

Mass Spectrometry (MS)

from chapter(s) _____ in the recommended text

A. Introduction

B. Components Of Mass Spectrometers

mass-to-charge.

molecular mass

without fragmentation).

- create ions in the gas phase
- separate ions on the basis of m/z (ie an analyzer)
- detect the number of ions of each m/z

an ionization source / an analyzer / a detector.

ionization.

for analysis.

or analysis.

for analysis.

or ionization.

Fourier transform (FT) analysis.

Electron Impact (EI) ionization.

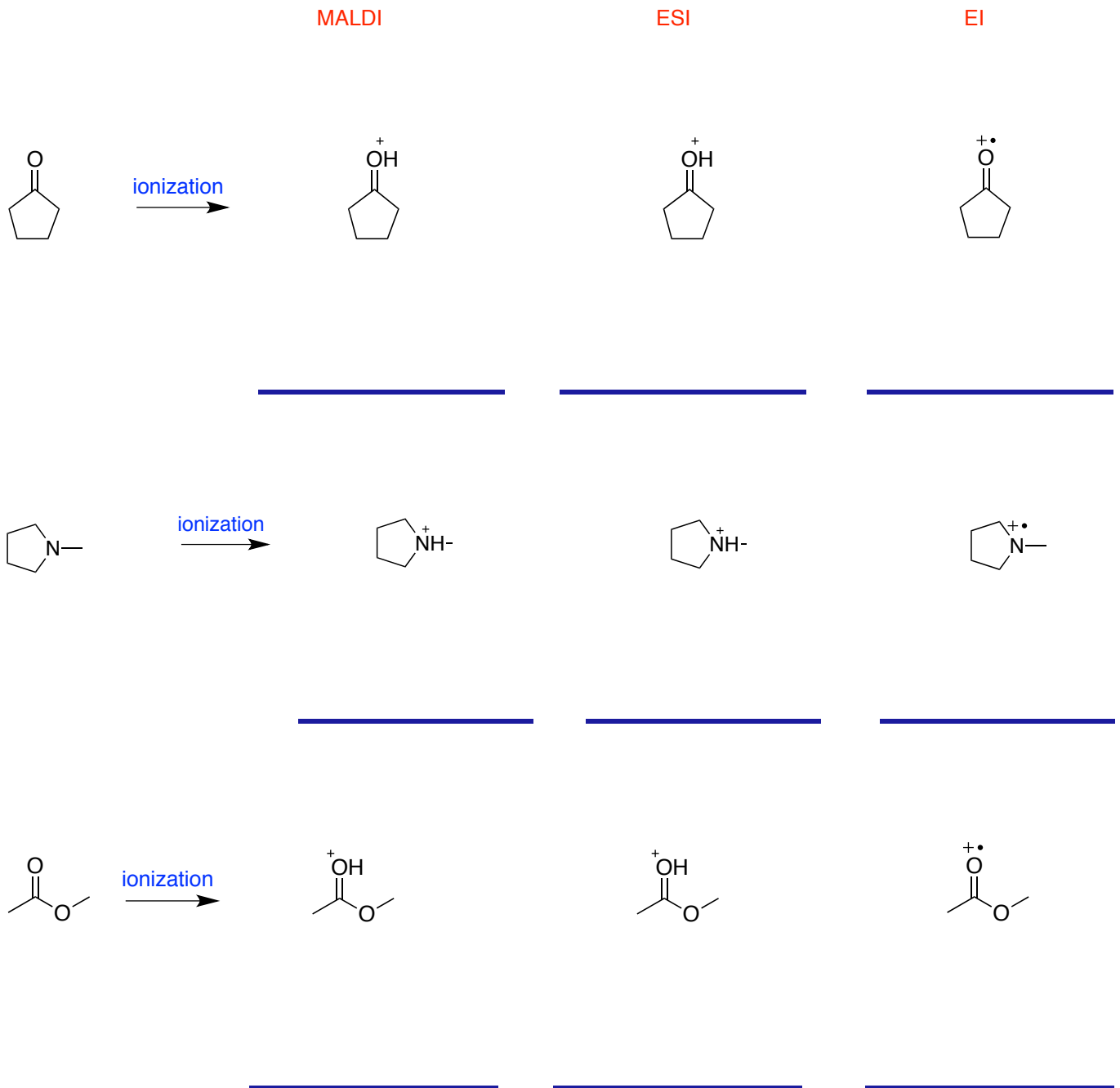
Detectors in MS electron multipliers.

MALDI-TOF is a valid description but ESI-MALDI is not.

C. Primary Ions Formed In Different Ionization Techniques

MALDI
ie $[M + 1]^+$.

ESI
 $[M + 1]^+$



an electron from molecules to give radical cations
ie $[M]^+$.

Resolution
sensitivity.

most sensitive forms of MS.

D. Isotopes In Mass Spectrometry

Element	Isotope	Abundance (%)	Mass number	Exact mass
hydrogen	^1H	99.99	1	1.00783
carbon	^{12}C	98.89	12	12.00000
carbon	^{13}C	1.11	13	13.00335
nitrogen	^{14}N	99.64	14	14.00307
oxygen	^{16}O	99.76	16	15.99492
fluorine	^{19}F	100	19	18.99840
phosphorus	^{31}P	100	31	30.97376
sulfur	^{32}S	95.00	32	31.97207
chlorine	^{35}Cl	75.77	35	34.96886
chlorine	^{37}Cl	24.23	37	36.96590
bromine	^{79}Br	50.69	79	78.91835
bromine	^{81}Br	49.31	81	80.91635
iodine	^{127}I	100	127	126.904468

CO

C₂H₄C₂H₅³⁵Cl

27.99492

exact mass

28.03132

exact mass

64.00801

*exact mass*CH₃⁷⁹BrCH₃⁸¹BrC₂H₅³⁷Cl

93.94184

exact mass

95.93984

exact mass

66.00505

*exact mass*can distinguish

1.99704 atomic mass units (amu's) in a ratio of 3.13:1

1.99800 amu's in a ratio of 1.03:1.

3 molecular ions in a 1:2:1

4 molecular ions in a 1:3:3:1

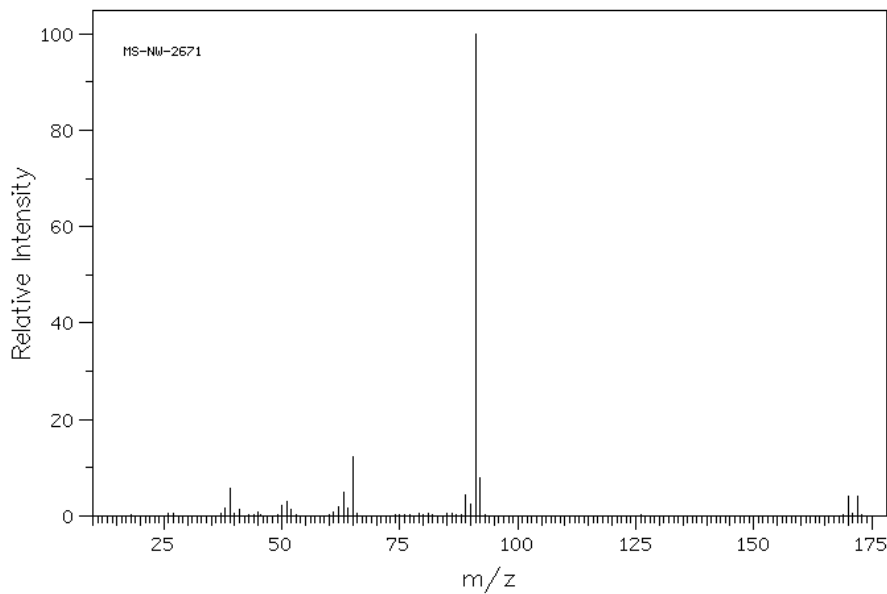
Illustrative Interpretation Of Isotopes In MS

the chlorine-containing compound A is number: 2

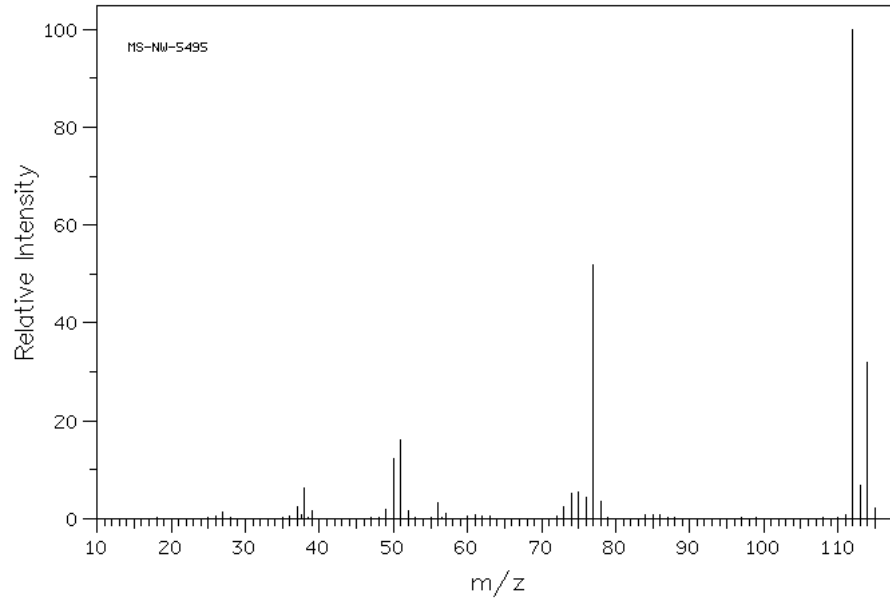
the bromine-containing compound B is number: 1

the non-halogenated compound C is number: 3

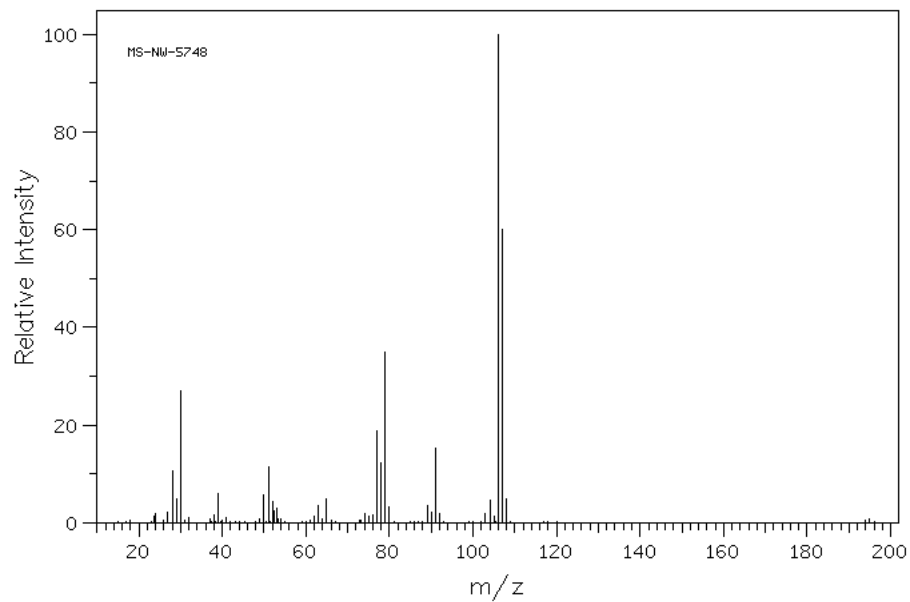
1 ($m/z = 170$ and 172):



2 ($m/z = 112$ and 114):



3 ($m/z = 107$):



always have odd molecular ion m/z values.

E. Fragmentation

radicals

the most stable one that is most likely to be observed.

electron impact

ESI does not.

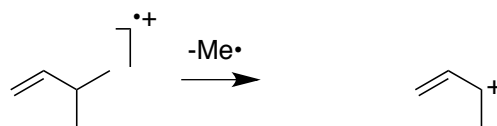
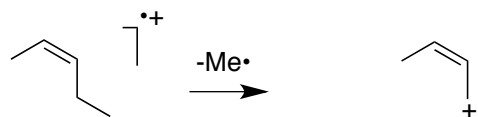
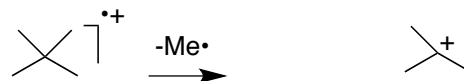
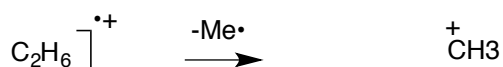
ESI is widely used in contemporary MS, but EI

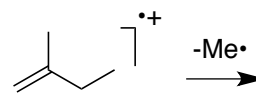
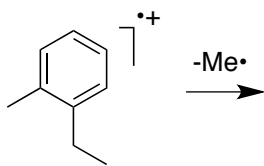
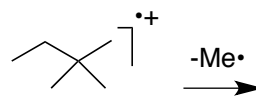
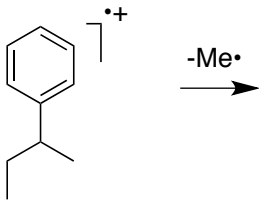
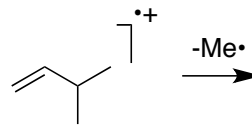
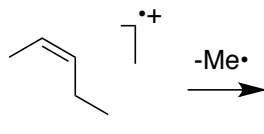
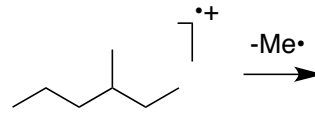
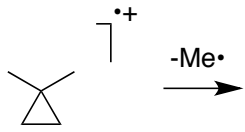
Fragmentation is usually undesirable

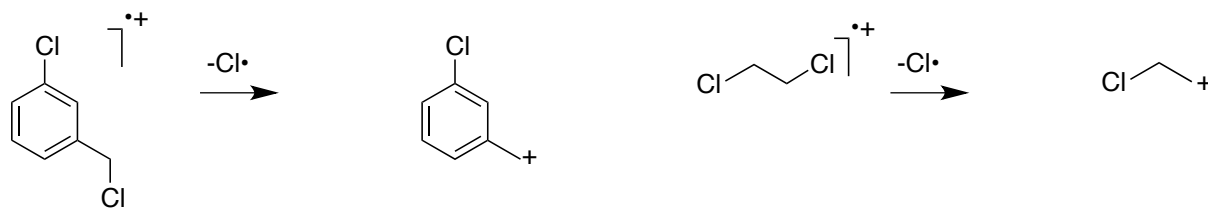
is useful when complementary methods

MS/MS

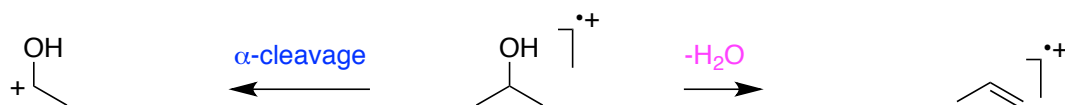
tandem

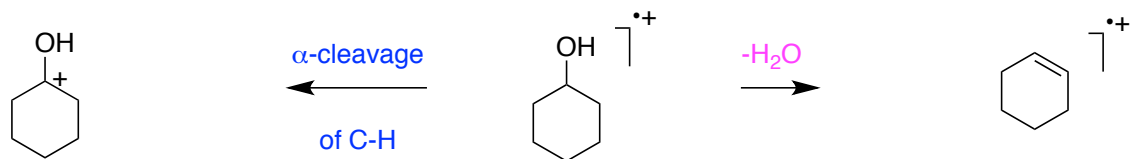
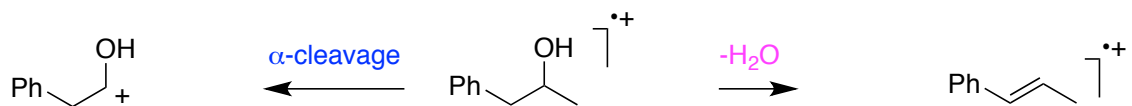
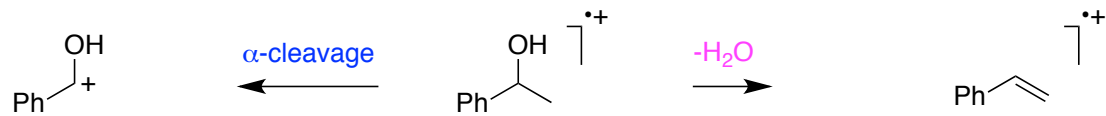


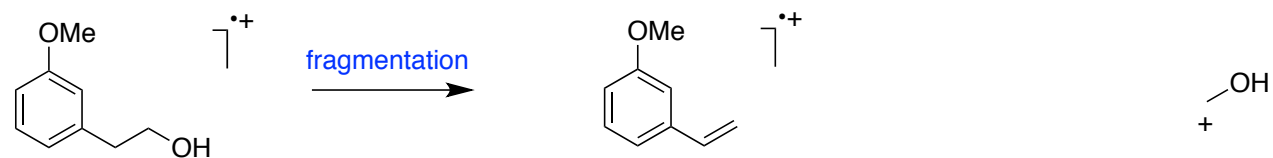
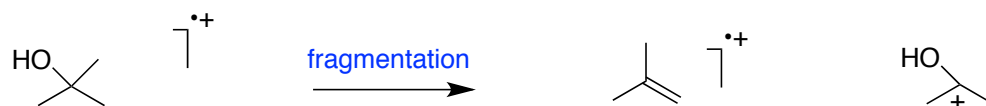
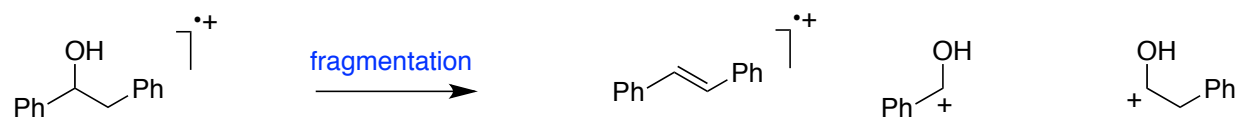


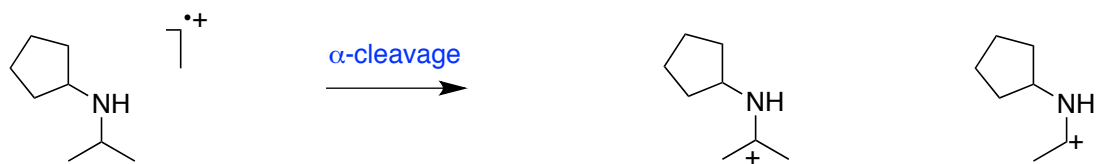


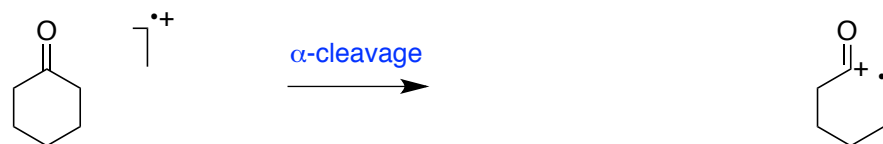
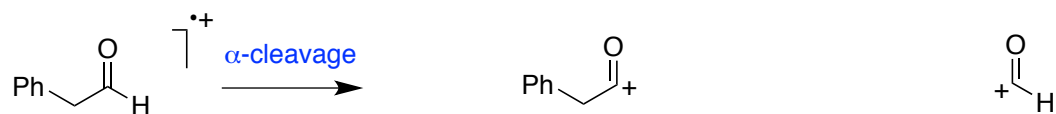
α -Cleavage

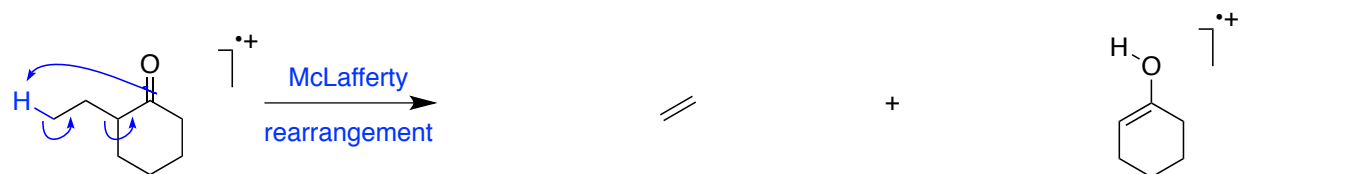
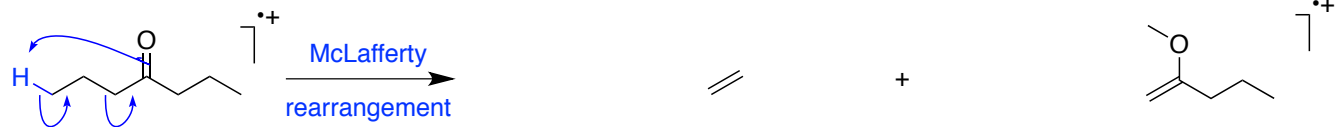












Molecule on the left can undergo *McLafferty rearrangement* since it has γ -hydrogen whereas molecule on the right does not.