Putting It Together
Solving a Structure Problem Using Combined Spectroscopic Techniques

1. Context
This is missing from most canned spectroscopy problems.
Where is the sample from? What are the likely functional groups? Carbon skeleton?
This can rule out many possibilities.

2. Mass Spectrometry
Molecular weight
Halogen substitution (from M+2 peak)
Number of carbons (from M+1 peak and 1.1% $^{13}$C abundance)
Sometimes, you can derive the molecular formula. If so, you should calculate the
degree of unsaturation, also known as the index of hydrogen deficiency (Carey
section 13.22). Remember that halogens replace hydrogens, and nitrogens
requires an extra H each.

3. Infrared Spectroscopy
Functional groups
Note that the C=O, O—H, C—O, N—H functional groups produce strong,
characteristic bands that are easy to see. Consequently, if you don't see them,
they are not there. On the other hand, non-polar groups like C=C, C==C, etc are
weak. Failure to see bands for these does not necessarily mean that they are
absent.
Remember to note functional groups that are absent (especially the C=O).
Remember to account for degree of unsaturation if possible.
You can often begin making simple substructures at this point (for example, C=O,
C—O—H, etc.)

4. Carbon NMR Spectroscopy
Chemical environments around carbons.
[With off-resonance decoupling] # H's on each carbon. This allows a different kind
of substructure to be determined: individual carbon environments with attached
hydrogens. This may or may not add up to the number of carbons.
[With gated decoupling] # C's in each chemical environment.

5. Proton NMR Spectroscopy
Chemical environments
# H's in each environment
Coupling gives information about connections. This may be where you begin piecing
together substructures into the full structure.

6. Substructure analysis
Concept: Treat a portion of the structure somewhat like an atom—that is, it has
valences (# things it can bond to). This is a useful way to collect information.
Example substructures, with valences:

<table>
<thead>
<tr>
<th>Substructure</th>
<th>Valence</th>
<th>Substructure</th>
<th>Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃—</td>
<td>1</td>
<td>CH₃CH₂—</td>
<td>1</td>
</tr>
<tr>
<td>(CH₃)₂CH—</td>
<td>1</td>
<td>CH₃(CH₂)nCH₂—</td>
<td>1</td>
</tr>
<tr>
<td>—CH₂—</td>
<td>2</td>
<td>—CH₂CH₂—</td>
<td>2</td>
</tr>
<tr>
<td>C=O</td>
<td>2</td>
<td>C—H</td>
<td>3</td>
</tr>
</tbody>
</table>