The order of energy required to remove electron is as follows—

σ electrons > non-conjugated π > conjugated π > non bonding or lone pair of electrons.

Isotope patterns for -Cl , -Br and S

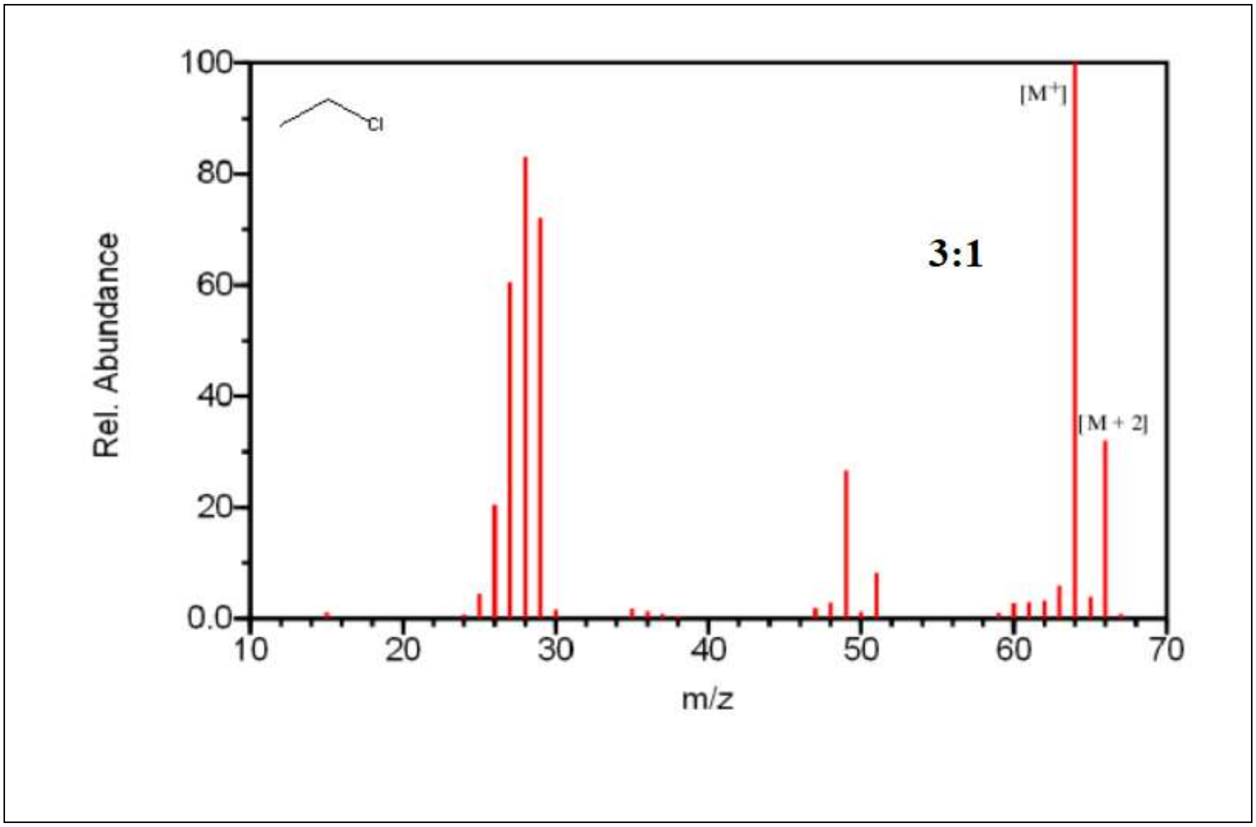
TABLE 1.3 Relative Isotope Abundances of Common Elements.

Elements	Isotope	Relative Abundance	Isotope	Relative Abundance	Isotope	Relative Abundance
Carbon	^{12}C	100	^{13}C	1.11	^{14}C	1×10^{-10}
Hydrogen	^{1}H	100	^{2}H	0.016		
Nitrogen	^{14}N	100	^{15}N	0.38		
Oxygen	^{16}O	100	^{17}O	0.04	^{18}O	0.2
Fluorine	^{19}F	100				
Silicon	^{28}Si	100	^{29}Si	5.1	^{30}Si	3.35
Phosphorus	^{31}P	100				
Sulfur	^{32}S	100	^{33}S	0.78	^{34}S	4.4
Chlorine	^{35}Cl	100			^{37}Cl	32.5
Bromine	^{79}Br	100			^{81}Br	98
Iodine	^{127}I	100				

- Isotopes are different types of the atoms that have the same atomic number (*i.e.* same number of protons in the nulceus) but different mass numbers (because there are a different number of neutrons in the nucleas). Hence they are the same element but the isotopes have dfferent masses.

- Mass spectrometers are capable of separating and detecting individual ions even those that differ only by a single atomic mass unit (note in reality mass spectrometers are far more sensitive than that !)
- As a result, molecules containing different isotopes can be distinguished.
- This is most apparent (at this level) when atoms such as bromine or chlorine are present in a molecule because those elements naturally exist with a significant % of the heavier isotope.
- For example, while C has 2 common isotopes, ^{12}C and ^{13}C, ^{13}C represents only about 1% of natural carbon. In contrast, Cl has 2 common isotopes, ^{35}Cl and ^{37}Cl, with about 25% being ^{37}Cl.

^{35}Cl : ^{37}Cl exists naturally in an almost 3:1 ratio, so we observe peaks at "M" (molecules with an atom of ^{35}Cl) and "M+2" (molecules an atom of ^{37}Cl) are obtained with relative intensity 3:1



$[M]^+$ are the molecular ion peaks with an m/z of 64 and 66 corresponding to the M ion **$[C_2H_5{}^{35}Cl]^+$** and the M+2 ion **$[C_2H_5{}^{37}Cl]^+$.**

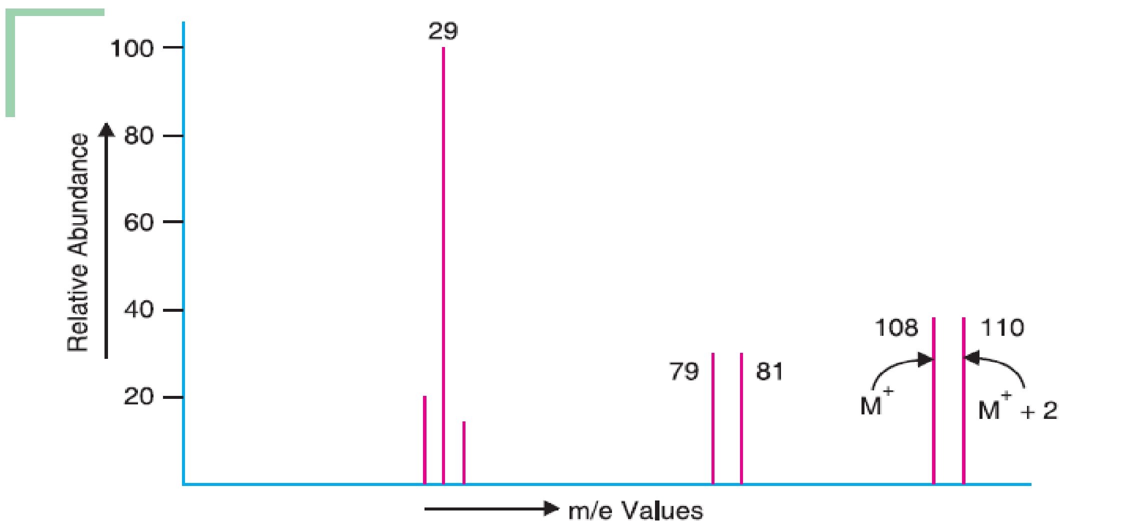
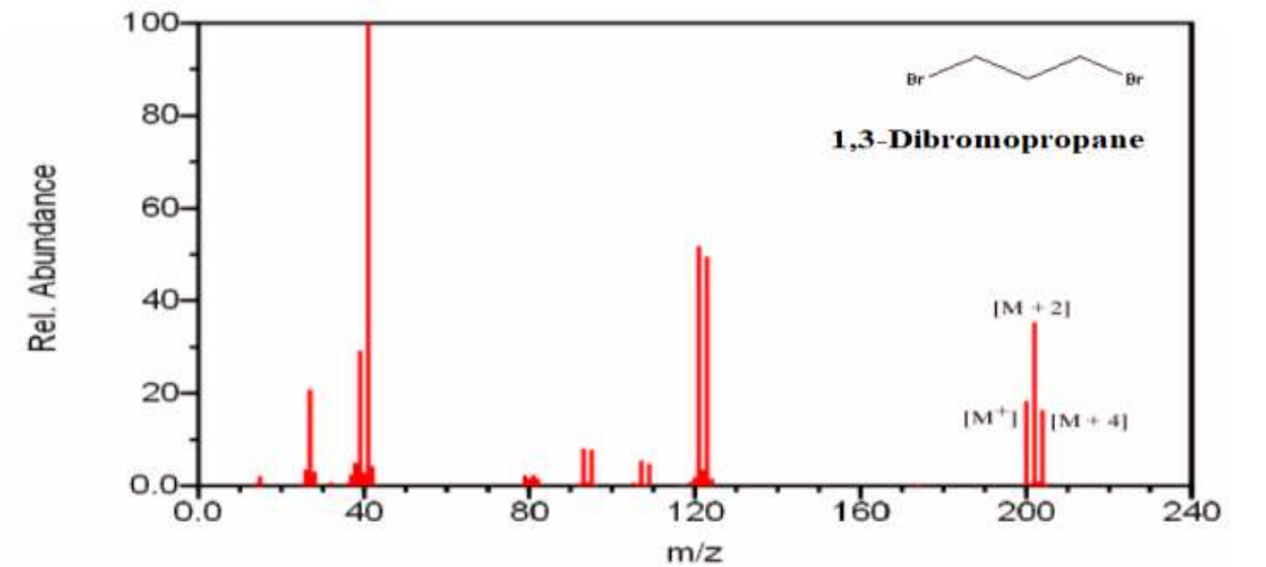
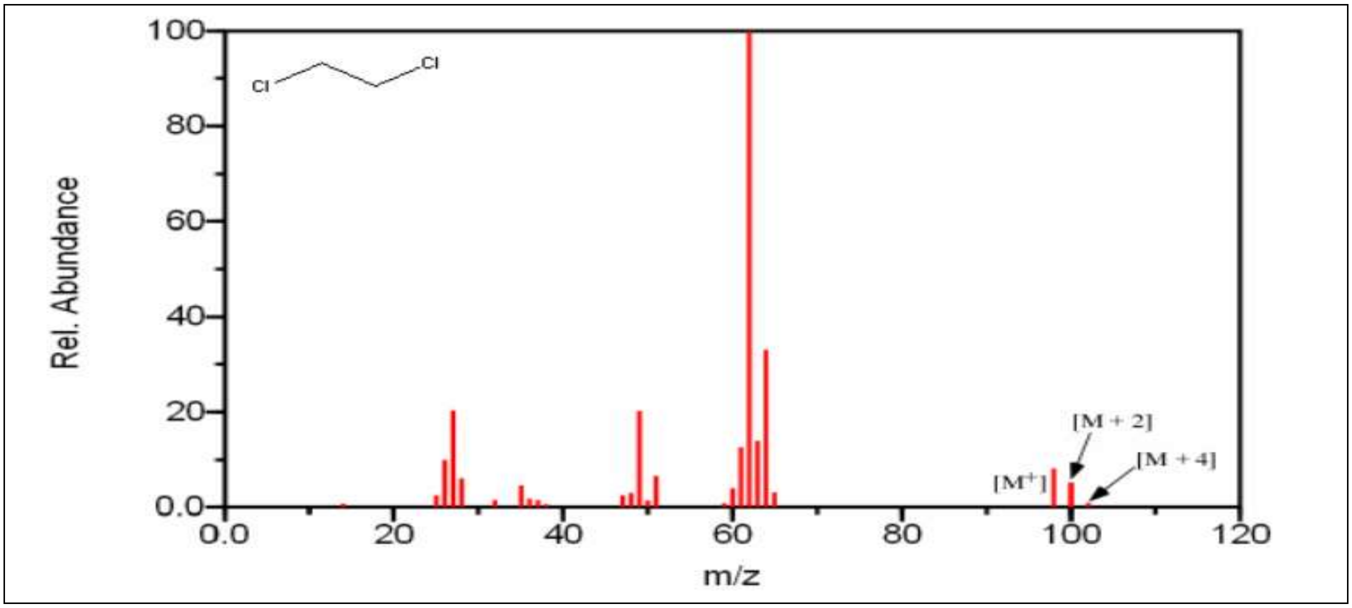


Fig. 7.5. Mass spectrum of Ethyl bromide.

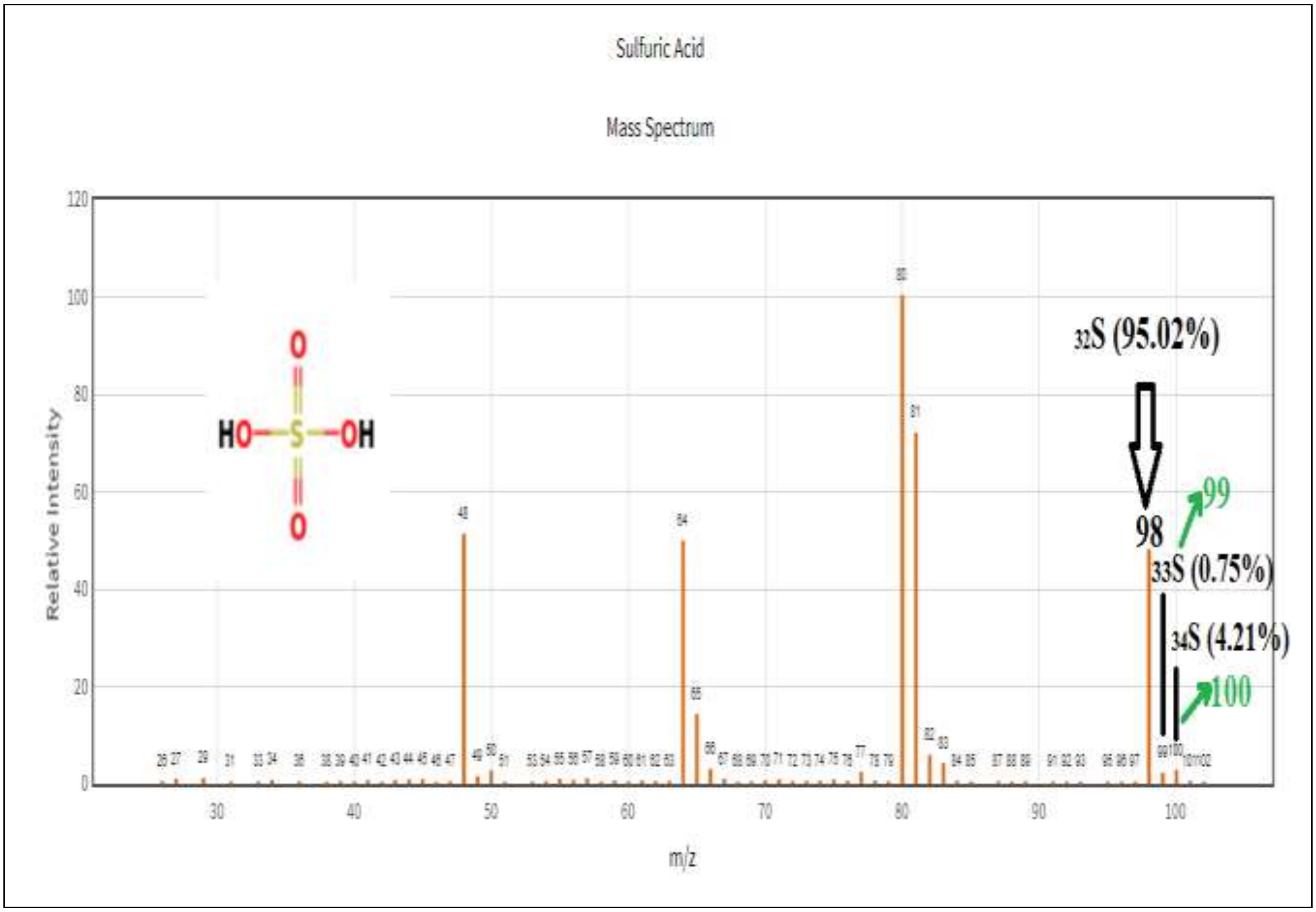
bromoethane has a characteristic [M + 2] peak that has a similar intensity as the [M+] peak . $[M]^+$ are the molecular ion peaks with an m/z of 108 and 110 corresponding to the M ion **$[C_2H_5{}^{79}Br]^+$** and the M+2 ion **$[C_2H_5{}^{81}Br]^+$.**



A compound containing two bromines will have a [M + 2] peak twice the size of the $[M^+]$ peak , and a [M + 4] peak the same size as the [M^+] peak. [$M]^+$ are the molecular ion peaks with an m/z of 200, 202 and 204 corresponding to the M ion **[$C_3H_6{}^{79}Br_2]^+$** , the M+2 ion **[$C_3H_6{}^{81}Br]^+$, and the M+4 ion [$C_3H_6{}^{81}Br2]^+$.**



[$M]^+$ are the molecular ion peaks with an m/z of 200, 202 and 204 corresponding to the M ion **[$C_2H_4{}^{35}Cl_2]^+$** , the M+2 ion **[$C_2H_4{}^{37}Cl]^+$, and the M+4 ion [$C_2H_4{}^{37}Cl_2]^+$.**



Nitrogen rule:

If a compound contains an even number of nitrogen atoms (0, 2, 4, ...), its monoisotopic molecular ion will be detected at an even-numbered nominal m/z value. While, on the other hand, an odd number of nitrogen atoms (1, 3, 5, . . .) is indicated by an odd-numbered nominal m/z. **This fact arises from the fact that nitrogen has an even mass(14) and an odd valency(3)[Valency of nitrogen is three as nitrogen has 5 electrons in its valence shell].**

Table 6.7 Examples illustrating the nitrogen rule

Number of nitrogens	Examples	$M^{+\bullet}$ at *m/z*
0	methane, CH_4	16
0	acetone, C_3H_6O	58
0	chloroform, $CHCl_3$	118
0	[60]fullerene, C_{60}	720
1	ammonia, NH_3	17
1	acetonitrile, C_2H_3N	41
1	pyridine, C_5H_5N	79
1	*N*-ethyl-*N*-methyl-propanamine, $C_6H_{15}N$	101
2	urea, CH_4N_2O	60
2	pyridazine, $C_4H_4N_2$	80
3	triazole, $C_2H_3N_3$	69
3	hexamethylphosphoric triamide, HMPTA, $C_6H_{18}N_3OP$	179

The rule may also be extended for use with fragment ions. This makes a practical tool to distinguish even-electron from odd-electron fragment ions and thus simple bond cleavages from rearrangements.

Applying the nitrogen rule to methane Reactions 6.2–6.6 were suggested as a way to make understand the mass spectrum of methane. They all follow the rule.

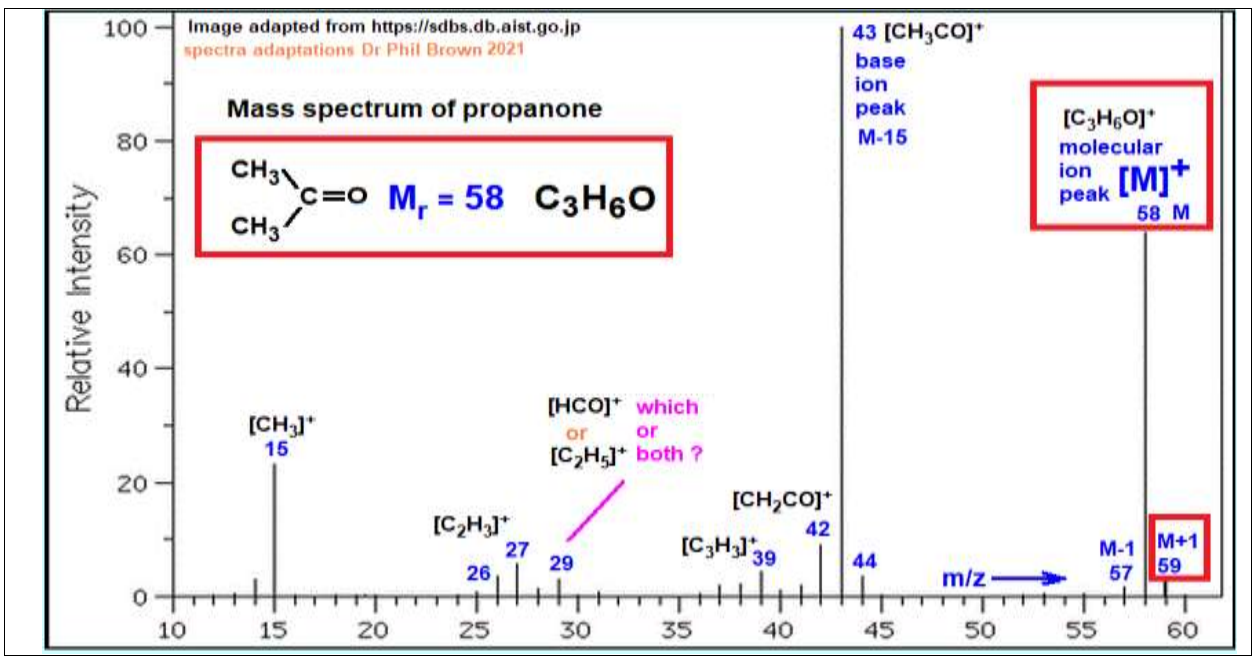
$$CH_4^{+\bullet} \rightarrow CH_3^{+} + H^{\bullet}; m/z\ 16 \rightarrow m/z\ 15 \quad (6.2)$$

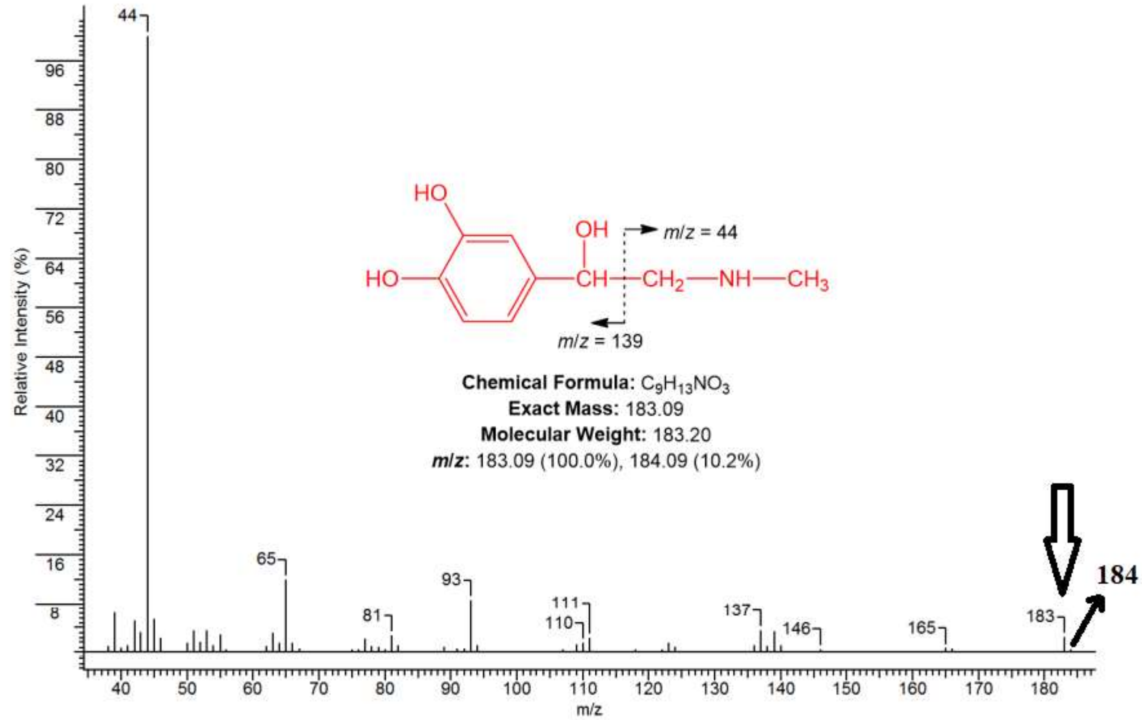
$$CH_4^{+\bullet} \rightarrow CH_2^{+\bullet} + H_2;\ m/z\ 16 \rightarrow m/z\ 14 \quad (6.3)$$

$$CH_2^{+\bullet} \rightarrow C^{+\bullet} + H_2;\ m/z\ 14 \rightarrow m/z\ 12 \quad (6.4)$$

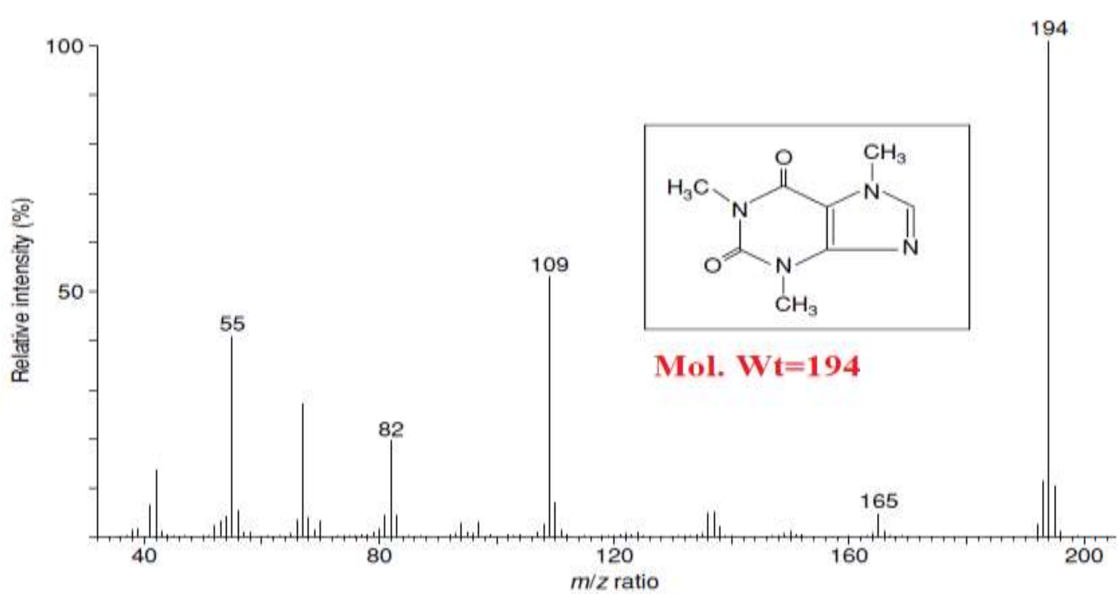
$$CH_2^{+\bullet} \rightarrow CH^{+} + H^{\bullet};\ m/z\ 14 \rightarrow m/z\ 13 \quad (6.5)$$

$$CH_3^{+} \rightarrow CH^{+} + H_2;\ m/z\ 15 \rightarrow m/z\ 13 \quad (6.6)$$





EI-MS spectrum of epinephrine (adrenaline)



electron ionization mass spectrum of caffeine