Structure 3.2 HL

IB CHEMISTRY HL

25	16		6	2	25
Mn	**S**	**J**	**C**	**He**	**M**n
Manganese	Sulfur		Carbon	Helium	Manganese
54.938045	32.065		12.0107	4.002602	54.938045

Structure 3.2.7
Understandings:
- Stereoisomers have the same constitution (atom identities, connectivities and bond multiplicities) but different spatial arrangements of atoms.

Learning outcomes:
- Describe and explain the features that give rise to *cis-trans* isomerism; recognize it in non-cyclic alkenes and C3 and C4 cycloalkanes.
- Draw stereochemical formulas showing the tetrahedral arrangement around a chiral carbon.
- Describe and explain a chiral carbon atom giving rise to stereoisomers with different optical properties. Recognize a pair of enantiomers as non-superimposable mirror images from 3D modelling (real or virtual).

Additional notes:
- Nomenclature using the E-Z system will not be assessed.
- The terms "chiral", "optical activity", "enantiomer" and "racemic" mixture should be understood.
- Different chemical properties of enantiomers can be limited to the fact that they behave differently in chiral environments.
- Wedge-dash type representations involving tapered bonds should be used for the representation of enantiomers.

cis-trans isomerism
- *cis-trans* isomerism occurs where there is restricted rotation around a bond either because of a double bond or a ring structure in a cyclic compound.
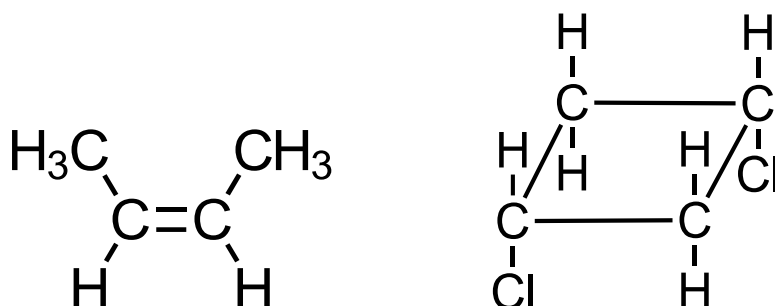

Molecules with carbon-to-carbon double bonds
- The π bond in the carbon-to-carbon double bond restricts rotation, forming two different isomers.
- For cis-trans isomerism to occur, there must be two different groups on each of the carbon atoms of the C=C bond.
- The molecule on the left cannot have cis-trans isomers, the molecule of the right can.
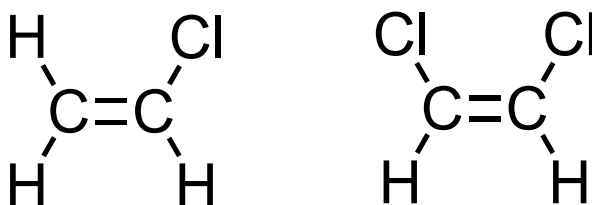
- *cis* isomers have the same groups on the same side of C=C bond.
- *trans* isomers have the same groups on opposite sides of C=C bond.

cis-but-2-ene   trans-but-2-ene
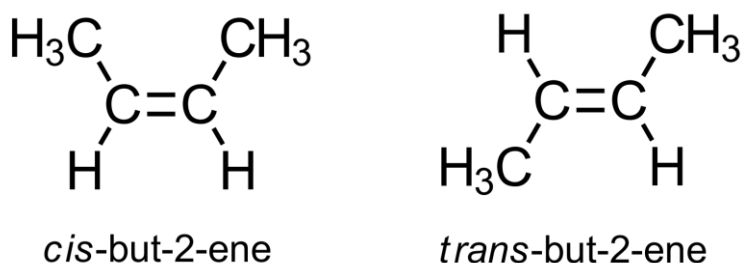
- *cis*-but-2-ene has the CH_3 groups on the same sides of the C=C bond.
- *trans*-but-2-ene has the CH_3 groups on opposite sides of the C=C bond.

Cyclic compounds

- Cyclic compounds have a ring structure that restricts rotation.
- When the molecule contains two or more different substituents attached to the ring, two different isomers are formed.
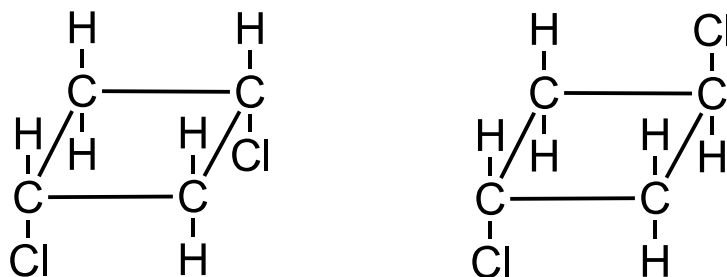
*cis*-1,3-dichlorocyclobutane *trans*-1,3-dichlorocyclobutane

- *cis* isomers have the substituents on the same side of the ring (above or below) and *trans* isomers have the substituents on opposite sides of the ring.

**Exercise:** Classify the isomers below as *cis* or *trans.*
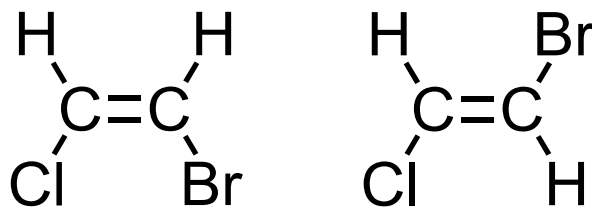
Optical isomerism

- Optical isomerism is shown by chiral molecules that have a carbon atom bonded to four different atoms or groups (chiral center or asymmetric carbon).
- A chiral carbon is a carbon atom bonded to four different atoms or groups.
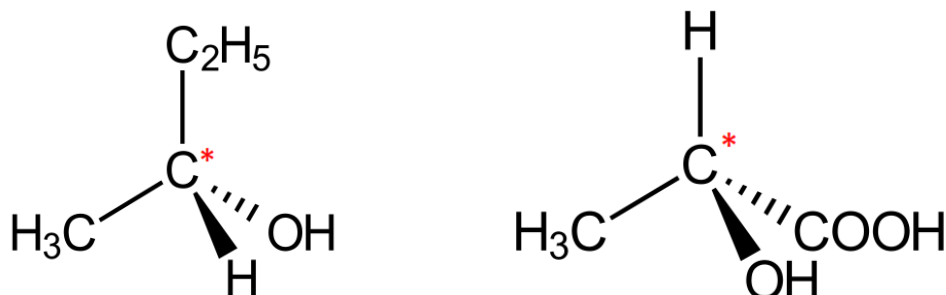
- The four groups can be arranged in two three dimensional configurations which are mirror images of each other.
- The two mirror images are non-superimposable and are known as enantiomers.
- The number of enantiomers for a particular molecule depends on the number of chiral centers in the molecule.
- There are 2^n optical isomers for an organic molecule with n chiral centers. For example, butan-2-ol has one chiral center and has $2^1 = 2$ optical isomers.
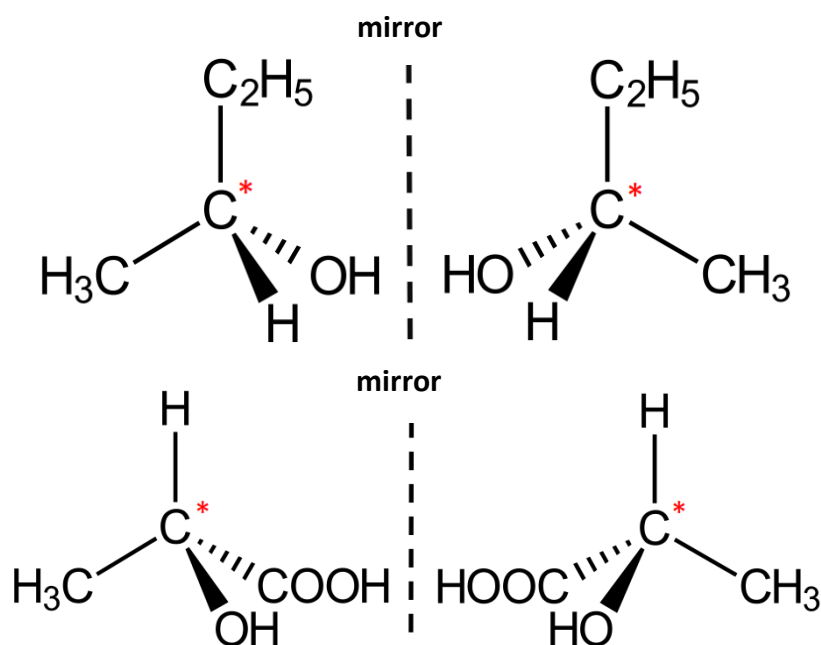
- The two optical isomers (enantiomers) are optically active with plane-polarised light - they rotate the plane of plane-polarised light by the same amount but in opposite directions.

Exercises:

   1. Deduce which of the following molecules contain a chiral carbon atom.

A. Propanone

B. 2-bromopropane

C. 2-bromobutane

D. 3-bromopentane

E. Pentan-2-ol

F. 2,2-dichloropentane
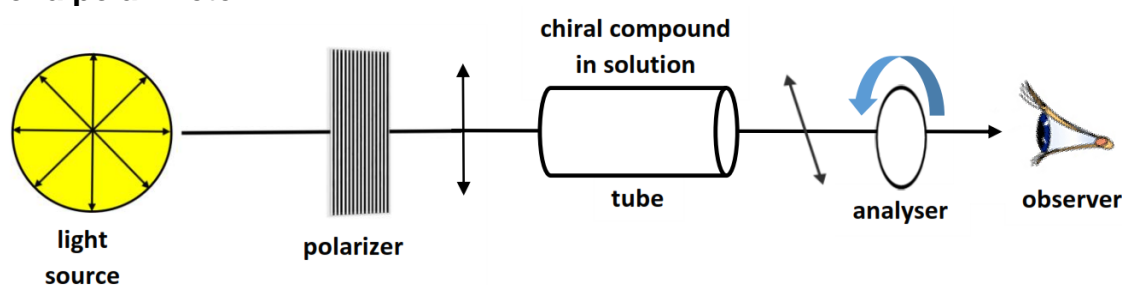
G. Propan-2-amine

H. 4-hydroxybutanoic acid

   2. Deduce the number of chiral centers and the number of optical isomers for $(CH_3)_2CHCHClCHBrCH_3$.

Plane-polarised light

- Ordinary light consists of waves that vibrate in all planes perpendicular to its direction of travel.
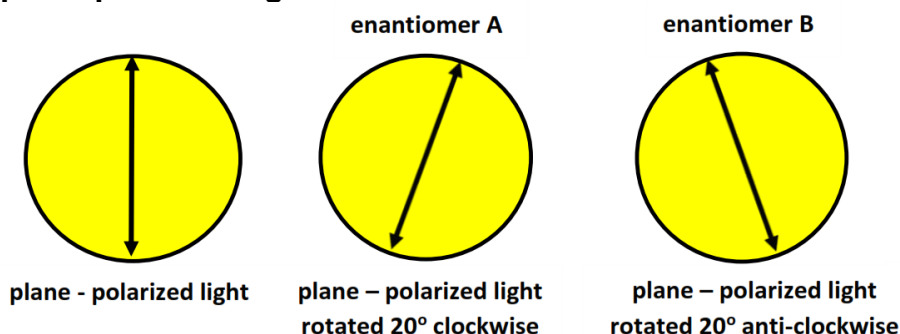- Plane-polarised light consists of waves vibrating in one plane only.

ordinary light   polarizer   plane - polarized light

Use of a polarimeter

chiral compound in solution
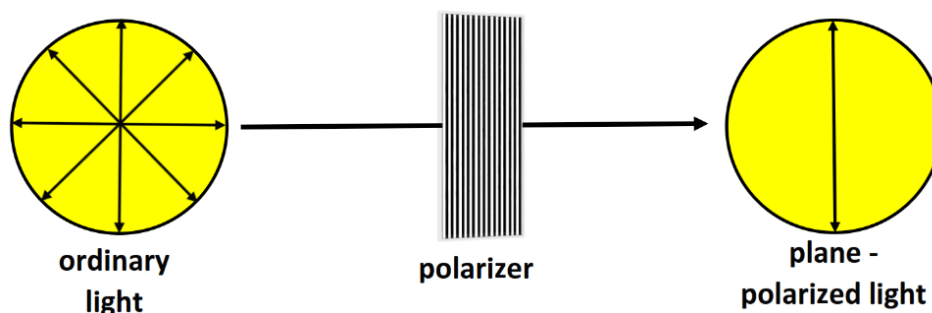
light source   polarizer   tube   analyser   observer

- Plane-polarised light is passed through a tube containing a solution of optical isomers.
- The plane of the plane-polarised light is rotated which then passes through the analyser.
- The analyser is rotated until the light passes through and the extent and direction of rotation can be determined.

Rotation of plane-polarised light

enantiomer A   enantiomer B

plane - polarized light   plane – polarized light rotated 20° clockwise   plane – polarized light rotated 20° anti-clockwise

- The two enantiomers of a chiral compound rotate the plane of plane-polarised light in equal amounts but in opposite directions.
- This property can be used to distinguish between the two enantiomers of a chiral compound.

Racemic mixture

enantiomer A		enantiomer B	
plane - polarized light	plane – polarized light rotated 20° clockwise	plane – polarized light rotated 20° anti-clockwise	no overall rotation – optically inactive
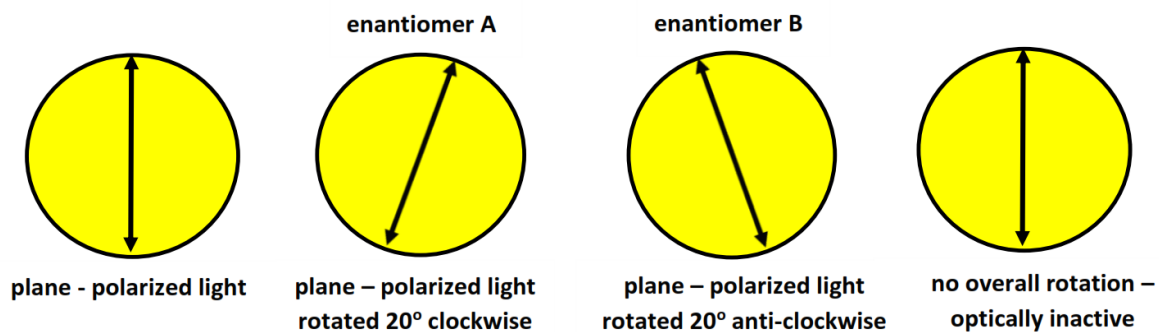
- A solution containing equal amounts of both enantiomers is known as a racemic mixture (racemate).
- If both enantiomers are present in equal amounts the two rotations cancel each other out and the mixture is said to be optically inactive.

Structure 3.2.8
Understandings:
- Mass spectrometry (MS) of organic compounds can cause fragmentation of molecules.

Learning outcomes:
- Deduce information about the structural features of a compound from specific MS fragmentation patterns.

Additional notes:
- Include reference to the molecular ion.
- Data on specific MS fragments are provided in the data booklet.

Mass spectrometry

- Mass spectrometry is used to determine the relative atomic mass (A_r) of an element; it can also be used to determine the structure of an organic compound.
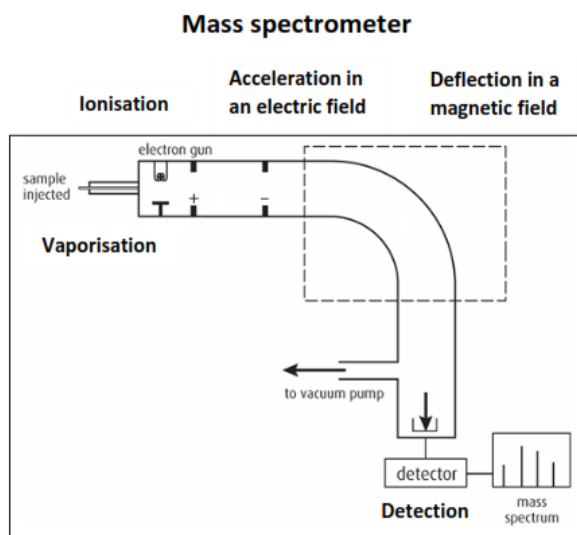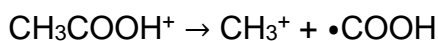
Mass spectrometer

- When the vaporised organic compound passes into the ionisation chamber of a mass spectrometer, it is bombarded by a stream of electrons forming a positive ion, $M^+(g)$.

$$M(g) + e^- \rightarrow M^+(g) + 2e^-$$
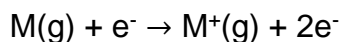
- The $M^+(g)$ ion is known as the molecular ion.
- Inside the mass spectrometer, some of the molecular ions break down to produce fragments.
- Using ethanoic acid (CH_3COOH) as an example:

$$CH_3COOH(g) + e^- \rightarrow CH_3COOH^+(g) + 2e^-$$
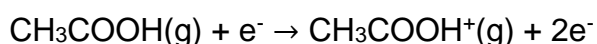
- The molecular ion (CH_3COOH^+) can break up as follows:

$$CH_3COOH^+ \rightarrow CH_3^+ + \cdot COOH$$

- The CH_3^+ fragment will be detected in the mass spectrometer and appear on the fragmentation pattern.
- The $\cdot COOH$ fragment is known as the neutral fragment lost (it is lost in the mass spectrometer).
- Section 22 has the mass lost and possible neutral fragment lost.

22. Mass spectral fragments lost

| Mass lost (M_r)	Possible neutral fragment lost
15	•CH_3
17	•OH
18	H_2O
28	$CH_2{=}CH_2$ CO
29	•CH_2CH_3 •CHO
31	•OCH_3
45	•COOH

Example: mass spectrum of ethanoic acid (CH_3COOH)
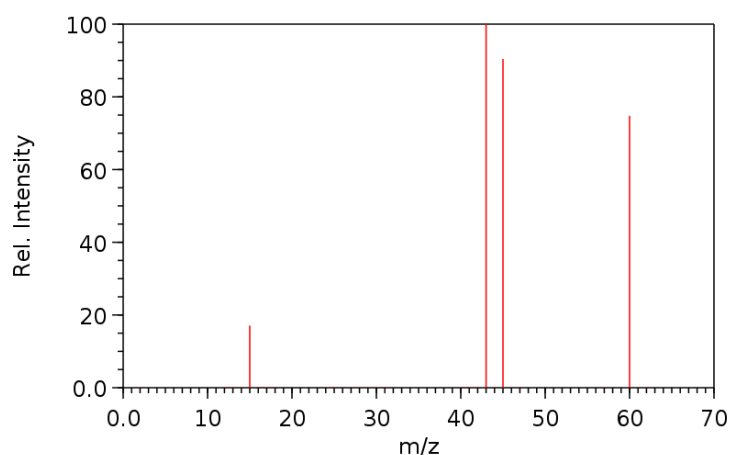
- The mass spectrum has peaks at m/z 15, 43, 45 and 60.
- The peak at m/z 60 is produced by the molecular ion (M^+). This can be used to determine the molar mass (M) or relative formula mass (M_r) of the compound.
- To determine the mass lost use the following equation:

$$\text{Mass lost} = \text{mass of molecular ion} - m/z \text{ of fragment}$$

- The peak at m/z = 45 is produced by the loss of a CH_3 group (60 – 45 = 15).
- The peak at m/z = 43 is produced by the loss of an OH group (60 – 43 = 17).
- The peak at m/z = 15 is produced by the loss of a COOH group (60 – 15 = 45).

Peak	Fragment
45 (60 – 45 = 15)	$COOH^+$ (loss of CH_3)
43 (60 – 43 = 17)	$C_2H_3O^+$ (loss of OH)
15 (60 – 15 = 45)	CH_3^+ (loss of COOH)
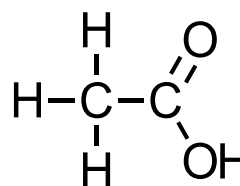
Exercise: From the following mass spectrum for an isomer of C_2H_6O, deduce the following.

1. The relative formula mass of the compound.
2. The neutral fragment lost that gives rise to the peak at *m/z* 29.
3. The neutral fragment lost that gives rise to the peak at *m/z* 31.
4. Determine the identity of the compound.
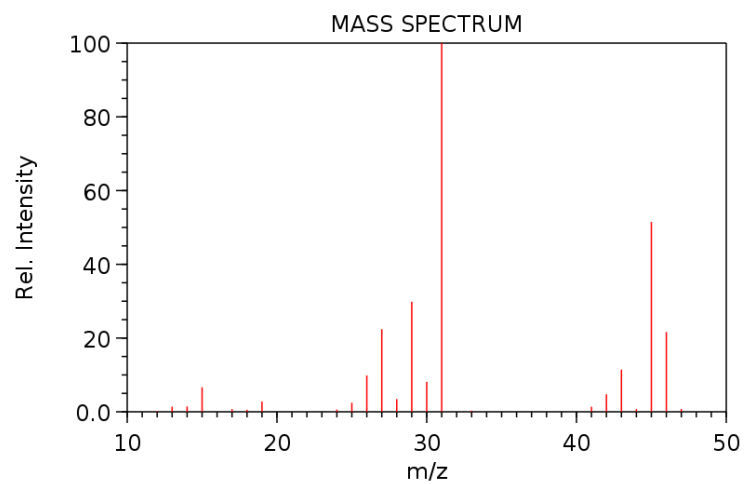
Structure 3.2.9
Understandings:
- Infrared (IR) spectra can be used to identify the type of bond present in a molecule.

Learning outcomes:
- Interpret the functional group region of an IR spectrum, using a table of characteristic frequencies (wavenumber/cm^{-1}).

Additional notes:
- Include reference to the absorption of IR radiation by greenhouse gases.
- Data for interpretation of IR spectra are given in the data booklet.

Linking questions:
- Reactivity 1.3 What properties of a greenhouse gas determine its "global warming potential"?

Infrared spectroscopy
- When molecules absorb energy in the infrared region of the electromagnetic spectrum, it causes the bonds between the atoms to vibrate (the bonds stretch and bend).
- The frequency of IR radiation absorbed by a bond is the wavenumber (cm^{-1}).
- Section 20 from the IB chemistry data booklet gives the wavelength of IR radiation absorbed by different bonds.

20. Infrared data

Characteristic ranges for infrared absorption due to stretching vibrations in organic molecules

Bond	Types of organic molecules	Wavenumber / cm^{-1}	Intensity
C — I	iodoalkanes	490–620	strong
C — Br	bromoalkanes	500–600	strong
C — Cl	chloroalkanes	600–800	strong
C — F	fluoroalkanes	1000–1400	strong
C — O	alcohols, esters, ethers	1050–1410	strong
C = C	alkenes	1620–1680	medium-weak; multiple bands
C = O	aldehydes, ketones, carboxylic acids and esters	1700–1750	strong
C ≡ C	alkynes	2100–2260	variable
O — H	carboxylic acids (with hydrogen bonding)	2500–3000	strong, very broad
C — H	alkanes, alkenes, arenes	2850–3090	strong
O — H	alcohols and phenols (with hydrogen bonding)	3200–3600	strong, broad
N — H	primary amines	3300–3500	medium; two bands

Example IR spectrum

- The region of an infrared spectrum in the range of about 500 to 1500 cm^{-1} is called the fingerprint region.
- This region of the spectrum is almost unique for any given compound and can be used to identify an unknown compound by comparing with the IR spectra of known compounds.
- The functional group region can be used to identify the bonds present in the compound.
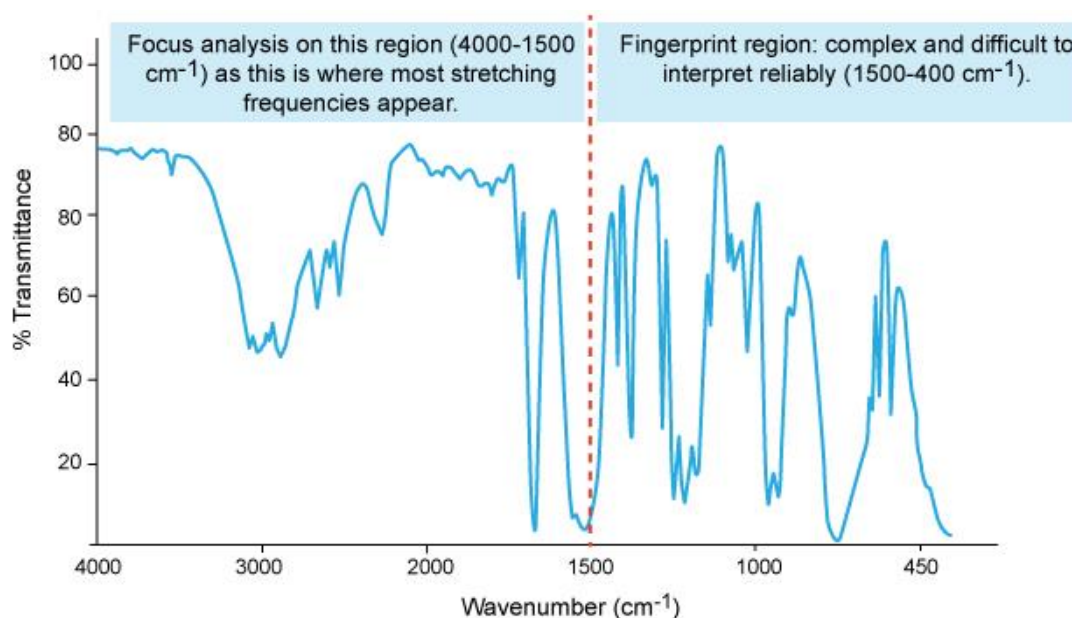
IR spectrum for ethanol C$_2$H$_5$OH
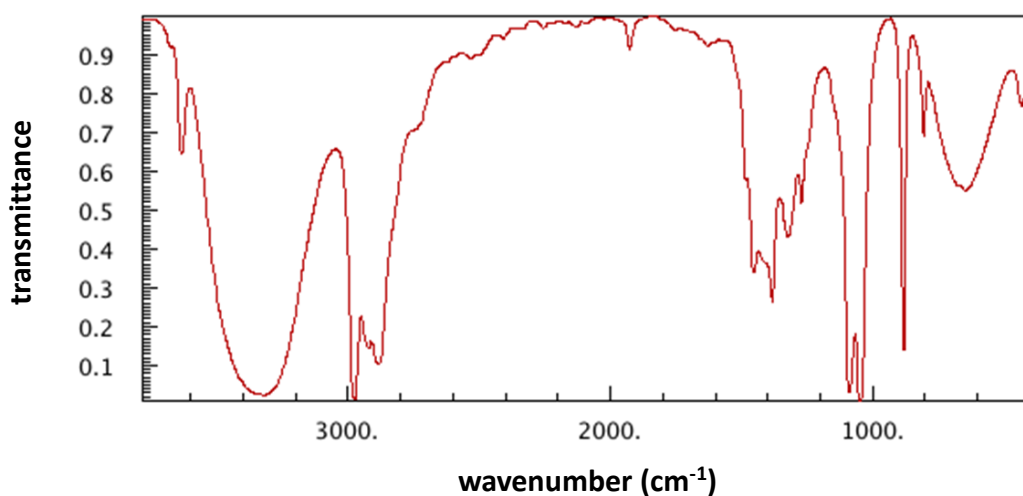
Exercise: use section 20 of the data booklet to identify the functional group present in the compound.

wavenumber (cm⁻¹)
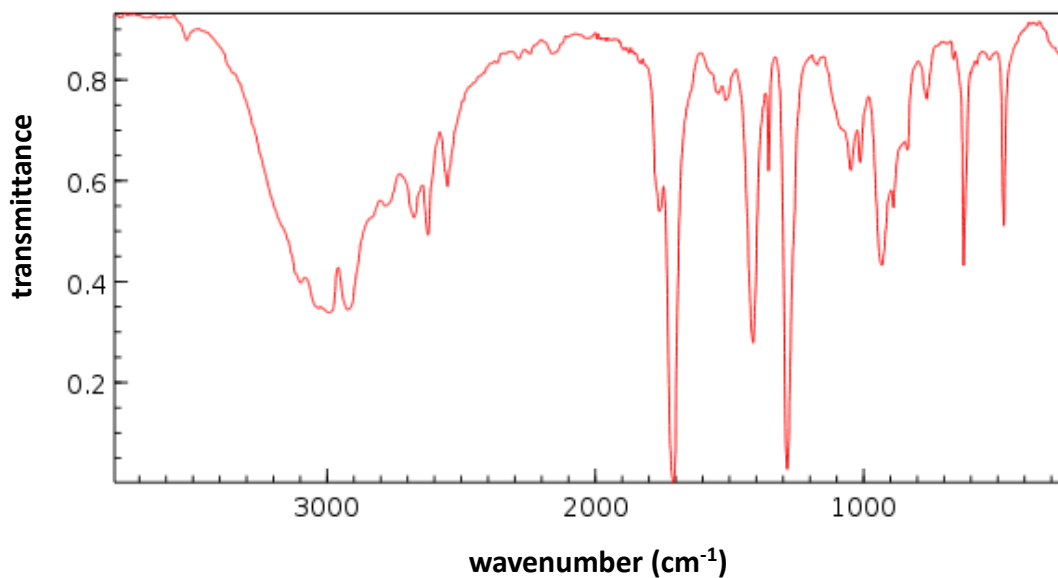
Exercise: The IR spectra below are for propanoic acid, propanal and propan-1-ol, but not in that order.

1. Draw the full structural formula of the three compounds and identify the functional group in each molecule.

2. Deduce which IR spectrum is for which compound, giving reasons for your choice.

Spectrum A

....
....
....
....

Spectrum B

....
....
....
....

Spectrum C

....
....
....
....

Structure 3.2.10
Understandings:
- Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) gives information on the different chemical environments of hydrogen atoms in a molecule.

Learning outcomes:
- Interpret ^{1}H NMR spectra to deduce the structures of organic molecules from the number of signals, the chemical shifts, and the relative areas under signals (integration traces).

Proton nuclear magnetic resonance spectroscopy ^{1}H NMR
- Hydrogen nuclei behave as little magnets, and a hydrogen nucleus can be aligned with an external magnetic field or opposed to it.
- The energy needed for the hydrogen nuclei to reverse their spin is very small and can be provided by radio waves.
- The number of peaks in a ^{1}H NMR spectrum gives the number of different chemical environments of hydrogen atoms.
- The position of the ^{1}H NMR signal is measured relative to the signal produced by TMS tetramethylsilane $Si(CH_3)_4$
- ^{1}H NMR data can be found in section 21 of the IB chemistry data booklet.

$$CH_3$$
$$H_3C-Si-CH_3$$
$$CH_3$$

^{1}H NMR spectrum for ethanal

| Type of proton	Chemical shift (ppm)
$-CH_3$	$0.9 - 1.0$
$\overset{O}{\underset{R}{\overset{||}{C}}}-H$	$9.4 - 10.0$

- There are two peaks (excluding the peak at zero ppm caused by TMS) on the spectrum so there are two different hydrogen environments.
- The peak at ppm 9.5 corresponds to the one proton in the CHO group.
- The peak at ppm 2.0 corresponds to the three protons in the CH_3 group.

Integrated trace
- The integrated trace goes up in steps which are proportional to the number of hydrogen atoms in the chemical environments.
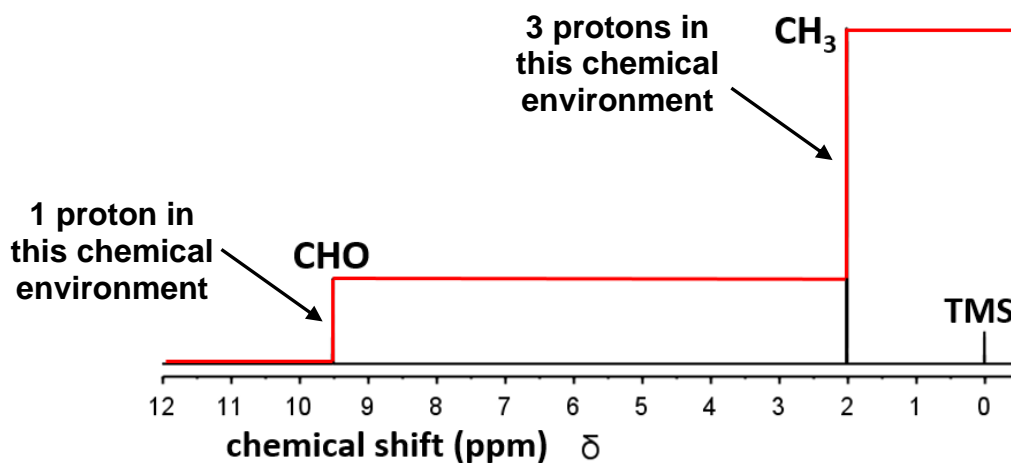
Exercises:
1. Use the ^1H NMR spectrum below to answer the following questions.
a) Outline the significance of the peak at 0 ppm.
b) Deduce the number of different chemical environments in which hydrogen atoms are located.
c) Determine the type of proton that produces the peak at 9.5 ppm.
d) Give the ratio of the hydrogen atoms in each peak.
e) The peaks at 1.3 and 2.2 correspond to a CH_3 and CH_2 group respectively. Determine the structural formula and name of the compound.
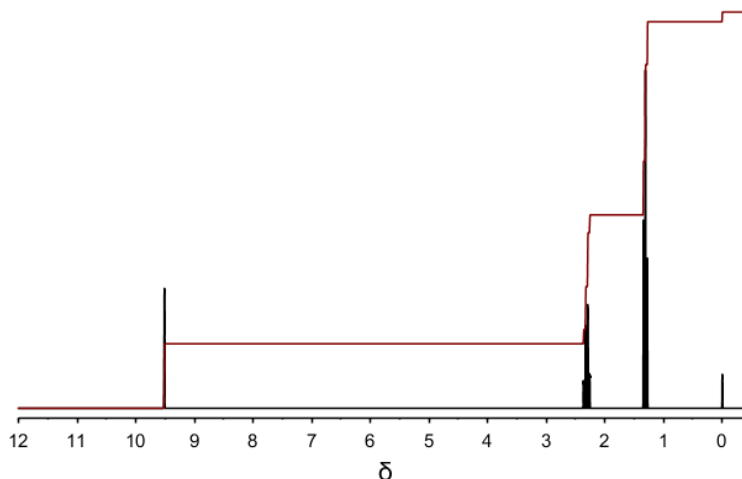
2. Predict the number of signals (peaks) in the ^{1}H NMR spectra for the following molecules. For each molecule, state the ratio of the protons in each compound.

a) Pentane, $CH_3CH_2CH_2CH_2CH_3$

b) Pentan-2-one, $CH_3COCH_2CH_2CH_3$

c) Pentanal, $CH_3CH_2CH_2CH_2CHO$

d) Propanoic acid, CH_3CH_2COOH

e) Ethoxyethane, $CH_3CH_2OCH_2CH_3$

Structure 3.2.11
Understandings:
- Individual signals can be split into clusters of peaks.

Learning outcomes:
- Interpret ^1H NMR spectra from splitting patterns showing singlets, doublets, triplets and quartets to deduce greater structural detail.

Additional notes:
- Data for interpretation of ^1H NMR spectra are given in the data booklet.

High resolution ^1H NMR
- In a high resolution ^1H NMR spectrum, what looked like single peaks in the low resolution spectrum are split into clusters of peaks.
- The number of peaks in a cluster tells you about the number of protons attached to the adjacent carbon atom(s).
- The number of peaks in a cluster is one more than the number of hydrogens (protons) attached to the adjacent carbon(s).
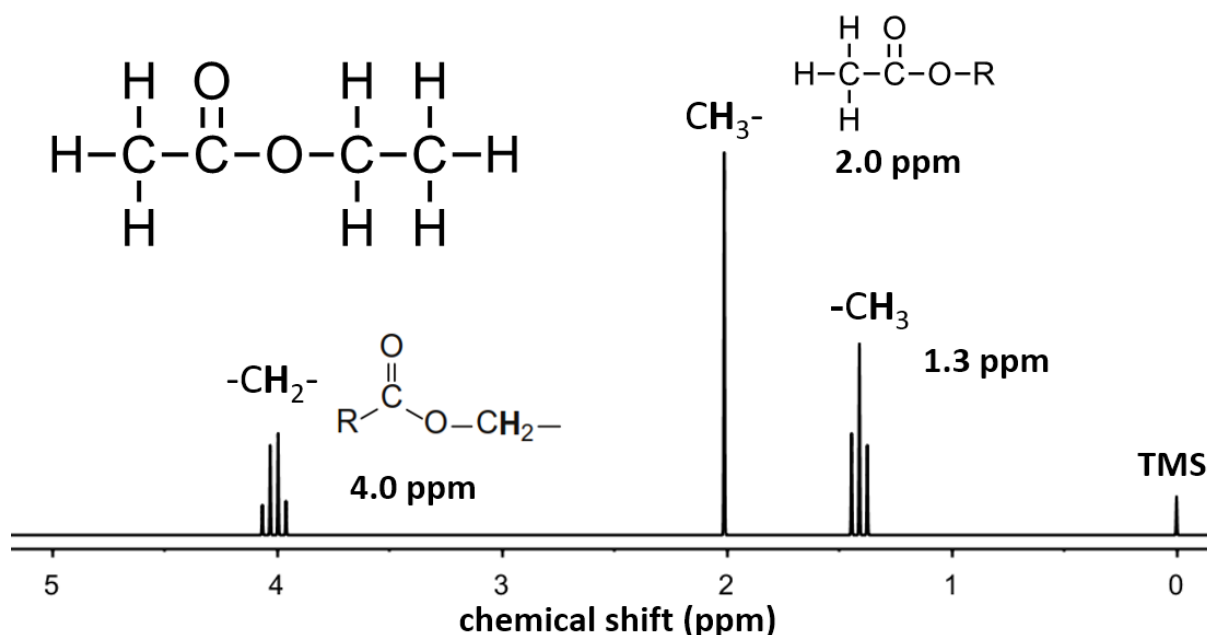
Number of adjacent protons	Number of peaks	Type of splitting	Relative intensities of peaks
0	1	singlet	1
1	2	doublet	1 1
2	3	triplet	1 2 1
3	4	quartet	1 3 3 1

Splitting patterns

- The splitting of the peaks occurs as the effective magnetic field, experienced by particular nuclei, is modified by the magnetic field produced by neighboring nuclei.
- This effect is known as spin-spin coupling.

Singlet	Doublet	Triplet	Quartet
1	1:1	1:2:1	1:3:3:1
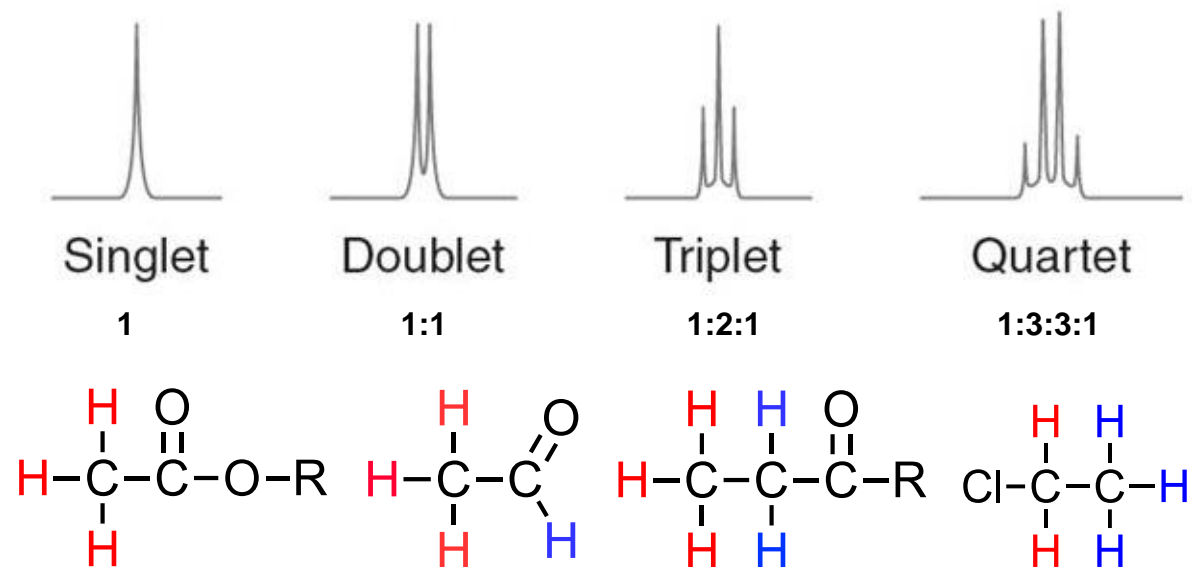
Example: High resolution ^1H NMR spectrum for ethyl ethanoate

- Triplet at 1.4 ppm caused by two protons on adjacent carbon (-CH₂-).
- Singlet at 2.0 ppm caused by zero protons on adjacent carbon (C=O).
- Quartet at 4.0 ppm caused by three protons on adjacent carbon (-CH₃).

Exercises:

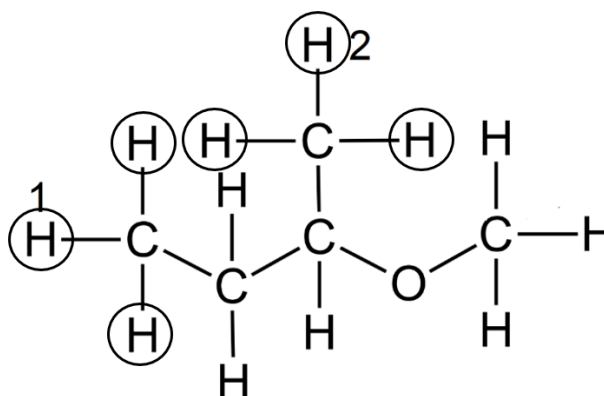1. Deduce the number of peaks and the splitting patterns in the ^1H NMR spectra of the following compounds.

a) Iodoethane

Number of peaks	
Splitting pattern(s)	

b) 2-bromo-2-methylpropane

Number of peaks	
Splitting pattern(s)	

2. The structure of 2-methoxybutane is shown below.

Predict the splitting patterns caused by the protons labelled 1 and 2.

1……………………………………
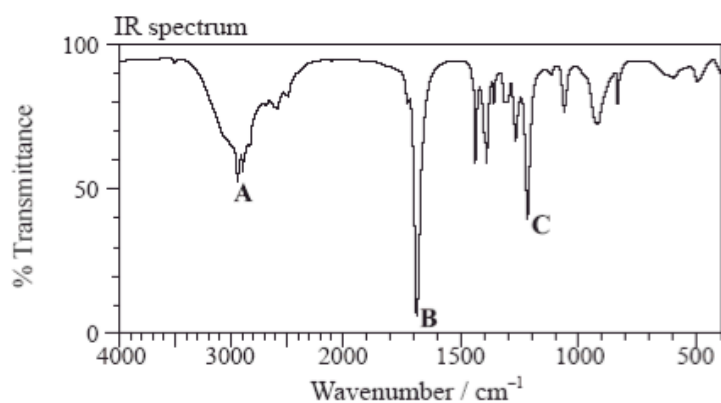
2……………………………………

Structure 3.2.12
Understandings:
- Data from different techniques are often combined in structural analysis.
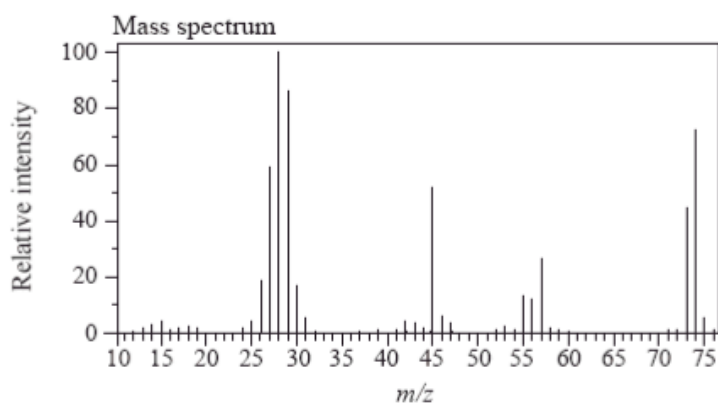
Learning outcomes:
- Interpret a variety of data, including analytical spectra, to determine the structure of a molecule.

Exercise: Deduce the structure of an unknown compound, X, which has the molecular formula $C_3H_6O_2$.

IR Spectrum

Mass spectrum

^1H NMR spectrum