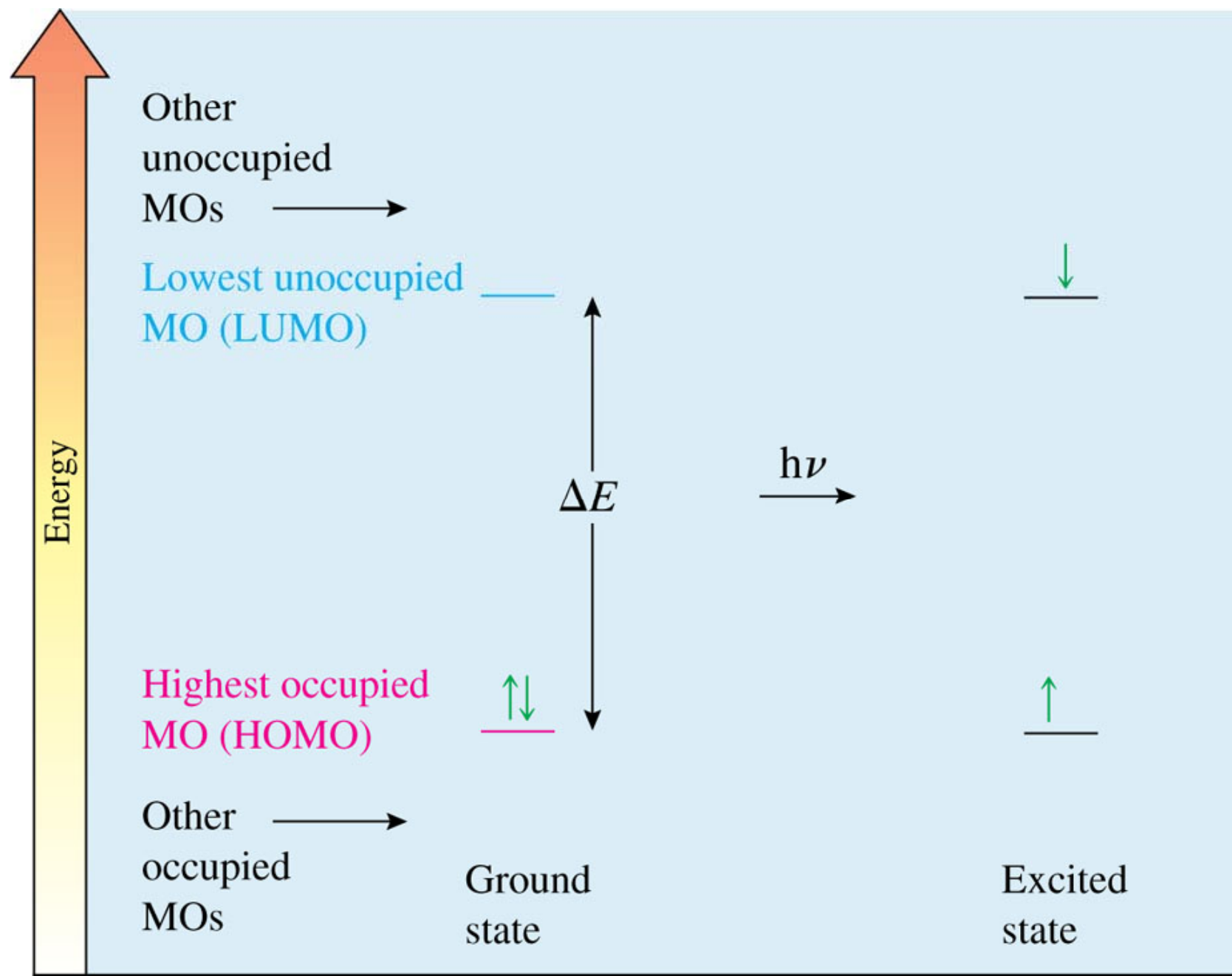# Chapter 15   Structure Determination by Spectroscopy II: UV-Vis & Mass

15.1 Ultraviolet-Visible Spectroscopy

UV region: 200 – 400 nm (143 - 71.5 Kcal/mol)
Visible region: 400 – 800 nm (71.5- 36 Kcal/mol)

$\Rightarrow$ **Electronic transition** in a molecule to excite an electron from an occupied MO to an antibonding MO is possible

Other unoccupied MOs $\longrightarrow$

Lowest unoccupied MO (LUMO) ____

ΔE

$h\nu$ $\longrightarrow$

Highest occupied MO (HOMO)

Other occupied MOs $\longrightarrow$

Ground state

Excited state

UV absorption

Much Broader than IR and NMR(radio wave)

∵each electronic state has numerous vibrational (IR region absorption) and rotational (microwave) sublevels

Absorbance (A)

$A = \log(I_o/I)$
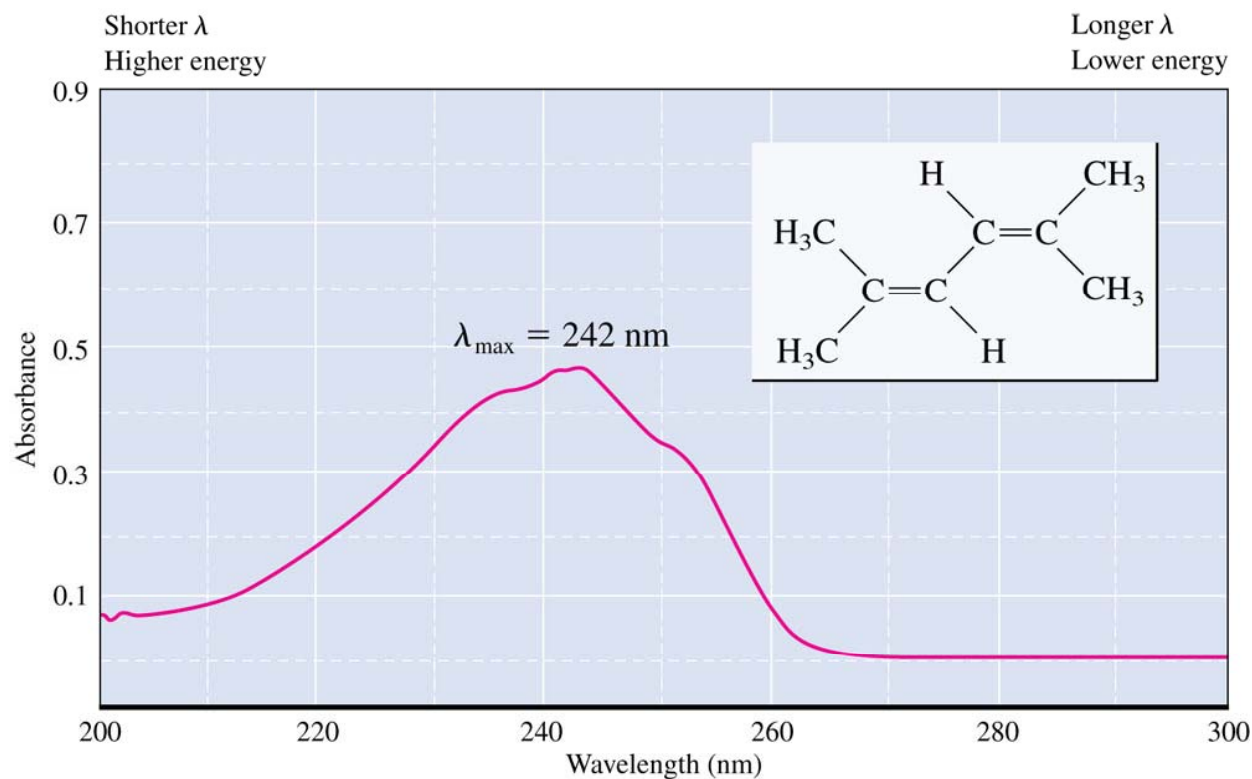
where I_o = the intensity of the light stricking the sample

I = the intensity of the light emerging from the sample

$A = \varepsilon cl$ at λ_{max} (Lambert-beer law)

Where ε = molar extinction coefficient, c=concentration, l= path length
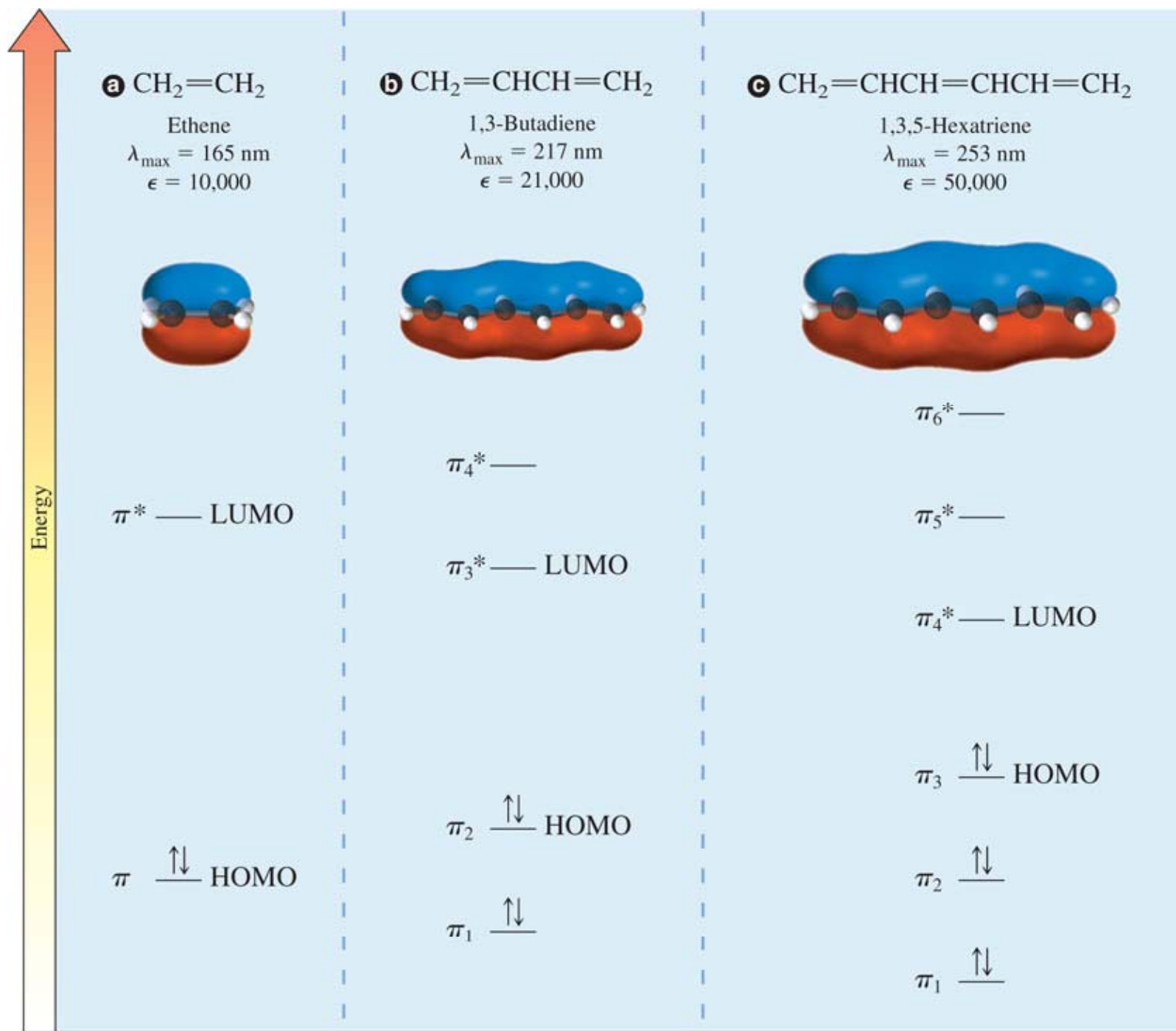
$\Rightarrow$ Quantitative analysis is possible

15.2 Types of Electronic Transition

$\sigma \rightarrow \sigma^*$ **transition of ethane:** λ_{max} **= 135nm**

$\pi \rightarrow \pi^*$ **transition of ethene:** λ_{max} **= 165nm, e = 10,000**

$\Rightarrow$ **No UV absorption ($\therefore$ alkane is good solvent for UV spectroscopy)**

λ_{max} **for $\pi \rightarrow \pi^*$ transition increases as the number of conjugated pi bond increases, then UV or Visible absorption is possible**

ⓐ $CH_2{=}CH_2$

Ethene
$\lambda_{max} = 165$ nm
$\epsilon = 10,000$

ⓑ $CH_2{=}CHCH{=}CH_2$

1,3-Butadiene
$\lambda_{max} = 217$ nm
$\epsilon = 21,000$

ⓒ $CH_2{=}CHCH{=}CHCH{=}CH_2$

1,3,5-Hexatriene
$\lambda_{max} = 253$ nm
$\epsilon = 50,000$

Energy

π_6^* ——

π_4^* ——

π^* —— LUMO

π_5^* ——

π_3^* —— LUMO

π_4^* —— LUMO

π_3 ⇅ HOMO

π_2 ⇅ HOMO

π ⇅ HOMO

π_2 ⇅

π_1 ⇅

π_1 ⇅

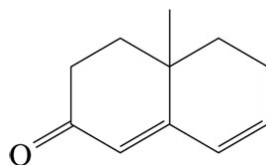# 15.3 UV-Visible Spectroscopy in Structure Determination

Quantitative analysis of known compound $\Rightarrow$ Good!

Qualitative analysis for unknown compound

$\Rightarrow$ not as good as IR and UV Good

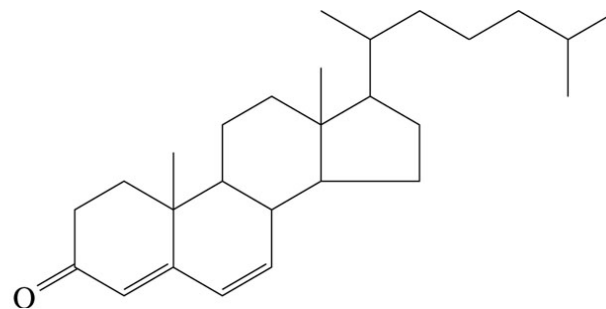**$\because$ peaks are broad and the same chromophore gives the same spectrum**

Chromophore: the part of the molecule that is responsible for the absorption of UV or visible light

$\lambda_{max} = 283$ nm

$\lambda_{max} = 284$ nm

OrgChem-C

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UV-B: 295~320 nm ⇒ causing sun-burn (cancer !)

sunscreen

    ozone in the upper atmosphere

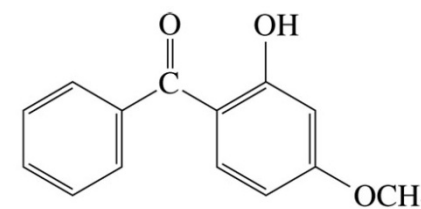   **PABA (p-benzoic acid) on the skin 📖 616 Focus On**
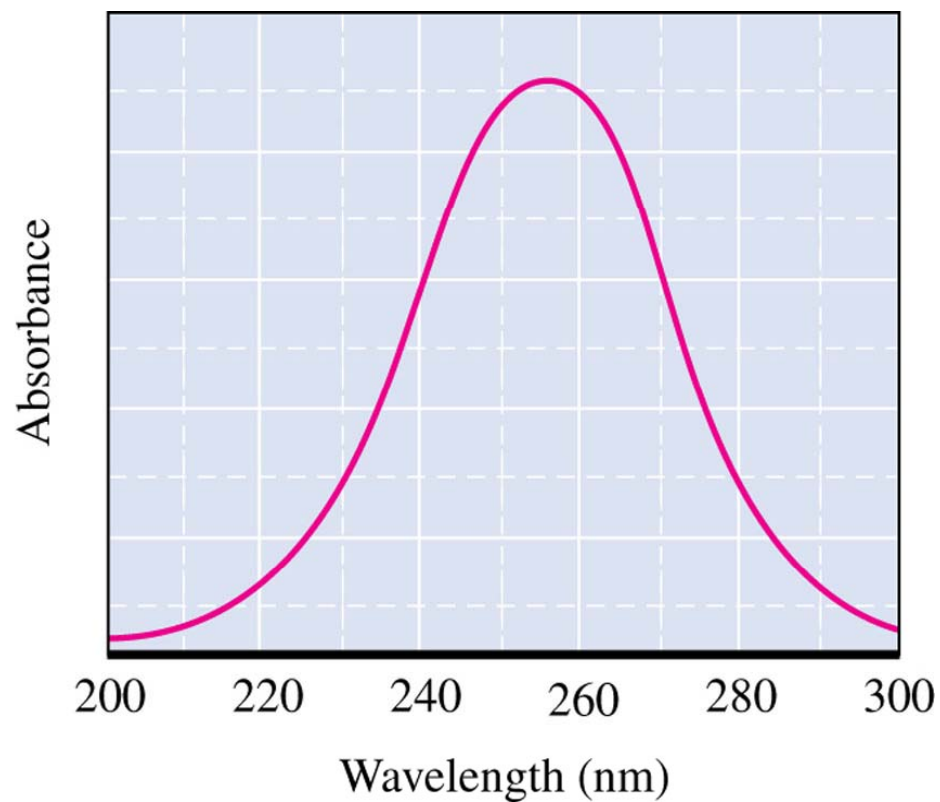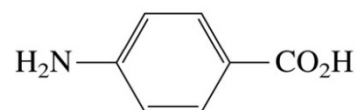
p-Aminobenzoic acid
PABA
$\lambda_{max} = 289$ nm

Oxybenzone
$\lambda_{max} = 284$ and 324 nm

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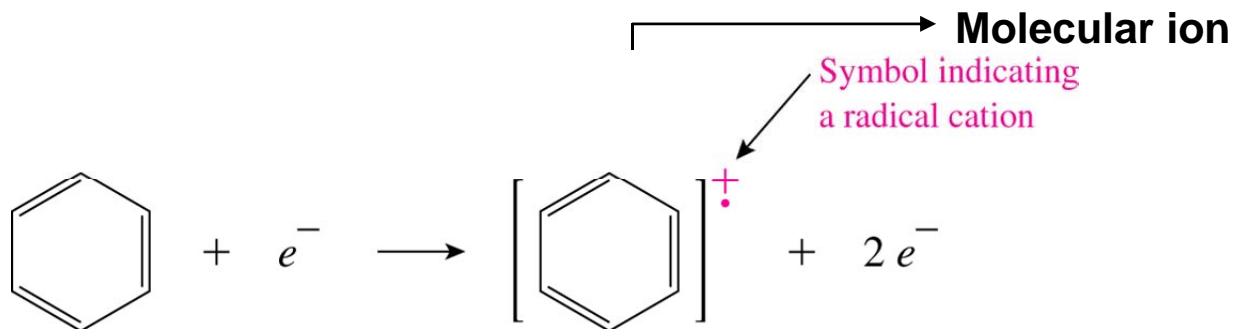
15.4 Mass Spectrometry
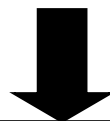
Used to measure the molecular mass of a compound, then the molecular formula can be speculated!

When molecules in the vapor phase is bombarded with high-energy electron beam, molecular ion (radical cation) is generated.

$\Rightarrow$**The molecular ion pass through a magnetic field. Here the charged ptcles are deflected according to mass to charge ratio (m/z).**

$\Rightarrow$ **Most abundant ion: base ion (value of 100)**

Molecular ion

Symbol indicating a radical cation

© 2006 Brooks/Cole - Thomson
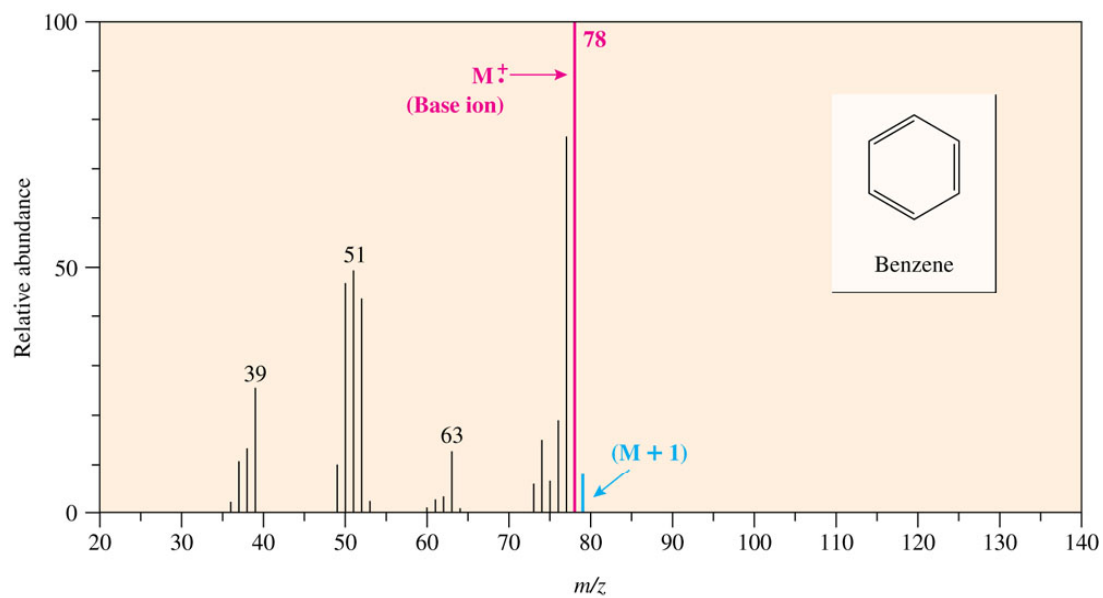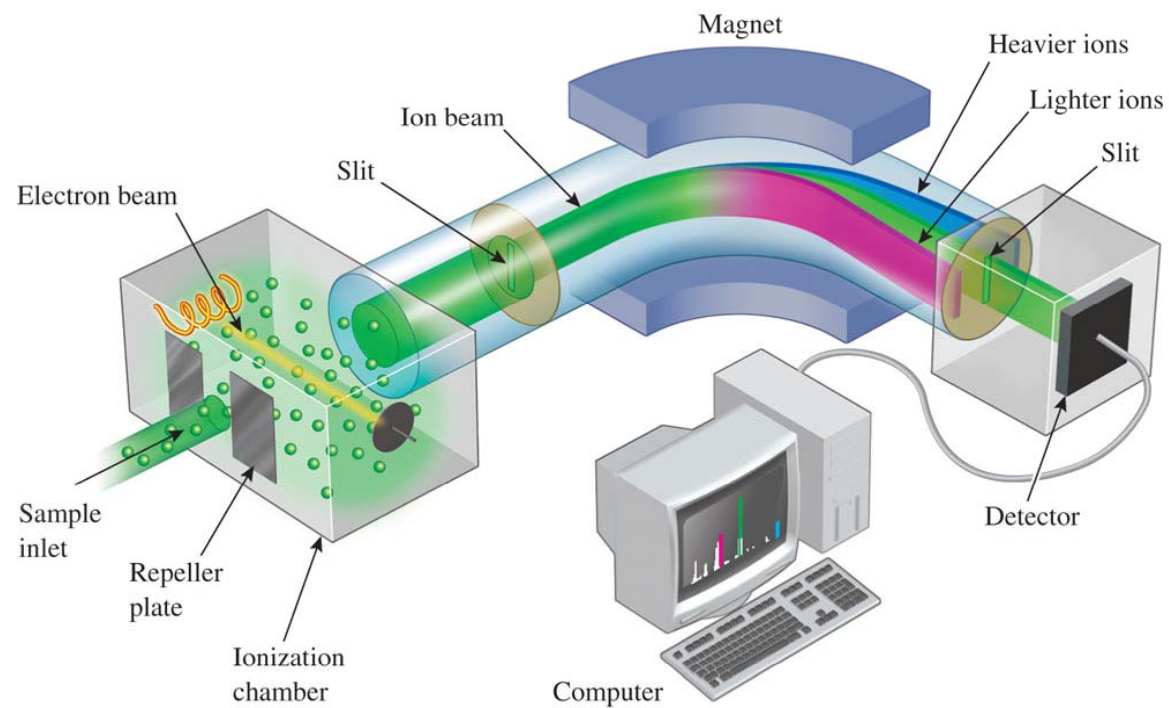
15.5 Determining the Molecular Formula

Low-resolution mass spectrometer (LRMS):provides the masses of the ions to the nearest whole number

High-resolution mass spectrometer (HRMS): provides the masses to several decimal places

Ex) CO_2, C_2H_4O, and C_3H_8

in LRMS m/z = 44

in HRMS m/z = 43.9898, 44.0262, and 44.0626, respectively

∴Using HRMS, atomic wt. & exact mass (📖 **619 Table 15.2**) and relative intensity of isotope peaks (📖 **620 Table 15.3**) can be obtained

∴Ex) benzene: $M^{+\bullet}$ = 78, M+1:6.8%, M+2:0.2% ∵^{13}C:1.1% of ^{12}C
📖 **previous page**

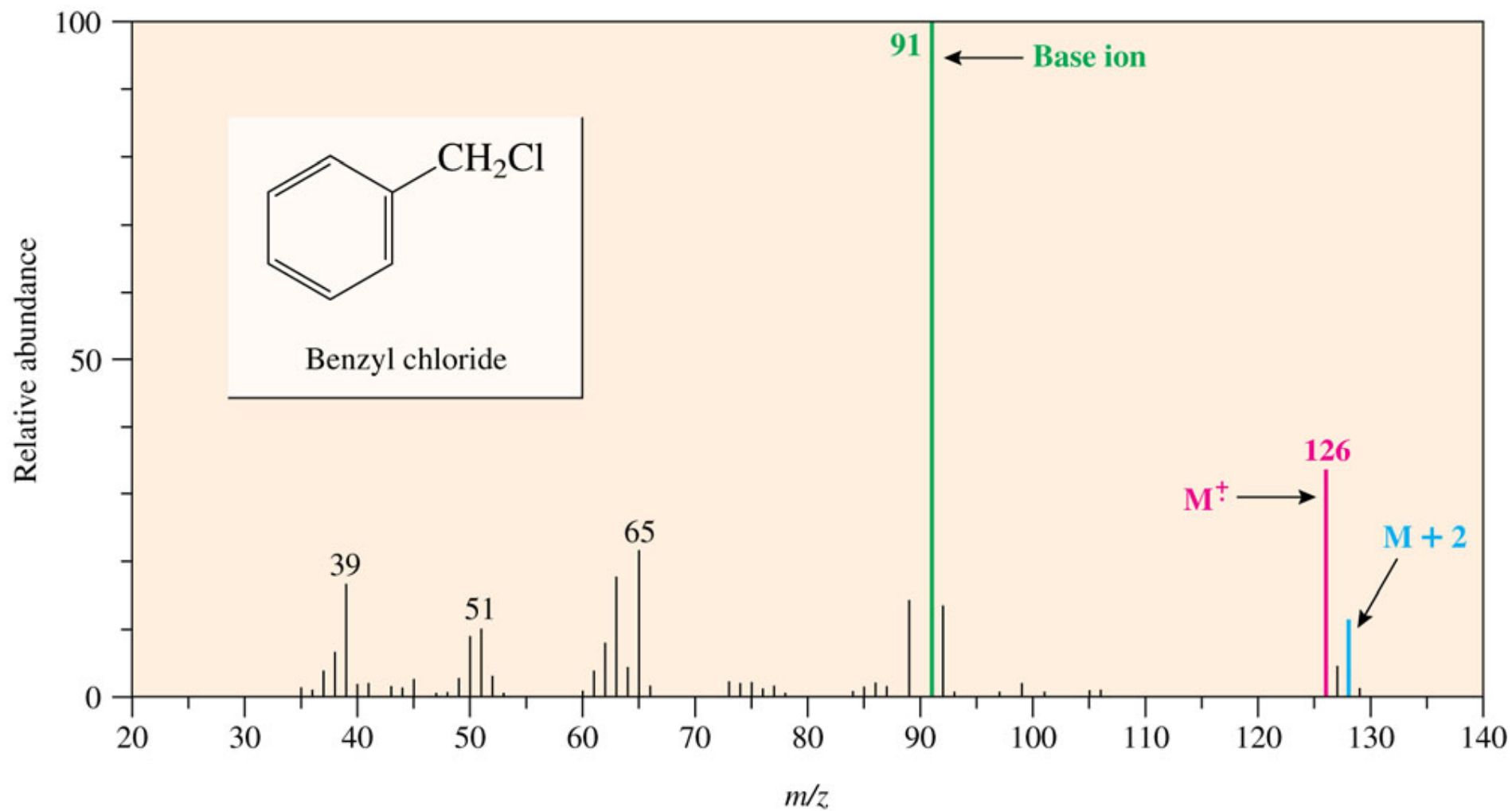| Isotope	Atomic Mass (amu)
^1H	1.00783
^{12}C	12.00000
^{14}N	14.0031
^{16}O	15.9949

These values are not the same as the atomic masses in the periodic table because these are the exact masses of individual isotopes. The masses in the periodic table are average masses of the element based on the masses and natural abundances of the isotopes of which it is composed.

Element	Major Isotope	RA	M + 1 Isotope	RA	M + 2 Isotope	RA
Hydrogen	^1H	100				
Carbon	^{12}C	100	^{13}C	1.1		
Nitrogen	^{14}N	100	^{15}N	0.4		
Oxygen	^{16}O	100			^{18}O	0.2
Fluorine	^{19}F	100				
Sulfur	^{32}S	100	^{33}S	0.8	^{34}S	4.4
Chlorine	^{35}Cl	100			^{37}Cl	32.5
Bromine	^{79}Br	100			^{81}Br	98.0
Iodine	^{127}I	100				

The relative abundance (RA) of the most abundant isotope is listed as 100, and the abundances of the other isotopes are listed relative to that number. The M + 1 isotope is the one that is responsible for the peak at m/z one unit higher than the peak for M⁺.

Mass spectrum of benzyl chloride ($C_6H_5CH_2Cl$). The base ion appears at $m/z = 91$ (Base ion). The molecular ion M^+ appears at $m/z = 126$, with the $M + 2$ peak due to chlorine isotope. Other fragment peaks appear at $m/z = 39$, 51, and 65.

15.6 Fragmentation of the Molecular Ion

The structure of the molecular ion (radical cation)

The compound with only sigma bond; the location of the odd electron and the positive charge is not certain.

$$CH_3CH_2CH_3 \quad + \quad e^- \quad \longrightarrow \quad \left[CH_3CH_2CH_3 \right]^{+\cdot} \quad + \quad 2\,e^-$$
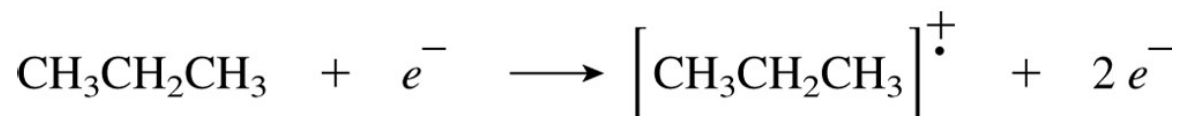
Propane

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The compound with nonbonding or pi electrons; the structure of radical cation is quite well known

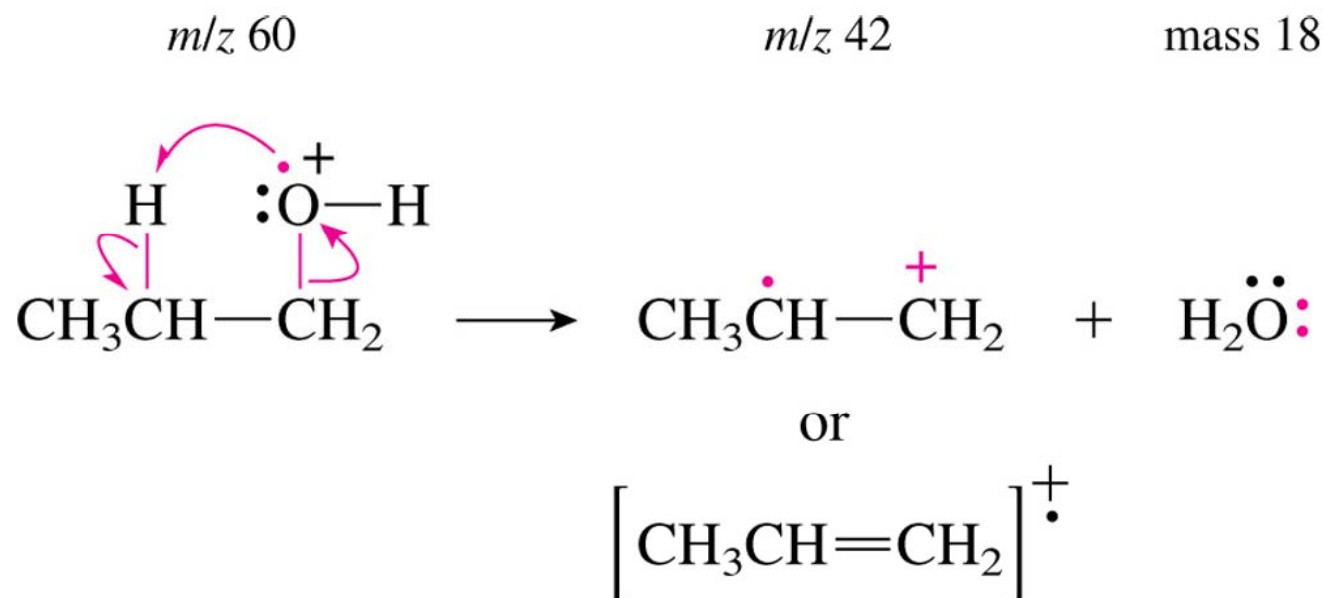$$CH_3 - \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} - H \quad + \quad e^- \quad \longrightarrow \quad CH_3 - \overset{\cdot\,+}{\underset{\cdot\cdot}{O}} - H \quad + \quad 2\,e^-$$

Methanol

Ethene

$+ \quad 2\,e^-$
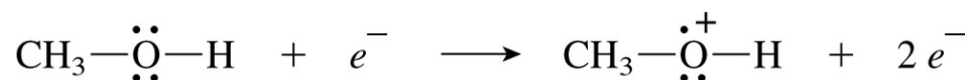
© 2006 Brooks/Cole - Thomson

Fragmentation of the radical cation; a small, stable molecule can be easily formed

m/z 60   *m/z* 42   mass 18

$$CH_3CH-CH_2 \longrightarrow CH_3CH-CH_2 \ + \ H_2O:$$

or

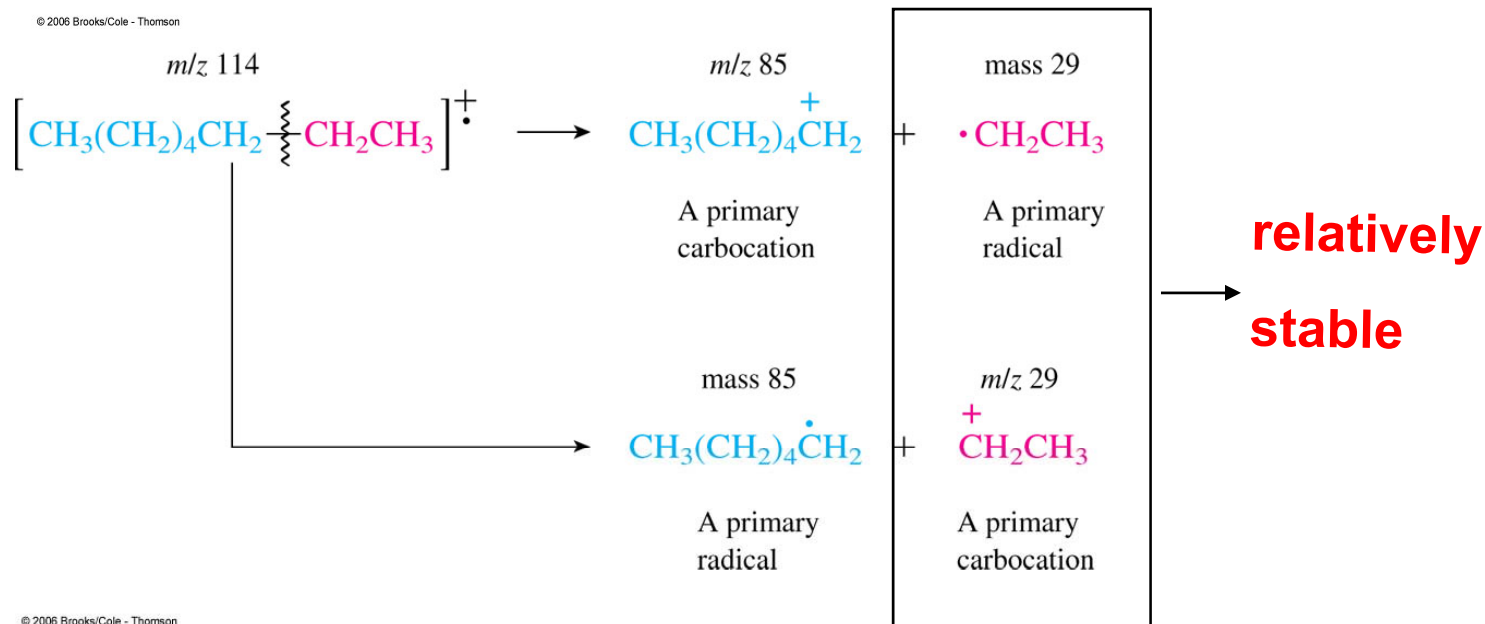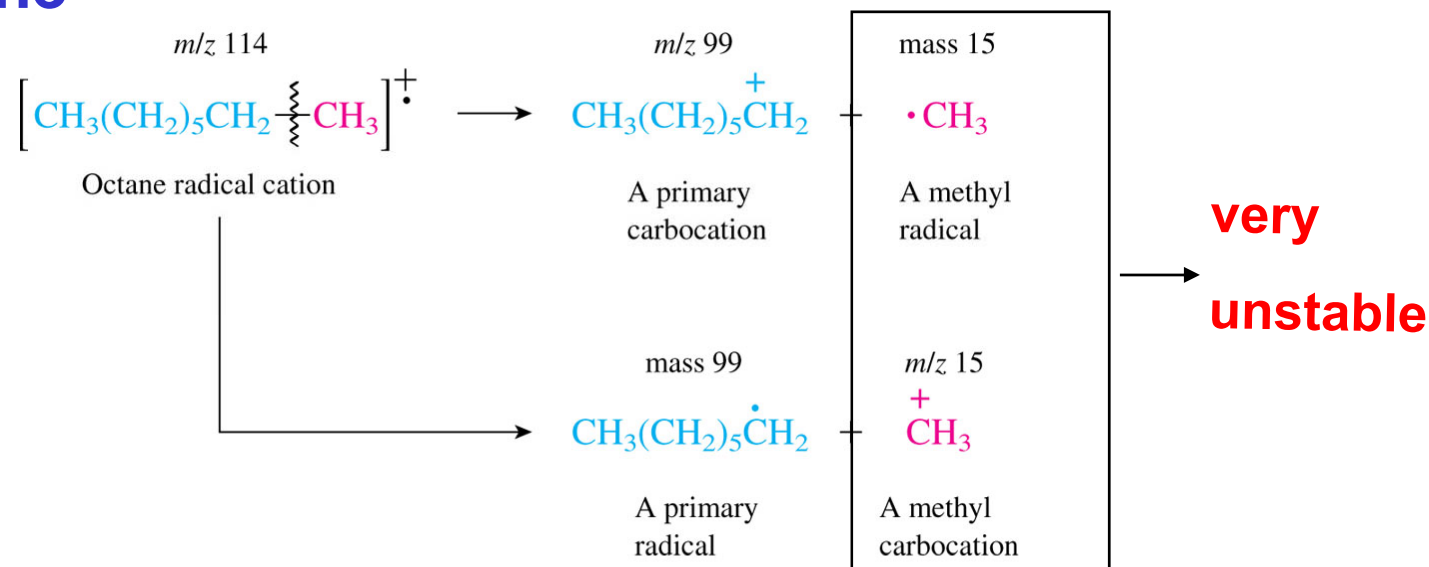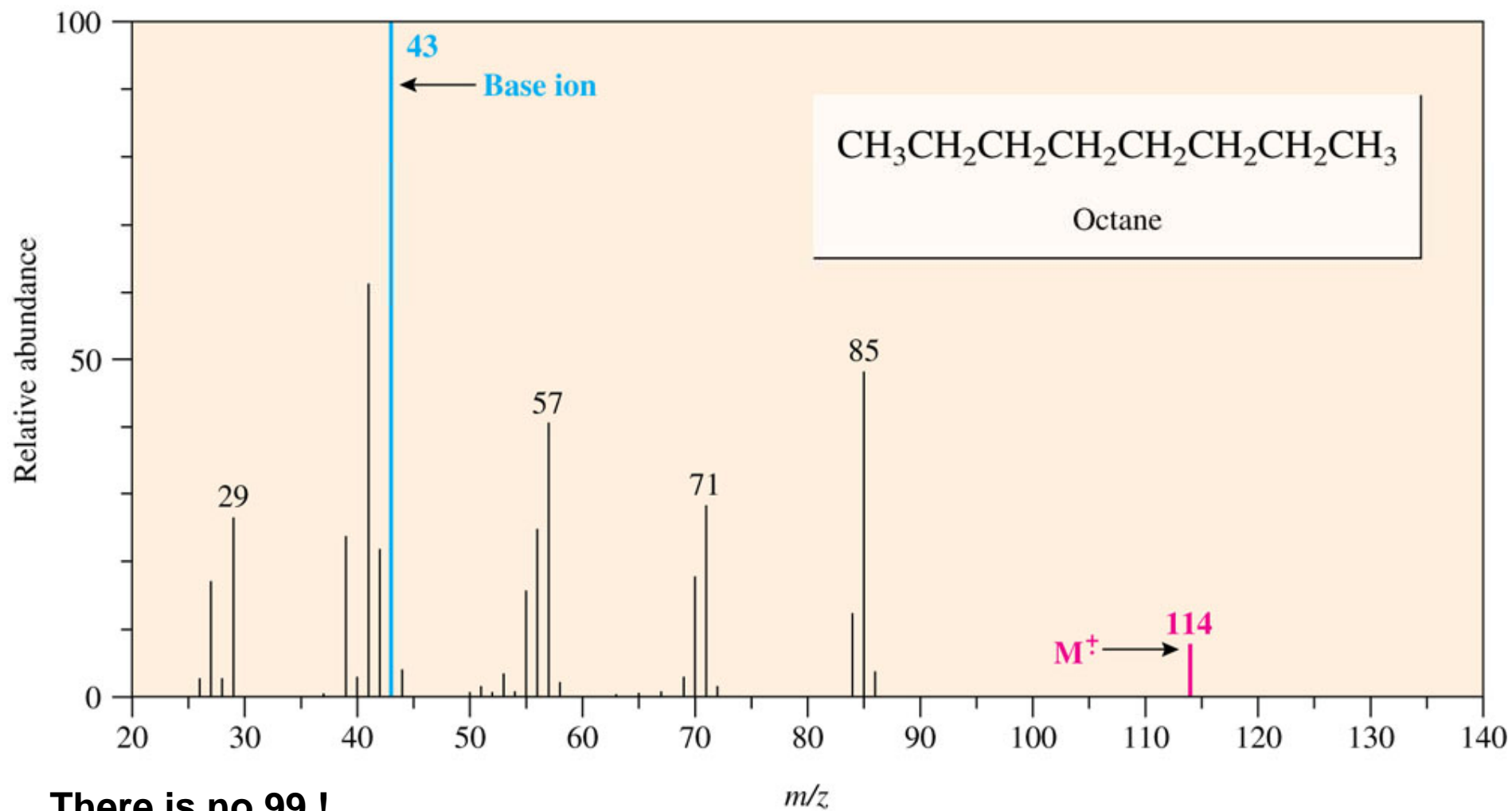$$\left[CH_3CH=CH_2 \right]^{+\cdot}$$

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Therefore the M⁺ peak is very small for primary and secondary alcohol.

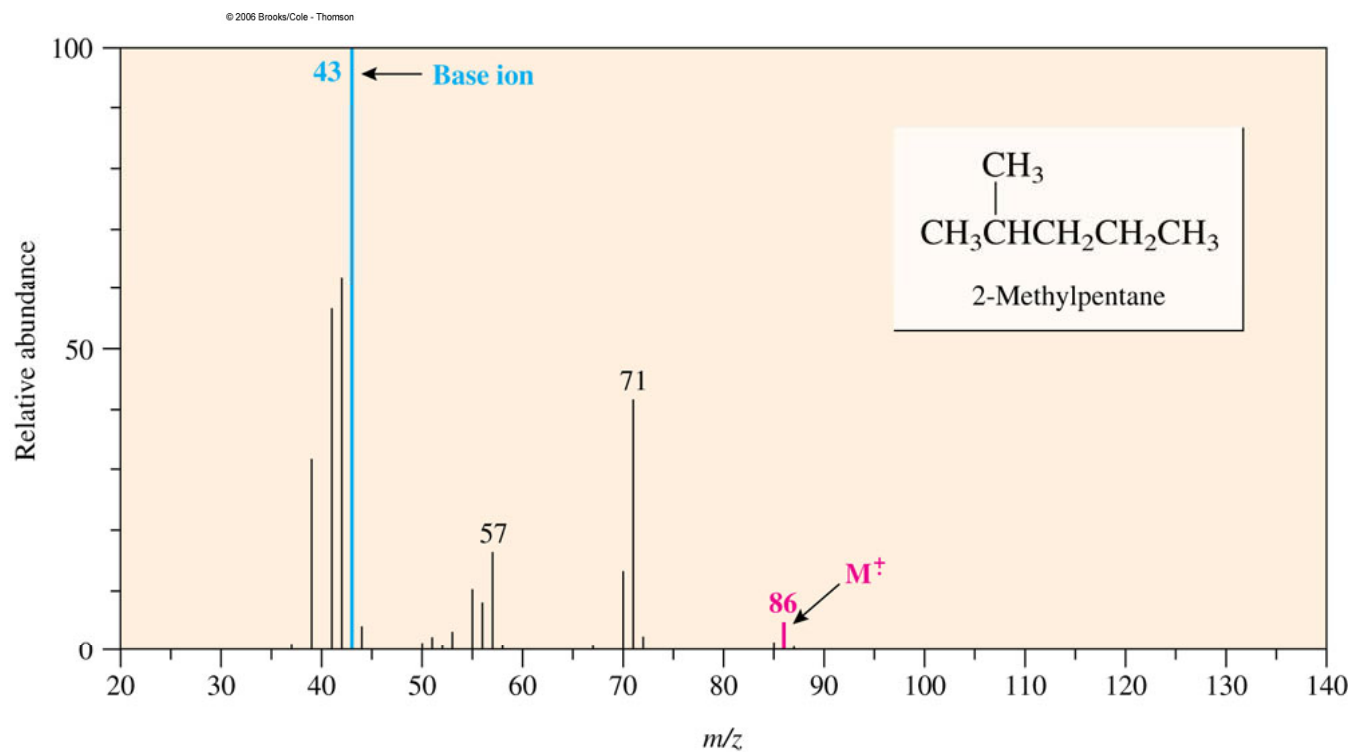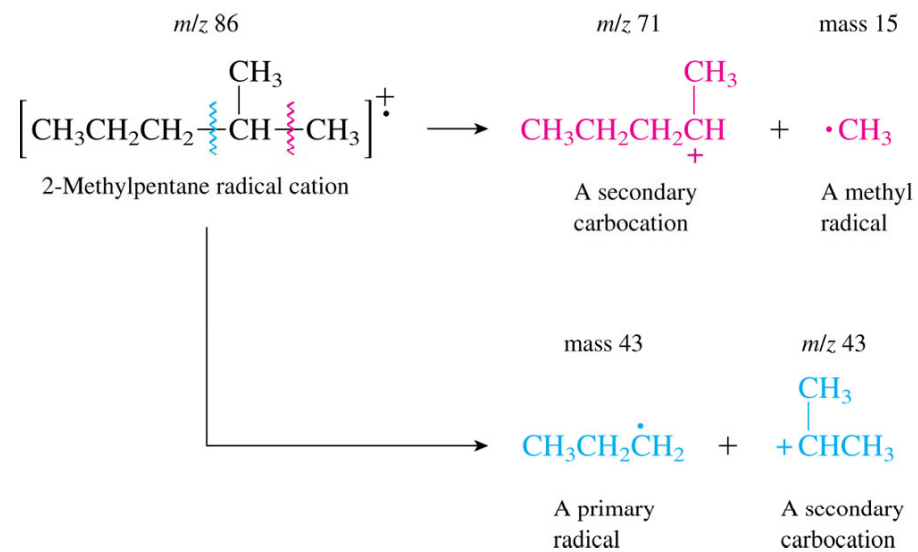**For terriary alcohol it is usually undetactable.**

Fragmentation of the Molecular Ion (radical cation)

Alkane

m/z 114

$$\left[CH_3(CH_2)_5CH_2 \nleftrightarrow CH_3 \right]^{+\cdot}$$

Octane radical cation

$\longrightarrow$

m/z 99

$CH_3(CH_2)_5\overset{+}{C}H_2$

A primary carbocation

mass 15

$\cdot CH_3$

A methyl radical

mass 99

$CH_3(CH_2)_5\overset{\cdot}{C}H_2$

A primary radical

m/z 15

$\overset{+}{C}H_3$

A methyl carbocation

very unstable $\longrightarrow$

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m/z 114

$$\left[CH_3(CH_2)_4CH_2 \nleftrightarrow CH_2CH_3 \right]^{+\cdot}$$

$\longrightarrow$

m/z 85

$CH_3(CH_2)_4\overset{+}{C}H_2$

A primary carbocation

mass 29

$\cdot CH_2CH_3$

A primary radical

mass 85

$CH_3(CH_2)_4\overset{\cdot}{C}H_2$

A primary radical

m/z 29

$\overset{+}{C}H_2CH_3$

A primary carbocation

relatively stable $\longrightarrow$

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Octane mass spectrum. Base ion at m/z 43; molecular ion M⁺· at m/z 114; fragment peaks at 29, 57, 71, 85.

There is no 99 !

m/z 86   m/z 71   mass 15

$$\left[CH_3CH_2CH_2 \overset{\displaystyle CH_3}{\underset{}{\overset{|}{CH}}} CH_3\right]^{+\cdot} \longrightarrow CH_3CH_2CH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{+}{CH}}} \quad + \quad \cdot CH_3$$

2-Methylpentane radical cation   A secondary   A methyl
                                            carbocation   radical

                                            mass 43   m/z 43

$$CH_3CH_2\overset{\cdot}{C}H_2 \quad + \quad \overset{\displaystyle CH_3}{\underset{+}{\overset{|}{C}HCH_3}}$$

                                            A primary   A secondary
                                            radical   carbocation

2-Methylpentane

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Alkene

$$\left[R\text{---}CH_2\text{---}CH\text{=}CH_2\right]^{+\cdot} \longrightarrow R\cdot + \overset{+}{C}H_2\text{---}CH\text{=}CH_2 \longleftrightarrow CH_2\text{=}CH\text{---}\overset{+}{C}H_2$$
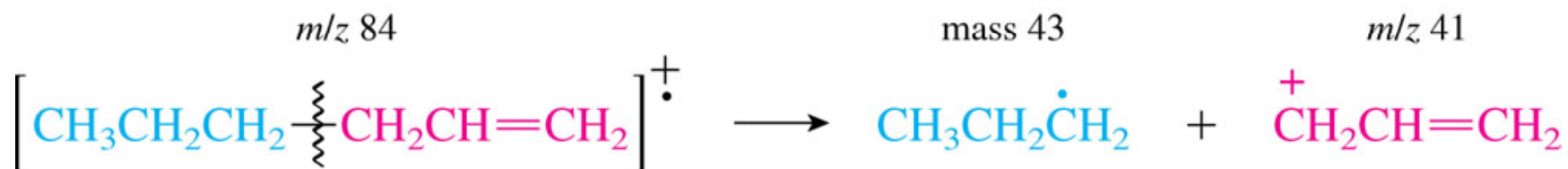
Major pathway   An allylic carbocation

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m/z 84   mass 43   *m/z* 41

$$\left[CH_3CH_2CH_2\text{---}CH_2CH\text{=}CH_2\right]^{+\cdot} \longrightarrow CH_3CH_2\overset{\cdot}{C}H_2 + \overset{+}{C}H_2CH\text{=}CH_2$$

1-Hexene radical cation

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$CH_2\text{=}CHCH_2CH_2CH_2CH_3$

1-Hexene

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Benzylic compound

m/z 134   *m/z* 91   mass 43

Butylbenzene radical cation   A benzylic carbocation

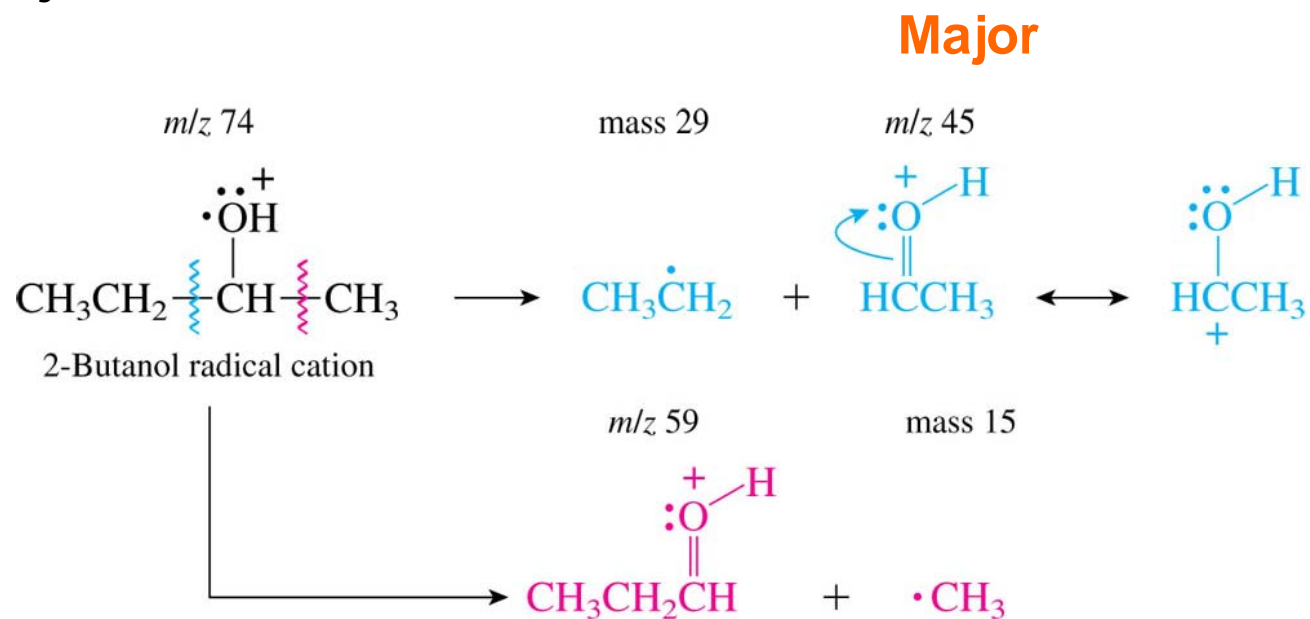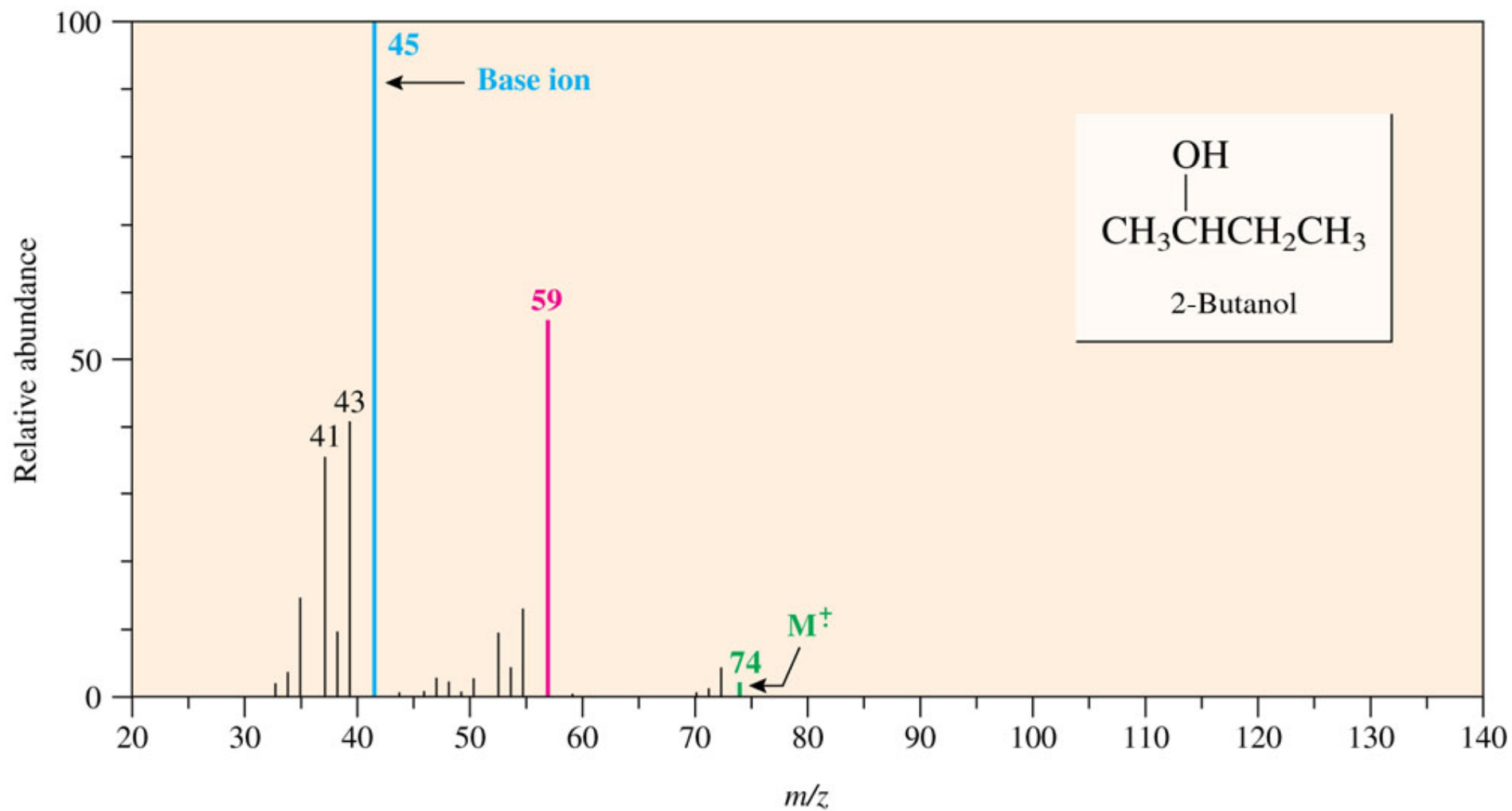© 2006 Brooks/Cole - Thomson

Butylbenzene
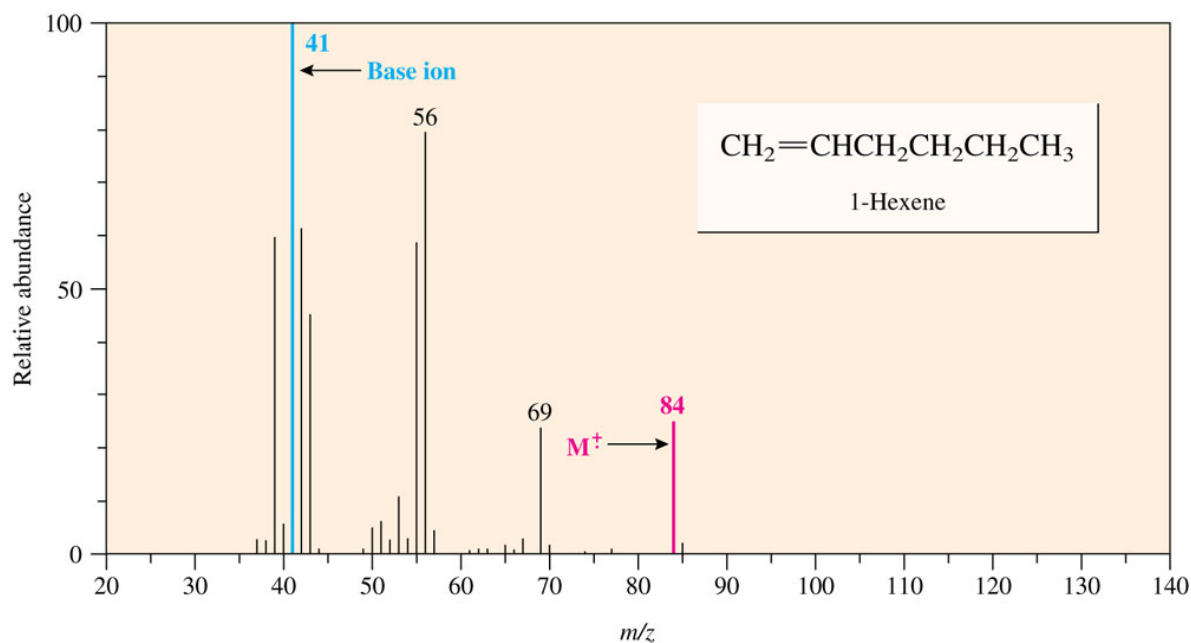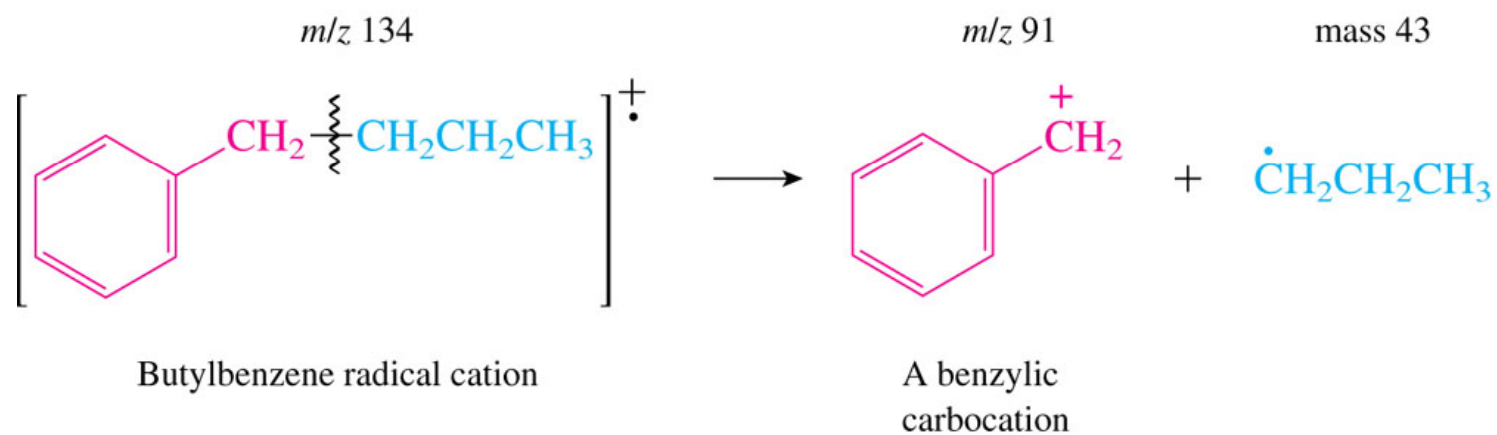
© 2006 Brooks/Cole - Thomson
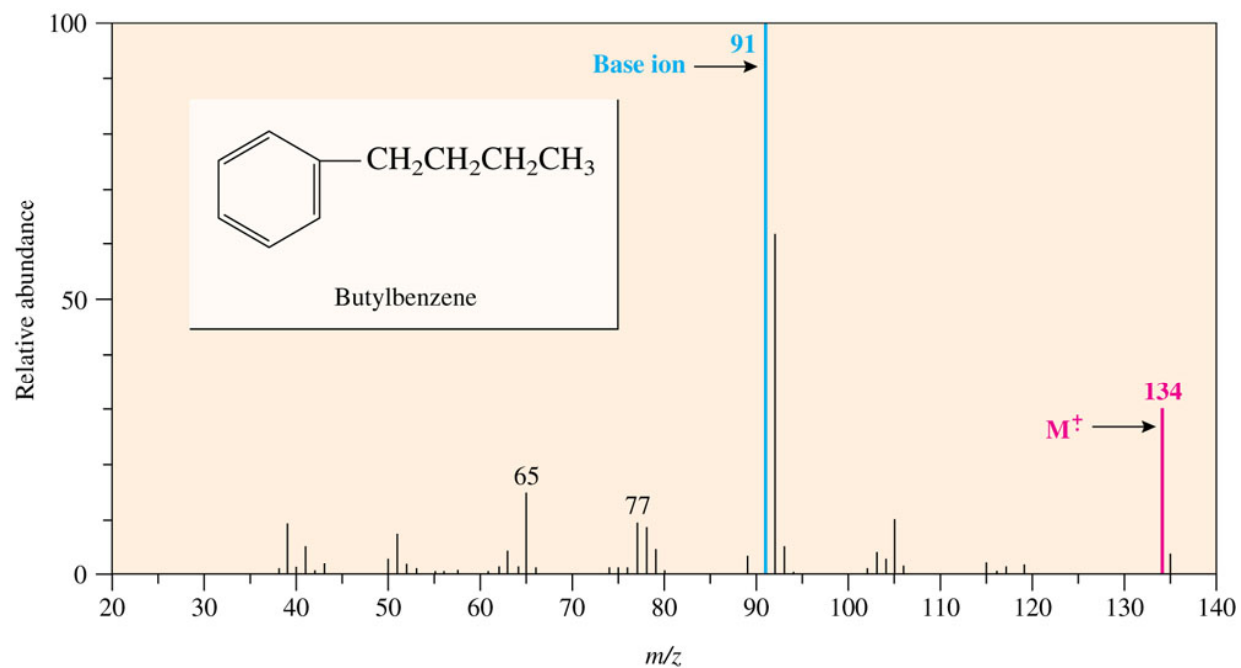
Alcohols

1) Elimination of water
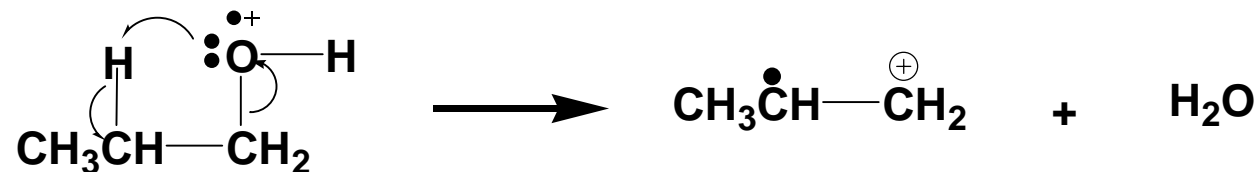
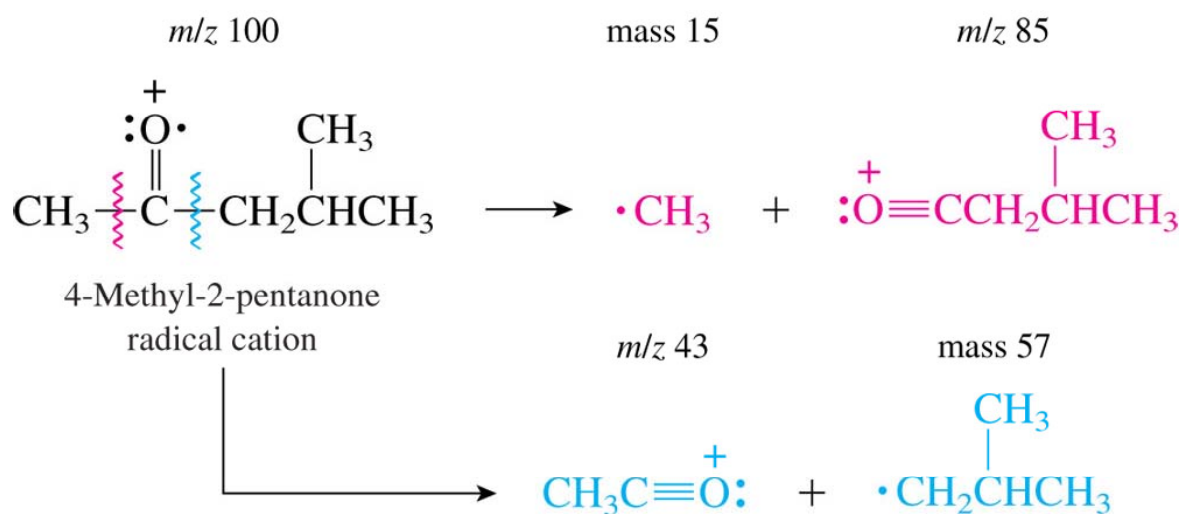## 2) Cleavage of the bonds between the hydroxy carbon and an adjacent carbon

Major

Aldehydes and Ketone

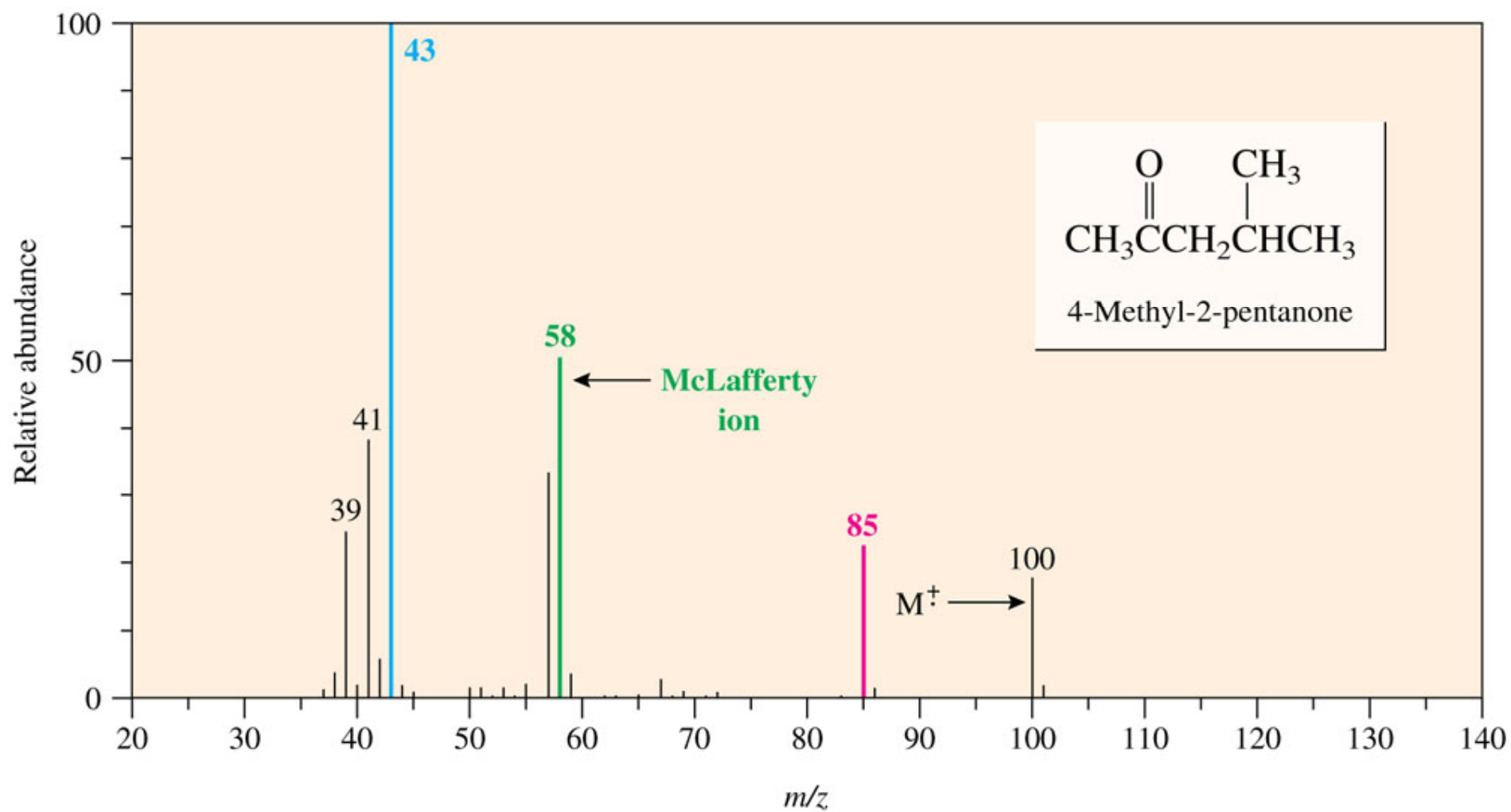**1) Major fragmentation pathway: the cleavage of the bonds to the carbonyl group**

4-Methyl-2-pentanone radical cation

2) McLafferty reattangement

4-Methyl-2-pentanone