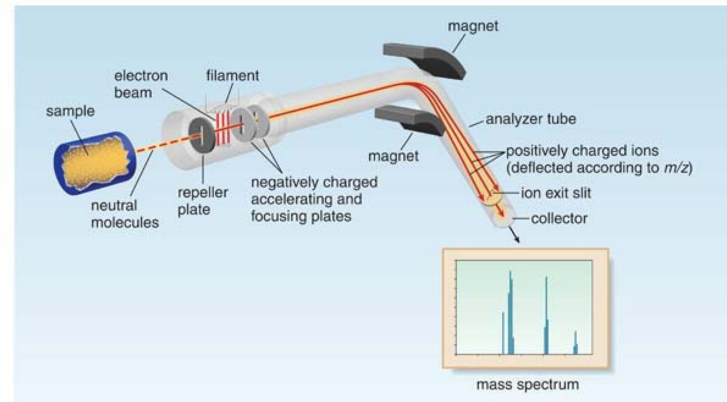
Mass Spectrometry

- **Mass spectrometry is a technique used for measuring the molecular weight and determining the molecular formula of an organic compound.**
- **In a mass spectrometer, a molecule is vaporized and ionized by bombardment with a beam of high-energy electrons (~ 1600 kcal, or 70 eV). It takes ~100 kcal of energy to cleave a typical σ bond.**
- **The electron beam ionizes the molecule by causing it to eject an electron – forming positive ions (the parent or molecular ion) and products from broken bonds (fragment ions).**

Mass Spectrometry

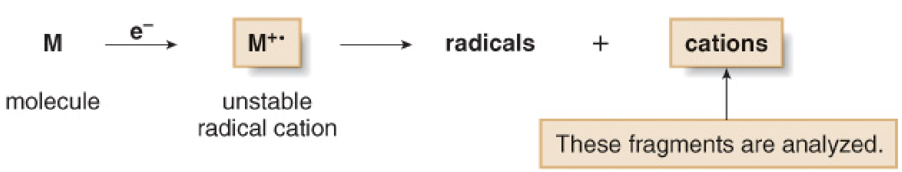
Instrumentation



In a mass spectrometer, a sample is vaporized and bombarded by a beam of electrons to form an unstable radical cation, which then decomposes to smaller fragments. The positively charged ions are accelerated toward a negatively charged plate, and then passed through a curved analyzer tube in a magnetic field, where they are deflected by different amounts depending on their ratio of mass to charge. A mass spectrum plots the intensity of each ion versus its *m/z* ratio.

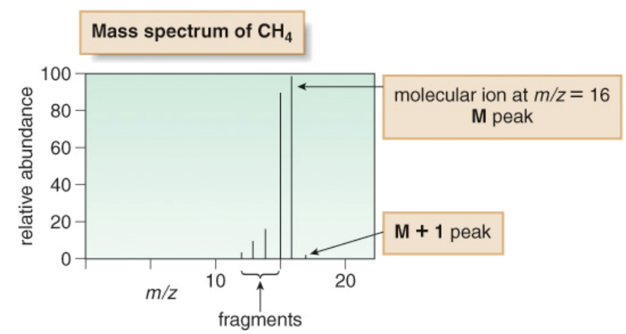
Mass Spectrometry

- **When the electron beam ionizes the molecule, the species that is formed is called a radical cation, and symbolized as $M^{+\bullet}$.**
- **The radical cation $M^{+\bullet}$ is called the molecular ion or parent ion.**
- **The mass of $M^{+\bullet}$ represents the molecular weight of M.**
- **Because $M^{+\bullet}$ is unstable, it decomposes to form fragments of radicals and cations that have a lower molecular weight than $M^{+\bullet}$.**
- **The mass spectrometer analyzes the masses of cations.**
- **A mass spectrum is a plot of the amount of each cation (its relative abundance) versus its mass to charge ratio (m/z, where m is mass, and z is charge).**
- **z is almost always +1, m/z actually measures the mass (m) of the individual ions.**



Mass Spectrometry

Consider the mass spectrum of CH_4 below:

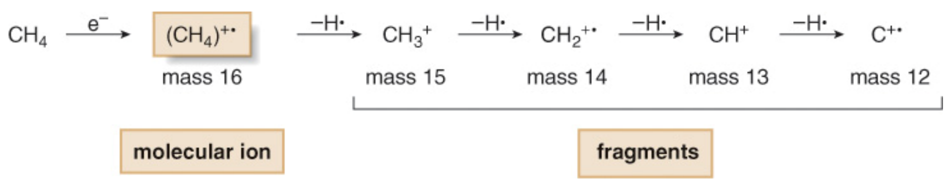


m/z	relative abundance
17	1.2
16	100.0 ← base peak
15	85.9
14	16.1
13	8.1
12	2.8

- **The tallest peak in the mass spectrum is called the base peak.**
- **The base peak is also the M peak, although this may not always be the case.**
- **Though most C atoms have an atomic mass of 12, 1.1% have a mass of 13. Thus, $^{13}CH_4$ is responsible for the peak at m/z = 17. This is called the M+1 peak.**

Mass Spectrometry

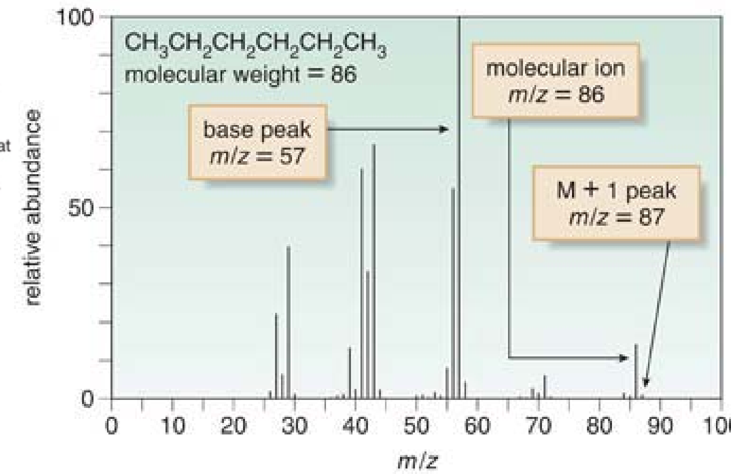
- **The mass spectrum of CH_4 consists of more peaks than just the M peak.**
- **Since the molecular ion is unstable, it fragments into other cations and radical cations containing one, two, three, or four fewer hydrogen atoms than methane itself.**
- **Thus, the peaks at m/z 15, 14, 13 and 12 are due to these lower molecular weight fragments.**



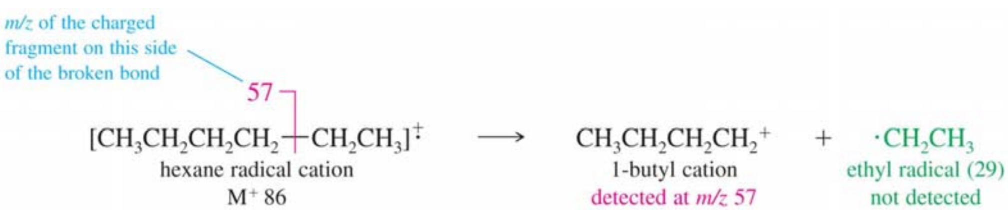
Mass Spectrometry

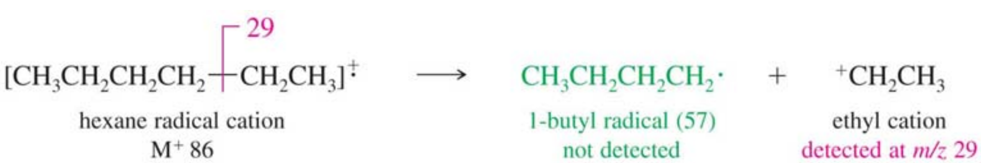
A mass spectrum:

- The molecular ion for hexane (molecular formula C_6H_{14}) is at m/z = 86.
- The base peak (relative abundance = 100) occurs at m/z = 57.
- A small M + 1 peak occurs at m/z = 87.

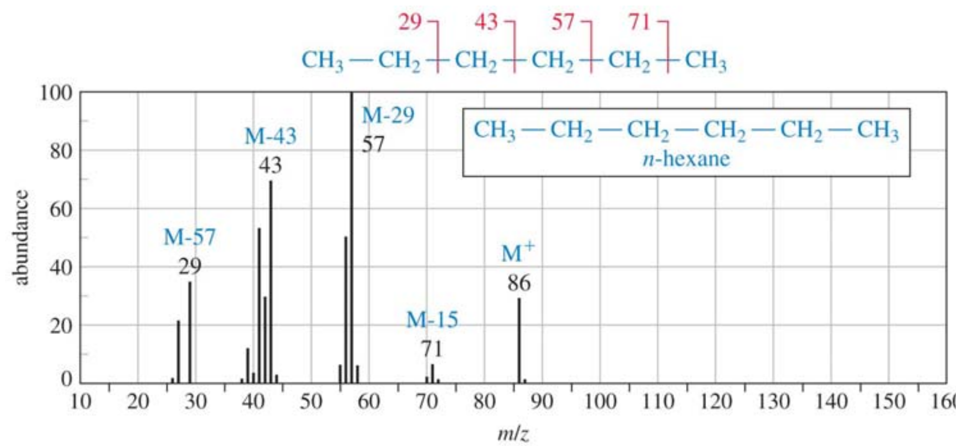


Fragmentation of the Hexane Radical Cation



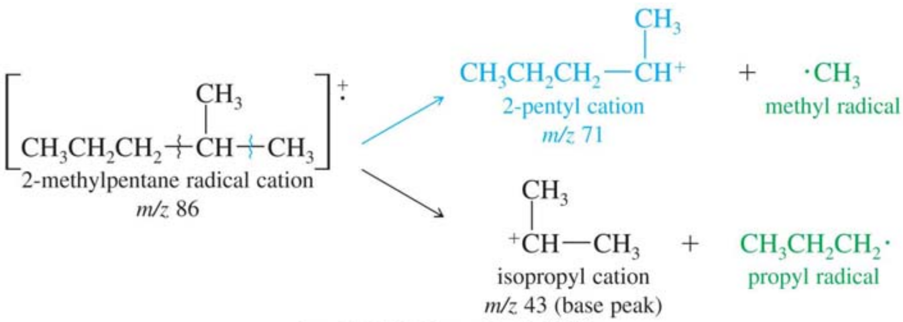


Mass Spectrum of *n*-Hexane



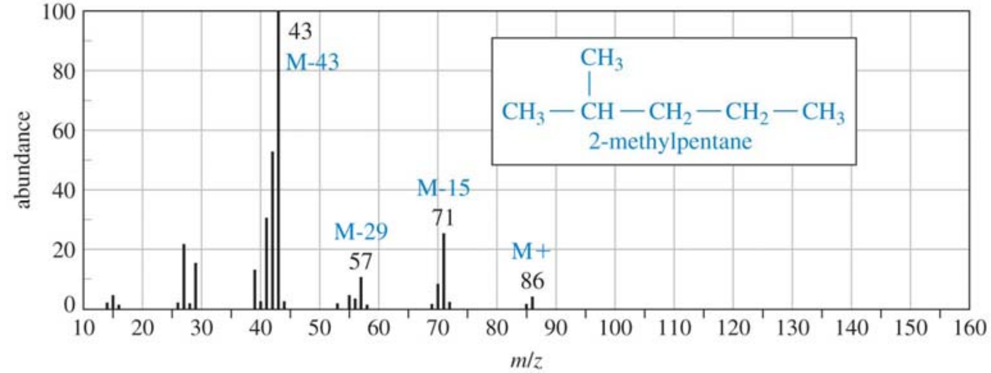
- Groups of ions correspond to loss of one-, two-, three-, and four-carbon fragments.

Fragmentation of Branched Alkanes



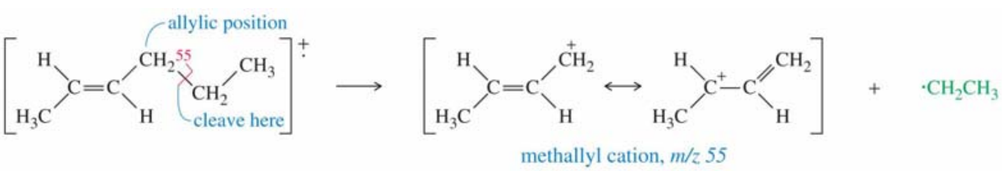
- The <u>most stable carbocation</u> fragments form in greater amounts.

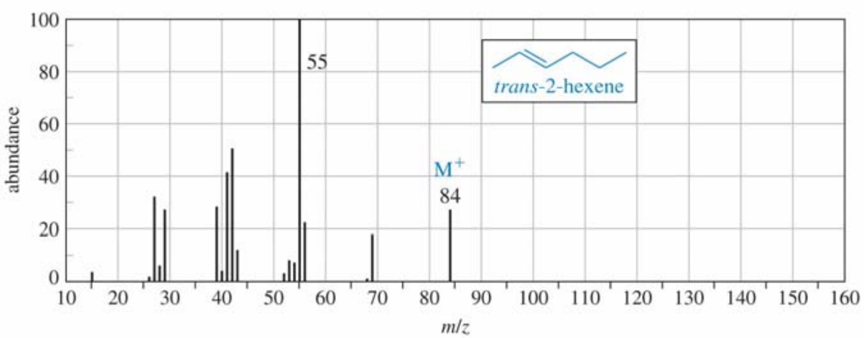
Mass Spectra of Alkanes



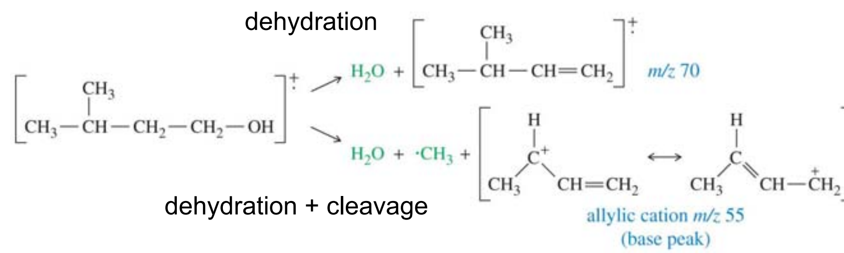
Mass Spectra of Alkenes

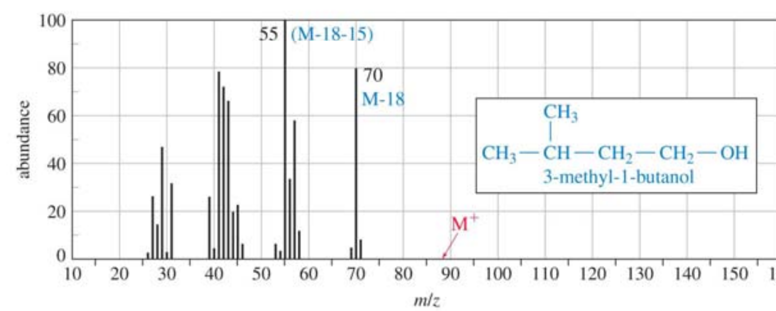
Resonance-stabilized cations favored.



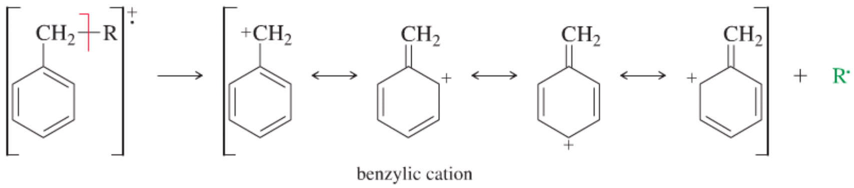


Mass Spectra of Alcohols

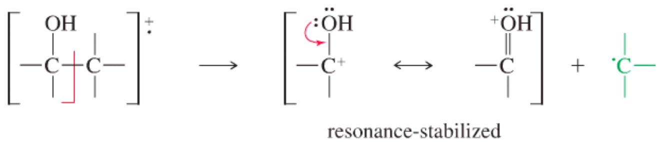




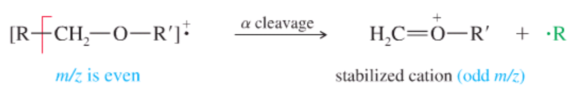
α-cleavage leading to stabilized ions



α cleavage of an alcohol

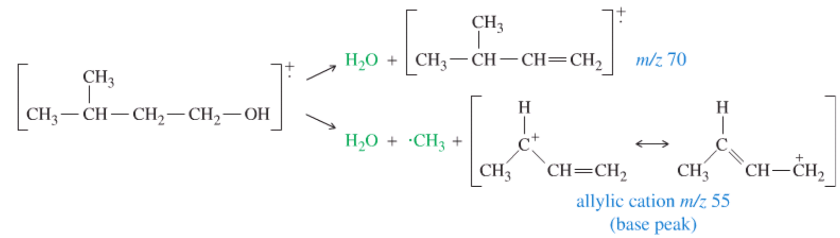


Ethers: α cleavage

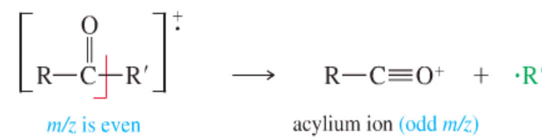


or loss of an alkyl group

Cleavage leading to stabilized ions



Ketones and aldehydes: loss of alkyl groups to give acylium ions



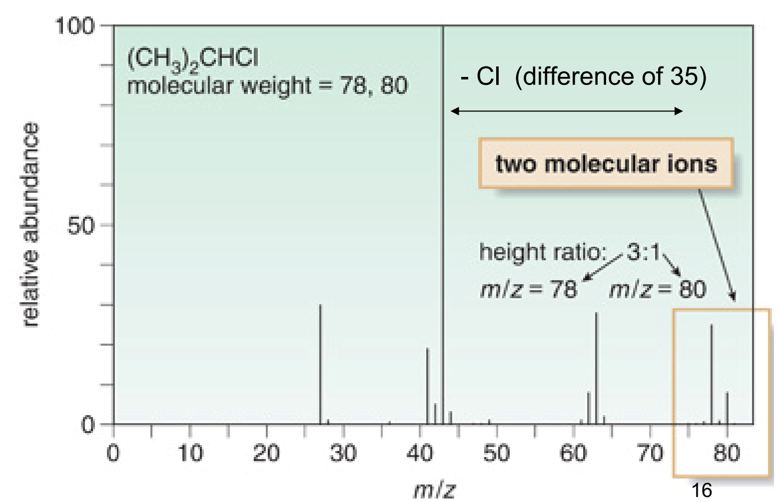
Mass Spectrometry

Alkyl Halides and the M + 2 Peak

- **Most elements have one major isotope, notable exceptions:**
- **Chlorine: ^{35}Cl and ^{37}Cl, which occur naturally in a 3:1 ratio.**
  - **Thus, there are two peaks in a 3:1 ratio for the molecular ion of an alkyl chloride.**
  - **The larger peak, the M peak, corresponds to the compound containing the ^{35}Cl. The smaller peak, the M+2 peak, corresponds to the compound containing ^{37}Cl.**
- **Br has two isotopes—^{79}Br and ^{81}Br, in a ratio of ~1:1. Thus, when the molecular ion consists of two peaks (M and M + 2) in a 1:1 ratio, a Br atom is present.**
- **Iodine may be lost as I$^+$ (127) – a gap of 127 in the spectrum as well as a peak at m/z = 127.**

Mass Spectrometry

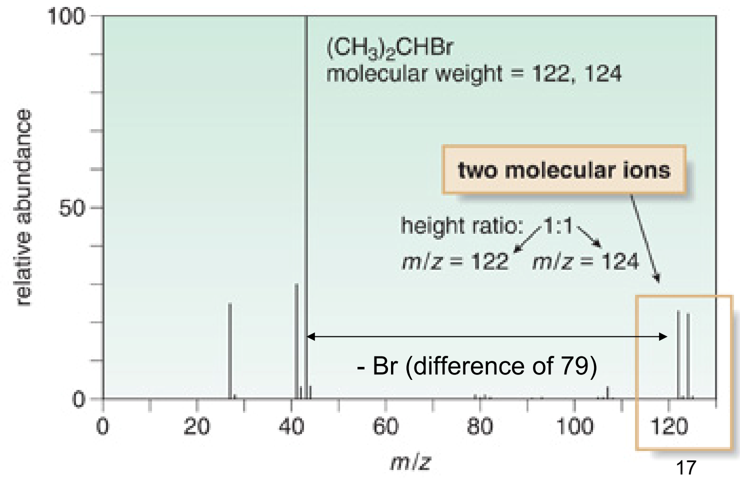
Alkyl chlorides and the M+2 peak



Mass Spectrometry

Alkyl bromides and the M+2 peak

Figure 14.4 Mass spectrum of 2-bromopropane [$(CH_3)_2CHBr$]



Mass Spectrometry

High Resolution Mass Spectrometers

- **Low resolution mass spectrometers report *m/z* values to the nearest whole number. Thus, the mass of a given molecular ion can correspond to many different masses.**
- **High resolution mass spectrometers measure *m/z* ratios to four (or more) decimal places.**
  - **This is valuable because except for ^{12}C whose mass is defined as 12.0000, the masses of all other nuclei are very close—but not exactly—whole numbers.**
  - **The Table lists the exact mass values for a few common nuclei. Using these values it is possible to determine the single molecular formula that gives rise to a molecular ion.**

Exact Masses of Some Common Isotopes

Isotope	Mass
^{12}C	12.0000
^{1}H	1.00783
^{16}O	15.9949
^{14}N	14.0031

Mass Spectrometry

High-Resolution Mass Spectrometers

- **Consider a compound having a molecular ion at *m/z* = 60 using a low-resolution mass spectrometer. The molecule could have any one of the following molecular formulas.**

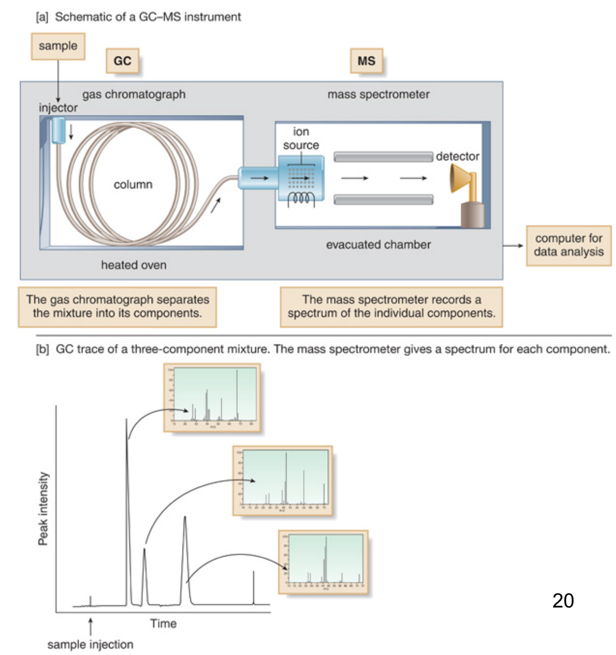
Formula	Exact mass
C_3H_8O	60.0575
$C_2H_4O_2$	60.0211
$C_2H_8N_2$	60.0688

Mass Spectrometry

Gas Chromatography-Mass Spectrometry (GC-MS)

Figure 14.5 Compound analysis using GC–MS

Used to detect drug and drug metabolites from bodily fluids – e.g. sport drug testing

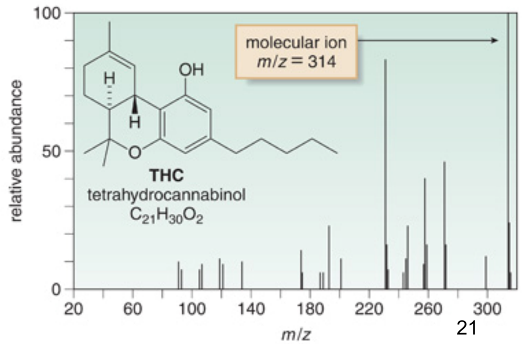


Mass Spectrometry

Gas Chromatography-Mass Spectrometry (GC-MS)

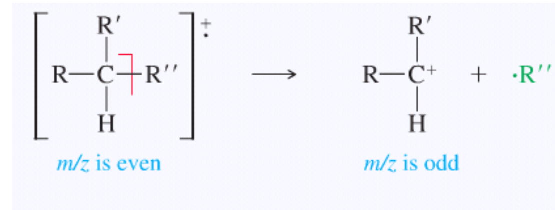
- **To analyze a urine sample for tetrahydrocannabinol, (THC) the principle psychoactive component of marijuana, the organic compounds are extracted from urine, purified, concentrated and injected into the GC-MS.**

- **THC appears as a GC peak, and gives a molecular ion at 314, its molecular weight.**



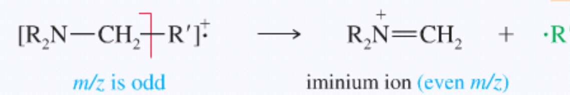
Mass Spectrometry
Other useful information

Compounds of carbon/hydrogen/oxygen have even mass number parent ions and odd mass number fragments, for example:



Compounds of that contain nitrogen, such as amines, have odd mass number parent ions and even mass number fragments, for example:

Amines: α cleavage next to the carbon bearing the nitrogen to give stabilized cations (Section 19-9)



Also an example of α-cleavage