Introduction to Mass Spectroscopy

The computer program, *Introduction to Spectroscopy: Mass Spectroscopy*, is a tutorial for the interpretation of electron impact mass spectra. Since the detailed analysis of mass spectra can be quite complicated, we will focus only on major features in the mass spectrum of a compound. You should not attempt to account for each peak in the mass spectrum. This program will assist you in correlating a proposed structure with the major features in a mass spectrum.

**Read the mass spectrometry chapter in your textbook** before you begin with the computer tutorial. We will focus on the mass spectroscopy of hydrocarbons, alkyl halides, alcohols, amines, aldehydes, and ketones (for now, we will skip carboxylic acids and esters).

The tutorial program is keyboard and menu driven. The main topic menu is shown below:

- General Instructions
- Sound On
- Introduction to Mass Spectroscopy
- Overview of Spectrum Analysis
- Fragmentation Patterns
- A Suggested Approach to Spectrum Analysis
- Spectrum Analysis Quiz
- Special Topics (skip this section)
- Quit - Exit to DOS

After you select a topic, a submenu will appear. Initially, you should work your way through the following topics in the order listed below:

**Introduction to Mass Spectroscopy** (do all topics)

**Overview of Spectrum Analysis**  
do all topics except rearrangements  
learn the 5 “fragmentation principles”

**Fragmentation Patterns**  
do all functional groups except carboxylic acids and esters  
(do aldehydes and ketones last)

**A Suggested Approach to Spectrum Analysis**  
read carefully and do example 1 and 4

**Spectrum Analysis Quiz**  
work the following problems: 5, 7-8, 10-15, 22, 25-27, 34, 37  
(these problems do not involve carbonyl compounds)  
✓ press the F1 key to display m/e for key fragment ions

At a later date, go back to the **Fragmentation Patterns** submenu and learn some of the fragmentation pathways that occur with aldehydes and ketones. Then you should attempt some of the problems that deal with aldehydes and ketones.
Mass Spectrometry: Interpretation of Spectra

General Considerations

The more stable a fragment (cation or cation radical), the more likely it will be observed in the mass spectrum. The stability of fragments observed in the mass spectrum is governed by the same principles of stability that apply to all radicals and cations.

benzylic / allylic > 3° > 2° > 1° > methyl

Fragmentation Principles

1) Cleavage is favored at branch points along a carbon chain.

2) If a C=C double bond is present in the molecule, cleavage to form an allylic carbocation is favored.

3) For alkylbenzenes, cleavage to produce a benzylic carbocation is favored. (benzylic carbocations rearrange to form tropylium carbocations)

4) α-cleavage: C–C bonds adjacent to a heteroatom (N, O, S, etc.) or C–C bonds adjacent to a carbonyl group are frequently cleaved.

5) Cleavage resulting in the elimination of small, neutral molecules is favored (for example, alcohols fragment to lose water resulting in a M–18 peak).

Some Common Fragment Ion Masses

<table>
<thead>
<tr>
<th>m/e</th>
<th>Ion(s)</th>
<th>m/e</th>
<th>Ion(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>CH₃⁺</td>
<td>57</td>
<td>C₄H₉⁺ (butyl, sec-butyl, isobutyl, or tert-butyl)</td>
</tr>
<tr>
<td>29</td>
<td>CH₃CH₂⁺</td>
<td>71</td>
<td>C₅H₁₁⁺ (various pentyl cations)</td>
</tr>
<tr>
<td></td>
<td>CHO⁺ (formyl)</td>
<td>77</td>
<td>C₆H₅⁺</td>
</tr>
<tr>
<td>41</td>
<td>CH₂=CH–CH₂⁺ (allyl)</td>
<td>91</td>
<td>C₆H₅CH₂⁺ (benzyl or tropylium ion)</td>
</tr>
<tr>
<td>43</td>
<td>CH₃CH₂CH₂⁺ (CH₃)₂CH⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[CH₃C=O]⁺</td>
<td></td>
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