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Investigation of Molecular Structure
SPECTROSCOPIC AND DIFFRACTION METHODS

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Investigation of Molecular Structure

SPECTROSCOPIC AND DIFFRACTION METHODS

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Generally-accepted values for bond lengths, bond enthalpies, and spectroscopic absorptions have been used; they have been obtained from a variety of sources including the data books and spectroscopic text-books cited in this text. Accurate relative atomic masses are from "Mass and Abundance Tables for use in Mass Spectrometry", by J. H. Beynon and A. E. Williams, Elsevier, Amsterdam, 1963, and fragmentation patterns from "Compilation of Mass Spectral Data", by A. Cornu and R. Massot, Heyden, London, 1966.

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B. C. Gilbert

York 1975

Introduction

This text is written for A level students and for those taking introductory courses in Chemistry at degree and National Certificate levels.

The inclusion of some aspects of spectroscopic and diffraction techniques in A level syllabuses and early in degree and National Certificate courses is a trend which is surely to be welcomed. There have been significant advances in recent years in the use of these methods, not only for obtaining an analysis of the elements and groups present in a given molecule but also for establishing the way in which the constituent atoms are arranged. These developments have had a profound effect in increasing our scientific knowledge, especially in the fields of chemistry and molecular biology; this is reflected in the elucidation of the structure and mode of action of a wide range of compounds including, for example, antibiotics, enzymes, and nucleic acids.

It is important that such work should find its place in A level curricula—not only as a means of training potential chemists but also as part of an education to show, through the study of modern chemistry, how advances are made.

The subjects of spectroscopy and diffraction are often taught as elegant mathematical descriptions, but then the reasons for *using* the techniques are lost. In this text I have reduced the mathematical content to a minimum. In introducing mass spectrometry, infra-red, visible and ultra-violet spectroscopy, nuclear magnetic resonance, and diffraction, I have outlined in each chapter the theoretical essentials which highlight the most important principles, such as the quantum theory, the electromagnetic spectrum, and magnetism. However, it is the *results* from these techniques which are equally important at this stage. These are introduced very early in each chapter, so that it is possible from these data to see, at first hand, how the identity of a compound may be found and how its detailed molecular structure can be determined. The examples of the great majority of the compounds I have used are from A level syllabuses although I have given other examples of general interest to show how the techniques are being developed.

When studying these techniques, one so often forgets that they are but one set of methods which chemists use, and it is important for students to realize that although spectroscopic and diffraction methods provide very important evidence, it must be backed up by other data—in particular, by investigation of the chemical reactions of the compounds concerned. However, in a short text such as this it is not possible to remind ourselves of this on every occasion a technique is discussed, and I hope that, in reading this book, it will be realized how much we depend on other knowledge to provide us with definitive evidence for our conclusions. Such reminders are given in worked examples in the text and in the problems at the end of chapters.

Further reading is encouraged and references to articles and books, helpful for an A level or first year university student, are given. Some more advanced points are described but these are reproduced in small print so they can be omitted on the first reading if necessary.

S.I. Units have been used throughout and the nomenclature adopted is essentially the I.U.P.A.C. system as recommended by the Association for Science Education in their booklet "Chemical Nomenclature, Symbols and Terminology" (1972). An exception is the retention of the generic name ether [e.g. diethyl ether rather than ethoxyethane], as allowed by I.U.P.A.C. References to well known 'trivial' names accompany the recommended names (in parenthesis).

Chapter 1

Mass Spectrometry

The technique of Mass Spectrometry, which owes its origin to pioneering experiments carried out at the beginning of the present century, is now established as a means for obtaining the formulae and structures of molecules. It enables many sophisticated structural problems to be solved rapidly, even when only minute quantities of material are available.

1.1 THE MASS SPECTROMETRY EXPERIMENT

The principle of the method is to obtain a positively charged ion characteristic of the substance under investigation, and then, effectively, to determine the *mass* of this ion using an approach closely related to that employed by J. J. Thomson for measuring the charge-to-mass ratio (e/m) for cathode rays (electrons). The procedure involves the use of electric and magnetic fields to deflect charged particles.

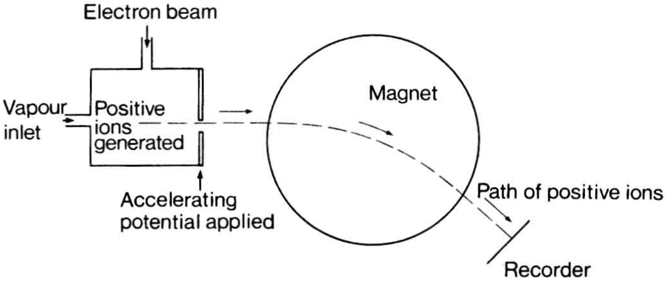
In 1912, Thomson had demonstrated the use of a magnetic field to deflect a beam of positive ions, obtained by the ionisation (loss of an electron) of neon atoms. Close examination of the trace produced by the positive ions as they impinged on a detector demonstrated that there were two different types of ion, which were characterised as those from the two neon **isotopes** (^{20}Ne and ^{22}Ne). These differ in their masses because of the different numbers of neutrons in their nuclei. This experiment not only demonstrated the existence of isotopes but also laid the foundation for the development of mass spectrometry.

The design of a simple mass spectrometer is shown in Figure 1.1. The substance to be studied (a gas or the vapour from a relatively volatile liquid) is introduced into the ionisation chamber which is kept at very low pressure (about 10^{-4} N m^{-2}). The vapour is bombarded with high energy electrons, and the collision between an electron and the molecule (or atom) under consideration causes an electron to be ejected from the latter, leaving a positively charged ion:

$$\mathrm{M} \longrightarrow \mathrm{M}^{+} + \mathrm{e}^{-}$$

The positively charged ions are attracted by an applied electrostatic potential and are hence accelerated towards the negative plate. Ions are allowed to pass through a slit in the plate and the resultant beam is passed into a magnetic field; the positive ions then become deflected by an amount which depends upon the *mass* and the *charge* of each. The lighter the ion and the greater its charge, the greater will be the deflection.* The derivation of the exact relationship is as follows:

For an accelerating potential V, the *potential energy* of an ion, of charge e, generated in the ion-chamber is eV.



1.1 Basic features of a simple mass spectrometer

The ion is accelerated through the slit, and in this process its potential energy is completely converted into *kinetic energy*, $\frac{1}{2}mv^2$, where m and v are the mass and velocity, respectively, of the ion. Thus:

$$\frac{1}{2}mv^2 = eV \tag{1.1}$$

When the positive ion passes into the magnetic field (of magnetic flux density B) it experiences a force at right angles both to the direction of motion and to the field direction. The magnitude of this force is Bev. The positive ion is now constrained to move in the arc of a circle of radius R, so that:

$$Bev = \frac{mv^2}{R} \tag{1.2}$$

Combination of equations (1.1) and (1.2) leads to the following expression:

$$\frac{m}{e} = \frac{B^2R^2}{2V} \tag{1.3}$$

This equation shows that for an ion of given mass (m) and charge (e) the radius of the circle of motion (R) is determined by B and V, i.e. the magnitudes of the magnetic and electric fields. In practice, R remains

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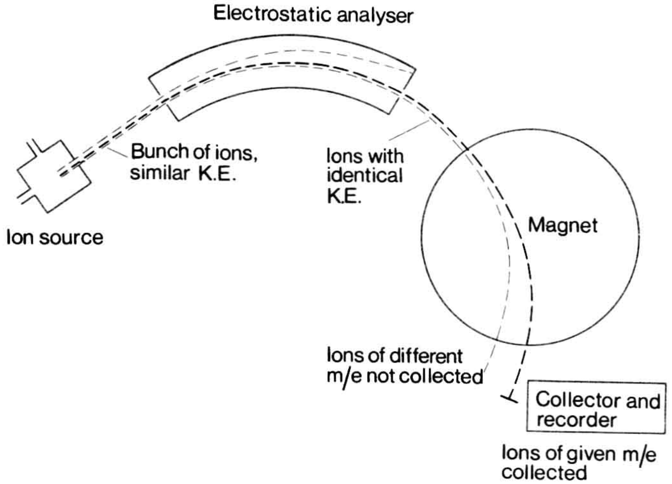
*A simply-constructed model is described by A. Farmer, *The School Science Review*, 1969, **50,** 594.

fixed by the geometry of the apparatus and the position of the detector. It can then be seen that if V is kept constant and B is varied, equation (1.3) will be satisfied for ions of different m/e for different values of B. In other words, the value of B needed to get a particular type of ion to be deflected to the recorder is a measure of m/e for that ion.

Most positive ions generated will have lost just one electron (that is, M is ionised to M^+, rather than M^{2+} or M^{3+}), and they will therefore have the same charge (opposite in sign, but equal in magnitude, to that of the electron). This means that, as B is varied, ions of different *mass* arrive at the recorder, and a spectrum of the masses of the various ions concerned can be plotted. Since the mass of the electron is very small compared with the mass of the nucleus (it is approximately one two-thousandth the mass of the proton) the experiment is effectively determining the masses of the parent molecules.

Early mass spectrometers worked almost exactly on this basis and achieved a reasonable resolution (separation of two fairly similar masses, such as ^{20}Ne and ^{22}Ne). Some modern mass spectrometers are designed with an extra focusing system which enables increased resolution to be obtained. As before, a narrow beam of positive ions with similar kinetic energies is produced. These ions have a small but finite range of kinetic energies, and this spread of energies must be reduced for more precise work so that equation (1.3) is strictly applicable. This criterion is achieved by passing the beam of ions through an electric field (this is called an electrostatic analyser) which deflects the ions according to their kinetic energies (Figure 1.2). Then only one

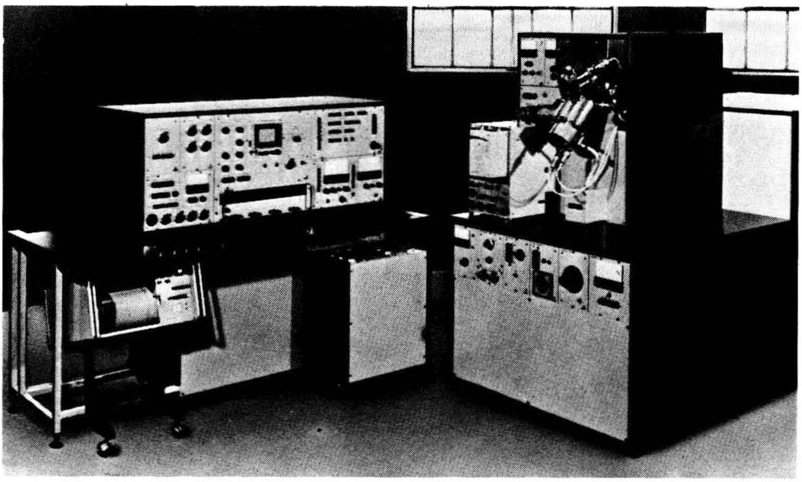


1.2 *Diagram of a double-focusing mass spectrometer* small component of the resulting beam, with a well-defined kinetic energy, is passed into the magnetic field for focusing of ions of given m/e values. As before, a scan of mass is obtained by varying B (although in certain circumstances it is possible to obtain a more rapid scan by varying V, with B constant). The detector usually comprises an electron multiplier as collector, and the arrival of ions appears as an electrical signal for display as a peak on an oscilloscope or recorder. This produces a **mass spectrum**—effectively a plot of the masses of the positive particles present against the relative number of ions of each mass. The scan is calibrated with a peak obtained from a substance of known relative atomic or molecular mass. The spectrum can usually be recorded in a few minutes, from less than a microgram of material.

Figure 1.3 shows the A.E.I. MS 50 Double-focusing Mass Spectrometer which operates on this basis and which can separate two masses differing by less than one part in 10^5.

1.2 MEASURING RELATIVE MOLECULAR AND ATOMIC MASSES

Modern mass spectrometers with a double-focusing facility can be used in two kinds of study. They may be employed to give fairly rapid scans of the relative masses of the ions from a variety of substances (this is also how a single-focusing instrument is employed). Alternatively, under carefully controlled conditions of high resolution, they can be used to separate closely spaced peaks and to determine the appropriate relative atomic and molecular masses with precision.



1.3 MS 50 Double-focusing mass spectrometer, A.E.I. Ltd. (Photo: Switchgear Testing Company, Manchester)

The following example should illustrate the advantages of the latter approach if the maximum amount of information is to be derived from an investigation. A peak which corresponds to mass 28 might be due to nitrogen ($^{14}N_2$), carbon monoxide ($^{12}C^{16}O$) or ethene ($^{12}C_2{}^1H_4$). However, these three molecules have slightly different relative molecular masses (these are based on the internationally accepted scale, with 12 exactly for the ^{12}C isotope):

$^{14}N_2$	28.0062
$^{12}C^{16}O$	27.9949
$^{12}C_2{}^1H_4$	28.0313

A modern mass spectrometer can readily be used to identify a peak exactly enough for it to be characterised as the positive ion from one of these. Further, if all three substances were to be present together, then under high-resolution conditions three separate peaks could be resolved. If one relative molecular mass is accurately known, this can be used to calibrate the field scan so that the other molecular masses can also be accurately determined.

Relative heights of separate peaks can also be used to obtain quantitative information. For example, from the mass spectrum of the monatomic gas neon can be measured not only the relative atomic masses of the constituent isotopes (^{20}Ne, ^{21}Ne, ^{22}Ne), to an accuracy of 1 part in 10^6, but also the relative abundance of the separate isotopes in the mixture:

	Relative atomic mass	Relative abundance %
^{20}Ne	19.9924	90.92
^{21}Ne	20.9940	0.26
^{22}Ne	21.9914	8.82

We must distinguish the *separate* isotopic atomic masses measured with the mass spectrometer from the *weighted average* obtained by other (chemical) methods. For example, ^{35}Cl has a relative atomic mass of 34.9688, and that of ^{37}Cl is 36.9659; the average atomic mass of the natural mixture of isotopes (75.53% ^{35}Cl, 24.47% ^{37}Cl) is 35.45).

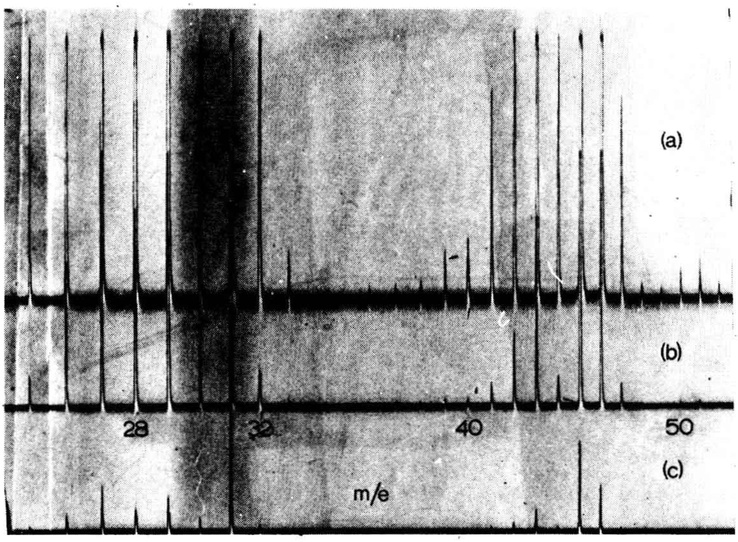
These investigations lead on to very interesting questions about the causes of the widespread natural occurrence of certain isotopes of some elements (^{12}C, ^{16}O, for example) and also about the magnitude of the mass difference between a given isotope and the sum of its constituent neutrons and protons (this is closely related to the binding energy of the nucleus). However, our concern here will be with the rather different application of mass spectrometry to the determination of molecular structure.

1.3 MASS SPECTROMETRY OF MOLECULES

When an organic compound is introduced into the spectrometer, the molecules become ionised, by the loss of an electron, and the positive ions produced pass through the focusing system, leading usually to a peak at the appropriate relative molecular mass. However, the mass spectrum of an organic compound also contains extra information which can be extremely useful.

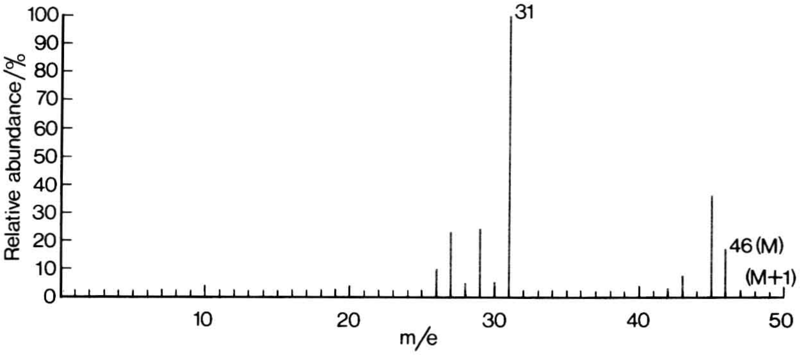
Figure 1.4 shows the mass spectrum of ethanol (CH_3CH_2OH); this is a plot of recorder signal (proportional to the number of ions of given m/e) against increasing m/e (in practice nearly all the ions have the same unit charge so this axis effectively corresponds to increasing mass; see page 11). The various traces indicated, (a)–(c), are recorded simultaneously with different degrees of amplification to allow the study of major and minor peaks.

Peaks occur at (or close to) most integral values (the extra precision possible with high resolution is not usually employed at this stage).



1.4 Mass spectrum of ethanol, CH_3CH_2OH

Many of the peaks are derived from ethanol by processes which will shortly be described. There are also peaks due to traces of air in the instrument; this gives rise to signals from N_2 (*m/e* 28) and O_2 (*m/e* 32), approximately in the expected ratio 4:1. These peaks may be used to calibrate the scan. For convenience, the spectrum is usually redrawn in somewhat simplified form (Figure 1.5) where only the major peaks from the organic compound are included. The peak heights are expressed as percentages of the height of the highest peak (the **base peak**), which is in this example the peak with *m/e* 31.



1.5 Stick diagram of the mass spectrum of ethanol

The mass spectrum of ethanol

The spectrum shows the expected peak at *m/e* 46, corresponding to the **molecular ion** (M^+) of the parent molecule (relative molecular mass is the sum of the relative atomic masses of $2C+6H+O$).

There is also a very small peak at *m/e* 47, called the $(M+1)$ peak, which corresponds to the relatively few ethanol molecules present which, because they contain a ^{13}C, ^{17}O, or ^{2}H atom, have a molecular mass of 47. (^{13}C has a natural abundance, compared with ^{12}C, of 1.1%; for ^{17}O, relative to ^{16}O, the figure is 0.04% and for ^{2}H, relative to ^{1}H, the abundance is 0.01%.)* An even smaller $(M+2)$ peak arises from the molecules which contain two ^{13}C atoms, or an ^{18}O atom, or a ^{13}C and a ^{17}O atom, etc. It must be stressed that these all have the same chemical composition as ethanol, but they contain naturally occurring low-abundance isotopes.

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* Isotope abundance tables can be found, for example, in "Book of Data: Chemistry, Physical Science, Physics", *Nuffield Advanced Science*, Penguin, London, 1972 (this also contains the accurate relative atomic masses of selected nuclei), and in "Chemistry Data Book", J. G. Stark and H. G. Wallace, SI Edn., John Murray, London, 1970.

The other peaks in the spectrum occur because some of the ethanol molecules which are first ionised to give M^+ then *fragment* to give smaller positively charged ions, a process which is understandable in terms of the high energy of the bombarding electrons. The positively charged fragments are accelerated in the usual way and are focused to be collected and recorded for their particular values of *m*/*e*.

The large peak in the mass spectrum of ethanol (the base peak) is at *m*/*e* 31; this corresponds to the positively charged fragment $[CH_2OH]^+$ obtained by loss of CH_3 from the parent ion $[CH_3CH_2OH]^{+\cdot}$. The structure of these and other positive ions will be discussed later (page 20), as will some guide-lines for interpreting fragmentation patterns, but it should at this stage be apparent that these peaks contain important clues about the structure of the molecule under investigation.

1.4 ANALYSIS OF MASS SPECTRA

The information of interest is contained mainly in the appearance of the peak from the molecular ion [with its associated $(M + 1)$ and $(M + 2)$ peaks] and in the fragmentation pattern. These features will now be considered in more detail.

(a) The Molecular Ion

For many molecules a peak of appreciable size from the molecular ion can be detected. It is usually a reliable guide that a molecule with π- or lone-pair electrons (e.g. benzene or ethanol, respectively) will give a detectable molecular ion (M) since one of these electrons can normally be lost (to give M^+) without the breakdown of the bonding framework in the molecule. However, because in some cases no peak from a molecular ion can be observed, care must be taken before it can be assumed that the peak at highest *m*/*e* is from the molecular ion.

It may be possible at this stage to determine very accurately the relative molecular mass of any given peak (if the high resolution facility is available) and this will then be carried out for the molecular ion itself. Because different atoms do not have exactly integral atomic masses and, in addition, because various combinations of similar mass are not identical (contrast, for example, C_2H_4 and N_2) the exact relative molecular mass (to 3 or 4 places of decimals) characterises the molecular formula exactly. For instance, a molecular peak with *m*/*e* almost exactly 60 could be from various possible molecules with different formulae, including $C_2H_4O_2$ [e.g. ethanoic acid (acetic acid), CH_3CO_2H] and C_3H_8O (e.g. propanol). The relative molecular masses