Section 2.9 Physical Properties of Organic Molecules

States of Matter:
- Gas
- Liquid
- Solid

Density, Solubility, mp, BP

What factor determines? => Intermolecular Forces/Attractions

Between molecules

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3 & \quad \text{CH}_3\text{CH}_2\text{OH} \\
\text{BP} = -42 \degree C & \quad \text{BP} = 78 \degree C \\
\text{Gas} & \quad \text{Liquid}
\end{align*}
\]

Gas \Rightarrow BP below 25 \degree C
Liquid BP 25 \Rightarrow 300 \degree C
Solids melting point (mp) above room temp.

Types of Intermolecular Attractions

- Small separation => weak forces
- Intermediate forces
- Strong

Van der Waals

\[
\begin{align*}
\text{C} & \quad \text{Cl} \\
\text{I} & \quad \text{S} \\
\text{S} & \quad \text{Cl}
\end{align*}
\]

Very small charges => (gas)

Strong intermolecular attractions \Rightarrow High mp/BP \Rightarrow Solids

Weak intermolecular attractions \Rightarrow Low BP \Rightarrow Gas

‘Shape’ of molecules:

Higher BP?
Surface area more \Rightarrow Higher BP

Branching
Solubility Rule → "Like dissolves like" — in regards to polarity.

Solubility in H₂O

Solubility in Alkanes (Hexane)

Biological Interactions

Glucose — Sugar

Serotonin

Binding site

Imitrex
How do we 'see' molecules

**Mass Spectroscopy (MS)**

1. **High Energy**
2. **Electron Beam**
3. **Electron**
4. **Molecule (M)**
5. **Lose 1e⁻**
6. **M⁺**
7. **Unstable**

**MW = 120**

**The mass spectrometers can measure the mass of a cation**

**Fragmentation**

**Parent ion**

**MW 120**

**Base peak** (Tallest)

**m-15 → methyl group**

**m-29 → CH₂CH₃**

**Mass Spectroscopy (MS)**

- **Infrared Spectroscopy (IR)**
- **Nuclear Magnetic Resonance (NMR)**

**m⁺ = radical (unpaired e⁻)**

**Cation**

**m/2 = 15**

**m/2 = 105**

**m/2 = 77**

**120/1 = 120**
Isotopes

Carbon 12/carbon 13

$^{12}C$  $^{13}C$

Halogens  

Br $\rightarrow$ Cl

79 Br 50% 35 Cl $\sim$ 65%

81 Br 50% 37 Cl $\sim$ 35%

Alcohol Fragmentations

+ CH$_2$  →  CH$_3$CH$_2$  

A cleavage  

Loss of H$_2$O

$^{1}H$ $^{1}O$ $^{1}O$ $^{1}N$ $^{1}H$

$^{1}C$ $^{1}C$ $^{1}C$ $^{1}C$ $^{1}C$

$^{1}H$ $^{1}H$ $^{1}H$ $^{1}H$ $^{1}H$

All compounds have unique fragmentation patterns.
How do we 'see' molecules → New eyes

1) Mass Spectroscopy (MS)
2) Infrared Spectroscopy (IR)
3) Nuclear Magnetic Resonance (NMR)

**Mass Spectroscopy**

\[ M \text{ (molecule)} \rightarrow M^+ + e^- \]

Example

\[
\begin{align*}
\text{C}_8\text{H}_8\text{O} \\
\text{MW} = 120
\end{align*}
\]

A mass spectrometer can measure the mass of cations (must have charge)

**Fragmentation**

High energy

Radical

\[ \text{MW} = 120 \]

\[ \text{MW} = 77 \]

What is its fate?

Molecular ion → Parent ion

Base peak = most abundant (largest) tail

**Spectrum**

<table>
<thead>
<tr>
<th>Mass/Abundance</th>
<th>15</th>
<th>43</th>
<th>77</th>
<th>105</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>M Parent ion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Molecular ion+ peak</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
ISOtopes

Carbon 12/Carbon 13

12C 13C

M + 1 peak

Halogens Br and Cl

Br 58% → 79Br
50% → 81Br

Cl 35Cl ≤ 65%
37Cl ≤ 35%

Alcohol Fragmentations

α-cleavage → to the OH

CH₃CH₂CH₂CH₃ → CN₂CH₂⁺

MW 74

α-cleavage

All compounds have unique fragmentation patterns.

what info do we get from ms?

(Molecular weight)

Fragmentation → stable cations produced
Infrared spectroscopy

Spectroscopy: How matter interacts with light (electromagnetic radiation)

Light—Both particle and wave properties

\[ \text{spread out} \]

Light is spectrum of wavelengths (\( \lambda \)) and frequencies (\( \nu \))

\( \lambda \) and \( \nu \) relate to the energy of light:

\[ E = \frac{hc}{\lambda} \quad \text{or} \quad E = h\nu \]

\[\text{adsorb}\]

Organic Molecules absorb light in 'Infrared' region

If full energy is absorbed \( \rightarrow \) becomes one with The molecule

In IR we use wavenumbers \( \nu \) units \( \text{cm}^{-1} \)

IR region \( 400 \text{ cm}^{-1} \rightarrow 4000 \text{ cm}^{-1} \)

Lower energy \( \rightarrow \) higher energy

How do organic molecules interact with light?

- Absorb \( \rightarrow \) increase vibrational motion

Nature of the Bond C-H

[Diagram of C-H bond with stretching and bending arrows]
Bonds absorb light at different frequencies:

- \( \text{C} - \text{C} \sim 1000 \text{ cm}^{-1} \)
- \( \text{C} = \text{C} \sim 1600 - 1650 \text{ cm}^{-1} \)
- \( \text{C} = \text{C} \sim 2350 \text{ cm}^{-1} \) (High energy)
- \( \text{C} - \text{O} \sim 1000 \text{ cm}^{-1} \rightarrow 1300 \text{ cm}^{-1} \)
- \( \text{C} = \text{O} \sim 1650 \rightarrow 1750 \text{ cm}^{-1} \)
- \( \text{C} - \text{H} \sim 2900 - 3100 \text{ cm}^{-1} \)
- \( \text{O} - \text{H} \sim 3300 \text{ cm}^{-1} \)

How an IR spectrum will look —> absorption bands:

3 Things to note about each absorption band (characteristics):

1. Location cm\(^{-1}\) —> Type of bond —> look at charts

2. Intensity — How strong — How deep is the absorption
   - Polar bonds are intense
   - # of bonds determine intensity

3. Shape — Narrow OR Broad
   - O-H are usually broad
     - Hydrogen Bonding
What to Ignore in IR

What to look for/pay attention to: $\approx 1500$

- O-H stretch $\approx 3200$ broad $\vee$
- C=O stretch $\approx 1700$ strong $\pm 50 \text{ cm}^{-1}$
- C-H $2900-3100 \text{ cm}^{-1}$
- C=C $\approx 2300 \text{ cm}^{-1}$ (weak)
- C≡N $\approx 2100 \text{ cm}^{-1}$ (medium)
- N-H $\approx 3200 \text{ cm}^{-1}$ (medium)

Nuances:

- Conjugation of $\ce{C=O}$: lower by about $30 \text{ cm}^{-1}$
- C-H $\text{sp}^2$ and $\text{sp}^3$ differences
- $\text{sp}^3$ C-H $\approx 2900-3000 \text{ cm}^{-1}$
- Esters $\ce{\text{O=C-R}}$: $1730 \text{ cm}^{-1}$ higher
- O-H on acids $\ce{\text{H-O-C}}$: $1705 \text{ cm}^{-1}$
- $\text{sp}^2$ C-H $\approx 1600 \text{ cm}^{-1}$
- $\text{sp}^2$ C-H $\approx 1700 \text{ cm}^{-1}$ (very broad)
- Benzene $\approx 1500-2100 \text{ cm}^{-1}$ weak Band of Benzene
- $\ce{\text{C=O-N}}$ $\approx 1700 \text{ cm}^{-1}$
- $\ce{\text{C-O-H}}$ $\approx 3200-2500 \text{ cm}^{-1}$ much lower