2.S Summary of Mass Spectrometry

Concepts & Vocabulary

2.1: Chapter Objectives and Preview of Mass Spectrometry

- Mass spectrometry is a way to determine the molecular weight of a structure to begin structure elucidation.

2.2 Instrumentation

- Mass spectrometry breaks apart molecules to detect fragments based on a mass to charge ratio.
- The particles in the sample (atoms or molecules) are bombarded with a stream of electrons, and some of the collisions are energetic enough to knock one or more electrons out of the sample particles to make positive ions.
- Most of the positive ions formed will carry a charge of +1 because it is much more difficult to remove further electrons from an already positive ion.
- Different ions are deflected by the magnetic field by different amounts, which depends on the mass of the ion and the charge of the ion.
- The output from the chart recorder is usually simplified into a "stick diagram". This shows the relative current produced by ions of varying mass/charge ratio.

2.3 Ionization Techniques

- There is a variety of ionization techniques. The ones discussed in this section are electron impact, chemical ionization, field ionization/desorption, electrospray ionization, matrix assisted laser desorption ionization, inductively coupled plasma mass spectrometry, and fast atom bombardment.
- Depending on the information desired from mass spectrometry analysis, different ionization techniques may be desired.

2.4 Mass Analyzers

- A mass analyzer is the component of the mass spectrometer that takes ionized masses and separates them based on charge to mass ratios and outputs them to the detector where they are detected and later converted to a digital output.
- There are six general types of mass analyzers that can be used for the separation of ions in a mass spectrometry (quadrapole, time of flight, magnetic sector, electrostatic sector, quadropole ion trap, and ion cyclotron resonance).

2.5 Applications of Mass Spectrometry

- Mass spectrometry is applicable across diverse fields with specific applications including, but not limited to drug testing and discovery, food contamination detection, pesticide residue analysis, isotope ratio determination, protein identification, and carbon dating.
- One of the new ways that clinical mass spectrometry is being used is to quantitatively detect small amounts of proteins, biomarkers, or drug molecules, with very low concentrations.

2.6 Interpretation of Mass Spectra

- Mass spectrum looks like a bar graph with the x axis as the m/z values and the y axis represents the intensity or relative abundance of a given m/z.
- The lines correspond to the fragments of the different ions with different m/z values.
- The more of a particular sort of ion that's formed, the higher its peak height will be. The tallest peak is called the base peak and is assigned 100% intensity.
- The peak that represents the unfragmented cation radical is called the parent peak or molecular ion (M^+).
- There is often an M+1 peak (one greater than the molecular ion), and it arises because of ^{13}C. This compound is referred to as an isotopomer.

2.7 Mass Spectrometry of Common Functional Groups

- Some fragment ions are very common in mass spectrometry often due to having no pathway available to break the ion down or the ion is relatively stable, so it forms easily.
- When alcohols are subjected to ionization, two fragmentation pathways can occur - alpha cleavage and dehydration.

- A general principle when nitrogen is part of a molecule is that if there is an odd number of nitrogens, then the molecular weight will be an odd number. This is also known as the nitrogen rule.
- Primary amines undergo a characteristic alpha cleavage.
- Other isotopomers are common when chlorine and bromine are part of the molecule. For chlorine and bromine there will be an additional M + 2 peak representing one of the isotopomers.
- Chlorine has two isotopes ^{35}C and ^{37}C with a 3:1 ratio (roughly), which appears in the mass spectrum in the fragments containing chlorine.
- The ratio of the relative abundance/intensity of the M:M + 2 is about 3:1, which reflecting the isotopic abundance of ^{35}C:^{37}C.
- With bromine, the isotopic distribution of ^{79}Br and ^{81}Br is more like 50:50. The ratio of the relative abundance/intensity of the M:M + 2 is about 50:50.
- Carbonyl compounds can undergoe an alpha cleavage and the McLafferty rearragnement.

Skills to Master

- Skill 2.1 Know what mass to charge means and measures.
- Skill 2.2 Distinguish between different types of ionization techniques.
- Skill 2.3 Determine the best mass analyzer to use for sample.
- Skill 2.4 Determine the ratio of different types of protons present in an organic compound.
- Skill 2.5 Interpret fragmentation patterns
- Skill 2.6 Interpret mass spectra
