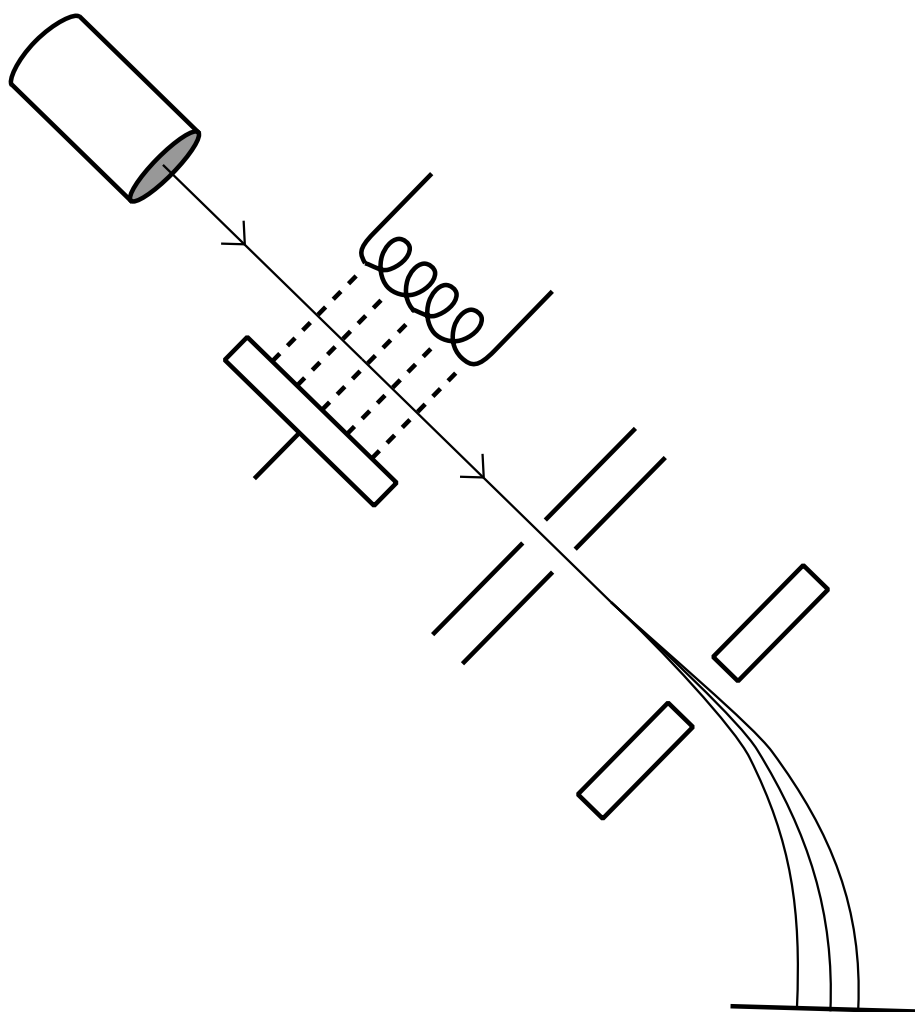# AN INTRODUCTION TO ...:

MASS SPECTROMETRY

*— A self-study booklet —*

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 process is carried out in an instrument known as a mass spectrometer. 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. Usually, it is possible to decide from the data what these pieces are and then work back to deduce the identity of the original substance. Mass spectra may also be used to determine the extent and location of isotopes of any atoms present in substance.

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

$$ \text{MOLECULE} \xrightarrow{\;electron\;bombardment\;} \text{MOLECULE}^{+}_{\bullet} \;+\; e^{-} $$

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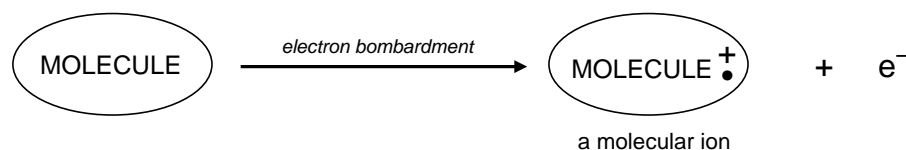
The resulting species is positively charged because it has lost an electron. The dot (•) represents the unpaired electron remaining from an electron pair when the other electron has been expelled.

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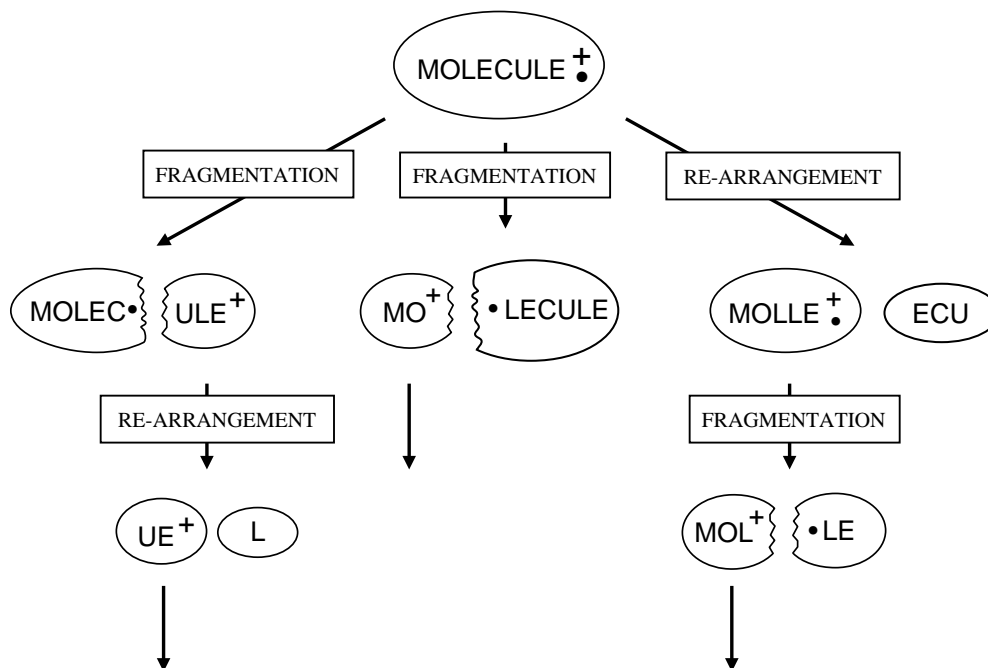

In addition to the steady **fragmentation** of pieces, **re-arrangement** of the structure can also take place giving rise to many other fragments.

The Mass Spectrometer

Operation   The sample pressure of a typical mass spectrometer is kept extremely low so that intramolecular fragmentations and re-arrangements can occur but the probability of any reactions occurring between species is highly unlikely. The relative concentrations of ions is dependent upon the relative rates of formation and subsequent fragmentation and re-arrangement of all the ions.

Instrumentation

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

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     ION   SOURCE              ANALYSER              DETECTOR
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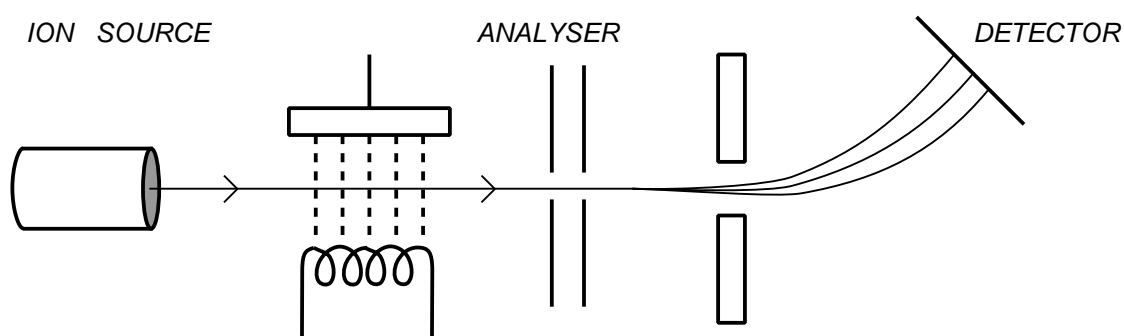

Ion source   The ion source is maintained at an extremely low pressure and the sample is heated to a temperature at which it will volatilize at the applied pressure. Very small samples (less than 10^{-3}g) of material are needed. A filament, usually made of rhenium or tungsten, is heated until it emits 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, (Nobel Prize winner in 1922), 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 can be found by comparing the peak intensities.
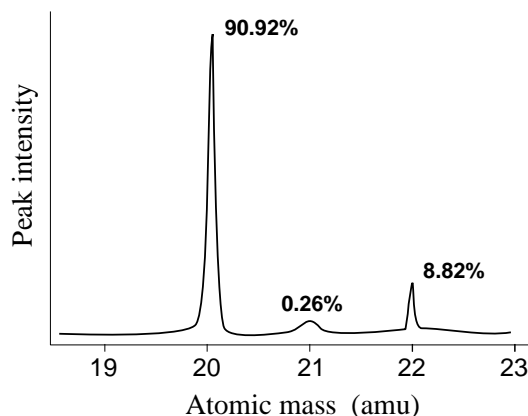

Fig. mass spectrum of the three neon isotopes

Molecules   Similar spectra are obtained for organic molecules but the number of peaks is significantly 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 $C_8H_{18}^+$.

The rest of the spectrum provides additional information of the molecule's structure.

Peaks appear due to characteristic fragments (e.g. 29 due to $C_2H_5^+$) and differences between two peaks also indicates the loss of certain units (e.g. 18 for H_2O, 28 for CO and 44 for CO_2). Many of the fragments do not show up themselves on the spectrum because they are not ions.
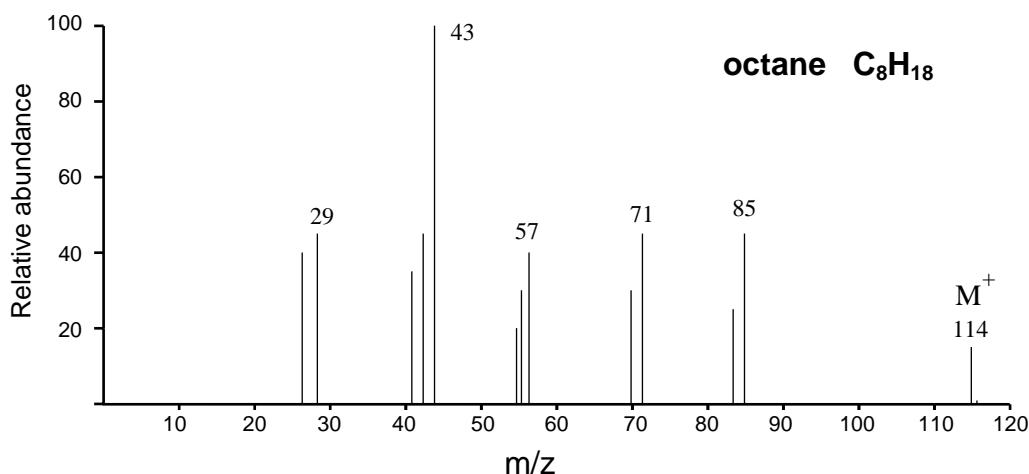
The small peak (M+1) at 115 due to the natural abundance (about 1%) of carbon-13. The height of this peak relative to that for the molecular ion depends on the number of carbon atoms in the molecule. The more carbons present, the larger the M+1 peak.
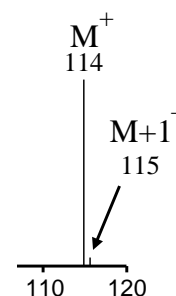
Isotopic
Abundance If several peaks occur in the molecular ion region it is due to naturally occurring isotopes of elements in the compound. In most cases the abundances of some of the isotopes is very small but, in the case of chlorine and bromine, the values can be significant.

Abundances of some natural isotopes

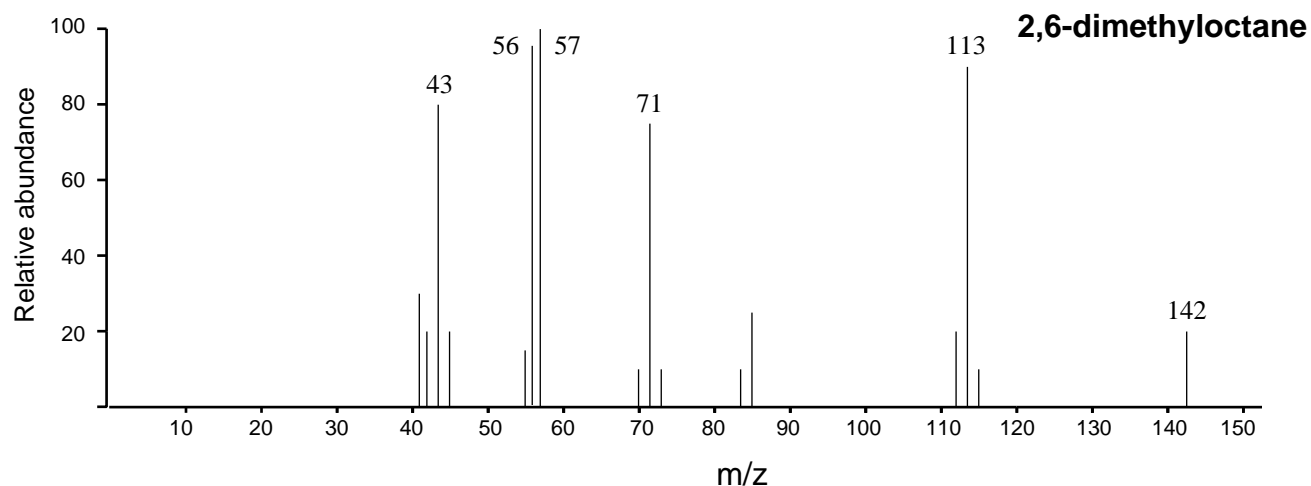|					
^{1}H	99.985%	^{2}H	0.015%		
^{12}C	98.893%	^{13}C	1.107%		
^{14}N	99.64%	^{15}N	0.36%		
^{16}O	99.759%	^{17}O	0.037%	^{18}O	0.204%
^{32}S	95%	^{33}S	0.76%	^{34}S	4.2%
^{19}F	100%				
^{35}Cl	75.8%	^{37}Cl	24.2%		
^{79}Br	50.537%	^{81}Br	49.463%		
^{172}I	100%				

FRAGMENTATION PATTERNS OF FUNCTIONAL GROUPS

Introduction Interpretation of thousands of spectra has shown that many classes of organic compound 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 ...

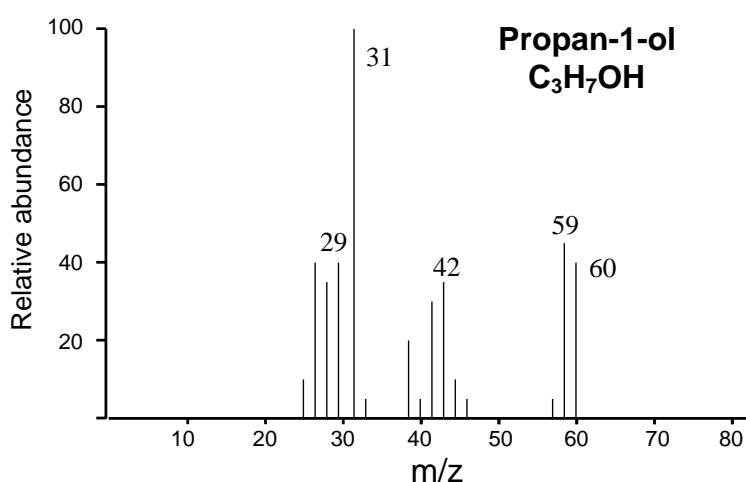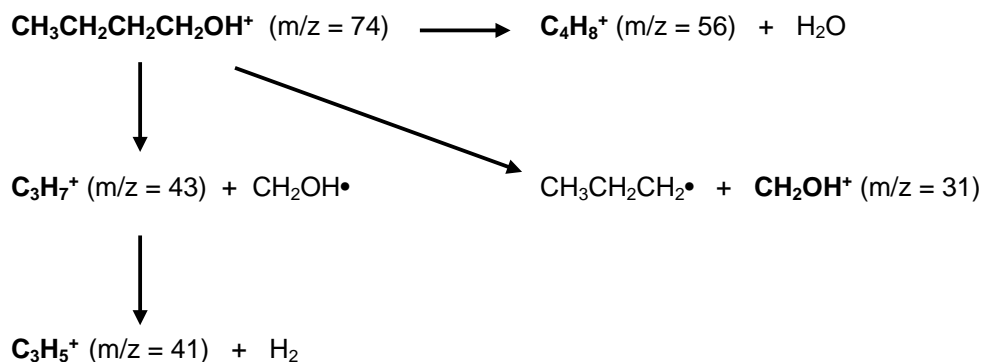| **m/z**	**15**	**29**	**43**	**57**	**71**	**85**	*etc.*
	CH_3^+	$C_2H_5^+$	$C_3H_7^+$	$C_4H_9^+$	$C_5H_{11}^+$	$C_6H_{13}^+$	

2,6-dimethyloctane

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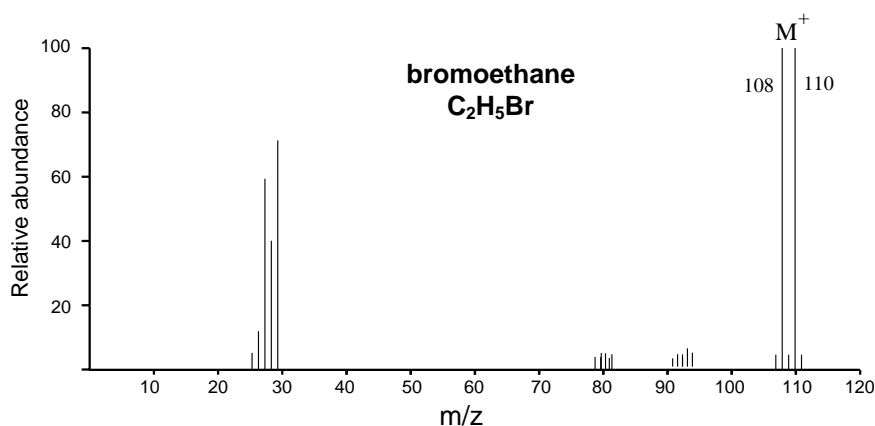
There are **two peaks for the molecular ion**, one for the molecule containing the isotope ^{79}Br and the other for the one with the ^{81}Br isotope. **Because the two isotopes are of similar abundance**, **the peaks are of similar height**.

Alcohols One of the most 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^+.

$$CH_3CH_2CH_2CH_2OH^+ \ (m/z = 74) \longrightarrow C_4H_8^+ \ (m/z = 56) \ + \ H_2O$$

$$C_3H_7^+ \ (m/z = 43) \ + \ CH_2OH\bullet \qquad CH_3CH_2CH_2\bullet \ + \ CH_2OH^+ \ (m/z = 31)$$

$$C_3H_5^+ \ (m/z = 41) \ + \ H_2$$

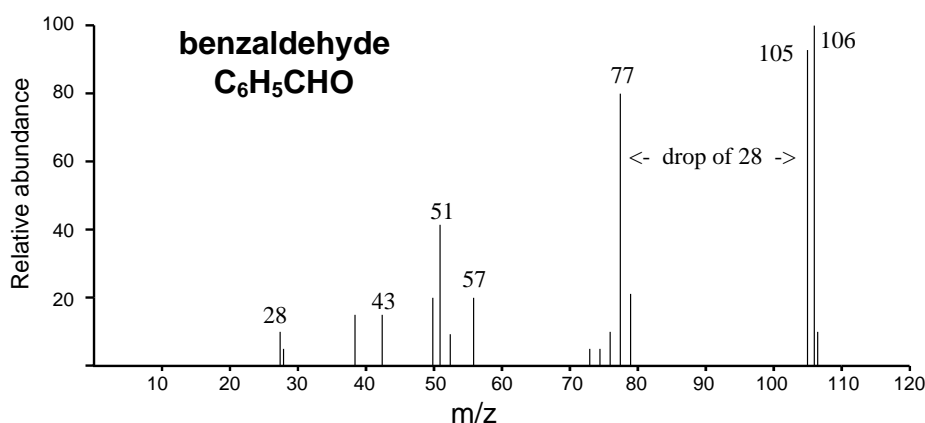| Peaks	
60	molecular ion
59	$C_3H_7O^+$
42	loss of water
31	CH_2OH^+
29	$C_2H_5^+$

**Aldehydes
& Ketones** Cleavage of bonds next to the carbonyl group (C=O) is a characteristic fragmentation of aldehydes and ketones. A **common fragment is carbon monoxide (CO)** but as it is a molecule and thus uncharged it will not produce a peak of its own. However, it will produce an **m/z drop of 28** somewhere in the spectrum.

*The position of the carbonyl group influences
the fragmentation pattern because the molecular
ion fragments either side of the carbonyl group.*

$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R' \nearrow RCO^+ + R'{\bullet}$$
$$\searrow R'CO^+ + R{\bullet}$$

**phenylethanone
$C_6H_5COCH_3$**

<- drop of 28 ->
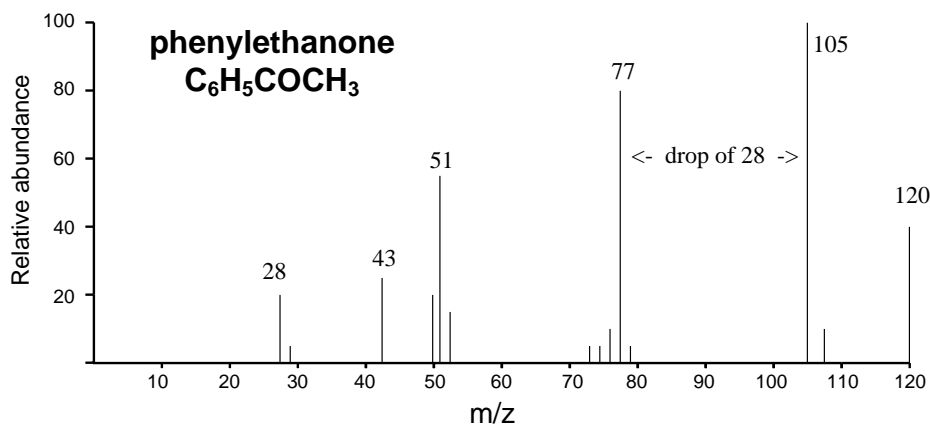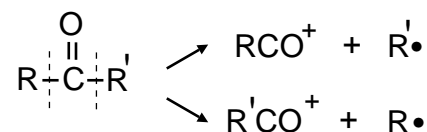
Peaks	
120	molecular ion
105	$C_6H_5CO^+$
77	$C_6H_5^+$
51	$C_4H_3^+$
43	CH_3CO^+
28	CO

**benzaldehyde
C_6H_5CHO**

<- drop of 28 ->

Peaks	
106	molecular ion
105	$C_6H_5CO^+$
77	$C_6H_5^+$
51	$C_4H_3^+$
43	CH_3CO^+
28	CO

Esters Cleavage of bonds next to the C=O group (see aldehydes and ketones) and evolution of carbon monoxide are common features of the mass spectra of these compounds.

$C_3H_7COOC_2H_5$
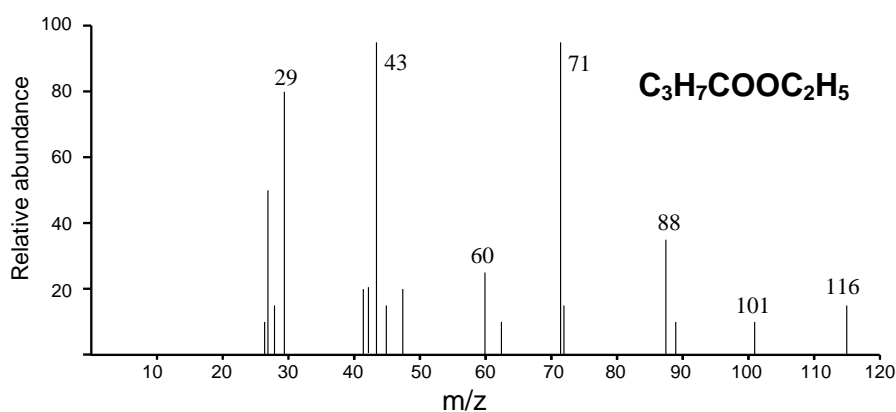
Peaks	
116	molecular ion
88	loss of CO
71	$C_3H_7CO^+$
43	$C_3H_7^+$
29	$C_2H_5^+$

Some common ions and their m/z value

The following table lists some groups commonly associated with
particular ions plus a possible inference for the compound

m/z	fragment	origin	m/z	fragment	origin
15	CH_3^+		58	$C_2H_6N^+$	*aliphatic amine*
18	H_2O^+		59	$COOCH_3^+$	*methyl ester*
26	$C_2H_2^+$			$CH_2OC_2H_5^+$	*ether*
27	$C_2H_3^+$		68	$C_3H_6CN^+$	
30	$CH_2NH_2^+$	*1° amine*	69	$C_5H_9^+$	
31	CH_2OH^+	*1° alcohol*	70	$C_5H_{10}^+$	
36/38 (3:1)	HCl^+		71	$C_5H_{11}^+$	
39	$C_3H_3^+$			$C_3H_7CO^+$	*ketone/ester*
40	$C_3H_4^+$		72	$C_3H_7CHNH_2^+$	*amine*
41	$C_3H_5^+$		73	$C_4H_9O^+$	
43	$C_3H_7^+$	*haloalkane*		$COOC_2H_5^+$	*ethyl ester*
	CH_3CO^+	*acyl halide*	76	$C_6H_4^+$	C_6H_5X
44	$C_2H_6N^+$	*amine*	77	$C_6H_5^+$	C_6H_5X
	$CONH_2^+$	*1° amide*	78	$C_6H_6^+$	C_6H_5X
	$CH_2CH(OH)^+$		79	$C_6H_7^+$	C_6H_5X
45	$CH_3CH(OH)^+$		79/81 (1:1)	Br^+	
49/51(3:1)	CH_2Cl^+		80/82 (1:1)	HBr^+	
50	$C_4H_2^+$	*aromatic*	80	$C_5H_6N^+$	
51	$C_4H_3^+$	C_6H_5X	81	$C_5H_5O^+$	
55	$C_4H_7^+$		85	$C_6H_{13}^+$	$C_6H_{13}X$
56	$C_4H_8^+$			$C_4H_9CO^+$	
57	$C_4H_9^+$	C_4H_9X			
	$C_2H_5CO^+$	*ketone/ester*			

Some common losses from molecular ions

The following table shows the groups commonly associated with mass lost from the
molecular ion (M) plus a possible inference for the compound under investigation.

M-1	H		M-33	HS	*thiol*
M-2	H_2			$CH_3 + H_2O$	
M-15	CH_3		M-34	H_2S	*thiol*
M-16	NH_2	*amide*	M-41	C_3H_5	*propyl ester*
M-17	OH		M-42	CH_2CO	*methyl ketone*
	NH_3			C_3H_6	*butyl ketone*
M-18	H_2O	*alcohol/carbonyl*	M-43	C_3H_7	*propyl ketone*
M-19	F	*fluoride*		CH_3CO	*methyl ketone*
M-20	HF	*fluoride*	M-44	CO_2	*ester/anhydride*
M-26	C_2H_2	*aromatic h/carbon*		C_3H_8	
M-27	HCN	*aromatic nitrile*	M-45	COOH	*carboxylic acid*
M-28	CO			OC_2H_5	*ethyl ester*
	C_2H_4	*ethyl ester*	M-46	C_2H_5OH	*ethyl ester*
M-29	CHO			NO_2	*nitrobenzenes*
M-29	C_2H_5	*ethyl ketone*	M-55	C_4H_7	*butyl ester*
M-30	C_2H_6		M-56	C_4H_8	
	CH_2O	*aromatic ether*	M-57	C_4H_9	*butyl ketone*
	NO	*nitrobenzenes*		C_2H_5CO	*butyl ketone*
M-31	OCH_3	*methyl ester*	M-58	C_4H_{10}	
M-32	CH_3OH	*methyl ester*	M-60	CH_3COOH	*ethanoate*