

Mass spectrometry for chemists and biochemists

SECOND EDITION

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1 The mass spectrum

1.1. FORMATION OF IONS

A mass spectrometer works with electrically charged particles and, before a mass spectrum can be obtained, the substance under examination must be ionized if it is not already ionic. Most research into mass spectrometry has been carried out on positive ions and these are discussed in detail. Negative ions are discussed as the occasion demands.

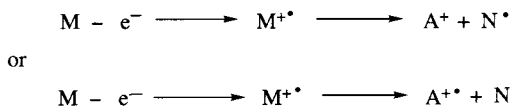
A molecule (M) can be ionized by removal or addition of an electron to give species ($M^{+\bullet}$ and $M^{-\bullet}$ respectively) having a mass which, for practical purposes, is identical to that of the original molecule, the mass of an electron being so small. Optionally, the molecule may be ionized by addition or subtraction of other charged species (X^+) to give ions ($[M + X]^+$ or $[M - X]^-$); in these cases, the resulting ions contain all or most of the original molecule but have masses that are different from that of the original so they are called *quasi-molecular* ions. Finally, the original substance may be a salt (M^+X^-), in which instance, it is ionized already and the oppositely charged species need only be separated prior to mass spectrometry.

Both currently and historically, the most widespread means of ionization has been the removal of an electron from a molecule to give $M^{+\bullet}$ through use of another electron (*electron ionization*, EI). Therefore, this discussion on the formation of a mass spectrum begins with EI, the other methods being introduced later.

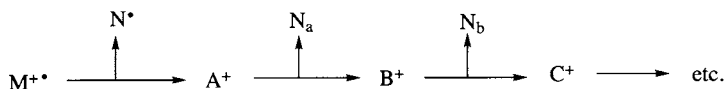
1.2. FORMATION OF THE MASS SPECTRUM FOLLOWING ELECTRON IONIZATION

When a molecule is ionized by removal of an electron, a *molecular ion* ($M^{+\bullet}$, a cation radical) is produced and this may contain sufficient excess of internal

energy to fragment by ejection of a neutral particle (N) with the formation of a *fragment ion* ($A^{+\bullet}$ or A^+). A neutral molecule gives a radical-cation as the molecular ion, and the fragment ion may be either a cation or a radical-cation. The ejected neutral particle (N) may be a radical or neutral molecule.



If the fragment ion (e.g. A^+) has sufficient excess of internal energy, then further decomposition may occur with the formation of new fragment ions (B^+ , C^+ , etc.) until there is insufficient excess of internal energy in any one ion for further reaction.



Such a series of decompositions when elucidated from a mass spectrum is a *fragmentation pathway*. The molecular ion ($M^{+\bullet}$) and any of the fragment ions (A^+ , B^+ , C^+ , etc.) may decompose by more than one pathway. The various fragmentation pathways together compose a *fragmentation pattern* characteristic of the compound under investigation. At one extreme, the fragmentation pattern might consist of only one pathway and result in a very simple mass spectrum. At the other extreme, the fragmentation pattern contains many, often interlocking pathways producing a complex spectrum. The extent to which fragmentation takes place along the individual pathways is determined by the excess of internal energy imparted to the molecular ion ($M^{+\bullet}$), its structure and the time allowed between ion formation and detection. Hence, the *mass spectrum* is not simply the fragmentation pattern but is the appearance of the fragmentation pattern at specified energies and times.

A mass spectrometer is designed to separate and measure the masses of ions by making use of their mass-to-charge (m/z) ratios. An ion is usually formed with a single positive charge ($z = 1$) so that m/z is then equivalent to m and gives the mass of the ion directly. Formerly, e and not z was used to represent the charge on the ion. Accordingly, many existing publications

represent the mass-to-charge ratio as m/e . The term m/z is used here to conform with IUPAC recommendations.

During any one interval of time in the spectrometer, molecular ions will be produced with various excesses of internal energy. Each molecular ion will fragment at a rate determined by its initial energy because, at the low pressures normally obtaining in an ion source, ion/ion and ion/molecule collisions are rare so that collisional equilibration of internal energies does not occur (except in techniques like chemical ionization). Some molecular ions may have insufficient energy to fragment whereas others have so much energy that decomposition proceeds right through a fragmentation pathway. Because of the initial range of internal energies in the molecular ions, a short period of time after ionization would see the presence of ions M^+ , A^+ , B^+ , C^+ , etc. in amounts determined by their individual rates of formation and decomposition and the initial energy imparted to M . If a sample of these ions in the ion source is obtained and their relative amounts measured, the results can be displayed with m/z values as abscissae and *ion abundances* as ordinates (figure 1.1). Such a picture of a sample of the ions in the ion source is the basis of the mass spectrum, which may be recorded on a cathode ray tube, paper chart, photographic plate or via a computer. An example of part of a mass spectrum recorded as peaks on a paper chart is shown in figure 1.2.

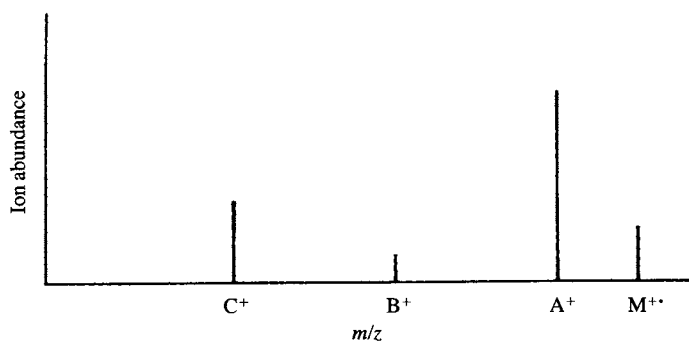


Figure 1.1. Abundances of ions M^+ , A^+ , B^+ and C^+ in a sample of ions drawn from an ion source.

As a standard practice, it is usual to make a record of a mass spectrum in either a *normalized* or *percentage relative abundance* (%RA) form or as a *percentage of total ion current* (%TIC). In a normalized record, the biggest peak in the spectrum is called the *base peak* and its height is put equal to 100 units; the relative heights of all other peaks are referred to this base peak and lie between 0 and 100 units (note that the base peak is not necessarily

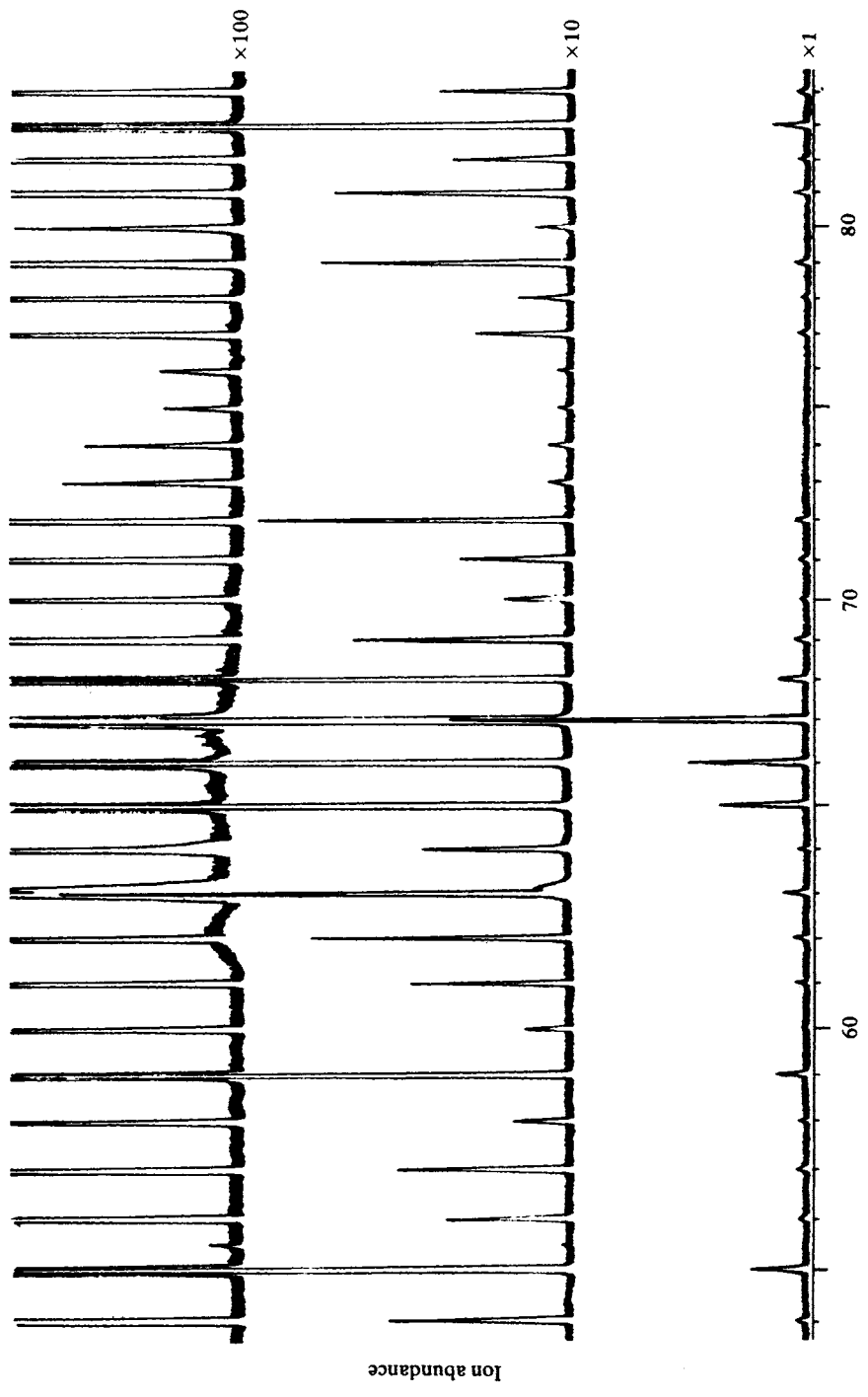


Figure 1.2. Part of a mass spectrum recorded on photographic paper (the three traces record the spectrum at increasing sensitivities from the lower to the upper trace).

Table 1.1. Normalized abundances^a in the mass spectrum of 1,3-dimethylbenzene.

| m/z | Abundance | m/z | Abundance | m/z | Abundance |
|-----|-----------|-----|-----------|-----|-----------|
| 38 | 1.2 | 65 | 5.5 | 102 | 1.1 |
| 39 | 7.1 | 74 | 1.1 | 103 | 6.1 |
| 50 | 2.8 | 77 | 18.3 | 104 | 2.6 |
| 51 | 9.1 | 78 | 5.1 | 105 | 28.7 |
| 52 | 5.0 | 79 | 6.5 | 106 | 61.7 |
| 54 | 2.2 | 89 | 1.9 | 107 | 5.4 |
| 62 | 1.6 | 91 | 100.0 | | |
| 63 | 4.2 | 92 | 7.8 | | |

Notes:

^a Ion abundances less than 1 per cent of the base peak have been omitted.

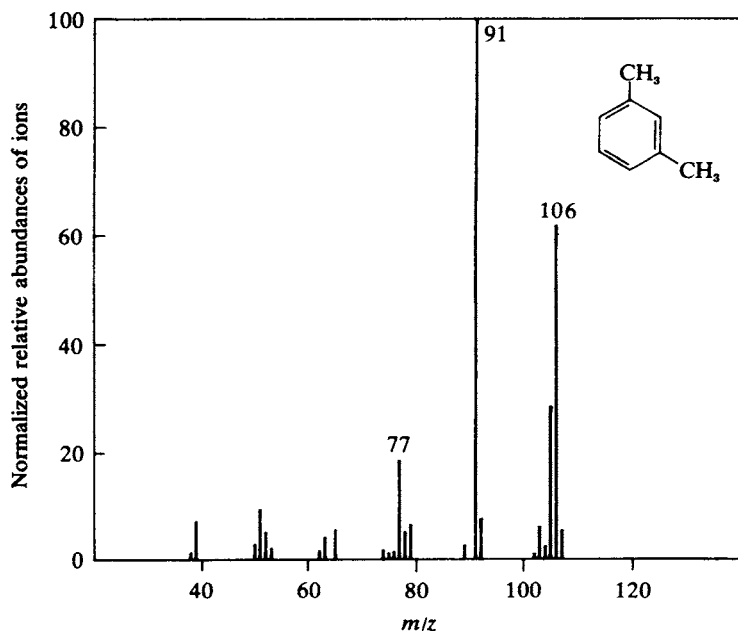


Figure 1.3. A line diagram showing normalized relative abundances of ions in the mass spectrum of 1,3-dimethylbenzene. Note that the base peak at m/z 91 is made equal to 100 units.

the molecular ion peak, although it may be). The height of a peak represents the abundance of ions at that particular m/z value. Table 1.1 illustrates part of the mass spectrum of 1,3-dimethylbenzene recorded in this way and figure 1.3 shows the same spectrum as a normalized line diagram. This form of output is typical of that provided by a computer. Very often not all the peaks in a mass spectrum appear in the normalized line diagram

since peaks of less than 1 per cent of the size of the base peak are frequently arbitrarily omitted as unimportant. Care must be exercised in this respect because, even though ions may not be abundant, they can be important for elucidating structures from mass spectra. For example, the molecular ions of a compound undergoing extensive fragmentation will have low abundance but they are still a very important feature of the spectrum. Fragment ions may decompose at about the same rate as they are formed, when again their abundance would be low but they could be important for unravelling a fragmentation pathway. For compounds of high molecular mass, the low-mass ions (e.g. below m/z 40) may be numerous and abundant but also may have little value for the interpretation of a spectrum; such low-mass ions are frequently omitted from the normalized line diagram.

To obtain a record of a mass spectrum by the percentage of total ion current method, abundances of all ions giving peaks of significant size, from the molecular ion down to a suitably chosen low mass (often about m/z 40 for electron ionization and possibly m/z 100 for other ionization methods) are added together as a measure of the total ion current (TIC). The relative contribution of each ion to this total is then calculated as a percentage (%TIC). Table 1.2 records part of the mass spectrum of 1,3-dimethylbenzene from m/z 38 to the molecular ion, with abundances of ions as %TIC. This last method of recording a mass spectrum is used less frequently than the normalization method but has some advantages in emphasizing the relative importance of an ion in the whole spectrum. It is helpful to know this relative importance when the mass spectrometer is used not to record a whole mass spectrum but to monitor ions of only one mass or a small number of masses in a mass spectrum (see later, chapter 7). Also, the percentage ion current method finds some favour in comparing the spectra of isomers, when changes in the relative contributions of certain ions to the total ion current may be sufficient to distinguish between the isomers. The difference between the two ways of recording spectra in tabular form is more apparent than real since the relative abundance of a peak in a normalized spectrum is simply related numerically to its value as a percentage of total ion current. However, if the spectrum has been processed to remove 'background' ions of constant, unwanted impurities such as chemical ionization reactant gases or decomposition products of the stationary phases of gas chromatography/mass spectrometry systems (section 4.4.2), this simple relationship may no longer exist. If such

Table 1.2. *Ion abundances^a in the mass spectrum of 1,3-dimethylbenzene as %TIC.*

| m/z | Abundance | m/z | Abundance | m/z | Abundance |
|-----|-----------|-----|-----------|-----|-----------|
| 39 | 2.5 | 65 | 1.9 | 92 | 2.7 |
| 50 | 1.0 | 77 | 6.4 | 103 | 2.1 |
| 51 | 3.2 | 78 | 1.8 | 105 | 10.0 |
| 52 | 1.7 | 79 | 2.2 | 106 | 21.6 |
| 63 | 1.5 | 91 | 35.1 | 107 | 1.9 |

Notes:

^a Ion abundances of less than 1 per cent are omitted

processing has been performed then the %TIC method is often replaced by an equivalent method: the percentage reconstructed ion current (%RIC). This latter sums the ion current from all consequential ions remaining after subtraction of 'background' ions.

It should be noted that the normalization method is likely to be the less accurate because a small irregularity in recording or measuring the base peak will markedly affect all the other ion abundances normalized against it. The measurement of the height of the base peak is prone to error, caused for example by the recording system becoming saturated. Usually, the percentage of total ion current method is virtually unaffected by such anomalies and is to be preferred, particularly if the mass spectral data are acquired and processed by a computer when the greater numerical difficulty of the method is unimportant. Most data systems allow either or both methods to be selected, with presentation of the spectrum in tabular or diagrammatic form. Table 1.3 shows a computer output listing of the mass spectrum of decahydronaphthalene in both %RA and %TIC forms.

Two main facets of mass spectrometry will be apparent from the above description. (i) In contrast with what happens in most other common methods of physicochemical spectroscopic analysis, some or all of the sample is consumed in mass spectrometry and is not recoverable. However, mass spectrometers are very sensitive instruments and spectra may be obtained from a few nanogrammes or even picogrammes of material. (ii) Unlike other physical methods, mass spectrometry does not deal with a well-defined property of a molecule. The appearance of a mass spectrum depends not only on the compound itself but also upon the interval of time between ionization and detection of ions, upon the initial

Table 1.3. *Ion abundances in the mass spectrum of decahydronaphthalene.^a*

| Mass | %RA | %TIC | Mass | %RA | %TIC |
|------|-------|------|------|-------|------|
| 41 | 64.02 | 5.25 | 80 | 5.99 | 0.49 |
| 42 | 9.79 | 0.80 | 81 | 86.55 | 7.10 |
| 43 | 7.19 | 0.59 | 82 | 78.53 | 6.44 |
| 50 | 0.67 | 0.06 | 83 | 15.70 | 1.29 |
| 51 | 3.02 | 0.25 | 84 | 17.16 | 1.41 |
| 52 | 1.82 | 0.15 | 85 | 0.82 | 0.07 |
| 53 | 12.99 | 1.07 | 91 | 2.14 | 0.18 |
| 54 | 21.23 | 1.74 | 93 | 2.87 | 0.24 |
| 55 | 46.84 | 3.84 | 94 | 3.50 | 0.29 |
| 56 | 25.85 | 2.12 | 95 | 60.05 | 4.93 |
| 57 | 1.94 | 0.16 | 96 | 99.19 | 8.14 |
| 63 | 0.46 | 0.04 | 97 | 11.35 | 0.93 |
| 65 | 3.73 | 0.31 | 108 | 0.81 | 0.07 |
| 66 | 8.24 | 0.68 | 109 | 30.31 | 2.49 |
| 67 | 100.0 | 8.20 | 110 | 9.07 | 0.74 |
| 68 | 59.97 | 4.92 | 111 | 0.42 | 0.03 |
| 69 | 35.17 | 2.89 | 123 | 0.89 | 0.07 |
| 70 | 3.19 | 0.26 | 137 | 0.91 | 0.07 |
| 71 | 0.45 | 0.04 | 138 | 99.35 | 8.15 |
| 77 | 5.02 | 0.41 | 139 | 10.37 | 0.85 |
| 78 | 1.08 | 0.09 | 140 | 0.31 | 0.03 |
| 79 | 9.43 | 0.77 | | | |

Notes:

^a All peaks over m/z 40 of greater than 0.3 per cent relative abundance are included.

energy distribution in the molecular ions and on the method of ionization, and partly upon the physical characteristics of the instrument and therefore on its design and manufacture.

For these reasons it is not possible to guarantee that a mass spectrum is accurately reproducible from instrument to instrument – even for instruments of the same manufacture when operating under apparently identical conditions. Normally, variations in ion abundance of a few per cent are acceptable in comparing spectra from different laboratories, but generally, good uniformity is found and not too much difficulty is experienced from small inconsistencies. The popular method of identifying compounds by

matching sample spectra against standard mass spectra stored in a computer library (section 4.4.3) is a testament to this.

1.3. MULTIPLY CHARGED IONS

In EI mass spectrometry, ions are generally produced with single positive charges ($z = 1$) but may sometimes have two, three or more charges so that the corresponding m/z ratios correspond to half, one-third, or lower fractional masses. A molecular ion with a single positive charge corresponds to a mass m , but with two positive charges it corresponds to $m/2$. Doubly charged ions are fairly common in the electron ionization mode, especially in the mass spectra of aromatic compounds, but more highly charged ions are rarer. Figure 1.4 shows part of a mass spectrum containing some prominent doubly charged ions amongst the singly charged ones. Assignment of doubly charged ions is obvious when peaks occur at half-integer m/z values but doubly charged ions occur at integer values if their mass, m , is even. In the latter case, some integer peaks may consist of superimposed peaks from singly and doubly charged ions. This should be borne in mind particularly when examining spectra of aromatic compounds and especially if a mass

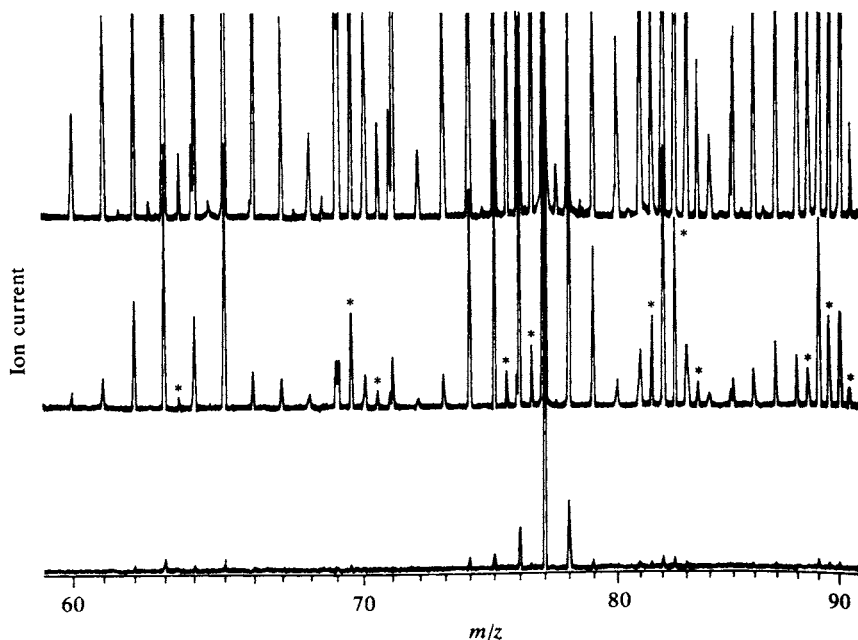


Figure 1.4. Part of a mass spectrum showing peaks due to multiply charged ions marked with an asterisk on the middle trace.

peak occurs at an m/z value corresponding to half the molecular mass of the compound under investigation. The doubly charged species may fragment either into two singly charged ions or into another doubly charged ion with ejection of a neutral particle.

There is one method of ionization, called electrospray (section 3.9), which relies on the formation of multiply charged ions. Large molecules like proteins are protonated at several (z) sites, giving $[M + zH]^{z+}$ ions. Even when the mass, m , is very large, the m/z values are not excessive for a large value of z . This makes ions of very large relative mass, and hence large molecules like proteins, compatible with simple mass spectrometers with upper m/z limits of just a few thousand.

1.4. ISOTOPES

Many elements in their natural states contain isotopes and, because a mass spectrometer measures mass-to-charge ratios, these isotopes appear in the mass spectrum. The most abundant isotope of carbon is ^{12}C , but natural carbon contains also ^{13}C and ^{14}C . Although as a beta-ray emitter the latter is extremely valuable for radio-tracer work, its natural abundance is so low as to make it almost inconsequential to mass spectrometry. Such is not the case for ^{13}C which occurs in a natural abundance of approximately 1.08 per cent in carbon. Hence, the mass spectrum of methane shows a molecular ion at m/z 16 ($^{12}\text{CH}_4$) together with an isotopic ion at m/z 17 ($^{13}\text{CH}_4$), the two ions having relative abundances of about 99 : 1. As the number of carbon atoms in a compound increases, so also do the chances of incorporating one ^{13}C atom into the molecule rather than a ^{12}C atom. A compound with ten carbon atoms would yield a molecular ion M^{+} , and an isotopic ion one mass unit greater $[M + 1]^{+}$, which would be about $10 \times 1.08 = 10.8$ per cent of the abundance of M^{+} (see, for example, the case of decahydronaphthalene, $\text{C}_{10}\text{H}_{18}$, for which the ^{13}C isotope peak at m/z 139 is nearly 11 per cent of the abundance of the ^{12}C molecular ion peak at m/z 138; the peak at m/z 140 represents some molecular ions containing two ^{13}C atoms (table 1.3). The chance of finding two ^{13}C atoms in the same molecule increases with increasing numbers of carbon atoms so that $[M + 2]^{+}$ ions then start to become more prominent. The chances of incorporating more than two ^{13}C atoms in a molecule are very small except with large numbers of carbon atoms and $[M + 3]^{+}$ ions from this source may be safely ignored. For a compound with ten

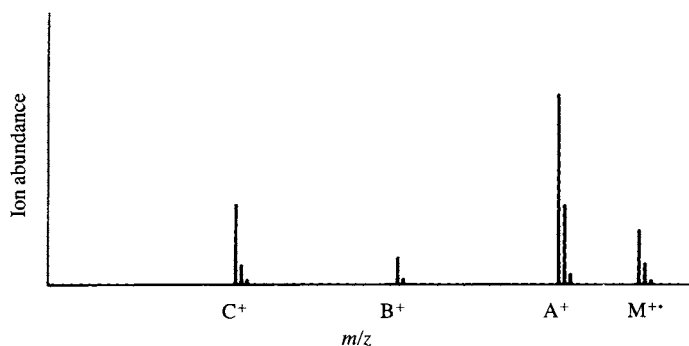


Figure 1.5. The simple mass spectrum of figure 1.1 repeated but with the addition of ^{13}C -isotopic masses for the ions M^{++} , A^+ , B^+ and C^+ .

carbon atoms, the approximate relative heights of the M^{++} , $[\text{M} + 1]^{++}$, $[\text{M} + 2]^{++}$ and $[\text{M} + 3]^{++}$ peaks are 100 : 10 : 0.45 : 0.01 from which it can be seen how unimportant are carbon isotope peaks greater than $[\text{M} + 2]^{++}$. Tables are available giving the relative heights of M^{++} , $[\text{M} + 1]^{++}$ and $[\text{M} + 2]^{++}$ peaks for many elemental compositions (Beynon and Williams, 1963) or are incorporated as options in computer software packages for mass spectrometry. All carbon compounds yield molecular and fragment ions accompanied by isotopic ions 1 and 2 mass units greater, making the appearance of the spectrum more complex. Figure 1.5 shows figure 1.1 modified so as to illustrate the appearance of the mass spectrum with ^{13}C isotopes included. Conversely, an estimate of the number of carbon atoms in an ion may be made by measuring the relative heights of the M^{++} and $[\text{M} + 1]^{++}$ peaks, but the method does not yield good results when there are more than about ten or twelve carbon atoms. Note that, in this discussion, the molecular ion (M^{++}) is considered to contain the isotopes of lowest mass. Then, the notation $[\text{M} + x]^{++}$ can be used for ions containing the isotopes of higher mass. Strictly, M^{++} and $[\text{M} + x]^{++}$ ions are all molecular ions.

Table 1.4 gives, for some elements commonly met in mass spectrometry, the approximate natural abundances of the more significant isotopes. It should be noted that sulphur, chlorine and bromine have particularly abundant isotopes separated by 2 mass units. For this reason, chlorine- and bromine-containing compounds especially are readily recognized in mass spectrometry and, by examining the isotope pattern in the molecular ion region, the numbers of chlorine and bromine atoms in the original molecule may be determined (Beynon, 1960; Biemann, 1962). Figure 1.6 shows the appearance of the molecular ion region for a dichlorobenzene; note the major peaks spaced 2 mass units apart due to the ^{35}Cl and ^{37}Cl isotopes of the

Table 1.4. *The more important natural isotope abundances for elements commonly occurring in mass spectrometry.*^a

| Element | Isotope (percentage of natural abundance) ^b | | |
|------------|--------------------------------------------------------|-------------------------|------------------------|
| Hydrogen | ¹ H (99.99) | | |
| Boron | ¹⁰ B (19.8) | ¹¹ B (80.2) | |
| Carbon | ¹² C (98.9) | ¹³ C (1.1) | |
| Nitrogen | ¹⁴ N (99.6) | ¹⁵ N (0.4) | |
| Oxygen | ¹⁶ O (99.8) | ¹⁸ O (0.2) | |
| Fluorine | ¹⁹ F (100.0) | | |
| Silicon | ²⁸ Si (92.2) | ²⁹ Si (4.7) | ³⁰ Si (3.1) |
| Phosphorus | ³¹ P (100.0) | | |
| Sulphur | ³² S (95.0) | ³³ S (0.7) | ³⁴ S (4.2) |
| Chlorine | ³⁵ Cl (75.5) | ³⁷ Cl (24.5) | |
| Bromine | ⁷⁹ Br (50.5) | ⁸¹ Br (49.5) | |
| Iodine | ¹²⁷ I (100.0) | | |

Notes:

^a Metals frequently possess many abundant isotopes and, because of the diversity of organometallic compounds, a listing of metal isotopes has not been included here. Many reference texts contain listings of isotope abundances; see also Beynon (1960) and Kiser (1965).

^b With the exception of hydrogen, percentages are given correct to the first decimal place. Trace isotopes are not included because they have little consequence in mass spectrometry at their natural abundance levels.

chlorine atoms and the minor peaks caused by contributions from the ¹³C isotope. A method of calculating simple isotopic patterns is presented in section 12.2.

Normalized mass spectra are sometimes drawn with the isotopic contributions simplified. For example, for two peaks at m/z 253 and 254 of relative heights as shown in figure 1.7(a), the ¹³C isotope contribution of m/z 253 contributes to the height of the peak at m/z 254; the ¹³C isotope of m/z 254 occurs at m/z 255. If there were eighteen carbon atoms in the elemental composition of the ion at m/z 253, then approximately $18 \times 1.1 = 19.8$ per cent of its peak height is the ¹³C contribution in m/z 254. By subtracting this ¹³C contribution from m/z 254, the relative abundances of the ions appear as in figure 1.7(b). Similarly, the ¹³C isotope peak of m/z 254 at m/z 255 disappears. This device of removing isotope contributions is

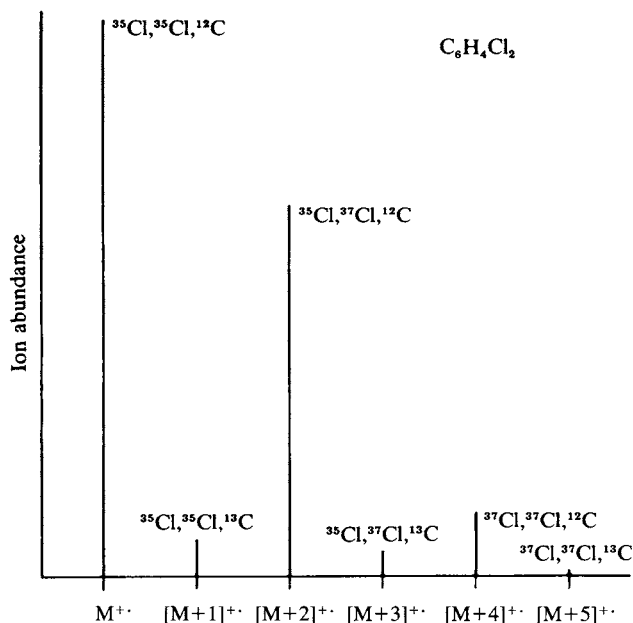


Figure 1.6. Contributions of carbon and chlorine isotopes to the pattern of peaks in the molecular ion region of a dichlorobenzene. The molecular ion (M^{+}) is usually considered to be the one having contributions from the isotopes of lowest mass but, strictly, all six ions are molecular ions.

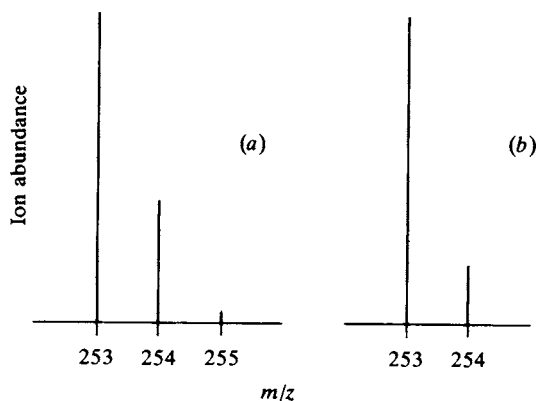


Figure 1.7. The appearance of part of the mass spectrum (m/z 253–255) of a compound having 18 carbon atoms. (a) With ^{12}C - and ^{13}C -isotope contributions and (b) with the ^{13}C -isotope contribution removed to leave only the ^{12}C -isotopes.

extremely helpful for many organometallic compounds since metals frequently have several isotopes and so yield complex-looking spectra; for example, mercury has seven isotopes spread over 9 mass units. Ions containing metal atoms can therefore afford many isotope peaks and removing their separate contributions simplifies the interpretation of such a spectrum. Figure 1.8 shows the mass spectrum of diethylmercury both with and without the isotope contributions; the spectrum without isotope peaks is much easier to interpret. For many elements, the isotope pattern serves as a

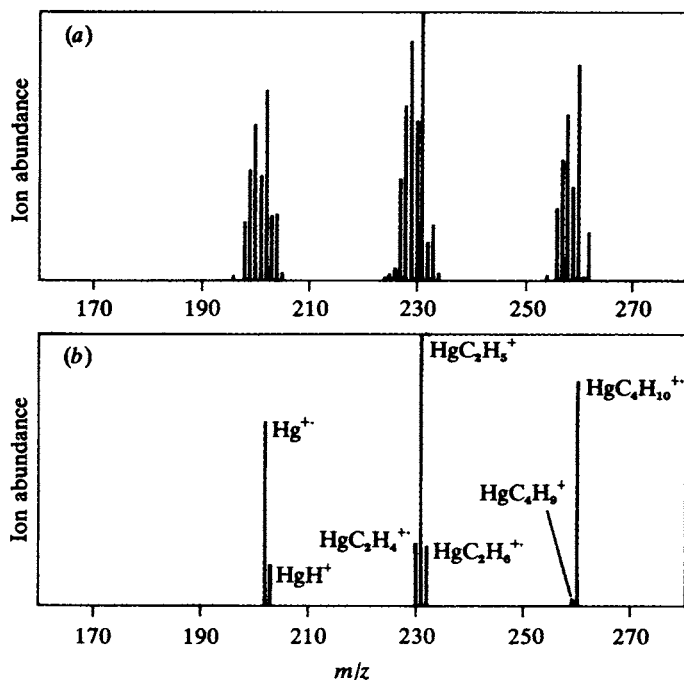


Figure 1.8. A partial mass spectrum of diethyl mercury, (a) including all isotope peaks, and (b) showing a mono-isotopic spectrum based on ^{202}Hg and ^{12}C .

fingerprint to identify the element and to define how many atoms of it are present in the molecule (section 12.2).

1.5. METASTABLE IONS

The sharp peaks of the normal ions in a mass spectrum are usually accompanied by some much broader, smaller peaks caused by decomposition of *metastable ions*. The maxima of these peaks arising from metastable ion decomposition frequently occur at non-integral m/z values and are easily distinguished from those due to normal ions (figure 1.9). The peak shapes are approximately Gaussian but occasionally flat-topped or dish-shaped ones are found extending over several mass units. The origin and fragmentation of metastable ions are discussed later (chapter 8). These ions are very useful for determining fragmentation pathways. For example, in magnetic sector mass spectrometers, if a metastable ion of mass m_1 decomposes to give an ion of mass m_2 , then a peak will be found at an apparent mass, $m^* = m_2^2/m_1$. Therefore, observation of a peak at mass m^* confirms the fragmentation of a *precursor ion* (m_1) to a *product ion* (m_2). In the mass spectrum of

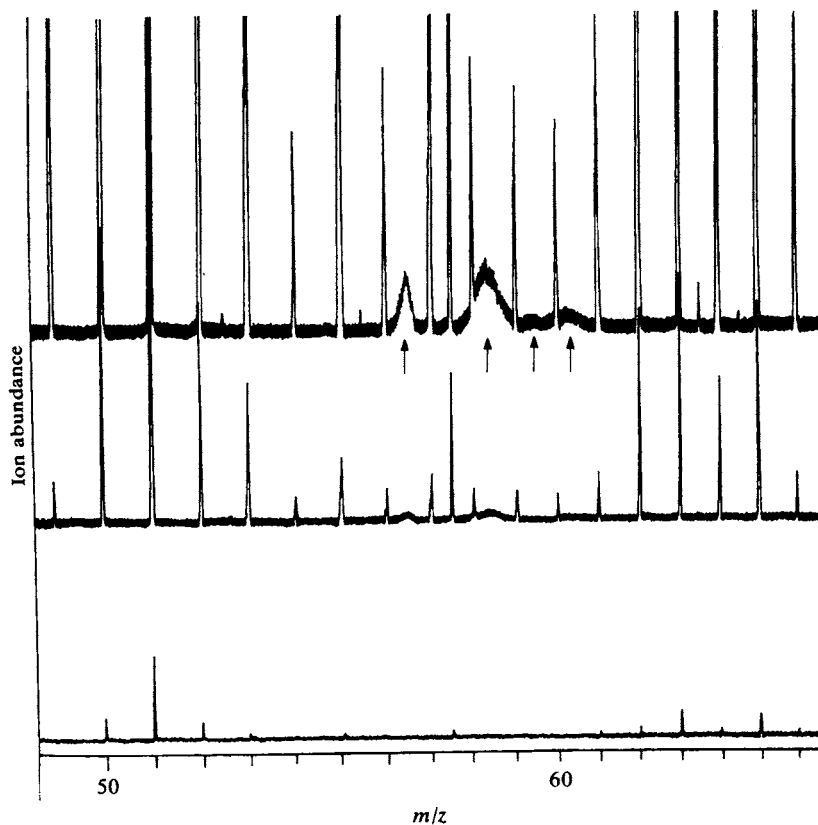


Figure 1.9. Peaks in a mass spectrum (indicated by arrows) representing product ions arising from fragmentation of metastable precursor ions. Normal product ions (produced in the ion source) give rise to narrow peaks at integral mass but product ions from metastable decomposition outside the source are usually seen as broad peaks at non-integral mass. Note also the fairly abundant doubly charged ions at m/z 57.5.

toluene, abundant ions occur at m/z 91 ($C_7H_7^+$) and m/z 65 ($C_5H_5^+$) and the appearance of a broad peak at m/z 46.4 ($= 65^2/91$) indicates that at least some of the ions at m/z 65 arise through ejection of C_2H_2 (26 mass units) from the ion at m/z 91. Computerized acquisition of data has resulted in the deletion of peaks for metastable ions from the routine mass spectrum and the output of spectra from such systems shows only narrow peaks (lines) representing normal ions. However, metastable ion decomposition can be examined conveniently by 'linked scanning' (see later – section 8.3.1).

1.6. ELEMENTAL COMPOSITIONS OF IONS

On the atomic scale, ^{12}C is given a mass of 12.0000 but other elements have fractional masses, e.g. 1H has mass 1.0078 and ^{16}O has mass 15.9949 (table 1.5). Because of this, the masses of most ions in a mass spectrum fall near but not at integer values. For instance, the molecular ion of acetone at m/z 58

Table 1.5. *Accurate masses of some elements commonly occurring in spectrometry.*^a

| Isotope | Atomic mass | Isotope | Atomic mass |
|------------------|-------------|------------------|-------------|
| ¹ H | 1.007 83 | ²⁹ Si | 28.976 49 |
| ² H | 2.014 10 | ³⁰ Si | 29.973 76 |
| ¹⁰ B | 10.012 94 | ³¹ P | 30.973 76 |
| ¹¹ B | 11.009 31 | ³² S | 31.972 07 |
| ¹² C | 12.000 00 | ³⁴ S | 33.967 86 |
| ¹³ C | 13.003 35 | ³⁵ Cl | 34.968 85 |
| ¹⁴ N | 14.003 07 | ³⁷ Cl | 36.965 90 |
| ¹⁵ N | 15.000 11 | ⁷⁹ Br | 78.918 39 |
| ¹⁶ O | 15.994 91 | ⁸¹ Br | 80.916 42 |
| ¹⁹ F | 18.998 40 | ¹²⁷ I | 126.904 48 |
| ²⁸ Si | 27.976 93 | | |

Notes:

^a Given correct to five decimal places. Notice how on this atomic scale, with ¹²C taken as standard, the masses fall either just above or just below integral values.

actually has a mass of 58.0418. The resolving power of a mass spectrometer is a measure of its ability to separate two ions of any defined mass difference. Basically, for two overlapping peaks M_1 and M_2 (figure 1.10), the resolution may be defined in terms of the mass difference (ΔM) between them such that the peaks are said to be resolved if $(b/H) \times 100 \leq 10$, where H is the height of the peaks and b measures the depth of the 'valley' between them. The resolution is then the value of $M_1/\Delta M$ when $(b/H) \times 100$ is equal to 10. For example, when two masses (100.000 and 100.005) are separated by a 10 per cent valley, the resolution of the instrument is $100.000/0.005$, i.e. 20 000. There are other, less common, definitions of resolution. An instrument of even modest resolving power can distinguish readily between adjacent integral masses; to separate m/z 100 from m/z 101 a resolution of only 100 is required. A high-resolution instrument, however, can separate an ion at m/z 100.000 from one at m/z 100.005. At low resolution, a mass spectrum consists of a series of peaks at integer m/z values but at medium resolution any of these peaks may be split due to the presence of ions of different elemental compositions. As an example, an ion at m/z 28 might have the composition N_2 or CO or C_2H_4 ; if all three ions were present, a low-resolution spectrum would show only one peak at m/z 28 but a medium-to-high-resolution instrument would reveal the three ion types at m/z 28.0061, 27.9949 and

28.0313 respectively (figure 1.11). Thus, at higher resolution, small mass differences can be detected and this property is utilized for accurate mass measurement of ions, as described in section 4.4.1.

1.7. APPEARANCE OF THE MASS SPECTRUM

Beginning with the simple picture of ion decomposition, and introducing the complications of isotopes, multiply charged ions, metastable ions, and peak

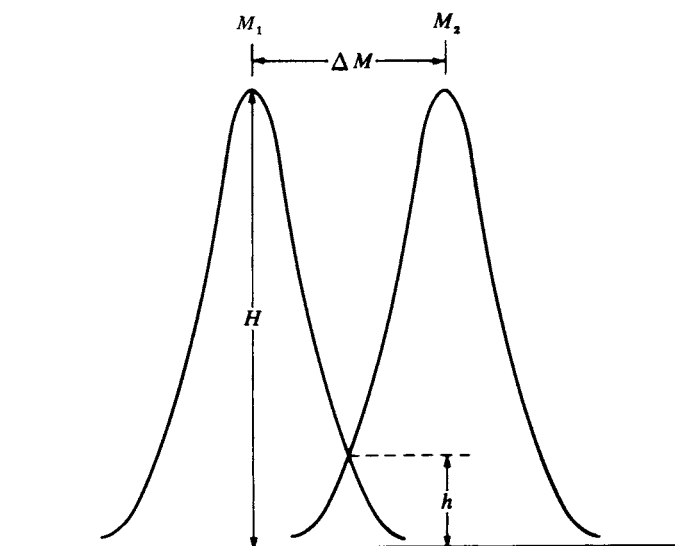


Figure 1.10. Two overlapping ion peaks M_1 and M_2 of height H and overlap b . If $(b/H) \times 100 \leq 10$, these peaks are considered to be resolved.

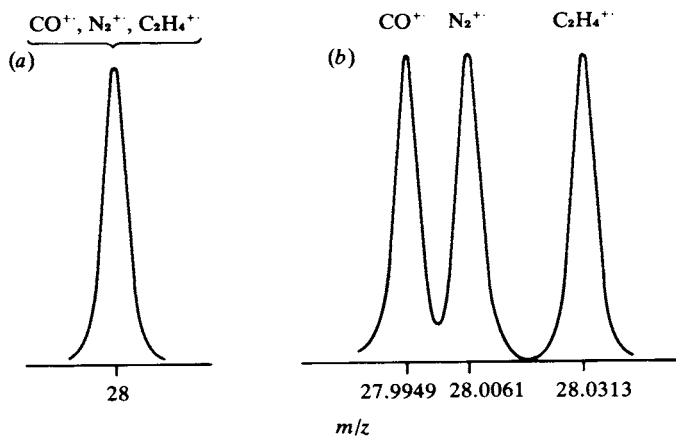


Figure 1.11. The appearance of the molecular ion region of a mass spectrum of a mixture of CO, N_2 and C_2H_4 at m/z 28 with (a) low resolving power showing no separation of masses and (b) medium resolving power (3000) showing good separation.