Mass Spectroscopy

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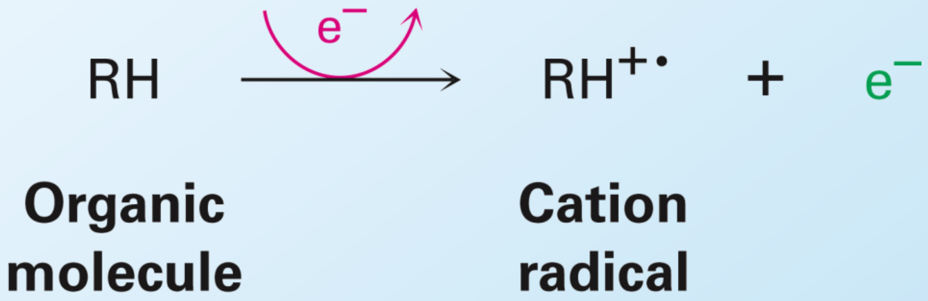
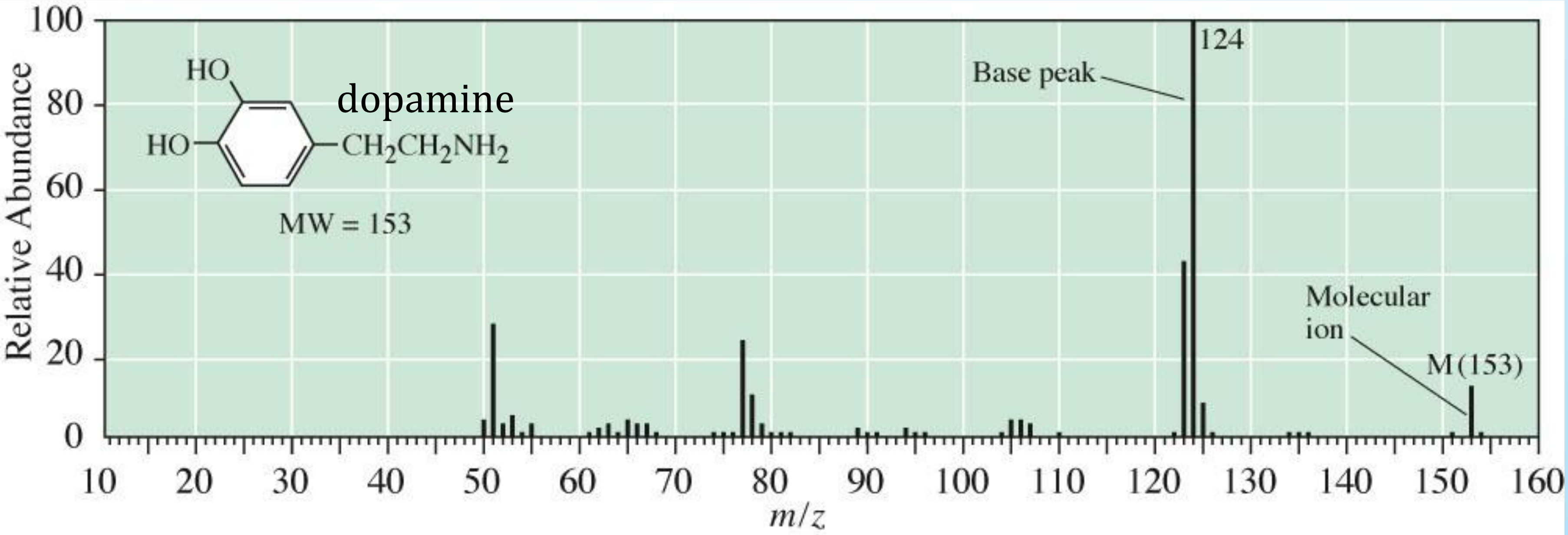
What is Mass Spectroscopy

- It is an analytical technique for measuring the mass-to-charge ratio (m/z) of ions in the gas phase.
- Mass spectrometry is our most valuable analytical tool for determining accurate molecular masses.
- Also can give information about structure.



The Mass Spectrum

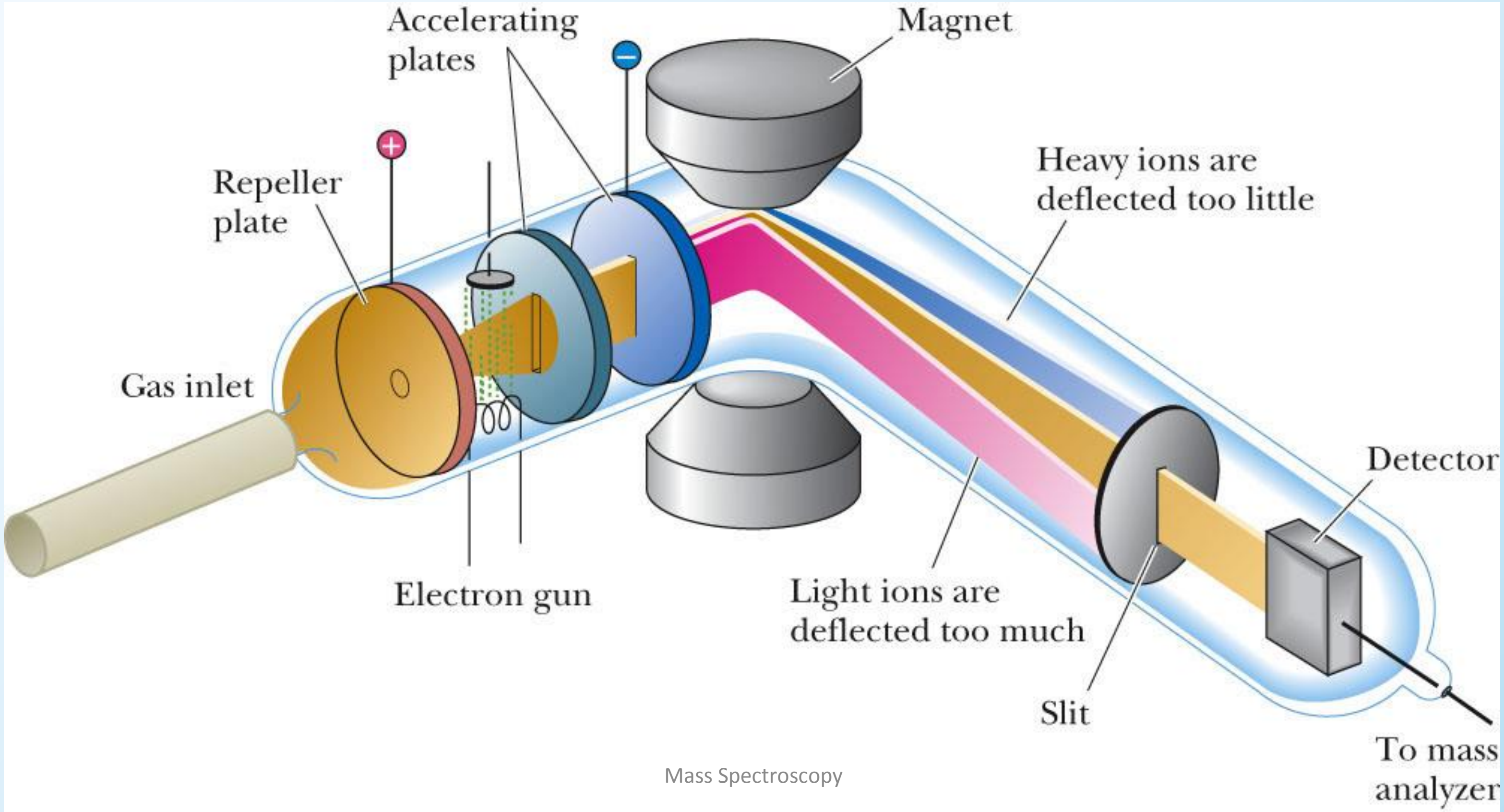
- The plot is of mass of ions (m/z) (x-axis) versus the intensity of the signal (y-axis)
- Most abundant ion peak is **base peak** (100%)
- Other peaks listed as the % of the base peak
- Usually the last peak is the unfragmented radical cation, called the **molecular ion peak** (M+)



The Instrument

The mass spectrophotometer does the following:

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



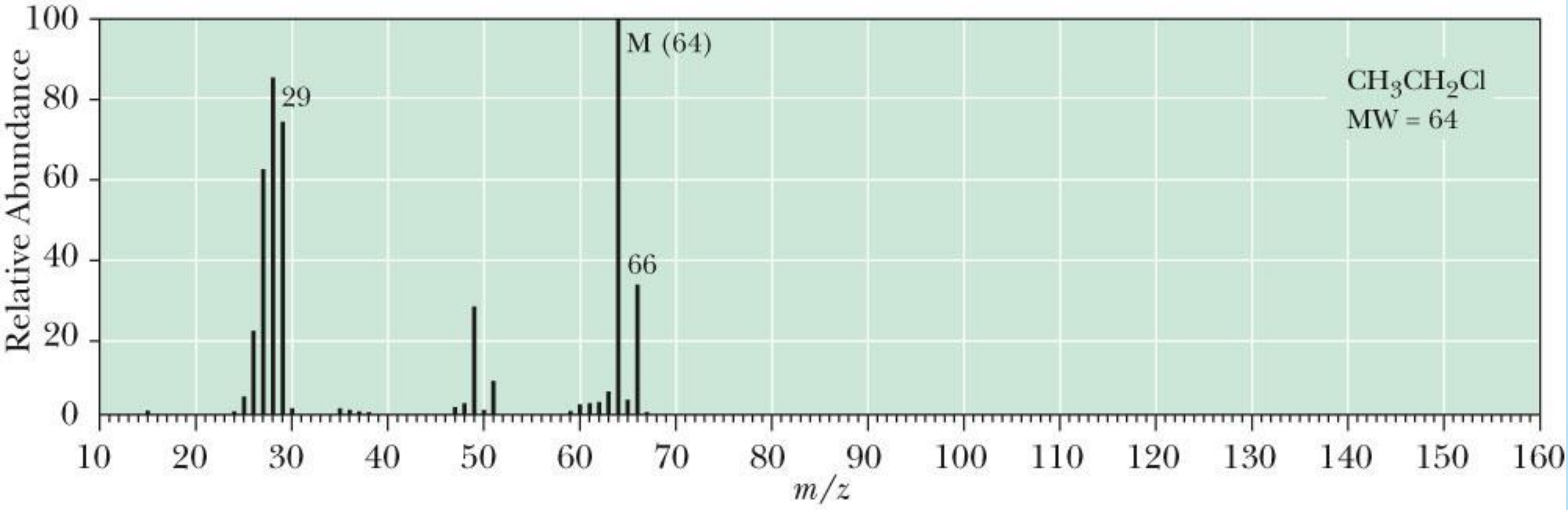
Isotopes

Virtually all elements common to organic compounds are mixtures of isotopes. All isotopes will show up on MS.

Element	Atomic weight	Isotope	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
		^{18}O	17.9992	0.20
sulfur	32.066	^{32}S	31.9721	100
		^{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

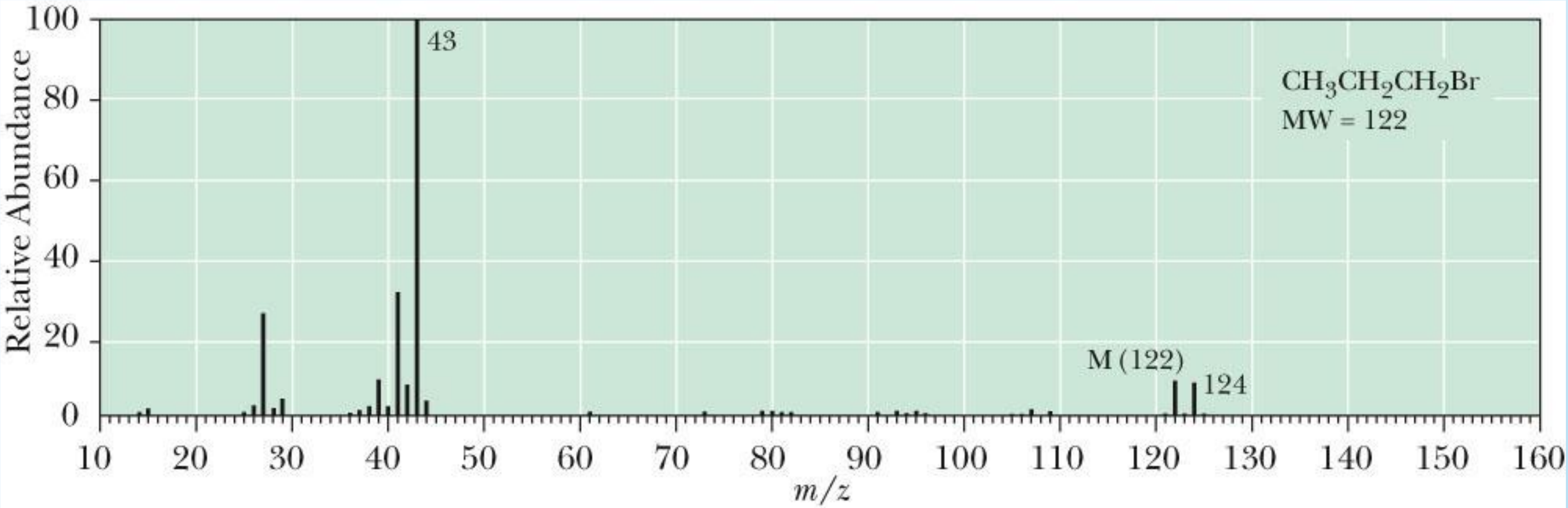
M+2 and M+1 Peaks

- The most common elements giving rise to significant 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, as seen in the MS of chloroethane.



M+2 and M+1 Peaks

- 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 atom in a compound, as seen in the MS of 1-bromopropane.

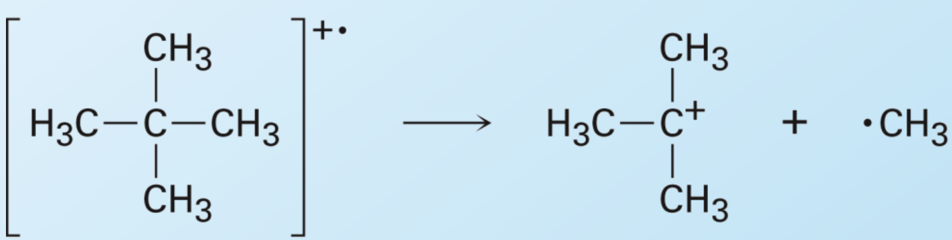


Fragmentation in MS

- The way molecular ions break down can produce characteristic fragments that help in identification
  - The spectrum as a “fingerprint” for comparison with known materials in analysis (used in forensics)
  - Fragmentation gives a cation and radical, only cations are detected by the MS
  - Positive charge goes to fragments that best can stabilize it

CH_3^+	<	1°	<	2° 1° allylic 1° benzylic	<	3° 2° allylic 2° benzylic	<	3° allylic 3° benzylic

  - Rearrangements occur in the MS instrument but the mass is the same; so one has to look at the fragmentation patterns to find the actual structure.



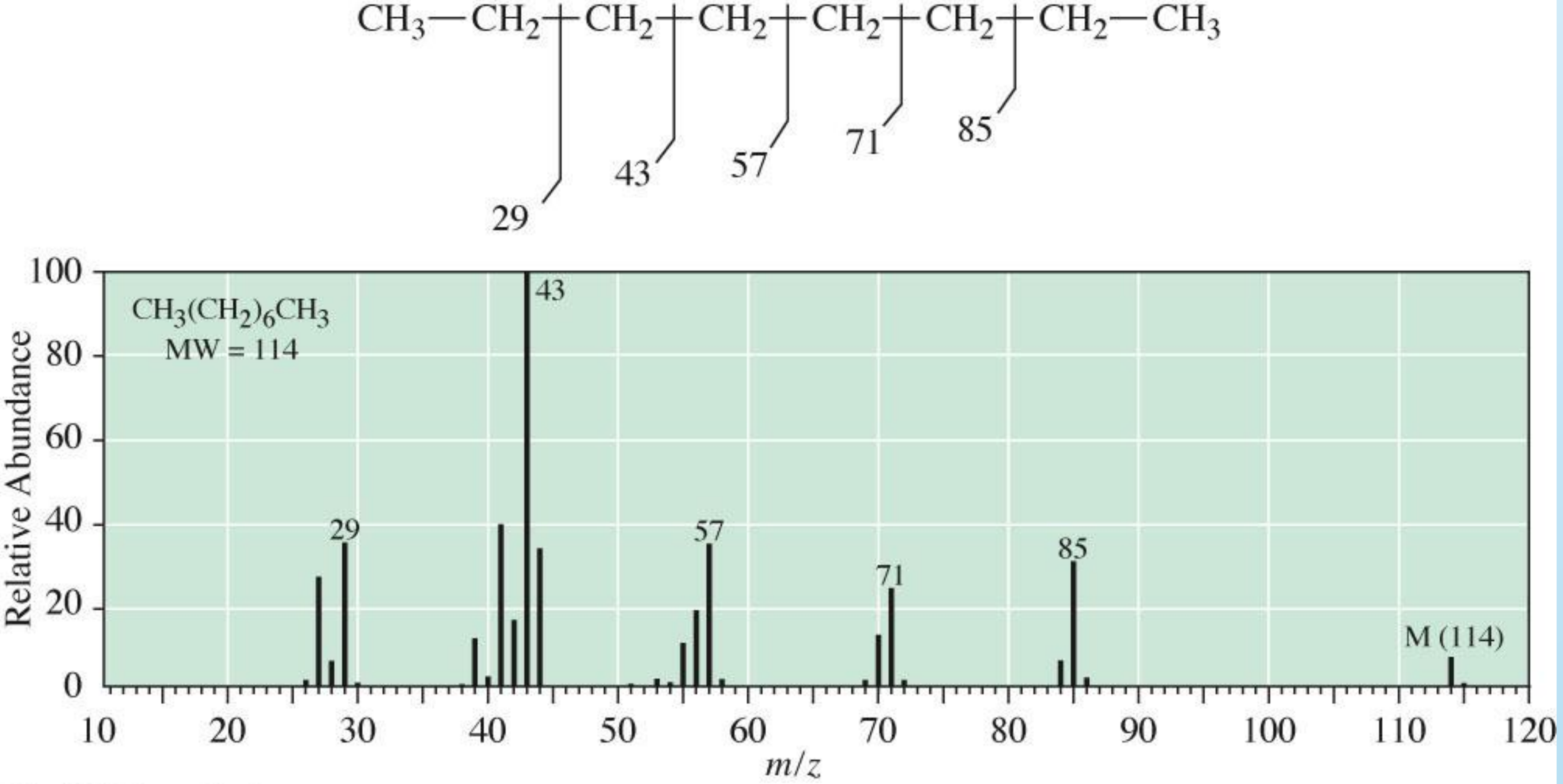
$m/z = 57$

Interpretation of MS

- The only elements to give significant M + 2 peaks are Cl and Br.
  - If no large M + 2 peak is present, these elements are absent.
- Is the mass of the molecular ion odd or even?
- 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, its molecular ion will have an odd m/z value.

Alkanes

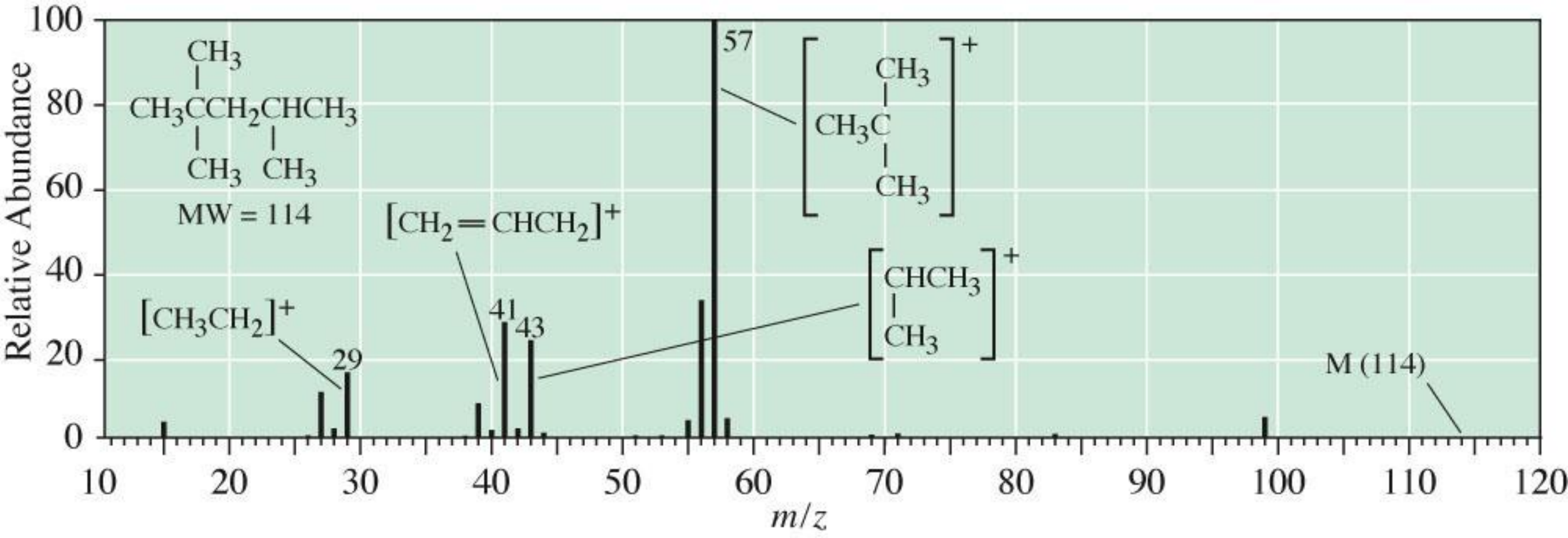
Mass spectrum of Octane. Note that there is no methyl cation peak. The base peak is for 43 which is propyl cation $C_3H_7^+$



Alkanes

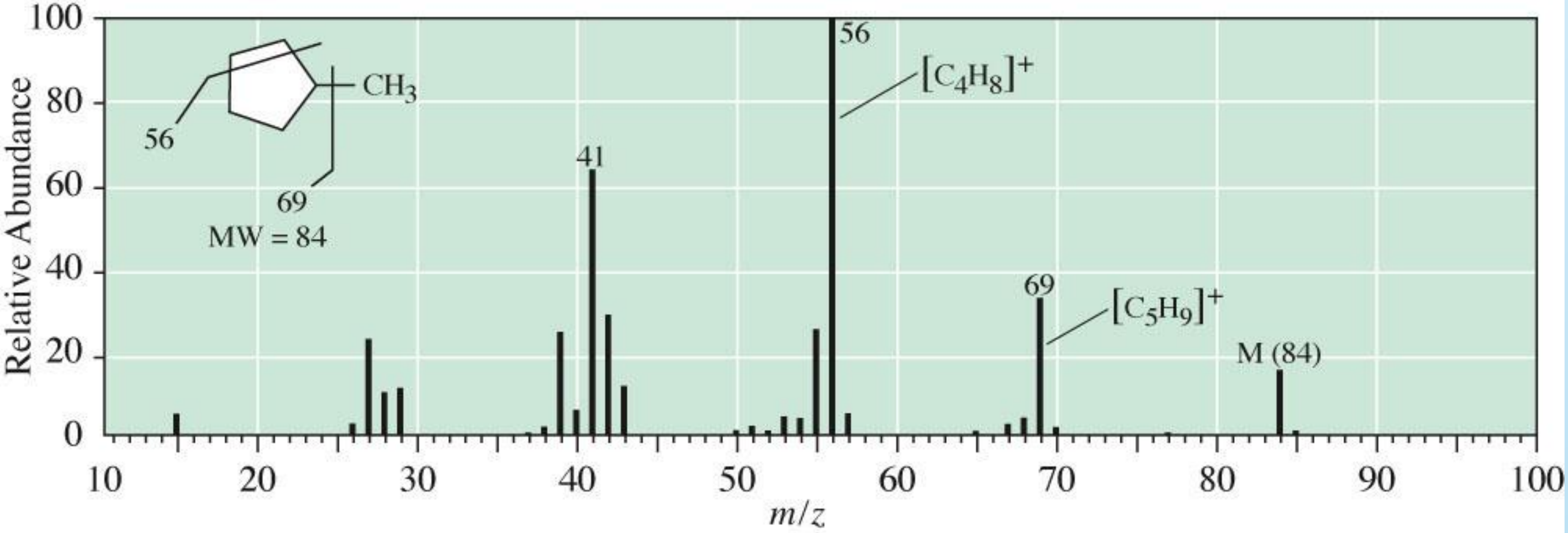
Mass spectrum of 2,2,4-trimethylpentane.

Note the base peak is 57 for t-butyl cation; the M+ is almost absent as everything has fragmented. The alkene cation is a result of rearrangement.



Alkanes

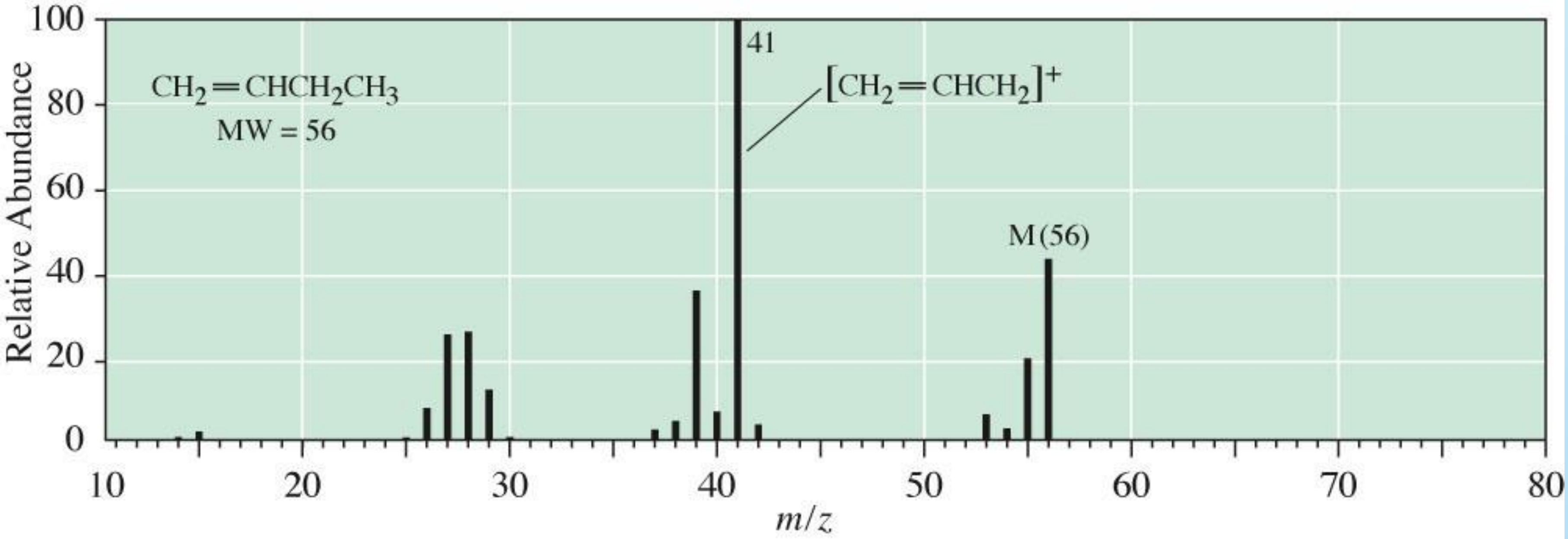
Mass spectrum of methylcyclopentane. The M+ peak is evident. Base peak is for butyl cation (4C), although the 5C fragment is also present.



Alkenes

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

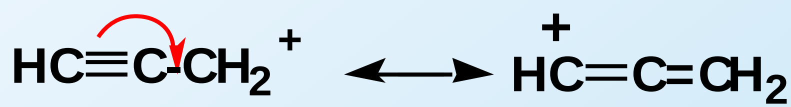
$$[CH_2{=}CHCH_2CH_2CH_3]^{\bullet +} \longrightarrow CH_2{=}CHCH_2^{\,+} + \bullet CH_2CH_3$$

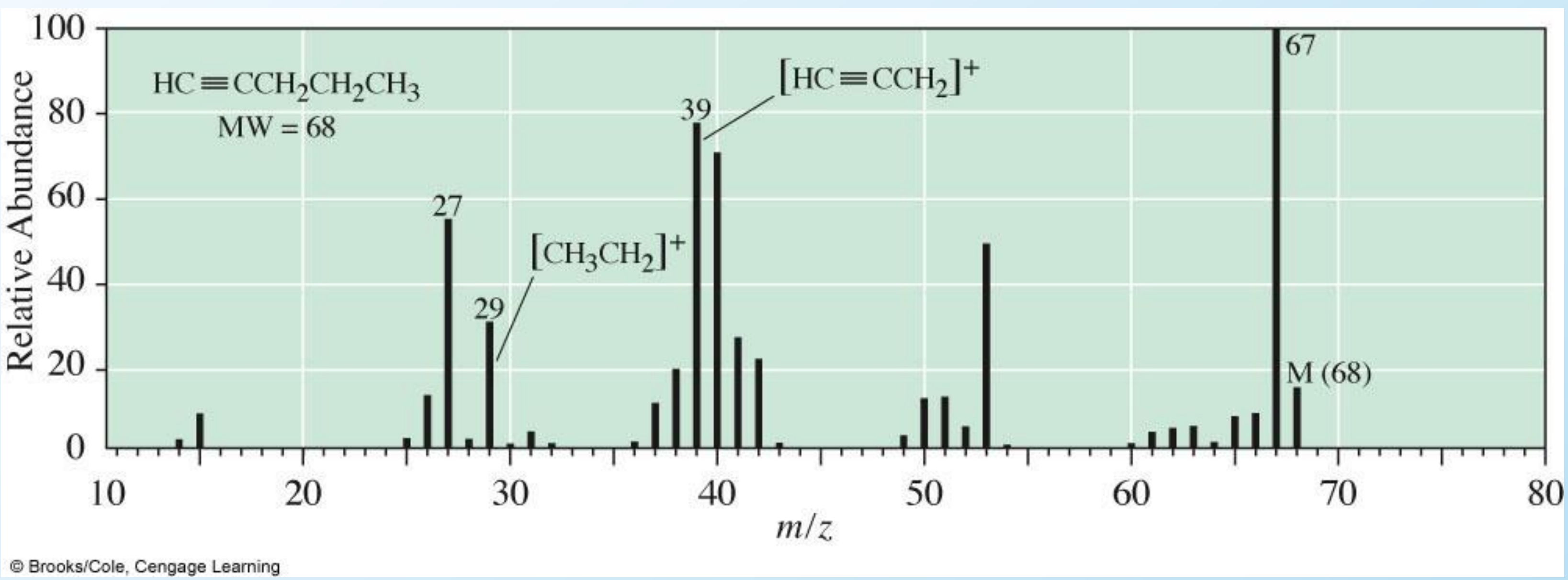


Alkynes

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

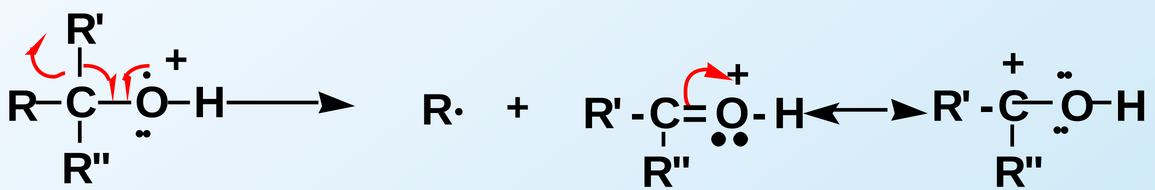
3-Propynyl cation (Propargyl cation)





Alcohols

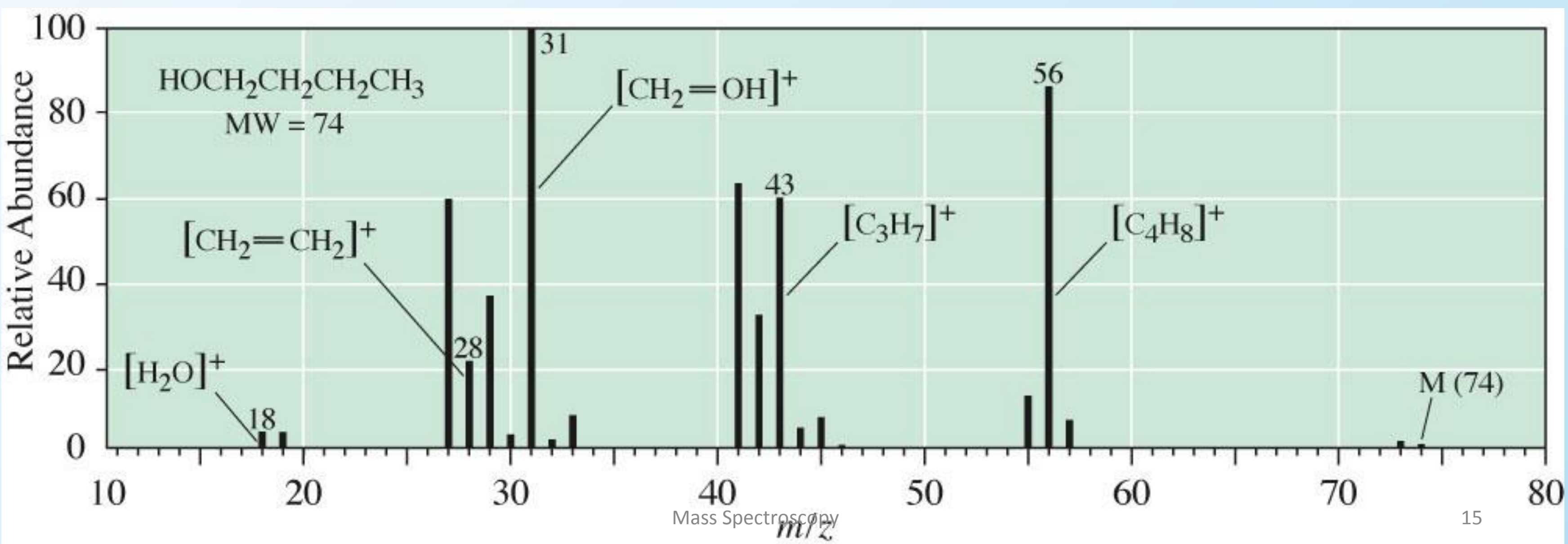
- The most common fragmentation patterns of alcohols is loss of H_2O to give a peak which corresponds to M-18.
- Another common pattern is loss of an alkyl group from the carbon bearing the OH to give a resonance-stabilized oxonium ion and an alkyl radical.



Molecular ion (a radical cation)

A radical

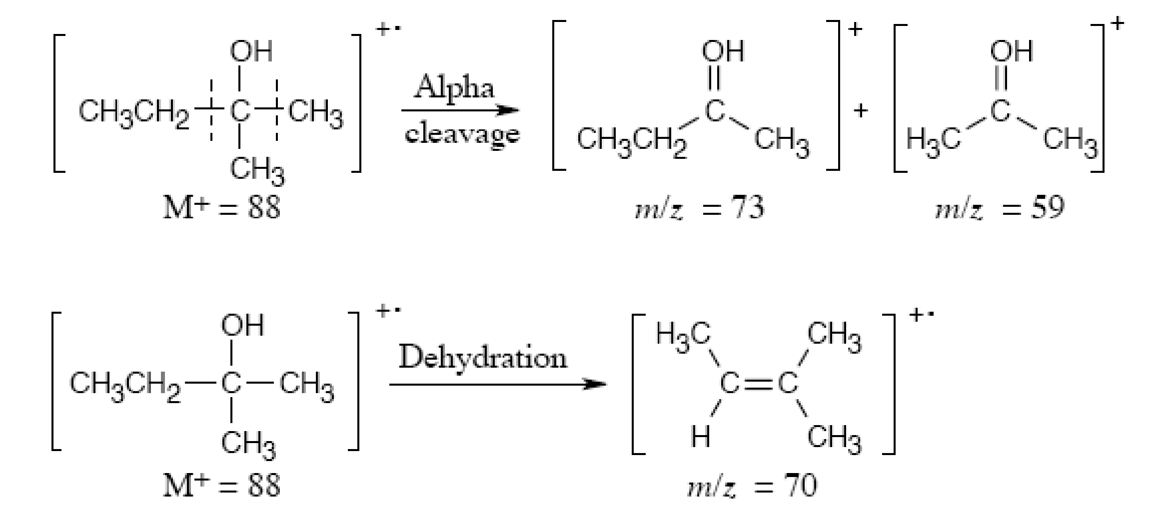
A resonance-stabilized oxonium ion



Problem

Propose structures for a compound that fits the following data: It is an alcohol with M^+ = 88 and fragments at m/z = 73, m/z = 70, and m/z = 59

Answer: We must first decide on the formula of an alcohol that could undergo this type of fragmentation via MS. We know that an alcohol possesses an O atom (MW=16), so that leads us to the formula $C_5H_{12}O$ for an alcohol with M^+ = 88, with a structure of:



One fragmentation peak at 70 is due to the loss of water, and alpha cleavage can result in m/z of 73 and 59.

Key Concepts

- Know how MS works
- Know about fragmentation patterns
- Know about base peak and molecular ion peak
- Be able to predict structure from fragmentation pattern and vice versa.