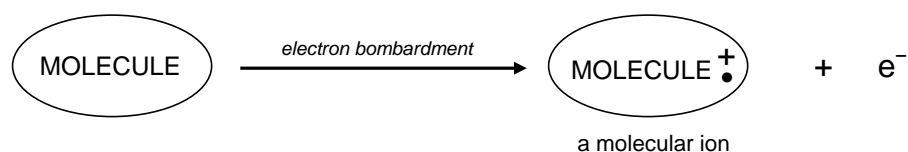


MASS SPECTROMETRY

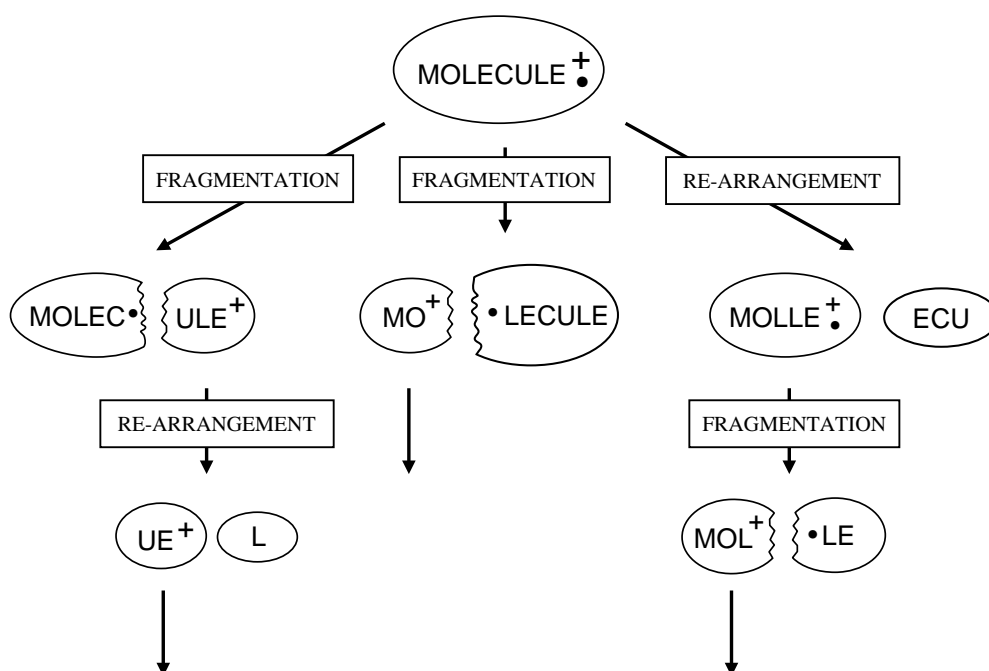
Introduction A mass spectrum can be thought of as being the record of the “damage” done to a molecule when it is bombarded in the gas phase by a beam of electrons. The process is carried out in an instrument known as a mass spectrometer. The starting molecules are destroyed and broken down into smaller 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 ...



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

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.

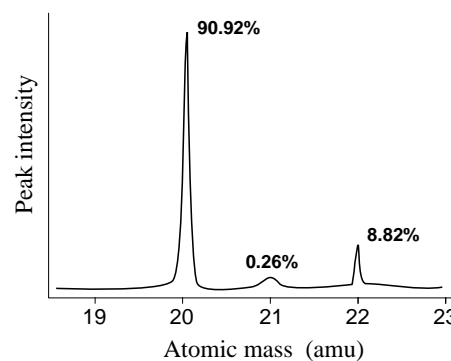


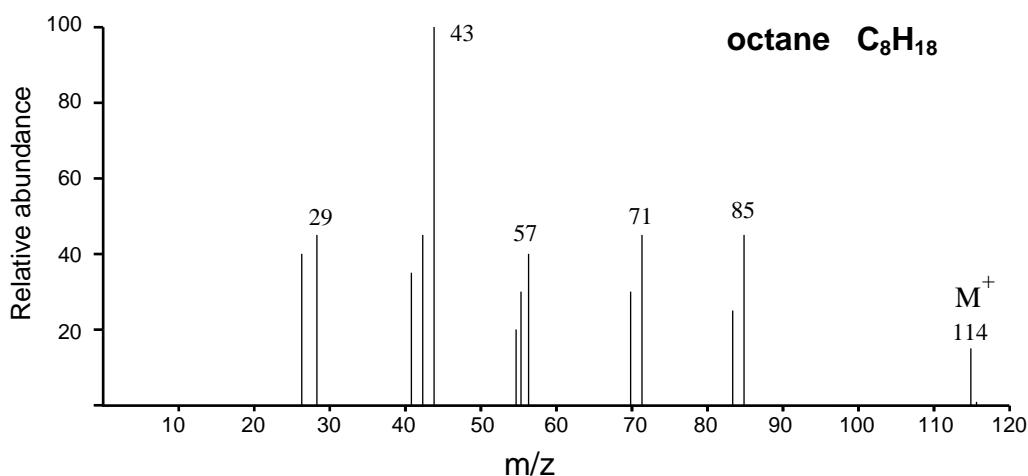
Fig. mass spectrum of the three neon isotopes

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.

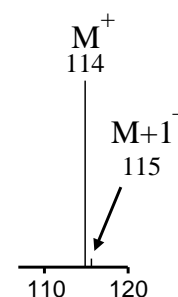
- **highest m/z value usually corresponds to the molecular ion**
- its position **provides information about the molecular mass** of a substance
- in the spectrum of octane (below), a signal occurs at 114 due to the species $\text{C}_8\text{H}_{18}^+$
- The **tallest** peaks come from the **most stable** species

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 because they are not charged 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.



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 ...

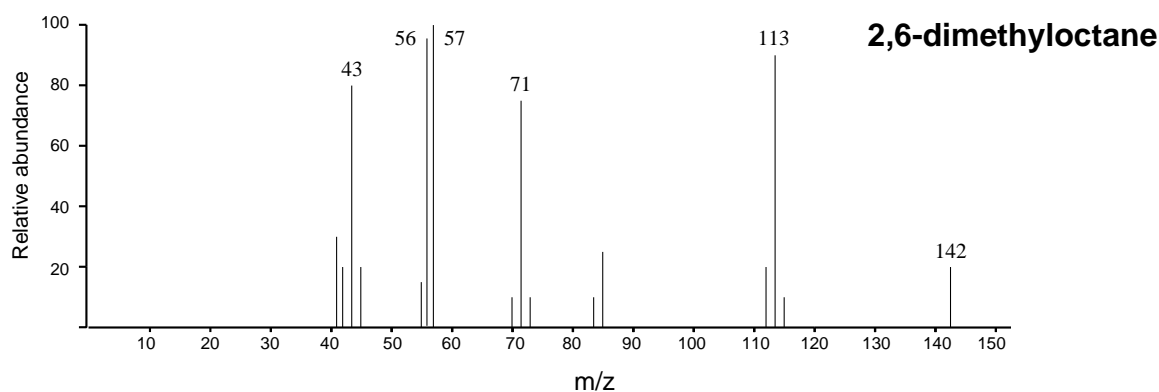
- position of peaks
- differences between major peaks

Alkanes

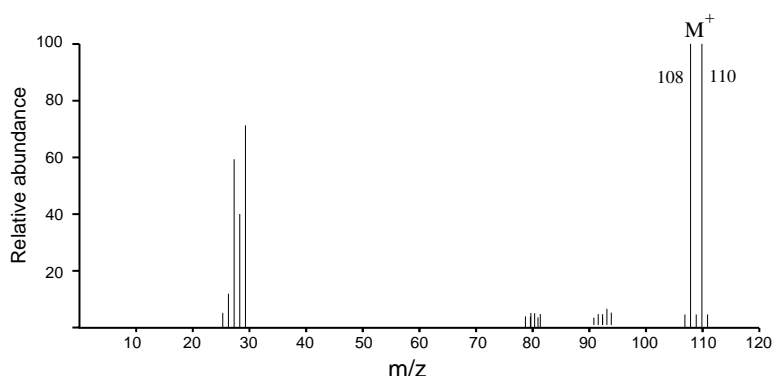
The mass spectra of these simple hydrocarbons have peaks at m/z values corresponding to the ions produced by breaking C-C bonds. Peaks can occur at ...

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

- the stability of the carbocation formed affects its abundance
- the more stable the cation the higher the peak
- the more alkyl groups attached to the carbocation the more stable it is
- *most stable* tertiary $3^\circ >$ secondary $2^\circ >$ primary 1° *least stable*
- alkyl groups are electron releasing and stabilise the cation



Haloalkanes The spectrum of a haloalkane often shows **multiple peaks in the molecular ion region** due to the **different isotopes** of the halogens.

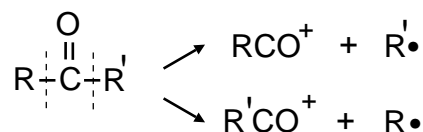


There are **two peaks for the molecular ion**, one for the molecule containing the isotope ^{79}Br and the other for the one with the ^{81}Br isotope. **Because the two isotopes are of similar abundance, the peaks are of similar height.**

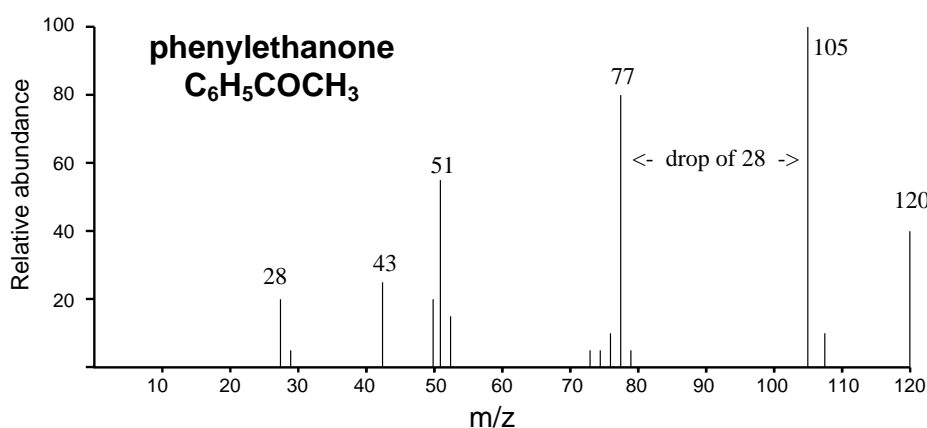
Aldehydes & Ketones

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.

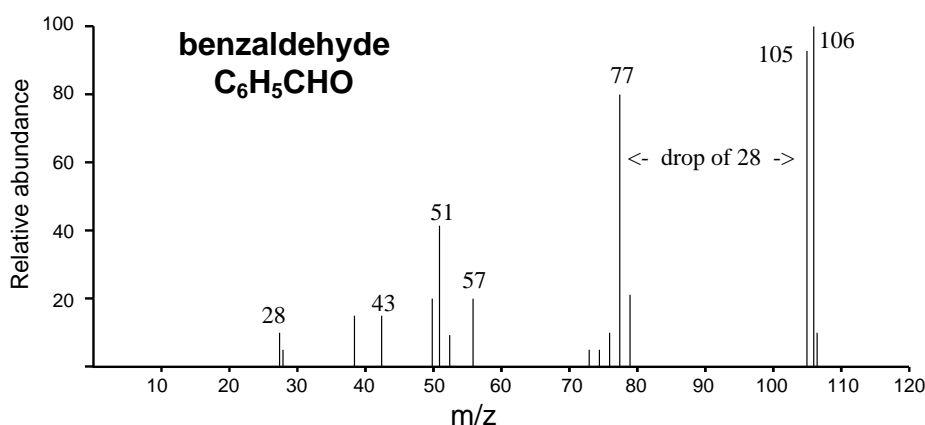
The position of the carbonyl group influences the fragmentation pattern because the molecular ion fragments either side of the carbonyl group



- the **more stable the acylium ion RCO⁺** the more abundant it will be
- the **more abundant the species** the taller its peak



| Peaks | |
|-------|---|
| 120 | molecular ion |
| 105 | C ₆ H ₅ CO ⁺ |
| 77 | C ₆ H ₅ ⁺ |
| 51 | C ₄ H ₃ ⁺ |
| 43 | CH ₃ CO ⁺ |
| 28 | CO |



| Peaks | |
|-------|---|
| 106 | molecular ion |
| 105 | C ₆ H ₅ CO ⁺ |
| 77 | C ₆ H ₅ ⁺ |
| 51 | C ₄ H ₃ ⁺ |
| 43 | CH ₃ CO ⁺ |
| 28 | CO |

Q.1 Give the m/z value of some peaks which might occur in the mass spectrum of...

- ethylbenzoate
- ethylethanoate
- methylethanoate
- C₆H₅COC(CH₃)₂