ALL ABOUT SOLVING PROTON-NMR

What is $^1$H-NMR?
$^1$H-NMR is NMR (Nuclear Magnetic Resonance) spectroscopy in which the proton nuclear spin is manipulated. It revolves around the idea that the energy required to cause nuclear spin flip is a function of the magnetic environment of an atom’s nucleus.

How can we find structure from NMR?
We find structure through the information NMR relays to us. These pieces of information include:
- Number of signals [which is the number of nonequivalent proton sets in a molecule]
- Position of signals [also known as chemical shift, which is the magnetic environment in which protons are in]
- Relative intensity of signals [also known as integration, which is the ratio of equivalent proton types]
- Splitting of signals [also known as spin-spin coupling, which is the amount of proton neighbors present]

How to solve for number of signals present
The number of signals depends on the equivalency of protons. Protons are equivalent if they have nuclei with the same magnetic environment. In other words, they have to be the same in every possible way. It is easier to find nonequivalent protons.

How to solve for the position of signals/chemical shift
Chemical shift is defined as the position of a signal in an NMR spectrum. It is dependent on different influences, such as the $\Delta E$ of the spin state energy (which is controlled by the magnetic field at the nucleus), and electronegativity (as chemical shift increases, electronegativity of atoms near the proton increases). The positions of signals will be given to us on a test so IT IS NOT MANDATORY TO MEMORIZE THEM!
### Characteristic Proton NMR Chemical Shifts (ppm)

<table>
<thead>
<tr>
<th>Proton Type</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCH₃</td>
<td>0.9</td>
</tr>
<tr>
<td>RCH₂R acyclic</td>
<td>1.3</td>
</tr>
<tr>
<td>RCH₂R cyclic</td>
<td>1.5</td>
</tr>
<tr>
<td>R₃CH</td>
<td>1.5 - 2.0</td>
</tr>
<tr>
<td>R₂CH</td>
<td>1.8</td>
</tr>
<tr>
<td>CH₂</td>
<td>2.0 - 2.6</td>
</tr>
<tr>
<td>CH₃</td>
<td>2.2 - 3.0</td>
</tr>
<tr>
<td>benzene-CH₃</td>
<td>2.3</td>
</tr>
<tr>
<td>benzene-CH₂R</td>
<td>2.6</td>
</tr>
<tr>
<td>RCH=CH</td>
<td>2.5</td>
</tr>
<tr>
<td>RCH₂X (X = Cl, Br, I)</td>
<td>3.5</td>
</tr>
<tr>
<td>RCH₂NR₂</td>
<td>2.3 - 2.7</td>
</tr>
<tr>
<td>R₂C=CH₂</td>
<td>5.0</td>
</tr>
<tr>
<td>RCH=CR₂</td>
<td>5.3</td>
</tr>
<tr>
<td>benzenè-H</td>
<td>6.5 – 8</td>
</tr>
<tr>
<td>aldehyde RCHO</td>
<td>9.5 – 11</td>
</tr>
<tr>
<td>RNH₂</td>
<td>1 – 3</td>
</tr>
<tr>
<td>benzenè-NH₂</td>
<td>3 – 5</td>
</tr>
<tr>
<td>OCH₃</td>
<td>3.3 – 4.0</td>
</tr>
<tr>
<td>OCH₂R</td>
<td>3.6 – 4.6</td>
</tr>
<tr>
<td>ROH</td>
<td>1 – 5</td>
</tr>
<tr>
<td>benzene-OH</td>
<td>4 – 7</td>
</tr>
<tr>
<td>RCOOH</td>
<td>10 – 13</td>
</tr>
</tbody>
</table>

This table will be given to us on an exam.

Chemistry 14C Lecture Supplement PowerPoint CD

**Chemical Shift Trend**

RCH₃ < RCH₂R < R₃CH (*because the electronegativity of C in R > electronegativity of H*)

**How to solve for the relative intensity of signals/integration**

Integration is the measurement of peak areas on the NMR spectrum. It corresponds to the amount of energy absorbed or released by all nuclei participating in chemical shift during the nuclear spin flip process. It is used to determine the ratio of hydrogens that correspond to the signal. It is proportional to relative number of equivalent protons.

**NOTE:** Integrals do not always relay the exact amount of protons present within a molecule!

**Example:**

In this molecule, there are three signals, A, B, and C. In the entire structure, one can see that there are **14** hydrogen atoms.

- A contains **9** equivalent protons in its signal
- B contains **2** equivalent protons in its signal
- C contains **3** equivalent protons in its signal

In order to determine what the integral is for these three signals, set the signal with the least amount of protons as an integral of 1. In this case, B would have an integral = 1. The ratio is then set to 2:1, in that 2 hydrogen atoms correspond to an integral that equals 1. This means that you multiply the number of hydrogens by ½. You can then apply this ratio to the other two signals.

- A has 9 hydrogens, so its integral will equal 4.5
- C has 3 hydrogens, so its integral will equal 1.5
How to solve for the splitting of signals
Spin-spin coupling is determined by the number of magnetic fields affecting the nucleus of a molecule. This causes splitting of the NMR signals. The general rule for splitting is the signal for a proton with \( n \) neighbors is split into \( n+1 \) lines.

There are some rules and restrictions we must follow when working with signal splitting:
1. Only non-equivalent protons can couple
   - If protons are equivalent, then they do not couple
2. Protons that are separated by three or more single bonds usually do not couple

In this example, \( H_a \) and \( H_d \) do not couple because they are four bonds apart (see red bonds). However, \( H_a \) and \( H_c \) can couple because they are two bonds apart (see green bonds).

- Pi bonds do not count towards the bond limit, but the splitting constant \( J \) (which is the spacing between lines in a splitting pattern) may be too small to see, so it may be there
  - For purposes of coupling, just pretend the pi bond isn't there [IT'S A FREE SPACER]! To be safe, add a +1 to the amount of bonds counted excluding the pi bond.
- Benzene rings count as one big free spacer
  - All protons couple with each other because of resonance
  - \( J \) may be small
  - Think of benzene as a “gated community” – hydrogen atoms bonded to the benzene ring can only couple with other hydrogens bonded to the benzene ring. They cannot bond with other hydrogens present in the molecule

The hydrogen atoms present in the methyl attached to the benzene ring cannot couple with the hydrogen atoms bonded directly to the benzene ring. The hydrogen atoms bonded directly to the ring can only bond to other hydrogens attached to the ring.

3. Signals for O-H and N-H
Example of how to solve an $^1$H-NMR Spectroscopy problem

We can deduce a lot from $^1$H-NMR, especially the molecular structure of a molecule. Here is an example of a typical $^1$H-NMR spectroscopy problem when the molecular formula is given, and the steps you take in order to solve it.

Formula: $C_6H_{14}O$

H-NMR: 3.3 ppm (triplet; integral = 1)
        1.6 ppm (sextet; integral = 1)
        0.90 ppm (triplet; integral = 1.5)

1. The first step is to calculate the DBE (double bond equivalency) value, which will tell us how many pi bonds are present or if there is a potential benzene ring present in the structure.

   $\text{DBE} = \# \text{of carbons} - (\# \text{of hydrogens} \div 2) + (\# \text{of nitrogens} \div 2) + 1$
   
   $= 6 - (14/2) + (0/2) + 1$
   
   $= 0$ (this means there are no pi bonds within the structure)

2. Knowing that the integral is proportional to the relative number of equivalent hydrogen atoms present within the structure, we can use the integral information given in the problem and the number of hydrogens, also given in the problem through the molecular formula, to find the factor in which to multiply the integral by so as to determine how many hydrogen atoms are present within each signal.

   The first signal had an integral = 1
   The second signal had an integral = 1
   The third signal had an integral = 1.5

   ➔ If you multiply each of these numbers by a factor of four, then you get:

   - 4 hydrogen atoms for the first signal
   - 4 hydrogen atoms for the second signal
   - 6 hydrogen atoms for the third signal

   Adding all of these up, we get 14 hydrogen atoms present, which is equivalent to the amount of hydrogens given in the formula, so we know we found the right factor to multiply by.

3. Now you can determine the implications for each integral and splitting pattern.

   - Before you find each implication, you need to find the number of neighbors each signal has. This is revealed through the splitting pattern given in the problem.

   The first signal is a triplet. From the general rule stated above, the signal for a proton with $n$ neighbors is split into $n+1$ lines. Because there are 3 splits in the signal, this means that there are 3-1 neighbors, which equals two neighbors.

   The second signal is a sextet. This means that there are 6-1 neighbors, which equals five neighbors.
The third signal is a triplet. This means that there are 3-1 neighbors, which equals two neighbors.

- Now you can find the implications, which deal with the C-H skeleton of a molecule (or N-H/O-H if they are present in the IR spectrum/molecular formula).

First Signal: has two neighbors → means that the underlined C-H part of the skeleton that we are looking at has two protons as neighbors

2x: -CH₂CH₂
Two neighboring protons

2x: CHCH₂CH
Two total neighboring protons

4x: -CHCH₂
Two neighboring protons

4x: CHCHCH
Two total neighboring protons

** The 2x and 4x before the C-H skeleton refer to the factor in which you multiply the number of hydrogen atoms underlined by. This will give you the total number of equivalent hydrogens you calculated before in Step 2.

Second Signal: has five neighbors

2x: CH₃CH₂CH₂
4x: CH₃CH(CH)₂

Third Signal: has two neighbors

2x: CH₃CH₂
3x: CH₂CH₂
3x: CHCH₂CH
6x: CHCH₂
6x: CHCHCH

4. After finding the implications, you then look at all of them and find the most likely implication that would make up a molecular structure [MOST LIKELY STRUCTURE = LEAST NUMBER OF ATOMS]. Always look for the simplest implications! Additionally, look for implications that can be eliminated based on validity (YOU CANNOT HAVE A CARBON WITH MORE THAN FOUR BONDS!).

- First Signal:

2x: -CH₂CH₂
2x: CHCH₂CH

Second Signal

2x: CH₂CH₂CH₂
4x: CH₃CHCH₂

Third Signal:

2x: CH₃CH₂
3x: CH₂CH₂
6x: CHCH₂
6x: CHCHCH

These cannot be possible implications because they are the only implications that are multiplied by a factor of 3. Therefore, they can be discarded.

These cannot be possible implications because they form hexavalent carbons, and carbons can only form four bonds.

Both of these implications have CH₂CH₂ in them, so we can assume they are part of the molecular structure.

Because the implications circled green both have CH₃CH₂ in them and can therefore be confirmed as part of the structure, we now need to find a final implication that will coincide with them. Because this implication is very similar to the ones we have already picked out, and because it contains a CH₂CH₂, just like the implication from the second signal, we can therefore conclude that this is the final implication that will make up our molecular structure.
5. Now we know that our molecular structure is composed of three implications that make up 2 CH$_3$CH$_2$CH$_2$ structures. But if you look at the circled implication from the First Signal, there is an attachment on the first CH$_2$ (-CH$_2$CH$_2$). This means that something attaches to this carbon.

If we look at the original formula given to us, we see that we have accounted for everything except the oxygen [there are 7 hydrogen atoms x 2 = 14 hydrogen atoms total; there are 3 carbon atoms x 2 = 6 carbons total $\rightarrow$ this is how many carbons and hydrogens were in the given molecular formula]. Now we have to account for the oxygen atom. Because there is an attachment to the CH$_2$, we can attach the oxygen to this carbon. Our structure will therefore look like this:

$$\text{CH}_3\text{CH}_2\text{CH}_2\cdot\text{O} \cdot \text{CH}_2\text{CH}_2\text{CH}_3$$

And there’s your molecular structure for the molecule!

**Note:** Make sure to check your work! Check the formula, integrals, number of signals, splitting, etc. and make sure they are all correct. Always perform an atom check and compare it to the formula given. Additionally, check to see if your structure agrees with the DBE for the molecule.

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Now let’s do another example involving mass spectroscopy and infrared spectroscopy.

Mass spectrum: m/z = 154 (M; 100%), m/z = 155 (11.23%), and m/z = 156 (0.26%)

IR spectrum:

$^{1}$H-NMR: 2.1 ppm (singlet; integral = 2), 1.9 ppm (singlet; integral = 1), and 1.1 ppm (singlet, integral = 6)
1. We first need analyze what the information the mass spectroscopy is telling us. The first m/z value is the M peak, which tells us how many nitrogen atoms are present in the molecular formula. If the m/z value is even, then there are zero or an even amount of nitrogen atoms. If the m/z value is odd, then there are an odd amount of nitrogen atoms.

In this example, the M peak has an intensity of 154. This is an even number, so there are 0 or an even amount of nitrogens in the structure.

The second value is the M+1 peak, which tells us how many carbons are present in the structure. How you find this is by dividing the relative abundance of the M+1 peak by 1.1%. **MAKE SURE YOU DO NOT DIVIDE BY 1%; THIS WILL NOT GIVE YOU THE RIGHT ANSWER.**

In this example, the M+1 peak relative abundance is 11.23%. You divide this by 1.1% and you get 10.209%. This means that the structure has either 10 or 11 carbons.

The third value is the M+2 peak, which tells us how many (if any) bromine, chlorine, or sulfur atoms are present within the structure. If the relative abundance is approximately 4%, then sulfur is present. If the relative abundance is approximately 33%, then chlorine is present. If the relative abundance is approximately 100%, then bromine is present.

In this example, the M+2 peak relative abundance is 0.26%. This does not correspond to any of the above stated elements, and is too small to be sulfur, so there is no chlorine, bromine or sulfur atoms present in this molecule.

We can now use this information to find a molecular formula for this structure.

C_{10} Possibility
154 – (12 amu per C x 10C) = 34 amu left for hydrogen, nitrogen and oxygen

<table>
<thead>
<tr>
<th>O</th>
<th>N</th>
<th>H</th>
<th>Formula</th>
<th>Does it work?</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>34</td>
<td>C_{10}H_{34}</td>
<td>No, violates H-Rule</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>18</td>
<td>C_{10}H_{18}O</td>
<td>Acceptable</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2</td>
<td>C_{10}H_{2}O_{2}</td>
<td>Acceptable</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>6</td>
<td>C_{10}H_{6}N_{2}</td>
<td>Acceptable</td>
</tr>
</tbody>
</table>

In this case, we can rule out C_{10}H_{6}N_{2} because the IR spectrum shows that there is a carbonyl in Zone 4, thus revealing an oxygen in the formula. C_{10}H_{6}N_{2} lacks an oxygen. You can also rule out C_{10}H_{2}O_{2} because it does not correspond with the integrals given in the ^1H-NMR. The integral equals 9 (2+1+6), and H_{2} is not a proportionate ratio. That leaves us with C_{10}H_{18}O as our formula.

C_{11} Possibility
154 – (12 amu per C x 11C) = 22 amu left for hydrogen, nitrogen and oxygen

<table>
<thead>
<tr>
<th>O</th>
<th>N</th>
<th>H</th>
<th>Formula</th>
<th>Does it work?</th>
</tr>
</thead>
</table>

In this case, we can rule out C_{10}H_{6}N_{2} because the IR spectrum shows that there is a carbonyl in Zone 4, thus revealing an oxygen in the formula. C_{10}H_{6}N_{2} lacks an oxygen. You can also rule out C_{10}H_{2}O_{2} because it does not correspond with the integrals given in the ^1H-NMR. The integral equals 9 (2+1+6), and H_{2} is not a proportionate ratio. That leaves us with C_{10}H_{18}O as our formula.
C_{11}H_{22} and C_{11}H_{8}N can be ruled out because they lack an oxygen. C_{11}H_{6}O can also be ruled out because it does not correspond to the integral given to us on the $^1$H-NMR.

**Therefore, our final formula is C_{10}H_{18}O.**

The last step is to calculate the DBE: $10 - (18/2) + (0/2) + 1 = 2$ (possibly two rings or 2 pi bonds or a ring and a pi bond)

2. Now we have to analyze the IR spectrum. We do this by looking at each zone and seeing if there are peaks that correspond to different functional groups.

Zone 1: Alcohol O-H: absent; no peak present  
Amine/Amide N-H: absent; no peak, no nitrogen in formula  
Terminal Alkyne $\equiv$C-H: absent; no peak in zone 3  
Zone 2: Aryl/Vinyl sp² C-H: absent; no peak > 3000 cm⁻¹  
Alkyl sp³ C-H: present; peaks < 3000 cm⁻¹  
Aldehyde C-H: absent, no peak at approx. 2700 cm⁻¹  
Carboxylic Acid C-H: absent; no broad peak  
Zone 3: Alkyne C≡C: absent; no peak  
Nitrile C≡N: absent; no peak, no nitrogen in the formula  
Zone 4: Carbonyl C=O: present, peak at 1716 cm⁻¹ $\rightarrow$ ketone  
Zone 5: Benzene C=C: absent; no peak, not enough DBE
Alkene C=C: absent; no peak

From the IR spectrum, we see that there is a ketone and alkyl sp$^3$ C-H bonds within the structure.

3. Now we have to analyze the $^1$H-NMR given to us. First, put all given information into a table:

<table>
<thead>
<tr>
<th>ppm</th>
<th>Neighbors</th>
<th>Integration</th>
<th># H</th>
<th>Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 ppm</td>
<td>Singlet</td>
<td>Integration = 2</td>
<td>2x2 = 4</td>
<td>2x: CH$_2$ 4x: CH</td>
</tr>
<tr>
<td>1.9 ppm</td>
<td>Singlet</td>
<td>Integration = 1</td>
<td>1x2 = 2</td>
<td>CH$_2$ 2x: CH</td>
</tr>
<tr>
<td>1.1 ppm</td>
<td>Singlet</td>
<td>Integration = 6</td>
<td>6x2 = 12</td>
<td>12x: CH 4x: CH$_3$ 6x: CH$_2$</td>
</tr>
</tbody>
</table>

Now we have to calculate how many hydrogen atoms are present for each signal. When you add up each integral value, you get a total of 9. There are 18 hydrogen atoms (as seen in the molecular formula), so it is a 1:2 ratio. This means that you multiply each integral by 2 to get the number of hydrogens:

Now we have to fill in the implications:

<table>
<thead>
<tr>
<th>ppm</th>
<th>Neighbors</th>
<th>Integration</th>
<th># H</th>
<th>Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 ppm</td>
<td>Singlet</td>
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<td>6x2 = 12</td>
<td>12x: CH 4x: CH$_3$ 6x: CH$_2$</td>
</tr>
</tbody>
</table>

The circled pieces are the skeletons that we can see are part of the structure. They were each chosen because they were the more likely of the implications assigned for their specific signal.

4. Now we have to put the pieces all together.
   - We see from the DBE that we could have two pi bonds, two rings, or a pi bond and a ring. The ketone uses one DBE, so we have one left (either a ring or a pi bond).
   - We see from the IR spectrum that we have a ketone and alkyl sp$^3$ C-H bonds.
   - We see from the $^1$H-NMR that we have 4x: CH$_3$, 2x: CH$_2$ and a CH$_2$. The 2x CH$_2$ will be more deshielded, which is evident by their higher ppm value. This means that they will be closer to an electronegative atom, such as the oxygen in the ketone.
The blue CH₂ groups are closest to the ketone because they are deshielded, as seen in their ppm, thus suggesting that they are close to an electronegative atom, like oxygen.

And here’s our molecular structure!

**Note:** Make sure to check your work! Check the formula, integrals, number of signals, splitting, etc. and make sure they are all correct. Always perform an atom check and compare it to the formula given. Additionally, check to see if your structure agrees with the DBE for the molecule.

Trial and error is huge in solving proton NMR problems. The more practice you do, the better you will be. PRACTICE, PRACTICE, PRACTICE!

Good luck, and I hope this helped!

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**Works Cited**

Dr. Hardinger’s Chemistry 14C Lecture Supplement  
Dr. Hardinger’s Chemistry 14C Lecture Supplement PowerPoint CD  
Dr. Hardinger’s Chemistry 14C Thinkbook  
http://www.chem.ucla.edu/harding/index.html [Illustrated Glossary]