Lecture 6 Agenda...
Mass Spectrometry (12.1-12.3)
Group Question #2

Suggested Ch 12 Problems:
12.2, 12.3(a,c,d), 12.4, 12.13, 12.23, 12.24, 12.26, 12.41, 12.42, 12.44

Exam 1: Tues, June 3
Covers Lectures 2 to 7

A GC-MS instrument.
Found in organic labs, crimes labs...
Mass spectral data (most of the time) gives the mass of the molecule. Fragment peaks = pieces of the molecule.

Mass Spectrum of Ethanol, $^{12}\text{C}_2^{1}\text{H}_6^{16}\text{O}$ (MW = 46)
Acquiring a mass spectrum of a molecule (M) is rather simple.

In EIMS, high energy electrons ionize the molecule, M, to the molecular ion, M⁺⁺. Lone pairs ionize the easiest, then pi electrons, then sigma electrons.

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

M⁺⁺ breaks up into fragment ions (F⁺) and neutral species.

The detector only detects charged species \( \Rightarrow m/z \) ratio (mass/charge).

The intensity of the signals is proportional to the number of ions. The more intense the signal, the more stable that ion is.
Mass spec is useful for detecting isotopes in compounds. Molecular Ions = sum of atomic weight(s) of all isotopes of all elements in a molecule.

If you had 10,000 atoms of each type of element below in a molecule, here’s the breakdown of each isotope of each element within that molecule:

- **C:** 9890 $^{12}\text{C}$ atoms 110 $^{13}\text{C}$ atoms
- **H:** 9999 $^{1}\text{H}$ atoms 1 $^{2}\text{H}$ atoms
- **O:** 9985 $^{16}\text{O}$ atoms, 4 $^{17}\text{O}$ atoms, 20 $^{18}\text{O}$ atoms
- **N:** 9963 $^{14}\text{N}$ atoms 37 $^{15}\text{N}$ atoms
- **Cl:** 7577 $^{35}\text{Cl}$ atoms 2423 $^{37}\text{Cl}$ atoms (3:1 $^{35}\text{Cl}$:$^{37}\text{Cl}$)
- **Br:** 5069 $^{79}\text{Br}$ atoms 4931 $^{81}\text{Br}$ atoms (1:1 $^{79}\text{Br}$:$^{81}\text{Br}$)
Mass spec data can will also give the mass (or fragments) of isotope incorporation in a molecule.

**MW at m/z 47 is for $^{13}\text{C}^{12}\text{C}^{1}\text{H}_6\text{O}$**

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The mass spec of chlorobenzene shows two significant peaks: $M^{+*}$ and $M+2$ peaks - shows the two main isotopes of chlorine in chlorobenzene! Look at the intensities too!
The two isotopes of bromine in bromobenzene can also be seen in the mass spec. Again, check out the intensities of the $M^{+\ast}$ and $M+2$ peaks.

$C_6H_5^{79}\text{Br} = m/z$ 156

$C_6H_5^{81}\text{Br} = m/z$ 158

$M^{+\ast} = 156$

$M+2 = 158$
Fragment ions are pieces of the molecule generated by the fragmentation of the $M^{+\ast}$ or further fragmentation of an $F^+$.

For each $F^+$, there is a neutral loss (a non-charged pieces).

Determining the identity of a neutral loss is useful when interpreting the fragment ions in the spectrum.
Here are some common pieces that result from fragmentations under mass spec conditions. This list will NOT be given with exams.

15 = CH₃
17 = OH (usually)
18 = H₂O
28 = CO or CH₂=CH₂
29 = CH₃CH₂ or CHO
31 = CH₃O
35/37 = Cl (look for 3:1 M⁺:M+2 pattern)
42 = CH₂=C=O

43 = \[
\begin{array}{c}
\text{C₃H₇} \\
\end{array}
\]
\quad \text{or} \quad \begin{array}{c}
\text{H₃C} \\
\end{array}

45 = CH₃CH₂O or CO₂H

57 = \[
\begin{array}{c}
\text{C₄H₉} \\
\end{array}
\]
\quad \text{or} \quad \begin{array}{c}
\text{H₃C} \\
\end{array}

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Common pieces continued...

71 = \[
\begin{align*}
\text{C}_5\text{H}_{11} \\
\text{or} \\
\text{C}_5\text{H}_{11}
\end{align*}
\]

77 = \[
\begin{align*}
\text{C}_6\text{H}_5
\end{align*}
\]

79/81 = Br (look for 1:1 \( M^+:M+2 \) pattern)

85 = \[
\begin{align*}
\text{C}_6\text{H}_{13} \\
\text{or} \\
\text{C}_6\text{H}_{13}
\end{align*}
\]

91 = \[
\begin{align*}
\text{CH}_2
\end{align*}
\]

105 = \[
\begin{align*}
\text{O}
\end{align*}
\]
Amines, alcohols, and carbonyl-containing compounds can undergo alpha-cleavage fragmentation.
Heteroatom-containing compounds (amines, alcohols, ethers) carbonyl-containing compounds can undergo inductive cleavage, \(i\).

\[
\text{R}^+ + \dot{\text{Y}} - \text{R} \quad \text{R}^+ + \dot{\text{Y}} - \text{R}
\]
Compounds that possess a heteroatom, a $\pi$ system, and an abstractable $H\gamma$ to the $\pi$ system can undergo a **McLafferty Rearrangement** (an intramolecular rearrangement).

The $\alpha$, $\beta$, and $\gamma$ notations are location identifiers; locations of carbons with respect to the carbonyl (C=O) bond.

Protons attached to the $\gamma$ carbon are $\gamma$ hydrogens.
The Nitrogen Rule.

- If a compound contains zero or an even number of nitrogen atoms, its molecular ion will be at an even mass number.

- If the molecular ion is an odd mass number, it may contain an odd number of nitrogens.
The mass spectrum for ethyl acetate is given below; structure is also shown. Determine the fragment ion structures for the peaks at $m/z$ 88, 73, 45, 43, and 29.