

## SOLVING COMBINED SPECTROSCOPY PROBLEMS:

Lecture Supplement: page 50-53 in Thinkbook

CFQ's and PP's: page 216 – 241 in Thinkbook

### Introduction:

The structure of an unknown molecule can be determined using three methods, which each reveal different aspects of the whole:

- **Mass Spectrometry** → indicates formula (by varying the magnetic field to manipulate the flight path of ions and plotting the number of ions recorded)
- **Infrared (IR) Spectroscopy** → indicates presence/absence of functional groups (using the principle that similar functional groups absorb photons of similar energies)
- **Nuclear Magnetic Resonance (NMR) Spectroscopy** → indicates how atoms are attached to give the “structural skeleton” (by using differences in nuclear spin flip energies)

### Procedure:

Note: On the majority of practice problems, the given information will not be presented in a way that is easy to read; it will just be listed. So to help solve the problem, it's always a good idea to organize the data in a table or some other form that makes it easy to understand.

1. **Mass Spectrometry:** The first set of data that should be analyzed is the Mass Spectrometry. This process will yield the formula for the molecule.

<u>Molecular Ion:</u>	<u>m/z:</u>	<u>Relative Intensity:</u>
M	mass of M	100% ← *M should always be set to 100%
M+1	mass of M+1	relative intensity of M+1
M+2	mass of M+2	relative intensity of M+2

- \*M should always be set to 100% relative intensity. If it is anything other than 100%, you must set it to 100% and scale the M+1 and M+2 peaks by the same factor.

For example: (Example is from page 50 of the Thinkbook)

<u>Molecular Ion:</u>	<u>m/z:</u>	<u>Relative Intensity:</u>
M	120	48% → 48 * 2.083 → 100%
M+1	121	4.85% → 4.85 * 2.083 → 10.104%
M+2	122	<0.1% → 0.1 * 2.083 → <0.208%

To make the M peak equal to 100% it must be multiplied by a factor of  $(100/48) = 2.083$ . You must then multiply M+1 and M+2 by this factor as well.

- Next, you should analyze the data from the mass spectrum:
  - M: gives information about the presence of Nitrogen using the *Nitrogen Rule*:

- If  $m/z$  for M is even, then there is an even number of N (0, 2, 4 ...)
- If  $m/z$  for M is odd, then there is an odd number of N (1, 3, 5 ...)
- M+1: indicates the number of Carbons in the molecule:  
 $\# \text{ of Carbons} = \frac{\text{Intensity of M+1 peak}}{1.1}$ 
  - \*It is divided by 1.1 because 1.1% of Carbon isotopes contribute to the M+1 peak.
  - \*If dividing these numbers gives a remainder of less than 0.3, round down. If you get a remainder of greater than 0.7, round up. If you get a remainder between 0.4 and 0.7, you should continue the problem considering both cases (for example: if you get 10.5, then consider the case of 10 Carbons and 11 Carbons).
- M+2: indicates the presence of Br, Cl, and S.
  - If  $M+2 = \sim 50\%$ , then there is a Br in the molecule.
  - If  $M+2 = \sim 33\%$ , then there is a Cl in the molecule.
  - If  $M+2 = \sim 4\%$ , then there is a S in the molecule.

Note: there could be more than one of these atoms in molecule. For example,  $M+2 = 66\%$  would indicate that there are two Cl atoms. However, these cases are rare in the problems given in the Thinkbook, OWLS, and old exams.

- Finally, you must use this information to generate possible formulas for the molecule.
  - Begin by noting the  $m/z$  for the M peak. Using this number, you will subtract the mass of any atoms you know for certain will be in the formula
    - The number of Carbons determined from the M+1 peak multiplied by the mass of Carbon-12 (12 amu) tells you the mass of Carbon that can be subtracted from the  $m/z$ .
    - If you found from the  $m/z$  for M that there are an odd number of Nitrogens, you know for certain that there is at least one N so you can subtract its mass (14 amu) from the  $m/z$ . If even, you cannot subtract anything in this stage because there may be zero N.
    - If M+2 indicated the presence of Br, S, or Cl, you can subtract the mass of the atom found. (For example, you can subtract 35 amu if  $M+2 = 33\%$  indicating Cl).
  - Next, use the *Hydrogen Rule* to calculate the maximum number of Hydrogen in the formula:  
 $\text{Max. \# of H} = 2c + n + 2,$   
 $c = \# \text{ of Carbon and}$   
 $n = \# \text{ of Nitrogen}$
  - Using the number of amu left (and taking into consideration the maximum number of Hydrogens), construct possible formulas using C, H, O, N (and Br, S, or Cl if you determined that they were present in previous steps). You should not consider other elements like Iodine or Fluorine unless indicated in the problem.
  - For example: (Example is from page 218 of the Thinkbook).

<u>Molecular Ion</u>	<u>m/z</u>	<u>Relative Intensity</u>	<u>Conclusions:</u>
M	132	100%	MW = 132 Even number of N
M+1 1	33	6.89%	$6.89 \div 1.1 = 6.26$ Six Carbons
M+2	134	1.42%	No S, Cl, Br

$M - (6 \text{ Carbons}) = 132 - (6 \times 12) = 60 \text{ amu left for O, N, H}$   
 Maximum # of H =  $2c + n + 2 = (2)(6) + 0 + 2 = 14 \text{ H's}$

<u>Oxygen</u>	<u>Nitrogen</u>	<u>60 - O - N = H</u>	<u>Formula</u>	<u>Notes</u>
0	0	$60 - 0 - 0 = 60$	$C_6H_{60}$	Violates H-rule
1	0	$60 - 16 - 0 = 44$	$C_6H_{44}O$	Violates H-rule
2	0	$60 - 32 - 0 = 28$	$C_6H_{28}O_2$	Violates H-rule
3	0	$60 - 48 - 0 = 12$	$C_6H_{12}O_3$	Reasonable
0	2	$60 - 0 - 28 = 32$	$C_6H_{32}N_2$	Violate H-rule
0	4	$60 - 0 - 56 = 4$	$C_6H_4N_4$	Reasonable
1	2	$60 - 16 - 28 = 16$	$C_6H_{16}N_2O$	Reasonable
2	2	$60 - 32 - 28 = 0$	$C_6N_2O_2$	Reasonable

2. **Proton NMR Spectroscopy:** The next set of data that should be analyzed is the NMR data.

(It is possible to analyze the IR before analyzing NMR. However, analyzing NMR first gives the advantage of knowing the number of Hydrogens in the molecule, which will help indicate the correct formula from the list of possibilities. Having the correct formula will tell the number of DBE's, a useful tool in analyzing the IR spectrum).

- Information will be given about chemical shifts, splitting patterns, and integrals. Arrange this data in a table (like shown below) to make it easy to read. Using this data, you will learn how many sets of equivalent protons are in the molecule and how many neighbors they have. This information will give you structural information about the molecule.

For example: (Example is from page 218 of the Thinkbook).

<u>Chemical Shift</u>	<u>Splitting</u>	<u>Integration</u>	<u>#H</u>	<u>Implication</u>
4.0 ppm	triplet	1.0	2 H	<u>CH<sub>2</sub></u> CH <sub>2</sub>
3.9 ppm	singlet	1.5	3 H	<u>CH<sub>3</sub></u>
3.0 ppm	singlet	1.0	2 H	<u>CH<sub>2</sub></u>
1.3 ppm	sextet	1.0	2 H	CH <sub>3</sub> <u>CH<sub>2</sub></u> CH <sub>3</sub>
0.9 ppm	triplet	<u>1.5</u>	<u>3 H</u>	<u>CH<sub>2</sub></u> CH <sub>3</sub>
		6.0	12 H	

- The integration does not tell you how many of each type of proton you have. Instead, it tells you the ratio of equivalent protons in the molecule. If the integration does not add up to the number of Hydrogens in your

possible formulas, then multiply it by an integer until it matches with one of the formulas. (A decimal in the integrations usually indicates that it must be multiplied by a factor of at least “2” to give you the correct number of Hydrogens).

In this case, the integration adds up to 6. None of the possible formulas we found has six Hydrogens. However, only one formula has 12 Hydrogens, a multiple of 6, so we can rule out the other possibilities. Our formula is:  $C_6H_{12}O_3$ .

- After you have determined #H, list out the possible arrangements of these protons under Implications. Most of the time, the correct arrangement will be the one that requires the LEAST number of atoms so this should be your first guess. If you are unable to put together a reasonable structure using these guesses, then consider using alternatives.

3. **IR Spectroscopy:** Use the IR data to indicate which functional groups are present. In order to do this, use the table provided on page 35 of the Thinkbook.

- Zone 1:
  - Alcohol O-H: usually the broadest peak in the spectrum; stretches from 3650 to 3200; intensity is variable
  - Amine/amide N-H: usually broad peak; stretches from 3500 to 3300; medium intensity
  - Alkyne  $C-H$ : strong peak @  $\sim 3300$
- Zone 2:
  - Alkane  $sp^3 C-H$ : peak LEFT of 3000; intensity is variable
  - Aryl/vinyl  $sp^2 C-H$ : peak RIGHT of 3000; intensity is variable
  - Aldehyde C-H: medium peaks at BOTH 2700 and 2900
  - Carboxylic Acid O-H: broad peak; stretches from 3000 to 2500 (This OH peak occurs at lower frequency than the zone 1 OH peak because it is conjugated. Conjugation = lower energy = lower frequency).
- Zone 3:
  - Triple bonds: Alkyne  $C-C$  and Nitrile  $C-N$   
It is difficult to distinguish these two types of peaks from just the stretching frequency. Instead, the absence/presence of N in the formula and chemical shift information from the NMR data should be used.
- Zone 4:
  - Carbonyl  $C=O$ : produces the most intense peak of any functional group in the five zones. The table on page 35 of the Thinkbook gives values for the characteristic stretching frequencies for different types of carbonyls (ester, ketone, etc.)
  - Aromatic overtones: usually appear between 1950 and 1750 as 4 small bumps. They indicate the presence of a benzene ring.

(Aromatic overtones may not always be distinct so check for the benzene peaks in zone 5).

- Zone 5:
  - Benzene C=C: shows as two peaks at 1600 and 1500; intensity is variable; also look for aromatic overtones in zone 4.
  - Alkene C=C: peak between 1680 and 1620; intensity is variable

### **IMPORTANT!!!**

- When analyzing the IR spectrum, it is important to write down the functional groups present AS WELL AS the functional groups that are definitely not present. This will help when putting the molecule together from the NMR data.
- Never rule out the possibility of a functional group until you are CERTAIN that it is not present. Eliminating possibilities too early can result in a wrong final answer.
- Sometimes, it will be unclear if an absorption is truly a peak or if it is just from interference. Use the number of DBE's and knowledge of the formula to help you decide.  
Example 1: If you know for certain that there is a benzene and there is only 4 DBE's, you know that there cannot be a triple bond or an alkene.  
Example 2: If there is no oxygen in the formula, then there cannot be a carbonyl or alcohol absorption.

### Some important facts about IR spectrum:

- Carbonyl has the most intense absorption in the IR spectrum. This is because intensity increases as the bond dipole increases. C and O have the largest difference in electronegativity so the C=O bond will have the greatest dipole moment and the most intense absorption.
  - A tertiary amine (Nitrogen bonded to three Carbons) will not show in the five zones because it does not have an N-H bond. N-C only shows in the fingerprint region.
  - Alkynes (C-C bond) will not show peaks in cases where the molecule is symmetric about it. In these cases, stretching does not cause a change in dipole moment, so the bond won't absorb an infrared photon and will not have absorption.
  - The carboxylic acid O-H occurs at a lower frequency than the O-H in zone 1 because it is conjugated. Conjugation lowers energy, so it also lowers frequency.
4. Lastly, put the molecule together using the formula you obtained from the Mass Spectrometry data and including the functional groups that were indicated in the IR Spectrum. When deciding if the structure is correct, check to make sure that:
- its protons produce the correct chemical shifts (For example, if one proton has a higher chemical shift than another, consider putting it closer to an Oxygen or

some other electronegative atom which would deshield it and move it downfield)..

- that you used all the DBE's
- that you used all the atoms indicated by the formula

Example:

This example is from page 221 of the Thinkbook.

### Mass Spectrum:

<u>Molecular Ion:</u>	<u>m/z:</u>	<u>Relative Intensity:</u>
M	149	100% → <b>Since m/z is odd, there must be an odd number of Nitrogen</b>
M+1	150	11.3% → <b>#C = 11.3 ÷ 1.1 = 10.27</b> <b>10 Carbon</b>
M+2	151	<0.1% → <b>No S, Cl, Br</b>

$$\text{Amu left: } 149 - (10 \text{ Carbons}) - 1 \text{ Nitrogen} = 149 - (10 \times 12) - 14 = 15$$

$$\text{Max H's} = 2c + n + 2 = (2)(10) + 1 + 2 = 23 \text{ H's}$$

<u>Oxygen</u>	<u>Nitrogen</u>	<u>15 - O - N = H</u>	<u>Formula</u>	<u>Notes</u>
0	0	15 - 0 - 0 = 15	C10H15N	Reasonable

In this case, there is not enough amu left for Oxygen (requires 16 amu). There is enough for another Nitrogen (requires only 14 amu), but we cannot consider this cause because we know that there must be an odd number of Nitrogen. So this is the only possible formula.

Because there is only one possible formula, there is no need to do NMR first (to use the ratio of Hydrogens to determine which is the correct formula).

### IR Spectrum:

$$\text{DBE} = \# \text{tet} - \# \text{mono}/2 + \# \text{tri}/2 + 1 = 10 - 15/2 + \_ + 1 = 4 \leftarrow \text{possible benzene}$$

#### Zone 1:

- No absorptions, so there is no OH, NH, or H-C<sub>≡</sub>

#### Zone 2:

- Aryl/vinyl sp<sup>2</sup> C-H present because there is a peak to the left of 3000
- Alkane sp<sup>3</sup> C-H present because there is a peak to the right of 3000
- Aldehyde absent because no peaks at 2900 and 2700 (also no Oxygen in formula and no zone 4 C=O absorption)

- Carboxylic acid absent because peak not broad enough (also no Oxygen in formula and no zone 4 C=O absorption)

Zone 3:

- No absorptions, so there is no triple bonds.

Zone 4:

- Carbonyl C=O absent because no intense absorption (also no Oxygen in formula)
- Aromatic overtones present because of small bumps (indicates benzene)

Zone 5:

- Benzene ring present because of peaks at 1600 and 1500
- Alkene must be absent because there are not enough DBE's left (only 4 DBE indicated by formula which have already been assigned to benzene).

NMR:

<u>Chemical Shift</u>	<u>Splitting</u>	<u>Integration</u>	<u>#H</u>	<u>Implication</u>
7.0 – 7.5 ppm	multiplet	1.25	5 H	<b>Monosubstituted Benzene Ring</b>
3.6 ppm	quartet	1.0	4 H	2 x <u>CH<sub>2</sub></u> CH <sub>3</sub>
1.4 ppm	triplet	<u>1.5</u> 3.75	<u>6 H</u> 15 H	2 x CH <sub>2</sub> <u>CH<sub>3</sub></u>

Since the total of the integrations does not add up to the number of Hydrogen from our formula, we must multiply each integral by a factor of 4.

DBE Check:

From the formula, we calculated that there would be 4 DBE. We used them all with the benzene.

Atom Check:

$C_6H_5$  (benzene) + 2 x  $CH_2$  + 2 x  $CH_3$  = 10 Carbons  
15 Hydrogen

The Nitrogen has not been accounted for.

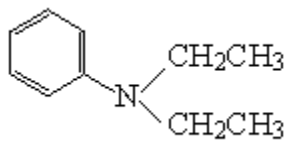
Pieces:

Monosubstituted benzene ring

2 x  $CH_2CH_3$  (Note that the methylene and methyl groups are attached to each other).

N

Final Structure:



\*Note that this structure produces chemical shifts that match the data given. The methylene protons are closer to the Nitrogen so they will have a larger chemical shift than the methyl protons.