

HL Infrared spectroscopy (1)

VIBRATION OF BONDS

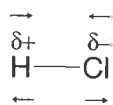
When molecules vibrate they absorb energy. This energy lies in the frequency range $1.2 \times 10^{14} - 1.2 \times 10^{13} \text{ s}^{-1}$ (Hz), i.e. wavelengths of $2.5 \times 10^{-6} - 2.5 \times 10^{-5} \text{ m}$ which is in the infrared region of the electromagnetic spectrum. For simple diatomic molecules made up of different atoms, such as HCl, there is only one form of vibration. This is stretching where the atoms alternatively move further apart then closer together. Different molecules absorb at different frequencies as the energy needed to excite a vibration depends on the bond enthalpy. Weaker bonds require less energy.

Molecule	Bond enthalpy / kJ mol^{-1}	Absorption / cm^{-1}
H-Cl	431	2886
H-Br	366	2559
H-I	299	2230

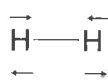
Note that infrared absorptions are usually given in cm^{-1} . Frequency and wavelength are related by the equation $c = \lambda f$ where c is the velocity of light in a vacuum. Since c is a constant the reciprocal of wavelength is a direct measure of frequency. This reciprocal of wavelength ($1/\lambda$) is known as the **wavenumber** and has the units cm^{-1} . Hence an absorption of 2886 cm^{-1} corresponds to a wavelength of $3.465 \times 10^{-6} \text{ m}$. The longer the wavelength the lower the energy and the smaller the value of $1/\lambda$ in cm^{-1} . Conversely the higher the wavenumber the higher the energy.

CHANGE IN BOND POLARITY

Not all vibrations absorb infrared radiation. For absorption there must be a change in the dipole moment (bond polarity) as the vibration occurs. Thus diatomic gas molecules containing only one element, such as H_2 , Cl_2 , and O_2 , do not absorb infrared radiation.



Stretching involves a change in dipole: IR active

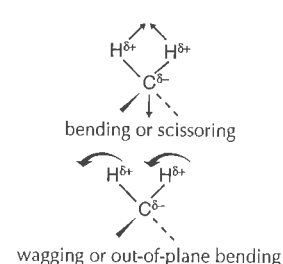
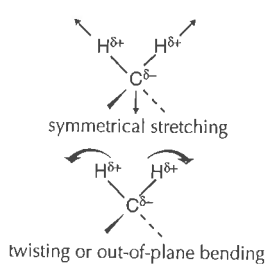
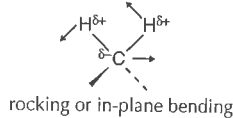
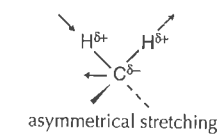


Stretching involves no change in dipole: IR inactive

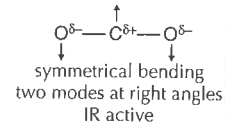
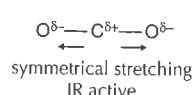
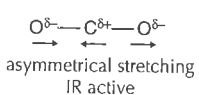
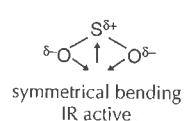
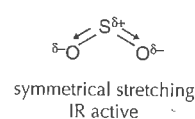
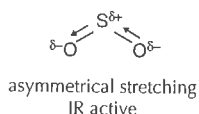
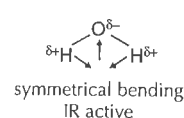
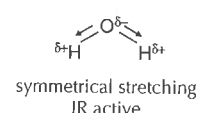
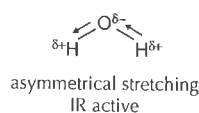
For more complex molecules only those vibrations which result in a dipole change will be infrared active. For example, the symmetrical stretch in carbon dioxide will be infrared inactive whereas the asymmetric stretch and the bending are both infrared active as they result in a dipole change.

Stretching and bending are the main modes of vibration but bending can be sub-divided into rocking, scissoring, twisting and wagging as exemplified by the $-\text{CH}_2-$ group.

Vibrations of $-\text{CH}_2-$ group



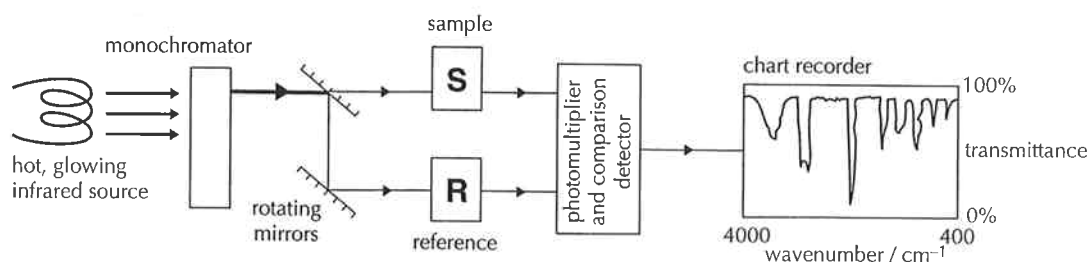
Vibrations of H_2O , SO_2 , and CO_2



HL Infrared spectroscopy (2)

THE OPERATING PRINCIPLES OF A DOUBLE BEAM INFRARED SPECTROMETER

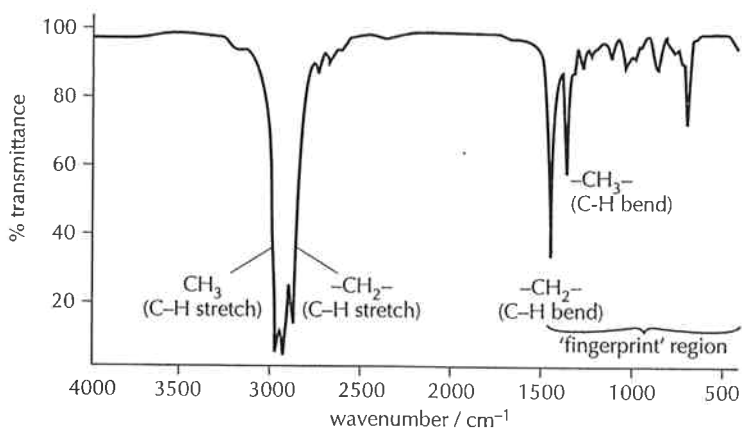
Traditional infrared spectrometers work by scanning wavelengths from about 2.5×10^{-6} m (4000 cm^{-1}) to 2.5×10^{-5} m (400 cm^{-1}). By using a rotating mirror the beam of monochromatic radiation is alternately passed through the sample and a reference. A photomultiplier converts photons of radiation into an electrical current. The spectrum is generated by comparison of the currents produced by the sample and the reference beams. Modern spectrometers pass all the wavelengths through the sample at the same time and a mathematical technique known as Fourier transformation is used to automatically analyse the transmission at each wavelength. Modern spectrometers are also linked to computers which store the spectra of known compounds. This enables an unknown compound to be identified by exact matching with the spectrum of a known compound.



Schematic diagram of a double beam infrared spectrometer

USE OF INFRARED SPECTROSCOPY

Infrared spectrum of hexane C_6H_{14}



Note that infrared spectra normally show percentage transmittance, rather than absorption, from a base of 100% transmittance.

Because of all the different vibrations possible most molecules actually have quite complex spectra and can be identified from the 'fingerprint' region, that is the region between about $1400\text{--}400 \text{ cm}^{-1}$. However, for simple laboratory use there are several main absorptions which can be used to identify particular functional groups. The most common of these have been mentioned previously in 11. Topic 20 – Organic Chemistry and are the --OH , C=O , C--H , C=C , and C--O bonds. The precise region at which these absorb is determined by the neighbouring atoms as these will influence the bond enthalpy. The main use of infrared spectroscopy is thus to confirm the presence of particular functional groups. The intoximeter for determining the amount of alcohol in the breath (see 14. option B – Medicines and Drugs) provides a good example of how it can also be used to give quantitative data on the amount of sample present.