

Unit 6.4 Mass spectroscopy (Marks 10)

Mass spectroscopy - principle – idea of mass spectrometer – fragmentation pattern –nitrogen rule - simple applications in structure elucidation (butane, ethane, acetone) –McLafferty rearrangement (hexanoic acid, pentanal).

What is Mass Spectroscopy ?

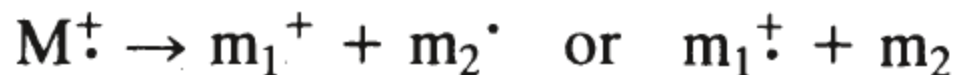
Mass spectrometry is an analytical tool useful for measuring the **mass-to-charge ratio** (m/z) of one or more molecules present in a sample. These measurements can often be used to calculate the **exact molecular weight** of the sample components as well.

Applications of mass spectrometry:

- (1) to measure *relative molecular masses (molecular weights) with very high accuracy* ; from these can be deduced exact molecular formulae
- (2) to detect within a molecule the places at which it *prefers to fragment* ; *from this* can be deduced the presence of recognizable groupings within the molecule and
- (3) as a method for identifying analytes by comparison of their mass spectra with libraries of digitized mass spectra of known compounds.

Basic Principles of Mass Spectrometry

In the simplest mass spectrometer (figure 5.1) , organic molecules are bombarded with electrons and converted to highly energetic positively charged ions (*molecular ions or parent ions*), which can break up into smaller ions (*fragment ions, or daughter ions*) ; the loss of an electron from a molecule leads to a radical cation, and we can represent this process as $M \rightarrow M^+$. The molecular ion M^+ commonly decomposes to a pair of fragments, which may be either a radical plus an ion, or a small molecule plus a radical cation. Thus,



The molecular ions, the fragment ions and the fragment radical ions are separated by deflection in a variable magnetic field according to their mass and charge, and generate a current (the *ion current*) at the collector in proportion to their *relative abundances*.

Basic Principles of Mass Spectrometry

A mass spectrum is a plot of relative abundance against the ratio mass/charge (the m/z value). For singly charged ions, the lower the mass the more easily is the ion deflected in the magnetic field. Doubly charged ions are occasionally formed: these are deflected twice as much as singly charged ions of the same mass, and they appear in the mass spectrum at the same value as do singly charged ions of half the mass, since $2m/2z = m/z$.

Neutral particles produced in the fragmentation, whether uncharged molecules (m_2) or radicals (m_2^{\bullet}), cannot be detected directly in the mass spectrometer.

Figure 5.1 shows a block layout for a simple mass spectrometer. Since the ions must travel a considerable distance through the magnetic field to the collector, very low pressures ($= 10^{-6}$ to 10^{-7} mmHg $= 10^{-4}$ Nm⁻²) must be maintained by the use of diffusion pumps.

Basic Principles of Mass Spectrometry

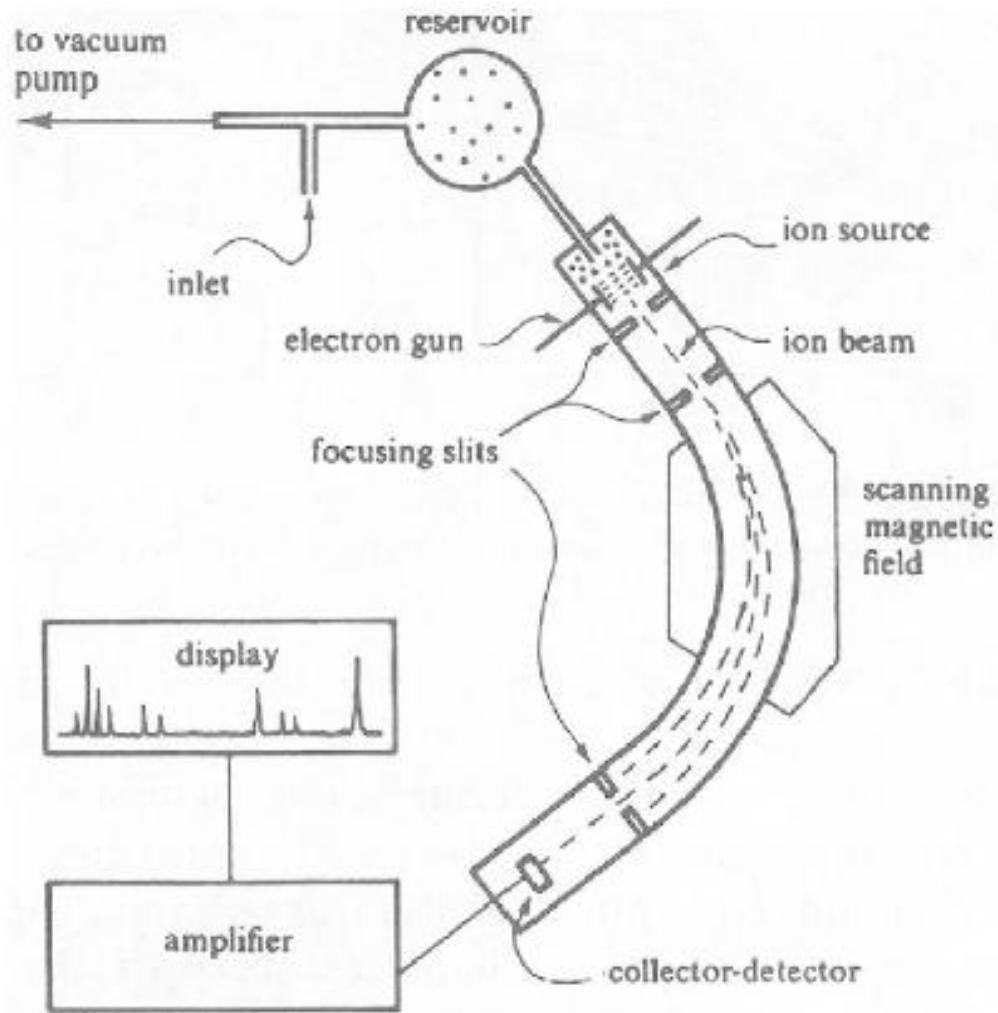


Figure 5.1 *A simple mass spectrometer. Molecules drift from the reservoir into the ion source, where they are ionized by electron bombardment. The resulting ion beam consists of molecular ions, fragment ions and neutral fragments; the ions are deflected by the magnetic field onto the collector-detector.*

Mass Spectrum of 2-methylpentane

Figure 5.2 shows a simplified line-diagram representation of the mass spectrum of 2-methylpentane (C_6H_{14}). The most abundant ion has an m/z value of 43 (corresponding to $C_3H_7^+$), showing that the most favored point of rupture occurs between C_x , and C_y : *this most abundant ion (the base peak) is given an arbitrary abundance of 100, and all other intensities are expressed as a percentage of this (relative abundances).* The small peak at m/z 86 is obviously the molecular ion. The peaks at m/z 15, 29 and 71 correspond to CH_3^+ , $C_2H_5^+$ and $C_5H_{11}^+$, respectively, etc.: the fragment ions arise from the rupture of the molecular ion, either directly or indirectly, and the analysis of many thousands of organic mass spectra has led to comprehensive semiempirical rules about the preferred *fragmentation modes of every kind of organic molecule.*

Mass Spectrum of 2-methylpentane

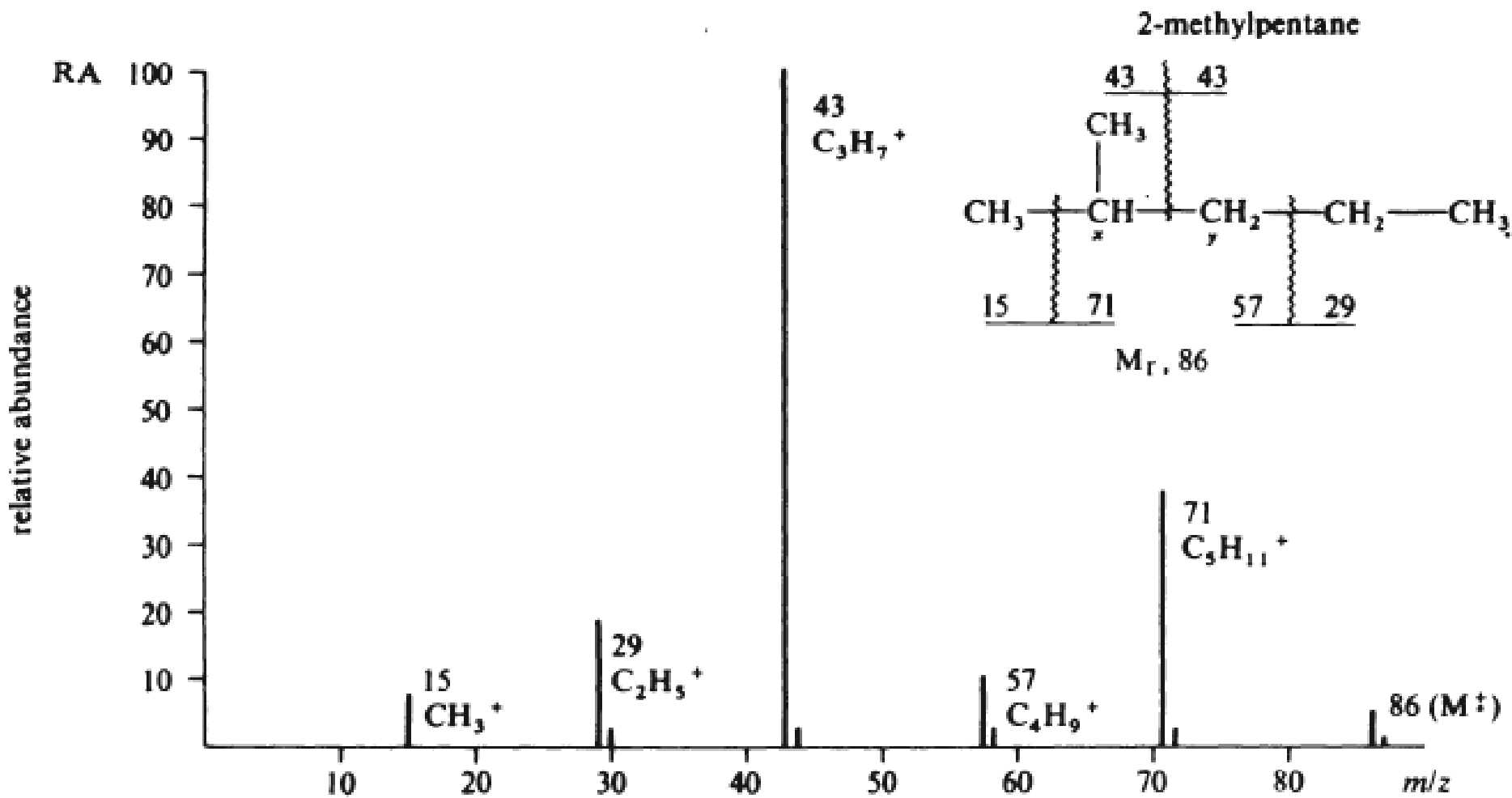


Figure 5.2 Simplified mass spectrum of 2-methylpentane showing how the chain can break in several places; but breaks occur preferentially at the branching point, the most abundant ion being m/z 43 ($C_3H_7^+$).

Disadvantages of Mass Spectrometry Technique

The mass spectrum of a compound can be obtained on a smaller sample size (*in extremis* down to 10^{-12} g) than for any other of the main spectroscopic techniques, the principal disadvantages being the destructive nature of the process, which precludes recovery of the sample, the difficulty of introducing small enough samples into the high-vacuum system needed to handle the ionic species involved and the high cost of the instruments. Mass spectrometry is unlike the other spectroscopic techniques does not measure the interaction of molecules with the spectrum of energies found in the electromagnetic spectrum, but the output from the instrument has all other spectroscopic characteristics, in showing an array of signals corresponding to a spectrum of energies; to highlight this distinction, the name *mass spectrometry* is preferred.

Instrumentation of Mass Spectrometer

1. SAMPLE INSERTION-INLET SYSTEMS: Organic compounds that have moderate vapor pressures at temperatures up to around 300°C (including gases) can be placed in an ampoule connected via a reservoir to the ionization chamber. Depending on volatility, it is possible to cool or heat the ampoule, etc ., to control the rate at which the sample volatilizes into the reservoir, from which it will diffuse slowly through the sinter into the ionization chamber. Samples with lower vapor pressures (for example, solids) are inserted directly into the ionization chamber on the end of a probe, and their volatilization is controlled by heating the probe tip .

Instrumentation of Mass Spectrometer

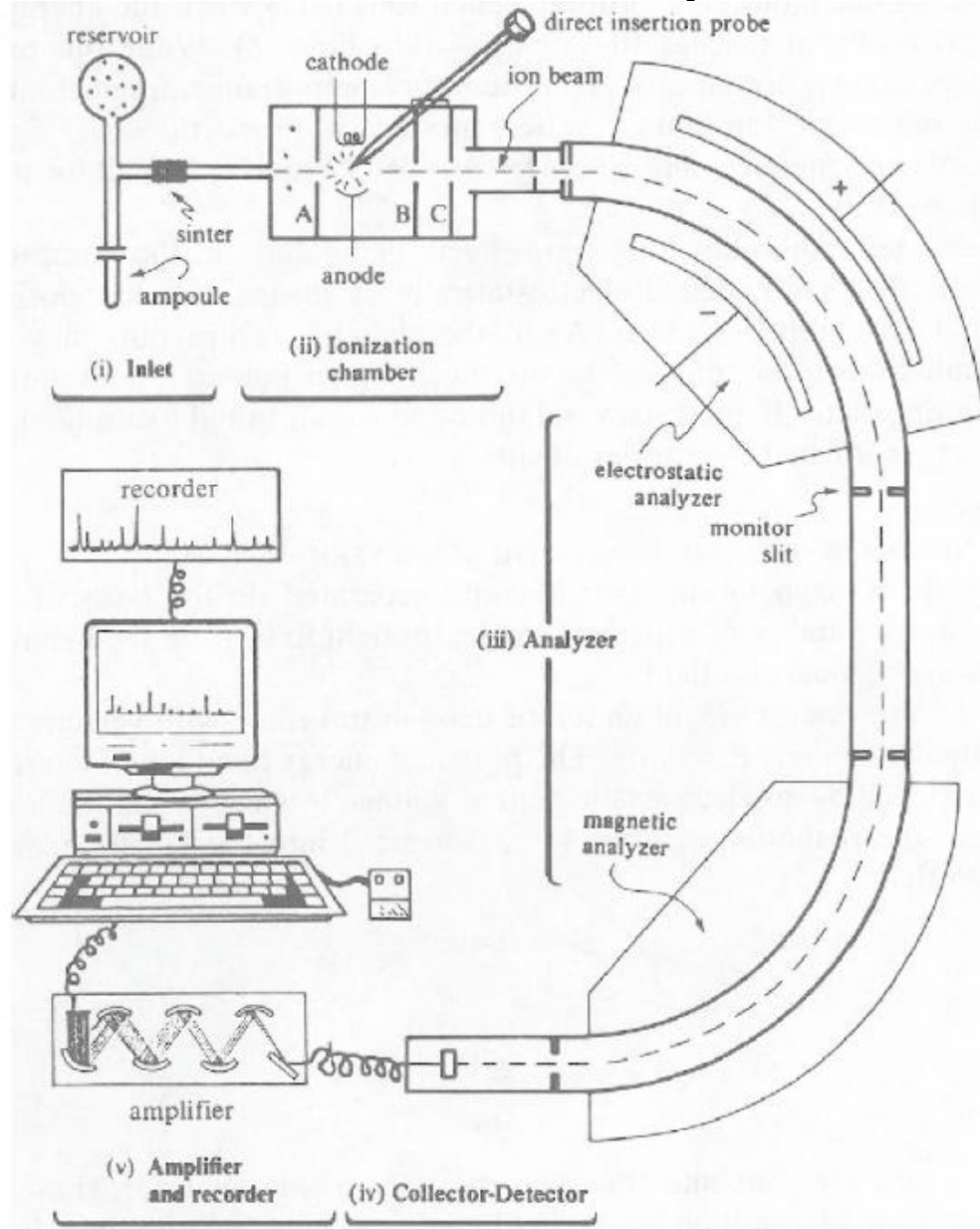


Figure 5.3 High-resolution, double-focusing mass spectrometer. (Evacuation system not shown.)

Instrumentation of Mass Spectrometer

2. ION PRODUCTION IN THE IONIZATION CHAMBER: The several methods available for inducing the ionization of organic compounds are discussed in section 5S.1, but electron bombardment is routinely used. Organic molecules react on electron bombardment in two ways: either an electron is captured by the molecule, giving a radical anion, or an electron is removed from the molecule, giving a radical cation:



The latter is more probable by a factor of 10^2 , and positive-ion mass spectrometry is the result. Most organic molecules form molecular ions (M^+) when the energy of the electron beam reaches 10-15 eV ($\sim 10^3$ kJmol⁻¹). While this minimum *ionization potential is of great theoretical importance, fragmentation* of the molecular ion only reaches substantial proportions at higher bombardment energies, and 70 eV ($\sim 6 \times 10^3$ kJmol⁻¹) is used for most organic work. When the molecular ions have been generated in the ionization chamber, they are expelled electrostatically by means of a low positive potential on a repeller plate (A) in the chamber.

Instrumentation of Mass Spectrometer

Once out, they are accelerated down the ion tube by the much higher potential between the accelerating plates Band C (several thousand volts) . Initial focusing of the ion beam is effected by a series of slits.

3. SEPARATION OF THE IONS IN THE ANALYZER:

Theory. In a magnetic analyzer ions are separated on the basis of m/z values, and a number of equations can be brought to bear on the behavior of ions in the magnetic field. The kinetic energy, E , of an ion of mass m travelling with velocity v is given by the familiar $E = \frac{1}{2} mv^2$.The potential energy of an ion of charge z being repelled by an electrostatic field of voltage V is zV . When the ion is repelled, the potential energy, zV , is converted into the kinetic energy, $\frac{1}{2} mv^2$, so that

$$zV = \frac{1}{2}mv^2$$

Therefore,

$$v^2 = \frac{2zV}{m} \quad (5.1)$$

Instrumentation of Mass Spectrometer

When ions are shot into the magnetic field of the analyzer, they are drawn into circular motion by the field, and at equilibrium the centrifugal force of the ion (mv^2/r) is equalled by the centripetal force exerted on it by the magnet (zBv), where r is the radius of the circular motion and B is the field strength. Thus,

$$\frac{mv^2}{r} = zBv$$

Therefore,

$$v = \frac{zBr}{m} \quad (5.2)$$

Combining equations (5.1) and (5.2),

$$\frac{2zV}{m} = \left[\frac{zBr}{m} \right]^2$$

Therefore,

$$\frac{m}{z} = \frac{B^2 r^2}{2V} \quad (5.3)$$

Instrumentation of Mass Spectrometer

It is from equation (5.3) that we can see the inability of a mass spectrometer to distinguish between an ion m^+ and an ion $2m^{2+}$, since the ratio, m/z , between them has the same value of $(B^2r^2/2V)$, and these three parameters B , r and V dictate the path of the ions. To change the path of the ions so that they will focus on the collector and be recorded, we can vary either V (*the accelerating voltage*) or B (*the strength of the focusing magnet*) . *Voltage scans (the former) can be effected much more rapidly than magnetic scans and are used where fast scan speed is desirable .*

4. Resolution: *The ability of a mass spectrometer to separate two ions (the spectrometer resolution) is acceptably defined by measuring the depth of the valleys between the peaks produced by the ions . If two ions of m/z 999 and 1000, respectively, can just be resolved into two peaks such that the recorder trace almost reaches back down to the baseline between them, leaving a valley which is 10 per cent of the peak height, we say the resolution of the spectrometer is '1 part in 1000 (10 per cent valley resolution)' . Simple magnetic-focusing instruments have resolving powers of around 1 in 7500 on this basis.*

Isotope Abundances

Few elements are monoisotopic, and table 5.1 gives the natural isotope abundance of the elements we might expect to encounter in organic compounds. Ions containing different isotopes appear at different m/z values. For an ion containing n carbon atoms, there is a probability that approximately $1.1n$ per cent of these atoms will be ^{13}C , and this will give rise to an ion of mass one higher than the ion that contains only ^{12}C atoms. The molecular ion for 2-methylpentane (figure 5.2) has an associated $M + 1$ ion, whose intensity is approximately 6.6 per cent of that of the molecular ion; while the molecular ion has only ^{12}C atoms, the $M + 1$ ion contains ^{13}C atoms. (The contribution of ^2H atoms should not be over-looked, even though the probability of their presence is not as high as for ^{13}C , and in exact work the statistics of both ^{13}C and ^2H abundances must be calculated.)

Isotope Abundances

Table 5.1 Natural isotope abundances and isotopic masses ($^{12}\text{C} = 12.000\ 000$) for common elements

<i>Isotope</i>	<i>Natural abundance (%)</i>	<i>Isotopic mass/m_u</i>
^1H	99.985	1.007 825
^2H	0.015	2.014 102
^{12}C	98.9	12.000 000
^{13}C	1.1	13.003 354
^{14}N	99.64	14.003 074
^{15}N	0.36	15.000 108
^{16}O	99.8	15.994 915
^{17}O	0.04	16.999 133
^{18}O	0.2	17.999 160
^{19}F	100	18.998 405
^{28}Si	92.2	27.976 927
^{29}Si	4.7	28.976 491
^{30}Si	3.1	29.973 761
^{31}P	100	30.973 763
^{32}S	95.0	31.972 074
^{33}S	0.76	32.971 461
^{34}S	4.2	33.967 865
^{35}Cl	75.8	34.968 855
^{37}Cl	24.2	36.965 896
^{79}Br	50.5	78.918 348
^{81}Br	49.5	80.916 344
^{127}I	100	126.904 352

Isotope Abundances

A second associated peak can arise at $m/z M + 2$ if two ^{13}C atoms are present in the same ion (or if two ^2H atoms, or one ^{13}C and one ^2H , are present); these probabilities can be calculated and may be a help in deciding the formula for an ion in the absence of exact mass measurement. For example, the two ions $\text{C}_8\text{H}_{12}\text{N}_3^+$ and $\text{C}_9\text{H}_{10}\text{O}_2^+$ have the same unit mass (m/z 150), and the $M + 1$ relative abundances are similar (9.98 percent and 9.96 per cent, respectively); however, the $M + 2$ abundances are sufficiently different to enable differentiation of the structures (0.45 per cent and 0.84 per cent, respectively). The ability to see $M + 2$ peaks of such low abundance depends on there being a large M^+ peak. Ions containing one bromine atom create a dramatic effect in the mass spectrum because of the almost equal abundance of the two isotopes; pairs of peaks of roughly equal intensity appear, separated by two mass units.

Isotope Abundances

Equally characteristic are the ions from chlorine compounds engendered by the ^{35}Cl and ^{37}Cl isotopes; for ions containing one Cl atom, the relative intensities of the lines, separated by two mass units, is 3:1. Ions containing one sulfur atom also have associated $m + 2$ peaks. The picture becomes much more complicated when one considers the relative abundances of ions containing several polyisotopic elements; the presence of two bromine atoms in an ion gives rise to three peaks at m , $m + 2$ and $m + 4$, the relative intensities being 1:2:1, while for three bromines the peaks arise at m , $m + 2$, $m + 4$, $m + 6$, with relative intensities 1:3:3: 1. These figures ignore any contribution from ^{13}C that may be present.

Isotope Abundances

For each element in a given ion, the relative contributions to $m + 1$, $m + 2$ peaks, etc .. can be calculated from the binomial expansion of $(a + b)^n$, where a and b are the relative abundances of the isotopes and n is the number of these atoms present in the ion. Thus, for three chlorine atoms in an ion, expansion gives $a^3 + 3a^2b + 3ab^2 + b^3$. Four peaks arise; the first contains three ^{35}Cl atoms and each successive peak has ^{35}Cl replaced by ^{37}Cl until the last peak contains three ^{37}Cl atoms. The m/z values are separated by two mass units, at m , $m + 2$, $m + 4$, $m + 6$. Since the relative abundances of ^{35}Cl and ^{37}Cl are 3:1 (that is, $a = 3$, $b = 1$), the intensities of the four peaks (ignoring contributions from other elements) are $a^3 = 27$, $3a^2b = 27$, $3ab^2 = 9$, $b^3 = 1$ (that is, 27:27:9 :1).

