

Topic 2.11

ANALYTICAL TECHNIQUES

High Resolution Mass Spectrometry
Infra-red Spectroscopy

HIGH RESOLUTION MASS SPECTROMETRY

The technique of mass spectrometry was used in Unit 1 to:

- determine the relative abundances of different isotopes in a sample of an element and hence to deduce relative atomic masses
- identify the peak with the largest m/z ratio in a spectrum of a molecule and hence determine the rmm of the molecule

On closer inspection of the molecular ion peak, it is actually possible to reveal more information than just the relative molecular mass. If the mass spectrum is examined under high resolution, the complete molecular formula can be deduced.

Eg If an organic molecule is found to have a molecular ion peak of 58 in a mass spectrometer, it could be either C_4H_{10} or C_3H_6O . In other words, it is not possible to deduce the exact molecular formula.

However, the two molecules C_4H_{10} and C_3H_6O do not have exactly the same mass. The exact mass of ^{16}O , ^{12}C and 1H atoms on the $^{12}C = 12$ scale is:

isotope	Relative isotopic mass
^{16}O	15.994
^{12}C	12.000
1H	1.008

Therefore by measuring the m/z ratio of a molecular ion peak to three decimal places, it is possible to distinguish between C_4H_{10} and C_3H_6O and hence deduce the molecular formula:

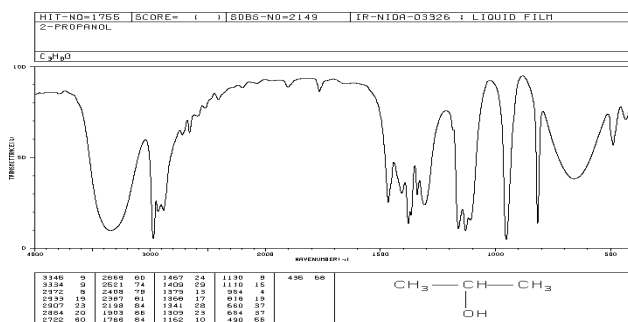
Eg A high resolution mass spectrum of a compound showed the molecular ion peak to have a m/z ratio of 58.042

C_4H_{10} has a relative molecular mass of 58.080 but C_3H_6O has a relative molecular mass of 58.042. So the molecular formula must be C_3H_6O .

INFRA-RED SPECTROSCOPY

a) Introduction

All molecules contain covalent bonds and these bonds are constantly rotating, bending and stretching with characteristic frequencies. When these bonds are subjected to infra-red radiation with the same frequency, they will bend or stretch more and the radiation of that frequency will be absorbed. Each bond absorbs one or two distinct frequencies only, so when infra-red radiation containing a full range of frequencies is passed through a sample of an organic compound, some frequencies are absorbed and others pass through unaffected. The resultant radiation can be detected and converted into a spectrum known as an infra-red spectrum. A typical infra-red spectrum is shown below:



The horizontal axis shows the **wave-number** in cm⁻¹. Wave-number is closely related to frequency. The vertical axis shows the **transmittance**, expressed as a percentage. If the transmittance is below 50%, then a significant quantity of the radiation at that frequency is absorbed. This is known as a peak. Some peaks occur at very precise frequencies – these are known as **sharp** peaks. Other peaks occur over a range of frequencies – these are known as **broad** peaks.

The infra-red spectrum above shows sharp peaks at 830 cm⁻¹, 950 cm⁻¹, 1140 cm⁻¹, 1180 cm⁻¹, 1300 cm⁻¹, 1380 cm⁻¹, 1500 cm⁻¹ and 2970 cm⁻¹, and a few others. It also shows broad peaks at 500 – 800 cm⁻¹, and 3100 – 3500 cm⁻¹.

Since different bonds absorb at different wavenumbers, the peaks in an infra-red spectra can be used to determine the different bonds present in the molecule.

Since almost all compounds contain C-H and C-C bonds, these peaks are almost always present in an infra-red spectrum:

Bond	Frequencies absorbed/ cm ⁻¹
C-H	2650 – 3310 (sharp)
C-C	720 – 1175 (sharp)

Any other bonds present, however, will give more distinctive peaks:

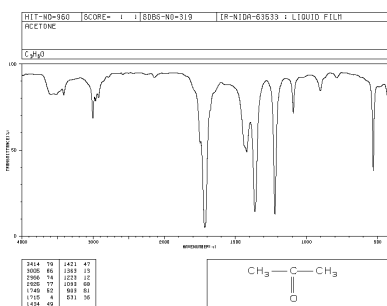
Bond	Frequencies absorbed/ cm^{-1}
C-O	1120 - 1310 (sharp)
C=C	1620 - 1690 (sharp)
C=O	1630 - 1815 (sharp)
O-H (alcohols)	3230 - 3350 (broad)
O-H (acids)	2500 - 3000 (broad)
C-O	1000 - 1300 (sharp)

It is easy to recognize the peaks due to the presence of the C=O and O-H bonds in particular, as the absorbance is very high (the transmittance is low). Note that whenever a bond is also involved in intermolecular hydrogen bonding, the peak becomes broad. Bonds which do not contain H atoms involved in hydrogen-bonding give sharper peaks.

b) Identifying functional groups

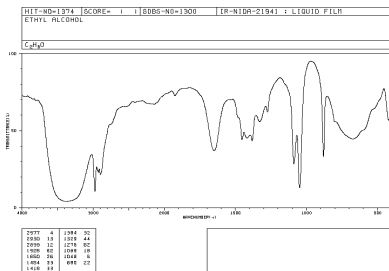
Functional groups can be identified by determining whether or not the peaks characteristic of the bonds present in that functional group are present in the infra-red spectrum. Some of these characteristic absorptions are shown below:

i) carbonyls (C=O):



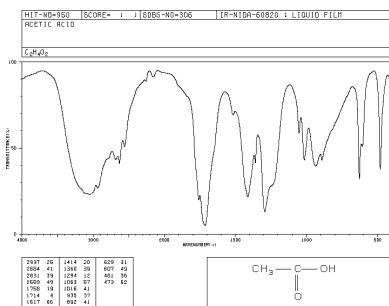
Note the strong sharp absorption at 1715 cm^{-1} , also found in carboxylic acids and esters.

ii) alcohols (C-O and O-H):



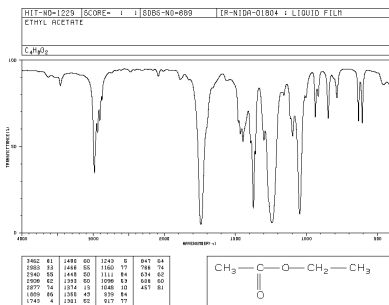
Note the strong broad absorption at $3100 - 3500\text{ cm}^{-1}$, characteristic of an O-H bond in an alcohol. Note also the sharp peak at 1050 cm^{-1} resulting from the C-O bond.

iii) carboxylic acids (C=O, C-O and O-H):



Note the very broad absorption at $2500 - 3000\text{ cm}^{-1}$, characteristic of an O-H bond in a carboxylic acid (it tends to mask the C-H peak completely). Note also the sharp peaks at 1710 cm^{-1} (C=O) and 1300 cm^{-1} (C-O).

iv) esters (C=O and C-O)



Note the sharp absorptions at 1250 cm^{-1} (C-O) and 1750 cm^{-1} (C=O) and in particular the **absence** of a broad absorption between 2500 and 3500 cm^{-1} (showing that no O-H bonds are present).

c) Identifying impurities

Often organic compounds contain impurities. The extent and nature of these impurities can be determined using infra-red spectroscopy. The bonds present in the impurity but not in the desired product will absorb radiation, giving peaks that would not be expected given the structure of the molecule.

Eg a sample of ethanal is believed to be impure and an infra-red spectrum of the sample is obtained. Only a sharp absorption at around 1700 cm^{-1} is expected in addition to the peaks resulting from C-C and C-H bonds.

If a broad peak between 3000 and 3500 cm^{-1} is also visible as well as a sharp peak between 1000 cm^{-1} and 1300 cm^{-1} , then an alcohol is also present as an impurity (probably ethanol).

If a broad peak between 2500 and 3000 cm^{-1} is also visible as well as a sharp peak between 1000 cm^{-1} and 1300 cm^{-1} , then a carboxylic acid is also present as an impurity (probably ethanoic acid).

If the infra-red spectrum matches the spectrum of a sample known to be pure, then no impurities are present. Infra-red spectroscopy is often used to ascertain the purity of organic compounds and to identify impurities.

d) Using the fingerprint region

Most of the functional groups give characteristic absorptions in the region of the spectrum between 1500 and 3500 cm^{-1} . It is this region that is typically used to identify the functional groups as there are few other peaks in this region (except the C-H peak which is easily identifiable). All the peaks in this region can thus be attributed to specific bonds.

The region of the spectrum between 500 and 1500 cm^{-1} , however, is much more complex and tends to consist of a large number of peaks close together which are difficult to identify. These peaks result from the structure of the molecule as a whole and not from specific bonds. This region is known as the **fingerprint** region and is completely different for each molecule – even those with the same functional group. Every molecule can thus be identified by close examination of the fingerprint region of its infra-red spectrum. The fingerprint regions of infra-red spectra of samples are compared to databases of pre-recorded infra-red spectra until a match is identified. This technique is known as “fingerprinting”.

e) **Global warming**

The ability of covalent bonds in molecules to absorb infra-red radiation is very useful for identifying molecules, functional groups and impurities. It is also, however, the cause of global warming.

Radiation from the sun (including visible and ultra-violet light) is absorbed by the earth and emitted at a lower frequency (usually in the infra-red region).

Molecules such as carbon dioxide, water and methane in the atmosphere do not absorb visible or ultra-violet light and so allow radiation of this frequency to reach the earth's surface. When the light is re-emitted by the earth in the infra-red region, however, it matches the natural frequency of vibration or rotation of bonds in these molecules and the radiation is therefore absorbed.

The ability of carbon dioxide and water vapour to absorb the radiation emitted by the earth is essential for keeping the planet warm enough to sustain life and is called the greenhouse effect.

Increasing levels of carbon dioxide in the atmosphere, however, is causing too much of the planet's heat to be trapped, causing global warming.