Part A.

1. Associate each of the following IR spectra with one of the following compounds and justify your answer.

   a. Propanoic acid: look for a carbonyl stretch and a broad OH stretch
   b. 2-Pentanol: look for an OH peak (broad). No carbonyl peak, no \( sp^3 \) CH's.
   c. Benzyl alcohol: Look for an OH peak and \( sp^3 \) CH's. No carbonyl peak.
   d. Acetophenone: Look for a carbonyl peak and \( sp^2 \) CH's. No OH peak.

Note: the key functional groups must be identified. Identifying the peaks on the spectrum directly is an straightforward way to do this.
Problem set 3 - Answers

Associate each of the following IR spectra with one of the following compounds and justify your answer.

c. 2-Propyn-1-ol: Look for an alkyne peak C=C plus an OH peak (broad) and a CH.

d. 1-Pentyne: Look for an alkyne peak C=C plus CH. No other key groups.

e. 4-Methylpentanenitrile: Look for a CN. No OH, C=O or CH.

Note: the key functional groups must be identified. Identifying the peaks on the spectrum directly is an straightforward way to do this.
2. Give the number of peaks expected for the indicated protons in each of the following structures:

**Note:** s = singlet, d = doublet, t = triplet, q = quartet

- a) [Diagram]
  - 2 (d) for H3C
  - 3 (t) for H2
  - 2 (d) for CH3

- b) [Diagram]
  - 3 (t) for H3C
  - 5 (quintet) for CH3

- c) [Diagram]
  - 2 (d) for Cl

- d) [Diagram]
  - 1 (s) for H
  - 1 (s) for CH2
  - 2 (d) for CH3

- e) [Diagram]
  - 4 (q) for H2
  - 1 (s) for CH3
  - Note: usually a broad singlet

- f) [Diagram]
  - 2 (d) for H2

3. How many signals would be expected in the following molecules?

- a) [Diagram]
  - 5 signals

- b) [Diagram]
  - 1 signal

- c) [Diagram]
  - 3 signals

- d) [Diagram]
  - 4 signals

- e) [Diagram]
  - 3 signals

- f) [Diagram]
  - 2 signals
4. Explain the following differences in chemical shift.

a) The "H" at 7.7 ppm is deshielded by resonance. Another way to put this is that resonance with the carbonyl group removes electron density from the proton.

\[ \delta = 7.1 \quad \delta = 7.7 \text{ ppm} \]

b) The "H" at 6.7 ppm is strongly deshielded by resonance. The proton at 6.1 ppm is deshielded only by proximity to the electron-withdrawing carbonyl group. This inductive effect is less powerful than the resonance effect.

\[ \delta = 6.1 \text{ ppm} \]

c) The oxygen of the ester is even more electronegative than the oxygen of the ether because resonance in the ester is strongly drawing electron density to the carbonyl oxygen. Electron density is consequently pulled more strongly away from the H's at 4.41 ppm.

\[ \delta = 3.6 \text{ ppm} \]

d) Resonance with the nitrogen pushes electron density onto the H at 4.2 ppm, effectively "shielding" it with electrons.
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5. Determine the structure of the following unknowns using the table to fill in your answers.

<table>
<thead>
<tr>
<th>Signal</th>
<th>δ</th>
<th>Integration</th>
<th>Multiplicity or Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>~4.3</td>
<td>1H</td>
<td>m (multiplet) or septet CH next to O (based on δ)</td>
</tr>
<tr>
<td>B</td>
<td>~2.0</td>
<td>3H</td>
<td>s CH₃ next to C=O</td>
</tr>
<tr>
<td>C</td>
<td>~1.3</td>
<td>6H</td>
<td>d 2 x CH₃ (identical) next to CH (i.e. an isopropyl group)</td>
</tr>
</tbody>
</table>

\[ DU = \frac{[5\times2 + 2 - 10]}{2} = 1 \]

Integration: \( \frac{6 \text{ mm} + 18 + 34}{10\text{H}} = 5.8 \text{ mm/H} \)

The pieces:

- \( \text{CH}_3 \)
- \( \text{CH}_3 \)
- \( \text{O} \)
- \( \text{CH}_3 \)

The molecule:

\( \left\{ \begin{array}{c} \text{CH}_3 \text{CH} \text{O} \text{CH} \text{CH}_3 \\ \text{C}_5\text{H}_{10}\text{O}_2 \end{array} \right\} \)
**Problem set 3 - Answers**

**b.**

![Molecular structure](image)

<table>
<thead>
<tr>
<th>Signal</th>
<th>δ</th>
<th>Integration</th>
<th>Multiplicity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>~7.8</td>
<td>2H (CH₂ or 2 x CH)</td>
<td>d</td>
<td>Not all the 2H’s can be CH₂ or there wouldn’t be enough carbons accounted for in the molecule (there are 10 carbons in the molecule); These H’s are in the aromatic region—they can’t be CH₂’s – only CH group exist on aromatic rings. Each CH is next to another CH</td>
</tr>
<tr>
<td>B</td>
<td>~7.2</td>
<td>2H (CH₂ or 2 x CH)</td>
<td>d</td>
<td>See explanation above</td>
</tr>
<tr>
<td>C</td>
<td>~2.7</td>
<td>2H (CH₂ or 2 x CH)</td>
<td>q</td>
<td>CH₂ next to CH₃ (b/c the peak is a quartet); not directly next to O, could be next to C=O (based on δ)</td>
</tr>
<tr>
<td>D</td>
<td>~2.6</td>
<td>3H</td>
<td>s</td>
<td>CH₃ next to C=O (based on δ) or on phenyl ring (which acts like an electron-withdrawing group)</td>
</tr>
<tr>
<td>E</td>
<td>~1.2</td>
<td>3H</td>
<td>t</td>
<td>CH₃ next to CH₂</td>
</tr>
</tbody>
</table>

**DU** = \([10(2) + 2 - 12]/2 = 5\)

**HINT:** DU of 4 = phenyl ring…

In this molecule, there is probably a phenyl ring (DU = 4) + one ring or one double bond

**Integration:** \((11 \text{ mm} + 11 + 11 + 17 + 17)/12\text{H’s} = 5.6 \text{ mm/H}\)
The pieces:

? = carbonyl or phenyl

The molecule:

Note: Carbonyl group should be placed at "X". We can tell this because $H_A$ is the most deshielded of the aromatic protons (by resonance with the carbonyl group).
Problem set 3 - Answers

c.

<table>
<thead>
<tr>
<th>Signal</th>
<th>δ</th>
<th>Integration</th>
<th>Multiplicity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>~3.4</td>
<td>2H</td>
<td>d</td>
<td>CH₂ (probably not 2 x CH, but keep this in mind, just in case), next to the CH, next to O (based on δ)</td>
</tr>
<tr>
<td>B</td>
<td>~3.3</td>
<td>3H</td>
<td>s</td>
<td>CH₃ isolated, next to O (based on δ)</td>
</tr>
<tr>
<td>C</td>
<td>~1.8</td>
<td>1H</td>
<td>m</td>
<td>CH multiplet (hard to say what the neighbors are)</td>
</tr>
<tr>
<td>D</td>
<td>~1.3</td>
<td>4H</td>
<td>m</td>
<td>2 x CH₂ (identical—symmetry exists in the molecule); hard to say what the neighbors are</td>
</tr>
<tr>
<td>E</td>
<td>~0.9</td>
<td>6H</td>
<td>t</td>
<td>2 x CH₃, identical in chemical environment, each next to CH₂ (also identical)</td>
</tr>
</tbody>
</table>

**DU** = \[\frac{7(2) + 2 - 16}{2}\] = 0 → no rings or double bonds

**Integration**: \(\frac{(12 \text{ mm} + 17 + 6 + 23 + 34)}{16 \text{ H’s}}\) = 5.8 mm/H

**The pieces:**

[Diagram of the pieces]

**The molecule:**

[Diagram of the molecule]

Note: the formula contains only one oxygen
6. Determine the most likely structure of a compound, with the molecular formula \( \text{C}_9\text{H}_{12} \), which gave a \(^1\text{H}\) NMR spectrum consisting of:
   - a doublet at \( \delta \ 1.25 \)
   - a septet at \( \delta \ 2.90 \) and
   - a multiplet at \( \delta \ 7.25 \)

\[ \text{\includegraphics[width=0.5\textwidth]{diagram.png}} \]

7. A compound with the molecular formula \( \text{C}_{10}\text{H}_{13}\text{Cl} \) gave the following \(^1\text{H}\) NMR spectrum:
   - singlet, \( \delta \ 1.6 \)
   - singlet, \( \delta \ 3.1 \)
   - multiplet, \( \delta \ 7.2 \) (5H)

The most likely structure for the compound is:

\[ \text{\includegraphics[width=0.5\textwidth]{diagram.png}} \]

8. Determine the likely structure for a compound \( \Lambda \ (\text{C}_6\text{H}_{10}\text{O}) \), which is found to decolorize bromine in carbon tetrachloride. Its spectral data is as follows:

\[ \begin{array}{c|c|c}
\text{\(^1\text{H}\) NMR} & \text{IR} & \\
\hline
\text{triplet, } \delta \ 1.0 & \text{singlet, } \delta \ 2.4 & 2200 \text{ cm}^{-1} \ (\text{sharp}) \\
\text{singlet, } \delta \ 1.4 & \text{singlet, } \delta \ 3.4 & 3300 \text{ cm}^{-1} \ (\text{sharp}) \\
\text{quartet, } \delta \ 1.6 & & 3500 \text{ cm}^{-1} \ (\text{broad}) \\
\end{array} \]

\[ \text{\includegraphics[width=0.5\textwidth]{diagram.png}} \]

9. Briefly explain how you might distinguish between the following substances by comparing their \(^1\text{H}\)-NMR spectra:
The main difference would likely be in the chemical shift of the methine proton of the isopropyl group. The methine proton in I is likely to be more deshielded, and produce a signal (septet) at about 3.5 ppm, while the analogous proton in II is likely to be found, also as a septet, at about 2.3 ppm.
10. An unknown compound has the formula C₆H₁₂O. Elucidate the structure of the molecule by scrutinizing its IR, ¹H NMR and ¹³C NMR spectra, shown below.

The molecule:

- **A**: ~2.4 ppm, 2H, Triplet (t), CH₂ next to CH₂ (based on multiplicity) and next to C=O (based on δ)
- **B**: ~2.1 ppm, 3H, Singlet (s), CH₃ next to C=O (based on δ)
- **C**: ~1.6 ppm, 2H, Multiplet (m), CH₂
- **D**: ~1.3 ppm, 2H, Multiplet (m), CH₂
- **E**: ~0.9 ppm, 3H, Triplet (t), CH₃ next to CH₂ (based on multiplicity)

**Integration**:

\[ \text{DU} = \frac{[6(2) + 2 - 12]}{2} = 1 \rightarrow C=O \text{ (based on IR)} \]

\[ \text{Integration: } \frac{9 \text{ mm} + 13 + 10 + 10 + 14}{12 \text{ H's}} = 4.7 \text{ mm/H} \]
An unknown compound, I, has the formula C₃H₇NO₂. Elucidate the structure of I by scrutinizing its IR, ¹H NMR and ¹³C NMR spectra, shown below.
### Problem set 3 - Answers

<table>
<thead>
<tr>
<th>Signal</th>
<th>( \delta )</th>
<th>Integration</th>
<th>Multiplicity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>~4.4</td>
<td>2H</td>
<td>Triplet (t)</td>
<td>( \text{CH}_2 ), next to ( \text{CH}_2 ) (based on multiplicity), next to O or ( \text{NO}_2 ) (based on ( \delta ))</td>
</tr>
<tr>
<td>B</td>
<td>~2.0</td>
<td>2H</td>
<td>M</td>
<td>( \text{CH}_2 )</td>
</tr>
<tr>
<td>C</td>
<td>~1.0</td>
<td>3H</td>
<td>t</td>
<td>( \text{CH}_3 ), next to ( \text{CH}_2 )</td>
</tr>
</tbody>
</table>

**DU** = \( \frac{3(2) + 2 +1 - 7}{2} = 1 \rightarrow \text{NOT a} \text{C}=\text{O based on IR… maybe NO}_2? \)

**Integration:** \( \frac{(17 \text{ mm} + 17 + 26)}{7 \text{H's}} = 8.6 \text{ mm/H} \)

**The molecule:**

![Molecule Diagram]
Part B. Identify the compound represented in each of the $^1$H NMR spectra

1. 2-pentanone

\[
\text{CH}_\text{\text{CH}}_\text{CH}_\text{CH}_\text{CH}_\text{C} = \text{O}
\]

2. Pentanal

\[
\text{CH}_\text{CH}_\text{CH}_\text{CH}_\text{C} = \text{O}
\]

3. 3-pentanone

\[
\text{CH}_\text{\text{CH}}_\text{CH}_\text{CH}_\text{CH}_\text{C} = \text{O}
\]

4. Methyl propanoate

\[
\text{CH}_\text{\text{CH}}_\text{CH}_\text{CH}_\text{C} = \text{O}
\]

5. Ethyl acetate

\[
\text{CH}_\text{\text{CH}}_\text{CH}_\text{CH}_\text{C} = \text{O}
\]

6. Butanoic acid

\[
\text{CH}_\text{\text{CH}}_\text{CH}_\text{CH}_\text{CH}_\text{C} = \text{O}
\]

7. 3-methyl butan-2-one

\[
\text{CH}_\text{\text{CH}}_\text{CH}_\text{CH}_\text{C} = \text{O}
\]

8. Isopropyl acetate

\[
\text{CH}_\text{\text{CH}}_\text{CH}_\text{CH}_\text{C} = \text{O}
\]

9. Methyl isobutyrate

\[
\text{CH}_\text{\text{CH}}_\text{CH}_\text{CH}_\text{CH}_\text{C} = \text{O}
\]

10. Isopropyl propionate

\[
\text{CH}_\text{\text{CH}}_\text{CH}_\text{CH}_\text{C} = \text{O}
\]

11. Ethyl isobutyrate
12. ethyl butyrate

13. propyl propionate

14. pentyl formate

15. hexanoic acid

16. butyl acetate

17. methyl pentanoate

18. \( \text{N,N-dimethylpropionamide} \)

19. butyramide

20. \( \text{N-methylbutyramide} \)

21. 1-propanol

22. 2-propanol
23. propanal

24. 1-bromobutane

25. 2-iodobutane

26. 1-chloro-2-methylpropane

27. 2-chloro-2-methylpropane

28. propylbenzene

29. isopropylbenzene

30. 1-ethyl-4-methylbenzene

31. 1,3,5-trimethylbenzene

32. (4-chlorobutyl)benzene

33. (2-chloro-2-methylpropyl)benzene
34. 1-(3-chloropropyl)-4-methylbenzene

35. (2-chlorobutan-2-yl)benzene

36. 3-methylpent-1-yn-3-ol

37. pent-3-yn-1-ol

38. pent-2-yn-1-ol

39. 2-methylbut-3-yn-2-ol

40. pent-4-yn-1-ol

41. 1-methoxypropane

42. ethoxyethane or diethyl ether

43. N-methylpropan-1-amine

44. methyl 4-aminobenzoate

45. 4-aminophenyl acetate
46. benzoyl bromide

47. 4-chlorobenzoic acid or \( p \)-chlorobenzoic acid

48. 1-(4-bromophenyl)propan-1-one

49. butyryl chloride

50. 4-chlorobutan-2-one

51. 2-aminopropanoic acid or alanine