F324: Rings, Polymers & Analysis
4.3.2 – Spectroscopy MARK SCHEME

1. (a) **infrared – 1 mark only**

shows (very broad) peak between 2500–3300 (cm^{-1})
(due to O–H bond) ✓

ALLOW *(very broad) peak around 3000 (cm^{-1})* ***OR*** *any stated value between 2500 and 3300 (cm^{-1}) for O–H*

DO NOT ALLOW *peak in range 3200–3550 (cm^{-1})*

IGNORE *any reference to C=O or C–O as both are also present in an ester* ***OR*** *to fingerprint region*

^{13}C NMR – 2 marks

$(CH_3)_2CHCH_2COOH$ has 4 peaks (due to 4 different C environments) ✓
$(CH_3)_3CCOOH$ has 3 peaks (due to 3 different C environments) ✓

ALLOW *'^{13}C NMR detects the number of/different C environments' for 1 ✓, suitable example for the 2nd mark 3*

3

(b) **splitting pattern**

explains any two in terms of '*n* + 1 rule' for two marks ✓✓
Explains any one peak for 1 mark ✓

1 mark *for correct ester*

if two splitting patterns are correctly analysed ***ignore*** *the third*

- *singlet* therefore adjacent C (if any) has no Hs

  ALLOW *singlet because next or bonded to an O*

- *multiplet* **OR** split into 7 therefore adjacent Cs have lots of/6 Hs

  ALLOW *multiplet/heptet because next to 2 CH_3s*

- *doublet* therefore adjacent C is bonded to 1H

  ALLOW *doublet because next to a CH*

must spell ***one*** *of multiplet / heptet, singlet, doublet correctly*

max = 2 marks

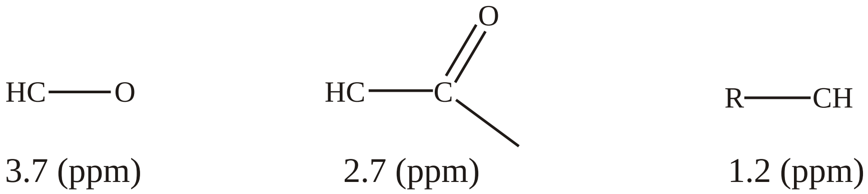
chemical shifts
two marks if any two absorptions are identified correctly ✓✓
one mark if any one absorption is identified correctly ✓

__ALLOW__ tolerance on δ values; 3.6–3.8, 2.6–2.8 and 1.1–1.3 (ppm)

- peak ~3.7 (ppm) – bonded to an O
- peak ~2.7 (ppm) – indicates it is next to a C=O
- peak ~1.2 (ppm) – bonded to other Cs **OR** part of a chain

max = 2 marks

__ALLOW__ any two gets 2 marks, any one scores 1 mark



__ALLOW__ peaks labelled on the spectrum
__ALLOW__ singlet must be bonded to O, multiplet to C=O and doublet to CH or R for both chemical shift marks

if two chemical shifts are correctly identified __IGNORE__ the third

compound identified as $(CH_3)_2CHCOOCH_3$ ✓✓

compound identified as $CH_3COOCH(CH_3)_2$ ✓

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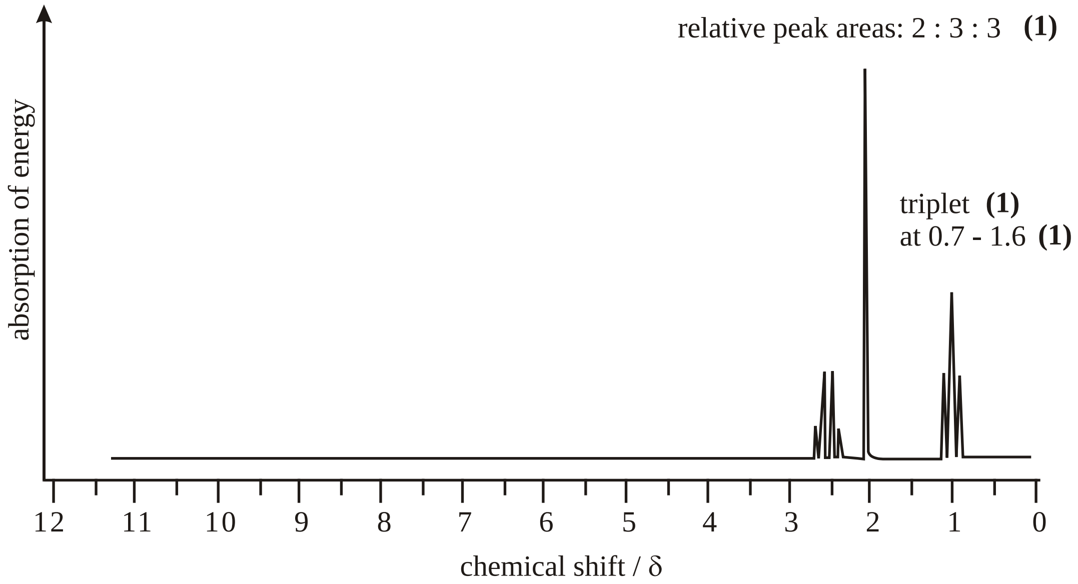
[9]

2. (i) the peak is due to the CH_3CO- group **(1)**

not split, so next to a C with no protons / has no neighbouring proton / δ value is in the range 2.0 – 2.9 **(1)** 2

(ii) adjacent to a C with three protons / to a CH_3 **(1)** 1

(iii) and (iv) 3



mark any additional incorrect peaks first

[6]

3. IR

Similarities
Any 2 of the following three peaks (must give the quoted range)
peak corresponding to OH in all three(3230 – 3550 cm^{-1}) **(1)**
peak corresponding to NH in all three(3100 – 3500 cm^{-1}) **(1)**
peak corresponding to CO in all three (1000 – 1300 cm^{-1}) **(1)** 2 max

Differences
only shown in the fingerprint region **(1)** 1

Mass Spec

similarities
M_r (75)/ base peak will be the same **(1)** 1
M + 1 peak same **(1)** 1

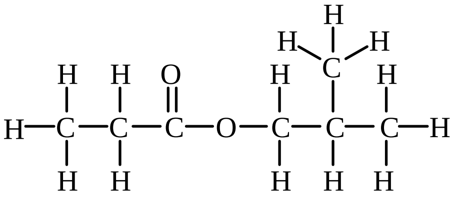
Differences
Fragmentation pattern may show differences between isomers / specific example, eg CH_3+ at m/e 15 **(1)** 1

(MAX 5)

QWC
Use of any two terms from: functional group / amino group / hydroxy group / fingerprint / fragmentation / fragment ion(s) / base peak or molecular ion / M + 1 peak / m/e 1

[6]

4. (a)



propanoate and ester group **(1)** 2-methyl propyl **(1)** 2

(b) propanoic acid **(1)**
(2-)methylpropan-1-ol **(1)**

heat **(1)**
conc. H_2SO_4 **(1)**
(allow ecf from part (a) for the equation)

$CH_3CH_2COOH + CH_3)_2CHCH_2OH \rightarrow CH_3CH_2COOCH_2CH(CH_3)_2 + H_2O$
reactants **(1)** products **(1)** 6

(c) mass spectrum / spectrometry **(1)**

molecular ion peak /
m/e or mass of the peak furthest right **(1) AW** 2

[10]

5. ***δ* value / chemical shift** gives the 'type' of proton /
chemical environment **(1) AW**
example quoted from data sheet **(1)**

number of peaks gives the number of different types of proton /
chemical environments **(1)**

relative / ratio of **(1)**
peak areas gives the number of protons (of each type) **(1)**

splitting gives number of neighbouring / adjacent protons **(1)**

description of *n* + 1 rule / example of doublet, triplet or quadruplet
showing 1, 2 and 3 protons neighbouring (carbon) atom **(1) AW**

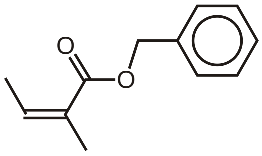
D_2O can be used to identify OH groups **(1)**
ANY 7 marks out of 8 7

Quality of written communication mark for correct use and
organisation of at least two of the following technical terms:
proton, environment, singlet (doublet *etc*.), ppm, equivalent,
chemical shift, splitting, labile, integration 1

[8]

6. (a) (i) alkene **(1)**
ester **(1)** 2
allow "C=C double bond"

i.



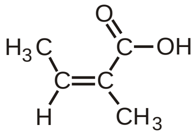
(1) 1

ii. $C_{12}H_{14}O_2$ **(1)** 1

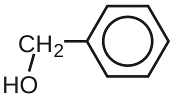
(b) same structural formula/order of bonds,
different spacial arrangement **AW (1)**

description or diagram showing **B** and how it is different from **A (1)**☐ 2

(c)



(1)



(1) 2

(d) (i) peak at 1680-1750 (cm^{-1}) due to C=O **(1)**

peak at 1000-1300 (cm^{-1}) due to C-O / **(1)** 2

(ii) 2500-3300 / 3230-3550 (cm^{-1}) **(1)**

O-H /carboxylic acid/alcohol is **not** present in **A (1)**

allow 1 mark for ~500-1500 (cm^{-1}) which is a unique
fingerprint region etc 2

[12]

7. (a) low boiling point / easily turns to a gas **AW (1)** 1

(b) 2,4-dinitrophenylhydrozine / 2,4-DNP(H) / Brady's reagent **(1)**

purify/recrystallise the product/solid (derivative) **(1)**

measure the melting point /mp **(1)**

compare the result with data book/known values **(1)** 4

[5]

8. (a) (i) Molecular ion peak: the peak caused by the unfragmented molecule / the peak with the highest m/e value / the peak that tells you the Mr. 1

Base peak : peak with the greatest (relative) intensity / peak representing most stable/abundant fragment
NOT the tallest / biggest / most common peak 1

(ii) The molecular ion is too unstable / will have been completely fragmented / may not carry a positive charge 1
NOT peak too small to be seen / too little ion present

(b) IR spectrum:
C=O peak at approx 1650 cm^{-1} (1680-1750 cm^{-1}) 1
broad O-H peak at value(s) between 2500-3300 cm^{-1} 1
ignore any references to C-O peak at 1000 – 1300 cm^{-1}

mass spectrum:
Fragment with m/e = 31 is CH_2OH^+ 1
Fragment at m/e = 45 is $COOH^+$ 1

penalise missing + sign once only

(c) 2 proton peak at δ = 3.3-4.3 – singlet ($-CH_2-$) 1
1 proton peak at δ = 3.5-5.5 – singlet (-OH) 1
1 proton peak at δ = 11.0-11.7 – singlet (-COOH) 1
(ranges of chemical shift (δ) values taken from data sheet)

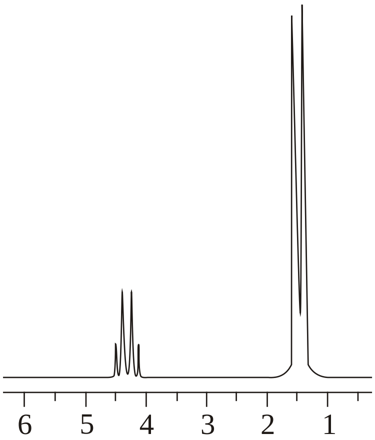
- penalise each error once only
- ignore peak areas/heights unless incorrectly labelled

Labelled diagram of the structure of G proposed by the student may be used to provide evidence for the positioning of peaks on the sketched spectrum.

Both OH and COOH protons disappear on shaking with D_2O 1

[11]

9. (i)



splitting:
doublet **(1)**
quartet **(1)**

ignore any other peaks

position:
doublet peak is at ~1.4 and
quartet peak is at ~4.3 **(1)**

allow ecf from ***one*** *incorrect splitting pattern*

areas:
1 and 3 on the correct peaks
(or either way round as ecf if any errors above) **(1)** 4

(ii) 4 **(1)**
OH/labile protons now visible AW **(1)** 2

[6]

10. (a) (i) Find the m /e of …. **(1)**
... the peak furthest to the right / with highest m /e or mass **(1)** 2

allow attempts to cater for the ^{13}C peak

$C_2H_3O_2$ /empirical formula has M_r = 59 **(1)**
so M_r of molecular formula is $^{118}/_{59}$ = 2 /twice the empirical formula **(1)** 2

(b) (i) OH <u>peak</u> disappears (with D_2O / on the second spectrum) 1

(ii) no of peaks: one **(1)**

splitting: none **(1)**

all four protons equivalent / in the same environment **(1)** 3

if the wrong structure is chosen allow ecf for:
two peaks ***(1)****,*
splitting ***(1)(1)*** *(as last 2 marks for part (ii))*

[8]

11. (i) **A** C_3H_6 **(1)** **B** C_4H_8 **(1)** 2

(ii) **A** $CH_3CH{=}CH_2$ (or displayed) ('sticks' penalised once) 1

(iii) $C_3H_5^+$ **(1)** for formula and **(1)** for charge 2

[5]