PART 4

Identification of Organic Compounds

Chapter
13. MS, IR, UV/Vis
14. NMR

Identification of organic comp'ds

- ❑ isolation [purification] first
  - ■ then ~ distillation, recrystallization
  - ■ now ~ distillation, recrystallization, and chromatography
- ❑ structure determination
  - ■ then ~ elemental analysis + spot tests   = + Br_2
  - ■ now ~ instrumental analysis
    - ❑ MS ~ fragmentation ~ molecular mass and formula
    - ❑ IR ~ vibration of bond ~ functional group
    - ❑ UV/Vis ~ absorption ~ (conj) double bonds
    - ❑ NMR ~ relaxation ~ environment Chapter 14

Classes of org comp'ds

Table 13.1 Classes of Organic Compounds

Class	Structure
Alkane	$-\overset{\mid}{\underset{\mid}{C}}-$ contains only C—C and C—H bonds
Alkene	$\overset{}{C}=\overset{}{C}$
Alkyne	$-C\equiv C-$
Nitrile	$-C\equiv N$
Alkyl halide	R—X X = F, Cl, Br, or I
Ether	R—O—R
Alcohol	R—OH
Benzene	(benzene ring)
Phenol	(benzene ring)—OH
Aniline	(benzene ring)—NH_2
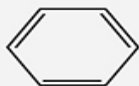
Class	Structure
Aldehyde	$R\overset{O}{\underset{}{\overset{\parallel}{C}}}H$
Ketone	$R\overset{O}{\underset{}{\overset{\parallel}{C}}}R$
Carboxylic acid	$R\overset{O}{\underset{}{\overset{\parallel}{C}}}OH$
Ester	$R\overset{O}{\underset{}{\overset{\parallel}{C}}}OR$
Amides	$R\overset{O}{\underset{}{\overset{\parallel}{C}}}NH_2$
	$R\overset{O}{\underset{}{\overset{\parallel}{C}}}NHR$
	$R\overset{O}{\underset{}{\overset{\parallel}{C}}}NR_2$
Amine (primary)	$R-NH_2$
Amine (secondary)	$R-\overset{R}{\underset{}{\overset{\mid}{N}}}H$
Amine (tertiary)	$R-\overset{R}{\underset{}{\overset{\mid}{N}}}-R$

Chapter 13

MS, IR, UV/Vis

Mass spectrometry
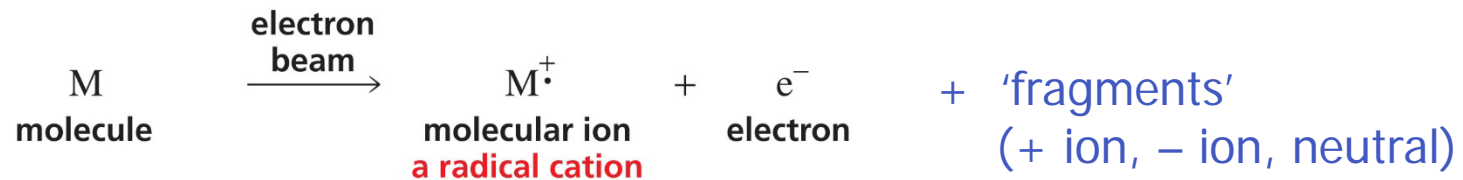
Infrared spectroscopy

UV and visible spectroscopy

Mass spectrometry [MS]

❑ Sample vaporized, ionized, and fragmented;

$$M \xrightarrow{\text{electron beam}} M^{+\cdot} + e^- + \text{'fragments'}$$

M
molecule

$M^{+\cdot}$
molecular ion
a radical cation

e^-
electron

'fragments'
(+ ion, – ion, neutral)

❑ (+) species moved [accelerated], deflected, and collected according to m/z [mass-to-charge ratio].
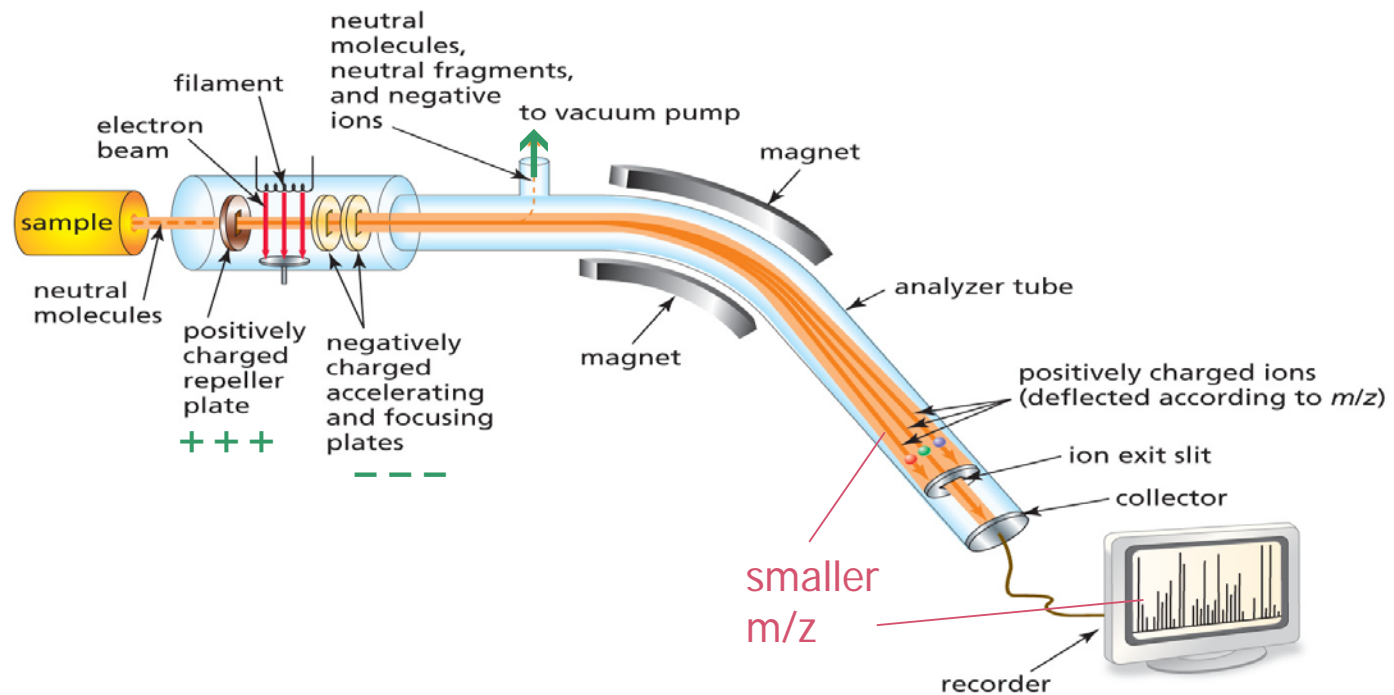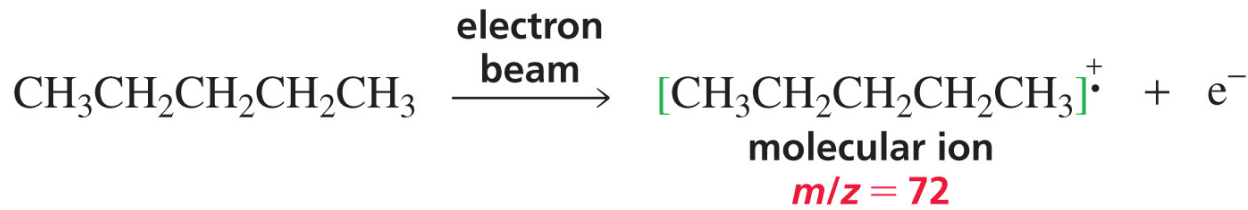
Mass spectrum
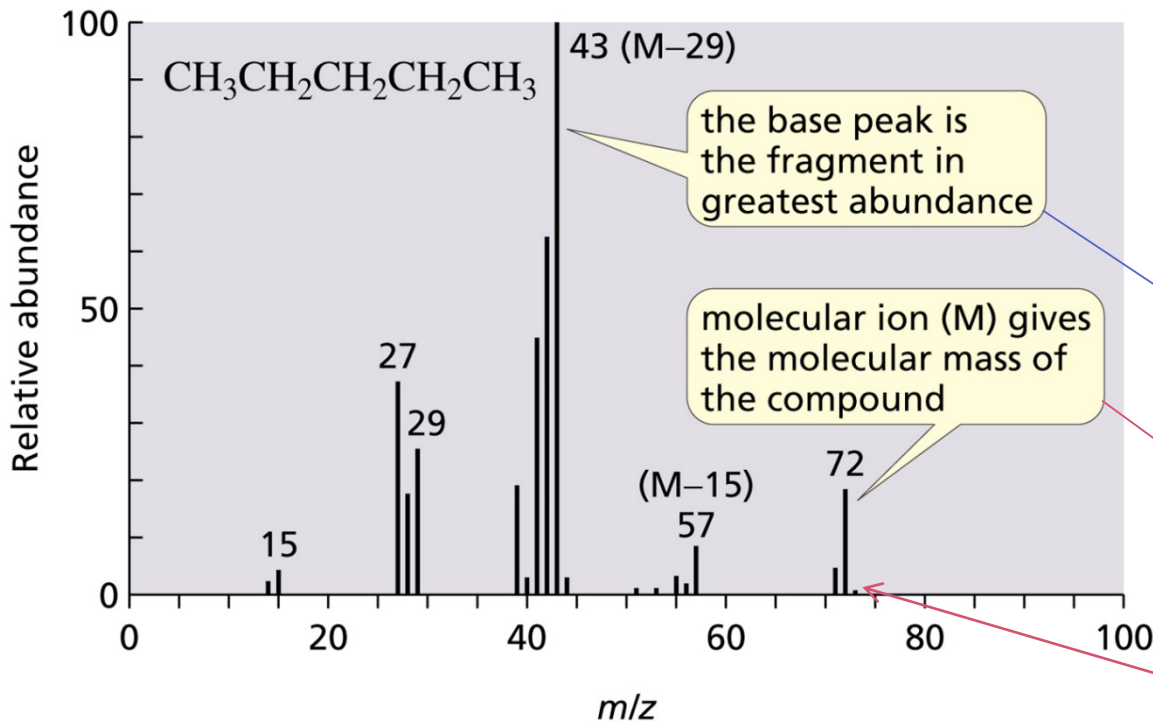
❑ relative abundance of fragments vs m/z

m/z = molecular mass
← z = 1 most cases

molecular mass [amu]
= molecular weight
molar mass [g/mol]

$CH_3CH_2CH_2CH_2CH_3$

43 (M−29)

the base peak is the fragment in greatest abundance

27
29
15

molecular ion (M) gives the molecular mass of the compound

(M−15)
57
72

base peak [base ion] = tallest peak

M = molecular ion
= m/z of M

M+1?

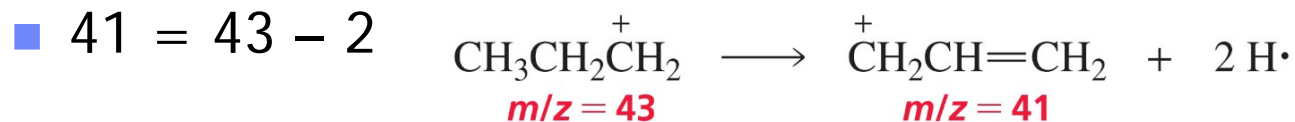$$CH_3CH_2CH_2CH_2CH_3 \xrightarrow{\text{electron beam}} [CH_3CH_2CH_2CH_2CH_3]^{+\bullet} + e^-$$
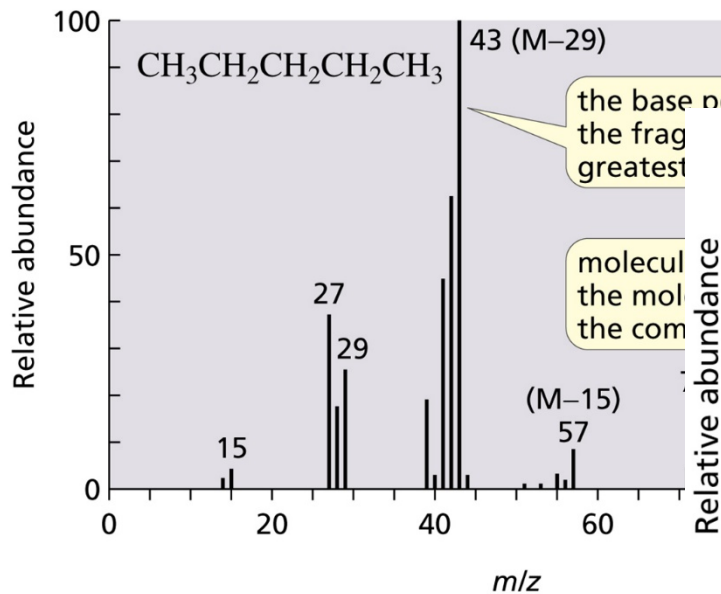
molecular ion
m/z = **72**

□ Abundance depends on

- bond strength ~ Weaker bonds break earlier.

- stability of fragment ~ More stable fragments formed more.

□ eg for pentane
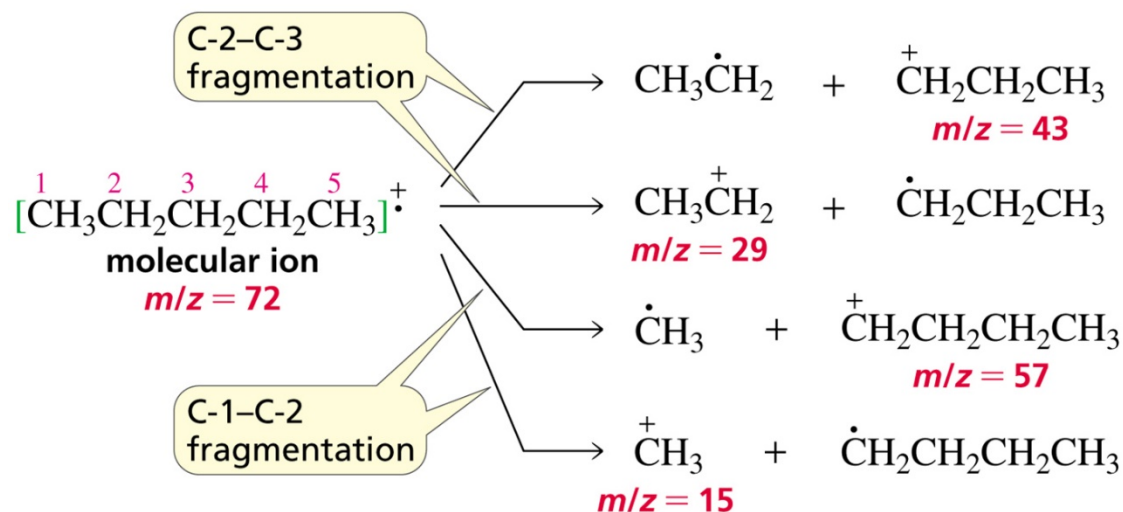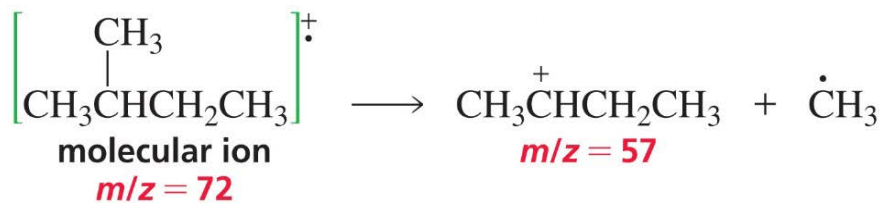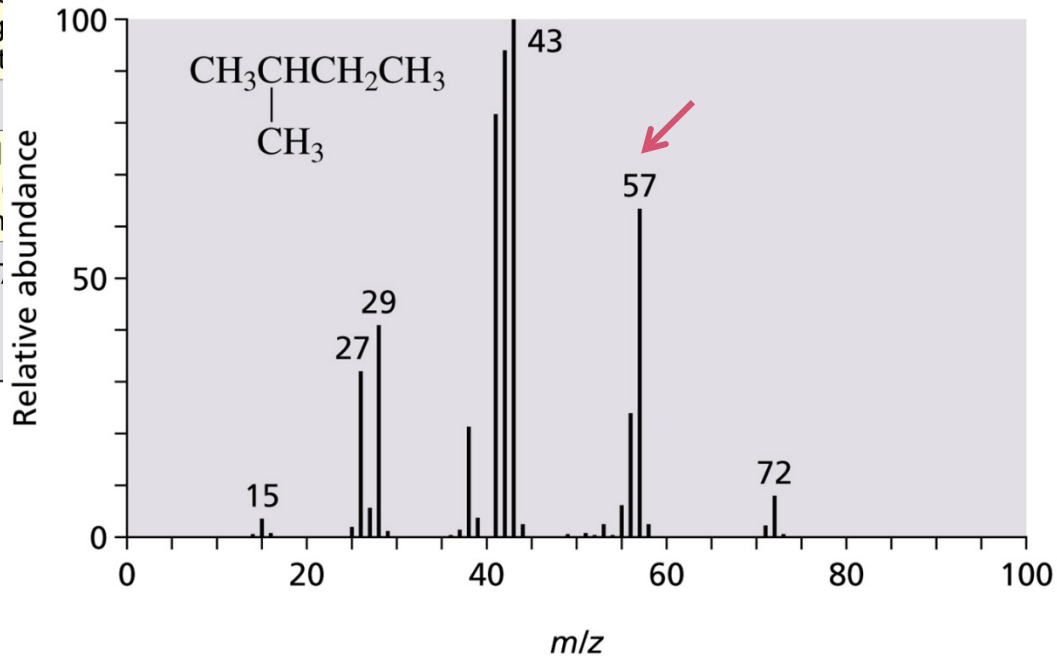

- 43 (base) & 29 are taller than 57 & 15. why?

- 41 = 43 − 2

❑ pentane vs 2-Me-butane

Calculating molecular formula

- □ from m/z of M (= M)

- □ 'base value' = # of C and # of H ← 'rule of 13'

  - ■ #C = M/13; #H = #C + leftover

    - □ M = 98 = 13*7 + 7 → base value = C_7H_{14}

- □ 1 O = CH_4; 1 N = CH_2

  - □ M = 98 with 1 O → $C_6H_{10}O$; with N & O → C_5H_8NO

- □ nitrogen rule

  - ■ If M is odd #, it contains odd # of N.

- ➢ Problem 5(d) p601: an amide with M = 115

  - ➢ C_8H_{19} → $C_6H_{13}NO$

- ➢ Do Problem 6 - 8

Isotopes in MS

- M+1 peak ← ^{13}C

- M+2 peak ← Cl or Br

  - others? ^{18}O? ^{13}C+D? 2 ^{13}C's? No.

  - Cl with 1/3 height; Br with 1/1
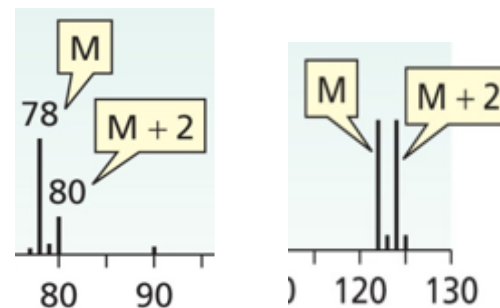
Table 13.2	The Natural Abundance of Isotopes Commonly Found in Organic Compounds		
Element	**Natural abundance**		
Carbon	^{12}C 98.89%	^{13}C 1.11%	
Hydrogen	^{1}H 99.99%	^{2}H 0.01%	
Nitrogen	^{14}N 99.64%	^{15}N 0.36%	
Oxygen	^{16}O 99.76%	^{17}O 0.04%	^{18}O 0.20%
Sulfur	^{32}S 95.0%	^{33}S 0.76%	^{34}S 4.22% ^{36}S 0.02%
Fluorine	^{19}F 100%		
Chlorine	^{35}Cl 75.77%		^{37}Cl 24.23%
Bromine	^{79}Br 50.69%		^{81}Br 49.31%
Iodine	^{127}I 100%		

High resolution MS

- gives exact mass to the precision of 0.0001

- gives molecular formula

Some Compounds with a Molecular Mass of 122 amu and Their Exact Molecular Masses and Molecular Formulas						
Exact molecular mass (amu)	122.1096	122.0845	122.0732	122.0368	122.0579	122.0225
Molecular formula	C_9H_{14}	$C_7H_{10}N_2$	$C_8H_{10}O$	$C_7H_6O_2$	$C_4H_{10}O_4$	$C_4H_{10}S_2$

- based on C = 12.0000 <u>not</u> 12.011

- eg Prob 10
  - C_6H_{14} = 12.0000 * 6 + 1.0078 * 14 = 86.1096

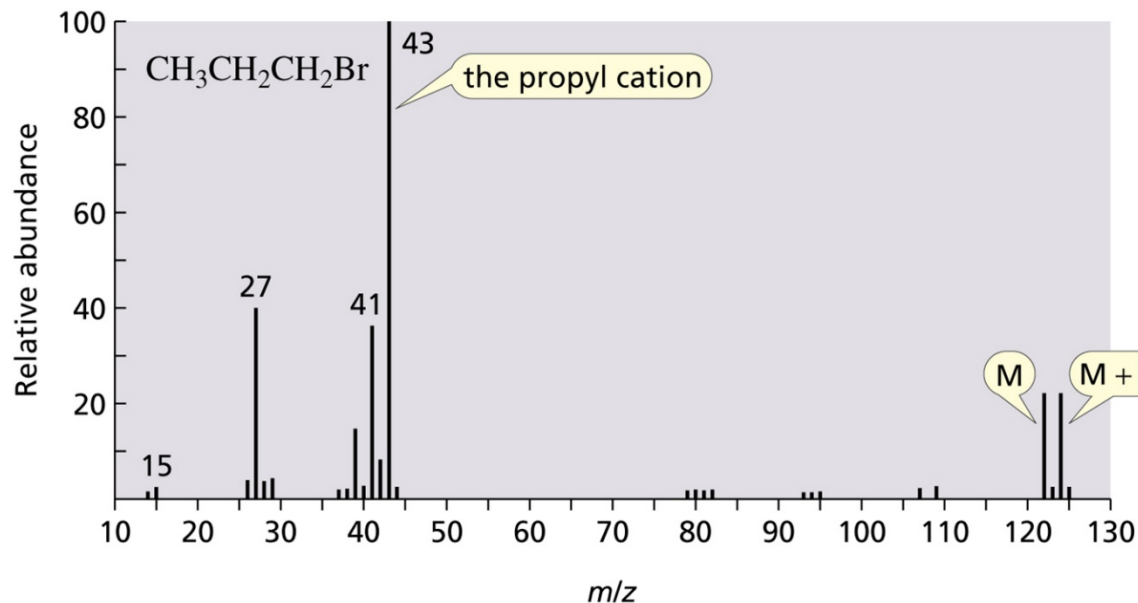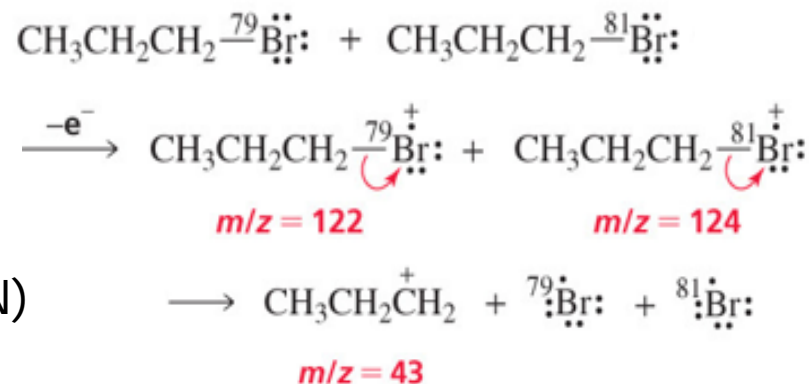| Table 13.3	The Exact Masses of Some Common Isotopes
Isotope	**Mass**
^1H	1.007825 amu
^{12}C	12.00000 amu
^{14}N	14.0031 amu
^{16}O	15.9949 amu
^{32}S	31.9721 amu
^{35}Cl	34.9689 amu
^{79}Br	78.9183 amu

Fragmentation patterns: RX

□ PrBr

- M/M+2 = 1/1 ~ Br

- M by giving up one of :, if any

- C–Br weakest

- heterolysis to Pr$^+$ + Br• (← Br more EN)

- base peak at 43 = M – 79 = M+2 – 81

$$CH_3CH_2CH_2{}^{79}\ddot{B}\ddot{r}: \quad + \quad CH_3CH_2CH_2{}^{81}\ddot{B}\ddot{r}:$$

$$\xrightarrow{-e^-} \quad CH_3CH_2CH_2 \overset{+}{\underset{79}{\ddot{B}}}\ddot{r}: \quad + \quad CH_3CH_2CH_2 \overset{+}{\underset{81}{\ddot{B}}}\ddot{r}:$$

m/z = 122   *m/z = 124*

$$\longrightarrow \quad CH_3CH_2\overset{+}{C}H_2 \quad + \quad {}^{79}\dot{:}\ddot{B}\ddot{r}: \quad + \quad {}^{81}\dot{:}\ddot{B}\ddot{r}:$$

m/z = 43

Bond Dissociation Energy
- C—Br = 71 kcal/mol ←
- C—Cl = 85 kcal/mol
- C—C = 89 kcal/mol
- C—H = 99 kcal/mol

2-Cl-propane

- M/M+2 = 3/1 ~ Cl

- base ion at 43 ← C–Cl heterolysis

  - C$^+$ + Cl•

- 63 and 65? C–C α-cleavage

❑ 2-Cl-Pr (cont'd)

- ■ α-cleavage
  - ❑ breaking α-C−C bond
    - ▪ α to Cl <u>not</u> to branch
  - ❑ resulting stable C⁺ (with complete octet)
  - ❑ a homolysis
  - ❑ occur in chlorides; <u>not</u> in bromides

the α-carbon

$$CH_3CH{-}^{35}\overset{+}{\ddot{C}l}: \;+\; CH_3CH{-}^{37}\overset{+}{\ddot{C}l}:$$

m/z = 78   *m/z = 80*

homolytic cleavage (α-cleavage)

$$CH_3CH{=\!=}^{35}\overset{+}{\ddot{C}l}: \;+\; CH_3CH{=\!=}^{37}\overset{+}{\ddot{C}l}: \;+\; 2\,{}^{\bullet}CH_3$$

m/z = 63   *m/z = 65*

product of α-cleavage   all the atoms have complete octets

$$CH_3CH{-}\overset{+}{\ddot{C}l}: \xrightarrow{\;\alpha\text{-cleavage}\;} CH_3CH{=}\overset{+}{\ddot{C}l}:$$

Fragment'n patterns: ROR′

- similar to RX ~ heterolytic C–O and homolytic C–C cleavage

87 taller than 101. why?
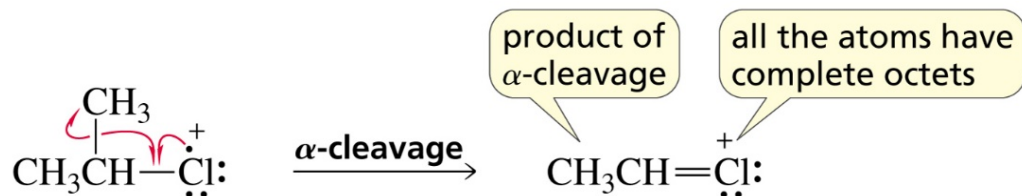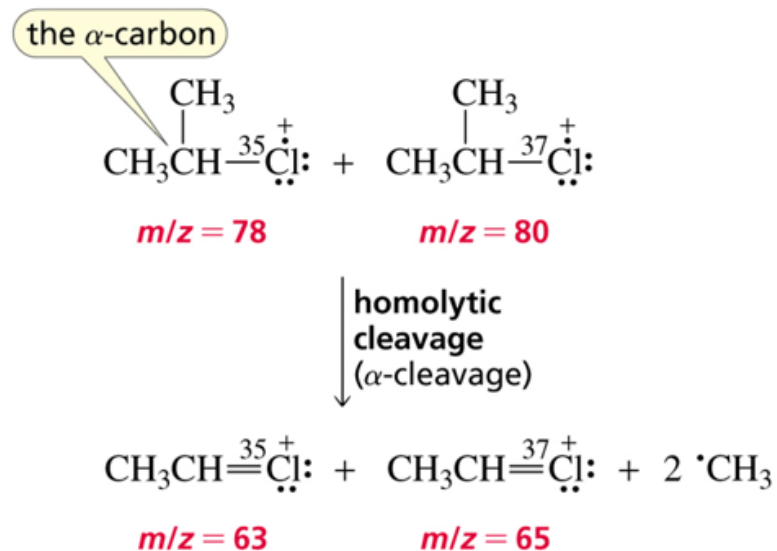
Fragment'n patterns: ROH

- ❑ M very short [little], if observable ← loss of H_2O facile

- ❑ α-cleavage

α-cleavage → $CH_3CH_2CH_2\dot{C}H_2$ + $CH_3CH=\overset{+}{\ddot{O}}H$ ⟶ base

$m/z = 45$

$:\ddot{O}H$ | $\ddagger\ddot{O}H$

$CH_3CH_2CH_2CH_2\overset{|}{C}HCH_3$ $\xrightarrow{-e^-}$ $CH_3CH_2CH_2CH_2\overset{|}{C}HCH_3$

2-hexanol | $m/z = 102$

α-carbon

α-cleavage → $CH_3CH_2CH_2CH_2CH=\overset{+}{\ddot{O}}H$ + $\dot{C}H_3$

$m/z = 87$
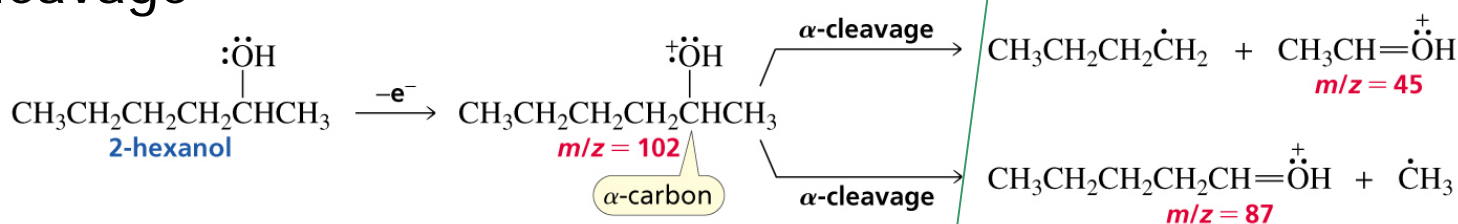
- ❑ two-bond cleavage
  - ▪ C−OH and C−γ-H

$CH_3CH_2CHCH_2CHCH_3$ ⟶ $CH_3CH_2\dot{C}HCH_2\overset{+}{C}HCH_3$ + H_2O

γ   β   α

$m/z = (102 − 18) = 84$

$CH_3CH_2CH_2CH_2CHCH_3$
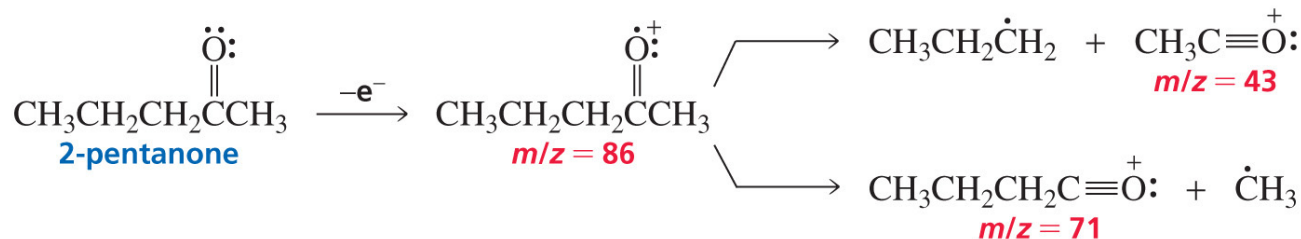 |
          OH
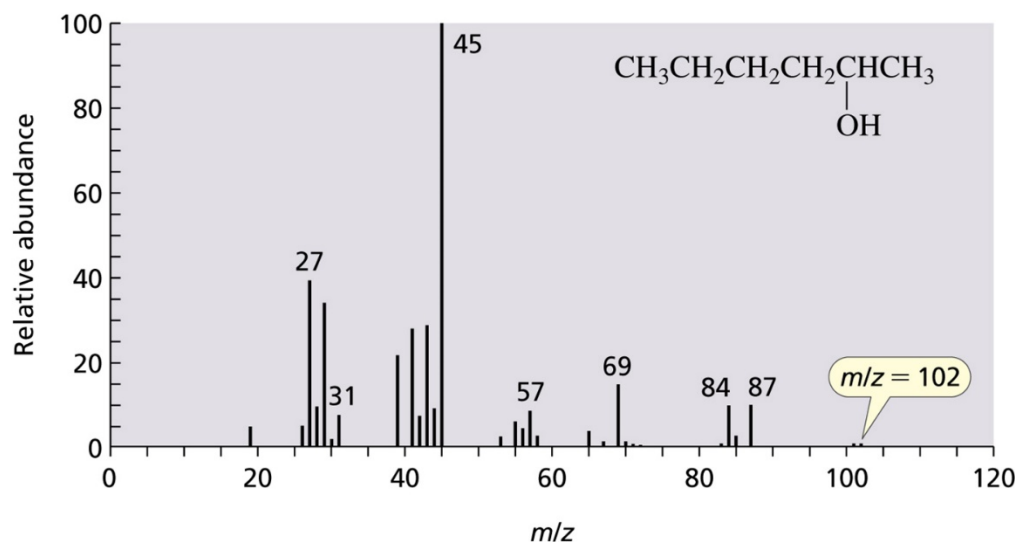
no 18?
fragmented to
(•−)+ neutral
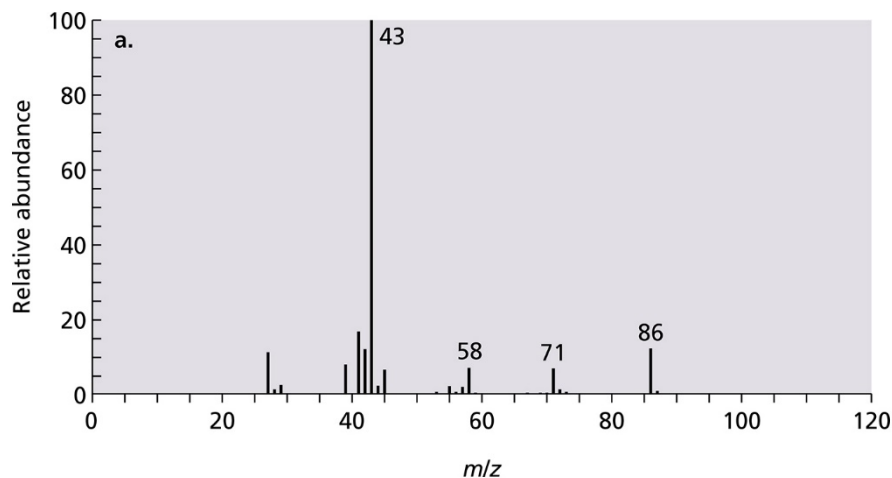
$m/z = 102$

✓ tiny M+
✓ not observable in 3°

Fragment'n patterns: ketones

- α-cleavage (of α-C–C(O))

- McLafferty rearrangement
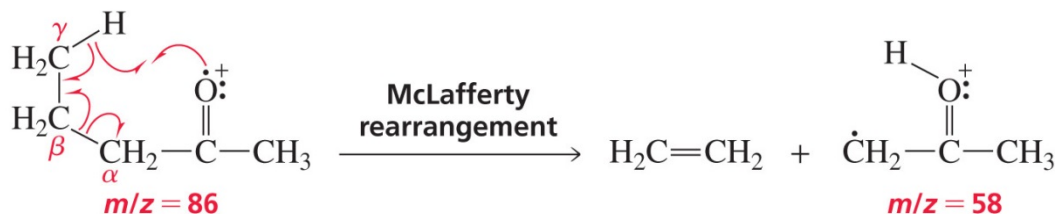
Summary of fragment'n

- ❑ The weakest bond breaks first.

- ❑ The cleavage resulting more stable fragment occurs more.

- ❑ M formed by giving up one of **:**, if any.

- ❑ C–O, C–N, C–X bonds break heterolytically.

- ❑ C–C, C–H bonds break homolytically.

why?

- ❑ Sometimes 2-bond cleavage occurs.

Variations of MS

- chemical ionization MS [CI-MS]

  - instead of e bombardment [EI-MS]

  - pre-ionized gas ionize sample by e (or H^+) transfer

  - less fragmentation → easy to measure M

- desorption ionization

  - for larger molecules that do not vaporize

  - dissolved in matrix, ionized, and ejected from matrix

  - SIMS, MALDI, FAB

- GC-MS

  - separation by gas chromatography, and

  - then MS