Differentiating in Spectroscopy: Putting it all together.

Example of a complete Spectrometry problem solved at the end.

Spectroscopy is the study of matter and its interaction with electromagnetic radiation (Hardinger). This tutorial will focus on Mass Spectrometry, Infrared Spectroscopy and H-NMR spectroscopy.

Mass Spectrometry
- Mass spectrometry is used to determine the chemical formulas of unknown materials.

*How it works:*

A mass spectrometer uses the different masses of atoms in order to differentiate among them. To carry out this differentiation, first the molecules must be turned into ions so they can be manipulated by electric and magnetic fields.

- First an unknown sample undergoes vaporization through evaporation to turn into a gas. This gas is then allowed to leak into the ion source chamber.
- Once in this chamber, the molecules are bombarded by an electron beam with an energy of 70 eV. This high energy beam succeeds in pushing out a single electron from the molecule thus making it a radical cation. The name radical cation refers to the fact that the ion now has a positive charge, as an electron has been removed, but it is also a radical as it has one unpaired electron. This intact ion is referred to as the Parent or Molecular Ion (M).
- Once the ion is created it is repelled by a positive charged repellor electrode that pushes it towards the accelerating plates.
- At the accelerating plates, the ion gains in velocity and speeds into the tube, which is surrounded by a perpendicular magnetic field. This magnetic field causes the path of the ion to curve. The amount of curvature or deflection is a function of the ions charge and mass.
  - The greater the mass or charge, the smaller the deflection. In the diagram above, this corresponds to the red line.
  - The smaller the mass or charge, the greater the deflection. In the diagram this corresponds to the orange line.
  - The magnetic field can be adjusted to cause ions of a specific mass to have a very specific deflection. For instance, in the above diagram, in order to direct the heavier ion, represented by the red line, to the collector slit, one would increase the magnitude of the magnetic field.
  - In this manner, the apparatus can be set to collect ions of a very specific mass.
• The ions then go to the detector and the number of ions with that specific weight is recorded by the computer. The process can then be repeated with a different magnetic field setting in order to gather ions of a different weight.
• The results are then graphed on a plot of mass-to-charge ratio (m/z) and Relative ion abundance. The mass-to-charge ratio corresponds to the mass and charge of the ion. Since the aim is for the ion to undergo ionization only once, the charge is +1. Thus mass is the only variable.
• m/z is plotted on the x-axis and the relative ion abundance is plotted on the y-axis.
• Now the question rises: if we put the same molecule in the ion chamber and they are all ionized only once, then how do different masses arise? The answer lies within the concept of Fragmentation. The electron beam used to ionize the molecule is much stronger than energy needed to break organic bonds. Thus, some of the kinetic energy from the electron beam may be transmitted to the ion, which makes it more volatile. Also since an electron has been removed from the molecule, a bond might have been weakened during this removal. This combination causes the molecular ion to break apart and form fragments.

Isotopes:
• Other differences in the mass of ions occur due to isotopes.
• Atomic weights are a weighted average of masses of an atom’s naturally occurring isotopes. Thus one can have very different masses for molecules made of the same atoms due to the use of different isotopes.
  o For example: carbon has two naturally occurring isotopes: $^{12}\text{C}$, which has a mass of 12 amu and $^{13}\text{C}$ which has a mass of 13 amu. If $^{12}\text{C}$ were to be used in methane, you would get the resulting mass of: $12+(1\times4)=16$ amu. However, if instead it were $^{13}\text{C}$ used in the methane, the mass would be: $13+(1\times4)=17$ amu. The different masses among isotopes results in difference in mass of ions.
  o Thus one can have M+1 as an ion which implies the mass of the molecular ion + 1 amu in mass. This difference is a result of the use of an isotope for one of the atoms. Or, we can even have, M+2, which signals the mass of the molecular ion +2 amu.

Mass Spectrum:

Mass Spectrum of Toluene:
• The mass spectrum is plotted with m/z on the x-axis and Relative Abundance (%) on the y-axis.
• **Base Peak**: is the ion with the greatest relative abundance. We set the base peak to a 100% relative abundance and shift the relative abundance of the other ions accordingly.
  • In this case, the molecular ion is the base peak but that is not always true.
• The mass of the molecular ion can be found by using the lowest mass isotopes.
For example: Toluene has a molecular formula of C\textsubscript{7}H\textsubscript{8}. Using the lowest mass isotopes we get the m/z of: \((7 \times 12) + (8 \times 1) = 92\) amu. Thus the molecular ion of toluene would have a mass of 92 amu.

**Rules to Know:**

- In nature, the \(^{13}\text{C}\) isotope occurs 1.1\% of the time. In M+1 ions of organic molecules, the carbon isotope contributes the most to the intensity of the peak. Thus, when the relative abundance of M is 100\%, then the abundance of the M+1 peak may be used to find the number of carbons in the formula.
  - For example: If one is given that the intensity of the M+1 peak is 6.9\%, you can find the approximate number of carbons by dividing 6.9\% by 1.1\%, which is the probability of finding the \(^{13}\text{C}\) isotope in nature. So \(6.9/1.1 = 6.3\) carbons \(\approx 6\) carbons.
  - Notice that when we are dividing by 1.1\% because the M+1 ions has one atom’s isotope in it. Since carbon has the greatest influence on the peak’s intensity, we divide the intensity by the chance of finding the carbon isotope.
  - For M+2 contributors, the contributors with the greatest influence are Sulfur, Chlorine and Bromine. Sulfur with a probability of 4\%; Chlorine with a probability of 33\% and Bromine with a probability of 100\%. Thus is the intensity of the M+2 peak is 4\%, you can conclude that Sulfur is intensifying the peak and thus there is sulfur in the formula. If the intensity of the M+2 peak is 33\%, then you can conclude that there is Chlorine in the formula. IF the M+2 peak intensity is 100\%, you can conclude there is Bromine in the formula.
  - If Fluorine or Iodine is present, it will be stated in the problem.
- **Nitrogen Rule:** if the m/z of the molecular ion is even, then there is an even number of nitrogens in the formula. If the m/z is odd, then there is an odd number of nitrogens in the formula.
  - For example: if we were simply give that the m/z of the molecular ion of toluene was 92, and we were trying to determine the molecular formula, we could say from the onset that the number of nitrogens is even. 0 counts as an even number.
- **Pi Bonds:** Each pi bond reduces the maximum count of hydrogen by 2.
- **Rings:** Each ring reduces maximum hydrogen count by 2. For this rule be sure to count individual rings and not the larger ring.
- **Hydrogen/Halogen Rule (H Rule):** The maximum number of hydrogens and halogens combined allowed are: \(2C+N+2\).

**Example will be presented at the end.**

**Infrared Spectroscopy:**

- Infrared Spectroscopy is used to determine the functional groups in a molecule.

**How it works:**

- Infrared Spectroscopy uses the absorption of infrared photons by molecules to determine the structure of the molecule.
  - Bonded atoms vibrate in space. This vibrational energy is quantized, meaning that there is a specific amount of energy that a molecule can absorb that will cause it to have a greater vibrational energy. The absorbed energy depends on the atoms involved and bond order. The photons that correspond to this energy level are the infrared protons.
  - The absorption of infrared photons causes a change in a molecule’s vibration. By knowing how the structure is related to the energy, which is absorbed, we can glean information about the structure of the molecule.
  - The results of the infrared spectroscopy are plotted with the stretching frequency on the x-axis and the photon quantity on the y-axis.
  - The stretching frequency is proportional to photon energy and has the units of cm\(^{-1}\). The stretching frequency is determined by the atoms that are bond together and the bond order. Thus one can say that functional groups determine stretching frequencies.
  - The bigger the atomic masses, the smaller the stretching frequency. The greater the bond order, the greater the stretching frequency.
- The intensity of the infrared peak is determined by the change in dipole moment. The bond dipole is a product of the electronegativity difference between bonded atoms and the bond length. The more polar the bond, the stronger the peak. Conversely, symmetrical (non-polar) or nearly symmetrical bonds have a weaker peak.

**Rules to Know:**
- To solve Infrared spectrum, we divide the graph into five zones and look for characteristic peaks to identify bonds in each zone. The Infrared Spectrum of Toluene is:

![Infrared Spectrum of Toluene]

- Each zone has a characteristic frequency and in each zone specific bonds have very specific peak intensities.
- By looking at the peaks in each zone, you can then use the characteristic frequencies chart to determine what functional group could possibly be in that zone.
- Characteristic Stretching Frequencies Table:

<table>
<thead>
<tr>
<th>Bond</th>
<th>Stretching Frequency</th>
<th>Shape and Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Zone 1: 3700-3200 cm⁻¹</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohol O-H</td>
<td>3650-3200 cm⁻¹</td>
<td>usually strong and broad</td>
</tr>
<tr>
<td>Alkyne =C-H</td>
<td>3340-3250 cm⁻¹</td>
<td>usually strong and sharp</td>
</tr>
<tr>
<td>Amine or amide N-H</td>
<td>3500-3300 cm⁻¹</td>
<td>medium; often broad</td>
</tr>
<tr>
<td><strong>Zone 2: 3200-2700 cm⁻¹</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aryl or vinyl sp² C-H</td>
<td>3100-3000 cm⁻¹</td>
<td>variable</td>
</tr>
<tr>
<td>Alkyl sp³ C-H</td>
<td>2960-2850 cm⁻¹</td>
<td>variable</td>
</tr>
<tr>
<td>Aldehyde C-H</td>
<td>~2900, ~2700 cm⁻¹</td>
<td>medium; two peaks</td>
</tr>
<tr>
<td>Carboxylic acid O-H</td>
<td>3000-2500 cm⁻¹</td>
<td>usually strong; very broad</td>
</tr>
</tbody>
</table>
• The Fingerprint region is unique to each molecule.
• The aryl $sp^2$-H is attached to a Benzene ring and the vinyl $sp^2$-H is attached to an alkene.
• $C=O$ frequencies of carbonyls are lowered by 20-40 cm$^{-1}$ due to conjugation with C-C pi bonds. This lowering of stretching frequency only affects the $C=O$ bond and only the conjugation of the C-C pi bond has this affect.
• When asked to find the functional groups attached to a molecule using the IR spectrum, you first need to find the Double Bound Equivalent. This number determines the amount of pi bonds and rings in the molecule. For example if you have a DBE of 4, then you have a Benzene ring. This is because Benzene has 3 double bonds and 1 ring thus equaling 4.
  o You can calculate the DBE through this formula. $DBE = C-H/2 + N/2 + 1$.
• Once you have determined the DBE, you can decide which functional group is possible for which zone depending on the peak characteristics and the number of pi bonds available.

Example will be presented at the end.

### Proton NMR Spectroscopy:

- H-NMR is used to find the C/H molecular skeleton.
- This method of spectroscopy makes use of the fact that the protons, neutrons and electrons of atoms have a spin. The movement of the charged particles creates a magnetic field. This spin is randomly aligned; however, when an external magnetic field ($B_0$) is applied to the atom, then the spins align to be either parallel or anti-parallel with the external magnetic field.
- There is an energy difference between the parallel alignment and anti-parallel alignment. The parallel alignment is the ground state and absorption of photons leads to a nuclear spin flip. This flip causes the parallel alignment to become anti parallel. Conversely, if a nucleus with an antiparallel spin releases a photon, the result could be a nuclear spin flip and the nucleus would then have a parallel alignment.
- The energy needed to go from one spin to the other is equal to the energy provided by radio waves. The greater the magnetic field strength of the nucleus, the greater the amount of photons that need to be absorbed to cause a nuclear spin flip. This can be restated to say that the greater the nuclear magnetic field, the greater the energy difference.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Stretching Frequency</th>
<th>Shape and Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 3: 2300-2000 cm$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkyne $C=C$</td>
<td>2260-2000 cm$^{-1}$</td>
<td>sharp and variable</td>
</tr>
<tr>
<td>Nitrile $C=N$</td>
<td>2260-2220 cm$^{-1}$</td>
<td>sharp and variable</td>
</tr>
<tr>
<td>Zone 4: 1850-1650 cm$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ketone $C=O$</td>
<td>1750-1705 cm$^{-1}$</td>
<td>strong</td>
</tr>
<tr>
<td>Ester $C=O$</td>
<td>1750-1735 cm$^{-1}$</td>
<td>strong</td>
</tr>
<tr>
<td>Aldehyde $C=O$</td>
<td>1740-1720 cm$^{-1}$</td>
<td>strong</td>
</tr>
<tr>
<td>Carboxylic acid $C=O$</td>
<td>1725-1700 cm$^{-1}$</td>
<td>strong</td>
</tr>
<tr>
<td>Amide $C=O$</td>
<td>1690-1650 cm$^{-1}$</td>
<td>strong</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond</th>
<th>Stretching Frequency</th>
<th>Shape and Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 5: 1680-1450 cm$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkene $C=C$</td>
<td>1680-1620 cm$^{-1}$</td>
<td>variable</td>
</tr>
<tr>
<td>Benzene $C=C$</td>
<td>~1600 and ~1500-1450 cm$^{-1}$</td>
<td>variable; 1600 cm$^{-1}$ often two peaks</td>
</tr>
</tbody>
</table>
Since the energy difference is controlled by the magnetic field at the nucleus, we can use the amount of energy absorbed to discern the strength of the magnetic field at the nucleus. For more energy to be absorbed, more photons must be absorbed. So the results of the procedure are plotted with the Spin Flip Energy, or photon energy, on the x-axis and the Intensity of the Signal, or photon quantity, on the y-axis.

**Rules to Know:**

- Each signal on the H-NMR spectrum corresponds to the groups of nonequivalent protons in the molecule.
  - Nuclei are equivalent if they are in the same magnetic environment. If there are 2 nuclei in two different magnetic environments then they are called nonequivalent. Equivalent protons must be identical in every way. This means they must have the same attachments and be connected to atoms with the same hybridization and so on. If you have more than one signal on the spectrum, it is an indication of nonequivalent proton groups. If all the protons are equivalent then you would just have 1 signal. If there are 2 groups of nonequivalent protons then you would have 2 signals and so on.
    - Single Bond rotation in an acyclic molecule allows for equivalency.
    - Mirror protons are equivalent.
    - It is much easier to test for nonequivalency.
- Since the magnetic field differs between NMR spectrometers a Chemical shift is applied. The chemical shift normalizes the spin flip energy scale to make it independent of the magnetic field strength. Since the chemical shift is the spin flip energy normalized, it too depends on the energy difference between the parallel and anti parallel alignment in an atom’s nucleus.
- The electron cloud of an atom shields the nucleus from the external magnetic field. The more shielded the nucleus is, the weaker the magnetic field it feels.
  - Graphically, this means that the more to the left the signal, is the more deshielded it is.

The more electronegative the atoms near the hydrogens the bigger the chemical shift. This is because the greater the electronegativity of the attached atom, the greater its electron greediness. Thus the more electronegative atom pulls the electrons away from the hydrogen thus leaving it deshielded and giving it a greater chemical shift.
  - The effect of electronegativity on an atom decreases with distance. The hydrogens of the methyl group in CH₃OH will be more deshielded than the hydrogens atoms of the methyl group in CH₃CH₂CH₂OH.
- There is a table that shows characteristic shifts for typical protons, however under 6.5 ppm these shifts are not dependable.
- Each signal on the spectrum is actually a very skinny triangle. Integrating under this triangle gives us a relative number of protons that make up that signal. Thus we can conclude that the relative intensities of NMR signals correspond to the relative number of hydrogens that make up the group that is symbolized by this signal.
• **Signal Splitting**: In this concept we are considering one single signal. So we are considering one group of equivalent protons. Do not confuse this with two different signals resulting from nonequivalent proton groups. A single signal can be split due to a nucleus being exposed to different magnetic environments. If a nucleus is exposed to one magnetic environment then the signal will be a singlet; if exposed to two different environments then the signal will be a doublet; if exposed to three different magnetic environments then the signal will be a triplet.

• A single nucleus may be exposed to different magnetic environments due to the spin direction of the adjacent nuclei. This concept is referred to as **Spin-Spin Coupling**.
  - Let's suppose nucleus A (nucleus of hydrogen atom A) has a spin parallel to the direction of the external magnetic field. This nucleus is in the ground state. Now suppose that there is another hydrogen atom (Atom B) near by and the nucleus of that atom also has a spin parallel to the external magnetic field. Nucleus A then feels the magnetic force of $B_0$ (the external field) + Nucleus B (the magnetic field of nucleus B). If, instead, nucleus B has an antiparallel spin then Nucleus A feels the magnetic force $B_0$ – Nucleus B. Thus Nucleus A can feel two different magnetic fields.
  - Since nucleus A feels two different magnetic field, it also feels two different spin flip energies. The two spin flip energies can then be defined as two chemical shifts. By defining the spin flip energies as chemical shifts, we make the spin flip energies independent of the magnetic field. Since there are now two different but very similar chemical shifts, the one signal of nucleus A is now split into a doublet.
  - This signal split gives rise to the **Coupling Constant** ($J$), which is the spacing between the lines in a splitting pattern.
  - As a general rule: A proton with $n$ neighbors is split into $n+1$ lines.
    - **Rules and Restrictions**:
      1. Only nonequivalent protons couple.
      2. Protons separated by more than three single bonds usually do not couple.
        - a. Pi bonds do not count towards this bond limit.
      3. Signals for O-H and N-H are usually singlets
        - a. This is due to hydrogen bonding. In order for coupling to occur, the hydrogens must stay in the same place for a while. However, due to hydrogen bonding, the hydrogens are being continually swapped between different molecules so no coupling can occur. Thus the signals can only be singlets.
  - Coupling in mutual between two hydrogens.

• **Benzene**: Benzene is a special case due to its resonance and partial pi bonds.

  From the structure of Benzene we can see that all the bond of the structure are partial pi bonds. Since there are partial pi bonds all around the circle we need not count the C-C bonds in the three-bond limit of coupling. Thus any hydrogen on the Benzene ring can couple with any other hydrogen on the benzene ring. Notice that the hydrogens around the Benzene, in this example, are nonequivalent. If we had just the Benzene molecule then the hydrogens could not couple because the hydrogens would be equivalent.

  Benzene ring proton coupling generally appears only as a singlet as the coupling constant is so small that distinct lines cannot be seen. This gives rise to a **Multiplet** which is a splitting pattern that is too complex to decipher.

  **First order Splitting**: gives rise to doublets, triplets etc. In this splitting pattern, the $J$ value are equal and the $n+1$ rule is obeyed. **Non-First order Splitting** gives rise to more complex splitting patterns as the coupling constants $J$ are unequal. In this case, the $n+1$ rule is not followed.

• Vinyl protons are deshielded due to the interaction of the external magnetic field ($B_0$) and the magnetic field induced by the electrons in the pi bond, C=C. Vinyl protons are attached to alkenes. When exposed to an external magnetic field, the electrons in the p-orbitals making the double bond also begin moving, concept referred to as **Magnetic Induction**. This movement gives rise to a new magnetic field. The two magnetic fields move in opposite directions so leaving the protons deshielded.

• Magnetic induction also causes Benzene ring proton chemical shifts ~6.5-8.0 ppm
• Magnetic induction by C=O bond causes aldehyde proton chemical shift ~9.5-11 ppm.

**Sample Problem:** Think Book, Pg. 174 Problem 1.

Mass Spectrum: m/z = 106 (M; 100%), m/z = 107 (8.91%), and m/z 108 (0.05%)

IR:

![IR spectrum graph]

H-NMR: 7.45-7.00 ppm (multiplet; integral=5), 2.63 ppm (quartet; integral =2), and 1.22 ppm (triplet; integral=3).

**Solution:**

Mass Spectrometry: Find the formula.

- m/z = 106 (M; 100%)  
  → **Nitrogen rule:** if the m/z of M is even then the number of nitrogens in the formula are also even. So we have an **even number of nitrogens**.

- m/z = 107 (M+1; 8.91%)
  → We use the value of M+1 to find the approximate number of carbons in the formula. Since the isotope of carbon occurs 1.1% naturally, we divide the ion abundance of M+1 by 1.1%. So 8.91%/1.1% = 8.1 carbons ≈ 8 carbons.

- m/z = 108 (M+2; 0.05%)
  → Had the abundance of M+2 been 4% we would have said there is sulfur in the formula. Had the abundance been 34%, we would have concluded there was chlorine in the formula. Had the abundance been 100%, we could have concluded there was Bromine in the formula.
  Since the abundance is 0.05%, we can conclude that there is no sulfur, chlorine or bromine in the formula.

- Amu for O and H = 106 (the m/z of the molecular ion)- (12x8) (subtract the mass of the carbon. We are using 12 as the mass because the lowest mass of a carbon isotope is 12. Also the mass of the molecule ion is the addition of the masses of the lowest mass isotopes of all the atoms present.)

  \[ \text{Amu} = 106-96 = 10 \text{ Amu for Oxygen and hydrogen.} \]

<table>
<thead>
<tr>
<th>Nitrogen</th>
<th>Oxygen</th>
<th>Hydrogen (Amu-O-N)</th>
<th>Formula</th>
<th>Validity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>10-16=6</td>
<td>C₈H₆O</td>
<td>NOT VALID</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>10-0=0</td>
<td>C₈H₁₀</td>
<td>VALID</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>10-(14x2)=-18</td>
<td>C₈H₁₈N₂</td>
<td>NOT VALID</td>
</tr>
</tbody>
</table>

Formula: C₈H₁₀.
IR: find functional groups

Formula (From Mass Spectrometry) = C\textsubscript{8}H\textsubscript{10}.

- DBE(Double Bound Equivalent= will tell how many double bonds or rings)= C- H/2 +N/2 +1.  
  8- 10/2 +0/2 +1 = 4 DBE → 4 double bonds or rings. ← suggests presence of Benzene Ring.

  - Zone 1 (3700-3200 cm\textsuperscript{-1}):  
    Alcohol O-H: Not Present. No peaks.  
    Amide or Amine N-H: Not Present. No Peaks.  
  - Zone 2 (3200-2700 cm\textsuperscript{-1}):  
    Aryl/ Vinyl sp\textsuperscript{2} C-H (>3000 cm\textsuperscript{-1}): Possible  
    Alkyl sp\textsuperscript{3} C-H (<3000 cm\textsuperscript{-1}): Possible  
    Aldehyde C-H: Not Present. No Peak at 2700 cm\textsuperscript{-1}.  
  - Zone 3 (2300-2000 cm\textsuperscript{-1}):  
    Alkyne C≡C: Not Present. No peaks.  
    Nitrile C≡N: Not Present No Peaks.
  - Zone 4 (150-1650 cm\textsuperscript{-1}):  
    C=O: Not present. No peaks.(Possibilities:Ketone, Ester,Aldehyde, Carboxylic Acid, Amide)  
  - Zone 5 (1680-1450 cm\textsuperscript{-1})  
    Benzene Ring: Present. There are two peaks at ≈1600 and 1500-1450 cm\textsuperscript{-1}.  
    Alkene C=C: Not Present. Not enough DBEs.

Solutions thus far: Formula: C\textsubscript{8}H\textsubscript{10}. DBE= 4.

Functional Groups: Aryl/ Vinyl sp\textsuperscript{2} C-H, Alkyl sp\textsuperscript{3} C-H, Benzene Ring.

H-NMR: C/H Molecular Structure

Given: 7.45-7.00 ppm (multiplet; integral=5), 2.63 ppm (quartet; integral =2), and 1.22 ppm (triplet; integral=3).

- 3 signals = 3 groups of equivalent protons.

<table>
<thead>
<tr>
<th>Shift</th>
<th>Splitting</th>
<th>Integral</th>
<th># of H</th>
<th>Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.45-7.00 ppm</td>
<td>multiplet</td>
<td>5</td>
<td>5H</td>
<td>C\textsubscript{8}H\textsubscript{5} (Benzene Ring: can tell because 5H and multiplet).</td>
</tr>
</tbody>
</table>
2.63 ppm  Quartet  2  2H  CH\sub{2}CH\sub{2}  2xCH in CHCH\sub{3}
3 neighbors   CH\sub{2}CH\sub{3}  2x CH in CHCHCH\sub{2}

1.22 ppm  Triplet  3  3H  CH\sub{3}CH\sub{2}  3 X CH in CHCHCH
2 neighbors  CH\sub{2}CH\sub{2}  3 X CH in CHCH\sub{2}

Totals: C\textsubscript{6}H\textsubscript{5} + CH\textsubscript{3} + CH\textsubscript{2} = C\textsubscript{8}H\textsubscript{10}.

Formula: Mass Spectrometry= C\textsubscript{8}H\textsubscript{10}; H-NMR: C\textsubscript{8}H\textsubscript{10}.

DBE: Mass Spectrometry= 4; H-NMR: 8- 10/2 + 0/2 +1= 4

DBE ✔

Pieces:
C\textsubscript{6}H\textsubscript{5} (Phenyl Group: Benzene Ring)
Aryl/ Vinyl sp\textsuperscript{2} C-H :  CH\textsubscript{2} in CH\textsubscript{2}CH\textsubscript{3}
Alkyl sp\textsuperscript{3} C-H:  CH\textsubscript{3} in CH\textsubscript{3}CH\textsubscript{2}

Assembled Structure:

How to Find the Implications of your H-NMR data:

- You must use all the data given to you. For example lets take the case of CH\sub{3}CH\sub{3} above.
  - From the data we have the information that the integral is 2H. Using the information from the formula and the integral you can calculate the relative number of hydrogens that correspond to that integral. To find the number of hydrogens that would correspond to 1 unit: total all the hydrogens from the formula and total all the numbers of the integral. Divide the total hydrogen number by the total integral number. Then take this number and multiply it by the unit number for each integral. In this case, the number of hydrogens per unit was 1H.
  - So we know for this particular piece of information, the integral is 2 and since the ratio is 1H per unit, we can conclude that the integral corresponds to 2H.
  - From the splitting pattern of a quartet we can surmise that there are 3H neighbors. The quartet follows the First Order splitting pattern, as there is a definite number of lines to be a quartet. Thus according to the First Order Splitting the pattern follows the n+1 rule. So if there are n+1 lines then there are n neighbors. Since a quartet has 4 lines, there are 3 neighbors.
  - You then find all the arrangements in which the carbon of interest should have two hydrogens attached and have three hydrogen neighbors:
    - CH\sub{2}CH\sub{2}CH\sub{2}: Here the carbon of interest in the bold carbon. That carbon has two hydrogens bonded to it. As you can also see that the carbons attached to the central carbon have three hydrogens total attached to them. These three hydrogens are the neighbors to the hydrogens that are attached to the carbon of interest.
    - CH\sub{2}CH\sub{2}: Once more the carbon of interest has two hydrogens attached to it. There is only one other carbon is attached to carbon of interest and that carbon has three hydrogens attached to it. These 3 hydrogens are the neighbors to the hydrogen attached to the carbon of interest.
    - 2 x CH in CHCHCH\sub{2}: In this case, there are 2 attached to the carbon of interest due to the 2 X CH. Once again, you can see the neighboring hydrogens equal 3H.

How to Pick the Correct Implication

- Since the number of hydrogens do not change in the different implications, we pick the implication in which the number of carbons would add up to equal the total number of carbons in the formula. This way you can eliminate or keep the implications that say 2 X CH depending on the number of carbons available. You must remember that you have to pick the implication that shows how the connection works as well. You need to try to visualize how the structure would connect and pick the implication that makes the most logical sense for connectivity and does not give you extra carbons that are not accounted for in the formula.
Works Cited


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