NMR & Mass Spectroscopy

Question 1

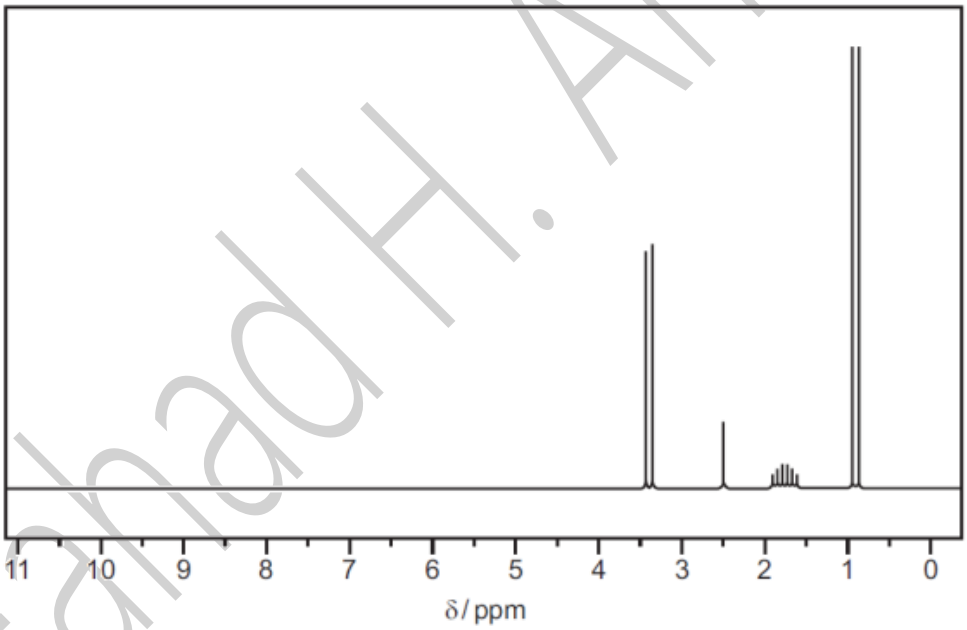
8 **T** is a saturated alcohol. It was analysed by mass spectroscopy and NMR spectroscopy.
In the mass spectrum, the molecular ion peak, M, was at an m/e value of 74 and the ratio of the heights of the M and M+1 peaks was 20.4 : 0.9.

(a) **(i)** Use the ratio of the heights of the M and M+1 peaks to calculate the number of carbon atoms in a molecule of **T**.

(ii) What is the molecular formula of **T**?

molecular formula = ...
[3]

(b) The NMR spectrum of **T** given below shows four absorptions. The absorption at 1.8 ppm is a multiplet and that at 2.5 ppm is a singlet.



(i) Use this information and your answer to **(a)(ii)** to deduce the structure of **T**.

T

(ii) Describe and explain which type of proton is responsible for each of the absorptions.

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(iii) The absorption at 1.8 ppm is a multiplet and that at 2.5 is a singlet.
State and explain the splitting patterns of the other absorptions, at 0.9 and 3.4 ppm.

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(iv) Describe and explain how the NMR spectrum of **T** dissolved in D_2O would differ from the one shown.

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[9]

[Total: 12]

w/14/qp41

Question 2

8 Instrumental analysis plays an increasingly important role in modern chemistry. Two important techniques are NMR spectroscopy and X-ray crystallography.

(a) Both techniques use part of the electromagnetic spectrum.
Which technique uses radiation with the longer wavelength, and in which part of the spectrum is it found?

.....

[1]

(b) NMR spectroscopy provides detailed information about protons, but X-ray crystallography is unable to detect them. Explain these facts.

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.....

[2]

(c) The protein found in hair contains the amino acid cysteine, $C_3H_7SNO_2$. Crystalline cysteine was examined using X-ray crystallography. State which atom produced the strongest reflection, explaining your answer.

.....

.....

[1]

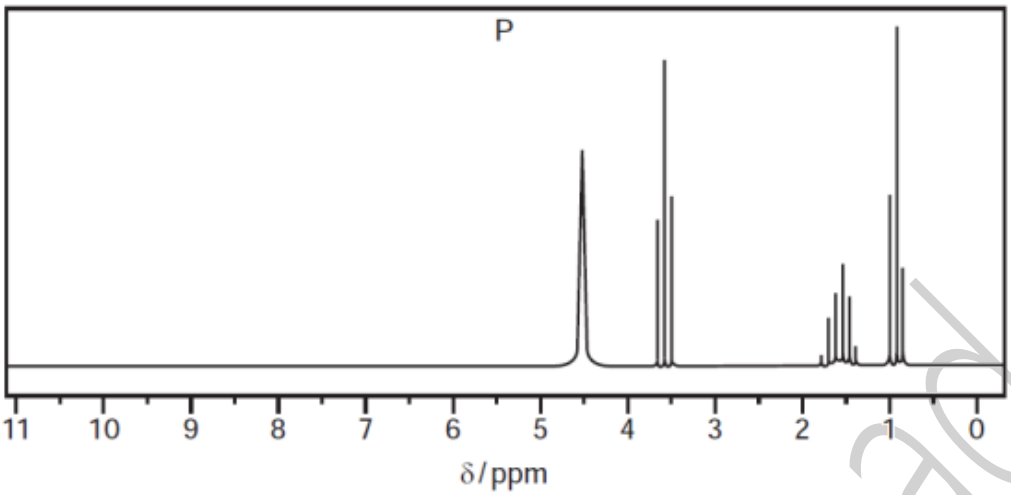
(d) Compound **P** is an alcohol that can be converted into compound **Q** in the following reaction sequence.

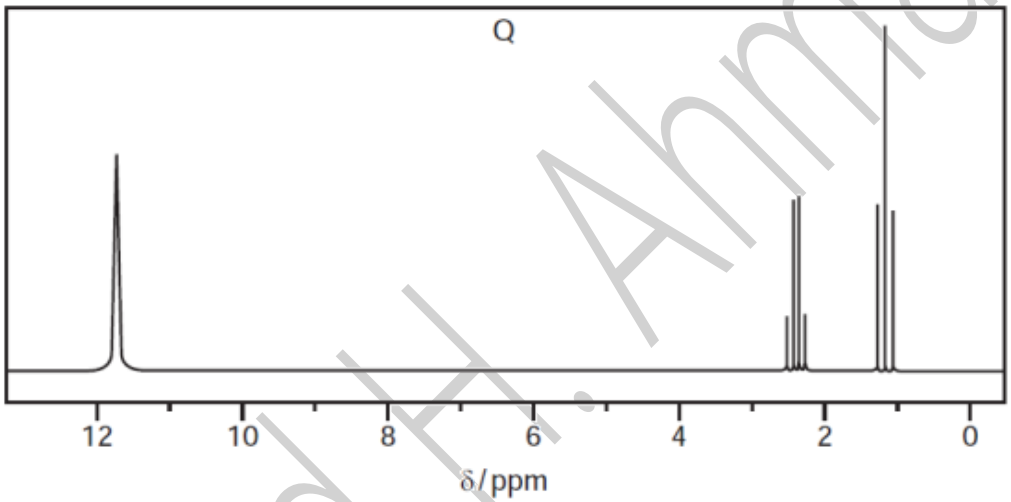
$$\mathbf{P} \rightarrow C_xH_6O \rightarrow \mathbf{Q}$$

Spectral analyses of **P** and **Q** were carried out.

(i) The mass spectrum of **P** shows an M : M+1 peak ratio of 4.5 : 0.15.
Calculate the number of carbon atoms in **P**.

The NMR spectra of **P** and **Q** are shown below.





(ii) In the spectrum of **P**, clearly label the peak due to the –OH group with an **X**.

(iii) State how many different proton environments are present in compound **Q**.

.....

(iv) What evidence is there in these spectra that **P** is a primary rather than a secondary alcohol?

.....

.....

.....

(v) Draw a structure for **Q**.

[6]

[Total: 10]

w/13/qp43

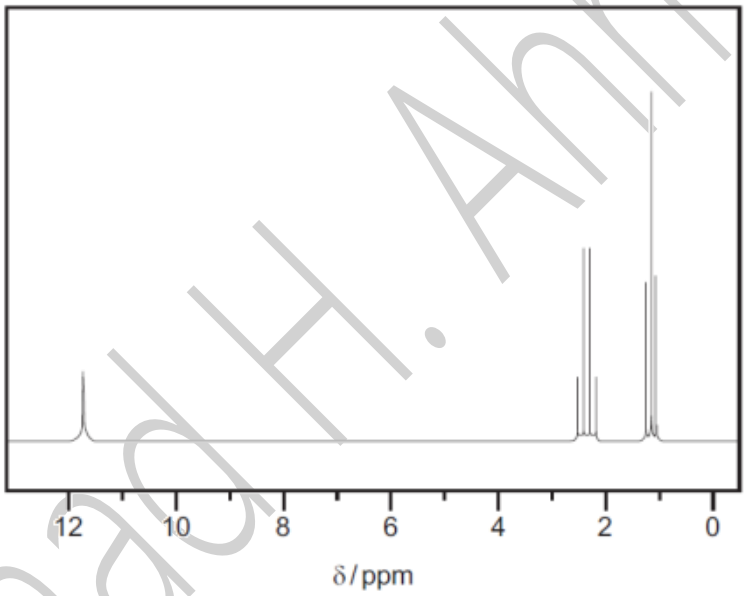
Question 3

7 The combination of mass spectroscopy and NMR spectroscopy provides a powerful method of analysis for organic compounds.

(a) The mass spectrum of a compound **G** contains M and M+1 peaks in the ratio of their heights of 74 : 2.5.
Use these data to calculate the number of carbon atoms present in **G**. Show your working.

[2]

(b) The NMR spectrum of compound **G** is shown.



(i) Use the *Data Booklet* and your knowledge of NMR spectroscopy to identify the type of proton responsible for each of the three absorptions.

δ / ppm	type of proton
1.1	
2.2	
11.8	

(ii) The addition of D_2O causes one of these absorptions to disappear.
Explain why this happens and state which absorption is affected.

.....

.....

(iii) Draw the structural formula of **G**.

[6]

(c) Several structural isomers of **G** exist.

(i) Draw the structural formula of an isomer of **G** with only two absorptions in its NMR spectrum.

(ii) Use the *Data Booklet* to suggest where these absorptions would occur.

peak	δ / ppm
1	
2	

[3]

[Total: 11]

s/14/qp41

Question 4

7 The techniques of mass spectrometry and NMR spectroscopy are useful in determining the structures of organic compounds.

(a) The three peaks of highest mass in the mass spectrum of organic compound **L** correspond to masses of 142, 143 and 144.
The ratio of the heights of the M : M+1 peaks is 43.3 : 3.35, and the ratio of heights of the M : M+2 peaks is 43.3 : 14.1.

(i) Use the data to calculate the number of carbon atoms present in **L**.

(ii) Explain what element is indicated by the M+2 peak.

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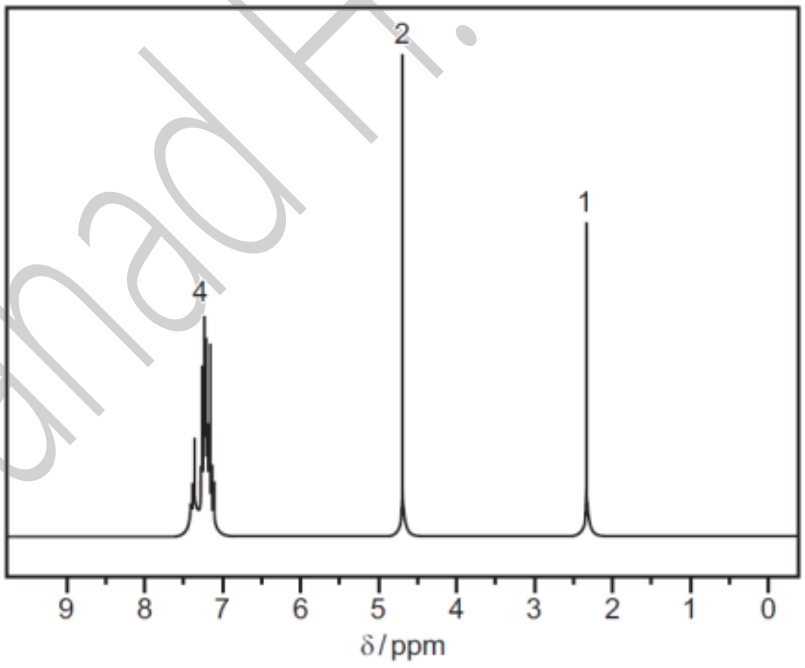
.....

Compound **L** reacts with sodium metal. The NMR spectrum of compound **L** is given below.



(iii) What does the NMR spectrum tell you about the number of protons in **L** and their chemical environments?

.....

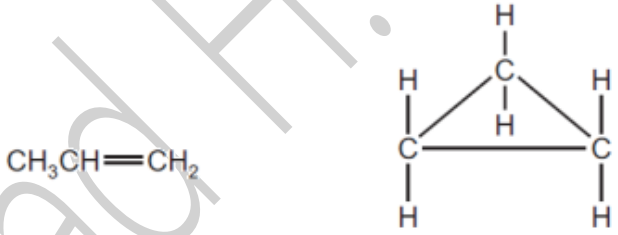
.....

(iv) Use the information given and your answers to **(i)**, **(ii)** and **(iii)** to deduce a structure for **L**.
Explain how you arrive at your answer.

structure of **L**

[7]

(b) The molecular formula C_3H_6 represents the compounds propene and cyclopropane.



propene cyclopropane

(i) Suggest **one** difference in the fragmentation patterns of the mass spectra of these compounds.

.....

.....

(ii) Suggest **two** differences in the NMR spectra of these compounds.

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.....

.....

[3]

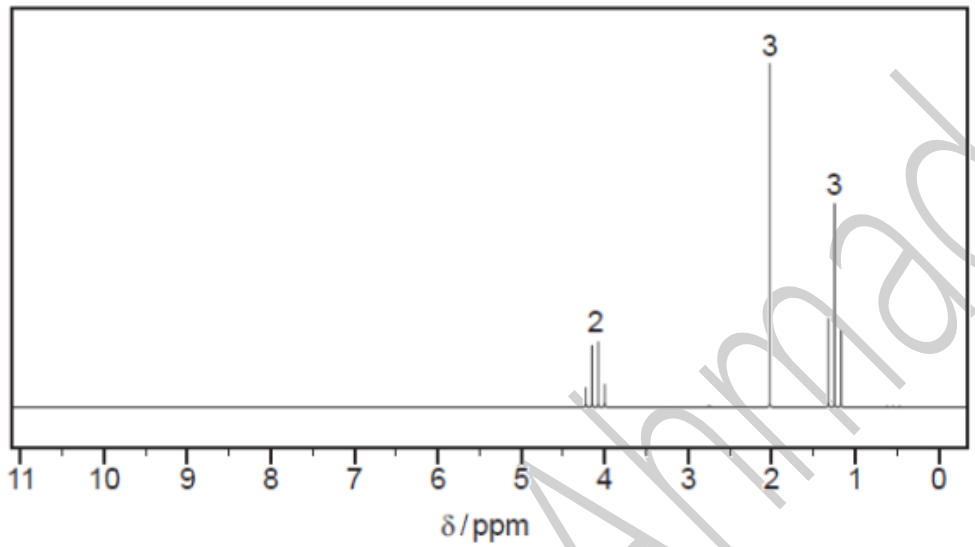
[Total: 10]

s/13/qp42

Question 5

(c) A sample of a liquid, **P**, was found at the scene of the crime and was analysed using mass spectrometry and NMR spectroscopy.

The mass spectrum has M and M+1 peaks in the ratio of 5.1: 0.22 with the M peak at *m/e* = 88.
The NMR spectrum is shown



Use the data to suggest a structure for **P**, explaining your answer.

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structure of **P**

[5]

Question 6

7 Different analytical techniques are used to build up a picture of complex molecules. Each technique on its own provides different information about complex molecules but together the techniques can give valuable structural information.

(a) Complete the table, identifying the technique which can provide the appropriate structural information.

structural information	analytical technique
three-dimensional arrangement of atoms and bonds in a molecule	
chemical environment of protons in a molecule	
identity of amino acids present in a polypeptide	

[3]

(c) A combination of mass spectrometry and NMR spectroscopy is often enough to determine the structure of a simple organic compound.
The organic compound **N** produced a mass spectrum in which the ratio of the M:M+1 peaks was 5.9:0.20, and which had an M+2 peak of similar height to the M peak.

(i) Calculate how many carbon atoms are present in one molecule of **N**.

(ii) Deduce which element, other than carbon and hydrogen, is present in **N**.

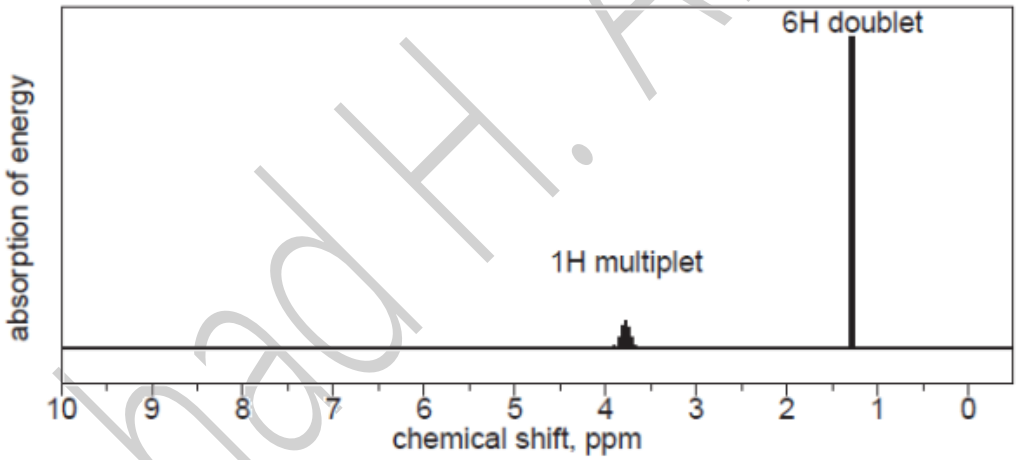
.....

(iii) Explain how many atoms of this element are present in one molecule of **N**.

.....

.....

The NMR spectrum of **N** is shown.



(iv) State the empirical formula of **N** and, using the NMR data, suggest the structural formula of **N**, explaining your reasons.

[6]

Question 7

(c) Another important technique used to examine the structure of proteins is X-ray crystallography. In this technique the position of individual atoms can be determined, and the distances between them measured.

(i) Hydrogen atoms never produce images using X-ray crystallography. Explain why this is the case.

.....

.....

(ii) Suggest and explain which one of the atoms in a molecule of cysteine, $H_2NCH(CH_2SH)CO_2H$, would show up most clearly using X-ray crystallography.

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.....

[3]

w/11/qp41

Question 8

(b) NMR spectroscopy is a very important analytical technique for use with organic compounds.

(i) Why is NMR spectroscopy particularly useful for organic compounds?

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.....

(ii) Two molecules, propanal and propanone, have the same molecular formula, C_3H_6O. Draw the displayed formula of each compound and explain briefly how NMR spectroscopy can distinguish between the two structures.

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.....

[4]

[Total: 9]

w/10/qp43

Question 9

8 **(a)** NMR spectroscopy and X-ray crystallography are two techniques that use electromagnetic radiation to look at the structures of large molecules.

For each technique state the sub-atomic particle involved, and explain how this particle interacts with the radiation.

NMR.....

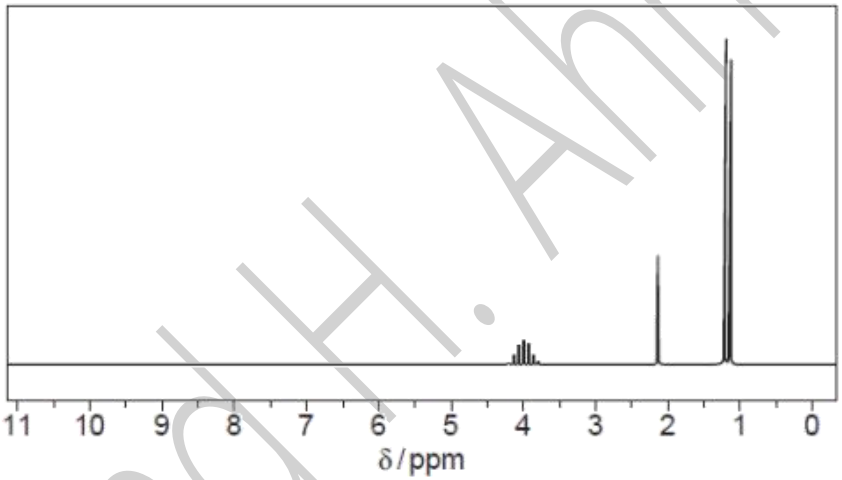
.....

X-ray .....

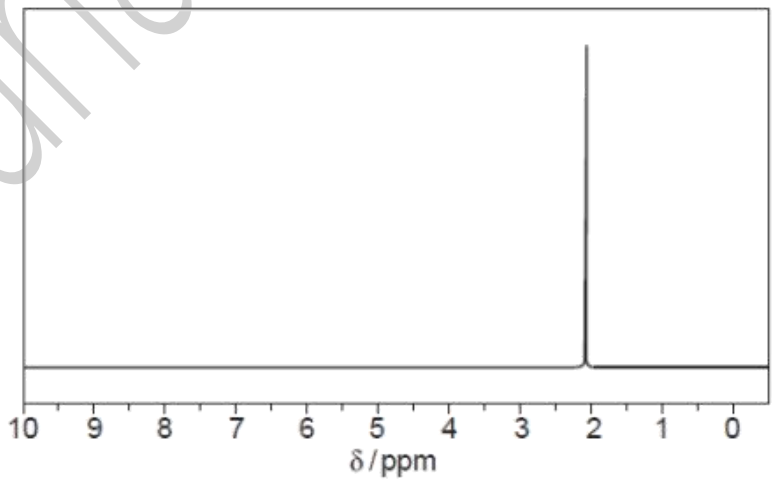
.....

[4]

(b) The two NMR spectra **1** and **2** were obtained before and after an alcohol, **Y**, was oxidised to give compound **Z**. The numbers of hydrogen atoms responsible for each peak have **not** been shown. All the peaks have been shown.



1



2

(i) State which spectrum, **1** or **2**, was produced by the alcohol, giving a reason for your answer.

spectrum .....

reason .....

.....

(ii) The mass spectrum of **Y** showed an M : M+1 peak ratio of 17.6:0.6.
Use this and other information in the question to suggest the identities of both **Y** and **Z**.

(iii) Draw a displayed formula for **Y** in the box provided

Y is

(iv) Explain why the NMR spectrum of **Z** only shows one peak.

.....

.....

[7]

[Total: 11]

Question 10

(c) Compounds used as pesticides may contain bromine or chlorine.

(i) What would be the difference in the ratio of the M: M+2 peaks if the pesticide contained one chlorine rather than one bromine atom?

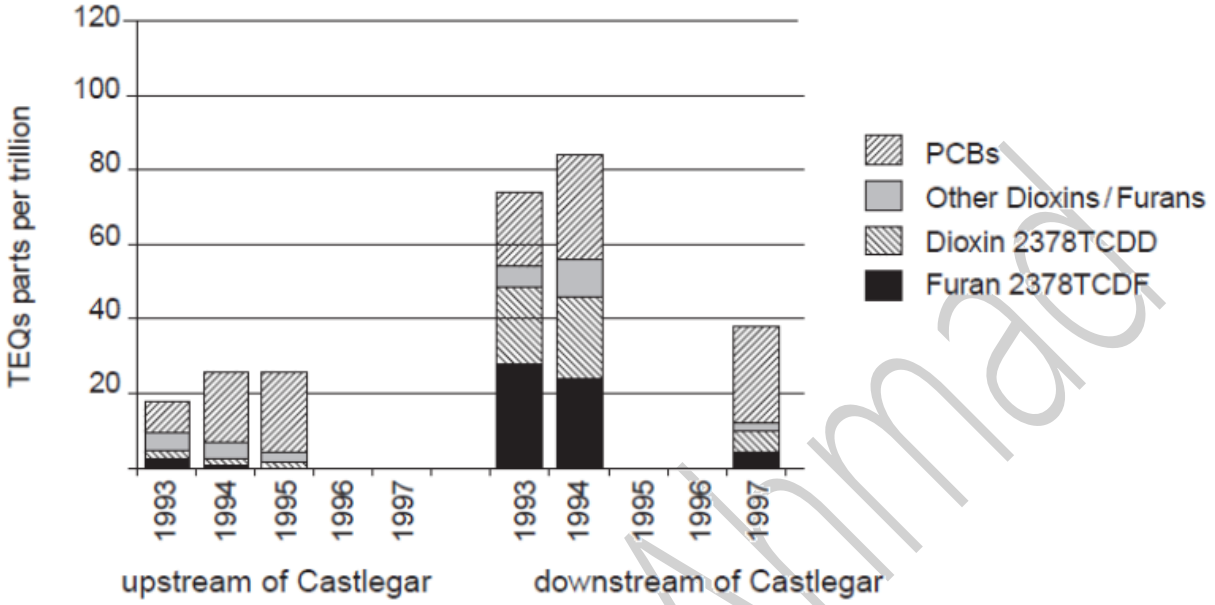
.....

(ii) If a given pesticide contains **two** chlorine atoms per molecule, deduce the relative heights of the M, M+2 and M+4 peaks.

[3]

(d) The following graph shows the occurrence of pesticide residues in the eggs of fish-eating birds of prey upstream and downstream of a paper mill at Castlegar on the Columbia River in Canada.

Columbia River Basin



PCBs, the dioxin 2378TCDD, and the furan 2378TCDF all come from chemicals containing chlorine.

(i) Suggest which compounds are present directly as a result of the paper mill.

.....

(ii) By studying the data for 1994, suggest which chemical(s) come from sources other than the paper mill.

.....

(iii) Compare the downstream data for 1994 with that for 1997. Suggest what might be responsible for the change.

.....

(iv) A molecule of 2378TCDD contains four chlorine atoms. How many molecular ion peaks would this compound show in its mass spectrum?

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[4]

w/09/qp42

Question 11

7 This question is about the modern techniques of analysis which may be used to determine molecular structures.

(a) In X-ray crystallography X-rays are diffracted by the electron clouds surrounding individual atoms in the structure.

(i) What useful information is provided by X-ray crystallography?

.....

.....

(ii) Why cannot hydrogen atoms in a structure be detected by this technique?

.....

[2]

(b) Suggest how structures of complex molecules such as enzymes, derived from X-ray crystallography, can help explain their biochemical behaviour.

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.....

..... [2]

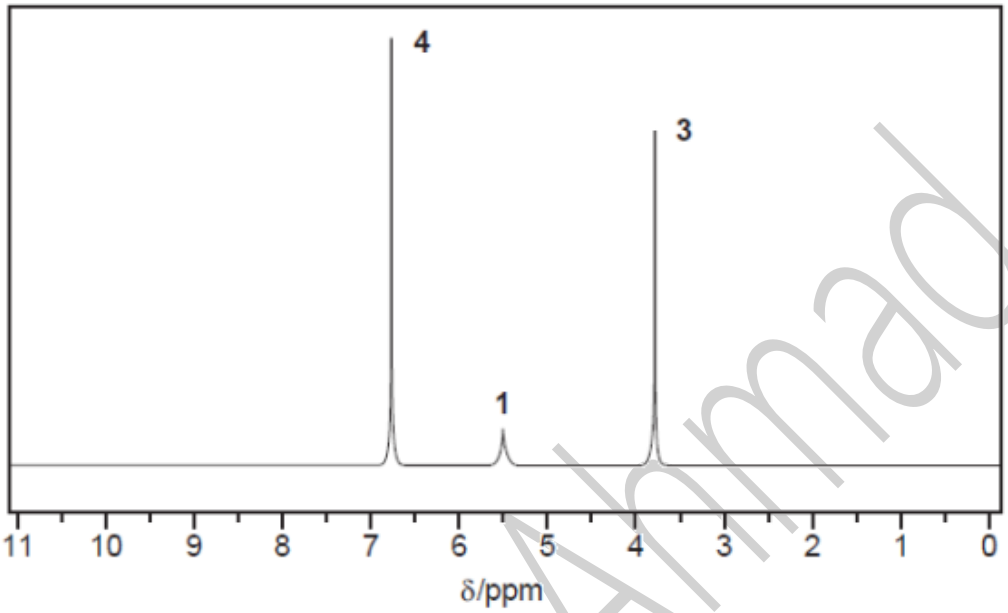
(c) NMR spectroscopy, in contrast to X-ray crystallography, is frequently used to examine protons in organic molecules.

(i) What feature of protons enables their detection by NMR spectroscopy?

.....

(ii) The NMR spectrum below was obtained from a compound **X**, $C_xH_yO_z$. In the mass spectrum of the compound, the M : M+1 ratio was found to be 25:2.

Determine the values of x, y and **z** in the formula of **X** and deduce a possible structure for the compound, explaining how you arrive at your conclusion.



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.....

Possible structure of **X**

[6]

[Total:10]

Question 12

(b) NMR and X-ray crystallography have made significant contributions to our knowledge of the structure of proteins and, in the pharmaceutical industry, how drugs react with target proteins.

(i) Suggest an advantage of **each** technique in helping to determine protein structure.

.....

.....

.....

(ii) MRI scanning is a medical technique based on NMR spectroscopy. It is particularly useful for looking for tumours in healthy tissue.

Suggest how this technique can distinguish tumour tissue from healthy tissue.

.....

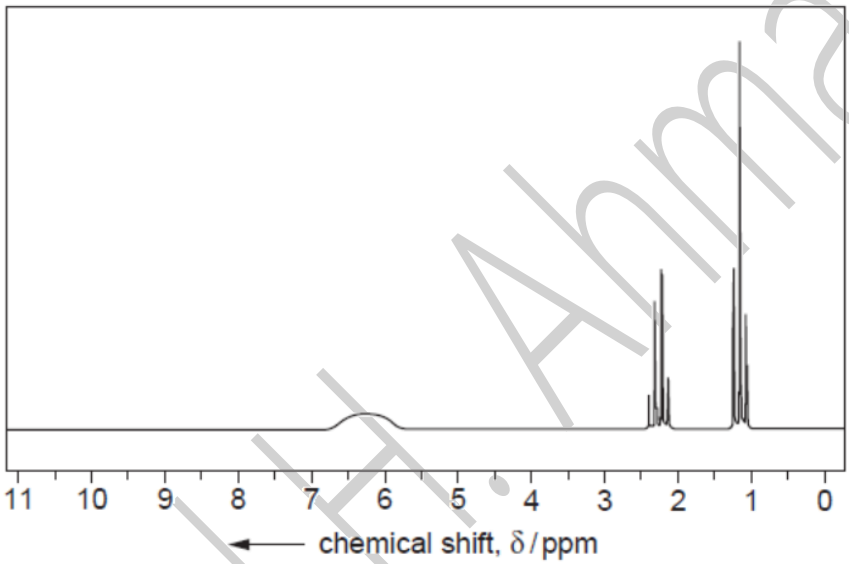
.....

[3]

(c) A saturated molecule of formula C_xH_yNO was subjected to analysis by mass spectrometry and NMR spectroscopy. In the mass spectrum of the compound, the M peak was at *m/e* 73 and the ratio of the heights of the M:M+1 peak was 48:1.7.

(i) Using the data from the mass spectrum, determine the values of *x* and *y* in the formula of the compound.

(ii) Use the data from **(i)** together with the NMR spectrum below to deduce a structure for the compound, explaining how you arrive at your answer.



w/08/qp4

Question 13

1 **(a)** Natural bromine consists of the two isotopes ^{79}Br and ^{81}Br in roughly equal proportions.

The mass spectrum of bromine consists of 5 peaks.

(i) Suggest the mass numbers for the 5 peaks and the identities of the species responsible for them.

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.....

.....

(ii) Suggest the ratios of the relative abundances of

- the three lines with the highest mass numbers,

.....

- the two lines with the lowest mass numbers.

.....

[4]

Esters of 2,3-dibromopropan-1-ol with phosphoric acid are useful flame retardants used in plastics and fibres.

2,3-dibromopropan-1-ol can be made from propenal by the following two-stage process.

(b) **(i)** Draw the structure of the intermediate **A** in the box opposite.

(ii) Suggest reagents and conditions for

- reaction I,

.....

- reaction II.

.....

[3]

(c) The mass spectrum of 2,3-dibromopropan-1-ol includes the following peaks.

mass number	relative abundance
31	100
106	44
108	45
185	0.3
187	0.6
189	0.3

(i) At what mass number would you expect the molecular ion to occur?

.....

(ii) Identify the molecular formula (including isotopic composition where relevant) of these 6 peaks.

mass number	molecular formula
31	
106	
108	
185	
187	
189	

[5]

Question 14

9 **(a)** Explain with reference to energy states how ^1H NMR can supply information about the structure of molecules.

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.....

.....

.....[3]

(b) Nuclear magnetic resonance is used in magnetic resonance imaging scanners. These scanners are increasingly used in hospitals to detect tumours. Suggest why magnetic resonance techniques are better than X-rays.

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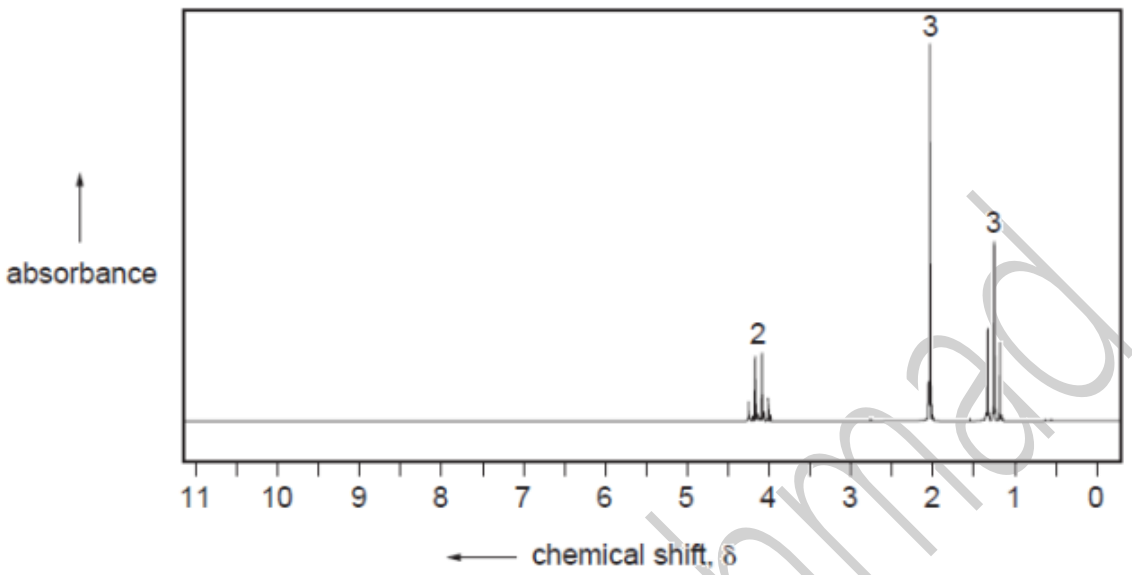
.....[2]

(c) The NMR spectrum shown below was obtained from a simple organic molecule, **G**, $C_xH_yO_2$. When a sample of **G** was placed in a mass spectrometer, the ratio of the M : M+1 peaks for the molecule was 14.5 : 0.66.



(i) Calculate how many carbon atoms there are in the molecule.

(ii) Use the NMR spectrum and the *Data Booklet* to work out the structure of **G**.

[5]

[Total: 10]

w/07/qp4

Question 15

7 NMR and X-ray crystallography are two important analytical techniques which can be used to study the structure and function of molecules.

(a) Nuclear magnetic resonance, NMR, arises because protons possess spin which generates a small magnetic moment. When an external magnetic field is applied the protons can align with or against the external field. If they are given a small amount of energy in the radio frequency range each can be 'promoted' so that their magnetic moment opposes the external field.

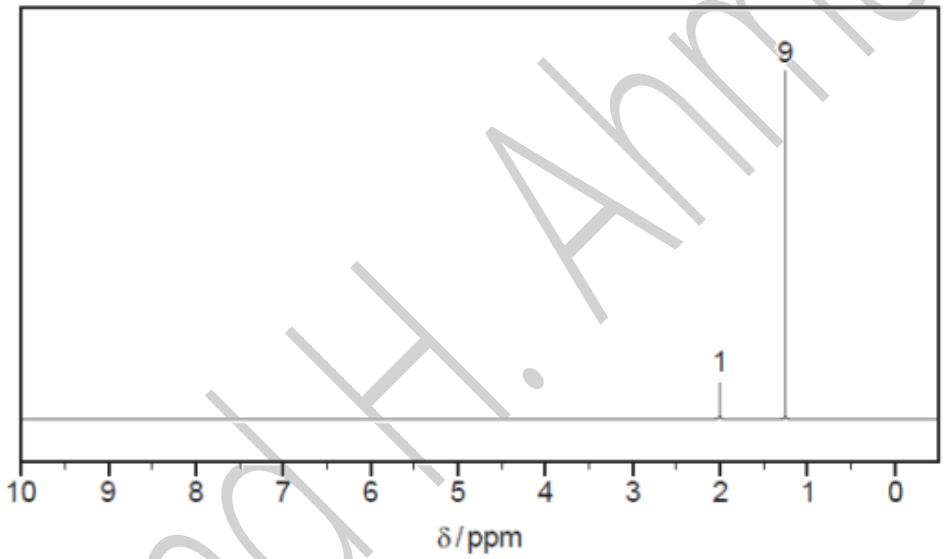
Two factors can influence the energy required for this promotion. What are they?

(i) .....

(ii) .....

[2]

(b) A compound, **J**, has the formula $C_4H_{10}O$. The NMR spectrum of **J** is shown.



(i) Indicate the groups responsible for each peak and hence deduce the structure of **J**.

peak at 1.26 δ ..... peak at 2.0 δ .....

structure of **J**

(ii) There are three other isomers of **J** containing the same functional group as **J**. Draw the structures of two of these three isomers and indicate how many different chemical shifts each would show in its NMR spectrum.

isomer 1 isomer 2

number of groups of peaks ..... number of groups of peaks .....

[6]

(c) X-ray crystallography can be useful in gathering information about the structure of large organic molecules, such as nucleic acids.

(i) Which element will show up most strongly in the X-ray crystallography of a nucleic acid? Explain your answer.

.....

.....

(ii) X-ray crystallography will **not** detect hydrogen atoms. Explain why this is so.

.....

.....

[2]

[Total: 10]

s/12/qp42

Question 16

(c) Propene was treated with bromine in the presence of chloride ions and the product analysed using mass spectrometry.

A group of peaks was found in the range *m/e* 156–160 with the following relative heights.

m/e	relative height
156	3
158	4
160	1

(i) Identify the species responsible for each of these peaks.

156 .....

158 .....

160 .....

A large peak was present in the spectrum with a *m/e* value of less than 20.

(ii) Suggest the *m/e* value for the peak and the species that produced it.

m/e .....

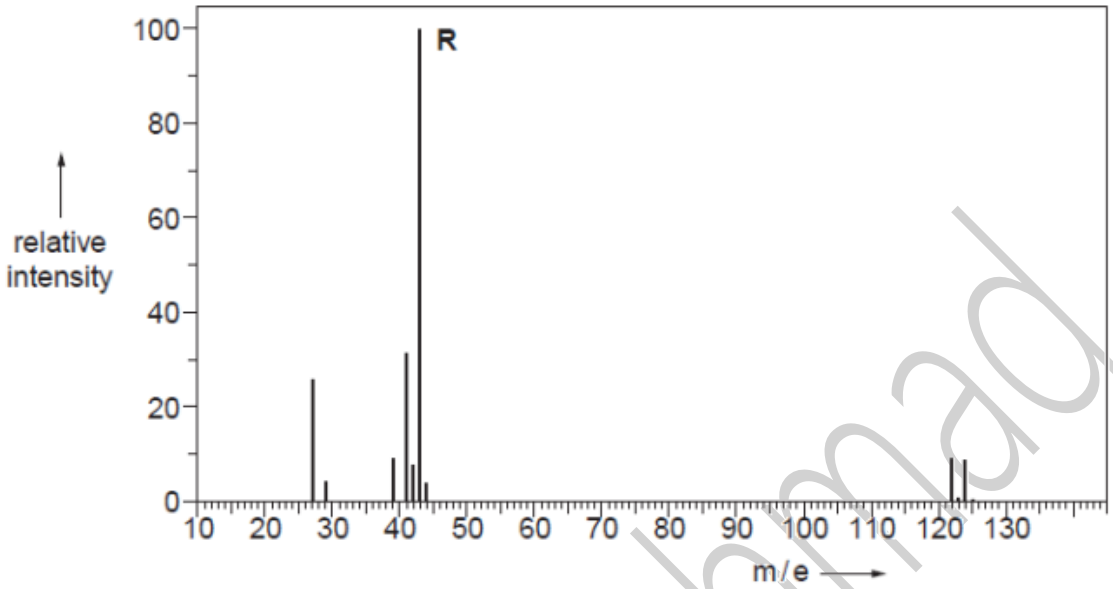
species .....

[4]

s/12/qp41

Question 17

(c) The mass spectrum shown was obtained from a compound of formula C_pH_qX, where X represents a halogen atom.



(i) Deduce the identity of X, giving a reason.

X is .....

.....

(ii) If the relative heights of the M and M+1 peaks are 9 and 0.3 respectively, calculate the value of p. Use this value and the m / e value of the molecular ion to calculate the value of q, and hence the molecular formula of the compound. Show your working.

(iii) Suggest a formula for the ion responsible for the peak labelled **R**.

..... [4]

(d) In the fragmentation of alcohols which occurs in a mass spectrometer, small stable, neutral molecules are sometimes produced. Suggest the identity of **two** such molecules, each with an M_r less than 30.

(i) ..... **(ii)** ..... [2]

[Total: 10]

s/11/qp41

Question 18

(d) When reacted with a small quantity of water, $SiCl_4$ produces an oxychloride **X**, $Si_xCl_yO_z$. The mass spectrum of **X** shows peaks at mass numbers of 133, 149, 247, 263 and 396. (You should assume that the species responsible for all these peaks contain the ^{16}O, the ^{35}Cl and the ^{28}Si isotopes only.)

(i) Use these data to deduce the molecular formula of **X**.

molecular formula .....

(ii) Suggest the structures of the fragments responsible for the peaks at the following mass numbers.

mass number	structure
133	
247	
263	

(iii) Hence suggest the displayed formula of **X**.

[5]

Question 19

9 A range of modern analytical techniques has made the identification of molecules, and atoms in compounds, much more rapid than traditional laboratory analysis.

(a) One instrumental technique is NMR spectroscopy, which uses the fact that under certain conditions protons can exist in two different energy states.
Explain how these different energy states arise.

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.....

.....[2]

(b) When methanol, CH_3OH, is examined using NMR spectroscopy, it absorbs at two different frequencies. Explain why, and predict the relative areas of the two peaks.

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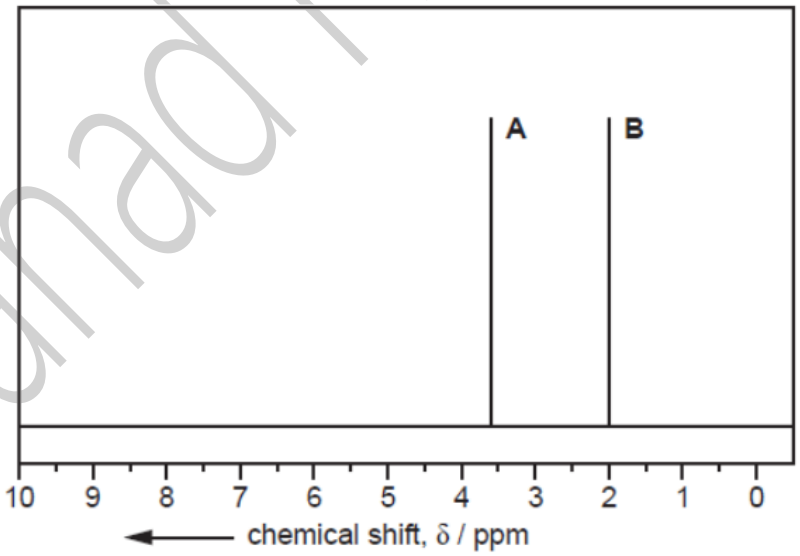
.....

.....[2]

(c) The NMR spectrum below is that of one of three possible isomers of molecular formula $C_3H_6O_2$.



The compound could be propanoic acid, methyl ethanoate or ethyl methanoate.

(i) In the boxes provided, draw the structures of the three compounds.

propanoic acid	methyl ethanoate	ethyl methanoate

(ii) Explain which compound produced the spectrum shown, indicating which protons are responsible for each of the peaks **A** and **B**.

.....

.....

.....

(iii) The NMR spectrum of another of the compounds has a peak at δ11.0.
State which compound this would be, and identify the proton(s) responsible for this peak.

compound .....

proton(s) .....

[4]

(d) X-ray crystallography is a technique used to identify the relative positions of atoms in a crystal of a compound.

(i) What further information about organic macromolecules can be deduced by the use of X-ray crystallography?

.....

.....

(ii) Which atoms cannot be located by X-ray crystallography?

.....

[2]

[Total: 10]

s/10/qp41

Question 20

(b) Nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry are also used in the detection of certain molecules, particularly those containing hydrogen atoms.

(i) Explain how and why the NMR spectrum of propanal, CH_3CH_2CHO, would be different from that of propanone, CH_3COCH_3, which contains the same atoms.

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(ii) Explain how and why the mass spectrum of the two compounds in **(i)** would be different.

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.....

[4]

(c) At one time, bromomethane, CH_3Br, was widely used to control insect pests in agricultural crops and timber. It is now known to break down in the stratosphere and contribute to the destruction of the ozone layer.

Samples can be screened for traces of bromomethane by subjecting them to mass spectrometry.

(i) Which peak(s) would show the presence of bromine in the compound?

.....

(ii) How could you tell by studying the M and M+2 peaks that the compound contained bromine rather than chlorine?

.....

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[3]

s/08/qp4

Question 21

(c) Gently heating ammonium nitrate, NH_4NO_3, in a test tube produces a mixture of two gases **A** and **B**. No residue remains in the tube.
The mass spectrum of gas **A** contains peaks at *m/e* (mass number) values of 16, 17 and 18, whereas that of gas **B** has peaks at *m/e* values of 14, 16, 28, 30 and 44.

(i) Identify the peaks in the mass spectra, and suggest the molecular formulae of the gases **A** and **B**.

.....

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.....

.....

(ii) Hence suggest an equation for the thermal decomposition of ammonium nitrate.

.....

[5]

s/07/qp4