

Principles of Infrared Spectroscopy

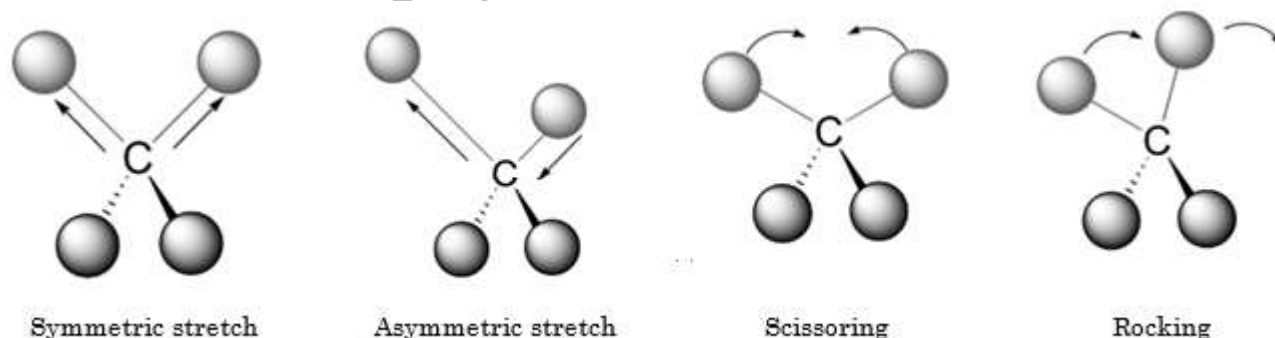
Infrared spectroscopy, which was first invented in the 1940s, is an essential tool in the determination of the presence, and equally importantly the absence, of functional groups.

Whilst microwaves can make molecules rotate and of great use in air pollution analysis, infrared spectroscopy involves the impact of infrared radiation on the stretching and twisting etc; of molecular bonds. The radiation increases the length of the bond without actually breaking it and is part of the electromagnetic spectrum known as non – ionising radiation (all regions with less energy i.e. lower frequency than x – rays).

An effective way to understand how infrared radiation impacts on a molecule is to stand up, legs apart and arms pointing above, and at 45°, to the shoulders, as if performing a star jump. The waist represents the central atom, arms and legs depict covalent bonds and the hands and feet represent the other bonding atoms.

- Twist from the waist so that the arms and hands are now at 90° to the body and this is, unsurprisingly, described as a **twist**.
- Standing straight again with hands close to the shoulders: Extend both arms, stretching as much as possible. This is a **symmetrical stretch**.
- Standing straight again with hands close to the shoulders, point with one hand as if landing a punch. Since one hand is as far from the body as possible whilst the other is close to the body this is an **asymmetrical stretch**.
- Arms in the air again pointing as far apart as possible but in line with the body and clap your hands together above your head. This motion is **scissoring**.
- Again standing straight put both arms in the air again, like a star jump move. Move, simultaneously, both arms from left to right or vice versa. This is **rocking**.

In molecular terms, some of these movements are illustrated below.



In these pictures a plain straight line links atoms in the plane of the paper, the hatched line indicates atoms behind the paper and the dark arrow indicates those in front of the page and are the standard way of displaying a three dimensional molecule in two dimensions.

When molecular atoms perform these actions many of the absorptions appear in the region below 1500 cm^{-1} , and can overlap making that part of the spectrum extremely difficult to interpret. The combination of peaks is important and unique to the specific compound and the specific wavenumbers are affected by the presence of isotopes since the differing masses affect the necessary wavenumbers. Since, however, they are unique to the compound they are immensely useful for comparison purposes and hence it is known as the *fingerprint region*.

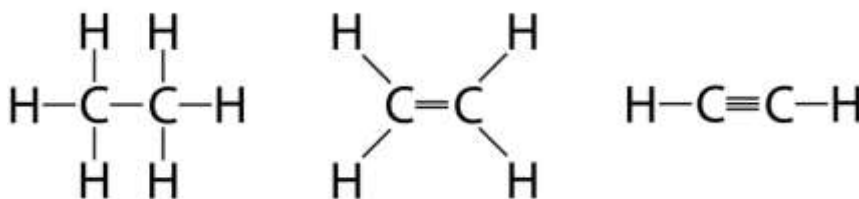
The Effects of Bond Strength and Electronegativity

The two principle reasons for the specific frequencies at which stretches occur within the infrared region are the masses of the two atoms and the bond strength. The *bond strength* depends on the atoms present and can be defined as the energy required to break the bond. It is also known as the *bond energy* and the *bond enthalpy* and is measured in kJ mol^{-1} . The term *bond strength* is used throughout this text as it is the most easily understood.

It is also possible to compare bond strengths by comparing bond lengths. The bond length is the distance between the nuclei of the two atoms and is measured in picometres (pm) which is equivalent to 10^{-12} m. The bond length is longer with a weaker bond, since the bonding electrons are less able to hold the atoms together and shorter for atoms held more tightly together. The other hugely important factor is the *electronegativity* of the bonding atoms. Bond strengths and electronegativity are discussed below.

Bond strength

Bond strengths, i.e. the energy required to break bonds can be compared by measuring the distance between the two atoms involved in the bond. For our purposes, the most instructive comparison is that of the bond lengths (the distances between the carbon atoms in the so called carbon – carbon single, double and triple bonds as shown below and becomes informative when we recall that the stronger the bond the shorter the bond length.



Molecule	ethane	ethene	ethyne
Bond length (pm)	154	133	120
Wavenumber (cm^{-1}) typical	1200	1650	2200

As discussed earlier, the concept of carbon – carbon single, double and triple bonds arose from the concept of valency and the requirement for carbon to form four bonds and hydrogen to form just one. It is clear from the bond lengths that a carbon = carbon double bond is *not* twice as strong as a carbon – carbon single bond since if so it would be half the length of a C – C bond and it is not. The same observation applies to the triple carbon – carbon bond. It is also noticeable that all the C – H bonds are of the same length and hence of the same strength. This is significant for clear chemical purposes but it also indicates that the nature of one non-polar bond has little if any effect on other bonds formed by the same atom. It is different for polar molecules which are discussed below when we also consider the relevant parts of the concept of electronegativity on spectroscopy. Finally, with reference to alkanes, alkenes and alkynes the carbon – carbon single, double and triple bonds the bond strength differences means that the energy required to stretch, twist, rock etc; the atoms explain why there are different absorbances for all three bonds and also explains why all C – H bonds appear in the same region.

Electronegativity

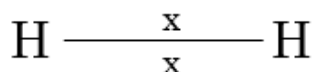
This concept has been discussed before but some concepts are worth reconsidering since they have different consequences and some are too difficult to only consider once and understanding increases with reiteration. It is also worth mentioning here that the fact that many atomic concepts are difficult to understand can be daunting to one new to the subject. There is nothing wrong with that since all of us have experienced the same difficulties both as pupils and the scientists who struggled to understand the meaning of their results. The only people who find these concepts trivial on introduction are those who not understand them at all.

Electronegativity is defined as *the ability of an atom to attract both of the bonding pair of electrons in a covalent bond towards itself*. The most electronegative atoms are nitrogen, oxygen, fluorine, chlorine and bromine and this is explained by calculation of the *effective atomic number* of the atoms.

The halogens all have an effective atomic number of seven whilst that of oxygen is six. The relative atomic number of hydrogen is simply one which means that oxygen has six times more power than hydrogen to attract the bonding pair whilst the halogens are even stronger and the bonds are even more distorted in terms of electron sharing.

The presence of electronegative elements causes a distortion in the distribution of the bonding electrons in a covalent bond as demonstrated by comparing the bonding distribution in the hydrogen molecule, the hydrogen chloride molecule and the water molecule.

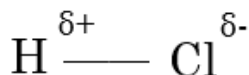
The **hydrogen** molecule, H_2 , contains two identical atoms obviously of the same electronegativity so the bonding pair can be visualised as in the middle of the bond where **x** represents one electron.



Chlorine is the third most electronegative element so so pulls the bonding pair of electrons towards itself as shown below in the **hydrogen chloride** molecule:



Since the hydrogen atom is deshielded and possesses less of the bonding pair than the chlorine, it is described as *electron deficient* and is represented by δ^+ whilst the chlorine atom, with more than its fair share of the bonding pair and so *electron rich* is represented by δ^- so we can now draw the, **polar**, HCl molecule as:



In these commonly used notations the term δ^+ and δ^- are not quantified, numerical values and simply signifies that the atom is partially charged.

The effect of electronegativity is clearly demonstrated by comparing the absorbances of the C – H and C – Cl which typically occur at $\sim 2950 \text{ cm}^{-1}$ and $\sim 750 \text{ cm}^{-1}$.

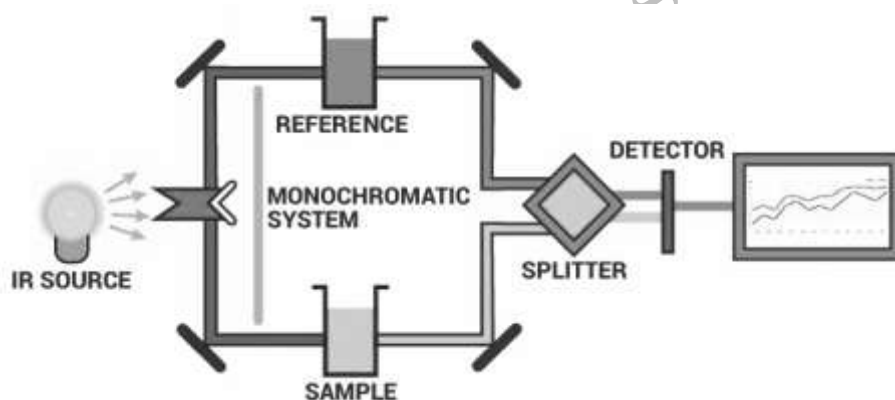
Infrared Spectroscopy in more detail

Infrared radiation causes the bond in a molecule to stretch (symmetrically and asymmetrically), rotate, rock or twist.

No molecule is ever at rest since at even the lowest temperatures it is still rotating but when electromagnetic radiation of slightly higher energy, in this case ir wavelengths, is absorbed, the molecule absorbs a portion of it, making use of it to stretch, twist, rock, scissor etc;

The radiation is then re-emitted when the bond releases the energy and the atoms return to their usual place. This is called *relaxation*. Whilst the ir radiation comes from one specific direction the emission of energy on relaxation occurs in all directions and effectively none of the absorbed and then emitted energy reaches the detector. This means that the molecule absorbs radiation and that this absorbed radiation does not reach the detector. In the actual experiment, if the compound is dissolved in a solvent, the ir beam is split through one reference container, containing the solvent only, and an identical container of the dissolved sample material. The difference in the received light represents the absorption by the sample.

The schematic arrangement of an infrared experiment is here.



Initially, an infrared spectrum can be daunting and appear incomprehensible however when the regions are broken down analysis can become much simpler than at first appears.

As explained above bonds can stretch, symmetrically and asymmetrically, and the bonded atoms can rock, scissor, twist etc; Each of these stretches requires a specific frequency of radiation. It is possible to calculate the frequency at which each of these will occur but that is unnecessary for structural analysis and is rarely performed by chemists.

Instead we look for the presence of specific functional groups whose presence can be confirmed by absorptions in specific regions and their absence can be completely ruled out by the absence of such peaks. This is made simpler by the fact that, irrespective of the structure of the molecule, particular stretches *always* occur in specific regions of the spectrum and can be identified. For example, a carboxylic acid will contain a – COOH group and will exhibit C = O, C – O and O – H peaks.

For our purposes the groups to look for are:



The first issue to be addressed is that of the unit, the *wavenumber*. The wavelengths or frequencies at which molecules absorb ir radiation can be very large or very small numbers respectively. This makes it difficult to compare them and so instead we use the concept of the wavenumber which has the unit cm^{-1} . The wavenumber is simply the number of waves present per centimetre and as such is a frequency. The frequency range now comprises numbers ranging between 4000 and $\sim 500 \text{ cm}^{-1}$, which are much more comprehensible. The reason why spectra stop at 500 cm^{-1} is for practical reasons only. The solid samples are dispersed with a paraffin wax known as nujol and contained between discs made of sodium chloride whilst solutions are contained within containers with sodium chloride or, more usually, potassium bromide windows. These materials are transparent to ir radiation between 4000 and 500 cm^{-1} but absorb all of it below 500 cm^{-1} .

There are specific regions to examine which may be used to identify the *presence* or the definite *absence* of particular functional groups. The most important are identified in this table and includes the $\text{C} \equiv \text{N}$ (nitrile) bond which has not been discussed to date.

Group	Wavenumber range (cm^{-1})	Group	Wavenumber range (cm^{-1})
O – H	~ 3500	C = O	~ 1750
N – H	~ 3500	C = C	~ 1650
S – H	~ 3500	C – O	~ 1450
C – H	3000 – 2900	$\text{C} \equiv \text{N}$	~ 2250

To summarise, the first three bonds occur at wavenumbers centred on 3500 cm^{-1} , carbonyl ($\text{C}=\text{O}$) peaks appear at around 1750 cm^{-1} , $\text{C}=\text{C}$ double bonds absorb at $\sim 1650 \text{ cm}^{-1}$ and $\text{C}-\text{O}$ stretches appear at around 1450 cm^{-1} so for structural determination purposes we only need to look at regions centred on 3500, 1750, 1650 and 1450 cm^{-1} . Since all organic compounds contain $\text{C}-\text{H}$ bonds the region to the right of 3000 cm^{-1} is useless for structural purposes since those peaks will always be there.

The matter is simplified even more if there are for example, oxygen atoms present but no sulfur or nitrogen atoms and it is made even easier using a correlation chart. The specific regions assignable to particular groups did not arise from complicated calculations; rather they were determined by the measuring the spectra of numerous examples of the same classes of compounds and assembling a correlation chart as shown above.

There are two other characteristics of an ir spectrum:

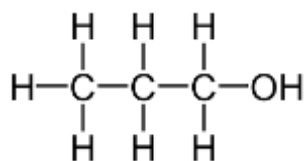
- Most of the stretches appears below 1500 cm^{-1} and cannot be assigned specifically but are a combination of peaks unique to that compound and, if a pure sample is available, the identity of a sample can be assessed by comparison hence this region is known as the *fingerprint region*.
- The peaks can be very broad (O – H), very strong (C = O and C = C) or can be very weak and everything else in between. Peaks are often described as the wavenumber with st, br, w, vw in brackets afterwards representing strong (st), broad (br), w (weak), very weak (vw) etc;

The presence or absence of these bonds, used in the analyses of the compounds in this series are of great significance in the determination of the functional groups that are present or absent and were of enormous importance in chemical advances in the 1950s and 1960s. It is easiest to understand this by actually looking at real spectra. We will look at three: a 3-carbon alcohol (**propanol**), **propanoic acid** and **cyclohexene**.

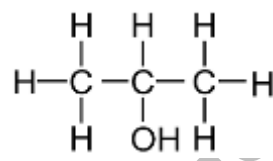
Propanol

The 3-carbon alcohol, **propanol**, has elemental composition C: 59.92% H: 13.45% O: 26.63% and a relative molecular mass (M_r) of 59.07 g mol⁻¹. The molecular formula is, therefore, C₃H₈O.

Since there is only one oxygen atom present the compound cannot be a carboxylic acid (which requires two oxygen atoms) and other possible classes could be aldehydes, ketones or alcohols. The only three carbon compound aldehyde, propanal, would have the formula CH₃CH₂CHO whilst the only possible three carbon ketone, propanone, will have the formula CH₃C(O)CH₃. This only leaves an alcohol and there are two possible structures (isomers) for propanol:



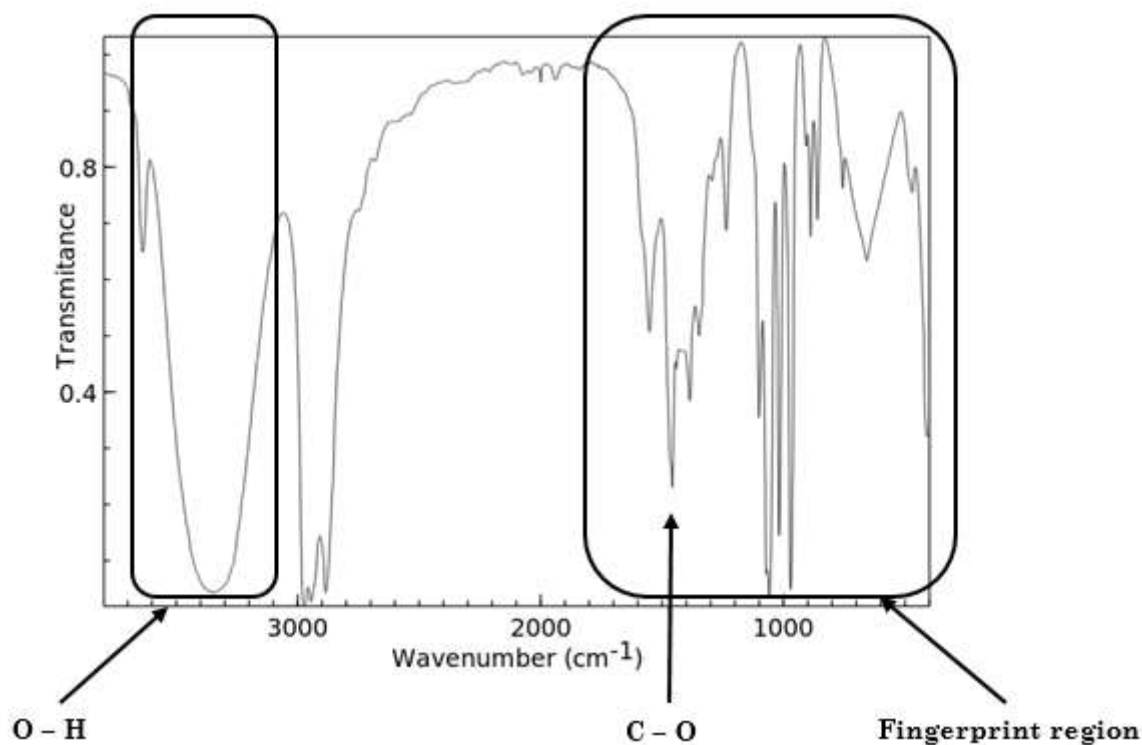
1 - propanol



2 - propanol

Remember that there cannot be a third isomer with the -OH group on the left most carbon as that is the same as 1 - propanol. which would be systematically named by the number of the carbon containing the O - H functional group as shown above.

The infrared spectrum shows the presence of C - H, O - H, C - C and C - O bonds but cannot differentiate between the two feasible structures from first principles.

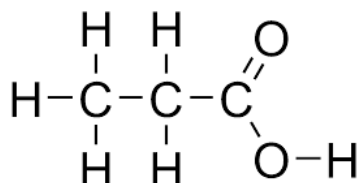


Propanoic acid

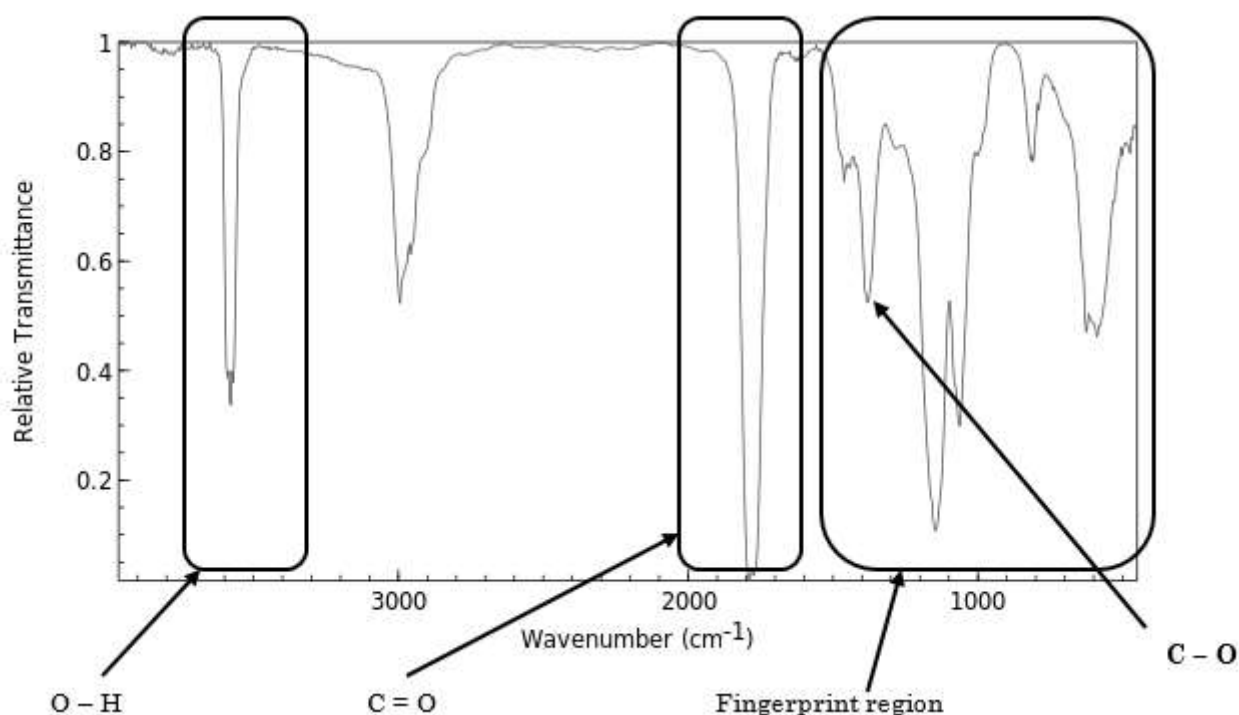
Propanoic acid has the elemental composition: C: 48.61% H: 8.18% O: 43.21% and a relative molecular mass of 74.06 g mol⁻¹ indicating that the molecular formula is C₃H₆O₂.

It is known to be acidic because a dilute aqueous solution has a pH of ~ 3 and it reacts with aqueous alkaline solutions.

Since a carboxylic acid has a -COOH group which from the number of bonds can only exist on the terminal carbon, the only feasible structure is



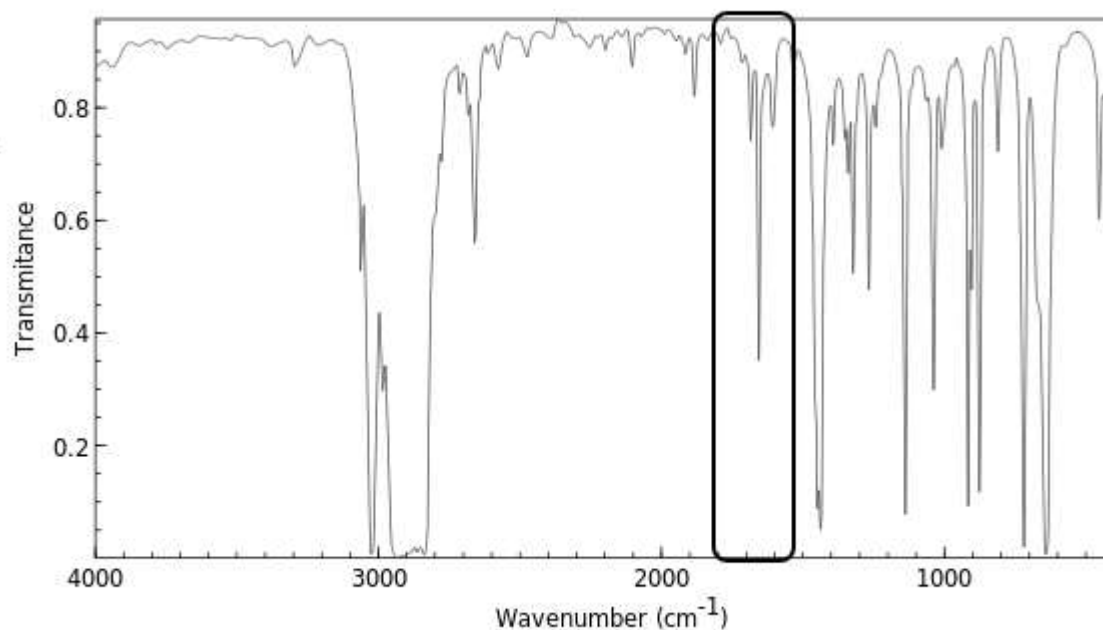
The infrared spectrum supports this suggestion since it demonstrates the existence of both an O - H bond and a C = O bond as well as a C - O bond as highlighted.



The C - O peak at ~1450 cm⁻¹ would be absent if the oxygen containing compound was a ketone or an aldehyde since neither class contains a single C - O bond.

Cyclohexene

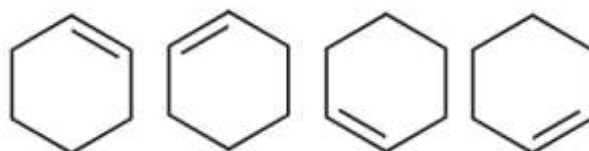
Cyclohexene has the molecular formula C_6H_{10} and a relative molecular mass of 82.10 g mol^{-1} . That it has a $C = C$ bond is indicated by the traditional test, decolourisation of bromine water and this is confirmed by the presence of a strong peak at $\sim 1650 \text{ cm}^{-1}$ as highlighted in its infra red spectrum:



Alkenes can be linear or cyclical but a linear six-carbon alkene would require thirteen hydrogen atoms i.e. the molecular formula would be C_6H_{12} . The only possibility is a cyclic structure as illustrated



No numbering of the carbons in the ring to indicate the position of the double bond is necessary since wherever we place it, simple rotation of the molecule would lead to the illustrated molecule. For example, the four molecules illustrated below are identical since each can be simply rotated in to all the others.



Although infrared spectroscopy is an extremely powerful tool for identifying the presence of functional groups, it has limitations when attempting to distinguish between theoretical isomers.

Another limitation is that although the experiment records the presence of absence of functional groups it does not quantify the number of such bonds. It reveals little information about the carbon – carbon backbone, and nor does it indicate and this nor completely justify the existence of each group in the molecule and this is where mass spectrometry and multinuclear nmr is of use.

Organic Mass Spectrometry

Mass spectrometry has already been discussed in relation to its application and role in the discovery of the isotopes of an atom but it is even more useful in determining the structural composition of organic molecules.

Essentially the mass spectrometric process can be described in a series of steps:

1. **Vaporisation** of the sample which can only be analysed in the gas phase. It is also essential that the entire process is conducted in evacuated apparatus since, otherwise, the charged fragments would be absorbed by the atmosphere present. Vaporisation is essential otherwise the ionisation process (step 2) would merely result in heating the sample and vaporise it anyway.

2. **Ionisation** of the sample.

This is effectively throwing something at the molecule [M] to knock out an electron and is analogous to throwing a rock at a vase and analysing the broken pieces to see what the vase was made up of – Don't do that!

The resulting molecular ion [M⁺] is inherently unstable and, under the exact same conditions, will break apart in exactly the same way every time the experiment is conducted. There are various ways to ionise the molecule. The two most important are:

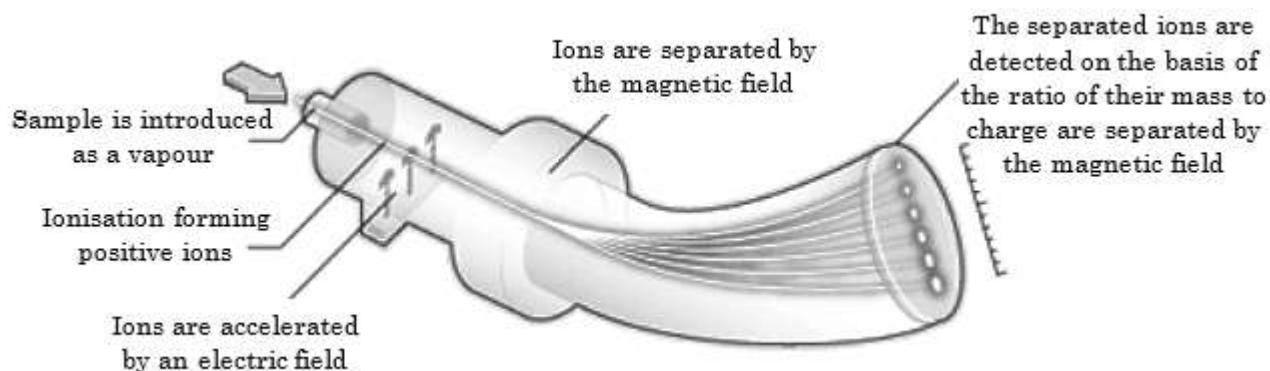
1. Throw electrons at it hoping that at least one electron will knock one out of the molecule. This is known as electronic ionisation.
2. Throw small molecules such as ammonia (NH₃) at the molecule. The ammonia molecules will do two things: eject an electron and then also bind to the target molecule. This creates an [M+NH₃]⁺ molecular ion. Naturally the presence of ammonia must be taken into account when studying the fragments.

Electron ionisation is by far the most commonly used, and useful, technique and is the only one we will consider here. In principle, a stream of electrons impinging on a target molecule could knock out more than one electron thus creating [M²⁺], [M³⁺] ions etc; In actuality although such events do occur they do so very rarely and so rarely that they can be ignored.

3. The molecular ion [M⁺] is then attracted towards the negative plate of an electric field and races towards it, passing through a hole in the plate. This is **acceleration**.
4. It then carries on to pass through a magnetic field. As discussed previously, a moving charge of whatever type will feel the presence of the magnetic field and its path will be altered depending on its mass/charge ratio (m/z). Such a change of path is known as **deflection** and causes separation of the peaks.
5. The fragments all change their paths very slightly but sufficiently so that they can be **detected** separately. The original measurements were made by using a photographic plate and a series of dots were produced. The lightness or darkness of these spots indicate the relative proportions of each fragments as a total of the whole. Nowadays the detector measures the electrical current generated at each m/z value.

Note: it is important to appreciate that the molecular ion is, by definition, unstable and will produce charged and neutral fragments. The neutral fragments are unaffected by an electric field and play no further part in the experiment.

A schematic diagram of the mass spectrometry process is shown below.

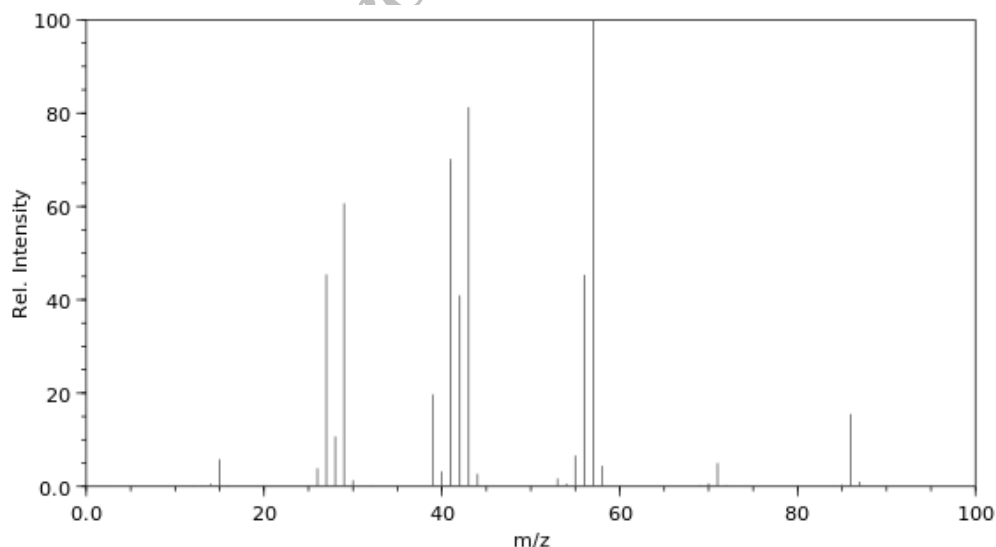


The mass spectrometry process

The charged fragments are, themselves, also unstable and can fragment as they travel producing further fragments which can produce further fragments. Some can also rearrange themselves into further charged species which can be detected. This can make the final spectrum of very large molecules extremely difficult to interpret but the task is worthwhile since it reveals much about the structure of molecules. All of this occurs within less than one second which is the typical time of flight of the molecular ion and its fragments from ionisation to detection. Such rearrangements are, however, beyond the scope of this introductory text.

If we consider an alkane of molecular formula C_6H_{14} .

The infra red spectrum of the molecule would be of limited value since it would only demonstrate the presence of C – C and C – H bonds together with the absence of a C = C bond. This molecule provides a very clear example of the benefits of the mass spectrometric analysis and the mass spectrum is displayed below.



Before we analyse the spectrum in depth there are two points to note.

- The analysis of the sample is **not** quantitative by mass and the peaks are scaled such that the most intense is set to be 100% and all other peaks are then of relative height and intensity to that peak. The 100% peak is known as the *base peak*.

- The molecular ion $[M]^+$ is **not** the peak with the greatest mass/charge (m/z) ratio. There is always one peak one mass unit greater, the so called $[M+1]$ peak which is always approximately 1% of the height of the molecular ion. This is due to the existence of isotopes of carbon.

The predominant carbon isotope (^{12}C) comprises approximately 99% of all carbon atoms. There are other carbon isotopes, notably ^{13}C which comprises $\sim 1\%$ of all carbon atoms and hence produces a peak one m/z unit higher than the molecular ion but which is ignored in spectrometric analysis. For every molecular ion fragment, however, there is also one peak one unit higher at 1% of the height of the major fragments. They can be ignored but their presence does account for numerous lines in the spectrum which are not determined.

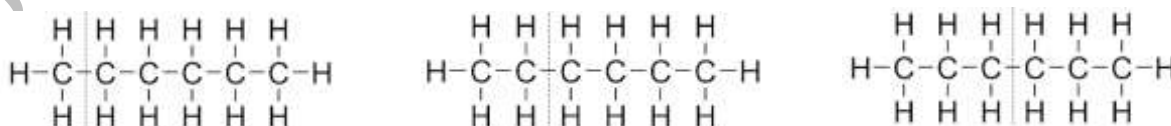
Returning to the above mass spectrum,

Hexane has the molecular formula C_6H_{14} and so has a relative molecular mass (M_r) of 86. The molecular ion $[M]^+$ has exactly this mass and it is clear that there is a tiny line one unit to the right due to the presence of ^{13}C in 1% of the total number of carbon atoms in the molecules.

There are two straightforward ways to determine the structure of particular fragments:

- The first looks at the lighter fragments and frequently pays dividends as there are few fragments which can form light fragments and there are a number of established rules:
 - A line at $m/z = 15$ can only be due to a $-\text{CH}_3$ group, that at m/z of 29 can only be due to a $-\text{C}_2\text{H}_5$ group, $m/z = 43$ indicates a $-\text{C}_3\text{H}_7$ group etc;
 - A line at $m/z = 12$ is just a ^{12}C atom whilst a line at $m/z = 16$ is oxygen and so on.
 - Two peaks at m/z of 35 and 37 in a relative intensity of 3:1 can only be due to the presence of a chlorine atom (caused by the ^{35}Cl and ^{37}Cl atoms which naturally exist in the proportion 3:1) whilst lines of equal height at m/z of 79 and 81 can only be assigned to a bromine atom of which two isotopes exist, ^{79}Br and ^{81}Br and which exist in roughly equal proportions. Naturally, the presence of a halogen atom would already be known from the elemental composition and from the specific tests for the presence of such atoms.
- The second way is a brute force method which is appropriate when a particular structure is suspected is a brute force method of determining the potential fragments. Essentially this involves drawing out the structure of the molecule and drawing lines across which bonds could be broken and then checking if these appear in the mass spectrum.

For example, hexane can be broken, theoretically, as shown below by the dashed lines.



$m/z:$ 15 71 29 57 43 43

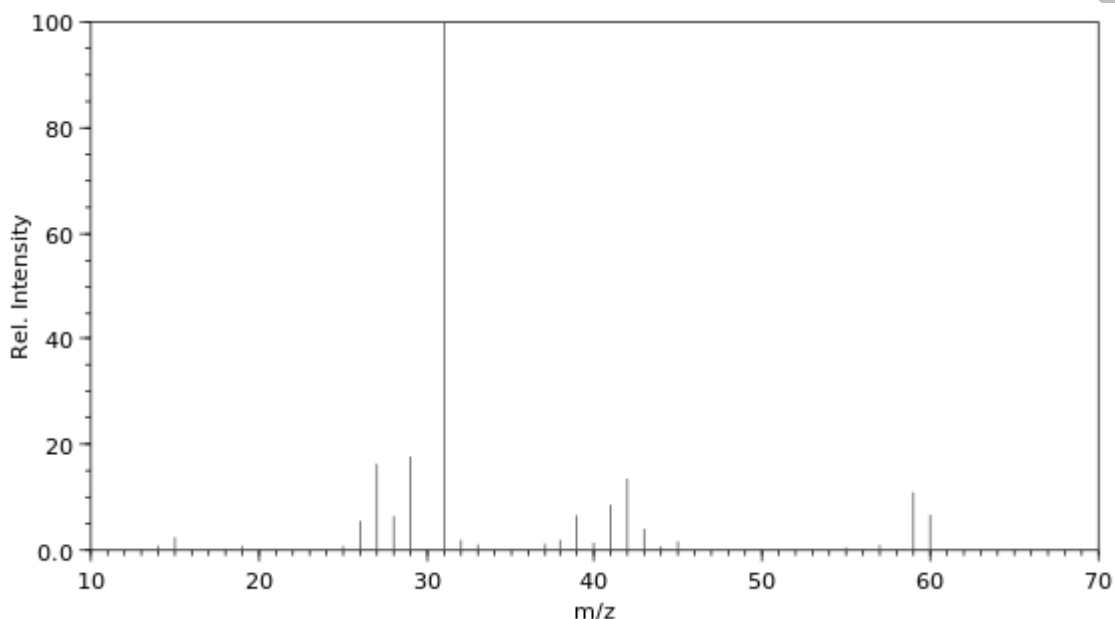
If the molecule has the structure proposed and fragments as suggested then we should expect to see peaks at $m/z = 15, 29, 43, 57, 71$ as indeed we do confirming the likelihood of this structure. The structure is confirmed later when we investigate ^1H and ^{13}C nuclear magnetic resonance (NMR).

Propan-1-ol or Propan-2-ol?

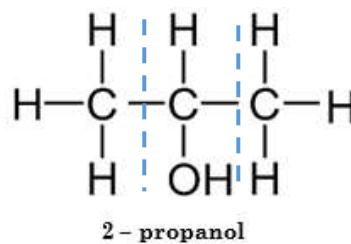
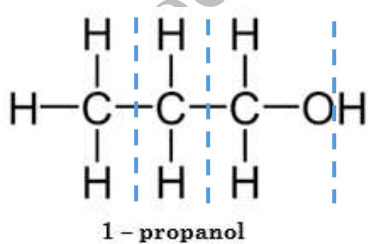
Returning to the three carbon molecule, **propanol**, which has elemental composition C_3H_8O and a relative molecular mass of 60.08 g mol^{-1} . Propanol has two isomers are possible as illustrated previously but also, for different purposes demonstrated again below.

We know from the ir spectrum that the molecule contains both an $O-H$ and a $C-O$ bond but no $C=O$ bond.

The infra red spectrum could not, however, determine if the $O-H$ functional group exists on the end or middle carbon atom. Unfortunately, mass spectrometry does not really help either as demonstrated below.



As before, it is important to check if the molecular ion M^+ is present and to then consider how the molecular ion could fragment and calculate the mass/charge ratios. Some of the possible fragments are indicated by the dashed lines and the masses of the fragments are shown below the diagram.



Fragments:

- CH_3 ($m/z = 15$)
- C_2H_5 ($m/z = 29$)
- C_2H_5O ($m/z = 45$)
- C_3H_7O ($m/z = 59$)

- CH_3 ($m/z = 15$)
- C_2H_5O ($m/z = 29$)
- C_2H_5 ($m/z = 45$)
- C_3H_7O ($m/z = 59$)

as well, in both cases, the molecular ion $[C_3H_8O]^+$ ($m/z = 60$).

The mass spectrum of the molecule we are considering is shown below. All the fragments are present and it is extremely difficult to differentiate between the two possible structures. This leads us on to the theory and application of Nuclear Magnetic Resonance (nmr) spectroscopy, which is discussed next and is used to answer this question.