Chapter 13: Mass spectrometry and Infrared spectroscopy

Learning Objectives:

1. Be able to predict the fragmentation patterns expected to arise in the mass spectrum of alkanes, alkyl halides, ethers, alcohols, and ketones.
2. Be able to describe what happens to a compound in a mass spectrometer
3. Be able to use the mass spectrum of a compound to find the molecular mass, and to help identify the structure of a compound.
4. Be able to describe what happens to a compound when it absorbs infrared radiation.
5. Be able to use of a chart of functional group IR absorptions, and to help identify the structure of a compound.
6. Be able to use result from elemental analysis to deduce the number of carbon, hydrogen, and nitrogen in the molecular formula.*

* Supplemental material, not included in the textbook

Sections:

13.1 Mass Spectrometry
13.2 The Mass Spectrum – Fragmentation
13.3 Isotope in Mass Spectrometry
13.4 Determination of Molecular Formulas: High-Resolution Mass Spectrometry
13.5 Fragmentation at Functional Groups*
13.6 Spectroscopy and the Electromagnetic Spectrum[#]
13.7 Infrared Spectroscopy
13.8 Characteristic Infrared Absorption bands
13.9 The Intensity of Absorption bands[#]
13.10 The position of Absorption bands
13.11 C-H Absorption Bands
13.12 The Shape of Absorption Bands*
13.13 Absence of Absorption Bands[#]
13.14 Infrared Inactive Vibrations[#]
13.15 Identifying Infrared Spectra
Additional material: Calculation of molecular formula using information from mass spectrometry and elemental analysis

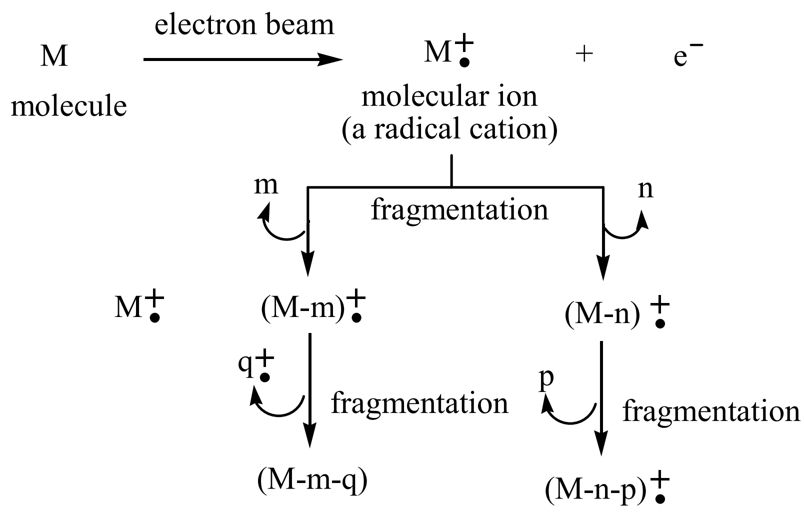
* Sections that will be focused
[#] Sections that will be skipped

Recommended additional problems

32, 45, 46, 50, 51, 54

Class Note

13.1 Mass Spectrometry and 13.2 The Mass Spectrum – Fragmentation



Cations detected by collector: $M^{+\bullet}$ $(M\text{-}m)^{+\bullet}$ $(M\text{-}n)^{+\bullet}$ $(M\text{-}n\text{-}p)^{+\bullet}$ $q^{+\bullet}$

A. Most of the instrument is designed to detect cations.

B. Relative abundance of fragmentation pattern depends on the energy of the electron beam.

13.3 Isotope in Mass Spectrometry

A. Relative abundance of carbon on molecular ion

^{12}C: 98.89% (0.989) (M) ^{13}C: 1.11% (0.011) (M+1)

Each carbon contributes 0.011 abundance to the abundance of M+1 peak =>

relative abundance of M+1 peak =
(number of carbon in the analyzed molecule) x relative abundance of M x 0.011

=> (number of carbon in the analyzed molecule) = relative abundance of M+1 peak ÷ (relative abundance of M x 0.011)

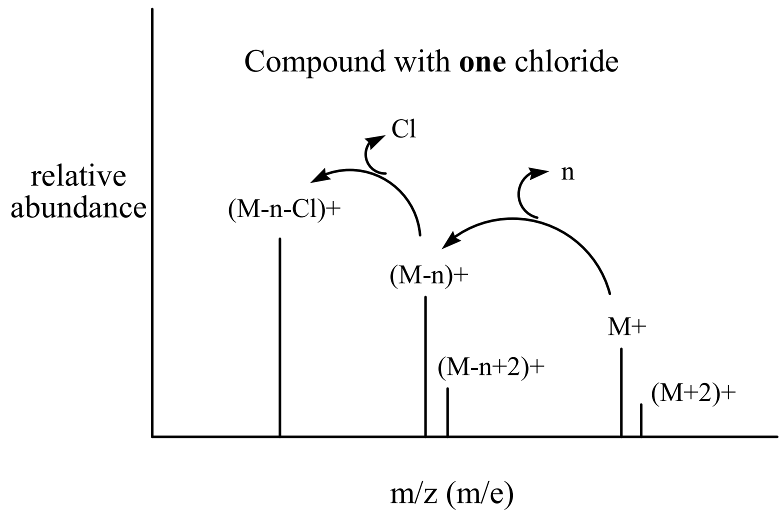
* Not very accurate for compound with high molecular weight

Example: M (150): 16.28 and (M+1) (151): 1.66

B. Relative abundance of Cl on molecular ion

^{35}Cl: 75.77% (0.76)　　　^{37}Cl: 24.23% (0.24)
(M)　　　　　　　　　　　　(M+2)

For compound with one Cl: M/(M+2) $\approx$ 3/1

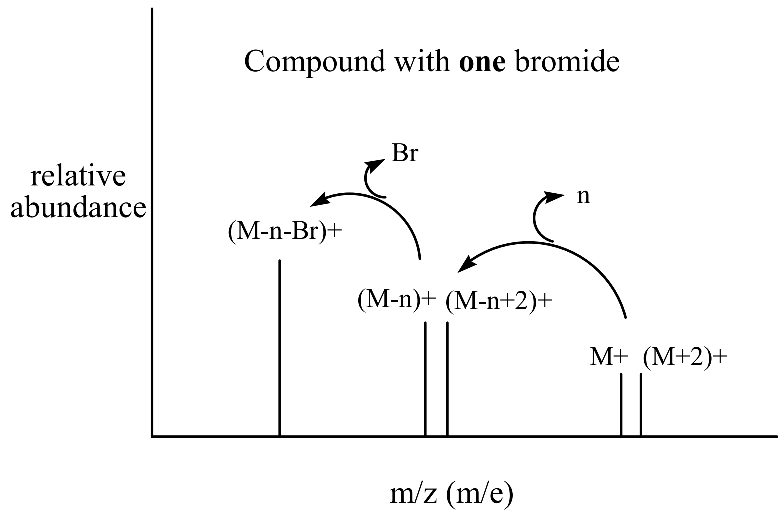


C. Relative abundance of Br on molecular ion

^{79}Br: 50.69% (0.51) (M)

^{81}Br: 49.31% (0.49) (M+2)

For compound with one Br: M/(M+2) ≈ 1/1



13.4 Determination of Molecular Formulas: High-Resolution Mass Spectrometry

Use Table 13.3

13.5 Fragmentation at Functional Groups*

A. Alkyl halides ($CH_3CH_2CH_2Br$ and $(CH_3)_2CHCl$)

B. Ethers ($CH_3CH_2CH(CH_3)OCH(CH_3)_2$)

C. Alcohols ($CH_3CH_2CH_2CH_2CH(OH)CH_3$)

D. Ketones ($CH_3CH_2CH_2COCH_3$)

13.7 Infrared Spectroscopy

Figure 13.12 (stretching and bending)

13.8 Characteristic Infrared Absorption bands

Table 13.4 (OH, NH, and C=O)

13.10 The position of Absorption bands

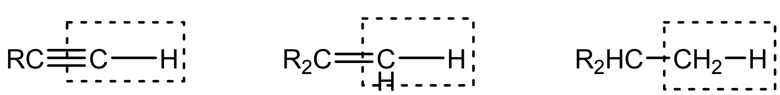
A. Effect of mass

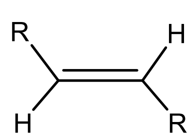
B. Effect of bond order

D. Effect of resonance and inductive effect

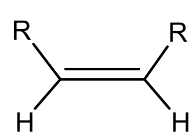
acyl halide > ester > aldehyde > ketone > amide

13.11 C-H Absorption Bands





trans



cis

* NMR provides more reliable characterization.

13.12 The Shape of Absorption Bands

NH, NH_2, OH, and CO_2H

13.15 Identifying Infrared Spectra

C=O and H-bond

Additional material: Calculation of molecular formula using information from mass spectrometry and elemental analysis

A. Example 1

From Mass Spec M^+: 99
From elemental analysis: C: 60.5%; H: 9.1%; N: 14.1%

B. Example 2

From Mass Spec M^+: 142, relative intensity: $(M^+/(M+2)^+ = 100/35$
From elemental analysis: C: 58.9%; H: 4.9%