

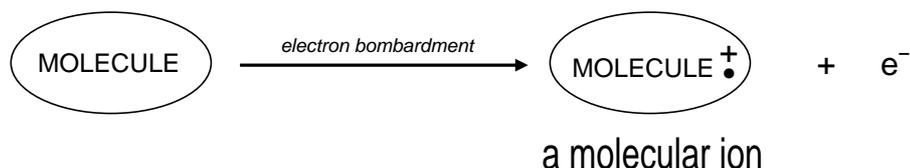
MASS SPECTROMETRY

Introduction A mass spectrum can be thought of as being the record of the “damage” done to a molecule when it is bombarded in the gas phase by a beam of electrons.

The starting molecules are destroyed and broken down into smaller pieces and these smaller pieces can, in turn, be broken down into even smaller pieces.

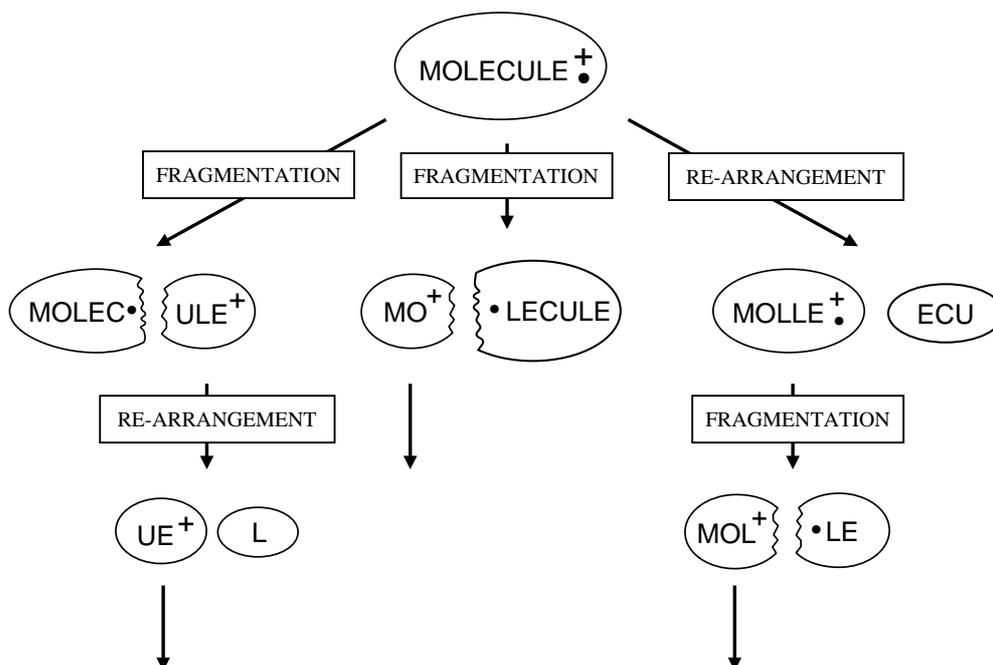
It is possible to decide from the data what these pieces are and then work back to deduce the identity of the original substance.

Theory When high energy electrons bombard molecule in a mass spectrometer, energy is transferred to that molecule. This can result in the molecule losing an electron.



The resulting species is positively charged because it has lost an electron. The dot (•) represents the unpaired electron remaining from an electron pair when the other electron has been expelled.

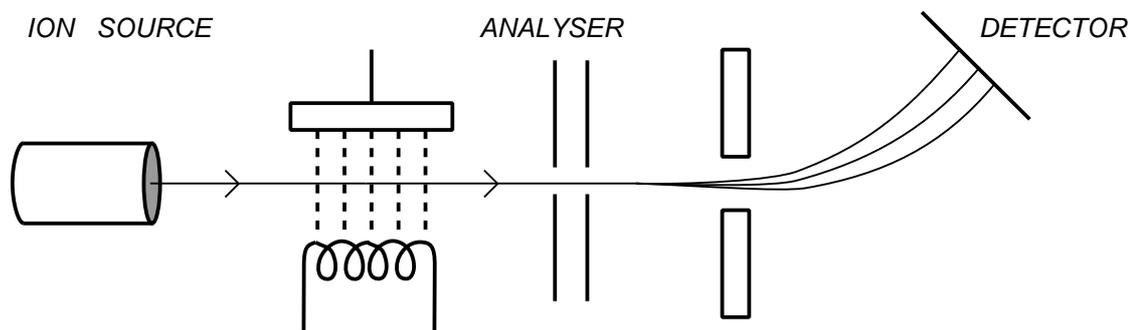
If it still has sufficient energy, the **molecular ion** can fragment further forming new ions, molecules or radicals. Radicals are neutral species containing an unpaired electron. A simple pattern showing possible fragmentations is shown below...



In addition to the steady **fragmentation** of pieces, **re-arrangement** of the structure can also take place giving rise to many other fragments.

The Mass Spectrometer

Operation A mass spectrometer consists of an ion source, an analyser and a detector.



Ion source The ion source is maintained at an extremely low pressure and the sample is heated to a temperature at which it will volatilize at the applied pressure. Very small samples (less than 10^{-3} g) of material are needed. A filament, usually made of rhenium or tungsten, is heated until it emits electrons; the energy of these electrons is very much higher than that required to break the bonds within a molecule. The fragmentation ions are accelerated out of the ion source by an electric field. Any parts of the sample that have not been ionised, plus any radicals or neutral molecules formed as a result of fragmentation or re-arrangement, will not be affected since they are uncharged and are not accelerated.

Analyser The analyser separates the ions according to their mass / charge (m/z). The radius of the path depends on the value of m/z ; ions of larger m/z values follow a curve of larger radius than those of lower m/z . Since most of the ions originating from organic molecules are singly charged (+1), the separation will be according to the mass of each fragment. Electric, magnetic or a combination of electric and magnetic fields can be used for the separation.

Detector Electric or photographic detection methods can be used to observe the presence of the ions. A mass spectrum records the mass/charge (m/z) values and the relative abundance for all fragments present. Instruments can have a range of sensitivities (resolving power). The greater the sensitivity, the finer the difference in mass/charge they can resolve. On a high resolution machine, the compounds $C_3H_6O_2$ and $C_4H_{10}O$ which have relative masses of 74.0604 and 74.0968 respectively can be distinguished by the appearance of two peaks but a low resolution instrument would show only one peak.

Data from low resolution instruments is routinely used by organic chemists as it provides...

- the exact molecular masses of molecules and
- structural information from interpretation of fragmentation patterns.

INTERPRETATION OF SPECTRA

Isotopes One of the first applications of the mass spectrum was the demonstration by F.W. Aston, that naturally occurring neon consisted of three isotopes ... ^{20}Ne , ^{21}Ne and ^{22}Ne . By comparing the positions of the peaks, one can calculate the atomic mass. In addition, the relative abundance of each isotope is found by comparing peak intensities.

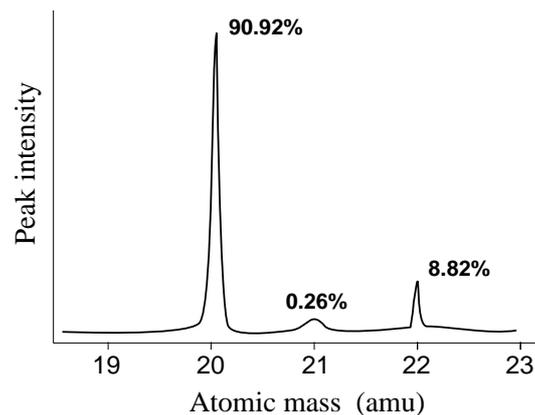


Fig. mass spectrum of the three neon isotopes

Elements Mass spectrometry is used in space probes for identification of elements in space.

Molecules Similar spectra are obtained for organic molecules but the number of peaks is much greater. Each peak is due to a particular fragment with a certain m/z value.

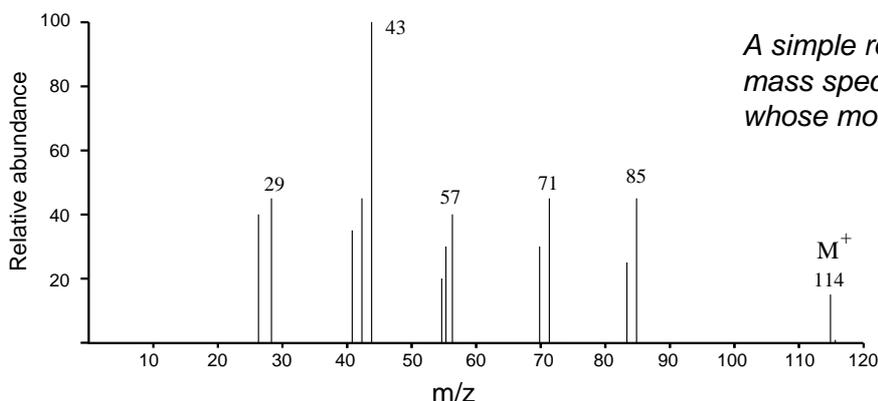
The **highest value usually corresponds to the molecular ion** and its position **provides information about the molecular mass** of a substance. In the spectrum of octane (below), a signal occurs at 114 due to the species $\text{C}_8\text{H}_{18}^+$.

The rest of the spectrum provides additional information about the structure.

Peaks appear due to

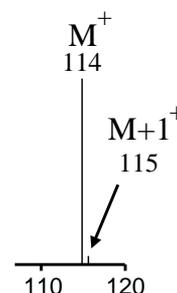
- characteristic fragments - e.g. 29 due to C_2H_5^+
- loss of small molecules such as H_2O , CO and CO_2

Many of the fragments do not show up because they are not ions.



A simple representation of the mass spectrum of a compound whose molecular mass is 114

The small peak ($M+1$) at 115 due to the natural abundance (about 1%) of carbon-13. The height of this peak relative to that for the molecular ion depends on the number of carbon atoms in the molecule. The more carbons present, the larger the $M+1$ peak.



Isotopic

Abundance If several peaks occur in the molecular ion region it is due to naturally occurring isotopes of elements in the compound. In most cases the abundance of some of the isotopes is very small but, for chlorine and bromine, the values are significant.

Abundances of some natural isotopes

^1H	99.985%	^2H	0.015%		
^{12}C	98.893%	^{13}C	1.107%		
^{14}N	99.64%	^{15}N	0.36%		
^{16}O	99.759%	^{17}O	0.037%	^{18}O	0.204%
^{32}S	95%	^{33}S	0.76%	^{34}S	4.2%
^{19}F	100%				
^{35}Cl	75.8%	^{37}Cl	24.2%		
^{79}Br	50.537%	^{81}Br	49.463%		
^{172}I	100%				

FRAGMENTATION PATTERNS OF FUNCTIONAL GROUPS

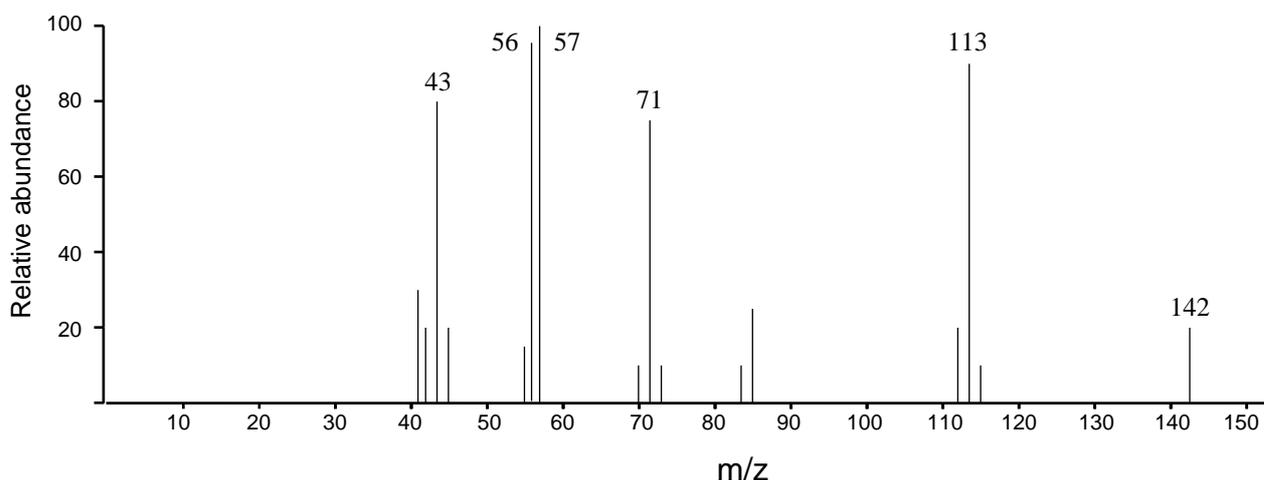
Introduction Interpretation of thousands of spectra shows classes of organic compounds show characteristic fragmentation patterns due to their functional groups. It is often possible to identify the type of compound from its spectrum by looking at the ...

- position of peaks
- differences between major peaks.

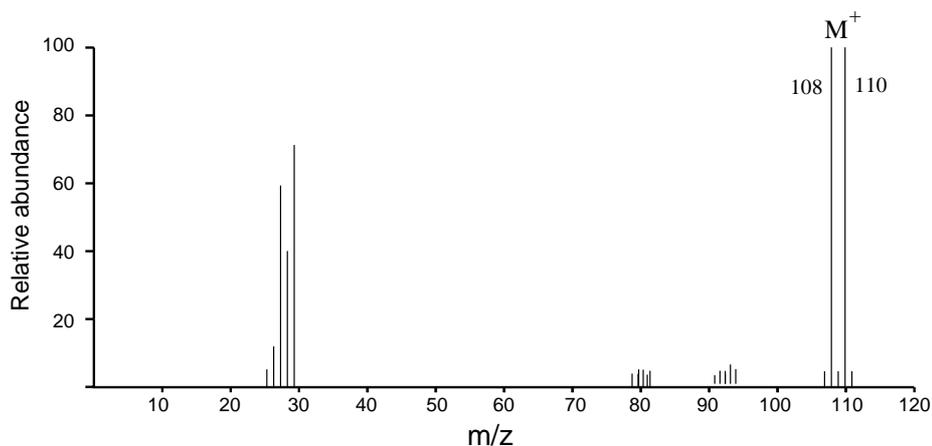
Alkanes

The mass spectra of these simple hydrocarbons have peaks at m/z values corresponding to the ions produced by breaking C-C bonds. Peaks can occur at;

m/z	15	29	43	57	71	85	<i>etc.</i>
	CH_3^+	C_2H_5^+	C_3H_7^+	C_4H_9^+	$\text{C}_5\text{H}_{11}^+$	$\text{C}_6\text{H}_{13}^+$	

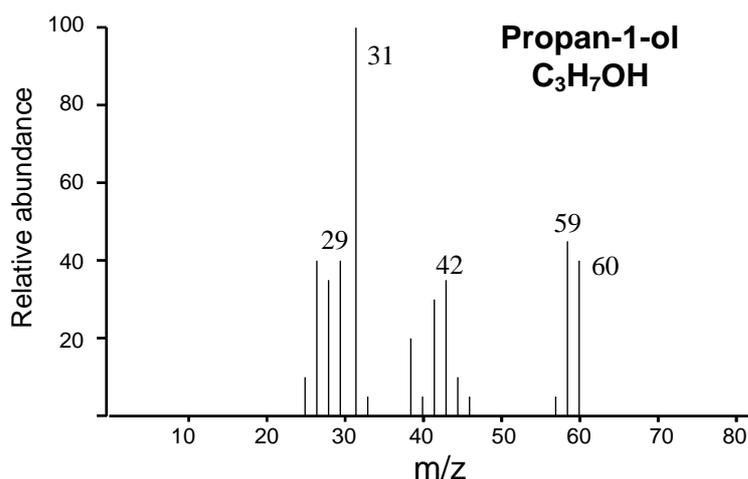
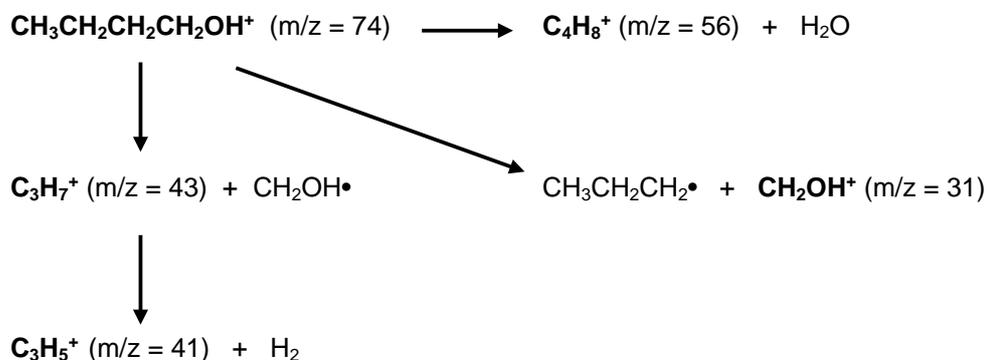


Haloalkanes The spectrum of a haloalkane often shows multiple peaks in the molecular ion region due to the different isotopes of the halogens. Elimination of a halogen radical is also common.



There are **two peaks for the molecular ion**, one for the molecule containing the isotope ^{79}Br and the other for the one with the ^{81}Br isotope. **Because the two isotopes are of similar abundance, the peaks are of similar height.**

Alcohols A characteristic aspects of the mass spectra of alcohols is the **loss of a water molecule giving a peak at 18 below the molecular ion**. Another common peak occurs at 31 due to the breaking of a C-C bond between the carbon bearing the OH group and an adjacent carbon; this produces an ion CH_2OH^+ .



Peaks	
60	molecular ion
59	$\text{C}_3\text{H}_7\text{O}^+$
42	loss of water
31	CH_2OH^+
29	C_2H_5^+