3. Infrared spectroscopy

Infrared spectroscopy can be used to detect the functional groups present in a sample, and information can sometimes be obtained about the proximity of one group to another. In some cases it is also possible to give data on the amount of sample present.

The theory

The atoms in molecules are not static, but vibrate about their equilibrium positions, even in the solid state. Each atom vibrates with a frequency which depends on its mass and the length and strength of any bonds it has formed. Molecular vibrations are stimulated by bonds absorbing radiation of the same frequency as the natural frequency of vibration of the bond (*ie* in the range $1.20 \times 10^{13} – 1.20 \times 10^{14}$ Hz) which is in the infrared region of the electromagnetic spectrum. So that the numbers are more manageable absorption is usually quoted in wavenumbers (units cm^{-1}, the reciprocal of wavelength in cm – *ie* the number of wavelengths that make up one centimetre). The relationship between frequency, wavelength, wavenumber and energy is shown in Table 1.

Table 1   Relationship between the frequency, wavelength, wavenumber, and energy of infrared radiation

Frequency (v) (Hz)	Wavelength (λ) (m)	Wavenumber (cm^{-1})	Energy ($kJ\ mol^{-1}$)
1.20×10^{13}	2.50×10^{-5}	400	4.79×10^3
1.20×10^{14}	2.50×10^{-6}	4000	4.79×10^4

Frequency, wavelength and energy are interrelated:

$$c = v\lambda$$

where c = velocity of light (3.00×10^8 ms^{-1})
            v = frequency in Hz
            λ = wavelength in m
and
            $E = hvL$ for a mole of photons

where E = energy
            h = Planck's constant (6.63×10^{-34} Js)
            L = Avogadro constant (6.02×10^{23} mol^{-1})

For most purposes it is assumed that each vibration occurs independently of all others around it (and that the atoms behave as simple harmonic oscillators). A variety of vibrations are possible. Some are shown in *Fig. 1*. The centre of mass of the molecule remains constant during these vibrations.
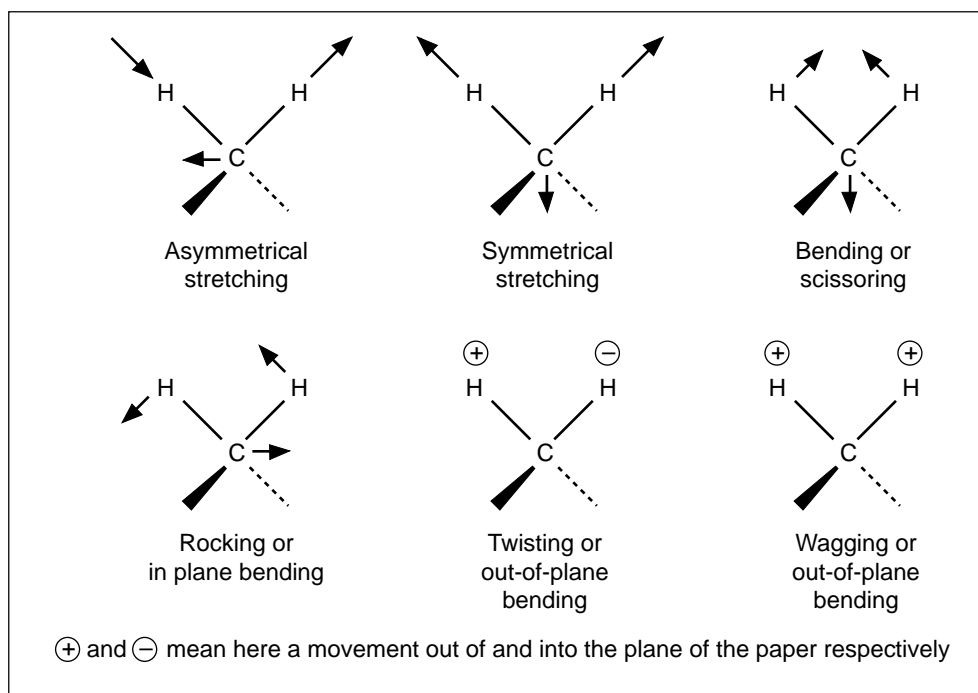
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Figure 1   Some modes of vibration

The spectrometer

Conventional infrared spectrometers (known as dispersive infrared spectrometers) have two beams of radiation, one passing through the sample, the other passing through a reference cell (*Fig. 2*).
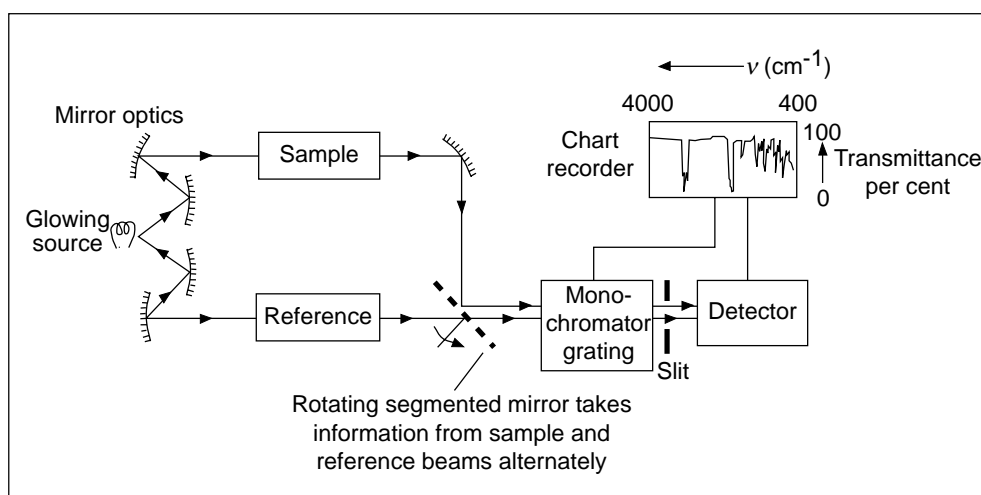

Figure 2   The infrared spectrometer

How it works

The infrared source used can be a simple coil of nichrome wire, or a more complex water cooled rod of silicon carbide. Radiation across the frequency range is passed

through the sample. As a particular frequency is absorbed by the sample less radiation is transmitted, and the detector compares the intensity passing through the sample with the intensity passing through the reference – the reference can be air. However, for solutions an identical cell containing the solvent is used as the reference so that the instrument does not record the absorption of the solvent as coming from the sample.

Detecting the radiation passing through the sample or reference cell is usually done by either a photomultiplier or a photodiode (which converts photons of radiation into tiny electrical currents); or a semiconducting cell (that emits electrons when radiation is incident on it) followed by an electron multiplier similar to those used in mass spectrometers (see page 8). Photocells containing triglycine sulphate (TGS) are commonly used, though a mercury cadmium telluride (MCT) cell is often used if fast scans using a very sensitive detector, are required (these operate at liquid nitrogen temperatures). In both cases the spectrum is generated by comparison of the currents produced by the sample and the reference beams.

The data system (a computer) records the spectrum as transmittance (the amount of radiation passing through the sample) against decreasing wavenumber (*ie* increasing wavelength – *eg Fig. 3*).
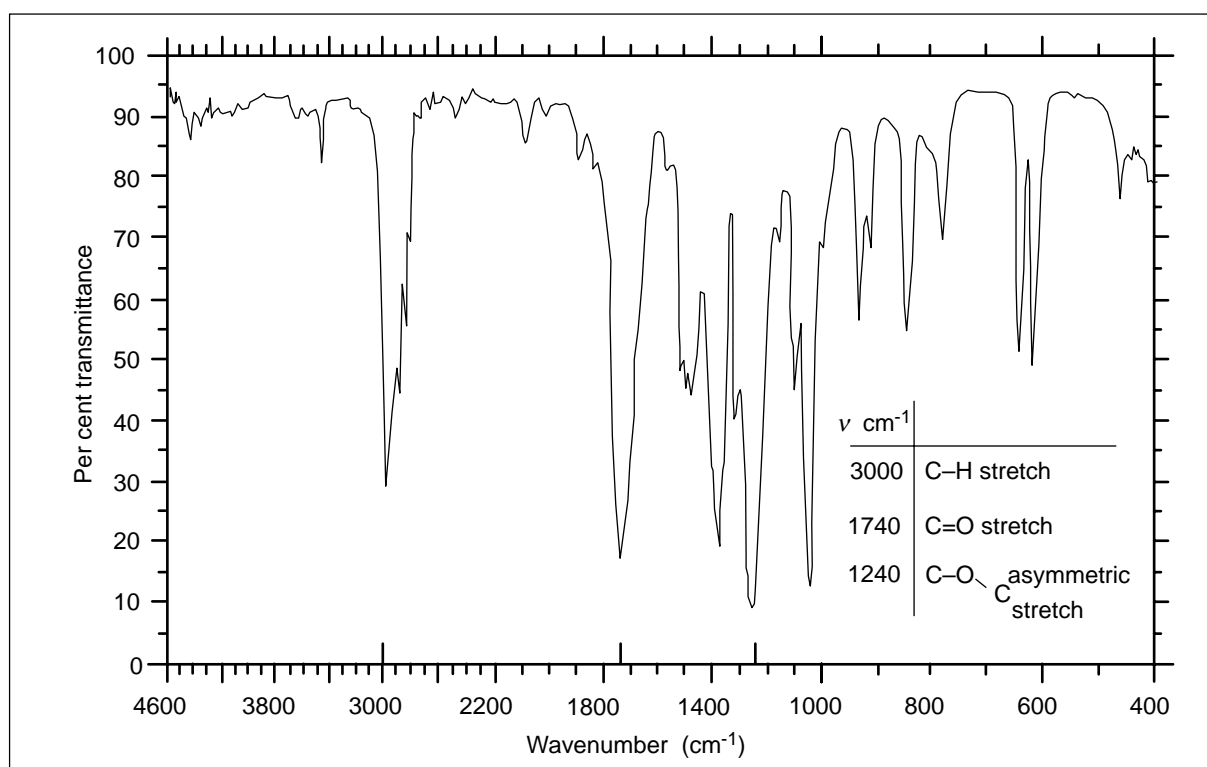

ν cm^{-1}	
3000	C–H stretch
1740	C=O stretch
1240	C–O asymmetric stretch

Figure 3   Infrared spectrum of ethyl ethanoate

Fourier transform infrared (FTIR)

Conventional infrared spectra are obtained by passing radiation through the sample and reference, and using a monochromator to select radiation of only one frequency at a time (monochromatic radiation). In FTIR only one beam is used and this means that all the required frequencies pass through the instrument simultaneously. A computer is used to interpret the resulting information (by a mathematical treatment known as Fourier transformation) and plot the spectrum.

The spectrum obtained by using this technique is sometimes slightly different from conventional scanning, but any variation is usually insignificant.

FTIR has a number of advantages over conventional infrared:

1   the whole spectrum can be run in a matter of a few seconds, rather than several minutes;

2   the faster scan speed means that the spectra of compounds leaving a chromatography column can be obtained as they exit the column without collecting them first;

3   the sensitivity of the technique is greater because the 'background noise' is at a much lower level;

4   the spectrum of a solvent or a known impurity can be removed from the observed spectrum because the information is initially converted to a digital signal – a computer can subtract one spectrum from another; and

5   a small sample can yield a spectrum by adding the information from several scans to produce a single spectrum.

Sample preparation

Infrared spectroscopy is not as sensitive as ultraviolet/visible spectroscopy because the energies involved in the vibration of atoms are far smaller than the energies of electronic transitions. However, very small amounts of sample will give good, reproducible, spectra if prepared correctly.

Gases

These are introduced into a special cell, typically 10 cm in length, although longer ones are available for gases with very low partial pressures.

Liquids

Liquids are used simply in the form of a thin film, kept in place by two potassium bromide discs made from single crystals (these are quite expensive). A drop of the liquid is placed on one disc and the second is placed on top and this spreads the sample into a thin film. Sodium chloride cannot be used across the whole frequency range because it absorbs radiation below 625 cm^{-1} and the data in the range 400 – 625 cm^{-1} would be lost. For many situations this is not a problem but where it is potassium bromide can be used instead of sodium chloride.

Solutions can also be held between discs, but if the concentration is very low a greater path length is required. A cell made of potassium bromide must be used. These are available with path lengths between 0.01 mm and 0.5 mm. Clearly, aqueous solutions cannot be used to clean potassium bromide discs or cells, otherwise they will dissolve, so the discs are cleaned with tetrachloromethane, followed by polishing to achieve a flat surface. In extreme cases washing with ethanol can be used so that the small water content in the alcohol dissolves the stained surface layer of the disc. Spectra of aqueous solutions are usually obtained by using special cells (*ie* zinc sulphide or zinc selenide) and the strong absorption peaks due to the water are disregarded or subtracted by computer.

Many organic solvents absorb in the infrared region, so reference cells of the same path length containing the pure solvent are put into the reference beam. Absorption bands of some solvents are shown in *Fig. 4*.
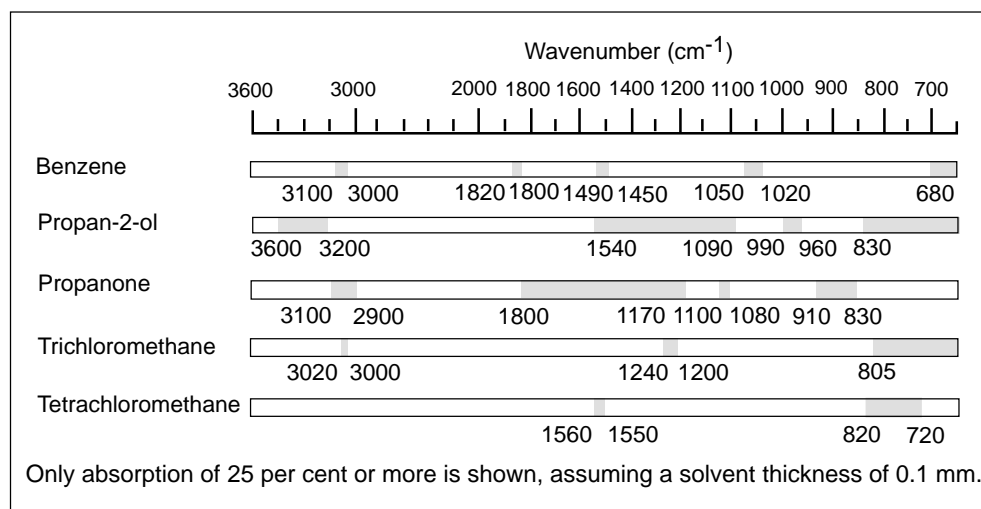
Wavenumber (cm⁻¹)

3600	3000	2000	1800	1600	1400	1200	1100	1000	900	800	700

Benzene
3100 3000   1820 1800 1490 1450   1050 1020   680

Propan-2-ol
3600 3200   1540   1090 990 960 830

Propanone
3100 2900   1800   1170 1100 1080 910 830

Trichloromethane
3020 3000   1240 1200   805

Tetrachloromethane
1560 1550   820 720

Only absorption of 25 per cent or more is shown, assuming a solvent thickness of 0.1 mm.

Figure 4   Absorption characteristics of some solvents

The solvent may have an effect on the spectrum. Hydrogen bonding of N-H and O-H groups is particularly responsible for changes in absorption frequency. Hydrogen bonding, for instance, causes bonds to broaden and shift to lower frequencies, see page 78.

Solids

A simple way of obtaining the infrared spectrum of a solid is to prepare a solution. Alternatively, the spectrum of the solid can be determined by first producing a disc or a mull.

A disc is made by grinding *ca* 1 mg of the solid with 100-250 mg of potassium bromide powder using a mortar and pestle. The very fine powder is then put into a circular die, and placed under a mechanical pressure of $1–7 \times 10^8$ Nm⁻² (15 000–100 000 pounds per square inch) under vacuum. The pressure is maintained for up to six minutes. The resulting transparent disc is used to record the spectrum. It is essential to produce a very fine powder, otherwise the radiation will simply reflect off the surface of the particles.

Making a mull involves grinding the solid to a fine powder, and then adding a liquid – *eg* Nujol (a long chain hydrocarbon) to produce a paste with a consistency like that of toothpaste. Other liquids can be used if Nujol masks the C–H bands of the sample, and these include hexachlorobutadiene, perfluorokerosene and chlorofluorocarbon grease. The mull is then placed between potassium bromide or sodium chloride discs. This method has the advantage that if the mull layer is too thick the discs can be pressed closer together reducing the thickness and producing a better spectrum – *ie* if the absorptions are too intense.

Vibrations absorbing infrared radiation

Only vibrations resulting in the change of a dipole moment, and having resonant frequencies in the infrared region of the spectrum, will absorb infrared radiation. Consequently, simple gas molecules such as H_2, Cl_2, and O_2 do not have infrared spectra (because they do not have dipoles).

Sulphur dioxide and carbon dioxide both potentially have three ways of absorbing energy and vibrating (*Fig. 5*).

The symmetrical stretch of carbon dioxide does not result in any change of the dipole of the molecule. Thus it would not be expected to absorb radiation, and this
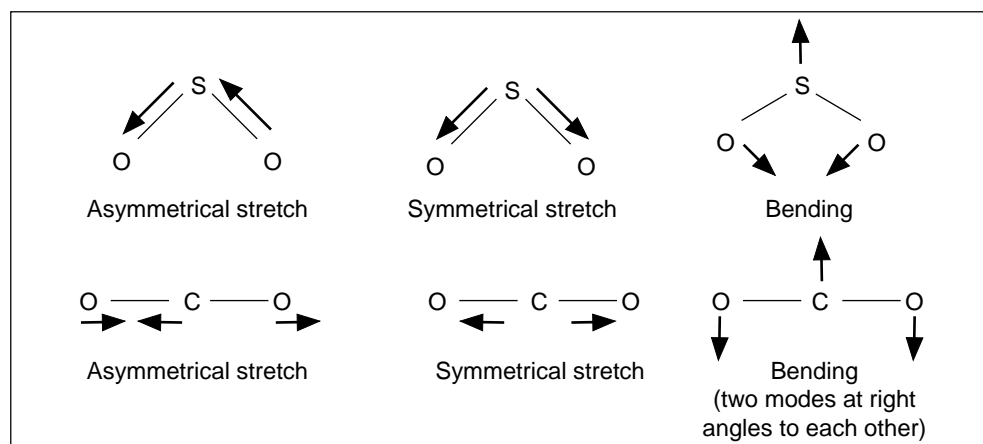
Figure 5   Vibrational modes of sulphur dioxide and carbon dioxide

mode is inactive. All the other modes of both molecules do change the molecular dipole, and absorb infrared radiation – *ie* they are active modes (*Figs. 6* and *7*).
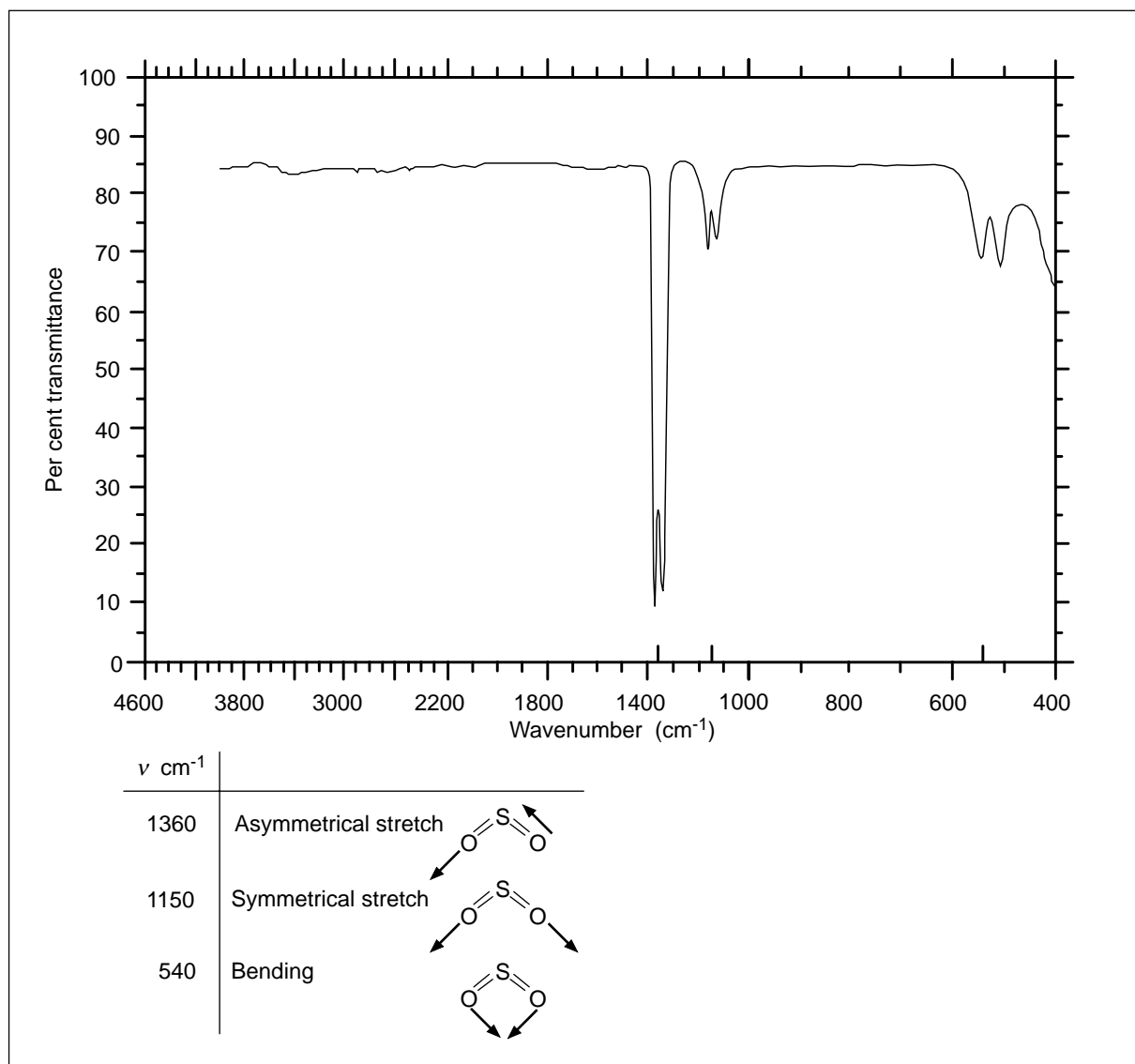
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v cm^{-1}		
1360	Asymmetrical stretch	O=S=O
1150	Symmetrical stretch	O=S=O
540	Bending	O=S=O

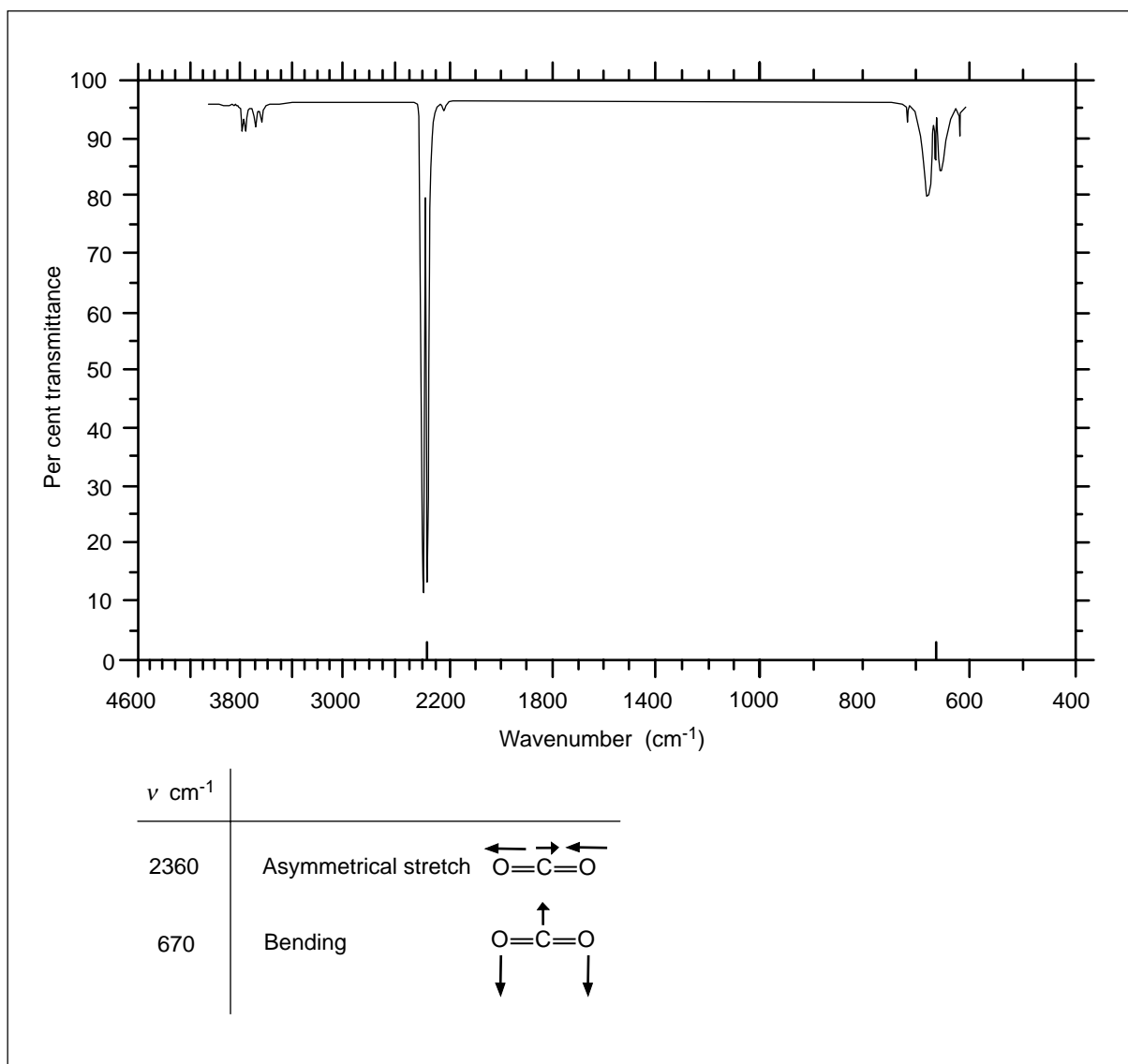**Figure 6**   Infrared spectrum of sulphur dioxide

**Figure 7**   Infrared spectrum of carbon dioxide

Interpretation of spectra

Simple molecules such as carbon dioxide and sulphur dioxide have spectra that are relatively easy to interpret. However, as the complexity of the sample increases it becomes more difficult to assign each absorption to a particular vibrational mode. This is not a great problem because although the exact description of the vibration is difficult, it is possible to assign particular peaks to the vibrations of functional groups. An example of this is the C=O bond stretching in organic molecules, which always occurs in the range 1640–1815 cm^{-1} (Table 2).

The infrared spectrum of propanal illustrates this, because the strong absorption at 1730 cm^{-1} falls into the range expected for an aliphatic aldehyde (1740–1720 cm^{-1}, *Fig. 8*).

Table 2   Characteristic absorptions of carbonyl groups

		Wavenumber (cm^{-1})
RCOCl	acyl chloride	1815–1790
RCOOR'	aliphatic ester	1750–1730
RCHO	aliphatic aldehyde	1740–1720
RCOOH	aliphatic acid	1725–1700
RCOR'	aliphatic ketone	1725–1700
ArCHO	aromatic aldehyde	1715–1695
ArCOR	aromatic ketone	1700–1680
ArCOAr	diaromatic ketone	1670–1650
RCONH$_2$	aliphatic amide	1680–1640
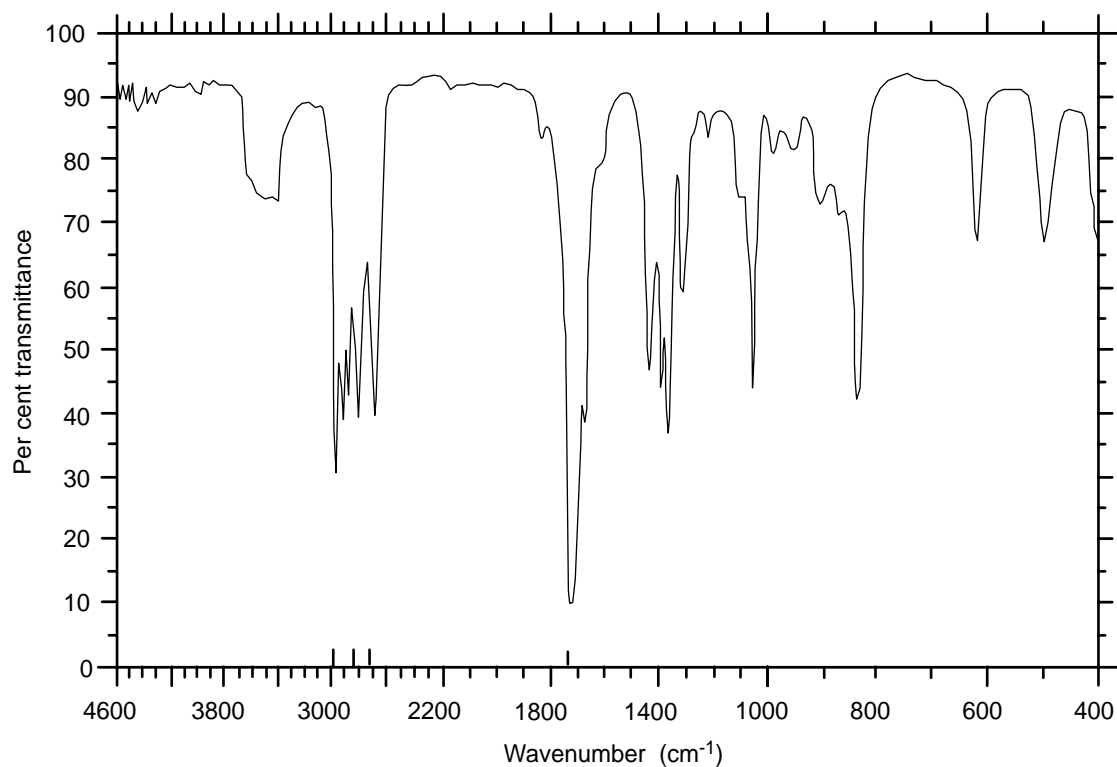
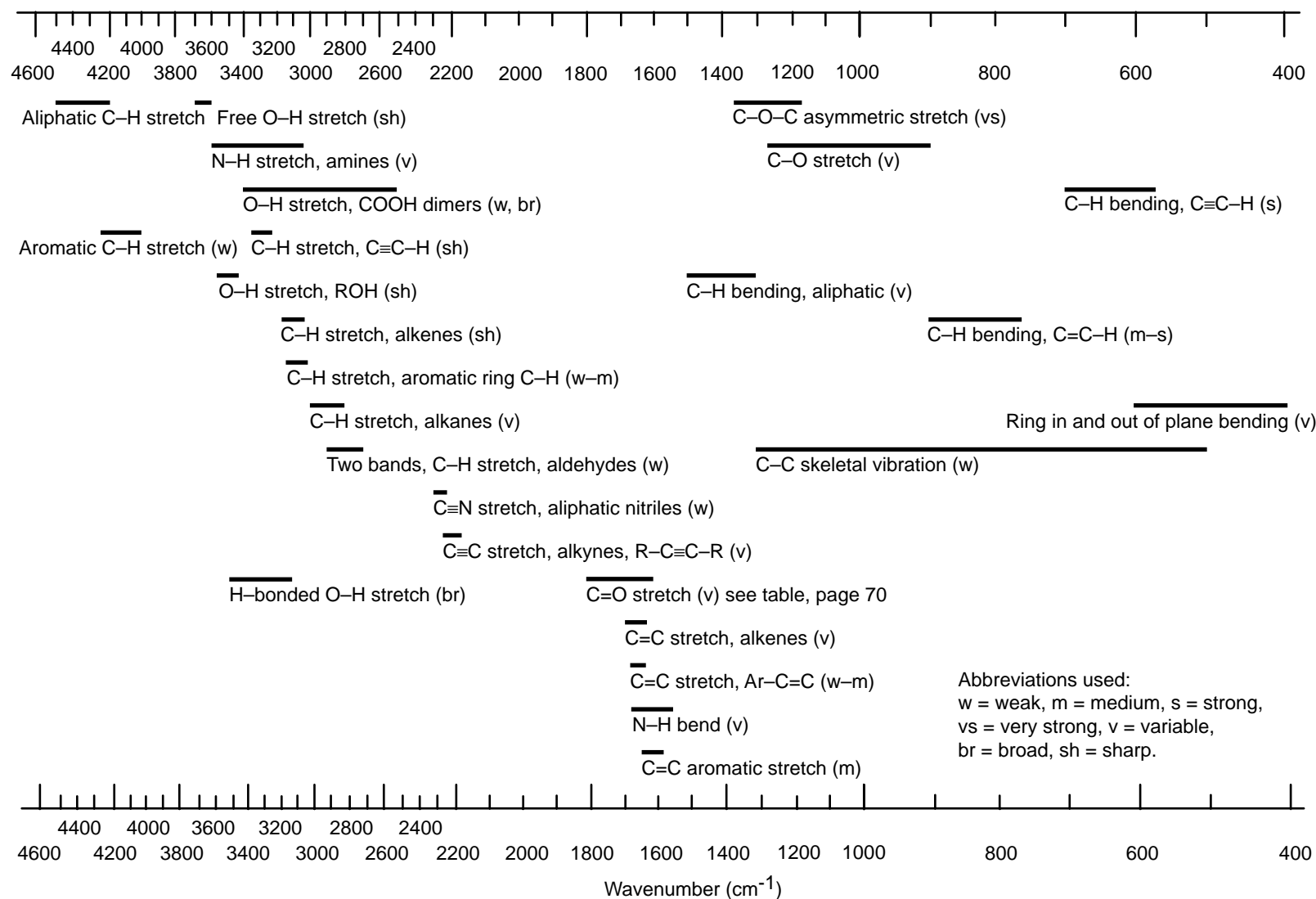| v cm^{-1}	
2980	Aliphatic C–H stretch
2830	C–H stretch of CHO group
2720	
1730	C=O stretch of CHO group

Figure 8   Infrared spectrum of propanal

Because particular types of vibration always occur at a similar frequency it is possible to build up a table of characteristic absorption frequencies. So, when the infrared spectrum of a compound of unknown structure is presented, it is probable that sufficient information can be derived from the spectrum to identify the functional groups present. In most cases more information is normally required to determine the structure.

The fact that functional groups give absorptions at particular frequencies can be used to show the purity of a sample. Contamination owing to solvent residues or by-products will show absorptions not observed in the pure compound. This is used extensively in industry, where it is possible to find that the same compound is marketed by a number of manufacturers but the infrared spectra of the products are slightly different. This happens in the pharmaceutical industry, particularly, where the infrared spectrum of a drug or its formulation is often included in its patent.

It is quite common for correlation tables to include data on the usual intensity and/or band width of absorption peaks as well as their wavenumbers (Table 3).

Table 3   Correlation table for infrared spectroscopy

| | | | | | | | | | | | | | | | | | | | | | | | | |
4400   4000   3600   3200   2800   2400
4600   4200   3800   3400   3000   2600   2200   2000   1800   1600   1400   1200   1000   800   600   400

Aliphatic C–H stretch   Free O–H stretch (sh)

C–O–C asymmetric stretch (vs)

N–H stretch, amines (v)

C–O stretch (v)

O–H stretch, COOH dimers (w, br)

C–H bending, C≡C–H (s)

Aromatic C–H stretch (w)   C–H stretch, C≡C–H (sh)

O–H stretch, ROH (sh)

C–H bending, aliphatic (v)

C–H stretch, alkenes (sh)

C–H bending, C=C–H (m–s)

C–H stretch, aromatic ring C–H (w–m)

C–H stretch, alkanes (v)

Ring in and out of plane bending (v)

Two bands, C–H stretch, aldehydes (w)

C–C skeletal vibration (w)

C≡N stretch, aliphatic nitriles (w)

C≡C stretch, alkynes, R–C≡C–R (v)

H–bonded O–H stretch (br)

C=O stretch (v) see table, page 70

C=C stretch, alkenes (v)

C=C stretch, Ar–C=C (w–m)

Abbreviations used:
w = weak, m = medium, s = strong,
vs = very strong, v = variable,
br = broad, sh = sharp.

N–H bend (v)

C=C aromatic stretch (m)

| | | | | | | | | | | | | | | | | | | | | | | | | |
4400   4000   3600   3200   2800   2400
4600   4200   3800   3400   3000   2600   2200   2000   1800   1600   1400   1200   1000   800   600   400

Wavenumber (cm^{-1})

The infrared spectrum can conveniently be split into four regions for interpretation:

4000–2500 cm^{-1}: absorption of single bonds to hydrogen – *eg* C–H, O–H, N–H

2500–2000 cm^{-1}: absorption of triple bonds – *eg* C≡C and C≡N

2000–1500 cm^{-1}: absorption of double bonds – *eg* C=C, C=O

1500–400 cm^{-1}:   absorption owing to other bond deformations – *eg* rotating, scissoring and some bending.

There are some exceptions – *eg* N–H bending is observed at 1550-1620 cm^{-1}.

4000–2500 cm $^{-1}$

The high frequency is explained by the low mass of the hydrogen atom. The spectrum is altered if ^{2}H is present – *ie* the C–H stretch of CHCl$_3$ is at a higher frequency than that of CDCl$_3$ (*Figs 9* and *10*).

v cm^{-1}	
3020	C–H stretch
1530	C–Cl stretch overtone
1220	C–H bend
765	C–Cl stretch
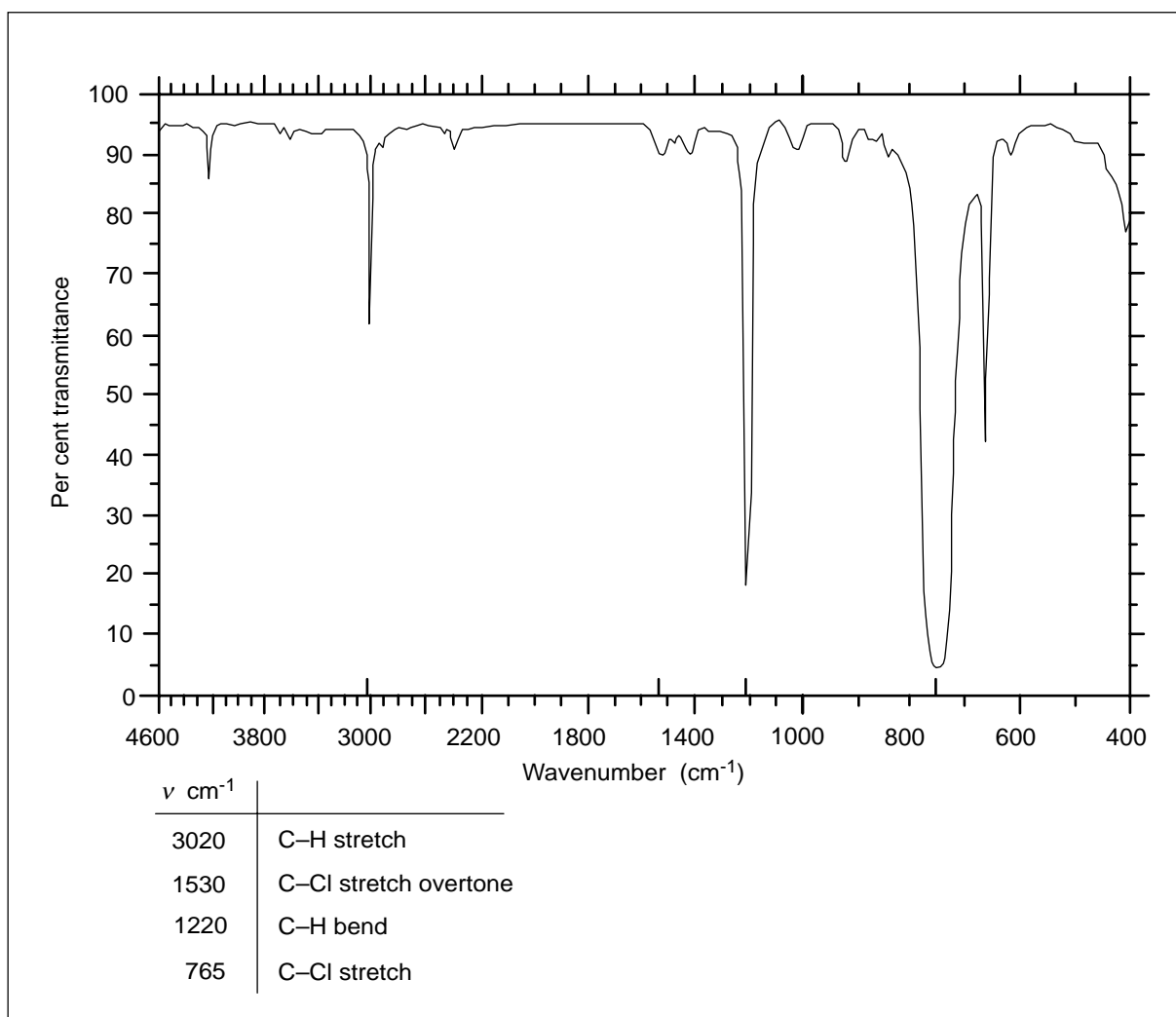
Figure 9   Infrared spectrum of CHCl$_3$

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ν cm^{-1}	
2260	C–D stretch
1480	C–Cl stretch overtone
915	C–D bend
740	C–Cl stretch
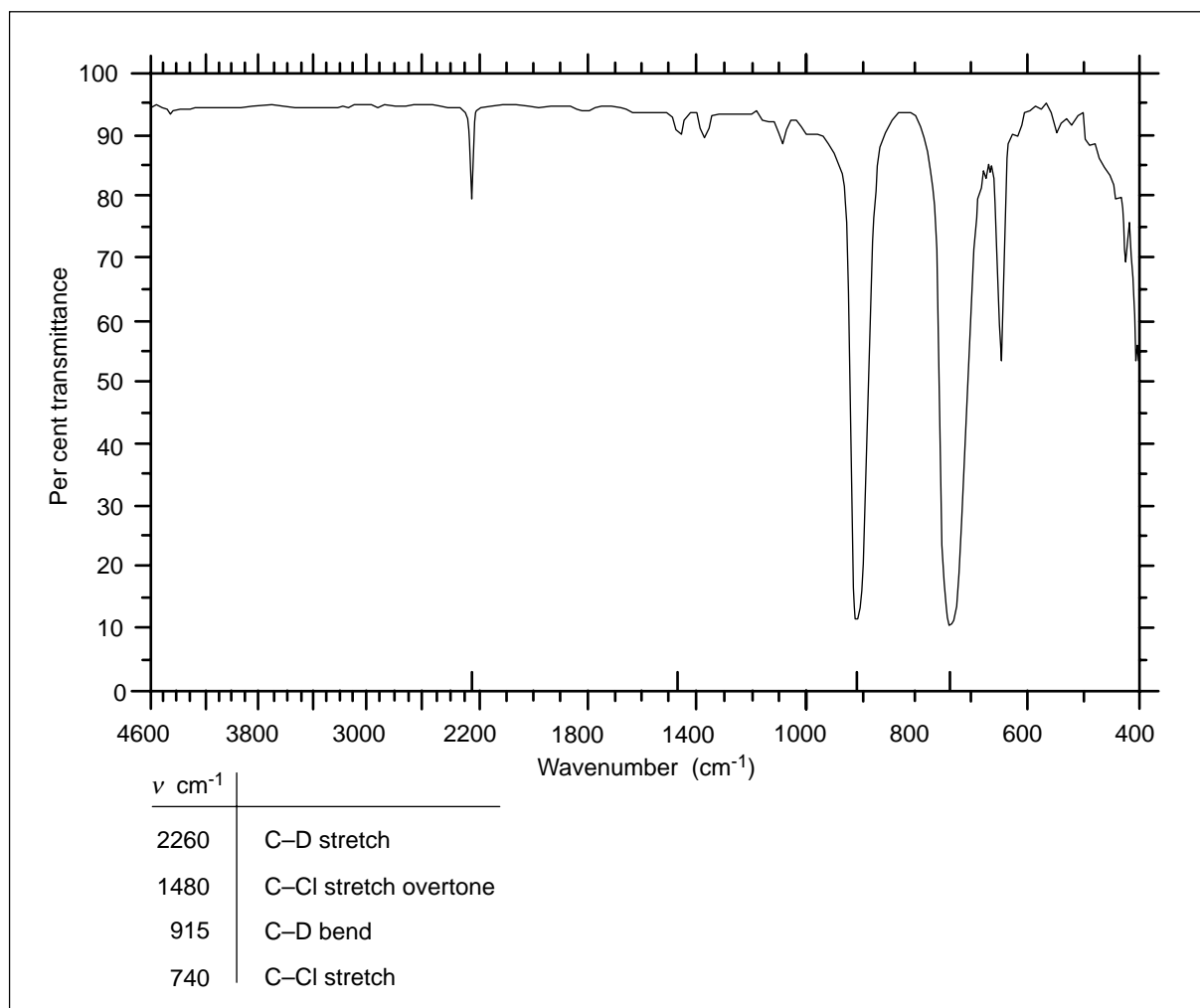
Figure 10   Infrared spectrum of CDCl$_3$

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2500–2000 cm^{-1}

Relatively high frequencies are required to provide the high energies necessary to make the strong triple bonds vibrate – *eg* $CH_3CH_2C{\equiv}N$ (*Fig. 11*).
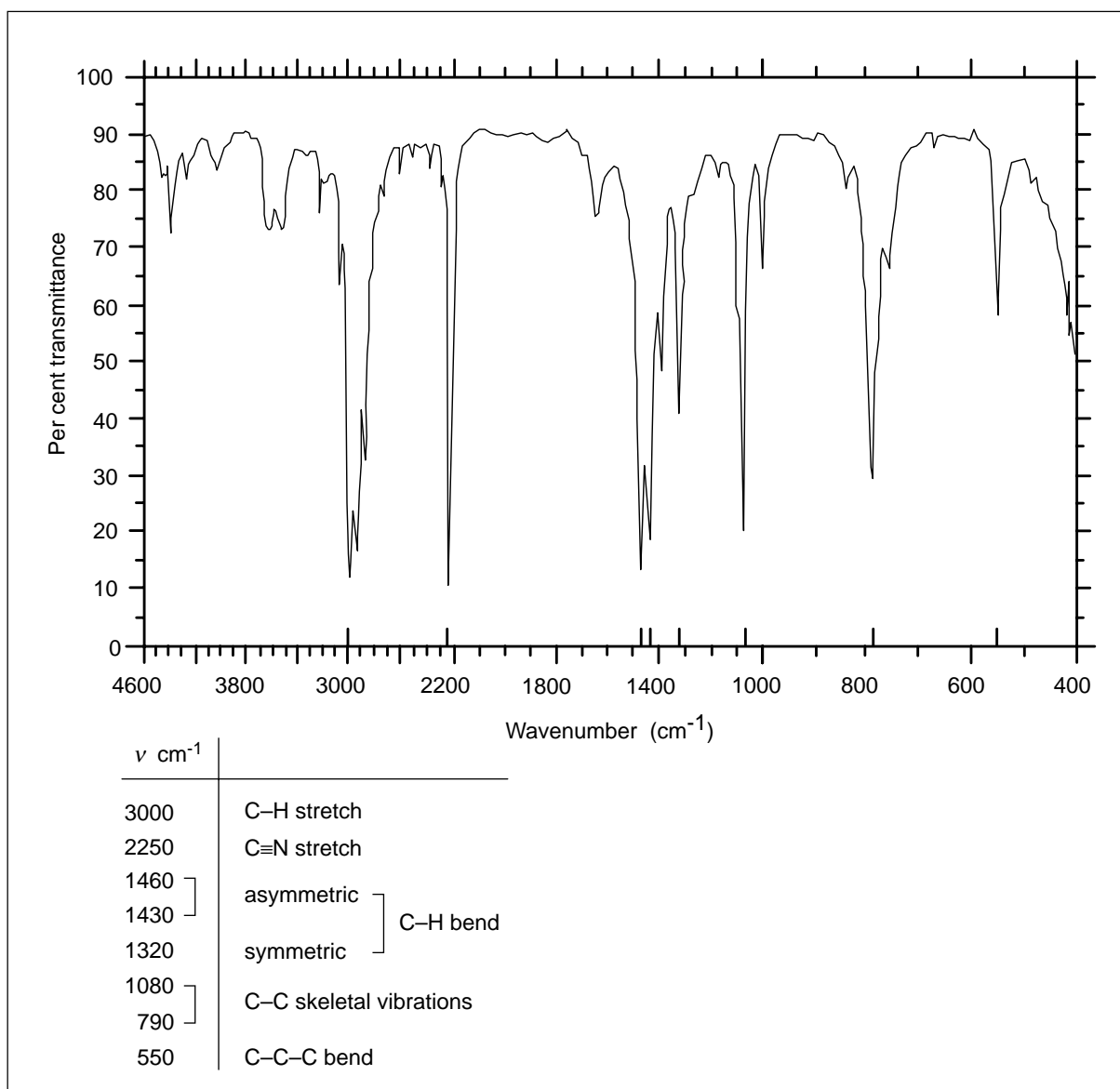
ν cm^{-1}	
3000	C–H stretch
2250	C≡N stretch
1460	asymmetric ⎫
1430	⎭ ⎫ C–H bend
1320	symmetric ⎭
1080	C–C skeletal vibrations ⎫
790	⎭
550	C–C–C bend

Figure 11   Infrared spectrum of propanonitrile, $CH_3CH_2C{\equiv}N$

2000–1500 cm⁻¹

Double bonds generally absorb in this region – *eg* C=O in propanal (*Fig. 8*). *Figure 12* shows the spectrum of hex-1-ene, with a sharp absorption peak due to the C=C stretch at 1640 cm⁻¹. Other groups absorbing here include C=N and C=O.

v cm⁻¹	
3080	C–H stretch of C=C–H
2970	C–H stretch
1640	C=C stretch
1460 ⎤	
990	C–C skeletal vibrations
910 ⎦	
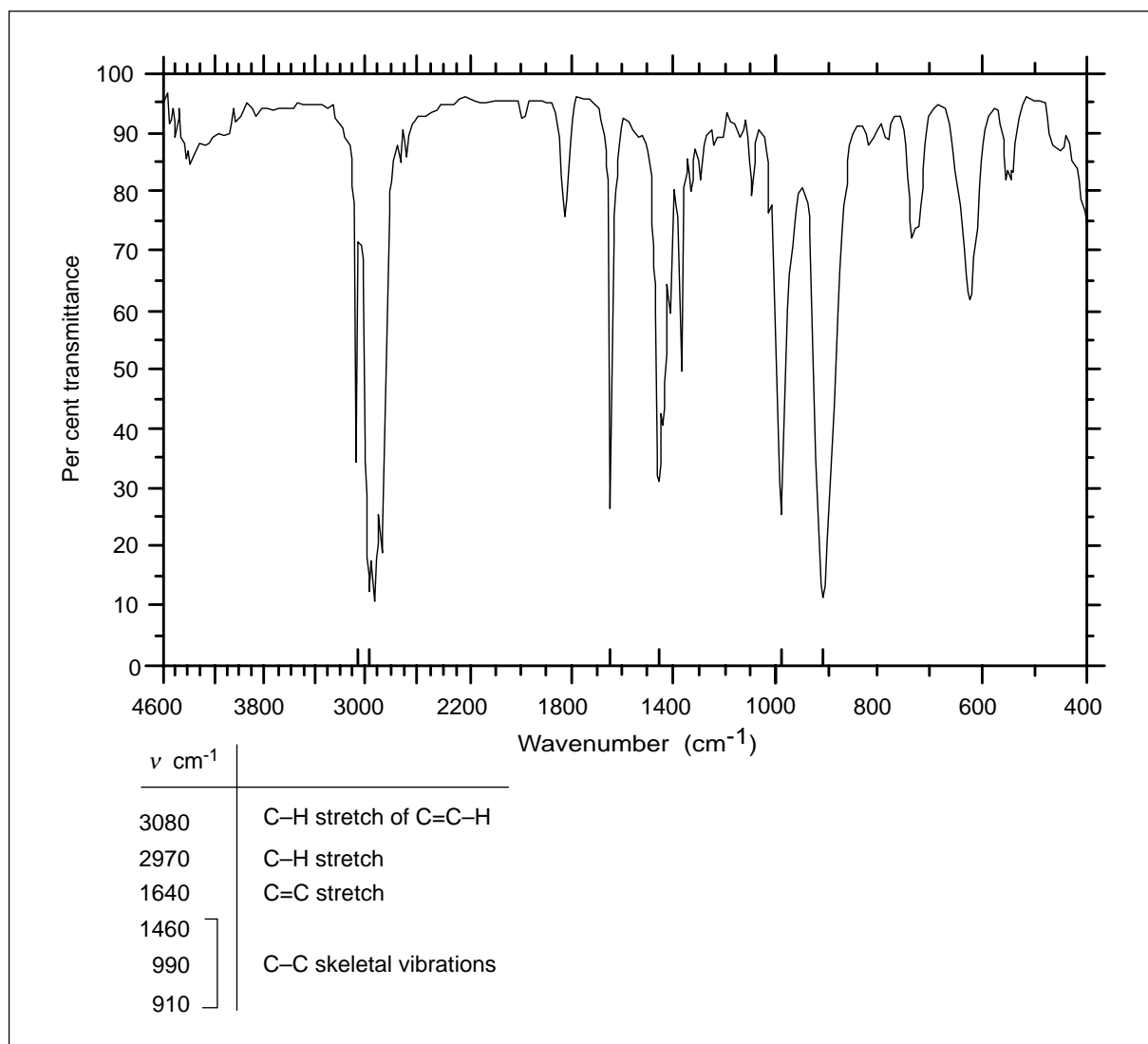
Figure 12   Infrared spectrum of hex-1-ene

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1500-400 cm⁻¹

Absorption owing to deformations such as rotating, scissoring and some bending depend on the combination of bonds in the molecule. This part of the spectrum is unique to each compound and is often called the 'fingerprint' region. It is rarely used for identifying particular functional groups, but some generalisations can be made – *eg* C–O absorbs at 1300–1020 cm⁻¹ (although absorption here is not exclusive to C–O). However, the fingerprint region can help identify particular molecules because no other compound will have the same pattern of absorptions. Many research organisations have reference databases of stored spectra, including the fingerprint region.

Figure 13 shows the infrared spectrum of phenol, which has extensive absorption in the fingerprint region. The other significant absorption at 3600 cm⁻¹ is due to the O–H vibration.

ν cm⁻¹	
3380	O–H stretch
3050	Aromatic C–H stretch
1500	C–C skeletal vibrations
1220	C–O stretch
1160	O–H bend
770	O–H in-plane bend
690	H-bonded O–H out-of-plane bending
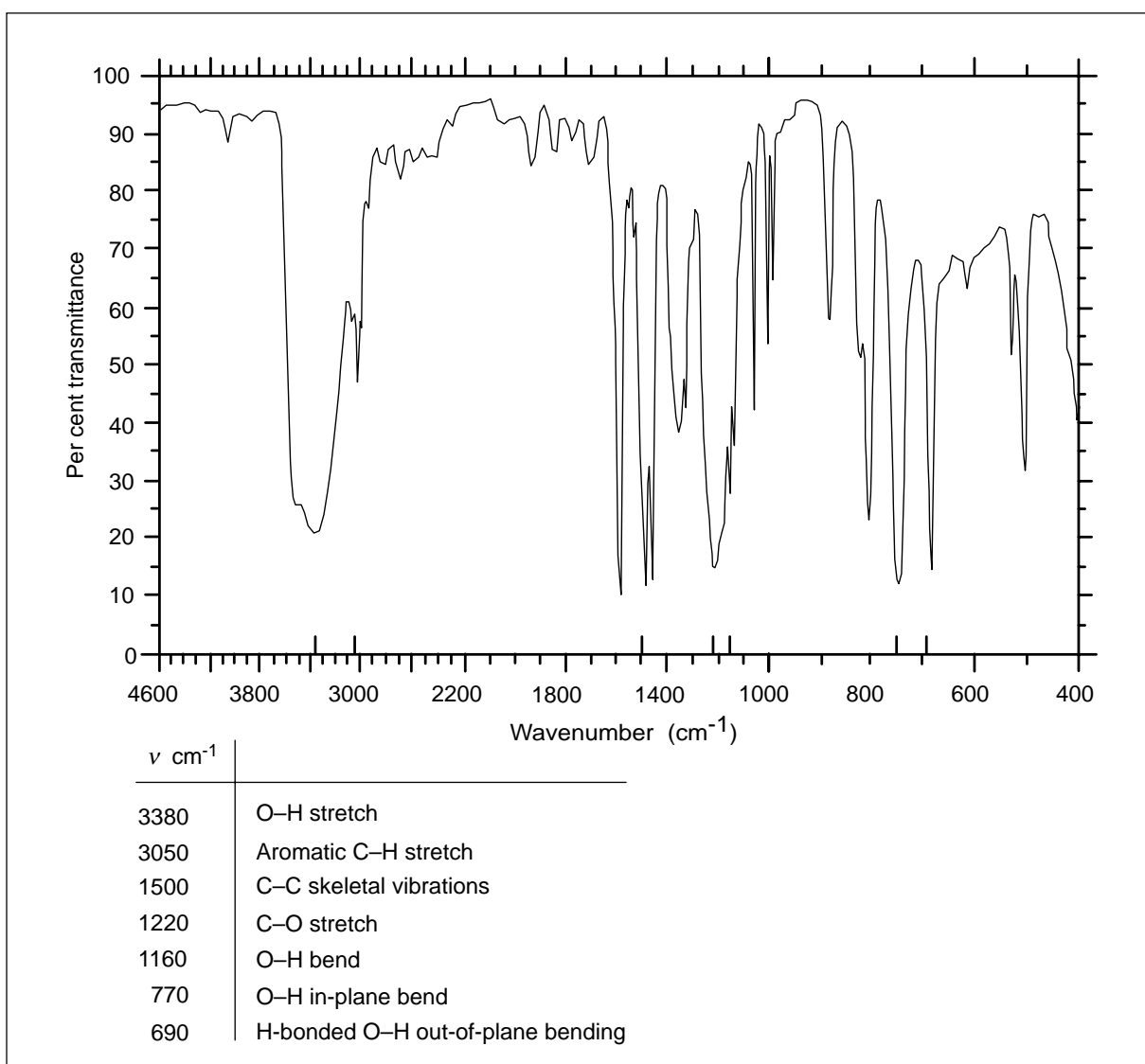
Figure 13   Infrared spectrum of phenol

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Hydrogen bonding

The absorption of the O–H group in alcohols and carboxylic acids does not usually appear as a sharp peak. Instead a broad band is observed because the vibrational mode is complicated by hydrogen bonding. Precisely how broad the band is depends on the degree of hydrogen bonding, and the frequency of an alcoholic O–H stretch depends on whether the alcohol is primary, secondary or tertiary. *Figures 14* and *15* show the spectra of methanol and methanoic acid.

ν cm^{-1}	
3330	O–H stretch
2940	C–H stretch
2820	
1450	O–H bend
1030	C–O stretch
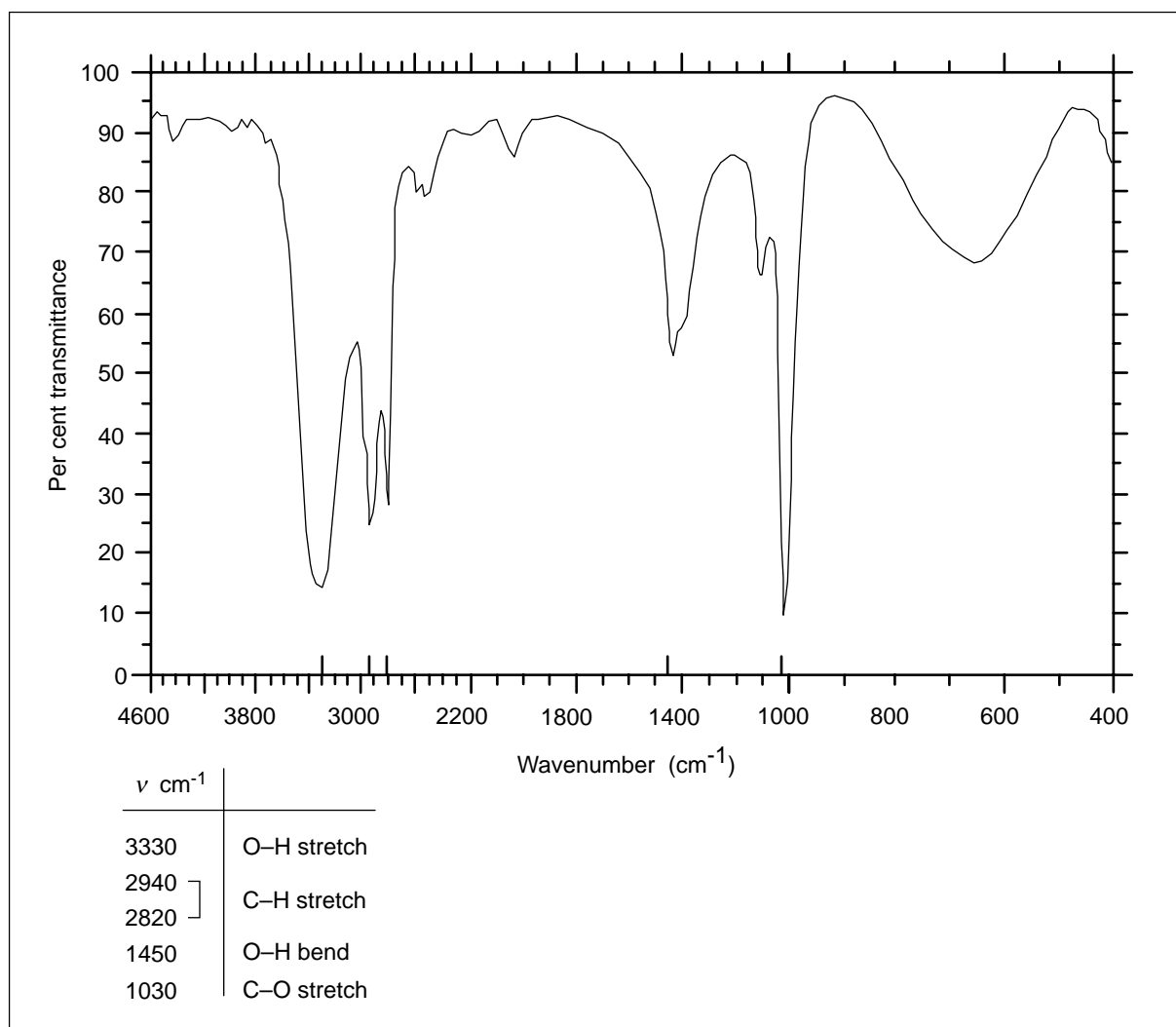
Figure 14 Infrared spectrum of methanol
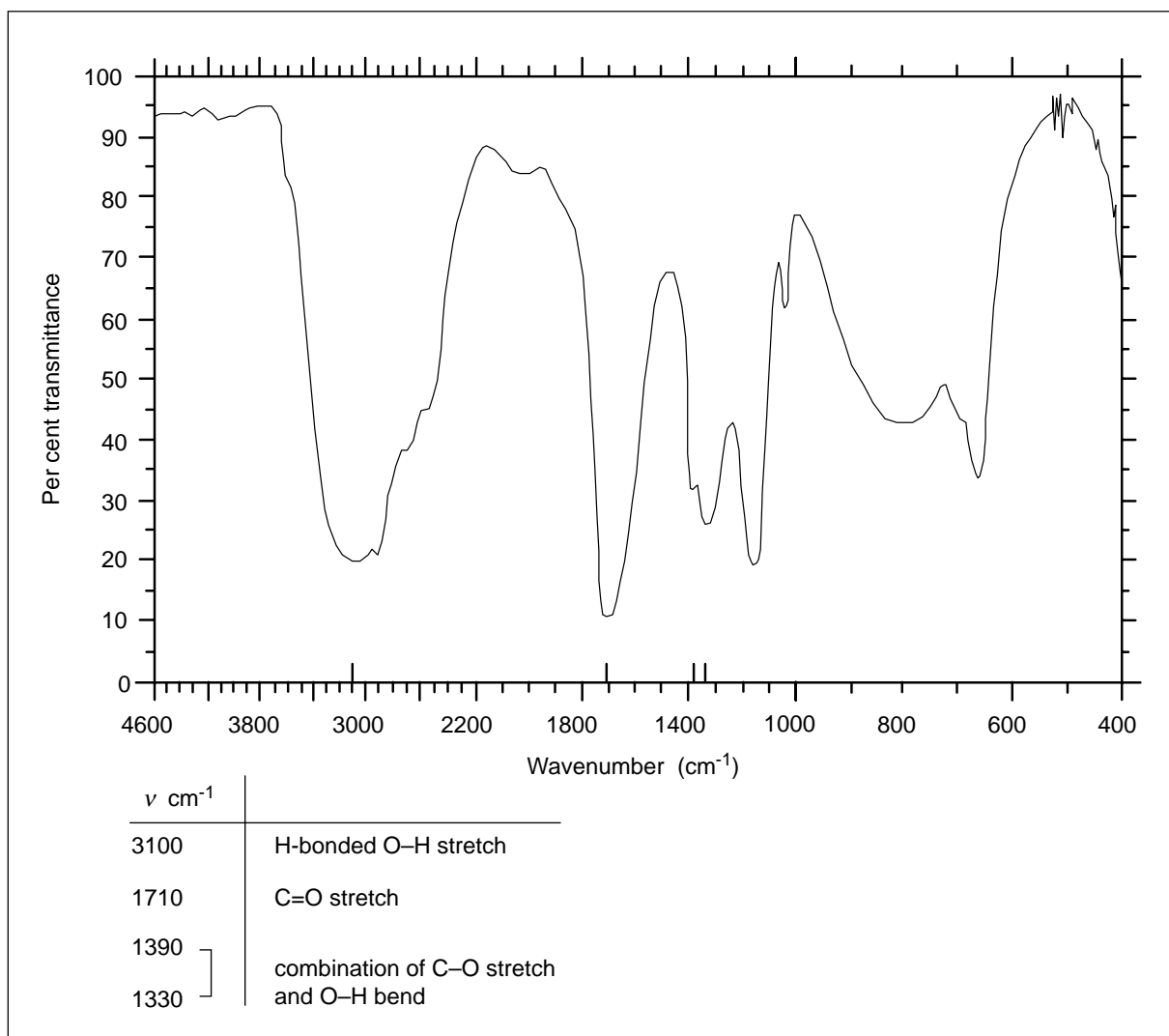
Figure 15   Infrared spectrum of methanoic acid

Differentiating between intermolecular and intramolecular bonding requires a series of spectra at different dilutions. An absorption band that diminishes as the solution becomes more dilute comes from intermolecular hydrogen bonding (between molecules) – whereas intramolecular bonding shows a much smaller effect.

Applications of infrared absorption

Advances in instrumentation and accessories available now make it possible to obtain spectra of materials previously thought too difficult. In many cases the sample size or concentration was too small, but this problem has been overcome by the construction of specialist cells. These have reflecting surfaces on their insides so that the path length through a liquid, for example, is increased (*Fig. 16*). An increased path length increases absorption according to Beer's Law (page 95).
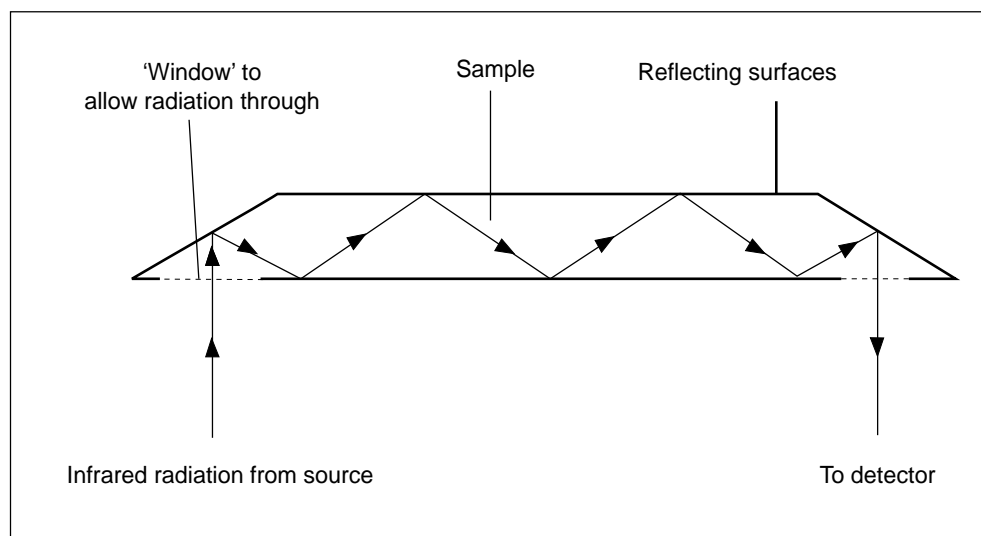
Figure 16   Schematic diagram of a reflectance cell

The infrared spectra of proteins were once rather difficult to observe because of the absorptions due to the solvents used (*ie* water, D_2O and methanol – all of which absorb infrared radiation). By using a reflectance cell and a computer it is now possible to record the spectra of proteins in solution and the pure solvent digitally, and by subtracting one from the other the spectrum of the protein can be obtained.

The secondary structure of proteins changes with pH, solvent, temperature, and exposure to lipids, and it is possible to use the vibrational frequencies of the protein backbone to determine the proportions of α-helix, β-pleated sheet and disordered protein in a sample. Significant regions of the spectrum in this respect are 1670–1620 cm^{-1} and 1305–1200 cm^{-1}.

The trend away from saturated fats in foods has meant that it is now necessary to measure the degree of unsaturation in oils and fats. Oils such as peanut oil can be placed in a reflectance cell to record their spectra and by measuring the areas under the peaks corresponding to unsaturated and saturated environments (*eg* at 3009 cm^{-1} and 2854 cm^{-1} respectively) it is possible to calculate the ratio of unsaturated:saturated bonds.

Microbiological systems can also be identified by using infrared spectroscopy because research has shown that bacteria can be categorised by their unique spectra. The spectra appear as broad complex contours rather than sharply defined peaks, and contain information on the total composition of the bacteria including RNA (ribonucleic acid) and DNA (deoxyribonucleic acid). Studies have extended to the successful identification of viruses, fungi, yeasts and amoebae, by using colonies of fewer than 10^4 cells which measure less than 4×10^{-5} m across.

In the past, some compounds have not yielded useful spectra because of their absorption characteristics – *eg* the spectra of black rubbers, which absorb radiation of all frequencies, have now been recorded. They can be ground to a powder in liquid nitrogen before being made into a potassium bromide pellet. Alternatively, thermogravimetric analysis and FTIR can be combined so that the sample is heated under controlled conditions to provide data on weight loss, and the species lost during heating are analysed by passing them through a cell in an infrared spectrometer. Spectra are collected continuously and are stored on a computer. If the spectra generated suggest that a number of compounds are produced at the same time it is possible to separate them by passing the mixture down a heated gas chromatography column (see Chapter 5 for details of gas chromatography).

The most spectacular combination of techniques is probably the linking of an optical microscope to an FTIR spectrometer. By using this system it is possible to study an object visually on a microscopic scale, and then obtain its infrared spectrum. To cut out stray radiation and to eliminate the risk of recording the spectrum of the background, different sized apertures are used to eliminate the unwanted regions of the visual image. Because some substances reflect radiation from their surfaces it is also possible to obtain two types of infrared spectrum through the microscope:

1 transmissive spectra in which the radiation passing through the sample is measured; and

2 reflective spectra whereby the radiation reflected back towards the radiation source is measured.

Sample sizes down to 2×10^{-5} m can be used, although many scans are necessary and the individual scans have to be added together to obtain the final spectrum.
Examples of other applications of infrared spectroscopy include:

1 the study of particles blocking air filters – the information obtained can be used to discover plant operation difficulties;

2 the study of how fats crystallise in margarines and low fat spreads – this is important because the physical properties of these foodstuffs depend on the crystal structures within them;

3 the categorising or identification of fibres and paint chips in forensic analysis; and

4 the screening of illicit substances – many illicit drugs are diluted or 'cut' by addition of other powdered materials and individual crystals can be identified from their spectra. Many of the powders added to dilute the pure drugs contain carbohydrates.

Drink-driving

A more familiar application (to some!) of infrared absorption is in the analysis of breath samples given by drivers who have been drinking.

Once alcohol has been consumed it is absorbed by the blood through the walls of the stomach and is transported to the liver, where it is removed at a slow rate – approximately one unit per hour. (One unit is the amount of alcohol contained in a glass of sherry, port or wine, a single measure of a spirit, or half a pint of beer.) The consumption rate is usually far greater than this, and the alcohol that cannot be removed by the liver passes through to the heart. From there it is pumped via the blood to the lungs where it is oxygenated prior to being distributed around the rest of the body.

It is while the blood is passing through the lungs that some alcohol is transferred to the breath (*Fig. 17*).
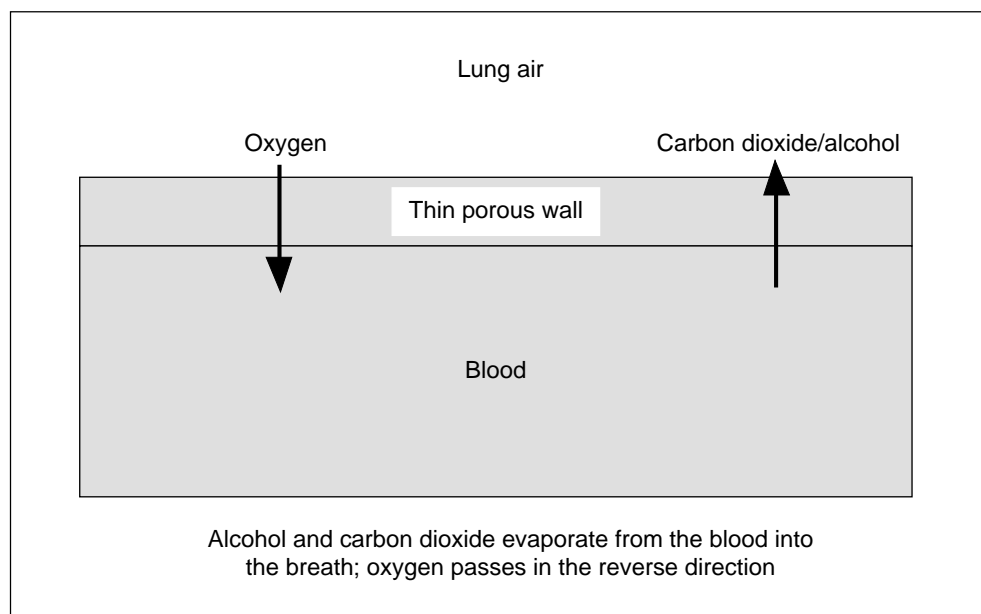
Lung air

Oxygen   Carbon dioxide/alcohol

Thin porous wall

Blood

Alcohol and carbon dioxide evaporate from the blood into
the breath; oxygen passes in the reverse direction

Figure 17   Transfer of alcohol from the blood to the breath

A static equilibrium cannot be established between the blood and breath concentrations of alcohol because the body is not a closed system. However, the relationship between the two concentrations at a given time has been determined and the 'blood/breath ratio' is accepted to be 2300:1 (therefore breath alcohol concentrations in µg per 100 cm^3 can be converted to blood alcohol concentrations in mg per 100 cm^3 by multiplying by 2.3). A small variation does exist from person to person.

Because the concentration of alcohol on the breath is proportional to the concentration in the blood the analysis of exhaled air has become an accepted means of determining whether a person is driving illegally (this is not always the same thing as being fit to drive). The current upper limit to remain within the law (1992) is 35 µg of alcohol per 100 cm^3 of breath, or 80 mg of alcohol per 100 cm^3 of blood.

Although the legal limit is 35 µg per 100 cm^3, the national policy is that prosecution does not follow unless a breath alcohol concentration is at least 40 µg of alcohol per 100 cm^3 of breath. This allows for some variation in the ratio of blood to breath alcohol (the instruments are recalibrated regularly so no compensation need be made for any inaccurate machines). Between 40 and 50 µg of alcohol per 100 cm^3 of breath means that the 'client' is given the option of having a blood or urine test, in which case the sample taken is divided into two. The police have one portion analysed, and the 'client' has the option of having an independent analysis of the other one. If a blood sample, for example, is taken then the figure used to decide whether to take a case to court is the blood alcohol concentration. If the figure is above 50 µg alcohol per 100 cm^3 of breath the 'client' is not given the option of a blood or urine test because the breath alcohol concentration is itself sufficient to convict a driver, and will not disguise a blood alcohol concentration within the legal limit.

Roadside and personal breath test instruments usually contain fuel cells. Typically these consist of a thin permeable film of sintered glass, a ceramic or a polymer, impregnated with a liquid or gel of sodium hydroxide and/or phosphoric acid. The

membrane is coated on both sides with a precious metal such as platinum or silver and the metal on one side of the film catalyses the oxidation of the alcohol vapour on the breath of the operator, while the oxygen on the other side of the membrane is reduced. An electromotive force (EMF) is generated, and is converted to a signal which indicates how close the operator is to the legal limit. In the UK these instruments are not used to provide evidence as they are less automated and do not provide a printout.

If a roadside breath test suggests that a driver has too high an alcohol level on their breath, they are taken to a police station where two further breath samples are analysed. (The sample with the lower concentration is used in evidence, the higher reading being disregarded.) British police forces currently use two models, one manufactured by Lion Laboratories and the other by Camic. Both work on the basis of the absorption of infrared radiation by alcohol vapour. (The following description relates to the Lion instrument, the Intoximeter 3000.)

The infrared spectrum of ethanol (*Fig. 18*) shows that the major absorptions are found at 3340 and 2950 cm^{-1}. These correspond to the O–H and C–H vibrations. Alcohol concentrations cannot be determined from the O–H vibration because of the water vapour present in both the atmosphere and the 'client's' breath, therefore the C–H vibration is used.

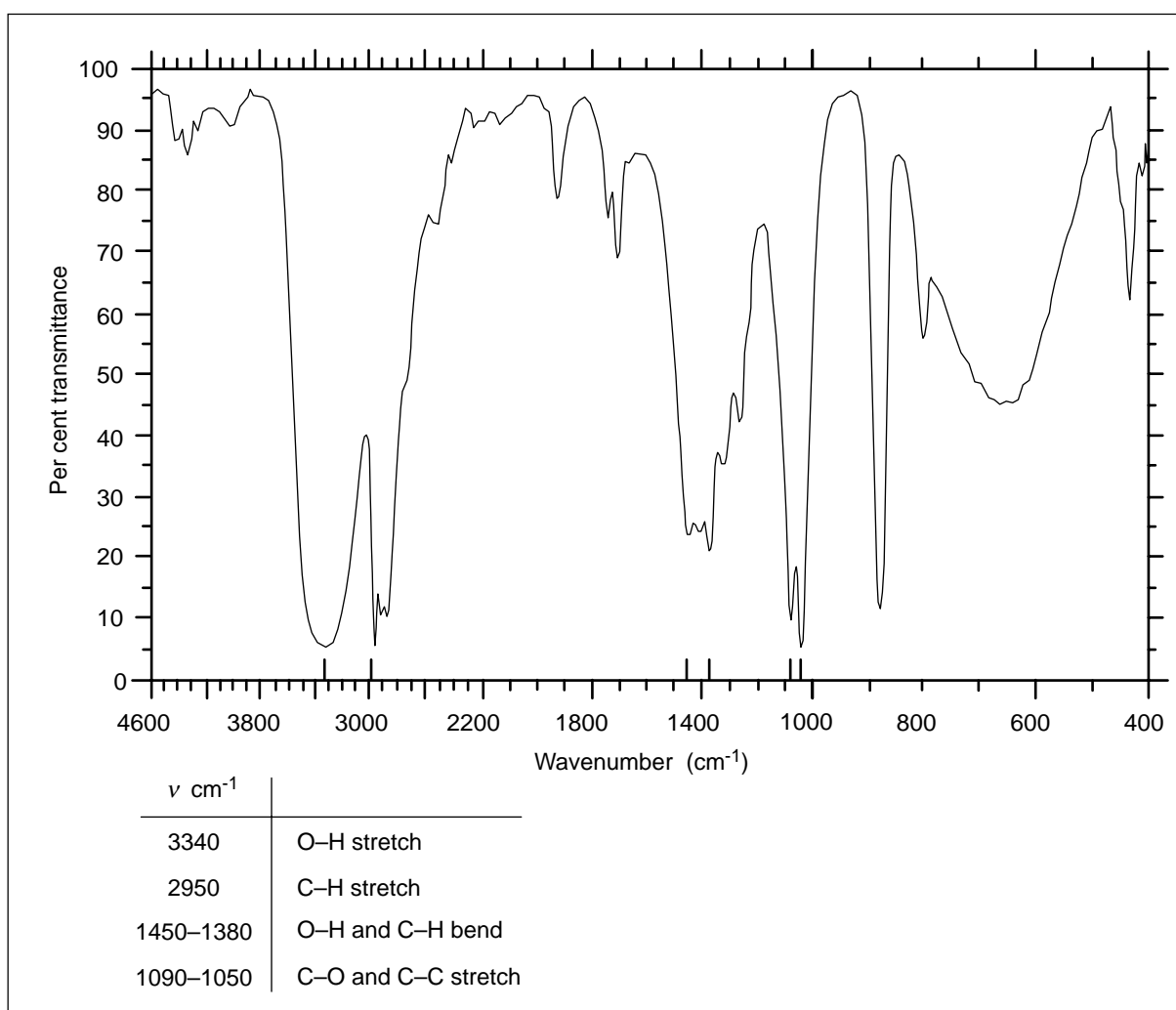| ν cm^{-1}	
3340	O–H stretch
2950	C–H stretch
1450–1380	O–H and C–H bend
1090–1050	C–O and C–C stretch

Figure 18   Infrared absorption spectrum of ethanol

The Intoximeter 3000 uses a nichrome filament operating at 800 °C as its radiation source, and the beam is split by a rotating chopper so that it passes alternately through the sample chamber and an identical reference chamber (*Fig. 19*). The chamber is 280 mm long and has a volume of 70 cm^3, rather larger than the cells used in routine infrared analysis. So that the alcohol does not condense, the chamber is thermostatically heated to 45 °C. The radiation passes through a filter mounted on the solid state photoconducting detector so that only the absorbance at 2950 cm^{-1} is measured. This eliminates interference from other materials on the breath that do not absorb at this frequency.
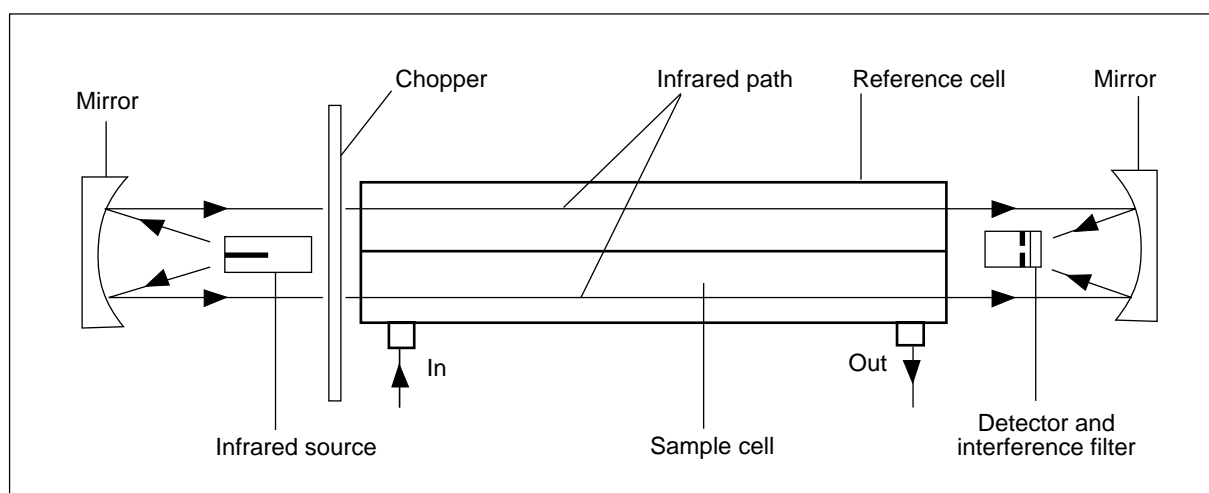
Figure 19   Components of the infrared analyser unit of the Lion Intoximeter 3000

Absorption follows the Beer–Lambert law, and the non-linearity of absorption at higher concentrations is compensated for by suitable software. The instrument is calibrated against a standard, and the absorption is converted to a measure of breath alcohol concentration. This is the figure that is finally given by the machine.

Some other substances also absorb at 2950 cm^{-1}. Of butane, 1,1,1-trichloroethane, and methylbenzene used in solvent abuse only butane registers on the machine. Trials have shown that any signal from butane disappears within the 20 minute period that must elapse between a drink being taken and the test being carried out.

More significantly, propanone absorbs at 2950 cm^{-1} and is found on the breath of some individuals (those with high protein intakes or who are diabetics). A second semiconducting detector is therefore built into the intoximeter that is more sensitive to propanone than to ethanol, while the infrared detector is more sensitive to the alcohol. When the instrument is calibrated the ratio of sensitivity of the two sensors to the two substances is measured and is stored in the computer memory. As a result, if propanone is present on the client's breath the semiconducting sensor will give a higher signal than if ethanol alone is present. The change in ratio of the two signals is then reduced, eliminating the contribution to the infrared absorption by the propanone.

Recent developments

A new technique based on infrared spectroscopy called photoacoustic spectroscopy has been developed over the past decade. In this technique infrared radiation passes through the window of a detector cell and strikes the solid sample. The absorption of the radiation results in sample heating and thermal waves are produced in the sample. These waves are transmitted as pressure waves to the gas around the sample.

In the gas they are acoustic waves with the same frequency as the infrared radiation absorbed, and are detected by a microphone in the cell. The detector cell has a sealed window to allow the infrared radiation through, but not any sounds or vibrations that the microphone might detect.

The waves are generated from within the sample so this method allows investigation of samples at different depths under the surface, depending on the conditions. The technique appears to show most potential in studies of polymers and surface coating properties.

Exercises

It is rare for a structure to be determined on the basis of an infrared spectrum alone. It is more common to use the technique to confirm the presence of functional groups or to support the structures suggested by other techniques. With sufficient other information it is possible to derive a lot of information about the structure or isomer of a compound from its infrared spectrum. Alternatively, the fingerprint region can be used to confirm the presence or otherwise of a compound in a sample.

Exercise 1

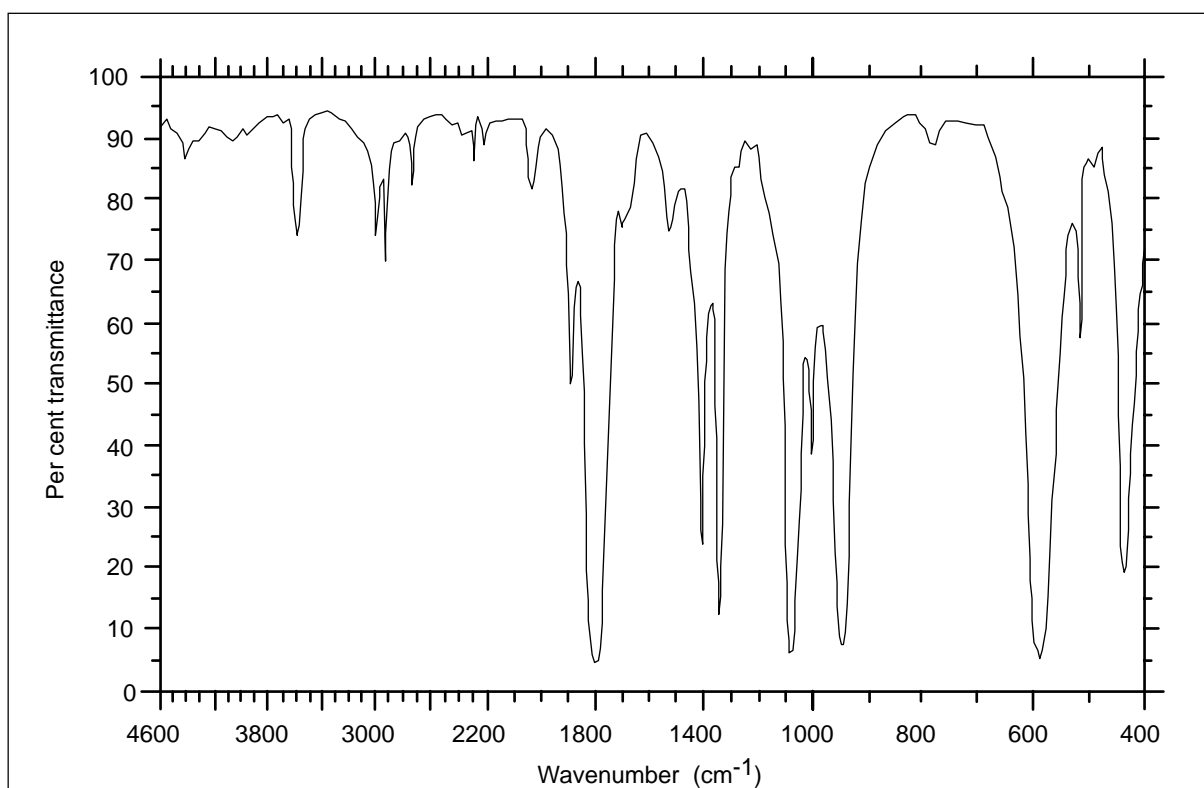The sample appears as a colourless mobile liquid of relative mass 78.5.

Figure 20

The strong absorption at 1790 cm^{-1} suggests an acid chloride, and the non-integral relative mass suggests that chlorine is present. Subtracting the mass of the COCl group leaves 15 mass units, which corresponds to a methyl group. Therefore the substance is ethanoyl chloride, CH_3COCl.

Exercise 2

A solid sample has a composition C 68.9 per cent, H 4.9 per cent, O 26.2 per cent by mass, and a relative mass of 122. From this information and the spectrum alone, it is possible to determine the structure.
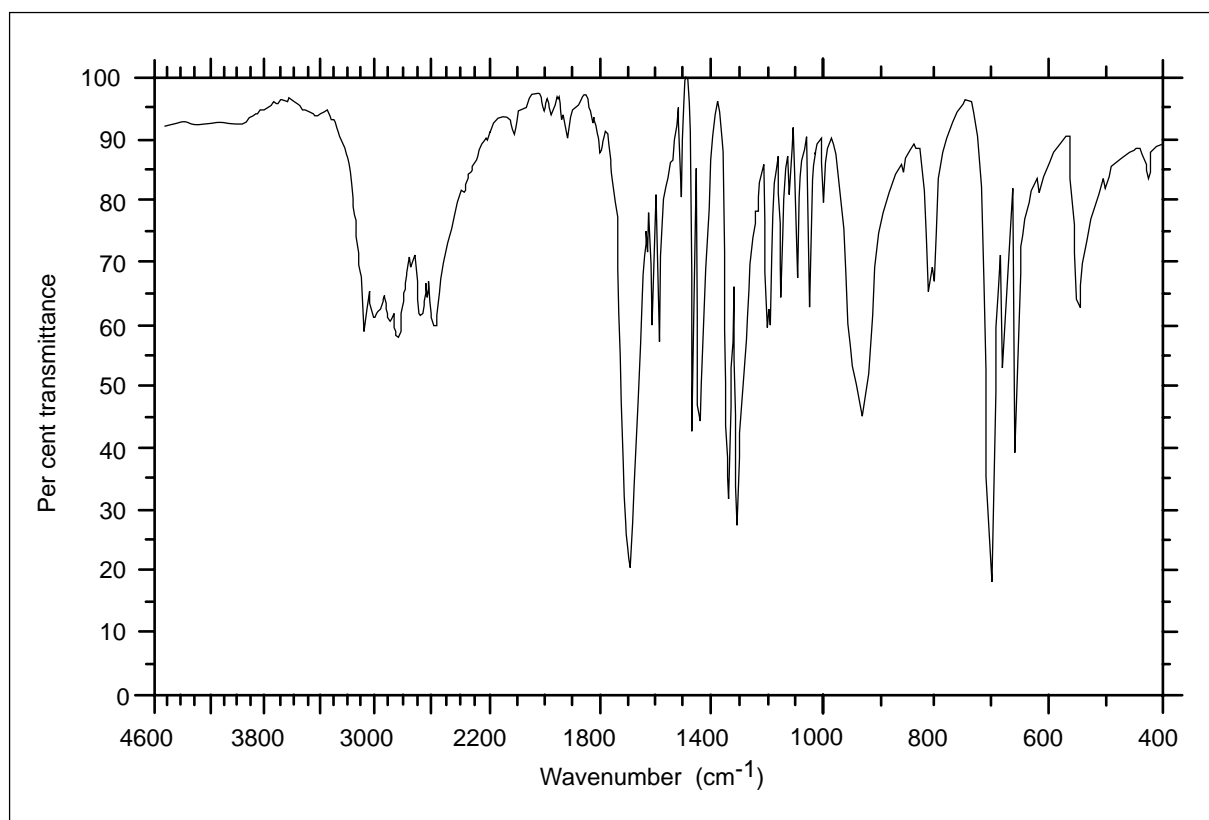

Figure 21

The percentage composition data gives the empirical formula $C_7H_6O_2$. This has relative mass 122. From the infrared spectrum, the strong absorption at 1680 cm^{-1} suggests a carbonyl group, and the peak at 2930 cm^{-1} is consistent with a carboxylic O–H stretch. The sharp peak at 1480 cm^{-1} indicates the C–C stretch of an aromatic ring. This should be accompanied by a sharp spectral line at 2950-3050 cm^{-1} as the aromatic ring hydrogen atoms vibrate. This is observed at the side of the carboxylic O–H absorption peak. The structure is effectively solved now, because an aromatic ring bonded to a carboxylic acid group gives a relative mass of 77+45=122. Thus we can conclude that the sample is benzoic acid, C_6H_5COOH.

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Exercise 3

The spectra below are known to be of ethanoic acid and ethanoic anhydride.
Determine which is which and explain the difference between the spectra.
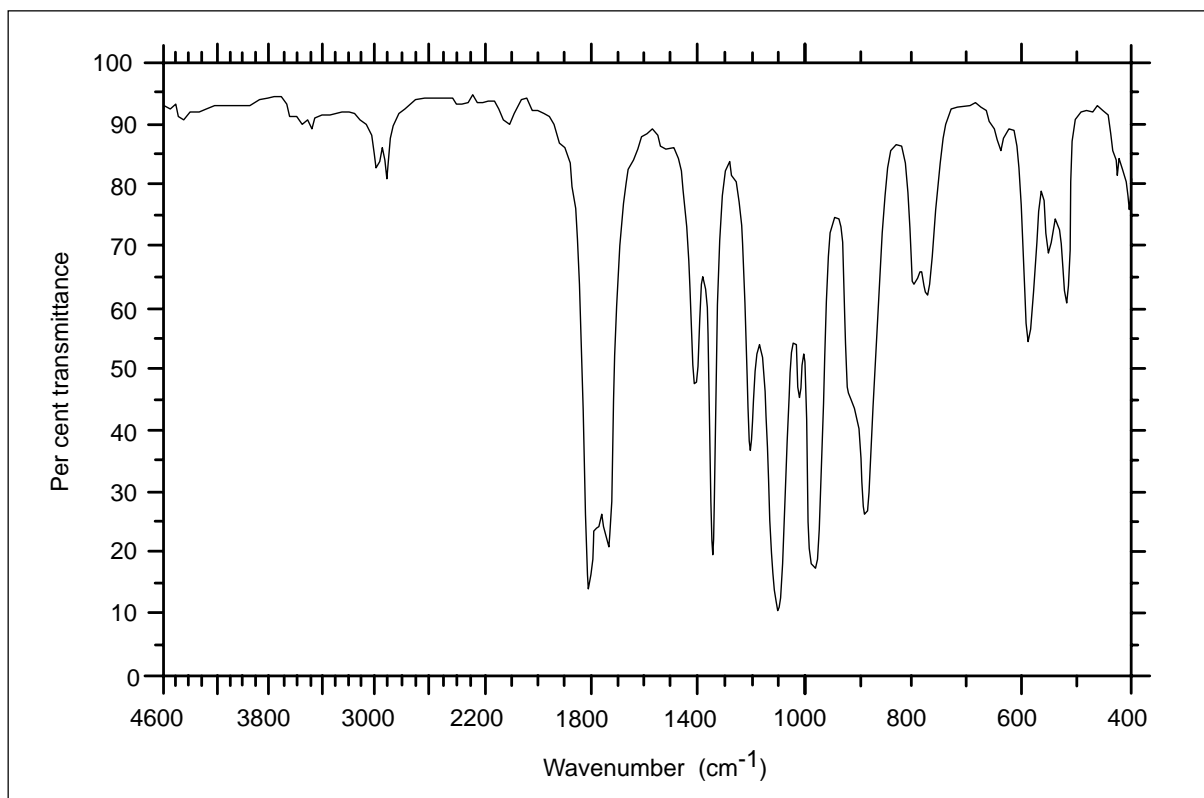

Figure 22

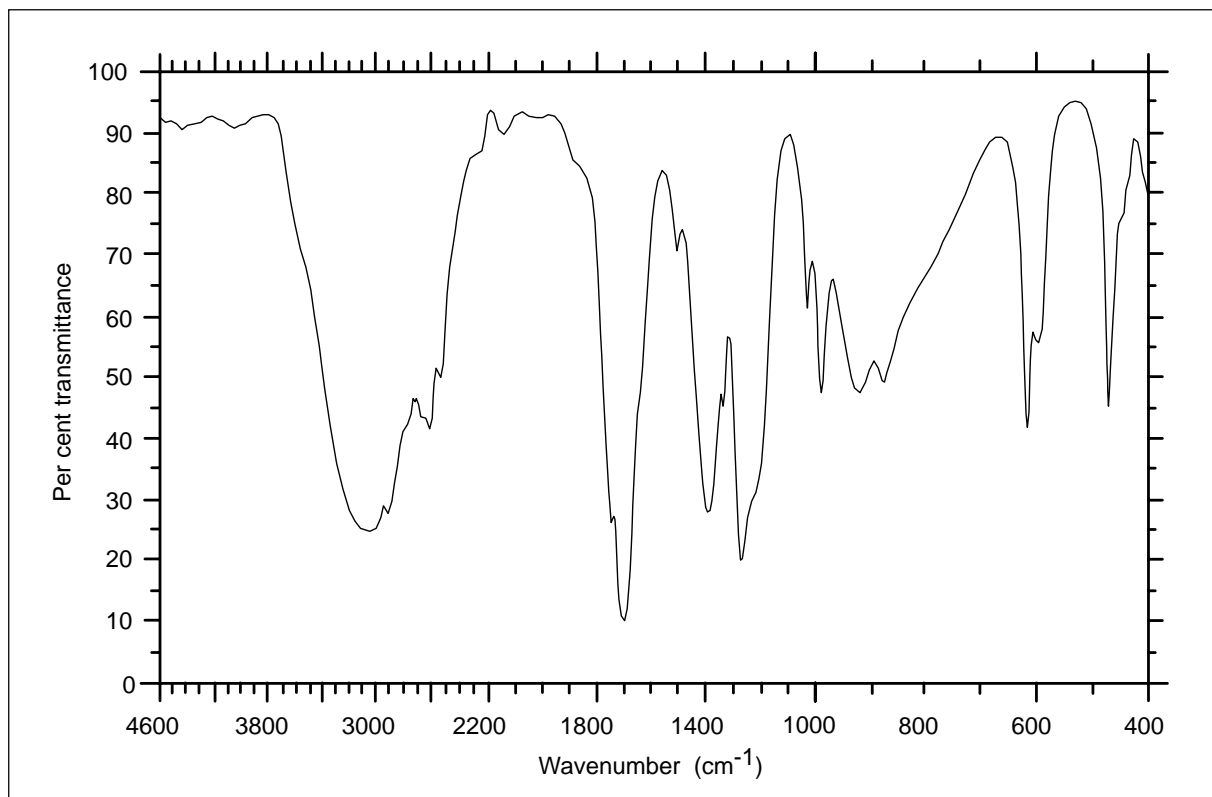**Figure 23**

Both spectra contain absorptions in the 1600–1800 cm^{-1} region due to the carbonyl stretch. However, only *Fig. 23* has an absorption corresponding to the hydrogen bonded O–H bond found in the acid. This is at 2600–3400 cm^{-1}. Thus, *Fig. 22* is the spectrum of ethanoic anhydride, and *Fig. 23* is the spectrum of ethanoic acid.

Exercise 4

The spectrum below (*Fig. 24*) is of a C_6 straight chain hydrocarbon. One bond is not a single bond. What is the compound?
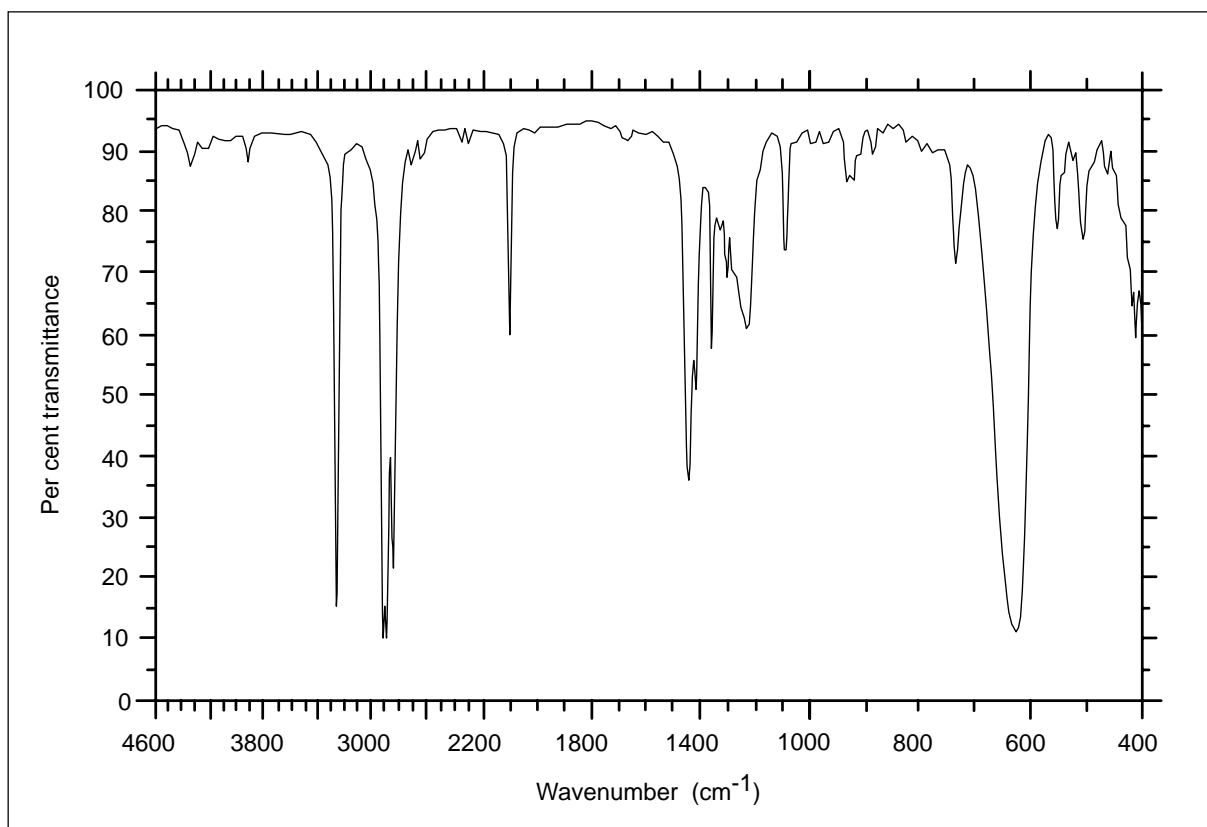

Figure 24

Figure 24 shows an absorption at 2120 cm^{-1}, indicating the presence of a triple bond, C≡C. Therefore, the compound is a hexyne. The position of the triple bond can be determined from the peak at 3350 cm^{-1}, because this suggests an ethynic hydrogen vibration, C≡C–H. Therefore, the triple bond is at the end of the chain, and *Fig. 24* is the spectrum of hex-1-yne. This is supported by the C–H bending frequency of the C≡C–H group centred on 615 cm^{-1}.

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Exercise 5

Figures 25 and 26 are the infrared spectra of the isomers ethoxyethane, $(C_2H_5)_2O$ and butan-1-ol, $CH_3CH_2CH_2CH_2OH$. From the spectra decide which is which.
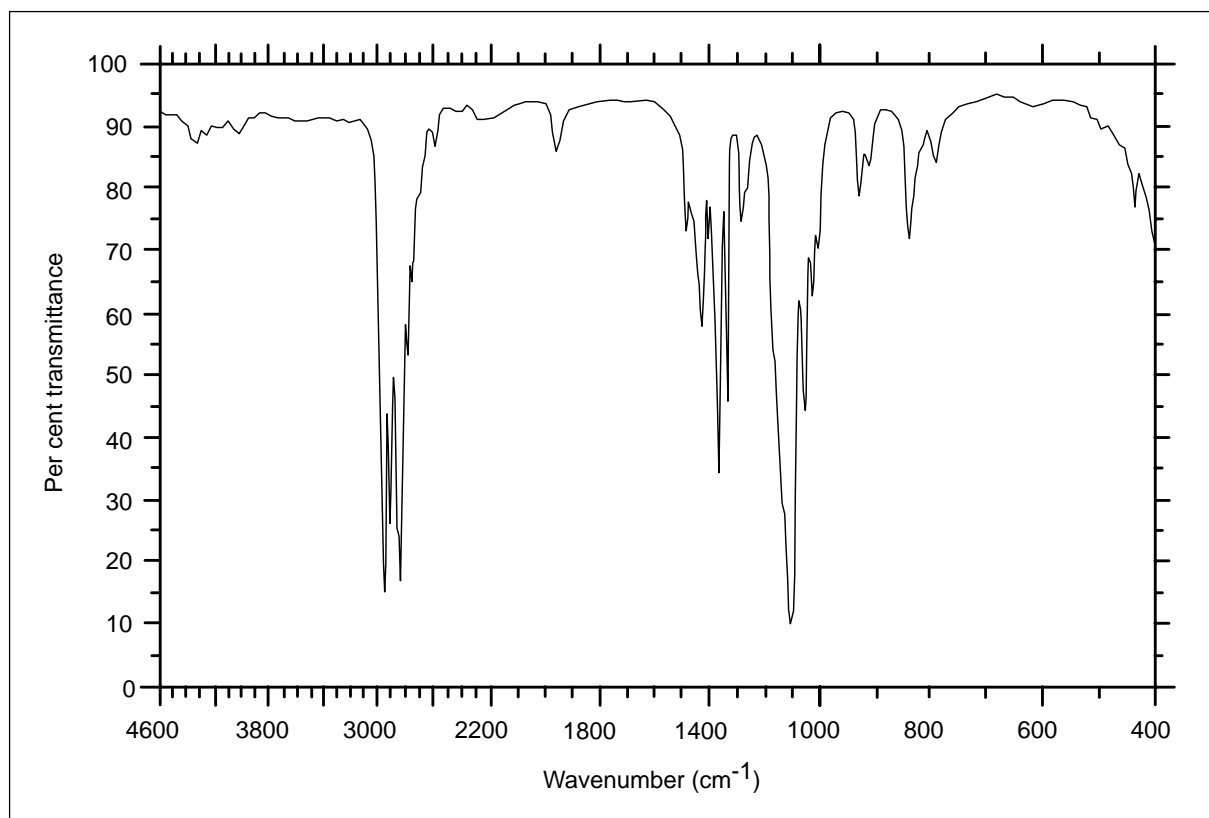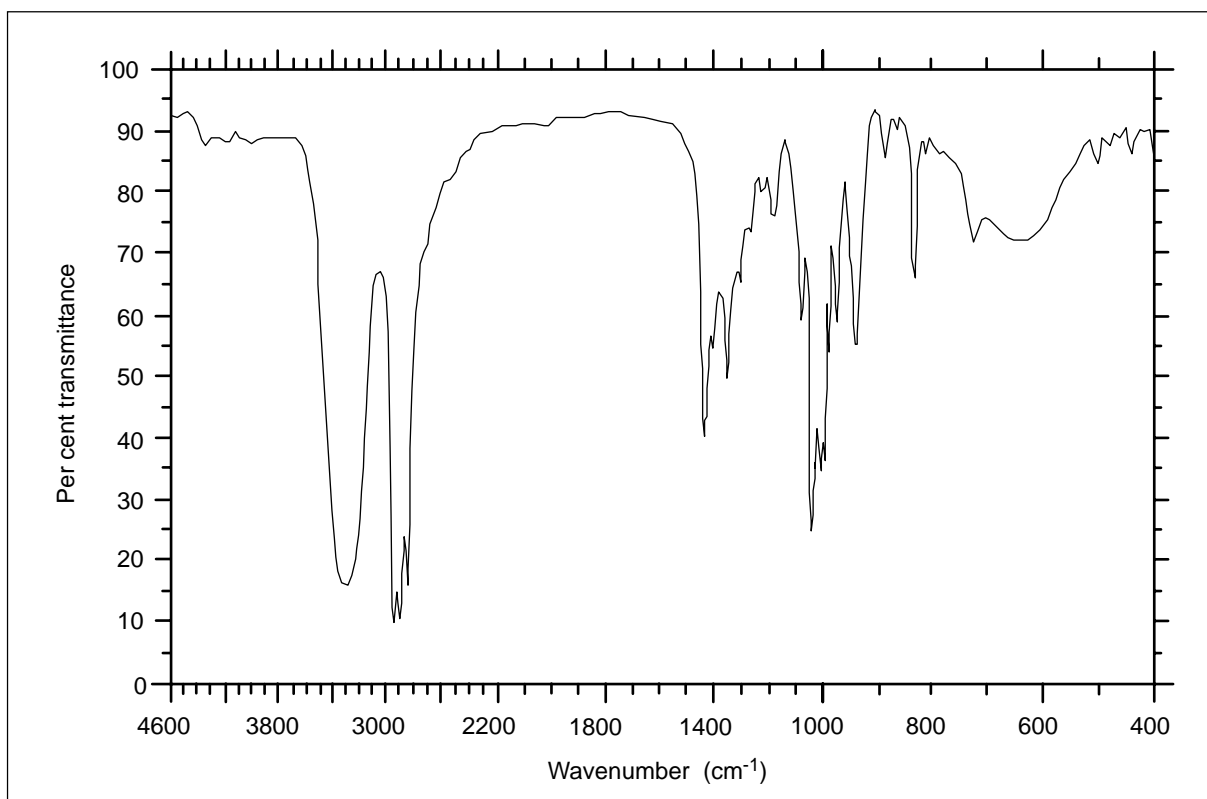

Figure 25

Figure 26

Both spectra show absorptions at *ca* 3000 cm^{-1}, consistent with the vibration of the C–H bond in saturated compounds. *Figure 26* also shows an absorption at 3300 cm^{-1} due to the hydrogen bonded O–H stretch of an alcohol, so *Fig. 26* represents the spectrum of butan-1-ol. There is a very strong absorption at 1150-1300 cm^{-1} in *Fig. 25*. Although this is in the fingerprint region, we know that we are looking for data consistent with an ether, and it is so strong and correlates so well with the C–O stretching frequency that there is little doubt that it is the ether, ethoxyethane. It could be argued that in cases like this, once one isomer has been conclusively identified the other one needs no further analysis, but real life situations are rarely that simple!