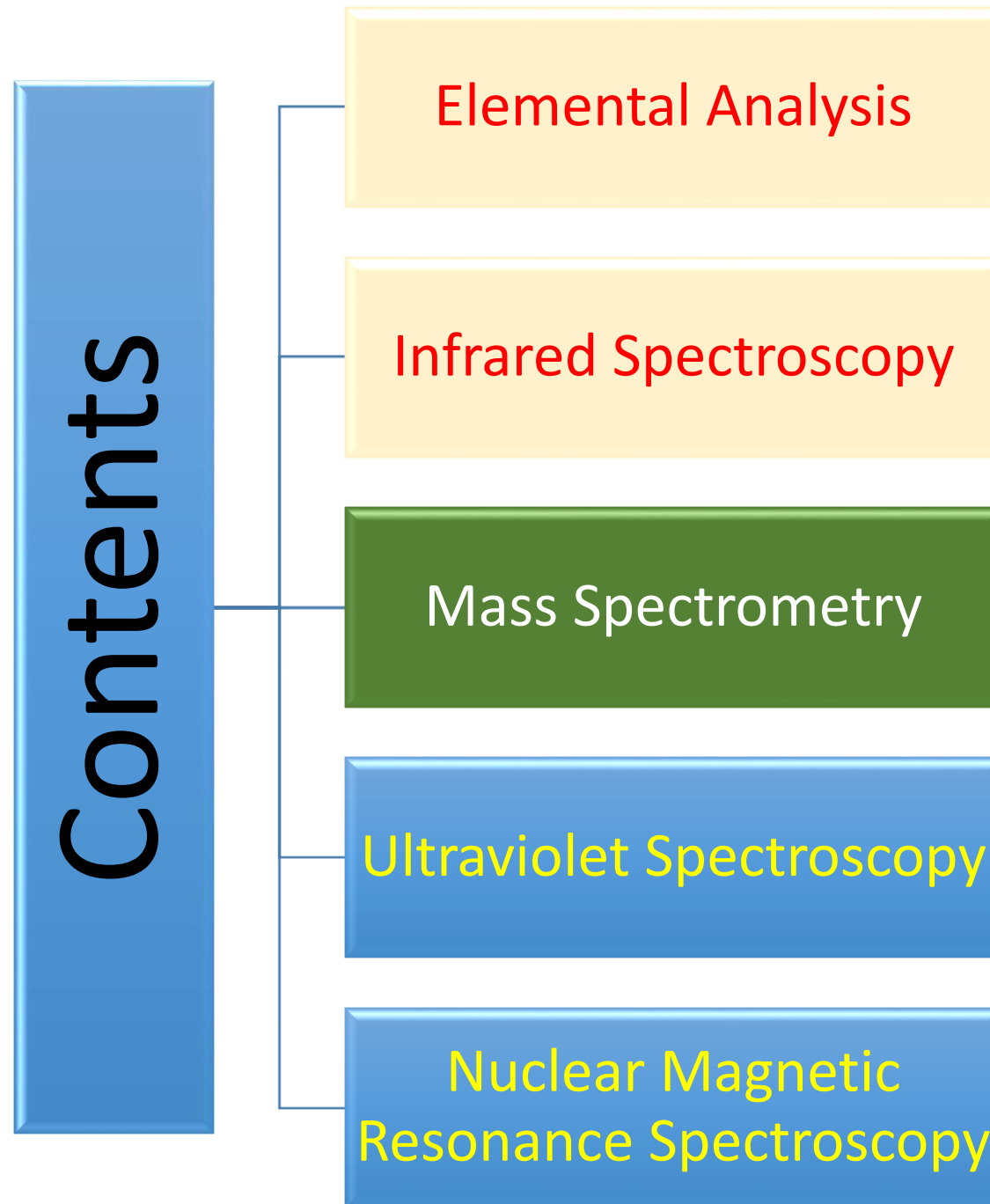


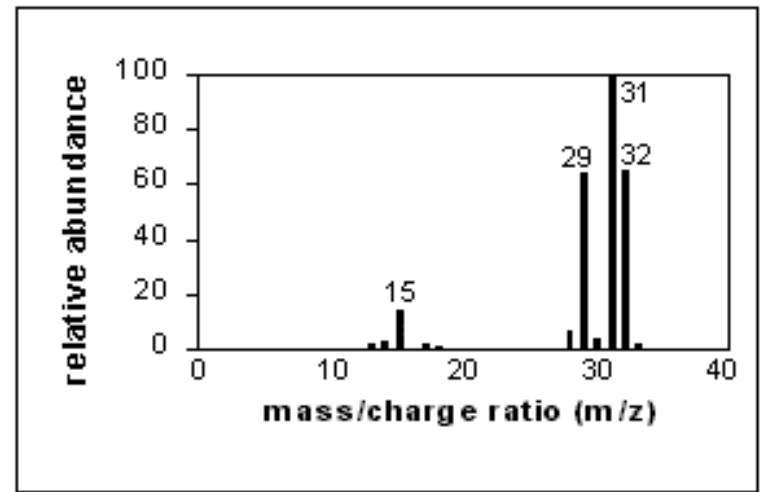


# INTRODUCTION TO SPECTROSCOPY

**Dr. Tarek Bedair**

Lecturer at Chemistry Department, Faculty of Science,  
Minia University





# PART III: MASS SPECTROMETRY

# Goals of Part (III)

1

- Use a mass spectrum to determine a compound's molecular weight, and propose which elements are likely to be present

2

- Given a structure, predict the major ions that will be observed in the mass spectrum from fragmentation of the molecular ion

# 13. INTRODUCTION TO MASS SPECTROMETRY

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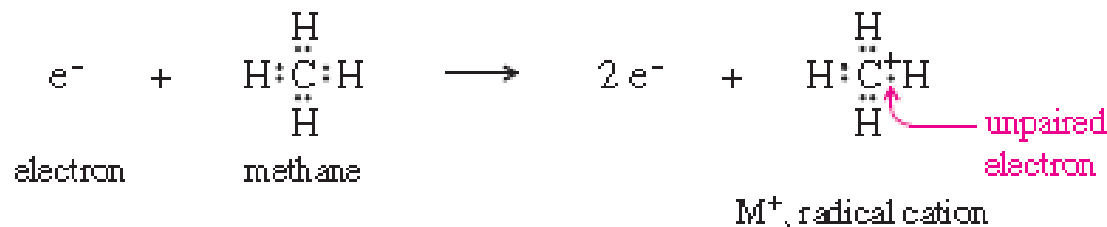
- **Mass spectrometry (MS)** provides the molecular weight and valuable information about the molecular formula, using a very small sample. The mass spectrum also provides structural information that can confirm a structure derived from NMR and IR spectroscopy.
- **Mass spectrometry** is fundamentally different from *spectroscopy*. Spectroscopy involves the absorption (or emission) of light over a range of wavelengths. Whereas, mass spectrometry does not use light at all.
- In the **mass spectrometer**, a sample is struck by high-energy electrons, breaking the molecules apart. The masses of the fragments are measured, and this information is used to reconstruct the molecule.

# 13A. The Mass Spectrometer

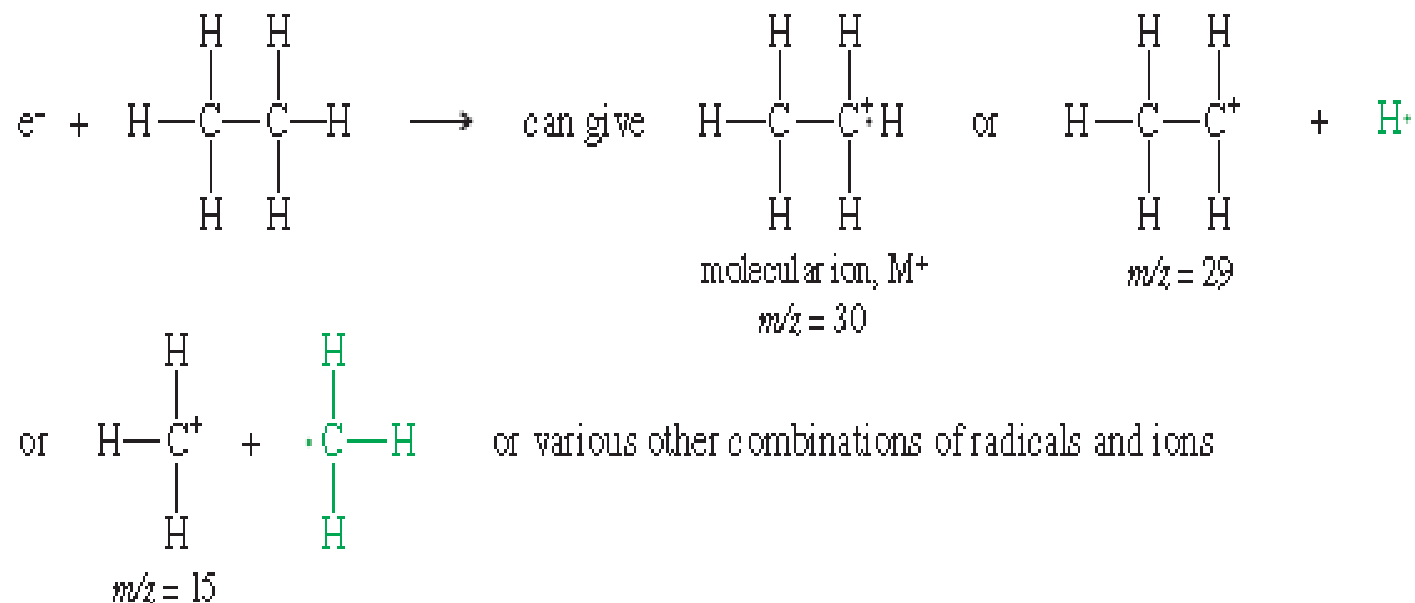
- A mass spectrometer ionizes molecules in a high vacuum, sorts the ions according to their masses, and records the abundance of ions of each mass.
- A mass spectrum is the graph plotted by the mass spectrometer, with the masses plotted as the x axis and the relative number of ions of each mass on the y axis.
- **Electron Impact Ionization:** In the ion source, the sample is bombarded by a beam of electrons. When an electron strikes a neutral molecule, it may ionize that molecule by knocking out an additional electron.



When a molecule loses one electron, it then has a positive charge and one unpaired electron. The ion is therefore a radical cation. The electron impact ionization of methane is



- The ions of smaller molecular weights are called *fragments*.
- Bombardment of ethane molecules by energetic electrons, for example, produces the molecular ion and several fragments. Both charged and uncharged fragments are formed, but *only the positively charged fragments are detected by the mass spectrometer*. We will often use green type for the “invisible” uncharged fragments.

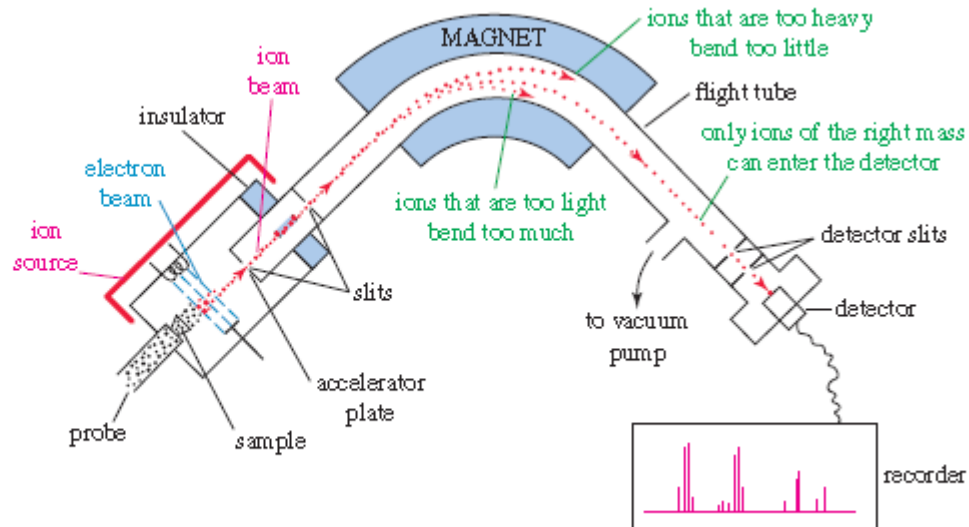


A double-focusing mass spectrometer. This one is combined with a gas chromatograph to use as a GC-MS. The gas chromatograph separates a mixture into its components and injects the purified components into the ion source of the mass spectrometer.

- **Separation of Ions of Different Masses:** Once ionization and fragmentation have formed a mixture of ions, these ions are separated and detected. The most common type of mass spectrometer, shown in Figure 12-16, separates ions by *magnetic deflection*.
- After ionization, the positively charged ions are attracted to a negatively charged accelerator plate, which has a narrow slit to allow some of the ions to pass through. The ion beam enters an evacuated flight tube, with a curved portion positioned between the poles of a large magnet. When a charged particle passes through a magnetic field, a transverse force bends its path. The path of a heavier ion bends less than the path of a lighter ion.
- The exact radius of curvature of an ion's path depends on its mass-to-charge ratio, symbolized by  $m/z$  (or by  $m/e$  in the older literature). In this expression,  $m$  is the mass of the ion (in amu) and  $z$  is its charge in units of the electronic charge.

**FIGURE 12-16**

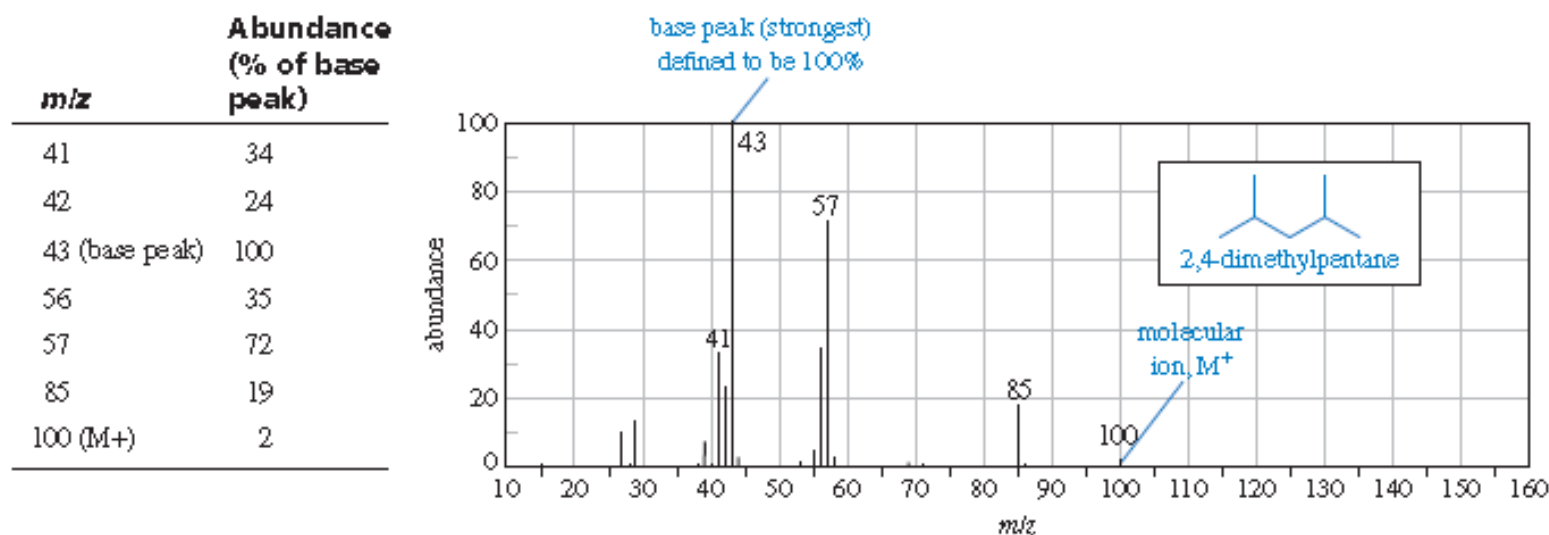
Diagram of a mass spectrometer. A beam of electrons causes molecules to ionize and fragment. The mixture of ions is accelerated and passes through a magnetic field, where the paths of lighter ions are bent more than those of heavier ions. By varying the magnetic field, the spectrometer plots the abundance of ions of each mass.





# 13B. The Mass Spectrum

- In the printed mass spectrum, all the masses are rounded to the nearest whole-number mass unit. The peaks are assigned abundances as percentages of the strongest peak, called the **base peak**. Notice that *the base peak does not necessarily correspond to the mass of the molecular ion*.
- A molecular ion peak (also called the *parent peak*) is observed in most mass spectra.



**FIGURE 12-17**

Mass spectrum of 2,4-dimethylpentane, given both as a bar graph and in tabular form. Abundances are given as percentages of the strongest peak (the base peak). In this example, the base peak is at  $m/z$  43 and the molecular ion peak (parent peak) is at  $m/z$  100. Notice that the molecular ion has an even mass number, while most of the fragments are odd.

# 14. DETERMINATION OF THE MOLECULAR FORMULA BY MASS SPECTROMETRY

## 14A. High-Resolution Mass Spectrometry (HRMS)

- Consider a molecular ion with a mass of 44. This approximate molecular weight might correspond to  $\text{C}_3\text{H}_8$  (propane),  $\text{C}_2\text{H}_4\text{O}$  (acetaldehyde),  $\text{CO}_2$ , or  $\text{CN}_2\text{H}_4$ . Each of these molecular formulas corresponds to a different exact mass:

$\text{C}_3\text{H}_8$		$\text{C}_2\text{H}_4\text{O}$		$\text{CO}_2$		$\text{CN}_2\text{H}_4$	
3 C	36.00000	2 C	24.00000	1 C	12.00000	1 C	12.00000
8 H	8.06260	4 H	4.03130			4 H	4.03130
		1 O	15.99491	2 O	31.98983	2 N	28.00610
44.06260		44.02621		43.98983		44.03740	

TABLE 12-3  
"Exact" Masses of Common  
Isotopes

Isotope	Atomic Mass (amu)
$^{12}\text{C}$	12.000000
$^1\text{H}$	1.007825
$^{16}\text{O}$	15.994914
$^{14}\text{N}$	14.003060

- If the HRMS measured the exact mass of this ion as 44.029 mass units, we would conclude that the compound has a molecular formula of  $\text{C}_2\text{H}_4\text{O}$ , because the mass corresponding to this formula is closest to the observed value.

# 14B. Use of Heavier Isotope Peaks

- Most elements do not consist of a single isotope, but contain heavier isotopes in varying amounts. These heavier isotopes give rise to small peaks at higher mass numbers than the major **M<sup>+</sup> molecular ion peak**. A peak that is one mass unit heavier than the M<sup>+</sup> peak is called the **M+1 peak**; two units heavier, the **M+2 peak**; and so on.
- Table 12-4 gives the isotopic compositions of some common elements, showing how they contribute to **M+1** and **M+2 peaks**.
- Iodine is recognized by the presence of the iodonium ion, I<sup>+</sup>, at  $m/z = 127$ .

TABLE 12-4

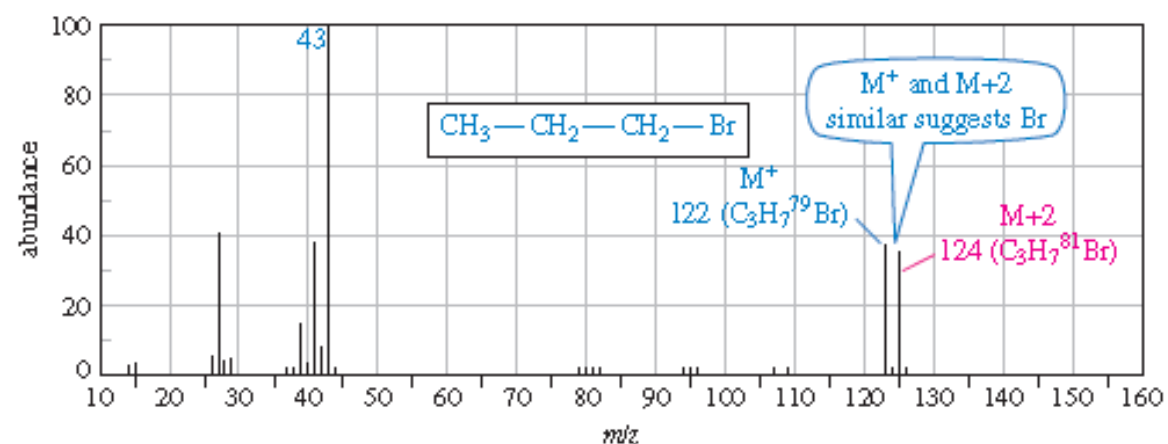
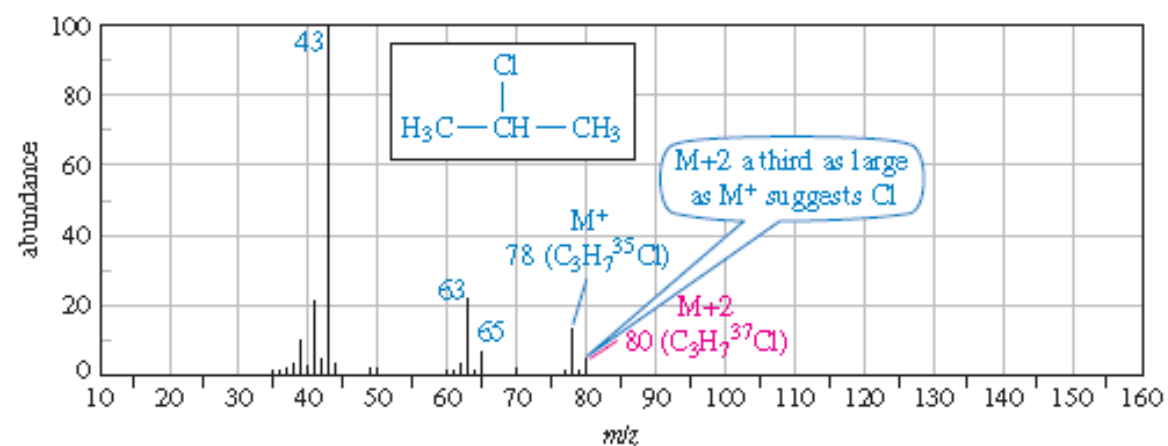
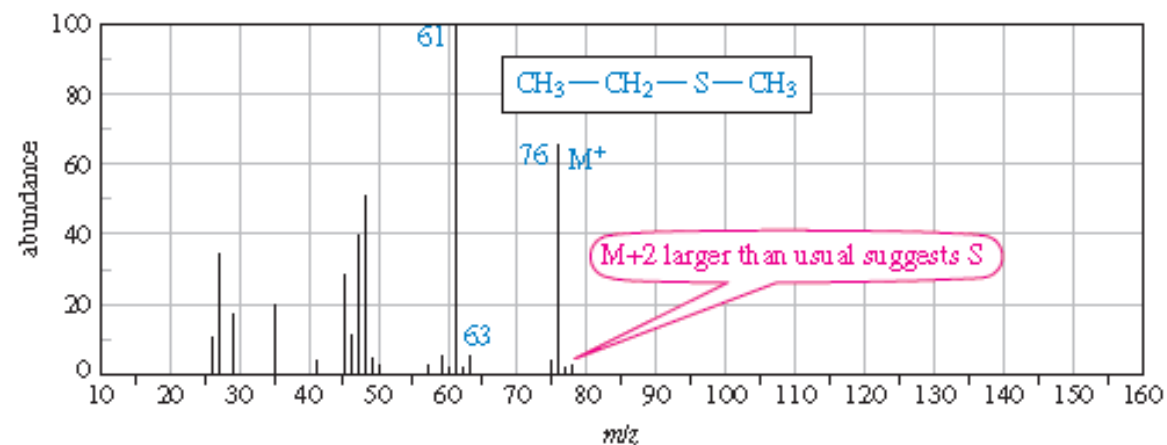
Isotopic Composition of Some Common Elements

Element		M <sup>+</sup>		M + 1		M + 2
hydrogen	<sup>1</sup> H	100.0%				
carbon	<sup>12</sup> C	98.9%	<sup>13</sup> C	1.1%		
nitrogen	<sup>14</sup> N	99.6%	<sup>15</sup> N	0.4%		
oxygen	<sup>16</sup> O	99.8%			<sup>18</sup> O	0.2%
sulfur	<sup>32</sup> S	95.0%	<sup>33</sup> S	0.8%	<sup>34</sup> S	4.2%
chlorine	<sup>35</sup> Cl	75.5%			<sup>37</sup> Cl	24.5%
bromine	<sup>79</sup> Br	50.5%			<sup>81</sup> Br	49.5%
iodine	<sup>127</sup> I	100.0%				

*Recognizable elements in the mass spectrum*

Br	M+2 as large as M <sup>+</sup>
Cl	M+2 a third as large as M <sup>+</sup>
I	I <sup>+</sup> at 127; large gap
N	odd M <sup>+</sup> , some even fragments
S	M+2 larger than usual (4% of M <sup>+</sup> )

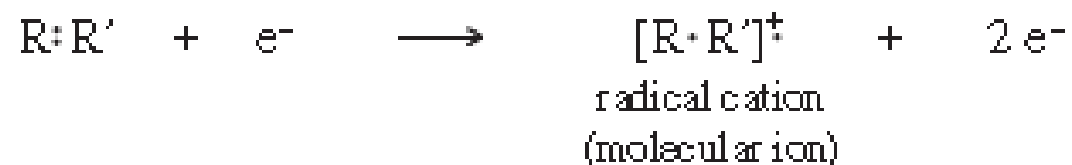
The following spectra show compounds containing sulfur, chlorine, and bromine.



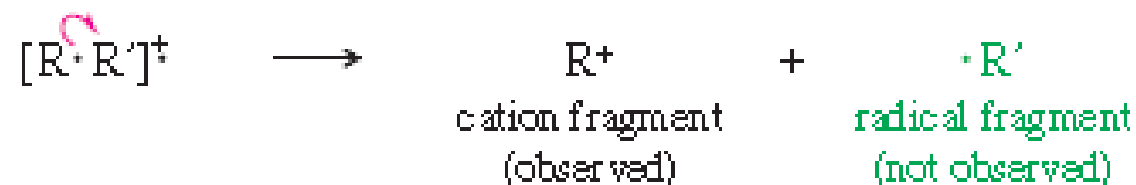
# 15. FRAGMENTATION PATTERNS IN MASS SPECTROMETRY

- An electron with a typical energy of 70 eV (6740 kJ/mol or 1610 kcal/mol) has far more energy than needed to ionize a molecule. The impact forms the radical cation, and it often breaks a bond to give a cation and a radical. The resulting cation is observed by the mass spectrometer, but the uncharged radical is not accelerated or detected. We can infer the mass of the uncharged radical from the amount of mass lost from the molecular ion to give the observed cation fragment.
- This bond breaking does not occur randomly; it tends to form the most stable fragments. By knowing what stable fragments result from different kinds of compounds, we can recognize structural features and use the mass spectrum to confirm a proposed structure.

## *Ionization*



## *Fragmentation*



# 15A. Mass Spectra of Alkanes

- The mass spectrum of hexane (Figure 12-19) shows several characteristics typical of straight-chain alkanes. Like other compounds not containing nitrogen, **the molecular ion ( $M^+$ )** has an even-numbered mass, and most of the **fragments** are odd-numbered. The base peak ( $m/z = 57$ ) corresponds to loss of an ethyl group, giving an ethyl radical and a butyl cation. The neutral ethyl radical is not detected, because it is not charged and is not accelerated or deflected.

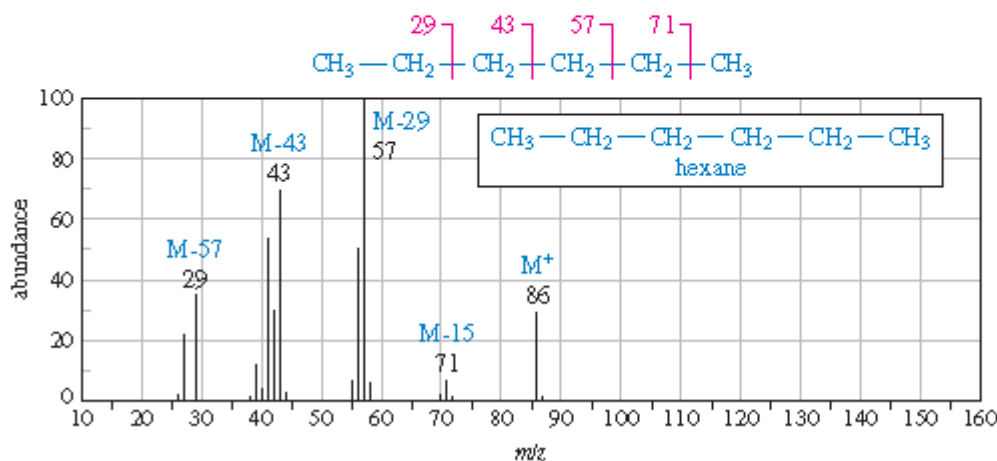
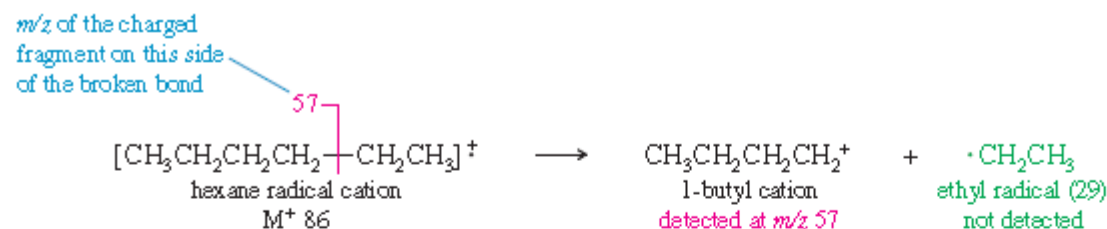
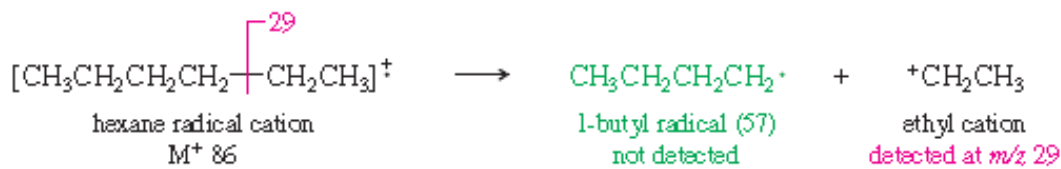
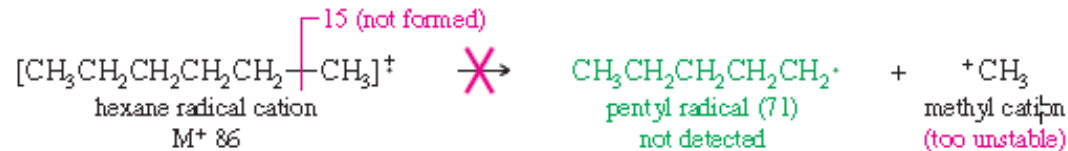
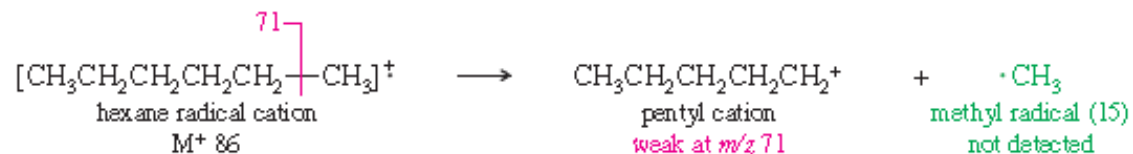
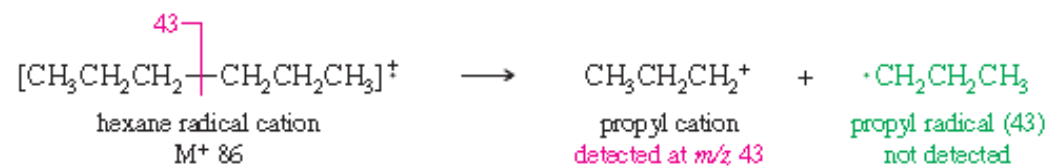


FIGURE 12-19

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



Symmetric cleavage of hexane gives a propyl cation and a propyl radical.



- Cation and radical stabilities help to explain the mass spectra of branched alkanes as well.
- Figure 12-20 shows the mass spectrum of 2-methylpentane.
- Fragmentation of a branched alkane commonly occurs at a branch carbon atom to give the most highly substituted cation and radical. Fragmentation of 2-methylpentane at the branched carbon atom can give a secondary carbocation in either of two ways:

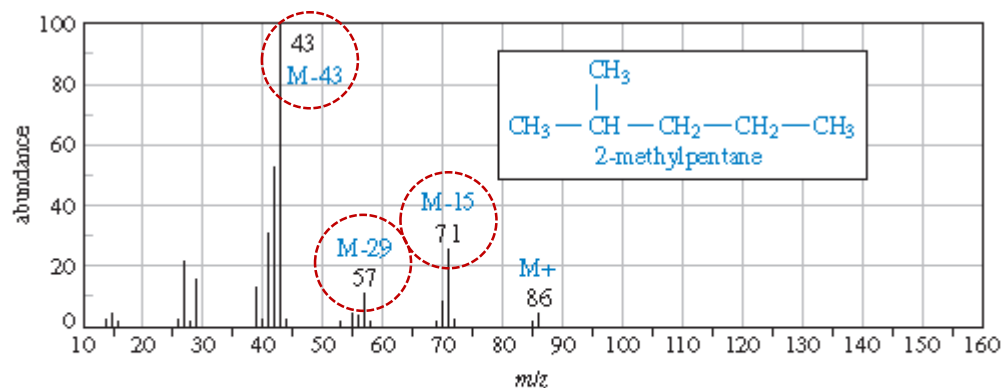
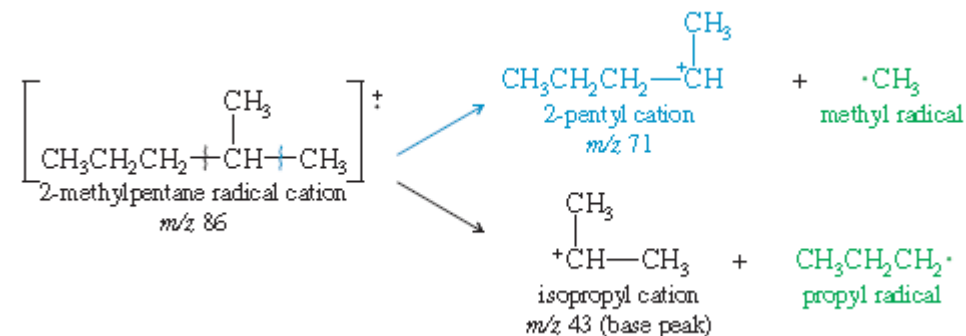


FIGURE 12-20

Mass spectrum of 2-methylpentane. The base peak corresponds to loss of a propyl radical to give an isopropyl cation.



# 15B. Fragmentation Giving Resonance-Stabilized Cations

- Fragmentation in the mass spectrometer gives resonance-stabilized cations whenever possible. The most common fragmentation of alkenes is cleavage of an allylic bond to give a resonance-stabilized allylic cation.

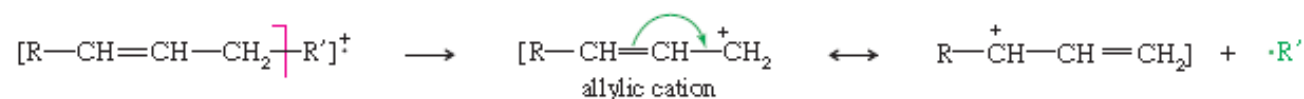
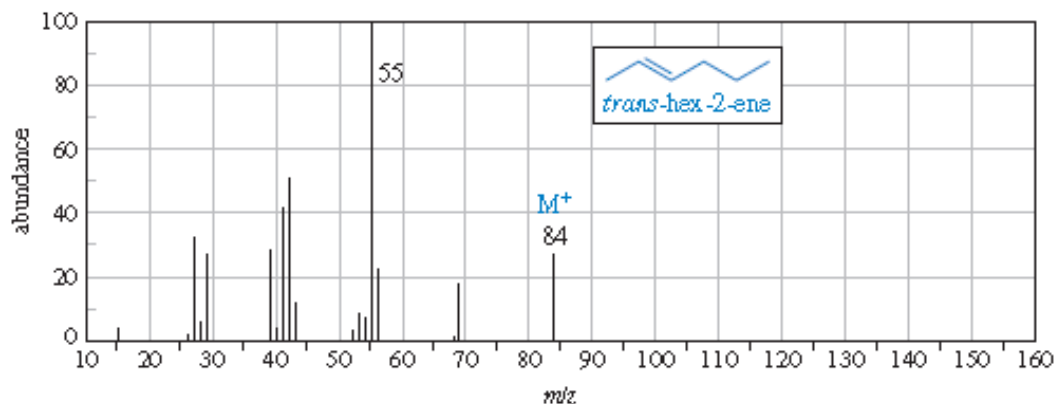
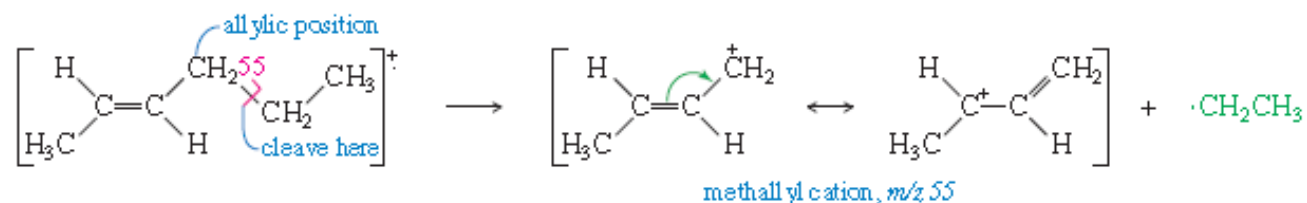


Figure 12-21 shows how the radical cation of *trans*-hex-2-ene undergoes allylic cleavage to give the resonance-stabilized cation responsible for the base peak at  $m/z$  55.

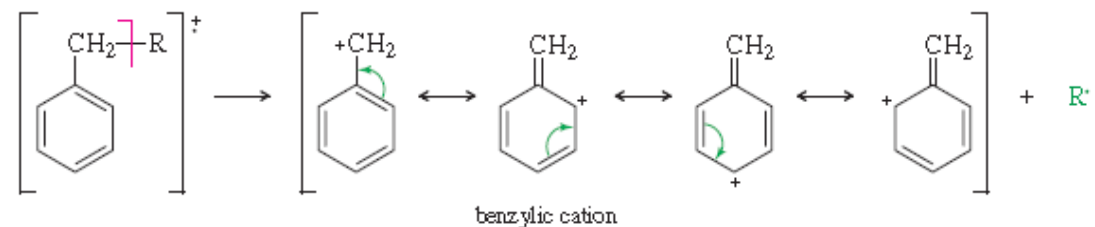


**FIGURE 12-21**

The radical cation of *trans*-hex-2-ene cleaves at an allylic bond to give a resonance-stabilized methallyl cation,  $m/z$  55.

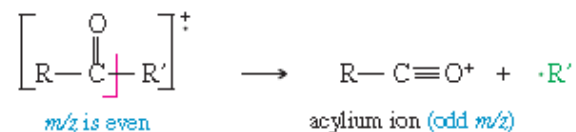


- Compounds containing aromatic rings tend to fragment at the carbon (called a benzylic carbon) next to the aromatic ring. Such a cleavage forms a resonance-stabilized benzylic cation.

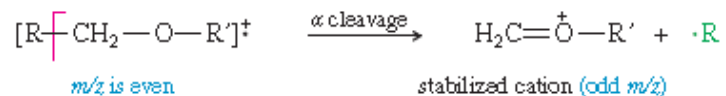


- Ethers, amines, and carbonyl compounds can also fragment to give resonance stabilized cations. The oxygen and nitrogen atoms in these compounds have nonbonding electrons that can stabilize the positive charge of a cation through resonance forms with octets on all the atoms.
- Common fragmentations often cleave the bond next to the carbon atom bearing the oxygen or nitrogen.

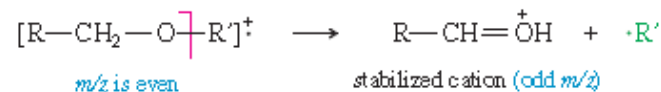
*Ketones and aldehydes: loss of alkyl groups to give acylium ions*



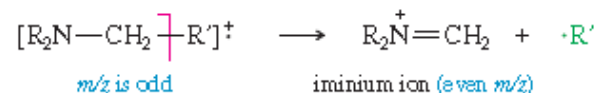
*Ethers: α cleavage*



*or loss of an alkyl group*



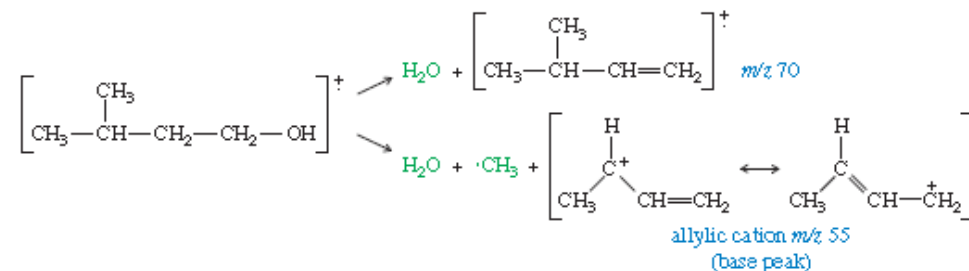
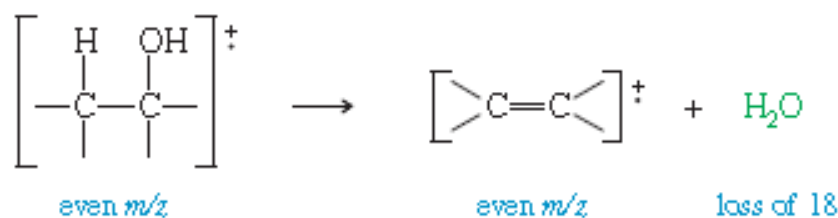
*Amines: α cleavage to give stabilized cations*



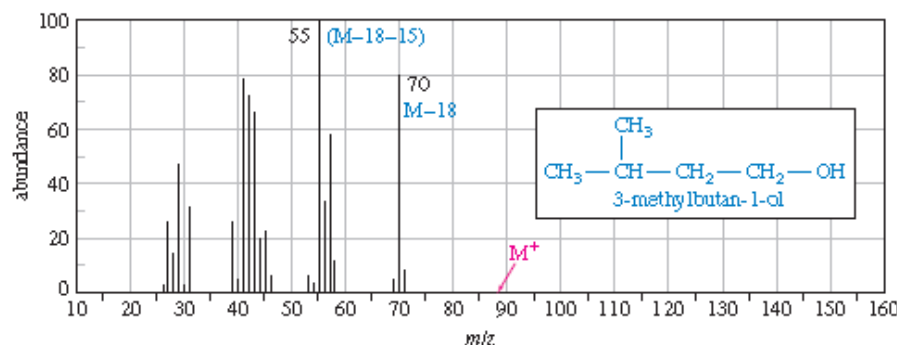
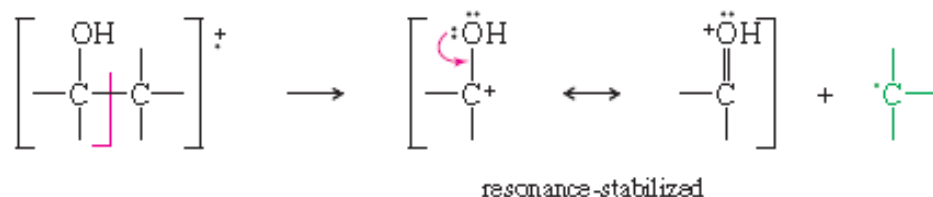
# 15C. Fragmentation Splitting Out a Small Molecule; Mass Spectra of Alcohols

- Mass spectral peaks are often seen corresponding to loss of small, stable molecules. Loss of a small molecule is usually indicated by a fragment peak with an even mass number, corresponding to loss of an even mass number. A radical cation may lose water (mass 18), CO (28), CO<sub>2</sub> (44), and even ethene (28) or other alkenes.

*Alcohols often lose water.*



*a cleavage of an alcohol*



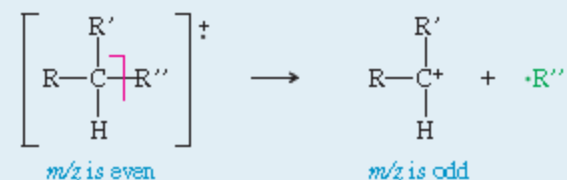
**FIGURE 12-22**

The mass spectrum of 3-methylbutan-1-ol. The strong peak at  $m/z$  70 is actually the M-18 peak, corresponding to loss of water. The molecular ion is not visible because it loses water easily.

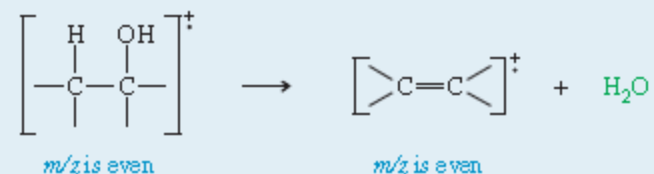
## SUMMARY Common Fragmentation Patterns

This summary is provided for rapid reference to the common fragmentation patterns of simple functional groups. Some of these functional groups are discussed in more detail in later chapters.

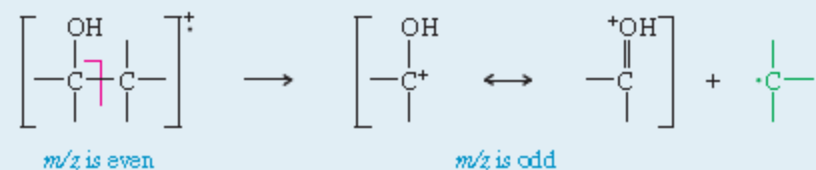
1. *Alkanes*: cleavage to give the most stable carbocations (Section 12-15A)



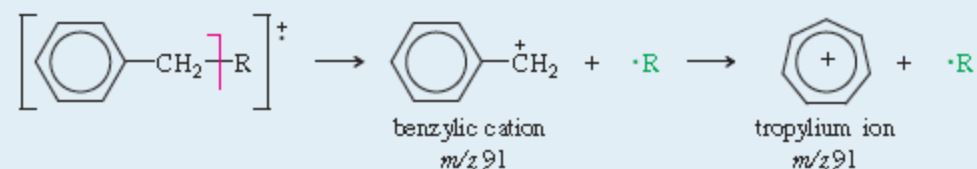
2. *Alcohols*: loss of water (Section 12-15C)



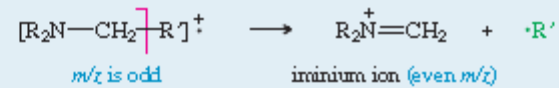
or  $\alpha$  cleavage (Section 12-15C)



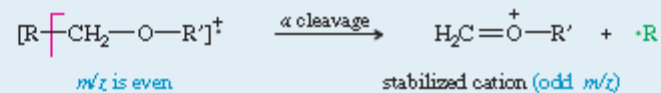
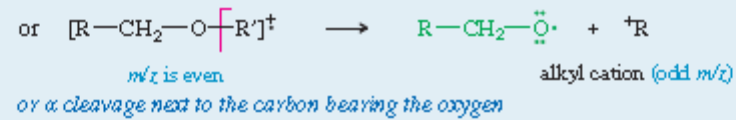
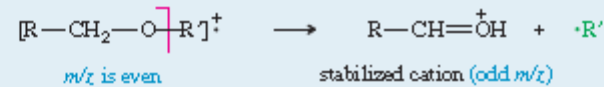
3. *Alkenes and aromatics*: cleavage to give allylic and benzylic carbocations (Section 12-15B and Section 16-15)



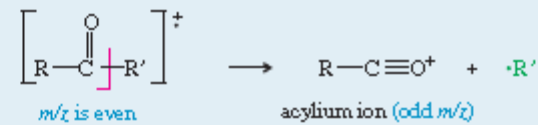
4. *Amines*:  $\alpha$  cleavage next to the carbon bearing the nitrogen to give stabilized cations (Section 12-15B and 19-8D)



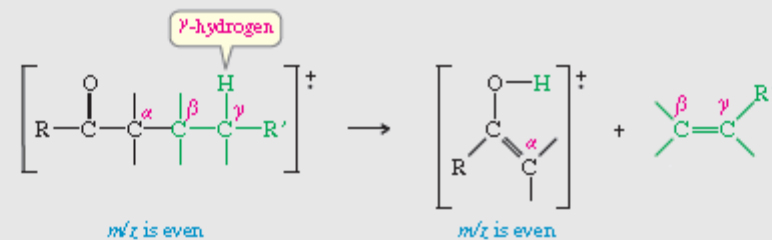
5. *Ethers*: loss of an alkyl group (Sections 12-15B and 14-4)



6. *Ketones and aldehydes*: loss of alkyl groups next to the carbon bearing the oxygen to give acylium ions (Section 12-15B and 18-5)



The McLafferty rearrangement splits out alkenes (covered in Section 18-5).



## Essential Terms

<b>absorption spectroscopy</b>	The measurement of the amount of light absorbed by a compound as a function of the wavelength. (p. 556)
<b>base peak</b>	The strongest peak in a mass spectrum. (p. 586)
<b>conjugated double bonds</b>	Double bonds that alternate with single bonds, allowing their pi bonding orbitals to overlap with each other. (p. 565)
<b>electromagnetic spectrum</b>	The range of all possible electromagnetic frequencies from zero to infinity. In practice, it ranges from radio waves up to gamma rays. (p. 558)
<b>fingerprint region</b>	The portion of the infrared spectrum between 600 and 1400 $\text{cm}^{-1}$ , where many complex vibrations occur. So named because no two different compounds (except enantiomers) have exactly the same absorptions in this region. (p. 561)

<b>FT-IR</b>	<b>(Fourier-transform infrared spectrometer)</b> Infrared light passes through both the sample and a scanning interferometer to give an interference pattern (interferogram). The interferogram is digitized, and the Fourier-transformed spectrum is calculated. (p. 563)
<b>fragmentation</b>	The breaking apart of a molecular ion upon ionization in a mass spectrometer. (p. 585)
<b>frequency (<math>\nu</math>)</b>	The number of complete wave cycles that pass a fixed point in a second; or the number of reversals of the electromagnetic field per second. (p. 557)
<b>gas chromatograph (GC)</b>	An instrument that vaporizes a mixture, passes the vapor through a column to separate the components, and detects the components as they emerge from the column. Mass spectrometry is one of the methods used to detect the components. (p. 587)
<b>HRMS</b>	<b>(high-resolution mass spectrometer)</b> A mass spectrometer that measures masses very accurately, usually to 1 part in 20,000. This high precision allows calculation of molecular formulas using the known atomic masses of the elements. (p. 588)
<b>infrared spectrometer</b>	A device that measures a compound's absorption of infrared light as a function of frequency or wavelength. (p. 562)
<b>infrared spectrum</b>	A graph of the infrared energy absorbed by a sample as a function of the frequency ( $\bar{\nu}$ , expressed as a wavenumber, $\text{cm}^{-1}$ ) or the wavelength ( $\lambda$ , expressed in $\mu\text{m}$ ). (p. 559)
<b>interferometer</b>	The light-measuring portion of an FT-IR spectrometer. The light is split into two beams. One beam is reflected from a stationary mirror, and the other from a moving mirror. The beams are recombined to form an interference pattern called an <b>interferogram</b> . Fourier transformation of the interferogram gives the spectrum. (p. 563)
<b>IR-active</b>	A vibration that changes the dipole moment of the molecule and thus can absorb infrared light. (p. 562)
<b>IR-inactive</b>	A vibration that does not change the dipole moment of the molecule and thus cannot absorb infrared light. (p. 562)

<b>mass spectrometer</b>	An instrument that ionizes molecules, sorts the ions according to their masses, and records the abundance of ions of each mass. (p. 584)
<b>mass spectrum</b>	The graph produced by a mass spectrometer, showing the masses along the <i>x</i> axis and their abundance along the <i>y</i> axis. (p. 584)
<b><i>m/z</i> (formerly <i>m/e</i>):</b>	The mass-to-charge ratio of an ion. Most ions have a charge of +1, and <i>m/z</i> simply represents their masses. (p. 585)
<b>molecular ion, <math>M^+</math></b>	<b>(parent ion)</b> In mass spectrometry, the ion with the same mass as the molecular weight of the original compound; no fragmentation has occurred. (p. 585)
<b><math>M + 1</math> peak:</b>	An isotopic peak that is one mass unit heavier than the major molecular ion peak. (p. 588)
<b><math>M + 2</math> peak:</b>	An isotopic peak that is two mass units heavier than the major molecular ion peak. (p. 588)
<b>overtone</b>	A relatively weak absorption at a multiple of (usually double) the fundamental vibration frequency. Occurs with very strong absorptions, such as those of carbonyl (C=O) groups. (p. 562)
<b>photon</b>	A massless packet of electromagnetic energy. (p. 557)
<b>radical cation</b>	A positively charged ion with an unpaired electron; commonly formed by electron impact ionization, when the impinging electron knocks out an additional electron. (p. 585)
	$R \cdot R + e^- \longrightarrow [R \cdot R]^+ + 2e^-$ <p style="text-align: center;">radical cation</p>
<b>source (ion source)</b>	The part of a mass spectrometer where the sample is ionized and undergoes fragmentation. (p. 585)
<b>wavelength (<math>\lambda</math>)</b>	The distance between any two peaks (or any two troughs) of a wave. (p. 557)
<b>wavenumber (<math>\bar{\nu}</math>)</b>	The number of wavelengths that fit into one centimeter ( $\text{cm}^{-1}$ or reciprocal centimeters); proportional to the frequency. The product of the wavenumber (in $\text{cm}^{-1}$ ) and the wavelength (in $\mu\text{m}$ ) is 10,000. (p. 558)