

## Chapter 14

# Understanding How to Analyze Structures of Products (Part 1): Mass Spectrometry (MS)

### Key Concepts

In EI mass spectrometry, a radical cation is created when an electron is knocked off a molecule. Non-bonded electrons, which are held by only one nucleus, are more loosely held and therefore more likely to be removed than bond electrons, which are held by two nuclei. Because of the resulting instability, the molecule often fragments in characteristic ways, with carbocation stability being an important consideration in many cases. Only those molecules or fragments that have a positive charge are registered by the detector.

To simplify analysis of a mass spectrometry fragmentation pattern, focus on the following key features:

1. The **M+ peak** (which allow you to determine overall mass as well as the potential number of carbons. The mass of a CH<sub>3</sub> group is 15 g/mole. Each additional alkyl carbon group averages 14 g/mole.)
2. Characteristic **isotope patterns associated with the M+ peak** (which allow you to determine the type of functional group present).

Characteristic patterns include:

Alkyl Bromides      M+2 peak that is the same height as the M+ peak

Alky Chlorides      M+2 peak that is 1/3 the height of the M+ peak

Alcohols            Are often missing the M+ peak, and have a characteristic M-18 peak caused by the loss of water. Alcohols often also have unusual m/z values of 31, 45, etc. caused by the loss of an R-OH group.

Amines              If an odd number of nitrogens are present, the M+ peak is an odd number

An aldehyde or ketone may undergo a McLafferty rearrangement if it has at least one  $\gamma$  hydrogen.

3. The **base peak** value as well as the difference between the base peak and M+ value provide structural information since they indicate where fragmentation most often occurred.

## **What You Need To Learn, Understand, and Apply**

1. The types of information gained from a mass spectrum.
2. The general theory of mass spectrometry.
3. The definition for each of the following:  $m/z$ ,  $M^+$ ,  $M+1$ ,  $M+2$ , base peak.
4. The ability to determine the most common ways a cation radical fragments.
5. The ability to identify unique characteristics of fragmentation patterns for alkanes, alkyl halides, ethers, alcohols, amines, aldehydes and ketones.
6. The skills needed to apply the material and avoid common errors.