CHEMISTRY 2600

Topic #3: Using Spectroscopy to Identify Molecules:

Radicals and Mass Spectrometry (MS)

Fall 2018

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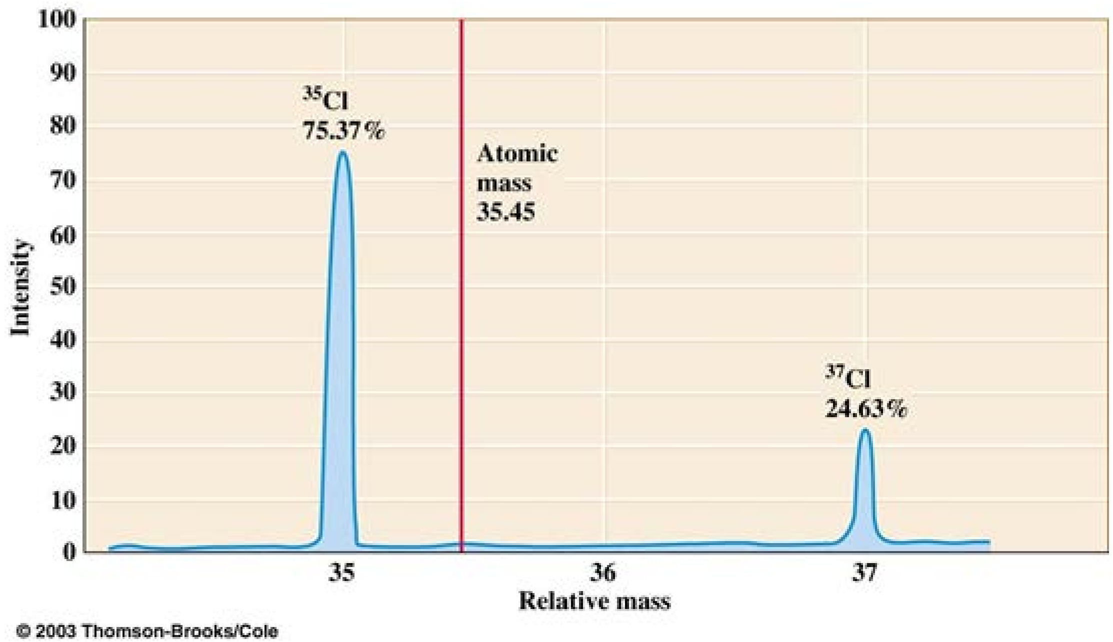
Mass Spectrometry: How Does It Work?

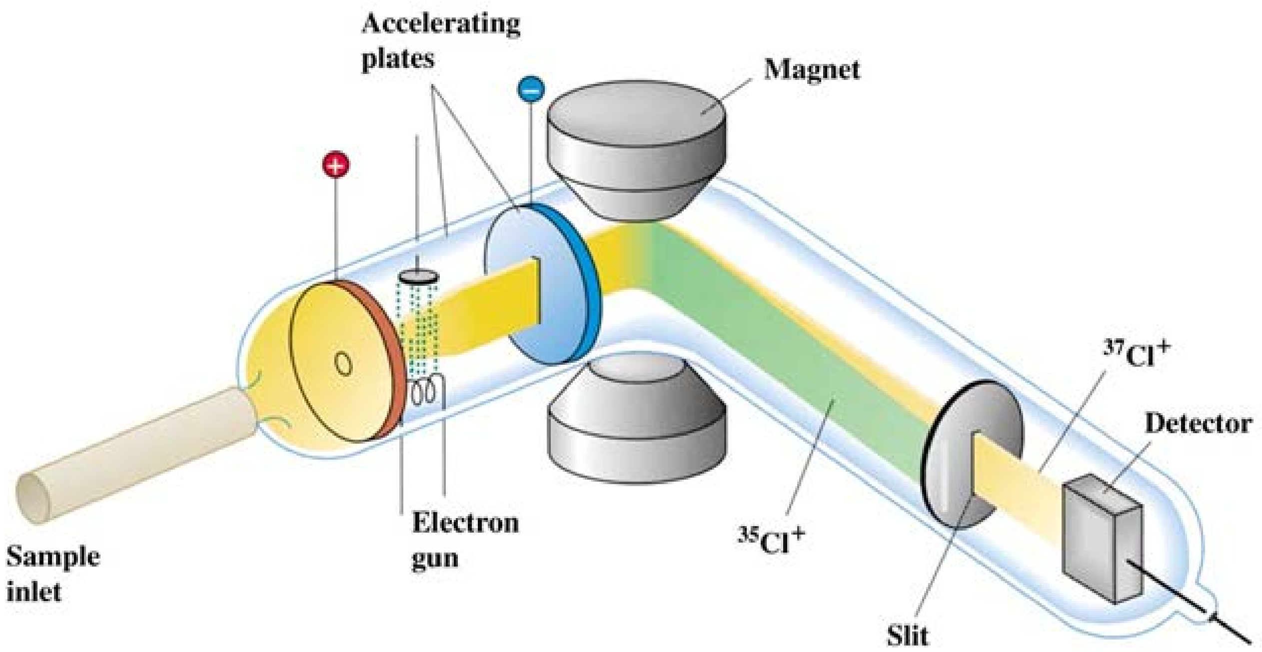
- In CHEM 1000, you saw that mass spectrometry can be used to identify which isotopes are present in a sample of an element:



The molar mass of chlorine is 35.4527 g/mol, but the mass spectrum shows us that a sample of chlorine atoms actually consists of ^{35}Cl and ^{37}Cl in a 3 : 1 ratio.

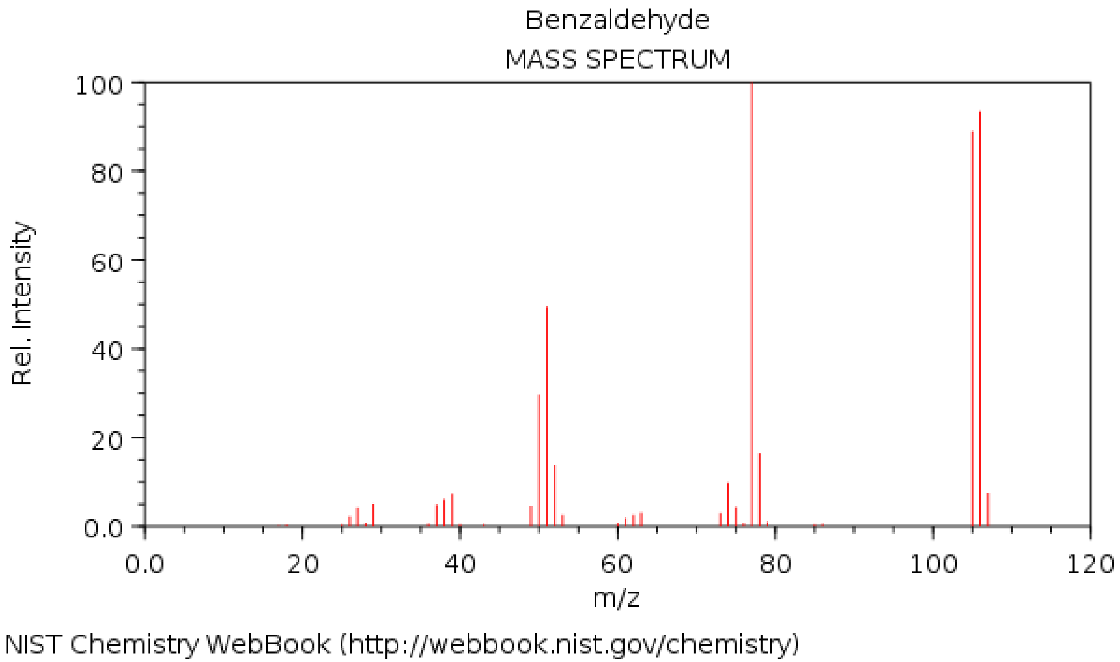
Mass Spectrometry: How Does It Work?

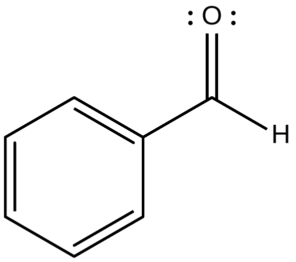
- What is the main difference between isotopes of an element?
- How can we take advantage of that difference?



Mass Spectrometry: How Does It Work?

- Molecules can also be subjected to mass spectrometry (MS), generating spectra like the one below:

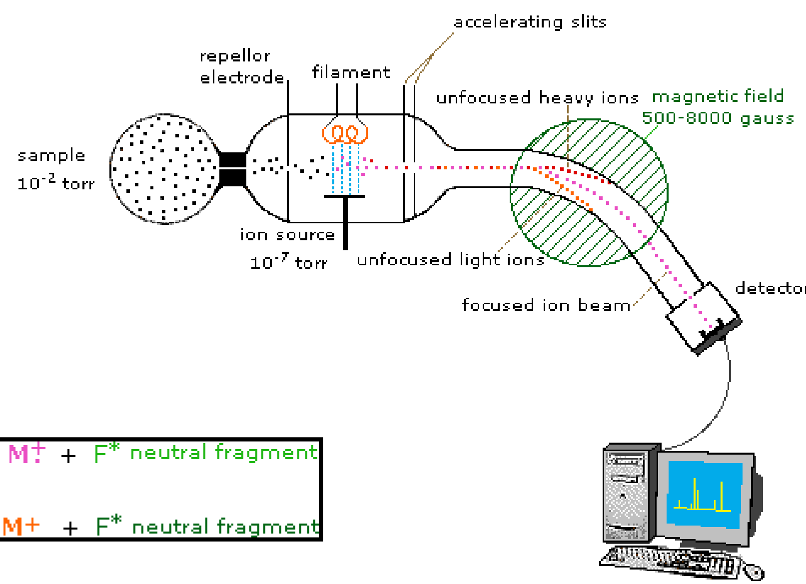


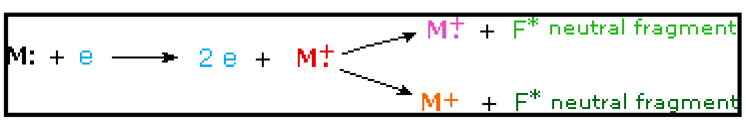


- Often, the rightmost significant peak is the **molecular ion**, giving the molecule's molar mass (106 g/mol for benzaldehyde).
- m/z refers to the mass-to-charge ratio of each fragment; only charged fragments appear on a mass spectrum. In most cases, z = 1 so m/z usually gives the mass of a fragment directly.

Mass Spectrometry: How Does It Work?

- One of the more common approaches to generating an ion in mass spectrometry is **electron ionization** (EI).
- Essentially, the molecule is bombarded with electrons. When it gets hit by an electron, another electron is ejected from the molecule, leaving behind a radical cation (the molecular ion):





Animated image from http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/MassSpec/masspec1.htm

The Molecular Ion

- Most molecular ions are even. An odd molecular ion usually indicates an odd number of nitrogen atoms in the molecule.

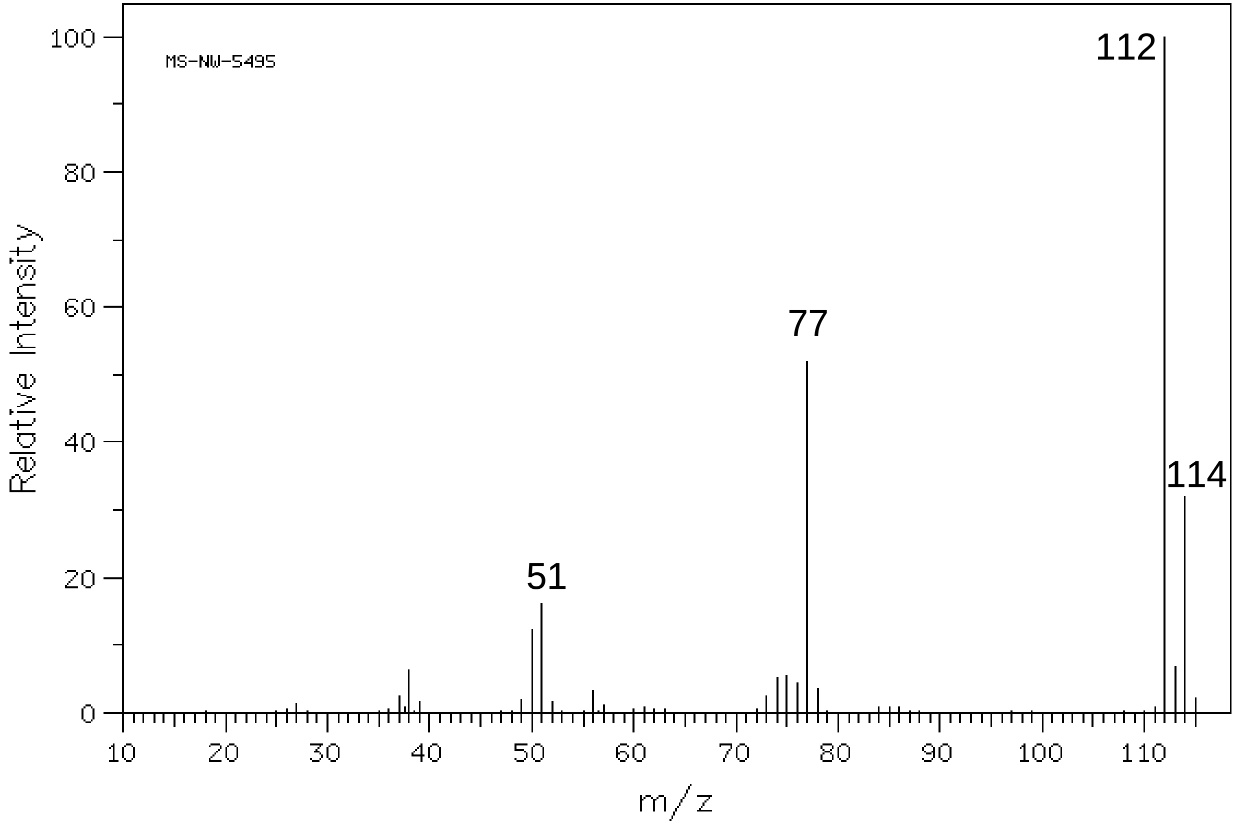
- The mass of the molecular ion can be combined with elemental analysis data to find a molecular formula.

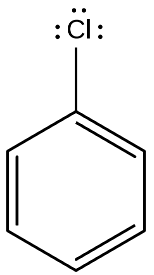
  e.g. A mass spectrum shows a molecular ion with m/z 114. Elemental analysis shows this species to be 63.16% C, 3.53% H 33.30% F. What is the molecular formula for this species?

- Alternatively, the exact mass from a high resolution mass spectrum (HRMS) can be used to determine the molecular formula.

Mass Spectrometry and Halogens (Cl)

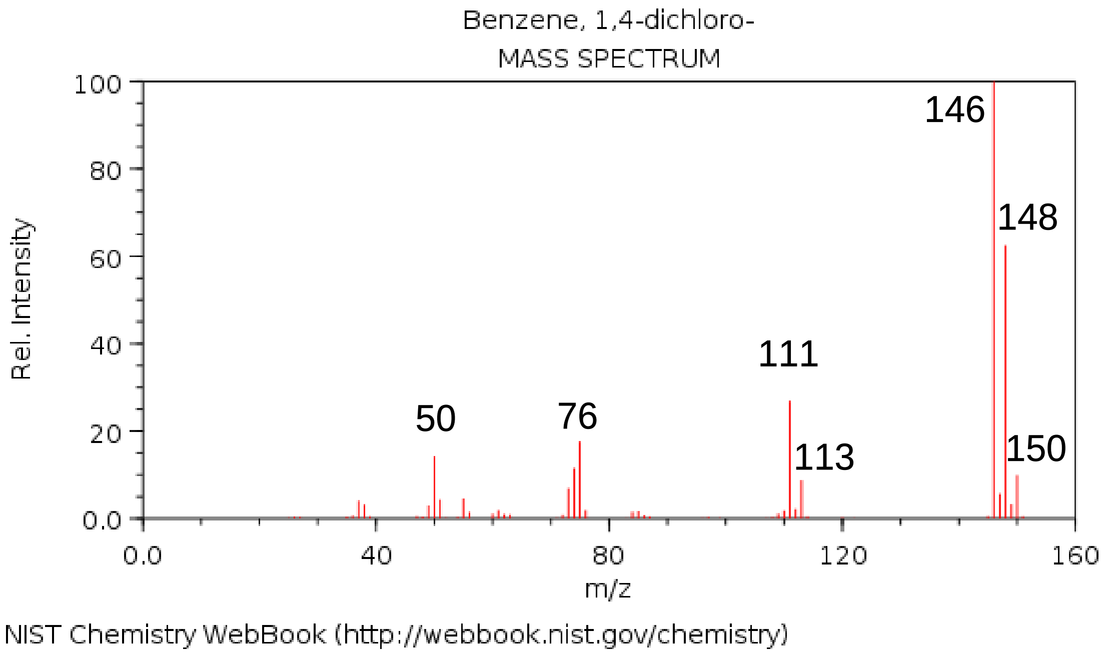
- As we saw on page 2, chlorine exists as a 3 : 1 mixture of isotopes. This means that every fragment containing a single chlorine atom will appear as a pair of peaks 2 units apart with a 3 : 1 ratio:

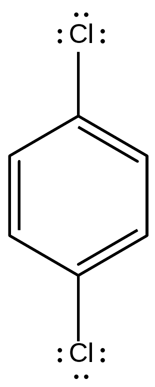




Mass Spectrometry and Halogens (Cl)

- It also means that every fragment containing two chlorine atoms will appear as a trio of peaks 2 units apart with a 9 : 6 : 1 ratio:

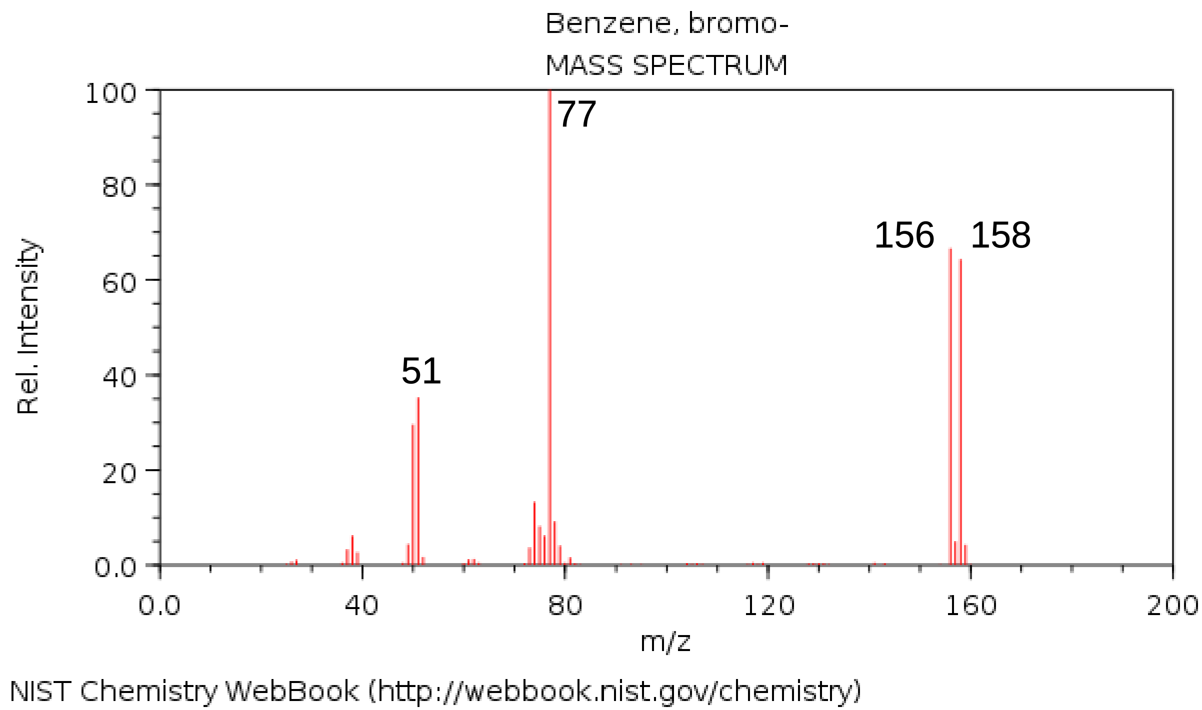


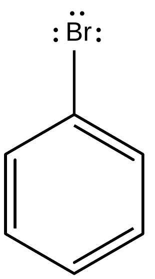


- Why is it a 9 : 6 : 1 ratio?

Mass Spectrometry and Halogens (Br)

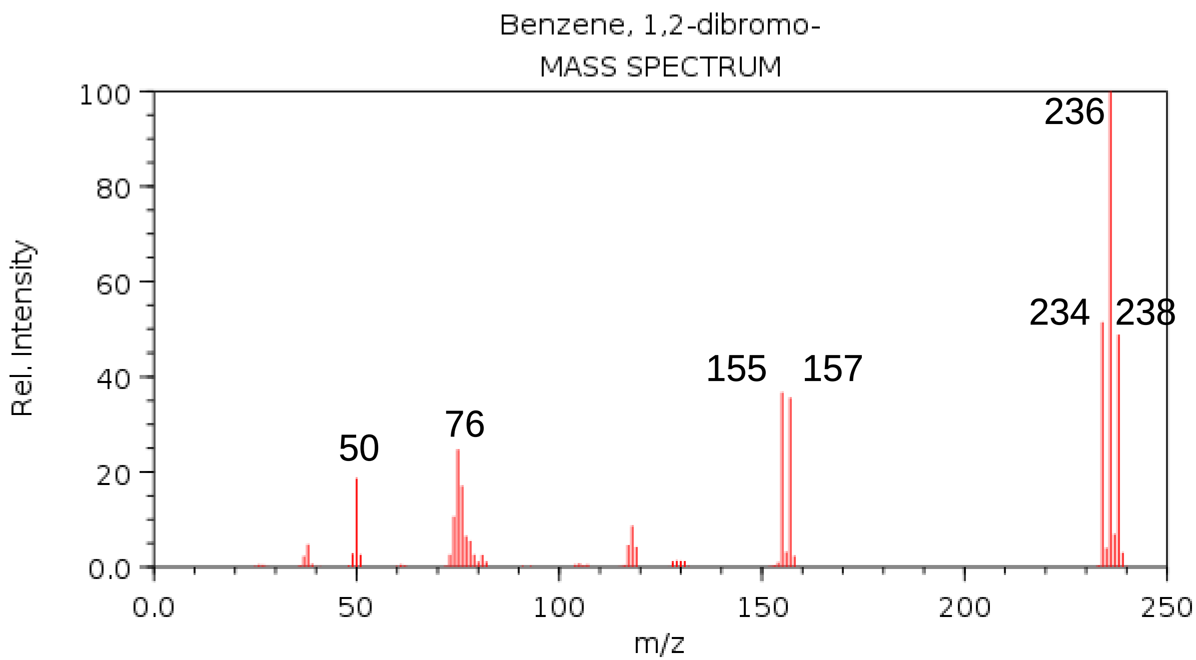
- Bromine exists as a 1 : 1 mixture of isotopes. This means that every fragment containing a single bromine atom will appear as a pair of peaks 2 units apart with a 1 : 1 ratio:



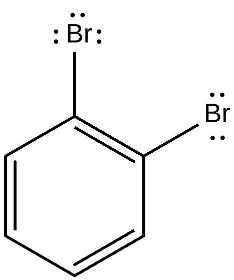


Mass Spectrometry and Halogens (Br)

- It also means that every fragment containing two bromine atoms will appear as a trio of peaks 2 units apart with a 1 : 2 : 1 ratio:



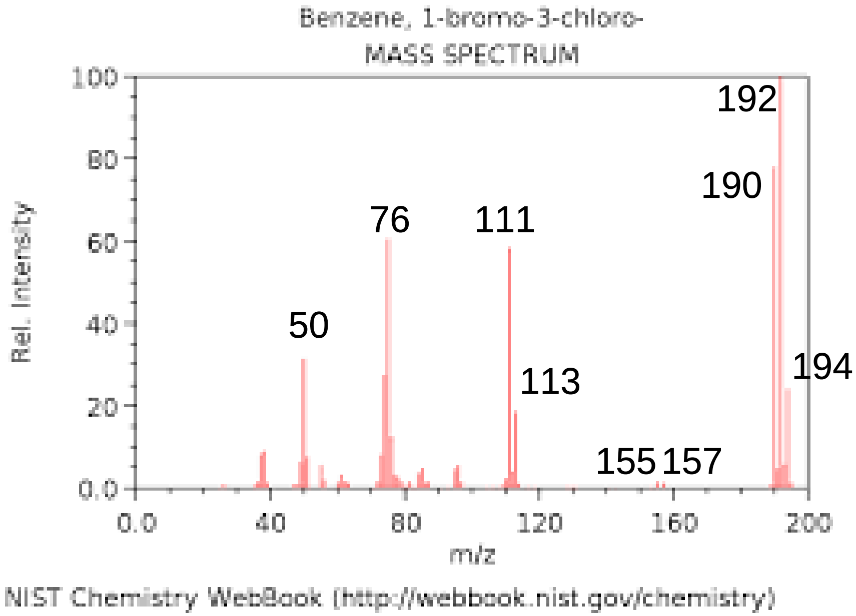
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

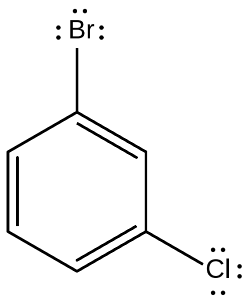


- Why is it a 1 : 2 : 1 ratio?

Mass Spectrometry and Halogens (Cl and Br)

- You can also recognize other combinations of chlorine and/or bromine atoms. For example, the mass spectrum below is for a molecule containing one chlorine and one bromine atom:

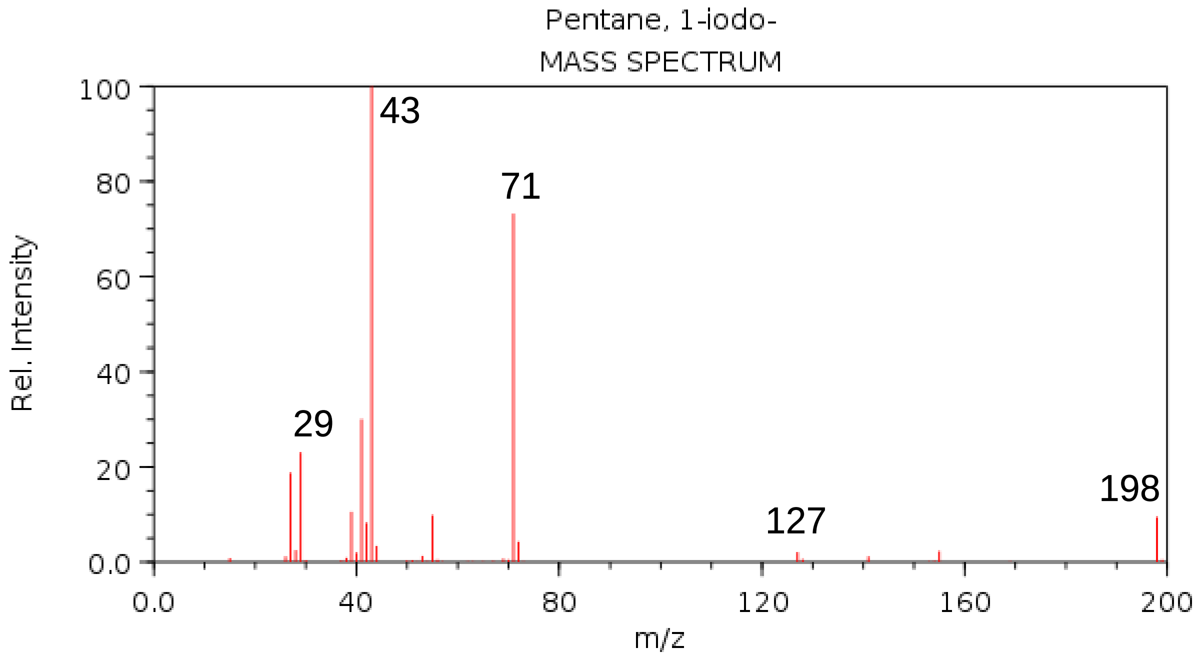


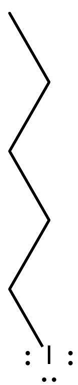


- What's the height ratio for this molecular ion? (M : M+2 : M+4)

Mass Spectrometry and Halogens (I)

- Note that the mass spectra involving Br have large gaps from the molecular ion to the next largest fragment. This is simply because Br has a much higher atomic mass than H, C, N, O, etc.
- We can use similar logic to recognize molecules containing I (even though I only has one significantly abundant isotope), looking for the molecular ion (M), the M-127 peak and/or a peak at m/z 127.





NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

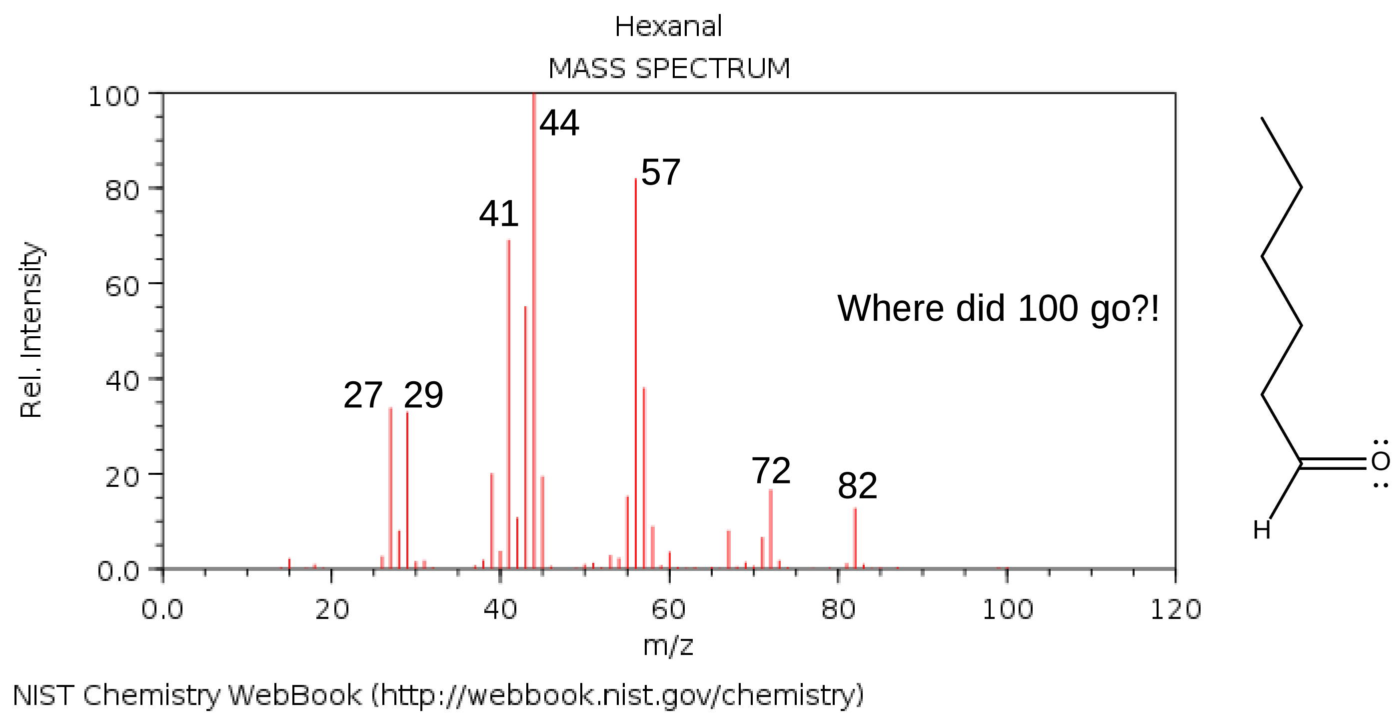
Mass Spectrometry and Halogens

- Percent abundances of relevant isotopes for MS of organic molecules:

Isotope	Abundance	Isotope	Abundance
^{1}H	99.98 %	^{19}F	100 %
^{2}H	0.01 %		
^{12}C	98.89 %	^{35}Cl	75.53 %
^{13}C	1.11 %	^{37}Cl	24.47 %
^{14}N	99.63 %	^{79}Br	50.54 %
^{15}N	0.37 %	^{81}Br	49.46 %
^{16}O	99.76 %	^{127}I	100 %
^{17}O	0.04 %		
^{18}O	0.20 %		

Fragmentation Patterns

- The molecular ion isn't the only useful piece of information on a mass spectrum – which is a good thing since sometimes it isn't even visible! The molar mass of hexanal is 100 g/mol.



- The mass spectrum contains other peaks corresponding to fragments formed via homolytic (radical) bond cleavage.

Fragmentation Patterns

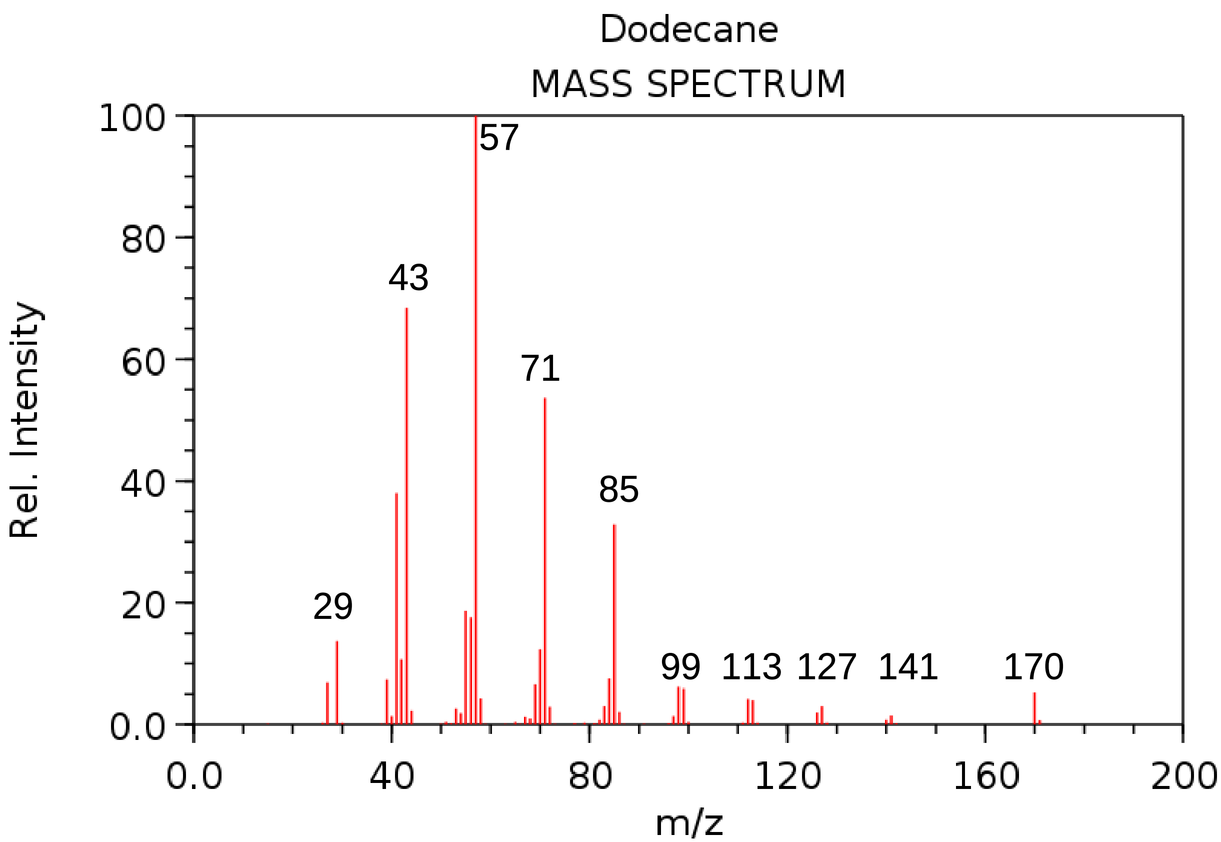
- Looking back at the mass spectra in these notes for aromatic molecules, we can see that all of the monosubstituted benzene rings contained a significant peak at m/z 77. What fragment was it for?

- We can also see that all of the disubstituted benzene rings contained a significant peak at m/z 76. What fragment was it for?

- Another peak common to many aromatic compounds is m/z 91. What fragment would that be for?

Fragmentation Patterns

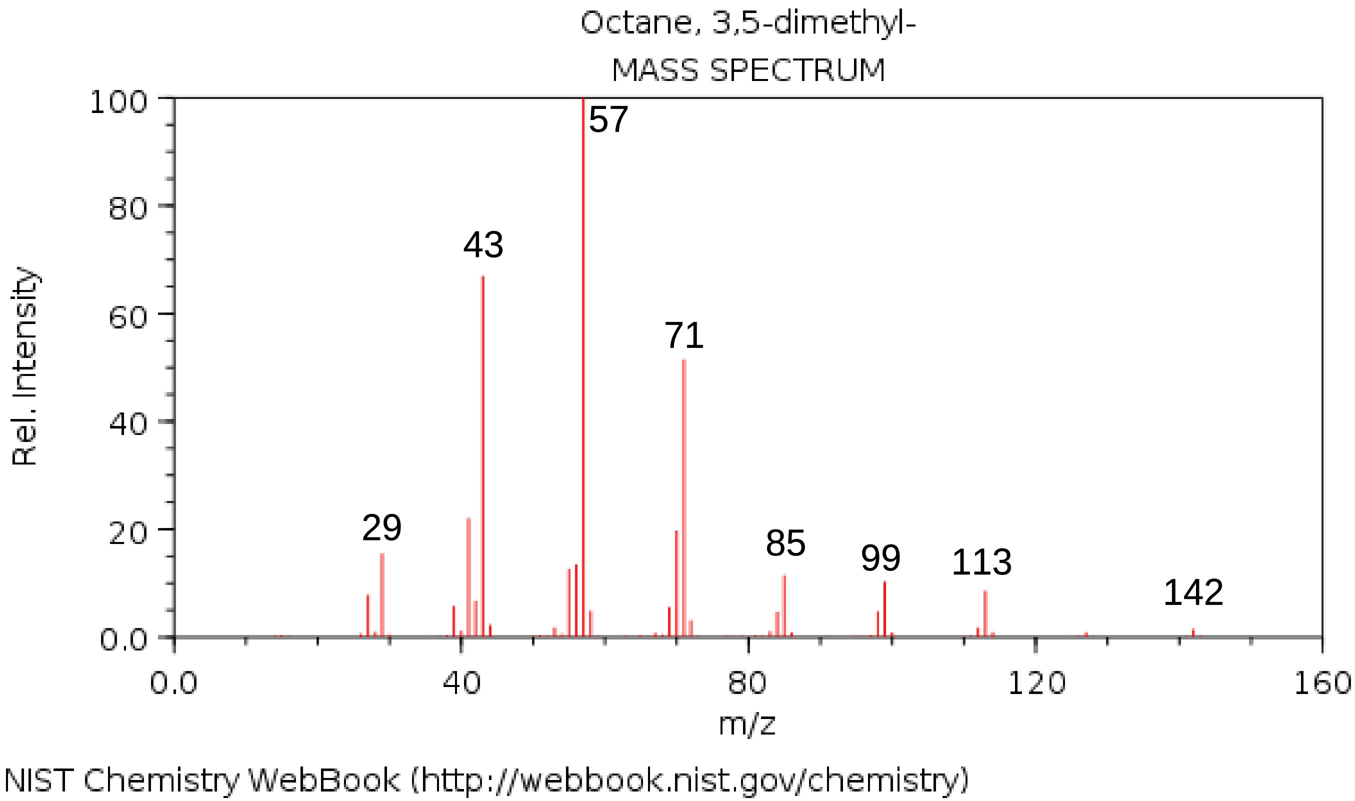
- Mass spectra for compounds containing long saturated carbon chains tend to have a series of peaks m/z 14 apart (mass of a $-CH_2-$ unit):

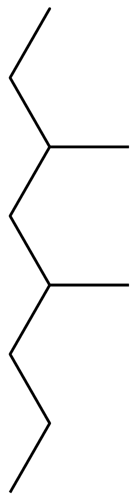


NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Fragmentation Patterns

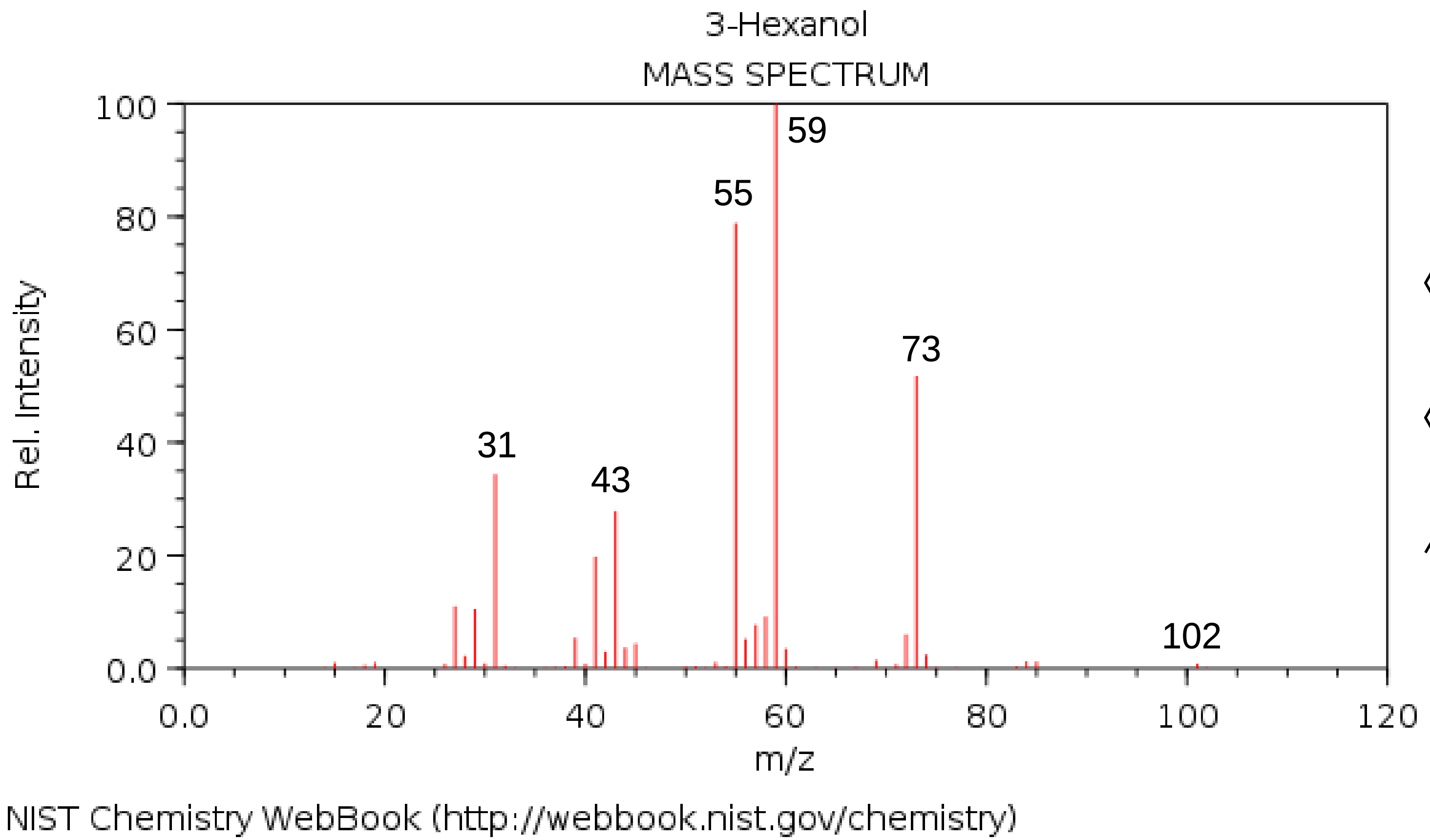
- The carbon chains can also contain branches:

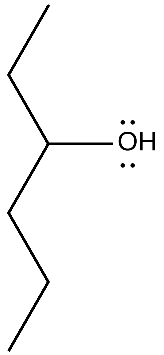




Fragmentation Patterns

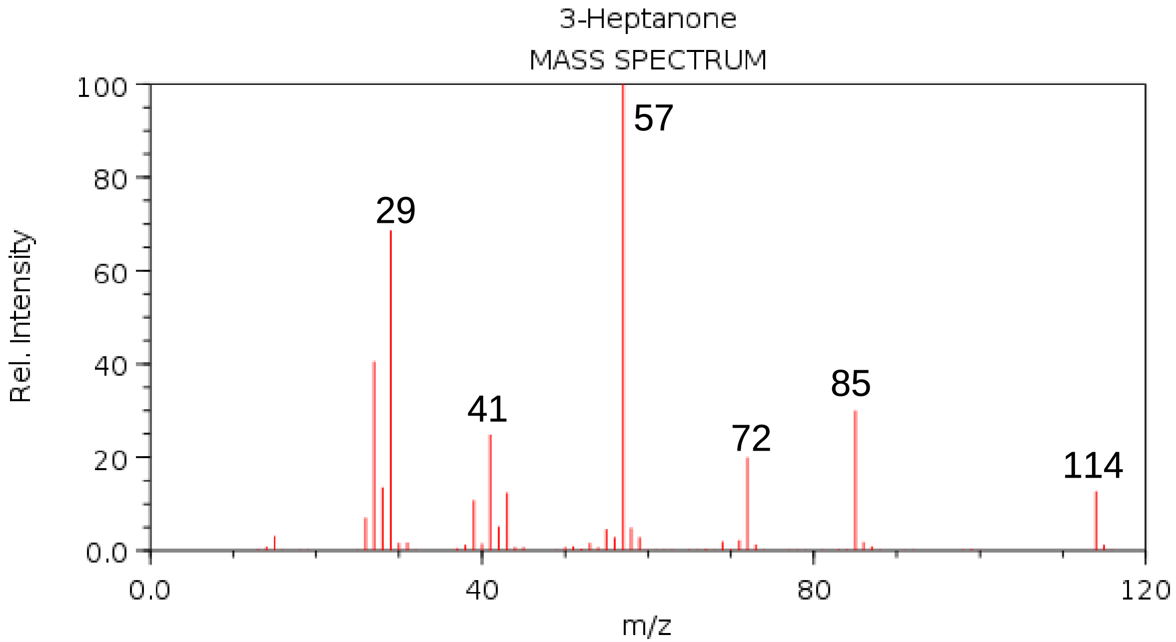
- Sometimes, fragments are formed via elimination reactions. You may see elimination of water in the MS of an alcohol:

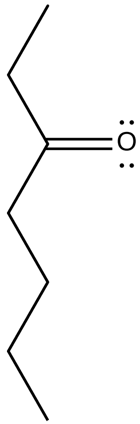




Fragmentation Patterns

- You may also see elimination of an alkene from a molecule containing an H atom that is three bonds away from a pi bond:





NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

- This is called a McLafferty rearrangement:

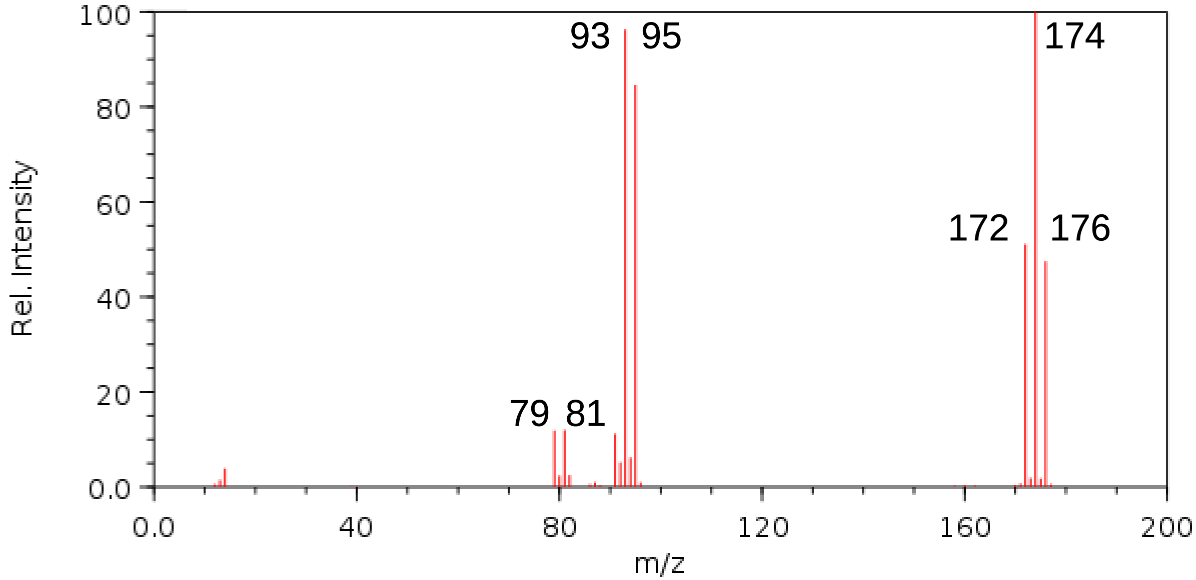
Fragmentation Patterns

- Even aromatic compounds can undergo McLafferty rearrangements:

- McLafferty rearrangements can sometimes be used to distinguish between constitutional isomers:

Practice Questions

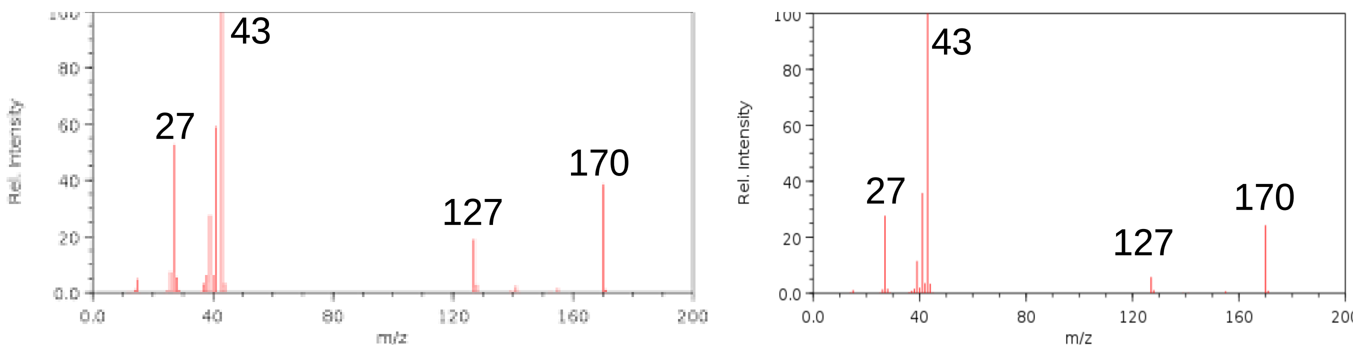
- Identify the molecular ion on this mass spectrum, and suggest the most likely molecular formula for this compound.



- How could you use other spectroscopic techniques to confirm this compound's identity?

Practice Questions

- These mass spectra are for two isomers:



- Identify the molecular ion on each spectrum, and suggest the most likely molecular formula for these compounds.

- How could you use other spectroscopic techniques to distinguish between these two compounds?