

NMR SPIN COUPLING

The Basis of Spin-Coupling

- Review how NMR signals arise (excitation and relaxation in a magnetic field, at different frequencies)
- Slight differences in the chemical environment cause detectable changes in the allowed energy states
- Nearby protons (or other nuclei) can be in one of two spin states, giving rise to two (or more) possible chemical environments for a nucleus to resonate in. This causes an NMR signal to show up as two (or more) peaks. This phenomenon is known as *spin-coupling*.

FIGURE: showing the different spin states of a nucleus in a magnetic field. These different states increase or decrease the effective magnetic field experienced by a nearby nucleus, allowing for two distinct signals. Include a splitting tree to show how this gives rise to two signals.

- The distance between the peaks of a multiplet is called the *coupling constant*. More on the coupling constant in a following section.
- Multiplets are formed when there is more than one nucleus nearby that is affecting the nucleus being examined. They follow Pascal's triangle as far as the number of peaks and those peaks' relative intensity go. The total area of the entire multiplet will correspond to the number of (equivalent) resonating nuclei. The number of peaks will correspond to $n + 1$, where n is the number of nuclei splitting the resonating one.

FIGURE: Pascal's triangle

FIGURE: Show the splitting trees for a triplet and quartet, then the signal they give rise to. For now, only consider AX and AX₂ (so J's are all the same).

- Multiplets are centered around the chemical shift expected for a non-split nucleus.
- The total area of a multiplet corresponds to the number of nuclei being observed. The number of peaks corresponds to $n + 1$ ($n = \#$ of nuclei which are splitting the nucleus.)
- When the nearby protons are different from each other (i.e. when they themselves are in different chemical environments than each other), then they possess different coupling constants. This causes splitting that does not follow Pascal's triangle. Instead, you get things like a doublet of doublets, etc.

FIGURE: Show the splitting tree for AX'X and the doublet of doublets it gives rise to. Possibly also include the same for AX'X₂ (a doublet of triplets)

Spin Coupling in Molecules

So far, we've talked theoretically, without considering the molecules that might give rise to the peaks we've talked about. Now we will look at some concrete examples and discuss the specific questions that arise when looking at an actual molecule rather than a hypothetical nucleus that happens to be near some non-equivalent nuclei.

EXAMPLE: Ethanol and its NMR spectrum

Point out that while one group of nuclei splits another, it is also split by the one it is splitting. In this way they are *coupled*.

Looking at an actual molecule raises the question, which nuclei can cause splitting?

Discuss the following factors:

- Only nonequivalent protons (explain distinction between magnetically equivalent and non-equivalent protons)
- Distance between the nuclei.
- Heteroatoms (of the same or different spins values)

Coupling Constants

- The distance between the peaks of a multiplet is called the *coupling constant*. It is independent of the field strength used (though multiplets can be better resolved at higher field strengths).
- Coupling constants are sometimes written nJ to denote the number of bonds (n) between the coupled nuclei.
- Walk through the calculation of a coupling constant...

Second-order Coupling

- When two groups of nuclei that split each other have similar chemical shifts* (i.e. they are not far apart from each other on the δ axis), then more complex coupling occurs. This is called *second-order coupling*.
 - *More specifically, when the difference in chemical shifts is close in size to the coupling constant.
- In second-order coupling, the multiplets "lean" toward each other. The inner peaks are higher than their outer peaks.

FIGURE: Example of spectrum showing second-order coupling. (Possibly $\text{CH}_3\text{O}(\text{CH}_2)_3\text{OCH}_3$ or $\text{Cl}(\text{CH}_2)_5\text{Cl}$?)

- Why does second order coupling matter?...
 - Leaning can help you identify which nuclei are coupling which
 - Strong second-order coupling effects can make some spectra hard to predict/interpret.
 - (Anything else?)

FIGURE: example of spectrum showing strong second-order coupling effects (possibly $\text{C}_5\text{H}_{11}\text{BrO}_2$?)