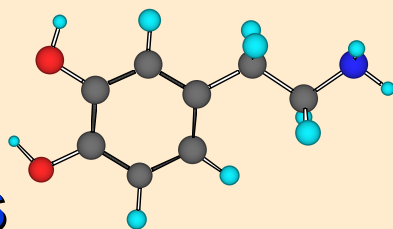


12



# Mass Spectrometry

Chapter 12

12-1

## 12 Mass Spectrometry (MS)

- ◆ An analytical technique for measuring the mass-to-charge ratio ( $m/z$ ) of ions, most commonly positive ions, in the gas phase
- ◆ Today, mass spectrometry is our most valuable analytical tool for the determination of precise molecular weights

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## 12 A Mass Spectrometer

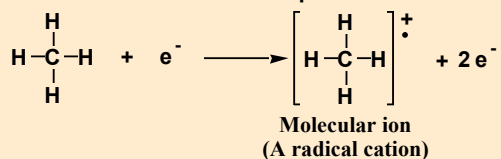
- ◆ A mass spectrometer is designed to do three things
  1. convert neutral atoms or molecules into a beam of positive (or negative) ions
  2. separate the ions on the basis of their mass-to-charge ratio ( $m/z$ )
  3. measure the relative abundance of each ion

12-3

## 12 A Mass Spectrometer

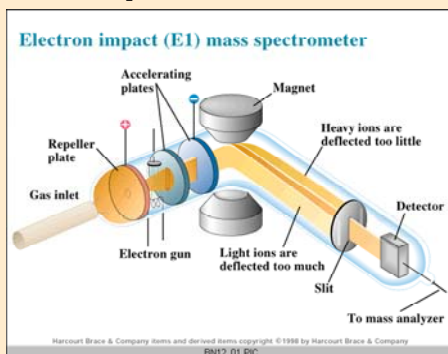
### ◆ Electron Ionization MS

- in the ionization chamber, the sample is bombarded with a beam of high-energy electrons
- collisions between these electrons and the sample result in loss of electrons from sample molecules and formation of positive ions



12-4

## 12 Mass Spectrum



12-5

## 12 Resolution

- ◆ **Resolution:** a measure of how well a mass spectrometer separates ions of different mass
  - low resolution - capable of distinguishing among ions of different nominal mass, that is ions that differ by at least one or more mass units
  - high resolution - capable of distinguishing among ions that differ in mass by as little as 0.0001 mass unit

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## 12 Resolution

- $C_3H_6O$  and  $C_3H_8O$  have nominal masses of 58 and 60, and can be distinguished by low-resolution MS
- these two compounds each have nominal mass of 60. Distinguish between them by high-resolution MS

Molecular Formula	Nominal Mass	Precise Mass
$C_3H_8O$	60	60.05754
$C_2H_4O_2$	60	60.02112

12-7

## 12 M+2 and M+1 Peaks

- ◆ The most common elements giving rise to  $M + 2$  peaks are chlorine and bromine
- ◆ Chlorine in nature is 75.77%  $^{35}Cl$  and 24.23%  $^{37}Cl$ 
  - a ratio of  $M$  to  $M + 2$  of approximately 3:1 indicates the presence of a single chlorine in a compound
- ◆ Bromine in nature is 50.7%  $^{79}Br$  and 49.3%  $^{81}Br$ 
  - a ratio of  $M$  to  $M + 2$  of approximately 1:1 indicates the presence of a single bromine in a compound

12-8

## 12 Fragmentation of M

- ◆ To attain high efficiency of molecular ion formation and give reproducible mass spectra, it is common to use electrons with energies of approximately 70 eV (1600 kcal/mol)
- ◆ This energy is sufficient not only to dislodge one or more electrons from a molecule, but also to cause extensive fragmentation
- ◆ These fragments may be unstable as well and, in turn, break apart to even smaller fragments

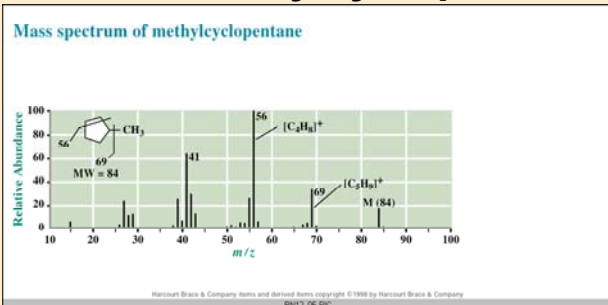
12-9

## 12 Interpreting MS

- ◆ The only elements to give significant  $M + 2$  peaks are Cl and Br. If no large  $M + 2$  peak is present, these elements are absent
- ◆ Is the mass of the molecular ion odd or even?
- ◆ **Nitrogen Rule:** if a compound has
  - zero or an even number of nitrogen atoms, its molecular ion will appear as a even  $m/z$  value
  - an odd number of nitrogen atoms, its molecular ion will appear as an odd  $m/z$  value

12-10

## 12 MS of methylcyclopentane



12-11

## 12 Combustion Analysis

94.08% C and 5.92 % H,  $M^+$  is 102.14g

$$\frac{102.14 \text{ g}}{\text{mole}} \times \frac{5.92 \text{ g C}}{100 \text{ g}} \times \frac{\text{mole C}}{1.0079 \text{ g C}} = 6 \text{ H}$$

$$\frac{102.14 \text{ g}}{\text{mole}} \times \frac{94 \text{ g C}}{100 \text{ g}} \times \frac{\text{mole C}}{12.011 \text{ g C}} = 8 \text{ C}$$

12-12

## 12 Units of Unsaturation

$$\begin{aligned} \text{double bonds + rings} &= \frac{(2 \times C) + 2 - H - X + N}{2} \\ &= \frac{(2 \times 8) + 2 - 6 - 0 + 0}{2} \end{aligned}$$