Isolation and Purification of Organic Compounds
<table>
<thead>
<tr>
<th>Technique</th>
<th>Aim</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Filtration</td>
<td>To separate an insoluble solid from a liquid (slow)</td>
</tr>
<tr>
<td>2. Centrifugation</td>
<td>To separate an insoluble solid from a liquid (fast)</td>
</tr>
<tr>
<td>3. Recrystallization</td>
<td>To separate a solid from other solids based on their different solubility in suitable solvent(s)</td>
</tr>
<tr>
<td>4. Solvent extraction</td>
<td>To separate a component from a mixture with a suitable solvent</td>
</tr>
<tr>
<td>5. Distillation</td>
<td>To separate a liquid from a solution containing non-volatile solutes</td>
</tr>
<tr>
<td>Technique</td>
<td>Aim</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>6. Fractional distillation</td>
<td>To separate miscible liquids with widely different boiling points</td>
</tr>
<tr>
<td>7. Steam distillation</td>
<td>To separate liquids which are <strong>immiscible with water</strong> and decompose easily below their boiling points</td>
</tr>
<tr>
<td>The mixture boils below 100°C</td>
<td></td>
</tr>
<tr>
<td>8. Vacuum distillation</td>
<td></td>
</tr>
<tr>
<td>9. Sublimation</td>
<td>To separate a mixture of solids in which only one can sublime</td>
</tr>
<tr>
<td>10. Chromatography</td>
<td>To separate a complex mixture of substances (large/small scale)</td>
</tr>
</tbody>
</table>
Tests for Purity

- If the substance is a **solid**, its *purity* can be checked by determining its *melting point*.
- If it is a **liquid**, its *purity* can be checked by determining its *boiling point*.

Chromatography for Complex Mixtures
Use of Infra-red Spectroscopy in the Identification of Functional Groups
Infra-red Spectroscopy

Arises from absorption of IR radiation by organic compounds

Causes atoms and groups of atoms of organic compounds to vibrate with increased amplitude about the covalent bonds that connect them
Modes of vibrations

Two basic modes: stretching and bending

Two atoms joined by a covalent bond can undergo a stretching vibration where the atoms move back and forth as if they were joined by a spring.

![Diagram showing stretching vibration](image)
Modes of vibrations

Symmetrical stretching:

Asymmetrical stretching:
Modes of vibrations

Bending (scissoring): - two modes

- Behind paper
- Out of paper
Modes of vibrations

Symmetric stretching

Asymmetric stretching

An in-plane bending (scissoring)

An out-of-plane bending (twisting)

Rocking

Wagging
The **frequency** \( (\nu) \) of a given stretching vibration of a covalent bond depends on

\[
\nu \propto \sqrt{\frac{k}{\mu}}
\]

For a diatomic molecule \( X - Y \)

\[
\mu = \frac{m_x m_y}{m_x + m_y}
\]

**Bond strength**

**Reduced mass of the system**
Bond strength $\uparrow$

$\Rightarrow k \uparrow$

$\Rightarrow \nu \uparrow$

$C - C < C = C < C \equiv C$

$C - O < C = O$

Increasing frequency of vibration

$\nu \propto \sqrt{\frac{k}{\mu}}$
Masses of bonding atoms ↓

$\Rightarrow \mu \downarrow$

$\Rightarrow \nu \uparrow$

$\sqrt{k}/\mu$

$\nu \propto \sqrt{k}/\mu$

Chemical bonds containing H atoms have high frequency of vibration due to the small mass of H
Infra-red Spectroscopy

- Molecular vibrations are quantized; the molecules absorb IR radiation of a particular amount of energy only.

\[ E = h\nu \]

- Only IR radiation with the same frequency as the vibrational frequency can be absorbed by the molecules.
Infra-red Spectroscopy

After the absorption of a quantum of energy ($h \nu$), the amplitude of vibration ↑ but the frequency of vibration ($\nu$) remains unchanged.

$$E = h \nu$$
The electromagnetic spectrum

Wavelength (m) →

← Frequency (Hz / s⁻¹)

UV / visible / Near IR → electronic transition
The electromagnetic spectrum

Wavelength (m) →

← Frequency (Hz / s⁻¹)

Mid IR → vibrational transition
The electromagnetic spectrum

Wavelength (m) →

← Frequency (Hz / s⁻¹)

Far IR / microwave → rotational transition
Important: As the wavelength gets shorter, the energy of the radiation increases.
Infra-red Spectroscopy

• Different functional groups (e.g. C=O, O-H) have different vibration frequencies
  → They have characteristic absorption frequencies

• Functional groups can be identified from their characteristic absorption frequencies
Infra-red Spectroscopy

• The stretching vibrations of single bonds involving hydrogen (C—H, O—H and N—H) occur at relatively high frequencies

<table>
<thead>
<tr>
<th>Bond</th>
<th>Range of wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—H</td>
<td>2840 - 3095</td>
</tr>
<tr>
<td>O—H</td>
<td>3230 - 3670</td>
</tr>
<tr>
<td>N—H</td>
<td>3350 - 3500</td>
</tr>
</tbody>
</table>

Characteristic absorption wavenumbers of some single bonds in infra-red spectra
**Infra-red Spectroscopy**

- Triple bonds are **stronger** and vibrate at **higher frequencies** than double bonds

<table>
<thead>
<tr>
<th>Bond</th>
<th>Range of wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C \equiv C)</td>
<td>2070 - 2250</td>
</tr>
<tr>
<td>(C \equiv N)</td>
<td>2200 - 2280</td>
</tr>
<tr>
<td>(C = C)</td>
<td>1610 - 1680</td>
</tr>
<tr>
<td>(C = O)</td>
<td>1680 - 1750</td>
</tr>
</tbody>
</table>

Characteristic absorption wavenumbers of some double bonds and triple bonds in infra-red spectra
Infra-red Spectroscopy

• An IR spectrum is obtained by scanning the sample with IR radiations from $1.2 \times 10^{13}$ Hz to $1.2 \times 10^{14}$ Hz

Or,

Wavenumber : $400 \text{ cm}^{-1}$ to $4000 \text{ cm}^{-1}$

wavenumber (cm$^{-1}$) = $\frac{1}{\lambda} = \frac{\nu}{c}$

• % transmittance rather than absorbance is displayed
Dips (peaks) show absorptions by functional groups

Cyclic hexene

$\text{C}_6\text{H}_{10}$

$\text{C}=\text{C}$
IR spectrum of propanal

Band region

Fingerprint region
Infra-red Spectroscopy

- Infra-red spectrometer is used to
  - measure the amount of energy absorbed at each wavelength of the IR region
Infra-red Spectroscopy

- A beam of IR radiation is passed through the sample
- the intensity of the emergent radiation is carefully measured
- The spectrometer plots the results as a graph called infra-red spectrum
- shows the absorption of IR radiation by a sample at different frequencies
Use of IR Spectrum in the Identification of Functional Groups

- When a compound absorbs IR radiation,
  - the intensity of transmitted radiation decreases
  - results in a decrease in percentage of transmittance
  - a dip in the spectrum
  - often called an absorption peak or absorption band
Use of IR Spectrum in the Identification of Functional Groups

- In general, an IR spectrum can be split into **four regions** for interpretation purpose
<table>
<thead>
<tr>
<th>Range of wavenumber (cm(^{-1}))</th>
<th>Interpretation</th>
</tr>
</thead>
</table>
| 400 – 1500                       | • Often consists of many **complicated bands** (*stretching and bending*)  
|                                  | • **Unique** to each compound  
|                                  | • Often called the **fingerprint region**  
|                                  | • **Not used for identification of particular functional groups** |
| 1500 – 2000                      | Absorption of **double bonds**,  
|                                  | e.g. \(C = C, C = O\) |
| 2000 – 2500                      | Absorption of **triple bonds**,  
|                                  | e.g. \(C \equiv C, C \equiv N\) |
| 2500 – 4000                      | Absorption of **single bonds involving hydrogen**, e.g. \(C \rightleftharpoons H, O \rightleftharpoons H, N \rightleftharpoons H\) |
Use of IR Spectrum in the Identification of Functional Groups

- The region between 4 000 cm\(^{-1}\) and 1 500 cm\(^{-1}\) is often used for identification of functional groups from their characteristic absorption wavenumbers.
**What is the characteristic range of wavenumber of $C=\text{N}$ bond?**

**Bond strength/wavenumber : $C=C < C=\text{N} < C=\text{O}$**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Characteristic range of wavenumber (cm$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>Alkenes</td>
<td>$C = C$</td>
<td>1610 – 1680</td>
</tr>
<tr>
<td>Aldehydes, ketones, acids, esters</td>
<td>$C = O$</td>
<td>1680 – 1750</td>
</tr>
<tr>
<td>Alkynes</td>
<td>$C \equiv C$</td>
<td>2070 – 2250</td>
</tr>
<tr>
<td>Nitriles</td>
<td>$C \equiv N$</td>
<td>2200 – 2280</td>
</tr>
<tr>
<td>Acids (hydrogen-bonded)</td>
<td>$O \rightleftharpoons H$</td>
<td>2500 – 3300</td>
</tr>
<tr>
<td>Alkanes, alkenes, arenes</td>
<td>$C \rightleftharpoons H$</td>
<td>2840 – 3095</td>
</tr>
<tr>
<td>Alcohols, phenols</td>
<td>$O \rightleftharpoons H$</td>
<td>3230 – 3670</td>
</tr>
<tr>
<td>(hydrogen-bonded)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary amines</td>
<td>$N \rightleftharpoons H$</td>
<td>3350 – 3500</td>
</tr>
</tbody>
</table>
Strategies for the Use of IR Spectra in the Identification of Functional Groups

1. **Focus** at the IR absorption peak **at or above** 1500 cm\(^{-1}\)

   ➔ Concentrate initially on the **major absorption peaks**
Strategies for the Use of IR Spectra in the Identification of Functional Groups

2. The absence and presence of absorption peaks at some characteristic ranges of wavenumbers are equally important.

- the absence of particular absorption peaks can be used to eliminate the presence of certain functional groups or bonds in the molecule.
Limitation of the Use of IR Spectroscopy in the Identification of Organic Compounds

1. Some IR absorption peaks have very close wavenumbers and the peaks always coalesce.

2. Not all vibrations give rise to strong absorption peaks.
3. **Not all absorption peaks** in a spectrum can be associated with a **particular bond or part of the molecule**

4. **Intermolecular interactions** in molecules can result in **complicated infra-red spectra**
Absorption Slightly above 3000 cm\(^{-1}\)

Alkene Arene

1680-1750 cm\(^{-1}\)

1610-1680 cm\(^{-1}\)

C=C bonds in benzene are weaker ⇒ ~1610 cm\(^{-1}\)
Aldehyde, Ketone, Ester

Carboxylic acid

Y

Broad
2500-3300 cm\(^{-1}\)

Y

Y

Contain oxygen

N

1680-1750 cm\(^{-1}\)

N

2070-2280 cm\(^{-1}\)

Aldehyde: lower C-H absorption at 2720-2820 cm\(^{-1}\)
2070-2280 cm\(^{-1}\) contains nitrogen

Nitrile
2200-2280 cm\(^{-1}\)

Contain nitrogen

Y

2070-2250 cm\(^{-1}\) for terminal alkyne, \(-\text{C}≡\text{C-H}\)

Additional sharp peak \(~3250\text{ cm}^{-1}\) for terminal alkyne, \(-\text{C}≡\text{C-H}\)

3200-3700 cm\(^{-1}\)
Amine (3350-3500 cm⁻¹)

Contain nitrogen

Y

Alcohol, phenol (3230-3700 cm⁻¹)

Contain oxygen

N

3200-3700 cm⁻¹

N

Alkane (2840-3000 cm⁻¹)

Single peak for 2° amine; double peaks for 1° amine
Several peaks (2840-3000 cm\(^{-1}\)) due to different modes of Symmetrical & asymmetrical stretching

Different modes of C-H bending (~1400 cm\(^{-1}\))
Q.82
Q.82
Q.82

[Diagram of infrared spectra with labels for OH, C=O, C-O, and chemical structures for compounds with these functionalities.]
Q.83

2840-3000

2720-2820

NEAT

C=O

NEAT

C=O
Q.83

\[ \text{2840-3000} \quad \text{2720-2820} \]

NEAT

\[ \text{CH}_3\text{CH}_2\text{CH}_2-\text{CH} \]

C=O

\[ \text{CH}_3\text{CH}_2-\text{C}-\text{CH}_3 \]

C=O

NEAT