ANDERSON SERANGOON JUNIOR COLLEGE
H3 CHEMISTRY
INFRA-RED (IR) SPECTROSCOPY

CONTENT

LEARNING OUTCOMES

Students should be able to:

(a) explain the origin of IR spectroscopy in simple molecules in terms of
  (i) stretching vibrations
  (ii) bending vibrations [detailed knowledge of instrumentation is not required]

(b) predict the number of IR absorptions for a given simple molecule (e.g. CO_2 or SO_2), and identify the molecular vibrations which give rise to them

(c) identify characteristic IR absorptions in the IR spectrum of a compound which may contain different functional groups [Absorptions of common functional groups will be provided in the Data Booklet.]

(d) suggest structures for a compound from its IR spectrum

(e) predict the characteristic IR absorptions that will be present in the IR spectrum of a compound, given its structure

1. INTRODUCTION

Infra-Red (IR) spectroscopy covers the IR radiation of the electromagnetic spectrum that has a longer wavelength and lower energy than visible light. The energy available is insufficient to cause electronic transitions, but it is enough to cause molecular vibrations and rotations.

Molecules are not motionless entities with the rigid bond lengths and angles that we are used to seeing in books. The atoms in a molecule actually display periodic motions known as vibrations, which arise from the bending or stretching of bonds.

1.1 Basic Principle

The absorption of IR is, like other absorption processes, a quantized process. A molecule absorbs only selected frequencies (energies) of IR radiation. The absorption of IR corresponds to energy changes in the order of 8 to 40 kJ/mol. Radiation in this energy range corresponds to the range encompassing the stretching and bending vibrational frequencies of the bonds in most covalent molecule.

In other words, the absorption of IR radiation is associated with small energy differences in the possible vibrational states / energy levels (i.e. stretching and bending of bonds). If the frequency of the radiation matches the energy gap between vibrational energy levels of the molecule, radiation will be absorbed, causing a change in the amplitude of molecular vibration.

Note, a molecule will absorb IR radiation corresponding to the frequency of the bond's natural vibration only if that particular mode of vibration causes the dipole moment of the molecule to change.

Using information on the absorptions, IR spectroscopy can be used to identify specific functional groups present in a molecule.

2 MOLECULAR VIBRATIONS

2.1 Types of Molecular Vibrations

The relative positions of atoms in a molecule are not fixed but instead fluctuate continuously as a consequence of a multitude of different types of vibrations and rotations about the bonds in the molecule.

Vibrations fall into the basic categories of stretching and bending. A stretching vibration involves a continuous change in the interatomic distance along the axis of the bond between the two atoms. Bending vibrations are characterised by a change in the angle between two bonds and are of the four types: scissoring, rocking, wagging and twisting.

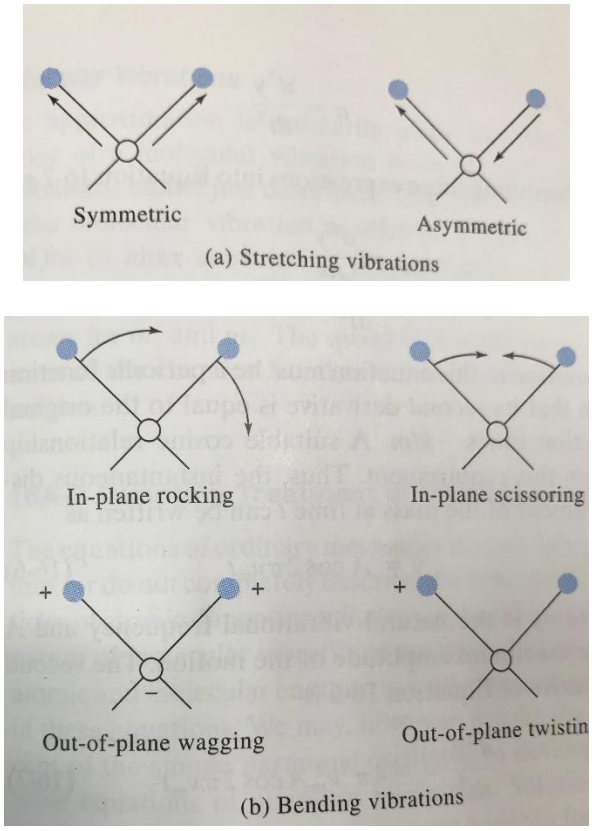


Figure 1
Type of molecular vibrations. Note that + indicates motion from the page towards the reader and – indicates motion away from the reader.

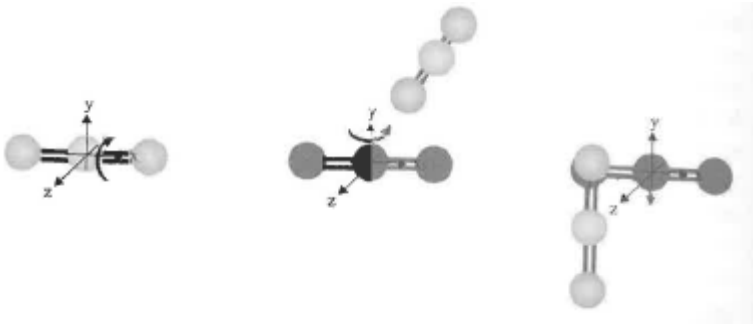
2.2 Number of vibrational modes

A molecule can move freely about in one of the three ways – translation, rotation and vibration. Each of these motions involves a change in the position and orientation of the atoms in the molecule in space. To describe a motion, we make use of the Cartesian coordinate axes (x, y and z). Hence a polyatomic molecule containing N atoms has 3N degrees of freedom when we treat each of the N atoms to be moving independently from each other.

Regardless of the value of N, any molecule will have three degrees of freedom attributed to the translational motion along the three Cartesian axes.

For a non-linear molecules, the other 3 degrees of freedom correspond to rotation about each axis. For a H_2O molecule, its rotation is depicted as:

But for a linear molecule, such as CO_2, there are only two degrees of freedom pertaining to rotation about the axes. As shown below, rotating the molecule along the x-axis, in which the atom lie, does not displace any atom from its position and hence does not count towards one degree of freedom.



Hence, subtracting the translational and rotational degrees of freedome (six for a non-linear molecule and five for a linear molecule) from the total 3N degrees of freedom will give us the vibrational degrees of freedom.

Type of degrees of freedom	*Linear*	*Non-linear*
Total	3N	3N
Translational	3	3
Rotational	2	3
Vibrational	**3N – 5**	**3N – 6**

Knowing the number of fundamental vibrations allow us to predict the number of absorption peaks in an IR spectrum. But the number of peaks observed may be fewer than expected. This is because in order for a particular vibrational mode to be IR active, the vibrational mode must involve a change in net dipole moment of the molecule during the vibration. In addition, the energy levels of some vibration modes may be too close to each other such that the different peaks become convoluted.

2.3 Predicting the number of IR absorption

<table>
<tr><th>Molecule type</th><th>Example</th><th>No. of vibration modes</th><th>Vibrations and IR absorptions involved</th></tr>
<tr><td rowspan="2">diatomic</td><td>HCl
(polar)</td><td></td><td></td></tr>
<tr><td>O=O
(non polar)</td><td></td><td></td></tr>
<tr><td>triatomic</td><td>Non linear

H_2O</td><td></td><td></td></tr>
<tr><td></td><td>Linear

CO_2</td><td>3(3) – 5 = 4</td><td>Two IR absorptions:
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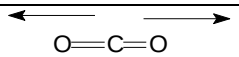
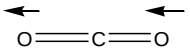
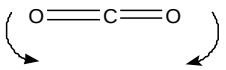
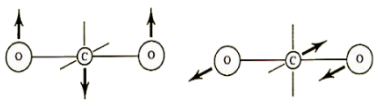
<tr><td> 
</td><td>The _____ mode results in no change in overall dipole of the molecule.

This is because the change in one of the C=O bond dipole on stretching is exactly compensated by the change in the other C=O bond dipole. Hence this vibrational mode is not IR active.</td></tr>
<tr><td> 

asymmetrical stretching</td><td>_____ mode causes one IR absorption.</td></tr>
<tr><td> 

bending</td><td>There are _____ modes.

However, they have the same energy (i.e. they are degenerate) as the two bending modes as similar motions that only differ in the plane in which they occur.
=> 1 IR absorption observed.
  </td></tr>
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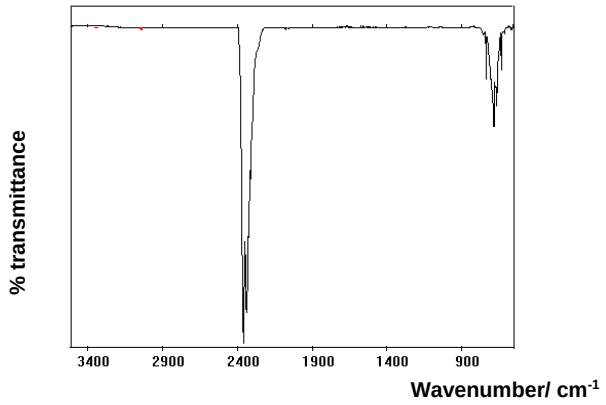
			IR spectrum of CO_2 

3 INTERPRETATION OF IR SPECTRUM

IR spectra is plotted as a graph of transmittance against wavenumber (cm^{-1}). *Wavenumbers* is the reciprocal of the wavelength in cm, or the number of wavelengths per cm.

$$\text{Wavenumber, } \tilde{\nu}\ (cm^{-1}) = \frac{1}{\lambda\ (cm)}$$

The higher the wavenumer, the higher the energy involved.

Wavenumber is related to frequency (Hz) as follows:

$f = c \times 1/\lambda$ where $c = 3 \times 10^{10}$ cm s^{-1}

We can use the IR absorption frequencies to determine <u>bond types</u> and <u>functional groups</u> in an organic compound. Full interpretation of an IR spectrum is almost impossible because most organic molecules are so large resulting in many complicated absorbances. It is important **not to over-interpret IR spectra.**

The useful IR region is from 4000 – 400 cm^{-1}. The lower frequency part of the spectrum (1500 cm^{-1} to around 400 cm^{-1}) of a molecule is called the "**fingerprint region**". This part serves as a **unique fingerprint of a specific compound**.

The following table lists various absorption peaks that can be associated with particular bonds.

7 Characteristic infra-red absorption frequencies for some selected bonds

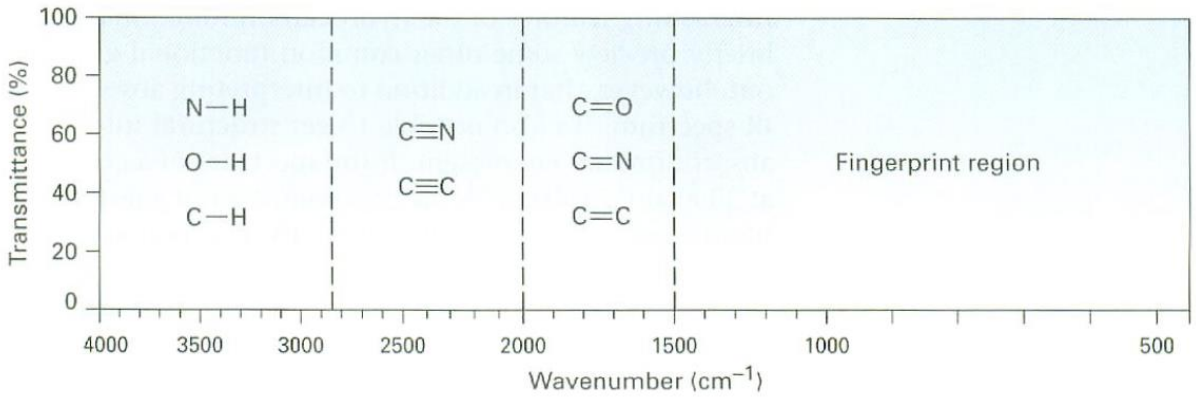
Bond	Functional groups containing the bond	Absorption range (in wavenumbers) / cm^{-1}	Appearance of peak (*s = strong, w = weak*)
C–C*l*	chloroalkanes	700–800	***s***
C–O	alcohol ether ester carboxylic acids	970–1260 1000–1310 1050–1330 1210–1440	***s*** ***s*** ***s*** ***s***
C=C	aromatic alkenes	1475–1625 1635–1690	***s*** ***w***
C=O	amides ketones and aldehydes carboxylic acids esters	1640–1690 1670–1740 1680–1730 1710–1750	***s*** ***s*** ***s*** ***s***
C≡C	alkynes	2150–2250	***w*** unless conjugated
C≡N	nitriles	2200–2250	***w***
C–H	alkanes, CH_2–H alkenes/arenes, =C–H	2850–2950 3000–3100	***s*** ***w***
N–H	amines, amides	3300–3500	***w***
O–H	carboxylic acid, RCO_2–H H-bonded alcohol/phenol, RO–H free alcohol, RO–H	2500–3000 3200–3600 3580–3650	***s*** and very broad ***s*** ***s*** and sharp

Some generalisation:

- Alkanes, alkenes and arenes show C-H stretches around 2800-3100 cm^{-1}. Absorptions above 3000 cm^{-1} due to =C-H stretches is a good indication the presence of aromatic rings.

- Broad and strong peaks around 2500-3000 cm^{-1} region could be due to O-H stretch in RCOOH. Presence of relative broad and strong or weak peaks around similar region of 3000-3500 cm^{-1} could be due to O-H and N-H stretches are in alcohols, amines or amides. Hence, use of other data may be required to confirm the structure.

- Strong absorption around 1600-1800 cm^{-1} indicate the presence of C=O. C=O in esters tend to have higher waveumber.



3.1 Factors affecting the IR absorption frequencies

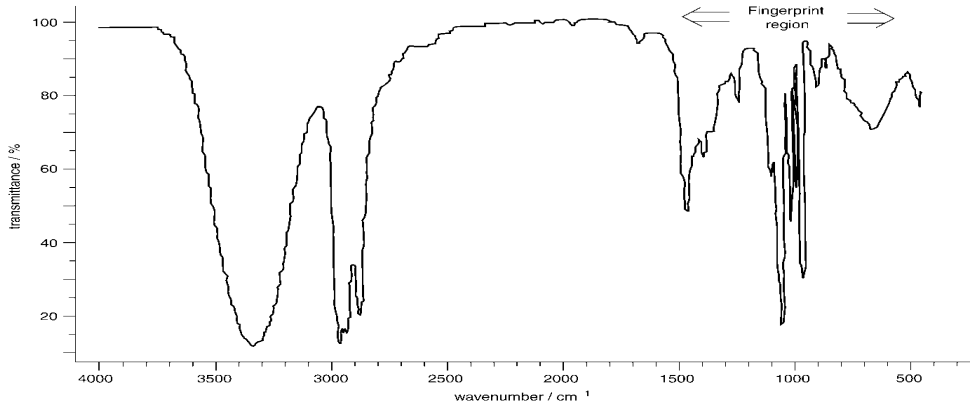
A bond can be modelled as a spring between 2 atoms.

(i) Type of vibration
More energy is required to stretch than to bend a spring. IR absorptions due to bending modes occur at lower wavenumbers than that of stretching modes.
E.g. C-H stretch in an alkane: 2600 – 2800 cm^{-1};
C-H bend in an alkane: 1365 – 1485 cm^{-1}

(ii) Bond order
The stronger the bond, the stiffer the spring. More energy is required to stretch multiple springs connected in parallel as compared to a single spring. The higher the bond order, the more energy required for vibration and hence higher wavenumbers for the IR absorption.
E.g. C≡C: 2150 – 2250 cm^{-1}; C=C (alkene): 1635 – 1690 cm^{-1}

(iii) Mass of atoms
The lighter the masses at the end of a spring, the quicker the vibration. This means that lighter masses vibrate at a higher frequency than heavier ones. Bonds containing a hydrogen atom (e.g. O-H, N-H, C-H), the lightest atom, vibrate at high frequencies in the region of 2500 – 4000 cm^{-1}.

3.2 Example – IR spectrum of propan-1-ol



Wavenumber of absorbance / cm^{-1}	**Interpretation (bond, functional group responsible)**
at 3350 cm^{-1}	Broad and strong peak peak due to O-H bond stretch
2800-3000 cm^{-1}	Strong peaks due to C-H stretch vibrations.
Between 1500 cm^{-1} and 500 cm^{-1}	This is the “fingerprint region”. Most of the peaks here cannot be associated with any particular bond, but the **pattern is unique** to propan-1-ol.

4 CHARACTERISTIC IR ABSORPTION FREQUENCIES