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**CHEMISTRY**
**PAPER No. 12: Organic spectroscopy**
**MODULE No. 24 : Mass Spectrometry: Theory,  
 instrumentation and modifications**

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## 1. Learning Outcomes

After studying this module, you shall be able to

- Know what is mass spectrometry
- Learn the principle of mass spectrometry
- Identify molecular ion peak
- Evaluate a mass spectrum
- Analyse the various types of mass spectrometers

## 2. Introduction

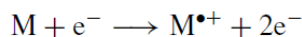
Mass Spectrometry (MS) is an analytic technique used to determine the relative masses of molecular ions and fragments by calculating the degree of deflection of charged particles in a magnetic field. It provides a great deal of information with very small amount of samples. Mass spectrometry is used to:

- Determine molecular mass
- Determine molecular formula of a compound
- Determine structural features of the compound
- Find out the structure of an unknown substance
- Provide data on isotopic abundance
- Verify the identity and purity of a known substance

**Mass spectrometry** is an instrumental technique that does not involve electromagnetic radiation. Thus, it is called spectrometry, whereas the others such as UV, NMR, IR are called spectroscopy.

The principle of mass spectrometry involves the generation of ions from either inorganic or organic compounds, to separate the ions by their mass-to-charge ratio ( $m/z$ ) and to detect them qualitatively and quantitatively by their  $m/z$  value and relative abundance.

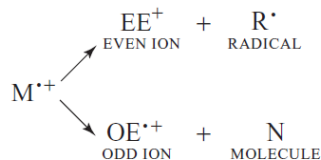
In the first step a beam of energetic electron produce gas phase ions of the compound. Removal of one electron from the molecule ( $M$ ) results into generation of parent ion ( $M^{\bullet+}$  or molecular ion). The molecular mass of the compound is equal to the  $m/z$  value of the parent ion.



This parent ion or molecular ion normally undergoes fragmentations (fragment ions or daughter ions). The parent ion ( $M^{\bullet+}$ ) is a radical cation with an odd number of electrons, it can fragment to

give either a radical ( $R^\cdot$ ) and an ion with an even number of electrons ( $EE^+$ ), or a molecule (N)

and a new radical cation ( $OE^+$ ).



These two types of ions derived from the molecular ion can, further undergo fragmentation, and so on. All these ions formed are then separated by the mass spectrometer according to their mass-to-charge ratio. Only positively charged species reach the collector. The charge ( $z$ ) on all the fragments is +1, therefore  $m/z$  is equal to the molecular mass ( $m$ ) of the fragment. A graph of the relative abundance of each fragment plotted against its  $m/z$  value is called a mass spectrum.

For example, in the case of methane ( $CH_4$ ), the impact of high energy electrons causes the molecule to lose an electron and form a radical cation with  $m/z$  16. A species, with a positive charge and one unpaired electron is called radical cation.

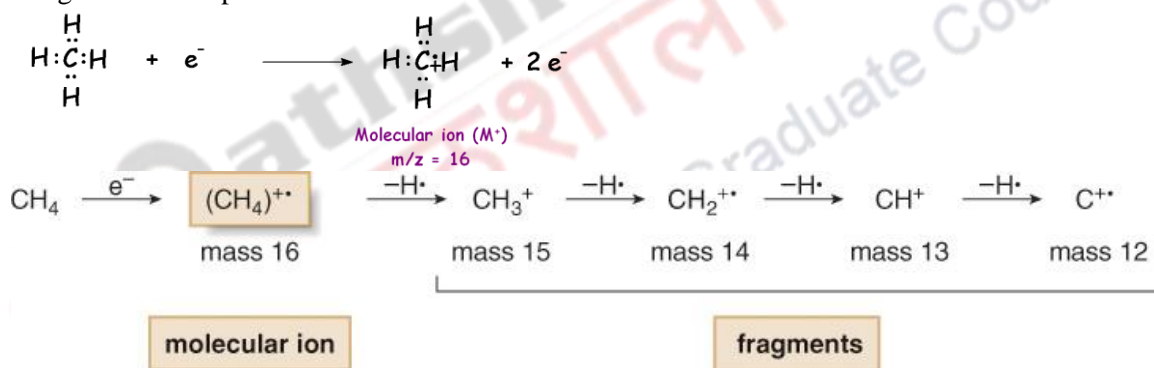


Figure 1: Fragmentation in methane

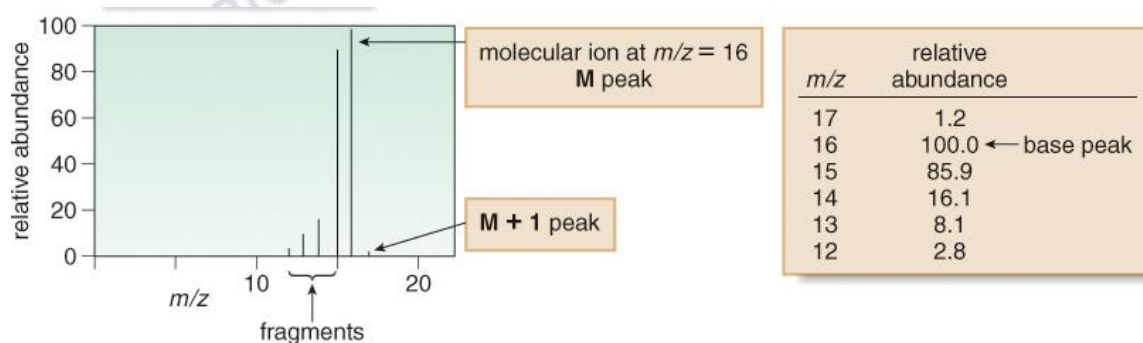


Figure 2: Mass spectrum of methane

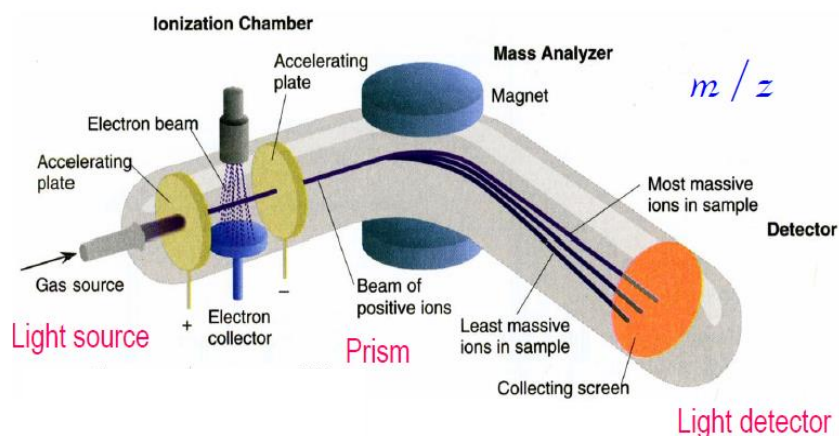
### 3. Instrumentation: Mass Spectrometer

The mass spectrometer consists of:

**3.1 Ion source**

**3.2 Mass analyzer**

**3.3 Ion detector**



**Figure 3: Diagram of mass spectrometer**

#### 3.1 Ion source (Ionisation):

In the first step a little amount of a compound is evaporated. The vaporized sample is, then ionized by bombardment with a beam of high energy electrons (usually 70 eV). The electron beam knocks out an electron from the molecule of the injected sample, creating a molecular ion (a radical cation). The molecular ion further breaks into fragments as it travels through the mass spectrometer as loss of electron weakens its bonds and collision gives it extra kinetic energy.

There is a pair of oppositely charged plates in the ionization chamber. The positively charged one causes the positively charged radical cation to accelerate into an analyzer tube.

The energy required for removing one electron from the neutral parent molecule is usually 10 eV. With this much energy, no fragmentation of the parent ion takes place. But the energy of the bombarding electron is around 70 eV, the additional energy is consumed in fragmenting the parent ion. This results in the formation of fragment ions of the daughter ions.

#### 3.2 Mass analyzer:

The separation of ions takes place in the analyzer at a pressure of about 10<sup>-8</sup> mbar. The analyzer tube is surrounded by a curved magnetic field, which causes the path of the radical cation to be deflected in proportion to its mass-to-charge ratio (m/z). The flight path of the ion depends on its molecular mass, its charge, and the strength of the magnetic field. Thus, at a given magnetic field strength, ions of only one specific mass collide with the detector and are recorded.

#### 3.3 Ion detector:

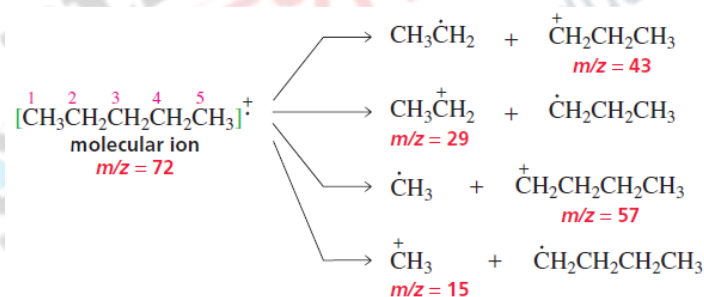
The ions which are separated by the analyser are detected and measured electrically or photographically. After the ions have passed the exit-slit, they collide on a collector-electrode. The resulting current is amplified and registered as a function of the magnetic-field force or the accelerating voltage.

The strength of the magnetic field is varied in increments to produce a mass spectrum, which is a plot of  $m/z$  (on the x axis) against relative abundance (on the y axis). If we assume that all ions have a charge of +1, then the peaks give the mass ratios and their heights give the proportions of ions of different masses.

#### 4. Fragmentation in pentane

The  $m/z$  value is the **nominal molecular mass** of the fragment and it is the molecular mass to the nearest whole number.

For example, pentane has a molecular mass of 72.0939 and a nominal molecular mass of 72. Pentane undergoes fragmentation, between carbon-carbon bonds to form various radical cations with different  $m/z$  value. Weak bonds break in preference to strong bonds, and bonds that break to form more stable fragments break in preference to those that form less stable fragments.



Mass spectra can be shown either as bar graphs or in tabular form.

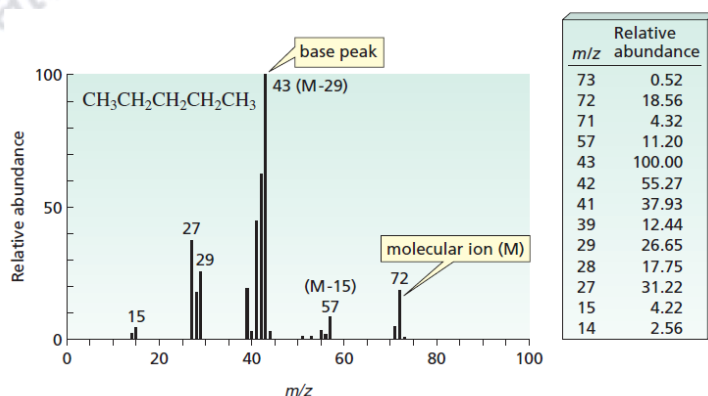


Figure 4: Mass spectrum of pentane (bar graph and tabular form)



The peak with the highest  $m/z$  72 value in the spectrum of pentane is due to the fragment that results when an electron is knocked out of a molecule (figure 4). It is called **molecular ion** peak and it is equal to molecular mass of pentane.

Peaks with  $m/z$  values less than 72 are called fragment ion peaks. The peak at  $m/z$  43 with the greatest intensity is called **base peak**.

## 5. Types of Mass Spectrometer

Depending upon the methods of ionization, ion separation and detection, there are various types of mass spectrometers as shown.



### **Ionisation**

#### **Ion Source**

Electron Ionisation (EI)

Chemical Ionisation (CI)

Fast Atom Bombardment (FAB)

Electrospray Ionisation (ESI)

Matrix-Assisted Laserdesorption/  
Ionisation (MALDI)

### **Ion Separation**

#### **Mass Analyser**

Quadrupole

Magnetic Sector Field

Electric Sector Field

Time-Of-Flight (TOF)

Ion Trap

### **Ion Detection**

#### **Detector**

Electron Multiplier

Multichannel plate

Faraday Cup

## 5.1 Ionization Methods in Organic Mass Spectrometry

There are many types of ionisation methods available with their own, advantage and disadvantage. The ionisation method to be employed depends on the type of sample under investigation and the mass spectrometer available.

**The various ionization methods are following:**

- Electron Impact Ionisation (EI)
- Chemical Ionisation (CI)
- Fast Atom Bombardment (FAB)
- Electrospray Ionisation (ESI)
- Matrix Assisted Laser Desorption Ionisation (MALDI)

Most of the ionisation methods create both positively and negatively charged sample ions, depending on the proton affinity of the sample. In **positive ionisation** mode the **protonated molecular ions** ( $M+H^+$ ) are generated. In **negative ionisation** mode the **deprotonated molecular ions** ( $M-H^-$ ) are usually generated.

## 5.2 Analysis and Separation of Sample Ions

The main function of the mass analyser is to separate, or resolve, the ions formed in the ionisation source of the mass spectrometer according to their mass-to-charge ( $m/z$ ) ratios. There are a number of mass analysers currently available, the better known of which include quadrupoles, magnetic sectors, electric sectors, time-of-flight (TOF) analysers, and both Fourier transform and quadrupole ion traps.

**Tandem mass spectrometers** are instruments that have more than one analyser and so can be used for structural and sequencing studies. Two, three and four analysers have all been incorporated into commercially available tandem instruments, and the analysers do not necessarily have to be of the same type, in which case the instrument is a hybrid one. More popular tandem mass spectrometers include those of the quadrupole-quadrupole, magnetic sector-quadrupole, and more recently, the quadrupole-time-of-flight geometries.

## 5.3 Detection and recording of sample ions

The detector monitors the ion current, amplifies it and the signal is then transmitted to the data system where it is recorded in the form of mass spectra. The  $m/z$  values of the ions are plotted against their intensities to show the number of components in the sample, the molecular mass of each component, and the relative abundance of the various components in the sample.

The type of detector is supplied to suit the type of analyser; the more common ones are the electron multiplier, the multi-channel plate and Faraday cup detectors.



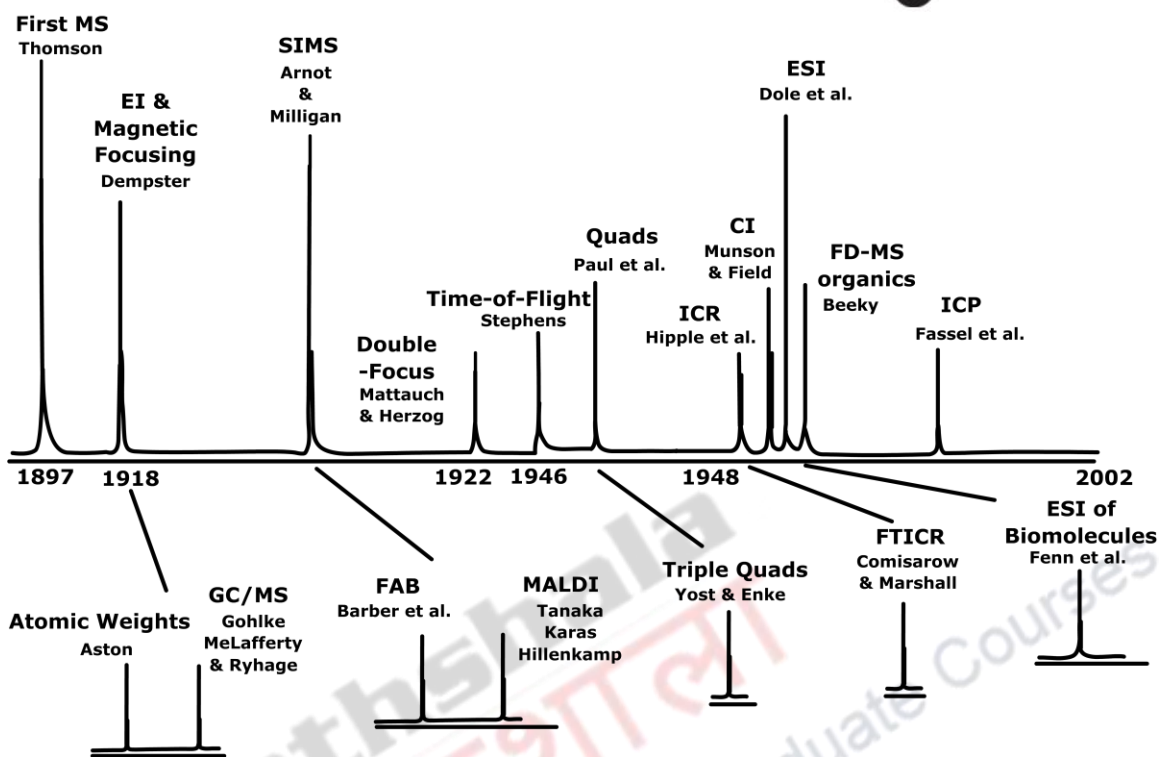


Figure 5: Historical development of mass spectrometry techniques

## 5. Summary

- Mass Spectrometry (MS) is an analytic technique used to determine the relative masses of molecular ions and fragments by calculating the degree of deflection of charged particles in a magnetic field.
- The mass spectrometer consists of ion source, mass analyzer and ion detector.
- The vaporized sample is, then ionized by bombardment with a beam of high energy electrons (usually 70 eV).
- The electron beam knocks out an electron from the molecule of the injected sample, creating a molecular ion (a radical cation).
- The separation of ions takes place in the analyzer.
- The ions which are separated by the analyser are detected and measured electrically or photographically.
- The  $m/z$  value is the nominal molecular mass of the fragment and it is the molecular mass to the nearest whole number.
- Mass spectra can be shown either as bar graphs or in tabular form.
- Peaks with  $m/z$  values less than parent ion are called fragment ion peaks.
- The peak with the greatest intensity is called base peak.
- The various ionization methods are Electron Impact Ionisation (EI), Chemical Ionisation (CI), Fast Atom Bombardment (FAB), Electrospray Ionisation (ESI) and Matrix Assisted Laser Desorption Ionisation (MALDI).
- The various types of mass analysers include quadrupoles, magnetic sectors, electric sectors, time-of-flight (TOF) analysers and both Fourier transform and quadrupole ion traps.
- The common type of detectors are the electron multiplier, the multi-channel plate and Faraday cup detectors.