

Nuclear Magnetic Resonance Spectroscopy Learning Objectives

As we study this chapter, you should...

- 1) **Know that nuclei that possess the property called *spin* are NMR active.** NMR active nuclei either contain an odd mass or an odd atomic number. An NMR active nucleus is one that behaves like a tiny magnet and aligns itself either with (lower energy situation) or against (higher energy situation) an external magnetic field. Transitions between these energy states are what give rise to NMR signals.
- 2) **Understand that symmetry (or lack thereof) affects the number of signals that show up in an NMR spectrum.**
- 3) **Know that NMR signals are affected by the environment of their nuclei.** The 'environment' includes: a) electron density surrounding a nucleus, b) neighboring groups, c) solvent, and d) other magnetic fields or nuclei. In practice, these factors influence the chemical shift and the splitting patterns of a signal as follows:

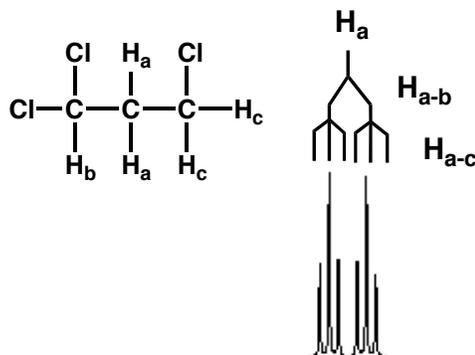
a) **Chemical shift**

- i) groups (or situations) that remove electron density (or lower the field strength) *deshield* a nucleus. *Deshielded* peaks are to the left.
- ii) groups (or situations) that increase electron density (or increase the field strength) *shield* a nucleus. *Shielded* peaks are to the right.

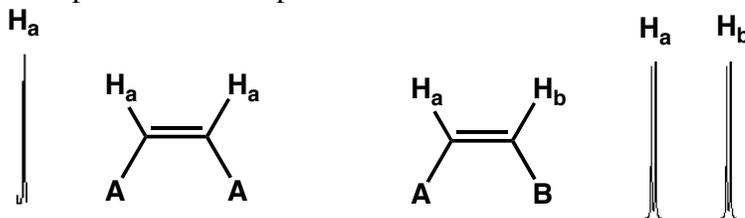
b) **Signal splitting (spin-spin coupling)**

- i) a proton NMR signal will be split into $n+1$ peaks where n = the number of *equivalent* neighboring protons
- ii) complex splitting must be used when neighboring protons are nonequivalent.

e.g.



- iii) equivalent protons do not split each other.

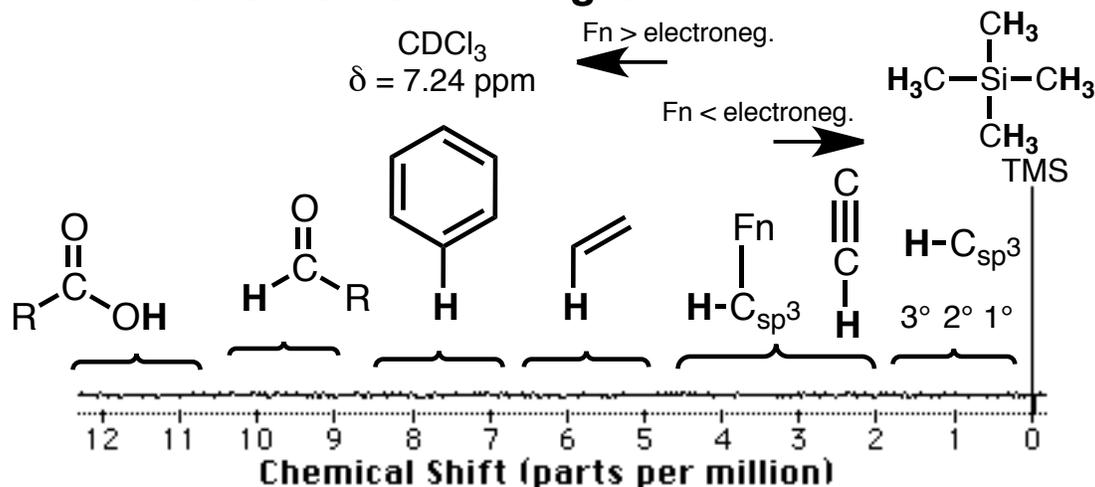


no splitting

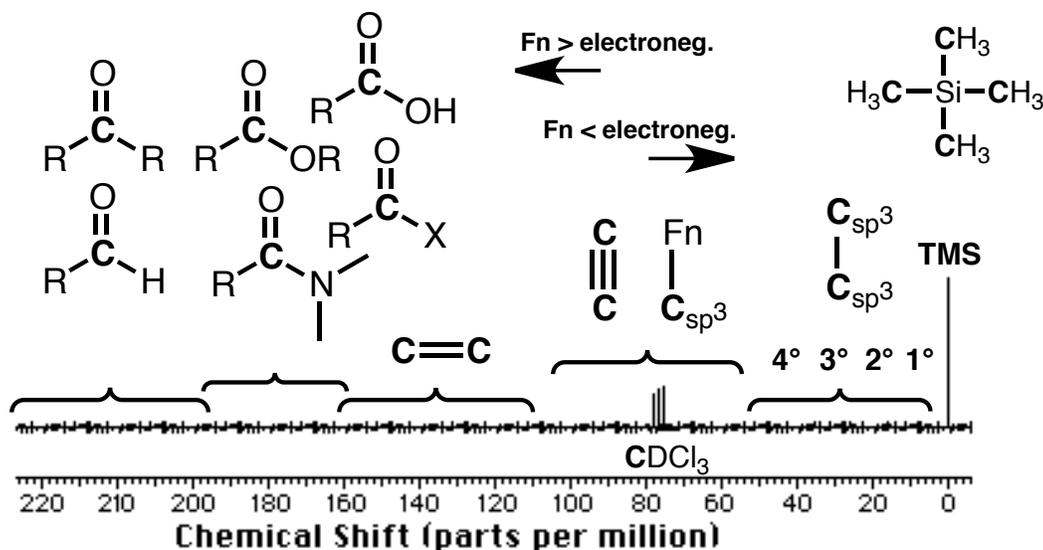
- 4) **Know that the area underneath ^1H NMR signals is proportional to the number of protons for each signal (integration).** By integrating the ^1H NMR peaks, we can determine the relative numbers of protons for each signal.
- 5) **Know that ^{13}C NMR spectra are simplified.** Due to the way ^{13}C NMR signals are obtained, we do not consider splitting or integration when interpreting these spectra.

¹H NMR Provides...

Information about...	How do we Determine this?
Symmetry in a molecule	Compare the number of peaks to the number of H's in the molecular formula
Functionality of a molecule	Look at the chemical shift of peaks
Relative ratio of H's	Look at the integration (then compare it to the actual no. of H's to get the <i>absolute</i> ratio)
The number of H's that are neighbors to the H's giving a signal/set of peaks	Look at the splitting pattern

¹H NMR Chemical Shift Ranges**¹³C NMR Provides...**

Information about...	How do we Determine this?
Symmetry in a molecule	Compare the number of peaks to the number of C's in the molecular formula
Functionality of a molecule	Look at the chemical shift of peaks

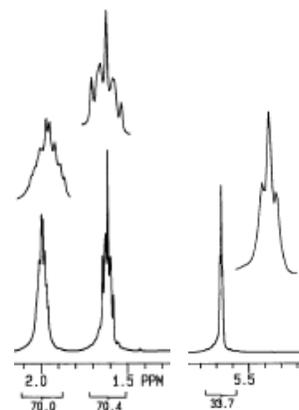
¹³C NMR Chemical Shift Ranges

A Suggested Procedure for Approaching NMR (and integrated) Spectral Problems

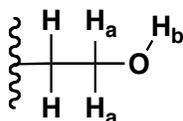
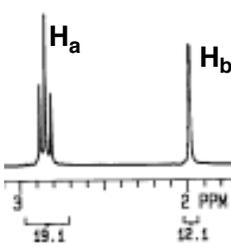
- I. Determine the Degrees of Unsaturation
- II. Use any data provided to you (^1H or ^{13}C NMR, UV-Vis, IR, MS, reactivity data, etc.) to figure out what these degrees of unsaturation represent (in terms of functional groups).
 - A. For NMR, that means looking at the chemical shifts.
 - B. For IR, that means looking at the shape, size and location of the peaks.
 - C. For UV-Vis, that means determining whether the molecule contains C=O or is conjugated.
 - D. For MS, that means looking at fragmentation patterns.
- III. Once you figure out what the degrees of unsaturation represent, try to spot any other functional groups present (repeat step II)
- IV. Then use the NMR to try to put the pieces together
 - A. Analyze the symmetry based on the number of different C's or H's in a molecule (based on the **number of peaks** present).
 - B. Determine the number of CH's, CH₂'s, CH₃'s based on the **Integration**.
 - C. Determine the exact types of partial fragments by analyzing the number of neighbors each proton has (based on the **splitting pattern**).
- V. All this info should give you pieces of the puzzle. Now try to put these pieces together and propose some structures (write them down, make guesses!). Then verify your guesses with the info that the NMR gives.

Below are some real-world artifacts that you might see in NMR spectra...

Splitting of signals is not always perfect...

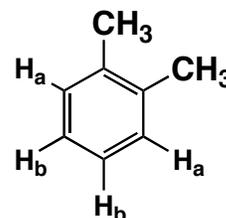
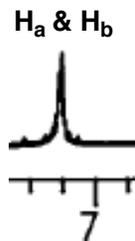
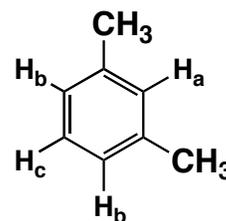
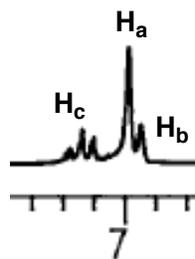


These are not broad singlets; they are either the result of small coupling constants or poor resolution from the NMR instrument (not everyone can have a 300 MHz NMR like us!).



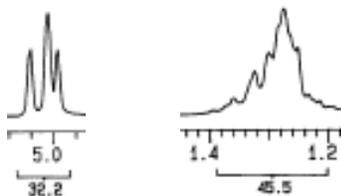
Coupling often doesn't occur through oxygen or nitrogen.

Benzene ring protons sometimes show splitting and sometimes NOT...



Sometimes you can use the splitting in your interpretation. Other times, just use the integration value to determine how many protons are on a benzene ring.

Peaks overlap...

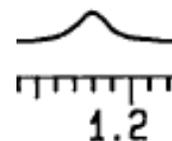
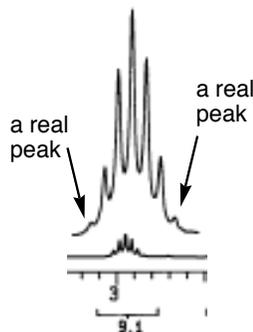


This represents two overlapping alkene protons.

This is the signal from two different (nonequivalent) CH₂ groups that happen to have similar chemical shifts.

Overlapping peaks can be difficult to interpret. Sometimes you just use the overall integration to get a sense for the number of protons. Or, if the splitting is crazy, you just assume that there are many neighbors.

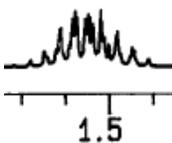
Sometimes peaks disappear into the baseline...



OH, NH, or SH peaks can be broadened out due to H-bonding or some other interaction.

Sometimes the end peaks are too small to see. 'Not much you can do, but use your *other* evidence to make sense of the structure.

Some splitting patterns are just not worth interpreting...



It is often just as informative to assume that the proton(s) giving such a signal are next to many different types of neighbors and leave it at that!