



Infrared Spectroscopy (IR)

Introduction to Infrared Spectroscopy (IR)

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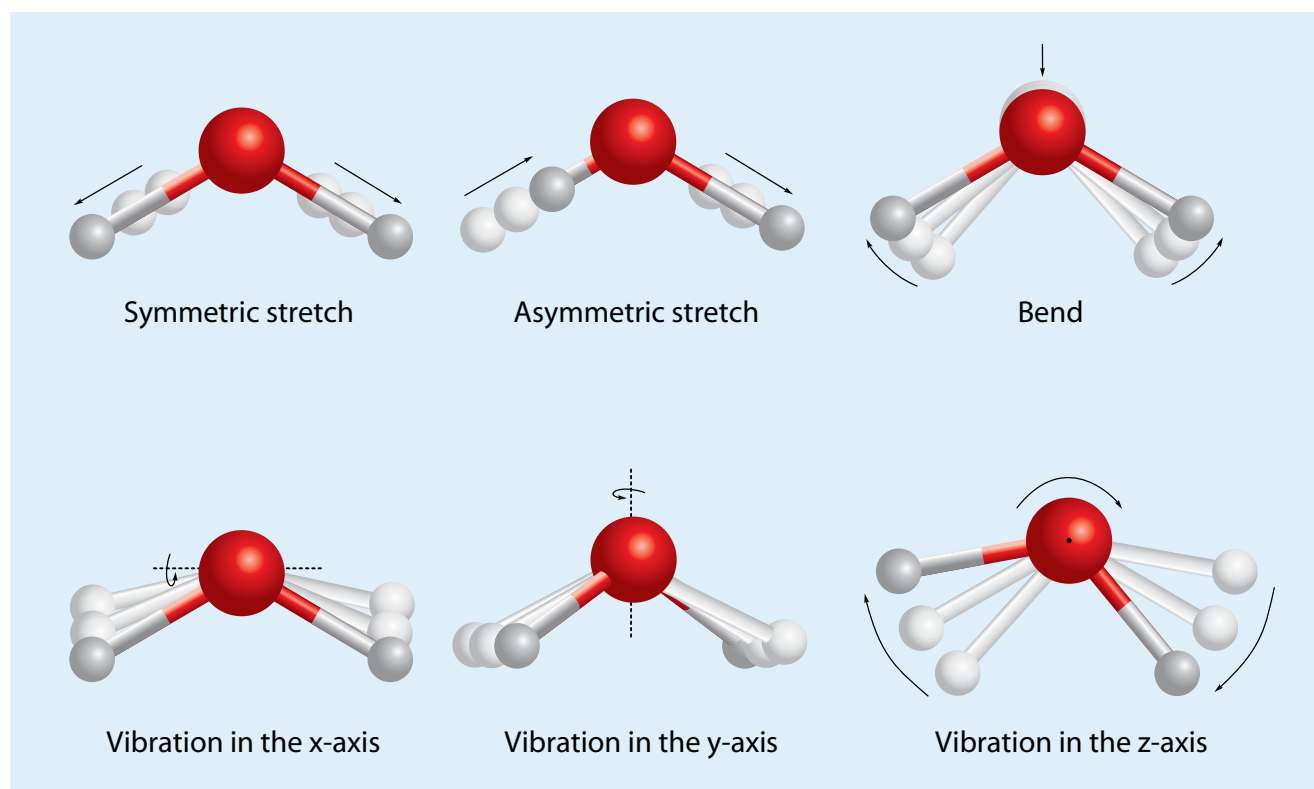
One of the first scientists to observe infrared radiation was William Herschel in the early 19th century. He noticed that when he attempted to record the temperature of each colour in visible light, the area just beyond red light gave a marked increase in temperature compared to the visible colours. However it was only in the early 20th century that chemists started to take an interest in how infrared radiation interacted with matter and the first commercial infrared spectrometers were manufactured in the USA during the 1940s.

Interaction with matter

The bonds within molecules all vibrate at temperatures above absolute zero. There are several types of vibrations that cause absorptions in the infrared region. Probably the most simple to visualise are bending and stretching, examples of which are illustrated below using a molecule of water.

If the vibration of these bonds result in the change of the molecule's dipole moment then the molecule will absorb infrared energy at a frequency corresponding to the frequency of the bond's natural vibration. This absorption of energy resulting in an increase in the amplitude of the vibrations is known as **resonance**.

An IR spectrometer detects how the absorption of a sample varies with wavenumber, cm^{-1} , which is the reciprocal of the wavelength in cm ($1/\text{wavelength}$). The wavenumber is proportional to the energy or frequency of the vibration of the bonds in the molecule.

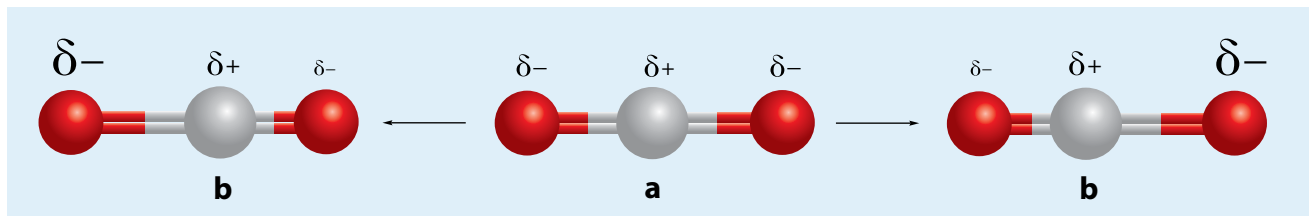


Carbon dioxide and IR

Carbon dioxide is probably the molecule most people associate with the absorption of infrared radiation, as this is a key feature of the greenhouse effect. If carbon dioxide was perfectly still it would not have a permanent dipole moment as its charge would be spread evenly across both sides of the molecule.

However the molecule is always vibrating and when it undergoes an asymmetric stretch, an uneven distribution of charge results. This gives the molecule a temporary dipole moment, enabling it to absorb infrared radiation.

Hence even some molecules without a permanent uneven distribution of charge can absorb IR radiation.



(a) No permanent dipole moment when the molecule is stationary due to equal and opposite dipoles.

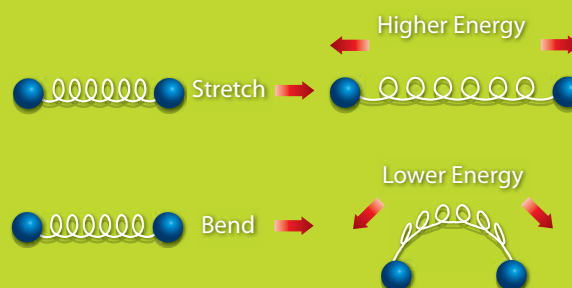
(b) As molecules undergo asymmetric stretch the permanent dipoles become uneven and temporary dipole moments are created.

Factors that affect vibrations

Type of Vibration

The energy absorbed when particular bonds vibrate depends on several factors. To get your head around this it is helpful to use an analogy; you can think of a bond as a spring between two atoms. Imagine trying to bend or stretch the spring. Generally it is easier to bend than stretch, so bending vibrations are of lower energy than stretching vibrations for the same bond.

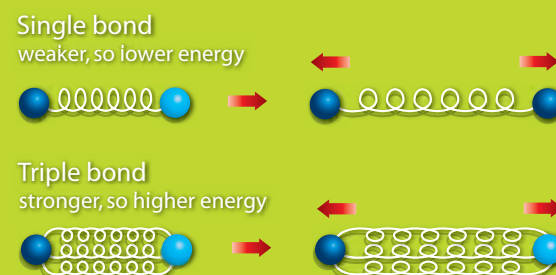
Therefore, absorptions due to bending tend to occur at lower wavenumbers than stretches.



Hence a C–H Stretch in an alkane absorbs at $2600\text{--}2800\text{ cm}^{-1}$ but a C–H Bend in an alkane absorbs at $1365\text{--}1485\text{ cm}^{-1}$

Strength of Bonds

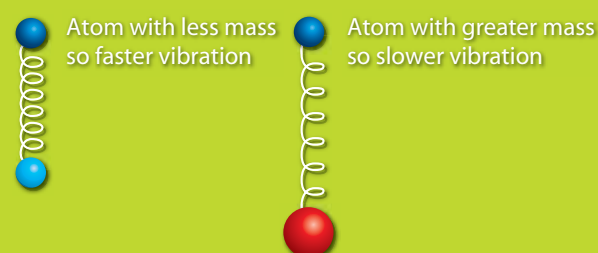
You can think of a strong bond as a stiff spring. This will need more energy to make the 'spring' bond vibrate, so stronger bonds absorb at higher wavenumbers.



Hence C–N absorbs at roughly $1050\text{--}1650\text{ cm}^{-1}$ but a C≡N absorbs at roughly 2200 cm^{-1}

Mass of Atoms

Finally the atoms in the bond can be thought of as masses at the end of the spring. Heavy masses on a spring vibrate more slowly than lighter ones. Using this analogy we can imagine that heavier atoms vibrate at a lower frequency than lighter ones. Therefore you would expect a C–Br bond to absorb at a lower frequency than a C–Cl bond as bromine is heavier than chlorine.



Hence C–Cl bond absorbs at about $600\text{--}800\text{ cm}^{-1}$ but a C–Br bond absorbs at about $500\text{--}600\text{ cm}^{-1}$

Infrared Spectrometers

Infrared spectrometers work in a variety of ways but all of them pass infrared radiation across the full IR range through a sample. The sample can be a thin film of liquid between two plates, a solution held in special cells, a mull (or paste) between two plates or a solid mixed with potassium bromide and compressed into a disc. The cells or plates are made of sodium or potassium halides, as these do not absorb infrared radiation.

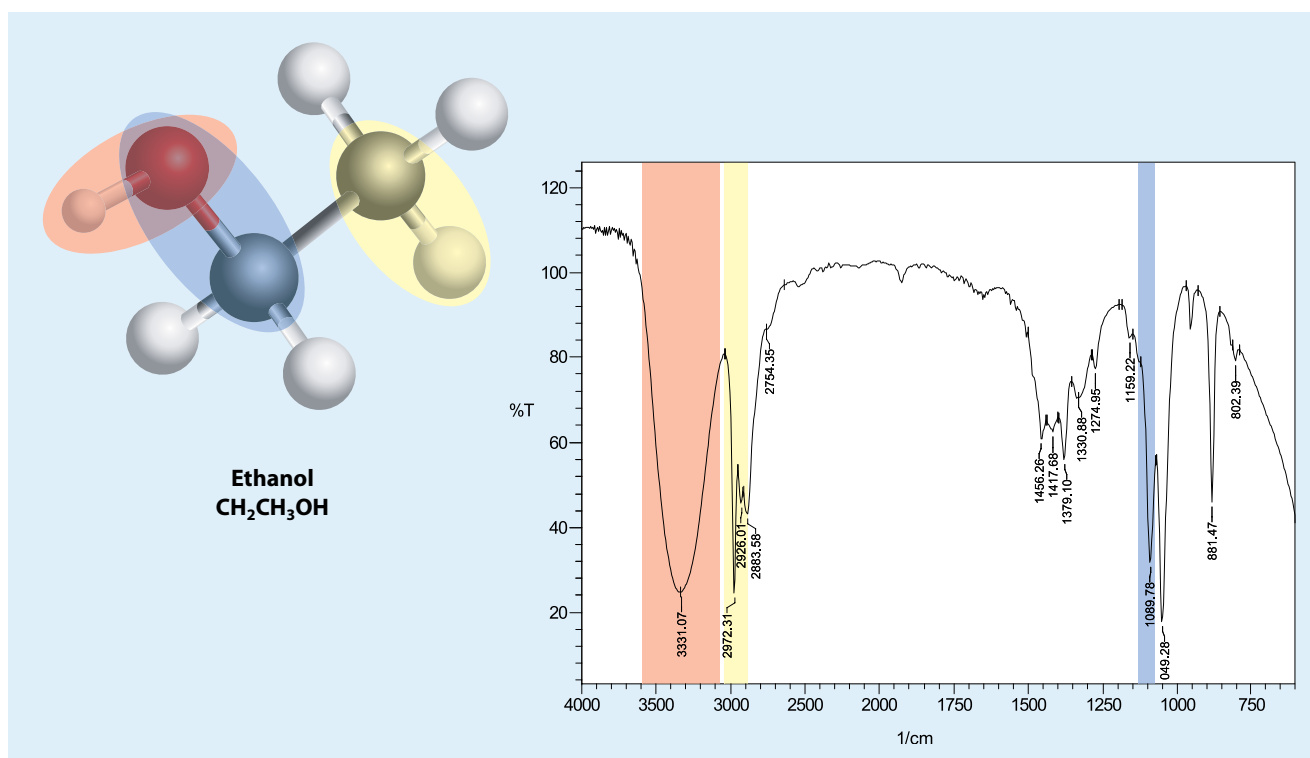
However the IR spectrometer 'in the suitcase' can use a technique called **attenuated total reflectance (ATR)**, which allows IR spectra to be run on solid and liquid samples without any additional preparation.

Interpreting a spectrum

As molecules often contain a number of bonds, with many possible vibrations, an IR spectrum can have many absorptions. This can be helpful as it results in each molecule's spectrum being unique. If the spectrum of a molecule has already been recorded on a database, any spectrum produced can be compared to that database to help identify the molecule. The spectrum can also be used to highlight specific bonds and hence functional groups within a molecule, to help determine its structure.

Look at this spectrum of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, to see which bonds are responsible for particular absorptions.

Although IR is not able to provide enough information to find the exact structure of a 'new' molecule, in conjunction with other spectroscopic tools, such as NMR and mass spectrometry, IR can help provide valuable information to help piece together the overall structure.



Uses of IR spectroscopy

Students and research chemists regularly use IR in structure determination and IR continues to have a wide range of applications in both research chemistry and wider society. For instance, IR is being used to help identify the structure of complex molecules in space and to help determine the time scale for the folding of complex protein structures into functioning biological molecules.

Many police forces across the world now routinely use IR, almost certainly without realising it. This is because many 'breathalysers' used to collect evidence to determine levels of alcohol in breath are IR spectrometers that look specifically for absorptions at around 1060 cm^{-1} , which corresponds the vibration of the C-O bond in ethanol!



BASIC ORGANIC FUNCTIONAL GROUP REFERENCE

Aliphatic	Methyl	2960	C-H
	Methylene	2930	
Unsaturated	Alkenes	3050	C=C
	Vinyl	910	
	Vinylidene	890	
	Cis	700	
	Trans	965	
	Alkynes	3200	
Aromatics	Mono	750	700
	Ortho	750	
	Meta	782	
	Para	817	
Oxygen Group	Ether	1100	C-O
	Alcohol	1100	
Carbonyl Compounds	Aldehyde	2700	C=O
	Ketone	1700	
	Ester	1740	
	Carboxylic Acid	1720	
		1200	
Nitrogen Groups	Amide	1640	N-H
	Amine	3300	
	Nitrile	2250	
		3200	

Methyl	Methylene		
CH ₃ —	—CH ₂ —		
Vinyl	Vinylidene	Cis	Alkene
		Trans	Alkyne

Mono	Ortho	Meta	Para

Ether	Alcohol
C—O—C	—OH

Aldehyde	Ketone	Ester	Carboxylic Acid

Amide	Amine	Nitrile
	C—N	C≡N

INSTRUMENT SETUP - Setting up the IR equipment

- **Check you have all the equipment**

You should have an IR Spectrometer and power lead, laptop computer and power lead, printer and power lead, two USB cables and a flat head screwdriver.

- **Choose a spot to set up**

You'll need to be close to 3 mains power sockets.


- **Plug in the spectrometer**

Place the spectrometer on the left of your setup area and attach the power cable to the socket marked Power Supply on the back of the spectrometer. Use the screwdriver to secure it and plug the other end into the mains.

- **Plug in the laptop**

Place the laptop to the right of the spectrometer and use the laptop power cable to connect the laptop to the mains.


- **Connect the spectrometer to the laptop**

Plug one end of a USB cable into the socket marked 'USB' on the back of the spectrometer; plug the other end into a USB socket on the laptop. The laptop socket will be marked with the  symbol.

- **Plug in the printer**

Position the printer to the right of the laptop and use the printer power cable to plug the printer into the mains.

- **Connect the printer to the laptop**

Plug one end of a USB cable into the USB socket on the printer and the other end into a free USB socket on the laptop. Both sockets are marked with this symbol: .

- **Switch the spectrometer, laptop and printer on at the mains**

- **Switch the computer on and let it boot up**

- **Switch the printer on**

- **Switch the spectrometer on**

The switch is on the back.

- **Open EZ OMNIC**

On the laptop, double-click on the EZ OMNIC icon.

You are now ready to run a spectrum...

Running spectra using macros

Two macros have been constructed for SIAS experiments and can be accessed through the EZ OMNIC software.

1. IR Liq: This macro will take you through recording spectra of liquid samples.
2. IR Solid: This macro will take you through recording spectra of solid samples and requires the use of the Thunderdome (ATR) unit.

*[Macros are located in the
C:\My Documents\OMINC\Macro directory]*