Chapter 5. Mass spectrometry

ionization and fragmentation

\[
\text{\includegraphics[width=0.2\textwidth]{molecule.png}}
\]

• which fragmentations?
mass and frequency, m/z and count rate

Reading:
Pavia
Chapter 8
Don’t need 8.3 B-D, 8.4 B-D
Use the text to clarify what’s covered on the slides.
1. General

- not a spectroscopic technique (no absorption of radiation)

spectroscopy

\[ A \]

\[ \lambda, \nu, \nu \]

spectrometry

count rate

\[ m/z \]

count rate: usually in %

: “relative abundance”

\[ m/z: \text{mass-to-charge ratio, here } z = 1 \]

and: sample is often destroyed through fragmentation
2. Spectrometer

- simplest version: electron ionization, magnetic sector mass analyzer

desired event:
\[ M + e^- \rightarrow M^{++} + 2 \ e^- \]

from accelerator:
\[ E_{\text{kin}} = \frac{1}{2}mv^2 = eV = zV \]

in the analyzer:
\[ r = \frac{mv}{eB_0} \]
\[ \frac{m}{z} = \frac{m}{e} = \frac{B_0^2r^2}{2V} \]
3. Mass spectrum

- from electron ionization (EI)
  \[ M + e^- \rightarrow M^{**} + 2 \, e^- \]
- \( M^{**} \): radical cation (or cation radical)
  : often incorrectly called “molecular ion, \( M^+ \)”
  : often the last peak in the spectrum, largest m/z: gives molar mass
- most abundant fragment (relative 100%): “base peak”
- other peak intensities given as % of base peak
  - fragment “ions”
  - “isotope peaks”

Figure 8.38  
Figure 8.40
4. Molecular ion, $M^{+•}$

**Difficulties:**
- $M^{+•}$ is not always the last peak in the mass spectrum
- last m/z can be
  
  a) smaller than the molar mass

  : $M^{+•}$ is too unstable, fragments before it reaches the detector

  
  detected: $M^{+•} - 18$

  detected: $M^{+•} - 1$

  
  can be more extreme than in these examples!

Figure 8.36

Figure 8.48
4. Molecular ion, $M^+$, continued

**Difficulties:**

- $M^+$ is not always the last peak in the mass spectrum
- last m/z can be

**b1) greater than the molar mass, first case**

: isotopes of higher mass are present in $M^{**}$

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Mass</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}\text{C}$</td>
<td>12</td>
<td>99%</td>
</tr>
<tr>
<td>$^{13}\text{C}$</td>
<td>13</td>
<td>1%</td>
</tr>
<tr>
<td>$^{35}\text{Cl}$</td>
<td>35</td>
<td>76%</td>
</tr>
<tr>
<td>$^{37}\text{Cl}$</td>
<td>37</td>
<td>24%</td>
</tr>
</tbody>
</table>

**Figure 8.57**

**Figure 8.82**
4. Molecular ion, $M^+$, continued

- isotope peak patterns for Cl- and Br-containing ions

**Figure 8.18**

**Table 8.8**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Isotope Peak Pattern</th>
<th>Mass Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>1:1</td>
<td>100 to 98</td>
</tr>
<tr>
<td>Br$_2$</td>
<td>1:2:1</td>
<td>51 to 100 to 49 or 100 to 195 to 95</td>
</tr>
<tr>
<td>Cl</td>
<td>10:3</td>
<td>100 to 33</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>10:6:1</td>
<td>100 to 65 to 11</td>
</tr>
</tbody>
</table>
4. Molecular ion, $M^+$, continued

**Difficulties:**
- $M^+$ is not always the last peak in the mass spectrum
- last m/z can be

  **b2) greater than the molar mass, second case**
  - $M$ collects a proton: $M^+ + 1$
  - sometimes for amines, hydrazines, azo compounds; carbonyls

*Figure 8.14*
5. Fragmentation considerations

a) Energy

- weak bonds break more readily
- fragmentations that lead to stabilized species are preferred
  - electron octet
  - resonance
  - charge on the most likely atom

\[
[R-O-\text{CH}_2-\text{CH}_2\ldots]^\ast\ast \rightarrow [R-O-\text{CH}_2 \leftrightarrow R-O=\text{CH}_2] + \text{radical}
\]

\[
\Rightarrow R-O^+ \text{ or } R-O-\text{CH}_2-\text{CH}_2
\]

but

\[
[A\text{r}-O-\text{CH}_2-\text{CH}_2\ldots]^\ast\ast \rightarrow A\text{r}-O^+
\]
\[
[A\text{r}-\text{CH}_2-\text{CH}_2\ldots]^\ast\ast \rightarrow A\text{r}-\text{CH}_2
\]

+ radical

resonance stabilization
5. Fragmentation considerations continued

b) Ions with an odd or even number of electrons

I. Odd electron ions (OE⁺⁺)

- possess an unpaired electron, such as M⁺⁺
- eliminate radicals R⁺ or neutral, closed-shell species N

\[
OE^{++} \rightarrow EE^+ + R^+
\]

\[
OE^{++} \rightarrow OE^{++} + N
\]

II. Even electron ions (EE⁺)

- possess all paired electrons, such as M⁺
- eliminate neutral, closed-shell species N

\[
EE^+ \rightarrow EE^+ + N
\]

\[
R-\overset{=}O=CH_2 \rightarrow R^+ + O=CH_2
\]

\[\text{+ and \cdot balance!}\]
5. Fragmentation considerations continued

c) Ionization energy, IE
- follows from
  \[ \text{OE}^{\ddagger\ddagger} \rightarrow \text{OE}^{\ddagger\ddagger} + N \]
- fragment with the smallest IE carries the charge (Stevenson's rule)

preferred: conjugated system has the higher HOMO
: easier to excite (UV-Vis)
: easier to ionize
5. Fragmentation considerations continued

Important to remember:
- ionization is the first event: fragmentations start from M\(^+\), not from M
- \(^+\) and \(^-\) balance
- H atom balance: it might be good to draw all H not to forget any
- mass balance
- \(R^*\) and N are not detected, do not give signals:
  \(\Rightarrow\) masses for \(R^*\) and N are listed differently:

\[
\begin{align*}
\text{CH}_3 & \quad \text{\textbullet}^+ \\
\text{\textbullet} \quad \text{\rightarrow} \\
(96) & \quad (81)\quad \text{15au} \quad \text{indicating that for this particular one-molecule fragmentation there is no signal at m/z 15}
\end{align*}
\]
6. Fragmentations

a) $\alpha$-cleavage

- For carbonyls

- For $R-X-R$, $X = O, N, S$

(- for phenyl)

Which is more likely?

Figure 8.60
6. Fragmentations

a) $\alpha$-cleavage continued

Decarbonylation

![Mass spectrum diagram](image)

- M**
- M (72)
- 29
- 57
- 43

- M**
- M (72)
- 29
- 57
- 43

- H$_3$C
- - CO
- +CH$_2$CH$_3$
- 28 au
- (29)

- H$_3$C
- - CO
- H$_3$C$^+$
- 28 au
- (15)

not observed

- H$_3$C
- CH$_3$
- 15 au
- (57)

- H$_3$C
- CO
- 29 au
- (43)

Figure 8.60
6. Fragmentations continued

b) benzyl and allyl cleavage
- for aromatic compounds
- for unsaturated compounds

Figure 8.44

Figure 8.31

![Diagram](image1.png)

![Diagram](image2.png)

highly delocalized, very stable

 tropyl ion

delocalized: allyl cation
6. Fragmentations continued

b) benzyl cleavage continued

Figure 8.44

tropylium fragmentation

\[
\text{C}_{10}\text{H}_{14} \\
\text{MW } = 134.22
\]

\[
\text{M}^{+} \text{ (134)}
\]

\[
\text{M}^{+} \text{ (91)} \\
\rightarrow \text{C}_{2}\text{H}_{2}^{-} \rightarrow \text{C}_{2}\text{H}^{-} \rightarrow +\text{C}_{3}\text{H}_{3}
\]

\[
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{134}
\]

\[
\text{C}_{2}\text{H}^{-} \rightarrow +\text{C}_{3}\text{H}_{7} \\
\text{43au}
\]

\[
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{77}
\]

\[
\text{26au} \\
\text{26au} \\
\text{26au}
\]

\[
\text{not observed}
\]

phenyl fragmentation

\[
\text{H} \\
\text{H} \\
\text{134}
\]

\[
\text{26au} \\
\text{26au}
\]

\[
\text{25au}
\]

highly delocalized, very stable

tropylium ion
6. Fragmentations continued

c) retro-Diels-Alder cleavage - for 6-membered rings with double bonds

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

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

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

"or" is irrelevant: paths are identical \((C_5H_8)\)

Figure 8.34
6. Fragmentations continued

c) retro-Diels-Alder cleavage continued

Figure 8.35
6. Fragmentations continued

d) McLafferty rearrangement - for longer chains with double bonds (C=O, C=C, C=N)

if C=C is part of an aromatic ring, the aromaticity is destroyed!

Figure 8.65
6. Fragmentations continued

e) oxonium rearrangement - for compounds with $X = O, N, P, S$ and charge on $X$

$$\text{M}^+ \rightarrow \text{O} - \text{CH}_3$$

Figure 8.65