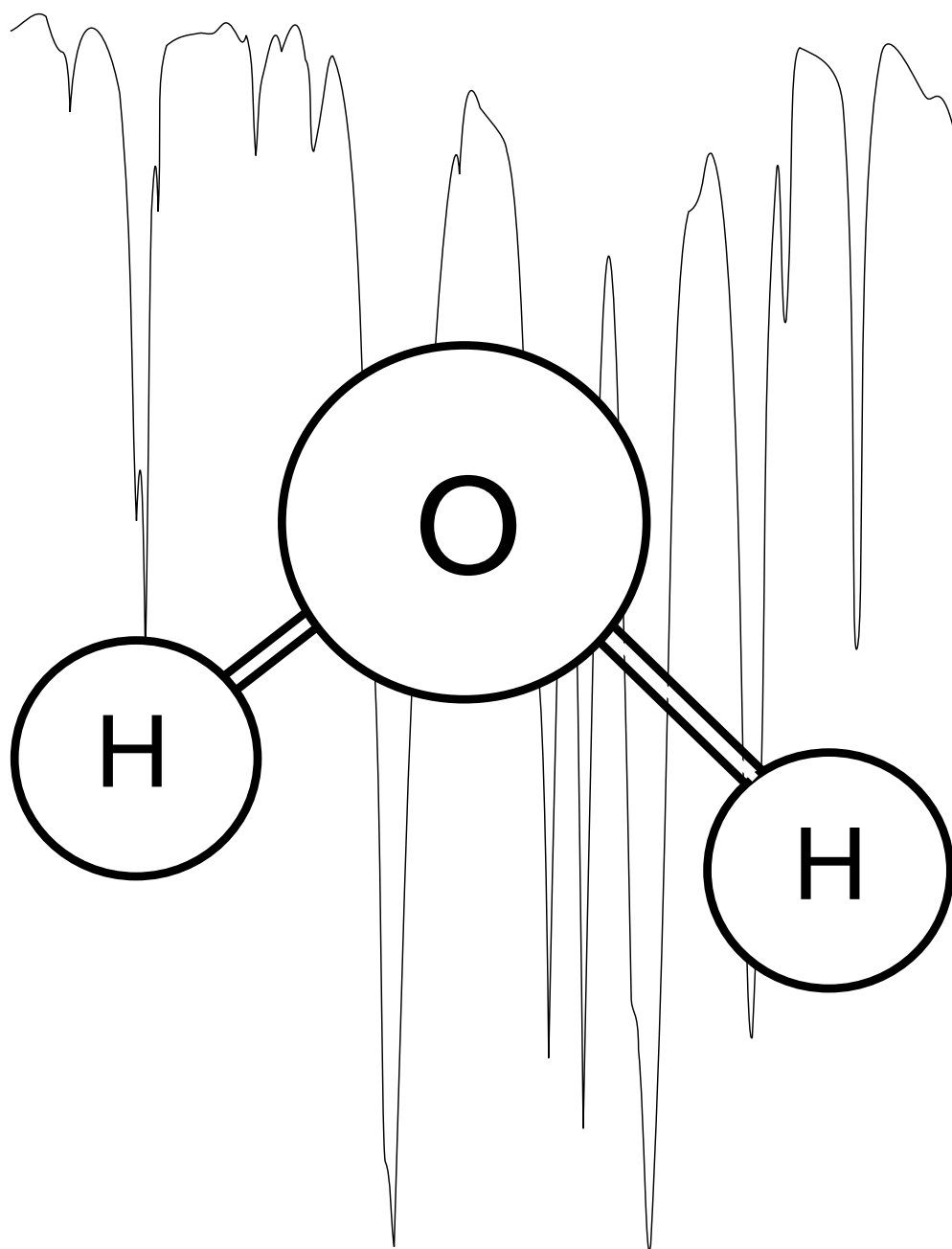


AN INTRODUCTION TO ...

INFRA RED SPECTROSCOPY

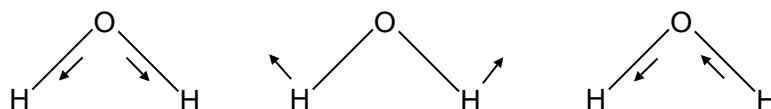


— *A self-study booklet* —

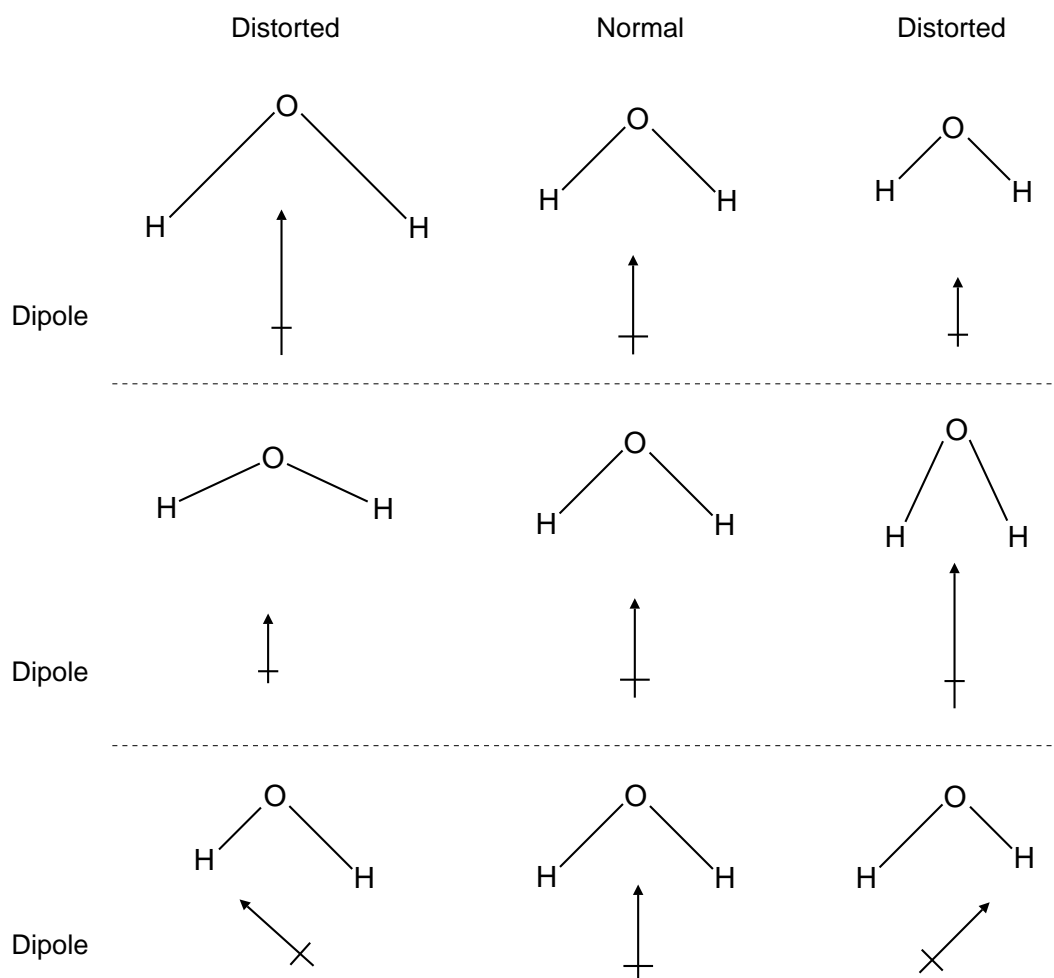
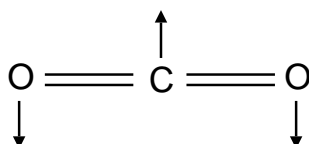
INFRA - RED SPECTROSCOPY

Introduction Different covalent bonds have different strengths due to the masses of different atoms at either end of the bond. As a result, the bonds vibrate at different frequencies (imagine two balls on either end of a spring). The frequency of vibration can be found by detecting when the molecules absorb electro-magnetic radiation.

Various types of vibration are possible. **Bending** and **stretching** are two such examples and can be found in water molecules. Each one occurs at a different frequency.

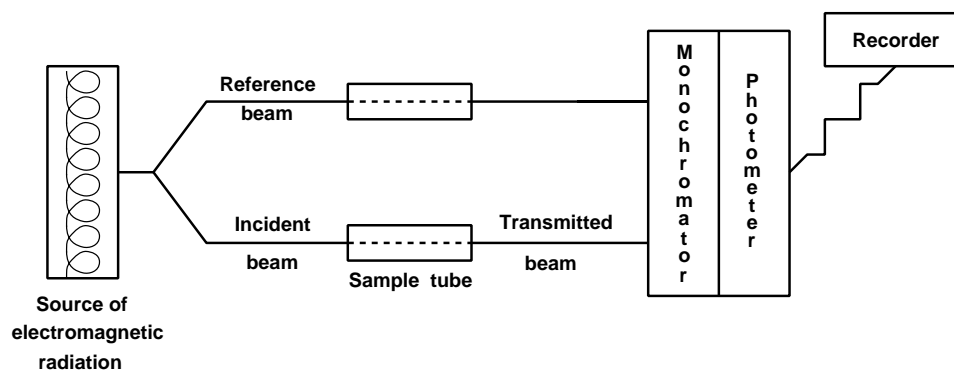


An equivalent bend at 667cm^{-1} occurs in a carbon dioxide molecule.



As molecules vibrate, there can be a change in the dipole moment of the molecule.

The Infra-red Spectrophotometer



Operation The intensity of the incident beam and reference beam is measured (they are the same). The intensity of the transmitted beam is also measured. The difference in intensity between the incidence beam and the transmitted beam is a measure of the amount of radiation absorbed by the sample. The frequency of radiation is examined continuously by the monochromator. In the photometer the relative intensities of the reference and transmitted beams are compared; the percentage of the reference beam found in the transmitted beam can be plotted as a function of frequency, or wavenumber.

Component parts

Source A filament of a rare earth metal oxide or carborundum maintained at red, or white, heat.

Optical Path The beam is guided and focussed by silvered mirrors. Ordinary lenses and mirrors are unsuitable because glass absorbs strongly over most of the frequencies used. Any windows must be made from mineral salts (e.g. NaCl) which have been highly polished to reduce the scattering of light.

Sample Infra-red spectra can be obtained as follows ...

liquids placed between polished salt cells about 1cm thick

gases placed in glass cells of 5 - 10 cm in length with end windows of salt.

solids scatter too much light if analysed on their own so they are ...

- finely ground and dissolved in a solvent (e.g. Nujol, a paraffin-based oil) or
- mixed with potassium bromide and compressed into a thin disc.

Monochromator Modern instruments use a rotating grating to produce the desired frequency.

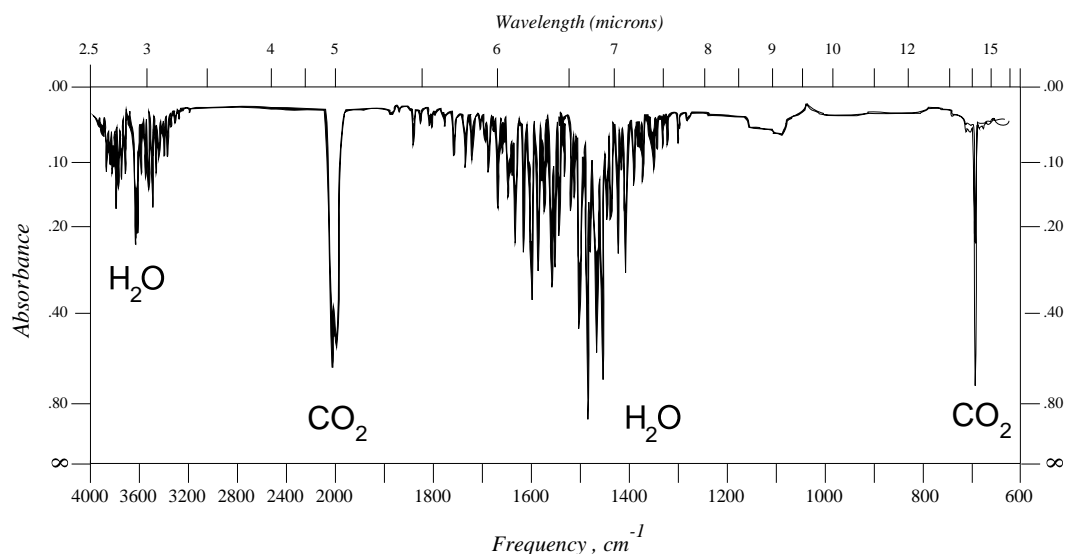
Detector A thermocouple is used.

Recorder The spectrum can be plotted out on a chart recorder to obtain hard copy. Modern instruments possess data handling devices for storage, recall and comparison of spectra.

It is usual for spectra to be plotted out as light transmitted from 0% to 100%. The maximum absorbance is indicated by a minimum on the chart. A transmittance close to 100% indicates that the molecule is transparent to frequencies in that region. The spectra have broad bands rather than single line peaks. This is because vibrational energy levels have a number of rotational energy levels associated with them.

The Double - Beam Spectrophotometer

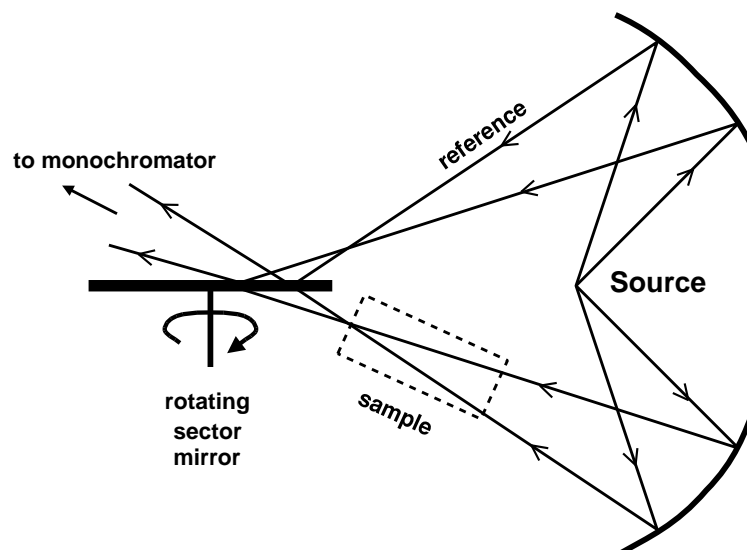
The infra-red spectrum of atmospheric air looks like this.



The absorbances due to atmospheric carbon dioxide and water vapour are considerable. They affect the composition of the spectrum not only by adding extra peaks but also the intensity of peaks can be affected by variations in the amount of water vapour present.

In order to reduce this problem, an instrument can be designed for double-beam use. In such an instrument, the source radiation is divided into two by means of mirrors and the different beams are passed alternately through the monochromator. Using electronics, the beams are balanced to remove the offending parts of the spectrum.

Another advantage of this type of machine is that when analysing a substance in solution, it is possible to pass one beam through the solution and the other beam through a sample of pure solvent. The spectrum due to the solvent can be subtracted from that of the solution to produce a spectrum of the dissolved solute.



Infra-red spectra

Interpretation Infra-red spectra are very complex due to the many types of vibration which occur in each molecule. Total characterisation of a substance based only on its IR spectrum is almost impossible unless one has computerised data handling facilities for comparison of the obtained spectrum with one in memory. However, the technique is useful when used in conjunction with other analytical methods such as nuclear magnetic resonance (nmr) spectroscopy and mass spectroscopy.

The position of a peak depends on the

- **bond strength**
- **masses of the atoms** joined by the bond

- **strong bonds** and **light atoms** absorb at **lower wavenumbers**
- **weak bonds** and **heavy atoms** absorb at **high wavenumbers**

Fingerprint Region

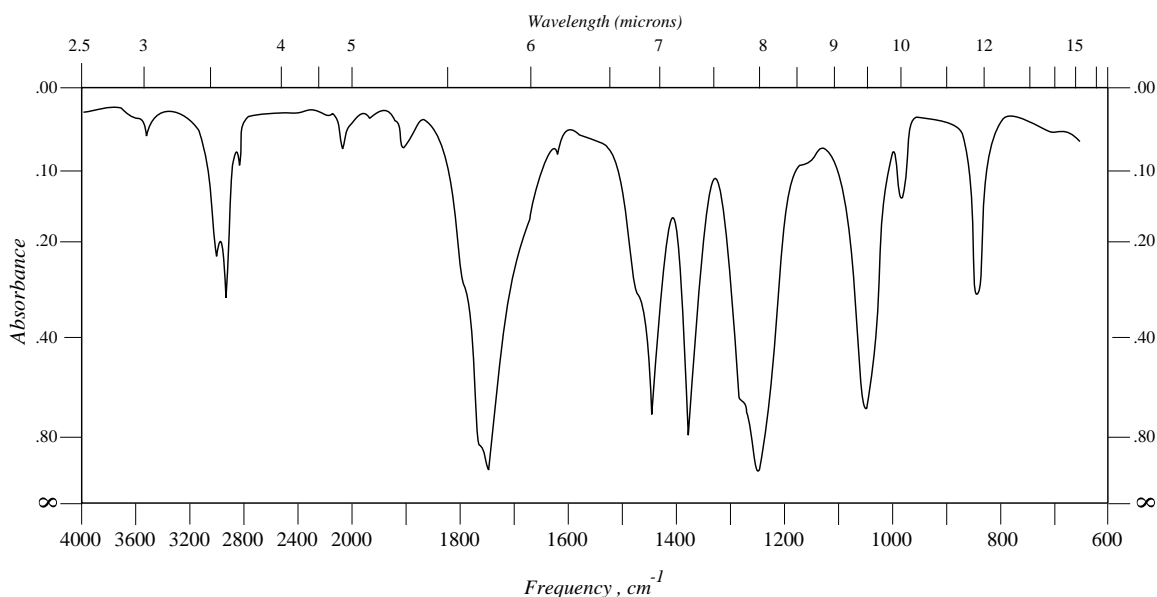
The technique is widely used in the analysis of the structure of organic compounds. As these tend to have a lot of C-C and C-H bonds within their structure, spectra obtained will have peaks in the 1400 cm^{-1} to 800 cm^{-1} range. This region is referred to as the “**fingerprint**” region as the pattern obtained is characteristic of a particular compound. The frequency of any absorption is also affected by adjoining atoms or groups.

One can also analyse the purity of a substance by checking the spectrum for unwanted peaks. The presence of a strong absorption due to a C=O bond can tell if an alcohol has been oxidised to the equivalent carbonyl compound.

The spectrum **Vertical axis** **Absorbance** the stronger the absorbance the larger the peak.

Horizontal axis **Frequency** **wavenumber** (waves per centimetre) / cm^{-1}
or **Wavelength** microns (μ); 1 micron = 1000 nanometres

A typical IR spectrum



This is the IR spectrum of the ester, methyl ethanoate (*acetate*). An obvious feature is the strong signal between 1750 cm^{-1} and 1730 cm^{-1} due to the carbonyl group.

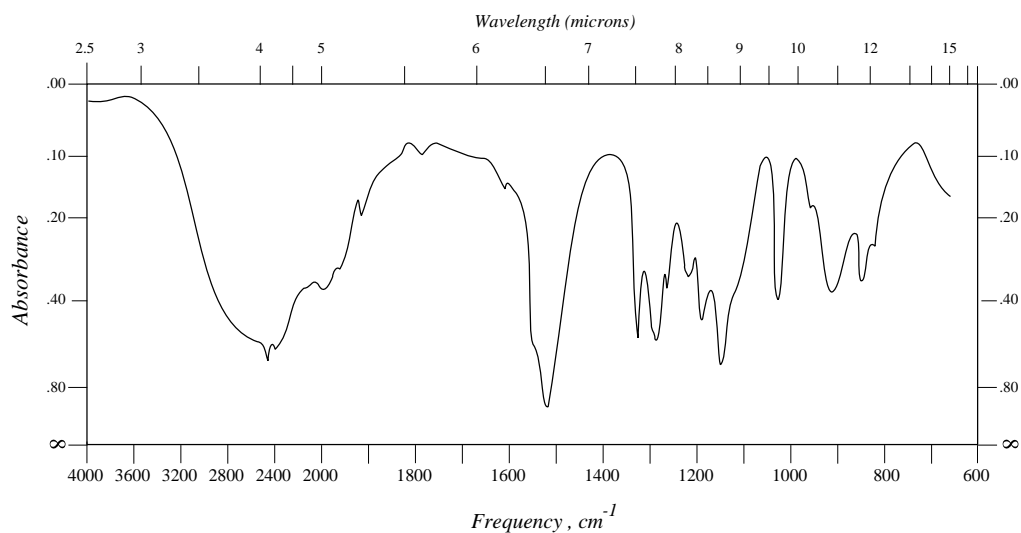
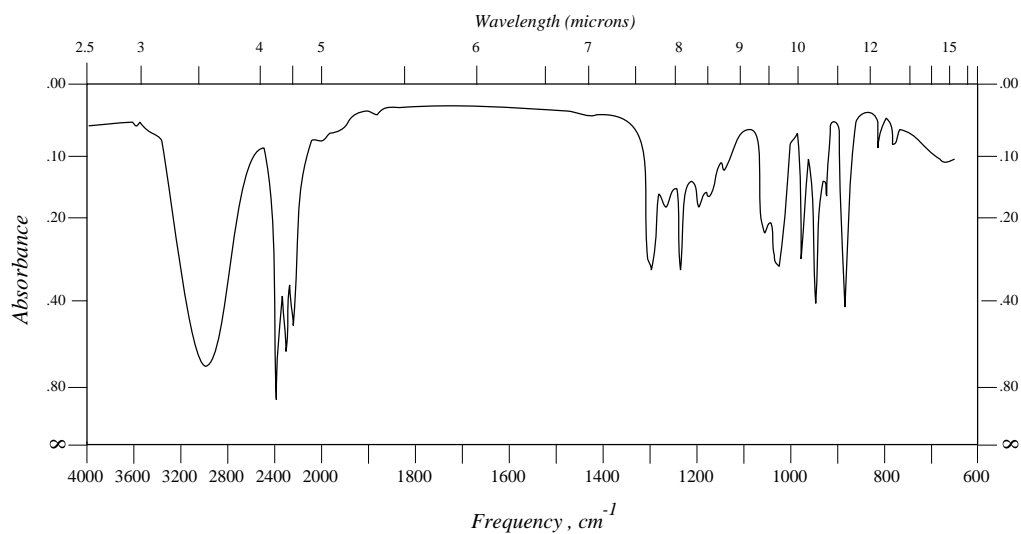
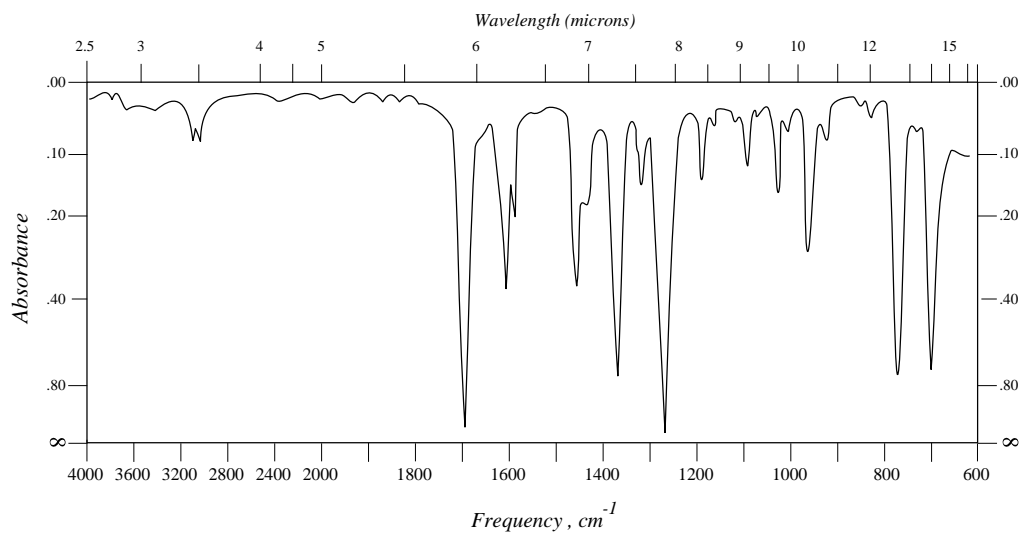
CHARACTERISTIC ABSORPTION FREQUENCIES OF SOME FUNCTIONAL GROUPS

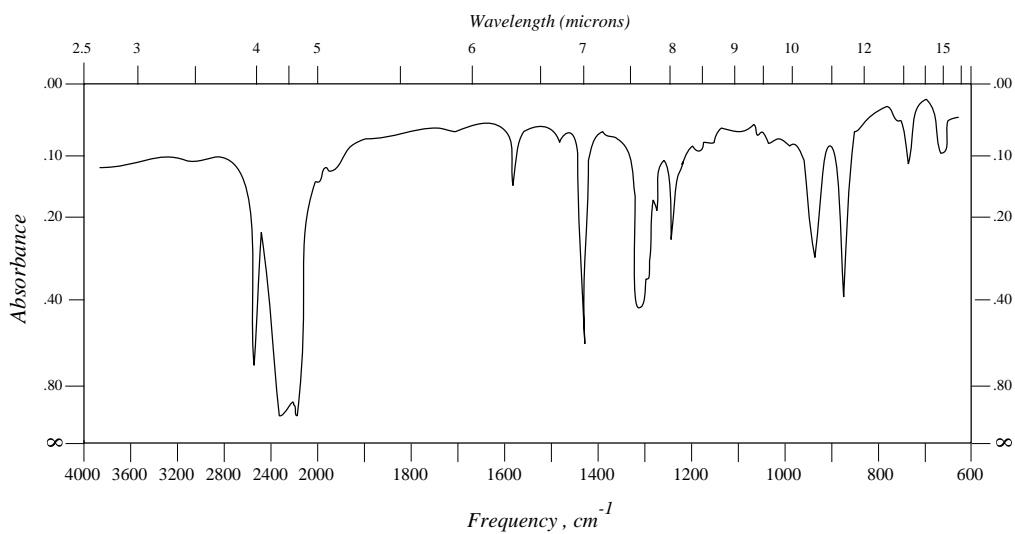
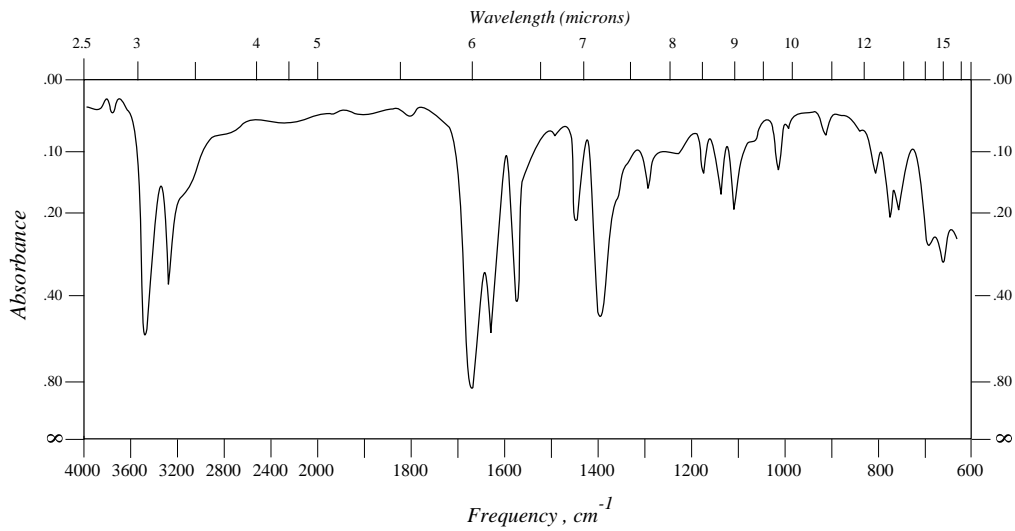
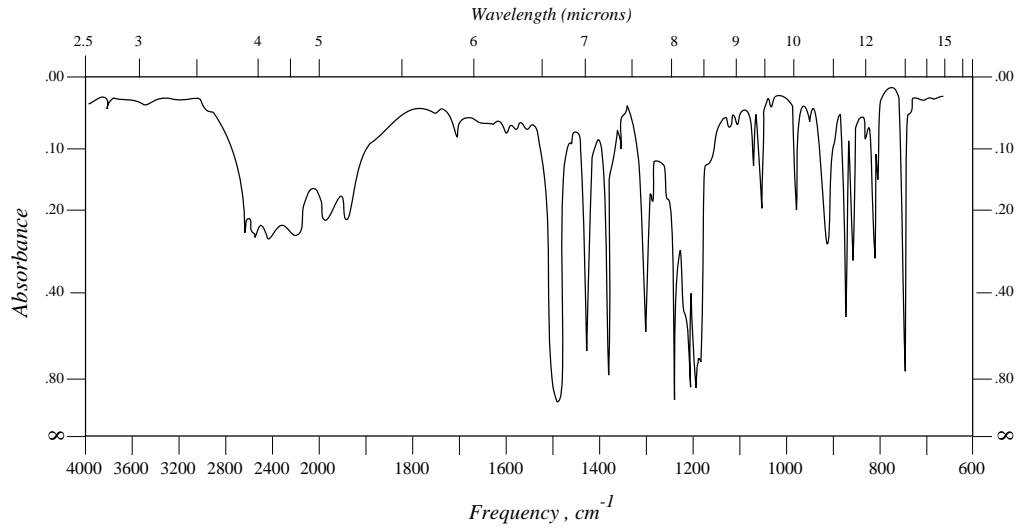
<i>Bond</i>	<i>Class of compound</i>	<i>Range, cm⁻¹</i>	<i>Intensity</i>
C-H	Alkane	2965 - 2850	strong
	CH ₃ -	1450	medium
		1380	medium
	CH ₂ -	1465	medium
	Alkene	3095 - 3010	medium
		1000 - 700	strong
	Alkyne	3300 (approx)	strong
Aldehyde		2900 - 2820	weak
		2775 - 2700	weak
C-C	Alkane	1200 - 700	weak
C=C	Alkene	1680 - 1620	variable
C≡C	Alkyne	2260 - 2100	variable
C=O	Ketone	1725 - 1705	strong
	Aldehyde	1740 - 1720	strong
	Carboxylic acid	1725 - 1700	strong
	Ester	1750 - 1730	strong
	Amide	1700 - 1630	strong
	Anhydride	1850 - 1800	strong
C-O	Alcohol, ester, ether carboxylic acid	1300 - 1000	strong
O-H	Alcohol (monomer)	3650 - 3590	variable, sharp
	Alcohol (H-bonded)	3420 - 3200	strong, broad
	Carbox. acid (H-bonded)	3300 - 3250	variable, broad
N-H	Amine (1°), Amide (1°)	3500 (approx)	medium
	Amine (2°), Amide (2°)	3500	medium
C≡N	Nitrile	2260 - 2240	medium
C-X	Fluoride	1400 - 1000	strong
	Chloride	800 - 600	strong
	Bromide	600 - 500	strong
	Iodide	500 (approx)	strong

QUESTIONS

Assign the following compounds to the six I.R. spectra on Pages 7 and 8

**benzamide , butan-2-ol , 4-nitrobenzoic acid
oct-1-ene , phenylethanone , propanoic acid**





ANSWERS phenylethanone, butan-2-ol, propanoic acid, 4-nitrobenzoic acid, benzamide, oct-1-ene