SPECTROSCOPY

Programme Code- MSCCH-17/18/19

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Block – 3 Mass Spectrometry-I

Lecture-4

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❖***LEARNING OUTCOMES***

After studying this Chapter, you shall be able to:

❖To know about mass spectrometry

❖Principle of mass spectrometry

❖Identify molecular ion peak

❖Evaluate a mass spectrum

❖Analyze the various types of mass spectrometers

❖ ***WHAT IS MASS SPECTROMETRY (MS):***

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

Important: 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.

❖ **Principle of mass spectrometry:**

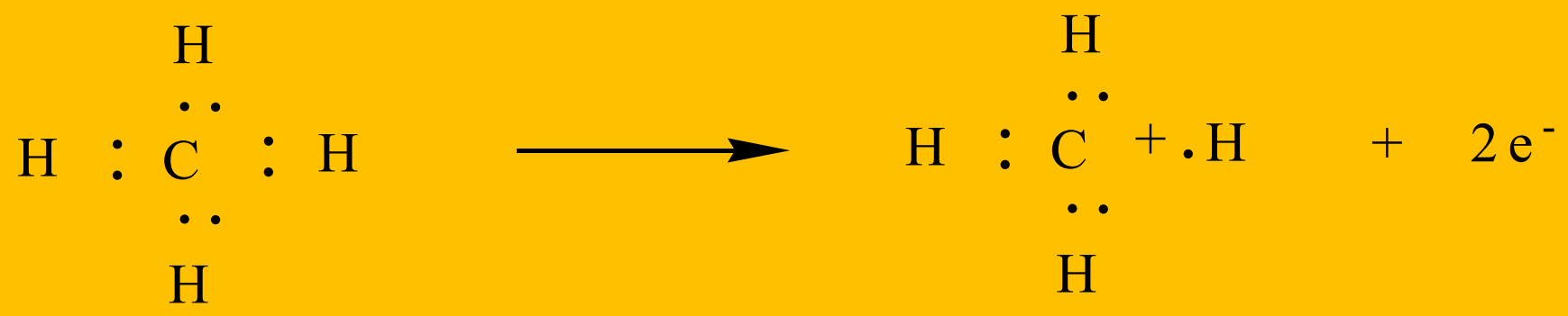
It involves the generation of ions from either inorganic or organic compounds, to separate the ions by their mass-to-charge ratio (m/z) and to detect them qualitatively and quantitatively by their m/z value and relative abundance.

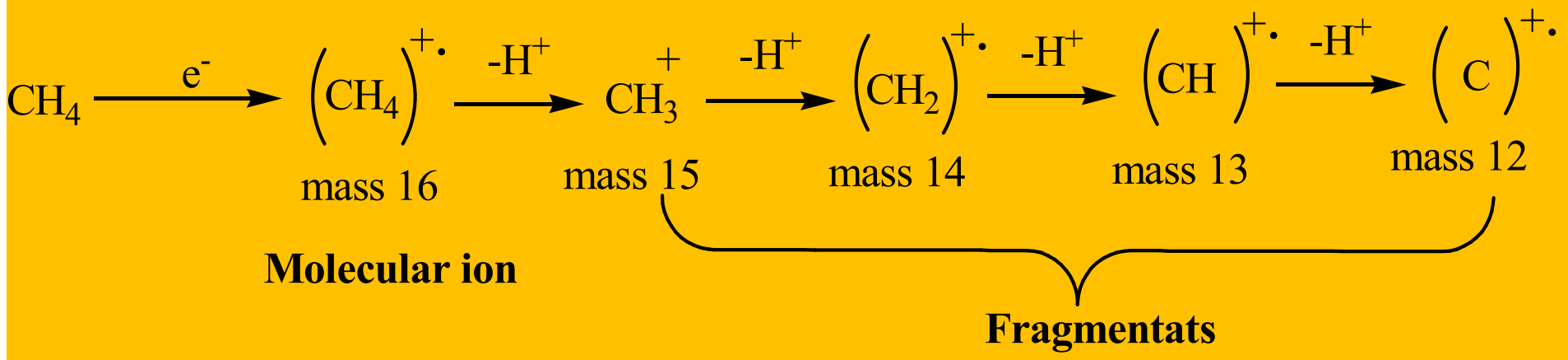
$$M + e^- \longrightarrow M^{\bullet +} + 2e^-$$

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.+ or molecular ion).

This parent ion or molecular ion normally undergoes fragmentations (fragment ions or daughter ions). The parent ion (M.+) is a radical cation with an odd number of electrons, it can fragment to give either a radical (R.) and an ion with an even number of electrons (EE+), or a molecule (N) and a new radical cation (OE.+).

For example, in the case of methane (CH4), 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.





Fragmentation of methane

❖ ***Instrumentation of Mass Spectrometer:***

The mass spectrometer act as three components:

1. Ion source

2 . Mass analyzer

3. Ion detector

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.

2. Mass analyzser:

The separation of ions takes place in the analyzer at a pressure of about 10-8 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.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.

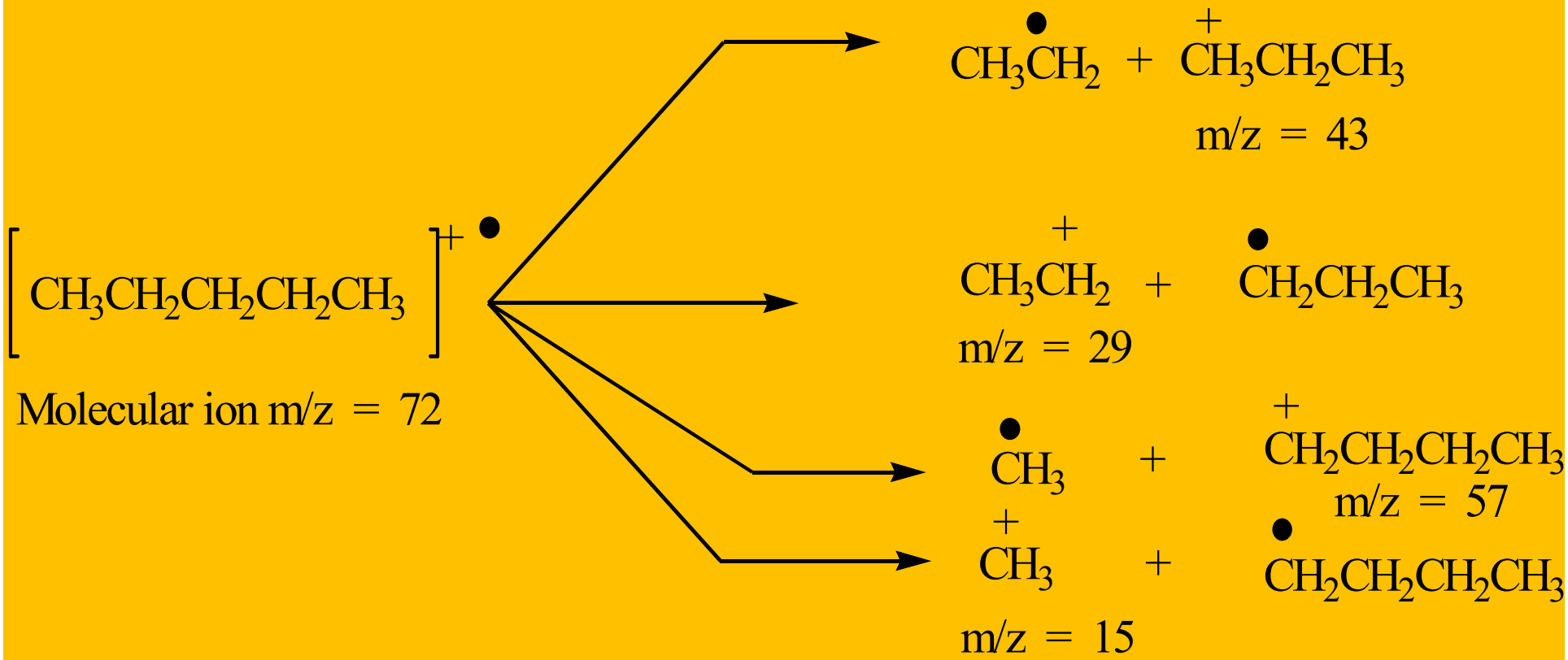
The strength of the magnetic field is varied in increments to produce a mass spectrum, which is a plot of m/z (on the x axis) against relative

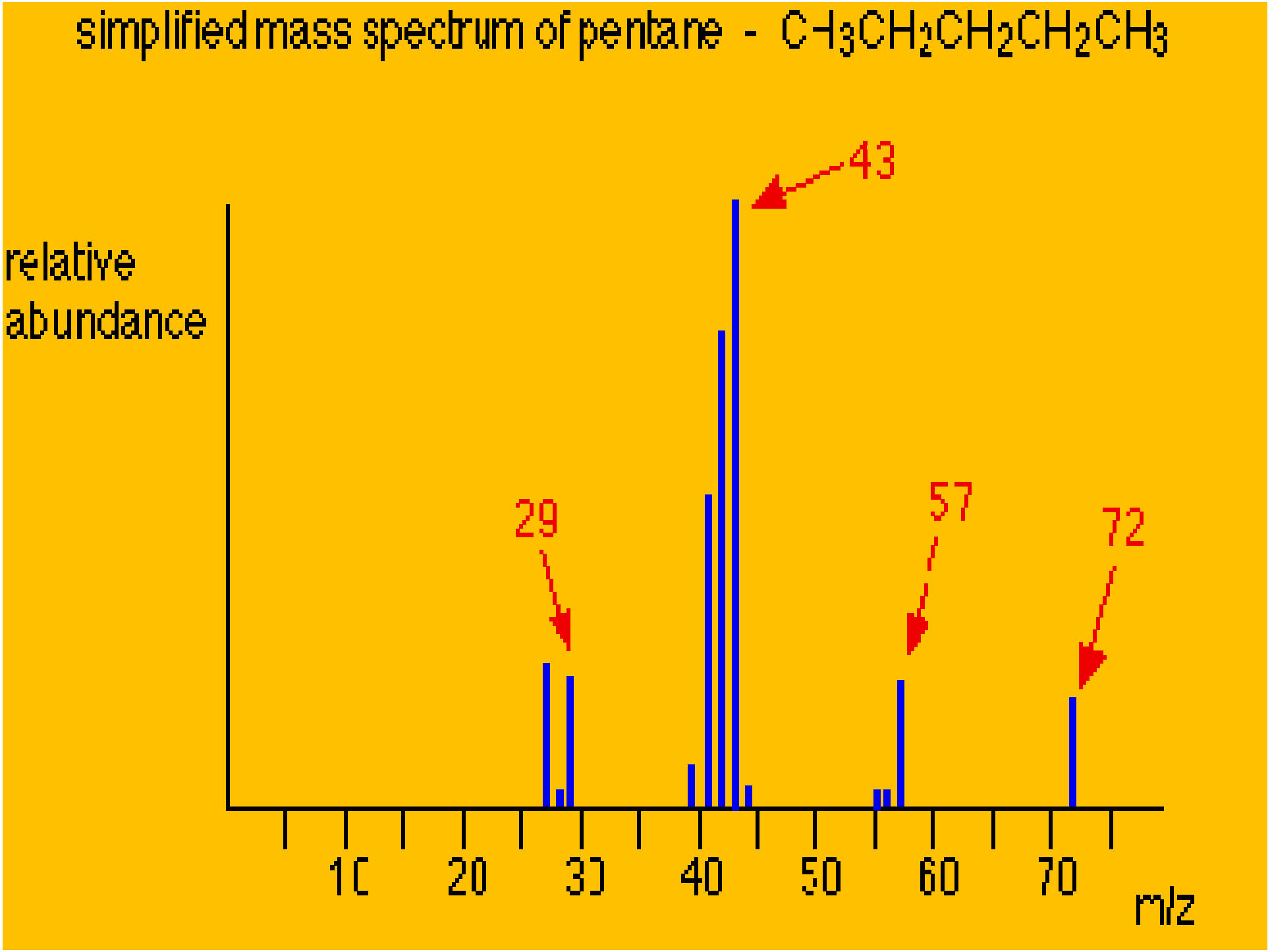
abundance (on the y axis). If we assume that all ions have a charge of +1, then the peaks give the mass ratios and their heights give the proportions of ions of different masses.

❖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.


$[CH_3CH_2CH_2CH_2CH_3]^{+\bullet}$
Molecular ion m/z = 72
$CH_3\overset{\bullet}{C}H_2 + \overset{+}{C}H_3CH_2CH_3$
m/z = 43
$\overset{+}{C}H_3CH_2 + \overset{\bullet}{C}H_2CH_2CH_3$
m/z = 29
$\overset{\bullet}{C}H_3 + \overset{+}{C}H_2CH_2CH_2CH_3$
m/z = 57
$\overset{+}{C}H_3 + \overset{\bullet}{C}H_2CH_2CH_2CH_3$
m/z = 15


simplified mass spectrum of pentane - CH3CH2CH2CH2CH3
relative abundance
43
29
57
72
10
20
30
40
50
60
70
m/z

❖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)

THANK YOU