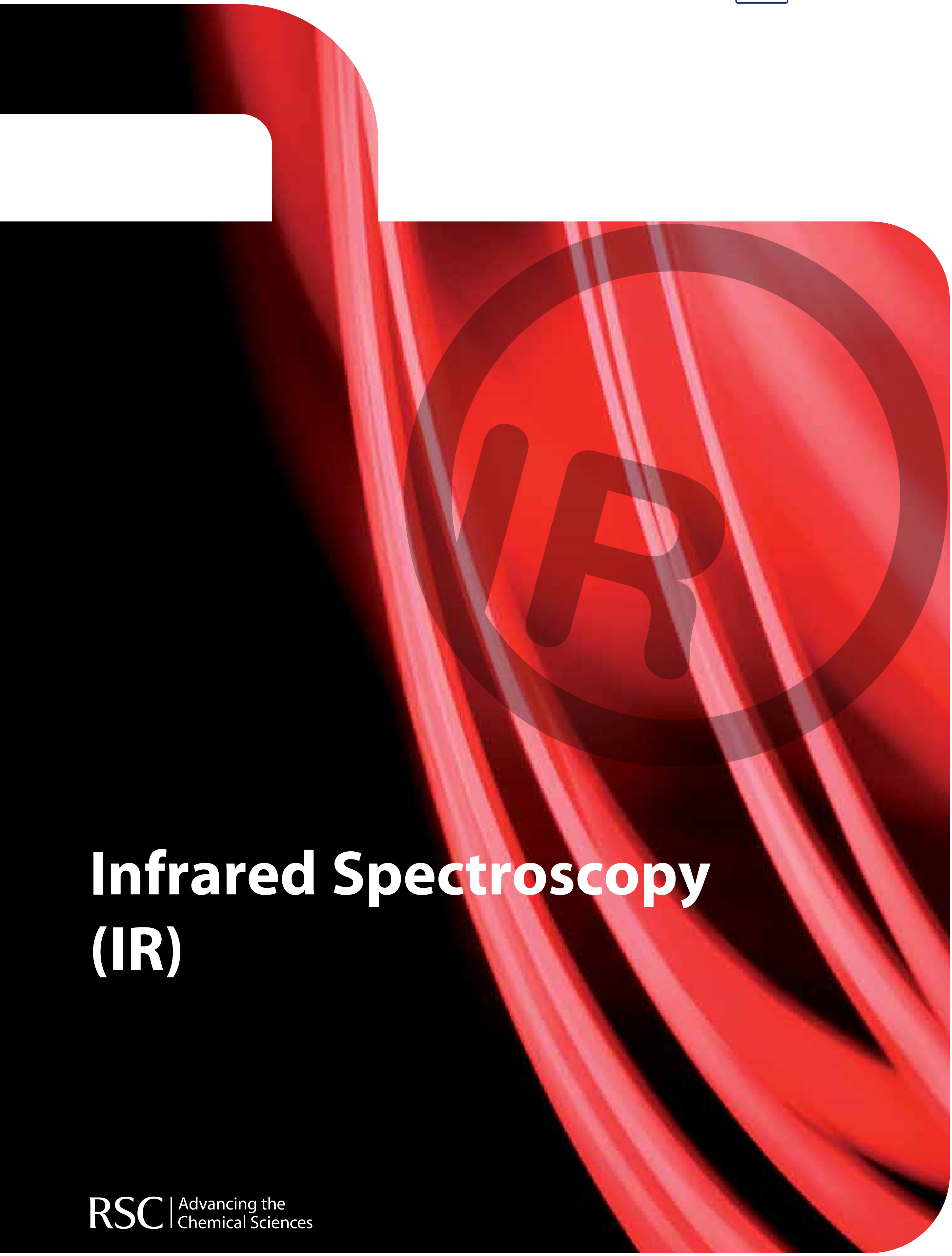
Spectroscopy in a Suitcase



Infrared Spectroscopy (IR)

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Introduction to Infrared Spectroscopy (IR)

Infrared Spectroscopy (IR)

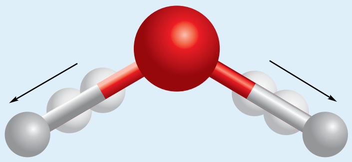
One of the first scientists to observe infrared radiation was William Herschel in the early 19th century. He noticed that when he attempted to record the temperature of each colour in visible light, the area just beyond red light gave a marked increase in temperature compared to the visible colours. 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

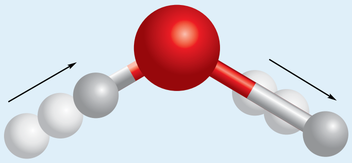
The bonds within molecules all vibrate at temperatures above absolute zero. There are several types of vibrations that cause absorptions in the infrared region. Probably the most simple to visualise are bending and stretching, examples of which are illustrated below using a molecule of water.

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**.

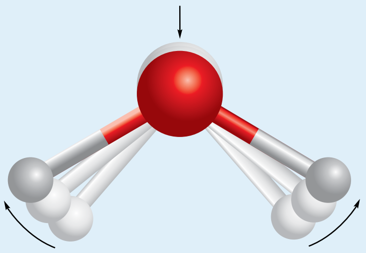
An IR spectrometer detects how the absorption of a sample varies with wavenumber, cm^{-1}, which is the reciprocal of the wavelength in cm (1/wavelength). The wavenumber is proportional to the energy or frequency of the vibration of the bonds in the molecule.



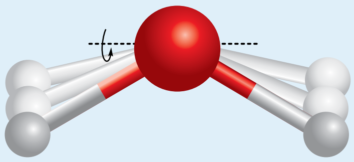
Symmetric stretch



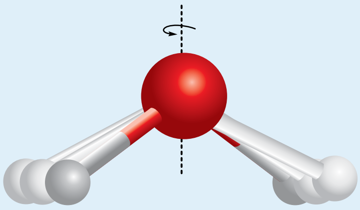
Asymmetric stretch



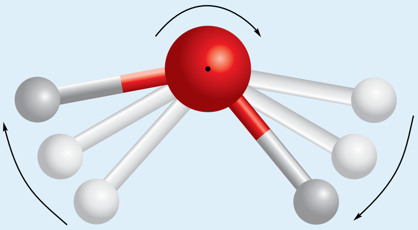
Bend



Vibration in the x-axis



Vibration in the y-axis



Vibration in the z-axis

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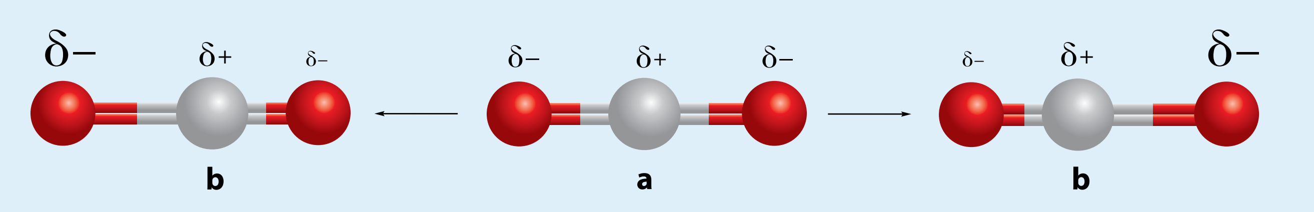
Carbon dioxide and IR

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.

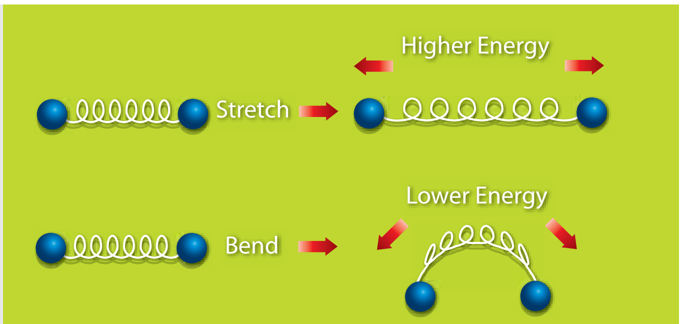


(a) No permenant dipole moment when the molecule is stationary due to equal and opposite dipoles.
(b) As molecules undergo assymmetric stretch the permenant dipoles become uneven and temporary dipole moments are created.

Factors that affect vibrations

Type of Vibration

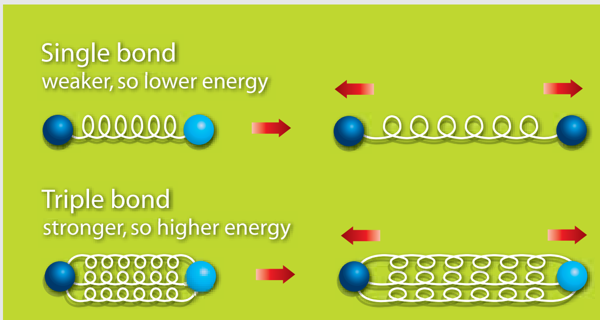
The energy absorbed when particular bonds vibrate depends on several factors. To get your head around this it is helpful to use an analogy; you can think of a bond as a spring between two atoms. Imagine trying to bend or stretch the spring. Generally it is easier to bend than stretch, so bending vibrations 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 2600-2800 cm^{-1}
but a C–H Bend in an alkane absorbs at 1365-1485 cm^{-1}

Strength of Bonds

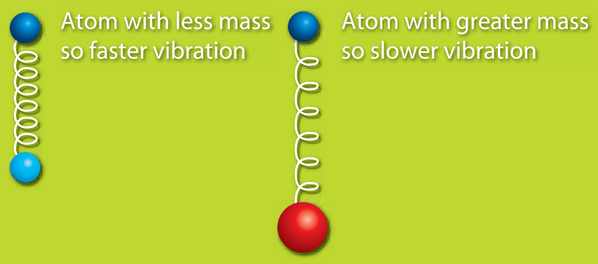
You can think of a strong bond as a stiff spring. This will need more energy to make the ‘spring’ bond vibrate, so stronger bonds absorb at higher wavenumbers.



Hence C–N absorbs at roughly 1050 - 1650 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 600-800 cm^{-1}
but a C–Br bond absorbs at about 500-600 cm^{-1}

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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.

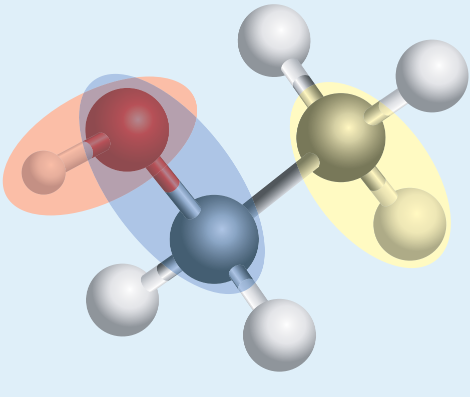
However the IR spectrometer 'in the suitcase' can use a technique called **attenuated total reflectance (ATR)**, which allows IR spectra to be run on solid and liquid samples without any additional preparation.

Interpreting a spectrum

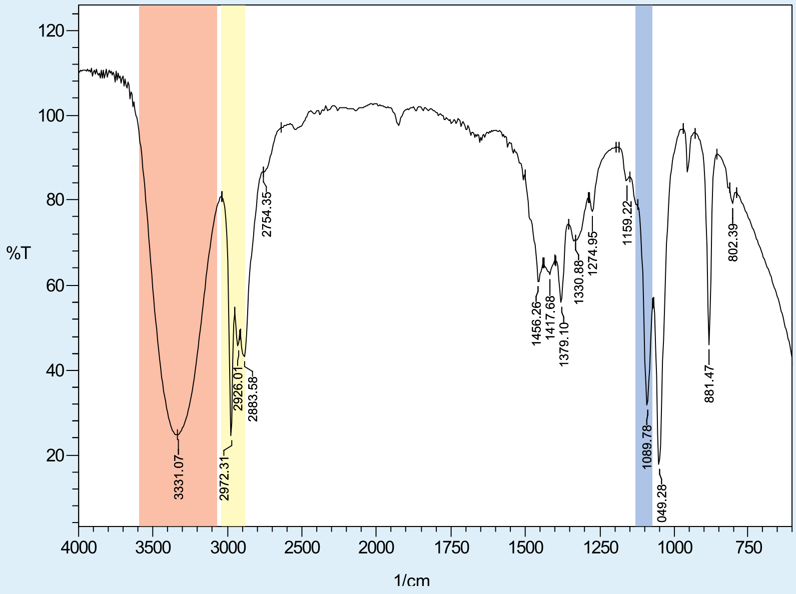
As molecules often contain a number of bonds, with many possible vibrations, an IR spectrum can have many absorptions. This can be helpful as it results in each molecule's spectrum being unique. If the spectrum of a molecule has already been recorded on a database, any spectrum produced can be compared 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, CH_3CH_2OH, 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.



Ethanol
CH_2CH_3OH



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!

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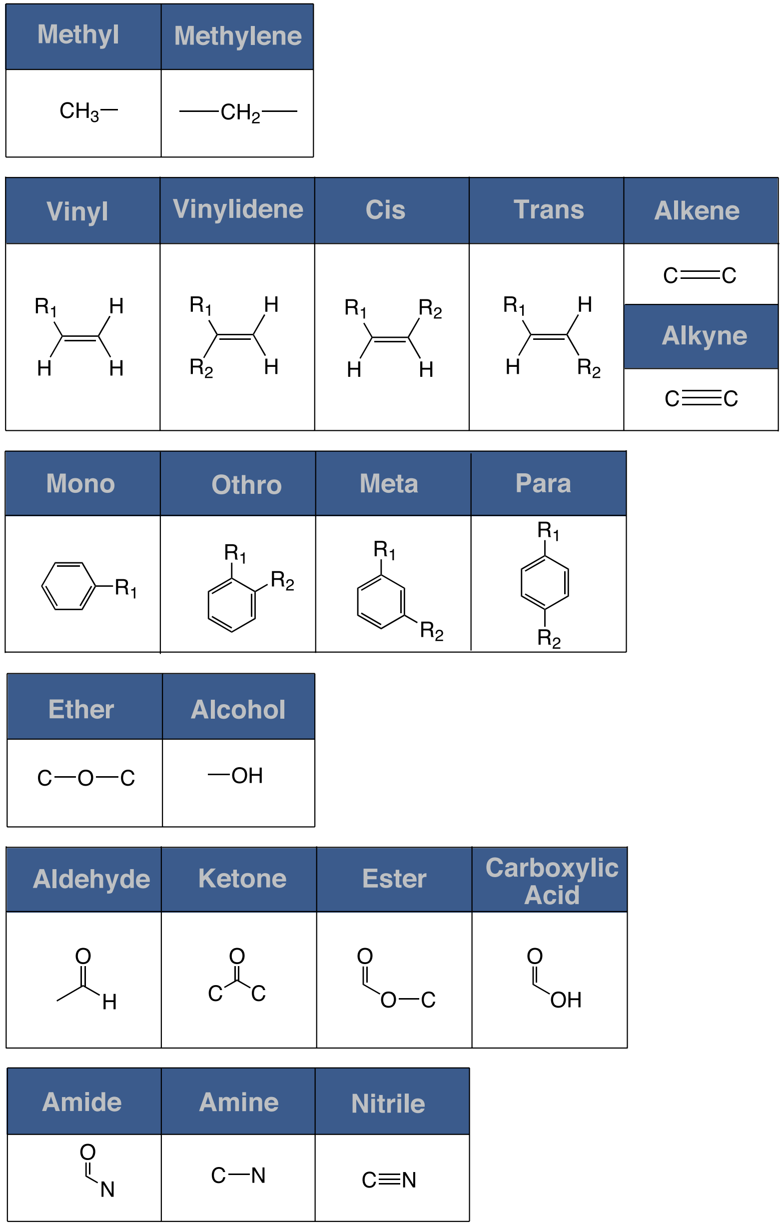
BASIC ORGANIC FUNCTIONAL GROUP REFERENCE

	C—H	C=C	C≡C	C—O	O—H	C=O	N—H	C≡N
Aliphatic								
Methyl	2960							
Methylene	2930							
Unsaturated								
Alkenes	3050	1640						
Vinyl	910	1640						
Vinylidene	890	1640						
Cis	700	1640						
Trans	965	1670						
Alkynes	3200		2200					
Aromatics								
Mono	750		700					
Ortho	750		-					
Meta	782		700					
Para	817		-					
Oxygen Group								
Ether				1100				
Alcohol				1100	3100			
Carbonyl Compounds						1750		
Aldehyde	2700					1730		
Ketone						1700		
Ester				1200		1740		
Carboxlic Acid					3100	1720		
Nitrogen Groups								
Amide						1640	3200	
Amine							3300	
Nitrile								2250



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