13.21
Mass Spectrometry
Atom or molecule is hit by high-energy electron

Principles of Electron-Impact Mass Spectrometry
Atom or molecule is hit by high-energy electron

\[ e^- \]

electron is deflected but transfers much of its energy to the molecule
Atom or molecule is hit by high-energy electron

$e^{-}$

electron is deflected but transfers much of its energy to the molecule
This energy-rich species ejects an electron.
This energy-rich species ejects an electron, forming a positively charged, odd-electron species called the *molecular ion*.
Molecular ion passes between poles of a magnet and is deflected by magnetic field. The amount of deflection depends on the mass-to-charge ratio. The highest m/z is deflected the least, while the lowest m/z is deflected the most.

*Principles of Electron-Impact Mass Spectrometry*
If the only ion that is present is the molecular ion, mass spectrometry provides a way to measure the molecular weight of a compound and is often used for this purpose.

However, the molecular ion often fragments to a mixture of species of lower m/z.
The molecular ion dissociates to a cation and a radical.
The molecular ion dissociates to a cation and a radical.

Usually several fragmentation pathways are available and a mixture of ions is produced.
mixture of ions of different mass gives separate peak for each m/z

intensity of peak proportional to percentage of each ion of different mass in mixture

separation of peaks depends on relative mass
A mixture of ions of different mass gives separate peaks for each m/z.

The intensity of each peak is proportional to the percentage of each atom of different mass in the mixture.

The separation of peaks depends on the relative mass.
Some molecules undergo very little fragmentation

Benzene is an example. The major peak corresponds to the molecular ion.
Isotopic Clusters

93.4% all H are \(^1\text{H}\) and all C are \(^{12}\text{C}\)

6.5% one C is \(^{13}\text{C}\)

0.1% one H is \(^2\text{H}\)
Isotopic Clusters in Chlorobenzene

visible in peaks for molecular ion

$m/z$
**Isotopic Clusters in Chlorobenzene**

- No m/z 77, 79 pair; therefore ion responsible for m/z 77 peak does not contain Cl.
Alkanes undergo extensive fragmentation

Decane

CH$_3$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$

Relative intensity

m/z

0 20 40 60 80 100 120

Decane

43 57 71 85 99 142
Propylbenzene fragments mostly at the benzylic position
13.22
Molecular Formula
as a
Clue to Structure
**Molecular Weights**

CH₃(CH₂)₅CH₃  \[\text{Heptane}\]

CH₃CO \[\text{Cyclopropyl acetate}\]

**Molecular formula**

- CH₃(CH₂)₅CH₃: C₇H₁₆
- CH₃CO: C₅H₈O₂

**Molecular weight**

- CH₃(CH₂)₅CH₃: 100
- CH₃CO: 100

**Exact mass**

- CH₃(CH₂)₅CH₃: 100.1253
- CH₃CO: 100.0524

**Mass spectrometry can measure exact masses. Therefore, mass spectrometry can give molecular formulas.**
Knowing that the molecular formula of a substance is $\text{C}_7\text{H}_{16}$ tells us immediately that is an alkane because it corresponds to $\text{C}_n\text{H}_{2n+2}$.

$\text{C}_7\text{H}_{14}$ lacks two hydrogens of an alkane, therefore contains either a ring or a double bond.
Index of Hydrogen Deficiency

relates molecular formulas to multiple bonds and rings

\[
\text{index of hydrogen deficiency} = \frac{1}{2} \left( \text{molecular formula of alkane} - \text{molecular formula of compound} \right)
\]
Example 1

\[ \text{index of hydrogen deficiency} \]

\[ = \frac{1}{2} \left( \text{molecular formula of alkane} - \text{molecular formula of compound} \right) \]

\[ = \frac{1}{2} \left( \text{C}_7\text{H}_{16} - \text{C}_7\text{H}_{14} \right) \]

\[ = \frac{1}{2} \left( 2 \right) = 1 \]

Therefore, one ring or one double bond.
Example 2

\[ C_7H_{12} \]

\[ = \frac{1}{2} (C_7H_{16} - C_7H_{12}) \]

\[ = \frac{1}{2} (4) = 2 \]

Therefore, two rings, one triple bond, two double bonds, or one double bond + one ring.
Oxygen has no effect

\[ \text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{OH} \text{ (1-heptanol, C}_7\text{H}_{16}\text{O)} \text{ has the same number of H atoms as heptane} \]

\[ \text{index of hydrogen deficiency} = \frac{1}{2} (\text{C}_7\text{H}_{16} - \text{C}_7\text{H}_{16}\text{O}) = 0 \]

\[ \text{no rings or double bonds} \]
Oxygen has no effect

\[
\begin{align*}
\text{index of hydrogen deficiency} & = \\
\frac{1}{2} \left( \text{C}_5\text{H}_{12} - \text{C}_5\text{H}_8\text{O}_2 \right) &= 2 \\
\text{one ring plus one double bond}
\end{align*}
\]

Cyclopropyl acetate
If halogen is present

Treat a halogen as if it were hydrogen.

\[
\text{C}_3\text{H}_5\text{Cl}
\]

same index of hydrogen deficiency as for \(\text{C}_3\text{H}_6\)
Rings versus Multiple Bonds

Index of hydrogen deficiency tells us the sum of rings plus multiple bonds.

Catalytic hydrogenation tells us how many multiple bonds there are.