

University of Babylon
College of Science
Department of Chemistry
Course No. Chsc 424



Undergraduate Studies
Physical chemistry
Fourth year - Semester 2
Credit Hour: 3 hrs.
Scholar units: three units

Lectures of Molecular Spectroscopy
Second Semester, Scholar year 2018-2019
Prof. Dr. Abbas A-Ali Draea

Lecture No. Nine : Mass Spectroscopy

- 1-Introduction
 - 2-Basic Principle
 - 3-Components
 - 4-Ion Free Path
 - 5-Ion source of mass spectrometer
 - 6-Chemical Ionization
-

1-Introduction:

- Mass spectrometry is a powerful analytical technique used to quantify known materials and identify unknown compounds within a sample, and to elucidate the structure and chemical properties of different molecules.
- The complete process involves the conversion of the sample into gaseous ions, with or without fragmentation, which are then characterized by their mass to charge ratios (m/z) and relative abundances.
- This technique basically studies the effect of ionizing energy on molecules.

- It depends upon chemical reactions in the gas phase in which sample molecules are consumed during the formation of ionic and neutral species.

At 1912, J.J. THOMSON constructs the first mass spectrometer (then called a parabola spectrograph). He obtains mass spectra of O₂, N₂, CO, CO₂ and COCl₂. He observes negative and multiply charged ions. He discovers metastable ions. In 1913, he discovers isotopes 20 and 22 of neon.

2-Basic Principle:

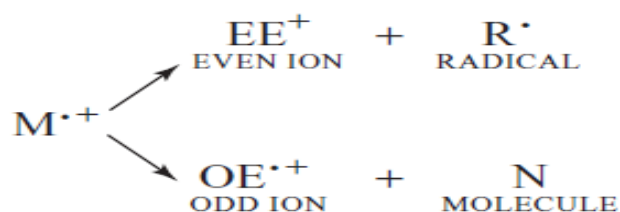
In general, a mass spectrometer generates multiple ions from the sample under investigation, it then separates them according to their specific mass-to-charge ratio (m/z), and then records the relative abundance of each ion type.

They found several steps for analysis process:-

First step in the mass spectrometric, involve analysis of compounds it is the production of gas phase ions of the compound, basically by electron ionization.



Second step, This molecular ion normally undergoes fragmentations. Because it is a radical cation with an odd number of electrons, it can fragment to give either a radical or an ion with an even number of electrons, or a molecule and a new radical cation. The important of difference between these two types of ions and the need to write them correctly:



-----2

These two types of ions have different chemical properties. Each primary product ion derived from the molecular ion can, in turn, undergo fragmentation, and so on.

Thired step, All these ions are separated in the mass spectrometer according to their mass-to-charge ratio, and are detected in proportion to their abundance.

Fourth step, A mass spectrum of the molecule is thus produced. It provides this result as a plot of ion abundance versus mass-to-charge ratio.

As illustrated in Figure 1, mass spectra can be presented as a barograph or as a table. In either presentation, the most intense peak is called the base peak and is arbitrarily assigned the relative abundance of 100 %. The abundances of all the other peaks are given their proportionate values, as percentages of the base peak. Many existing publications label the y axis of the mass spectrum as number of ions, ion counts or relative intensity.

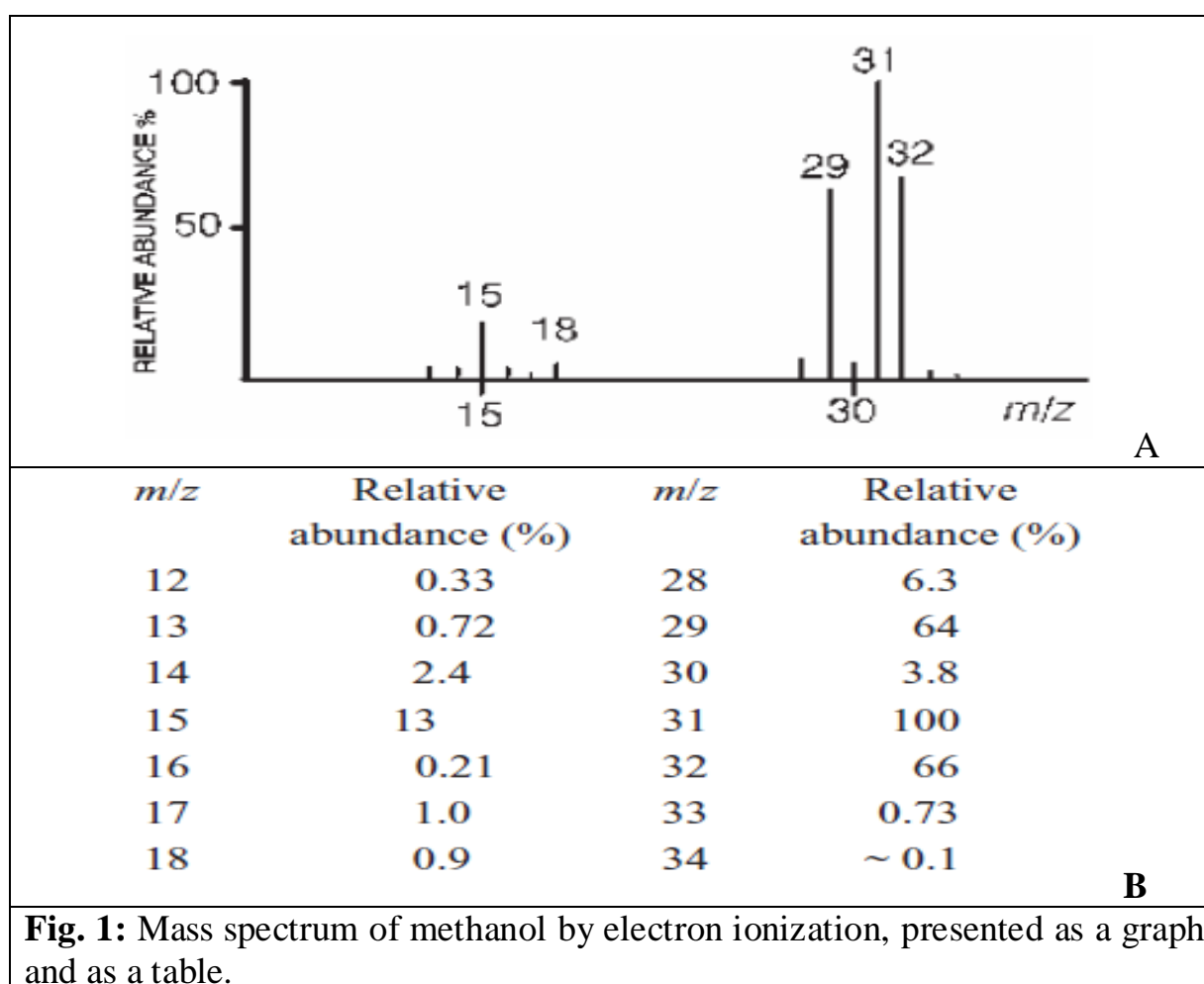


Fig. 1: Mass spectrum of methanol by electron ionization, presented as a graph and as a table.

But the term relative abundance is better used to refer to the number of ions in the mass spectra.

Most of the positive ions have a charge corresponding to the loss of only one electron. For large molecules, multiply charged ions also can be obtained. Ions are separated and detected according to the mass-to-charge ratio. The total charge of the ions will be represented by q , the electron charge by e and the number of charges of the ions by z :

$$q = ze \quad \text{and} \quad e = 1.6 \times 10^{-19} \text{ C} \quad \text{-----3}$$

The x axis of the mass spectrum that represents the mass-to-charge ratio is commonly labelled m/z . When m is given as the relative mass and z as the charge number, both of which are unitless, m/z is used to denote a dimensionless quantity.

Generally in mass spectrometry, the charge is indicated in multiples of the elementary charge or charge of one electron in absolute value ($1e = 1.602177 \times 10^{-19} \text{ C}$) and the mass is indicated in atomic mass units ($1 \text{ u} = 1.660540 \times 10^{-27} \text{ kg}$). As already mentioned, the physical property that is measured in mass spectrometry is the mass-to-charge ratio. When the mass is expressed in atomic mass units (u) and the charge in elementary charge units (e) then the mass-to-charge ratio has u/e as dimensions. For simplicity, a new unit, the Thomson, with symbol Th , has been proposed. The fundamental definition for this unit is

$$1\text{Th} = 1\text{u}/e = 1.036\,426 \times 10^{-8} \text{ kg C}^{-1} \quad \text{----4}$$

Ions provide information concerning the nature and the structure of their precursor molecule. In the spectrum of a pure compound, the molecular ion, if present, appears at the highest value of m/z (followed by ions containing heavier isotopes) and gives the molecular mass of the compound. The term molecular ion refers in chemistry to an ion corresponding to a complete molecule regarding occupied valences. This molecular ion appears at m/z 32 in the spectrum of methanol, where the peak at m/z 33 is due to the presence of the ^{13}C isotope, with an intensity that is 1.1% of that of the m/z 32 peak. In the same spectrum, the peak at m/z 15 indicates the presence of a methyl

group. The difference between 32 and 15 that is 17 is characteristic of the loss of a neutral mass of 17Da by the molecular ion and is typical of a hydroxyl group. In the same spectrum, the peak at m/z 16 could formally correspond to ions CH_4^+ , O^+ or even CH_3OH_2^+ , because they all have m/z values equal to 16 at low resolution. However, O^+ is unlikely to occur, and a doubly charged ion for such a small molecule is not stable enough to be observed.

3-Components:

The instrument consists of three major components:

1. **Ion Source:** For producing gaseous ions from the substance being studied.
2. **Analyzer:** For resolving the ions into their characteristics mass components according to their mass-to-charge ratio.
3. **Detector System:** For detecting the ions and recording the relative abundance of each of the resolved ionic species.

In addition, a sample introduction system is necessary to admit the samples to be studied to the ion source while maintaining the high vacuum requirements ($\sim 10^{-6}$ to 10^{-8} mm of mercury) of the technique; and a computer is required to control the instrument, acquire and manipulate data, and compare spectra to reference libraries.

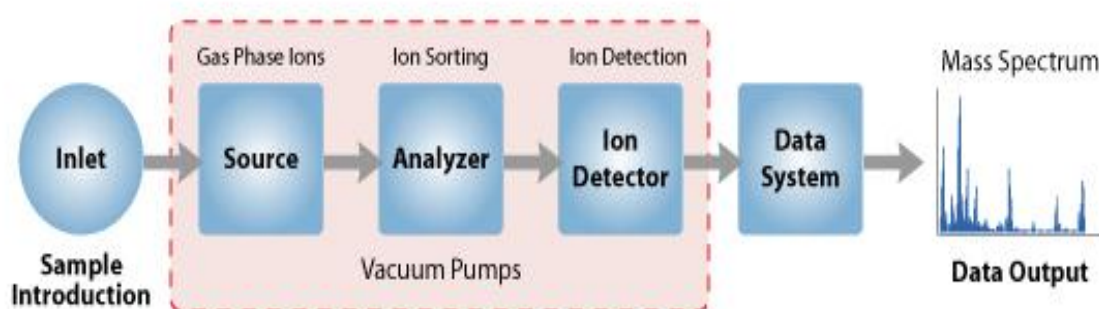


Fig.2: Components of a Mass Spectrometer.

With all the above components, a mass spectrometer should always perform the following processes:

1. Produce ions from the sample in the ionization source.
2. Separate these ions according to their mass-to-charge ratio in the mass analyzer.
3. Eventually, fragment the selected ions and analyze the fragments in a second analyzer.
4. Detect the ions emerging from the last analyzer and measure their abundance with the detector that converts the ions into electrical signals.
5. Process the signals from the detector that are transmitted to the computer and control the instrument using feedback.

4-Ion Free Path:

All mass spectrometers must function under high vacuum (low pressure). This is necessary to allow ions to reach the detector without undergoing collisions with other gaseous molecules. Indeed, collisions would produce a deviation of the trajectory and the ion would lose its charge against the walls of the instrument. On the other hand, ion–molecule collisions could produce unwanted reactions and hence increase the complexity of the spectrum. Nevertheless, we will see later that useful techniques use controlled collisions in specific regions of a spectrometer. According to the kinetic theory of gases, the mean free path L (in m) is given by:

$$L = \frac{kT}{\sqrt{2}p\sigma} \text{-----5}$$

Where k is the Boltzmann constant, T is the temperature (in K), p is the pressure (in Pa) and σ is the collision cross-section (in m²); $\sigma = \pi d^2$ where d is the sum of the radii of the

stationary molecule and the colliding ion (in m). In fact, one can approximate the mean free path of an ion under normal conditions in a mass spectrometer ($k=1.38 \times 10^{-21} \text{ JK}^{-1}$, $T \approx 300 \text{ K}$, $\sigma \approx 45 \times 10^{-20} \text{ m}^2$) using either of the following equations where L is in centimeters and pressure p is, respectively, in Pascals or milliTorrs.

Large differences in pressure are controlled with the help of an efficient pumping system using mechanical pumps in conjunction with turbo molecular, diffusion or cryogenic pumps. The mechanical pumps allowed vacuum of about 10^{-3} Torr to be obtained. Once this vacuum is achieved, the operation of the other pumping systems allows a vacuum as high as 10^{-10} Torr to be reached.

The sample must be introduced into the ionization source so that vacuum inside the instrument remains unchanged. Samples are often introduced without compromising the vacuum using direct infusion or direct insertion methods. For direct infusion, a capillary is employed to introduce the sample as a gas or a solution. For direct insertion, the sample is placed on a probe, a plate or a target that is then inserted into the source through a vacuum interlock. For the sources that work at atmospheric pressure and are known as atmospheric pressure ionization (API) sources, introduction of the sample is easy because the complicated procedure for sample introduction into the high vacuum of the mass spectrometer is removed.

5-Ion source of mass spectrometer:

The tool of Ion Sources is make ions from sample molecules (Ions are easier to detect than neutral molecules). There are several types of ionization methods in mass spectrometry. Most common methods are:

- A-Matrix-assisted laser desorption/ionization (MALDI).
- B- Electrospray Ionization (ESI).
- C- Electron ionization.

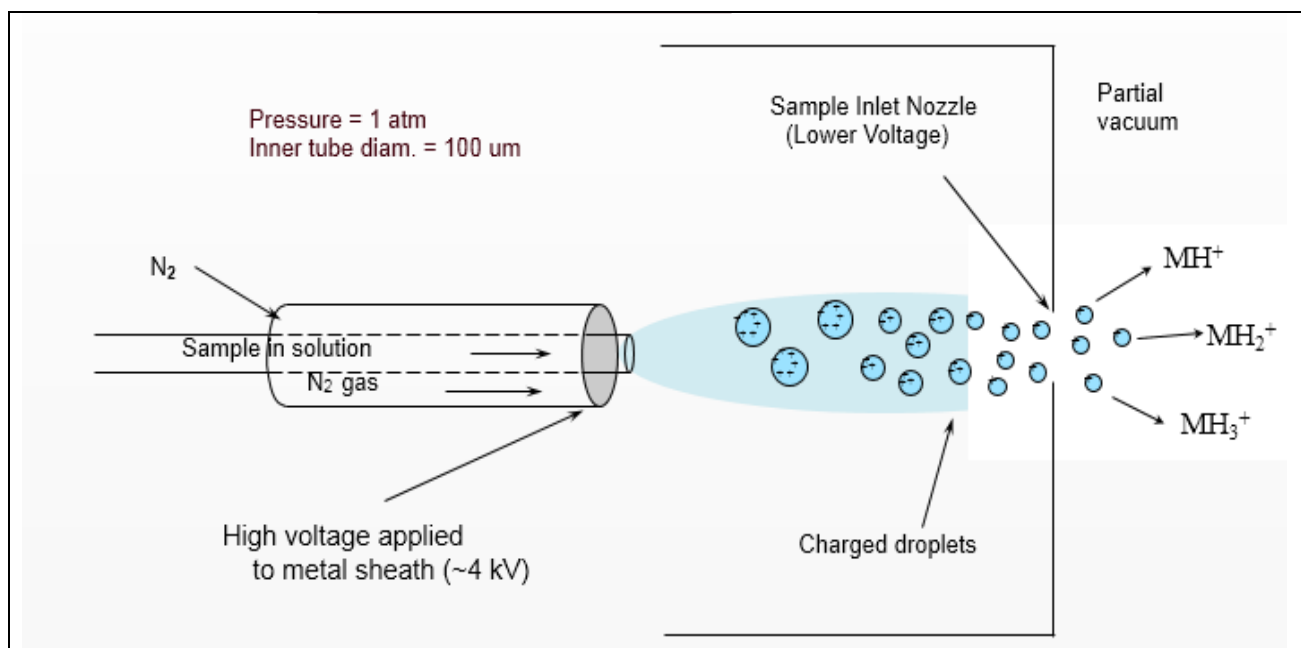


Fig. 3: General diagram of electrospray ionization mechanism.

A-Matrix-assisted laser desorption/ionization (MALDI)

- Method of ionization is a soft ionization method and results in minimum fragmentation of sample.
- Method is used for non-volatile, and thermally labile compounds such as proteins, oligonucleotides, synthetic polymers.
- Sample is mixed with 1000 times molar excess of sample and spotted onto a metal plate and dried.
- Matrix plays a key role in this technique by absorbing the laser light energy and causing a small part of the target substrate to vaporize.
- Although, the process of forming analyte ions is unclear, it is believed that matrix which has labile protons, such as carboxylic acids, protonates neutral analyte molecules after absorbing laser light energy.

1. Sample is mixed with matrix (X) and dried on plate.
2. Laser flash ionizes matrix molecules.
3. Sample molecules (M) are ionized by proton transfer:
 $\text{XH}^+ + \text{M} \rightarrow \text{MH}^+ + \text{X}^\cdot$

B- Electrospray Ionization (ESI):

- Electrospray Ionization (ESI) is a preferred method of ionization when the sample is in liquid form.
- A soft method of ionization and results in less fragmentation.
- ESI is a very valuable method for analysis of biological samples.
- The analyte is introduced either from a syringe pump or as the eluent flow from liquid chromatography with a flow rate $1\mu\text{l min}^{-1}$.
- The analyte solution passes through the electrospray needle (Stainless steel capillary with 75-150 μm internal diameters) that has a high potential difference (with respect to the counter electrode) applied to it (typically in the range from 2.5 to 4 kV).
- This forces the spraying of charged droplets from the needle with a surface charge of the same polarity to the charge on the needle.
- As droplet moves towards counter electrode cone (which passes it to analyzer), solvent evaporation occurs and droplet shrinks until it reaches the point that the surface tension can no longer sustain the charge (the Rayleigh limit) and at that point droplets break.
- This produces smaller droplets and the process is repeated.
- Finally after all solvent evaporated, charge is passed on to analyte.
- These charged analyte molecules can have single or multiple charges

C-Electron ionization:

- Method is work well for many gas phase molecules, but it results in extensive fragmentation and molecular ions are not observed for many compounds.
- Fragmentation mass spectra are sometime useful because it provides structural information of a molecule.
- The electron beam is produced by a filament of rhenium or tungsten wire by thermionic emission.

- When cathode filament of rhenium or tungsten is heated at temperature over 1000 K, electrons are emitted.
- The generated electrons are accelerated to 70 eV which results in electron beam.
- The volatile sample or sample in gaseous phase containing neutral molecules is introduced to the ion source in a perpendicular direction to the electron beam.
- Electron impact on the analyte results in either loss of electron (to produce cation) or gain of electron (to produce anion).
- Chemical bonds in organic molecules are formed by pairing of electrons.
- Electron impact may knock out one of the electron.
- This leaves the bond with a single unpaired electron.
- Radical as well as being cation written as M^+ , where (+) indicates ionic state while (·) indicates radical.
- Electron impact may result in electron capture (extra unpaired electron).
- This generates a radical as well as being anion written as M^- , where (-) indicates ionic state while (·) indicates radical.

6-Chemical Ionization:

They found several steps for analyst to be chemical ionization, as follow:

- A reagent gas like CH_4 is injected in the ion chamber.
- Due to electron impact, the reagent gas in the chemical ionization source gets ionized.
- Injection of analyst molecule is followed up.
- Analyst molecules undergo many collisions with the reagent gas.
- The reagent gas ions in this cloud react and produce adduct ions, which are excellent proton donors for analyst.

1-Electron impact on reagent gass $CH_4 + e^- \longrightarrow CH_4^+ + 2e^-$

2- reaction of reagent gas to form 1 on $CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3^·$

3- reaction of reagent gas 1 on with analyst. $CH_5^+ + M \longrightarrow CH_4 + CH_4 + MH^+$