Spectroscopic Methods in Organic Chemistry

CHEM-6124, Organic Chemistry (Minor)

Online Lectures (MS)

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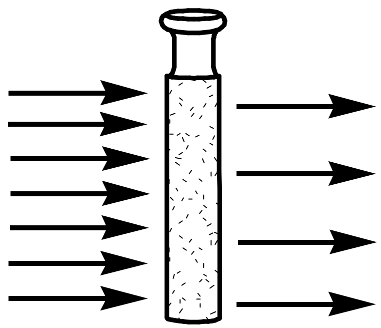
Spectroscopy *vs* Spectrometry

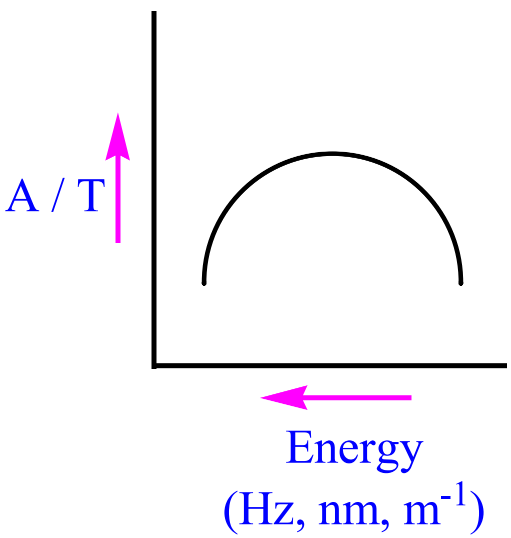
1) Involves a physical change



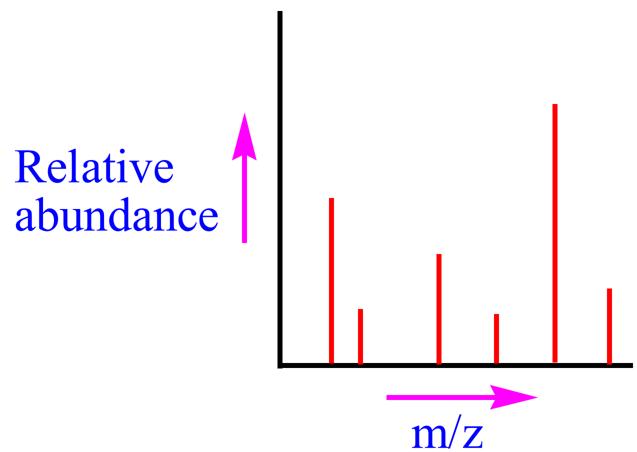
1) Involves a chemical change

$$\dot{M}^{\bullet +} + 2\,\bar{e} \longleftarrow \ddot{M} + \bar{e} \longrightarrow \dot{M}^{\bullet -}$$

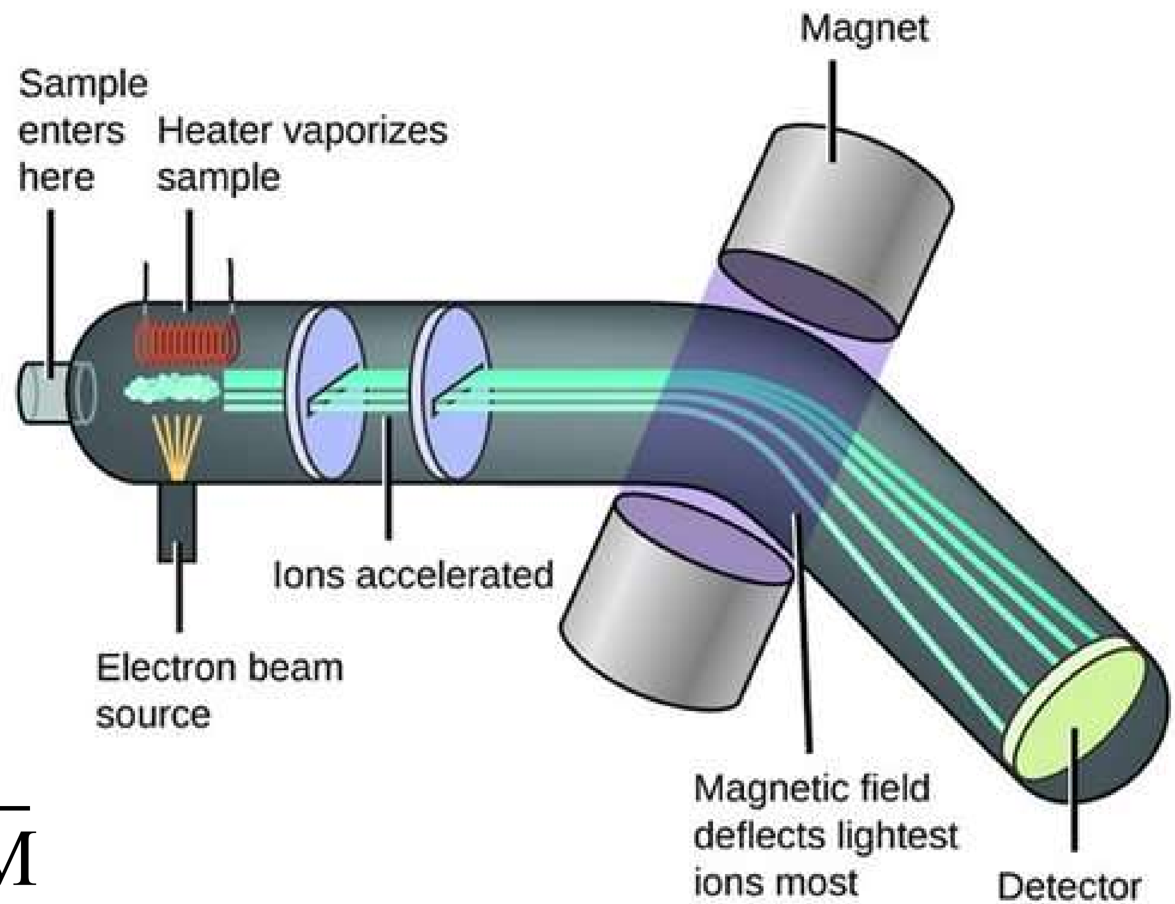
2) a spectrum



2) a spectrum



Mass Spectrometry



$$M \xrightarrow[(1\text{-}10\ eV)]{\bar{e}} M^{\bullet -}$$

$$M \xrightarrow[(70\ eV)]{\bar{e}} M^{\bullet +}$$

Energy of Accelerated Electrons

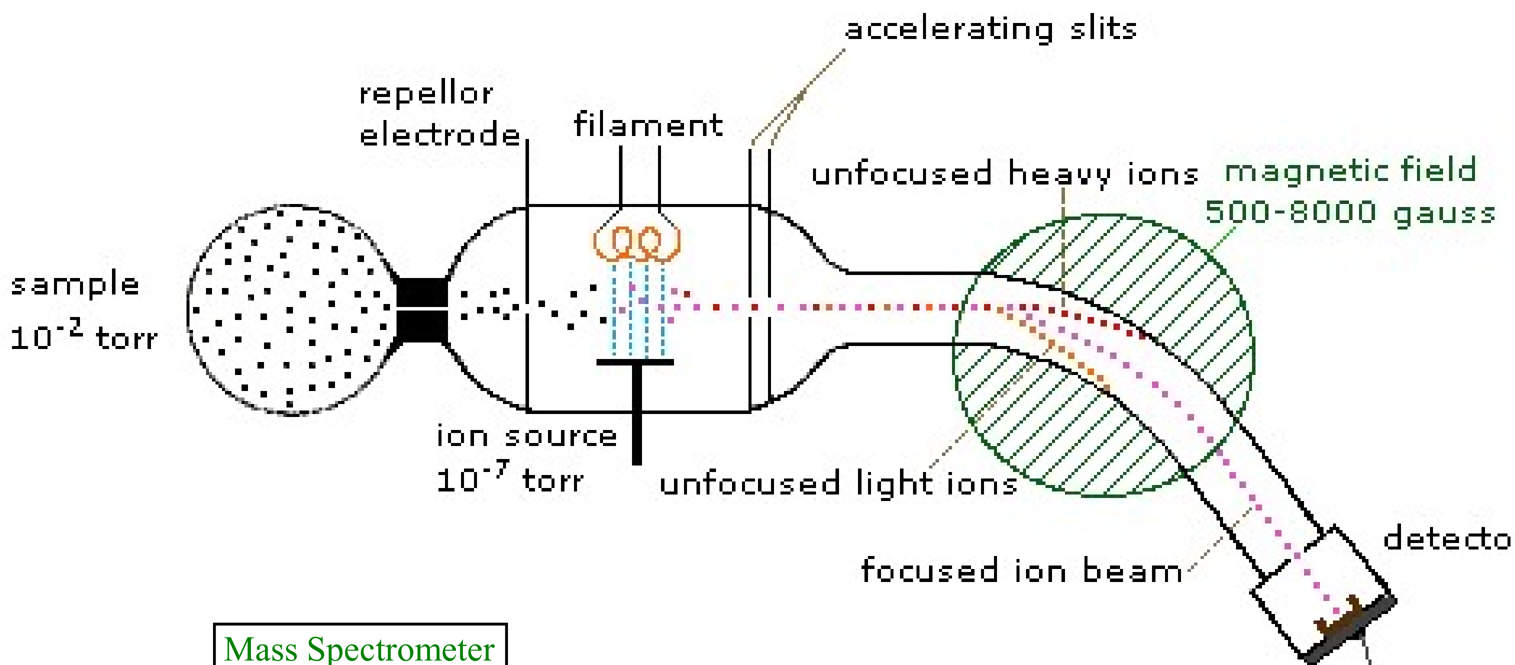
$70\ eV = 70 \times (1.6 \times 10^{-19}) = 1.12 \times 10^{-17}\ \text{J / partical} \times (6.02 \times 10^{23})$
$= 6.75 \times 10^{6}\ \text{J . mol}^{-1} = 6.75 \times 10^{3}\ \text{kJ . mol}^{-1}$

since E = hν so = E/h = $\dfrac{1.12 \times 10^{-17}\ \text{J}}{6.63 \times 10^{-34}\ \text{J.s}} = 1.69 \times 10^{16}\ \text{s}^{-1}$ (Hz)

since c = ν λ so λ = c/ν = $\dfrac{3 \times 10^{8}\ \text{m.s}^{-1}}{1.69 \times 10^{16}\ \text{s}^{-1}} = 1.78 \times 10^{-8}\ \text{m}$

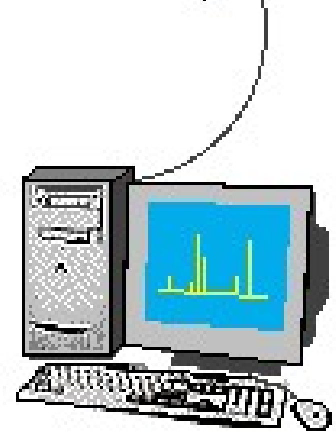
λ = 17.8 nm = 178 A^{o} (VUV: 3 - 200 nm)

A Mass Spectrometer

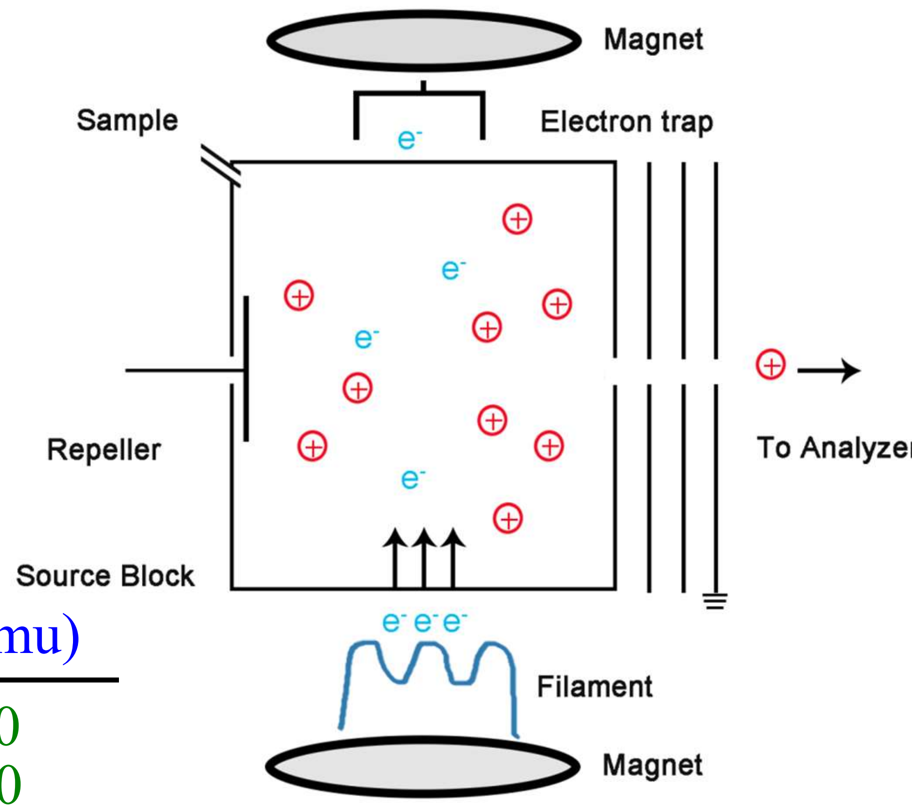


Mass Spectrometer

- **Vaporizer**
  - i) Heating
  - ii) Reduced Pressure
  - iii) Any / both
  - $P = 10^{-9}$ to 10^{-12} bar
  - (10^{-4} to 10^{-7} $N.m^{-2}$)
- **Ionizer**
  - i) 70 *eV*
  - ii) 1-10 *eV*
- **Fragmenter**
  - Magnetic & Electric field
- **Detection**

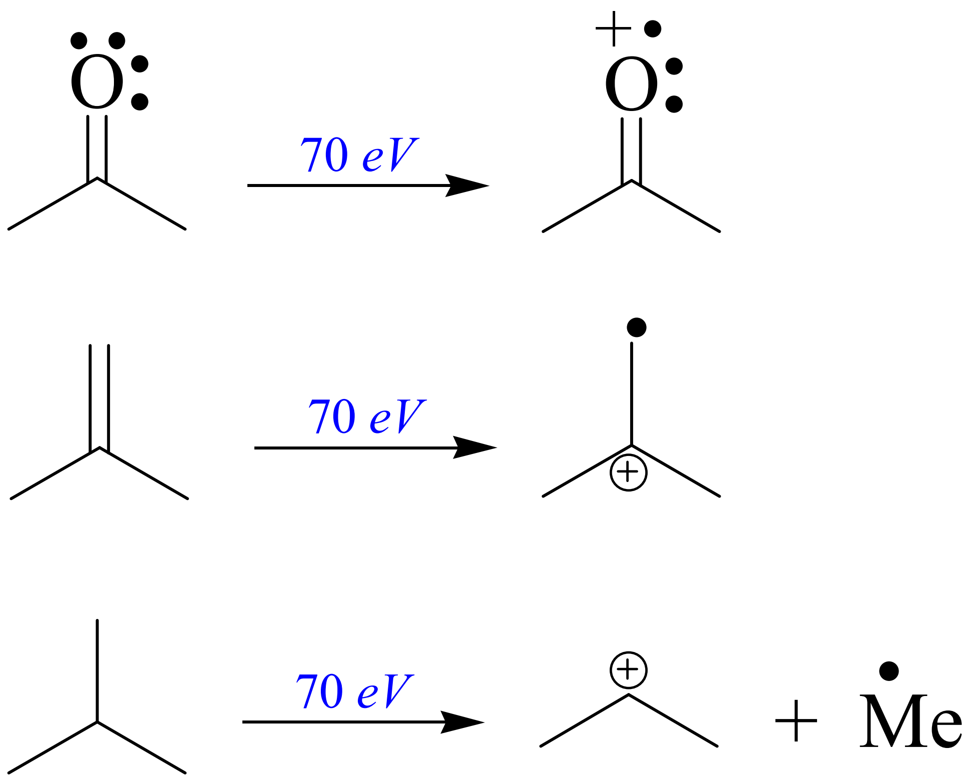


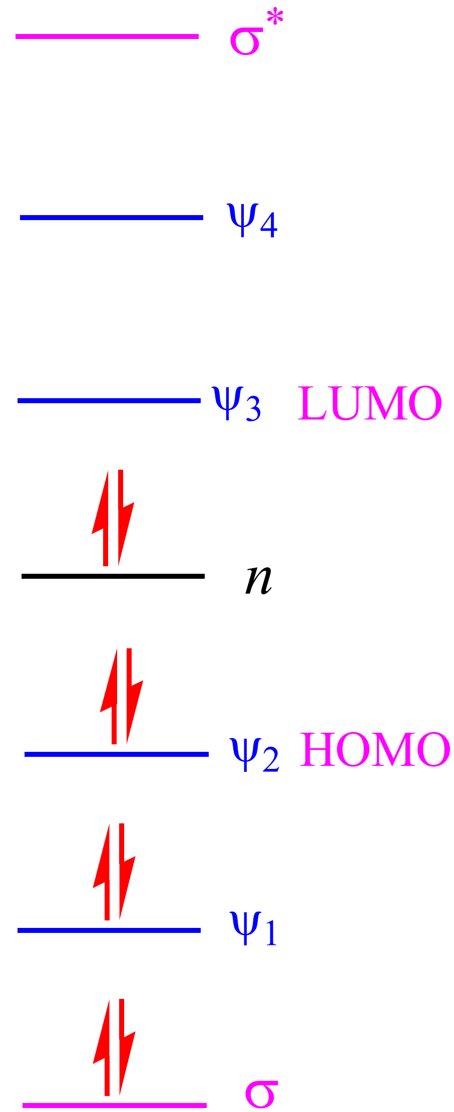
Ionization Techniques

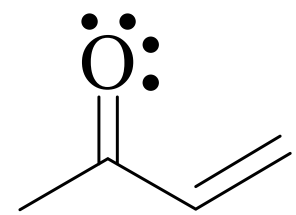


Techniques	MM (amu)
Electron Impact (EI)	1,000
Chemical Ionization (CI)	1,000
Atmospheric pressure Chemical Ionization (APCI)	2,000
Fast Atomic Bobmardment (FAB)	6,000
Electro Spray Ioniozation (ESI)	10,000
Matrix Assisted Laser Desorption Ionization (MALDI)	500,000

Electron Impact (EI)







Chemical Ionization (CI)

$$1\bar{e} + CH_4 \xrightarrow{70\ eV} CH_4^{\bullet +} + 2\bar{e}$$

$$CH_4^{\bullet +} + CH_4 \longrightarrow CH_5^{\oplus} + {}^{\bullet}CH_3$$

$$CH_5^{\oplus} + M \longrightarrow CH_4 + MH^{\oplus}$$

$$1\bar{e} + CH_4 + M \longrightarrow MH^{\oplus} + {}^{\bullet}CH_3 + 2\bar{e}$$

$$1\bar{e} + \ddot{N}H_3 \xrightarrow{70\ eV} NH_3^{\bullet +} + 2\bar{e}$$

$$NH_3^{\bullet +} + NH_3 \longrightarrow NH_4^{\oplus} + {}^{\bullet}NH_2$$

$$NH_4^{\oplus} + M \longrightarrow NH_3 + MH^{\oplus}$$

$$1\bar{e} + NH_3 + M \longrightarrow MH^{\oplus} + {}^{\bullet}NH_2 + 2\bar{e}$$

APCI / ESI

$$1\bar{e} + \ddot{O}H_2 \xrightarrow{70\ eV} \overset{\bullet +}{O}H_2 + 2\bar{e}$$

$$\overset{\bullet +}{O}H_2 + OH_2 \longrightarrow \overset{\oplus}{O}H_3 + \dot{O}H$$

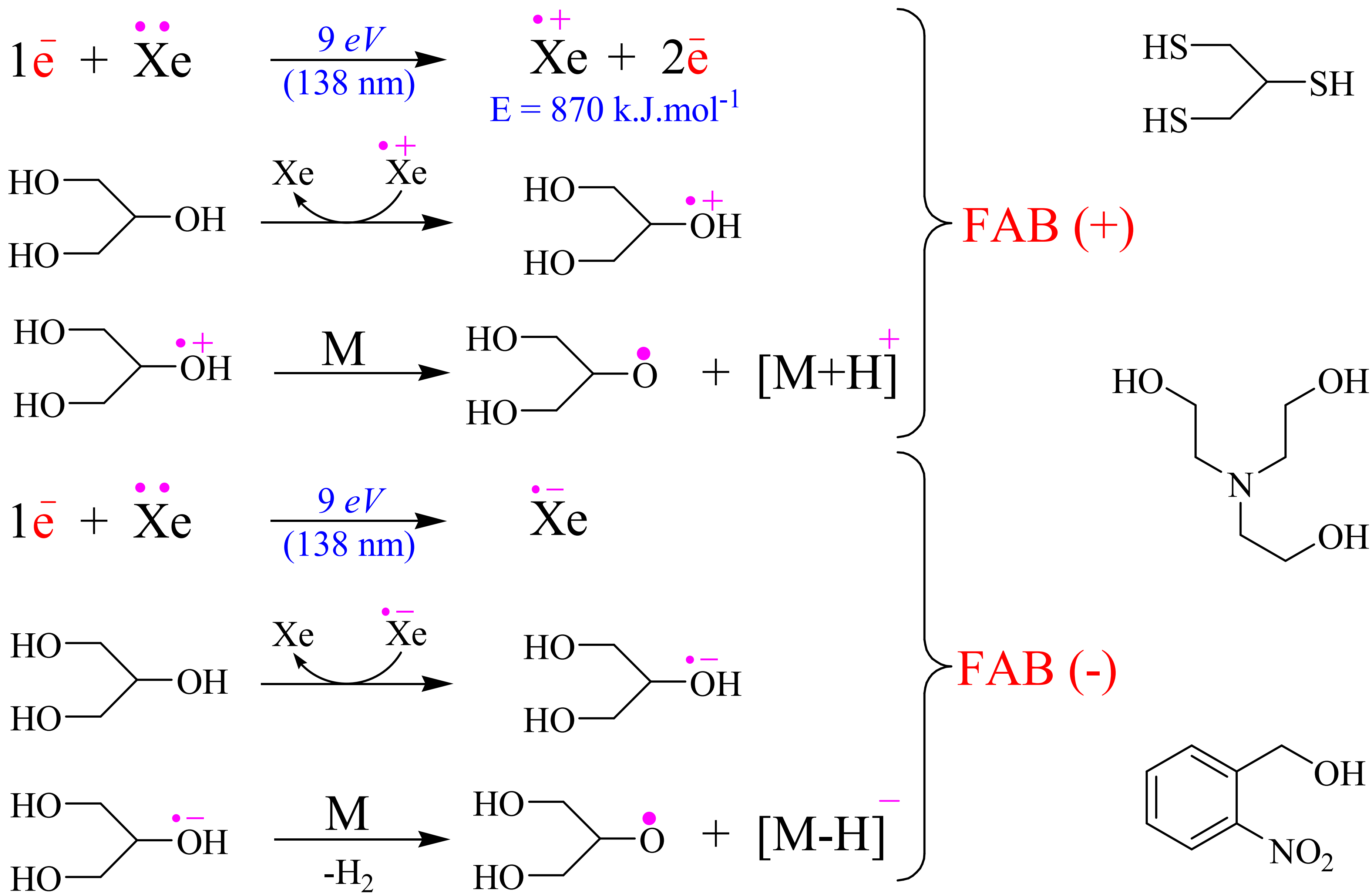
$$\overset{\oplus}{O}H_3 + M \longrightarrow OH_2 + \overset{\oplus}{M}H$$

$$1\bar{e} + H_2O + M \longrightarrow \overset{\oplus}{M}H + \dot{O}H + 2e^-$$

ESI:

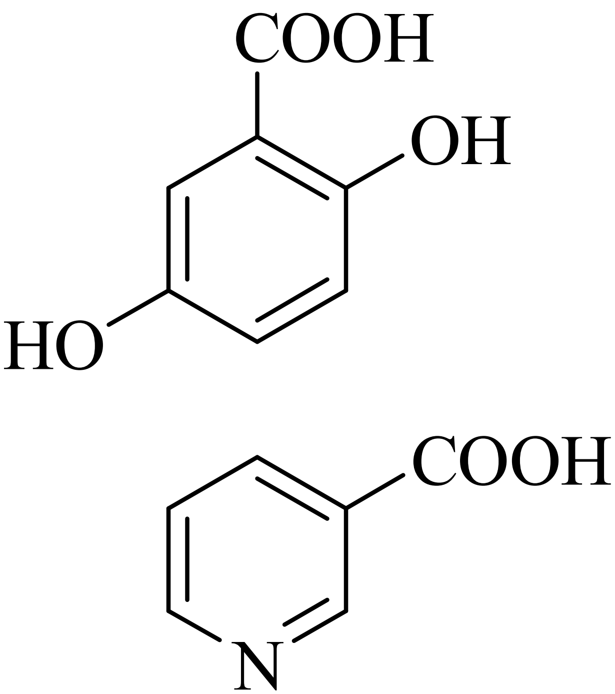
1) Ionization takes place first rather vaporization
2) Analyte may be an organic molecule or a polymer/ biopolymer
3) Matrix is a buffer of K^+, Na^+, $^+NH_4$ ions
4) Molecular ions [M+H], [M+Na], [M+K], [M+NH_4]

Fast Atomic Bombardment (FAB)

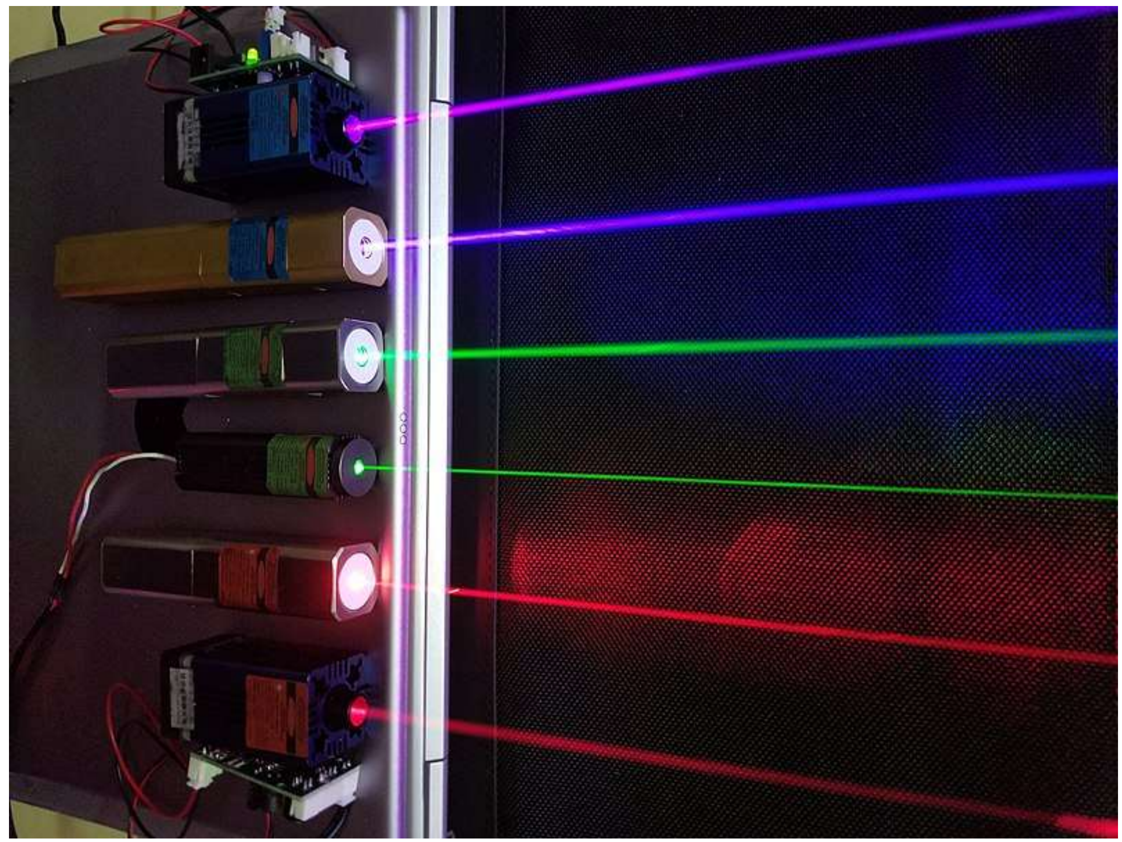


MALDI

Matrix Assisted Laser Desorption Ionization

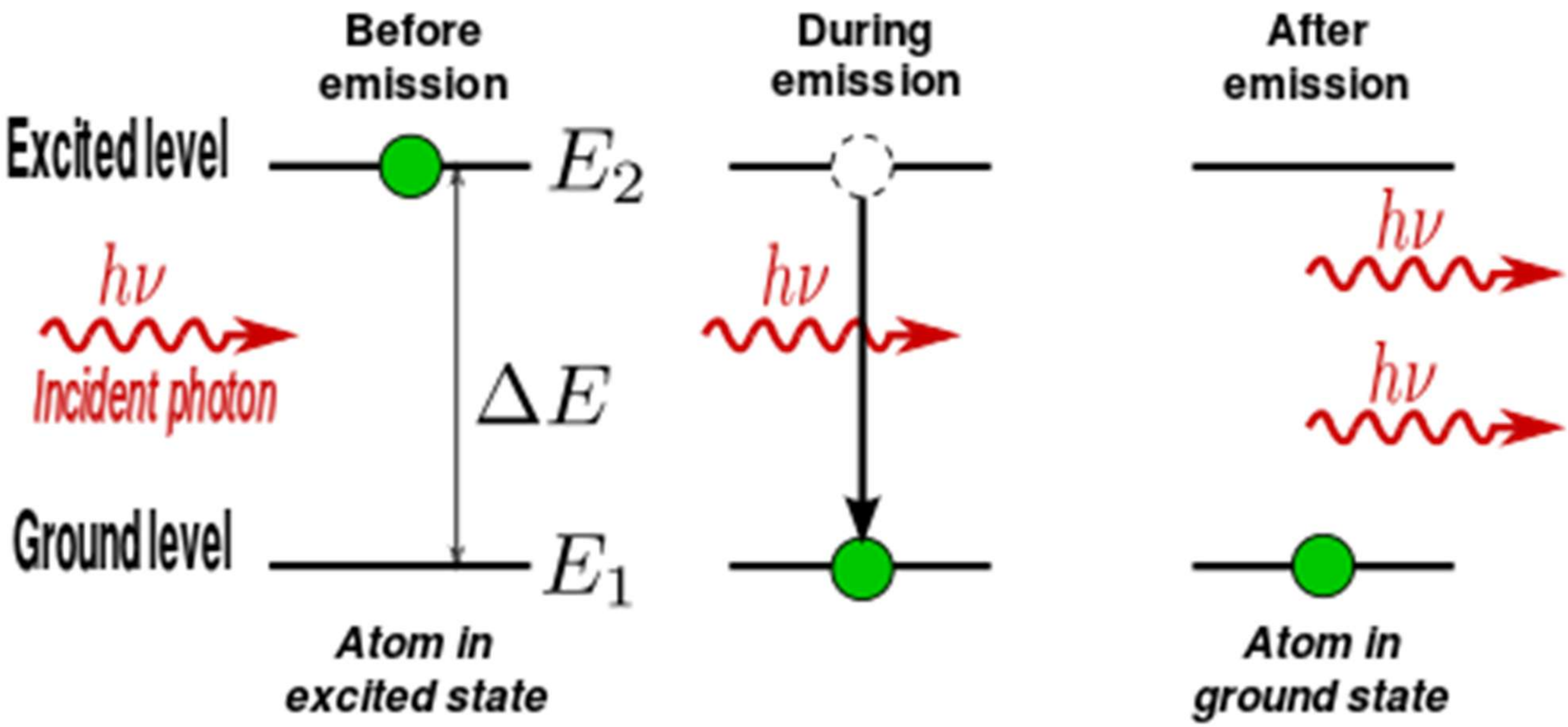


Matrix (λ_{max})



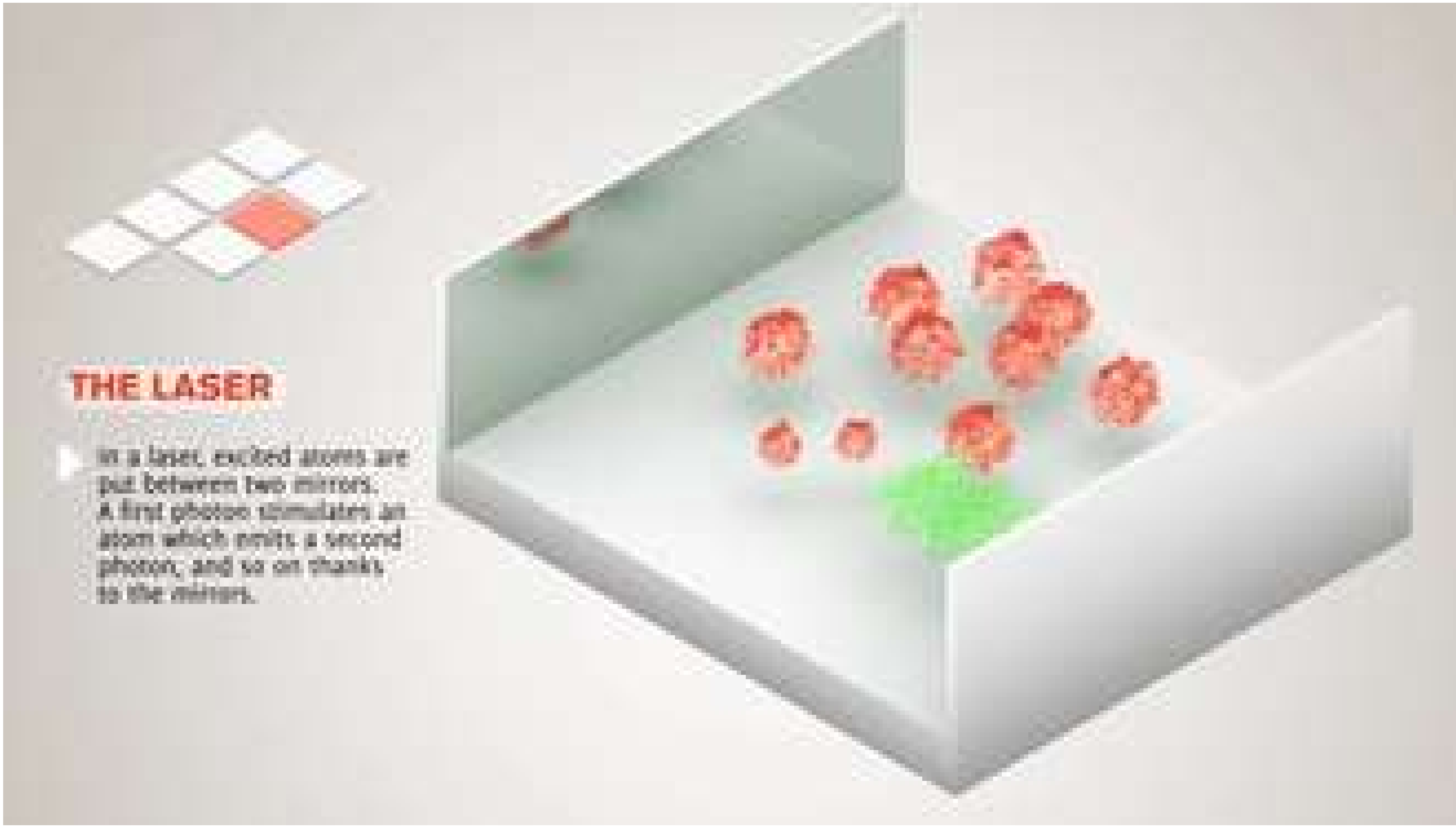
LASER Principle

Light Amplification by Stimulated Emission of Radiations

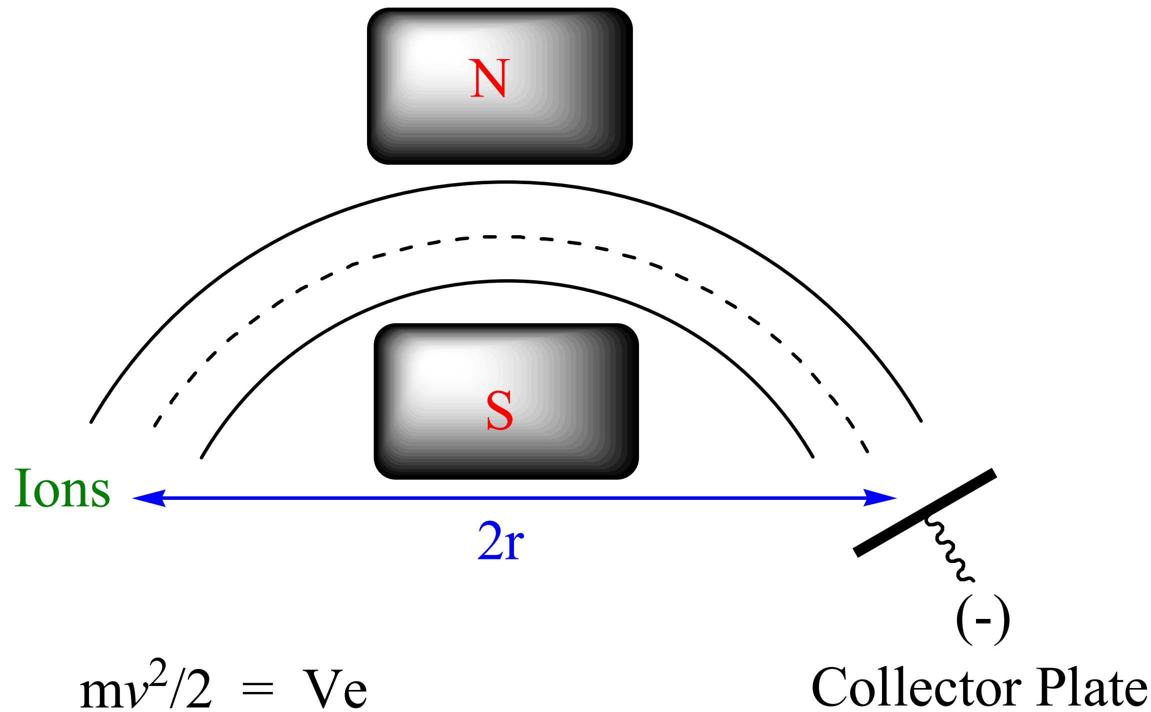


$$E_2 - E_1 = \Delta E = h\nu$$

LASER Principle



Fragmentation



K.E. = Ve $\Longrightarrow$ $mv^2/2$ = Ve

v^2 = 2 V e / m .... eq 1

since Fc α H v

mv^2/r = H e v v^2 / v = H e r / m

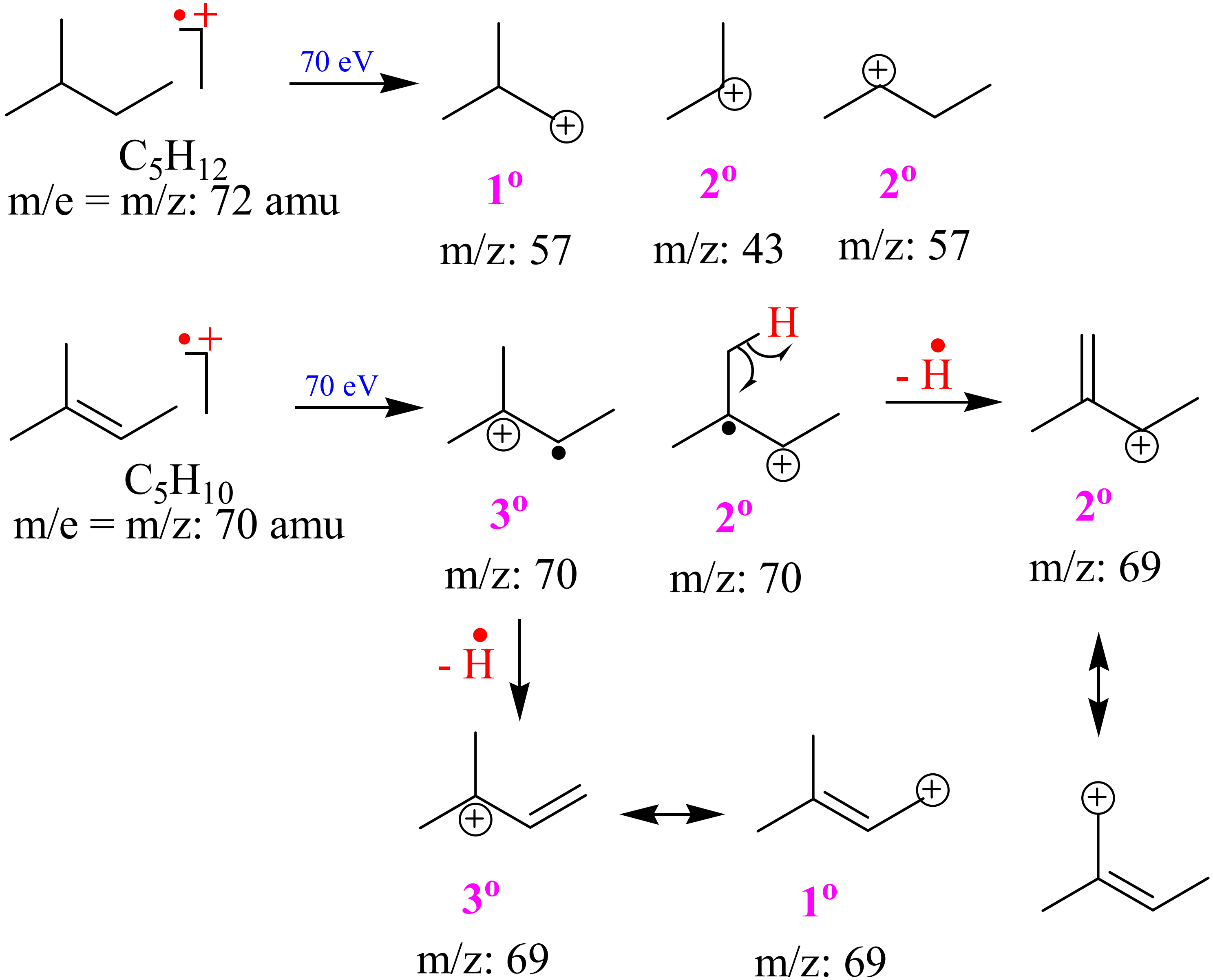
v^2 = $H^2 e^2 r^2 / m^2$ .... eq 2

$H^2 e^2 r^2 / m^2$ = 2 V e / m

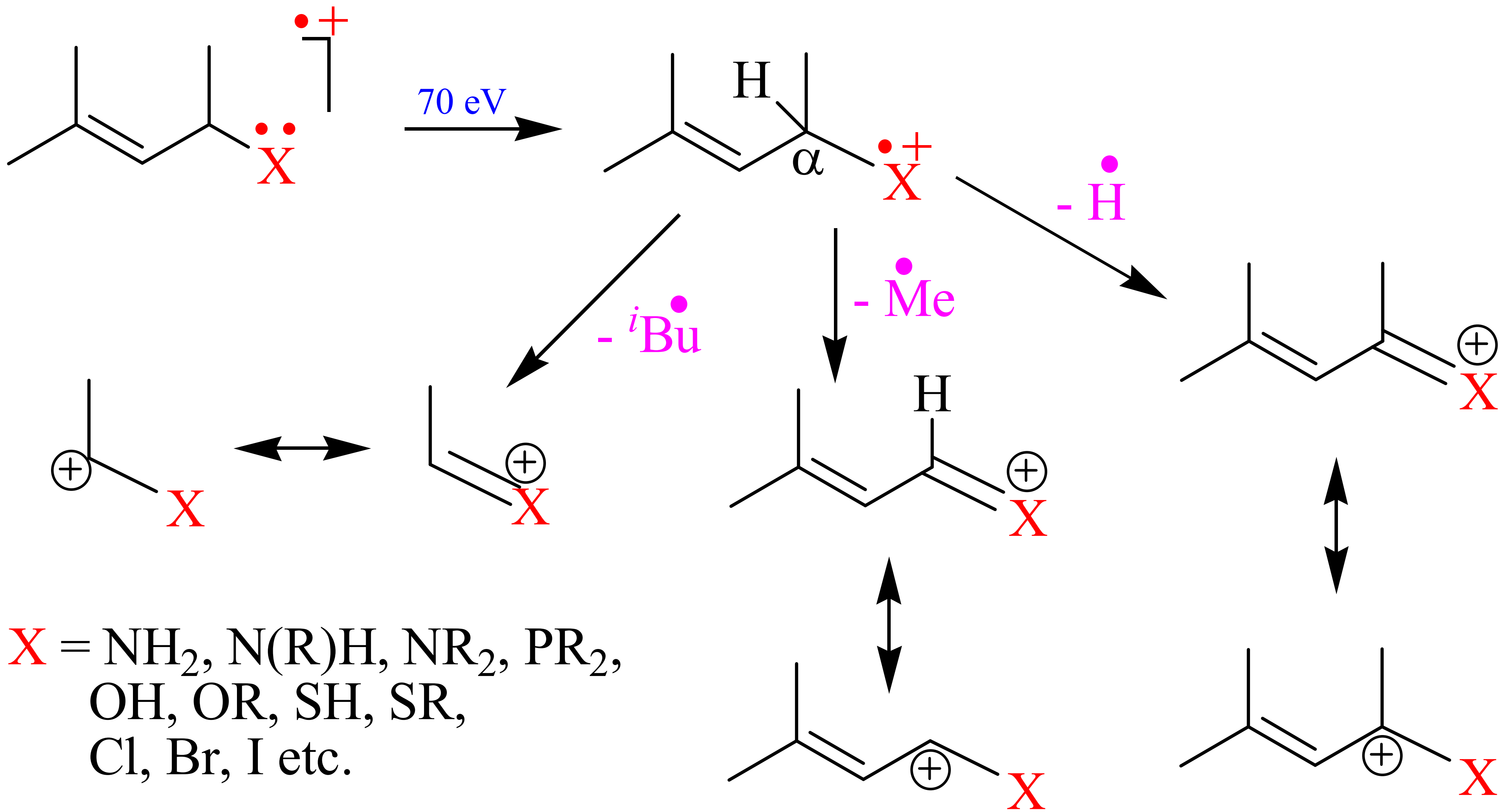
2 V / $H^2 r^2$ = e / m

m / e = $H^2 r^2$ / 2 V

α-Cleavage

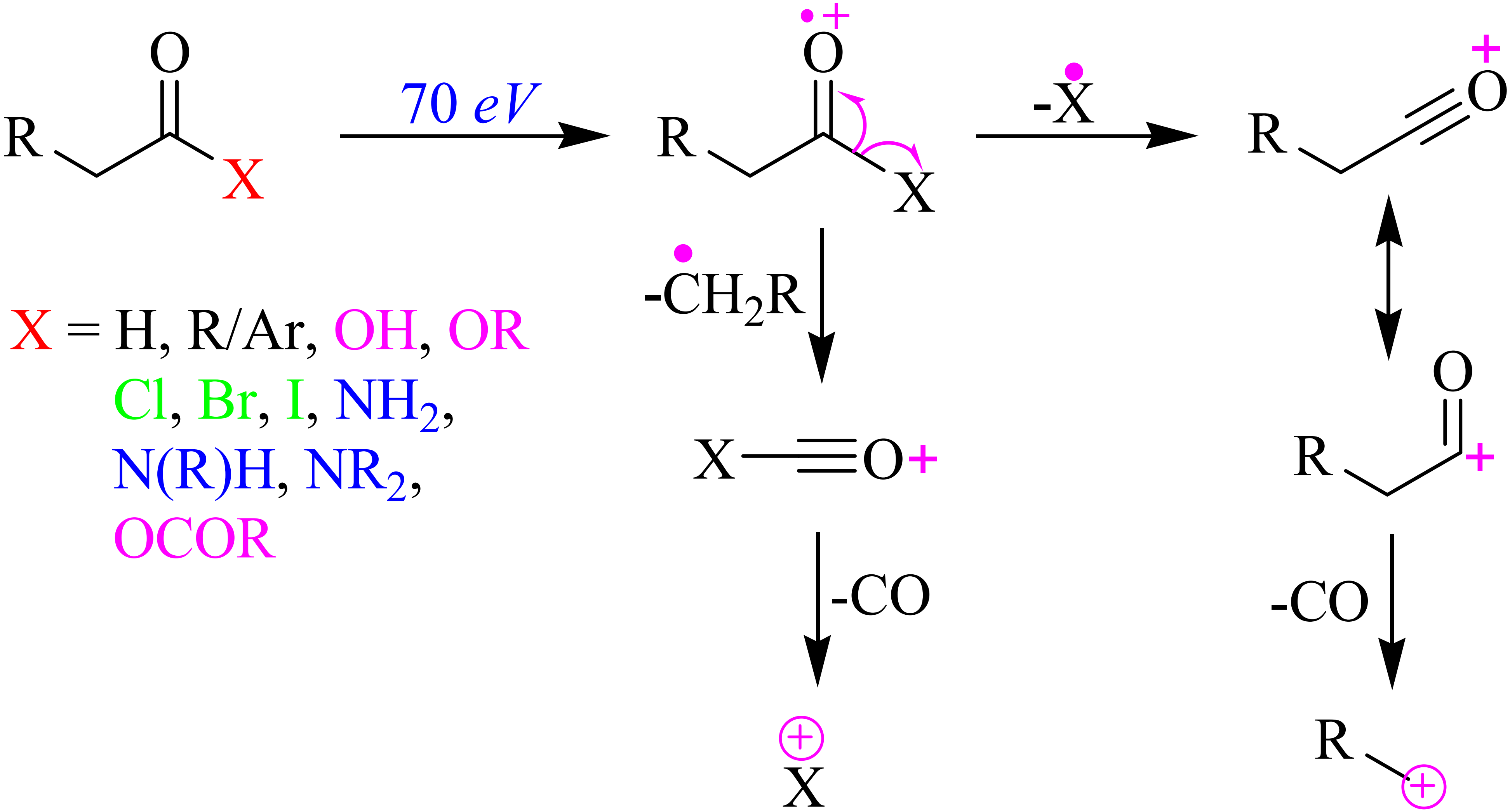

70 eV
C_5H_{12}
m/e = m/z: 72 amu
1°
m/z: 57
2°
m/z: 43
2°
m/z: 57
70 eV
C_5H_{10}
m/e = m/z: 70 amu
H
- H
3°
m/z: 70
2°
m/z: 70
2°
m/z: 69
- H
3°
m/z: 69
1°
m/z: 69

α-Cleavage



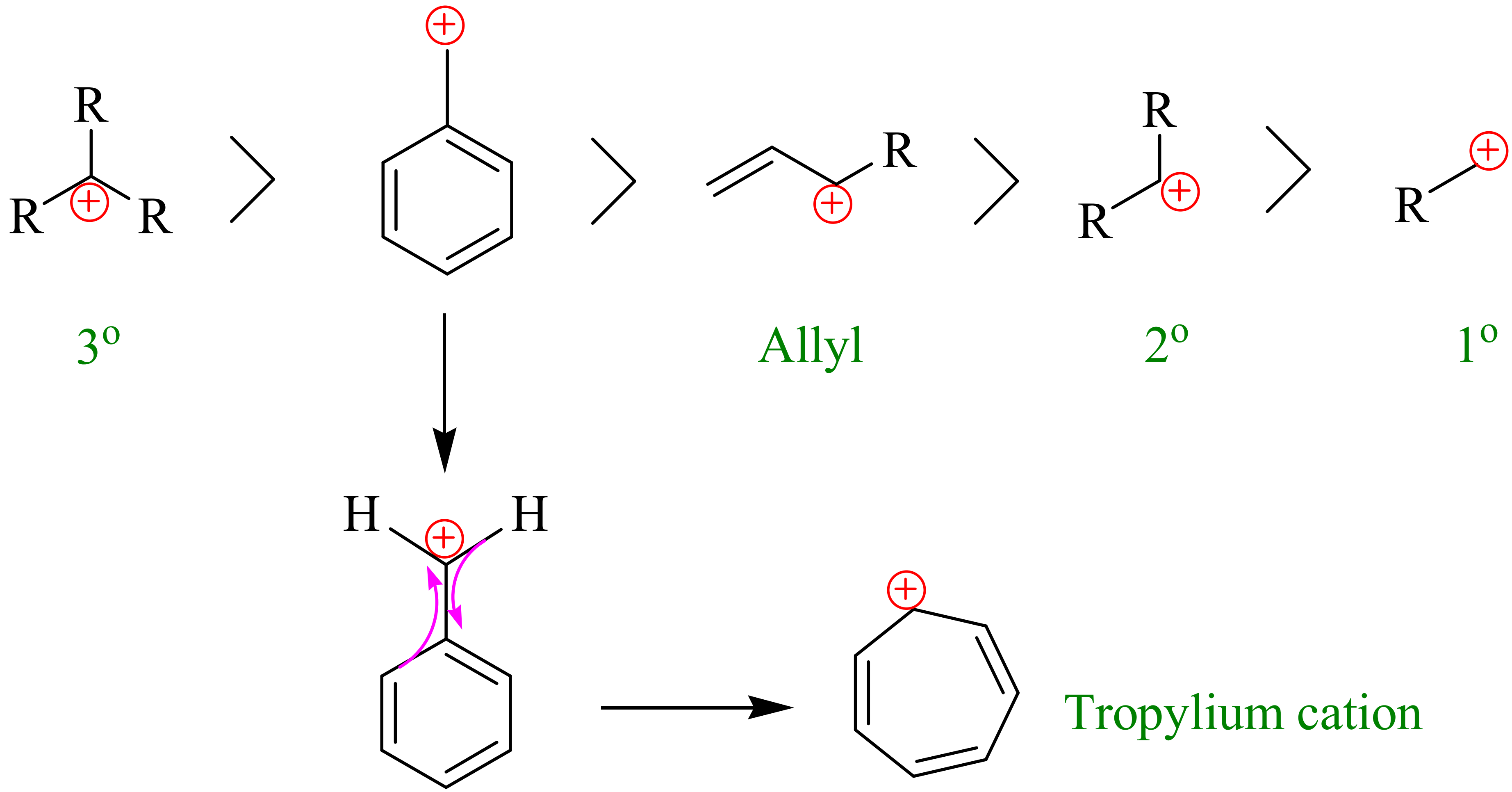
X = NH_2, N(R)H, NR_2, PR_2,
OH, OR, SH, SR,
Cl, Br, I etc.

Fragmentation (α-Cleavage)

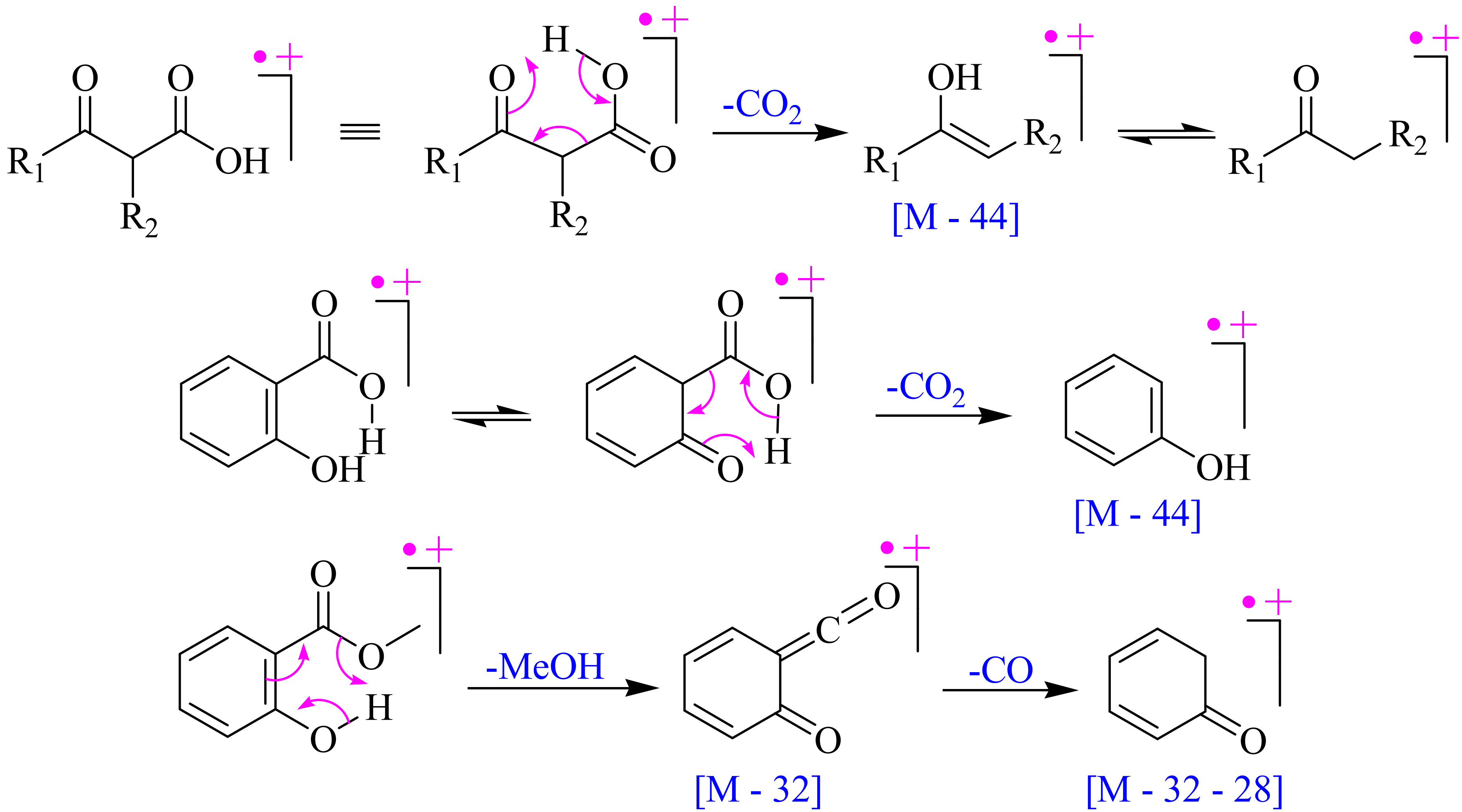


X = H, R/Ar, OH, OR, Cl, Br, I, NH_2, N(R)H, NR_2, OCOR

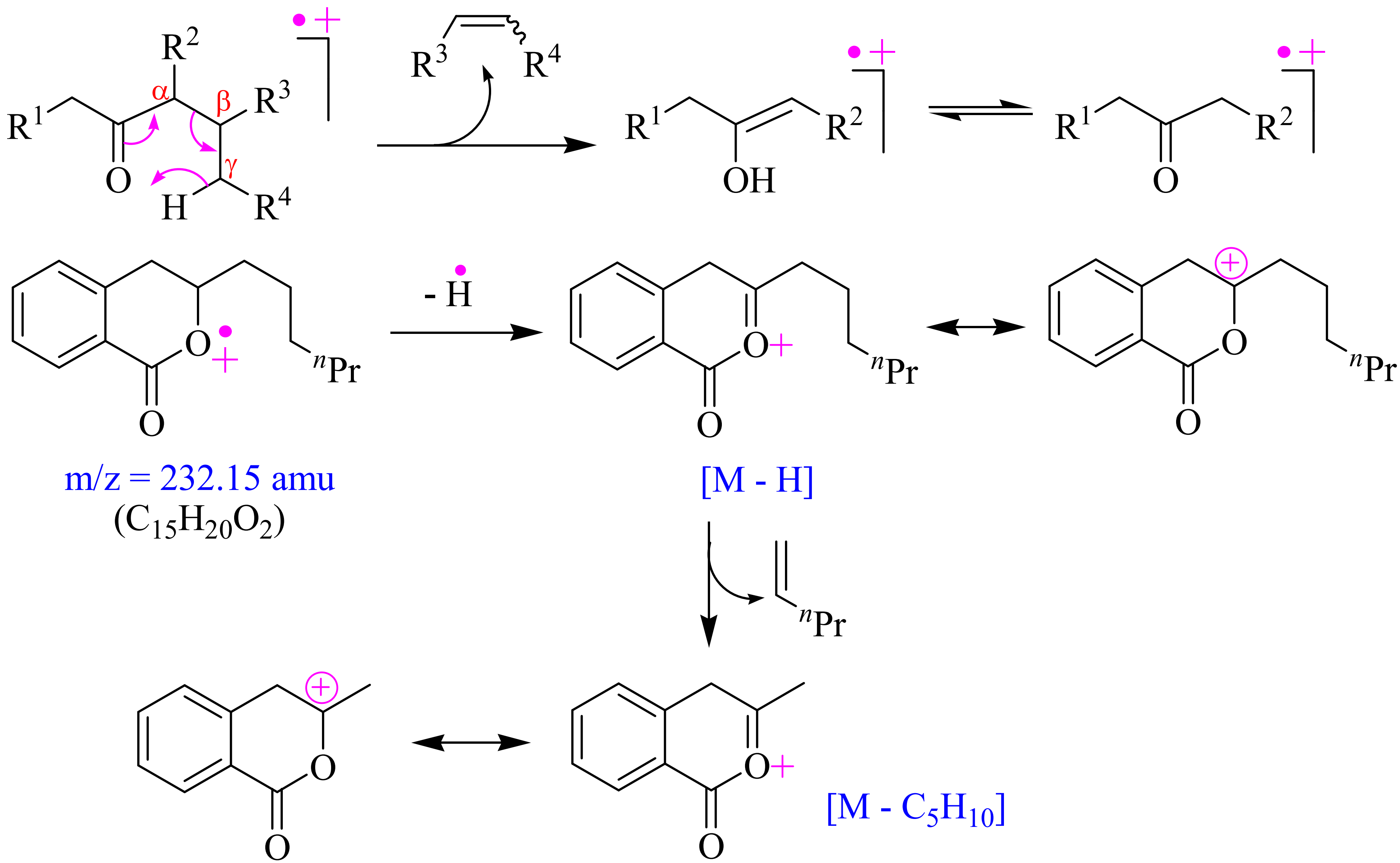
Stability of Carbocation



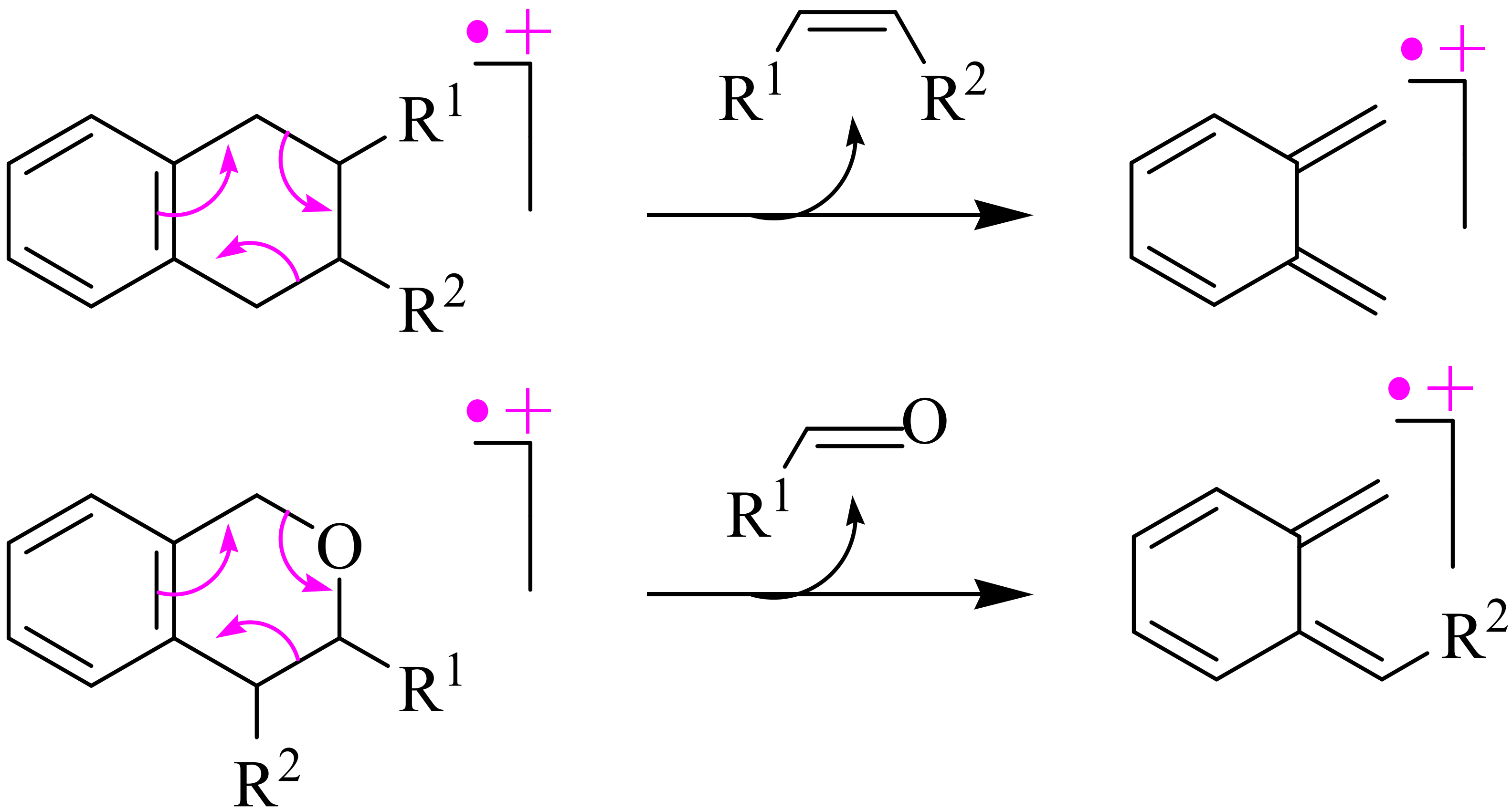
β-Ketoacid Rearrangement



McLafferty (γ-H) Rearrangement



Retro Diels-Alder



Isotopic Abundances of Cl

Number of [M] in MS spectrum = n + 1; where n = number of halogens

Ratio of lines in MS spectrum = $(a + b)^n$; where n = number of halogens

$$(a + b)^1 = 0.75a + 0.25b$$
$$= 3a + 1b$$

$$(a + b)^2 = a^2 + 2ab + b^2$$
$$= (0.75)^2a^2 + 2(0.75)a\,(0.25)b + (0.25)^2b^2$$
$$= (0.56)a^2 + (0.38)ab + (0.06)b^2$$
$$= 9a^2 + 6ab + 1b^2$$

$$(a + b)^3 = a^3 + 3a^2b + 3ab^2 + b^3$$
$$= (0.75)^3a^3 + 3(0.75)^2a^2\,(0.25)b + 3(0.75)a\,(0.25)^2b^2 + (0.25)^3\,b^3$$
$$= (0.42)a^2 + (0.42)a^2b + (0.14)ab^2 + (0.016)b^3$$
$$= 30a^3 + 30a^2b + 10ab^2 + 1b^3$$

Isotopic Abundances of Br

$(a + b)^1 = 0.5a + 0.5b$

$= 1a + 1b$

$(a + b)^2 = a^2 + 2ab + b^2$

$= (0.5)^2a^2 + 2\,(0.5)a\,(0.5)b + (0.5)^2b^2$

$= (0.25)a^2 + (0.5)ab + (0.25)b^2$

$= 1a^2 + 2ab + 1b^2$

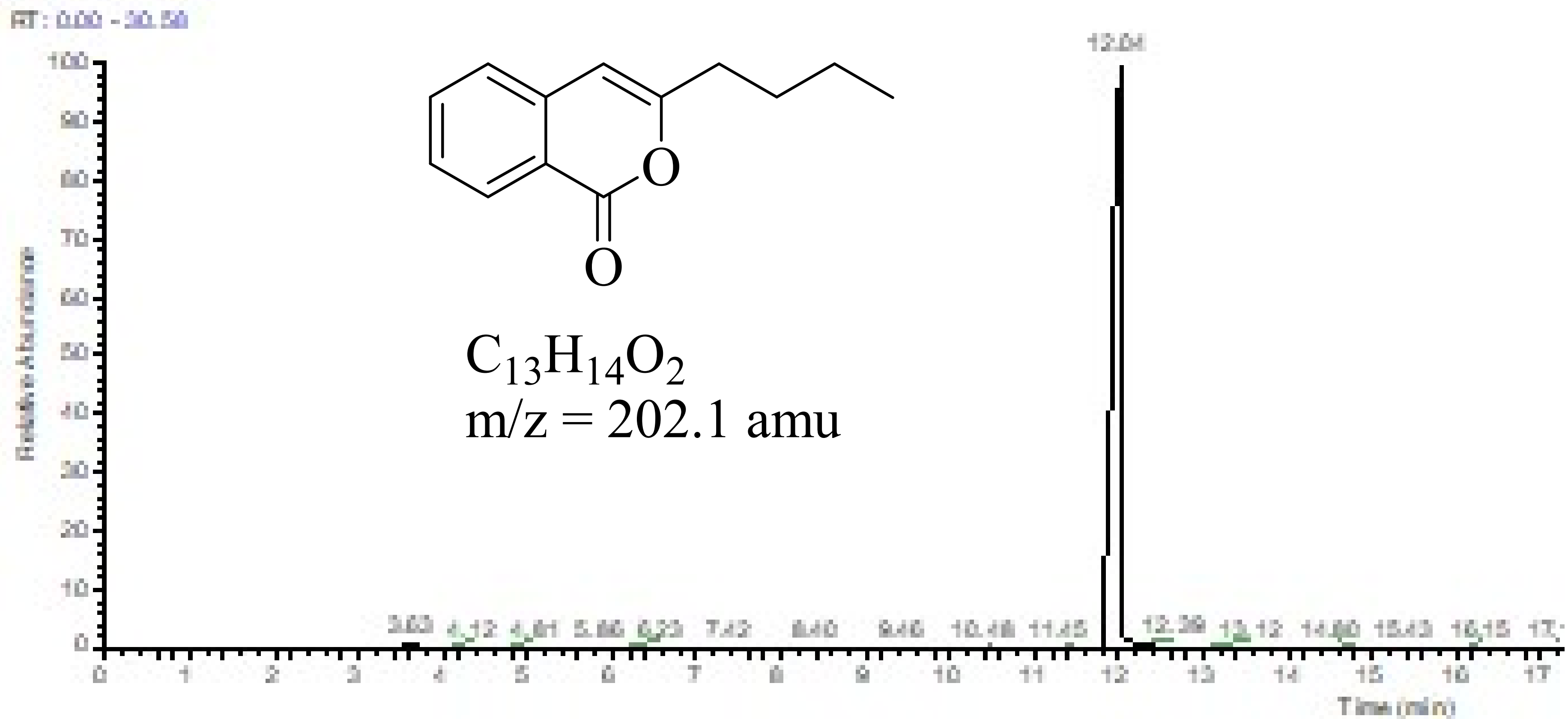
$(a + b)^3 = a^3 + 3a^2b + 3ab^2 + b^3$

$= (0.50)^3a^3 + 3(0.50)^2a^2\,(0.50)b + 3(0.50)a\,(0.50)^2b^2 + (0.50)^3$

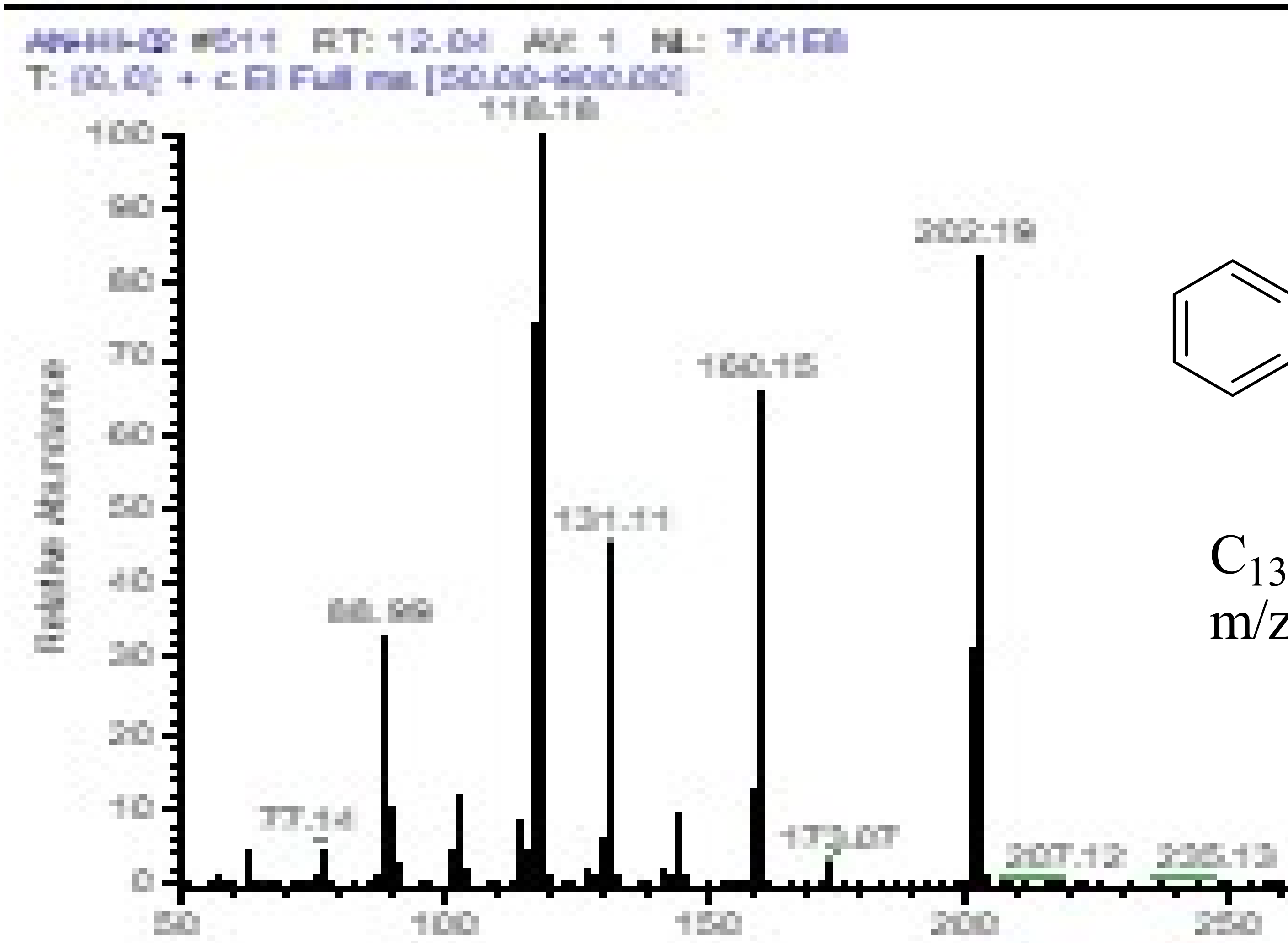
$= (0.125)a^3 + (0.375)a^2b + (0.375)ab^2 + (0.125)b^3$

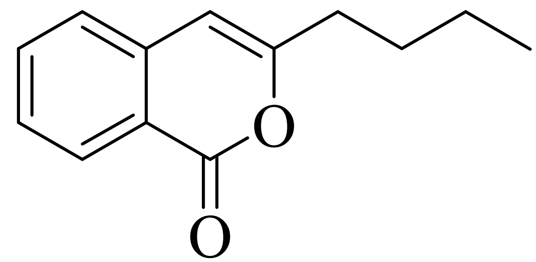
$= 1a^3 + 3a^2b + 3ab^2 + 1b^3$

GCMS


RT: 0.00 - 30.50
12.04
Relative Abundance
Time (min)
O
O
$C_{13}H_{14}O_2$
m/z = 202.1 amu

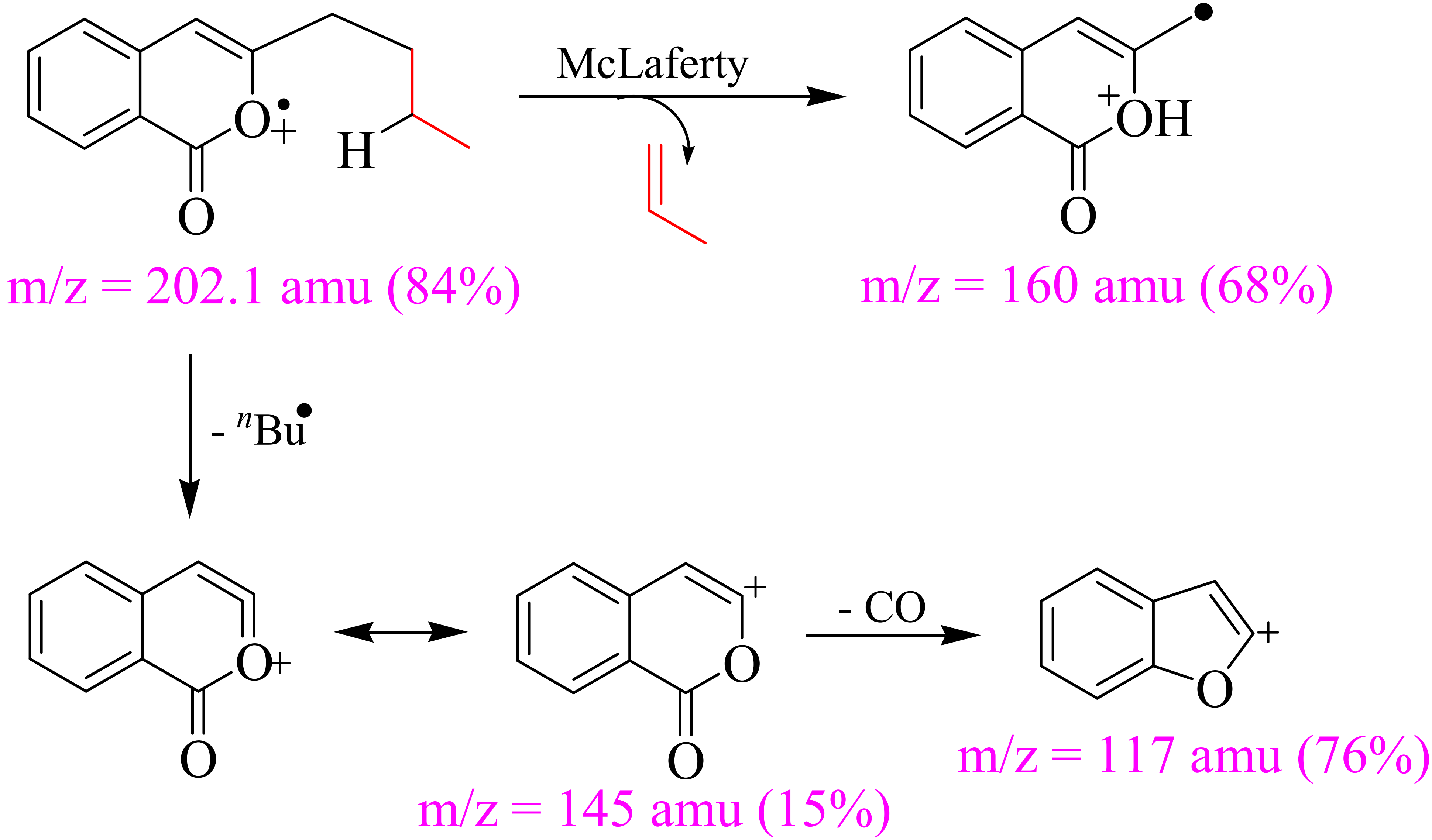
GC EIMS



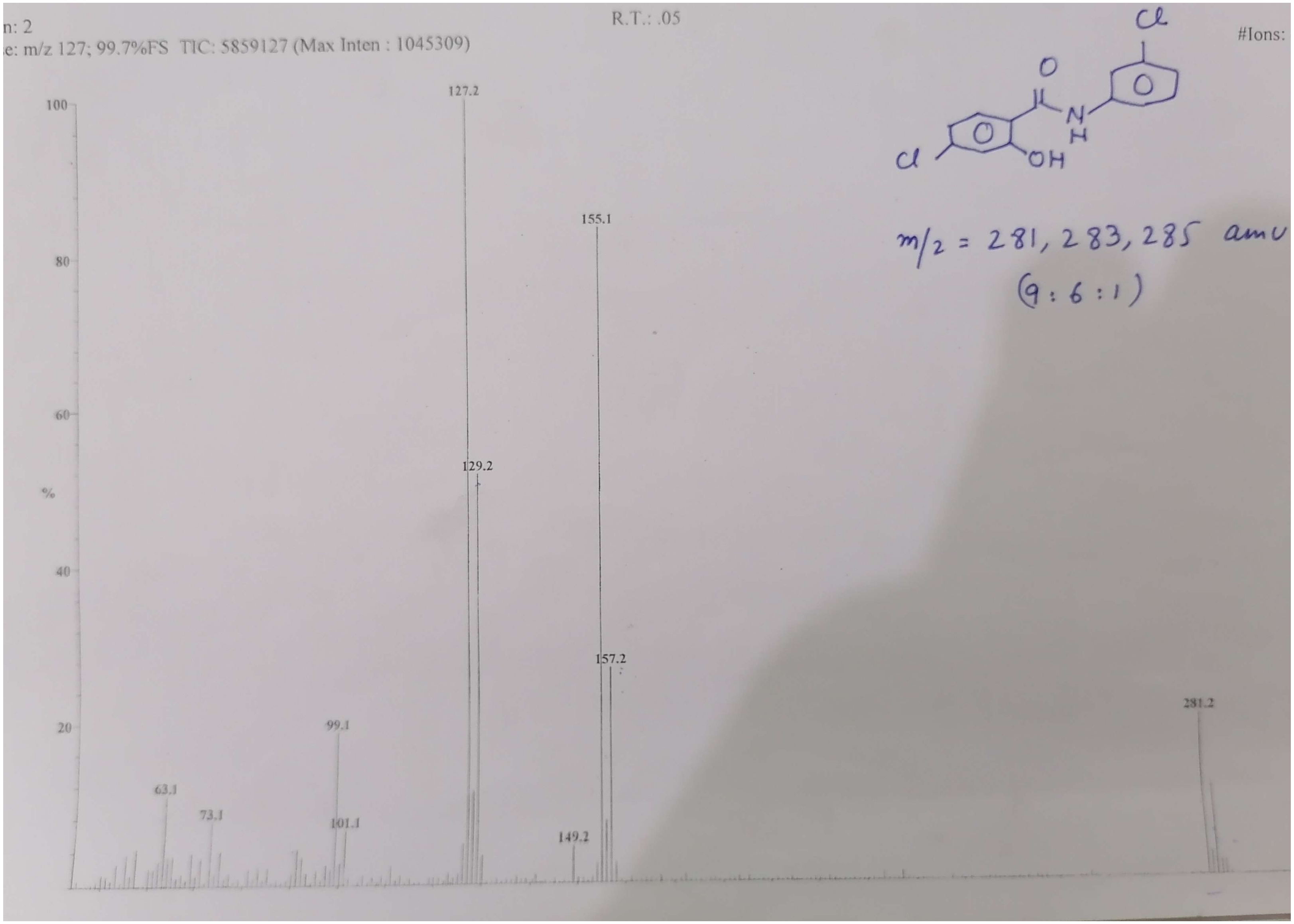


$C_{13}H_{14}O_2$
m/z = 202.1 amu

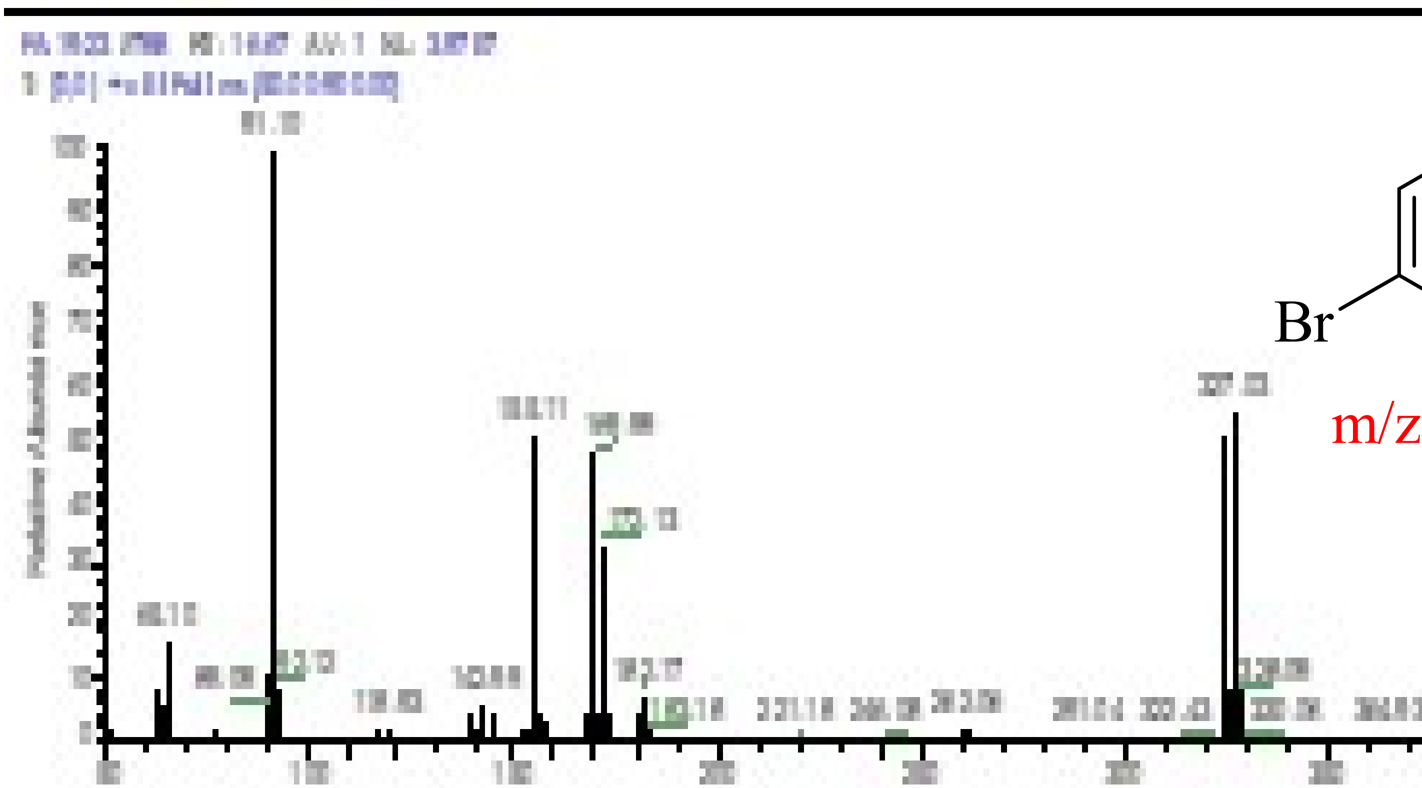
Fragmentation

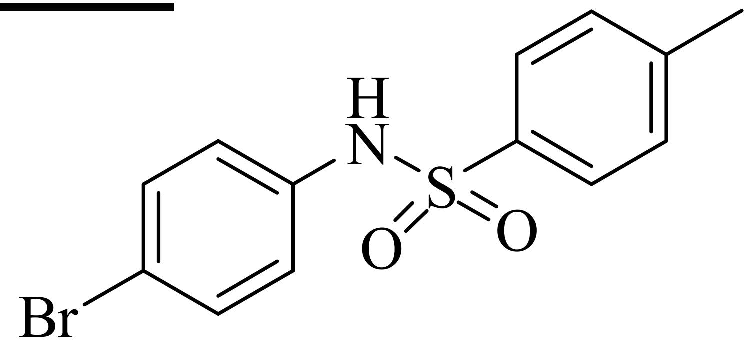


EIMS


R.T.: .05
n: 2
e: m/z 127; 99.7%FS TIC: 5859127 (Max Inten : 1045309)
#Ions:
127.2
155.1
129.2
157.2
281.2
99.1
63.1
73.1
101.1
149.2
100
80
60
40
20
%
m/z = 281, 283, 285 amu
(9 : 6 : 1)

EIMS



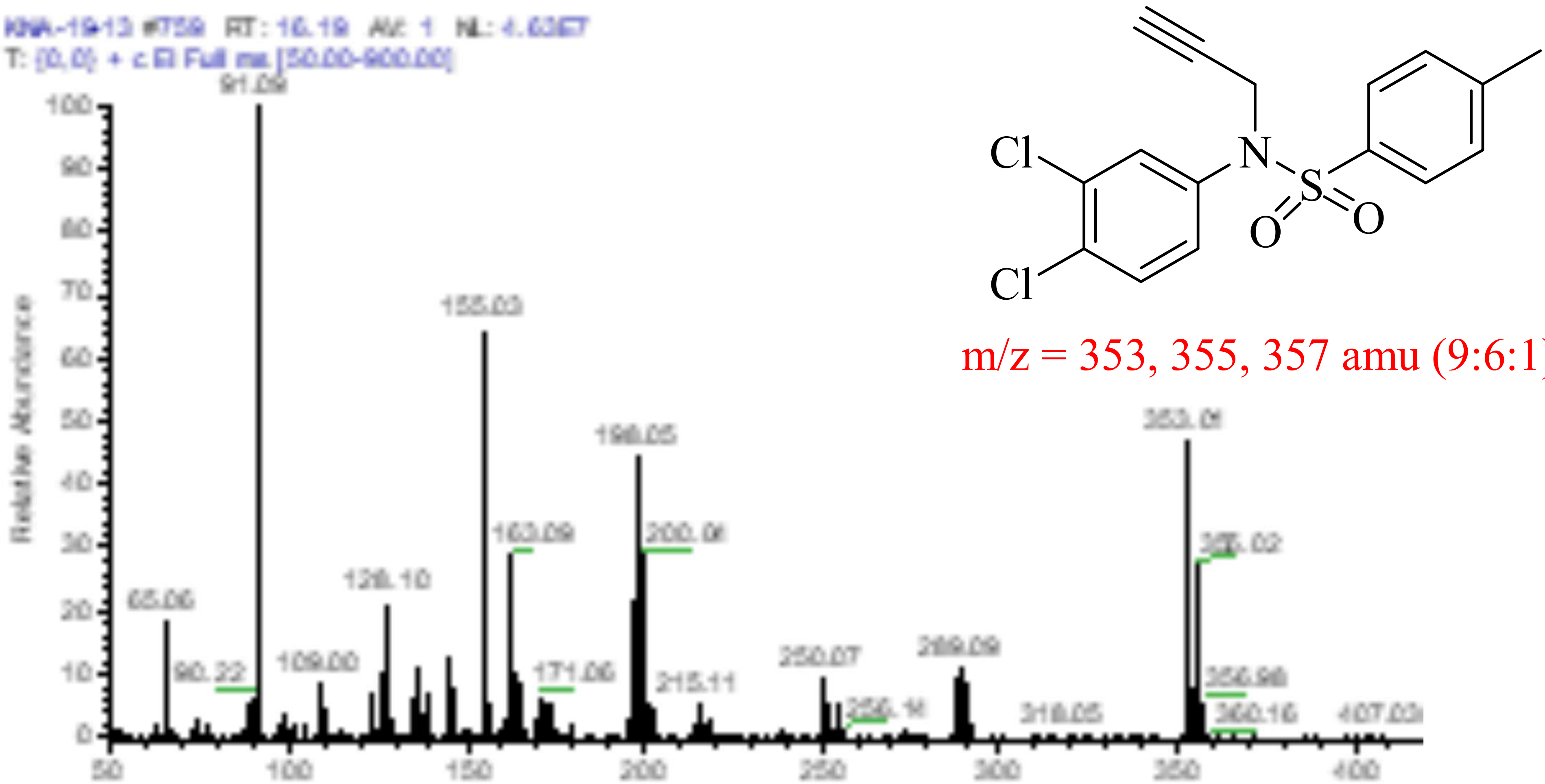


m/z = 325, 327 amu (1:1)

EIMS

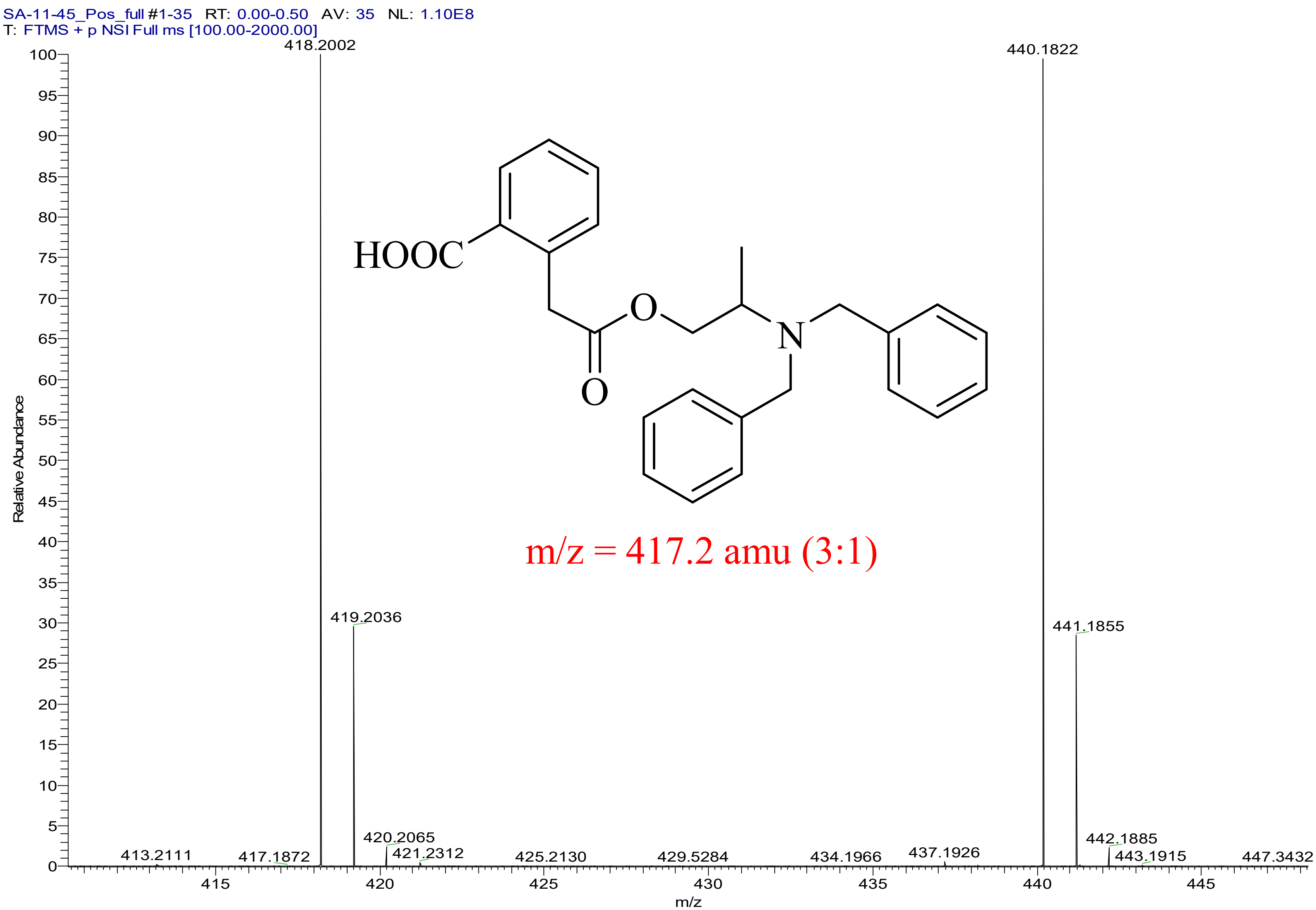
m/z = 319, 321 amu (3:1)

EIMS

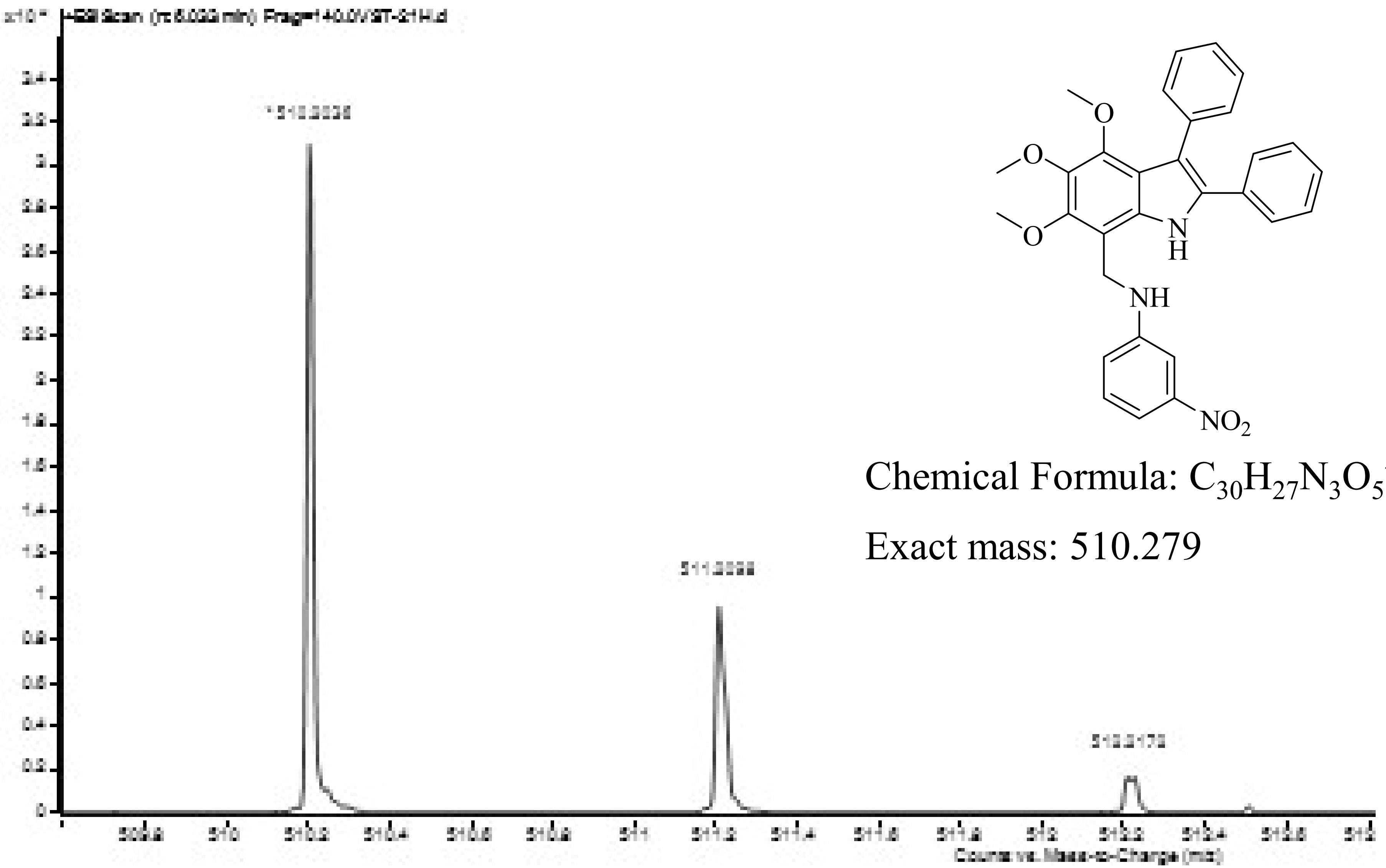


m/z = 353, 355, 357 amu (9:6:1)

High Resolution ESIMS



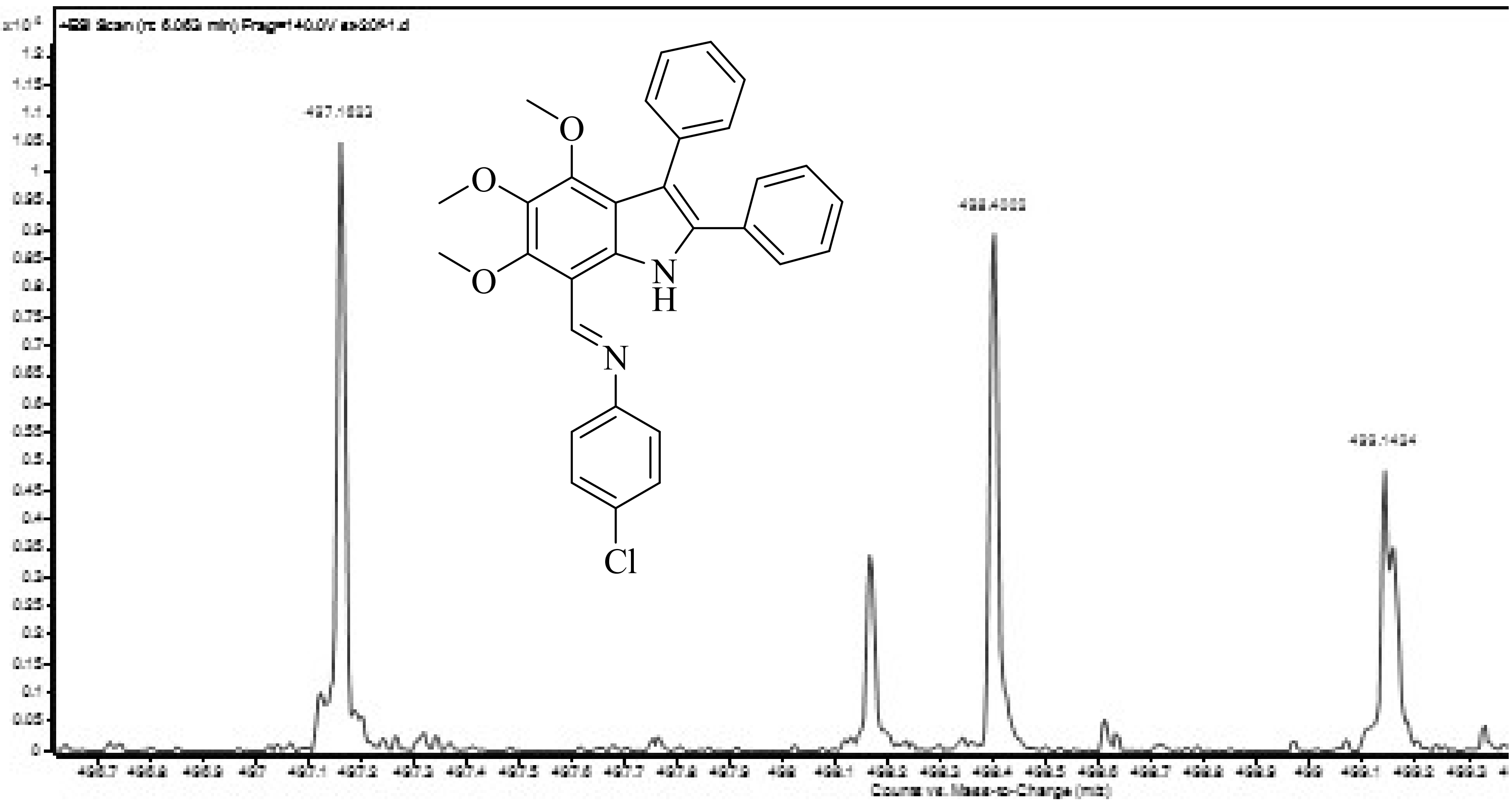
High Resolution ESIMS



Chemical Formula: $C_{30}H_{27}N_3O_5^+$

Exact mass: 510.279

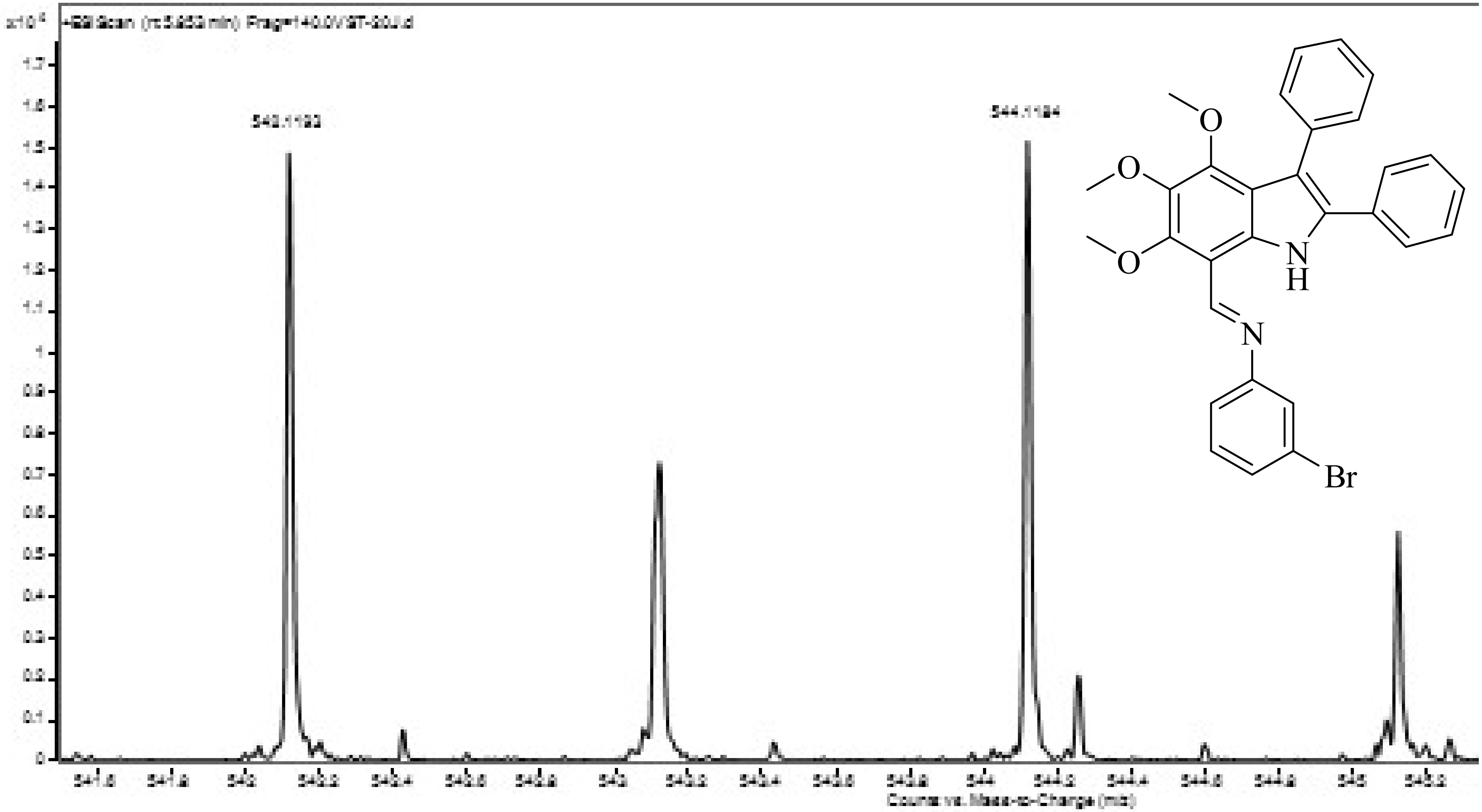
High Resolution ESIMS



Chemical Formula: $C_{30}H_{25}ClN_2O_3^+$

Exact mass: 497.163 amu

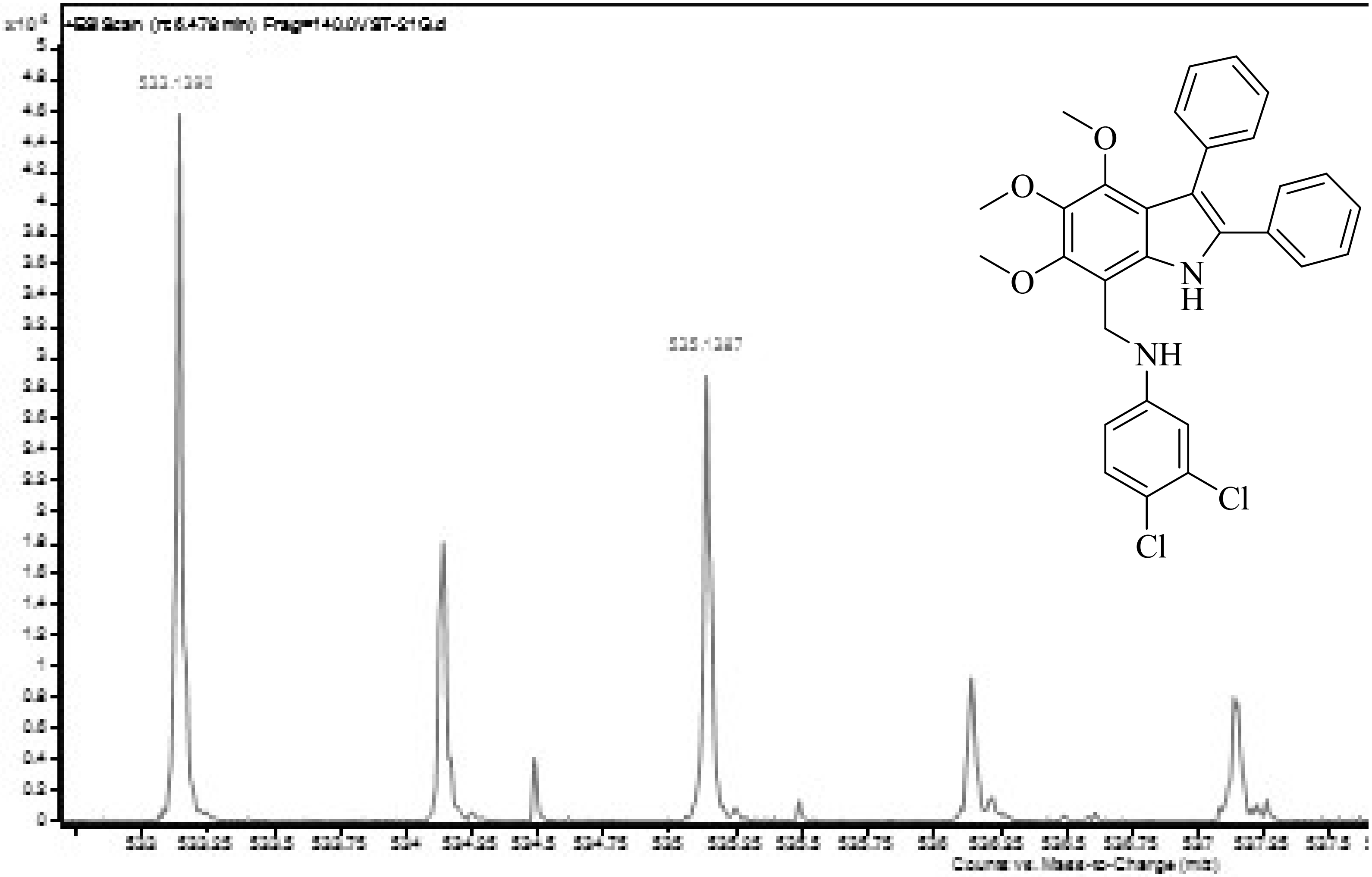
High Resolution ESIMS



Chemical Formula: $C_{30}H_{25}BrN_2O_3^{+}$

Exact mass: 541.112 amu

High Resolution ESIMS



Chemical Formula: $C_{30}H_{26}Cl_2N_2O_3^{+}$

Exact mass: 532.13 amu