Mass Spectometry

1. – $M^{\cdot+}$ get the M/z & the Molecular formula
   - Identify $M^{\cdot+}$
   - use rule of 13
   - use ^{13}C isotope ratio to help identify # of Carbons

2. – Isotope effects to identify
   - $M^{\cdot+}$ || $(M^{\cdot+}+2)$ | 1
   - Br 50/50 rel ab in $M^{\cdot+}$ (2amu)
   - Cl 75/25 rel ab in $M^{\cdot+}$

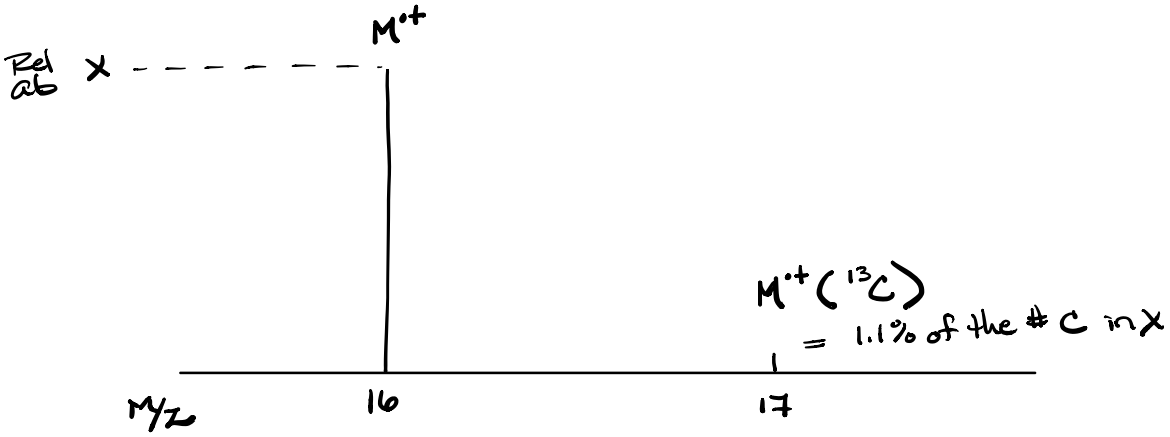
3. – Fragmentations
   - Identify functional groups
   - Molecular Sub-units
   - Help ID a molecule from possible structural candidates

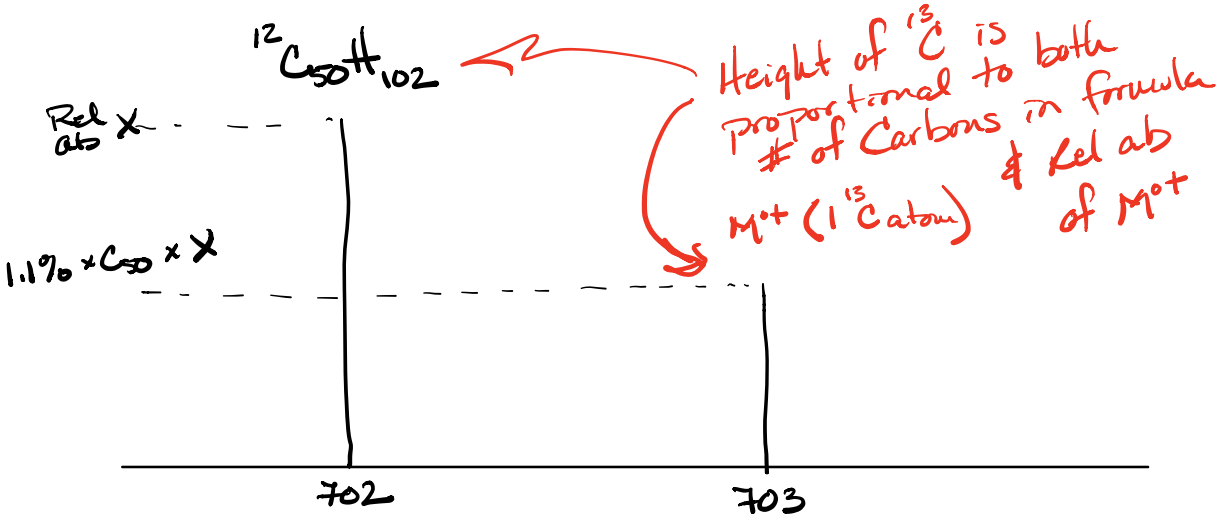
mass # = p + n

^{12}C	^{13}C	^{14}C
98.9%	1.1%	0%
amu	12amu	13amu	14amu

$^{12}CH_4$ = 16 m/z

$^{13}CH_4$ = 17 m/z

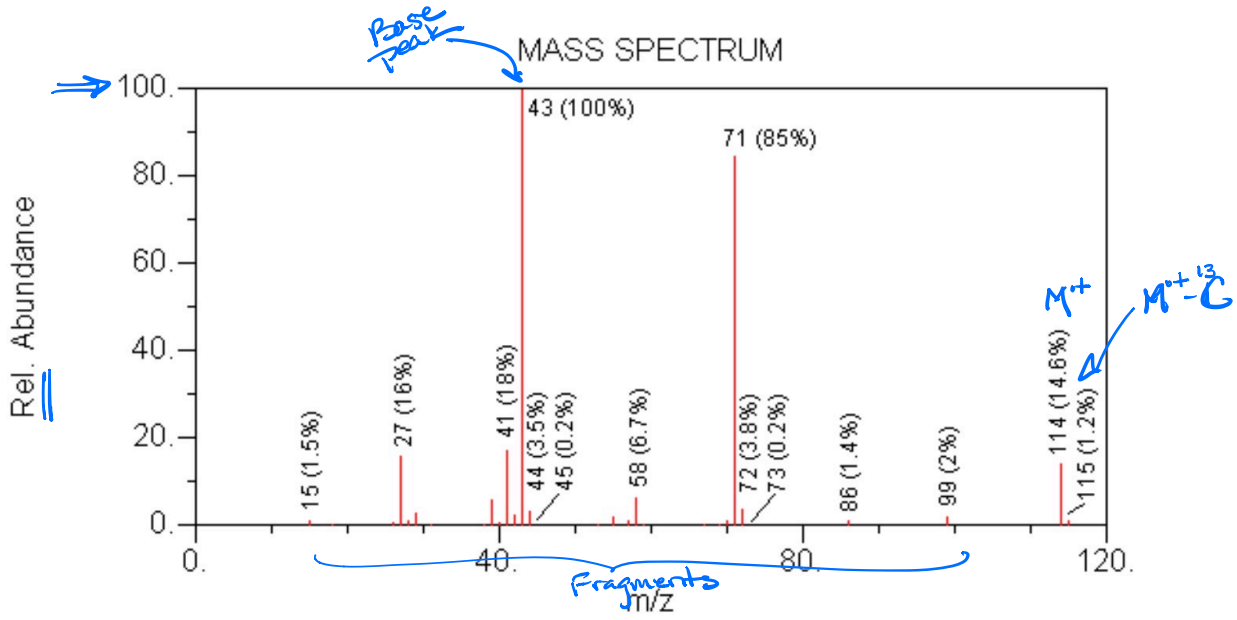




It is possible to back calculate the # of Carbons in formula using Rel ab of $M^{\cdot+}$ & Rel ab of $M^{\cdot+}$-^{13}C.

$$\frac{\left[\frac{\text{Relative abundance of } M^{\cdot+}\text{-}{}^{13}C}{\text{Relative abundance of } M^{\cdot+}} \times 100\right]}{1.1} = \#C \text{ in formula}$$

- Identify $M^{\cdot+}$
- Rule of 13 to find possible formulas
- $M^{\cdot+}$-^{13}C peak to find # of Carbons in molecule
- find actual molecular formula



$M^{\cdot+} = 114 \quad (14.6\%)$

$M^{\cdot+}-{}^{13}C = 115 \quad (1.2\%)$

Rule 13

$$13 \overline{)\,114}\;\;8 \qquad -104 \qquad 10$$

$C_8H_{8+10} = C_8H_{18}$

C_8H_{18} $-CH_4$ $+0$ → $C_7H_{14}O$

$C_7H_{14}O$ $-CH_4$ $+0$ → $C_6H_{10}O_2$

$C_6H_{10}O_2$ $-CH_4$ $+0$ → $C_5H_6O_3$

^{13}C isotope

Natural rel ab ^{13}C %

$$\left(\frac{M^{\cdot+}-{}^{13}C}{M^{\cdot+}} \times 100\right) \div 1.1 = \#C$$

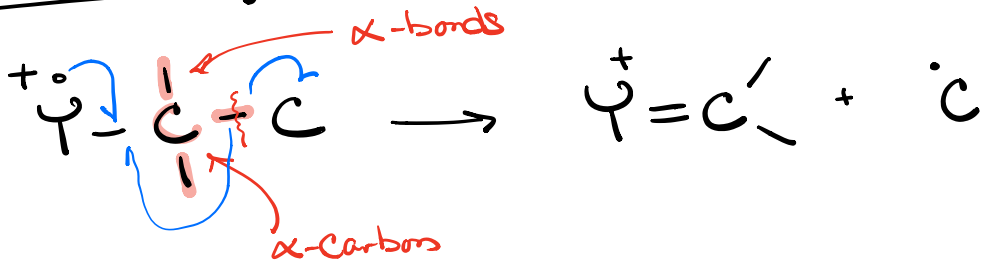
$$\left[\frac{1.2}{14.6} \times 100\right] \div 1.1 = 7$$

Fragmentations

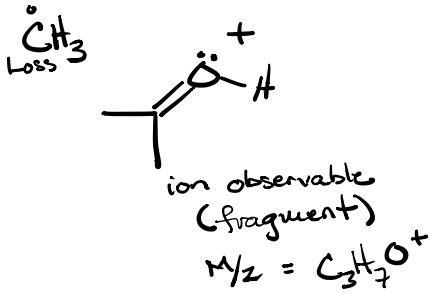
2 main types

- α - Cleavage
  - Homolytic
  - Heterolytic
- McLafferty

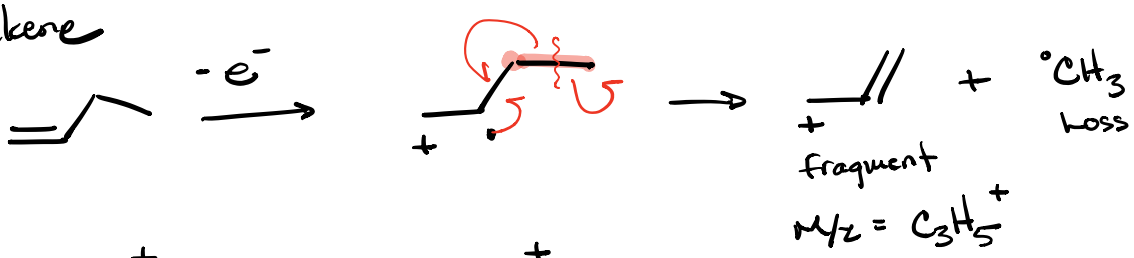
Homolytic α - Cleavage – the cleavage of an α-bond

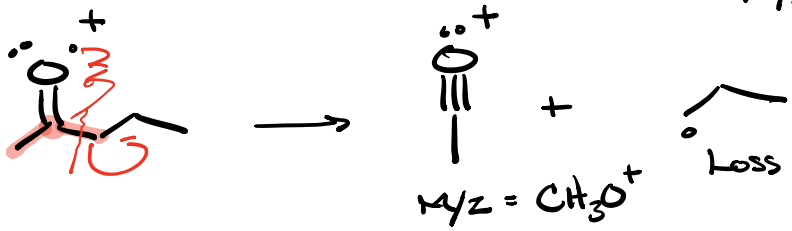


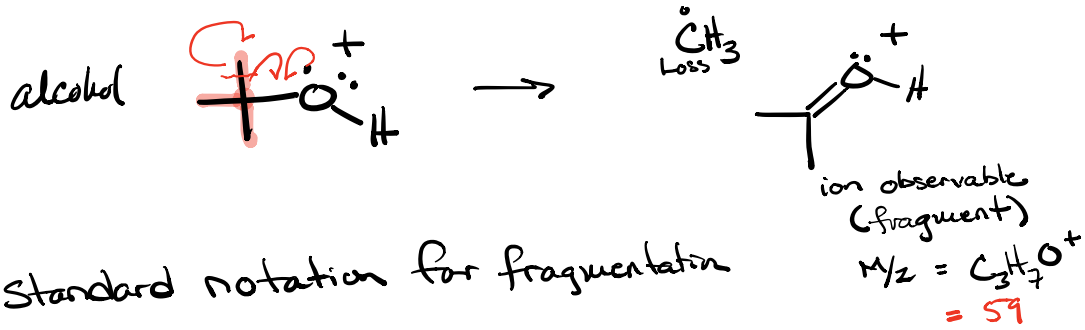
alcohol



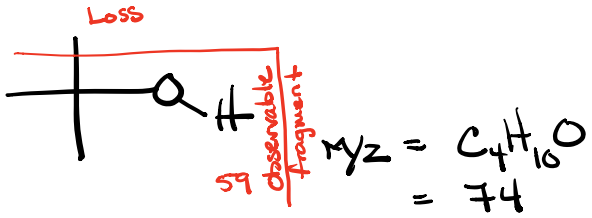
alkene

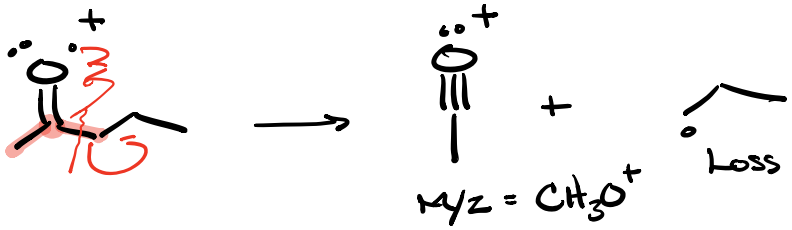


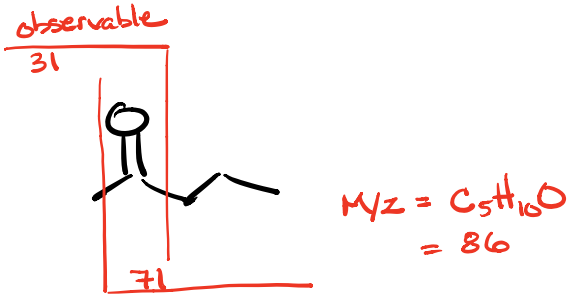




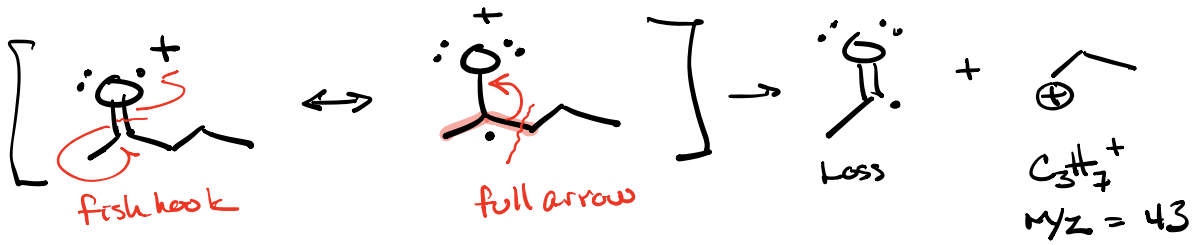
Standard notation for fragmentation

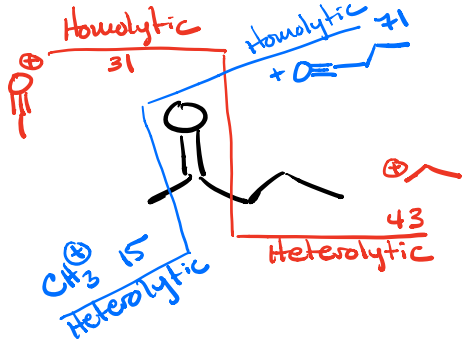




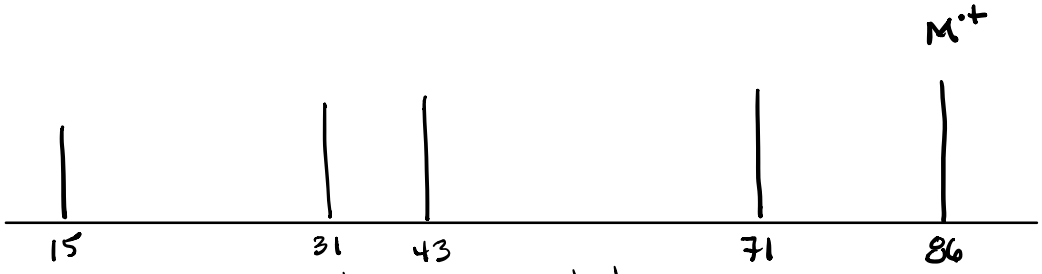


Heterolytic α-Cleavage (Carbonyl Compounds)





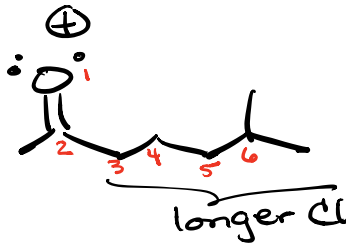
Ketone
aldehydes
Carboxylic acid
esters
amide
lactone
lactams



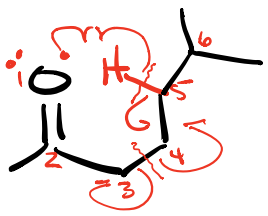
possible fragmentations

They may not all show up

McLafferty – Common pattern w/ Carbonyl Compounds

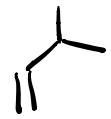


$M/z = C_8H_{16}O = 128$



Concerted Rearrangement & fragmentation →

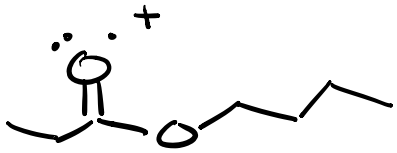
Stable ∝ Radical



neutral molecule Loss

Hydrogen on atom #5
Starting from oxygen as #1

$M/z = C_3H_6O^{+\cdot}$
$= 58$



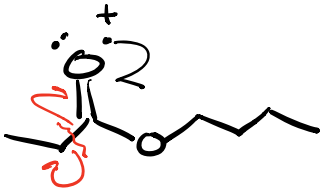
M/z = ?

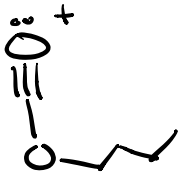
expected α cleavages (4 - 2 homo, 2-hetero)

McLafferty

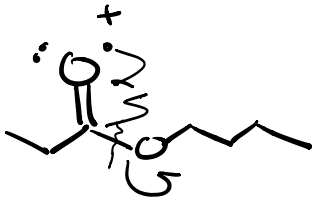
$C_7H_{14}O_2^{\cdot+}$ = 130 ✓

homolytic α's

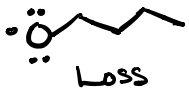




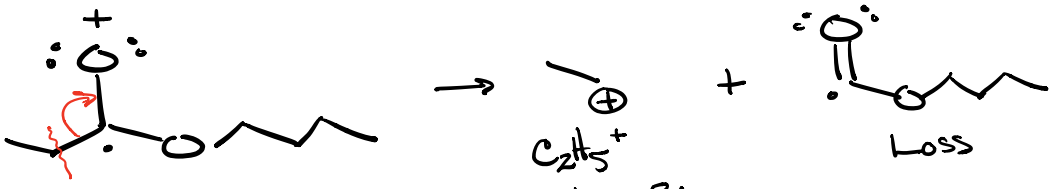
M/z = $C_5H_9O_2$
= 101

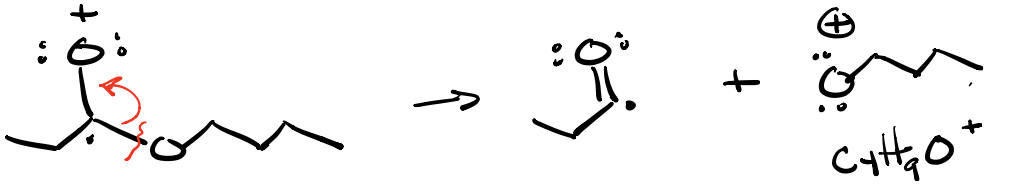


M/z = C_3H_5O
= 57

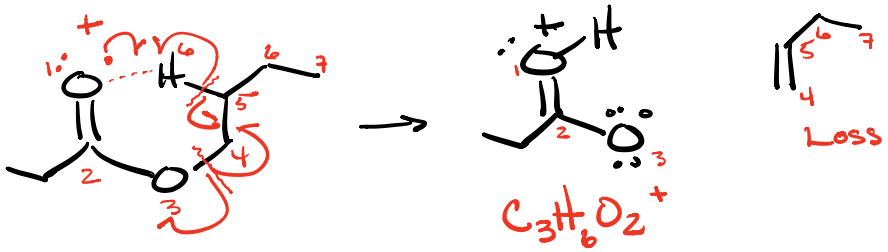


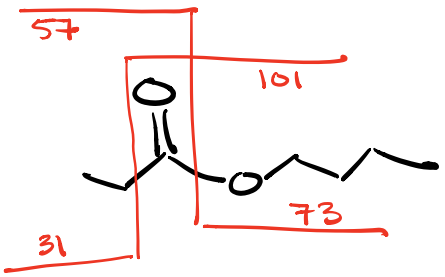
Heterolytic α's





McLafferty





mclafferty = 84