Mass Spectroscopy

Dr. Sapna Gupta

Introduction - Mass Spectroscopy

Mass spectrometry is our most valuable analytical tool for determining accurate molecular masses.

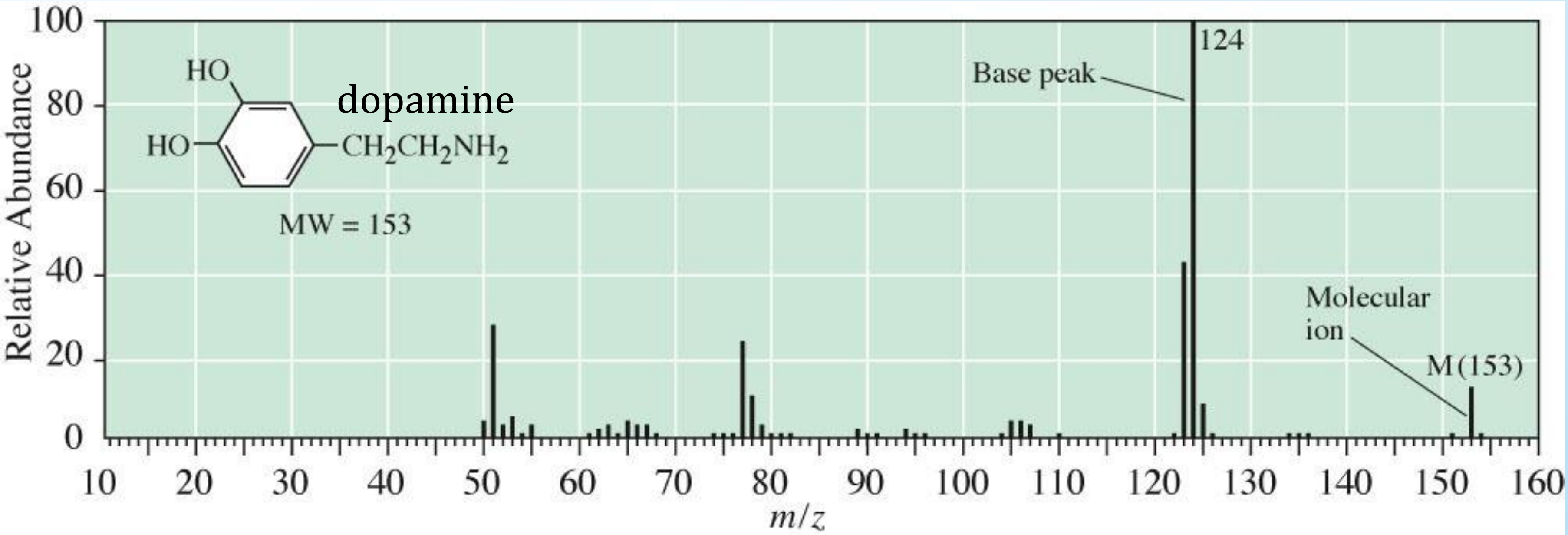
It is an analytical technique for measuring the mass-to-charge ratio (m/z) of ions in the gas phase.

It can also give information about structure.

RH	$\longrightarrow$	$RH^{+\bullet}$	+	e^-
organic molecule		Cation Radical		

The Mass Spectrum – A First Look

- 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+).



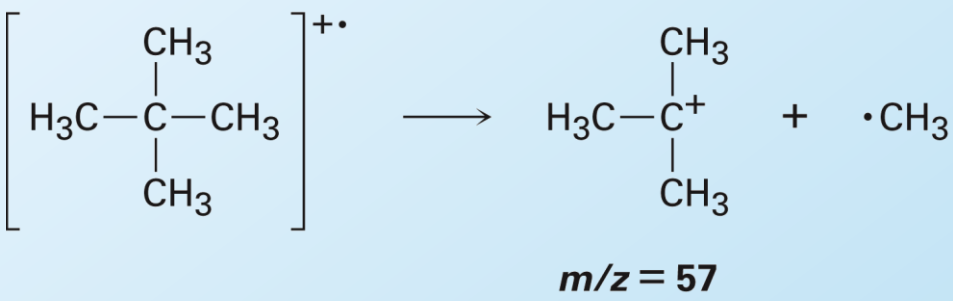
Theory – Mass Spectroscopy

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° < 3° < 3° allylic

- 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.



Isotope Use in Mass Spectroscopy

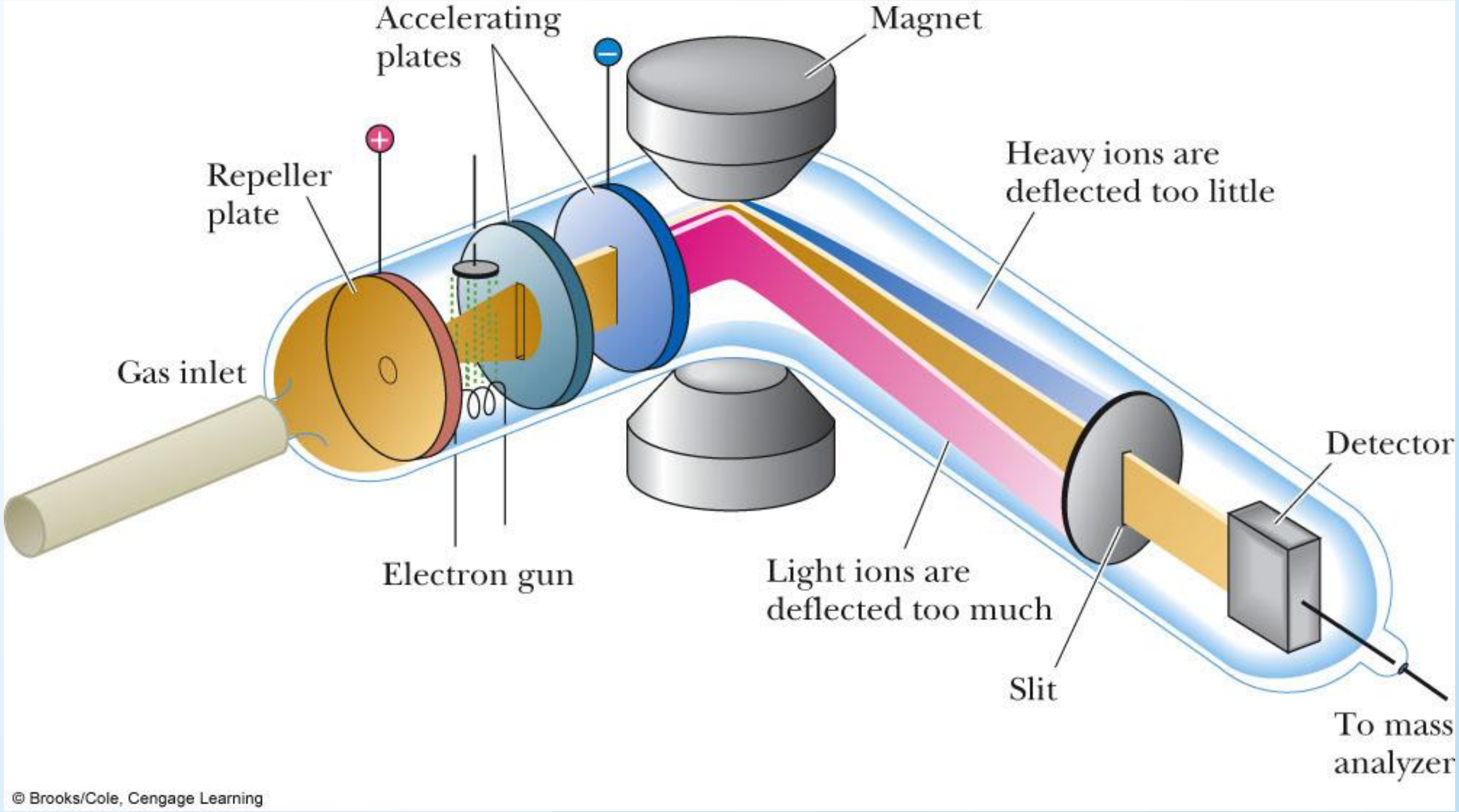
Virtually all elements common to organic compounds are mixtures of isotopes. All isotopes will show up on MS.

Element	Atomic Weight	Isotope	Mass (amu)	Relative Abundance
Hydrogen	1.0079	^{1}H ^{2}H	1.00783 2.01410	100 0.016
Carbon	12.011	^{12}C ^{13}C	12.0000 13.0034	100 1.11
Nitrogen	14.007	^{14}N ^{15}N	14.0031 15.0001	100 0.38
Oxygen	15.999	^{16}O ^{18}O	15.9949 17.9992	100 0.20
Sulfur	32.066	^{32}S ^{34}S	31.9721 33.9679	100 4.40
Chlorine	35.453	^{35}Cl ^{37}Cl	34.9689 36.9659	100 32.5
Bromine	79.904	^{79}Br ^{81}Br	78.9183 80.9163	100 98.0

The Mass Spectrophotometer

The mass spectrophotometer does the following:

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



Interpretation of MS

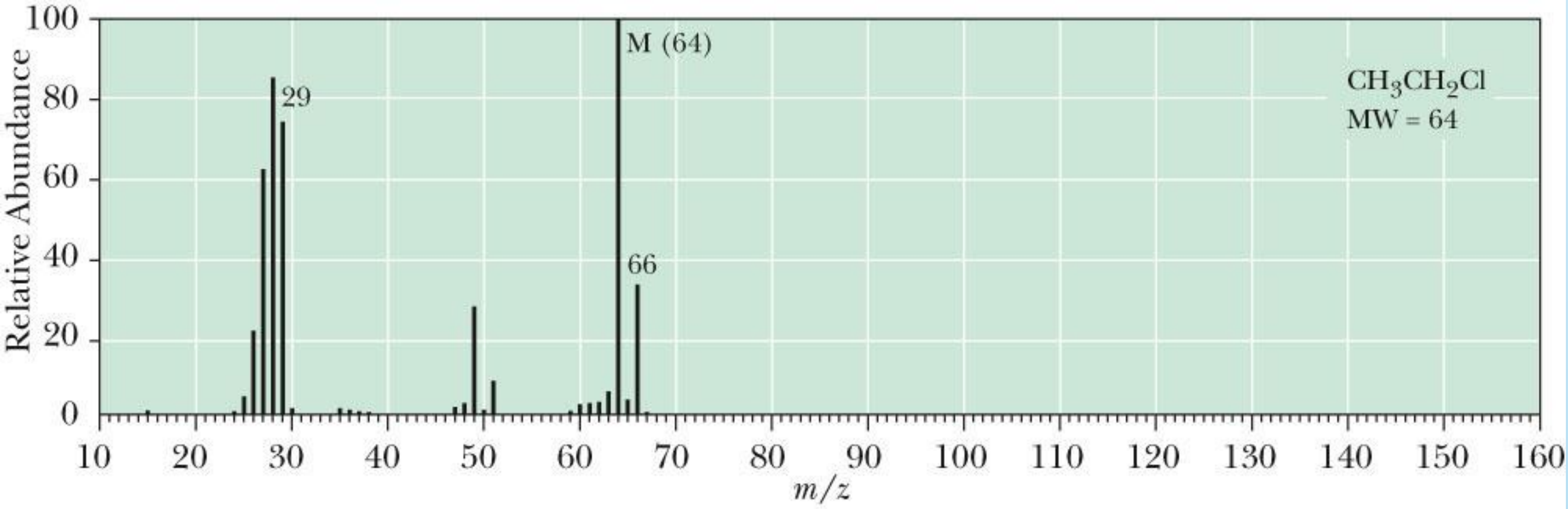
1. The only elements to give significant M + 2 peaks are Cl and Br.
   If no large M + 2 peak is present, these elements are absent.
2. Is the mass of the molecular ion odd or even?
3. Nitrogen Rule: If a compound has:
   - zero or an even number of nitrogen atoms, its molecular ion will have an even m/z value.
   - an odd number of nitrogen atoms, its molecular ion will have an odd m/z value.

M+2 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.

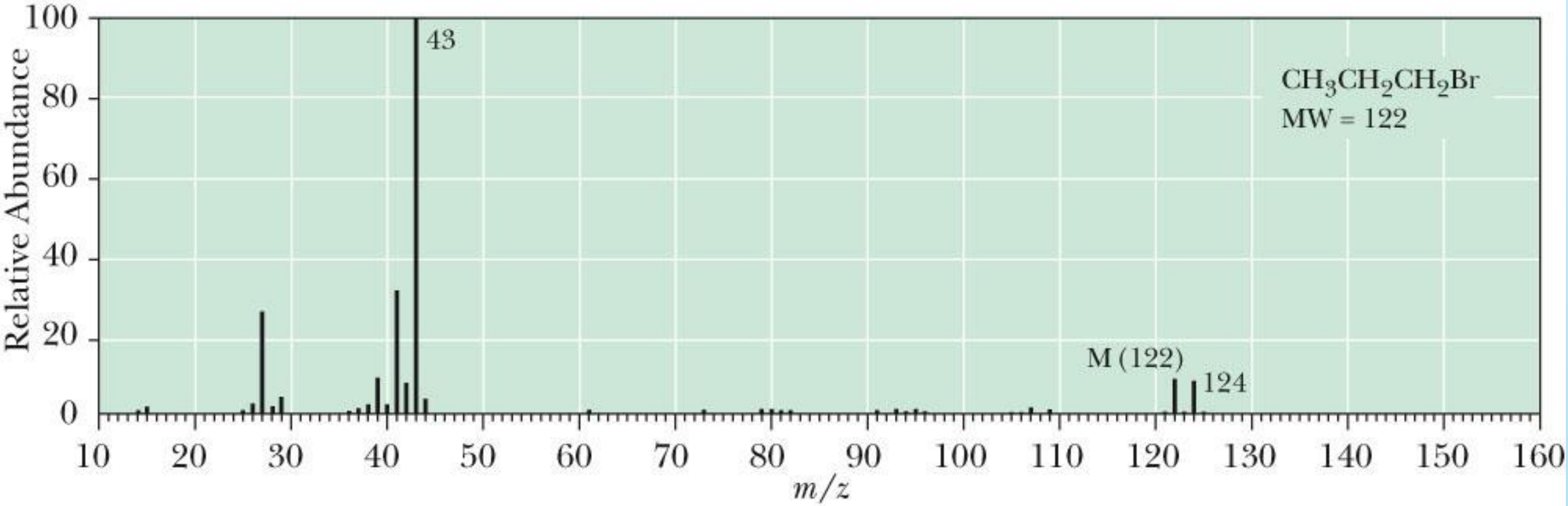
A ratio of **M to M + 2 of approximately 3:1** indicates the presence of a single chlorine in a compound, as seen in the MS of chloroethane.



M+2 Peaks

Bromine in nature is 50.7% ^{79}Br and 49.3% ^{81}Br.

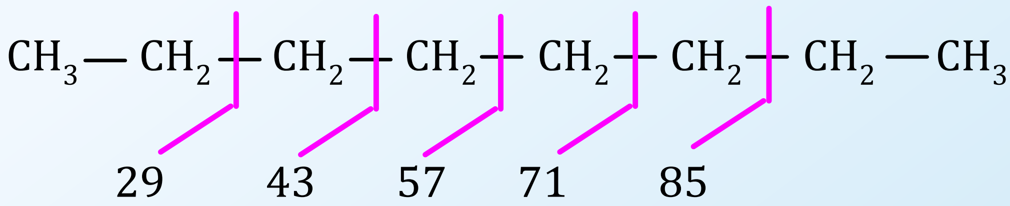
A ratio of M to M + 2 of approximately 1:1 indicates the presence of a single bromine atom in a compound, as seen in the MS of 1-bromopropane.

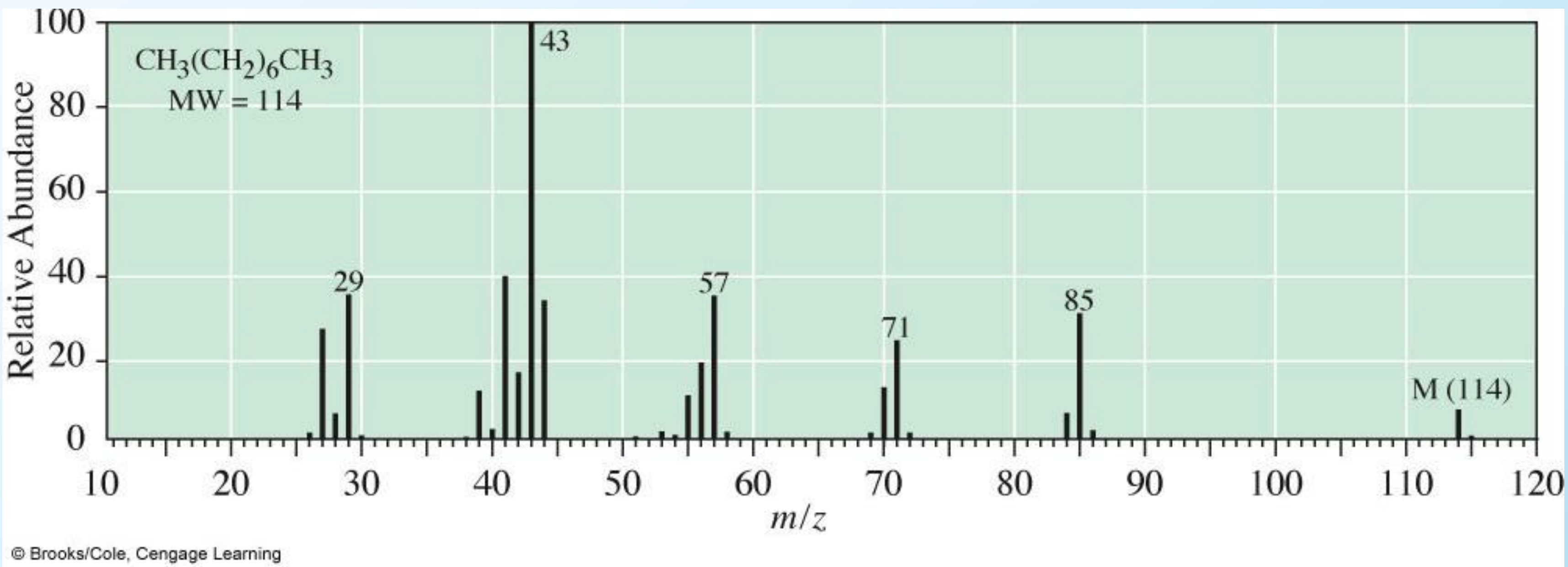


MS - Alkanes

Mass spectrum of Octane.

- Note that there is no methyl cation peak.
- The base peak is for 43 which is propyl cation $C_3H_7^+$

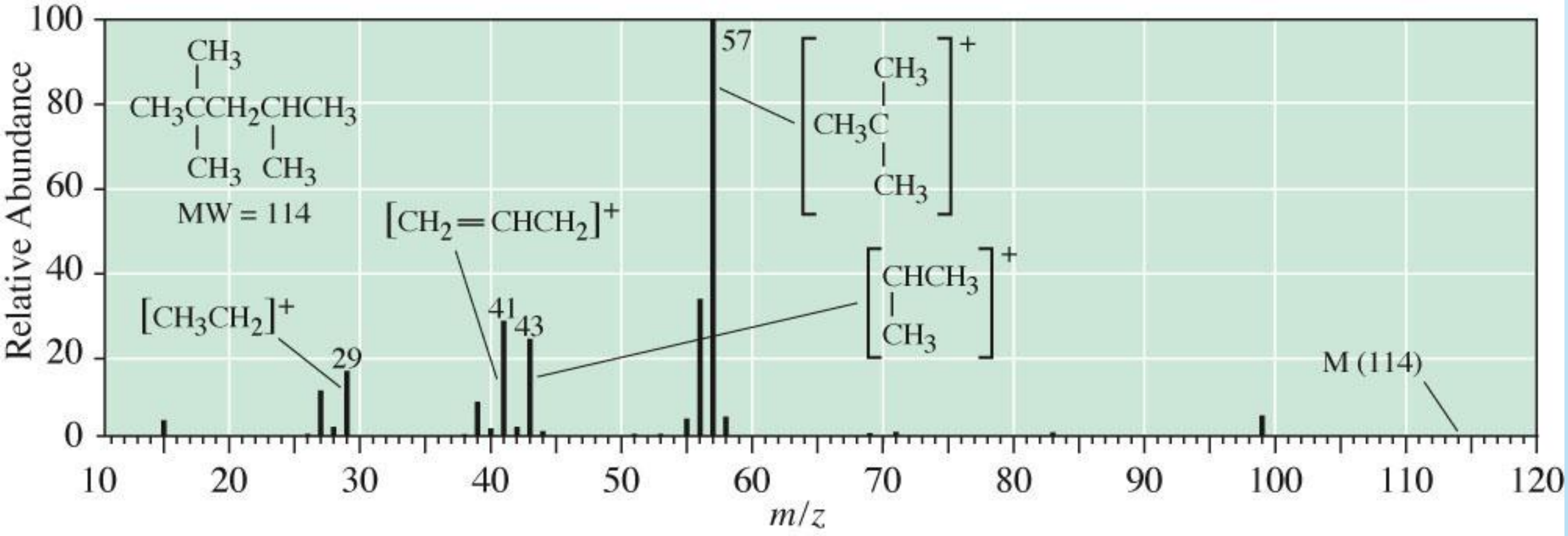




MS - Alkanes

Mass spectrum of 2,2,4-trimethylpentane.

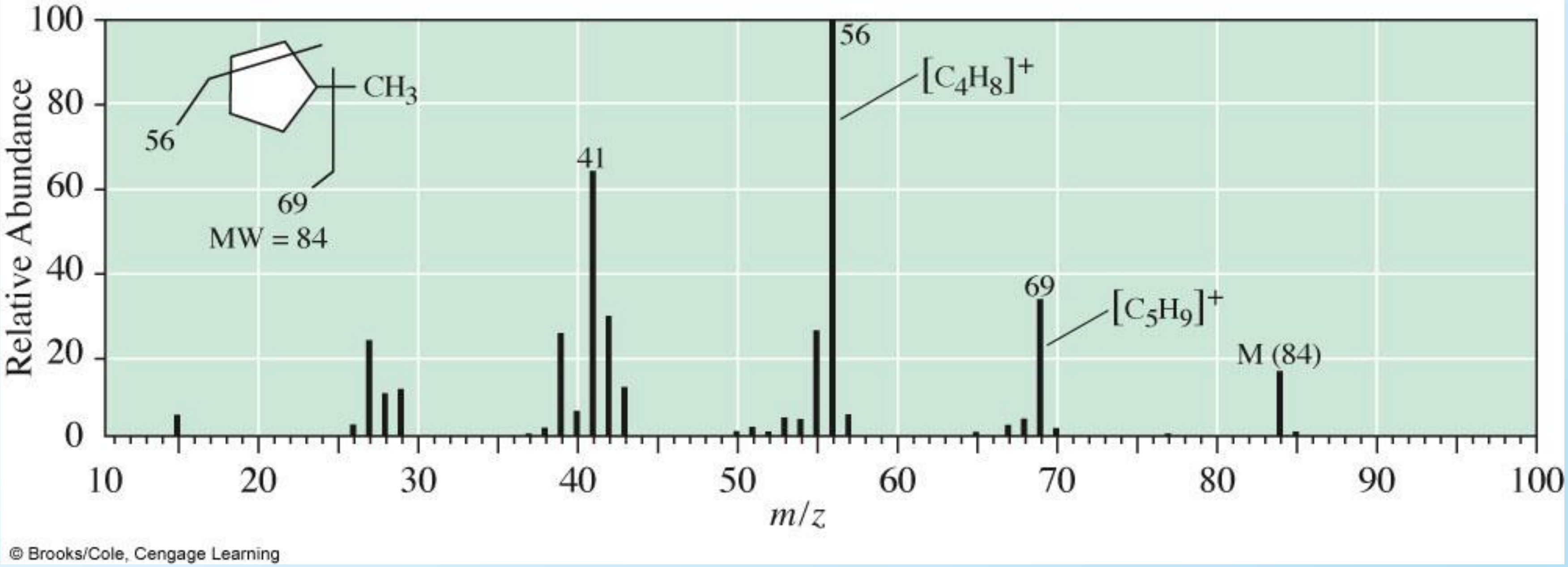
- Note the base peak is 57 for t-butyl cation; the M+ is almost absent as everything has fragmented.
- The alkene cation is a result of rearrangement.



MS - Alkanes

Mass spectrum of methylcyclopentane.

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

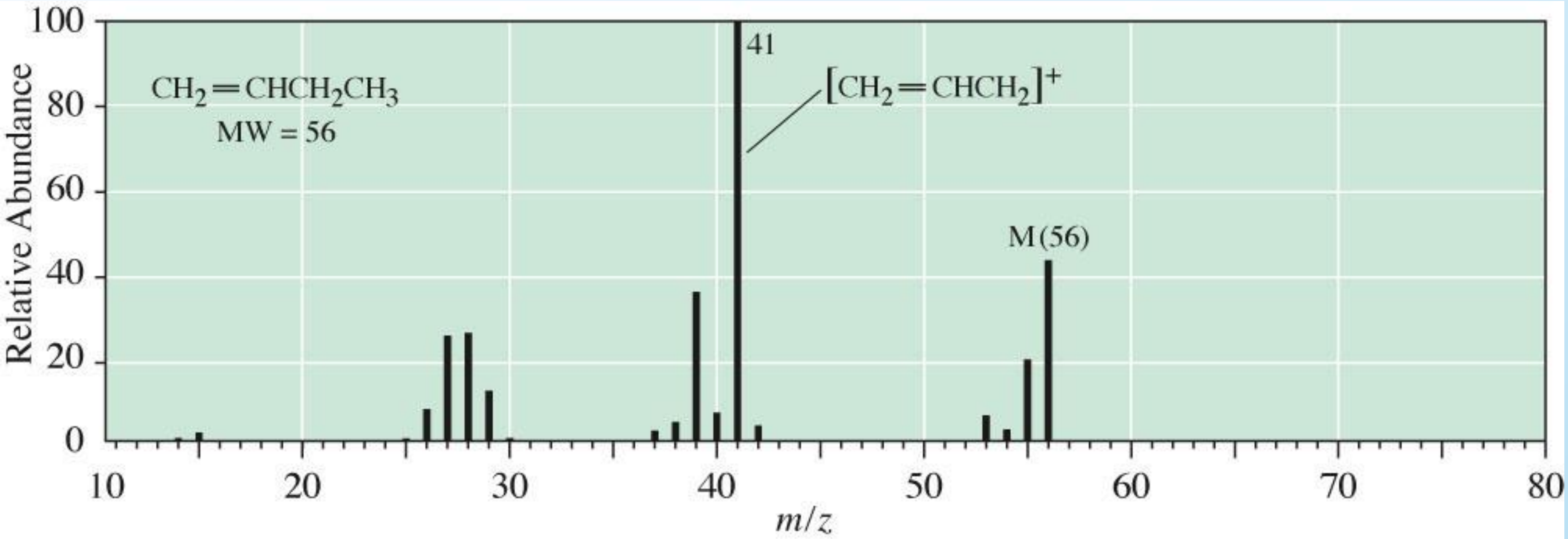


MS - Alkenes

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

Below is the example of 1-butene. Note that the fragmentation does not indicate that there are 5 carbons in the original molecule. Molecules fragment in different ways and these are examples of two fragments.

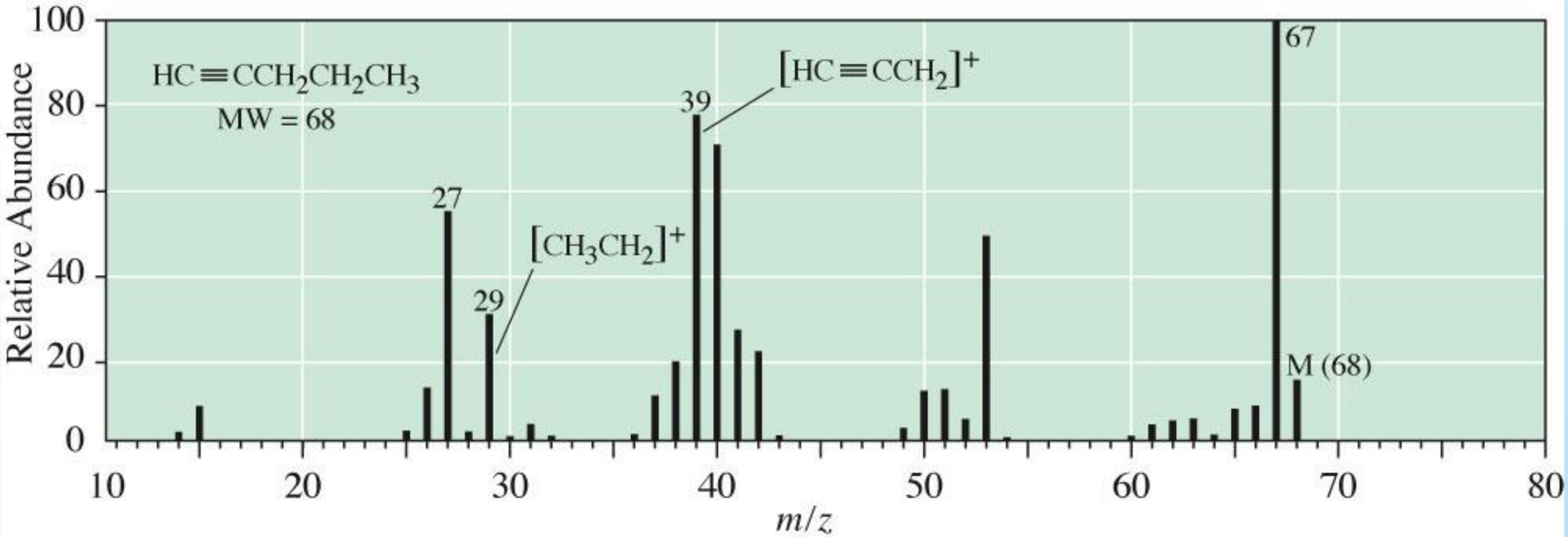
$$[CH_2{=}CHCH_2CH_3]^{\bullet +} \longrightarrow CH_2{=}CHCH_2^{+} + {}^{\bullet}CH_2CH_3$$



MS - Alkynes

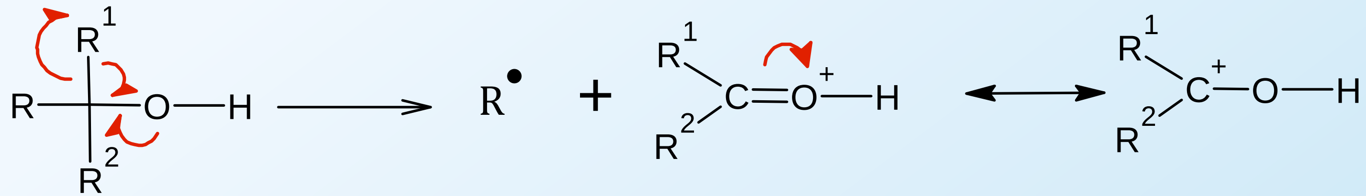
Alkynes typically show a strong molecular ion peak and cleave readily to form the resonance-stabilized propargyl cation or substituted propargyl cations.

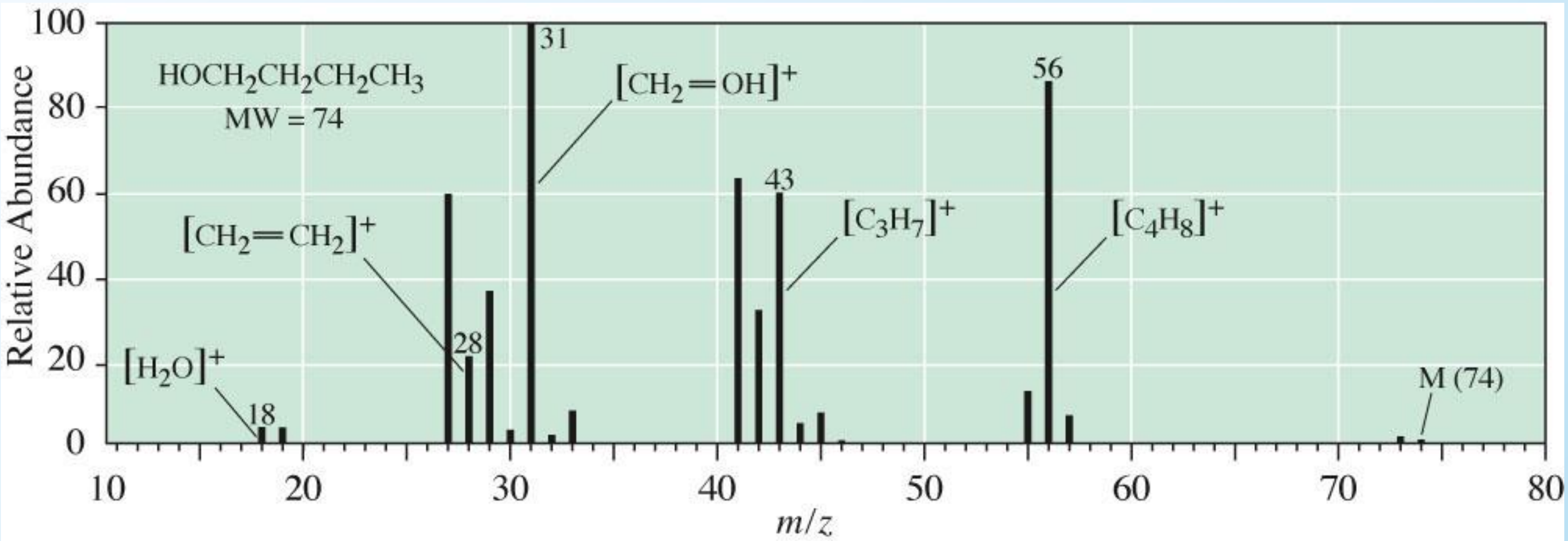
Below is the MS for 1-pentyne.



MS - 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.
- Below is the MS for 1-butanol.

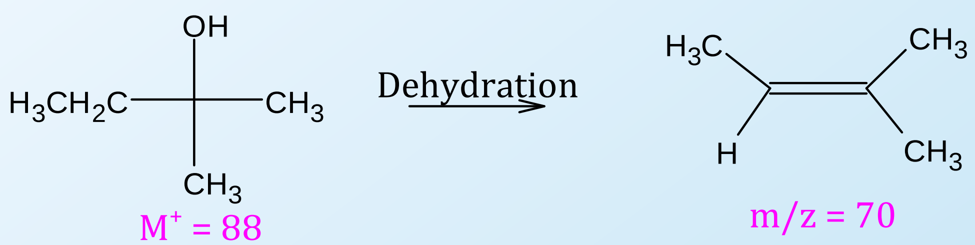


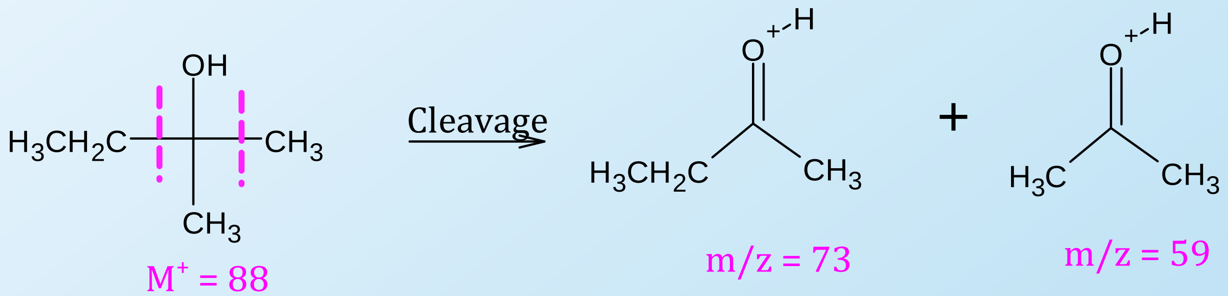


<u>Solved Problem</u>: Propose structures for a compound that fits the following data: It is an alcohol with $M^+ = 88$ and fragments at $m/z = 73$, $m/z = 70$, and $m/z = 59$

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.