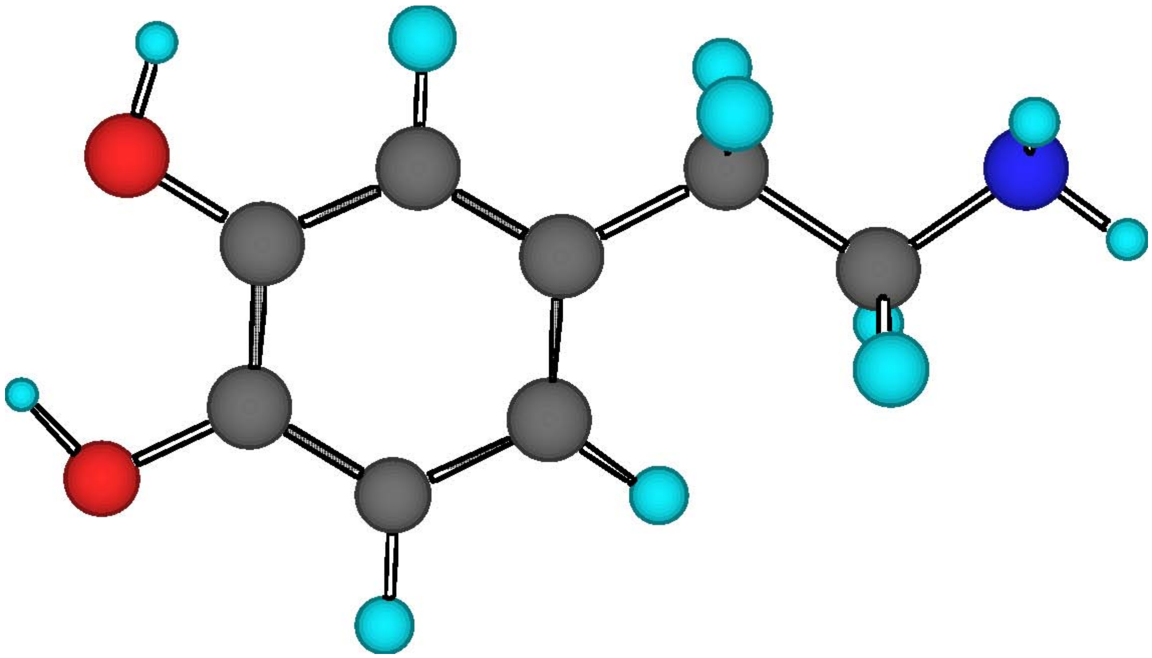
Mass Spectrometry



Top five list for Mass Spectrometry

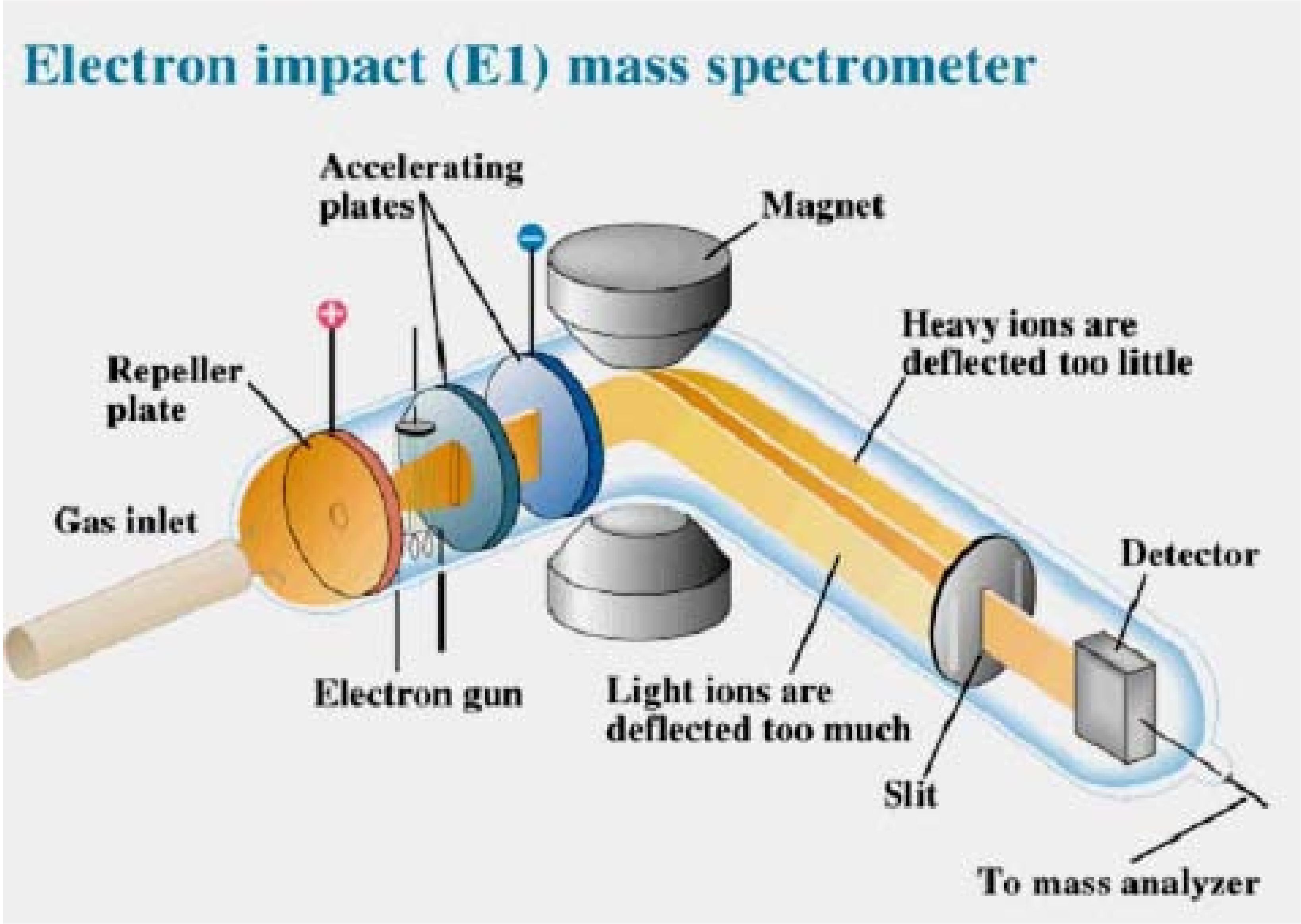
- 1. Molecular weight
- 2. Fragmentation pattern
- 3. Isotope ratio
- 4. Nitrogen rule
- 5. Exact mass

A Mass Spectrometer

A mass spectrometer is designed to do three things

- 1. Convert neutral atoms or molecules into a beam of positive (or negative) ions
- 2. Separate the ions on the basis of their mass-to-charge ratio (m/z)
- 3. Measure the relative abundance of each ion

A Mass Spectrometer



A Mass Spectrometer

- Electron ionization MS

- In the ionization chamber, the sample is bombarded with a beam of high-energy electrons
- Collisions between these electrons and the sample result loss of electrons from sample molecules and formation of positive ions

Molecular Ion

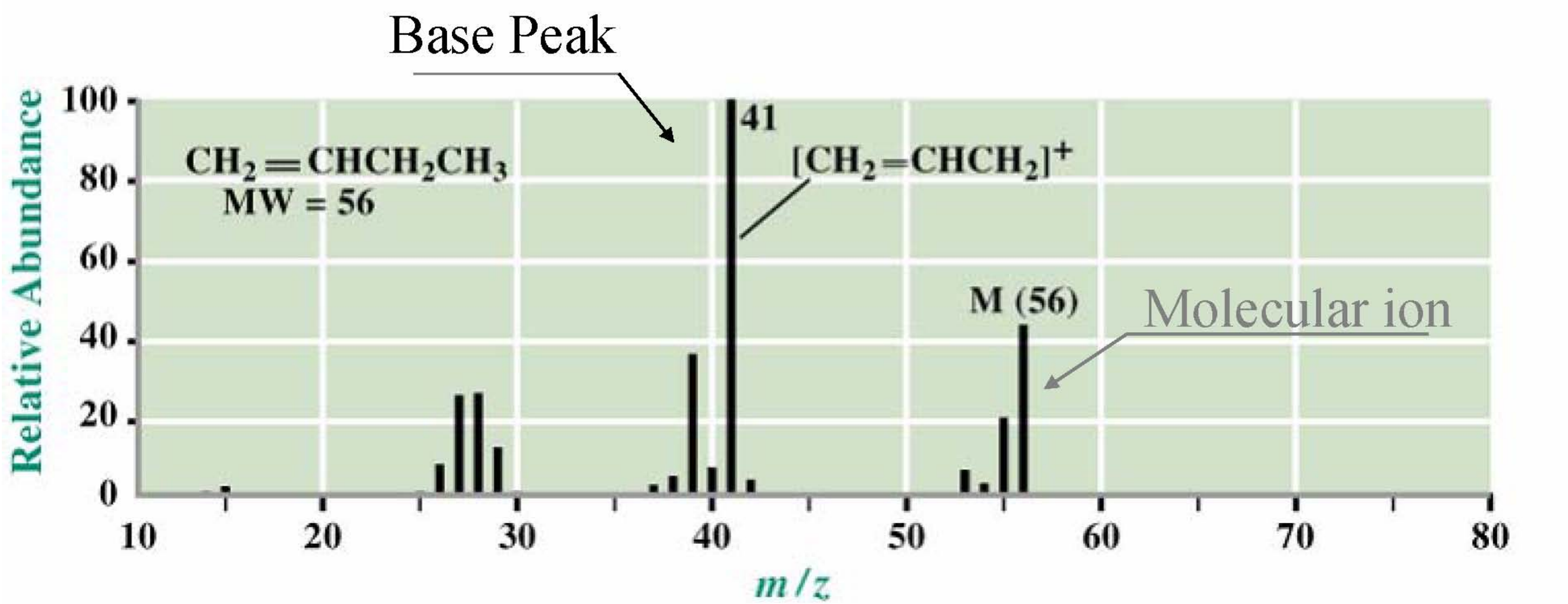
- Molecular Ion (M+): the species formed by removal of a single electron from a molecule

- For our purposes, it does not matter which electron is lost; at high energies, radical cation character is generally delocalized throughout the molecule. Therefore, we write the molecular formula of the parent molecule in brackets with: [M]+•
- A plus sign to show that it is a cation
- A dot to show that it has an odd number of electrons

Mass Spectrum

- Mass spectrum: a plot of the relative abundance of each ion versus mass-to-charge ratio
- Base peak: the most abundant peak; Assigned an arbitrary intensity of 100
- The relative abundance of all other ions is reported as a % of abundance of the base peak

Mass Spectrum of 1-Butene



Other MS Techniques

- What we have described is called electron ionization mass spectrometry (EI MS)

  - Other techniques, which work better but which require more expensive instruments, include:

    Fast atom bombardment (FAB)

    Matrix-assisted laser beam desorption ionization (MALDI)
    Chemical ionization (CI)

- And many others….

Resolution

- Resolution: a measure of how well a mass spectrometer separates ions of different mass

- Low resolution-capable of distinguishing among ions of different nominal mass, that is ions that differ by at least one or more mass units
- High resolution-capable of distinguishing among ions that differ in mass by as little as 0.0001 mass unit

Multiple Magnets or Quadrupole Magnet are Used for HRMS

- These "sectors" are often combined to permit even better resolution.

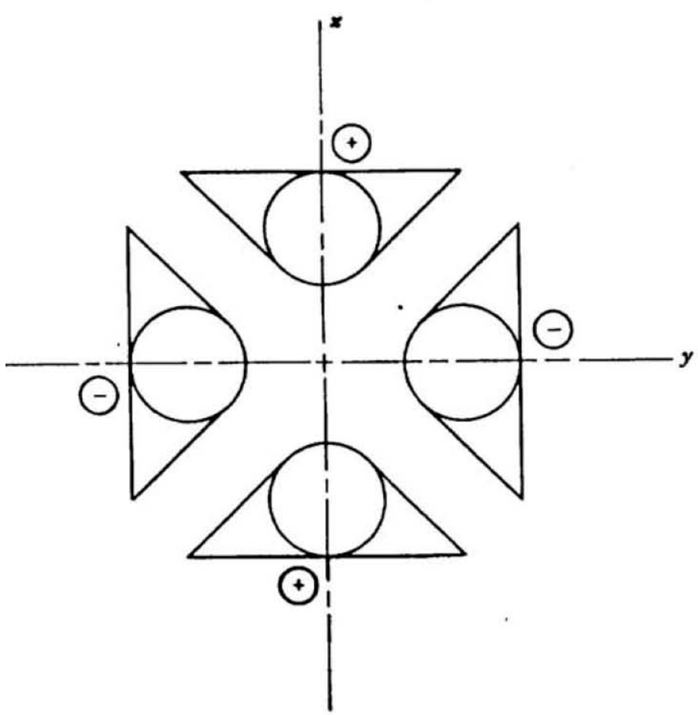


Figure 3. *Quadrupole arrangement.*

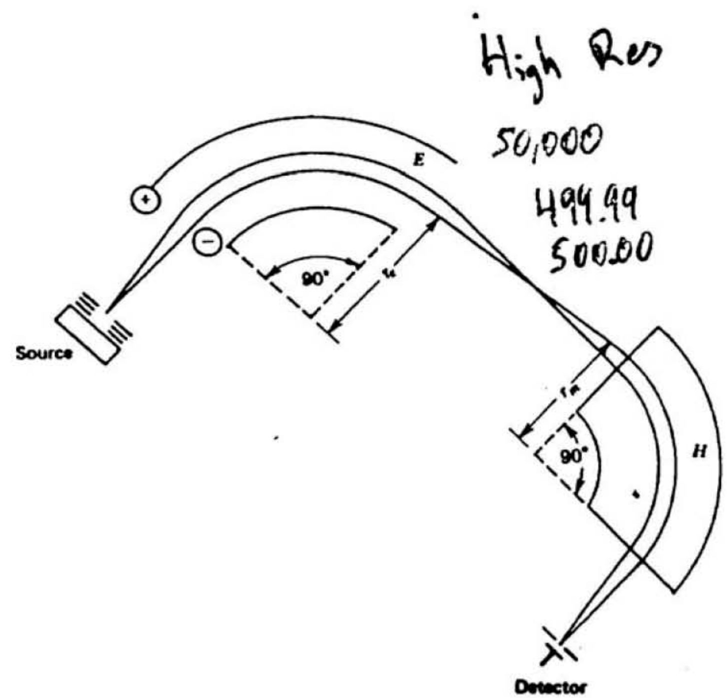


Figure 4. *Nier-Johnson double-focusing mass analyzer. E = electric field. H = magnetic field.*

Isotopes

- Carbon, for example, in nature is 98.90% ^{12}C and 1.11% ^{13}C. Thus, there are 1.11 atoms of carbon-13 in nature for every 100 atoms of carbon-12

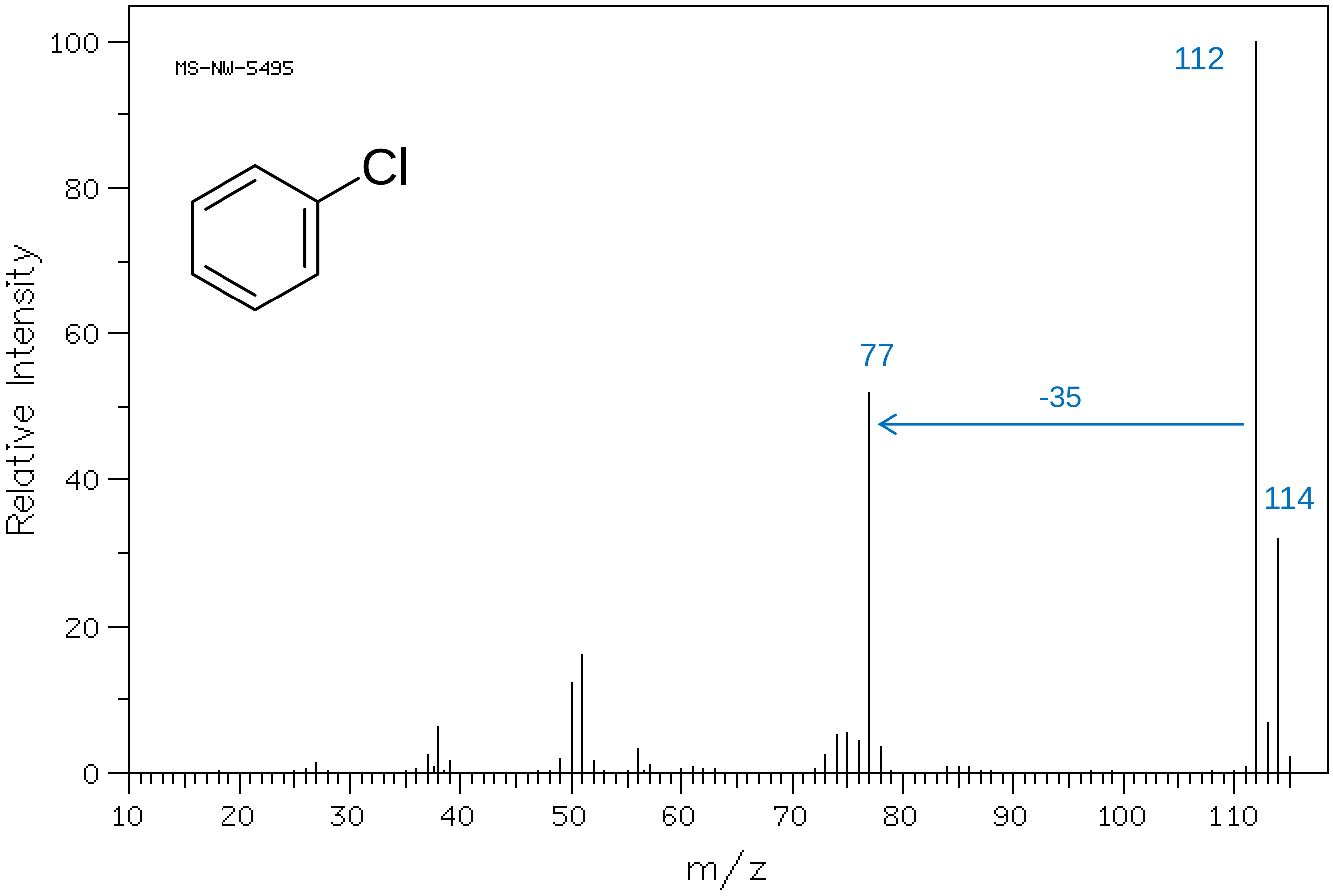
- **1.10 x 100 = 1.11 atoms ^{13}C per 100 atoms ^{12}C**

- **98.90**

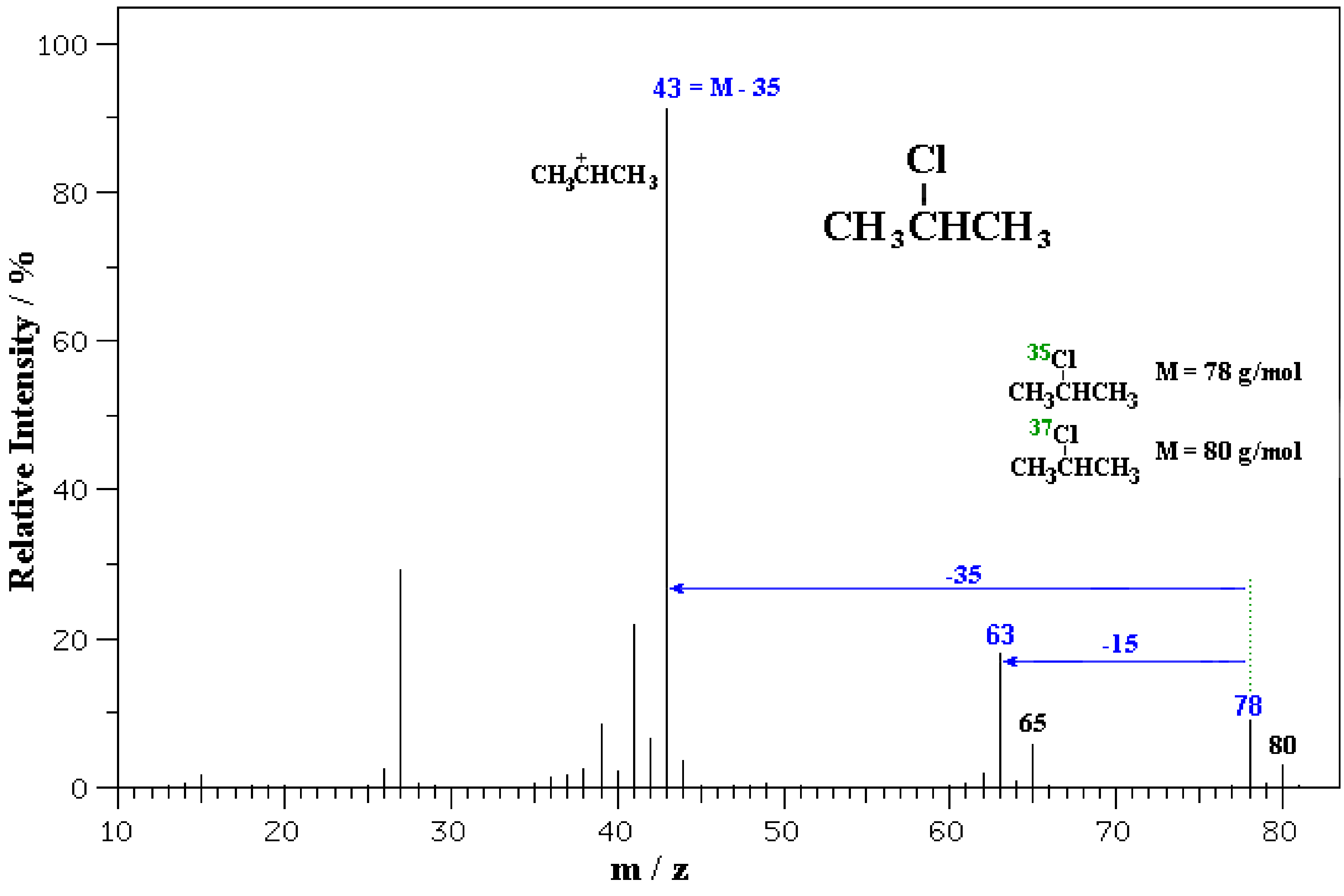
Precise masses and natural abundances of isotopes

Element	Atomic Weight	Isotope	Precise Mass (amu)	Relative Abundance
hydrogen	1.0079	^{1}H	1.00783	100
		^{2}H	2.01410	0.016
carbon	12.011	^{12}C	12.0000	100
		^{13}C	13.0034	1.11
nitrogen	14.007	^{14}N	14.0031	100
		^{15}N	15.0001	0.38
oxygen	15.999	^{16}O	15.9949	100
		^{17}O	16.9991	0.04
		^{18}O	17.9992	0.20
sulfur	32.066	^{32}S	31.9721	100
		^{33}S	32.9715	0.78
		^{34}S	33.9679	4.40
chlorine	35.453	^{35}Cl	34.9689	100
		^{37}Cl	36.9659	32.5
bromine	79.904	^{79}Br	78.9183	100
		^{81}Br	80.9163	98.0

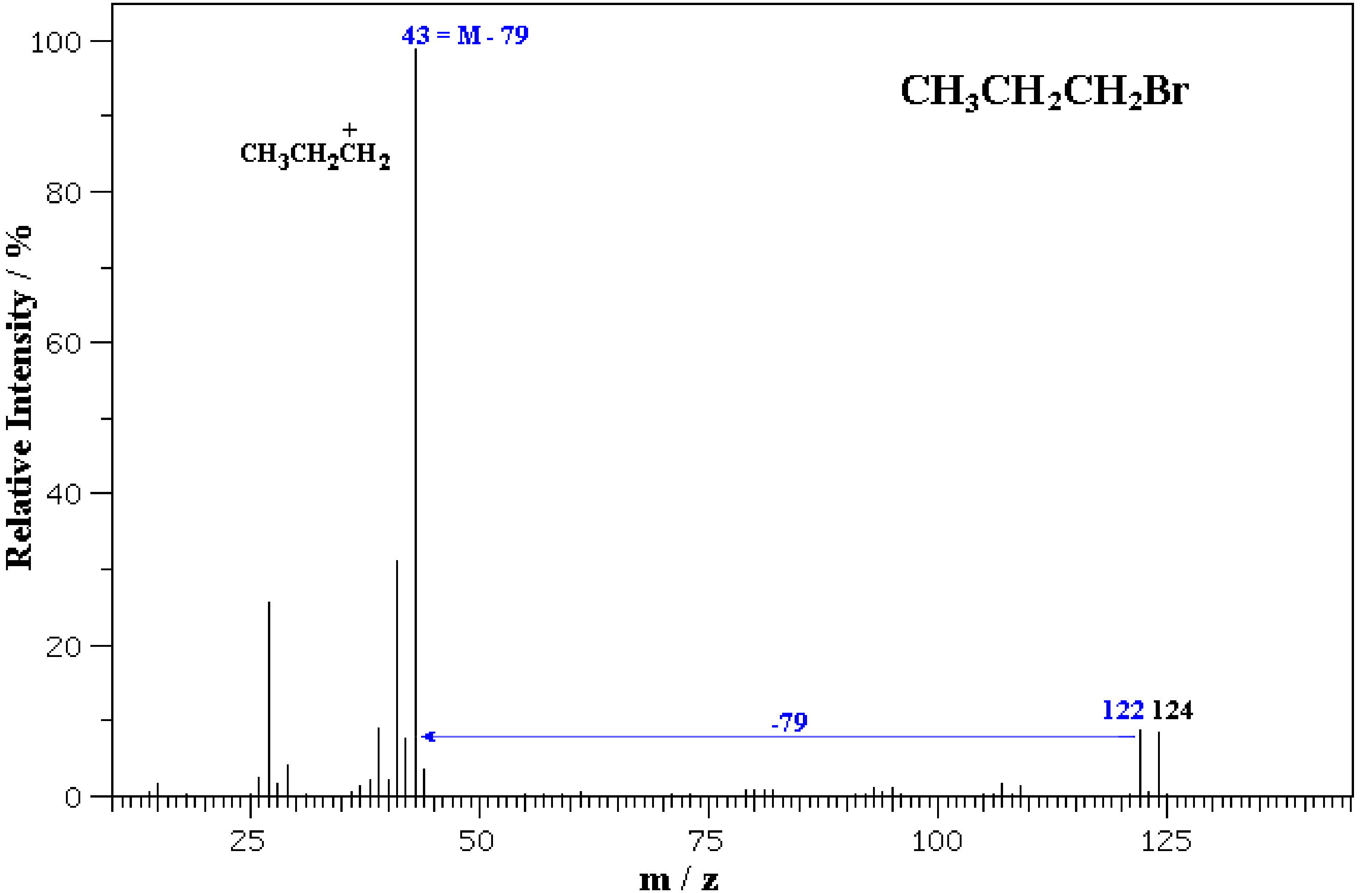
Chlorobenzene mass spectrum



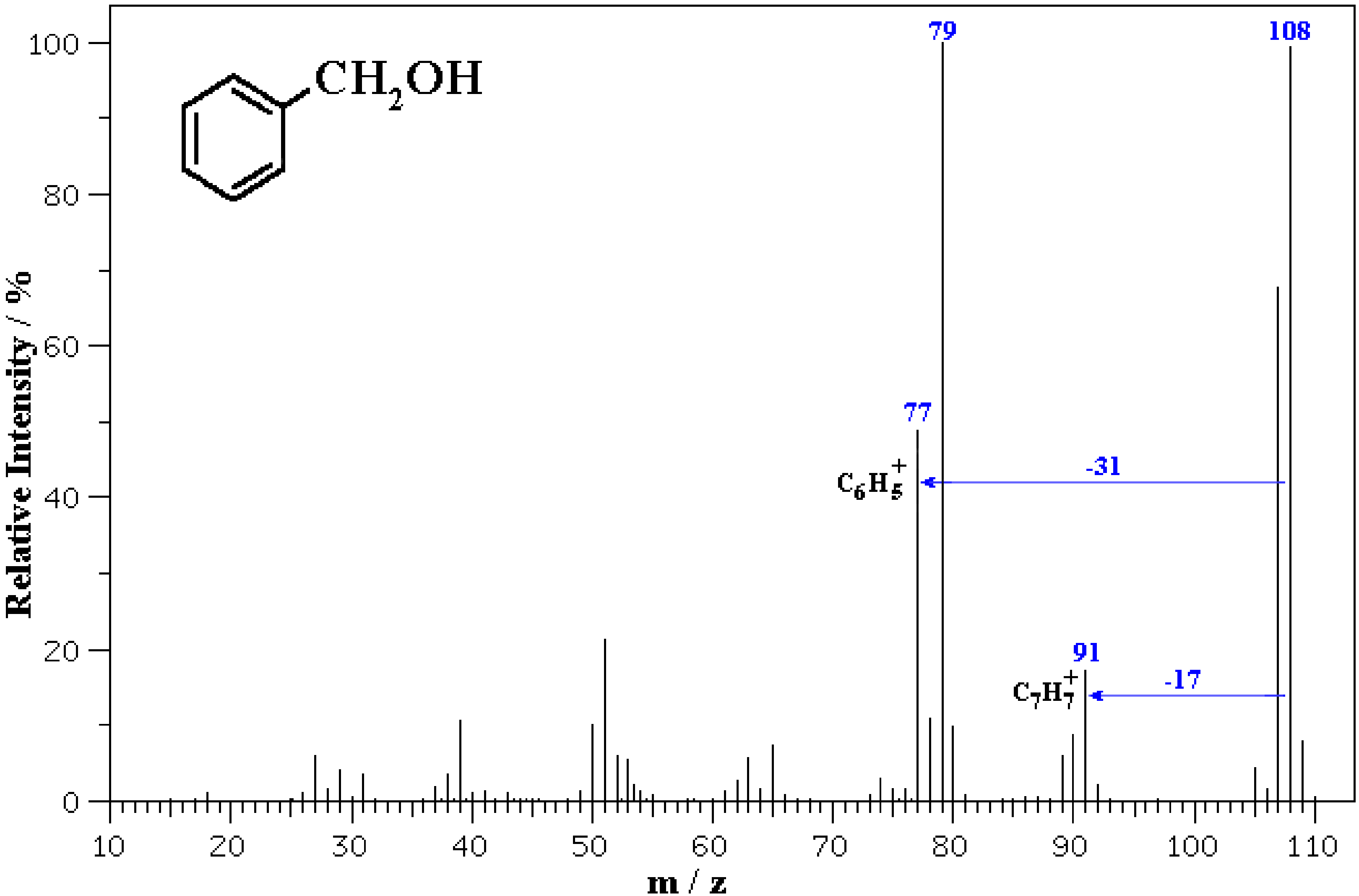
Mass spectrum: 2-chloropropane



Mass spectrum: n-propyl bromide



Benzyl alcohol mass spectrum

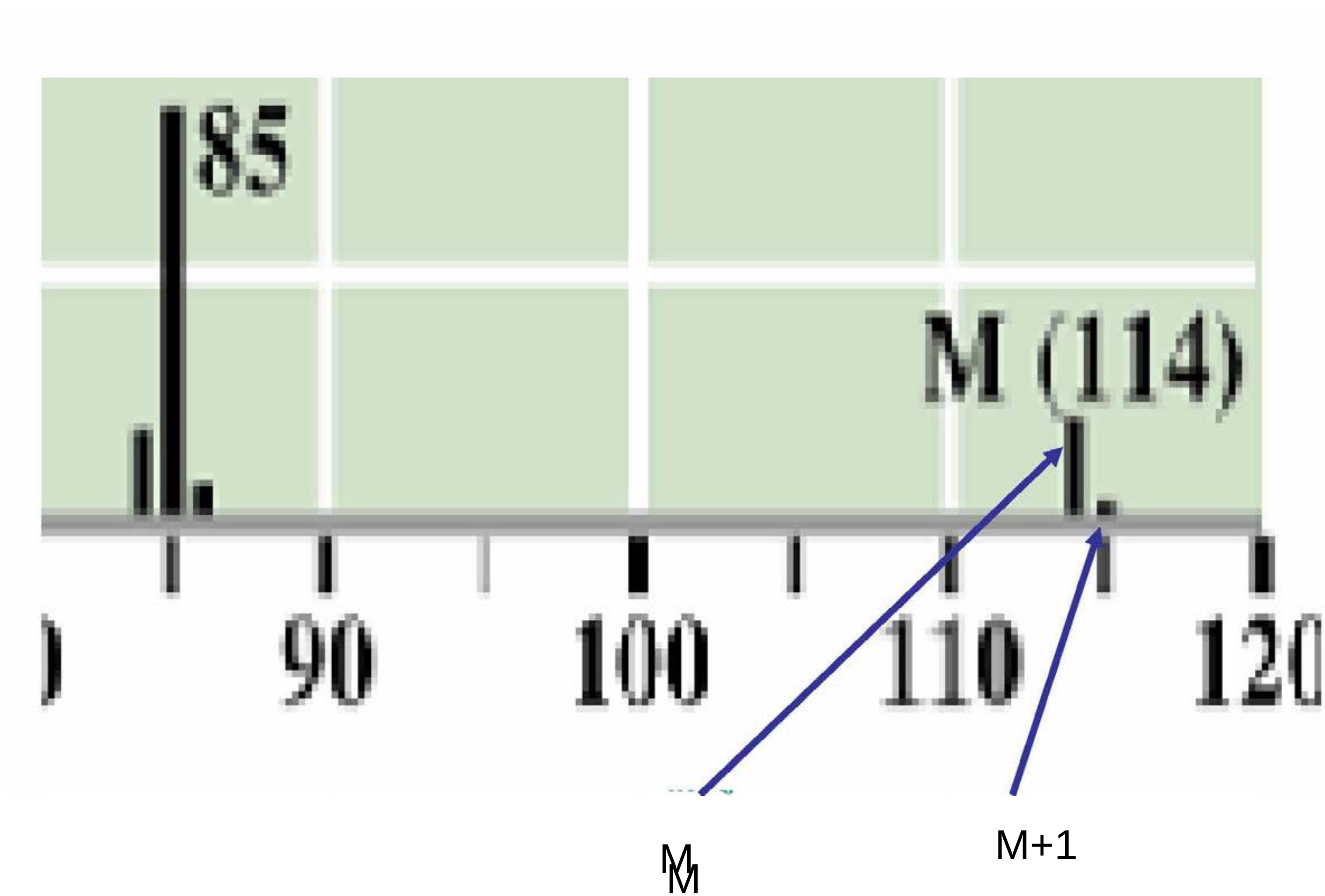


Resolution

- **C_3H_6O and C_3H_8O have nominal masses of 58 and 60, and can be readily distinguished by low-resolution MS**
- But, these two compounds both have a nominal mass of 60.
- **C_3H_8O 60.05754**
  $C_2H_4O_2$ 60.02112
- Distinguish between them by high-resolution MS

M+2 and M+1 Peaks

- Each unique combination of isotopes gives rise to a separate peak.
- The intensity of the peaks is determined by the probability of occurrence
- For carbon mass 13.000, the abundance is 1.11% (see above)
- For some elements, this number is large

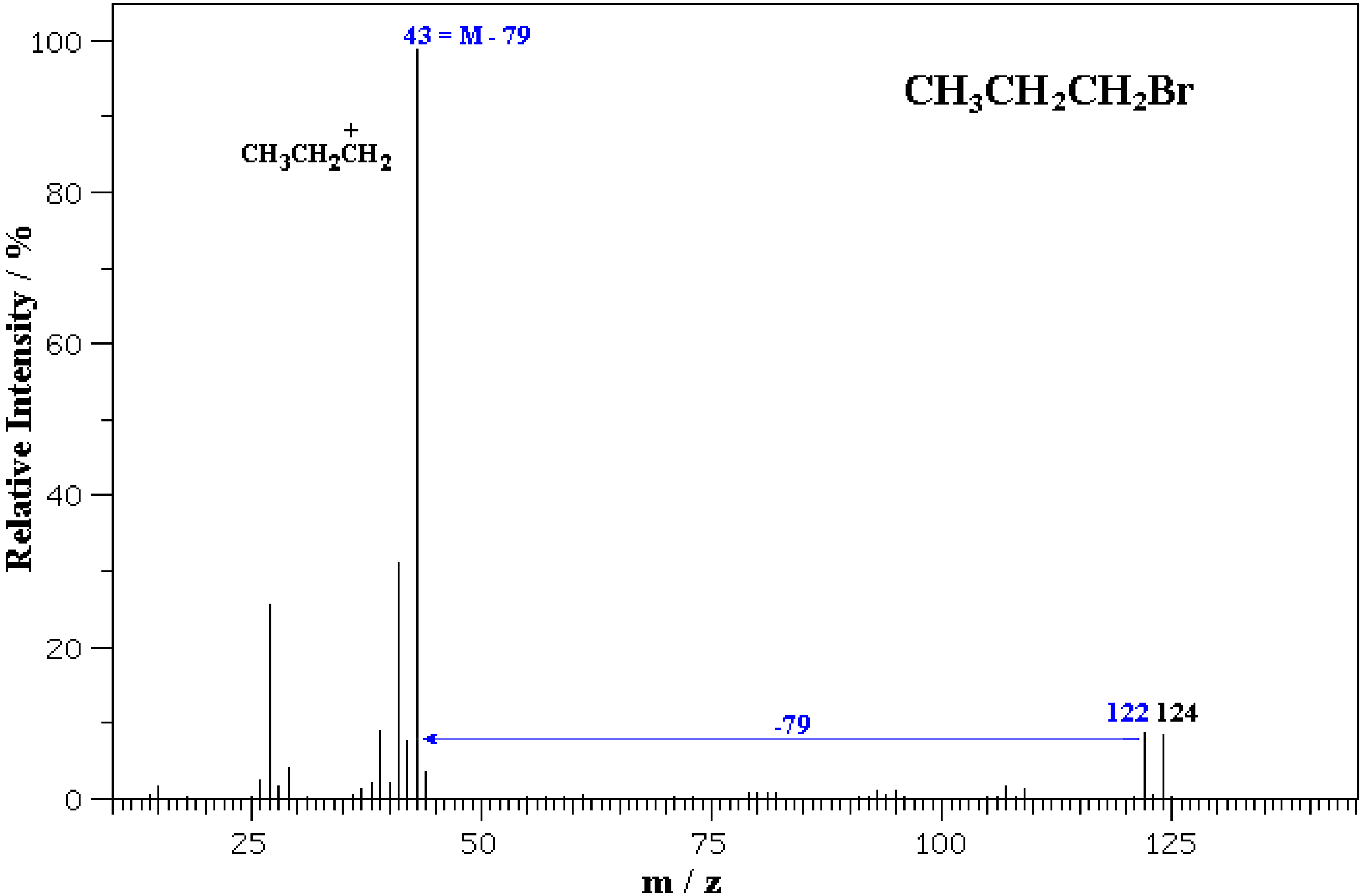


85
M (114)
90
100
110
120
M
M+1

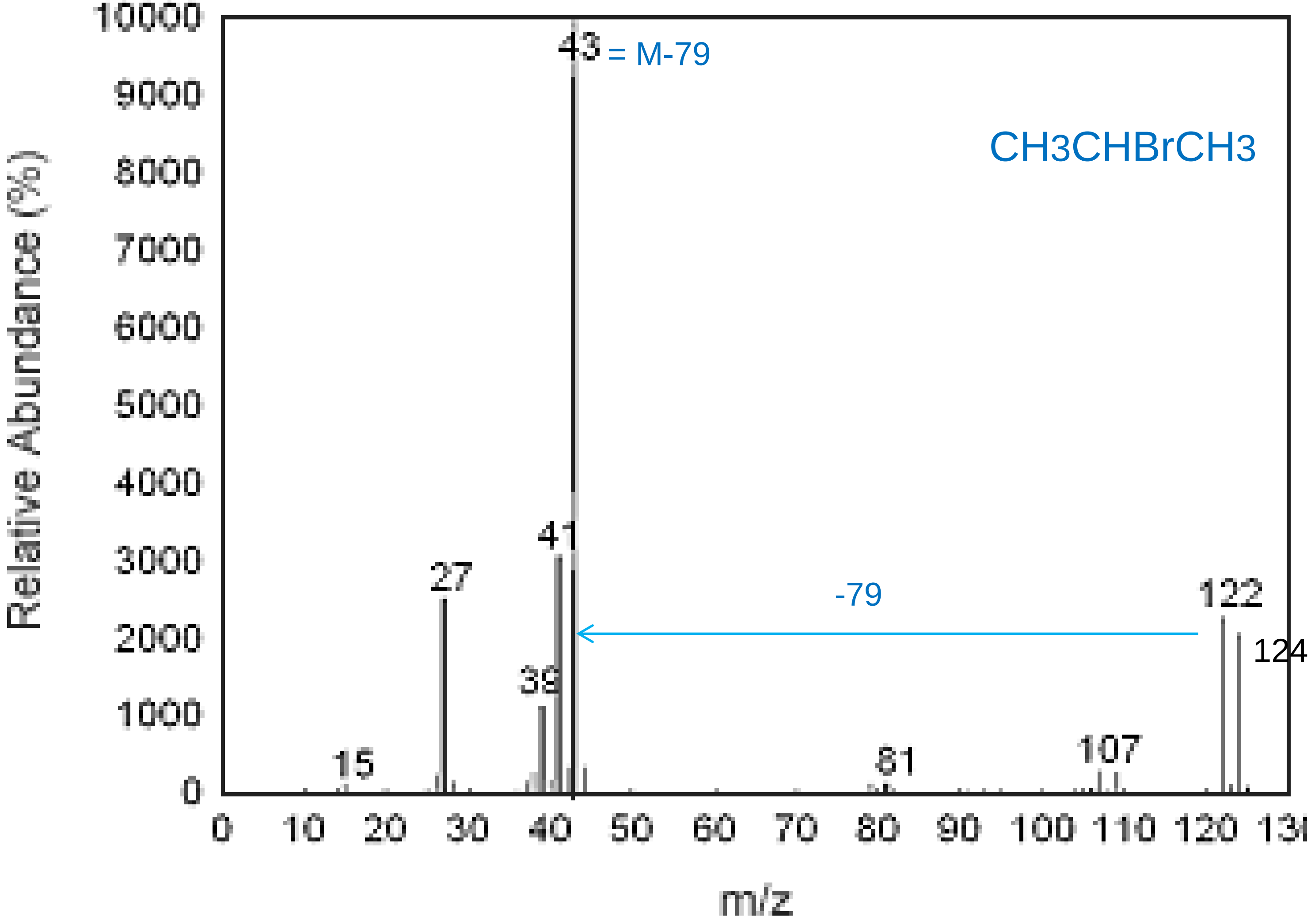
M+2 and M+1 Peaks

- The most common elements giving rise to M + 2 peaks are chlorine and bromine
- Chlorine in nature is 75.77% ^{35}Cl and 24.23% ^{37}Cl
- a ratio of M to M + 2 of approximately 3:1 indicates the presence of a single chlorine in a compound
- Bromine in nature is 50.7% ^{79}Br and 49.3% ^{81}Br
- a ratio of M to M + 2 of approximately 1:1 indicates the presence of a single bromine in a compound

Mass spectrum: n-propyl bromide



2-Bromopropane mass spectrum



M+2 and M+1 Peaks

Sulfur is the only other element common to organic compounds that gives a significant M + 2 peak and it is small

^{32}S = 95.02% and ^{34}S = 4.21%

Because M + 1 peaks are relatively low in intensity compared to the molecular ion and often difficult to measure with any precision, they are generally not useful for accurate determinations of molecular weight

Isotopes

- ^{16}O 15.9949 100
- ^{17}O 16.9991 0.04
- ^{18}O 17.9992 0.20

- ^{32}S 31.9721 100
- ^{33}S 32.9715 0.78
- ^{34}S 33.9679 4.40

- ^{35}Cl 34.9689 100
- ^{37}Cl 36.9659 32.5

- ^{79}Br 78.9183 100
- ^{81}Br 80.9163 98.0

Interpreting MS

1. Check the M+2 region of the spectrum The only elements to give significant M + 2 peaks are Cl and Br. If there is no large M + 2 peak then there is no Cl or Br! (remember sulfur, S, is “small”)

2. Is the mass of the molecular ion odd or even?

The Nitrogen Rule

- Nitrogen rule: if a compound has

- zero or an even number of nitrogen atoms, its molecular ion will have an even m/z value

- an odd number of nitrogen atoms, the molecular ion will have an odd m/z value

Fragmentation of Molecular ion

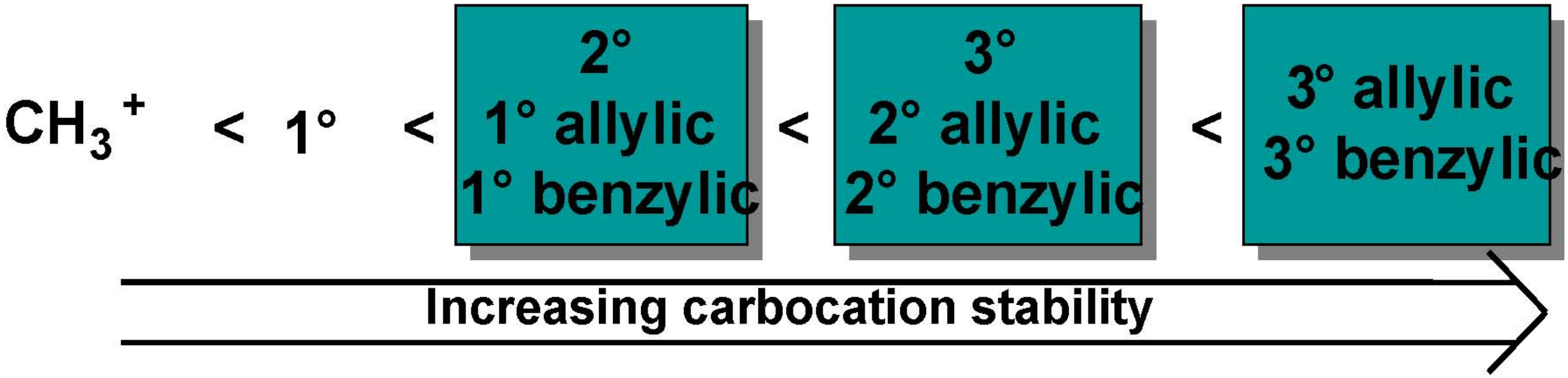
- To attain high efficiency of molecular ion formation and give reproducible mass spectra, it is common to use electrons with energies of approximately 70 eV (1600 kcal/mol)
- This energy is sufficient not only to dislodge one or more electrons from a molecule, but also to cause extensive fragmentation
- These fragments may be unstable as well and, in turn, break apart to even smaller fragments

Fragmentation of Molecular ion

- Fragmentation of a molecular ion, M, produces a radical and a cation. Only the cation is detected by MS
- The chemistry of ion fragmentation can be understood in terms of the formation and relative stabilities of carbocations in solution
- Where fragmentation occurs to form new cations, the mode that gives the most stable cation is favored

Fragmentation of M

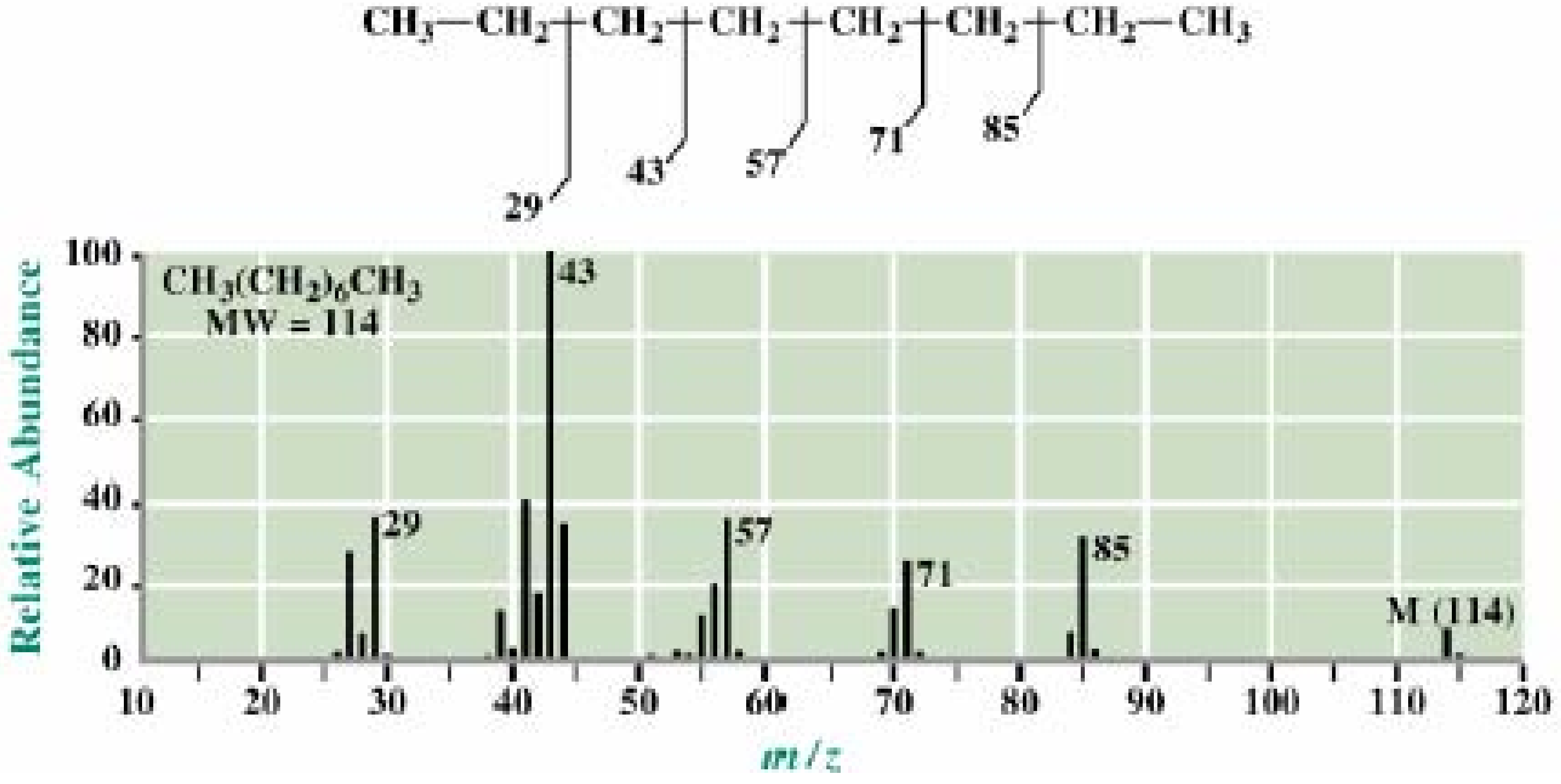
- The probability of fragmentation to form new carbocations increases in the order



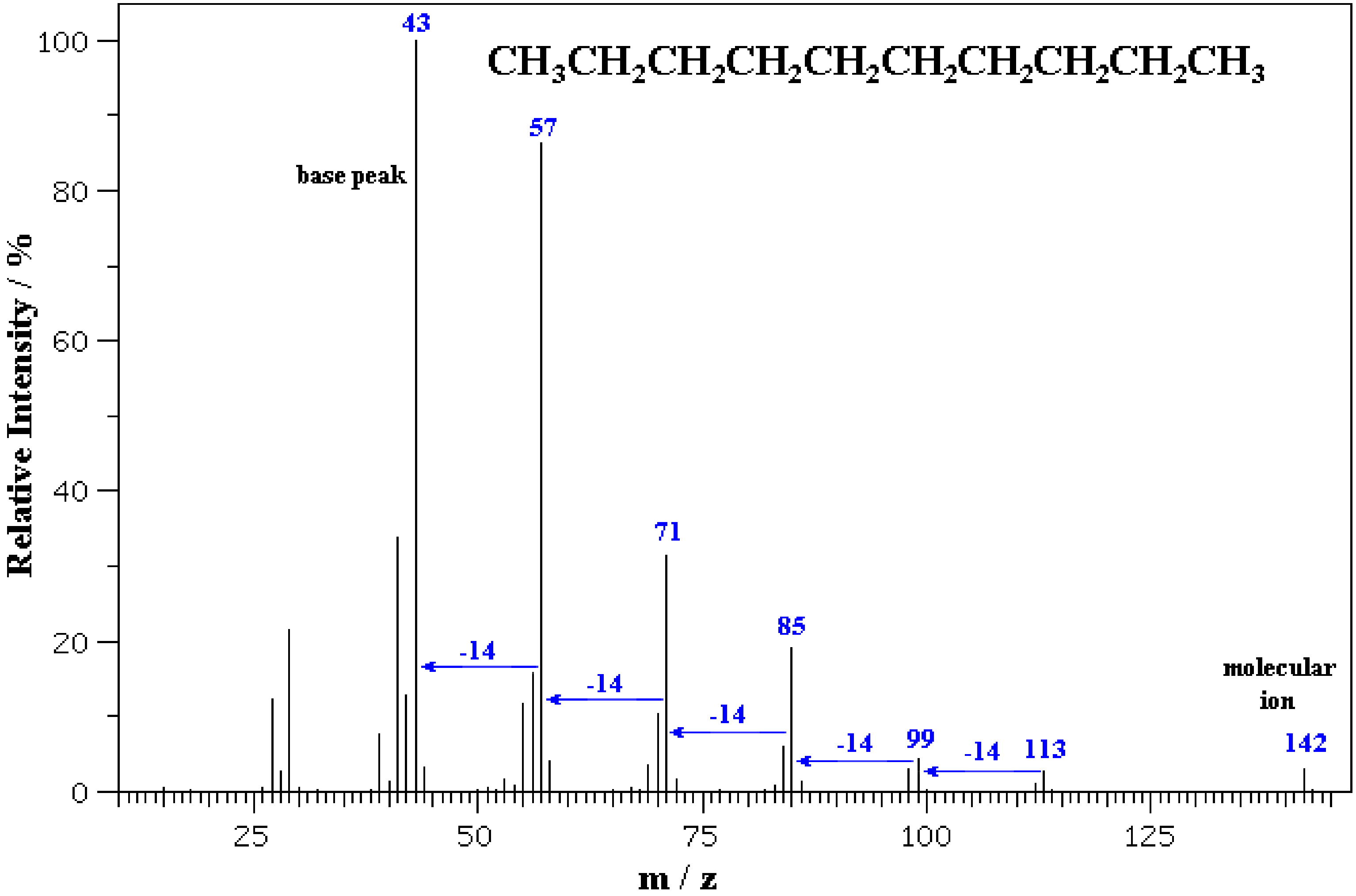
Alkanes

- Fragmentation tends to occur in the middle of unbranched chains rather than at the ends
- The difference in energy between allylic, benzylic, 3°, 2°, 1°, and methyl cations is much greater than the difference among comparable radicals
- where alternative modes of fragmentation are possible, the more stable carbocation tends to form in preference to the more stable radical

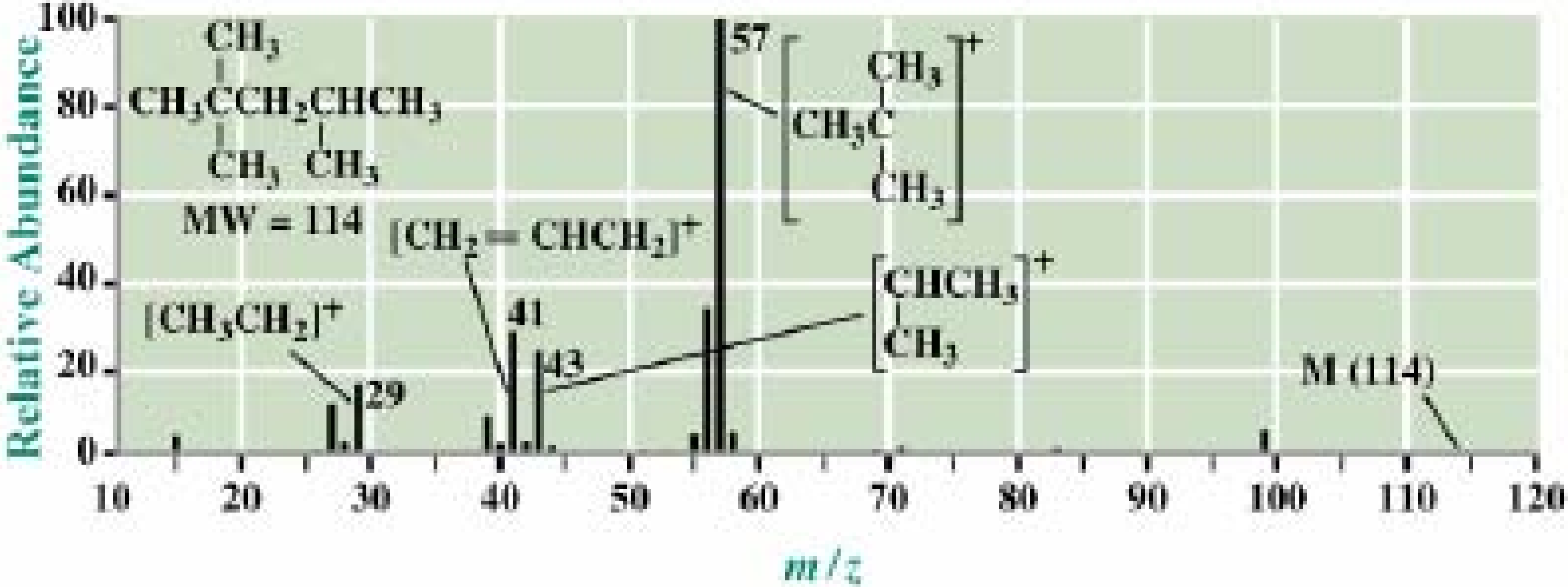
Mass spectrum of octane



Mass spectrum: n-decane



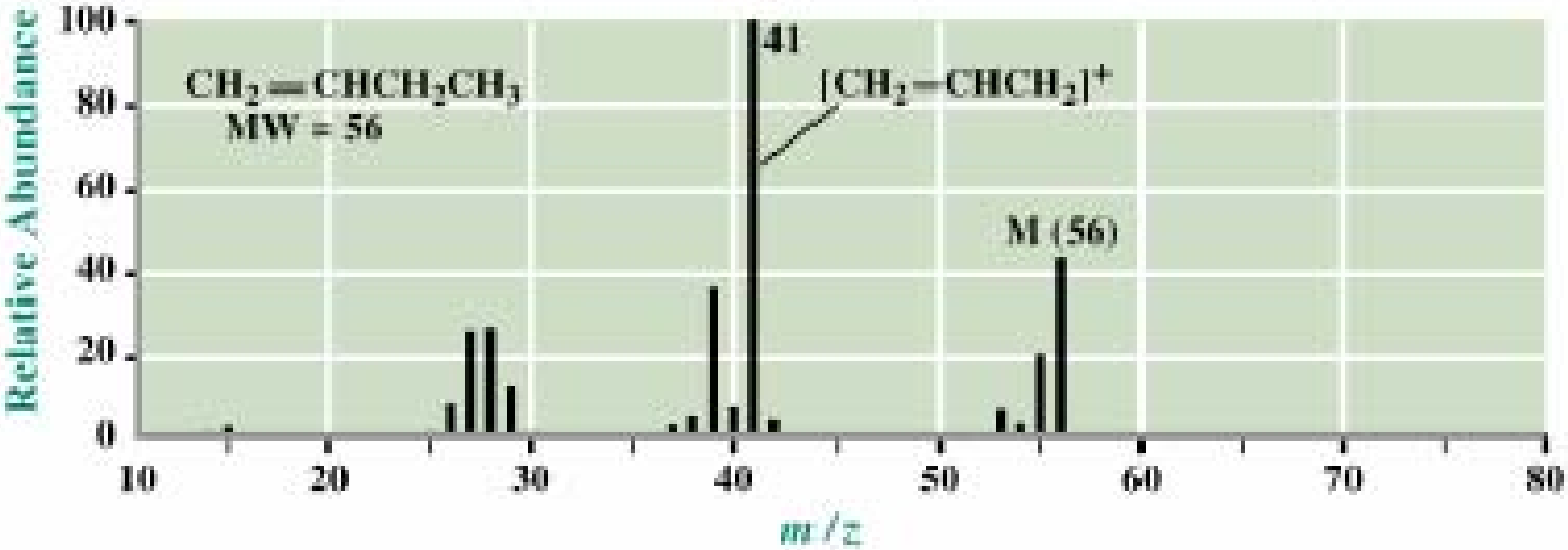
Mass spectrum of 2,2,4-trimethylpentane



Alkenes

- Alkenes characteristically show a strong molecular ion peak
- They cleave readily to form resonance-stabilized allylic cations

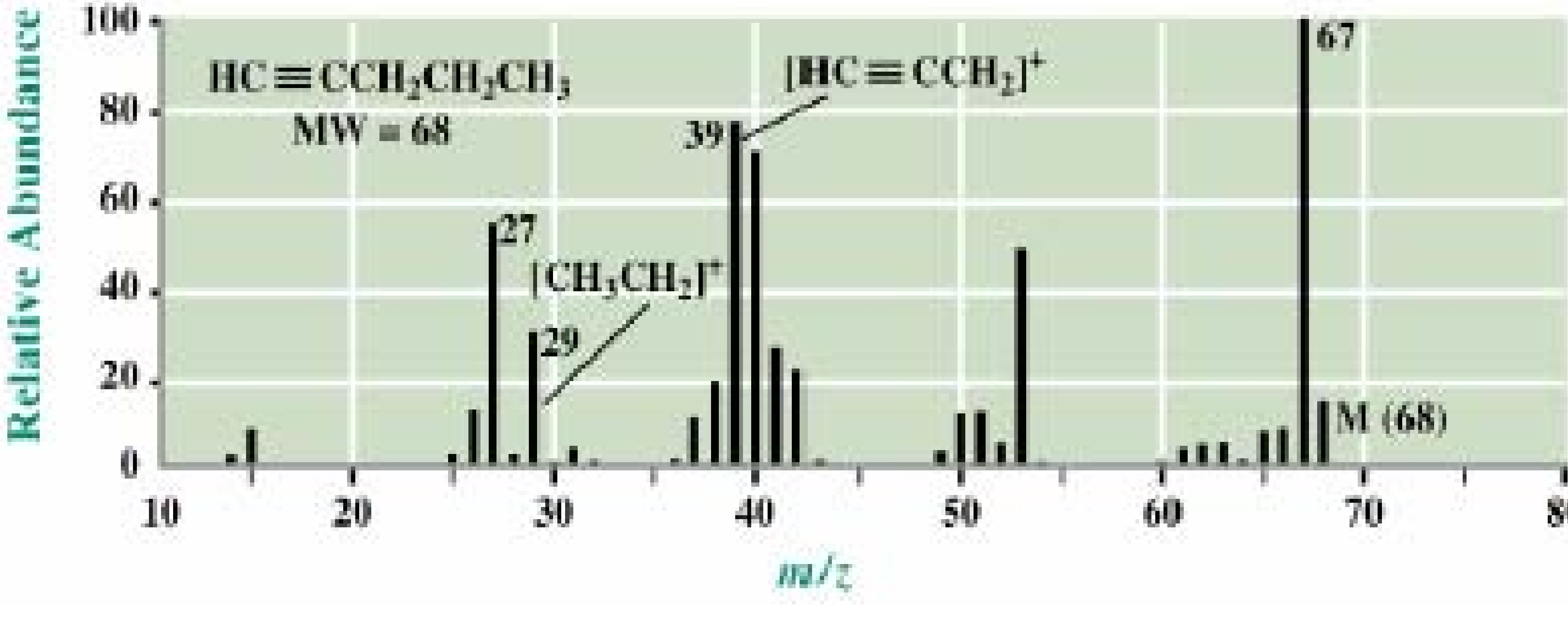
Mass spectrum of 1-butene



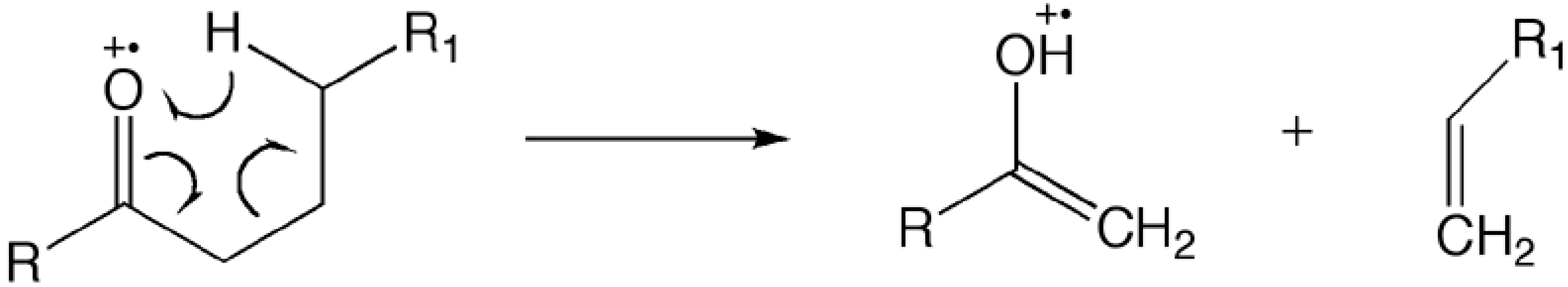
Alkynes

- Alkynes typically show a strong molecular ion peak
- They cleave readily to form the resonance-stabilized propargyl cation or a substituted propargyl cation

Mass spectrum of 1-pentyne



McLafferty Rearrangement



http://www.chem.arizona.edu/massspec/example_html/examples.html