An Introduction to Mass Spectrometry

By

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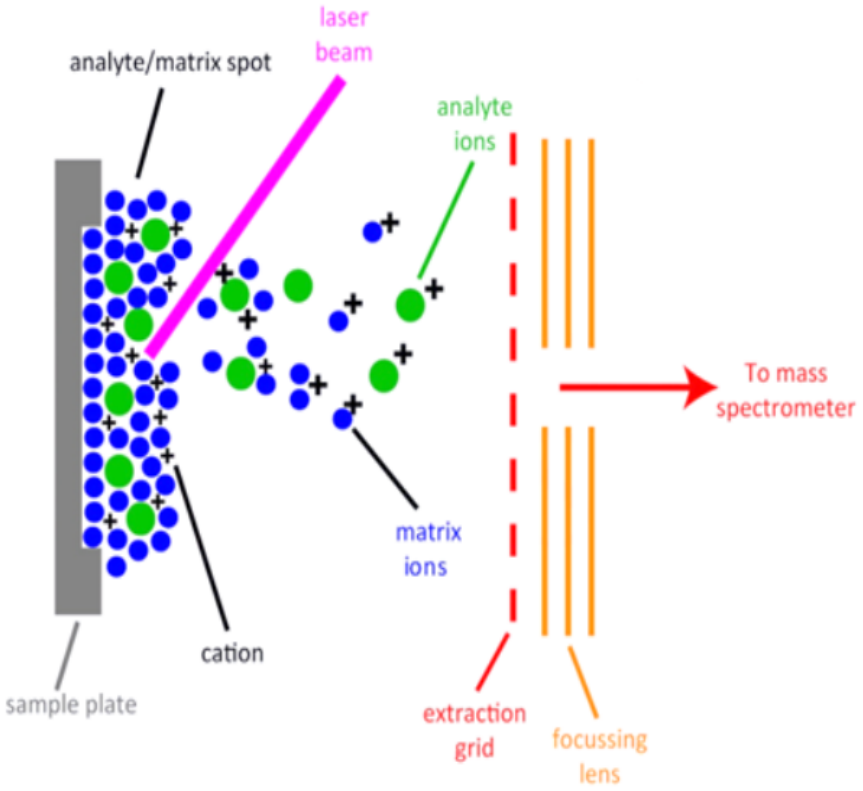

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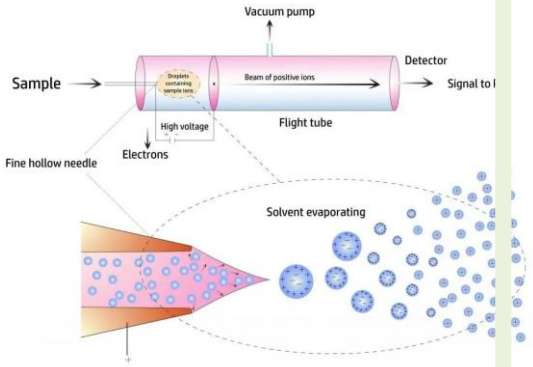
Preface



Mass spectrometry is an analytical technique that allows to the determination of the molecular masses of the compounds analyzed as well as their identification and quantification. It is based on the separation and detection of ions formed in an ionization source or in a collision chamber.

This work presents initiations on mass spectrometry. It conforms to the basic program of university training in some technological sectors, particularly the basic sciences. It is intended for students of institutes and universities, teachers in particular for the first year of Master of Organic Chemistry. The structure of this book consists of four parts that explain this module, it provides students of the exact sciences with the basic notions necessary to properly explain of the mass spectrometry. These are generally, the definitions, Ion and desorption sources and mass analyzers.

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Part 1

Introduction

In mass spectrometry, one generates ions from a sample to be analyzed. These ions are then separated and quantitatively detected. Separation is achieved on the basis of different trajectories of moving ions with different mass/charge (*m/z*)** ratios in electrical and/or magnetic fields.

Mass-spectrometry has evolved from the experiments and studies early in the 20th century that tried to explain the behavior of charged particles in magnetic and electrostatic force fields. Well-known names from these early days are J. J. Thompson *investigation into the behavior of ionic beams in electrical and magnetic fields* (1912), A. J. Dempster *directional focussing* (1918) and F. W. Aston *energy focussing* (1919).

In this way a refinement of the technique was achieved that allowed important information concerning the natural abundance of isotopes to be collected.

The first analytical applications then followed in the early forties when the first reliable commercial mass spectrometers were produced. This was mainly for the quantitative determination of the several components in complex mixtures of crude oil.

In the beginning of the sixties the application of mass-spectrometry to the identification and structure elucidation of more complex organic compounds,

including polymers and biomolecules, started. Since then, the technique has developed to a powerful and versatile tool for this purpose, which provides information partly complementary to and overlapping with other techniques, such as NMR.

It is perhaps surprising that a technique that at first sight does not appear to give more information than the weight of a particle should be so important, since it is difficult to imagine a more prosaic property of a molecule than its molecular weight.

The controlled fragmentation of the initial molecular ions yields interesting information that can contribute to structure elucidation. In addition, the weights can now be determined with sufficient accuracy to allow elemental compositions to be derived.

These lecture notes were first drafted in Dutch by Peter van Galen in 1992, when the only mass spectrometer in the Faculty of Science was the Department's double sector instrument. They were translated into English in 2005, and gradually updated by Peter van Galen and Martin Feiters to include the descriptions of new instruments based on new principles and with new applications.

1.1 Principles of Mass Spectrometry

Mass spectrometry is a sophisticated instrumental technique that produces, separates, and detects ions in the gas phase. The basic components of a mass spectrometer are shown in Figure 1. Samples are introduced into an ionization source through some type of inlet system. Depending on the phase and nature of the sample and the analytes, different ionization sources will be more or less optimal for producing ions.

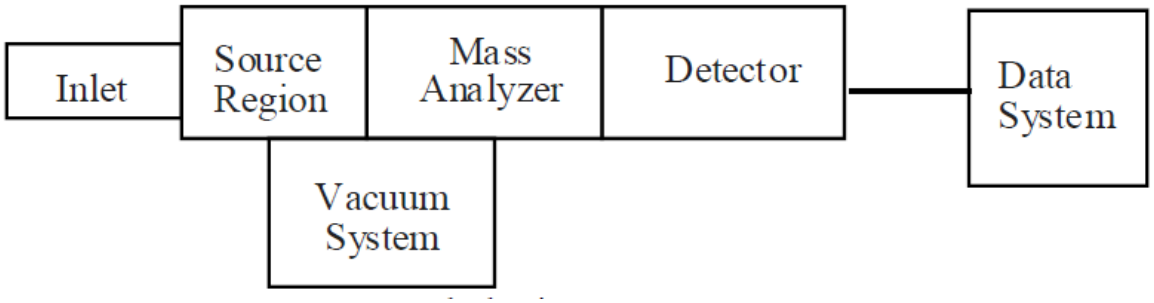

Figure 1.1 Mass Spectrometer Block Diagram.

***The mass to charge ratio (m/z) is used to describe ions observed in mass spectrometry. By convention, m is the numerical value for the mass of the ion and z is the numerical value for the charge of the ion. The unified atomic mass (u) and the elementary charge units (e) are used for these values. The unified atomic mass is defined as 1/12 the mass of an atom of ^{12}C. Older terms still in use but not accepted as SI units include the atomic mass unit (amu) and the dalton (Da).*

The amu is no longer acceptable because there are conflicting definitions. The dalton is frequently used for polymers, peptides and other large molecules. The elementary charge unit is defined as z is an integer equal to the number of electrons lost (or gained for negative ions). For most experiments one electron is lost during ionization so z is +1 and the m/z value is equivalent to the relative molecular mass of the ion. Because the unified atomic mass and the charge number are pure numbers the mass-to-charge ratio is a number and does not have any units. For

Mass spectrometry is based upon the motion of a charged particle, called an ion, in an electric or magnetic field. The mass to charge ratio (*m/z*) ** of the ion effects this motion. Since the charge of an electron is known, the mass to charge ratio a measurement of an ion's mass. Typical mass spectrometry research focuses on the

formation of gas phase ions, the chemistry of ions, and applications of mass spectrometry.

1.2 Principles Measurement

In Figure 2, the essential parts of an analytical mass spectrometer are depicted. Its procedure is as follows:

1. A small amount of a compound***, typically one micromole or less, is evaporated. The vapor is leaking into the ionization chamber where a pressure is maintained of about 10^{-7} mbar (high-vacuum).

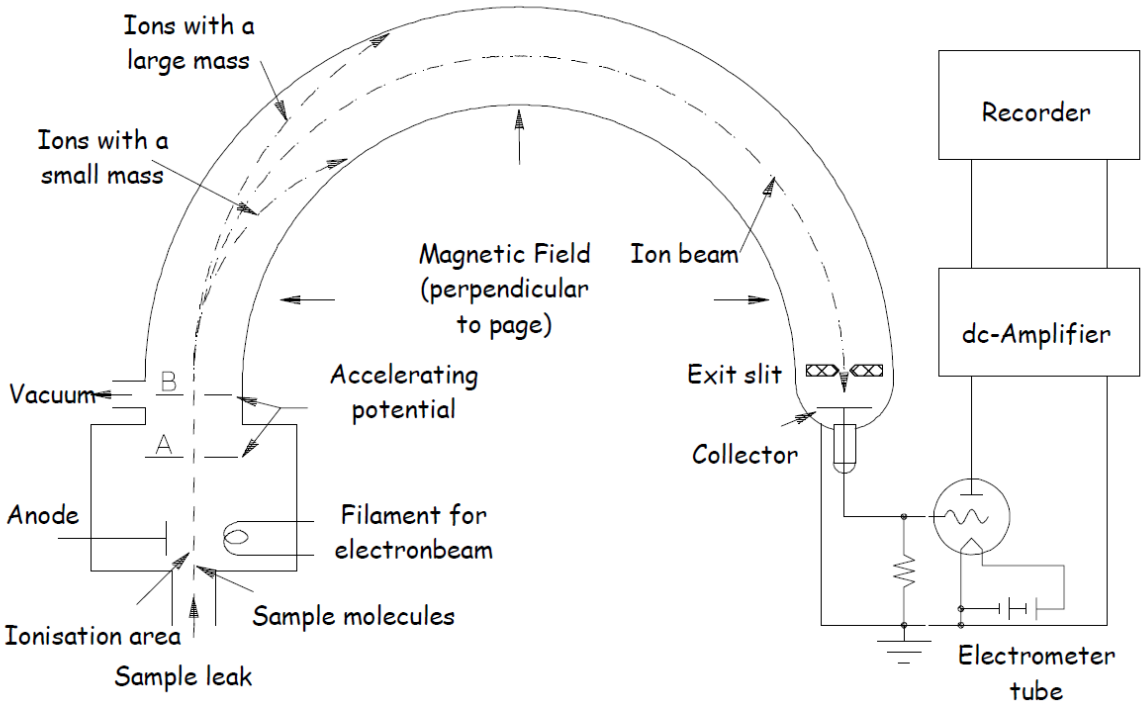

Figure 1.2 Schematic representation of a mass spectrometer.

2. The vapor molecules are now ionized by an electron-beam. A heated cathode, the filament, produces this beam. Ionization is achieved by inductive effects rather than strict collision. By loss of valence electrons, mainly positive ions are produced.

3. The positive ions are forced out of the ionization chamber by a small positive charge (several Volts) applied to the repeller opposing the exit-slit (A). After the ions have left the ionization chamber, they are accelerated by an electrostatic field (A>B) of several hundreds to thousands of volts before they enter the analyzer.

****Samples are introduced into an ionization source through some type of inlet system. Depending on the phase and nature of the sample and the analytes, different ionization sources will be more or less optimal for producing ions.*

4. The separation of ions takes place in the analyzer, in this example a magnetic sector, at a pressure of about 10-8 mbar. A strong magnetic field is applied perpendicular to the motional direction of the ions. The fast-moving ions then will follow a circular trajectory, due to the Lorentz acceleration, whose radius is determined by the mass/charge ratio of the ion and the strength of the magnetic field. Ions with different mass/charge ratios are forced through the exit-slit by variation of the accelerating voltage (A>B) or by changing the magnetic-field force.

5. 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.

Part 2

Ion sources

2.1 Definition

A Variety of ionization techniques are used for mass spectrometry. Most ionization techniques excite the neutral analyze molecule which then ejects an electron to form a radical cation ($M^{+\cdot}$)**. Other ionization techniques involve ion molecule reactions that produce adduct ions (MH^{+})***. The most important considerations are the physical state of the analyte and the ionization energy.

In Figure 3, the scheme of an ionization chamber, ion-source, typically electron impact, is presented. In this chamber in several ways, ions of the compound to be investigated can be produced. The most common way is to bombard vapor-molecules of the sample with electrons of about 70 eV. These electrons are generated by heating a metal wire (filament), commonly used are tungsten or rhenium. A voltage of about 70 Volts (from 5 to 100) accelerates these electrons towards the anode.

***$M^{+\bullet}$ is the molecular ion produced by removing a single electron to form a radical cation. M is the molecule, + is the charge of the cation, and • is the remaining unpaired electron of the radical.*

****Adduct ions are produced by a chemical reaction between an ion and a neutral molecule. Many of these reactions cause the addition of a proton (H+) to the molecule (M) and produce an adduct ion (MH^{+}).*

During the bombardment, one or more electron can be removed from the neutral molecule thus producing positively charged molecular radical-ions. Only about one in 10^3 of the molecules present in the source are ionized. The ionization probability differs among substances, but it is found that the cross-section for most molecules is a maximum for electron energies from approximately 50 to 100 eV.

Most existing compilations of electron impact spectra are based on spectra recorded with approximately 70 eV electrons, since sensitivity is here close to a maximum and fragmentation is unaffected by small changes in electron energy around this value.

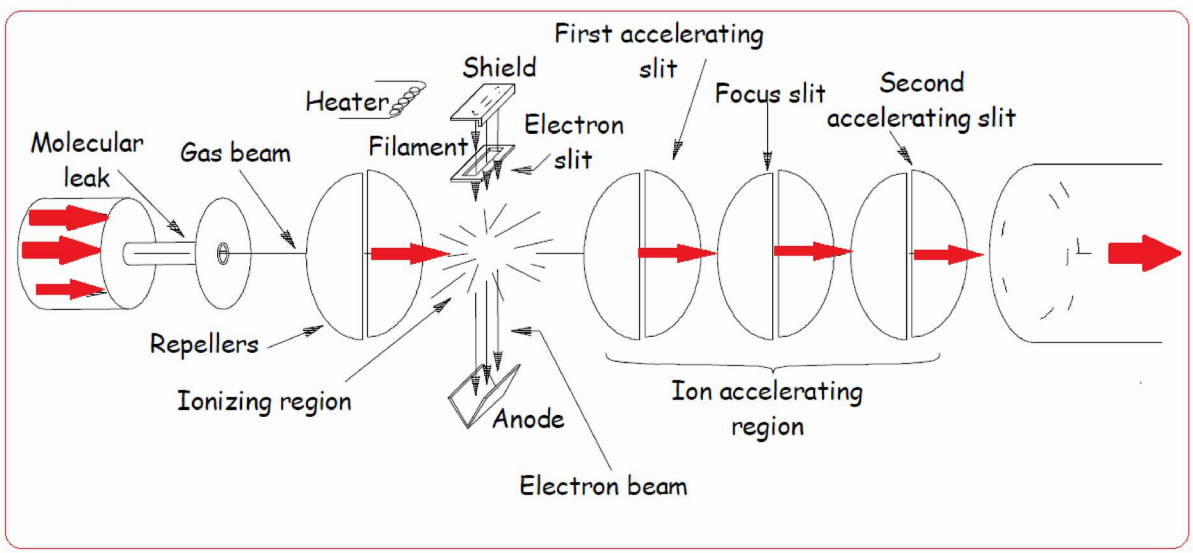

Figure 2.1 Schematic representation of an ion source.

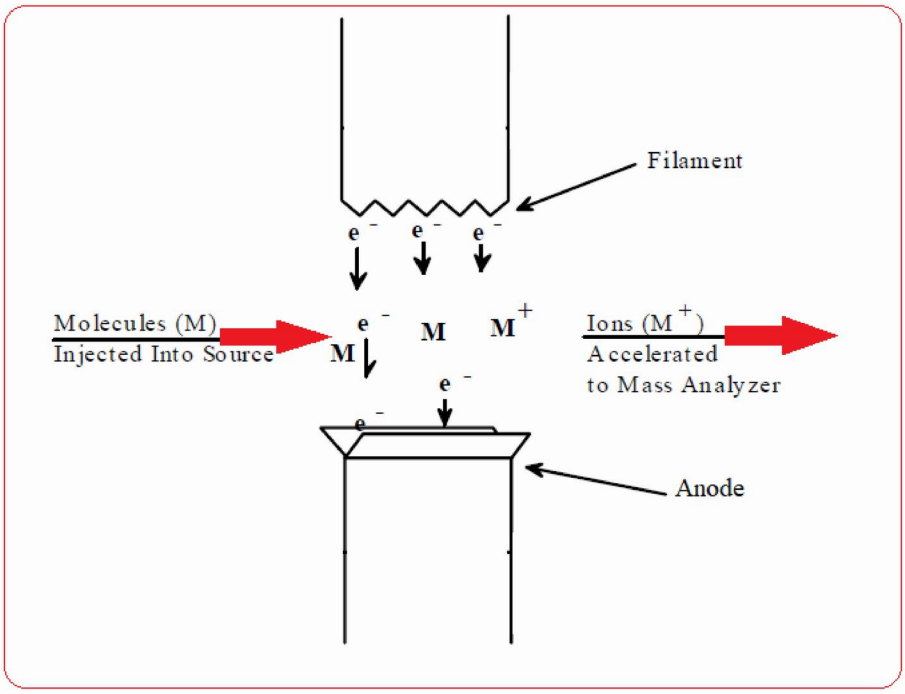

Figure 2.2 The ionizing region.

During this ionization, the radical-ions on average gain an excess energy enough to break one or more bonds en hence producing fragment-ions.

In Figure 4 the possible fragmentation of a molecule ABCD is presented.

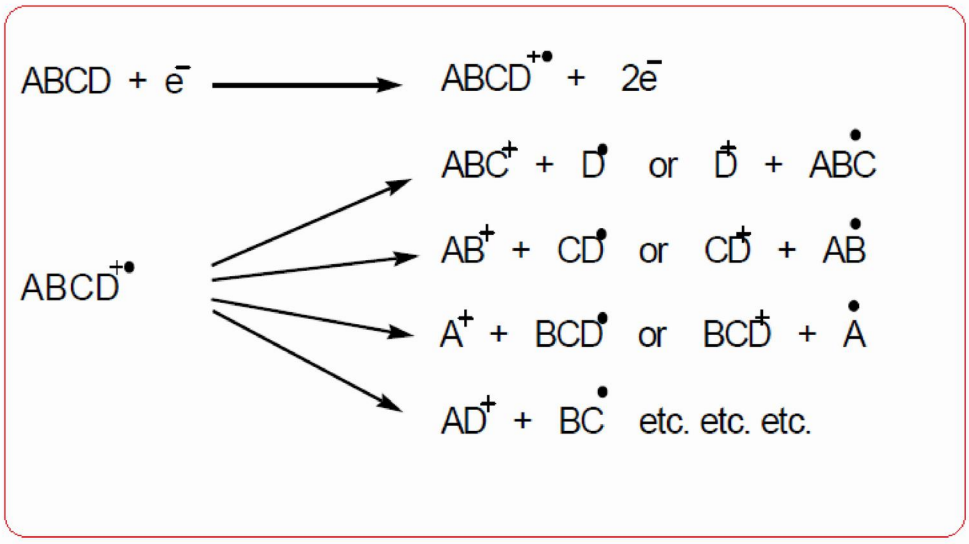

Figure 2.3 Possible fragmentation of a 'molecule' ABCD.

It should be stated here that this is a simplified presentation and that in real life a multitude of possible ways to form fragments even via re-arrangement reactions exists. Fragmentation of a molecular radical cation to give a neutral molecule and a new fragment radical cation is also possible.

2.2 Chemical Ionization

Chemical Ionization (CI) is a "soft" ionization technique that produces ions with little excess energy. As a result, less fragmentation is observed in the mass spectrum. Since this increases the abundance of the molecular ion, the technique is complimentary to 70 eV of EI. CI is often used to verify the molecular mass of an unknown. Only slight modifications of an EI source region are required for CI experiments.

In Chemical Ionization, the source is enclosed in a small cell with openings for the electron beam, the reagent gas and the sample. The reagent gas is added to this cell at approximately 10 Pa (0.1 torr) pressure. This is higher than the 10^{-3} Pa (10^{-5} torr) pressure typical for a mass spectrometer source.

At 10^{-3} Pa, the mean free path between collisions is approximately 2 meters and ion-molecule reactions are unlikely. In the CI source, however, the mean free path between collisions is only 10^{-4} meters and analyte molecules undergo many collisions with the reagent gas. The reagent gas in the CI source is ionized with an electron beam to produce a cloud of ions. The reagent gas ions in this cloud react and produce adduct ions like CH (Figure 6), which are excellent proton donors.

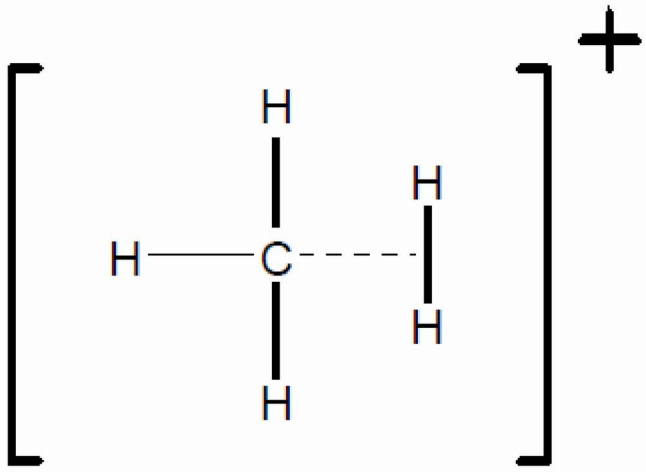

Figure 2.4 CH_5^+ ion.

When analyte molecules (M) are introduced to a source region with this cloud of ions, the reagent gas ions donate a proton to the analyte molecule and produce MH^+ ions.

The energetics of the proton transfer is controlled by using different reagent gases. The most common reagent gases are methane, isobutane and ammonia. Methane is the strongest proton donor commonly used with a proton affinity (PA) of 5.7 eV. For softer ionization, isobutane (PA 8.5 eV) and ammonia (PA 9.0 eV) are frequently used. Acid base chemistry is frequently used to describe the chemical ionization reactions. The reagent gas must be a strong enough Brønsted acid to transfer a proton to the analyte. Fragmentation is minimized in CI by reducing the amount of excess energy produced by the reaction. Because the adduct ions have little excess energy and are relatively stable, CI is very useful for molecular mass determination. Some typical reactions in a CI source are shown in Figure 2.5.

A) EI of reagent gas to form ions:

$$CH_4 + e^- \rightarrow CH_4^{+\bullet} + 2\,e^-$$

B) Reaction of reagent gas ions to form adducts:

$$CH_4^{+\bullet} + CH_4 \rightarrow CH_3^{\bullet} + CH_5^+$$

Or

$$CH_4^{+\bullet} \rightarrow CH_3^+ + H^{\bullet}$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

C) Reaction of reagent gas ions with analyte molecules:

$$CH_5^+ + M \rightarrow CH_4 + MH^+$$

$$C_2H_5^+ + M \rightarrow C_2H_4 + MH^+$$

$$CH_3^+ + M \rightarrow CH_4 + (M - H)^+$$

Figure 2.5 Chemical ionization reactions.

Part 3

Desorption Sources

3.1 Introduction

The ionization methods discussed so far require that the ionizing agents act on gaseous samples. Such methods are not applicable to non volatile or thermally unstable samples. A number of *desorption ionization* methods have been developed for dealing with this type of sample. These methods have enabled mass spectra to be obtained for thermally delicate biochemical species and species having molecular masses of greater than 100,000 Da. Desorption methods dispense with volatilization followed by ionization of the gaseous analyte molecules. Instead, energy in various forms is introduced into the solid or liquid sample in such a way as to cause direct formation of gaseous ions. As a consequence, spectra are greatly simplified and often consist of only the molecular ion or the protonated molecular ion. In most cases the exact mechanism of how ions are formed without fragmentation is not well understood.

3.2 Field Desorption Methods

In field desorption, a multi tipped emitter similar to that used in field ionization sources is used. In this case, the electrode is mounted on a probe that can be removed from the sample compartment and coated with a solution of the sample. After the probe is reinserted into the sample compartment, ionization again takes place by applying a high voltage to this electrode. With some samples it is necessary to heat the emitter by passing a current through the wire. As a result, thermal degradation may occur before ionization is complete.

3.2.1 Matrix-Assisted Laser Desorption/Ionization

Matrix-assisted laser desorption/ionization (MALDI) spectrometry is an ionization method that can be used to obtain accurate molecular mass information about polar biopolymers ranging in molecular mass from a few thousand to several hundred thousand Da. The method was first described nearly simultaneously in 1988 by two research groups, one German and the other Japanese Commercial instrumentation is available for MALDI. In the MALDI technique, a low concentration of the analyte is uniformly dispersed in a solid or liquid matrix deposited on the end of a stainless-steel probe or placed on a metal plate.

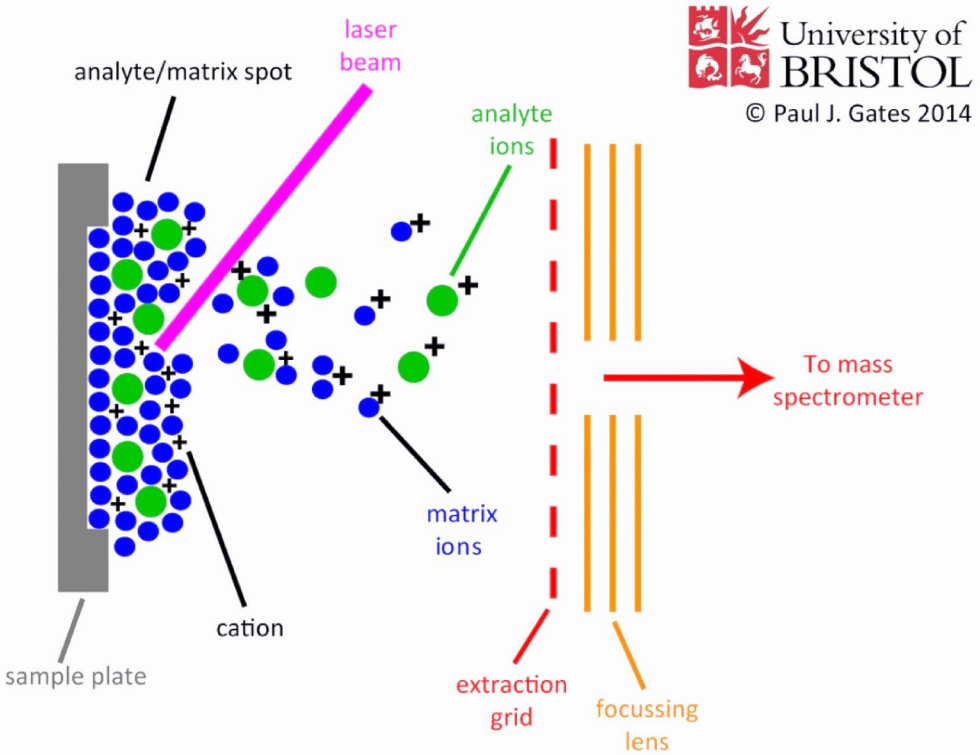

Figure 3.1 Mechanism of the Matrix-Assisted Laser Desorption/Ionization ***(Figure sent to us by Dr Paul Gates, University of Bristol, UK, used with permission).***

The plate is then placed in a vacuum chamber and a laser beam is focused onto the sample. In addition to the usual vacuum- chamber MALDI, atmospheric-pressure MALDI has also been described.

The MALDI matrix must strongly absorb the laser radiation. The matrix and analyte are then desorbed and ionized, creating an ion plume. The overall process is illustrated in Figure. The most common type of mass analyzer used with MALDI is the time-of-flight (TOF) analyzer.

A mass spectrum from a MALDI-TOF instrument is shown in Figure. Here, the matrix material was nicotinic acid, and the analyte was a monoclonal antibody from a mouse having a molecular mass of approximately 150,000 Da.

Note that the spectrum is characterized by very low background noise and a complete absence of fragmentation of the large analyte ion. Multiply charged ions are present as well as peaks for dimer and trimer species. Although the mechanism of the formation of the MALDI ion plume is not completely understood, it is thought to involve absorption of the laser beam by the matrix, followed by transfer of the energy from the matrix to the analyte. Desorption of the analyte and the matrix then occurs. The analyte is thought to desorbs as neutral molecules and then to be ionized by proton transfer reactions with protonated matrix ions in a dense phase over the surface containing the matrix. A series of photochemical reactions may produce the protonated matrix ions. Recently, the MALDI technique has been extended to imaging methods by scanning a localized laser beam over the dispersed sample. Mass spectral images of a variety of biopolymers have been obtained in this manner.

3.2.2 Electrospray Ionization (Nebulization- ionization)

Electrospray ionization–mass spectrometry (ESI/MS), which was first described in 1984, has now become one of the most important techniques for analyzing biomolecules, such as polypeptides, proteins, and oligonucleotides, having molecular weights of 100,000 Da or more. In addition, this method is finding more and more application to the characterization of

inorganic species and synthetic polymers. For their development of soft desorption ionization methods, such as electrospray ionization, John B. Fenn and Koichi Tanaka shared the **2002 Nobel Prize** in Chemistry.

Electrospray ionization takes place under atmospheric pressures and temperatures in an apparatus such as that shown in Figure. A solution of the sample is pumped through a stainless-steel capillary needle at a rate of a few microliters per minute. The needle is maintained at several kilovolts with respect to a cylindrical electrode that surrounds the needle.

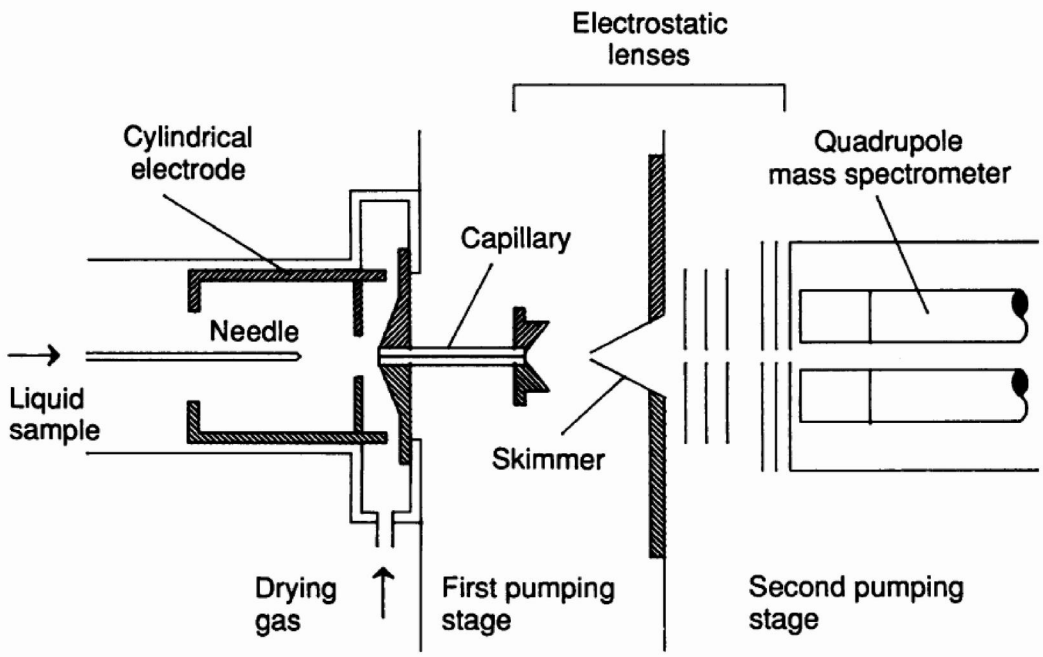

Figure 3.2 Electrospray deposition John B. Fenn and Koichi Tanaka

The resulting charged spray of fine droplets then passes through a desolating capillary, where evaporation of the solvent and attachment of charge to the analyte molecules take place. As the droplets become smaller as a consequence of evaporation of the solvent, their charge density becomes greater until, at a point called the *Rayleigh limit*, the surface tension

can no longer support the charge. Here a so-called *Coulombic explosion* occurs and the droplet is torn apart into smaller droplets. These small droplets can repeat the process until all the solvent is removed from the analyte, leaving a multiply charged analyte molecule. An interesting and useful feature of the electrospray process is that little fragmentation of large and thermally fragile biomolecules occurs because there is little extra energy retained by the analyte upon ionization. Furthermore, the ions formed are multiply charged so that their m/z values are small enough to make them detectable with a quadrupole instrument with a range of 1500 or less. This important property is demonstrated by the mass spectra of four proteins of varying molecular mass (M) shown in Figure. In these spectra, adjacent peaks are for analyte ions that differ by one charge. A striking feature of the spectra for proteins, such as those in the figure, is that the average charge state increases in approximately linear fashion with molecular mass. The charge state corresponding to each peak can be determined from peak distribution, thus making it possible to determine the molecular mass of a protein from spectra such as those shown in Figure. An important characteristic of electrospray ionization is that it is readily adapted to direct sample introduction from high-performance liquid chromatography and capillary electrophoresis columns. That there is little fragmentation of the analyte makes structural elucidation a difficult task. Usually, tandem mass spectrometry is used for this purpose. Here, the ions from the original ionization process are separated and the ion of interest is subjected to a fragmentation step before being mass analyzed.

Part 4

Mass Analyzers

4.1 Mass analyzers definitions

After ions are formed in the source region, they are accelerated into the mass analyzer by an electric field. The mass analyzer separates these ions according to their *m/z* value. The selection of a mass analyzer depends upon the resolution, ** (*26*) mass range, *** scan rate**** and detection limits required for an application. Each analyzer has very different operating characteristics and the selection of an instrument involves important tradeoffs.

*** Resolution in mass spectrometry refers to the separation of two ions where R=m/Δm. These terms are defined several different ways. The most common are the 10% valley definition "Let two peaks of equal height in a mass spectrum at masses m and m-Δm be separated by a valley that at its lowest point is just 10% of the height of either peak." and the peak width definition "For a single peak made up of singly charged ions at mass m in a mass spectrum, the resolution may be expressed as m/_m, where _m is the width of the peak at a height that is a specified fraction of the maximum peak height. It is recommended that one of three values 50 %, 5 % or 0.5 % be used."(34)*

****Mass range refers to the highest mass to charge ratio transmitted by the mass spectrometer.*

Analyzers are typically described as either continuous or pulsed. Continuous analyzers include quadrupole filters and magnetic sectors. These analyzers are similar to a filter or monochromator used for optical spectroscopy. They transmit a single selected *m/z* to the detector and the mass spectrum is obtained by scanning the analyzer so that different mass to charge ratio ions are detected.

Pulsed mass analyzers are the other major class of mass analyzer. These are less common but they have some distinct advantages. These instruments collect an entire mass spectrum from a single pulse of ions. This results in a signal to noise advantage similar to Fourier transform or multichannel spectroscopic techniques. ***Ion cyclotron resonance, Pulsed analyzers include time-of-flight,*** and ***quadrupole ion*** trap mass spectrometers.

4.2 Ion Cyclotron Resonance (Fourier-transform ion cyclotron resonance)

The Ion Cyclotron Resonance mass spectrometer (ICR-MS or FT-ICR-MS) uses a superconducting magnet to trap ions in a small sample cell. This type of mass analyzer has extremely high mass resolution. These instruments are very expensive and are typically used for specialized research applications. The ICR traps ions in a magnetic field that causes ions travel in a circular path (Figure 4.1). This is similar to the path of an ion in a magnetic sector, but the ions are not traveling as fast and the magnetic field is stronger. As a result, the ions are contained in the small volume of the trap.

The ion's cyclotron frequency (ω), is the angular frequency** of an ion's orbit. This frequency is determined by the magnetic field strength (B) and the *m/z* value of the ion.

$$\omega = \frac{B \times e}{m/z} \quad (4.1)$$

The angular frequency ($\boldsymbol{\omega}$**) is in radians per second.*

After ions are trapped in this cell, they are detected by measuring the signal at this cyclotron frequency. This signal is measured by placing electrodes on each side of the ions circular orbit. An RF voltage is applied to the transmitter electrodes at the cyclotron frequency of the ion of interest. This RF energy moves ions at the applied frequency to a larger orbit.

Due to the ion-trap nature of FT-MS, it is possible to measure the ions without destroying them, this enables further experiments to performed on the ions. Alan Marshall has a published a number of reviews of FT-ICR and its applications over the years [4].

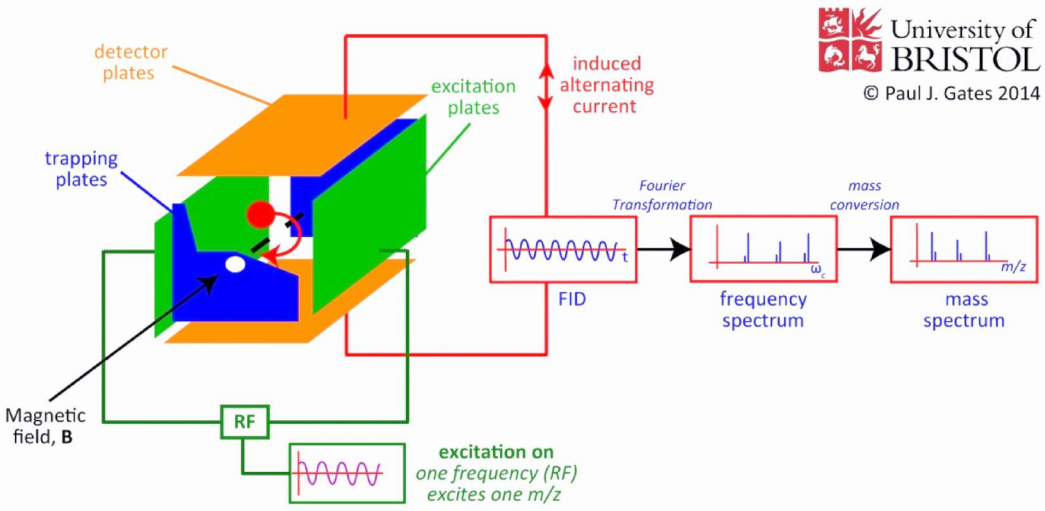

Figure 4.1 Ion Cyclotron Mass Spectrometer schematic.

*****The scan rate of a mass spectrometer refers to how fast it scans a mass spectrum. This is important for chromatography applications where the entire mass spectrum must be scanned faster than the elution time of the chromatographic peak. Ideally, a minimum of ten complete mass spectra are acquired for a single chromatographic peak.*

4.3 Time-of-Flight

The time-of-flight (TOF) mass analyzer separates ions in time as they travel down a flight tube (Figure 12). This is a very simple mass spectrometer that uses fixed voltages and does not require a magnetic field. The greatest drawback is that TOF instruments have poor mass resolution, usually less than 500. These instruments have high transmission efficiency, no upper *m/z* limit, very low detection limits, and fast scan rates. For some applications these advantages outweigh the low resolution. Recent developments in pulsed ionization techniques and new instrument designs with improved resolution have renewed interest in TOF-MS.

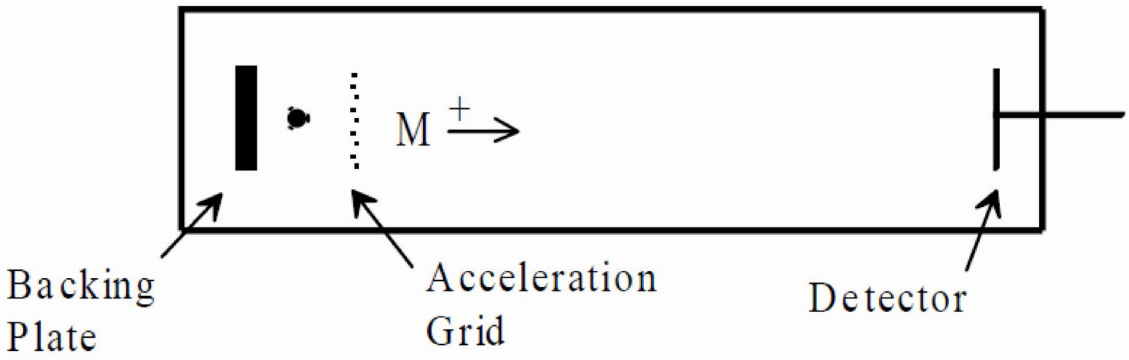

Figure 4.2 Time-of-Flight Mass Spectrometer.

In the source of a TOF analyzer, a packet of ions is formed by a very fast (ns) ionization pulse. These ions are accelerated into the flight tube by an electric field (typically 2-25 kV) applied between the backing plate and the acceleration grid. Since all the ions are accelerated across the same distance by the same force, they have the same kinetic energy. Because velocity (v) is dependent upon the kinetic energy ($E_{kinetic}$) and mass (m) lighter ions will travel faster.

$$E_{kinetic} = \frac{1}{2}mv^2 \tag{4.2}$$

$E_{kinetic}$ is determined by the acceleration voltage of the instrument (V) and the charge of the ion ($e \times z$). Equation 2 rearranges to give the velocity of an ion (v) as a function of acceleration voltage and m/z value.

$$v = \sqrt{\frac{2V \times e}{m/z}} \tag{4.3}$$

After the ions accelerate, they enter a 1 to 2 meter flight tube. The ions drift through this field free region at the velocity reached during acceleration. At the end of the flight tube, they strike a detector. The time delay (t) from the formation of the ions

to the time they reach the detector upon the length of the drift region (L), the mass to charge ratio of the ion, and the acceleration voltage in the source.

$$t = \frac{L}{\sqrt{2V \times e}} \times \sqrt{m/z} \qquad (4.4)$$

Equation 4.4 shows that low *m/z* ions will reach the detector first. The mass spectrum is obtained by measuring the detector signal as a function of time for each pulse of ions produced in the source region.

4.4 Quadrupole Ion Trap

The Quadrupole ion storage trap mass spectrometer (QUISTOR) is a recently developed mass analyzer with some special capabilities. Several commercial instruments are available and this analyzer is becoming more popular. QUISTORs are very sensitive, relatively inexpensive, and scan fast enough for GC/MS experiments. The sensitivity of the QUISTOR results from trapping and then analyzing all the ions produced in the source.

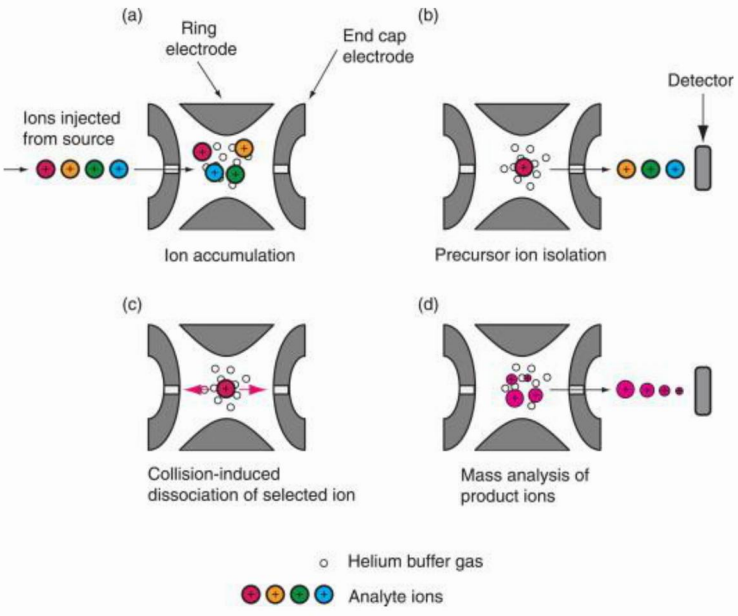

Figure 4.3 Quadrupole Ion Trap Mass Spectrometer [5].

The QUISTOR consists of a doughnut shaped ring electrode and two end cap electrodes. A cutaway view of this arrangement is shown in Figure 4.3.

A combination of RF and DC voltages is applied to the electrodes to create a quadrupole electric field similar to the electric field for the quadrupole mass analyzer. This electric field traps ions in a potential energy well at the center of the analyzer. The mass spectrum is acquired by scanning the RF and DC fields to destabilize low mass to charge ions. These destabilized ions are ejected through a hole in one end cap electrode and strike a detector. The mass spectrum is generated by scanning the fields so that ions of increasing *m/z* value are ejected from the cell and detected. The trap is then refilled with a new batch of ions to acquire the next mass spectrum. The mass resolution of the ion trap is increased by adding a small amount 0.1 Pa (10^{-3} torr) of Helium as a bath gas. Collisions between the analyte ions and the inert bath gas dampen the motion of the ions and increase the trapping efficiency of the analyzer.

4.5 Tandem mass spectrometry

Tandem mass spectrometry, also known as MS/MS or MS2, involves multiple steps of mass spectrometry selection, with some form of fragmentation occurring in between the stages. In a tandem mass spectrometer, ions are formed in the ion source and separated by mass-to-charge ratio in the first stage of mass spectrometry (MS1). Ions of a particular mass-to-charge ratio (precursor ions) are selected and fragment ions (product ions) are created by collision-induced dissociation, ion-molecule reaction, photodissociation, or other process. The resulting ions are then separated and detected in a second stage of mass spectrometry (MS2).

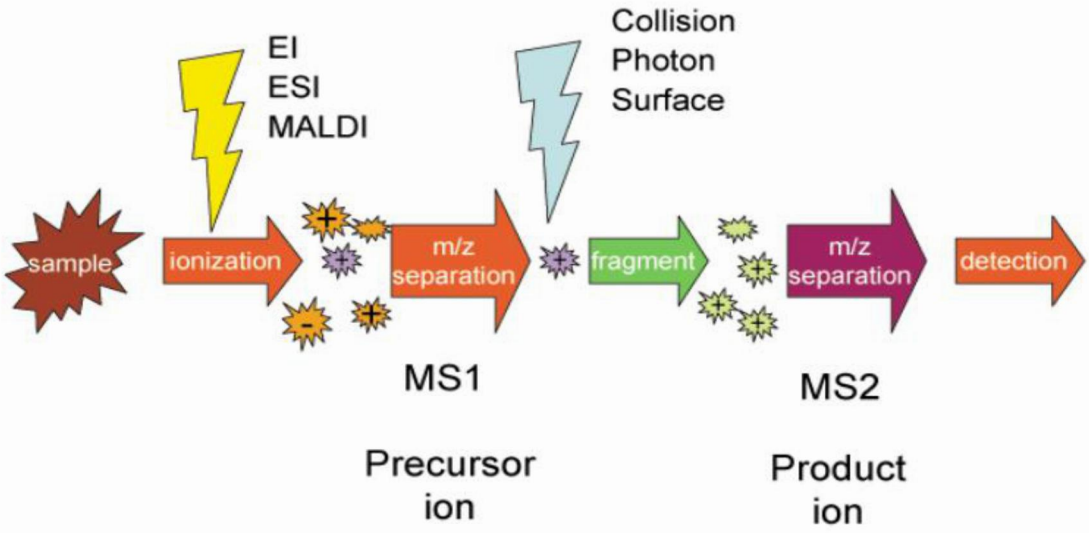

Figure 4.4 Schematic of tandem mass spectrometry.

The following scheme explains how Tandem MS works. Once samples are ionized (by ESI, MALDI, EI, etc.) to generate a mixture of ions, precursor ions of a specific mass-to-charge ratio (*m/z*) are selected (MS1) and then fragmented (MS2) to generate a product ion for detection. The selection-fragmentation-detection sequence can be further extended to the first-generation product ions. For example, selected product ions generated in MS2 can be further fragmented to produce another group of product ions (MS3) and so on.

4.6 Detectors

Detection of ions is based upon their charge or momentum. For large signals a faraday cup is used to collect ions and measure the current. Older instruments used photographic plates to measure the ion abundance at each mass to charge ratio. Most detectors currently used amplify the ion signal using a collector similar to a photomultiplier tube. These amplifying detectors include: electron multipliers, channeltrons and multichannel plates. The gain is controlled by changing the high

voltage applied to the detector. A detector is selected for its speed, dynamic range, gain, and geometry. Some detectors are sensitive enough to detect single ions.

4.7 Vacuum system

All mass spectrometers operate at very low pressure (high vacuum). This reduces the chance of ions colliding with other molecules in the mass analyzer. Any collision can cause the ions to react, neutralize, scatter, or fragment. All these processes will interfere with the mass spectrum. To minimize collisions, experiments are conducted under high vacuum conditions, typically 10^{-2} to 10^{-5} Pa (10-4 to 10^{-7} torr) depending upon the geometry of the instrument. This high vacuum requires two pumping stages. The first stage is a mechanical pump that provides rough vacuum down to 0.1 Pa (10^{-3} torr). The second stage uses diffusion pumps or turbomolecular pumps to provide high vacuum. ICR instruments have even higher vacuum requirements and often include a cryogenic pump for a third pumping stage.

Part 5

Applications

Summarizing all of the above we can say that the *Mass spectrometry* provides information about the *molecular mass* of an organic compound, and about how the organic compound *fragments* when it is has a large amount of excess energy.

5.1 Formation of Molecular and Fragment Ions (5.2A)

A **mass spectrometer** bombards a small sample of an organic compound with a beam of high energy electrons (e-) leading to the formation of positively charged **molecular ions** that subsequently decompose into **fragment ions**.

$$\text{Organic Compound} + e^- \rightarrow \text{Molecular Ions} \rightarrow \text{Fragment Ions}$$

The *mass spectrometer* detects the mass of the *molecular ions* as well as the masses of the *fragment ions*.

- ***Molecular Ion***

A *molecular ion* ($M^{+\bullet}$) forms when a high energy electron (e^-) collides with a molecule (**M**) in the sample causing it to lose one of its own electrons.

$$e^- + M \rightarrow M^{+\bullet} + 2\,e^-$$

The two electrons (2e-) that are products of this "reaction" include the electron from the electron beam that hit the molecule as well as the electron ejected from the molecule. The *molecular ion* ($M^{+\bullet}$) is positive because it has lost an electron and therefore has one less electron than it has protons.

Besides its positive (+) charge, we specifically show using the symbol (•) that the *molecular ion* has one *unpaired* (*unshared*) electron. Molecules have even numbers of electrons that exist as *pairs* in chemical bonds, as *pairs* of unshared electrons, or as *pairs* in inner shell atomic orbitals. As a result, the loss of one electron not only causes *M* to become (+), but also to have an odd number of electrons so that one is unpaired (•).

5.2 Fragment Ions

Molecular ions ($M^{+\bullet}$) possess a large amount of excess energy when they form. This causes many of them to decompose into smaller fragments that are positively charged (*cations)* and uncharged (neutral) species called **radicals**. We illustrate *molecular ion formation* and its subsequent *fragmentation* in a mass spectrometer using a generic molecule R_1-R_2 in which the chemical bond between R_1 and R_2 breaks during fragmentation.

$$e^- + \underset{(M)}{R_1\text{-}R_2} \rightarrow \underset{(M)^{+\bullet}}{(R_1\text{-}R_2)^{+\bullet}} + 2e^-$$

$$\underset{(M)^{+\bullet}}{(R_1\text{-}R_2)^{+\bullet}} \rightarrow R_1^+ + R_2^{\bullet} \quad \text{and/or} \quad R_1^{\bullet} + R_2^+$$

Figure 5.1 Fragment Ions.

Mass spectrometers detect the presence of positively charged ions and measure their masses. As a result, a mass spectrometer provides masses of *molecular ions* ($(R_1 - R2 +\bullet$) as well as masses of the positive *fragment ions* (R_1^+ and R_2^+) that result from fragmentation of the molecular ion.

Fragment ions are like pieces of a jig saw puzzle that chemists can often fit back together to give part or all of the detailed molecular structure of the original organic molecule.

5.3 Molecular and Fragment Ions from Methane

We use methane (CH4) to illustrate *molecular ion* formation and *fragmentation* because all of its chemical bonds are identical.

(a) Electron bombardment (formation of the molecular ion)

e^-	+	CH_4	→	$CH_4^{+\cdot}$	+	$2e^-$
		10p		10p		
1e		10e		9e		2e

Figure 5.2 Electron bombardment.

(b) Fragmentation (formation of radical and cation)

$CH_4^{+\cdot}$	→	$CH_3^{\cdot}$	+	H^+
10p		9p		1p
9e		9e		

Or

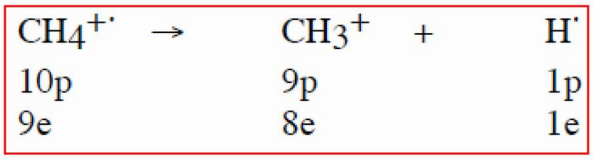

Figure 5.3 Fragmentation.

Each of these equations is *chemically* and *electrically* balanced. Both the total number of *protons* (*p*) as well as the total number of *electrons* (*e*) are the same on both sides of each equation, and the same is true for the net electrical charge on both sides of each equation. The relative numbers of protons (*p*) and numbers of electrons (*e*) for each species show you why a species has a negative (-) charge, a positive (+) charge, and/or an unpaired electron (•). The species with single (+) charges have one more *p* than *e*, while those labelled with a (•) have an odd number of *e's*. (By convention, we do not show a (•) on e- even though it is simply a single electron.)

This detailed analysis is a useful exercise, but you will not need to do it routinely in order to interpret results of *MS* structure determinations of organic compounds.

The ***two important points*** are that a mass spectrometer (a) generates and detects positively charged ions (*molecular* and *fragment ions*) from the original compound, and (b) determines their masses. We describe this in more detail in the following sections.

5.4 The Mass Spectrometer and Mass Spectrum

There are several different designs for mass spectrometers, but all of them form, detect, and measure the mass of positively charged species formed by electron bombardment.

5.4.1 Mass Spectrometer

We show the typical component parts of these mass spectrometers using the simple "block" diagram in Figure 5.4.

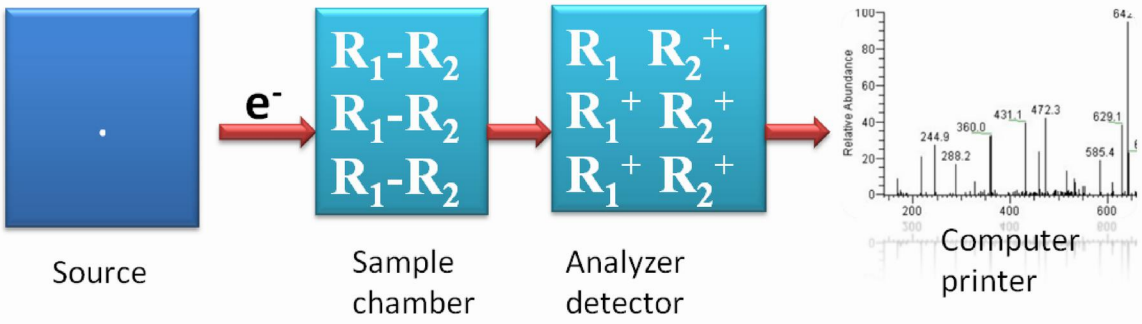

Figure 5.4 Typical component parts of these mass spectrometers.

The mass spectrometer bombards the organic sample in the **sample chamber** (Figure 5.4) with high energy electrons from the **source**, and detects the resulting positive ions in the **analyzer/detector** region of the spectrometer. The *analyzer* and *detector* are usually separate components, but some mass spectrometers, used for routine mass spectral analysis in organic laboratories, analyze and detect positive ions in the *sample chamber* where they form.

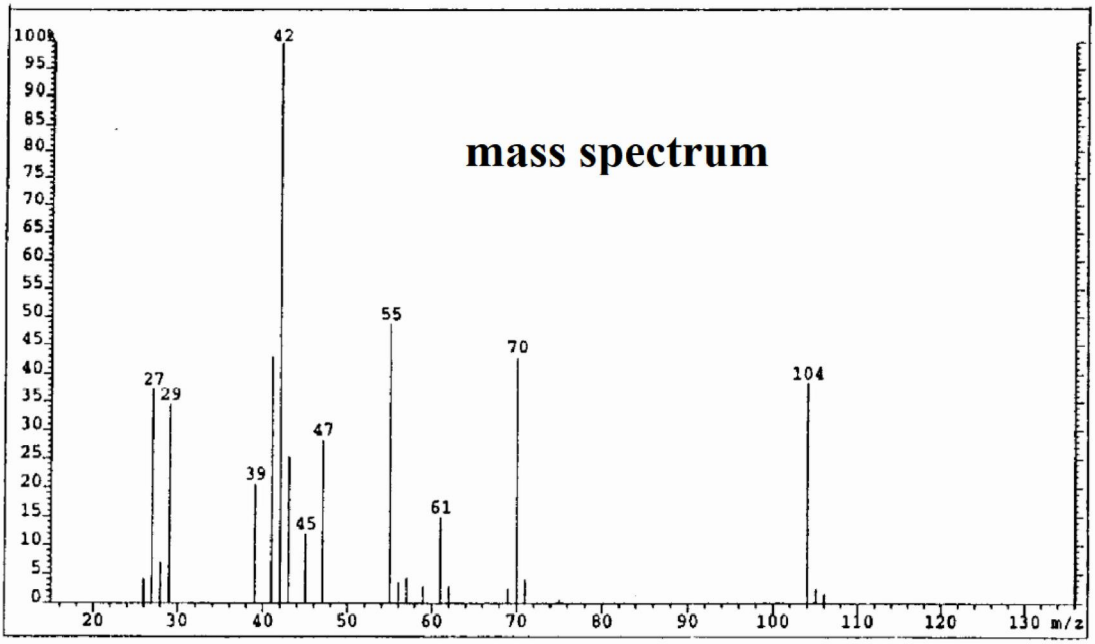

Figure 5.5 Mass spectrum illustration.

5.4.2 Mass Spectrum

The mass spectrometer determines the amount and mass of each positively charged species, stores these data in a computer, and subsequently prints out these results in a table or displays them as a **mass spectrum** (Figure 5.5).

A *mass spectrum* consists of a collection of *lines* at different **m/z** values (described below) along the horizontal axis or **base line** of the spectrum. Each line corresponds to a positively charged species detected by the spectrometer.

5.4.3 Mass-to-Charge Ratios (m/z Values).

The *m/z values* (**mass-to-charge ratios**) on the horizontal axis of the spectrum correspond to the mass (*m*) (*amu*) of each positively charged species divided by its electrical charge (*z*).

Most positive species formed in a mass spectrometer have a charge of +1 (z = +1), so their *m/z values* usually are the same as their masses (*m/z = m/(+1) = m*). The *m/z values* for the taller lines in the *mass spectrum* often appear as labels at the top of those lines.

The height of each *line* (or **signal** or **peak**) corresponds to the relative amount formed of the positive species with a particular *m/z* value. We call the tallest peak in any mass spectrum the **base peak** and usually assign it a value of 100% on the vertical axis. In the spectrum in Figure 5.5, the *base peak* is the line at m/z = 42. We describe the heights of the other peaks in the spectrum as a percentage of the *base peak*. We will see below that the positive ion giving the base peak is usually not the *molecular ion*, but is a particularly stable *fragment ion* whose structure depends on the particular compound giving the mass spectrum.

5.4.4 Peaks for the Molecular Ion and Fragment Ions

One of the most important lines in a mass spectrum is that of the *molecular ion* since its m/z value gives the *molecular mass* of the original compound. *Fragment ions* are pieces of the original molecule, but a knowledge of their structures is important in deducing the structure of the original molecule since we can often piece them together like pieces of a jigsaw puzzle. Their masses (m/z values) and an understanding of the reactivity of molecules helps us figure out the structures of fragment ions. We illustrate these points and other aspects of the use of MS by considering mass spectral results for **several different organic compounds.**

- **Hexane**

Our first example is the mass spectrum of the linear alkane *hexane*.

CH_3-CH_2-CH_2-CH_2-CH_2-CH_3

5.4.5 Mass Spectrum of Hexane

The hexane mass spectrum (Figure 5.6) has major lines (peaks) at *m/z values* of 15, 27, 29, 39, 41, 42, 43, 56, and 57, and smaller peaks at other *m/z values* including 71 and 86.

These m/z values all result from rounding off exact m/z values to **unit resolution** (*e.g.* an m/zvalue of 35.1 rounded off to *unit resolution* is 35).

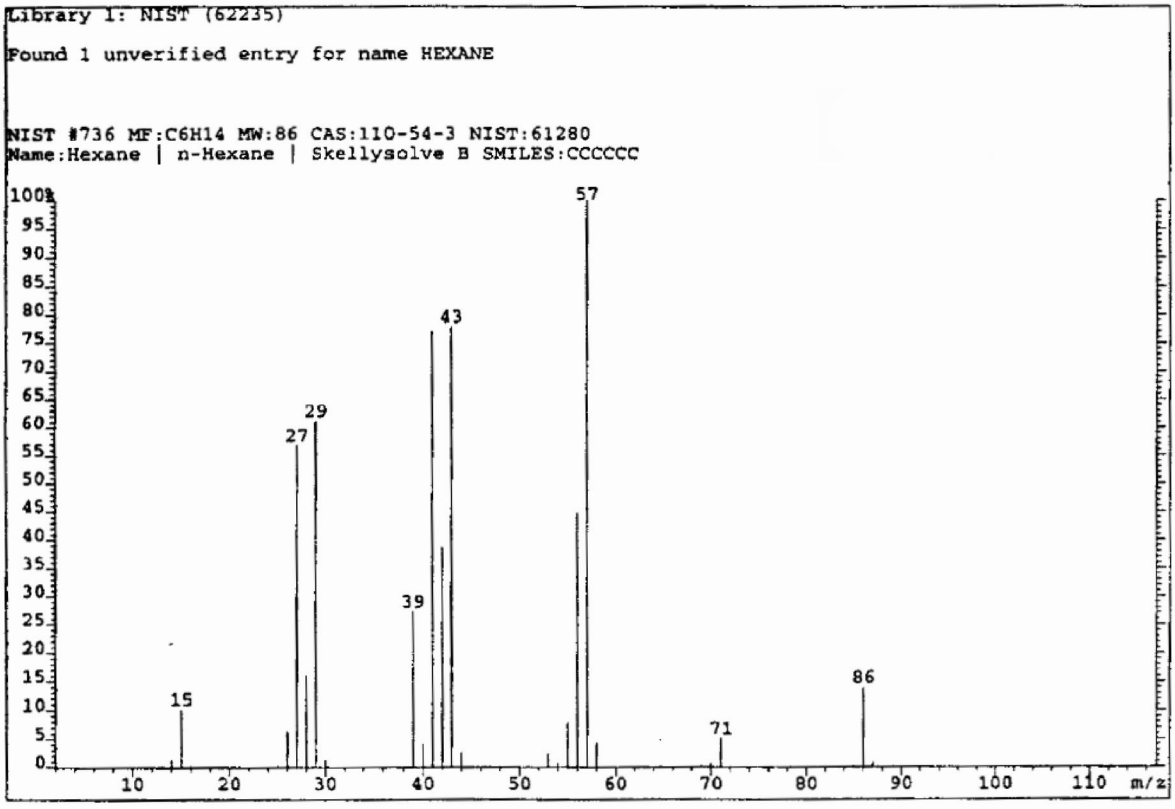

Figure 5.6 Mass Spectrum of Hexane.

What positive ions give these different peaks? Let's first look at the structure of hexane and consider how its *molecular ion* might fragment to form different *fragment ions*, and then see if the masses of these fragments are present in the spectrum.

5.4.6 Molecular Ion and Fragment Ions from Hexane

Bombardment of hexane (C_6H_{14}) with high energy electrons forms the *molecular ion* $(C_6H_{14})^{+\cdot}$ (Figure 5.7).

This *molecular ion* might then fragment by breaking any of its C-C bonds (Figure 5.7) and we show the *molecular ion* and possible *fragment ions* in Table 5.1 along with their *unit resolution* and exact *m/z values*.

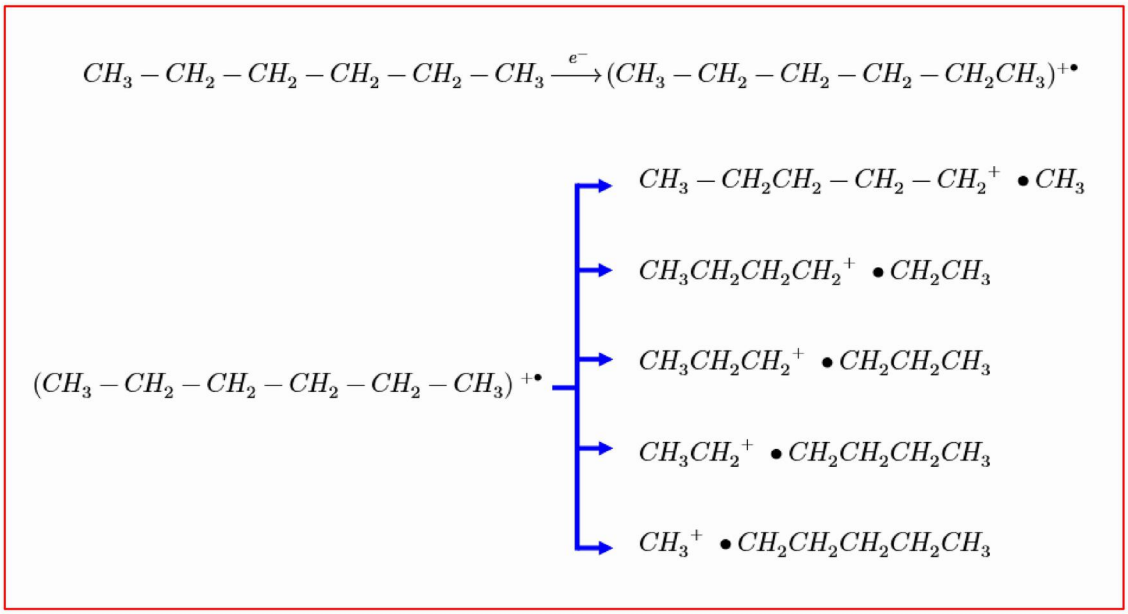

Figure 5.7 Bombardment of hexane with high energy electrons.

Table 5.1 Exact and Unit Resolution m/z Values for Cations formed from Hexane in a Mass Spectrometer.

Ion Structure		m/z Value (*amu*) Exact	Unit Resolution
$(C_6H_{14})^{+\cdot}$	$(CH_3CH_2CH_2CH_2CH_2CH_3)^{+\cdot}$	86.1096	86
$C_5H_{11}^{+}$	$(CH_3CH_2CH_2CH_2CH_2+)$	71.0861	71
$C_4H_9^{+}$	$(CH_3CH_2CH_2CH_2+)$	57.0705	57
$C_3H_7^{+}$	$(CH_3CH_2CH_2+)$	43.0548	43
$C_2H_5^{+}$	(CH_3CH_2+)	29.0391	29
CH_3^{+}	(CH_3+)	15.0235	15

You can see peaks at all of these m/z values in the hexane mass spectrum (Figure 5.6). In addition, there are prominent peaks for fragments that have m/z values other than those in Table 5.1. Some are 1 or 2 *amu* less than those mentioned in Table 5.1 and they correspond to ions with one or two fewer H atoms than the ions shown in Table 5.1. It is also important to note that there are several "groups" of peaks made up of individual peaks that are each 14 *amu* (the mass of a CH_2 group) larger or smaller than individual peaks in a neighboring group.

5.4.7 Exact Mass Values

The mass values of these peaks are shown at *unit resolution* in Figure 5.6, but **high-resolution** mass spectrometers give their *exact mass values*. The exact mass of the hexane molecular ion $(C_6H_{14})^{+\cdot}$ is virtually identical to the exact mass of a hexane molecule (C_6H_{14}) since $(C_6H_{14})+\cdot$ differs from (C_6H_{14}) by just one electron that has negligible mass. However, if you use atomic masses from a periodic table or the *Handbook of Chemistry and Physics* to calculate the molecular mass of hexane, you obtain a value of 86.18 amu rather than the exact mass value of 86.11 (86.1096

rounded off to 4 significant figures). These two values of 86.18 and 86.11 may seem very close to each other, but their difference of 0.07 amu is greater than any experimental or calculational error. A clue that we may have overlooked something in this analysis of hexane masses is the observation that the mass 86 peak is not the highest mass peak in this mass spectrum. If you look closely at Figure 5.6 you will see a very small peak at mass 87 that is not due to an impurity in our sample. We explain below both the origin of this **M+1 peak**, and why we cannot calculate *exact mass values* using atomic mass data from a *periodic table*.

5.4.8 M+1 Peaks and Isotopes

The *exact mass values* of all of the cations in Table 5.1 are slightly less than we would calculate using atomic mass values from a *periodic table*. This is because atomic masses of C and H from *periodic tables* are *weighted averages* of exact mass values of their naturally occurring *isotopes*. In contrast, mass spectrometers detect individual ions that do not have "average" isotopic distributions as we describe below.

The 12.01 amu atomic mass of C from a periodic table is a weighted average based on the 99% natural abundance of ^{12}C (6 protons, 6 neutrons, atomic mass 12.00000 amu) and 1% ^{13}C (6 protons, 7 neutrons, atomic mass 13.00335 amu).

Similarly, the 1.008 amu atomic mass of H from a periodic table is a weighted average based on the 99.985% natural abundance of ^{1}H (1 proton, 0 neutrons, atomic mass 1.007825 amu) and 0.015 % ^{2}H (1 proton, 1 neutron, atomic mass 2.0140 amu).

However, the detector of the mass spectrometer determines the masses of individual molecular fragments that cannot contain a statistical distribution of isotopes.

While most hexane molecular ions contain only ^{12}C and ^{1}H and are $(^{12}C_6\ ^{1}H_{14})^{+\cdot}$, there are also molecular ions in which one ^{12}C is replaced by a ^{13}C to give $(^{13}C_1\ ^{12}C_5\ ^{1}H_{14})^{+\cdot}$ that we call the M+1 peak. Their masses are both different from that calculated for $(C_6\ ^{1}H_{14})^{+\cdot}$ using atomic masses from a periodic table. In any sample we also expect a few molecular ions of hexane to contain two or more ^{13}C atoms, but their number is so small that they are not visible in the spectrum.

While an M+1 peak in the hexane spectrum could also reflect the presence of a ^{2}H atom in the molecular ion $(^{12}C_6\ ^{2}H_1\ ^{1}H_{13})^{+\cdot}$, the natural abundance of ^{2}H (0.015%) is so small that such ions constitute a trivial part of the M+1 peak.

Most *fragment ions* also contain just ^{12}C and ^{1}H, so their exact masses in Table 5.1 are also less than we would calculate using weighted average masses from a periodic table. However like the molecular ion, fragment ions with relatively intense peaks also have neighboring isotopic peaks one mass unit higher due to replacement of a ^{12}C by ^{13}C.

5.4.9 Mass Spectra of Hexane Structural Isomers

In order to see how mass spectra can provide information to help distinguish between isomers with the same molecular formula, we compare the mass spectrum of *hexane* with those of its isomers *2-methylpentane*, and *2,2-dimethylbutane* that are all C_6H_{14} (Figure 5.8).

5.4.10 The Molecular Ion Peaks

One of the most obvious differences between these spectra in Figure 5.8 is the molecular ion peak at 86. It is much weaker in the spectrum of 2-methylpentane than in that of *hexane*, and we cannot see it at all in the spectrum of *2,2-dimethylbutane*. This is an example of a general phenomenon in mass spectrometry that increasing branching in a molecule increases the probability of fragmentation of its molecular ion. An increase in ease of fragmentation of a molecular ion decreases its lifetime and decreases the possibility of observing it in a mass spectrum as we describe below.

5.4.11 Fragmentation

Fragmentation of the molecular ion due to branching occurs primarily at the **points of branching**. We mark these *points of branching* in 2-methylpentane and 2,2-dimethylbutane with the symbol (*) in Figure 5.9.

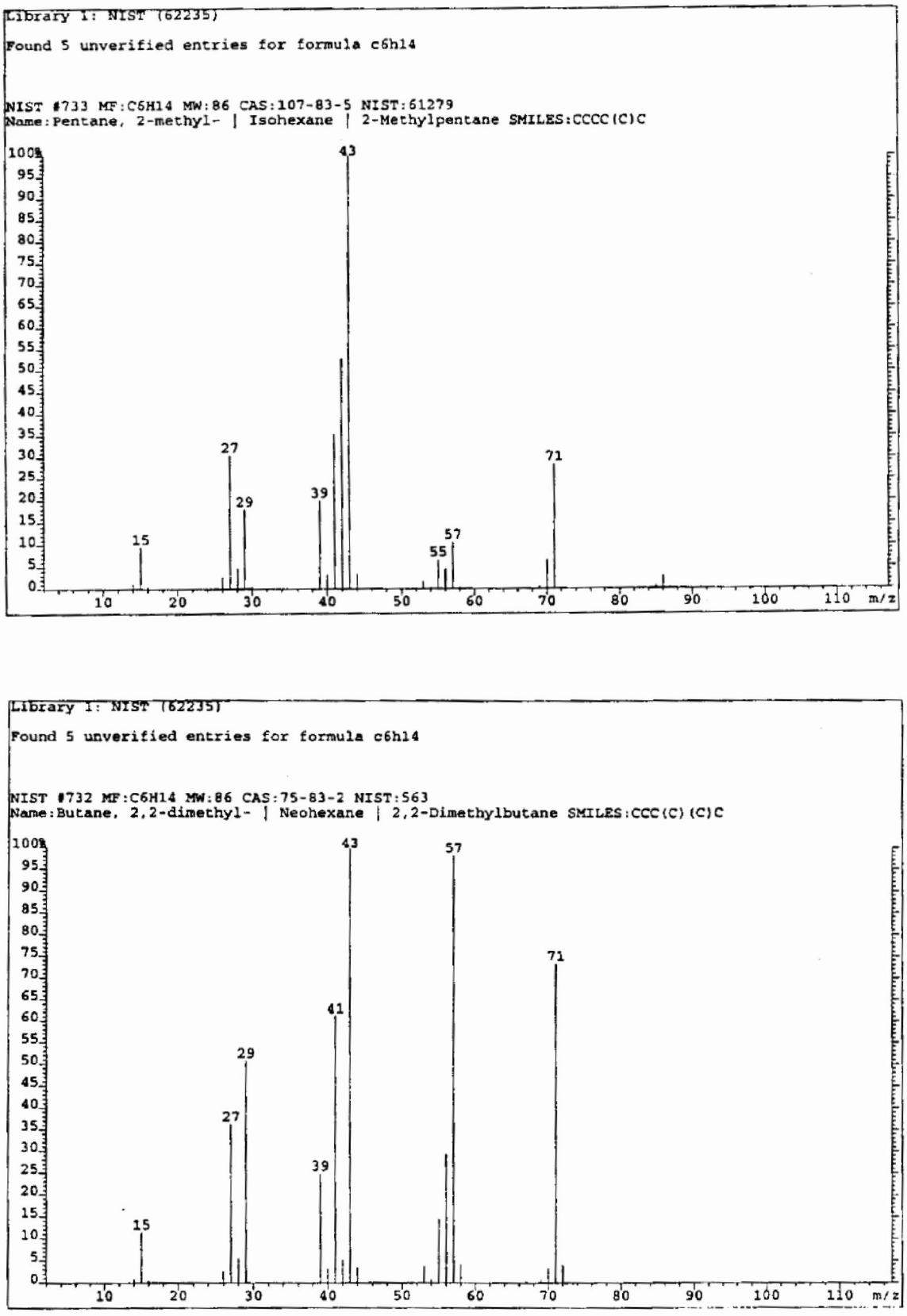

Figure 5.8 Presentation of Mass Spectra of Hexane Structural Isomers.

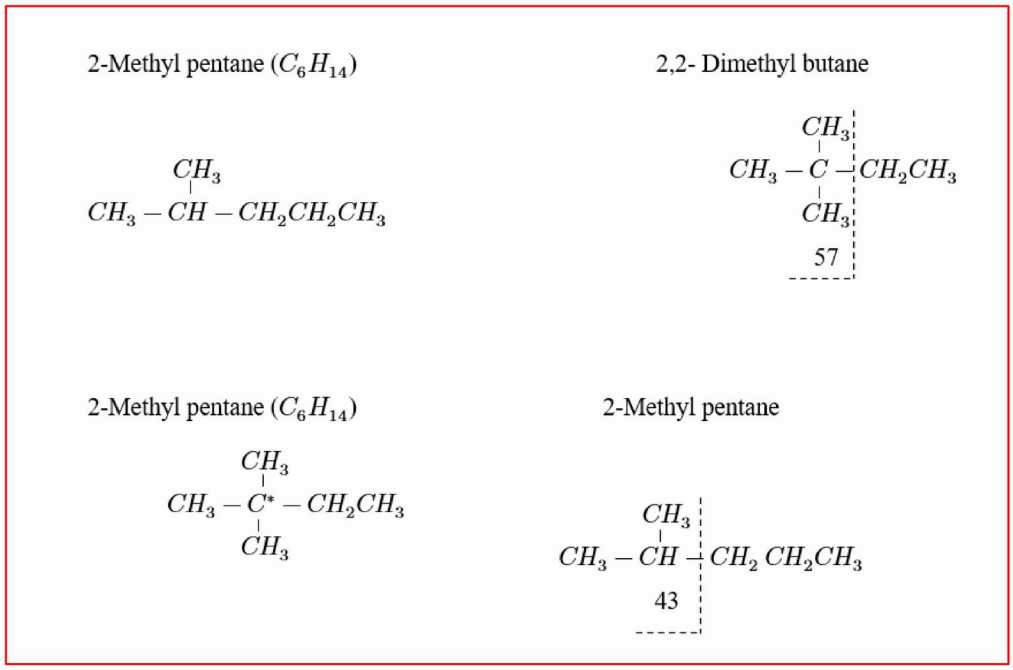

Figure 5.9 Possible C-C fragments for 2,2-dimethylbutane and for 2-methylpentane .

If $CH_3^{\cdot}$ is lost from C* in either of those compounds, we expect to see a mass 71 fragment ($C_5H_{11}^{+}$). Figure 5.8 shows that this mass 71 peak is largest for the most highly branched isomer *2,2-dimethylbutane*, less intense for *2-methylpentane*, and smallest for *hexane* since it is unbranched.

We show other possible C-C fragmentations in Figure 5.9 for *2,2-dimethylbutane* and for *2- methylpentane* at the branch points C*.

For *2,2-dimethylbutane*, we might expect to see a mass 57 peak ($C_4H_9^{+}$), while we might expect to see a mass 43 peak ($C_3H_7^{+}$) from *2-methylpentane*. We observe each of these in their respective spectra and they illustrate how mass spectra can distinguish between structural isomers.

Mass spectral results are not always easy to interpret in terms of simple fragmentation reactions. For example, while the mass 57 peak ($C_4H_9^+$) for *2-methylpentane* is very small confirming that a C_4 fragment cannot be formed by cleavage at C*, the mass 43 peak ($C_3H_7^+$) from *2,2- dimethylbutane* is unexpectedly large even though there is no obvious way of forming a C_3 fragment by a simple fragmentation reaction at any C-C bond. The molecule "knows what it is doing" and obviously wants to form this ion, but its origin is not easy to understand. Mass Spectro metrists say that such unexpected peaks arise by **random rearrangements**.

??? Why Branching Increases Fragmentation? You will learn later in the text that substitution of an alkyl group for an H on a C+ center increases the stability of that C+ center. This is the major reason why the positively charged species formed by C-C cleavage at branch points are so prominent in the mass spectra of branched alkanes.

5.4.12 Mass Spectra of Compounds with Functional Groups (5.2E)

Molecules with functional groups such as OH, NH2, or a halogen (X) have characteristic mass spectral features that help identify the presence of these functional groups. We illustrate these characteristic features using mass spectra of *1-pentanol*, *1-pentanamine*, *1-chloropentane*, *1- Bromo pentane*, and *1-iodopentane* (Figure 5.11).

5.5 General Features

All of these compounds in Figure 5.10 have the general structure $CH_3CH_2CH_2CH_2CH_2$-Y where Y is OH, NH_2, Cl, Br, or I. Electron bombardment in the mass spectrometer first gives molecular ions $(CH_3CH_2CH_2CH_2CH_2\text{-}Y)^{+\cdot}$ and these fragment into smaller cations and radicals.

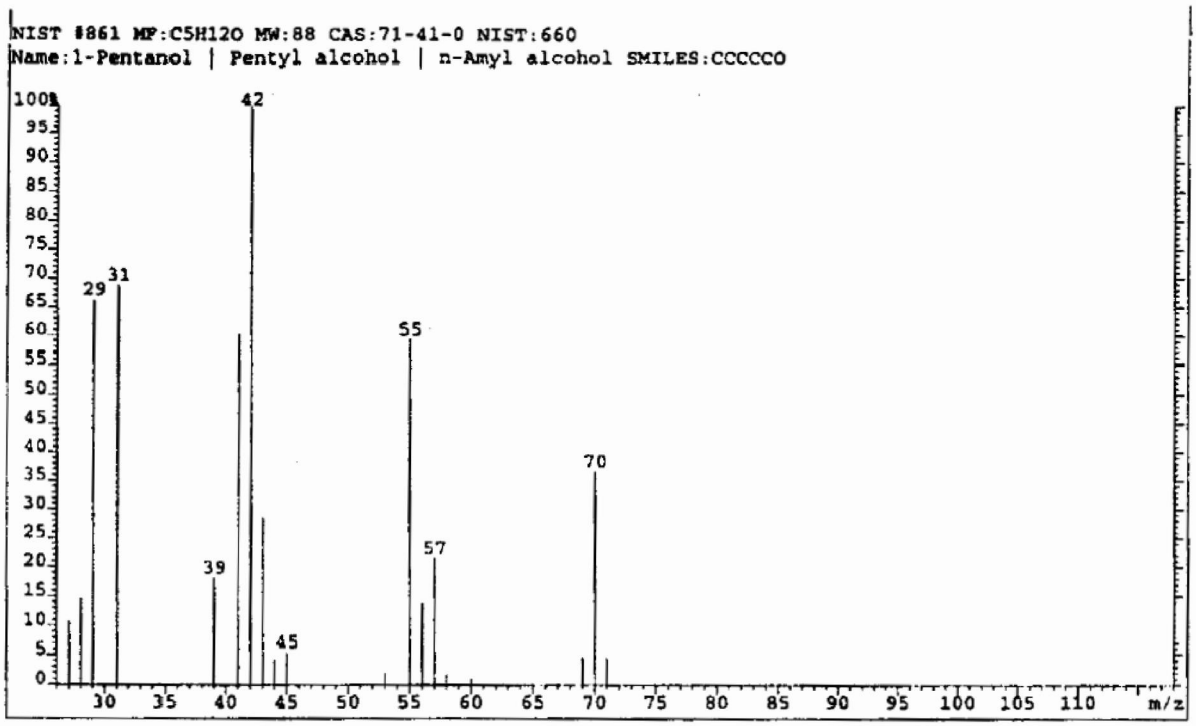

Figure 5.10.a) mass spectra of *1-pentanol*

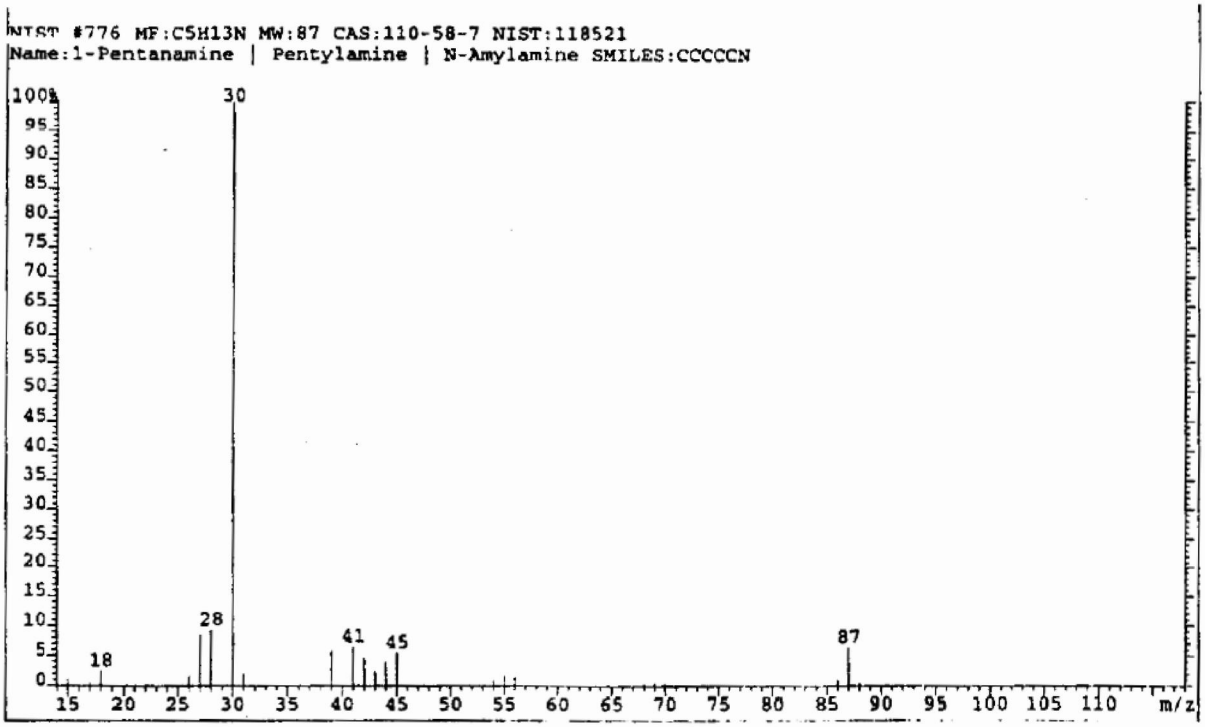

Figure 5. 10.b) mass spectra of *1-pentanamine*

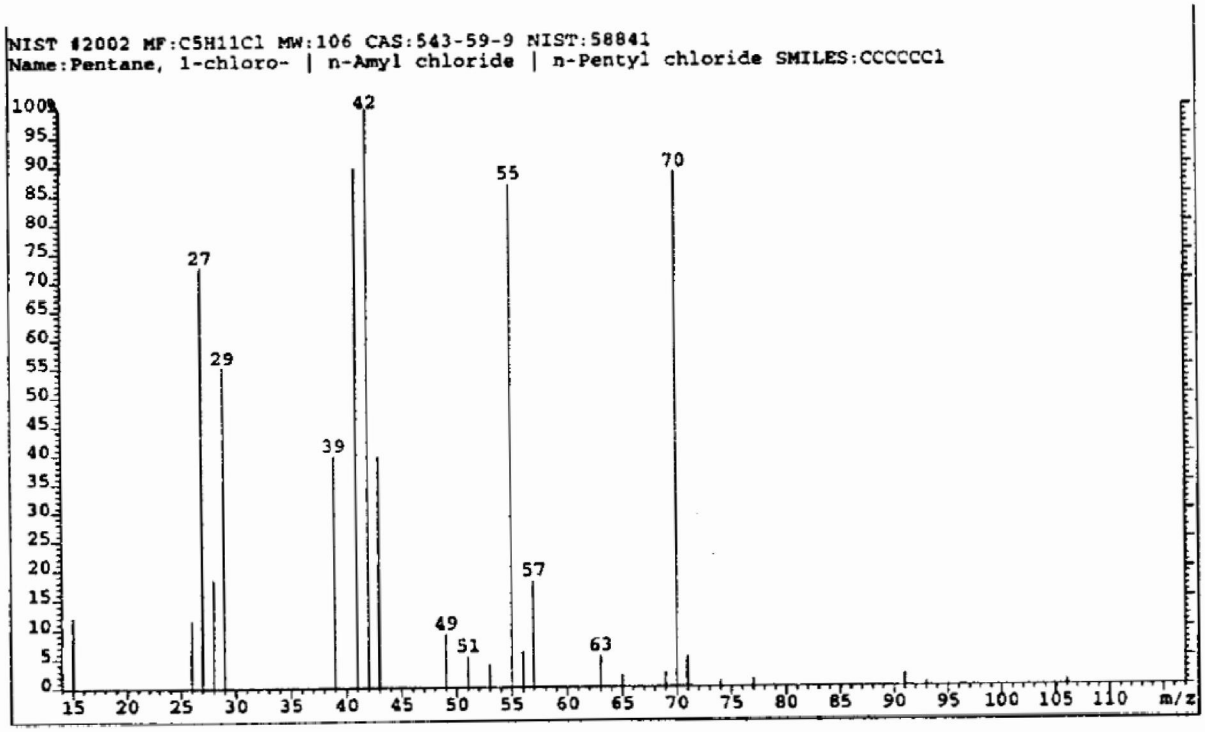

Figure 5. 10.c) mass spectra of *1-chloropentane*

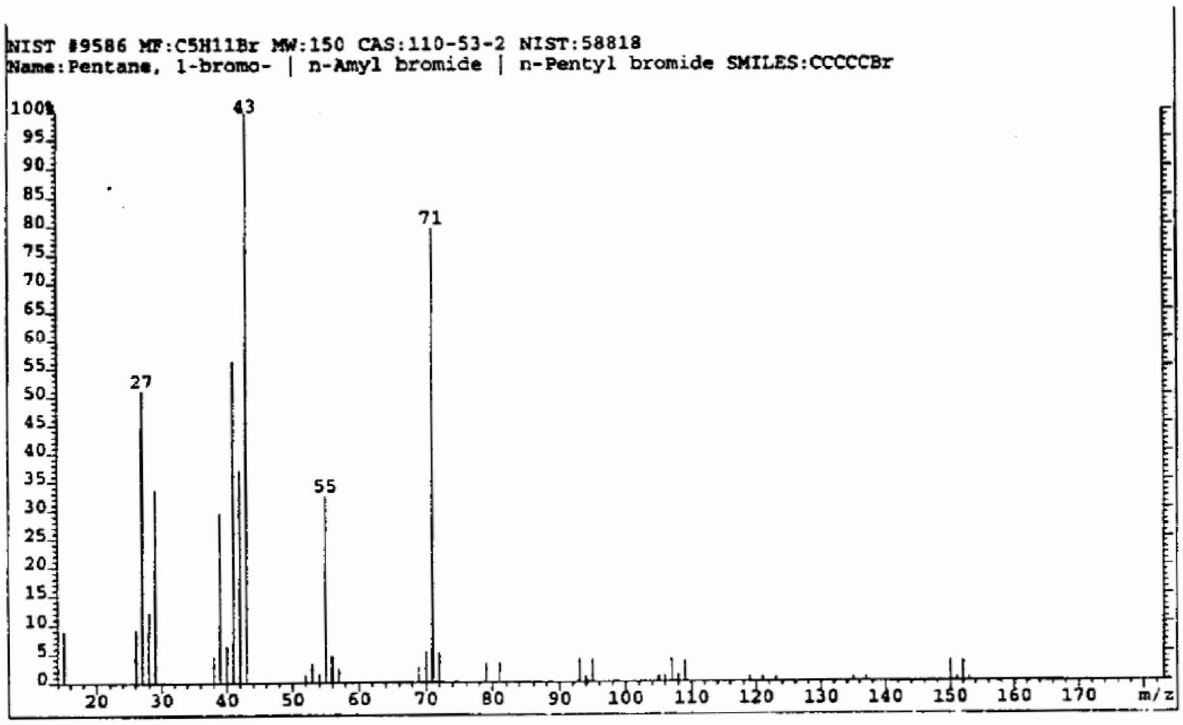

Figure 5. 10.d) mass spectra of *1- Bromo pentane.*

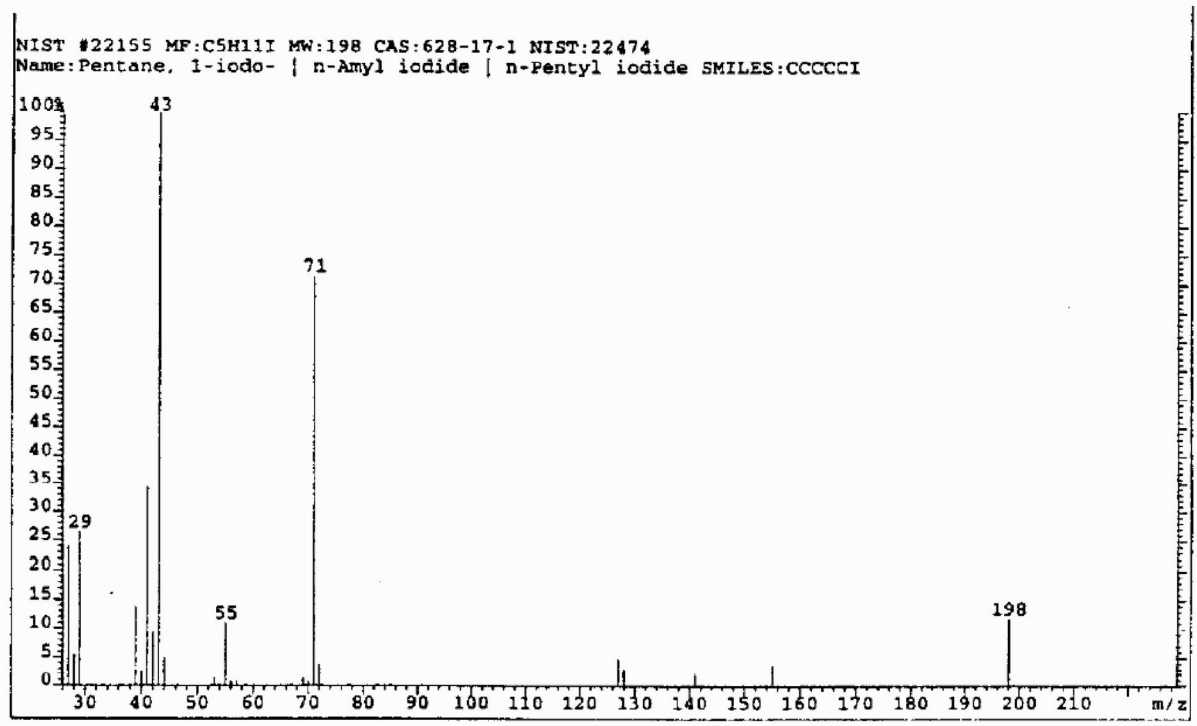

Figure 5.10.e) mass spectra of *1-iodopentane*

These fragments form by cleavage at C-C bonds as we saw for isomeric hexanes, but the functional group Y influences this fragmentation.

We will focus on the *molecular ion peaks*, on the *fragment peaks* corresponding to $^{+}CH_2$-*Y*, and on *fragment peaks* at mass values 55 ($C_4H_7^{+}$) and 70($C_5H_{10}^{+}$) that form as we show in Figure 5.11.

Each Y group causes an unusually large amount of fragmentation at its adjacent C-C bond giving the characteristic $^{+}CH_2$-*Y* fragment.

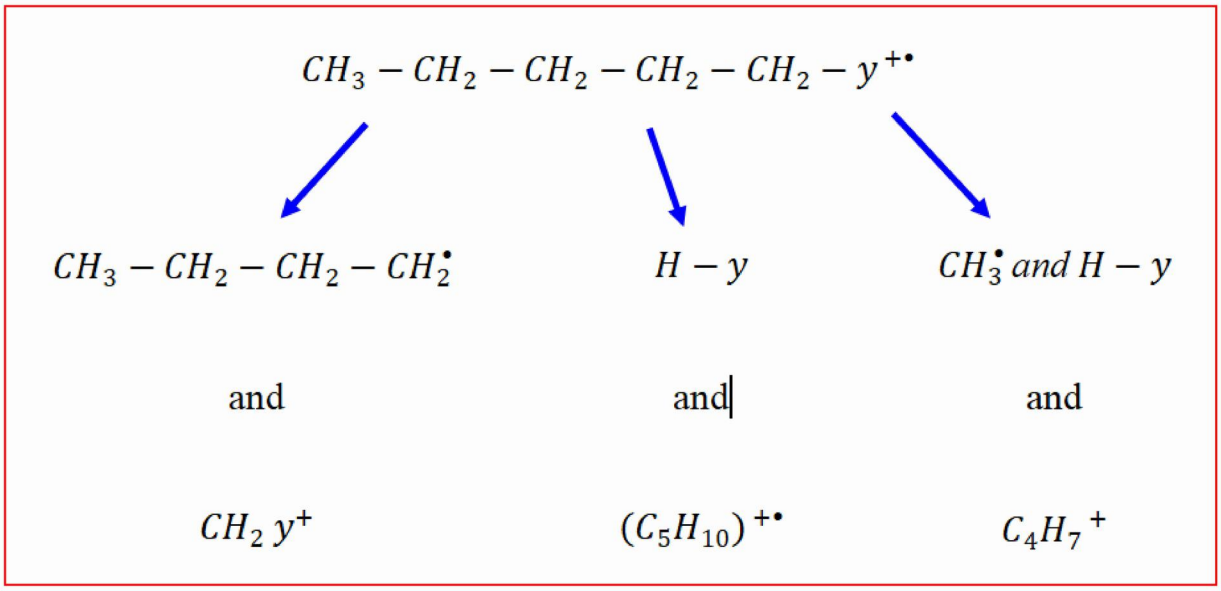

Figure 5.11 molecular ions $(CH_3CH_2CH_2CH_2CH_2\text{-}Y)^{+\cdot}$

The peak at m/z = 70 is due to the cation arising from loss of the molecular species H-Y (that is H-OH, H-NH_2, or H-X), while that at m/z = 55 arises from loss of both H-Y and $CH_3^{\cdot}$. We briefly highlight each functional group below.

a-Pentanol (Y = OH). The molecular ion peak (m/z = 88) in the mass spectrum of 1-pentanol ($CH_3CH_2CH_2CH_2CH_2$-OH) is very small and this is characteristic of alcohols (ROH).

In contrast, the *+CH2-OH* peak at m/z = 31 (+CH_2-*Y* where Y = OH) is intense and so are the peaks at m/z = 55 (loss of H-OH and $CH_3^{\cdot}$) and m/z = 70 (loss of H-OH).

b-Pentanamine (Y = NH_2). The molecular ion peak (m/z = 87) for 1-pentamine ($CH_3CH_2CH_2CH_2CH_2$-NH_2) is relatively more intense than the molecular ion peak from 1-pentanol and this is generally true for *amines* (*RNH2*) compared to *alcohols* (*ROH*). The $M^{+\cdot}$ line is sufficiently intense that its ^{13}C isotopic M+1 peak is also visible

in the spectrum. Although the peaks at m/z = 55 and 70 due to loss of H-NH_2 (ammonia) are barely visible, the $^{+}CH_2$-NH_2 peak ($^{+}CH_2$-Y where Y = NH_2) is so intense that it is the *base peak* in the spectrum. All of these observations are characteristic of the mass spectra of amines.

c-Chloropentane (Y = Cl). Molecular ions of chloroalkanes undergo extensive fragmentation, so the $M^{+\cdot}$ peak at m/z = 106 for 1-chloropentane ($CH_3CH_2CH_2CH_2CH_2$-Cl) is just barely visible. Consistent with this, the fragment peaks at m/z = 55 due to loss of both H-Cl and CH3·, and at m/z = 70 due to loss of H-Cl, are very intense.

The $^{+}CH_2$-Cl fragment ($^{+}CH_2$-Y where Y = Cl) is also visible in this spectrum, but you may be surprised to learn that it corresponds to the two separate peaks at m/z = 49 and 51. Natually occurring Cl is a mixture of the isotopes ^{35}Cl (76%) and ^{37}Cl (24%) so $^{+}CH_2$-Cl is an equivalent % mixture of $^{+}CH_2$-^{35}Cl (m/z = 49) and $^{+}CH_2$-^{37}Cl m/z = 51). The isotopic mixture for Cl also causes every cation containing Cl to give two peaks separated by 2 amu .

The molecular ion with the isotope ^{37}Cl (m/z =108) is not visible because it would be only one-fourth the size of the already tiny peak for the ^{35}Cl molecular ion at mass 106, but pairs of fragment ions with ^{35}Cl and ^{37}Cl appear at m/z = 63 and 65 ($C_2H_4Cl^{+}$), and at m/z = 91 and 93 ($C_4H_8Cl^{+}$).

d-Bromopentane (Y = Br). Since naturally occurring Br is almost an equimolar mixture of ^{79}Br (51%) and ^{81}Br (49%), cations containing Br also give two mass spectral peaks with almost equal intensities such as the two weak molecular ion peaks

from 1-bromopentane ($CH_3CH_2CH_2CH_2CH_2$-Br) at m/z =150 and 152. You can see other such isotopic pairs of peaks separated by 2 amu including those for $^{+}CH_2$-*Br* ($^{+}CH_2$-*Y* where Y = Br) at m/z = 93 and 95.

The characteristic fragment peaks at m/z = 55 and 70 for C_4H^{7+} and C_5H^{10+} are present, but significantly less intense than those from 1-chloropentane.

e-Iodopentane (Y = I). In contrast to Cl or Br, naturally occuring iodine (I) is almost entirely the single isotope ^{127}I. As a result, 1-iodopentane ($CH_3CH_2CH_2CH_2CH_2$-I) gives just a single molecular ion peak at m/z = 198 along with its small M+1 peak at m/z = 199 due to ^{13}C.

The mass spectrum of 1-iodopentane also illustrates that fragmentation is much less important for *iodoalkanes* than for *bromoalkanes* or *chloroalkanes*. The characteristic fragment peaks at m/z = 55 and 70, and at m/z = 141 for $^{+}CH_2$-*I* ($+CH_2$-*Y* where Y = I) are all relatively small.

However, you can see an intense peak at m/z = 71 in the mass spectrum of 1-iodopropane due to $C_5H_{11}^{+}$. This m/z = 71 peak is also present in the mass spectrum of 1-bromopentane and is due to molecular ion fragmentation at C-I or C-Br bonds forming $C_5H_{11}^{+}$ and I. or Br. atoms. We will see in a later chapter that the relative stability of halogen atoms is I. > Br. > Cl. and this explains the very small m/z = 71 peak in the mass spectrum of 1-chloropentane.

Conclusion

If you look back at the mass spectra that we have shown here, you may wonder how a material science specialist can possibly identify the compound giving that spectrum without knowing the answer in advance. Each spectrum has many peaks and it is not always clear how some of them formed.

These are valid feelings on your part, but chemists who use mass spectrometry as an analytical tool have had extensive training in which they have seen and studied thousands of mass spectra of a variety of different compounds. Like any other skill, the ability to use this technique requires extensive practice.

We have illustrated only a few of the basic concepts that chemists use to interpret mass spectra.

It is important to emphasize again that one of the most important uses of mass spectral data by organic chemists is the determination of a molecular mass for a compound from the m/z value of its molecular ion. Fragment ions are also important clues to molecular structure, that chemists use in conjunction with other spectrometric techniques.

Organic chemists often have some idea of the likely structure of an organic compound before they obtain its mass spectrum so mass spectrometry frequently provides confirmation of a suspected structure.

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Preface

Mass spectrometry is an analytical technique that allows to the determination of the molecular masses of the compounds analyzed as well as their identification and quantification. It is based on the separation and detection of ions formed in an ionization source or in a collision chamber.

This work presents initiations on mass spectrometry. It conforms to the basic program of university training in some technological sectors, particularly the basic sciences. It is intended for students of institutes and universities, teachers in particular for the first year of Master of Organic Chemistry. The structure of this book consists of four parts that explain this module, it provides students of the exact sciences with the basic notions necessary to properly explain of the mass spectrometry. These are generally, the definitions, Ion and desorption sources and mass analyzers.

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