F324: Rings, Polymers & Analysis
4.3.2 - Spectroscopy

1. An industrial chemist discovered five bottles of different chemicals (three esters and two carboxylic acids) that were all labelled $C_5H_{10}O_2$.

The different chemicals had the structural formulae below.

$CH_3CH_2COOCH_2CH_3$ **$(CH_3)_3CCOOH$** **$CH_3COOCH(CH_3)_2$**

$(CH_3)_2CHCH_2COOH$ **$(CH_3)_2CHCOOCH_3$**

(a) The chemist used both infrared and ^{13}C NMR spectroscopy to identify the two carboxylic acids and to distinguish between them.

How do both types of spectra allow the carboxylic acids to be identified and distinguished?

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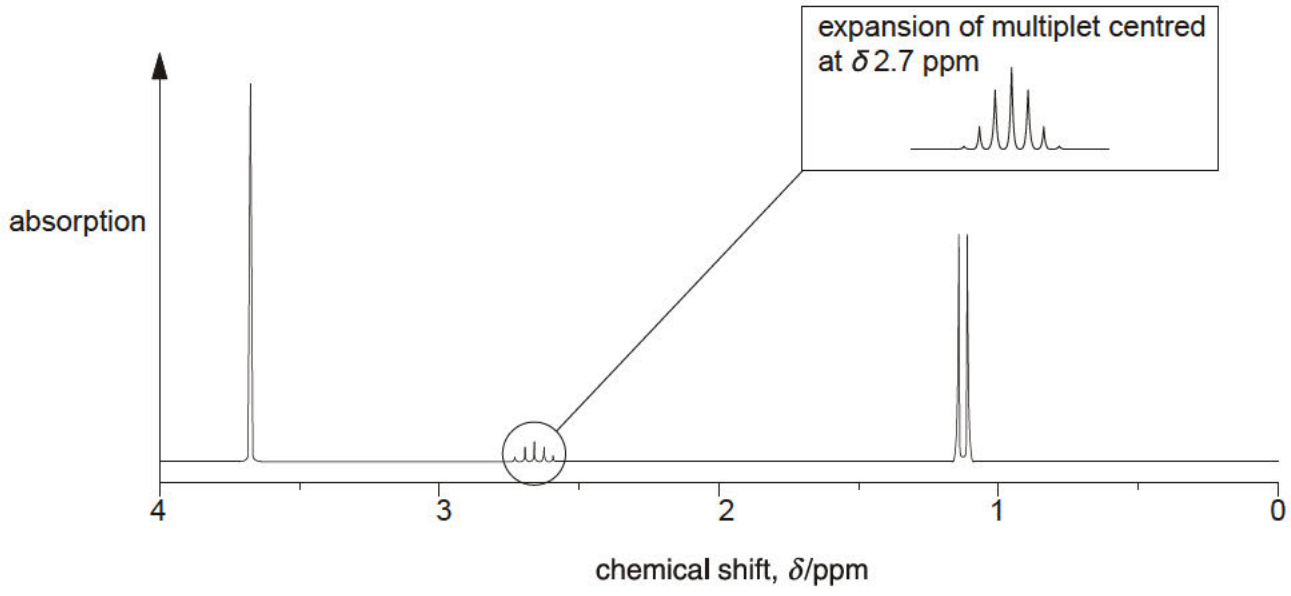
[3]

(b) The chemist analysed one of the esters by ^{1}H NMR spectroscopy. The spectrum is shown below.



Analyse the splitting patterns and the chemical shift values to identify the ester.

Give your reasoning.

In your answer, you should use appropriate technical terms, spelt correctly.

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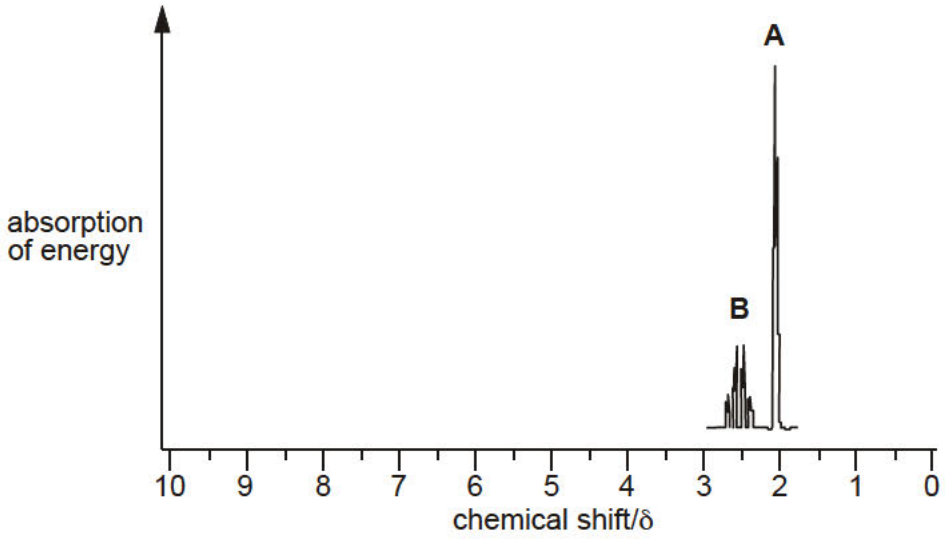
[6]

[Total 9 marks]

2. Unknown compounds are often identified by n.m.r. spectroscopy.

Part of the n.m.r. spectrum of **butanone** is shown on the axes below.



(i) State which part of the butanone molecule is responsible for peak **A** at $\delta = 2.1$.

Explain your reasoning.

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[2]

(ii) Explain why peak **B** is split into a quadruplet.

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[1]

(iii) Predict the remainder of the n.m.r. spectrum of butanone by sketching it on the axes above.

[2]

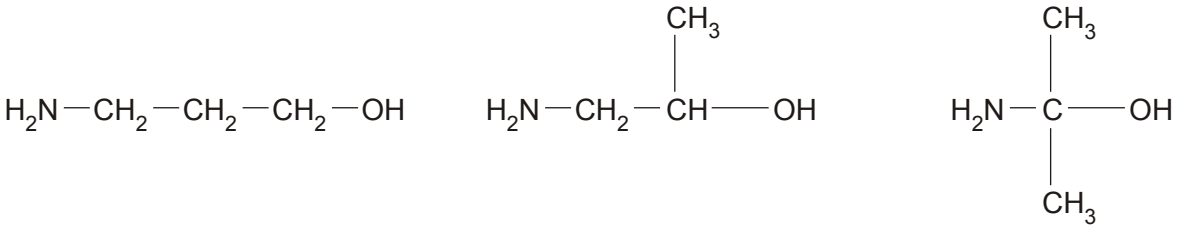
(iv) Write the relative peak area above each of the peaks on the completed spectrum of butanone.

[1]

[Total 6 marks]

3. In this question, one mark is available for the quality of use and organisation of scientific terms.

The structural formulae of three isomers of C_3H_9NO are shown below.



Describe the **similarities** and **differences** you would expect to see when comparing the

- infra-red spectrum of each isomer
- mass spectrum of each isomer.

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[5]

Quality of Written Communication [1]

[Total 6 marks]

4. An ester **D** with the formula, $CH_3CH_2COOCH_2CH(CH_3)_2$, is used in rum flavouring.

(a) Draw a displayed formula of ester **D**.

[2]

(b) Outline how you could obtain a sample of ester **D**, starting with a named carboxylic acid and a named alcohol.

Include any essential reaction conditions and write an equation for the reaction. You do not need to include any details of the separation or purification of the ester.

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[6]

(c) State a spectroscopic method that could be used to confirm that a sample of ester **D** has a molecular mass of 130.

Explain how you would obtain the molecular mass of **D** from the spectrum.

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[2]

[Total 10 marks]

5. In this question, one mark is available for the quality of the use and organisation of scientific terms.

Describe and explain the different ways that a high resolution n.m.r. spectrum can give information about a molecule.

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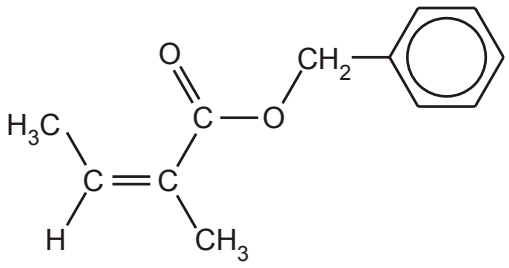
[7]

Quality of Written Communication [1]

[Total 8 marks]

6. Compound **A** is used to add the flavour of mushrooms to foods.



compound **A**

(a) (i) Apart from the benzene ring, name the two functional groups in compound **A**.

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[2]

(ii) Draw the skeletal formula of compound **A**.

[1]

(iii) Deduce the molecular formula of compound **A**.

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[1]

(b) Compound **B** is a stereoisomer of compound **A**.

Explain what is meant by the term *stereoisomerism*. Use compounds **A** and **B** to illustrate your answer.

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[2]

(c) If the food is cooked for a long time, naturally occurring acids catalyse the hydrolysis of compound **A**.

Draw structures to show the **two** organic compounds formed by the acid hydrolysis of compound **A**.

[2]

(d) The hydrolysis of compound **A** can be monitored by sampling the mixture at regular intervals, separating the components, and recording their infra-red spectra.

(i) State **two** absorptions that would be expected in the infra-red spectrum of compound **A**, and identify the parts of the molecule responsible for each.

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[2]

(ii) Suggest a wavenumber range within the spectrum that could be used to clearly distinguish compound **A** from the products formed by the hydrolysis reaction.

Explain your answer.

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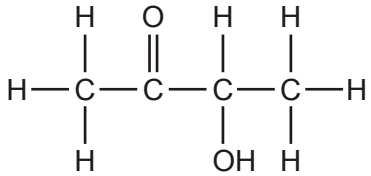
[2]

[Total 12 marks]

7. *Thua nao* is a traditional sauce made in Northern Thailand by fermenting cooked soybeans. Its unique flavour is due to a range of volatile compounds formed during the fermentation.

One of these volatile compounds is 3-hydroxybutanone.



3-hydroxybutanone

(a) State the meaning of the term *volatile*.

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[1]

(b) Several hydroxyketones with similar boiling points can be separated from the fermentation mixture.

Describe a method, which does **not** involve spectroscopy, that could be used to distinguish 3-hydroxybutanone from the other hydroxyketones.

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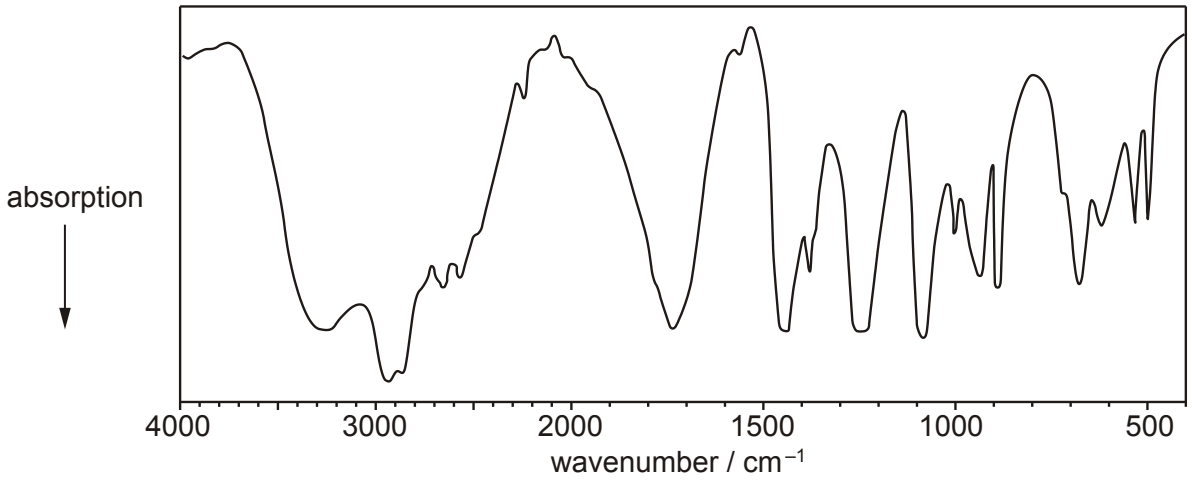
[4]

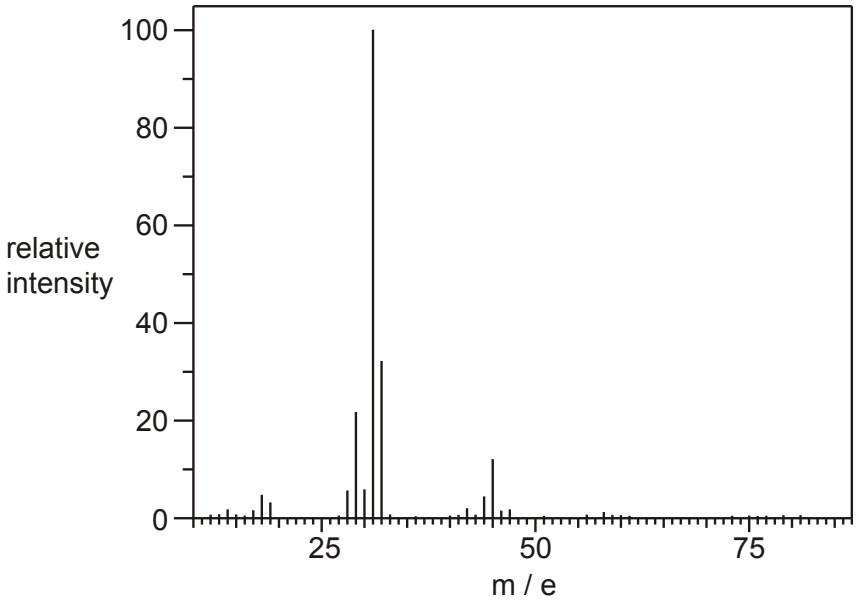
[Total 5 marks]

8. Compound **G** can be extracted from sugar-cane and is commonly used in 'rejuvenating' skin creams because it helps to remove some of the dead cells from the skin surface.

The molecular formula of **G** is $C_2O_3H_4$ and the compound contains **two different** functional groups containing oxygen atoms.

The infra-red and mass spectra of **G** are shown below.





(a) After inspection of the mass spectrum of **G**, an analyst wrote the comment:

'The molecular ion peak appears to be missing from the spectrum.
The base peak is due to a fragment ion with m / e = 31.'

(i) Explain what is meant by the following terms.

molecular ion peak .....

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base peak .....

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[2]

(ii) Suggest why the molecular ion peak is missing from the spectrum.

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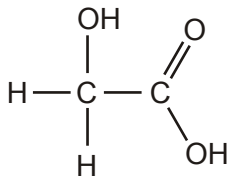
[1]

(b) The structure of compound **G** is shown below.



Show how the infra-red and mass spectra confirm this structure. In your answer, you should suggest a possible structure for the ion that gives the base peak at m / e = 31 in the mass spectrum.

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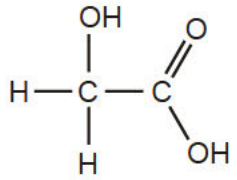
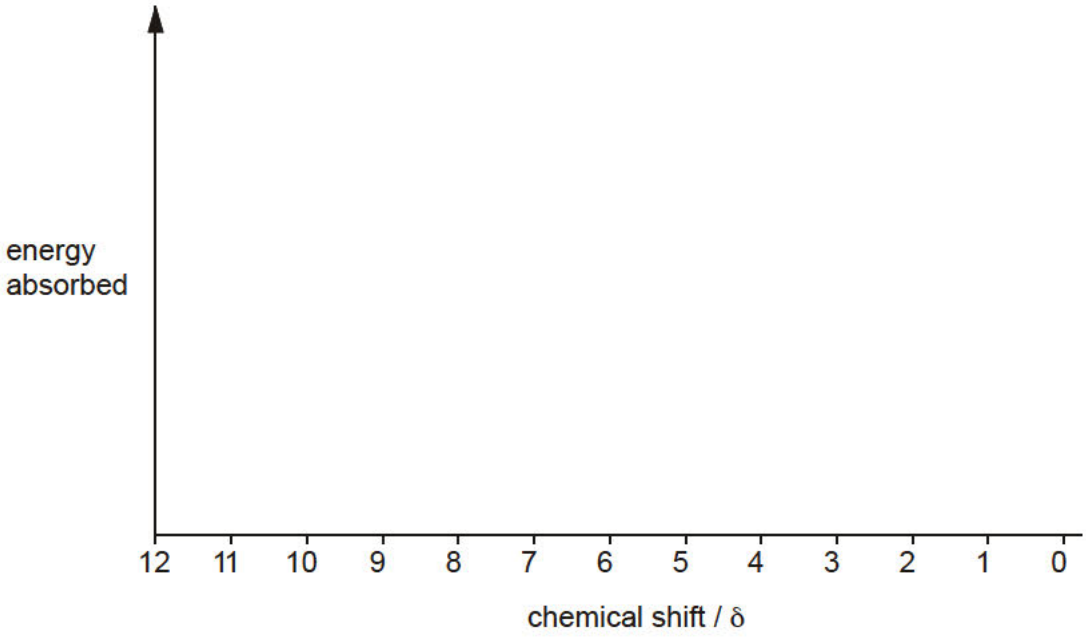
[4]

(c) The structure of compound **G** is shown below.



Sketch the ^{1}H n.m.r. spectrum of compound **G** and label the relative peak areas. Label any peaks that would be lost from the spectrum on shaking with D_2O.



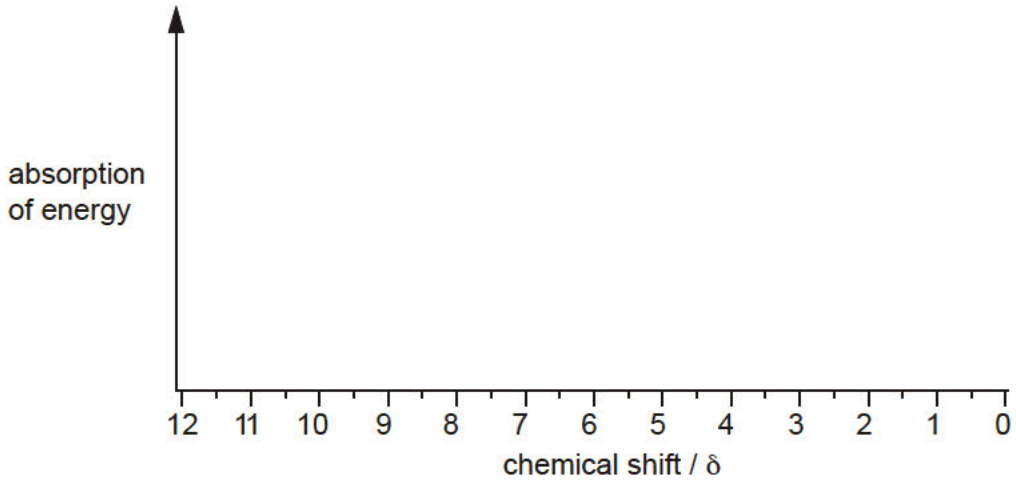
[4]

[Total 11 marks]

9. Lactic acid produces an n.m.r. spectrum in D_2O with peaks at chemical shift values of 1.4 ppm and 4.3 ppm.

(i) On the axes below, sketch the high resolution n.m.r. spectrum of lactic acid in D_2O.

Show any splitting patterns and state the relative areas of the two peaks.



[4]

(ii) How many peaks would you expect if the n.m.r. spectrum of lactic acid was run in an inert solvent rather than in D_2O? Explain your answer.

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[2]

[Total 6 marks]

10. Forest fires release a large number of organic compounds into the atmosphere. These include alcohols and carboxylic acids. An environmental chemist is trying to identify one of these compounds in a sample of air.

The unknown compound **X** is thought to be a carboxylic acid with empirical formula $C_2H_3O_2$.

(a) Mass spectrometry is used to help deduce the molecular formula of compound **X**.

(i) Describe how the mass spectrum of compound **X** is used to determine its relative molecular mass.

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[2]

(ii) The relative molecular mass of compound **X** is shown to be 118.

Explain how this relative molecular mass and the empirical formula are used to deduce that the molecular formula of compound **X** is C_4H_6O4. Show any working.

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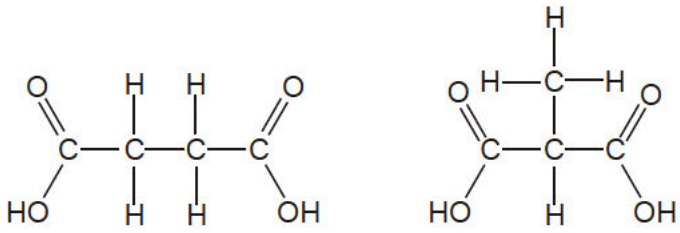
[2]

(b) The two dicarboxylic acids with molecular formula $C_4H_6O_4$ are shown below.



N.m.r. spectroscopy is used to deduce which of these is the unknown compound.

The environmental chemist obtains an n.m.r. spectrum of compound **X** and then adds some D_2O and obtains a second n.m.r. spectrum.

(i) What difference would you expect between these two n.m.r. spectra?

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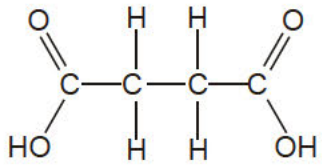
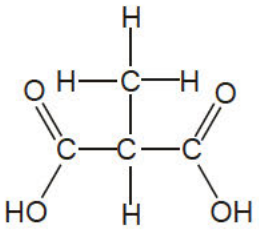
[1]

(ii) Predict the number of peaks and any spin-spin splitting expected on the n.m.r. spectrum of a solution in D_2O of the other acid with formula $C_4H_6O_4$.

Explain your reasoning.

(The two possible structures of compound **X** are shown again below.)





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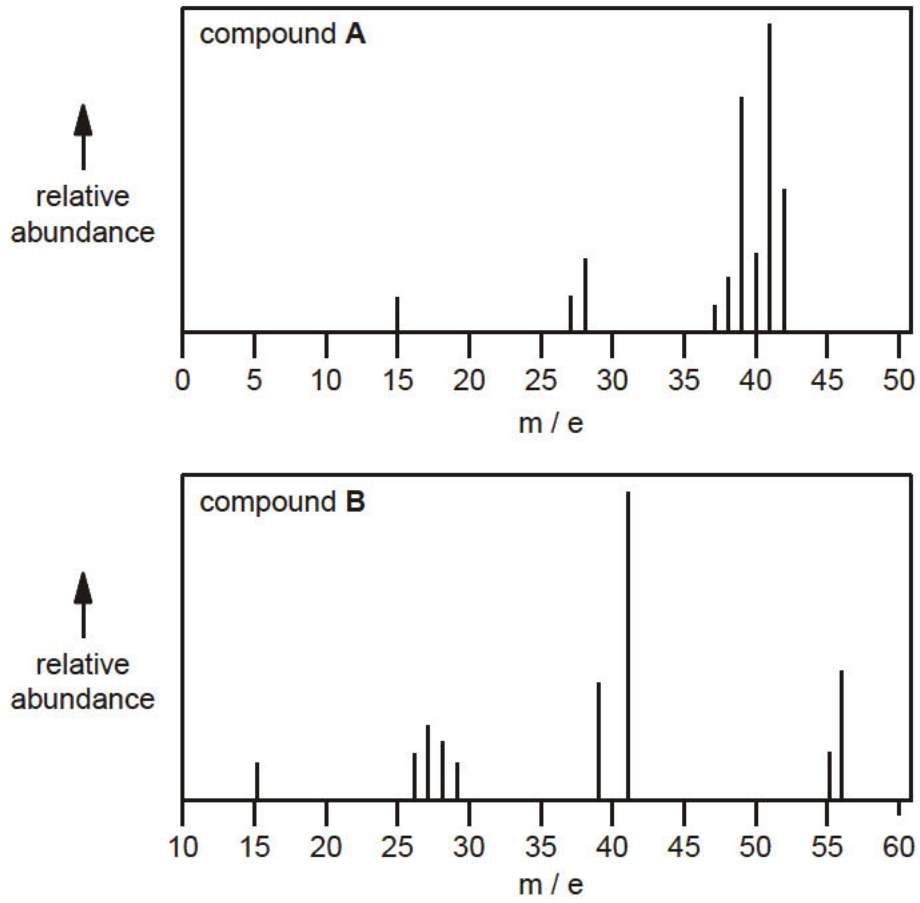
[3]

[Total: 8 marks]

11. This question is about the use of spectrometry in helping to gain information about the structure of organic molecules.

The major peaks in the mass spectra of two hydrocarbons **A** and **B** are shown below. Compounds **A** and **B** have the same empirical formula.



(i) Deduce the molecular formula of each compound.

Compound **A** .....

Compound **B** .....

[2]

(ii) Draw the structural formula of compound **A**.

[1]

(iii) Suggest the species responsible for the peak at *m/e* 41 in the spectrum of compound **B**.

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[2]

[Total 5 marks]