Mass Spectrometry

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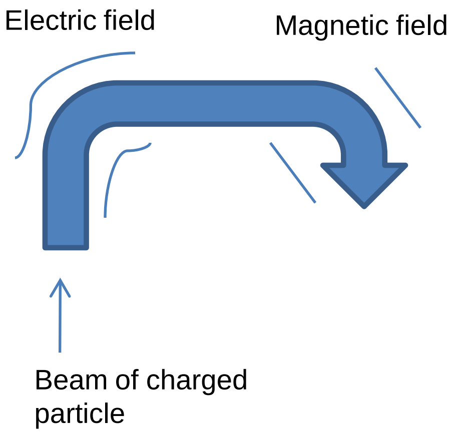
Mass spectrometry

- **Mass spectrometry**, also called **mass spectroscopy**, is an analytic technique by which chemical substances are identified by the sorting of gaseous ions in electric and magnetic fields according to their mass-to-charge ratios.
- The instruments used in such studies are called mass spectrometers and mass spectrographs, and they operate on the principle that moving ions may be deflected by electric and magnetic fields.
- The two instruments differ only in the way in which the sorted charged particles are detected.
- In the mass **spectrometer** they are detected electrically, in the **mass spectrograph** by photographic or other nonelectrical means; the term **mass spectroscope** is used to include both kinds of devices.
- Since electrical detectors are now most commonly used, the field is typically referred to as mass spectrometry.
- Mass spectrometry technique used to:
  - quantify known materials,
  - to identify unknown compounds within a sample, and
  - to elucidate the structure and chemical properties of different molecules.

History

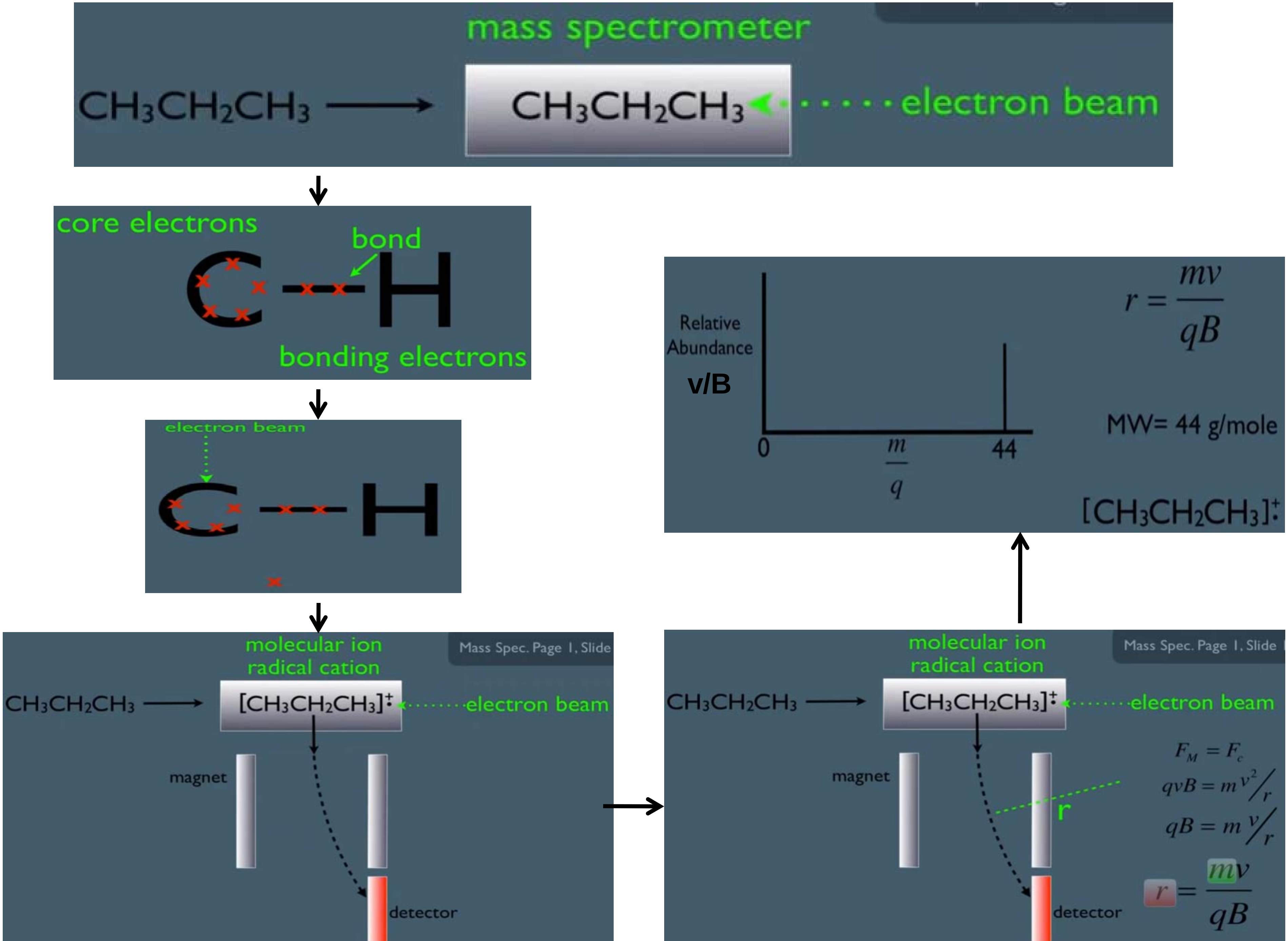
- The foundation of mass spectroscopy was laid in 1898, when **Wilhelm Wien**, a German physicist, discovered that beams of charged particles could be deflected by a magnetic field.
- In more refined experiments carried out between 1907 and 1913, the British physicist **J.J. Thomson**, who had already discovered the electron and observed its deflection by an electric field, passed a beam of positively charged ions through a combined electrostatic and magnetic field.

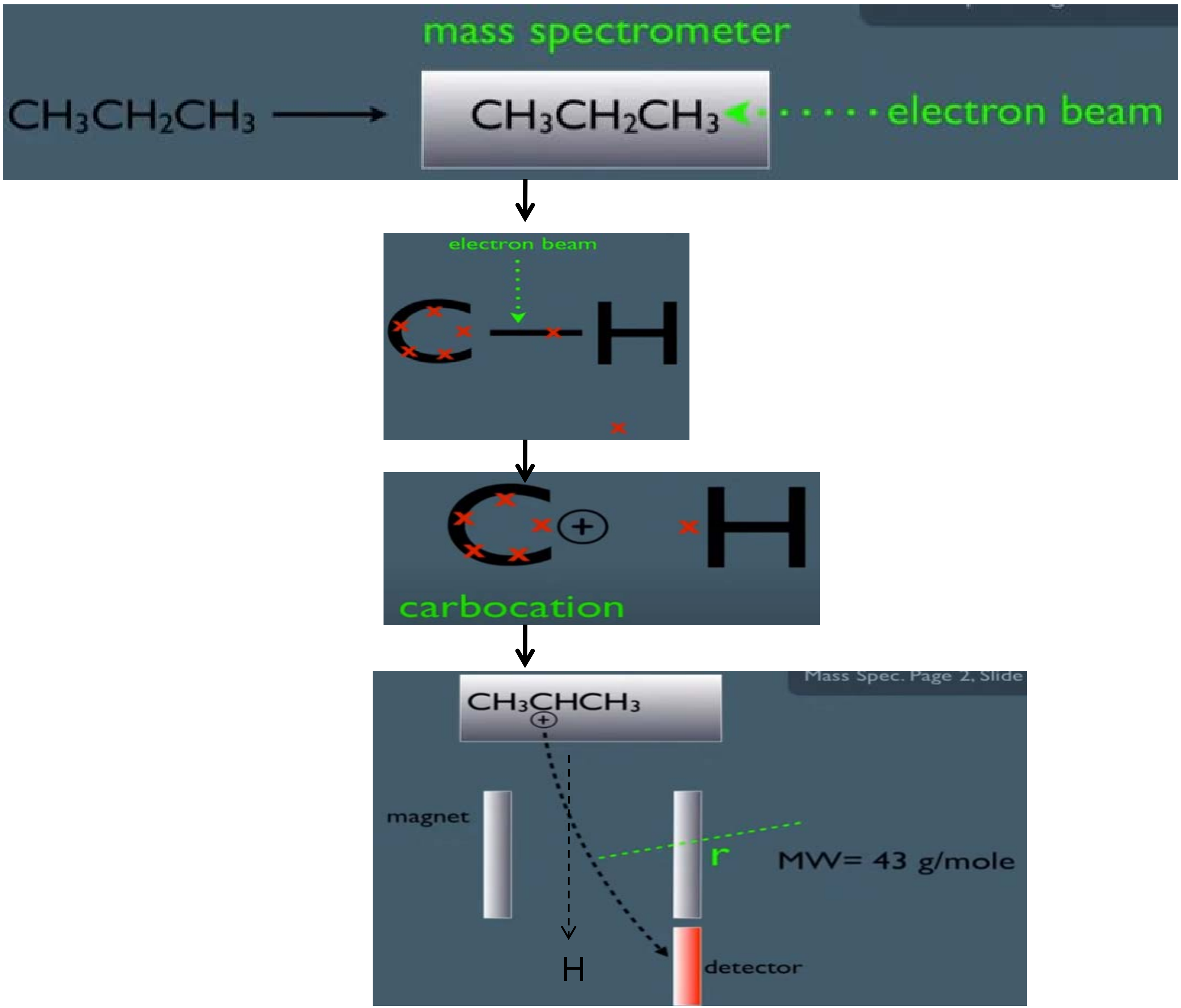


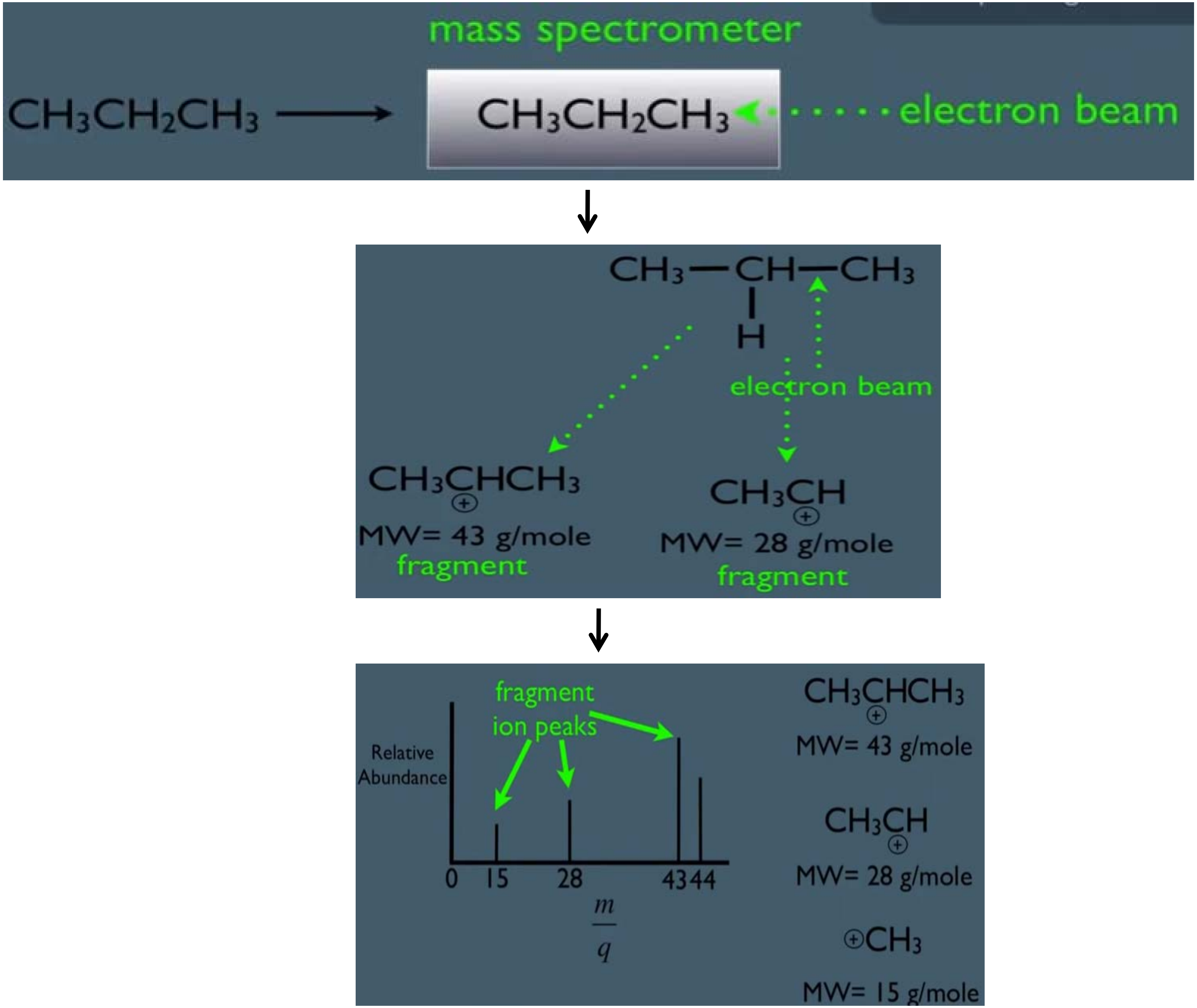
- The two fields in Thomson's tube were situated so that the ions were deflected through small angles in two perpendicular directions.
- The net result was that the ions produced a series of parabolic curves on a photographic plate placed in their paths.

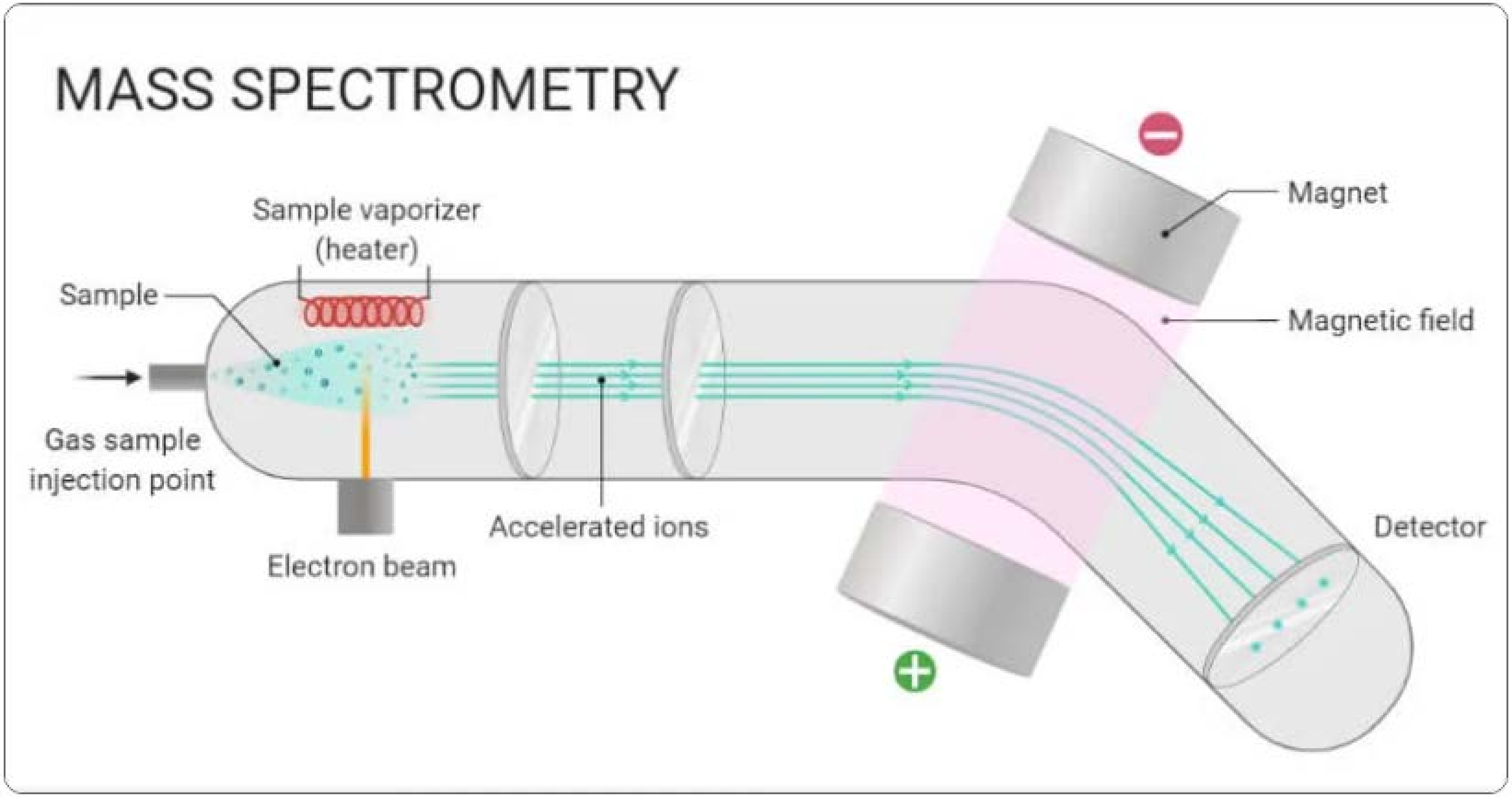
Principle of Mass Spectrometry (MS)

- In this technique, molecules are bombarded with a beam of energetic electrons.
- The molecules are ionized and broken up into many fragments, some of which are positive ions.
- Each kind of ion has a particular ratio of mass to charge, i.e. m/e ratio (value).
- For most ions, the charge is one, and thus, the m/e ratio is simply the molecular mass of the ion.
- The ions pass through magnetic and electric fields to reach the detector where they are detected and signals are recorded to give mass spectra.
- A mass spectrum is a plot of relative abundance against the ratio of mass/charge (m/e).
- These spectra are used to determine the elemental or isotopic signature of a sample, the masses of particles and of molecules, and to elucidate the chemical structures of molecules and other chemical compounds.


mass spectrometer
CH3CH2CH3
CH3CH2CH3
electron beam
core electrons
bond
bonding electrons
electron beam
molecular ion
radical cation
Mass Spec. Page 1, Slide
CH3CH2CH3
[CH3CH2CH3]+·
electron beam
magnet
detector
molecular ion
radical cation
Mass Spec. Page 1, Slide
CH3CH2CH3
[CH3CH2CH3]+·
electron beam
magnet
r
detector
F_M = F_c
qvB = mv^2/r
qB = mv/r
r = mv/qB
Relative Abundance
v/B
0
m/q
44
r = mv/qB
MW= 44 g/mole
[CH3CH2CH3]+·


mass spectrometer
CH3CH2CH3
CH3CH2CH3
electron beam
electron beam
C
H
C
H
carbocation
Mass Spec. Page 2, Slide
CH3CHCH3
magnet
r
MW= 43 g/mole
H
detector


mass spectrometer
$CH_3CH_2CH_3$
$CH_3CH_2CH_3$
electron beam
$CH_3-CH-CH_3$
H
electron beam
$CH_3\underset{\oplus}{C}HCH_3$
MW= 43 g/mole
fragment
$CH_3\underset{\oplus}{C}H$
MW= 28 g/mole
fragment
fragment
ion peaks
Relative
Abundance
0
15
28
43
44
$\frac{m}{q}$
$CH_3\underset{\oplus}{C}HCH_3$
MW= 43 g/mole
$CH_3\underset{\oplus}{C}H$
MW= 28 g/mole
$\oplus CH_3$
MW= 15 g/mole


MASS SPECTROMETRY
Sample vaporizer
(heater)
Sample
Gas sample
injection point
Electron beam
Accelerated ions
Magnet
Magnetic field
Detector

Working of Mass Spectrometry (MS)

- In a typical procedure, a sample, which may be solid, liquid, or gas, is ionized, for example by bombarding it with electrons.
- This may cause some of the sample's molecules to break into charged fragments. These ions are then separated according to their mass-to-charge ratio, typically by accelerating them and subjecting them to an electric or magnetic field:
- Ions of the same mass-to-charge ratio will undergo the same amount of deflection.
- The ions are detected by a mechanism capable of detecting charged particles, such as an electron multiplier. Results are displayed as spectra of the relative abundance of detected ions as a function of the mass-to-charge ratio.
- The atoms or molecules in the sample can be identified by correlating known masses (e.g. an entire molecule) to the identified masses or through a characteristic fragmentation pattern.

Instrumentation

A. Sample Inlet

- A sample stored in the large reservoir from which molecules reach the ionization chamber at low pressure in a steady stream by a pinhole called “Molecular leak”.

B. Ionization

- Atoms are ionized by knocking one or more electrons off to give positive ions by bombardment with a stream of electrons.
- These electrons move between cathode and anode.
- When the sample passes through the electron stream between the cathode and anode, electrons with high energy knock electrons out of the sample and form ions.
- Most of the positive ions formed will carry a charge of +1.
- Ionization can be achieved by :
  - Electron Ionization (EI-MS)
  - Chemical Ionization (CI-MS)
  - Desorption Technique (FAB)

... Instrumentation

C. Acceleration

- The ions placed between a set of charged parallel plates get attracted to one plate and repel from the other plate.
- The acceleration speed can be controlled by adjusting the charge on the plates.

D. Deflection

- Ions are deflected by a magnetic field due to differences in their masses.
- The lighter the mass, the more they are deflected.
- It also depends upon the no. of +ve charge an ion is carrying; the more +ve charge, the more it will be deflected.

… Instrumentation

E. Detection

- The ions with correct charge and mass move to the detector.
- The ratio of mass to charge is analyzed through the ion that hits the detector.
- When an ion hits the metal box, the charge is neutralized by an electron jumping from the metal onto the ion.
- Types of analyzers:
  - Time of Flight analyzers (TOF): does not use magnetic fields depends on the differing speeds of ions with the same energy but different masses.
  - Magnetic sector mass analyzers
  - Double focussing analyzers
  - Quadrupole mass analysers
  - Ion trap analyzer
  - Ion cyclotron analyser

Applications of Mass Spectrometry

- Environmental monitoring and analysis (soil, water, and air pollutants, water quality, etc.)
- Geochemistry – age determination, soil, and rock composition, oil and gas surveying
- Chemical and Petrochemical industry – Quality control
- Identify structures of biomolecules, such as carbohydrates, nucleic acids
- Sequence biopolymers such as proteins and oligosaccharides
- Determination of the molecular mass of peptides, proteins, and oligonucleotides.
- Monitoring gases in patients' breath during surgery.
- Identification of drug abuse and metabolites of drugs of abuse in blood, urine, and saliva.
- Analyses of aerosol particles.
- Determination of pesticides residues in food.

Applications of MS

Key application and field of application	Explanation
Elemental and isotopic analysis. Physics Radiochemistry Geochemistry	Elemental identification and isotopic abundance measurement of both short lived and stable species in physical and radioactivity in geochemistry and more recently in the life sciences.
Organic and bio-organic analysis Organic chemistry Polymer chemistry Biochemistry and medicine	Identification and structural characterization of molecules from small to very large as provided either by chemistry, physiological processes or polymer chemistry.
Structural elucidation Organic chemistry Polymer chemistry Biochemistry and medicine	Mass spectrometric experiments can be arranged consecutively to study mass selected ions in tandem mass spectrometry. Eventually products are subjected to a third level and so fourth.
Characterization of ionic species and chemical reactions Physical chemistry Thermochemistry	Tandem MS provide as elegant means for the study of unimolecular or bimolecular reactions of gas phase ions and for the determination of ion energetics.
Mass Spectral Imaging Biomedical studies Material sciences	Mass spectra can be obtained from micrometer sized areas on surfaces, translating the lateral distribution of compounds on surfaces into images, which in turn can be correlated to optical images.