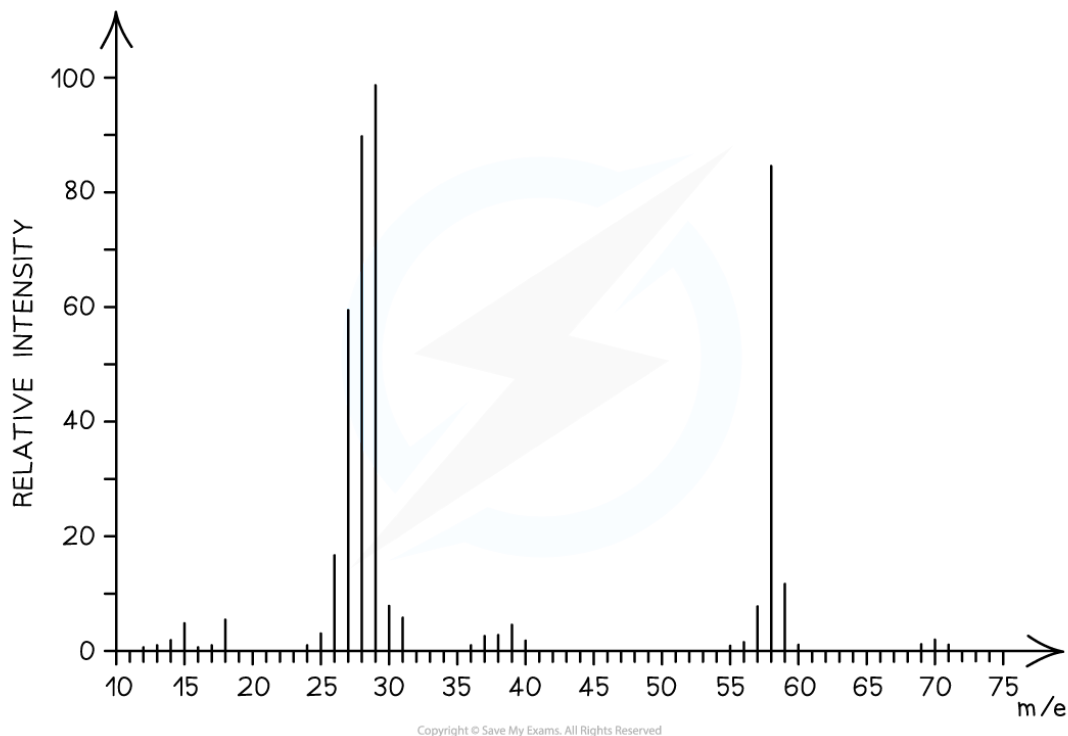
Answer:

- The mass spectrum corresponds to **propanal** as the molecular ion peak is at m/e = 58
- Propanal arises from the $CH_3CH_2CHO^+$ ion which has a molecular mass of 58
- Butanal arises from the $CH_3CH_2CH_2CHO^+$ ion which has a molecular mass of 72

Fragmentation Patterns

- The molecular ion peak can be used to identify the **molecular mass** of a compound
- However, different compounds may have the same molecular mass
- To further determine the structure of the unknown compound, **fragmentation analysis** is used
- Fragments may appear due to the formation of **characteristic fragments** or the **loss of small molecules**
  - For example, a peak at 29 is due to the characteristic fragment $C_2H_5^+$
  - Loss of small molecules give rise to peaks at 18 (H_2O), 28 (CO), and 44 (CO_2)
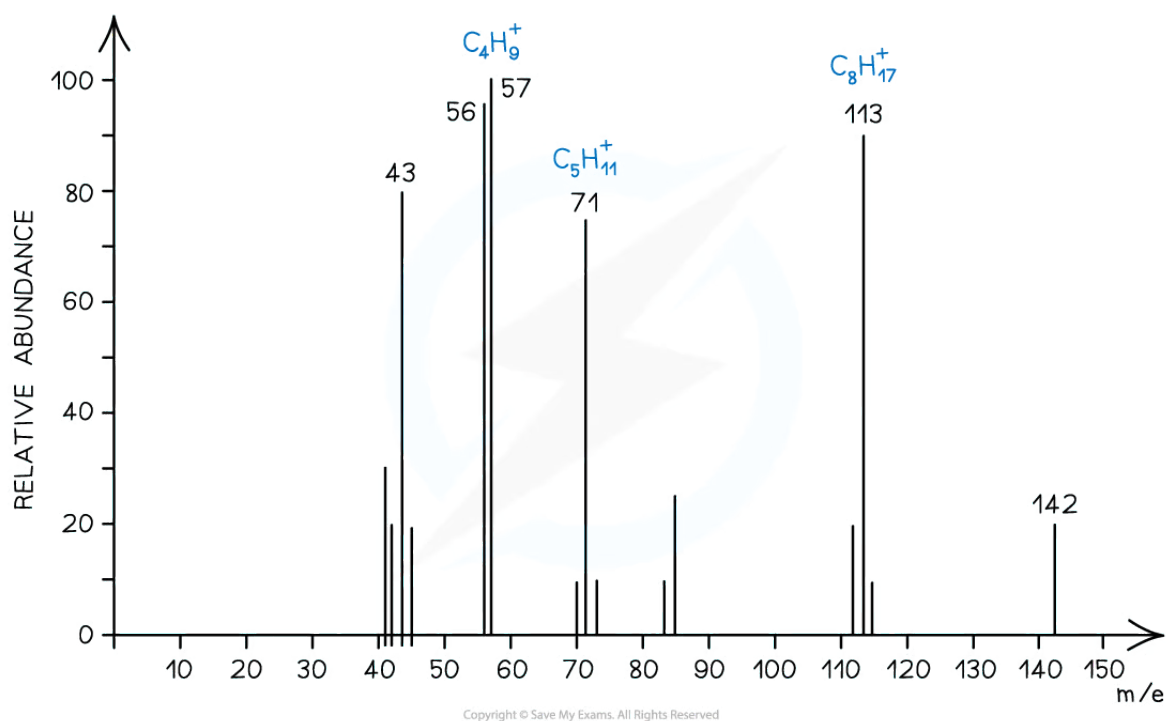
Alkanes

- Simple alkanes are fragmented in mass spectroscopy by breaking the C–C bonds
- **M/e** values of some of the common alkane fragments are given in the table below

m/e values of Fragments Table

Fragment	m/e
CH_3^+	15
$C_2H_5^+$	29
$C_3H_7^+$	43
$C_4H_9^+$	57
$C_5H_{11}^+$	71
$C_6H_{13}^+$	85

Your notes

Your notes

Mass spectrum showing fragmentation of alkanes

Halogenoalkanes

- Halogenoalkanes have often multiple peaks around the molecular ion peak
- This is caused by the fact that there are different isotopes of the halogens

Alcohols

- Alcohols often tend to lose a **water molecule** giving rise to a peak at **18 below the molecular ion**
- Another common peak is found at m/e value 31 which corresponds to the CH_2OH^+ fragment
- For example, the mass spectrum of propan-1-ol shows that the compound has fragmented in four different ways:
    - Loss of H to form a $C_3H_7O^+$ fragment with $m/e = 59$
    - Loss of a water molecule to form a $C_3H_6^+$ fragment with $m/e = 42$
    - Loss of a C_2H_5 to form a CH_2OH^+ fragment with $m/e = 31$
    - And the loss of CH_2OH to form a $C_2H_5^+$ fragment with $m/e = 29$

> 💡 **Exam Tip**
>
> A table of mass spectral fragments lost is included in the IB Chemistry Data Booklet Section 28 so you don't need to learn all the likely fragments

11.1.3 Nuclear Magnetic Resonance Spectroscopy

How NMR works

- **Nuclear Magnetic Resonance (NMR)** spectroscopy is used for analysing organic compounds
- Only atoms with **odd mass numbers** show signals on **NMR** spectra and have the property of **nuclear spin**
- In ^{1}**H NMR**, the magnetic field strengths of protons in organic compounds are measured and recorded on a spectrum
- Samples are irradiated with radio frequency energy while subjected to a strong magnetic field
- The nuclei can align themselves with or against the magnetic field
- Protons on different parts of a molecule (in different molecular environments) absorb and emit (**resonate**) different radio frequencies
- All samples are measured against a reference compound – **Tetramethylsilane (TMS)**
    - TMS shows a single sharp peak on an **NMR** spectrum, at a value of zero
    - Sample peaks are then plotted as a 'shift' away from this reference peak
    - This gives rise to 'chemical shift' values for protons on the sample compound
    - Chemical shifts are measured in **parts per million (ppm)**

Features of a NMR spectrum

- An **NMR** spectrum shows the intensity of each peak against their chemical shift
- The area under each peak is proportional to the number of protons in a particular environment
- The height of each peak shows the intensity/absorption from protons
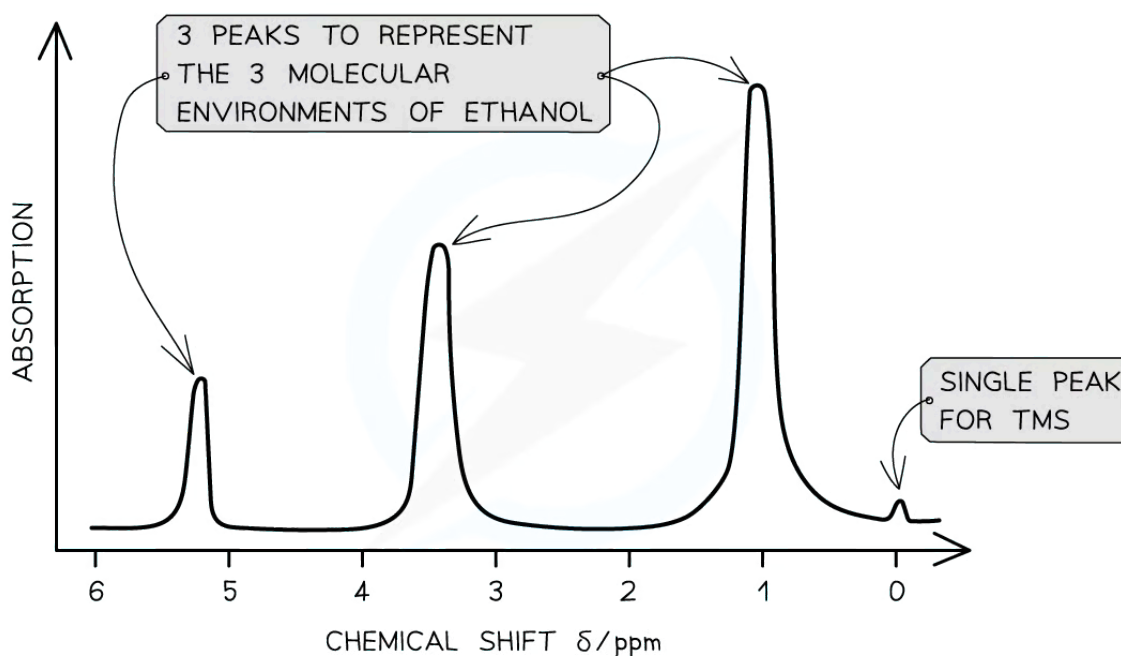
A low resolution ^{1}H NMR for ethanol showing the key features of a spectrum

Chemical Environments

Chemical environments

- Hydrogen atoms of an organic compound are said to reside in different chemical environments
  - Eg. Methanol has the molecular formula CH_3OH
  - There are 2 environments: $-CH_3$ and $-OH$

- The hydrogen atoms in these environments will appear at 2 different chemical shifts
- Different types of protons are given their own range of chemical shifts

| Aldehyde	HCOR	$9.3 - 10.5$
Alcohol	ROH	$0.5 - 6.0$
Phenol	$Ar - OH$	$4.5 - 7.0$
Carboxylic acid	RCOOH	$9.0 - 13.0$
Alkyl amine	$R - NH -$	$1.0 - 5.0$
Aryl amine	$Ar - NH_2$	$3.0 - 6.0$
Amide	RCONHR	$5.0 - 12.0$

> 💡 **Exam Tip**
>
> Typical proton chemical shift values are given in Section 27 of the IB Chemistry Data Booklet. The values alone do not identify specific protons as the values occur over a range that is sometimes overlapping, but they can be used in combination with other structural information to help confirm a feature

Interpreting an NMR Spectrum

- Protons in the same environment are chemically equivalent
- Each peak on a NMR spectrum relates to protons in the same environment
- Peaks on a low resolution NMR spectrum refers to environments of an organic compound
  - Eg. Ethanol has the molecular formula CH_3CH_2OH
  - This molecule as 3 separate environments: $-CH_3$, $-CH_2$, $-OH$
  - So 3 peaks would be seen on its spectrum at 1.2 ppm ($-CH_3$), 3.7 ppm ($-CH_2$) and 5.4 ppm ($-OH$)
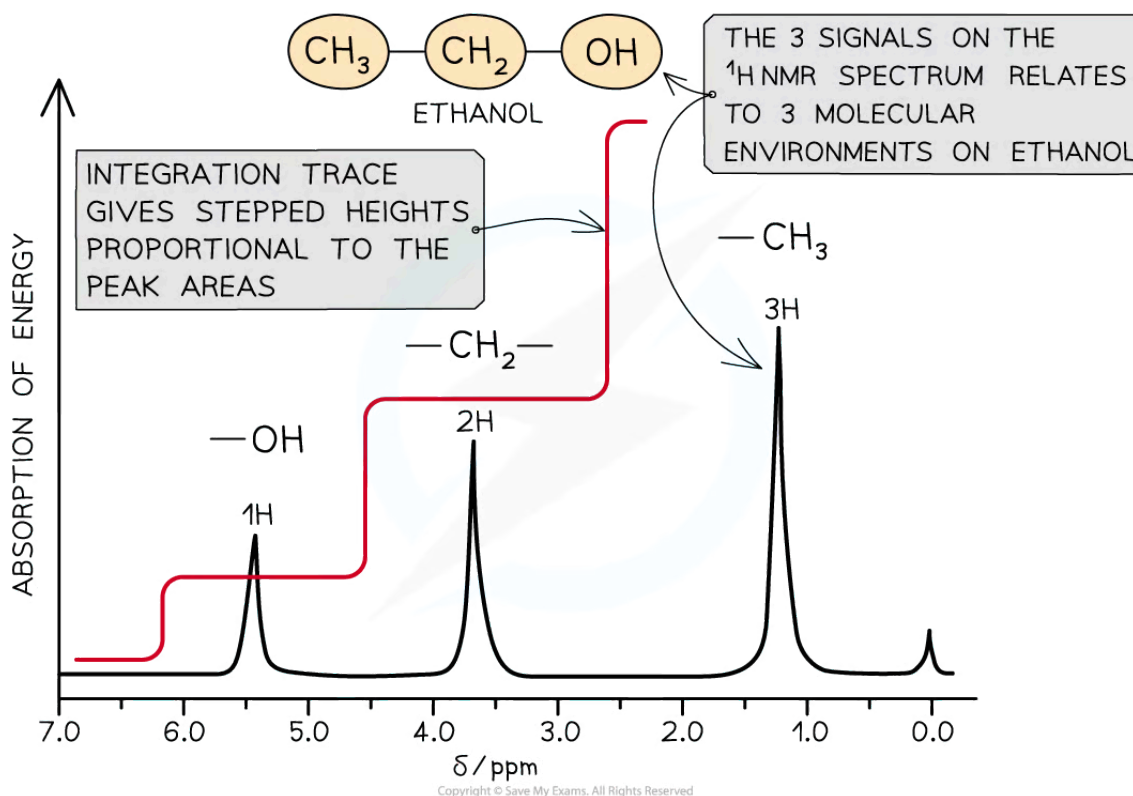
A low resolution NMR spectrum with integration trace

- The area under each peak is determined by computer and an **integration trace** overlaid on the spectrum
- The **integration trace** has stepped lines whose steps are in the same proportion as the peak areas
- This makes it easier to determine the relative abundance of the different proton environments

✏️ Worked example

Which of the following features can be found from a ^{1}H NMR spectrum?

      A. The total mass of hydrogen atoms present

B. The number of different hydrogen environments

C. The frequency vibration of C–O bonds

D. The first ionization energy of hydrogen

Answer:

The correct option is **B**.

- An NMR spectrum can tell you about the type of hydrogen environments and the relative proportion of the Hs in those environments
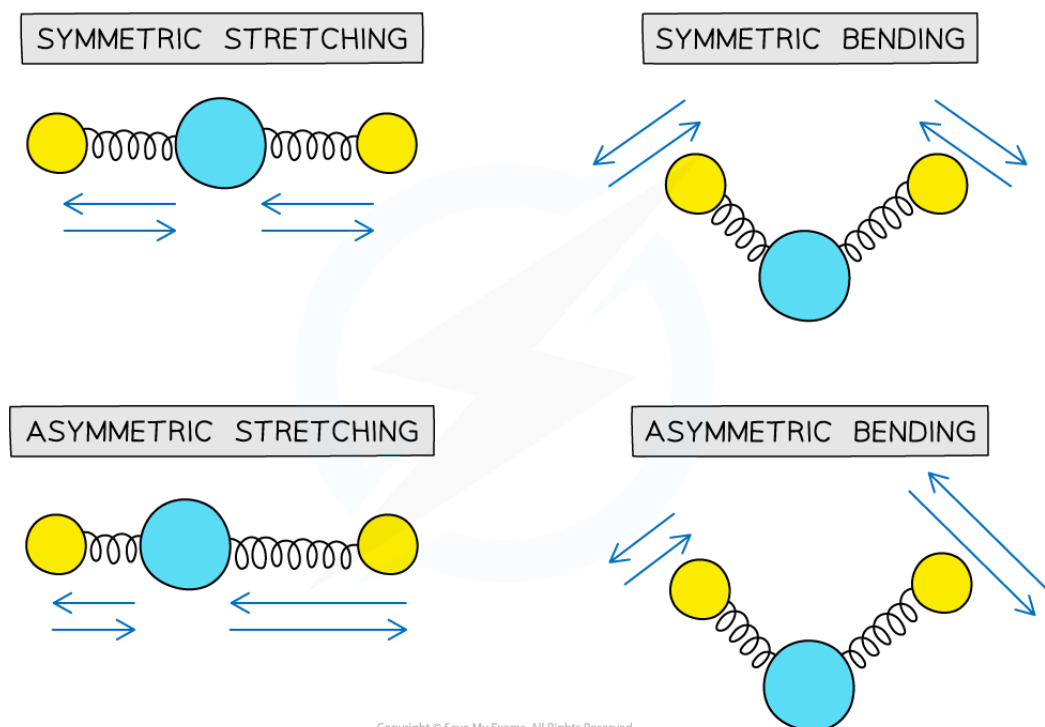
11.1.4 Infrared Spectroscopy

How IR Spectroscopy works

- All **covalent bonds** act rather like springs, as opposed to rigid bars
- Like springs, the bonds can vibrate in a number of different ways
- The frequency of vibration occurs in the **infra-red region** of the **electromagnetic spectrum**
- If an organic molecule is irradiated with **infra-red energy** that matches the **natural vibration frequency** of its bonds, it absorbs some of that energy and the amplitude of vibration increases
- This is known as **resonance**

Different modes of vibration in molecules. Each mode has a characteristic frequency of vibration

Infrared (IR) spectroscopy

- **Infrared (IR) spectroscopy** is a technique used to identify compounds based on changes in **vibrations** of atoms when they **absorb** IR of certain **frequencies**
- A **spectrophotometer** irradiates the sample with IR radiation and then detects the **intensity** of **IR radiation** absorbed by the molecule
- **IR energy** is absorbed only if a molecule has a **permanent dipole** that changes as it vibrates
  - Symmetrical molecules such as O_2 or H_2, are therefore **IR inactive**
- The **resonance frequency** is the specific frequency at which the bonds will vibrate

Your notes

- Rather than displaying frequency, an **IR spectrum** shows a unit called **wavenumber**
  - **Wavenumber** is the reciprocal of the **wavelength** and has units of cm^{-1}

- Characteristic absorptions can be matched to specific bonds in molecules
  - This enables chemists to determine the **functional groups** present

Absorption Range of Bonds

Bond	Functional groups containing the bond	Characteristic infrared absorption range (in wavenumbers) (cm^{-1})
C−O	Hydroxy, ester	1040−1300
C=C	Aromatic compound, alkene	1500−1680
C=O	Amide carbonyl, carboxyl ester	1640−1690 1670−1740 1710−1750
C≡N	Nitrile	2200−2250
C−H	Alkane	2850−2950
N−H	Amine, amide	3300−3500
O−H	Carboxyl, hydroxyl	2500−3000 3200−3600

- Due to some absorption bands overlapping each other, other analytical techniques such as **mass spectroscopy** should be used alongside **IR spectroscopy** to identify an unknown compound
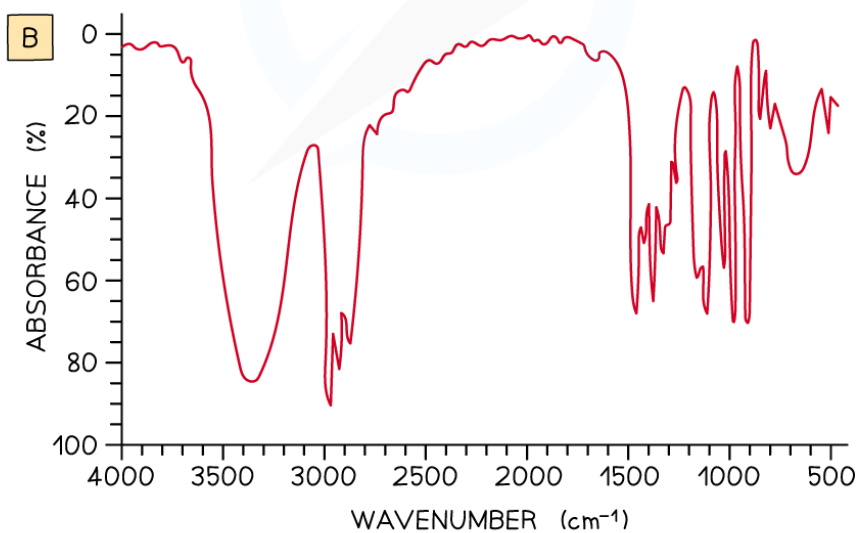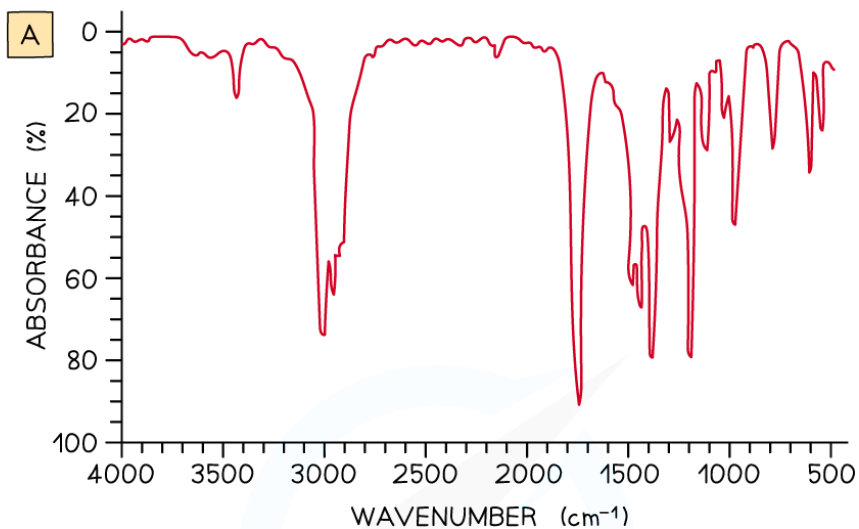
Interpreting an IR Spectrum

- The best way to understand how to interpret an **IR spectrum** is by looking at examples and becoming familiar with the characteristic features of an **IR spectrum**

✏️ Worked example

Examine the two spectra shown and determine which one belongs to propan-2–ol and which one belongs to propanone

Answer:

Your notes

- IR spectrum **A** is **propanone** and spectrum **B** is **propan-2-ol**.
- In IR spectrum **A** the presence of a strong, sharp absorption around 1710 cm^{-1} corresponds to the characteristic C=O, carbonyl, group in a ketone.
- In spectrum **B** the presence of a strong, broad absorption around 3200–3500 cm^{-1} suggests that there is an alcohol group present, which corresponds to the -OH group in propan-2-ol.

Fingerprint Region

- The region below about 1500 cm^{-1} is called the **fingerprint region** and is unique to every molecule
- It has many peaks that can be difficult to assign
- These peaks represent the complex vibrational interactions that occur between different bonds within a molecule
- The value of the **fingerprint region** is in being able to compare the **IR spectrum** to a known compund from a database and coming up with an exact match
- This is particularly useful, for example, in identifying a specific member of a **homologous series**
  - All members of the series will show the same type of bonds present, but no two molecules will have the same fingerprint region

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💡 **Exam Tip**

Infrared data is found in Section 26 of the IB Chemistry Data Booklet so there is no need to learn specific wavenumber ranges of bonds

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