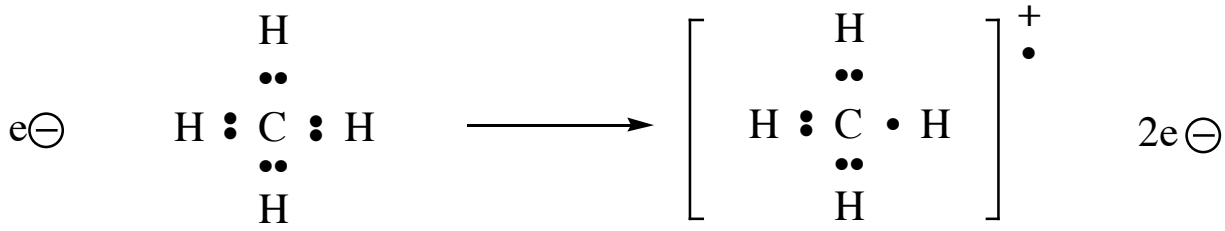
Mass Spectrometry

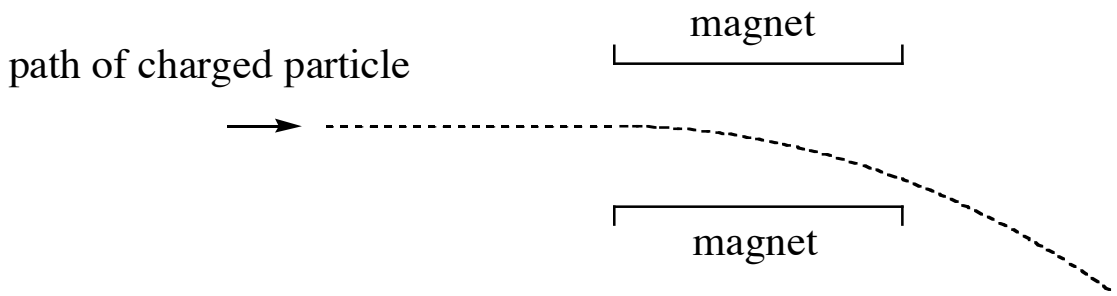
Can determine information about molecular weight and molecular structure

Electron impact ionization



by ejecting one electron the molecule becomes charged

When a charged species passes through a magnetic field the flight path is bent



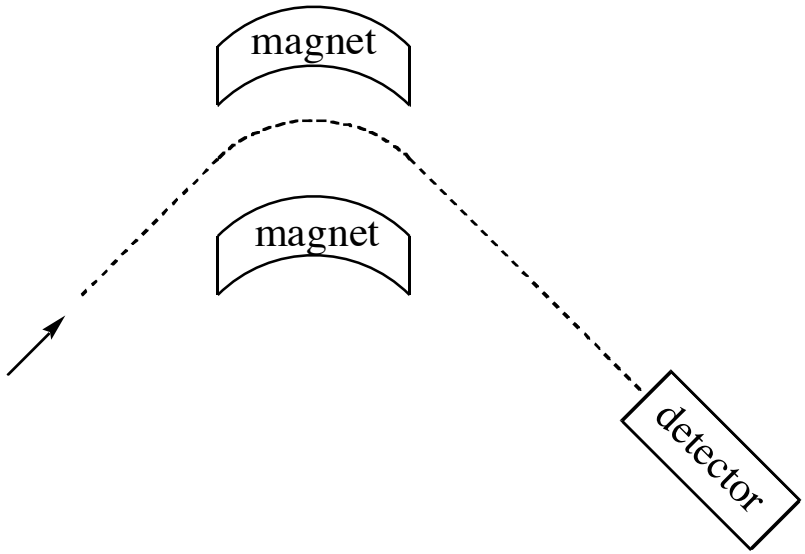
the charged particle is attracted to one 'pole' in the presence of a magnetic field

and hence its path is bent

the radius of curvature is m/z

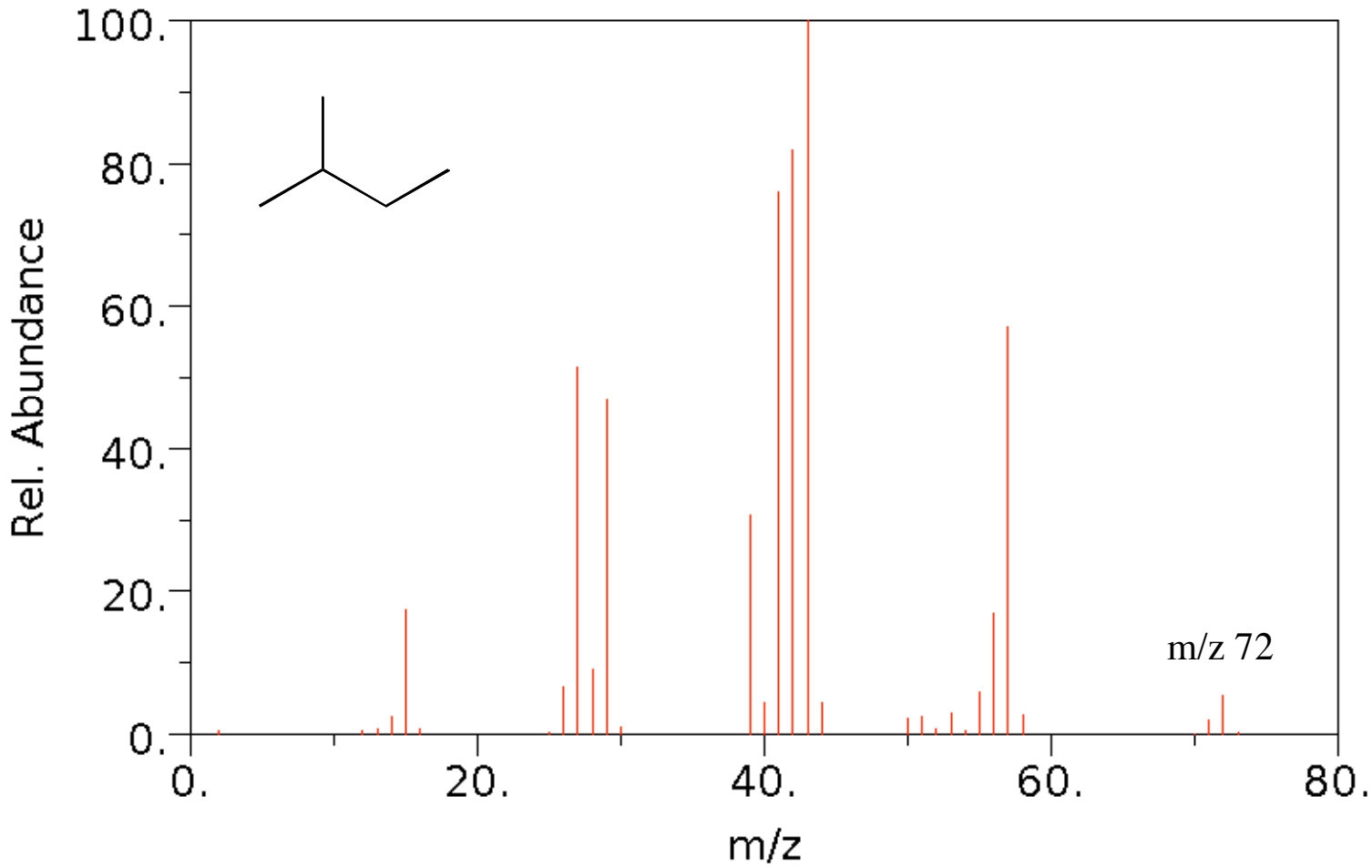
therefore lighter species bend more than heavier species with a given magnetic field

In practice the magnetic field is adjusted to achieve a desired radius of curvature



by adjusting magnetic field only a certain mass will be able to tranverse the curvature and reach the detector, you can then plot absorbance versus m/z for a given compound

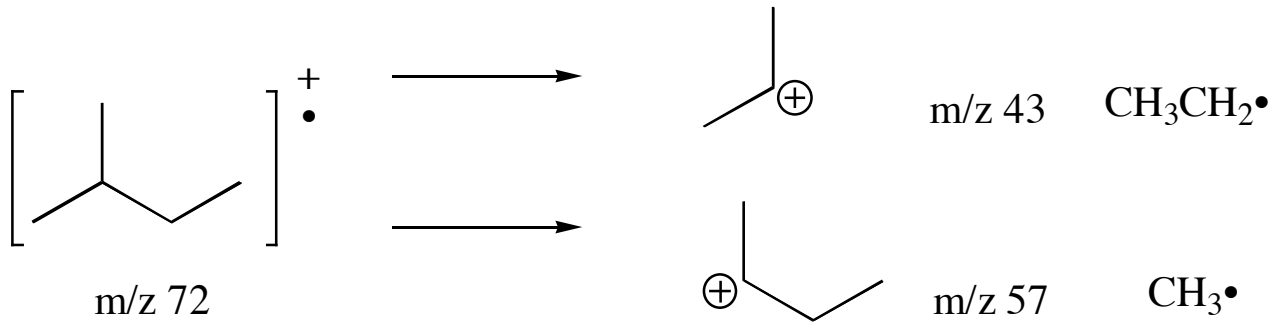
The parent ion is called the molecular ion peak (M+)



Can find molecular ion, but what are all the other peaks?

The molecular ion peak can fragment

Due to the high energy of the radical/cation generated, this species can fragment

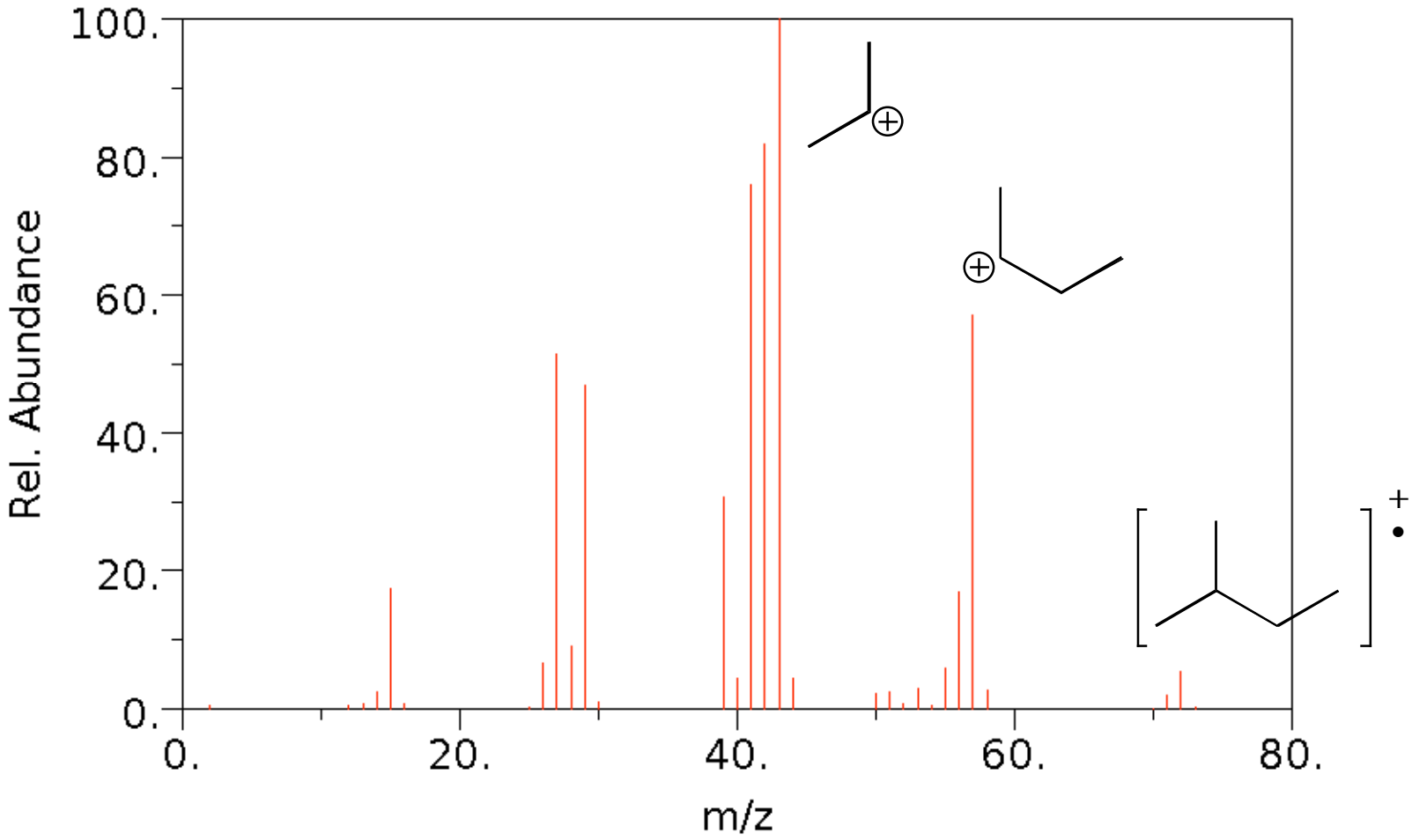


remember only the charged species will be detected

(the radical species will not be affected by the magnetic field)

the probability of obtaining a given fragment is due to the

STABILITY of the cations produced



the peaks below the molecular ion peak can therefore be assigned to these fragments

Effect of Isotopes

Remember that an isotope has the same number of protons and electrons,
but a different number of neutrons

since neutrons and protons are the "heavy" parts of an atom,
the extra number of neutrons will cause a greater mass

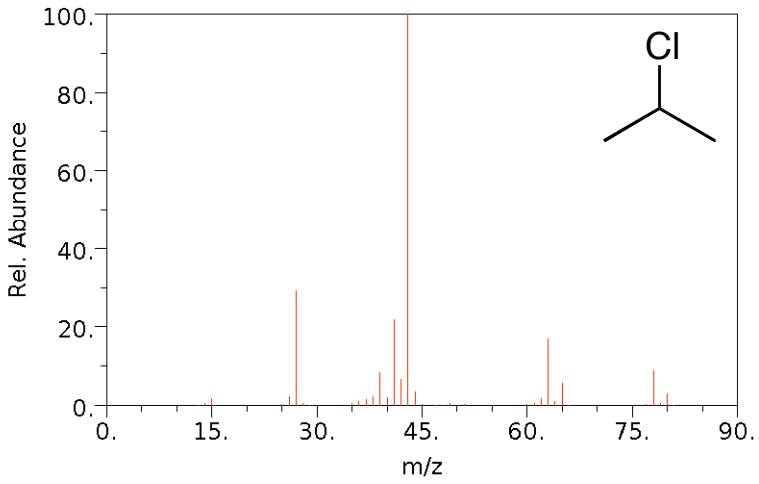
in a mass spectrometer we can see the effect of this by peaks
above the molecular ion peak (M, M+1, M+2)

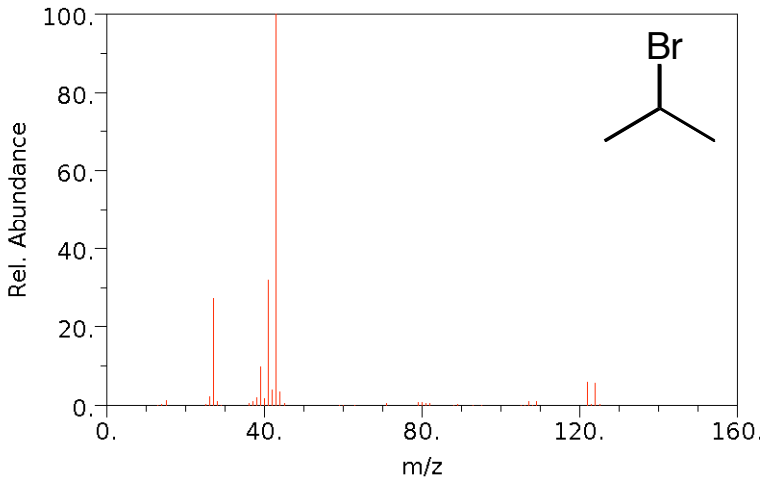
The ratio of these peaks is diagnostic of which atoms are present

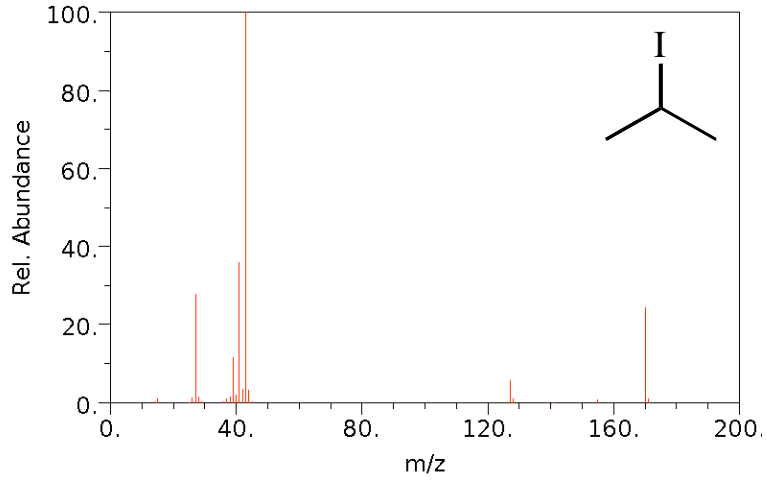
The natural abundance of isotopes is well known

	M	M+1	M+2
H	100%		
C	98.9%	1.1%	
S	95%	0.8%	4.2%
Cl	75.5%		24.5%
Br	50.5%		49.5%
I	100%		

Can distinguish atoms by the ratio of peaks above the molecular ion







Nitrogen

Nitrogen is also diagnostic in a mass spectrum due to the odd/even parity of the mass

Consider small molecules and their corresponding mass

CH_4	m/z 16
NH_3	m/z 17

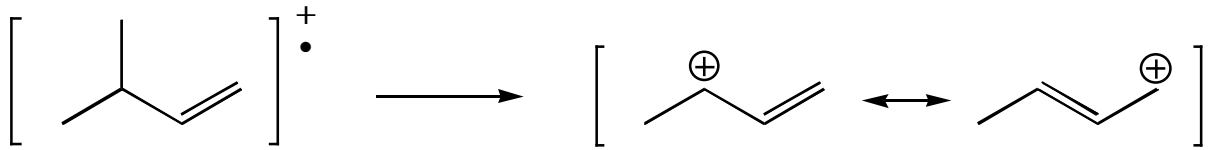
The molecular ion peak for a molecule with one nitrogen is odd

All other common atoms in an organic compound give a mass which is even

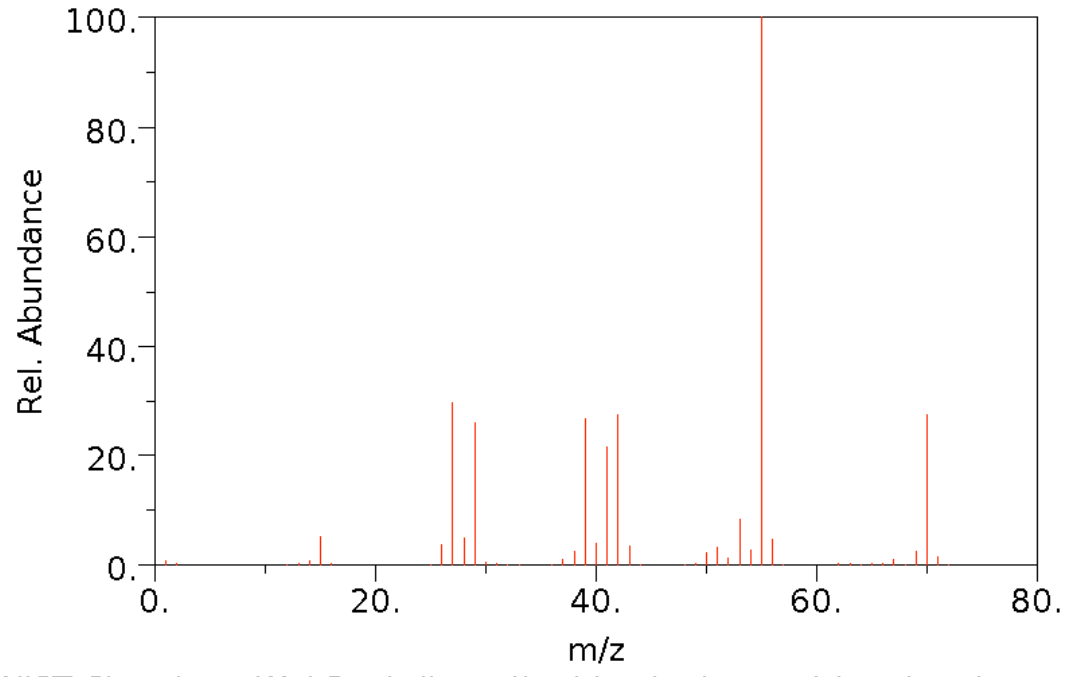
Fragmentation Behavior of Common Functional Groups

Alkenes

With an alkene the common fragmentation is to create an allylic carbocation



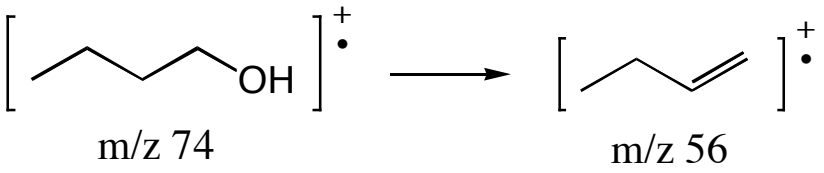
m/z 70 m/z 55



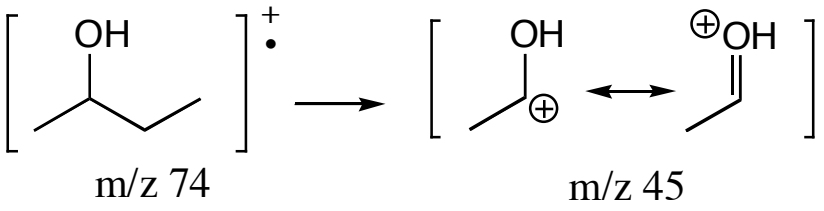
Alcohols

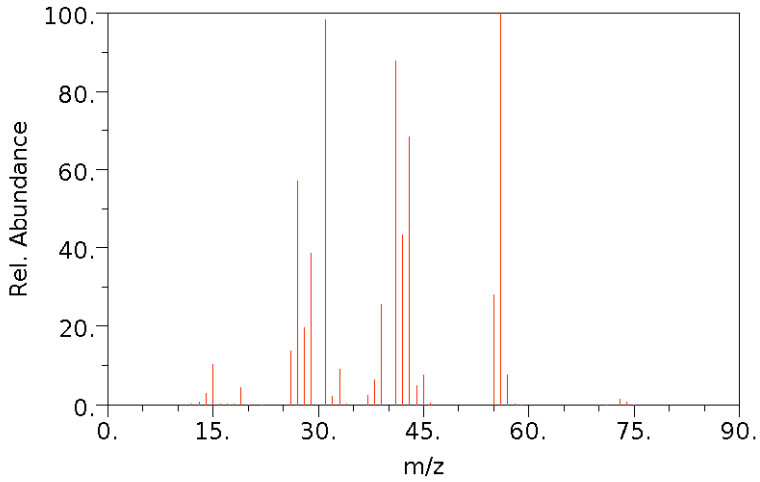
Two common effects

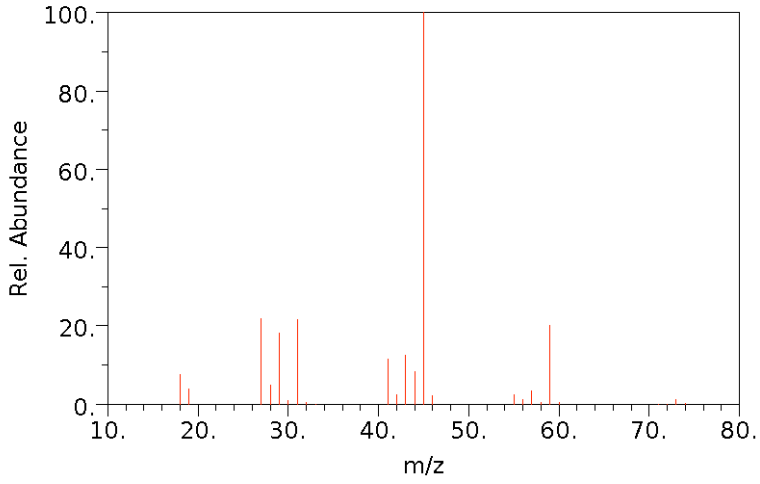
1) Lose water



2) α-cleavage

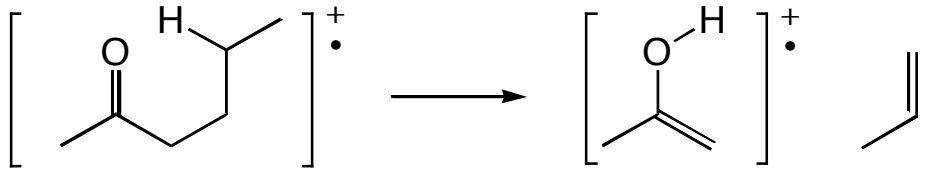




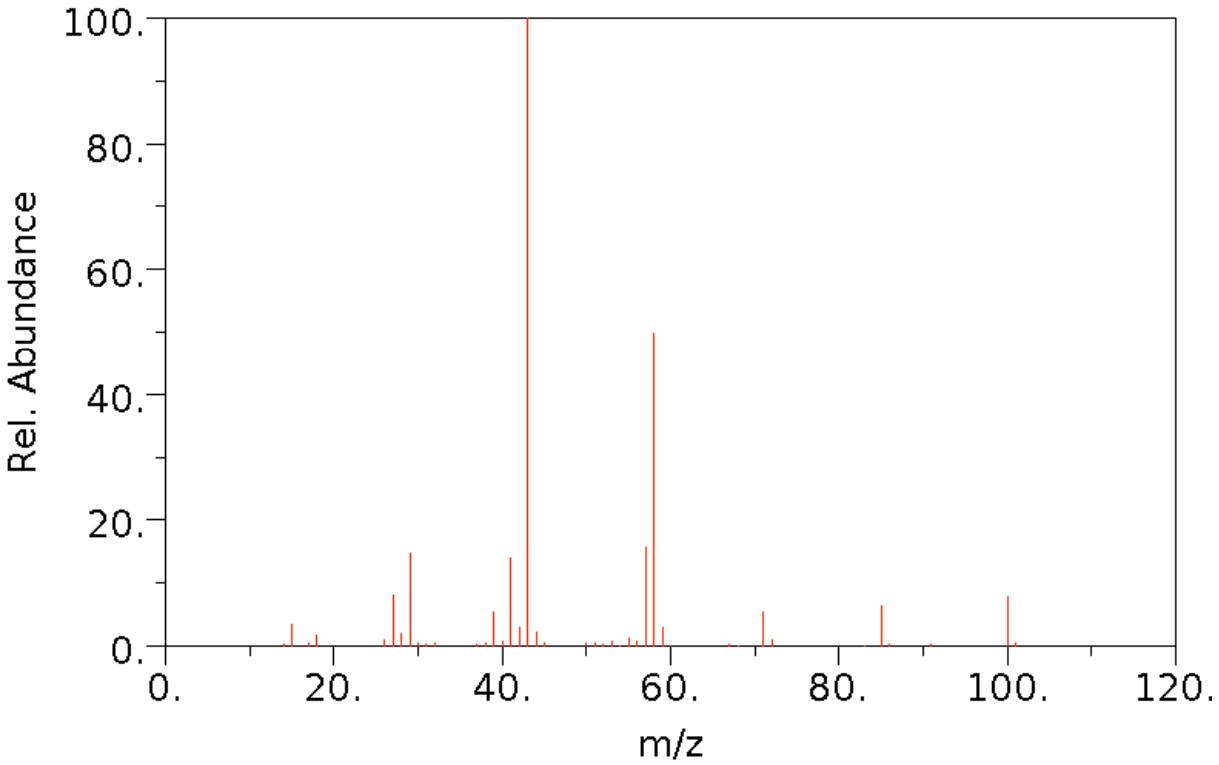


McLafferty Rearrangement

Any ketone containing a γ-hydrogen can rearrange to the enol form in a MS



m/z 100 m/z 58



High Resolution Mass Spectrometry (HRMS)

These high level mass spectrometers, called HRMS,
can be used to determine molecular formula

a HRMS can detect particle masses with an accuracy of 1/20,000
therefore > 0.0001 amu (atomic mass units)

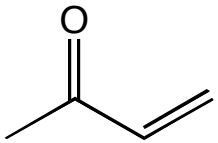
can use this to distinguish compounds with a similar rough mass
but with a different molecular formula

^{12}C	12.0000 amu (by definition)
^{1}H	1.0078 amu
^{16}O	15.9949 amu

Differentiating Structures Using HRMS

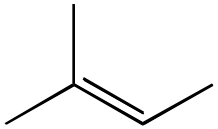
Many structures may have the same integer value molecular weight, but different molecular formulas

these structures can be differentiated with HRMS



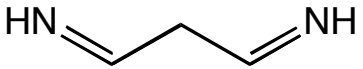
$C_4H_6O_1$

70.0418 amu



C_5H_{10}

70.0783 amu



$C_3H_6N_2$

70.0531 amu