

### 11.3 Spectroscopic identification of organic compounds

#### Analytical techniques

- **qualitative analysis:** the detection of the presence but not the quantity of a substance in a mixture; for example, forbidden substances in an athlete's blood
- **quantitative analysis:** the measurement of the quantity of a particular substance in a mixture; for example, the alcohol levels in a driver's breath
- **structural analysis:** a description of how the atoms are arranged in molecular structures; for example, the determination of the structure of a naturally occurring or artificial product.

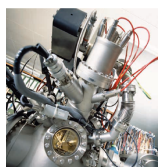
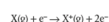
- **Infrared spectroscopy** is used to identify the bonds in a molecule.
- **Mass spectrometry** is used to determine relative atomic and molecular masses. The fragmentation pattern can be used as a fingerprint technique to identify unknown substances or for evidence for the arrangements of atoms in a molecule.
- **Nuclear magnetic resonance spectroscopy** is used to show the chemical environment of certain isotopes (hydrogen, carbon, phosphorus, and fluorine) in a molecule and so gives vital structural information.

#### Mass spectrometry

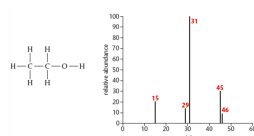
##### Determining the molecular mass of a compound

##### Fragmentation patterns

The ionization process in the mass spectrometer involves an electron from an electron gun hitting the incident species and removing an electron:



Very energetic collisions lead to "fragmentation patterns".



The molecular ion or parent ion is formed when a molecule loses one electron but otherwise remains unchanged.

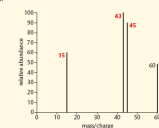
What does the relative abundance tell us?



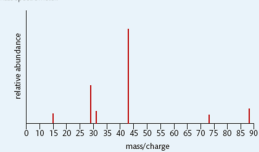
Full analysis of a mass spectrum can be a complex process. We make use of the mass difference between the peaks to identify the pieces which have fallen off. You are expected to recognize the mass fragments shown below. You are not expected to memorise the details as the data are given in section 28 of the IB data booklet.

Mass lost	Fragment lost
15	CH <sub>3</sub>
17	OH
18	H <sub>2</sub> O
28	CH <sub>2</sub> =CH <sub>2</sub> , C=O
29	CH <sub>3</sub> CH <sub>2</sub> , CHO
31	CH <sub>3</sub> O
45	COOH

**Worked example**  
A molecule with an empirical formula CH<sub>2</sub>O has the simplified mass spectrum below. Deduce the molecular formula and give a possible structure of the compound.



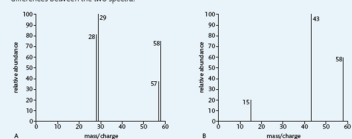
28 While working on an organic synthesis, a student isolated a compound X, which they then analysed with a mass spectrometer.



Identify X from the mass spectrum shown.

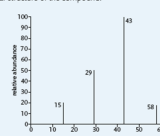
- A CH3CH2CH3 B C4H8CO2H C C3H5CO2CH3 D (CH3)2CHCO2H

29 The mass spectra of two compounds are shown below. One is propanone (CH3COCH3) and the other is propanal (CH3CH2CHO). Identify the compound in each case and explain the similarities and differences between the two spectra.



30 The simplified mass spectrum of a compound with empirical formula C<sub>2</sub>H<sub>4</sub> is shown below.

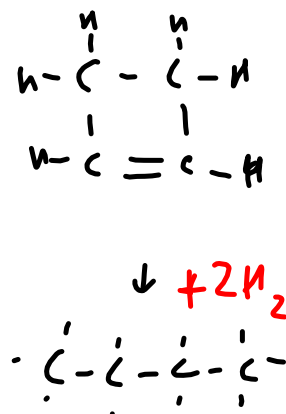
- (a) Explain which ions give rise to the peaks shown.  
(b) Deduce the molecular structure of the compound.



Mass lost	Fragment lost
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17	OH
18	H <sub>2</sub> O
28	CH <sub>2</sub> =CH <sub>2</sub> , C=O
29	CH <sub>3</sub> CH <sub>2</sub> , CHO
31	CH <sub>3</sub> O
45	COOH

## The degree of unsaturation/IHD

Molecule	Saturated non-cyclic target	Index of hydrogen deficiency (IHD)
$C_2H_4$	$C_2H_6$	1
$C_2H_2$	$C_2H_6$	2
cyclobutane and but-1-ene, $C_4H_8$	$C_4H_{10}$	1
$C_2H_5OH$	$C_2H_5OH$	0
$C_2H_4O$	$C_2H_6O$	1
$C_2H_5Cl$	$C_2H_5Cl$	0



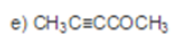
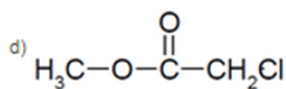
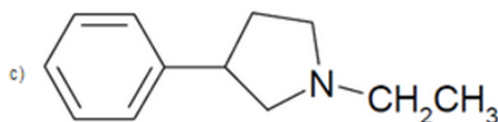
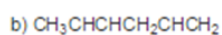
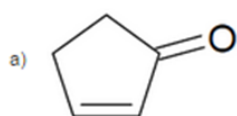
The number of  $H_2$  molecules required to convert molecule x into a saturated, non-cyclic molecule.

### Exercises

31 Deduce the IHD of the following by copying and completing the table below.

Molecule	Corresponding saturated non-cyclic molecule	IHD
$C_6H_6$	Hexane	4
$CH_3COCH_3$	propan-2-ol	1
$C_7H_6O_2$	Heptadiol	5
$C_2H_3Cl$	chloroethane	1
$C_4H_9N$	aminobutane	1
$C_6H_{12}O_6$	hexan	1

31



A

a)

b)

c)

d)

e)

Different regions of the electromagnetic spectrum give different information about the structure of organic molecules

- **wavelength ( $\lambda$ ):** the distance between successive crests or troughs
- **frequency ( $\nu$ ):** the number of waves which pass a point every second.

Type of electromagnetic radiation	Typical frequency ( $\nu$ ) / $s^{-1}$	Typical wavelength ( $\lambda$ ) / m
radio waves (low energy)	$3 \times 10^6$	$10^2$
microwaves	$3 \times 10^{10}$	$10^{-2}$
infrared	$3 \times 10^{12}$	$10^{-4}$
visible	$3 \times 10^{14}$	$10^{-7}$
ultraviolet	$3 \times 10^{15}$	$10^{-8}$
X rays	$3 \times 10^{16}$	$10^{-10}$
gamma rays	greater than $3 \times 10^{17}$	less than $10^{-14}$



- **Radio waves** can be absorbed by certain nuclei, causing them to reverse their spin. They are used in NMR and can give information about the environment of certain atoms.
- **Microwaves** cause molecules to increase their rotational energy. This can give information about bond lengths. It is not necessary to know the details at this level.
- **Infrared radiation** is absorbed by certain bonds causing them to stretch or bend. This gives information about the bonds in a molecule.
- **Visible light and ultraviolet light** can produce electronic transitions and give information about the electronic energy levels within the atom or molecule.
- **X rays** are produced when electrons make transitions between inner energy levels. They have wavelengths of the same order of magnitude as the inter-atomic distances in crystals and produce diffraction patterns which provide direct evidence of molecular and crystal structure.



### Infrared (IR) spectroscopy

#### The natural frequency of a chemical bond

A chemical bond can be thought of as a spring. Each bond vibrates and bends at a natural frequency which depends on the bond strength and the masses of the atoms. Light atoms, for example, vibrate at higher frequencies than heavier atoms and multiple bonds vibrate at higher frequencies than single bonds.



These vibrations are increased when energy in the IR region of the electromagnetic spectrum is absorbed.

However, this only occurs if the bond is permanently polar or has temporary dipoles when vibrating.

symmetric stretch $\Rightarrow 3600\text{ cm}^{-1}$	asymmetric stretch $\Rightarrow 3400\text{ cm}^{-1}$	asymmetric bend $\Rightarrow 1600\text{ cm}^{-1}$	symmetric bend $\Rightarrow 1500\text{ cm}^{-1}$
		As the molecule vibrates, it has a temporary dipole. It has no change in dipole.	As the molecule vibrates, it has a temporary dipole. It has no change in dipole.

Wavenumber  $\rightarrow$   $\frac{1}{\text{Wavelength (cm)}}$

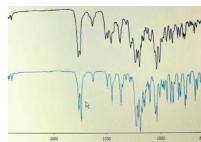
Bond	Wavenumber / $\text{cm}^{-1}$	Intensity
C-O	1050-1410	strong
C=C	1620-1680	medium-weak; multiple bands
C=O	1700-1750	strong
C=C	2100-2260	variable
O-H, hydrogen bonded in carboxylic acids	2500-3000	strong, very broad
C-H	2850-3090	strong
O-H, hydrogen bonded in alcohols and phenols	3200-3600	strong
N-H	3300-3500	strong

Some bonds can also be identified by the distinctive shapes of their signals: for example, the O-H bond gives a broad signal and the C=O bond gives a sharp signal.

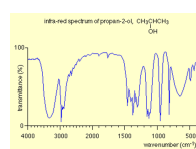
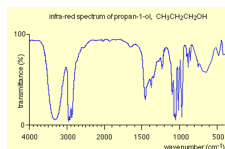
IR spectrum for a sample of pure heroin



Does the sample contain heroin?



The fingerprint region below  $1500\text{ cm}^{-1}$  can be used to positively identify a compound:



### Exercises

32 Which of the following types of bond is expected to absorb IR radiation of the longest wavelength?

Bond order	Mass of atoms bonded together
A 1	small
B 1	large
C 2	small
D 2	large

33 The infrared spectrum was obtained from a compound and showed absorptions at  $2100\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$ . Identify the compound.

A  $\text{CH}_3\text{COOCH}_3$  B  $\text{C}_6\text{H}_5\text{COOH}$  C  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  D  $\text{CH}_3\text{Cl}$

34 A molecule absorbs IR at a wavenumber of  $1720\text{ cm}^{-1}$ . Which functional group could absorption?

I aldehydes II esters III ethers

A I only B I and II C I, II, and III D none

35 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.

(a) Determine the empirical and molecular formulae of the compound.

(b) Deduce the IR of the compound.

(c) The IR spectrum shows an absorption band at  $1700\text{ cm}^{-1}$  and a very strong band between  $2500$  and  $3300\text{ cm}^{-1}$ . Deduce the molecular structure of the compound.

36 Draw the structure of a sulfur dioxide molecule and identify its possible modes of vibration. Predict which of these is likely to absorb IR radiation.

Bond	Wavenumber / $\text{cm}^{-1}$	Intensity
C-O	1050-1410	strong
C=C	1620-1680	medium-weak
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### Exercises

37 Identify the bonds which will produce strong absorptions in the IR region of the electromagnetic spectrum.

I C-O bond II C=C bond III C=O

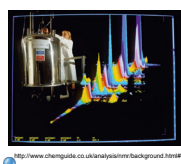
A I and II only B I and III only C II and III only D I, II, and III

38 State what occurs at the molecular level when IR radiation is absorbed.

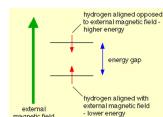
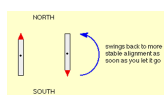
39 Cyclohexane and hex-1-ene are isomers. Suggest how you could use infrared spectroscopy to distinguish between the two compounds.

40 The ipecosimeter, used by the police to test the alcohol levels in the breath of drivers, measures the absorbance at  $2900\text{ cm}^{-1}$ . Identify the bond which causes ethanol to absorb at this wavenumber.

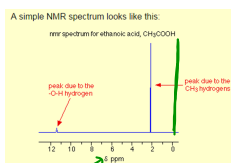
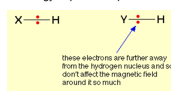
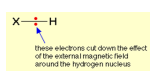
41 A molecule has the molecular formula  $\text{C}_4\text{H}_8\text{O}$ . The infrared spectrum shows an absorption band at  $1000\text{--}1300\text{ cm}^{-1}$ , but no absorption bands above  $3000\text{ cm}^{-1}$ . Deduce its structure.



# Nuclear magnetic resonance (NMR) spectroscopy → <sup>1</sup>H NMR



The environment of the H is important because electrons affect the energy required to flip the nucleus.



The signals are measured against the standard signal produced by the 12 hydrogen nuclei in tetramethylsilane (TMS), the structure of which is shown in Figure 11.26.



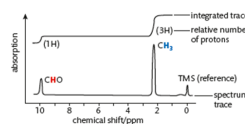
TMS is chosen as the standard because:

- > It has 12 hydrogen atoms all of which are in exactly the same environment. That produces a **single peak**, but it's also a strong peak (because there are lots of hydrogen atoms).
- > The electrons in the C-H bonds are closer to the hydrogens as Si is less electronegative than C. That means that these hydrogen nuclei are the most shielded from the external magnetic field, and so they **interact with radio waves with a higher frequency** than almost all other H-environments.

The net effect of this is that TMS produces a single peak on the spectrum at the extreme right-hand side. Almost everything else produces peaks to the left of it.

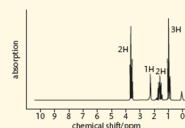
	9.0-10.0*
	10.0-12.0*
	4.5-6.0
	6.0-9.0
	2.0-2.5
	0.9-1.8
	2.1-2.7

Type of proton	Chemical shift / ppm
TMS	0
-CH <sub>3</sub>	0.9-1.8
	2.0-2.5



## Worked example

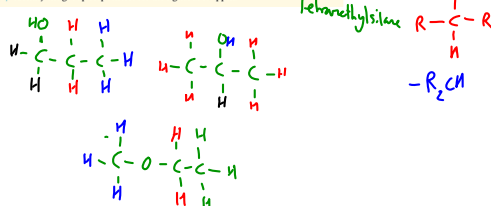
The NMR spectrum of a compound which has the molecular formula C<sub>3</sub>H<sub>6</sub>O is shown here.



	9.0-10.0*
	10.0-12.0*
	4.5-6.0
	6.0-9.0
	2.0-2.5
	0.9-1.8
	2.1-2.7

- Draw the full structural formulas and give the names of the three possible isomers of C<sub>3</sub>H<sub>6</sub>O.
- Identify the substance responsible for the peak at 0 ppm and state its purpose.
- Identify the unknown compound from the number of peaks in the spectrum.
- Identify the group responsible for the signal at 9.7 ppm.

(b) → TMS → Standard reference  
(c) → Tetramethylsilane R-C(R)(H)<sub>3</sub>



## Exercises

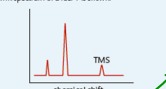
42. The <sup>1</sup>H NMR spectrum of a compound exhibits three major peaks and the splitting patterns below.

Chemical shift / ppm	Peak area
1.0	3
2.0	3
2.3	2

Identify the compound.

- A CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub> B CH<sub>3</sub>CH<sub>2</sub>CHO C CH<sub>3</sub>CH<sub>2</sub>COCH<sub>3</sub> D CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

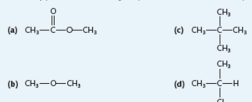
43. The low resolution <sup>1</sup>H NMR spectrum of a fuel Y is shown.



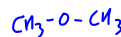
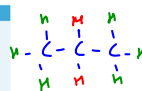
Identify Y.

- A CH<sub>3</sub>OH B C<sub>2</sub>H<sub>6</sub> C C<sub>2</sub>H<sub>5</sub>OH D CH<sub>3</sub>OCH<sub>3</sub>

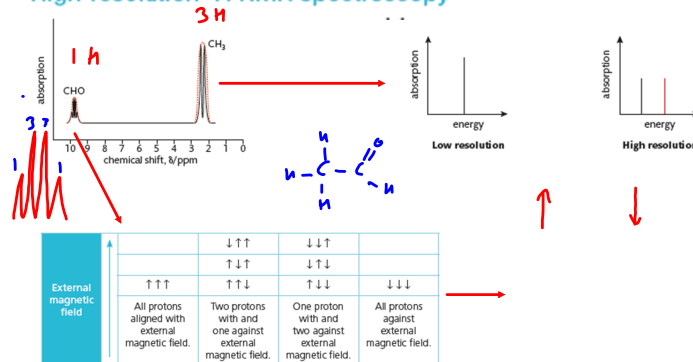
44. How many peaks will the following compounds show in their <sup>1</sup>H NMR spectra?



45. Describe and explain the <sup>1</sup>H NMR spectrum of CH<sub>3</sub>CH<sub>2</sub>OH.





High-resolution  $^1\text{H}$  NMR spectroscopy

quartet

## Worked example

Predict the splitting pattern produced by a neighbouring  $-\text{CH}_2-$  group.

## Solution

There are  $2^2$  different combinations.

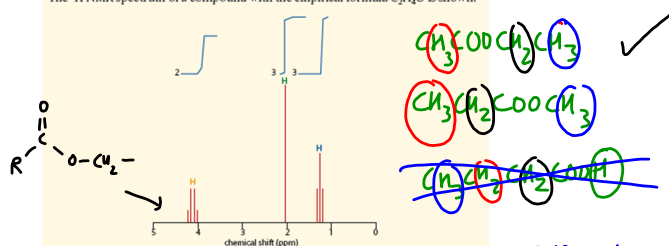
↑↑	↑↓	↓↓
Both protons aligned with external magnetic field.	One proton aligned with and one against external magnetic field.	Both protons aligned against external magnetic field.

Three lines are produced with relative intensities of 1, 2, 1.

Number of chemically equivalent protons causing splitting	Splitting patterns with relative intensities
0	1
1	1 1
2	1 2 1
3	1 3 3 1
4	1 4 6 4 1

singlet  
doublet  
triplet  
quartet  
quintet

## Worked example

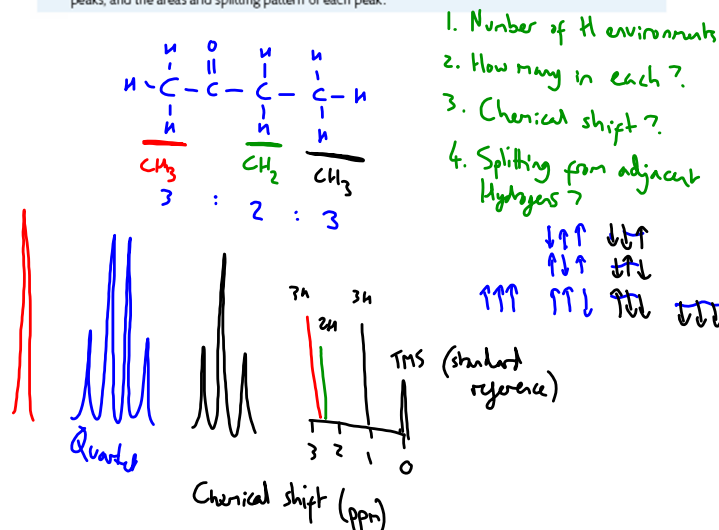
The  $^1\text{H}$  NMR spectrum of a compound with the empirical formula  $\text{C}_2\text{H}_4\text{O}$  is shown.

- (a) Deduce the molecular formula of the compound.  $\rightarrow \text{C}_4\text{H}_8\text{O}_2 \rightarrow \text{IHD} \rightarrow 1$
- (b) Draw possible structures of molecules with this molecular formula.
- (c) Use section 27 of the IB data booklet to identify a structure which is consistent with the  $^1\text{H}$  NMR spectrum and account for the number of peaks and the splitting patterns in the spectrum.

↑↑  
↑↓  
↓↓

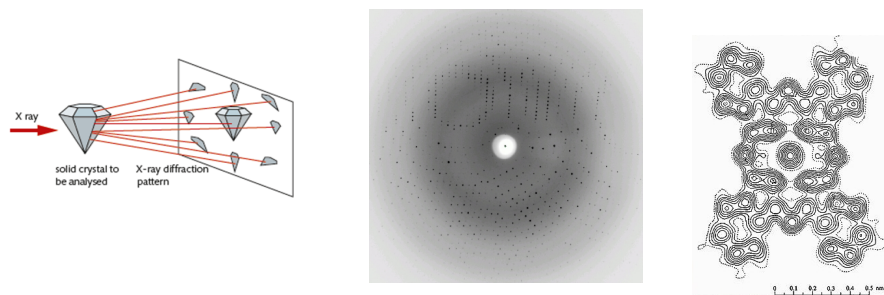
## Exercises

- 46 (a) Draw the molecular structure of butanone.
- (b) Use section 27 of the IB data booklet to predict the high resolution  $^1\text{H}$  NMR spectrum of butanone. Your answer should include the chemical shift, the number of hydrogen atoms, and the splitting pattern for the different environments of the hydrogen atoms.
- 47 Compare the  $^1\text{H}$  NMR spectra of ethanal and propanone. Your answer should refer to number of peaks, and the areas and splitting pattern of each peak.



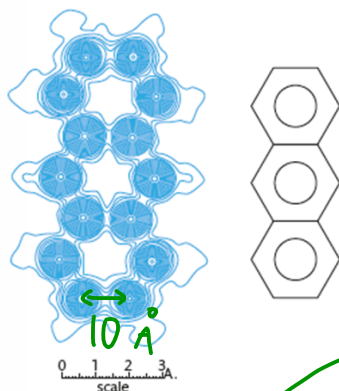
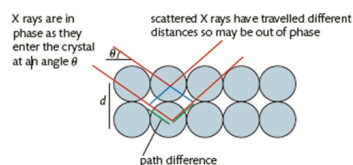
## X-ray diffraction

X-ray crystallography works by shining X-rays onto a very pure crystal of the substance you are interested in. The X-rays are diffracted (bent from their original path) when they interact with regions of high electron density and produce a diffraction pattern that can be converted into an electron density map.



We use monochromatic x-rays (waves of equal wavelength) so that we can easily relate the diffraction pattern and the crystal structure.

Why must we carry this out with the sample in a solid state?



The electron density map produced by anthracene.

The information can be used to calculate:

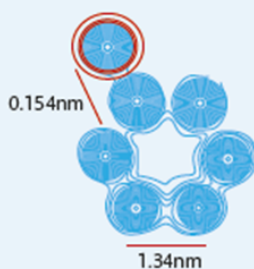
- Bond lengths
- Bond angles

Why can we not see the hydrogens in this diffraction pattern?



### Exercises

- 49 Which analytical technique would give bond length and bond angle data for a metal complex?
- 50 When monochromatic X rays are directed towards a crystal, some under by the term monochromatic and why is this important in X-ray crystallography?
- 51 Why do hydrogen atoms not appear in an electron density map produced by X-ray diffraction?
- 52 Explain why a sample must be in the solid state when X-ray diffraction is used to determine structure.
- 53 A simplified electron density map of a compound is shown.



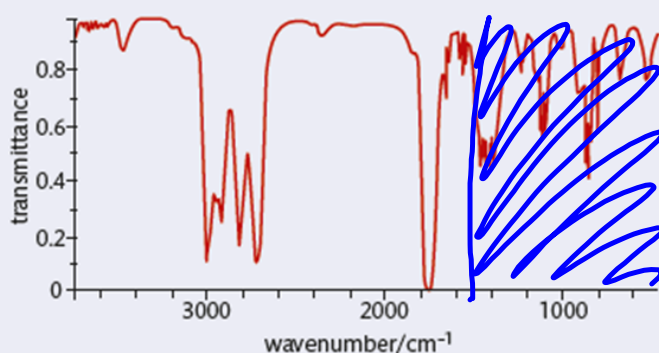
- (a) Identify the compound from its bond length data.
- (b) Explain why not all the atoms are shown in the electron density map.
- (c) Deduce the degree of IHD of the compound.

The angle of diffraction depends on the wavelength. If the X-rays have different wavelengths, different diffraction angles/pattern would be obtained. It would be impossible to match the angles with the wavelengths.

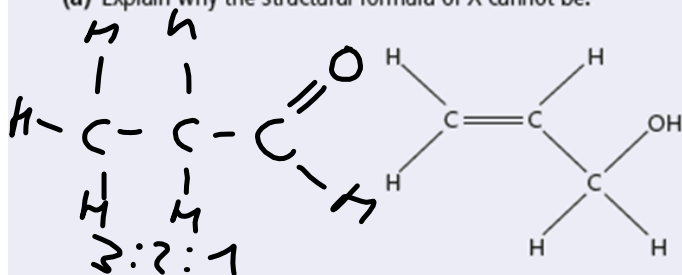
- 51 Hydrogen atoms have a low electron density.
- 52 The atoms must have a regular arrangement if an ordered diffraction pattern is to be produced.
- 53 (a)  $C_6H_6CH_3$   
(b) Hydrogen atoms do not appear because of their low electron density  
(c) The saturated non-cyclic compound is  $C_7H_{16}$   

$$IHD = \frac{1}{2}(16 - 8) = 4$$
 (the IHD of a benzene ring = 4)

9 The infrared spectrum of a substance, X, with empirical formula  $C_3H_6O$  is given below.



(a) Explain why the structural formula of X cannot be:



(2)

(b) The  $^1H$  NMR spectrum of X consists of three peaks. Deduce the structural formula of X and the relative areas under each peak.

(2)

(Total 4 marks)

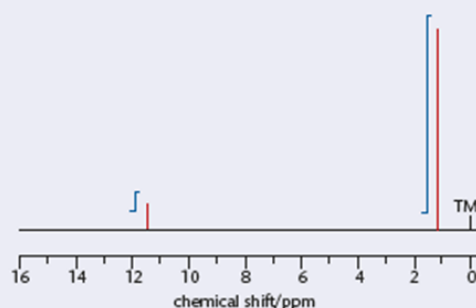
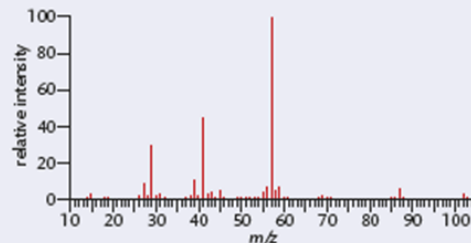
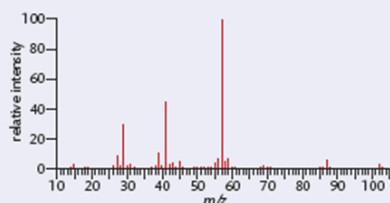
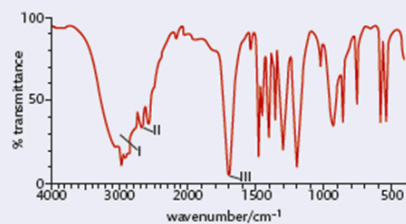
9 (a)

(b)

6 Infrared spectroscopy is commonly used as an analytical technique by inorganic, physical, and organic chemists.

(a) Explain why hydrogen bromide is IR active whereas bromine is IR inactive. (1)

(b) The IR spectrum, mass spectrum, and  $^1\text{H}$  NMR spectrum of an unknown compound, X, of molecular formula  $\text{C}_5\text{H}_{10}\text{O}_2$ , are as follows.



- (i) In the IR spectrum, identify the bond responsible for each of the absorptions labelled I, II, and III. (3)
- (ii) In the mass spectrum, deduce which fragments the  $m/z$  values at 102, 57, and 45 correspond to. (3)
- (iii) Identify the peak at 11.5 ppm in the  $^1\text{H}$  NMR spectrum. (1)
- (iv) State what information can be obtained from the integration traces in the  $^1\text{H}$  NMR spectrum about the hydrogen atoms responsible for the peak at 1.2 ppm. (1)
- (v) Deduce the structure of X. (1)
- (vi)  $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$  is an isomer of X. Deduce two differences between the  $^1\text{H}$  NMR spectrum of this isomer and that of X. (2)

6 (a) (stretches/vibrations in) HBr involve change in bond dipole / (stretches/vibrations in)  $\text{Br}_2$  do not involve change in bond dipole [1]

(b) (i) I: O—H  
II: C—H  
III: C=O [3]

Award [2] for C—H for I and O—H for II.

(ii)  $m/z$  102: molecular ion peak /  $(\text{CH}_3)_3\text{CCOOH}^+ / \text{C}_5\text{H}_{10}\text{O}_2^+ / \text{M}^+$   
 $m/z$  57:  $(\text{CH}_3)_3\text{C}^+ / (\text{M}-\text{COOH})^+ / \text{C}_4\text{H}_9^+$   
 $m/z$  45:  $\text{COOH}^+$  [3]

Penalize missing + once only.

(iii) (H of) COOH group [1]

(iv) nine hydrogens in the same environment /  $(\text{CH}_3)_3\text{C}-$  (group) [1]

(v)  $(\text{CH}_3)_3\text{CCOOH} / (\text{CH}_3)_3\text{CCOOH} / \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{COOH}$  [1]

(vi) no peak at 11.5 ppm in spectrum of isomer / different chemical shift values  
four peaks (instead of two) / different number of peaks;  
Three of these peaks can be split in actual spectrum, so allow for this in answers if exactly four peaks is not stated.  
different integration trace / different areas under the peaks / integration trace would have a 3:2:2:3 peak area ratio [2 max]  
Do not award mark if incorrect peak area ratios are given for the structure drawn in (v).