Mass Spectrometry
Learning Objectives

As we study this chapter, you should...

1) Be familiar with the theory behind the technique of mass spectrometry
2) Be familiar with the terminology of mass spectrometry
3) Be able to interpret a mass spectrum and use it to get clues about the structure and elemental make-up of an unknown compound
4) Be able to predict fragmentation patterns for organic compounds

The following concepts and trends are important to Mass Spectrometry:

1) Mass Spectrometry involves the ionization of molecules and the detection of these ions or their fragments based on mass and/or charge.

2) Only charged species can be detected in a mass spectrometer. In our spectrograms, all peaks will correspond to *cationic* fragments (positively charged species).

3) Fragmentation occurs soon after the molecule is ionized.

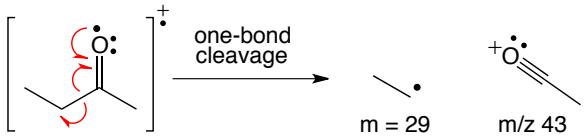
4) Fragmentation favors the more stable species. These will give the taller peaks. Try to remember the factors that make chemical species stable…these factors will also apply to MS fragments.

5) The Base Peak corresponds to the most intense peak (and probably the most stable product(s) of fragmentation).

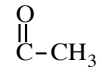
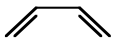
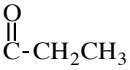
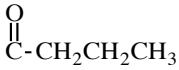
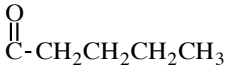
6) The Molecular Ion Peak is the peak that corresponds to the initially ionized compound (usually one of the rightmost peaks in the spectrum).

7) Some general fragmentation guidelines…

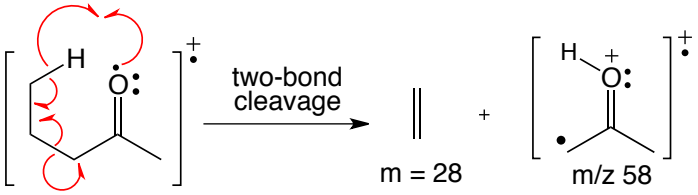
One-bond cleavage always gives a cation and a radical.



Common Fragments in Mass Spectrometry

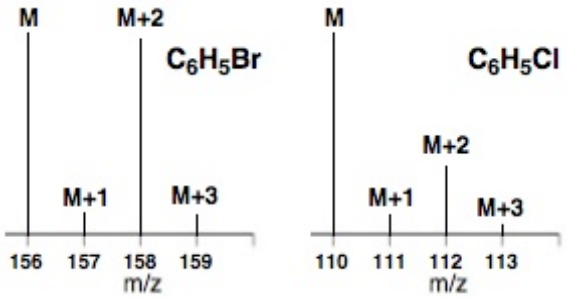
Mass	Fragment
15	• CH_3
18	H_2O
19	F •
28	CO , $H_2C{=}CH_2$
29	• CH_2CH_3 , 
35 & 37	Cl •
43	propyl , 
44	CO_2
54	
57	butyl , 
71	pentyl , 
79 & 81	Br •
85	hexyl , 

Two-bond cleavage always gives a neutral molecule and another radical cation.



Nitrogen rule: A molecule that contains an odd number of nitrogen atoms (i.e. 1, 3, 5, etc.) will have an odd value for its molecular ion peak (M).

M+2 Peaks: When a Cl or Br is present in a molecule, the Mass spectrum will show M+2 peaks that are approximately 1/3 or equal in height to the M peak, respectively.



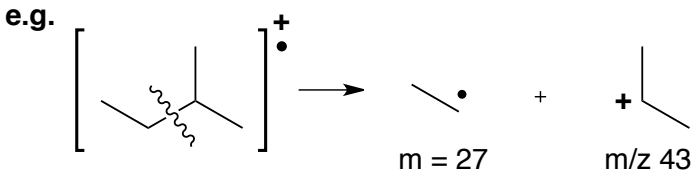
The following table shows the natural abundances of some commonly encountered elements…

Table of Isotopic Natural Abundances

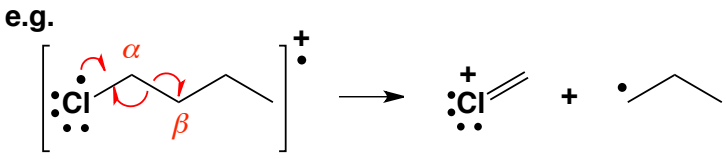
Element	Isotope (nat. abund.)	Isotope (nat. abund.)	Isotope (nat. abund.)
Hydrogen	^{1}H (99.99%)	^{2}H (0.01%)	^{3}H (0.00%)
Carbon	^{12}C (98.89%)	^{13}C (1.11%)	
Oxygen	^{16}O (99.76%)	^{17}O (0.038%)	^{18}O (0.205%)
Nitrogen	^{14}N (99.63%)	^{15}N (0.37%)	
Fluorine	^{19}F (100%)		
Chlorine	^{35}Cl (75.78%)		^{37}Cl (24.22%)
Bromine	^{79}Br (50.69%)		^{81}Br (49.31%)
Iodine	^{127}I (100%)		
Sulfur	^{32}S (94.93%)	^{33}S (0.76%)	^{34}S (4.29%)

8) Common fragmentations…

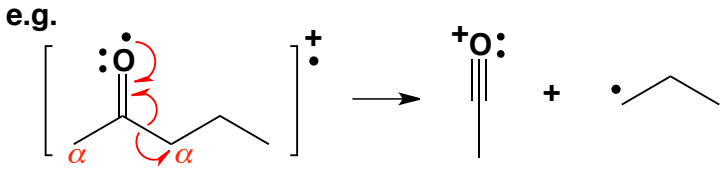
Alkyl group cleavage: A common fragmentation that occurs between the carbon-carbon bonds when one fragment can be a stable carbocation (2°, 3°, allylic)



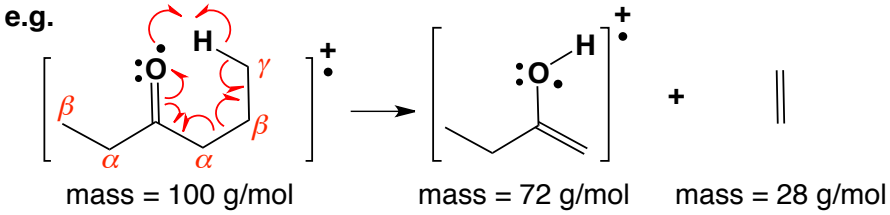
α-cleavage: A common fragmentation that occurs at the bond right after the α-carbon of an electron rich functional group (e.g. OH, OR, X, etc.)



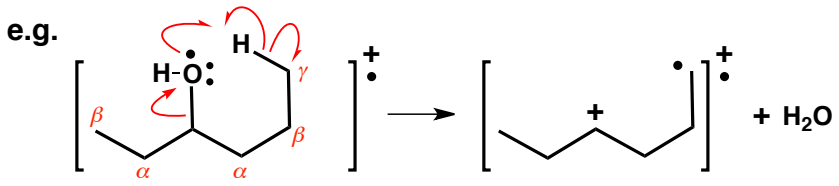
Carbonyl-cleavage: A common fragmentation that occurs between the carbonyl carbon and its α-carbon



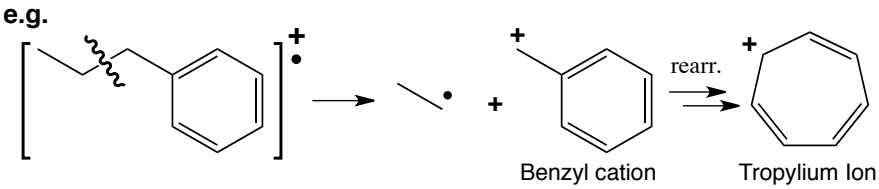
McLafferty Rearrangement: A two-bond cleavage fragmentation that sometimes occurs when a carbonyl compound has a γ-hydrogen.



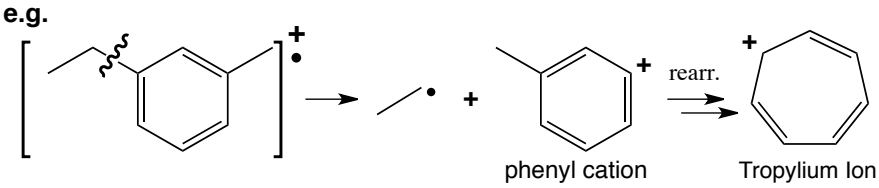
Loss of Water: A two-bond cleavage fragmentation that sometimes occurs when an alcohol has a γ-hydrogen (note: it can occur with hydrogens at other positions as well). The result is a loss of water and an M-18 peak.



Tropylium Ion: Many alkylbenzenes undergo fragmentation and rearrangement to form a very stable cation called a tropylium ion (mass = 91). Thus, an m/z = 91 peak in a mass spectrum is indicative of a benzene ring in the molecule.



Tropylium ions also form with one-bond cleavage at another substituent on a disubstituted toluene:



9) Anatomy of a Mass Spectrogram