Mass Spectrometry

Can determine information about the molecular weight and molecular structure

Electron impact ionization

An electron is accelerated toward the sample
Upon collision, an electron is expelled from the molecule
The sample thus becomes charged
When a charged species passes through a magnetic field the flight path is bent.

The charged particle is attracted to one “pole” in the presence of a magnetic field, hence the path is bent.

The radius of curvature is m/z. Therefore lighter species bend more than heavier species with a given magnetic field.
In practice the magnetic field is adjusted to achieve a desired radius of curvature

By adjusting the magnetic field only a certain mass will be able to transverse the curvature and reach the detector, the absorbance can thus be plotted versus m/z for a given compound
The parent ion is called the molecular ion peak (M+). Can find molecular ion, but what are the other peaks?
The molecular ion peak can fragment

Due to the high energy of the radical/cation generated, this species can fragment

Remember only the charged species will be detected
(the radical species will not be affected by the magnetic field)

The probability of obtaining a given fragment is due to the STABILITY of the cations produced
Effect of Isotopes

Remember that an isotope has the same number of protons and electrons, but a different number of neutrons.

Since neutrons and protons are the “heavy” parts of an atom, the extra number of neutrons will cause a greater mass.

In a mass spectrometer we can see the effect of this by peaks above the molecular ion peak (M, M+1, M+2, etc.).
The ratio of these peaks is diagnostic for which atoms are present.

The natural abundance of isotopes is well known.

<table>
<thead>
<tr>
<th></th>
<th>M</th>
<th>M+1</th>
<th>M+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>98.9%</td>
<td>1.1%</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>95%</td>
<td>0.8%</td>
<td>4.2%</td>
</tr>
<tr>
<td>Cl</td>
<td>75.5%</td>
<td></td>
<td>24.5%</td>
</tr>
<tr>
<td>Br</td>
<td>50.5%</td>
<td></td>
<td>49.5%</td>
</tr>
<tr>
<td>I</td>
<td>100%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Can distinguish atoms by the ratio of peaks above the molecular ion

Especially useful to distinguish which halogen is present

\[
\begin{align*}
\text{Cl} & : m/z 78, M/M+2 = 3 \\
\text{Br} & : m/z 122, M/M+2 = 1 \\
\text{I} & : m/z 170
\end{align*}
\]
Nitrogen

Nitrogen is also diagnostic in a mass spectrum due to the odd/even parity of the mass

Consider small molecules and their corresponding mass

\[
\begin{align*}
\text{CH}_4 & \quad \text{m/z} = 16 \\
\text{NH}_3 & \quad \text{m/z} = 17
\end{align*}
\]

The molecular ion peak for a molecule with one nitrogen is always odd, all other common atoms in an organic compound yield an even mass
Fragmentation Behavior of Common Functional Groups

Alkenes

With an alkene the common fragmentation is to create an allylic carbocation

\[
\begin{align*}
\text{m/z 70} & \quad \text{m/z 55}
\end{align*}
\]
Alcohols
Two common effects

1) Loss of water

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\[
\begin{align*}
\text{[CH₃CH₂CH(OH)]}^{+} & \rightarrow \text{[CH₃CH=CH]}' + \text{H₂O} \\
\text{m/z 74} & \rightarrow \text{m/z 56}
\end{align*}
\]
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Alcohols

2) \( \alpha \)-cleavage

\[
\begin{array}{c}
\text{OH} \\
\text{C}_3\text{H}_7 \\
m/z 74
\end{array}
\xrightarrow{\cdot^+} \begin{array}{c}
\text{OH} \\
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
m/z 45
\end{array}
\]

+ \cdot \text{CH}_2\text{CH}_3
McLafferty Rearrangement

Any ketone containing a γ-hydrogen can rearrange to the enol form in a MS
Ketones can also do $\alpha$-cleavage similar to alcohols.
High Resolution Mass Spectrometry (HRMS)

These high sensitivity mass spectrometers, called HRMS, can be used to determine molecular formula

a HRMS can detect particle masses with an accuracy of 1/20,000 therefore > 0.0001 amu (atomic mass units)

Can use this to distinguish compounds with a similar rough mass but with a different molecular formula

\[
\begin{align*}
^{12}\text{C} & \quad 12.0000 \text{ amu (by definition)} \\
^{1}\text{H} & \quad 1.0078 \text{ amu} \\
^{16}\text{O} & \quad 15.9949 \text{ amu}
\end{align*}
\]
Differentiating Structures Using HRMS

Many structures may have the same integer value molecular weight, but different molecular formulas.

These structures can be differentiated with HRMS.

For example:

\[
\begin{align*}
\text{C}_4\text{H}_6\text{O}_1 & \quad 70.0418 \text{ amu} \\
\text{C}_5\text{H}_{10} & \quad 70.0783 \text{ amu} \\
\text{C}_3\text{H}_6\text{N}_2 & \quad 70.0531 \text{ amu}
\end{align*}
\]