



台灣大學開放式課程



【本著作除另有註明，作者皆為蔡蘊明教授，所有內容皆採用 [創用CC 姓名標示-非商業使用-相同方式分享 3.0 台灣](#) 授權條款釋出】



Chapter 9 Mass Spectroscopy (質譜)

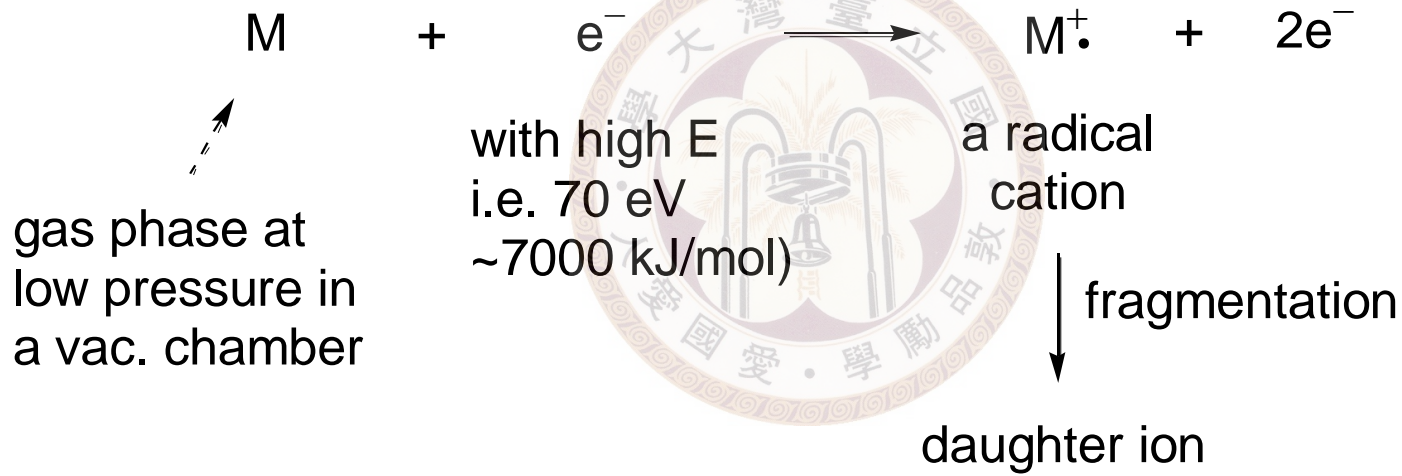
分子的點名器

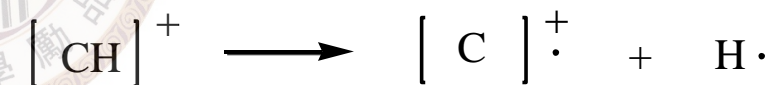
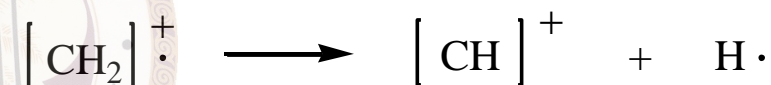
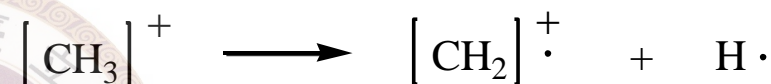
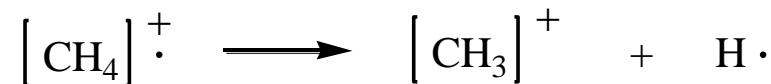
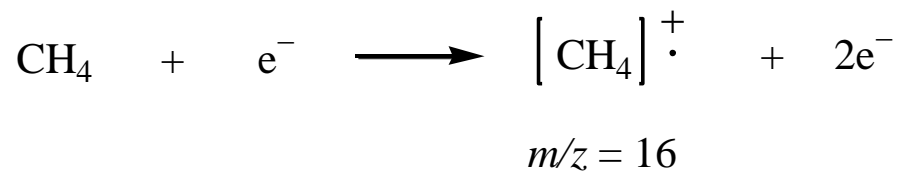
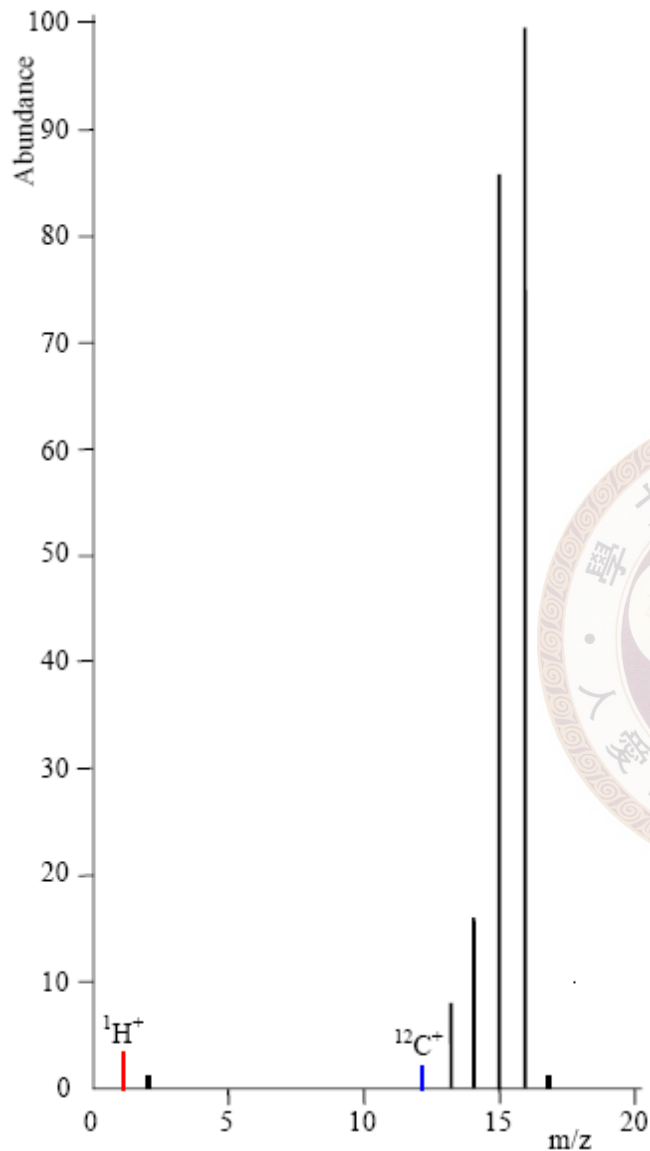




✧ Electron ionization (EI) MS

molecular ion (also called parent ion) carries high E

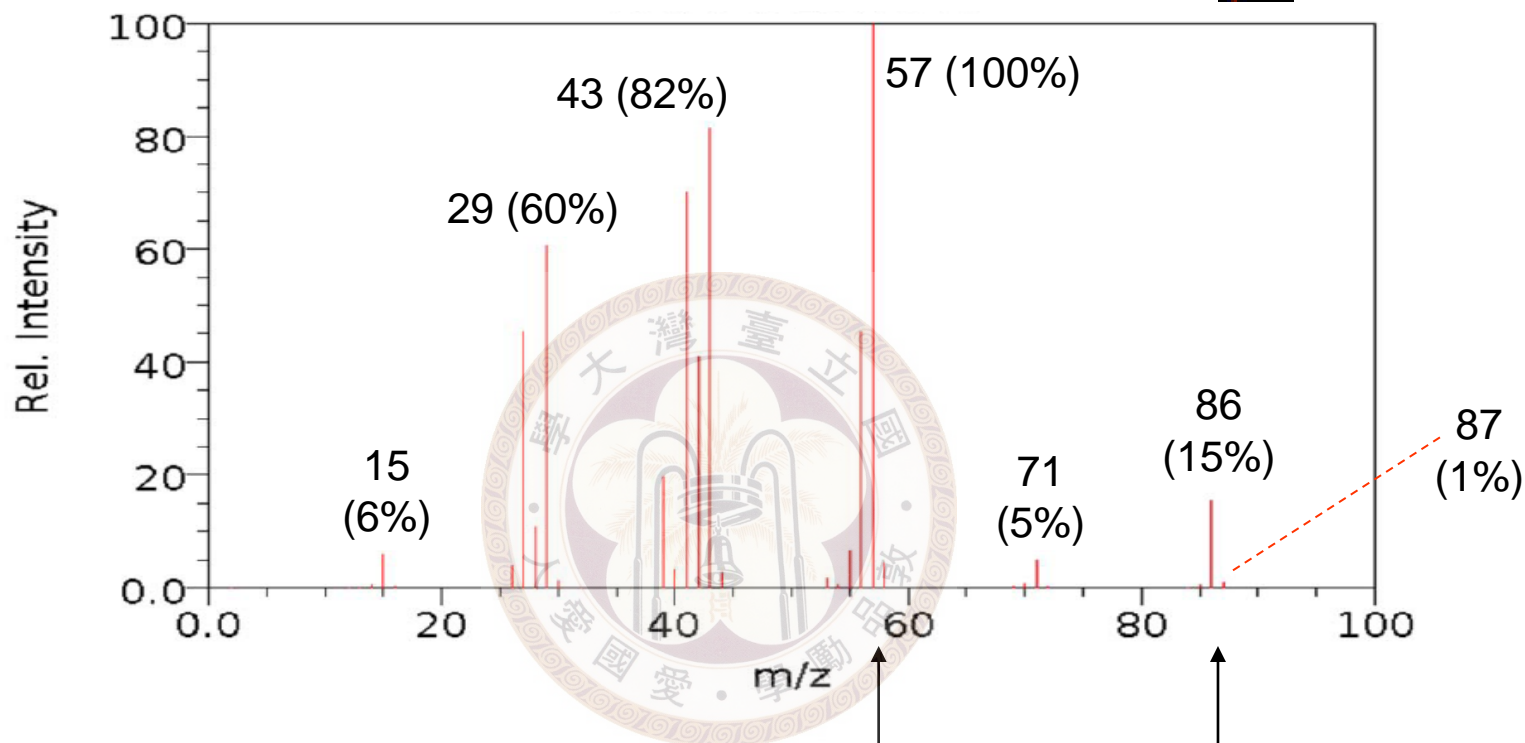




Mass spectrum shown as a bar graph

Mass spec. of hexane (C₆H₁₄)

NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

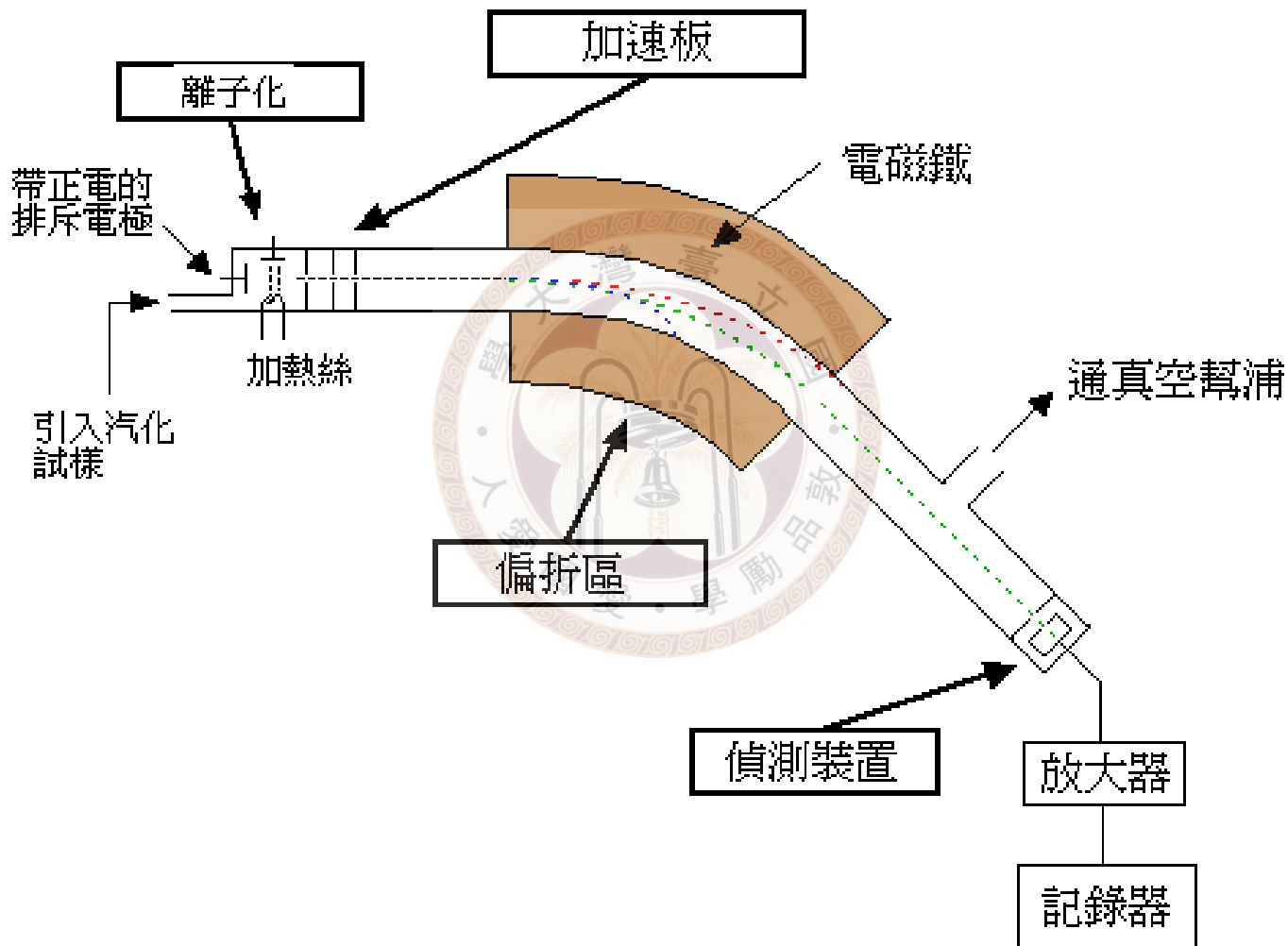


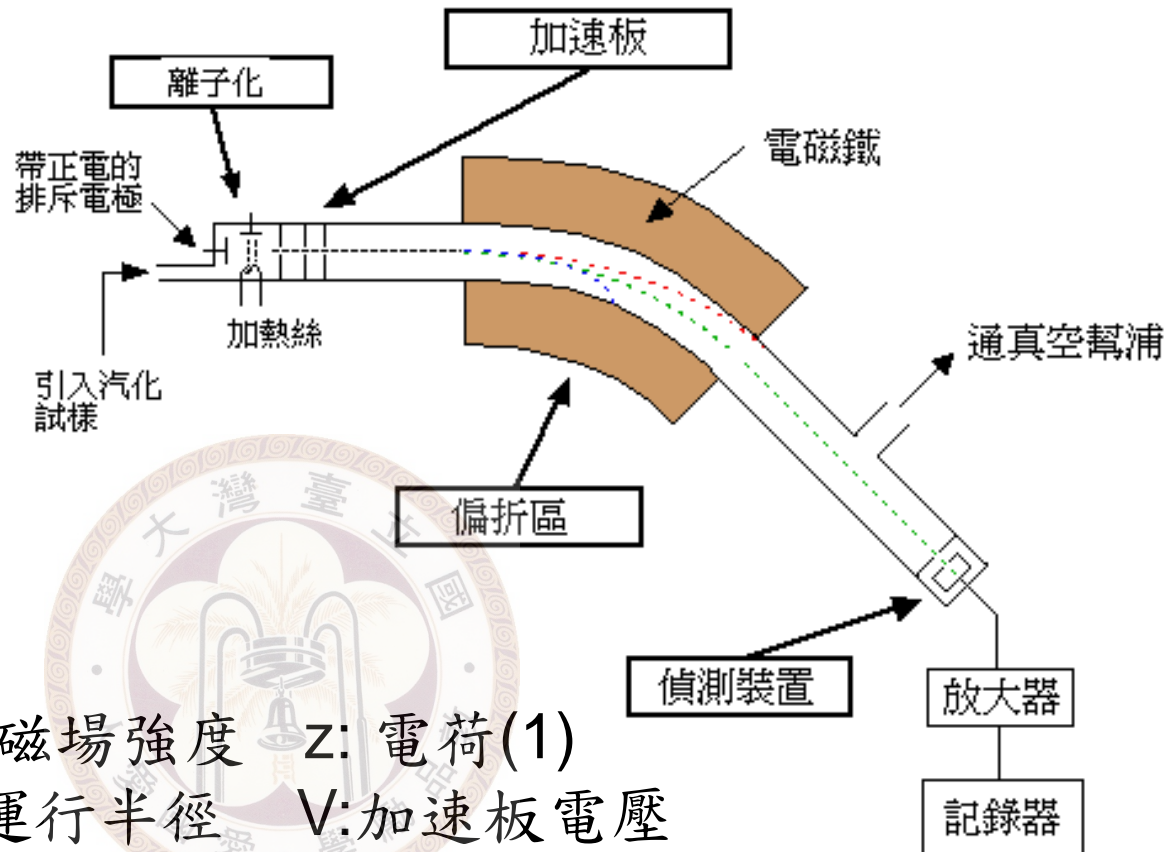
Base peak
Intensity = 100%
(最強的peak)

Molecular ion peak: M⁺
Usually the highest m/z
→ A good way to
determine molecular
mass



※ 質譜儀結構與設計概念





$$\frac{m}{z} = \frac{B^2 r^2 e}{2V}$$

m : 質量
e : 電量

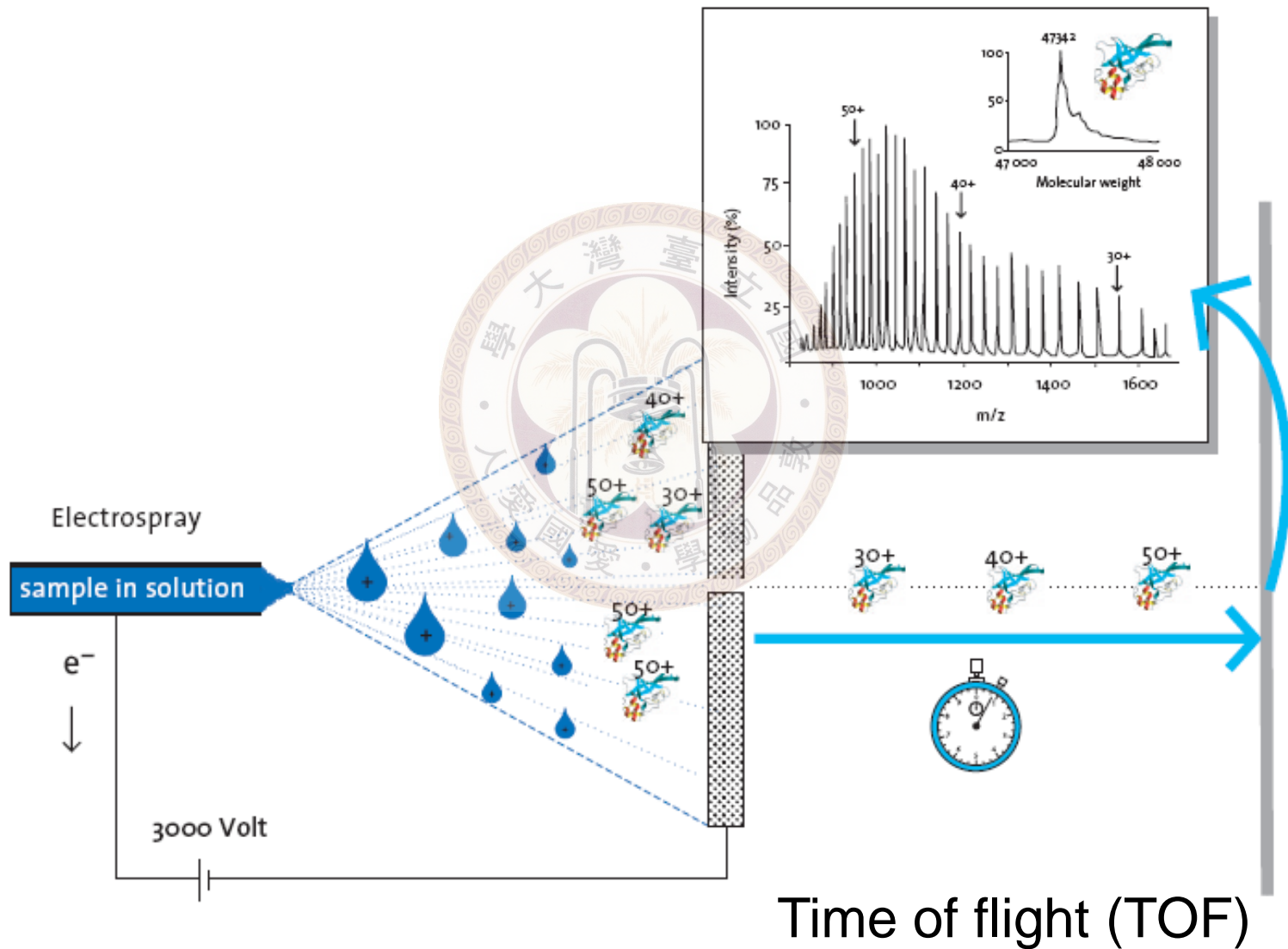
B : 磁場強度 z : 電荷(1)
r : 運行半徑 V : 加速板電壓

m愈大 ⇨ r愈大
B愈大 ⇨ r愈小

Scan B: fragments with different m/z will be registered.
Or scan accelerating voltage at constant B.

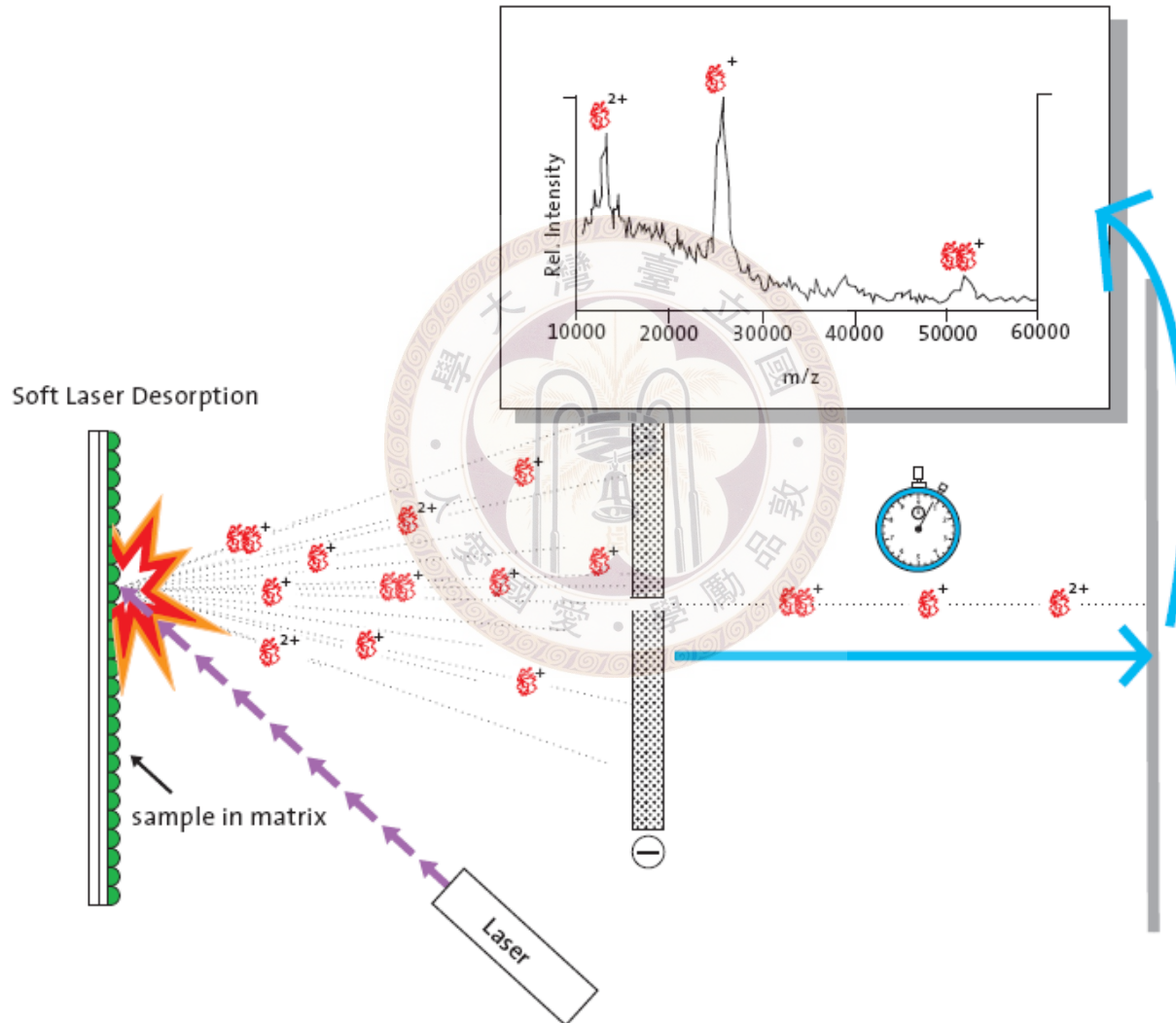


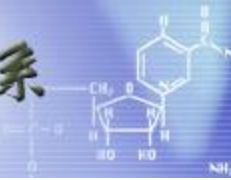
◎ 其它游離方式：電灑法





© MALDI (matrix-assisted laser-desorption ionization)





◎ Fast-atom bombardment (FAB)

Hit with a high energy atom such as Xe with sample in a nonvolatile matrix.





※ Some features

◎ The presence of isotopes

$M^+ + 1$ possible: due to isotopes

例 CH_4 : usual combination $\cdot {}^{12}\text{C}^1\text{H}_4$

Others: ${}^{13}\text{C}^1\text{H}_4$ or ${}^{12}\text{C}^1\text{H}_3{}^2\text{H} \rightarrow M^+ + 1$

Relative abundance for ${}^{13}\text{C}$: 1.08 ${}^2\text{H}$: 0.016

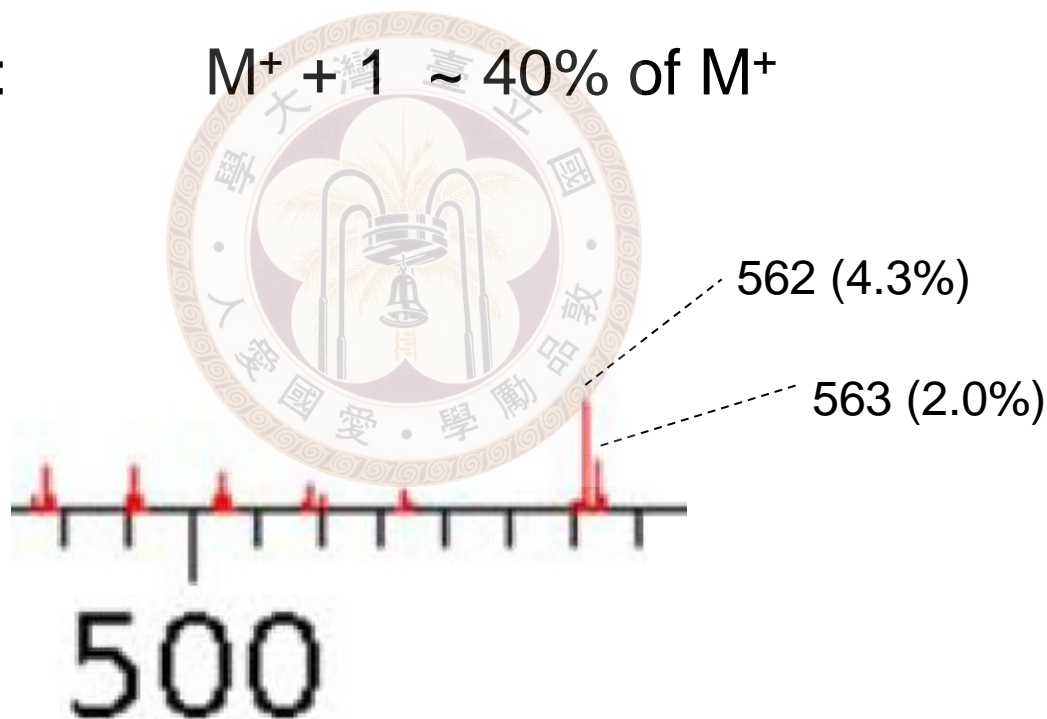
Probability for $m/z = 17$: $\sim 1.08 + 4(0.016) = 1.14\%$

For O, N: natural abundances of isotopes are small

→ $M^+ + 1$ depends largely on the number of C
(note: ^{15}N 0.366)

例 C_5H_{12} : $M^+ + 1 \sim 5\%$ of M^+

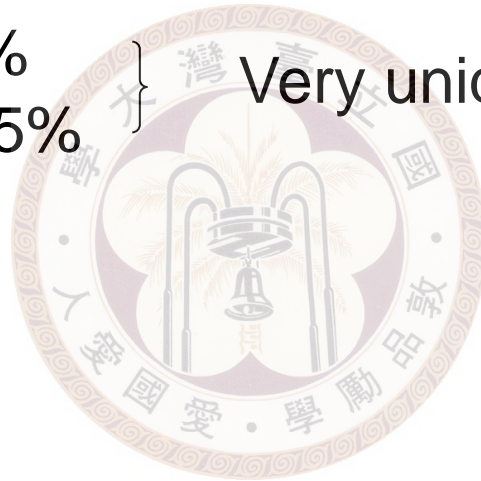
$\text{C}_{40}\text{H}_{82}$: $M^+ + 1 \sim 40\%$ of M^+



$M^+ + 2$

^{18}O : 0.2%
 ^{34}S : 4.4%
 ^{81}Br : 98%
 ^{37}Cl : 32.5%

} Very unique





◎ Resolution

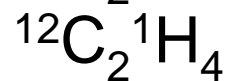
高解析度的質譜可用以區別：



27.9949



28.0062

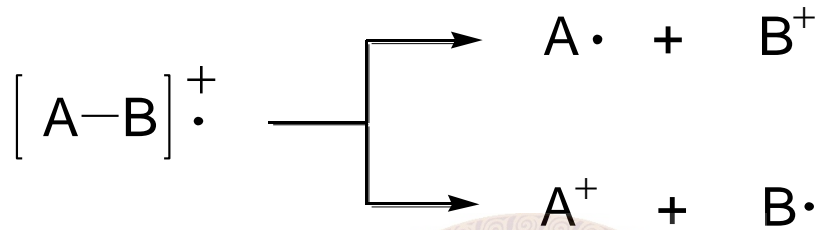


28.0312





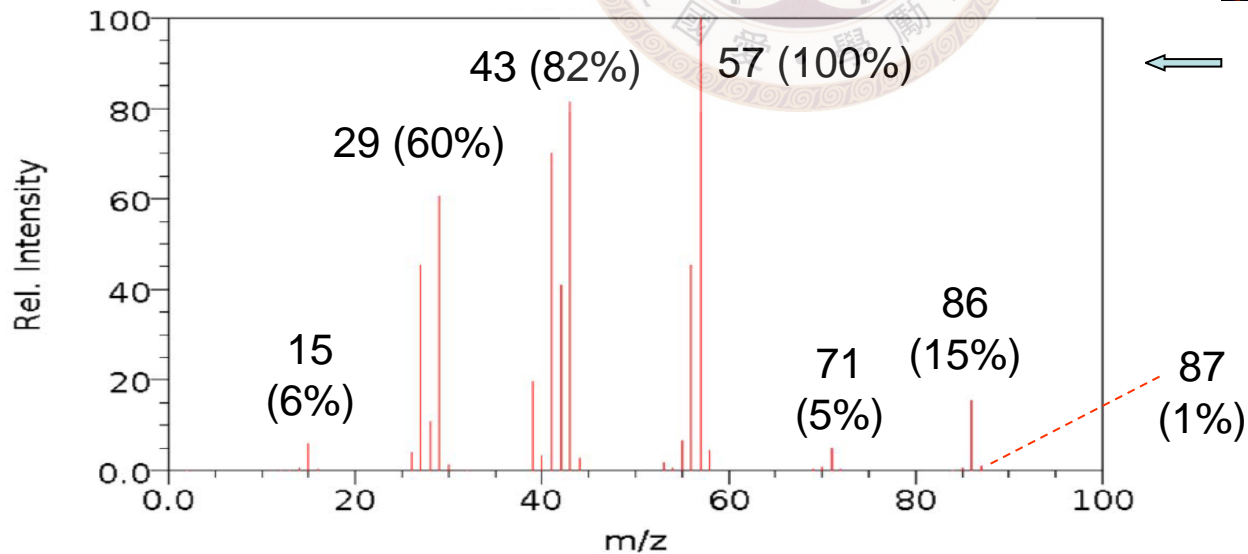
※ Fragmentation



Stability of the cation determines the pathway

Mass spec. of hexane (C₆H₁₄)

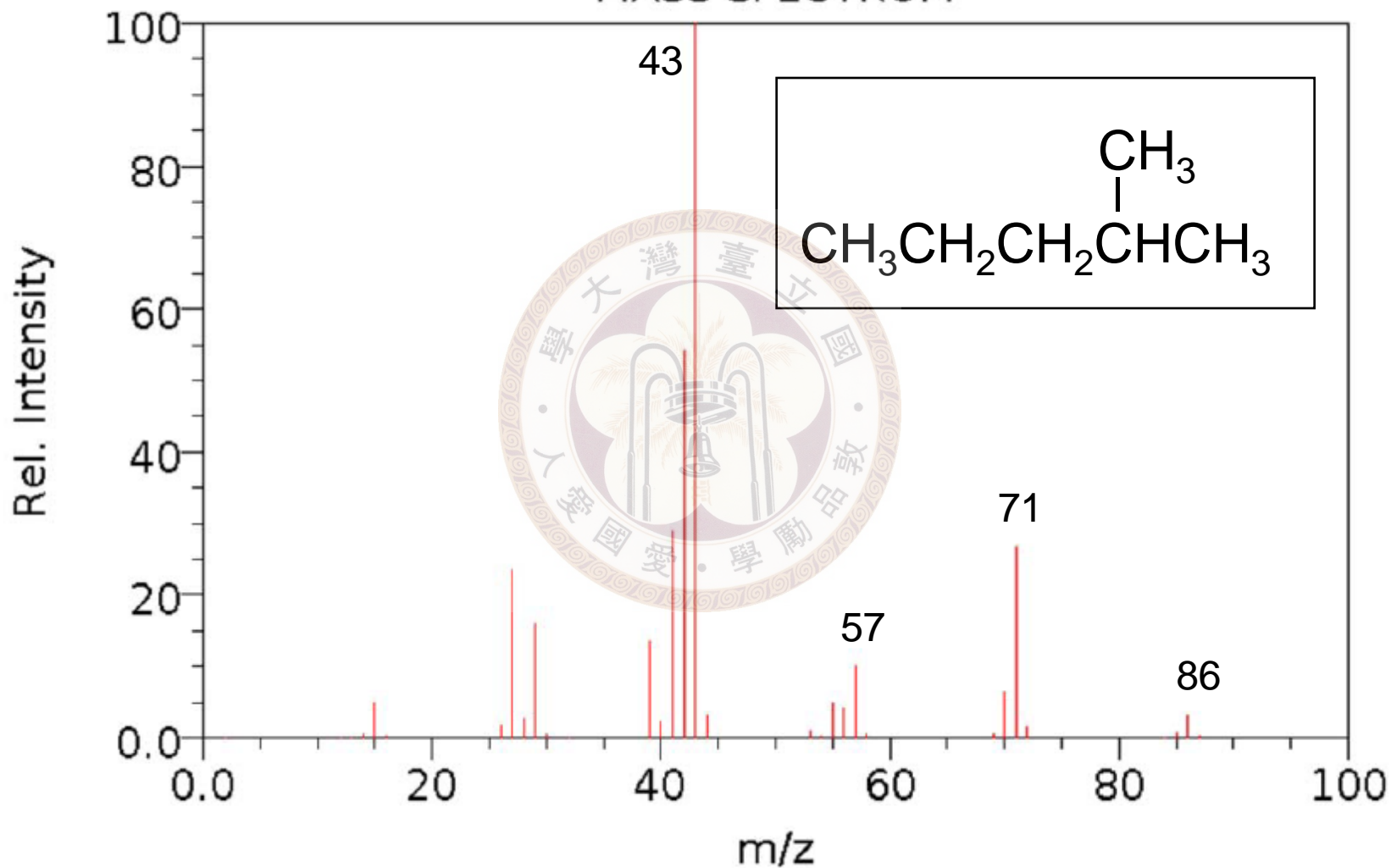
NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>) 

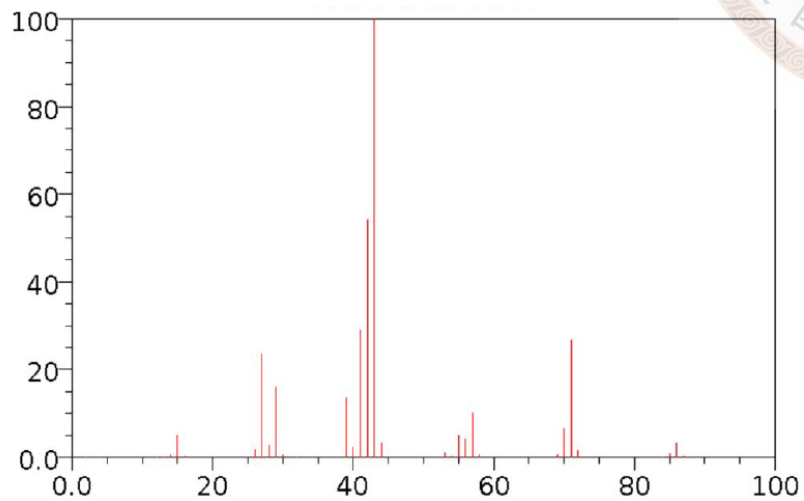
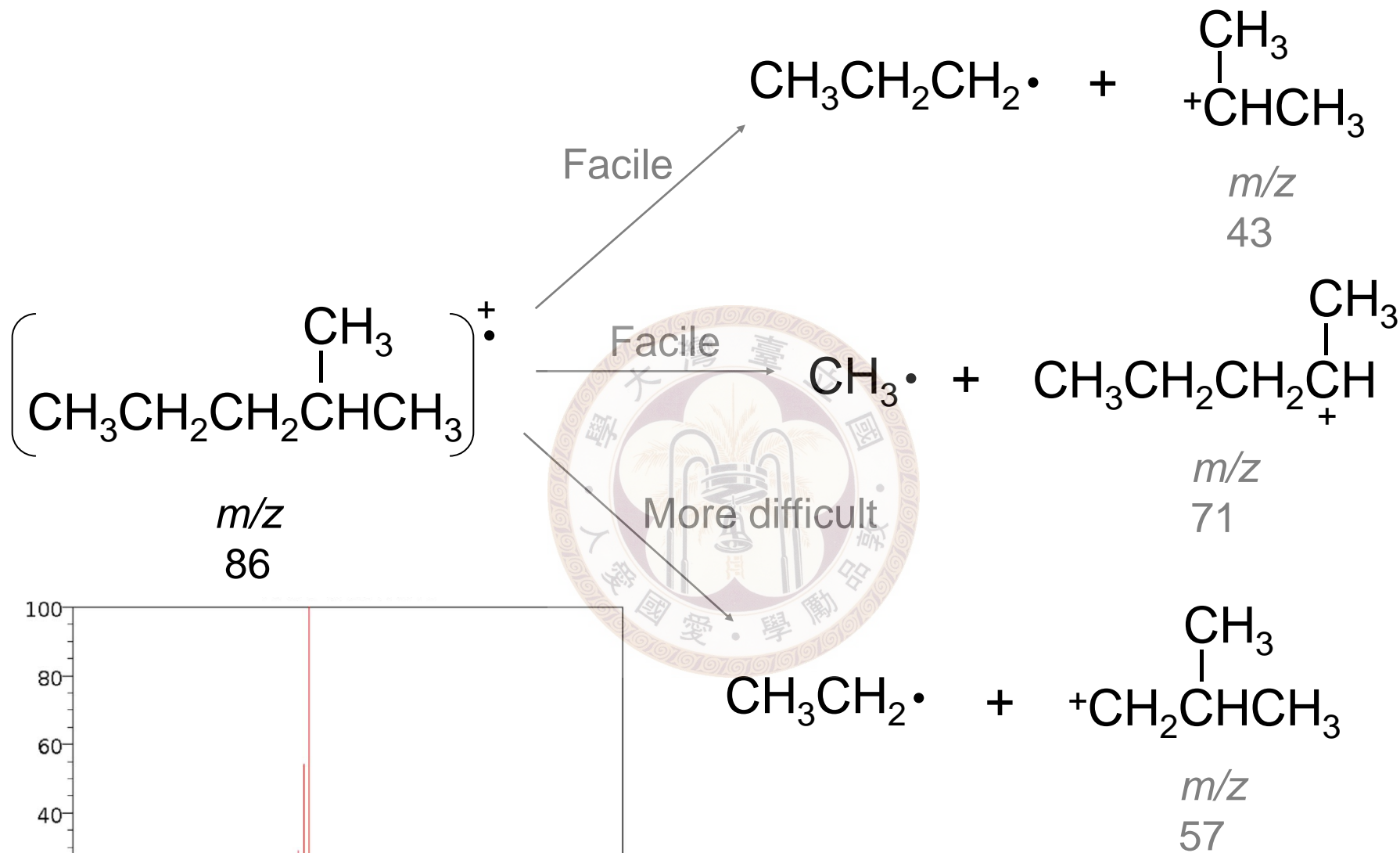


← Methyl cation (M⁺ = 15) is a very small peak

✓ Alkanes

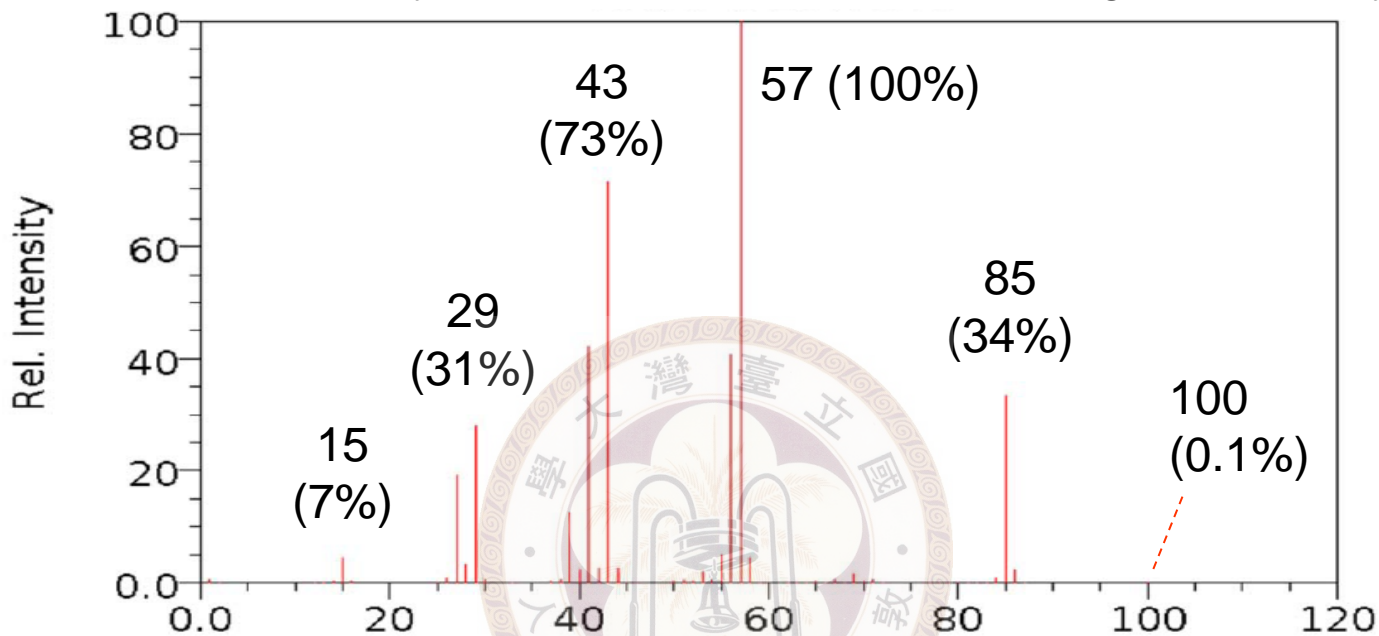
Pentane, 2-methyl-
MASS SPECTRUM



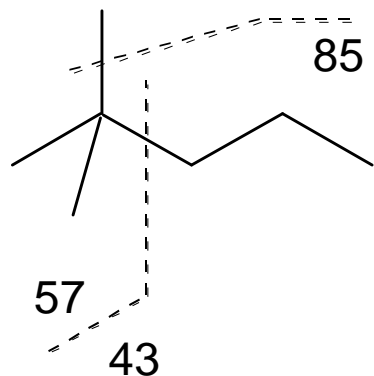


Mass spectrum of 2,2-dimethylpentane

NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)



2,2-dimethylpentane



Parent peak very small

Base peak corresponds to *t*-butyl cation

✓ Alkenes

Strong parent peak

Losing π e^- is easy

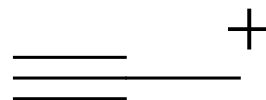


$m/z = 41$
base peak

✓ Alkynes

Strong parent peak

Forms propargyl ion easily

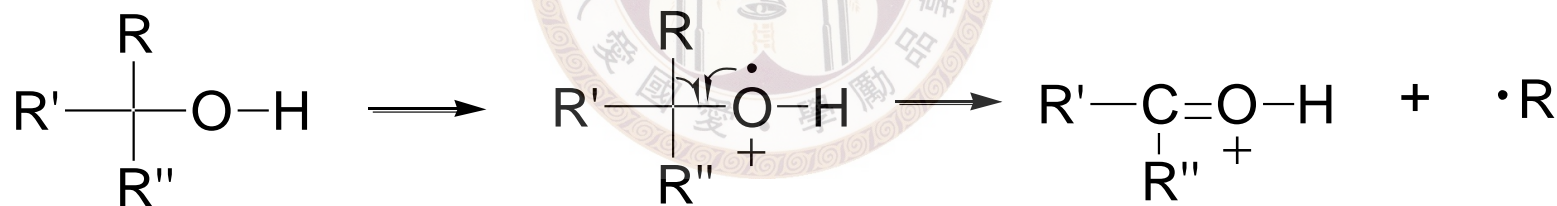


✓ Alcohols

$M^+ - 18$ occurs easily \longrightarrow Low parent ion



Breaks $\alpha - \beta$ bond easily (α -cleavage)



(similar for carbonyl compounds and amines)