4.11 ANSWERS TO EXERCISES

4.11 Exercise 1

1. 45 – $COOH^+$
   43 - $CH_3CH_2CH_2^+$
   equations: $CH_3CH_2CH_2COOH^{+\cdot} \rightarrow CH_3CH_2CH_2^+ + \cdot COOH$
   $CH_3CH_2CH_2COOH^{+\cdot} \rightarrow CH_3CH_2CH_2 + \cdot COOH^+$

   29 - $CH_3CH_2^+$
   59 - CH_2COOH^+
   equations: $CH_3CH_2CH_2COOH^{+\cdot} \rightarrow CH_3CH_2^+ + \cdot CH_2COOH$
   $CH_3CH_2CH_2COOH^{+\cdot} \rightarrow CH_3CH_2\cdot + CH_2COOH^+$

   15 – CH_3^+
   73 - $CH_2CH_2COOH^+$
   equations: $CH_3CH_2CH_2COOH^{+\cdot} \rightarrow \cdot CH_3 + CH_2CH_2COOH^+$
   $CH_3CH_2CH_2COOH^{+\cdot} \rightarrow CH_3^+ + \cdot CH_2CH_2COOH$

   Methylpropanoic acid contains no peaks at 29 and 59 as it contains no such fragments

2. Pentan-2-one gives a peak at 43 due to $CH_3CH_2CH_2^+$ and CH_3CO^+
   equations: $CH_3CH_2CH_2COCH_3^{+\cdot} \rightarrow CH_3CH_2CH_2^+ + \cdot COCH_3$
   $CH_3CH_2CH_2COCH_3^{+\cdot} \rightarrow CH_3CH_2CH_2\cdot + COCH_3^+$
   Pentan-3-one gives no peak at 43 as it contains no such fragments

3. a) 15 - $CH_3CH_2CH_2CH_2CH_3^{+\cdot} \rightarrow CH_3^+ + \cdot CH_2CH_2CH_2CH_3$
   29 - $CH_3CH_2CH_2CH_2CH_3^{+\cdot} \rightarrow CH_3CH_2^+ + \cdot CH_2CH_2CH_3$
   43 - $CH_3CH_2CH_2CH_2CH_3^{+\cdot} \rightarrow CH_3\cdot + {}^+CH_2CH_2CH_2CH_3$
   57 - $CH_3CH_2CH_2CH_2CH_3^{+\cdot} \rightarrow CH_3CH_2\cdot + {}^+CH_2CH_2CH_3$
   b) 15 - $CH_3COOCH_2CH_3^{+\cdot} \rightarrow CH_3^+ + \cdot COOCH_2CH_3$
   15 - $CH_3COOCH_2CH_3^{+\cdot} \rightarrow CH_3COOCH_2\cdot + {}^+CH_3$
   29 - $CH_3COOCH_2CH_3^{+\cdot} \rightarrow CH_3COO\cdot + {}^+CH_2CH_3$
   43 - $CH_3COOCH_2CH_3^{+\cdot} \rightarrow CH_3CO^+ + \cdot OCH_2CH_3$
   c) 15 - $CH_3CH_2COOH^{+\cdot} \rightarrow CH_3^+ + \cdot CH_2COOH$
   29 - $CH_3CH_2COOH^{+\cdot} \rightarrow CH_3CH_2^+ + \cdot COOH$
   57 - $CH_3CH_2COOH^{+\cdot} \rightarrow CH_3CH_2CO^+ + \cdot OH$
   d) 15 - $CH_3CH_2CH_2CH_2CHO^{+\cdot} \rightarrow CH_3^+ + \cdot CH_2CH_2CH_2CHO$
   29 - $CH_3CH_2CH_2CH_2CHO^{+\cdot} \rightarrow CH_3CH_2^+ + \cdot CH_2CH_2CHO$
   43 - $CH_3CH_2CH_2CH_2CHO^{+\cdot} \rightarrow CH_3CH_2CH_2^+ + \cdot CH_2CHO$
   57 - $CH_3CH_2CH_2CH_2CHO^{+\cdot} \rightarrow CH_3CH_2CH_2CH_2^+ + \cdot CHO$

4.11 Exercise 2

1. peak at 1.1 is CH_3- adjacent to -CH_2-
peak at 2.2 is -CH_2CO-, adjacent to CH_3-
peak at 11.8 is –COOH
so molecule is propanoic acid, CH_3CH_2COOH

2. a) peak at 1.2 is CH_3-, adjacent to -CH_2-
peak at 1.3 is also CH_3-, adjacent to -CH_2-
peak at 2.3 is -CH_2CO-, adjacent to CH_3-
peak at 4.1 is -CH_2O-, adjacent to CH_3-
so molecule is ethyl propanoate, $CH_3CH_2COOCH_2CH_3$

b) $CHCl_3$ is not used as a solvent because it contains a proton which will interfere with the spectrum of the substance being analysed.

c) TMS is a good standard because
- it contains 12 identical protons, giving a single intense peak
- it contains highly shielded protons, which do not interfere with the spectrum
- it is cheap and non-toxic

3. a) Propanal has three peaks, propanone has two
b) Both have three peaks, two with chemical shift between 0 and 50. However the third peak in propanone will have a chemical shift at 160 – 220, but the third peak in propan-2-ol will have a chemical shift at 50 - 90
c) i) 4 ii) 5 iii) 3

4.11 Exercise 3

1. Molecular formula = $C_5H_{10}O_2$

infra-red spectrum:
peak at 1710 cm^{-1} indicates a carbonyl
proton nmr spectrum:
peak at 0.8 is CH_3- adjacent to -CH_2-
peak at 1.1 is -CH_2- adjacent to CH_3- and -CH_2-
peak at 2.3 is -CH_2CO- adjacent to -CH_2-
peak at 3.7 is CH_3O-
so molecule is methyl butanoate, $CH_3CH_2CH_2COOCH_3$
mass spectrum:
peak at 43 from:
$CH_3CH_2CH_2COOCH_3^{+\cdot} \rightarrow CH_3CH_2CH_2^{+} + \cdot COOCH_3$
peak at 71 from:
$CH_3CH_2CH_2COOCH_3^{+\cdot} \rightarrow CH_3CH_2CH_2CO^{+} + \cdot OCH_3$