# 344 | Organic Chemistry Laboratory

## Introduction to Mass Spectrometry and GC-MS

Main topics

- Overview of gas chromatography (GC)

- Generation of molecular ions

- Fragmentation patterns

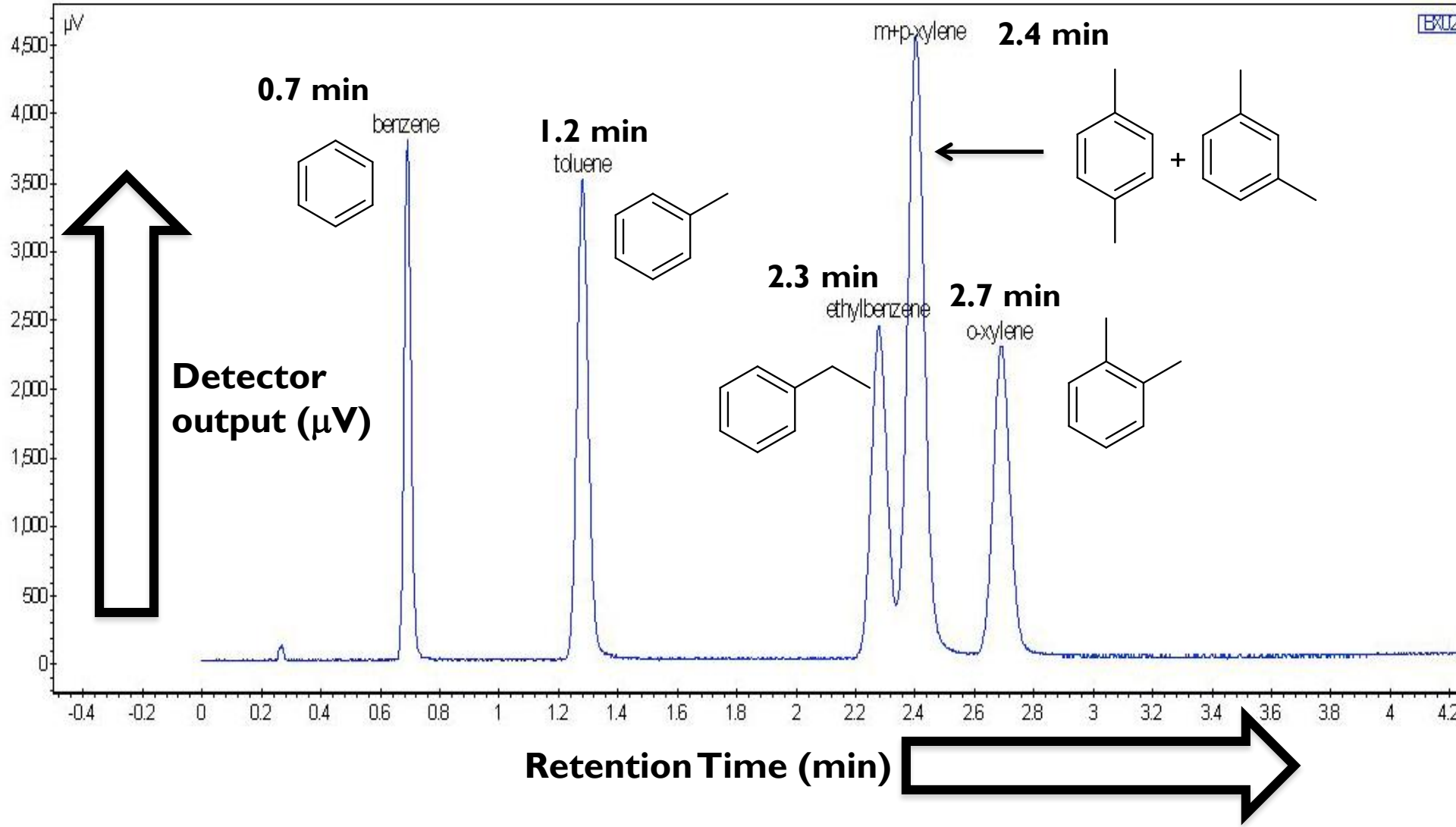
**Chromatography** – separation of a mixture into individual components

**Gas Chromatography (GC)** coupled to EI-MS

Organic sample needs to be sufficiently volatile to vaporize

**Stationary phase** = packed column **Mobile phase** = He

# GC trace – mixture of aromatic hydrocarbons (BTEX)

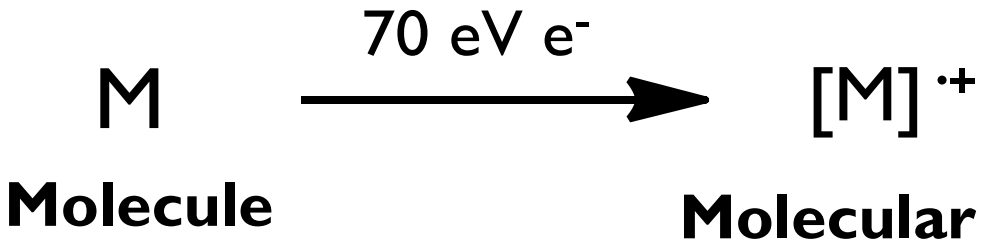



**GC-MS** - a mass spectrum is obtained for each compound as it elutes from the GC

# Electron Impact-Mass Spectrometry (EI-MS)

**Uses high energy electron beam (70 eV), sample in gas phase**

**Ionization energy for most organic molecules ~8-15 eV**




**Molecule** → **Molecular Ion**

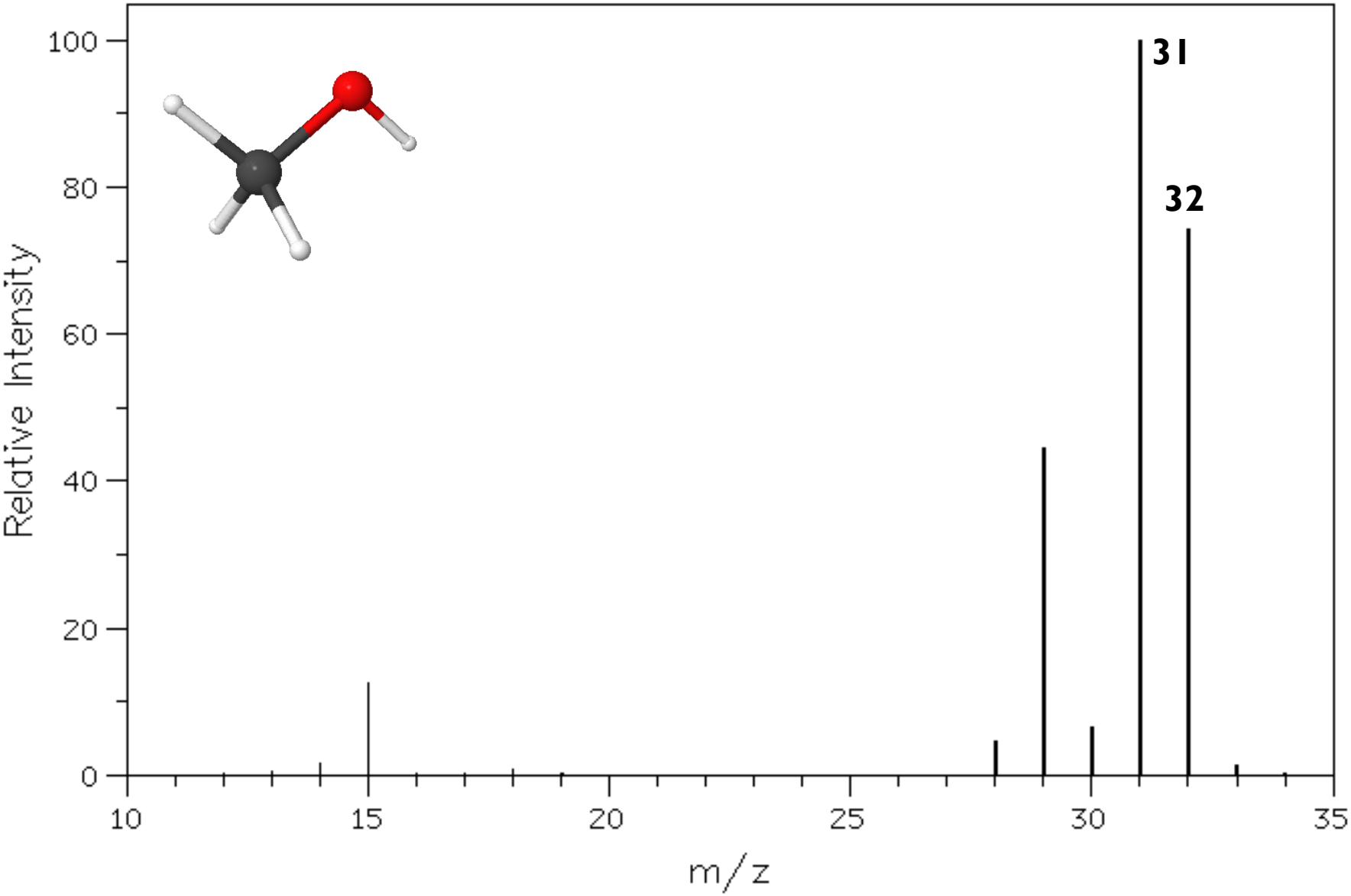
**$[M]^{\cdot+}$ gives the molecular mass in amu (m) of M**

**bond breaking** | **bond forming**

## Molecular Fragments

**Information on connectivity of the molecule, isotopes**

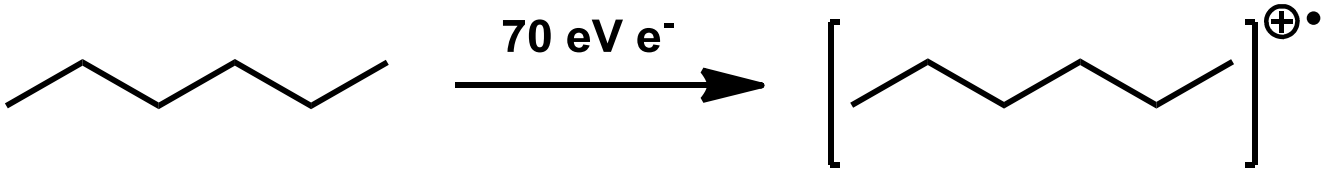
# EI-Mass Spectrum of Methanol $CH_3OH$



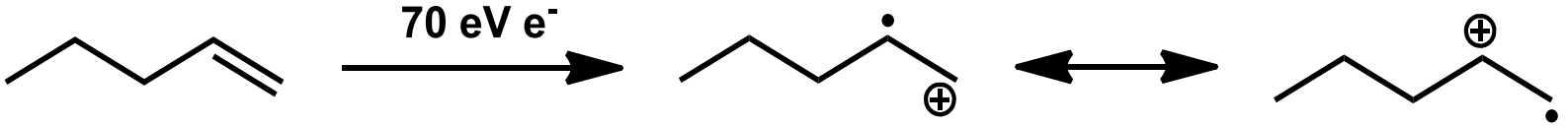
# Generation of $[M]^{\cdot+}$

From where on the molecule is the electron most likely to be removed?

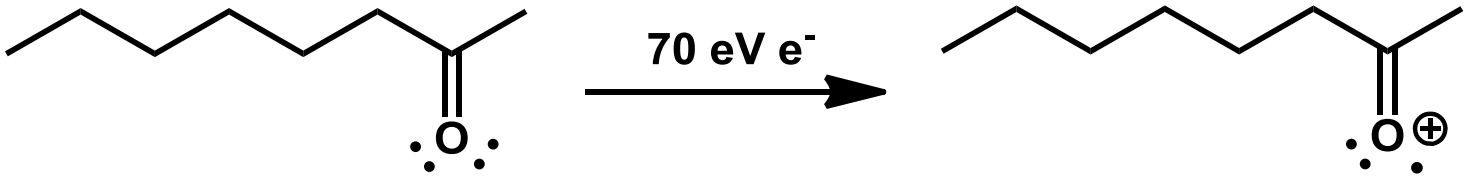
**Alkanes – σ bond**



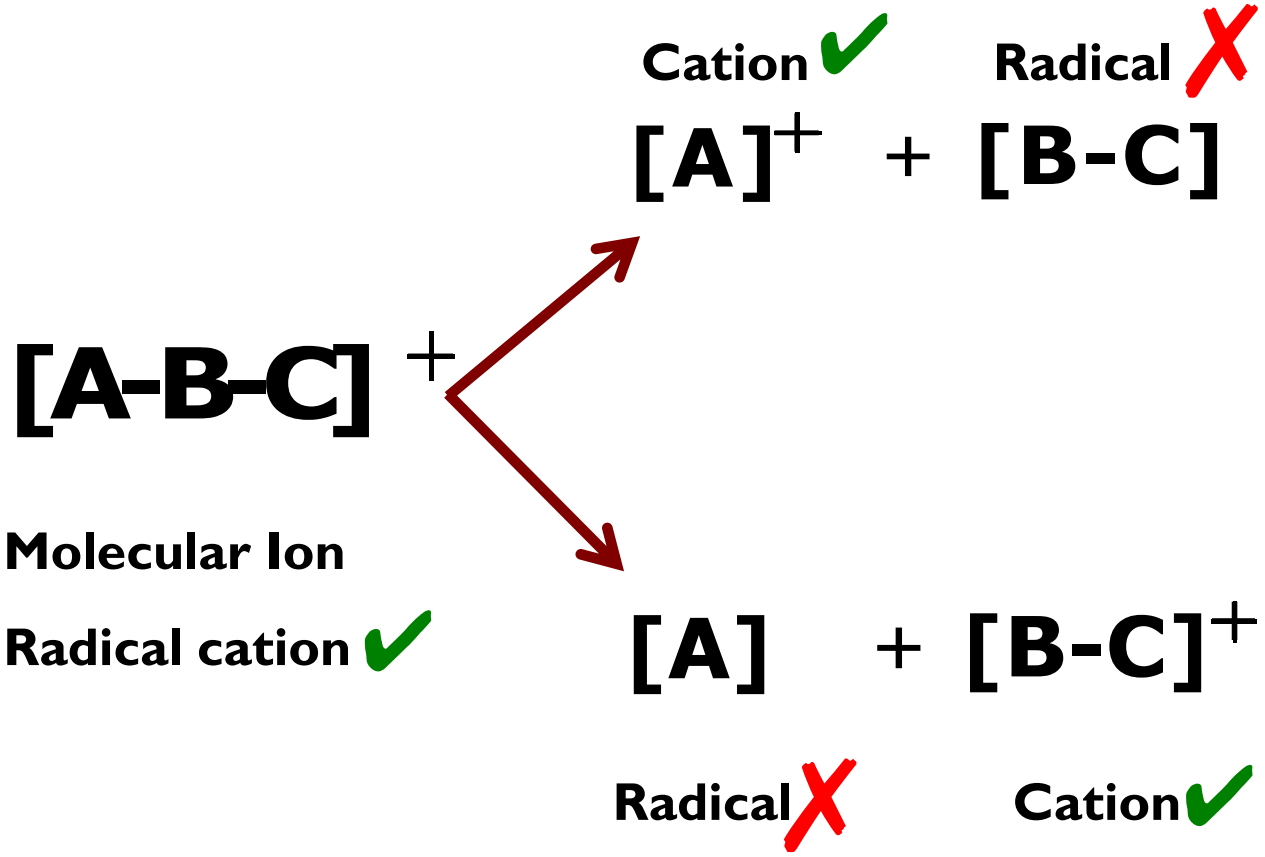

**Alkenes – π bond**




**Heteroatom compounds (O, N, S, etc.) – non-bonding lone pairs**



# Generation of fragments from $[M]^{\bullet+}$



# Generation of fragments from $[M]^{\bullet+}$

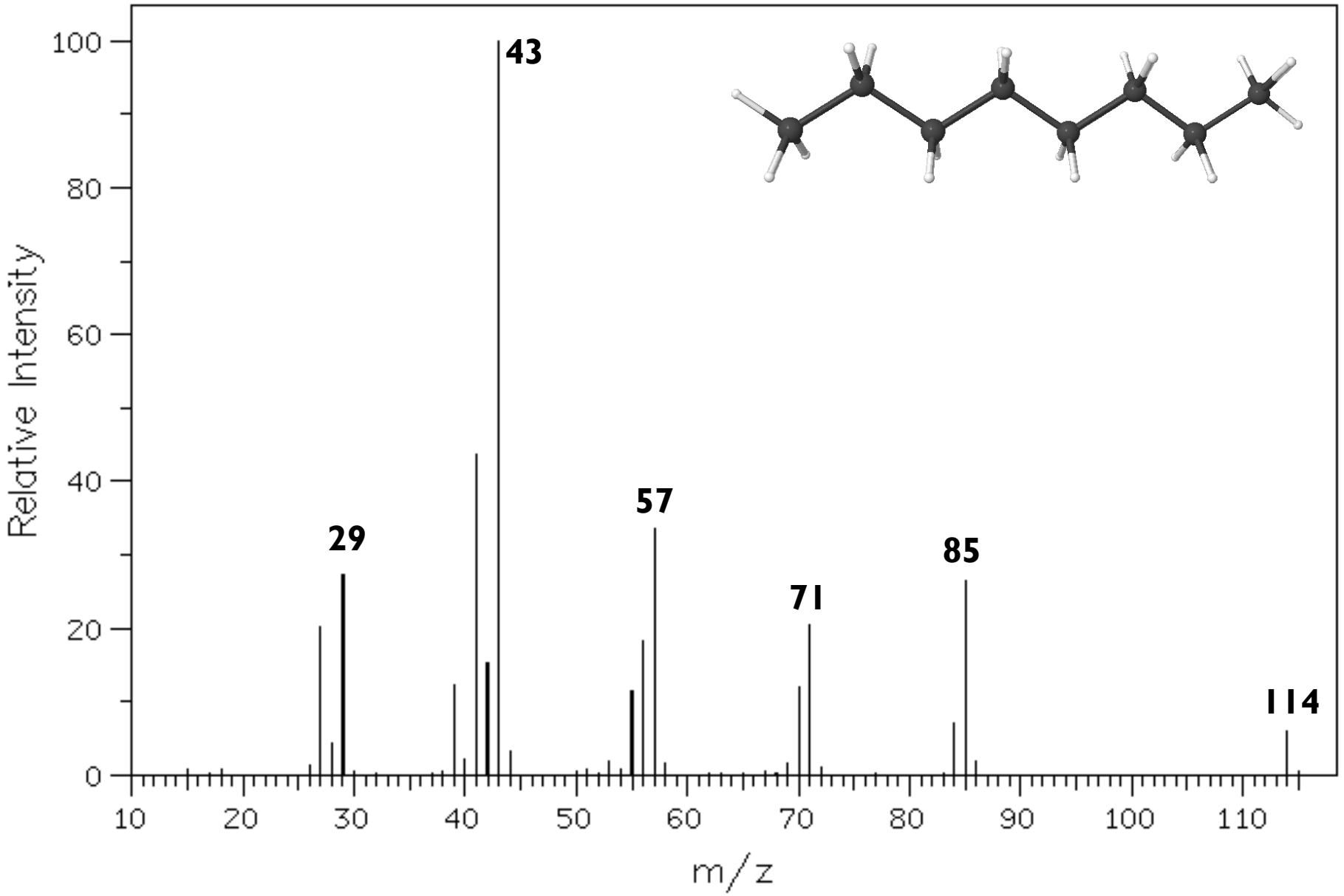

**Molecular Ion**

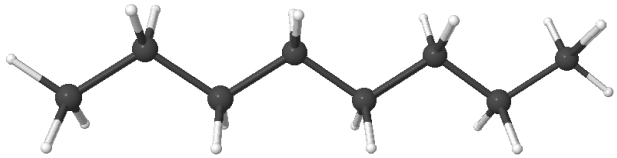
**Radical cation** ✔

**Only CATIONS and RADICAL CATIONS are detected by EI-MS.**

**Radicals and other neutral molecules (CO, $H_2O$, alkenes) <u>NOT</u> detected by EI-MS.**

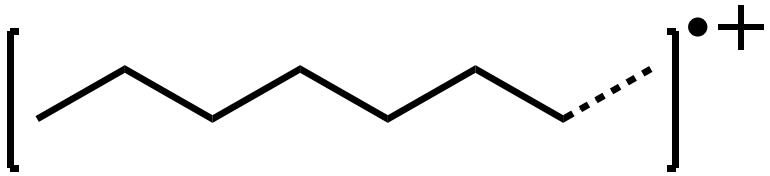
# EI-Mass Spectrum of Octane $C_8H_{18}$

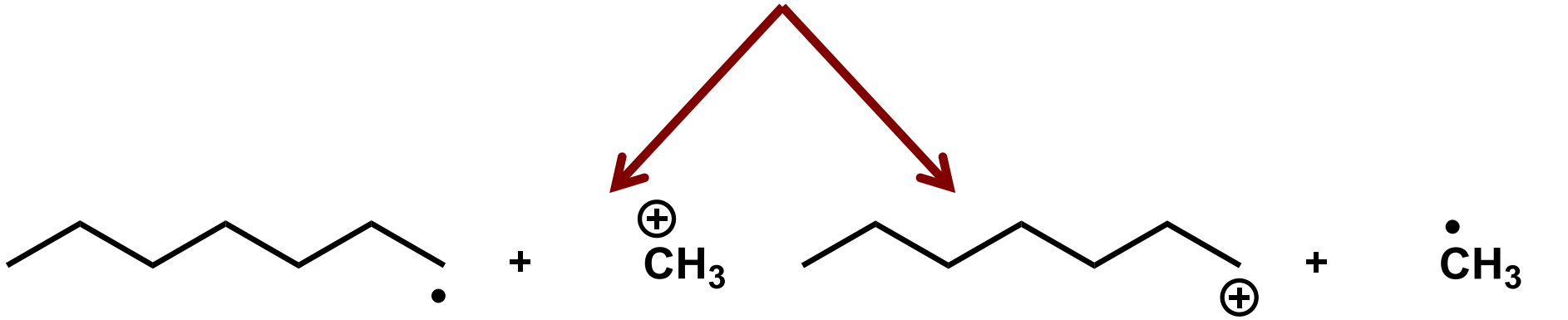




Octane

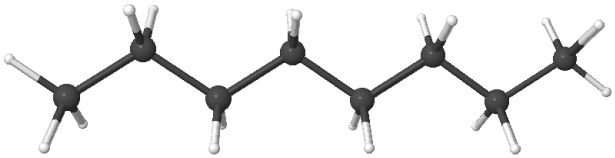
MW = 114 g/mol






**Both fragmentations involve formation of a Me radical or a Me cation**

# 3º > 2º > 1º > Me



Octane

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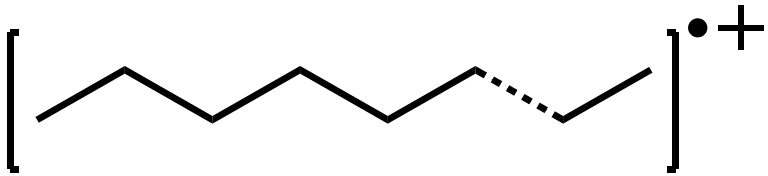
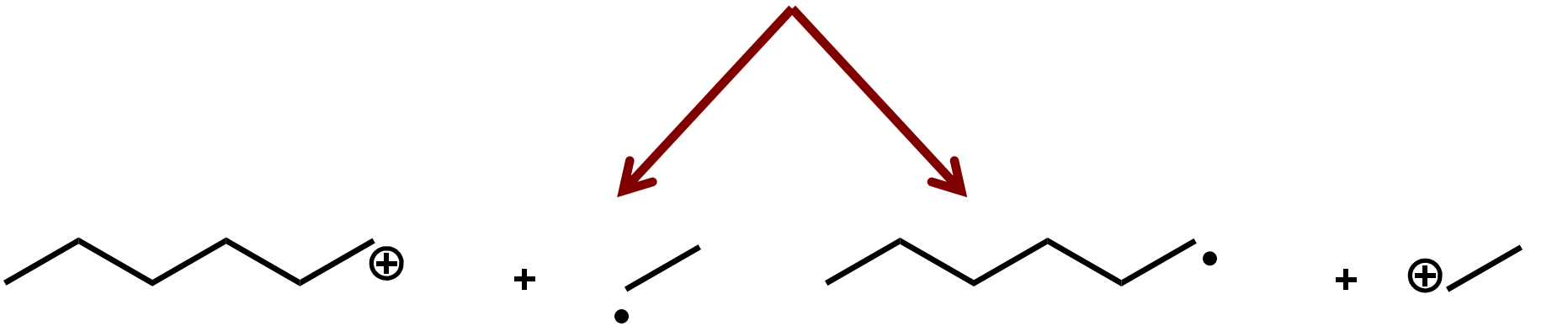
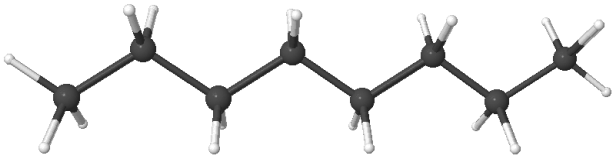




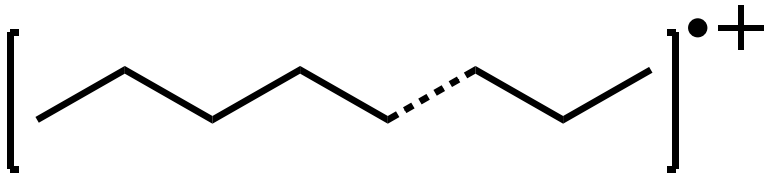
*m/z* = 85 ✔ mass = 29 mass = 85 ✔ *m/z* = 29

**Stability of cation and radical is important**

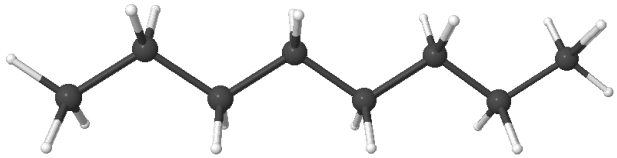


Octane

MW = 114 g/mol



*m/z* = 71 ✔ + mass = 43 mass = 71 + ✔ *m/z* = 43



Octane

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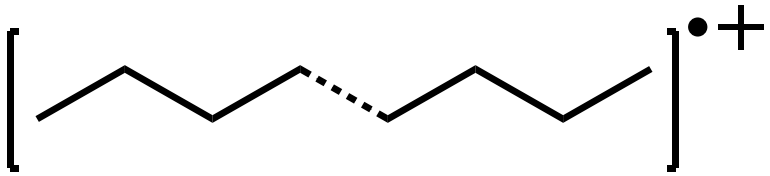
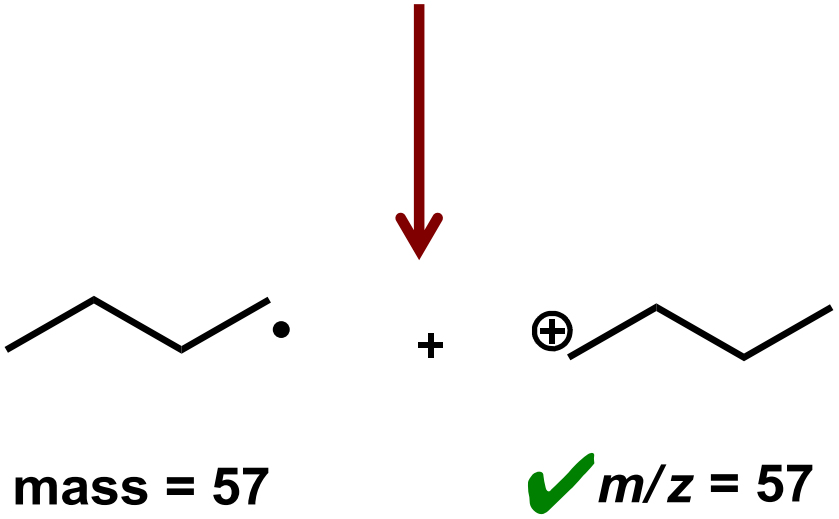
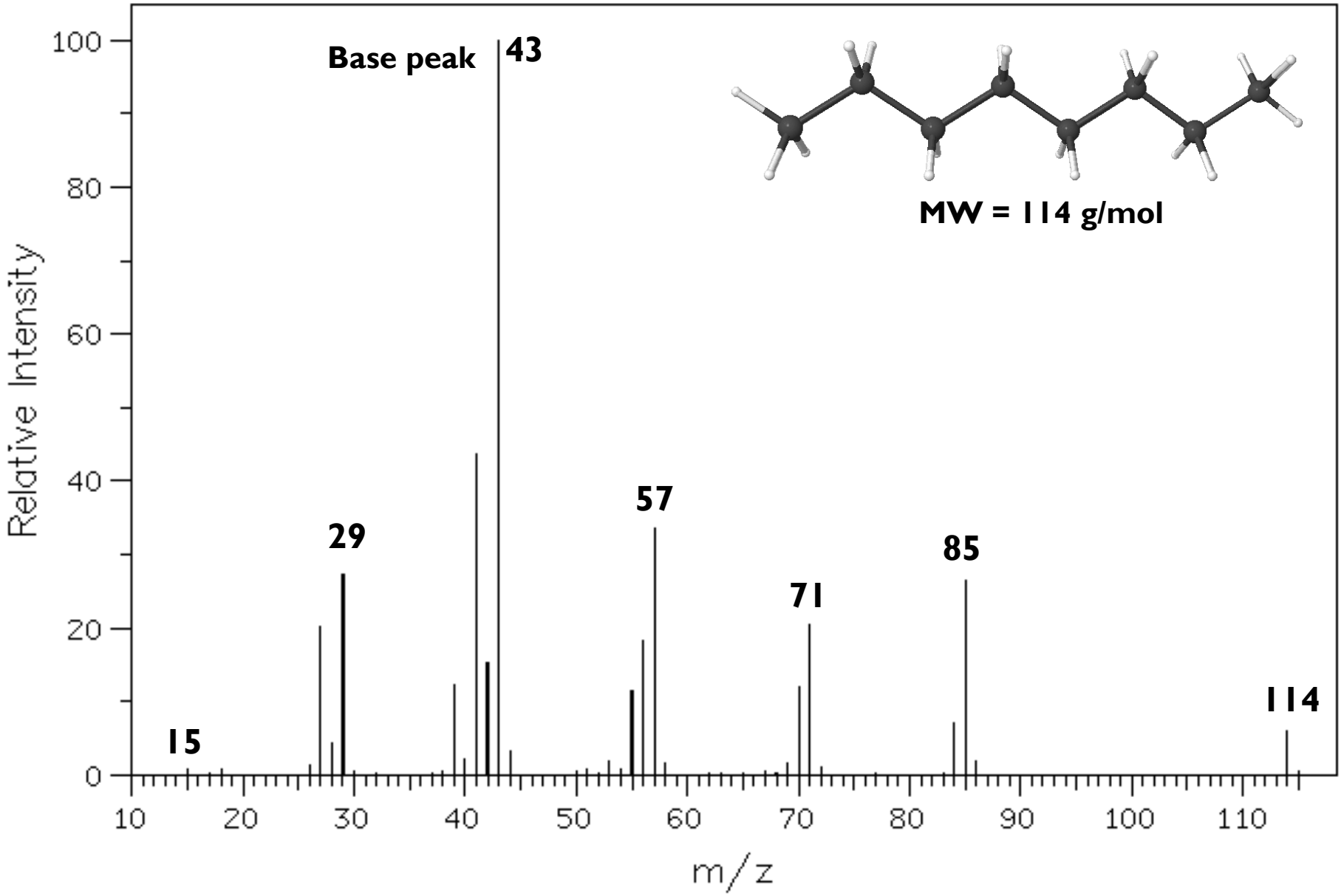




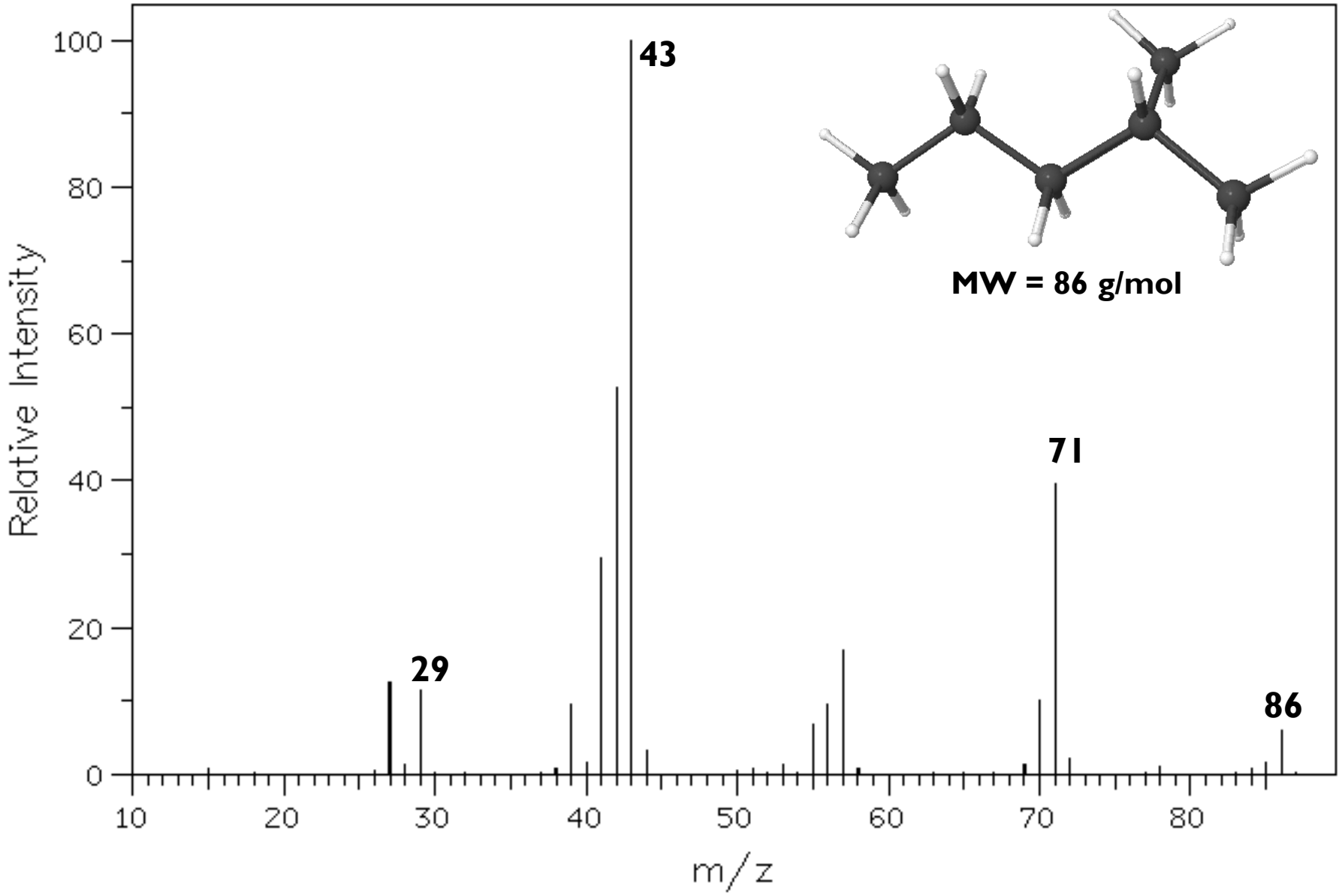

**Stability of cation and radical is important.**

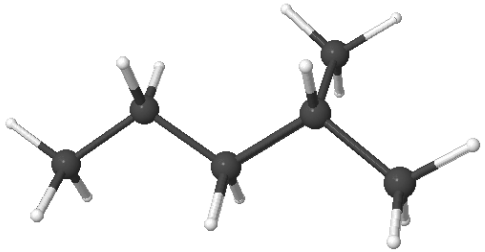
**Fragmentations involving formation of a Me species are disfavored.**

# EI-Mass Spectrum of Octane $C_8H_{18}$



# EI-Mass Spectrum of 2-methylpentane



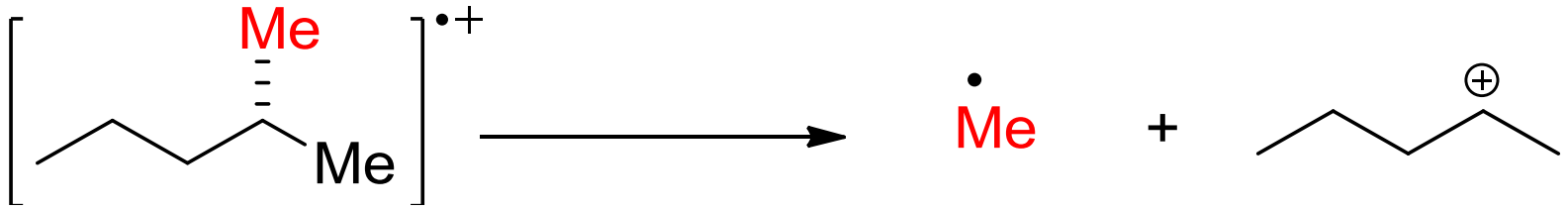


**2-Methylpentane**

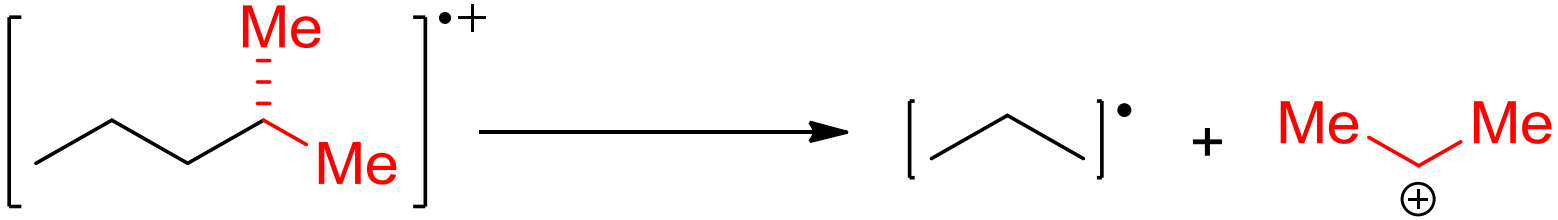
**MW = 86 g/mol**

**m/z = 43 forms readily and is persistent in the chamber.**

**m/z = 71 may form readily, but fragments more rapidly.**



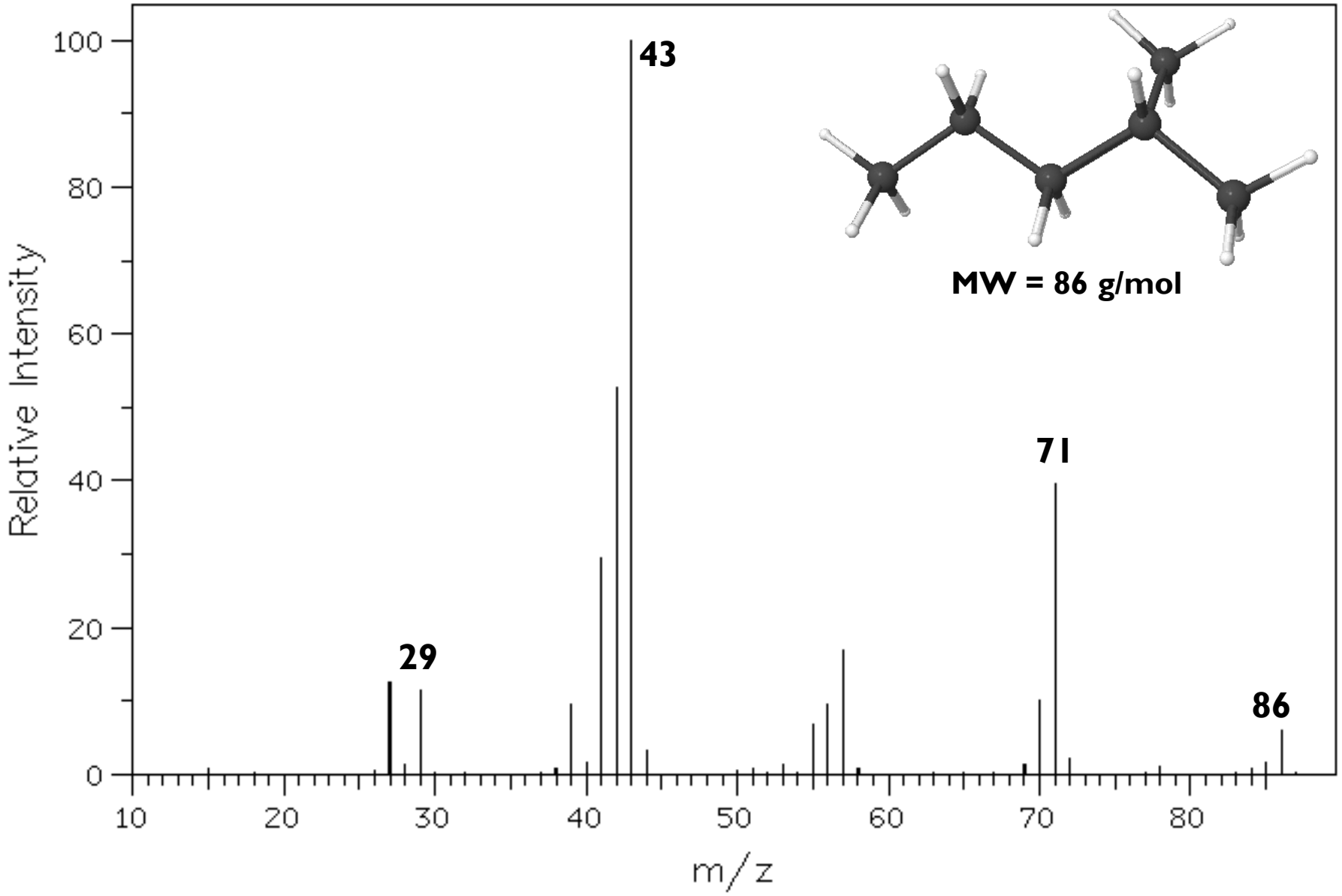

**m/z = 86** **mass = 15** **m/z = 71**




**m/z = 86** **mass = 43** **m/z = 43**

**Branched alkanes fragment either side of the branch point(s).**

# EI-Mass Spectrum of 2-methylpentane



# Isotope patterns

Atoms exist as isotopes (different # neutrons, same # protons)

$^{12}C$ is most abundant isotope of carbon

~1.08 % of C-atoms in any sample are $^{13}C$ isotope (NMR active, useful)

~0.016% of H-atoms in any sample are $^{2}H$ isotope (D)

~0.38% of N-atoms in any sample are $^{15}N$ isotope

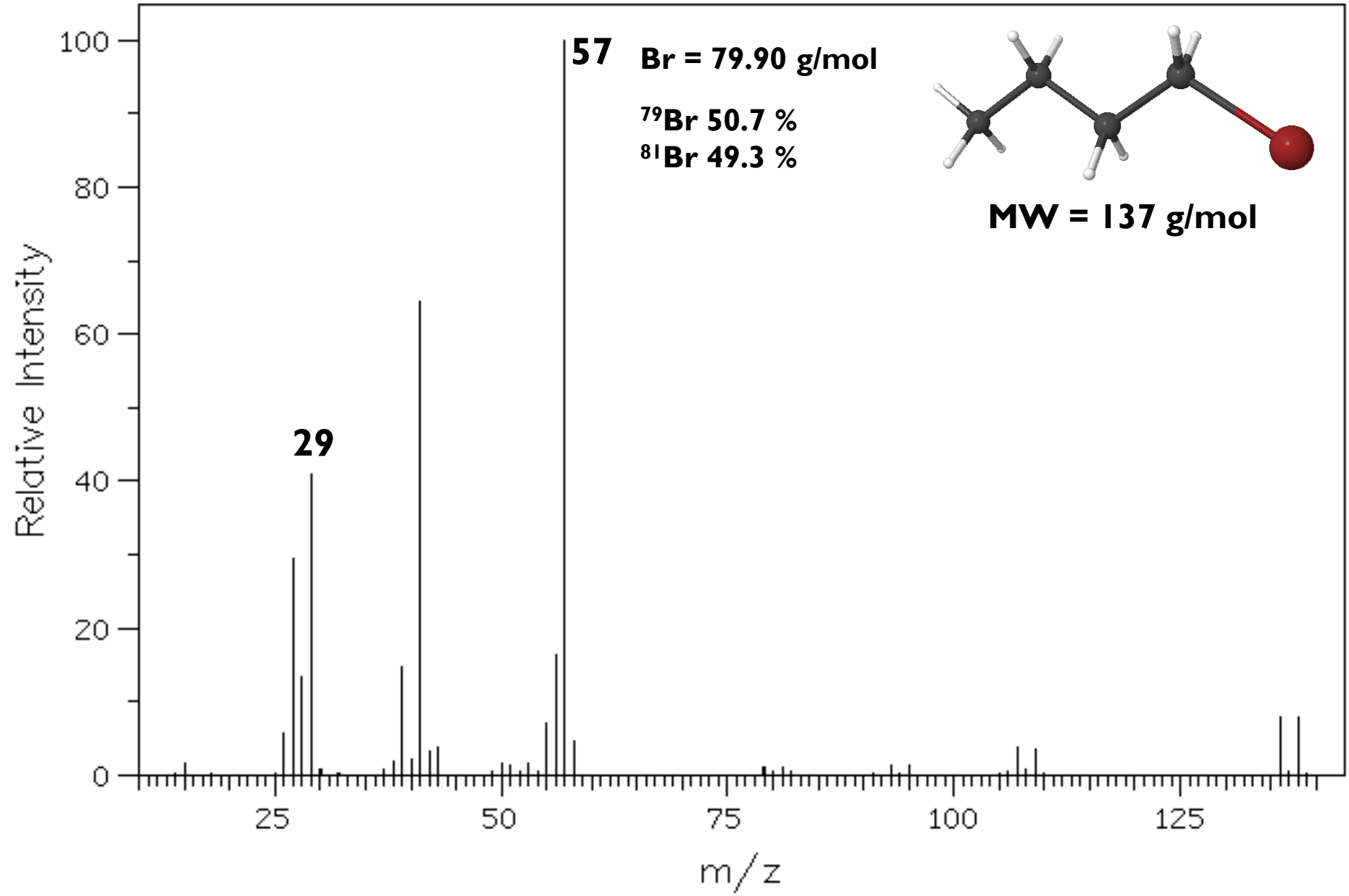
**Atomic mass Br = 79.90 amu**

**$^{79}$Br 50.7 %  $^{81}$Br 49.3 %  ~1:1 ratio of $^{79}$Br:$^{81}$Br isotopes**

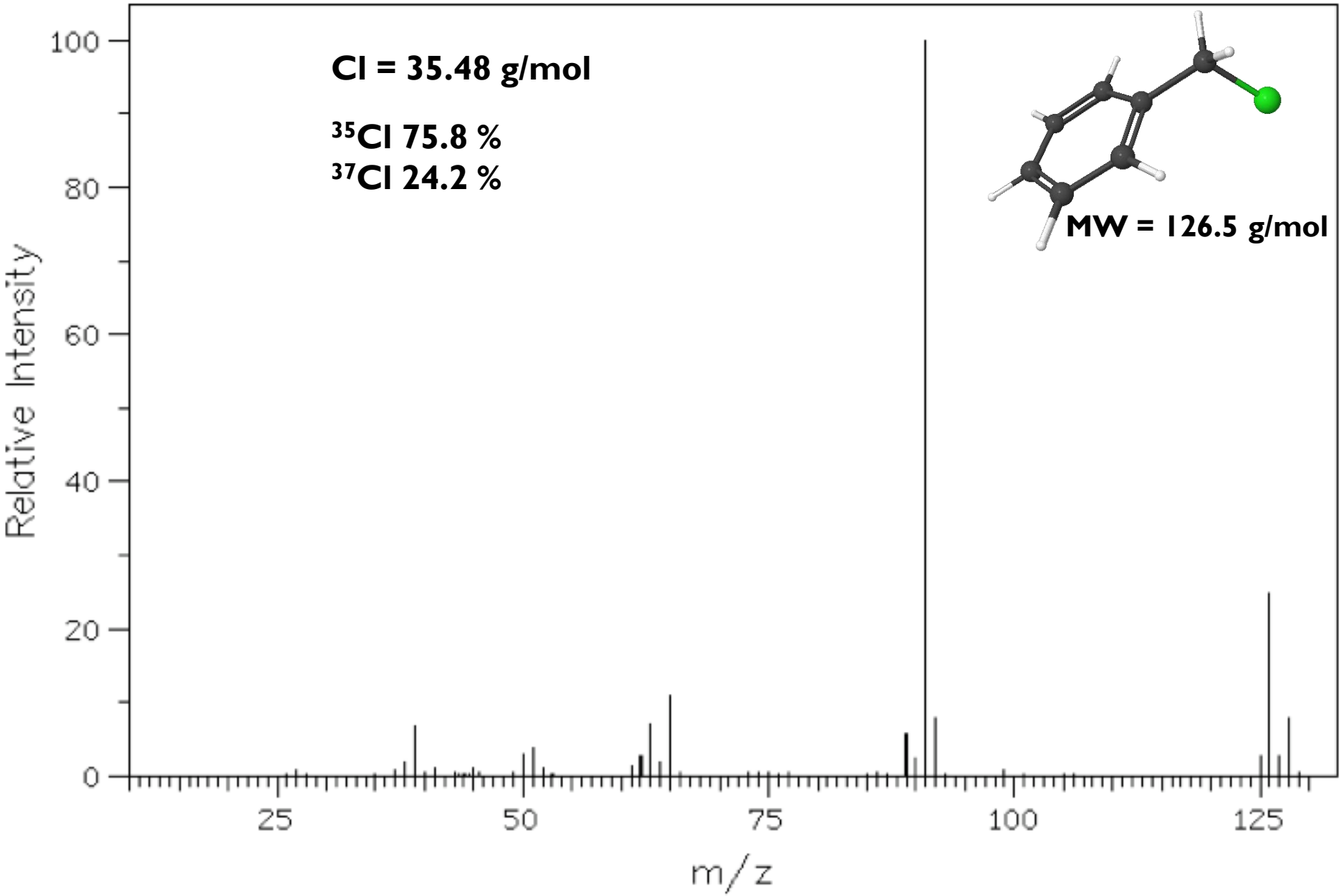
**Atomic mass Cl = 35.48 amu**

**$^{35}$Cl 75.8 %  $^{37}$Cl 24.2 %  ~3:1 ratio of $^{35}$Cl:$^{37}$Cl isotopes**

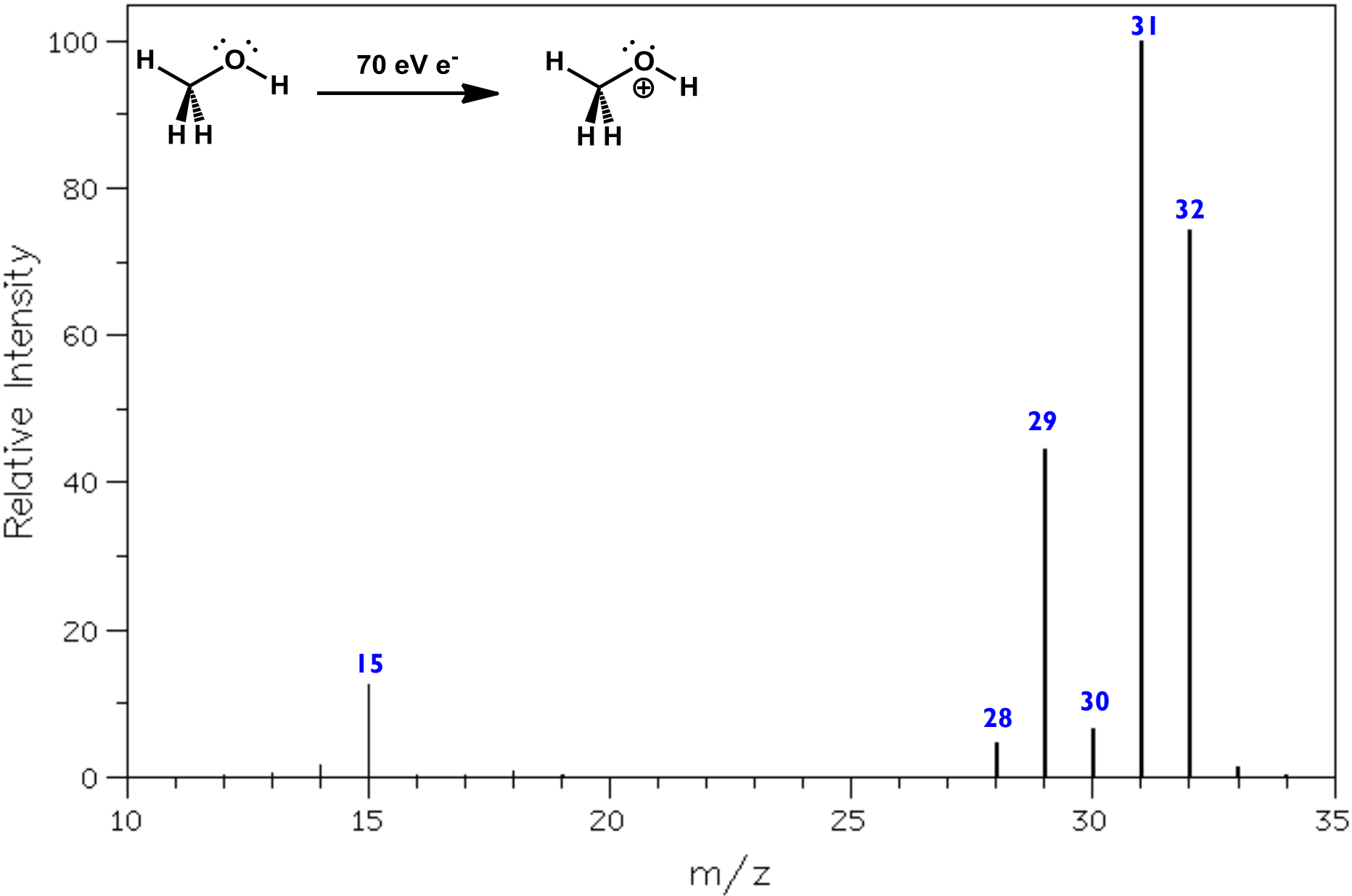
# EI-Mass Spectrum of 1-Bromobutane



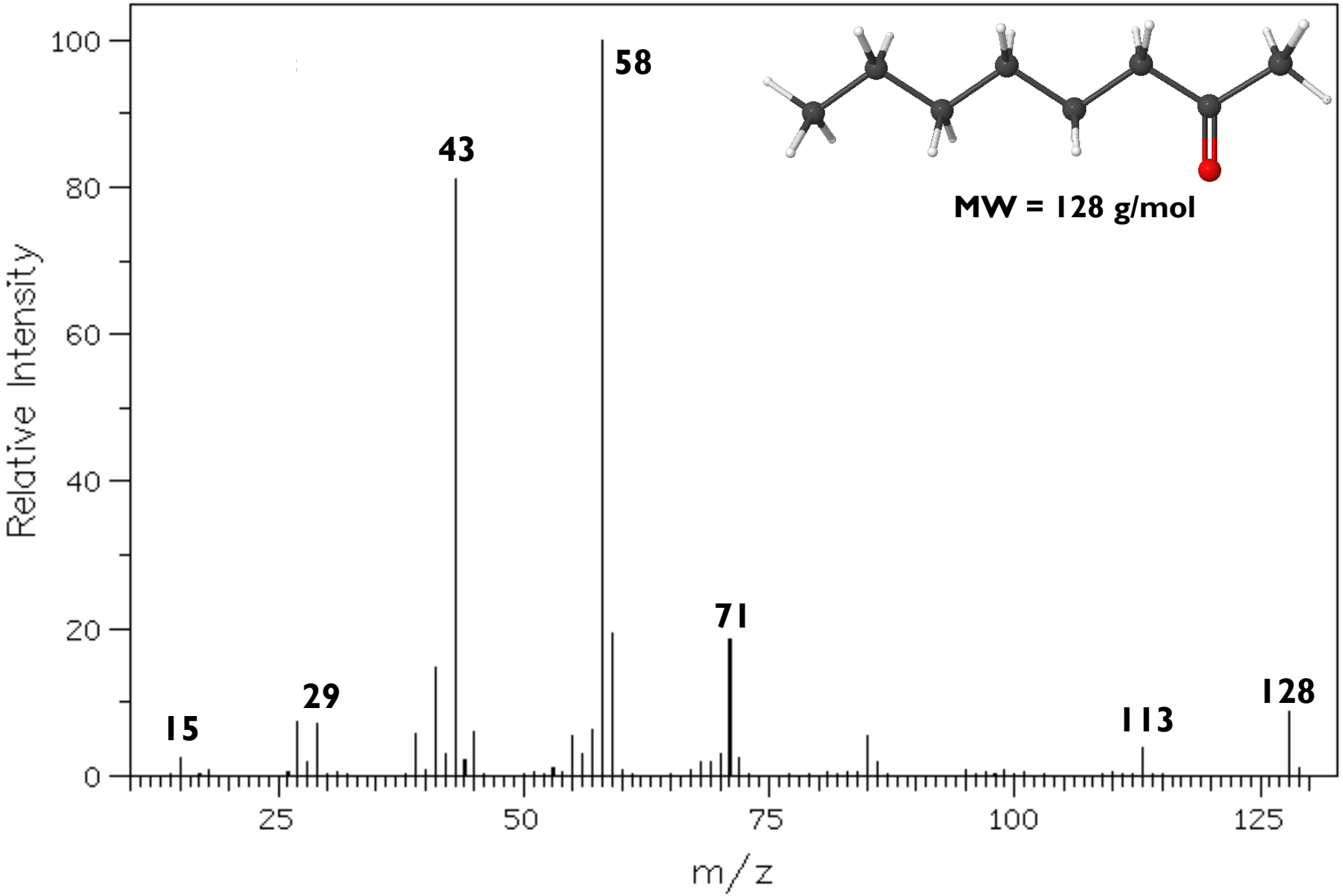
# EI-Mass Spectrum of Benzyl chloride

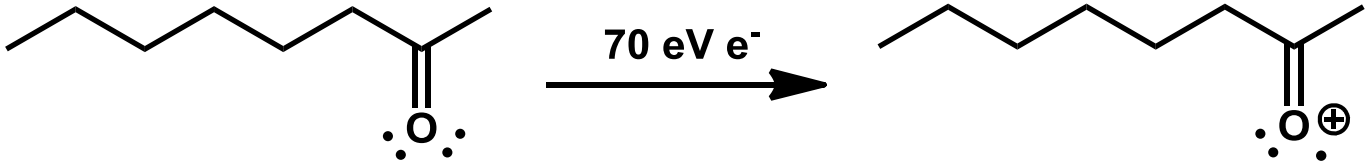


# EI-Mass Spectrum of Methanol $CH_3OH$



# EI-Mass Spectrum of 2-octanone




70 eV e-
O
O

# EI-Mass Spectrum of 2-octanone