University of Illinois at Chicago
UIC

Lecture 14
Organic Chemistry 1

Professor Duncan Wardrop

February 25, 2010

Mass Spectrometry

Sections: 13.24-13.25

Spectroscopy vs. Spectrometry

Spectroscopy

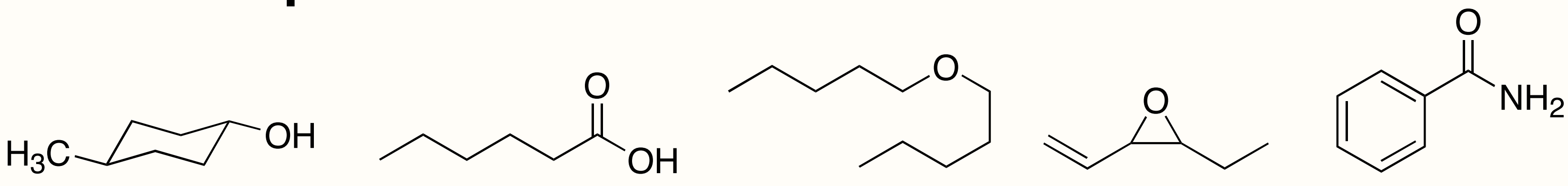
study of the interaction of electromagnetic radiation with matter; typically involves the absorption of electromagnetic radiation

Spectrometry

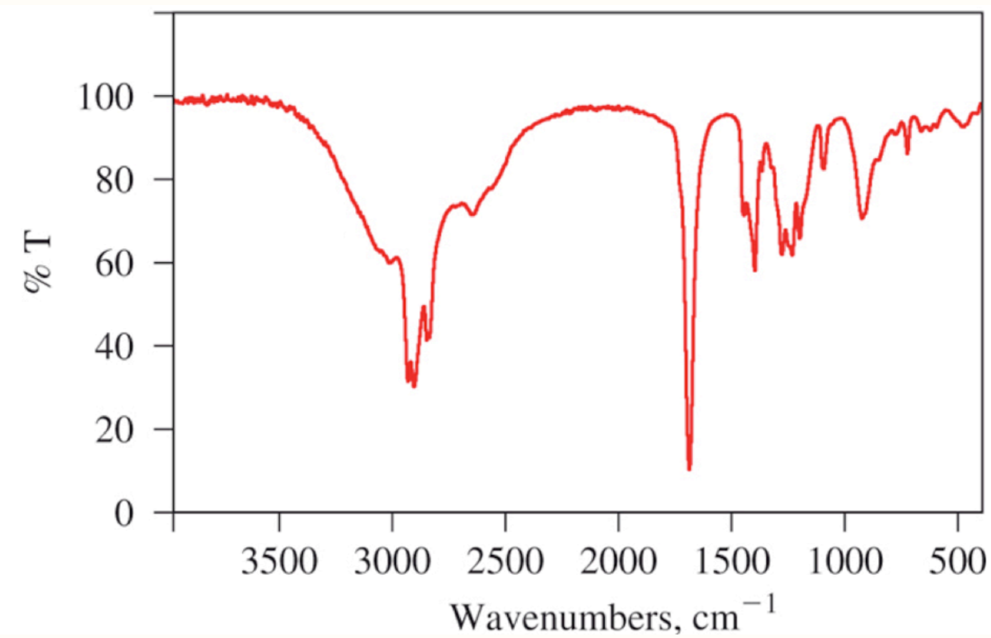
evaluation of molecular identity and/or properties that does not involve interaction with electromagnetic radiation

Self Test Question

Which molecule corresponds to the IR spectrum below?



a b c d e



A. a
B. b
C. c
D. d
E. e

Self Test Question

Which covalent bond, highlighted in bold (red) in the molecules below, would **not** be expected to exhibit an IR stretching band?

A	B	C	D	E
$O{=}C{=}O$	$H_3C{-}C{\equiv}N$	$H_3C{-}C{\equiv}N$	CH_4 (H−C−H, with H above and below C)	$H_3C{-}C{\equiv}C{-}CH_3$

CO2 has no dipole moment!

Mass Spectrometry

Section 13.24

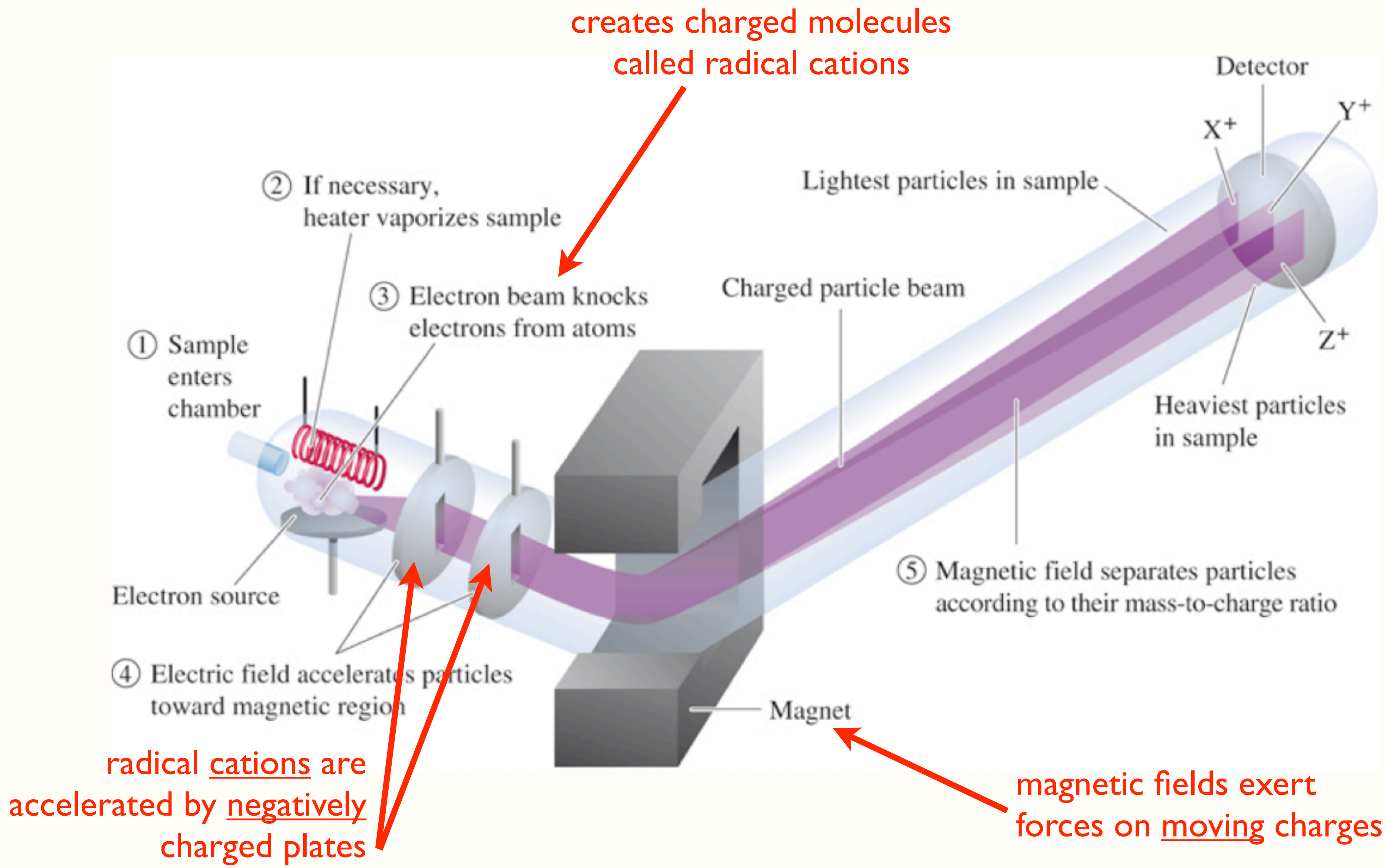
You are responsible for section 13.25!

Mass Spectrometry

Primary Applications:

1. Determine molecular mass.
2. Establish fragmentation patterns, which can be indexed in a database.
3. Determine presence of some heteroatoms.
4. Determine the exact mass of molecules.

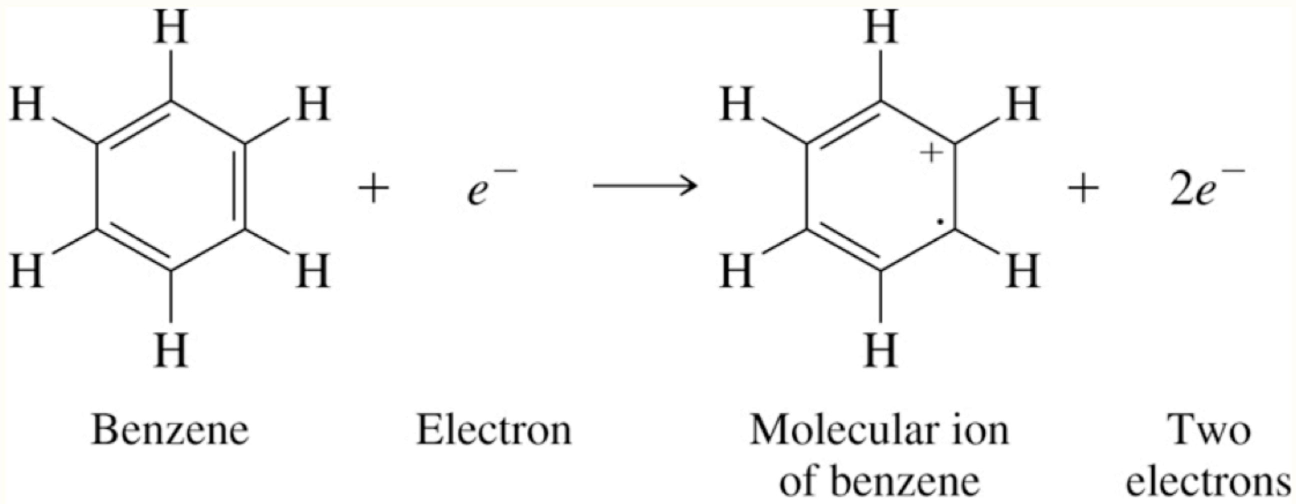
Mass Spectrometer Schematic



Formation of Radical Cations

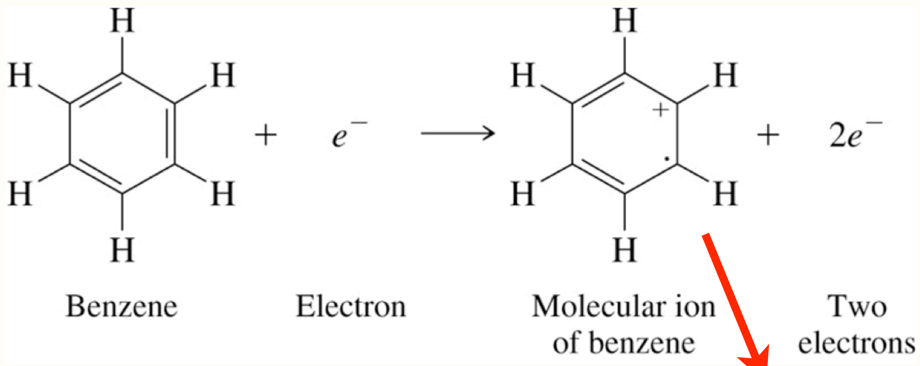
$$\mathrm{A{:}B} \quad + \quad e^- \quad \longrightarrow \quad \overset{+}{\mathrm{A{\cdot}B}} \quad + \quad 2e^-$$

Molecule | Electron | Cation radical | Two electrons

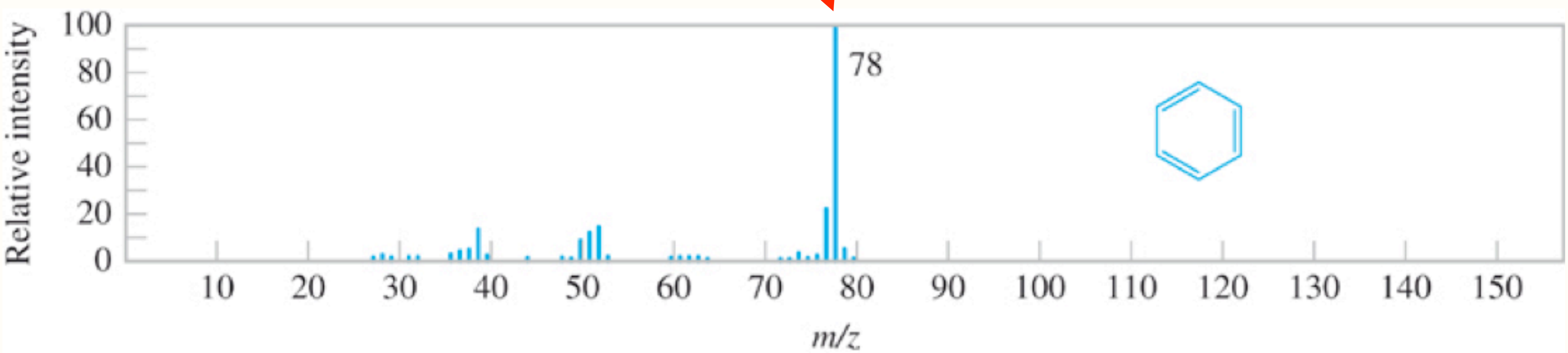


- organic molecules are bombarded with 70-eV electrons
- causes organic molecule to lose <u>one</u> electron from a covalent bond
- organic molecule is then charged
- the mass of charged species is determined by a mass spectrometer

Molecular Ion Peaks



C: 6 x 12 = 72
H: 6 x 1 = 6
Total = 78

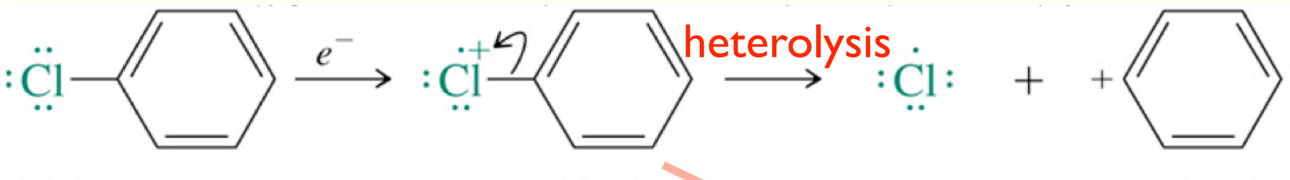


- molecular ion peak = highest m/z (mass/charge) peak
- since charge (z) is usually 1, molecular ion peak = molecular mass
- molecular ion peak does not have to have relative intensity of 100%
- most intense peak = base peak
- relative intensity = height of peak ÷ base peak

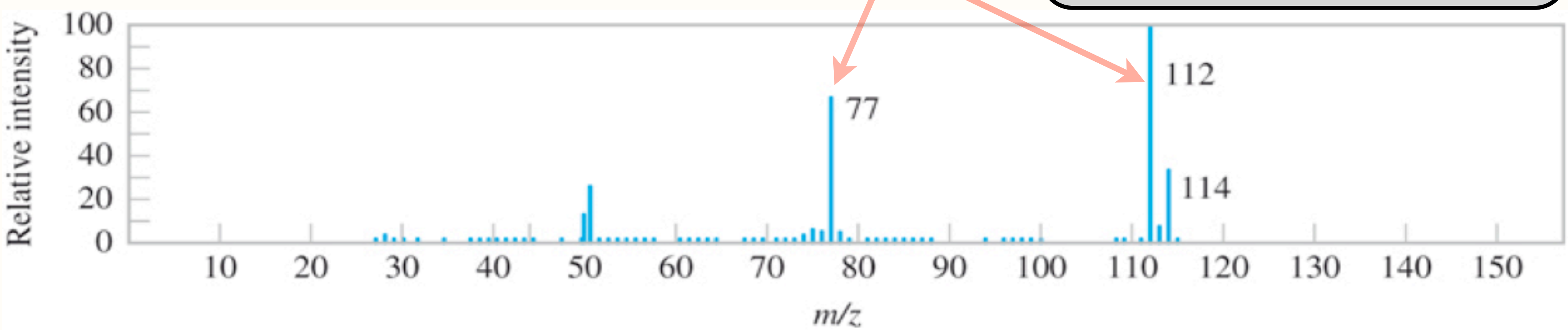
Fragmentation

$$A:B \;+\; e^- \longrightarrow \overset{+}{A\cdot B} \;+\; 2e^-$$

Molecule | Electron | Cation radical | Two electrons

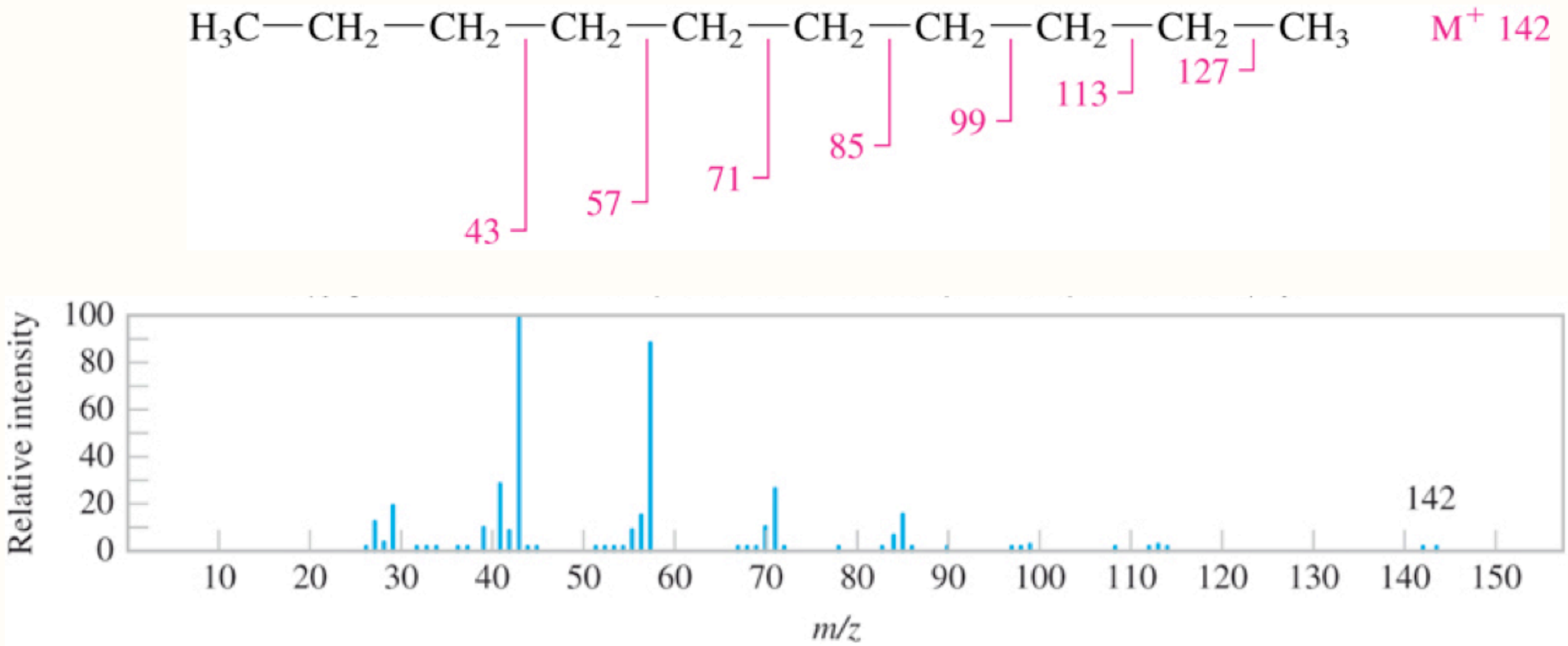


- radical cation fragments (heterolysis) to give a neutral radical species and a cation
- fragment contains less mass than parent ion
- relative intensity of the fragment depends on its concentration (likelihood of occurring)
- more stable cations are more likely; give more intense peaks



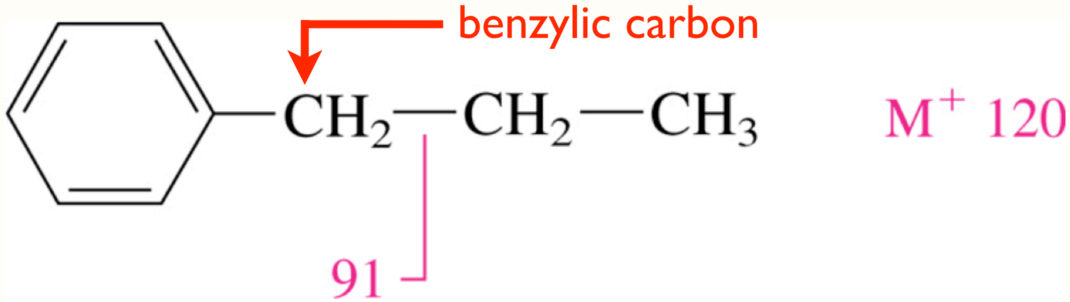
Fragmentation

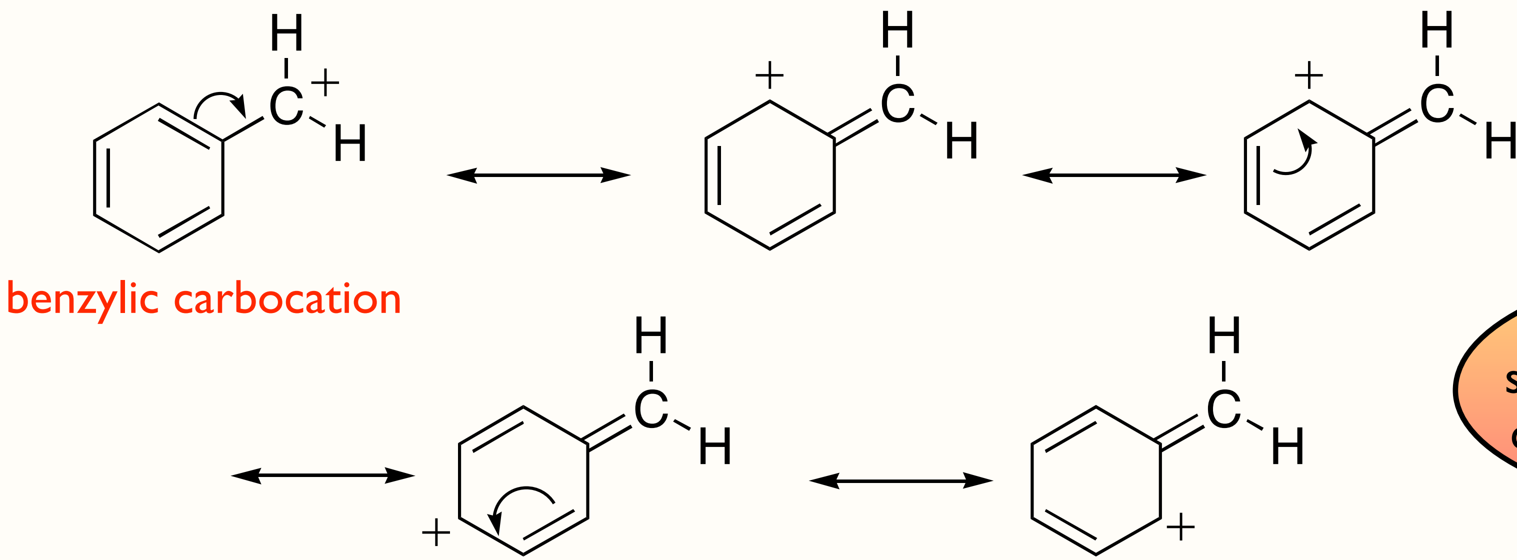
Common Fragmentation Pattern for Alkanes



Fragmentation

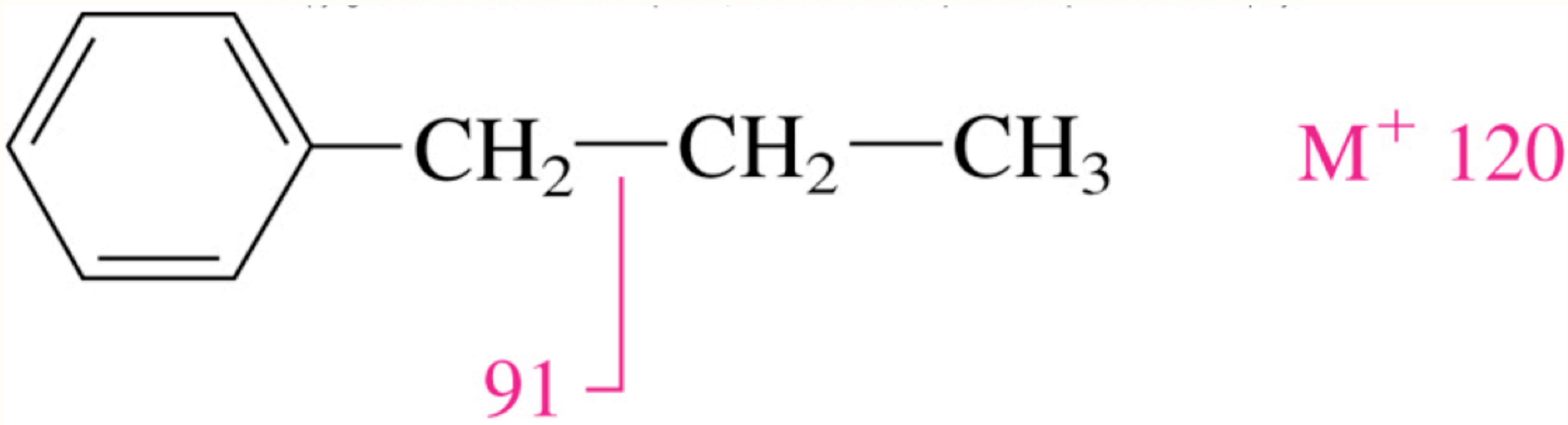
Common Fragmentation Pattern for Alkyl Benzenes

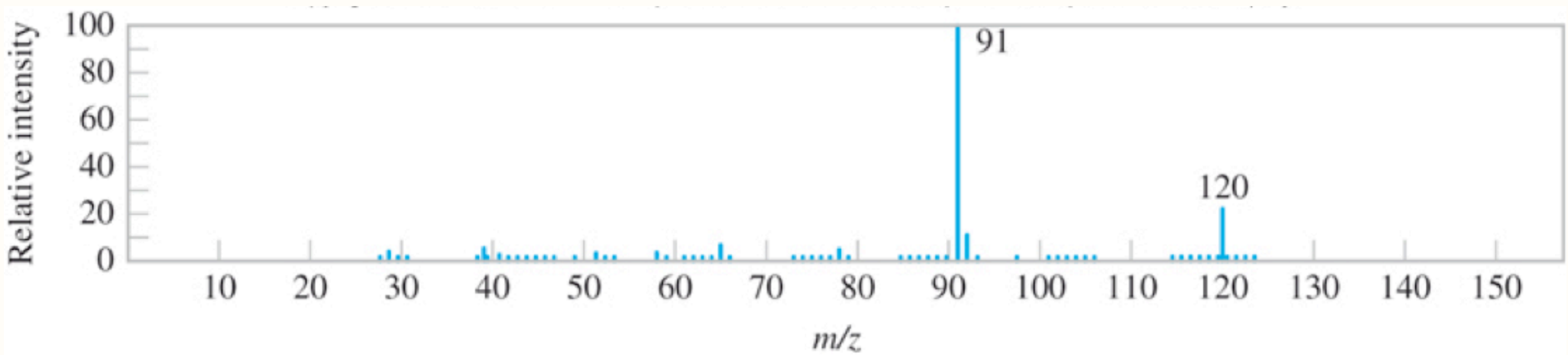




benzylic carbocation stabilized by <u>resonance</u> = common fragment in MS

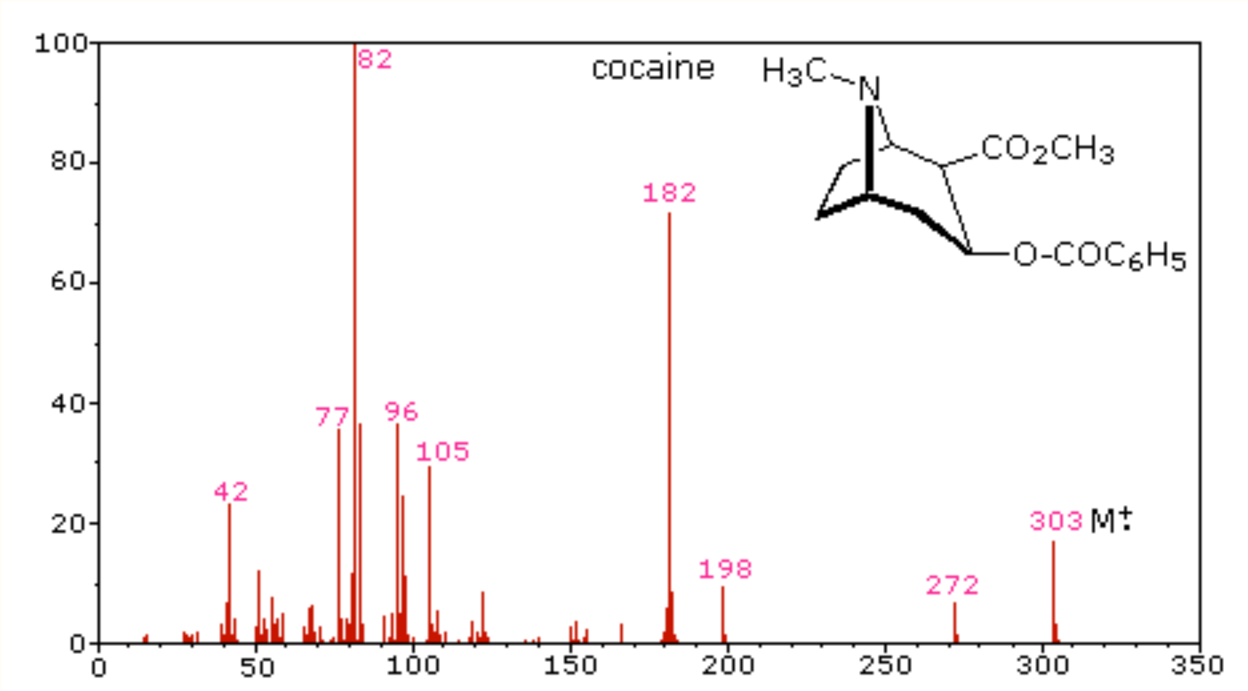
Fragmentation



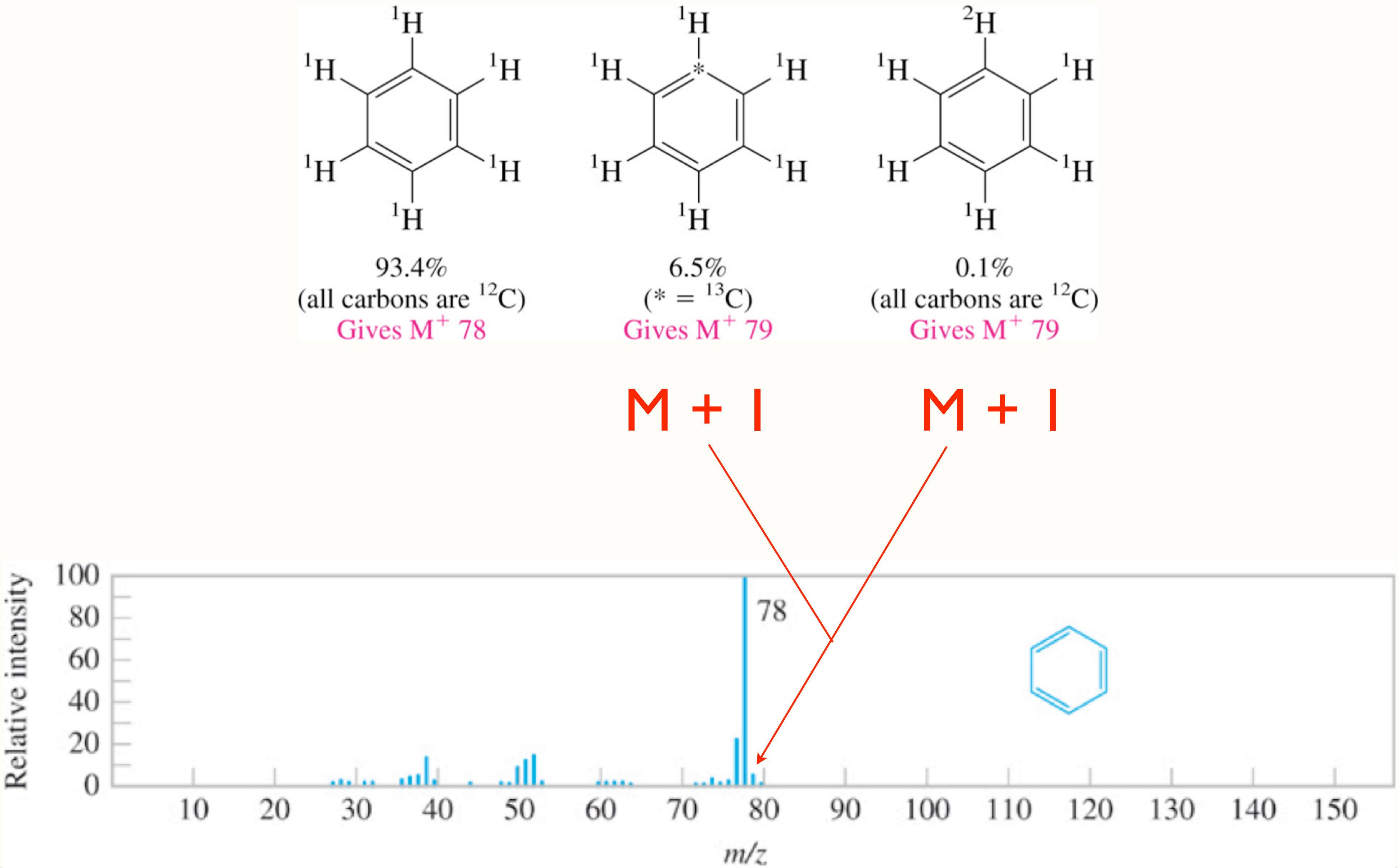


Fragmentation

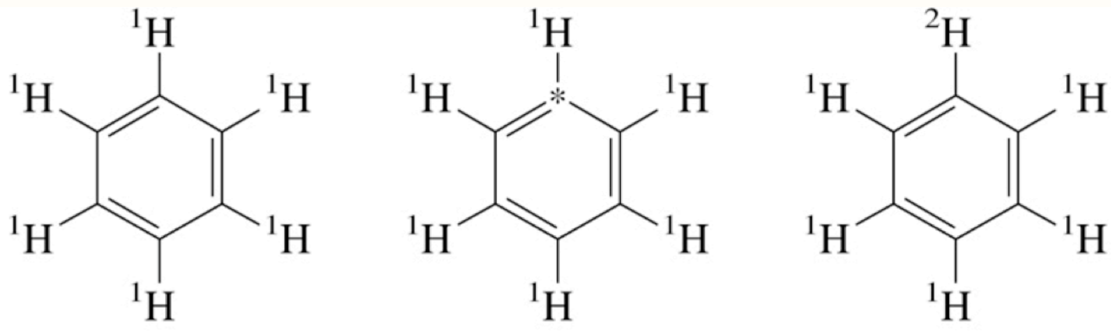
Since fragmentation patterns should be the same for identical molecules, they can be saved in a database and matched to unknowns later. CSI anyone?



Isotopic Clusters: Carbon and Hydrogen



Isotopic Clusters: Carbon and Hydrogen



93.4% (all carbons are ^{12}C) Gives M^+ 78

6.5% (* = ^{13}C) Gives M^+ 79

0.1% (all carbons are ^{12}C) Gives M^+ 79

M + 1 M + 1

Probability of M+1

6 x 1.1% = 6.6% of ^{13}C

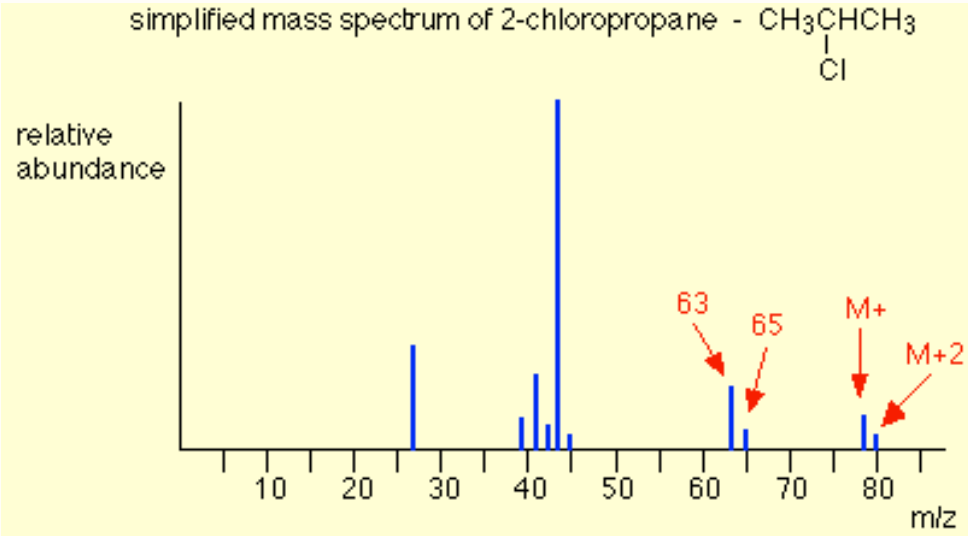
6 x 0.015% = 0.1% of ^{2}H

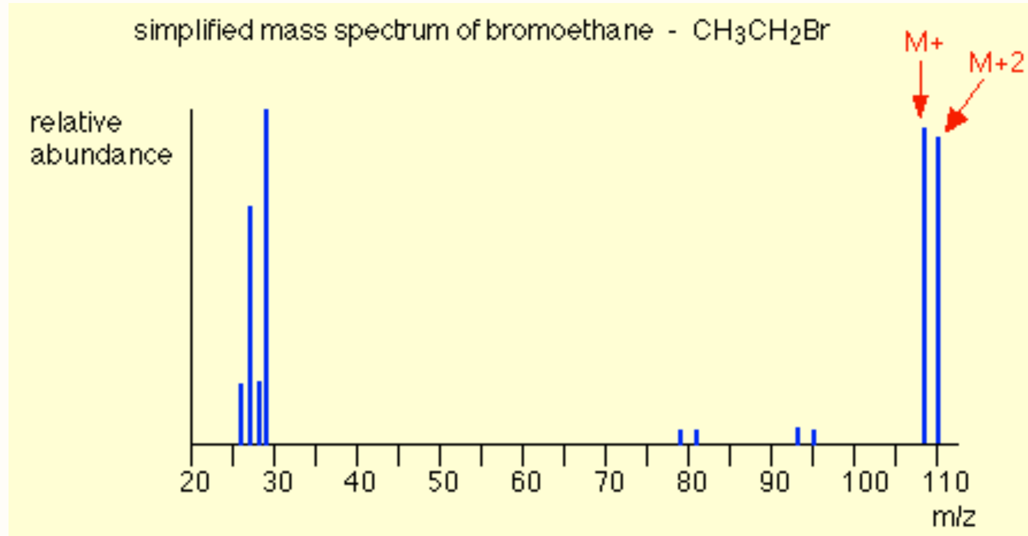
Total Probablility = 6.7%

Natural Abundance of Isotopes	
Isotope	Abundance
^{13}C	1.10%
^{12}C	98.90%
^{2}H (D)	0.015%
^{1}H	99.985%

- mass spectrometry is sensitive enough to resolve exact masses of isotopes
- intensity of the peaks corresponds to natural abundance of each isotope
- probability = number of atoms in molecule x natural abundance

Isotopic Clusters: Chlorine & Bromine





Natural Abundance of Isotopes	
Isotope	Abundance
^{35}Cl	75.77%
^{37}Cl	24.23%
^{79}Br	50.69%
^{81}Br	49.31%

- Chlorine: M:(M+2) ~ 3:1
- Bromine: M:(M+2) ~ 1:1
- probability = number of atoms in molecule x natural abundance

Spectroscopic Methods

Method	Measurement/Application
Infrared Spectroscopy	• vibrational states: stretching and bending frequencies of covalent bonds that contain a dipole moment • functional group determination
Ultraviolet-Visible (UV-vis)Spectroscopy	• electronic states: energy associated with promotion of an electron in a ground state to an exited state • chromophore determination
Mass Spectrometry	• molecular weight: of parent molecule and fragments produced by bombardment with "free" electrons • fragment and isotope determination
Nuclear Magnetic Resonance Spectroscopy	• nuclear spin states: energy associated with spin states of nuclei in the prescence of a magnetic field • determine structural groups and connectivity

Next Lecture. . .

Chapter 7: Sections 7.1-7.7

Bring your models!