

Introduction to ^1H -NMR Spectroscopy _____ Hydrogen NMR spectroscopy is considerably more complex than ^{13}C -NMR. The interpretation is more difficult. However, the extra complexity provides extra information that is unavailable from carbon NMR. In interpreting carbon NMR, we basically focused on only two things, how many carbon lines were present, and where they were located (chemical shifts). Both of these are also central to hydrogen NMR, but two additional factors, “integration” and “splitting”, are also useful.

The four facets of ^1H NMR spectroscopy can be summarized as follows:

1. The number of signal sets \Rightarrow the number of symmetry-unique hydrogen types
2. The chemical shifts (frequency) of each signal set \Rightarrow the chemical environment/hybridization/functional groups
3. The integration of each signal set \Rightarrow how many hydrogen atoms cause a signal.
 - $3\text{H} \Rightarrow \text{CH}_3$ group
 - $2\text{H} \Rightarrow \text{CH}_2$ group
 - $1\text{H} \Rightarrow \text{CH}$ or OH group
4. The splitting of each signal set \Rightarrow information about what is connected to a given carbon
 - N lines $\Rightarrow N-1$ “neighbor” H’s (when working from spectrum to structure)
 - N neighbors $\Rightarrow N+1$ lines (when you know what a structure is, and you’re trying to predict what it’s spectrum should look like)

Summary of Steps in ^1H NMR Interpretation: (Not all will be needed to get the Answers Today)

1. **Count how many signal sets** you have. **This will tell you how many types of hydrogen-bearing carbons** you have. (Hydrogens attached to symmetry-equivalent carbons will give equivalent signals)
2. **Check diagnostic “chemical shift” windows** of the lines **to provide yes-or-no answers regarding the presence or absence of key functional groups** in your molecule.
3. Check the integration of each signal set.
 - $3\text{H} \Rightarrow \text{CH}_3$ group $2\text{H} \Rightarrow \text{CH}_2$ group $1\text{H} \Rightarrow \text{CH}$ or OH group
4. Check the splitting of each signal set.
 - For a signal set with N lines $\Rightarrow N-1$ hydrogens will be attached to carbons directly connected to the carbon of the signal set

I. Number of Signal Sets

1. Nonequivalent H’s have different chemical environments and give different signals
2. Symmetry-equivalent H’s have the same chemical environment and give the same signal
 - Thus the number of signal sets tells you how many different types of hydrogens are present
3. Ways for the number of signal sets to differ from the number of carbons:
 - a. Symmetry duplication: two (or more) carbons give only one type of hydrogen and one signal set
 - b. Hydrogen-free Carbons: No attached H, no H signal! (Carbonyl carbons rarely have H’s...)
 - c. OH Groups: OH as well as CH’s give hydrogen signals
 - d. CH_2 H’s are NONEQUIVALENT in Two “Cis/Trans” Cases:
 - When there is a **chiral center** in the molecule. In 2-bromobutane, one of the CH_2 H’s on C-3 is cis to the bromine, the other is trans. The cis and trans H’s will give different signals.
 - In **Alkenes**. In propene ($\text{CH}_3\text{CH}=\text{CH}_2$), one of the CH_2 H’s is cis to the methyl, the other is trans. They are in different environments and would give different signals.
4. On an **achiral** molecule (alkenes excepted), hydrogens on a given carbon will be equivalent.
 - all three H’s on a CH_3 group will be equivalent
 - both H’s on a CH_2 group will be equivalent.
5. Strategy Keys:
 - a. If possible, determine how many signal sets you have in a spectrum. (Useful when working from spectrum to structure).
 - b. For a particular structure, determine how many signal sets you should have. (Useful when matching unknown candidate structures with actual spectra, as in today’s lab.)
 - c. **End-Check: Check that the number of signal sets in your spectrum matches with the structure you believe you actually have! If not, structure needs correction!**

II. “Chemical Shifts” of the Signal Sets

9's (9.0-10.0)	Aldehyde sp^2 hybridized C-H's
7's (6.5-8.4)	Aromatic sp^2 hybridized C-H's
5's (4.8-6.8)	Alkene sp^2 hybridized C-H's
3's (2.8-4.5)	Oxygenated sp^3 hybridized C-H's (halogenated and nitrogenated alkyl C-H's will also come in this window, although no candidates for today's lab). Oxygenated sp^3 -carbons are routinely present for the following functional groups that contain oxygen single bonds: <ul style="list-style-type: none"> • alcohols, • ethers, or • esters
2's (1.8-2.8)	Allylic sp^3 hybridized C-H's (sp^3 hybridized C-H's that has a double bond attached to the sp^3 hybridized C). Allylic signals routinely appear when one of the following double-bonded functional groups is present: <ul style="list-style-type: none"> • carbonyls, (ketones, esters, aldehydes, acids, amides) • alkenes, or • aromatics
1's (0.7-2.0)	sp^3 hybridized C-H's, with no attached Functional Groups <ul style="list-style-type: none"> • Note: Many molecules with non-functional alkyl portions will give a lot of signal in this area.
0-12 (anywhere!)	Alcohol/Acid O-H hydrogens (N-H hydrogens likewise) <ul style="list-style-type: none"> • alcohols, • carboxylic acids

How do I process and use what I see from my Chemical Shifts?**1. Recognize OH Hydrogens.**

- An OH can come anywhere, and can easily cause you to make a mistaken conclusion about a feature group. For example, if you have an OH and it comes in the 2's, and you conclude that you have an allylic C-H, that might send you down a bad blind alley. Or if you have an OH that appears in the 5's, you might falsely deduce that you have an alkene, etc.. Thus it is really helpful to recognize OH's when they appear so that they don't confuse you.
- **Two recognition factors for OH signals:**

1. They always **integrate for 1H**, never for 2H or 3H
2. They normally **appear as singlets, normally somewhat broad**. C-H signals tend to be sharper, and any C-H signal that integrates for one will have significant splitting. The only way to have a 1H that doesn't split is for it to be an OH.
3. If you have an OH signal, of course you will also have some C-H signals in the 3's area.

2. Check each of the zones. Each one gives you a yes or no answer about the presence of absence of the featured group.

- Do I have something in the 9's? If yes \Rightarrow aldehyde
- Do I have something in the 7's? (Other than a solvent singlet...)? If yes \Rightarrow aromatic
- Do I have something in the 5's? If yes \Rightarrow alkene
- Do I have something in the 3's? If yes \Rightarrow alcohol, ether, or ester
- Do I have something in the 2's? If yes \Rightarrow ketone, aromatic, or alkene
- Do I have something in the 1's? If yes \Rightarrow some nonfunctional alkyl carbons

3. End-Check: Check that the functional groups indicated by your chemical shift information match with the structure you believe you actually have! If not, structure needs correction!

Miscellaneous Chemical Shifts Notes

1. The regions are somewhat approximate, and have some spillover. But it's useful to basically talk about the “1's”, “2's”, “3's”, etc. to discuss the major windows. Even though something might actually come at 4.2, it's still useful to refer to that as appearing in the “3's” group and make conclusions accordingly. I'll still refer to something as coming in the “1's” group even if it comes at 0.8.
2. Notice that sp^2 hybridized C-H's come above 5, sp^3 hybridized C-H's come below
3. Notice that oxygenated C-H's come higher than non-oxygenated analogs. An sp^3 -hybridized C-H's with an attached oxygen comes higher than without (3's versus 1's), just as an sp^2 -hybridized C-H's comes higher with an attached oxygen (10's) than without (5's, 7's)
4. The above windows are sufficient for this week's lab. In future, and for more complex molecules, there are more complex ways for a C-H to come in some of the above window. For example, an sp^3 -hybridized C-H with two attached oxygens can come in the 5's, or an sp^3 -hybridized C-H that is doubly allylic (for example, two attached carbonyls) can come in the 3's. But for beginning, none of our C-H's will be impacted by more than one attached functional group at a time.
5. OH's are real wildcards because they can come anywhere, and can easily get you confused.

III. Integration In C-13 NMR we didn't really use the heights or sizes of the signal in any quantitative way. However, the sizes of H-NMR signal sets are very useful and informative.

1. All hydrogens give an equal amount of signal
2. When there is symmetry duplication of a hydrogen, the resulting signal will be multiplied accordingly!
3. The key is not the signal height, but rather the signal **area**.
4. The signal **area** is measured by “integration lines”. Make sure to differentiate integration marks, and what they mean, from signal lines themselves.
5. **Relative areas directly correlate ratios of H's**
6. These **must be simple whole-number ratios** (2:1, 3:1, 3:2, etc..)
 - Convert the “computer” ratios to simple whole-number ratios
 - Round off freely! The computer isn't normally very precise, easily 10% errors
7. Clean sets involving equivalent H's give clean, symmetric signal sets:
 - a. $1H \Rightarrow CH$ or OH
 - b. $2H \Rightarrow CH_2$
 - c. $3H \Rightarrow CH_3$
 - d. $6H \Rightarrow 2$ equivalent CH_3 groups
8. Unsymmetrical messy sets involving overlapping signal sets: (these will routinely not look nice and symmetric...)
 - a. $3H \Rightarrow OH$ overlapping a CH_2
 - b. $4H \Rightarrow$ two overlapping but not exactly equivalent CH_2 groups; or a CH_3 overlapping an OH or CH
 - c. $5H \Rightarrow$ common in the 7's, for 5 overlapping arene H's; also common in the 1's, when a CH_3 and CH_2 overlap
9. Unfortunately having signal sets overlap is all too common

How do I process and use what I see from my Integrations?

1. Distinguish “Clean” Signal Sets from Overlapping Signal Sets
 - o Clean ones look symmetric, overlapping sets do not
2. **For the Clean sets, the integration tells you what kind of group you have**
 - a. $1H \Rightarrow CH$ or OH (methine or hydroxyl group)
 - b. $2H \Rightarrow CH_2$ (methylene group)
 - c. $3H \Rightarrow CH_3$ (methyl group)
 - d. $6H \Rightarrow 2$ equivalent CH_3 groups
3. **End-Check: Check that the “groups” your integration shows match with the structure you believe you actually have! If not, your structure needs to be corrected!**

IV. Splitting In C-13 NMR all of our carbon lines came out as nice simple single lines. However, in H-NMR hydrogen signals are routinely split into multiple lines. The number of lines in a signal set tell us nothing about the C-H's themselves that cause the signal (whether it's a CH₃ or CH₂ group, whether it's an sp³ or sp² carbon, whether it's allylic or oxygenated...). But the splitting tells us something else that is really useful: what kind of CH groups are attached to the group of interest! Splitting tells us nothing about the group itself, but it does provide great information about neighbor groups.

Rules of "Splitting"

- **N-1 Rule:** N lines \Rightarrow N-1 neighbor H's (H's directly attached to carbons attached to the C-H group causing the signal)
 - The N-1 Rule is useful when working from spectrum to actual structure
 - **N+1 Rule:** N neighbor H's \Rightarrow N+1 lines
 - The N+1 Rule is useful when working from structure to actual spectrum
1. OH hydrogens don't participate in splitting (normally)
 2. Only C-H hydrogens participate in splitting (normally)
 3. For today's labs and for simple molecules, the N-1/N+1 rules are good. However, the rules actually are accurate only if the neighbor H's are equivalent. The rule can break down when some of the neighbor H's differ significantly from each other
 4. Splitting from H's further distant than neighbor carbons sometimes occurs, but usually the amount of splitting is too small to worry about
 5. Physics Origin: hydrogens are quantized little magnets. Having neighbor hydrogens is equivalent to having local magnets that can either reinforce the external field (spin up) or counteract the external magnetic field (spin down).

N+1 Rule (Given structure, how many lines a spectrum should give)										
Neighbors	2	3+2	2	0	Neighbors	0	-	2	2+3	2
Lines	3	6	3	1	Lines	1	-	3	6	3
(Notice: OH doesn't split...)										
N-1 Rule (Given spectrum, how many neighbors a structure should have)										
	Lines	1 (s)inglet		Lines	2 (d)oublet					
	Neighbors	0		Neighbors	1					
	Lines	3 (t)riplet		Lines	4 (q)uartet					
	Neighbors	2		Neighbors	3					
etc.										

6. Splitting nicknames:
 - 1 line \Rightarrow singlet (s) 2 lines \Rightarrow doublet (d) 3 lines \Rightarrow triplet (t)
 - 4 lines \Rightarrow quartet (q) 5 lines \Rightarrow pentet (p) >5 lines \Rightarrow multiplet (m)

How do I process and use what I see from my Splitting?

1. For a given signal set, use integration to determine if you have a CH₃, CH₂, or CH group
2. Then use the number of lines in the signal set and the N-1 Rule to see how many hydrogens must be present on neighboring carbons
3. **End-Check:** Check that the structure you believe you actually have would give the splitting you are actually seeing in your spectrum. If not, your structure needs to be corrected!

V. Standard Summary Report There is a standard summary report format for H-NMR's which addresses chemical shift, integration, and splitting. Normally an interpretation/correlation with the actual structure is also included.

Ex: $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3$ (I'll number the carbons from left to right...)

Standard report format (approximate chemical shift range, integration, splitting, and interpretation of which signal correlates to which group in the structure...)

3's, 3H, s (CH_3 -1)

3's, 2H, t (CH_2 -2)

1's, 2H, p (CH_2 -3)

2's, 2H, t (CH_2 -4)

2's, 3H, s (CH_3 -6)

VI. Miscellaneous

- 1. Subtracting the Solvent Lines: Don't Count the Singlet at 7.26** The sample is always diluted in a solvent. We will routinely use CDCl_3 , specifically because it has no H's! However, it is not totally pure, and usually is contaminated by a small amount of CHCl_3 , which gives a signal at 7.26. Ignore this signal!
- 2. Subtracting the Reference Line: Don't Count the Line at 0** A reference chemical $[(\text{CH}_3)_4\text{Si}]$ is normally included that gets used to define where “zero” is. This zero marker is present all the time, but is not part of your actual molecule. Ignore this signal!
- 3. Subtracting the Water Line:** Often a little moisture will be in the solution, probably because it gets into the CDCl_3 solvent bottle. This will often appear somewhere around 1.6, but it often drifts depending on hydrogen-bonding factors. Ignore this signal!
- 4. Subtracting the Acetone Line?** Sometimes students will have washed their NMR tube with acetone, but not all the acetone will have had a chance to evaporate. If residual acetone is present, it will give a singlet at 2.15. Unfortunately this is about the same place where other methyl groups that are connected to carbonyls come. One hint that a 2.15 line is acetone and not actually part of your molecule is if it integrates funny, i.e. is either too big or too small to integrate correctly. One other hint is to ask the instructor!
- 5. How do I know what's a real signal versus a signal arising from an impurity that I should ignore?** For today, if in doubt ask the instructor! The instructor will confirm which lines you should or shouldn't consider in doing your analysis. However, one useful recognition tip is if something integrates badly. Integrals are supposed to be nice whole-number ratios (1:1, 2:1, 3:2, etc.). So if something integrates at a 0.1:1 ratio compared to the next smallest signal set, it's likely just an impurity.
- 6. Beware of Overlapping.** Overlapping is most routine in the benzene area (7's), and also in the alkyl area (1's), but happens elsewhere as well. OH signals also often overlap other signals.

VII. Review + Summary

- Count **how many signal sets** you have.
- Check **“chemical shift” windows** of the lines to provide yes-or-no answers regarding the **presence or absence of key functional groups** in your molecule.
- Check the **integration** of each signal set.
 - 3H \Rightarrow CH_3 group 2H \Rightarrow CH_2 group 1H \Rightarrow CH or OH group
- Check the **splitting** of each signal set.
 - N lines \Rightarrow N-1 neighbor hydrogens
- Beware of misinterpreting overlapping signals
- Beware being confused by signal sets caused by solvents or impurities
- 5. End-Check: Check that the structure you believe you actually have would give the number of signal sets you have, the chemical shifts you have, the integrations you have, and the splittings that you have. If not, your structure needs to be corrected!**

