Lecture 17: Solving Spectroscopy Problems Part 2
Discussion Section Problems Solutions

1. Mass spectrum: \( m/z = 154 \) (M)  
   Zero or even number of nitrogens
   \( m/z = 155 \) (M+1): 11.23\% / 1.1 \% = 10.3 \( C_{10} \) or \( C_{11} \)
   \( m/z = 156 \) (M+2): < 4\%  No S, Cl or Br

Formula \((C_{10})\): 154 - 120 \( (C_{10}) = 34 \) amu for oxygens, nitrogens, and hydrogens.

<table>
<thead>
<tr>
<th>Oxygens</th>
<th>Nitrogens</th>
<th>34 - O - N = H</th>
<th>Formula</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>None’</td>
<td>34 - 0 - 0 = 34</td>
<td>( C_{10}H_{34} )</td>
<td>Violates H-rule</td>
</tr>
<tr>
<td>One</td>
<td>None</td>
<td>34 - 16 - 0 = 18</td>
<td>( C_{10}H_{18}O )</td>
<td>Possible</td>
</tr>
<tr>
<td>Two</td>
<td>None</td>
<td>34 - 32 - 0 = 2</td>
<td>( C_{10}H_{2}O_{2} )</td>
<td>More than two signals in NMR</td>
</tr>
<tr>
<td>None</td>
<td>Two</td>
<td>34 - 0 - 28 = 6</td>
<td>( C_{10}H_{6}N_{2} )</td>
<td>No oxygen for C=O in IR</td>
</tr>
</tbody>
</table>

Formula \((C_{11})\): 154 - 132 \( (C_{11}) = 22 \) amu for oxygens, nitrogens, and hydrogens.

<table>
<thead>
<tr>
<th>Oxygens</th>
<th>Nitrogens</th>
<th>22 - O - N = H</th>
<th>Formula</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>None</td>
<td>22 - 0 - 0 = 22</td>
<td>( C_{11}H_{22} )</td>
<td>No oxygen for C=O in IR</td>
</tr>
<tr>
<td>One</td>
<td>None</td>
<td>22 - 16 - 0 = 6</td>
<td>( C_{11}H_{6}O )</td>
<td>Does not fit NMR integration</td>
</tr>
</tbody>
</table>

DBE: \( C - (H/2) + (N/2) + 1 = 10 - (18/2) + (0/2) + 1 = 2 \)  
Two rings or two double bonds or one triple bond or one ring and one double bond.

IR:  
Zone 1: Alcohol O–H, amine/amide N–H and terminal alkyne \( \equiv C–H \): Absent – peaks too weak.

Zone 2: Aryl/vinyl C–H: Absent - no peaks > 3000 cm\(^{-1}\).  
Alkyl C–H: Present - peaks < 3000 cm\(^{-1}\).  
Carboxylic acid O–H: Absent - not broad enough; not enough oxygens.  
Aldehyde C–H: Probably absent; ~2700 cm\(^{-1}\) is weak.

Zone 3: Alkyne C≡C and nitrile C≡N: Absent – no peaks.

Zone 4: C=O: present at 1716 cm\(^{-1}\); ketone only; not enough oxygen for COOH.

Zone 5: Alkene C=C and benzene ring: Absent – no peaks ~1600 cm\(^{-1}\).
\(^1\)H-NMR:

<table>
<thead>
<tr>
<th>Chemical shift</th>
<th>Splitting</th>
<th>Integral</th>
<th># H</th>
<th>Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 ppm</td>
<td>singlet</td>
<td>2</td>
<td>4 H</td>
<td>2 x CH(_2) or 4 x CH</td>
</tr>
<tr>
<td>1.9 ppm</td>
<td>singlet</td>
<td>1</td>
<td>2 H</td>
<td>CH(_2) or 2 x CH</td>
</tr>
<tr>
<td>1.1 ppm</td>
<td>singlet</td>
<td>6</td>
<td>12 H</td>
<td>4 x CH(_3) or 6 x CH(_2) or 12 x CH</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td></td>
<td></td>
<td>9</td>
<td>18 H (2 x CH(_2)) + CH(_2) + (4 x CH(_3)) = C(<em>7)H(</em>{18})</td>
</tr>
</tbody>
</table>

Atom check: C\(_{10}\)H\(_{18}\)O (MS) - C\(_7\)H\(_{18}\) (NMR) - CO (IR) = C\(_2\). *These carbons may or may not be equivalent.*

DBE check: The C=O in the IR accounts for one of the two calculated DBE. There are not enough oxygens in the formula for the other DBE to be a C=O, and there is no evidence of an alkene from IR or NMR, so the remaining one DBE is probably due to a ring.

**Pieces:**  
2 x CH\(_2\)  
2 x C  
CH\(_2\)  
C=O  
4 x CH\(_3\)  
ring

Assembly: The pieces must now be assembled into a structure that is consistent with the spectra data, chiefly the NMR splitting pattern. The NMR signal for the CH\(_3\) groups show they are all equivalent and have no neighbors. This cannot be achieved by attachment to the C=O, so they must be attached to the two carbons that are not directly bonded to any hydrogens. The pieces are now:

2 x CH\(_3\)–C–CH\(_3\)  
CH\(_2\)  
ring

2 x CH\(_2\)  
C=O

These pieces can only be assembled in one way that is consistent with the NMR splitting pattern.

\[
\begin{array}{c}
\text{O} \\
3,3,5,5-\text{Tetramethylcyclohexanone}
\end{array}
\]

2. **Mass spectrum:** m/z = 112 (M): Even mass so *zero or even number of nitrogens*

m/z = 113 (M+1): 7.86% / 1.1% = 7.2 C\(_7\) or C\(_8\)

m/z = 114 (M+2): < 4% so *no sulfur, chlorine or bromine*
**Formula (C₇):** 112 – 84 (C₇) = 28 amu for oxygens, nitrogens, and hydrogens.

<table>
<thead>
<tr>
<th>Oxygens</th>
<th>Nitrogens</th>
<th>Formula</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>None</td>
<td>28 - O - N = H</td>
<td>C₇H₂₈</td>
</tr>
<tr>
<td>One</td>
<td>None</td>
<td>28 - 16 - 0 = 12</td>
<td>C₇H₁₂O</td>
</tr>
</tbody>
</table>

**Formula (C₈):** 112 - 96 (C₈) = 16 amu for oxygens, nitrogens and hydrogens. IR shows one oxygen (in C=O), leaving no amu for hydrogens. All C₈ formulas are therefore rejected.

**DBE:** C - (H/2) + (N/2) + 1 = 7 - (12/2) + (0/2) + 1 = 2. *Two pi bonds or two rings or one pi bond plus one ring.*

**IR:** Zone 1: Amine/amide N–H, alcohol O–H and terminal alkyne ≡C–H: Absent - no peaks.

Zone 2: Aryl/vinyl C–H: Present - peaks >3000 cm⁻¹.  
Alkyl C–H: Present - peaks < 3000 cm⁻¹.  
Aldehyde C–H: Absent - no peak ~2700 cm⁻¹; zone 4 inconsistent.  
Carboxylic acid O–H: Absent - not broad enough; zone 4 inconsistent.

Zone 3: Alkyne C≡C and nitrile C≡N: Absent - no peaks.

Zone 4: C=O: Absent - 1650 cm⁻¹ is low for C=O but good for alkene.

Zone 5: Alkene C=C: Present - 1650 cm⁻¹ suggests C=C.  
Benzene ring: Absent - not enough DBE.
**1H-NMR:**

<table>
<thead>
<tr>
<th>Chemical Shift</th>
<th>Splitting</th>
<th>Integral</th>
<th># H</th>
<th>Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.34 ppm</td>
<td>doublet</td>
<td>1</td>
<td>1 H</td>
<td>CH in CHCH chemical shift suggests alkene</td>
</tr>
<tr>
<td>4.64 ppm</td>
<td>doublet</td>
<td>1</td>
<td>1 H</td>
<td>CH in CHCH</td>
</tr>
<tr>
<td>3.96 ppm</td>
<td>triplet</td>
<td>2</td>
<td>2 H</td>
<td>CH₂ in CH₂CH₂ CH₂ in CHCH₂CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 x CH in CHCH₂CH₂ 2 x CH in CHCHCH</td>
</tr>
<tr>
<td>1.85 ppm</td>
<td>triplet</td>
<td>2</td>
<td>2 H</td>
<td>CH₂ in CH₂CH₂ CH₂ in CHCH₂CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 x CH in CHCH₂CH₂ 2 x CH in CHCHCH</td>
</tr>
<tr>
<td>0.94 ppm</td>
<td>singlet</td>
<td>6</td>
<td>6 H</td>
<td>2 x CH₃ or 3 x CH₂ or 6 x CH</td>
</tr>
</tbody>
</table>

**Totals** 12 12 H CH + CH + CH₂ + CH₂ + (2 x CH₃) = C₆H₁₂

**Atom Check:** C₇H₁₂O (MS) - C₆H₁₂ (1H-NMR) = CO. The IR spectrum suggests the molecule does not contain an OH or C=O functional group, so the oxygen atom must be part of an ether.

**DBE Check:** DBE (calculated) = 2. One of these is the alkene (IR 1650 cm⁻¹). All other functional groups that require DBE show up in the IR, so the other DBE in this unknown structure must be a ring.

**Pieces:**
- CH of CHCH (Probable alkene) 2 x CH₃
- CH of CHCH O of ether
- CH₂ of CH₂CH₂ C
- CH₂ of CH₂CH₂ ring

**Assembly:** The molecular skeleton fragments implied by the 1H-NMR splitting pattern suggest the two CH groups are attached to each other, and the two CH₂ groups are attached to each other. This reduces the piece list:

CHCH (Probable alkene) O of ether
CH₂CH₂ C
2 X CH₃ ring

The two equivalent methyl groups cannot be attached to the CHCH or CH₂CH₂ pieces because the 1H-NMR signal for the methyl groups is a singlet (no neighbors). Bonding the two methyls to the oxygen creates methyl ether, CH₃–O–CH₃. While this is a legitimate structure, the observed chemical shift (0.94 ppm) is not consistent with an OCH₃ (typically 3.8 ppm). Therefore the two methyls must be attached to the orphan carbon atom, further reducing the pieces list:
In order to be consistent with the observed $^1$H-NMR splitting patterns, the alkene CH could only be bonded to the other CH (HC=CH) or to the orphan carbon (HC=C(CH$_3$)$_2$). A methyl group attached to an alkene has a typical chemical shift of ~1.8 ppm, a bit higher than the actual CH$_3$ chemical shift of 0.94 ppm. This suggests the alkene is HC=CH, and the pieces are now:

- HC=CH
- O of ether
- CH$_2$CH$_2$
- ring
- CH$_3$–C–CH$_3$

The alkene is not symmetric (otherwise it would not have an IR stretch), and it is bonded to groups that do not cause extra splitting. Thus the alkene must be bonded to the ether oxygen and (CH$_3$)$_2$C groups. The piece list has been further reduced.

- (CH$_3$)$_2$C–CH=CH–O
- CH$_2$CH$_2$
- ring

These can only be assembled in one way:

4,4-Dimethyl-2,3-dihydropyran