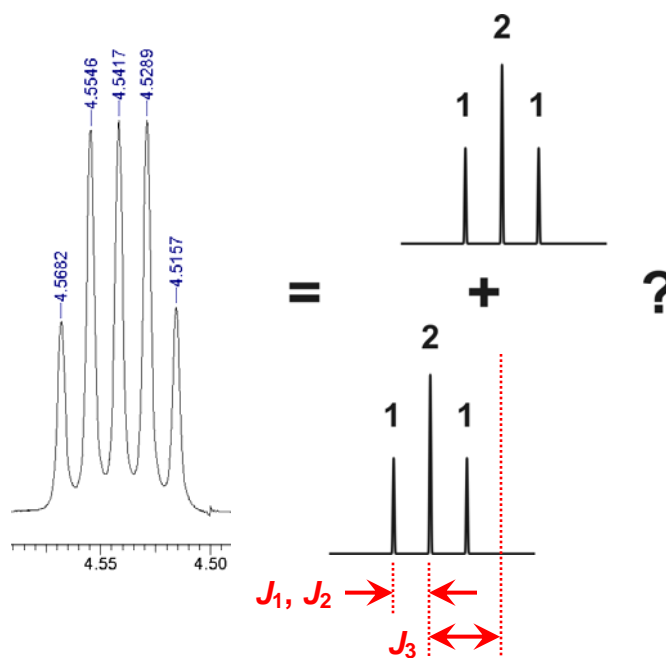


Discussion Section Exercise Solutions

^1H NMR Multiplets with Different Coupling Constants

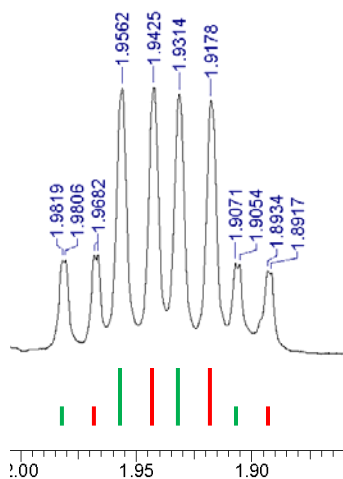
1&2. None of the multiplets in this NMR spectrum are simple—none of them have center peaks that are much taller than the outer peaks—but I think they are all pretty clearly derived from those simple multiplets. Take, for example, the multiplet at $\delta = 4.5$ ppm. This series of peaks isn't a simple multiplet, but it does look a little like the sum of two triplets—as if the multiplet were a doublet of triplets. If that were true, then the multiplet would have two different coupling constants: the J for each triplet component, and then the J representing the splitting of the triplet into two. Over the next couple of class periods, we will be talking about a slightly more complicated method for calculating multiple J values for really complex multiplets, but here I don't think we need that method. Here,



$$J_1 = J_2 = (\sim 0.128 \text{ ppm})(500 \text{ MHz}) = 6.4 \text{ Hz},$$

$$J_3 = 12.8 \text{ Hz}.$$

For our other multiplets:



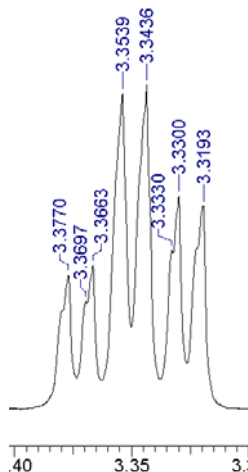
Maybe this one is a doublet of quartets? (See my green and red tick marks under the multiplet.) If so, then $J_1 = J_2 = J_3 =$ the distance between any two green lines (or two red ones), and $J_4 =$ the distance between red and green lines. So, here,

$$J_1 = J_2 = J_3 = 12.4 \text{ Hz},$$

$$J_4 = 6.8 \text{ Hz}.$$

The fine structure might be due to another, tiny

coupling constant in this multiplet, or it could be because some of the coupling constants we've assumed to be equal are not exactly equal. Let's leave it alone for now.

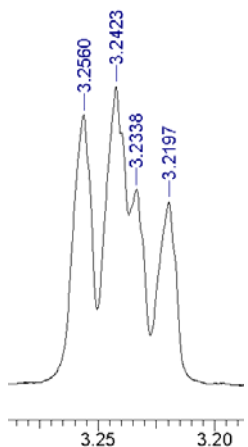


Doublet of triplets maybe?

$$J_1 = J_2 = 11.5 \text{ Hz,}$$

$$J_3 = 5.2 \text{ Hz.}$$

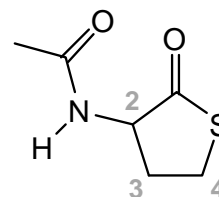
Again, tough to evaluate the fine structure.



A doublet of doublets, with at least one, and maybe more, tiny coupling constants hidden within each (broad-looking) peak. Thankfully, this one is pretty easy to calculate,

$$J_1 = 6.8 \text{ Hz, } J_2 = 11.3 \text{ Hz.}$$

3. Our molecule has a total of 9 H's to assign, but four of them are pretty easy; the acetyl -CH₃ group is coupled to nothing, and has to be the 3H singlet at $\delta = 2.1$ ppm. And chemical shift tables say that amide N-H protons are typically far downfield, so the broad "doublet" at $\delta = 6.3$ ppm must be the amide N-H. I don't know why the peak is doubled, but the separation between the two humps is too large to be a coupling constant. It could be that there are two most-stable, slowly interconverting conformations of the molecule that each contribute one of the two humps, but I don't think that's likely.



Out of the remaining 5 H's, the one that is farthest downfield, at $\delta = 4.5$ ppm, is probably H2, just because that carbon has two electron withdrawing groups attached. (You can confirm this with Pretsch's increment additivity table on p. 160, which predicts $\delta = 4.5$ ppm for this CH.) This proton has three sharp coupling partners in the NMR multiplet (dt), but only two vicinal neighbors, meaning that some long-range coupling to one of the H4 protons must contribute. The H4 protons must be the ones in the $\delta = 3.4$ - 3.2 ppm region, again based on Pretsch's tables; the one with the extra coupling constant must have a 4J . This sometimes for protons in a "W" arrangement, suggesting that H2 and an H4 have this arrangement.

