Materials Characterisations

1. Intro- Monday 3rd Feb

1.1. Polymers

You can characterise polymers at either:

1) Molecular Level: chemical composition chain structure via infra red/Raman spectroscopy (functional groups), nuclear magnetic resonance (functional groups), gel permeation chromatography (molecular weight and distribution)
2) Bulk: morphology, properties via x-ray diffraction/scattering (crystallinity/composition), differential scanning calorimetry (thermal properties), +ONE MORE

Infrared radiation & interaction w/ matter

Insert picture

High energy → low energy: Ionisation -> finish

Electromagnetic waves

Remember: oscillating charge → change in electric and magnetic field i.e. → electromagnetic wave

Summary

Polymer = macromolecule composed of many repeat unit
EM waves = radiating E. depending on their E, they will interact differently with matter.

1.2. Intro to characterisation

Characterisation = refers to the broad & general process by which a materials structure & properties are probed & measured. = fundamental process in materials.

FEG SEM = field emission gun
TEM = transmission electron microscopy

2 imaging moulds w/SEM = secondary electron imaging, backscattered electron imaging

Analysis: EBSD = electron backscattered diffraction – for phase identification & orientation measurement (grains)
EDS = energy dispersive spectroscopy – chemical composition

What can we study in SEM?

Topography & morphology (imaging)/rough or smooth?
Chemistry (need to use EDS with)
Crystallography (EBSD) - orientation & crystallography
Orientation of grains (EBSD)
In-situ experiment: reaction w/atmosphere, effects of temp, mechanical testing (e.g. micro bending test) – not tested

= focused beam of electrons is scanned across region of sample. Images formed via signal detected at each point the beam scans.

Magnification: M = L (screen size? - fixed no) / l (scanning length)

Secondary phases, sem

2. IR & Raman Spectroscopy - Monday 10th Feb

IR = causes vibrational & rotational transitions in molecules
For absorption = Hz of radiation corresponds to Hz of vibration in molecule

IR radiation range:
- Far-IR: 300-10 cm^{-1};
- Mid-IR: 4.000-300 cm^{-1}
- Near-IR: 14.000-4.000 cm^{-1}

Low transmittance = high absorption of that particular wavelength

Energy of molecule = absorption Hz

1. Theory of Infrared Absorption

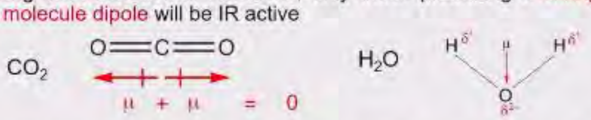
NUMBER OF VIBRATIONS: DEGREES OF FREEDOM OF A MOLECULE

A molecule consisting of *n* atoms has a total of 3*n* degrees of freedom, corresponding to the Cartesian coordinates of each atom.

Linear molecule: 2 rotational degrees (rotation around own axis leave molecule unchanged)
3 translational degrees
the rest (3n – 5) are fundamental vibrations

Non-linear molecule: 3 rotational degree
3 translational degree
the rest (3n – 6) are fundamental vibrations

Among the fundamental vibrations, only those producing a change in the molecule dipole will be IR active



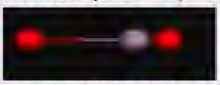
Homonuclear diatomic molecules (like H_2, N_2, Cl_2,etc) have (3*2 – 5) = 1 fundamental vibration, that doesn't change the molecule dipole, so they will be IR inactive

Linear Triatomic Molecule : CO_2

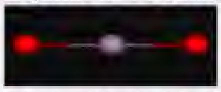
If we consider a linear molecule like CO_2:

3 atoms: (3*3) = 9 degree of freedom,

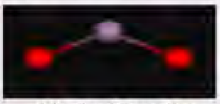
of which (3*3 – 5) = 4 fundamental vibrations



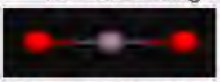
Asymmetric stretching



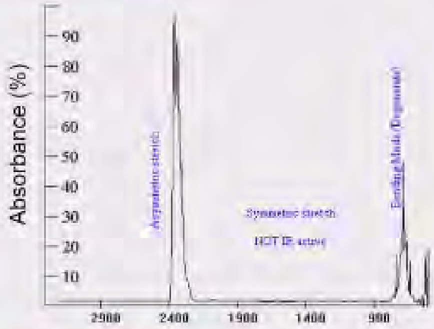
Symmetric stretching



Vertical bending



Horizontal bending



Bending vibrations usually occurs at **lower energy** (lower wavenumber) compared to stretching vibration

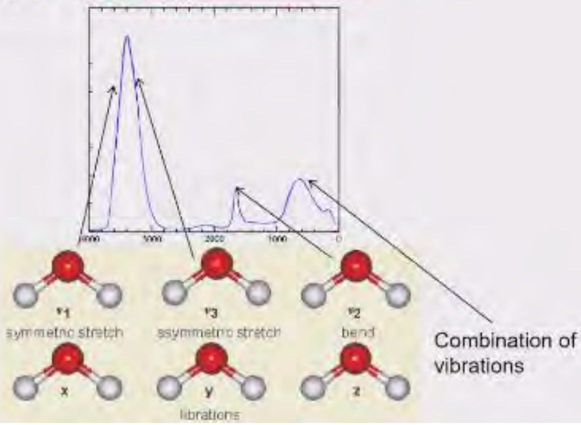
http://www.chemtube3d.com/vibrationsCO2.htm

Non-Linear Triatomic Molecule : H_2O

If we consider a non-linear molecule like H_2O:

3 atoms: (3*3) = 9 degree of freedom,

of which (3*3 – 6) = 3 fundamental vibrations



Generic $-CH_2-$ Fragment

More than 3 atoms involved, (3n – 6) does not apply!

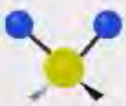
Asymmetrical stretching

Symmetrical stretching

Rocking (bending)

Scissoring (bending)

Twisting (bending)



Wagging (bending)

Energy of Vibrations: Harmonic Oscillator Model

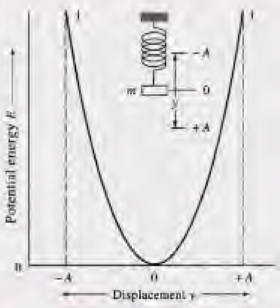
The stretching frequency of a bond can be approximated using the harmonic oscillator model:

Hooke's law: $F = -ky = ma = m\frac{d^2x}{dt^2}$

$y = A\cos(2\pi\nu - \varphi) \qquad E_p = \frac{1}{2}ky^2$

$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad \bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{m}}$

ν = frequency of vibration
$\bar{\nu}$ = wavenumber
k = force constant of spring
m = mass
y = displacement



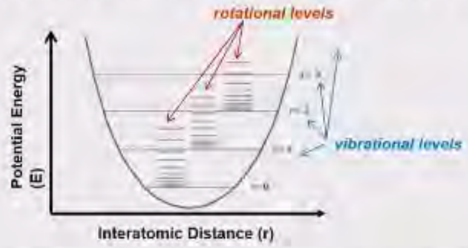
For two masses attached to a spring:

$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

With μ= reduced mass: $\mu = \frac{m_1 m_2}{m_1 + m_2}$

The model gives good estimation for the absorption, however the real values will be shifted and/or will give bands (instead of discrete lines) because:

- presence of rotational motions coupled with vibrational motions.



- Additional bands can appear due to overtones (multiples of the fundamental absorption) and combination of fundamental frequencies

- **Isotopic effect** – changes in reduced mass

1.What does happen in matter when we hit it with Infrared Radiation?

Bonds between atoms absorb some of the wavelengths and they vibrate faster; the wavelengths they absorb will depend upon the type of bond (single/double/triple) and the nature of the two atoms involved

2.What kind of information can we obtain from IR Spectroscopy?

In first instance, information about the functional groups present by looking mostly at the left part of the spectrum. If we have a database of IR spectra, we can try to find an exact match looking at the most complex right part

2.1. IR -17th Feb

<u>IR</u>

In industry – quality control and dynamic measurements

Forensic – identification for criminal and civil cases
Non destructive technique
Fast analysis

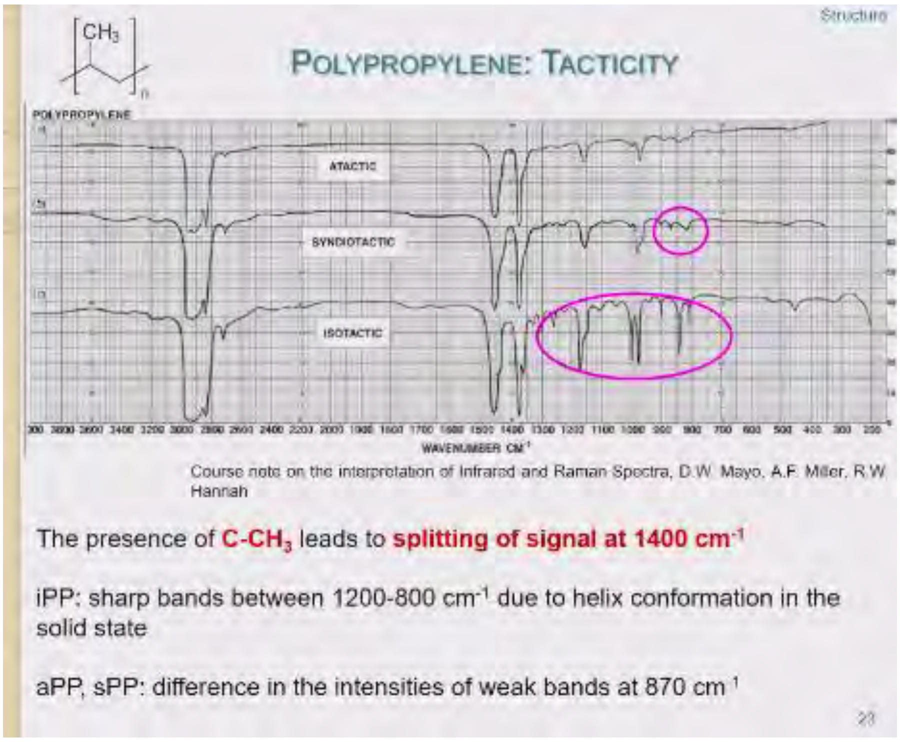
Good quality: intensity not too high or too low, resolution and background

Since C-C is symmetrical (lower dipole change), weak aborptions

<u>Tacticity</u>

= arrangement in space of side-groups on polymer

Isotactic = same side
Syndiotactic = alternating
Atactic = random



<u>Additives</u>