Chapter 05 – Mass Spectrometry

Topic A4 from the IB HL Chemistry Curriculum

	Assessment Statement	Obj	Teacher's Notes
A.4.1	Determine the molecular mass of a compound from the molecular ion peak.	3	
A.4.2	Analyze fragmentation patterns in a mass spectrum to find the structure of a compound.	3	Examples of fragments should include: • $(M_r - 15)^+$ loss of CH_3 • $(M_r - 17)^+$ loss of OH • $(M_r - 29)^+$ loss of C_2H_5 or CHO • $(M_r - 31)^+$ loss of CH_3O • $(M_r - 45)^+$ loss of COOH

Determining the molecular mass of a compound

The mass spectrometer was introduced in Chapter 04, where we saw it was used to find the mass of individual atoms and the relative abundances of different isotopes. The instrument can be used in a similar way to find the relative molecular mass of a compound. If the empirical formula is also known from compositional analysis, the molecular formula can be determined. The technique also provides useful clues about the molecular structure. The following exercise is designed to refresh your memory about empirical and molecular formulas and organic functional groups:

Exercise: An unknown compound has the following mass composition:

C, 40.0%; H, 6.7%; O, 53.3%.

The largest mass recorded on the mass spectrum of the compound corresponds to a relative molecular mass of 60. Calculate the empirical formula and determine the molecular formula of the compound. Use your knowledge of chemical formulas and organic chemistry to identify any functional groups that might be present. Show all work in the space below.

Mass spectrometry – instrumentation

In its simplest form, the mass spectrometer performs three essential functions. First, it subjects molecules to bombardment by a stream of high-energy electrons, converting some of the molecules to ions, which are accelerated in an electric field. Second, the accelerated ions are separated according to their mass-to-charge ratios in a magnetic or electric field. Finally, the ions that have a particular mass-to-charge ratio are detected by a device which can count the number of ions striking it. The detector's output is amplified and fed to a recorder. The trace from the recorder is a mass spectrum – a graph of the number of particles detected as a function of mass-to-charge ratio.
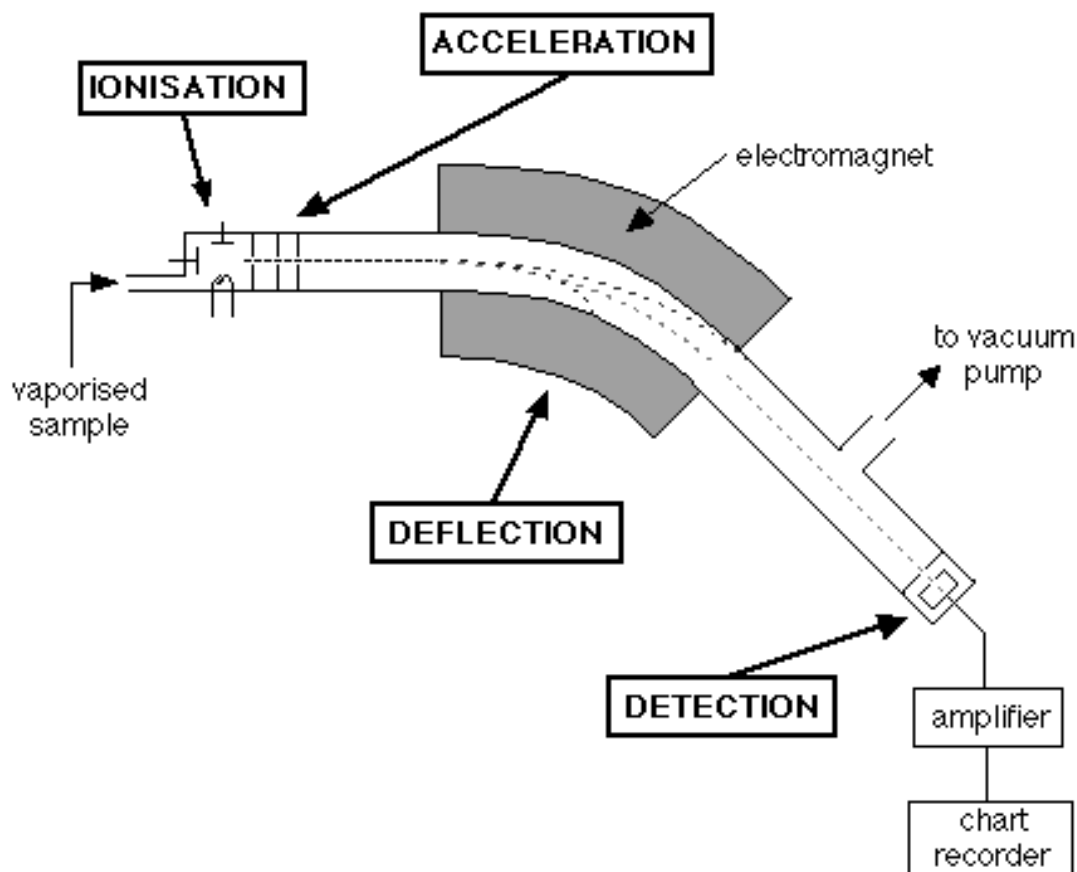

Figure 05.01: A diagram of a mass spectrometer.

When we examine each function in detail, we see that the mass spectrometer is actually somewhat more complex than just described. Before the ions can be formed, a stream of molecules must be introduced into the ionization chamber where the ionization takes place. A sample inlet system provides this stream of molecules.

A sample studied by mass spectrometry may be a gas, a liquid, or a solid. Enough of the sample must be converted to the vapor state to obtain the stream of molecules that must flow into the ionization chamber. With gases, of course, the substance is already vaporized, so a simple inlet system can be used. This inlet system is only partially evacuated so that the ionization chamber itself is at a lower pressure than the sample inlet system. The sample is introduced into a larger reservoir, from which the molecules of vapor can be drawn into the ionization chamber, which is at low pressure. To ensure that a steady stream of molecules is passing into the ionization chamber, the vapor travels through a small pinhole, called a molecular leak, before entering the chamber. The same system can be used for volatile liquids or

solids. For less volatile materials, the system can be designed to fit within an oven, which can heat the sample to provide a greater vapor pressure. Care must be taken not to heat any sample to a temperature at which it might decompose.

With rather nonvolatile solids, a direct-probe method of introducing the sample may be used. The sample is placed on the tip of the probe, which is then inserted through a vacuum lock into the ionization chamber. The sample is placed very close to the ionizing beam of electrons. The probe can be heated, thus causing vapor from the sample to be evolved in proximity to the beam of electrons. A system such as this can be used to study samples of molecules with vapor pressures lower than 10^{-9} mm Hg at room temperature.

Once the stream of sample molecules has entered the ionization chamber, a beam of high-energy electrons bombards it. This process converts the molecules to ions. The ions are then accelerated in an electric field. The following is a diagram of a typical ionization chamber.
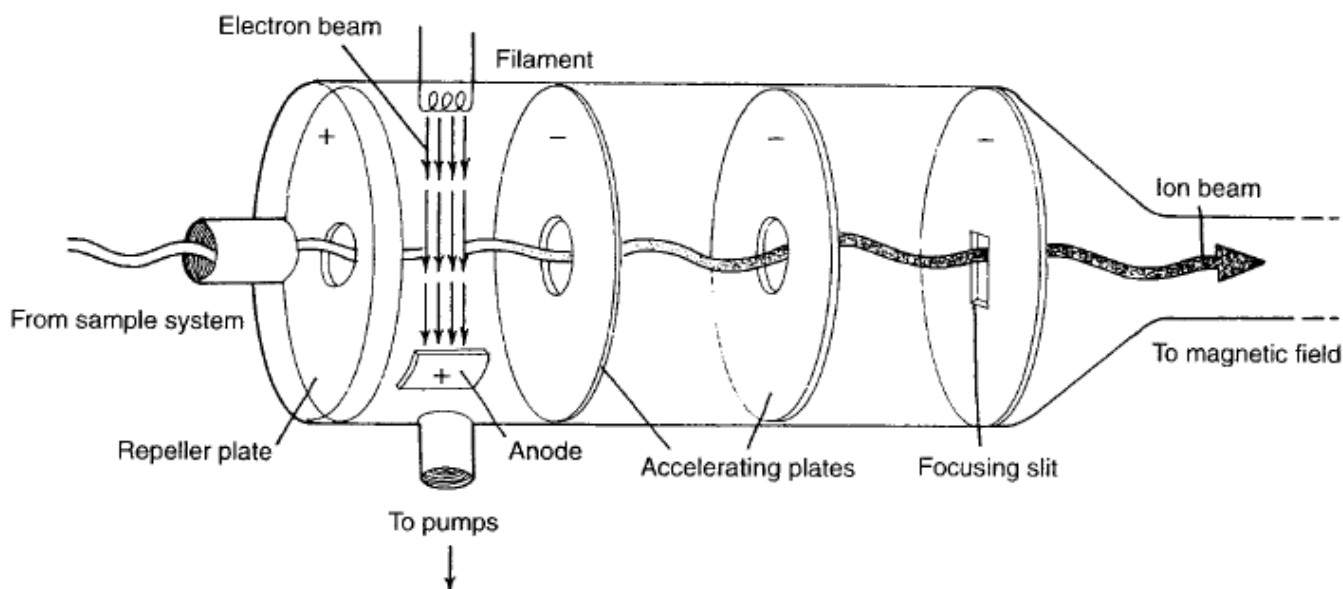

Figure 05.02: A typical ionization chamber and the nearby accelerating plates.

In the ionization chamber, the beam of high-energy electrons is emitted from a filament that is heated to several thousand degrees Celsius. In normal operation, the emitted electrons have an energy of about 70 electron volts (eV). These high-energy electrons strike the stream of molecules which has been admitted from the sample system and ionize the molecules in the stream by removing electrons from them; the molecules are thus converted to positive ions. A repeller plate, which carries a positive electrical potential, directs the newly created ions toward a series of accelerating plates. A large potential difference, ranging from 1 to 10 kilovolts (kV), applied across these accelerating plates produces a beam of rapidly traveling positive ions. One or more focusing slits direct the ions into a uniform beam.

Most of the sample molecules are not ionized at all but are continuously drawn off by vacuum pumps which are connected to the ionization chamber. Some of the molecules are converted to negative ions through the absorption of electrons. The repeller plate absorbs these negative ions. A small proportion of the positive ions which are formed may have a charge greater than one (a loss of more than one electron). These are accelerated in the same way as the singly charged positive ions.

The energy required to remove an electron from an atom or molecule is its ionization potential. Most organic compounds have ionization potentials between 8 and 15 eV. However, a beam of electrons does not create ions with high efficiency until it strikes the stream of molecules with a potential of 50 to 70 eV. In order to produce reproducible spectra, electrons of this energy range are used to ionize the sample.

From the ionization chamber, the beam of ions passes through a short field-free region. From there, it enters the deflector, the region where the ions are separated according to their mass to charge ratios. In the presence of a magnetic field, a charged particle describes a curved flight path. The greater the mass-to-charge (m/e) ratio of the ion, the larger the radius of the curved path.
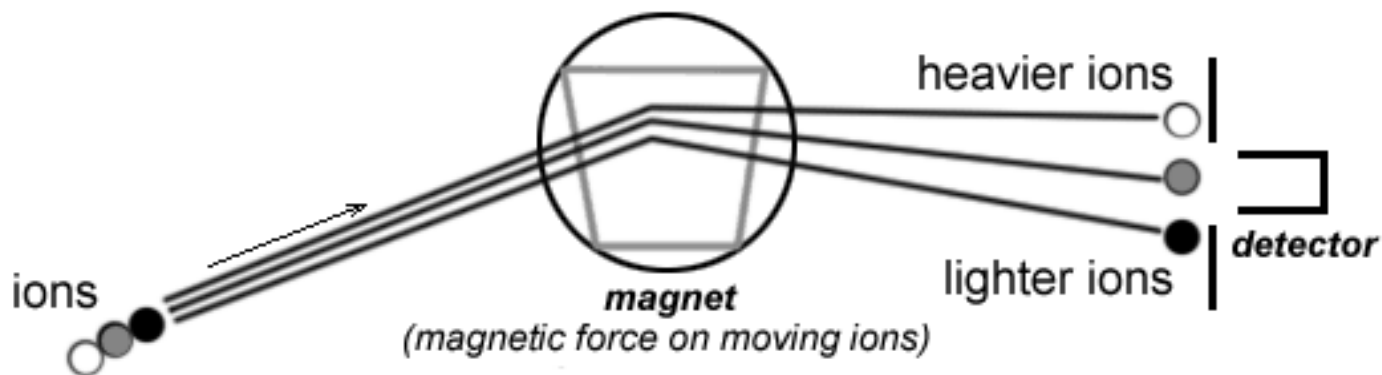

Figure 05.03: A closer, yet simplified look at the deflection of ions.

The analyzer tube of the instrument is constructed to have a fixed radius of curvature. A particle with the correct mass-to-charge ratio can negotiate the curved analyzer tube and reach the detector. Particles with mass-to-charge ratios which are either too large or too small strike the sides of the analyzer tube and do not reach the detector. The method would not be very interesting if ions of only one mass could be detected. Therefore, either the accelerating voltage or the magnetic field strength is continuously varied in order that all of the ions produced in the ionization chamber can be detected.

The detector of a typical instrument consists of a counter which produces a current that is proportional to the number of ions which strike it. Through the use of electron multiplier circuits, this current can be measured so accurately that the current caused by just one ion striking the detector can be measured. The signal from the detector is fed to a recorder, which produces the mass spectrum. In modern instruments, the output of the detector is fed through an interface to a computer. The computer can store the data, provide the output in both tabular and graphic forms, and compare the data to standard spectra, which are contained in spectra libraries also stored in the computer.

Mass spectrometry – the mass spectrum

The mass spectrum is a plot of ion abundance versus mass-to-charge ratio. The following figure is a portion of a typical mass spectrum – that of dopamine, a substance which acts as a neurotransmitter in the central nervous system.
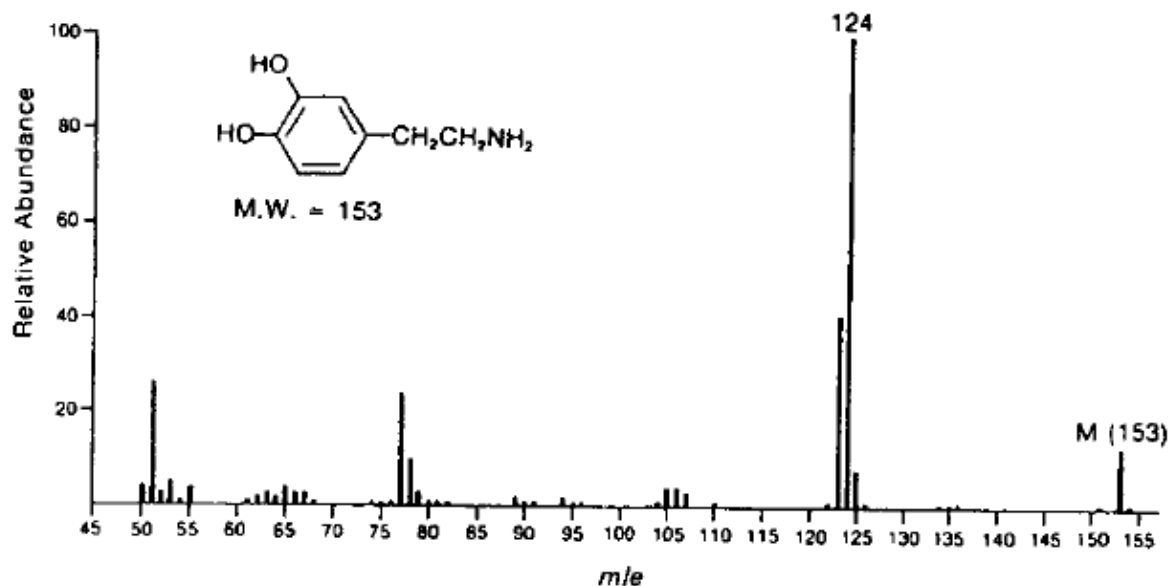

Figure 05.04: The mass spectrum of dopamine.

The most abundant ion formed in the ionization chamber gives rise to the tallest peak in the mass spectrum, called the base peak. In the mass spectrum of dopamine, the base peak is indicated at a m/e value of 124. The relative abundances of all of the other peaks in the spectrum are reported as percentages of the abundance of the base peak.

As mentioned earlier, the beam of electrons in the ionization chamber converts some of the sample molecules to positive ions. Some of these types of ions are of sufficient importance to warrant further examination. The simple removal of an electron from a molecule yields an ion whose weight is the actual molecular weight of the original molecule. This ion is the molecular ion, which is frequently symbolized by M^+. The value of m/e at which the molecular ion appears on the mass spectrum, assuming that the ion only has one electron missing, gives the molecular weight of the original molecule. If you can identify the molecular ion peak in the mass spectrum, you will be able to use the spectrum to determine the molecular weight of an unknown substance. Ignoring heavy isotopes for the moment, the molecular ion peak is the heaviest peak in the mass spectrum. Strictly speaking, the molecular ion is a radical-cation since it contains an unpaired electron as well as a positive charge.

Molecules in nature do not occur as isotopically pure species. Virtually all atoms have heavier isotopes which occur in characteristic natural abundances. Hydrogen occurs largely as ^1H, but about 0.02% of hydrogen atoms are the isotope ^2H. Carbon normally occurs as ^{12}C, but about 1.1% of carbon atoms are the heavier isotope ^{13}C. With the possible exception of fluorine and a few additional elements, most other elements have a certain percentage of naturally occurring heavier isotopes. Peaks caused by ions bearing those heavier isotopes also appear in mass spectra. The relative abundances of such isotopic peaks are proportional to the abundances of the isotopes in nature. Most often, the isotopes occur one or two mass units above the mass of the "normal" atom.

Therefore, besides looking for the molecular ion (M^+) peak, one would also attempt to locate the M + 1 and M + 2 peaks. The relative abundances of these two peaks can be used to determine the molecular formula of the substance being studied.

We have seen that the beam of electrons in the ionization chamber can produce the molecular ion. This beam is also sufficiently powerful to break some of the bonds in the molecule, producing a series of molecular fragments. The positively charged fragments are also accelerated in the ionization chamber, sent through the analyzer, detected, and recorded on the mass spectrum. These fragment ions appear at m/e ratios corresponding to their individual masses. Very often a fragment ion, rather than the parent ion, is the most abundant ion produced in the mass spectrum. A second means of producing fragment ions exists if the molecular ion, once it is formed, is so unstable that it disintegrates before it can pass into the accelerating region of the ionization chamber. The fragments which are charged then appear as fragment ions in the mass spectrum. A great deal of structural information about a substance can be determined from an examination of the fragmentation pattern in the mass spectrum. More will be written about this fragmentation pattern in a later section.

The molecular ion peak and molecular weight

When a beam of high-energy electrons impinges upon a stream of sample molecules, ionization of electrons from the molecules takes place. The resulting ions, called molecular ions, are then accelerated, sent through a magnetic field, and detected. If these molecular ions have lifetimes of at least 10^{-5} seconds, they reach the detector without breaking into fragments. The user then observes the m/e ratio which corresponds to the molecular ion in order to determine the molecular weight of the sample molecule.

In practice, molecular weight determination is not quite as easy as the preceding paragraph suggests. First, you must understand that the value of the mass of any ion accelerated in a mass spectrometer is its true mass, and not its molecular weight obtained through the use of chemical atomic weights. The chemical scale of atomic weights is based on weighted averages of the weights of all of the isotopes of a given element. The mass spectrometer can distinguish between masses of particles bearing the most common isotopes of the elements and particles bearing heavier isotopes. Consequently, the masses which are observed for molecular ions are the masses of the molecules in which every atom is present as its most common isotope.

In the second place, molecules subjected to bombardment by electrons may break apart into fragment ions. As a result of this fragmentation, mass spectra can be quite complex, with peaks appearing at a variety of m/e ratios. You must be quite careful to be certain that the suspected peak is indeed that of the molecular ion and not that of a fragment ion. This distinction becomes particularly crucial when the abundance of the molecular ion is low, as when the molecular ion is rather unstable and fragments easily.

Certain facts must apply to a molecular ion peak:

1. The peak must correspond to the ion of highest mass in the spectrum, excluding isotopic peaks that occur at even higher masses. The isotopic peaks are usually of much lower intensity than the molecular ion peak. At the sample pressures used in most spectral studies, the probability that ions and molecules will collide to form heavier particles is quite low.

2. The ion must have an odd number of electrons. When a molecule is ionized by an electron beam, it loses one electron to become a radical-cation. The charge on such an ion is one, thus making it an ion with an odd number of electrons.

3. The ion must be capable of forming the important fragment ions in the spectrum, particularly the fragments of relatively high mass, by loss of logical neutral fragments. These fragmentation processes will be explained in detail in a later section.

The observed abundance of the suspected molecular ion must correspond to expectations based on the assumed molecule structure. Highly branched substances undergo fragmentation very easily. Observation of an intense molecular ion peak for a highly branched molecule thus would be unlikely. The lifetimes of molecular ions vary according to the following generalized sequence.

> aromatic compounds > conjugated alkenes > alicyclic compounds > organic sulfides > unbranched hydrocarbons > mercaptans > ketones > amines > esters > ethers > carboxylic acids > branched hydrocarbons > alcohols

You must be careful when studying molecules containing chlorine or bromine atoms, since these elements have two commonly occurring isotopes. Chlorine has isotopes of 35 (relative abundance = 75.77%) and 37 (relative abundance = 24.23); bromine has isotopes of 79 (relative abundance = 50.5%) and 81 (relative abundance = 49.5%). When these elements are present, take special care to not confuse the molecular ion peak with a peak corresponding to the molecular ion with a heavier halogen isotope present.

In many of the cases which you are likely to encounter in mass spectrometry, the molecular ion can be observed in the mass spectrum. Once you have identified that peak in the spectrum, the problem of molecular weight determination is solved. However, with molecules which form unstable molecular ions, you may not observe the molecular ion peak. Molecular ions with lifetimes less than 10^{-5} second break up into fragments before they can be accelerated. The only peaks which are observed in such cases are those due to fragment ions. You will be obliged to deduce the molecular weight of the substance from the fragmentation pattern on the basis of known patterns of fragmentation for certain classes of compounds.

Fragmentation patterns

As we discussed in Chapter 04, the ionization process in the mass spectrometer involves an electron from an electron gun hitting the incident species and removing an electron:

$$X(g) \ + \ e^- \ \rightarrow \ X^+(g) \ + \ 2e^-$$
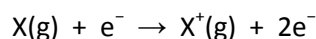
As mentioned earlier, the collision can be so energetic that it causes the molecule to break up into different fragments. The largest mass peak in the previous exercise corresponded to a parent ion passing through the instrument unscathed, but other ions, produced as a result of this break up, are also detected.

This **fragmentation pattern** can provide useful evidence for the structure of the compound. A chemist pieces together the fragments to form a picture of the complete molecule in the same way archaeologists find clues about the past from the pieces of artifacts discovered in the ground.

Consider Figure 05.05, below:
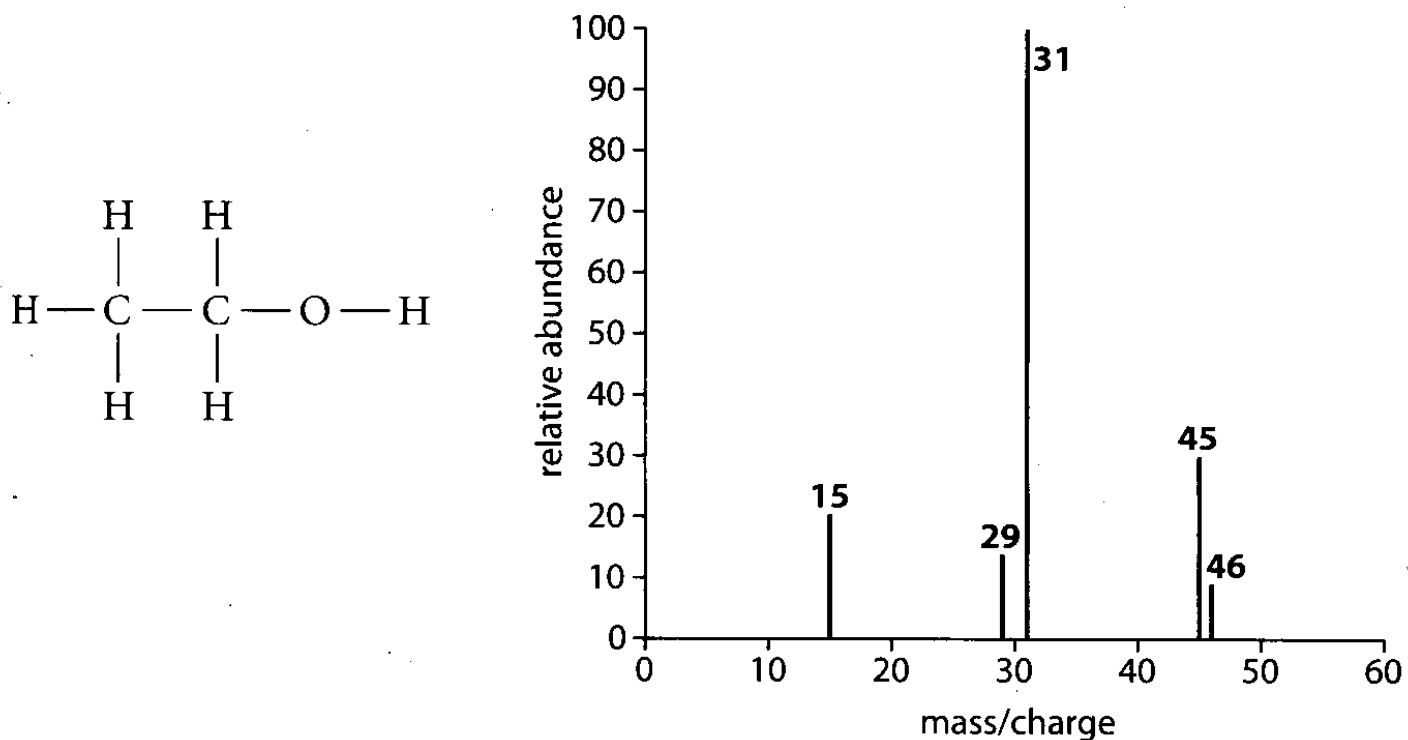
Figure 05.05: The structure of ethanol and its mass spectrum.

The molecular ion corresponds to the peak at 46. The ion that appears at a relative mass of 45, one less than the parent ion, corresponds to the loss of a hydrogen atom. Figure 05.06 shows a fragmentation path which explains the spectrum.
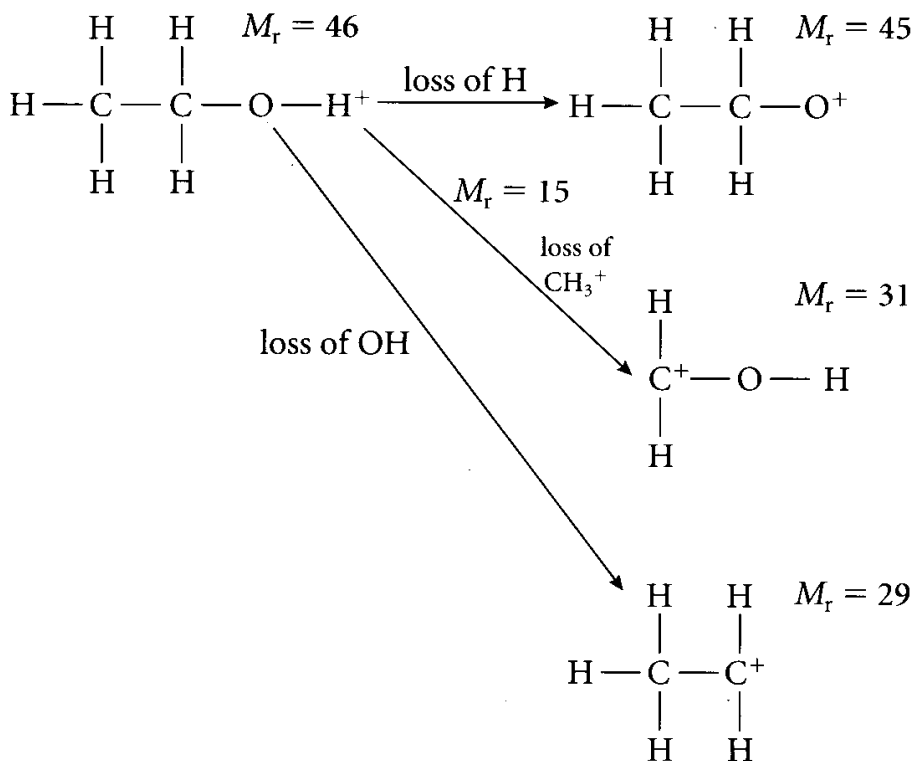
Figure 05.06: Possible fragmentation pattern produced when ethanol is bombarded with high energy electrons.

The parent ion can break up into smaller ions in a mass spectrometer. A compound is characterized by this fragmentation pattern.

For each fragmentation, one of the products keeps the positive charge. So, for example, if the C–C bond breaks in the ethanol molecules, two outcomes are possible as seen in Figure 05.07.

$$CH_3 + CH_2OH^+$$
$$31$$

$$C_2H_5OH^+$$

$$CH_3{}^+ + CH_2OH$$
$$15$$
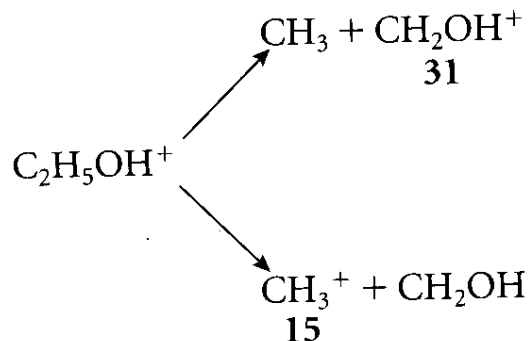
Figure 05.07: Two possible ways in which the C–C bond can break in ethanol. Only the charged species can be detected, as electric and magnetic fields have no effect on neutral fragments.

This explains the presence of peaks at both 15 and 31. Generally the fragment that gives the most stable ion is formed. The cleavage of the C–O bond leads to the formation of the $C_2H_5{}^+$ ion is in preference to the OH^+ ion in the example above, so there is an observed peak at 29 but not at 17.

Full analysis of the mass spectrum can be a complex process. We make use of the mass difference between the peaks to identify the pieces which have fallen off. You are expected to recognize the mass fragments shown in the table below.

Mass difference	Possible group
15	$CH_3{}^+$
17	OH^+
29	$C_2H_5{}^+$ or CHO^+
31	CH_3O^+
45	$COOH^+$

It is vitally important that you remember to write the positive charge on the ions when identifying different fragments.

<u>*Worked example*</u>: A molecule with an empirical formula CH_2O has the simplified mass spectrum below. Deduce the molecular formula and possible structure of the compound.
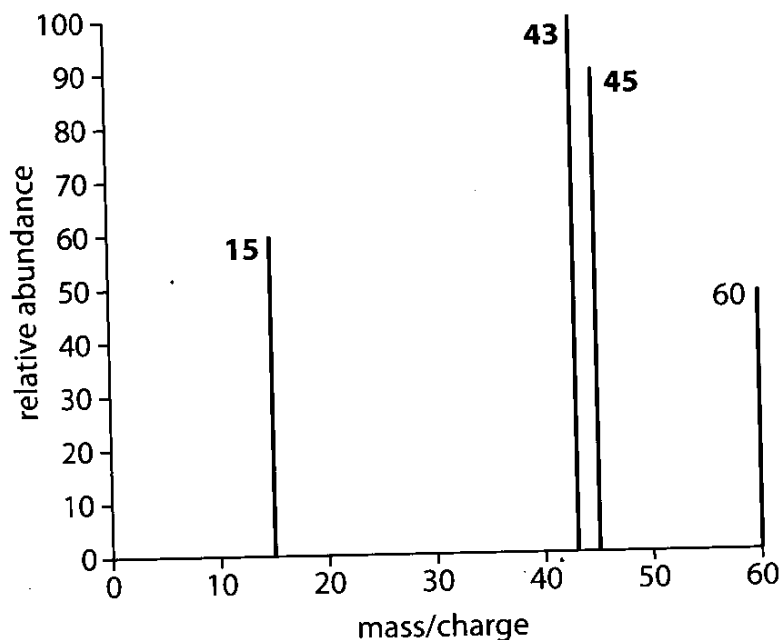
Solution:

Empirical formula = CH_2O; molecular formula = $C_nH_{2n}O_n$

We can see that the parent ion has a relative mass of 60.

M_r = n(12.01) + 2n(1.01) + n(16.00) = 30.03n

n = 60 ÷ 30.03 = 2

Molecular formula = $C_2H_4O_2$

From the spectrum we can identify the following peaks:

Peaks	Explanation
15 (60–45)	Presence of CH_3^+ - loss of COOH from molecule
43 (60–17)	Presence of $C_2H_3O^+$ - loss of OH from molecule
45 (60–15)	Presence of $COOH^+$ - loss of CH_3 from molecule

The structure consistent with this fragmentation pattern is:
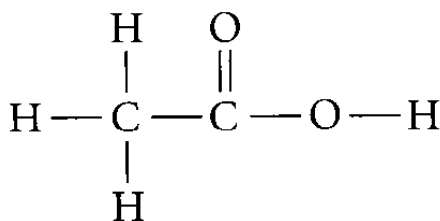
Exercise: The mass spectra of two compounds are shown below. One is propanone (CH_3COCH_3) and the other is propanal (CH_3CH_2CHO). Identify the compound in each case and explain the similarities and differences between the two spectra.
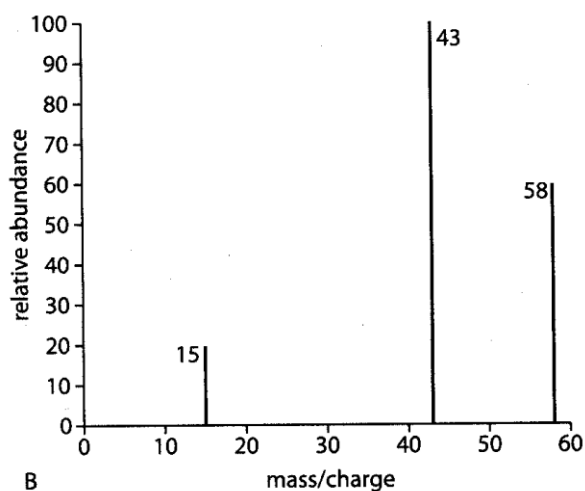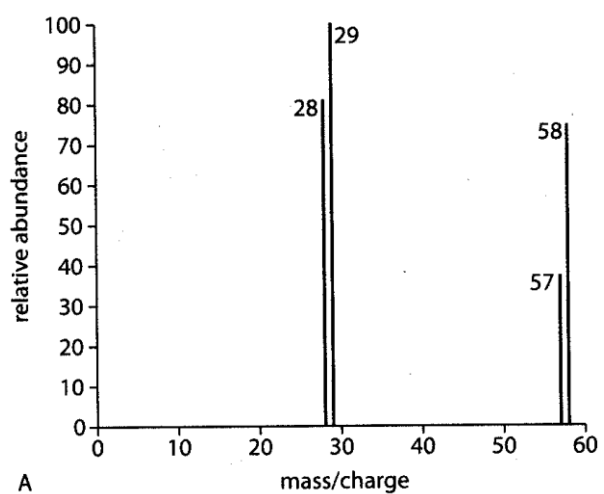
Exercise: The simplified mass spectrum of a compound with empirical formula C_2H_5 is shown below.
    (a) Explain which ions give rise to the peaks shown.
    (b) Deduce the molecular structure of the compound.
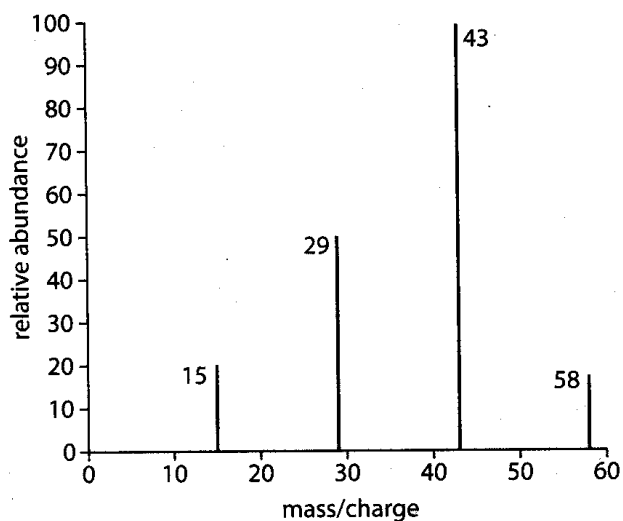
Reading a mass spectrum

When a molecule has been bombarded by high-energy electrons in the ionization chamber of a mass spectrometer, besides losing one electron to form an ion, the molecule also absorbs some of the energy transferred in its collision with the incident electrons. This extra energy places the molecular ion in an excited vibrational state. The vibrationally excited molecular ion may be unstable, and it may lose some of its extra energy by breaking apart into fragments. In a spectrum, one usually observes peaks corresponding to both the molecular ion and the fragments. For most classes of compounds, the mode of fragmentation is somewhat characteristic and hence predictable.

Let's take a look at some mass spectra for certain types of compounds. Identify the molecular ion peak, and the base peak for each of the spectra. What do these peaks tell you about the compounds in question? With your teacher's assistance, try to figure out what fragments are responsible for which peaks in the spectra. Keep an eye out for useful patterns.

Alkanes

For saturated hydrocarbons and organic structures containing large saturated hydrocarbon skeletons, the methods of fragmentation are quite predictable. What is known about the stabilities of carbocations in solution can be used to help us understand the fragmentation patterns of alkanes.

Mass spectrum. Relative abundance vs m/e. CH₃(CH₂)₆CH₃, M.W. = 114. Peaks labeled 29, 43, 57, 71, 85, M(114).

Mass spectrum. Relative abundance vs m/e. Isobutane structure CH₃—CH—CH₃ with CH₃ branch, M.W. = 58. Peaks labeled 43, M(58).

Aromatic Hydrocarbons

M(78)

M.W. = 78

Relative abundance

m/e

91

M(92)

M.W. = 92

Relative abundance

m/e

Alcohols

HO—CH₂CH₂CH₂CH₃
M.W. = 74

CH₃—CH—CH₂CH₃
|
OH
M.W. = 74

Halogen Compounds

Mass spectrum of $CH_3CH_2CH_2CH_2CH_2CH_2Br$, M.W. = 165, with peaks labeled 43, 85, 135, 137, M(164), M+2.

Mass spectrum of $CH_3CH_2CH_2CH_2CH_2-CH-CH_3$ with Cl substituent, M.W. = 134.6, with peaks labeled 56, 98, 99, 105, 107, M(134), M+2.

CH₃CH₂Cl
M.W. = 64.5

M(64)

M+2

Br—CH₂CH₃
M.W. = 109

M(108) M+2

Cl—CH₂—Cl
M.W. = 84.9

Br—CH₂—Br
M.W. = 173.8

Solve each of the following problems. Show any work required in the margins or on a separate piece of paper.

The separation of ions in a mass spectrometer depends on

A.   only the charge on the ions.

B.   only the mass of the ions.

C.   the mass and the charge of the ions.

D.   only the velocity of the ions.
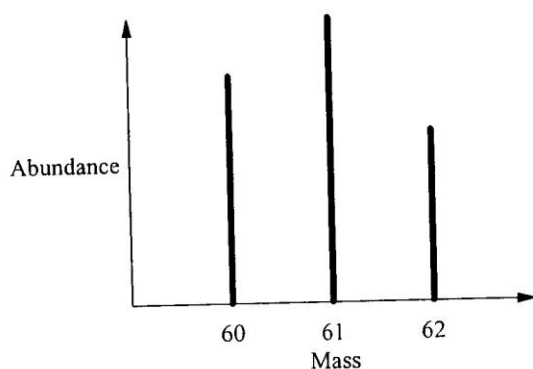
The mass spectrum of an element is shown above. Which statement about this element is correct?

A.   The three isotopes are separated after being converted to negative ions

B.   The isotope with mass 62 will be deflected more than the isotopes with masses 60 or 61

C.   The most abundant isotope contains 61 neutrons

D.   Its atomic mass will be between 60 and 61

What is the correct sequence for the processes occurring in a mass spectrometer?

A.   vaporization, ionization, acceleration, deflection

B.   vaporization, acceleration, ionization, deflection

C.   ionization, vaporization, acceleration, deflection

D.   ionization, vaporization, deflection, acceleration

The mass spectrum of $CH_3COOC_2H_5$ is **not** expected to show a major ion peak at which m/e ratio?

A.   88

B.   32

C.   29

D.   15

When injected into a mass spectrometer a compound gave a number of ion peaks. Two peaks, one of which was the molecular ion, had m/e values of 58 and 43. Which of the molecular fragments below might have been lost from the original molecule?

A. CH_3

B.   OH

C. C_2H_5

D.   CHO
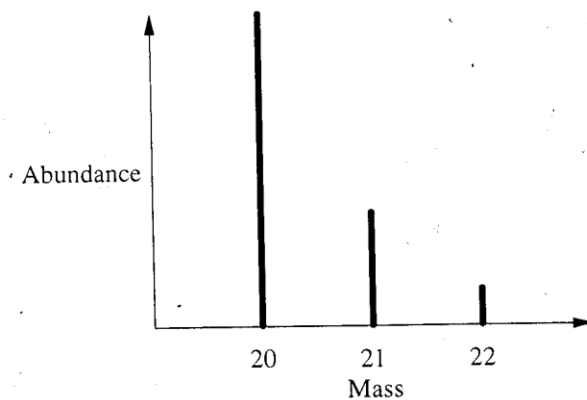
According to the mass spectrum above, the relative atomic mass of the element shown is best expressed as

A.   20.0.

B.   between 20.0 and 21.0.

C.   21.0.

D.   between 21.0 and 22.0.

Solve each of the following Paper 2 and 3 problems. Show any work in the space provided or on separate paper.

A sample of germanium is analysed in a mass spectrometer. The first and last processes in mass spectrometry are vaporization and detection.

(a)　(i)　State the names of the other three processes in the order in which they occur in a mass spectrometer.　　　*[2]*

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　　(ii)　For each of the processes named in (a) (i), outline how the process occurs.　　　*[3]*

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(b)　The sample of germanium is found to have the following composition:

Isotope	^{70}Ge	^{72}Ge	^{74}Ge	^{76}Ge
Relative abundance / %	22.60	25.45	36.73	15.22

　　(i)　Define the term *relative atomic mass*.　　　*[2]*

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　　(ii)　Calculate the relative atomic mass of this sample of germanium, giving your answer to two decimal places.　　　*[2]*

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(c)　Use the Aufbau principle to write the electron configuration of an atom of germanium.　　　*[1]*

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(d)   The successive ionization energies of germanium are shown in the following table:

	1st	2nd	3rd	4th	5th
Ionization energy / kJ mol^{-1}	760	1540	3300	4390	8950

(i)   Identify the sub-level from which the electron is removed when the first ionization energy of germanium is measured.   *[1]*

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(ii)   Write an equation, including state symbols, for the process occurring when measuring the second ionization energy of germanium.   *[1]*

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(iii)   Explain why the difference between the 4th and 5th ionization energies is much greater than the difference between any two other successive values.   *[2]*

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The existence of isotopes in magnesium can be shown using a mass spectrometer. The operation of a mass spectrometer can be described in terms of five main stages. The first is evaporation and the last is detection.

(a)   After evaporation, the magnesium is then ionised. Outline how it is ionised.   *[2]*

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(b)   State the names, in the correct order, of the other two stages, and in **each** case state the technique used.   *[4]*

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(c)   The relative abundances of the three isotopes of magnesium are as follows:

$$^{24}Mg = 78.6\,\%,\ ^{25}Mg = 10.1\,\%,\ ^{26}Mg = 11.3\,\%.$$
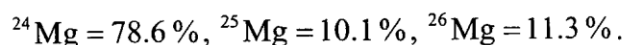
Calculate the relative atomic mass of magnesium using these values, giving your answer to three decimal places.   *[2]*

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(d)   Write the electronic configuration of magnesium using the spdf notation.   *[1]*

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The diagram below represents the spectrum of chlorine, consisting of five peaks, labelled I, II, III, IV and V respectively. **Peak I is due to the $^{35}Cl^+$ ion.**
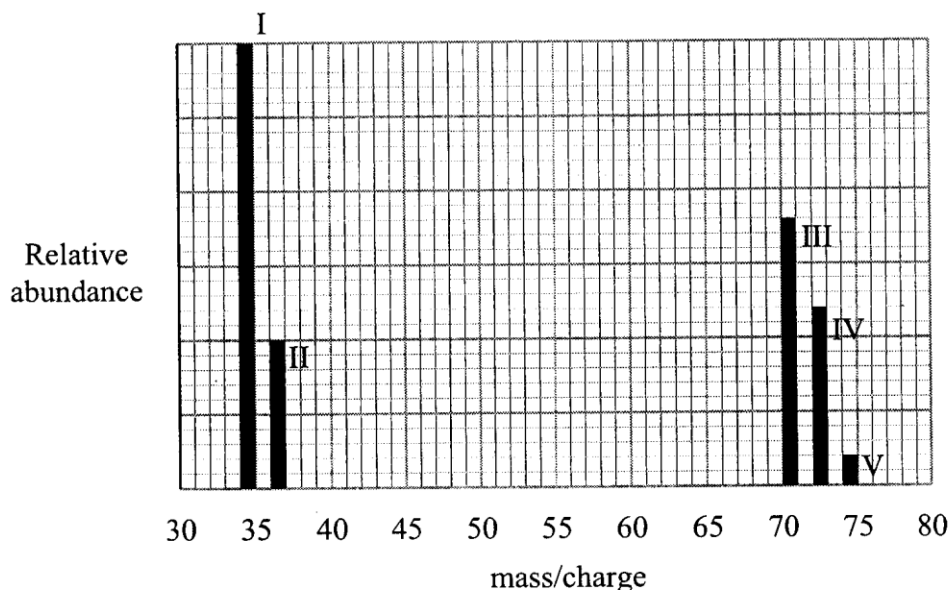
(a)　What analytical technique would give a spectrum like that shown above?　　　　*[1]*

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(b)　State why the spectrum of chlorine consists of more than two peaks.　　　　*[1]*

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(c)　Suggest what peaks II and IV might be due to.　　　　*[2]*

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(d)　Using the spectrum above, find the isotopic composition of chlorine and justify your answer.　　*[2]*

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(e)　(i)　How is a molecular ion formed?　　　　*[1]*

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　　(ii)　What information could be obtained from the mass/charge value of the molecular ion?　　*[1]*

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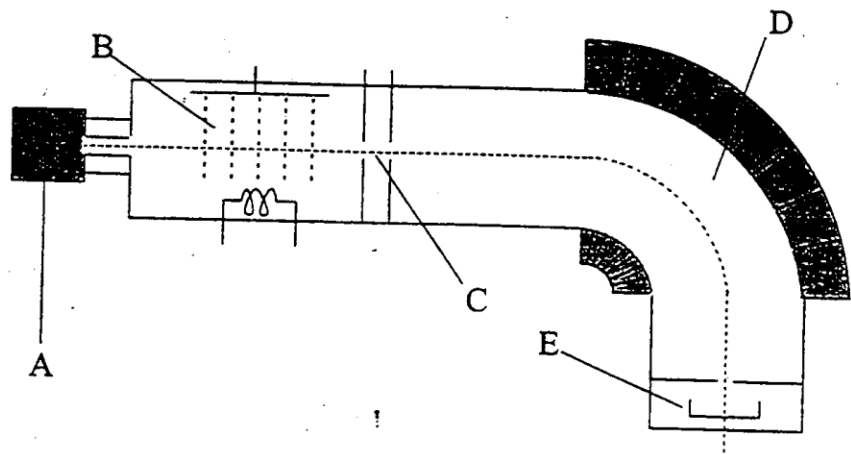
(a)   Above is a diagram of a simple mass spectrometer. State which of the sections below corresponds to which lettered part of the spectrometer.

Section	Letter
Accelerating potential	
Gaseous sample	
Electron bombardment ionisation	
Detector	
Magnetic field to deflect ions	

[3 marks]

(b)   Why must the inside of the spectrometer be kept at a high vacuum?   *[1 mark]*

. . . .

. . . .

(c)   The spectrometer is set up so that an ion X^+ is focussed on the detector. The settings are left unchanged and an ion with a mass less than that of X^+ travels through the magnetic field. State and explain whether this ion will be deflected more than, or less than, X^+.

[2 marks]

. . . .

. . . .

(d)   The mass spectrum of propane is shown below:

Ion intensity

m/z
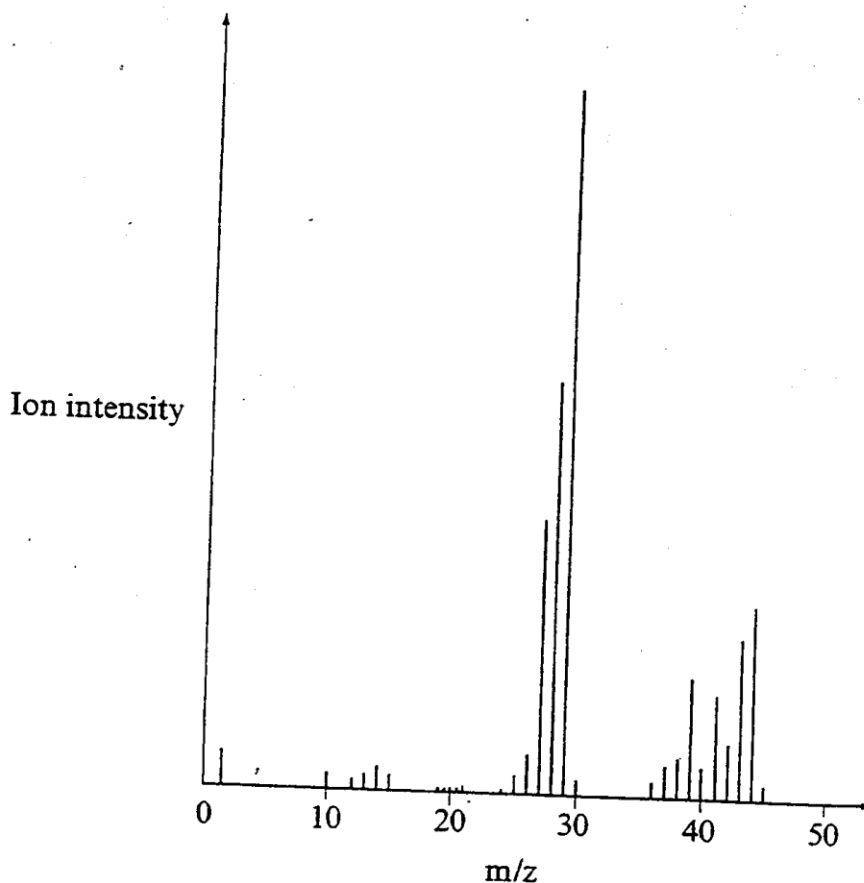
(i)   Why is there a small peak at m/z = 45 ?

                   [1 mark]

. . . .

. . . .

(ii)   Why are there no peaks at higher m/z values?

                   [1 mark]

. . . .

. . . .

(iii)   What is the formula of the ion responsible for the peak of greatest intensity?

                   [1 mark]

. . . .

. . . .