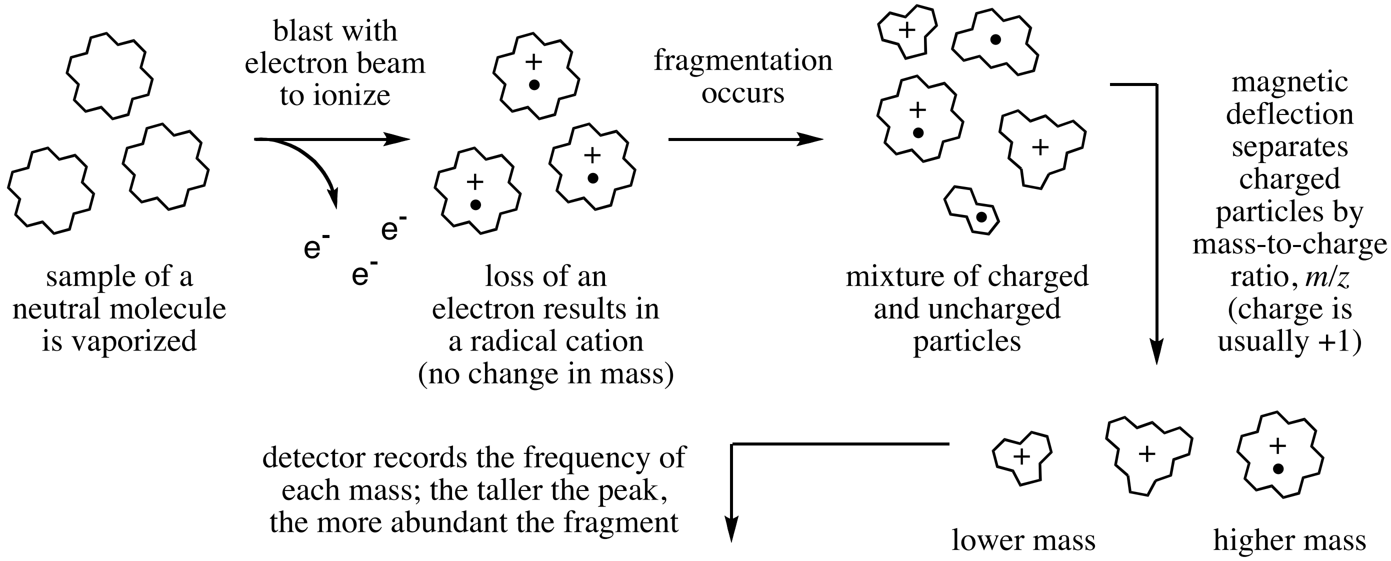
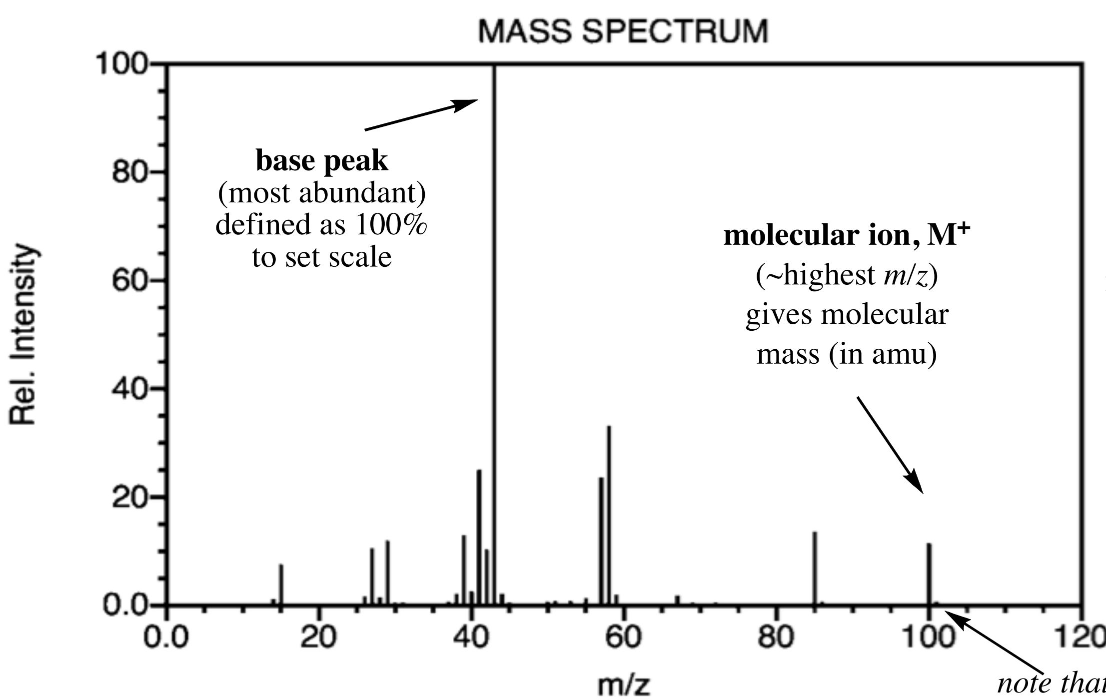
CHM 3150L Organic Chemistry II Laboratory, Dr. Laurie S. Starkey
Introduction to Mass Spectrometry

Mass spectrometry is used to determine a sample's **molecular mass** and **molecular formula**. Some structural information can also be determined by mass spec. This technique is especially valuable when used in conjuction with gas chromatography (called **GC-MS**); the GC separates the components of a mixture and then the mass spec analyzes each component. To obtain a **mass spectrum**, a sample is vaporized and then bombarded with a high energy beam of electrons (this technique is called electron-impact ionization, or EI). This ionizes the sample by knocking an electron out of the structure. A nonbonded or bonded electron is removed, resulting in radical cation species. Although it is now missing an electron, the intact molecule still has the same molecular mass and is known as the **molecular ion (M^+)**, or the parent ion. In addition, this high-energy environment causes the molecular ion to fragment and the various pieces can be analyzed to learn something about the original structure. All **charged species** are separated by mass as they are passed through a magnetic field and a detector records how many pieces of each mass have been formed. Note that because this technique does not involve the absorption or emission of energy, it is not called spectroscopy.





note that a small peak is observed at (M+1)

spectra have been reproduced from the NIST Chemistry WebBook http://webbook.nist.gov/chemistry

Spectral Analysis
In this spectrum, the sample has a molecular mass (M) of 100 amu. The most abundant fragment, called the base peak, has a *m/z* of 43 amu, or (M–57). This fragment was formed when a 57 amu segment of the molecule broke off. Many other fragments were formed; not all will be analyzed.

What is the mass of a single molecule?

CH_4 Mass = C + 4(H) =

but ~1% of carbon atoms exist as ^{13}C isotope!

$^{13}CH_4$ Mass = ^{13}C + 4(H) =

What ratio is expected for the molecular ion peaks of C_2H_6?

the number of carbon atoms affects the relative height of the M+1 peak

Other isotopes of high abundance

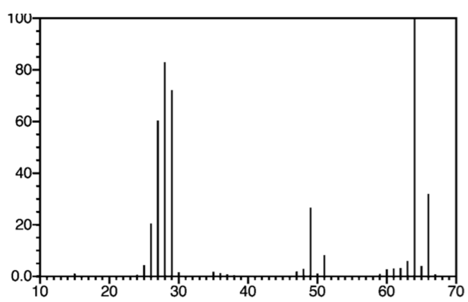
Cl (35.45 amu) atoms are 76% ^{35}Cl and 24% ^{37}Cl

Br (79.90 amu) atoms are 51% ^{79}Br and 49% ^{81}Br

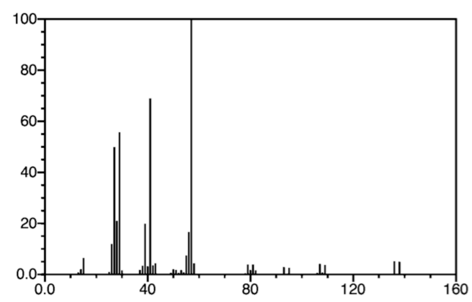
fragments containing Cl or Br have significant M+2 peaks

What ratios are expected for the molecular ion peaks of CH_2Br_2?

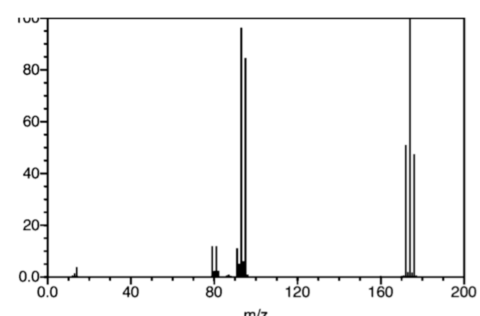
possible masses? CH_2 Br Br total amu



mass spec of chloroethane (M^+ 64)



mass spec of bromobutane (M^+ 137)



mass spec of dibromomethane (M^+ 172)

Determining molecular formula from high-resolution mass spectrometry (high-res mass spec)

exact masses of various elements:

^1H	1.007825 amu
^{12}C	12.000000 amu
^{14}N	14.003050 amu
^{16}O	15.994914 amu

these molecules all have a molecular mass of 98 g/mol

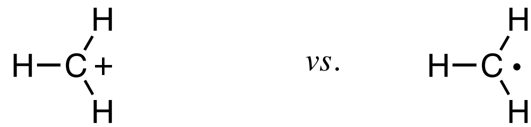
$C_4H_6N_2O$	98.0480 amu
$C_5H_6O_2$	98.0368 amu
$C_5H_{10}N_2$	98.0845 amu
$C_6H_{10}O$	98.0732 amu
C_7H_{14}	98.1096 amu

the molecular formula can be determined from precise molecular mass

Mass Spec Features of Various Functional Groups

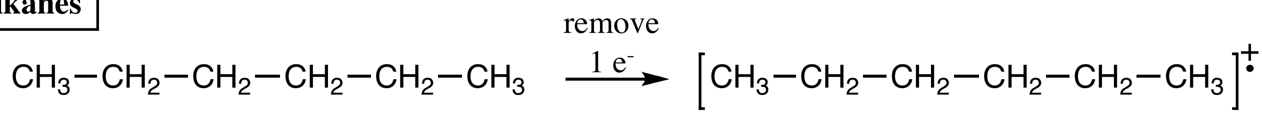
Fragmentation of the molecular ion

Which is more stable, a carbocation C^+ or a radical R• ?



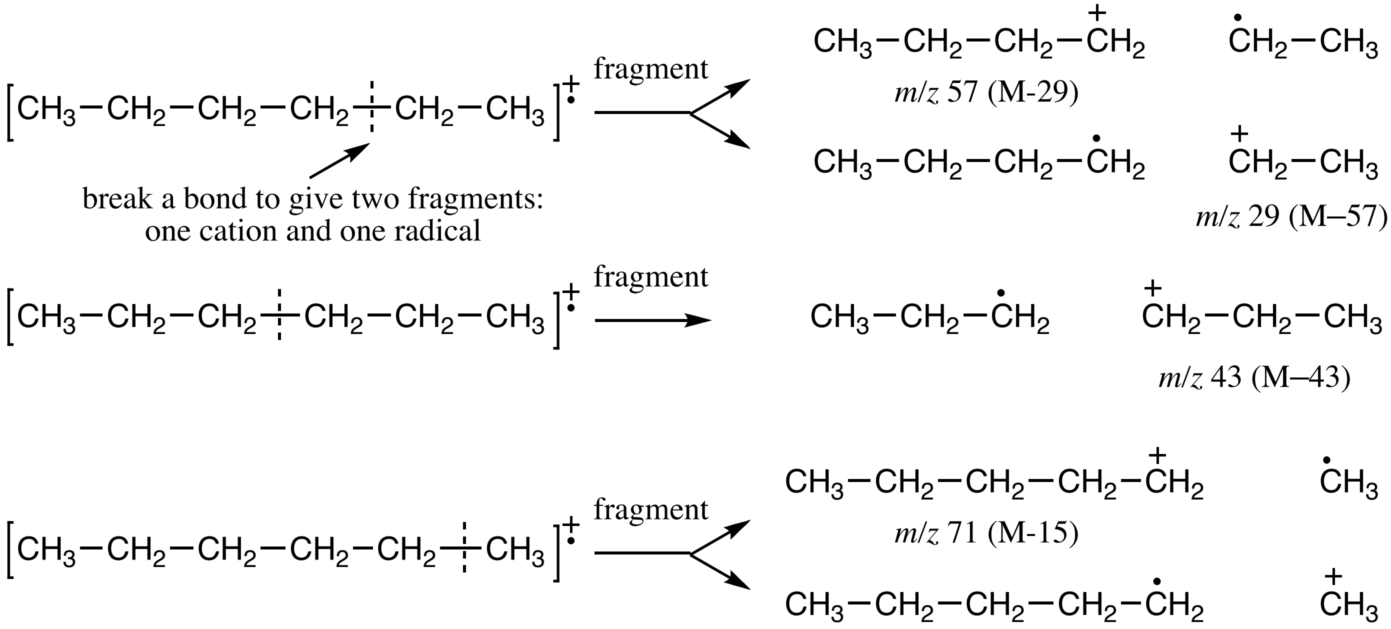
fragmentation is more likely if it gives more stable carbocations and radicals

Alkanes



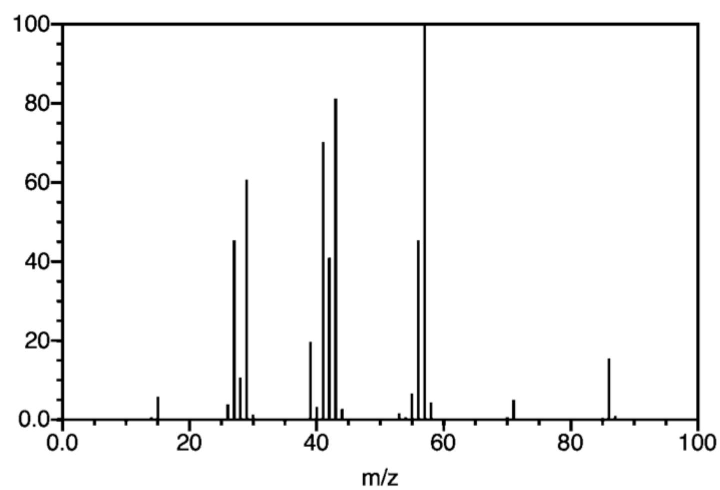
hexane

a radical cation (M^+) *m/z* 86



m/z 15 (M–71)

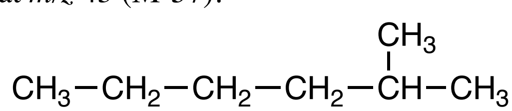
note: hexane has peaks at *m/z* 15, 29, 43, 57, 71, 86



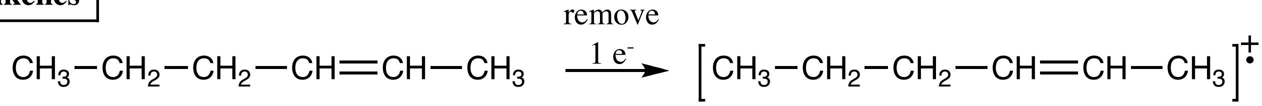
Why are the peaks at *m/z* 15 and 71 so small?

Branched Alkanes

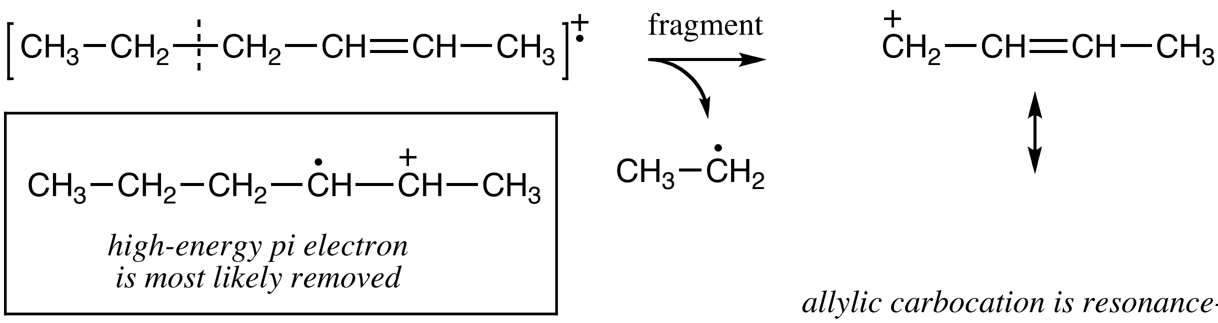
Explain why the base peak of 2-methylhexane is at *m/z* 43 (M-57).



Alkenes

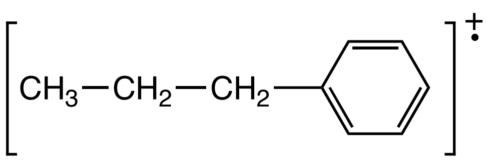


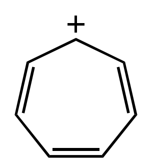
allylic cleavage gives stable carbocation



allylic carbocation is resonance-stabilized

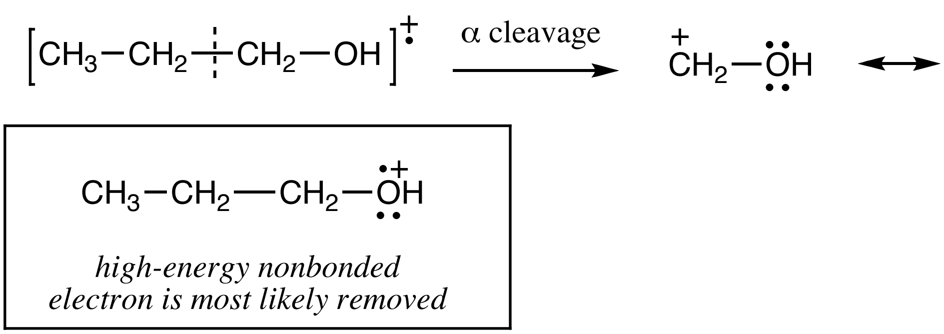
Aromatic





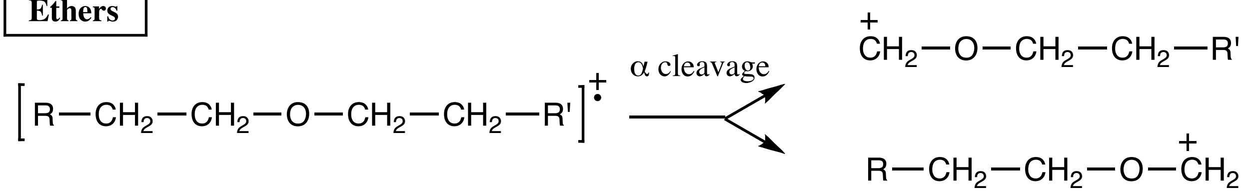
tropylium cation
m/z 91

Alcohols

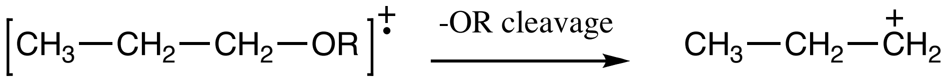


also, loss of H_2O (M–18) may be observed
(multistep mechanism first involves an intramolecular proton transfer)

Ethers

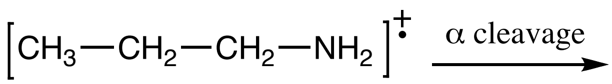


also, loss of RO• may be observed



m/z (M–OR)

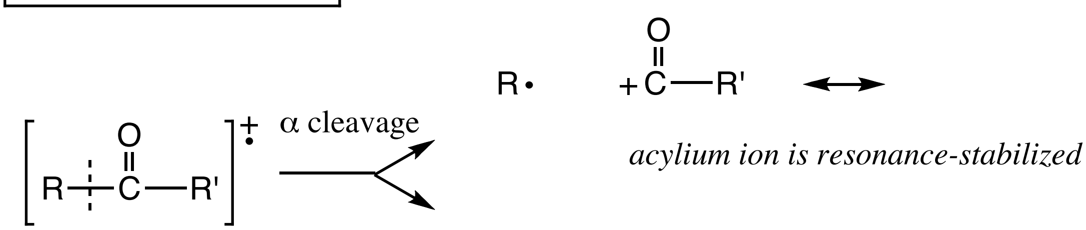
Amines



Nitrogen Rule: M^+ is odd if there are an odd number of nitrogens!

odd molecular mass indicates one nitrogen (or 3 or 5 or 7 nitrogens...)
even molecular mass indicates zero nitrogens (or 2 or 4 or 6 nitrogens...)

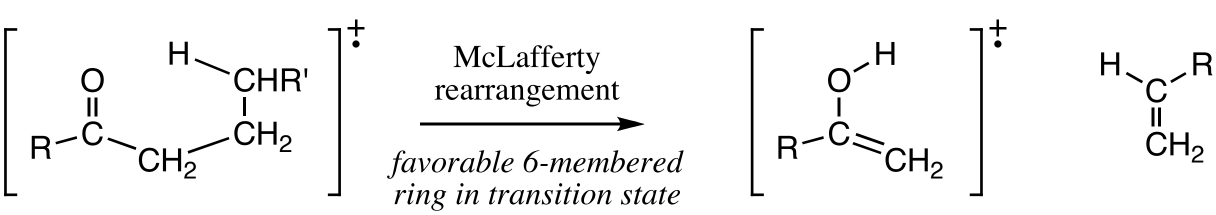
Aldehydes & Ketones



m/z (M–R)

loss of larger group more likely
(more stable R•)

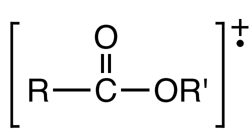
McLafferty rearrangement is a common fragmentation for carbonyl-containing molecules



molecular ion cleaves
between α and β carbons

Esters

esters can undergo α cleavage, McLafferty rearrangement, or loss of RO•



Mass Spectrometry Discussion Questions

For the given molecule (M=58), do you expect the more abundant peak to be *m/z* 15 or *m/z* 43? Explain.

$CH_3-CH_2-CH_2-CH_3$

For the given molecule (M=74), which peak do you expect to be most abundant: *m/z* 31, *m/z* 45 or *m/z* 59? Explain.

$HO-CH_2-CH_2-CH_2-CH_3$

Explain why the mass spectra of methyl ketones typically have a peak at *m/z* 43. Provide the structure of this fragment.

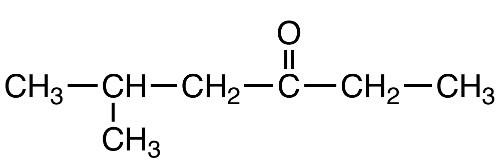
In the mass spectrum of the given molecule (M=88), provide structures for the peaks at *m/z* 45 and *m/z* 57.

$CH_3-O-CH_2-CH_2-CH_2-CH_3$

How could you use mass spectrometry to distinguish between the following two compounds (M=73)? Provide structures (and *m/z* values) for the significant fragments expected.

$CH_3-CH_2-CH_2-CH_2-NH_2$ and $CH_3-CH_2-CH_2-NH-CH_3$

What would be the *m/z* ratio for the fragment resulting from a McLafferty Rearrangement for the following molecule (M=114)? What fragment accounts for its base peak at *m/z* 57?



Mass spec problems (Wade 7th, 8th or 9th edition) Chapter 12: 8-11, 18, 20.