

- Thus, in Figure 1.22, our peaks are a 2H septet and a 6H triplet.
- The ratio of peaks forms **Pascal's Triangle**! You can Google why, if you're interested!!
- Sometimes, these peak patterns are called **multiplets**.
  - We tend to use the term “multiplet” when the splitting is either very complicated or low resolution, that is, when we cannot tell if the splitting is a triplet, quartet, septet, or something even more exotic (like what we'll discuss next class!).
- Note that identical protons do not couple themselves.<sup>[9]</sup>
  - This is why (for example) the septet in Figure 1.22 is not an octet: The two secondary protons do not couple to each other.
- **Coupling constant:** A measure of coupling. *Denoted by  $J$ . Units Hz.*
  - Protons that couple each other have identical  $J$  values.
- Coupled protons split via **roofing**.
- **Roofing:** A phenomenon in which coupled peaks slant towards each other.

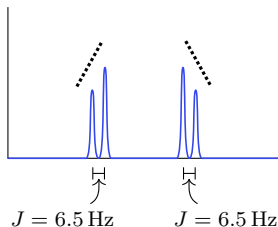


Figure 1.23: Roofing in NMR.

- When you couple two doublets, they have this extra fun shape that helps hint toward coupling.
- Next time: Where  $J$  comes from, compounds coupling, carbon NMR, and more!

## 1.5 Nuclear Magnetic Resonance - 2

- 9/13:
- Lecture 4 recap: A summary of the features in an NMR spectrum.
    1. Chemical shift ( $\delta$ ).
      - This tells us the ppm of the peak, specifically whether the proton is more downfield or upfield.
      - It indicates which functional group a proton is in or near, e.g., EWG/EDG (see Figure 1.20).
    2. Integration.
      - The integration is the area under the peak.
      - It tells us how many unique protons make up a peak.
    3. Coupling.
      - The coupling determines the shape of the peak.
      - It tells us how many protons are adjacent to the peak.
    4. Coupling constant ( $J$ ).
      - The coupling constant gives an exact, quantitative measure of the shape of the peak.
      - It tells us where (geometrically) the adjacent protons are.

<sup>9</sup>For a (heavily mathematical, quantum mechanical) explanation of why, see [this](#) resource.

- Today: More NMR.
  - Reading: Clayden et al. (2012), Chapter 13.
- Lecture outline.
  - More on the coupling constant.
  - $^{13}\text{C}$  NMR.
  - Guidelines for interpreting a  $^1\text{H}$  NMR spectrum.
- To begin, we will pick up where we left off in discussing  $J$ .
- What determines the magnitude of  $J$ ?
  - $J$  is determined by the geometry between protons, especially the **dihedral angle**.
  - The typical range of  $J$  values is 6 – 8 Hz.
- **Dihedral angle:** The angle between two coupled protons in a Newman projection sighted along the C–C bond connecting the coupled protons' carbons. *Denoted by  $\phi$ .*
- **Karplus equation:** An expression of the magnitude of  $J$  for two coupled protons as a function of their dihedral angle.

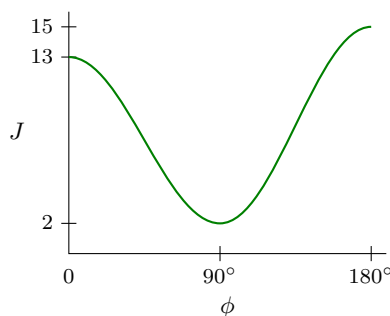


Figure 1.24: Karplus equation.

- Coupling is greatest when the protons are either directly aligned, or directly antiperiplanar ( $180^\circ$ ).
- Example coupling constants: In a vinyl group.

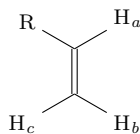


Figure 1.25: Coupling constants in a vinyl group.

- Since there is no free rotation around the double bond, the three proton pairs in this functional group all have distinct and recognizable couplings.
- In this functional group...
  - The *cis* protons couple at  $J_{\text{H}_{a,b}} \approx 6 - 12 \text{ Hz}$ ;
  - The *trans* protons couple at  $J_{\text{H}_{a,c}} \approx 12 - 18 \text{ Hz}$ .
  - The **geminal** protons couple at  $J_{\text{H}_{b,c}} \approx 1 - 3 \text{ Hz}$ .
- Implication: Geminal protons *can* couple (provided that they are not chemically equivalent).
  - In other words, protons do not *need* to be **vicinal** in order to couple.

- **Geminal** (atoms or groups): Two atoms or groups in a molecule that are both bonded to the same “parent” carbon atom.
- **Viscinal** (atoms or groups): Two atoms or groups in a molecule that are bonded to adjacent, viscinal carbon atoms (i.e., in a 1,2-relationship).
- Example coupling constants: In benzene.

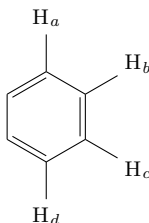
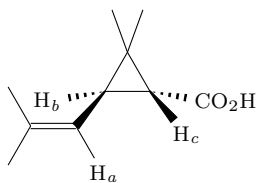
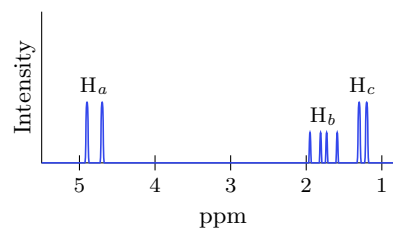
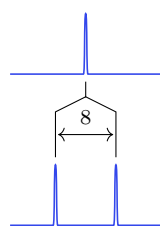


Figure 1.26: Coupling constants in benzene.

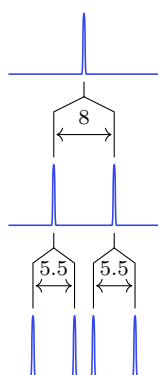
- Long range coupling is possible with  $\pi$ -systems.
  - Thus, protons *meta* and *para* to each other can couple even though they're not viscinal.
- $J_{\text{ortho}} \approx 7 - 10 \text{ Hz}$ .
- $J_{\text{meta}} \approx 2 - 3 \text{ Hz}$ .
- $J_{\text{para}} \approx 0 - 14 \text{ Hz}$ .
- Coupling to nonequivalent protons.



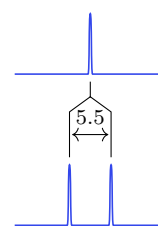
(a) An example molecule.

(b) The molecule's  $^1\text{H}$  NMR spectrum.

doublet

(c) Splitting diagram:  $\text{H}_a$ .

doublet of doublets

(d) Splitting diagram:  $\text{H}_b$ .

doublet

(e) Splitting diagram:  $\text{H}_c$ .

Figure 1.27: Nonequivalent proton coupling.

- Before covering this example in class, Prof. Elkin flags a typo from where this example is covered in Clayden et al. (2012).
  - Specifically, the molecule in Figure 1.27a is called chrysanthemic acid, and its  $^1\text{H}$  NMR spectrum is also covered on Clayden et al. (2012, p. 292).
  - However, when the authors of the textbook drew the molecule, they forgot to include the two methyl groups on the “top” carbon in Figure 1.27a: This is their mistake, not ours.
- We now return to analyzing the example.
- Maxim: If a proton is adjacent to multiple unique protons, it couples to each.
  - Indeed, the molecule in Figure 1.27a is interesting to us because  $\text{H}_b$  is vicinal to both  $\text{H}_a$  and  $\text{H}_c$  (so it will couple to both of them), but  $\text{H}_a$  and  $\text{H}_c$  are not chemically equivalent, i.e., are unique.
  - The resultant splitting is captured in Figure 1.27b.
  - Note, however, that some of chrysanthemic acid’s proton NMR peaks have been edited out of Figure 1.27b for the sake of clarity, e.g., those from the four methyl groups at the top and left of the molecule, as drawn in Figure 1.27a.
- To explain the splittings observed in Figure 1.27b, we draw **splitting diagrams**.
  - Figures 1.27c, 1.27d, and 1.27e constitute three such diagrams. Let’s go through them one by one.
- Figure 1.27c.
  - $\text{H}_a$  is vicinal to a single proton, namely  $\text{H}_b$ .
  - Thus,  $\text{H}_b$  will split  $\text{H}_a$  into a doublet.
  - Experimentally, we observe that the coupling constant is 8 Hz.
- Figure 1.27e.
  - Similarly to  $\text{H}_a$ ,  $\text{H}_c$  gets split by  $\text{H}_b$ .
  - However,  $\text{H}_c$  is distinct from  $\text{H}_a$ , and thus it interacts differently with  $\text{H}_b$ . This may be observed since  $\text{H}_b$  only splits  $\text{H}_c$  by 5.5 Hz.
- Figure 1.27d.
  - $\text{H}_b$  will get split by both  $\text{H}_a$  and  $\text{H}_c$ , however.
  - In particular,  $\text{H}_a$  will split it by 8 Hz, and  $\text{H}_c$  will split it by 5.5 Hz. But how does this splitting manifest itself?
  - To answer this question, we may think of  $\text{H}_a$  as splitting  $\text{H}_b$  “first,” and then  $\text{H}_c$  as splitting the resultant doublet “second.”
  - As an exercise, draw out this splitting diagram again, but switch the order of the splitting (i.e., let  $\text{H}_c$  do the splitting “first” and  $\text{H}_a$  do the splitting “second”). You will see that you get the exact same peak pattern!!<sup>[10]</sup>
- The peak pattern derived in Figure 1.27d is known as a **doublet of doublets** (dd).
- Note: Doublet of doublets *must* be symmetric.
  - For example, we couldn’t have 1 peak on the left more separated from the other 3.
- Doublets aren’t the only peak patterns that are susceptible to this kind of twofold splitting: Indeed, we can mix and match others!
  - For example, we can have a **triplet of doublets** or a **doublet of doublets of doublets of doublets**. (These are for you to dig into on your own, if you’re curious :)
- Note that a doublet of doublets is *not* a quartet; in a quartet, you have equal spacing between every peak and a 1 : 3 : 3 : 1 ratio of peak heights.

<sup>10</sup>An additional exercise you can try is figuring out why we can draw splitting diagrams for the splitting caused by equivalent protons, too. If you draw out a splitting diagram for the splitting caused by two (or more!) equivalent protons, you will see that the process is needlessly redundant since our rule in Table 1.3 summarizes everything well enough.

- Why do we use Hz for  $J$  but ppm for  $\delta$ ?
  - Chemical shifts and coupling are slightly different phenomena. In particular, they differ in the way they interact with the applied external magnetic field.
  - We use ppm for the chemical shift because ppm is a uniform scale for the chemical shift, even when we change the magnetic field strength of our NMR spectrometer.
  - We use Hz for coupling because Hz is a uniform scale for the coupling, even when we change the magnetic field strength of our NMR spectrometer!
- We now switch our focus from  $^1\text{H}$  NMR to  $^{13}\text{C}$  NMR for a bit.
- $^{13}\text{C}$  NMR vs.  $^1\text{H}$  NMR.
  - Recall from the lecture on mass spec that the  $^{13}\text{C}$  isotope makes up approximately 1% of carbon. (Most naturally occurring carbon is the NMR-silent isotope  $^{12}\text{C}$ .)
    - The fact that most carbon nuclei are NMR silent means that we get less signal from  $^{13}\text{C}$  NMR than  $^1\text{H}$  NMR.
  - Spectral window: 0 – 200 ppm for organics.
    - Note that this is much larger than the 0 – 12 ppm window for  $^1\text{H}$  NMR.
  - Coupling is rare; you almost always get singlets.
  - No integration; the peak height changes, but exactly why is complicated.
    - Google it if you're curious!!
  - Sometimes “cleaner” than  $^1\text{H}$  NMR, by which we mean that you get better resolution in the absence of splitting.
    - In other words, it's easier to interpret how many peaks you have in  $^{13}\text{C}$  NMR.
  - We can now see carbons without protons!
    - Examples: Carbonyl, tetrasubstituted, and quaternary carbons.
- Example  $^{13}\text{C}$  NMR spectrum: Cyclohexanol (C1CCCCC1O).

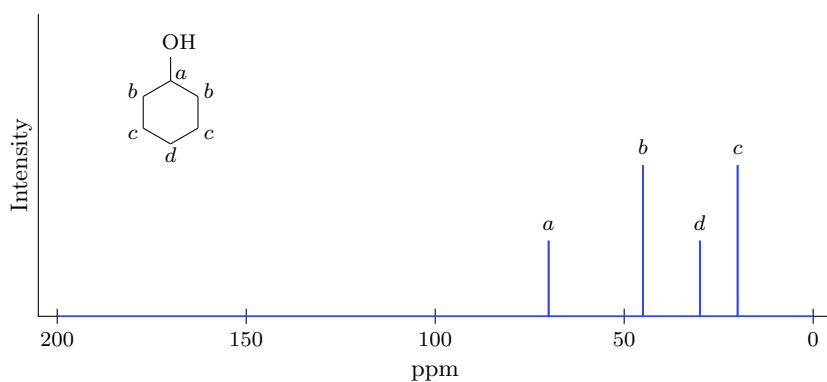


Figure 1.28:  $^{13}\text{C}$  NMR spectrum of cyclohexanol.

- When analyzing a  $^{13}\text{C}$  NMR spectrum, we label the carbons in our molecule with letters.
- Specifically, one letter is used for each *unique* carbon.
- This is why cyclohexanol (a symmetric molecule) only needs 4 letters instead of 6: It has 4 *unique* carbons and 6 total carbons.

- The example in Figure 1.28 illustrates one of the things for which  $^{13}\text{C}$  NMR is most useful: Telling us how many unique carbons we have!

Molecule	Cyclohexanol ( <chem>C1CCCCC1O</chem> )	2-Aminocyclohexanol ( <chem>C1CCCCC1O</chem> <chem>C1CCCCC1N</chem> )	Cyclohexane ( <chem>C1CCCCC1</chem> )
# carbons	6	6	6
# unique carbons	4	6	1

Table 1.4:  $^{13}\text{C}$  NMR identifies the number of unique carbons.

- Indeed, for almost identical molecules, we observe big differences in the  $^{13}\text{C}$  NMR spectrum.
  - For example, the asymmetric molecule 2-aminocyclohexanol has 6 unique carbons while the highly symmetric cyclohexane has only 1 unique carbon, despite the fact that all of these molecules only differ by a couple of functional groups!
- $^{13}\text{C}$  NMR — like  $^1\text{H}$  NMR — helps us identify key functional groups.

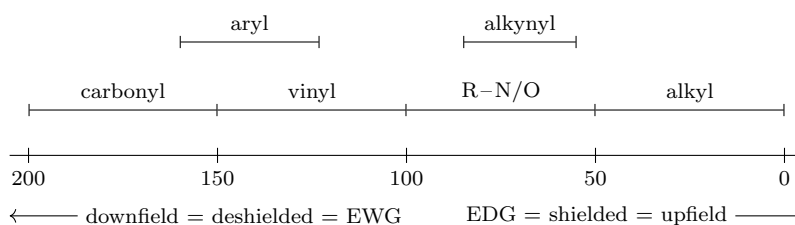


Figure 1.29: Chemical shifts of common carbon types.

- Note that we have a carbonyl region here that we did not have in Figure 1.20!
- If  $^{13}\text{C}$  NMR can be used for functional group identification, why would we ever want to use IR?
  - There are some functional groups between which  $^{13}\text{C}$  NMR can't distinguish.
    - Example:  $^{13}\text{C}$  NMR can't distinguish  $\text{C}=\text{N}$  from  $\text{C}=\text{O}$ , but IR can.
  - As a general rule, though, a chemist would collect data from both sources (as well as all the others) and make sure that the data is consistent.
    - For example, if  $^{13}\text{C}$  NMR suggests that a molecule has an alkynyl carbon but IR doesn't show a stretch at  $3300\text{ cm}^{-1}$ , we might have a problem!
    - One potential solution to this problem could be that we mistakenly identified a R-N/O peak in the  $^{13}\text{C}$  NMR spectrum as an alkynyl peak.
- We now return to  $^1\text{H}$  NMR for some guidelines on interpreting these spectra.
  - NMR can tell you how many distinct  $^1\text{H}/^{13}\text{C}$  groups you have, what kind of functional group they are, and how they're connected.
  - Example step-by-step workflow for  $^1\text{H}$  NMR.
    - Identify the number of unique peaks, and watch out for overlap!
    - Note the chemical shifts and propose likely functional groups.
    - Calculate or consider integrations.
    - Observe the peak shape and start hypothesizing about connectivity.
    - Calculate  $J$  to confirm or support connectivity.
    - Make sure that all the data is consistent.

- Let's now look at an example of how we could identify a compound from its  $^1\text{H}$  NMR spectrum using the above workflow.
- Example  $^1\text{H}$  NMR spectrum: 4,4-Dimethylcyclohex-2-en-1-one (CC1=C(C)CCC(=O)C1).

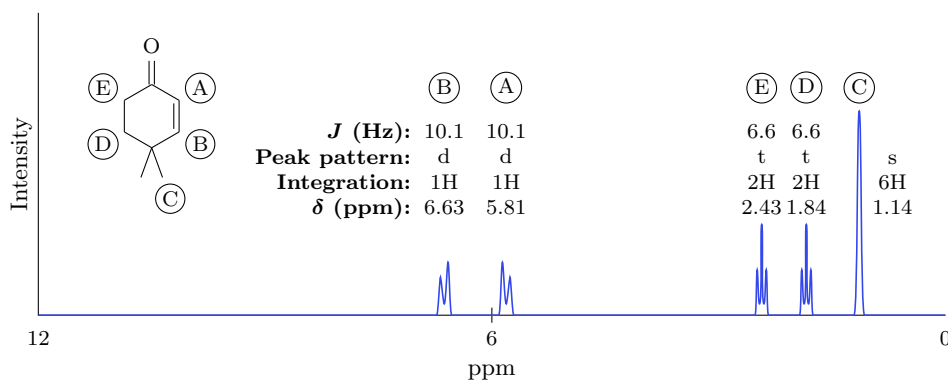


Figure 1.30:  $^1\text{H}$  NMR spectrum of 4,4-dimethylcyclohex-2-en-1-one.

- There are 5 unique peaks.
  - This means that there are 5 unique proton positions.
- There are 2 peaks in the vinyl region,<sup>[11]</sup> and 3 peaks in the alkyl region.
- The ratio of integrations is 1 : 1 : 2 : 2 : 6.
  - The 6H integration must be 2 identical groups of 3 protons (i.e., methyl groups)!
  - Similarly, if we saw 9H, it would probably be 3 identical methyl groups.
- There are 2 roofing doublets, 2 triplets, and 1 singlet.
  - The 2 roofing doublets correspond to the vinyl protons.
    - This implies that our vinyl protons are adjacent to each other.
    - Thus, part of our molecule looks like this: C=C
    - Note that we will not know that the vinyl protons are *cis* until Step 5; they could still be *trans* or geminal until the coupling constant tells us otherwise.
  - The 2 triplets correspond to some of the alkyl protons.
    - This splitting pattern implies the presence of two protons next to two protons.
    - Thus, part of our molecule looks like this: CH2-CH2
    - Note that this splitting pattern analysis lines up with the integrations as well!
  - The 1 singlet corresponds to the remaining alkyl protons.
    - Six chemically identical protons that are not split by anything implies geminal methyl groups on a tetrasubstituted carbon.
    - Thus, part of our molecule looks like this: C(C)(C)C
- The  $J$ 's agree with all the motifs we've proposed so far.
  - The 6.6 Hz splitting of the triplets doesn't get us much new information.
  - However, per Figure 1.25 and the associated discussion, a coupling constant of 10.1 Hz for the vinyl protons confirms that they are in a *cis* orientation, as drawn above.
- All of the data is, indeed, consistent with the proposed molecule's structure.

<sup>11</sup>Note that we include the peak at 6.63 ppm in the vinyl region even though it would normally fall in the aryl region (per Figure 1.20) due to the nearby carbonyl EWG.