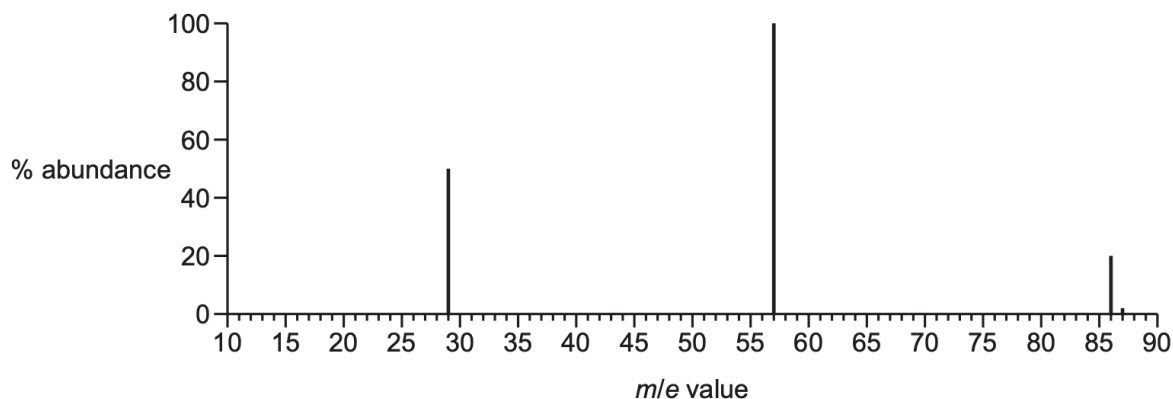


1.

(d) Fig. 5.1 shows the mass spectrum of ketone **Z**, $C_5H_{10}O$.

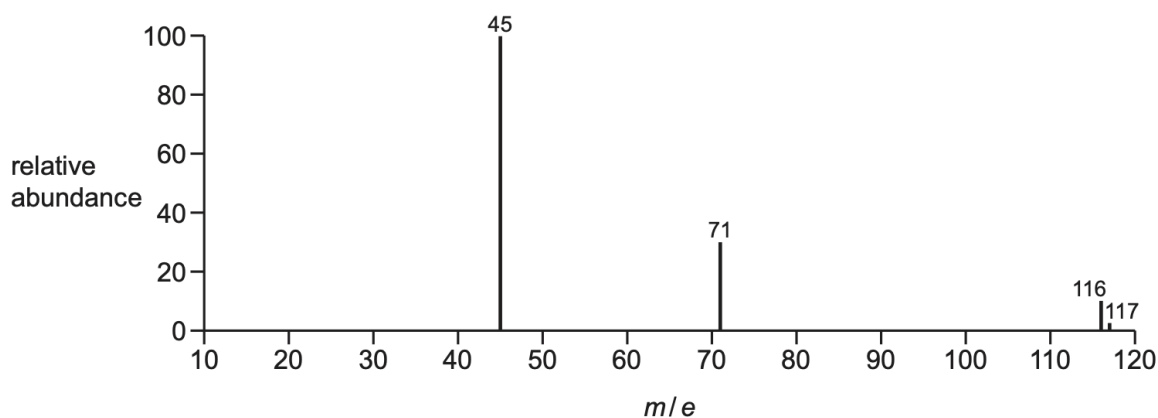


Use the information in Fig. 5.1 to suggest the formulae of the fragments with m/e peaks at 29 and 57. Deduce the identity of **Z**.

- $m/e = 29$: $C_2H_5^+$
- $m/e = 29$: $COCH_2CH_3^+$ OR $C_3H_5O^+$
- identity of **Z**: pentan-3-one

2.

(c) Fig. 6.1 shows the mass spectrum of **Z**.



Empirical formula of **Z** = CHO

a.

Deduce the molecular formula of **Z**. Explain your answer by referring to the molecular ion peak in Fig. 6.1 and the empirical formula of **Z**.

Look for some reference to 116 as the mass of the molecular ion **AND** mass of $C_{(1)}H_{(1)}O_{(1)} = 29$ to conclude molecular formula is $C_4H_4O_4$
 $116 / 29 = 4$ so $C_4H_4O_4$

b.

Use Fig. 6.1 to suggest the formulae of the fragments with m/e peaks at 45 and at 71.

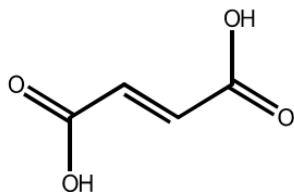
m/e 45

m/e 71

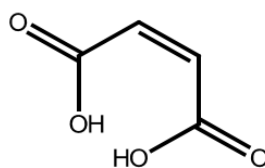
M1 m/e 45: $^+\text{COOH}$ OR $^+\text{CHO}_2$

M2 m/e 71: $\text{C}_3\text{H}_3\text{O}_2^+$

c. Suggest the structure of Z

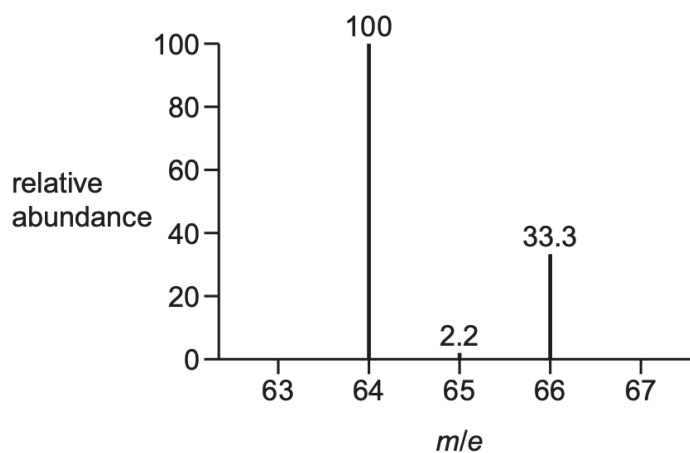


OR



3.

Z contains three types of atom: carbon, hydrogen and a halogen. The mass spectrum of **Z** is recorded. Fig. 5.1 shows a section of the mass spectrum at m/e greater than 63. The fragment at $m/e = 64$ is the molecular ion peak.



Deduce which halogen is present in Z using Fig. 5.1. Explain your answer.

- Chlorine AND
- peak at $M+2$ represents the molecular ion with 37-Cl OR
- relative abundance of (peaks) M : $M+2$ is $100:33.3 / 3:1$ (so peak at $M+2$ contains 37-Cl)

4.

Lactones are cyclic esters. Under suitable conditions, lactones form from molecules that have both an alcohol and a carboxylic acid functional group.

Equation 1 shows an example of the formation of a lactone.

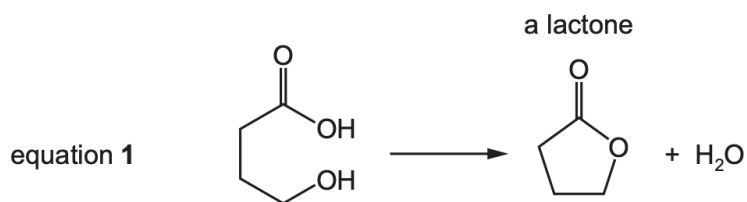


Fig. 5.1 shows the synthesis of lactone **P** from compound **M**.

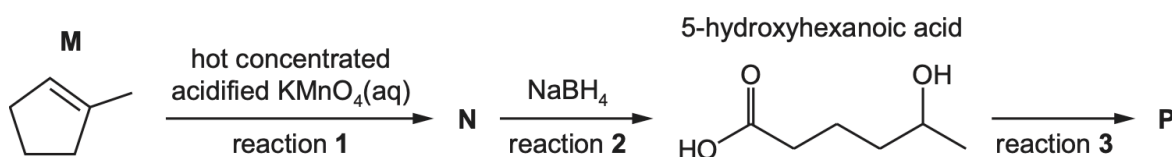


Table 5.1

bond	functional group containing the bond	characteristic infrared absorption range (in wavenumbers)/cm ⁻¹
C–O	hydroxy, ester	1040–1300
C=C	aromatic compound, alkene	1500–1680
C=O	amide carbonyl, carboxyl ester	1640–1690 1670–1740 1710–1750
C≡N	nitrile	2200–2250
C–H	alkane	2850–3100
N–H	amine, amide	3300–3500
O–H	carboxyl hydroxy	2500–3000 3200–3650

A student monitors the progress of reaction 2 using infrared spectroscopy. Use Table 5.1 to suggest why it is difficult to distinguish between **N** and 5-hydroxyhexanoic acid using infrared spectroscopy.

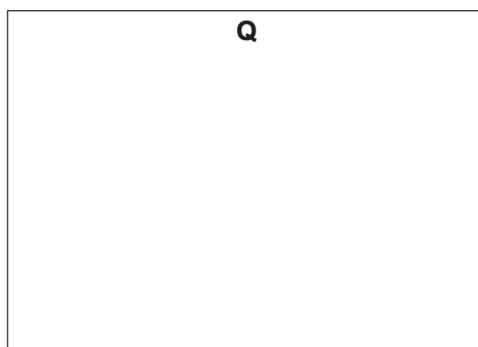
- absorptions will overlap / be similar / the same / indistinguishable
- both have some bonds in similar environments

- (c) Unknown lactone **Q** is analysed using mass spectrometry. Table 5.2 shows information from the mass spectrum.

Table 5.2

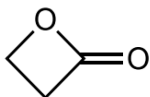
peak	<i>m/e</i>	abundance
M+	72	95.5
M+1	73	3.15

Use these data to deduce the structure of **Q**.
Show your working.



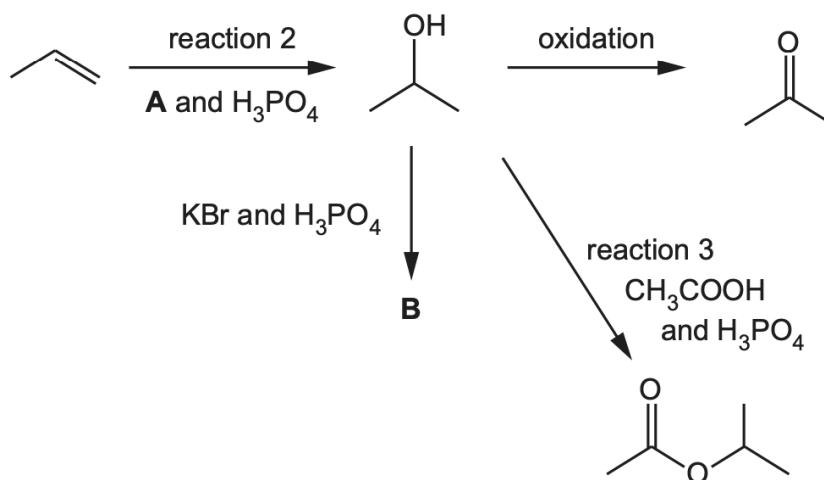
.....
.....

$$100 / 1.1 \div 95.5 / 3.15 = 3 \text{ carbon atoms}$$



5.

Fig. 3.1 shows a reaction scheme that involves H_3PO_4 in several reactions.



(iv) Reaction 3 is monitored using infrared spectroscopy. It is not possible to use the O—H absorption frequency to monitor the reaction.

Use Table 3.2 to identify a suitable bond whose absorption frequency can be used to monitor the progress of reaction 3.

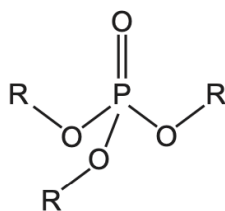
State the change you would see in the infrared spectrum during reaction 3.

- Bond: C=O
- Change in IR spectrum: absorption changes wavenumber from 1670–1740 to 1710–1750 cm^{-1}

6.

H_3PO_4 also reacts with alcohols to form organophosphates.

Organophosphates are compounds similar to esters. They have the general structure shown in Fig. 3.2.



R = alkyl group

Compound **T** is a simple organophosphate.

The mass spectrum of **T** shows a molecular ion peak at $m/e = 182$. This peak has a relative intensity of 12.7.

The relative intensity of the $M+1$ peak is 0.84.

Deduce the number of carbon atoms in **T**.
Hence suggest the molecular formula of **T**.

Assume that phosphorus and oxygen exist as single isotopes.

Show your working.

number of carbon atoms in **T** =

molecular formula of **T** =

[3]

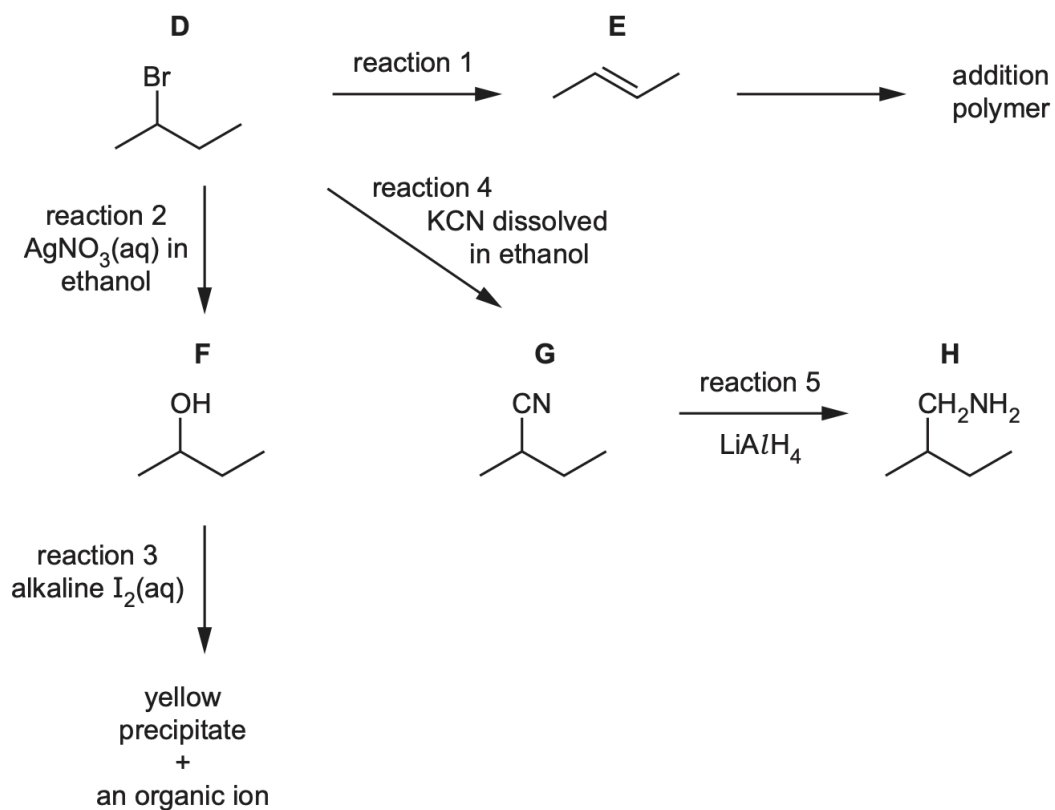
$$\frac{0.84}{12.7} \times \frac{100}{1.1} \quad (= 6.013)$$

no. of carbon atoms = 6

molecular formula = $C_6H_{15}O_4P$

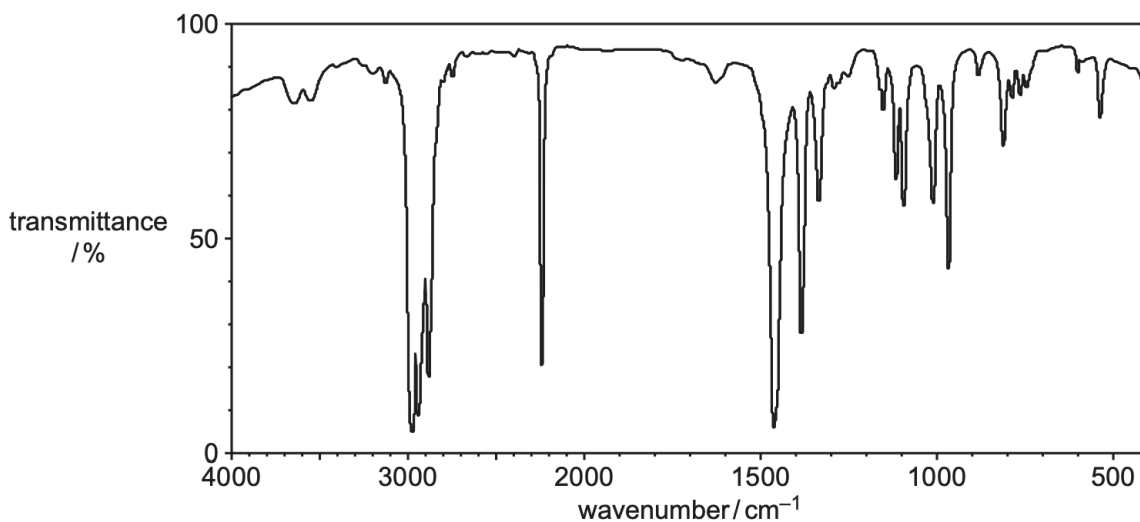
7.

Fig. 4.1 shows some reactions of compound **D**, 2-bromobutane.



bond	functional groups containing the bond	characteristic infrared absorption range (in wavenumbers) / cm^{-1}
C–O	hydroxy, ester	1040–1300
C=C	aromatic compound, alkene	1500–1680
C=O	amide carbonyl, carboxyl ester	1640–1690 1670–1740 1710–1750
C≡N	nitrile	2200–2250
C–H	alkane	2850–2950
N–H	amine, amide	3300–3500
O–H	carboxyl hydroxy	2500–3000 3200–3600

(d) (i) Fig. 4.2 shows the infrared spectrum of one of the compounds **D**, **E**, **F**, **G** or **H**.



Use information from the table to identify which of the compounds **D**, **E**, **F**, **G** or **H** produces the infrared spectrum in Fig. 4.2. Explain your answer.

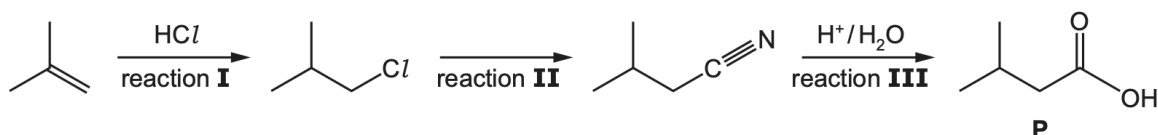
- **G**
- absorption at 2200–2250 cm⁻¹ AND C≡N

8. In the mass spectrum of **D**, the relative abundance of the molecular ion peak is 3.4. Predict the relative abundance of the M+2 peak for **D**. Explain your answer.

- 3.4 AND relative abundance of ⁷⁹Br:⁸¹Br ≈ 50:50 OR 1:1

9.

(e) **P** can be produced as shown.



a. The progress of reaction **I** can be monitored using infra-red spectroscopy. One absorption that can be used to monitor the progress of this reaction is that of C–Cl at 730cm⁻¹. Identify another absorption that can be used to monitor the progress of this reaction. In your answer, you should refer to the specific bond and its corresponding absorption range in wavenumbers.

- C=C AND 1500–1680

NOTE: question asks for reaction **I** specifically!! So CN group or COOH cannot be monitored!

b. The yield of reaction **I** is very low. Explain why.

- this reaction involves less stable intermediate: 1° carbocation intermediate is less stable than 3°
- explain difference in reactivity in terms of positive inductive effect – lower positive inductive effect / lower +I OR inductive effect of less alkyl groups

10.

X is a product of the substitution reaction that occurs when CHClF_2 reacts with Br_2 .

There is only one naturally occurring isotope of fluorine, ^{19}F .

The mass spectrum of **X** shows molecular ion peaks at $m/e = 164, 166$ and 168 .

Complete Table 3.3 to show **all** the molecular ions responsible for each peak.

Table 3.3

m/e	formulae of molecular ions
164	
166	
168	$(\text{CF}_2^{37}\text{Cl}^{81}\text{Br})^+$

M1 m/e 164 $(\text{CF}_2^{35}\text{Cl}^{79}\text{Br})^+$

M2 m/e 166 $(\text{CF}_2^{37}\text{Cl}^{79}\text{Br})^+$ **AND** $(\text{CF}_2^{35}\text{Cl}^{81}\text{Br})^+$

NOTE: REMEMBER to put both for 166!!

11.

The mass spectrum of a sample of pure copper is shown in Fig. 1.1.

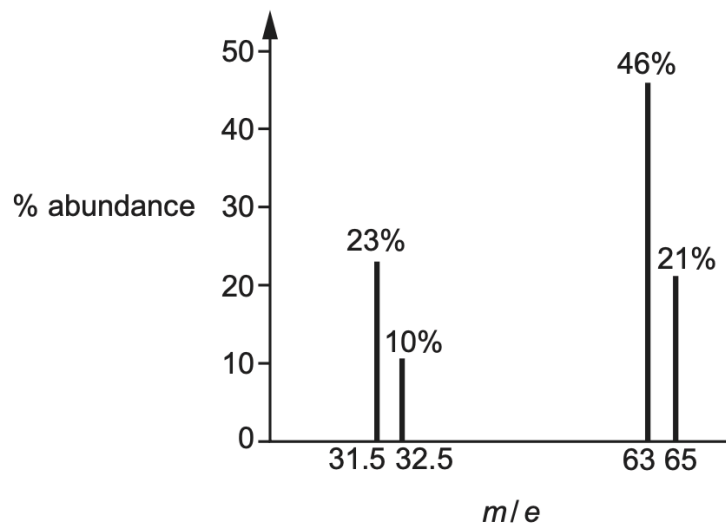


Fig. 1.1

Identify the ion with an abundance of 23% in the sample.

- Charge = +2
- Mass = $2 \times 31.5 = 63$
- Ion = ${}^{63}\text{Cu}^{2+}$

12.

- (c) Organic compound **E** contains three carbon atoms. **E** reacts with cold dilute acidified $\text{KMnO}_4(\text{aq})$ to form a single compound **F** with $M_r = 154.9$. Fig. 3.1 shows the infrared spectrum of **E**. Fig. 3.2 shows the infrared spectrum of **F**.

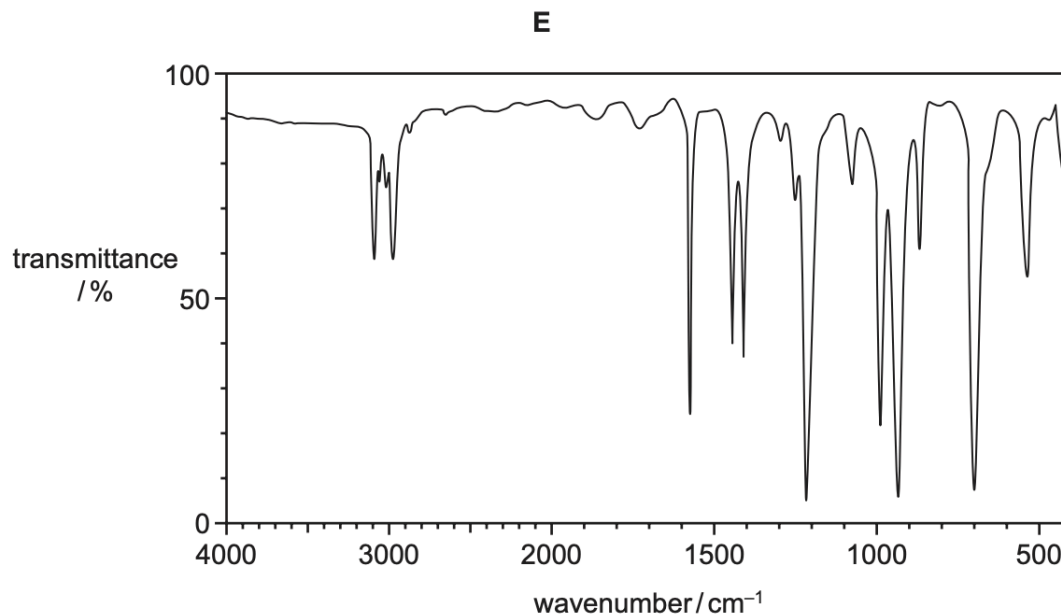


Fig. 3.1

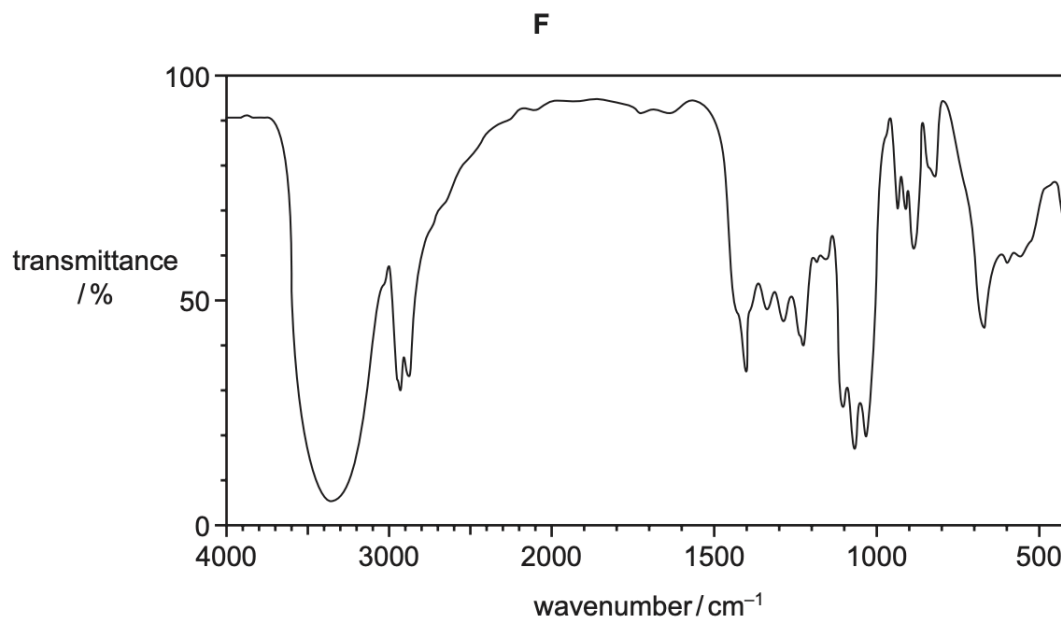


Fig. 3.2

The mass spectrum of **E** shows a molecular ion peak and an $M+2$ peak of approximately equal abundance at $m/e = 120$ and 122 . Deduce the relative molecular mass, M_r , of **E**.

- $M_r = (120 + 122) / 2 = 121$

Because they M+ and M+1 peaks have equal abundance