

Chapter 1: NMR Coupling Constants

NMR can be used for more than simply comparing a product to a literature spectrum. There is a great deal of information that can be learned from analysis of the coupling constants for a compound.

1.1 Coupling Constants and the Karplus Equation

When two protons couple to each other, they cause splitting of each other's peaks. The spacing between the peaks is the same for both protons, and is referred to as the coupling constant or J constant. This number is always given in hertz (Hz), and is determined by the following formula:

$$J \text{ Hz} = \Delta \text{ ppm} \times \text{instrument frequency}$$

Δ ppm is the difference in ppm of two peaks for a given proton. The instrument frequency is determined by the strength of the magnet, and will always be 300 MHz for all spectra collected on the organic teaching lab NMR.

Figure 1-1 below shows the simulated NMR spectrum of 1,1-dichloroethane, collected in a 30 MHz instrument. This compound has coupling between **A** (the quartet at 6 ppm) and **B** (the doublet at 2 ppm).

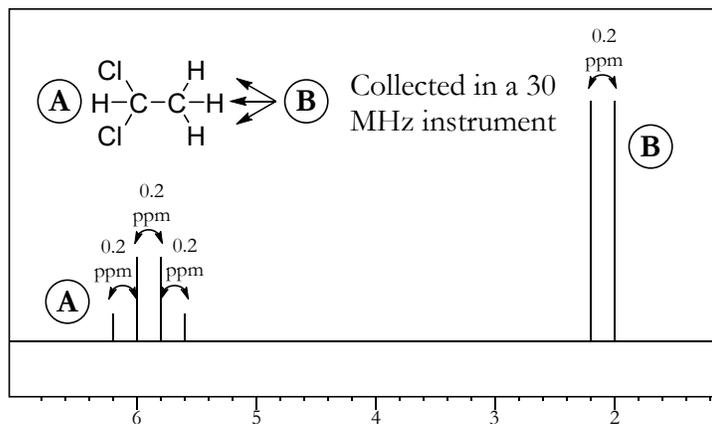


Figure 1-1: The NMR spectrum of 1,1-dichloroethane, collected in a 30 MHz instrument. For both A and B protons, the peaks are spaced by 0.2 ppm, equal to 6 Hz in this instrument.

For both **A** and **B**, the distance between the peaks is equal. In this example, the spacing between the peaks is 0.2 ppm (for example, the peaks for **A** are at 6.2, 6.0, 5.8, and 5.6 ppm). This is equal to a J constant of $(0.2 \text{ ppm} \cdot 30 \text{ MHz}) = 6 \text{ Hz}$. Since the shifts are given in ppm or parts per million, you should divide by 10^6 . But since the frequency is in megahertz instead of hertz, you should multiply by 10^6 . These two factors cancel each other out, making calculations nice and simple.

Figure 1-2 below shows the NMR spectrum of the same compound, but this time collected in a 60 MHz instrument.

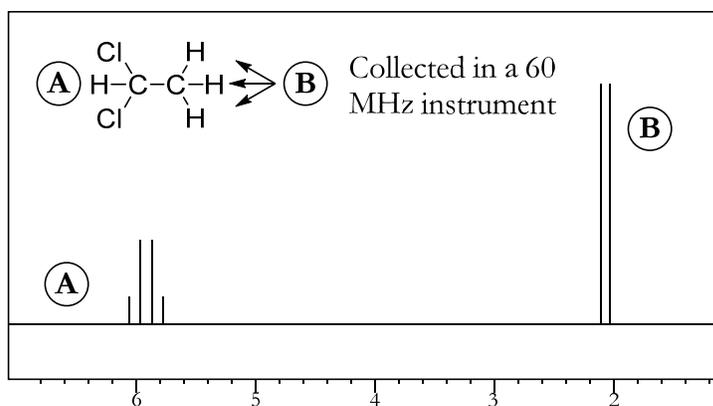


Figure 1-2: The NMR spectrum of 1,1-dichloroethane, collected in a 60 MHz instrument. For both A and B protons, the peaks are spaced by 0.1 ppm, equal to 6 Hz in this instrument.

This time, the peak spacing is 0.1 ppm. This is equal to a J constant of $(0.1 \text{ ppm} \cdot 60 \text{ MHz}) = 6 \text{ Hz}$, the same as before. This shows that the J constant for any two particular protons will be the same value in hertz, no matter which instrument is used to measure it.

The coupling constant provides valuable information about the structure of a compound. Some typical coupling constants are shown here.

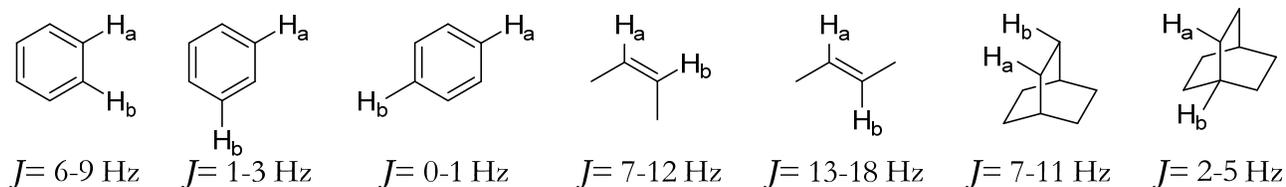


Figure 1-3: The coupling constants for some typical pairs of protons.

In molecules where the rotation of bonds is constrained (for instance, in double bonds or rings), the coupling constant can provide information about stereochemistry. The Karplus equation describes how the coupling constant between two protons is affected by the dihedral angle between them. The equation follows the general format of $J = A + B (\cos \theta) + C (\cos 2\theta)$, with the exact values of A, B and C dependent on several different factors. In general, though, a plot of this equation has the shape shown in Figure 1-4. Coupling constants will usually, but not always, fall into the shaded band on this graph.

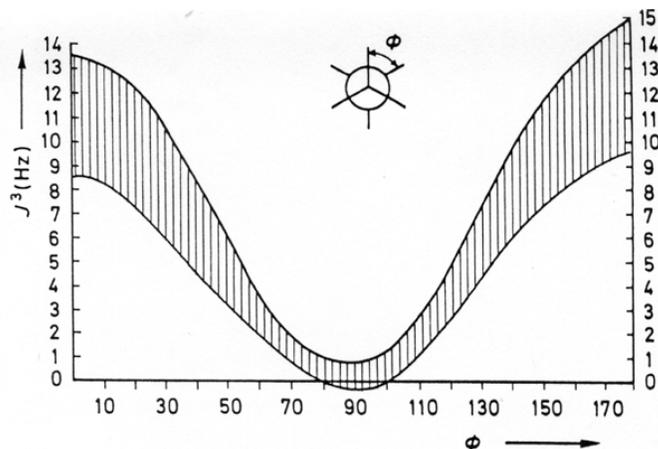


Figure 1-4: The plot of dihedral angle vs. coupling constant described by the Karplus equation.

The highest coupling constants will occur between protons that have a dihedral angle of either 0° or 180° , and the lowest coupling constants will occur at 90° . This is due to orbital overlap – when the orbitals are at 90° , there is very little overlap between them, so the hydrogens cannot affect each other's spins very much (Figure 1-5).

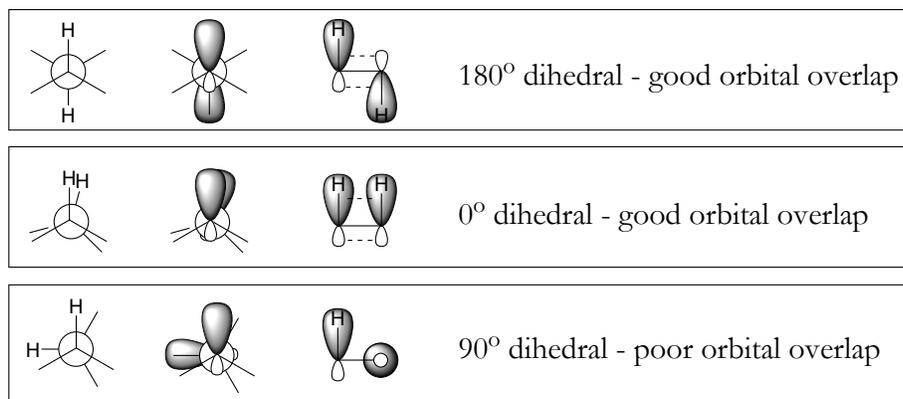


Figure 1-5: The best orbital overlap occurs at 180° or 0° , which is why the coupling constant is higher for those angles.

1.2 Calculating Coupling Constants in MestreNova

To calculate coupling constants in MestreNova, there are several options. The easiest one is to use the Multiplet Analysis tool. To do this, go to Analysis \rightarrow Multiplet Analysis \rightarrow Manual (or just hit the “J” key). Drag a box around each group of equivalent protons. A purple version of the integral bar will appear below each one, along with a purple box above each one describing its splitting pattern and location in ppm. As with normal integrals, you can right-click the integral bar, select “Edit Multiplet”, and set these integrals to whatever makes sense for that particular structure. For example, in Figure 1-6, each peak is from a single proton so each integral should be about 1.00.

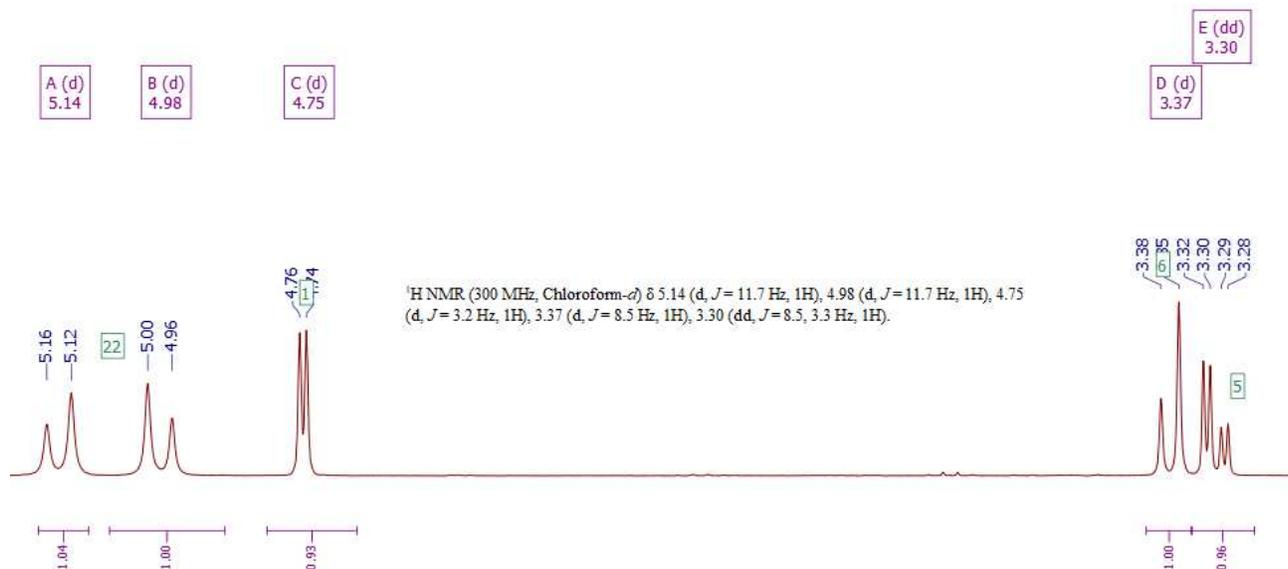


Figure 1-6: An example NMR spectrum with multiplet analysis.

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Once all peaks are labeled, you can go to Analysis → Multiplet Analysis → Report Multiplets. A text box should appear containing information about the peaks in a highly compressed format. You can then copy and paste this text into your lab report as needed. The spectrum shown above has the following multiplets listed:

^1H NMR (300 MHz, Chloroform-d) δ 5.14 (d, $J = 11.7$ Hz, 1H), 4.98 (d, $J = 11.7$ Hz, 1H), 4.75 (d, $J = 3.2$ Hz, 1H), 3.37 (d, $J = 8.5$ Hz, 1H), 3.30 (dd, $J = 8.5, 3.3$ Hz, 1H).

The first set of parentheses indicates that the sample was dissolved in Chloroform-d and placed in a 300 MHz instrument. After that, there is a list of numbers. Each number or range indicates the chemical shift of each of the peaks in the spectrum, in order of descending chemical shift. Each number also has a set of parentheses after it, giving information about that peak. These parentheses contain:

- A letter or letters to indicate the splitting of a peak (s=singlet, d=doublet, t=triplet, q=quartet); it is also possible to see things like dd for a doublet of doublets or b for broad. If MestreNova can't identify a uniform splitting pattern, it will name it a multiplet (m).
- The coupling constants or J-values for that peak – for example, the peak at 3.30 ppm has J-values of 8.5 and 3.3 ppm.
- The integral of the peak, rounded to the nearest whole number of H.

Using this information, you can determine which peaks in Figure 1-6 are coupling to each other based on which ones have matching J-values.

- Peaks **A** and **B** in Figure 1-6 both have J-values of 11.7 Hz, so these two protons are coupling to each other.
- Peaks **C** and **E** both have J-values of 3.2 or 3.3 Hz (similar enough, within a margin of error), so these two protons are coupling to each other.
- Peaks **D** and **E** both have J-values of 8.5 Hz, so these two protons are coupling to each other.

If the multiplet analysis tool is failing to determine J-values for any reason, you can always calculate them manually. To do this, you will need to get more precise values for your peak locations. Right-click anywhere in the empty space of the spectrum and select Properties, then go to Peaks and increase the decimals to 4 (Figure 1-7).

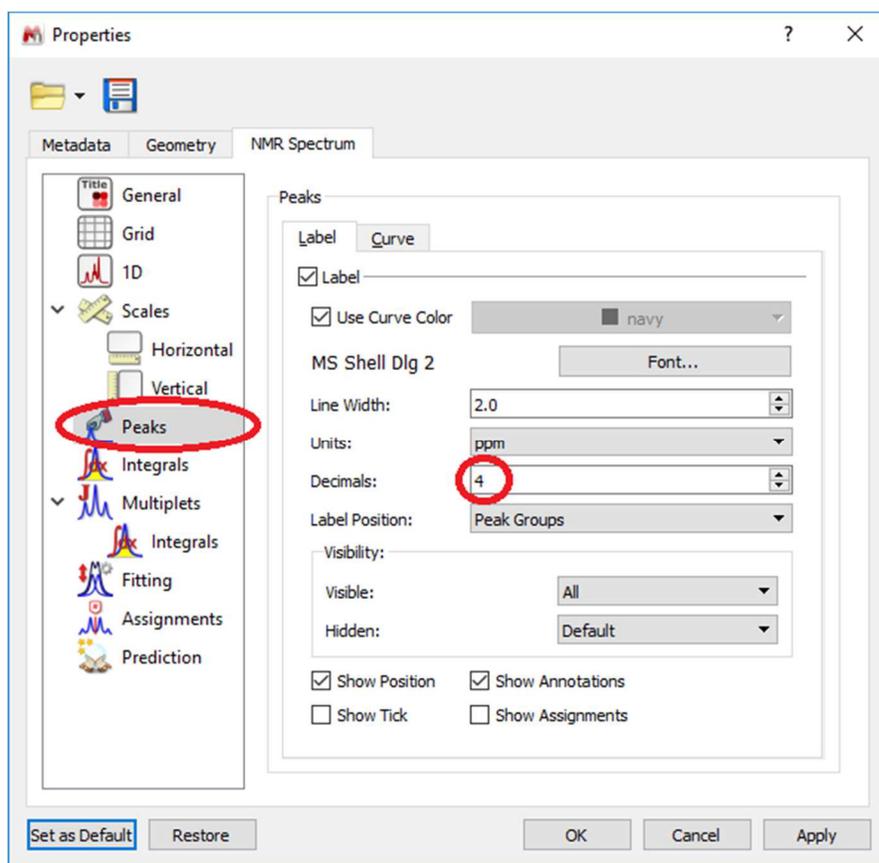


Figure 1-7: Changing the decimals on peak labeling.

Now if you do peak-picking to label the locations of the peaks, you should see them to 4 decimal places. This will allow you to plug these into the equation to find the J-values manually. For example, in Figure 1-8, the peaks around 4.7 ppm have a J-value of $(4.7550 \text{ ppm} - 4.7442 \text{ ppm}) \cdot 300 \text{ MHz} = 3.24 \text{ Hz}$. Note that this is in agreement with MestreNova's determination of 3.2 ppm for this J-value in Figure 1-6.

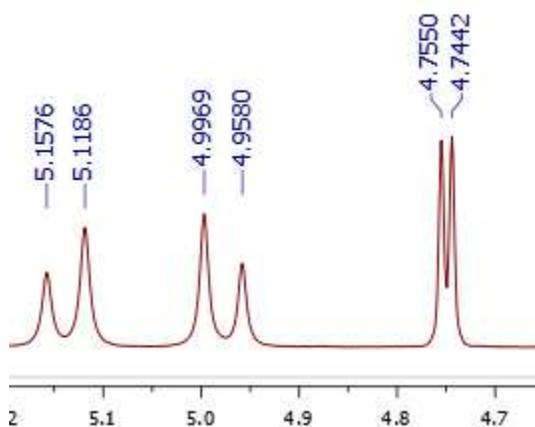


Figure 1-8: Peaks labeled with enough precision to allow you to calculate J-values manually.

1.3 Topicity and Second-Order Coupling

During the NMR tutorial, you learned about the concept of chemical equivalence: protons in identical chemical environments have identical chemical shifts. However, just because two protons have the same connectivity to the molecule does not mean they are chemically equivalent. This is related to the concept of **topicity**: the stereochemical relationship between different groups in a molecule. To find the topicity relationship of two groups to each other, you should try replacing first one group, then the other group with a placeholder atom (in the examples in Figure 1-9, a dark circle is used as the placeholder). If the two molecules produced are identical, then the groups are homotopic; if the molecules are enantiomers, then the groups are enantiotopic; and if the molecules are diastereomers, then the groups are diastereotopic. Groups that are diastereotopic are chemically inequivalent, so they will have a different chemical shift from each other in NMR, and will show coupling as if they were neighboring protons instead of on the same carbon atom.

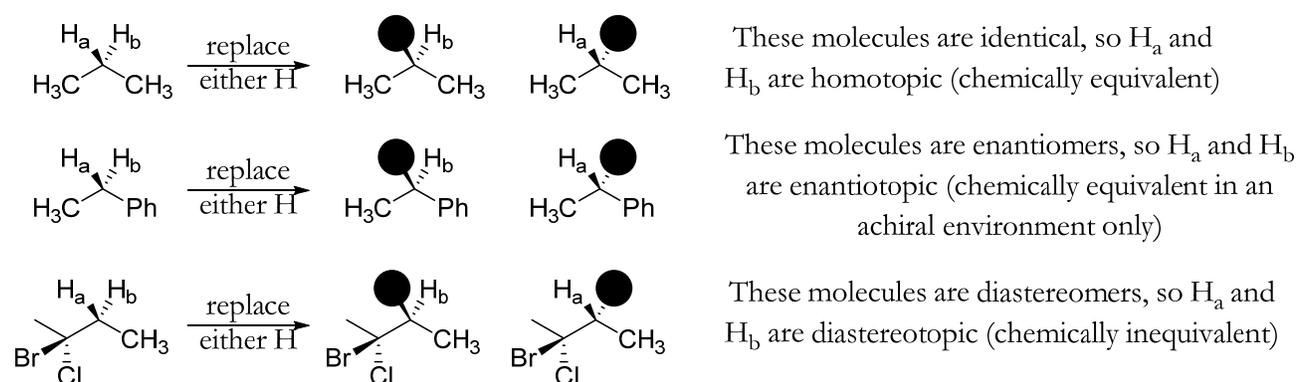


Figure 1-9: Some examples of homotopic, enantiotopic, and diastereotopic groups.

If two signals are coupled to each other and have very similar (but not identical) chemical shifts, another effect will appear: second-order coupling. This means that the peaks appear to “lean” toward each other – the peaks on the outside of the coupled pair are shorter, and the peaks on the inside are taller. (Figure 1-10).

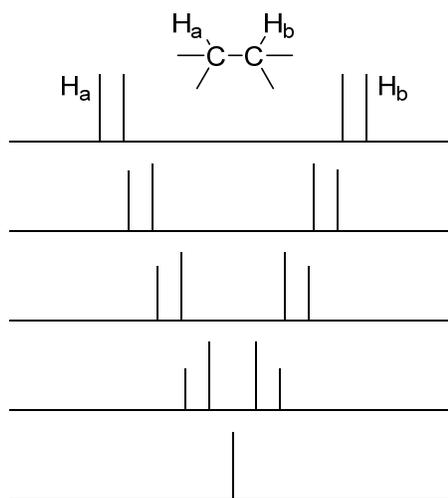


Figure 1-10: As the chemical shifts of H_a and H_b become more and more similar, the coupling between them becomes more second-order and the peaks lean more.

This is very common for two diastereotopic protons on the same carbon atom, but it appears in other situations where two protons are almost chemically identical as well. In Figure 1-8, note the two doublets at 4.98 and 5.14 ppm. These happen to be diastereotopic protons – they are attached to the same carbon, but are chemically equivalent.

Looking for pairs of leaning peaks is useful, because it allows you to identify which protons are coupled to each other in a complicated spectrum. In Figure 1-11, there are two different pairs of leaning peaks: two 1H peaks with a $J = 9$ Hz, and two 2H peaks with $J = 15$ Hz. Recognizing this makes it possible to pick apart the different components of the peaks towards the left of the spectrum: these are two overlapping doublets, not a quartet.

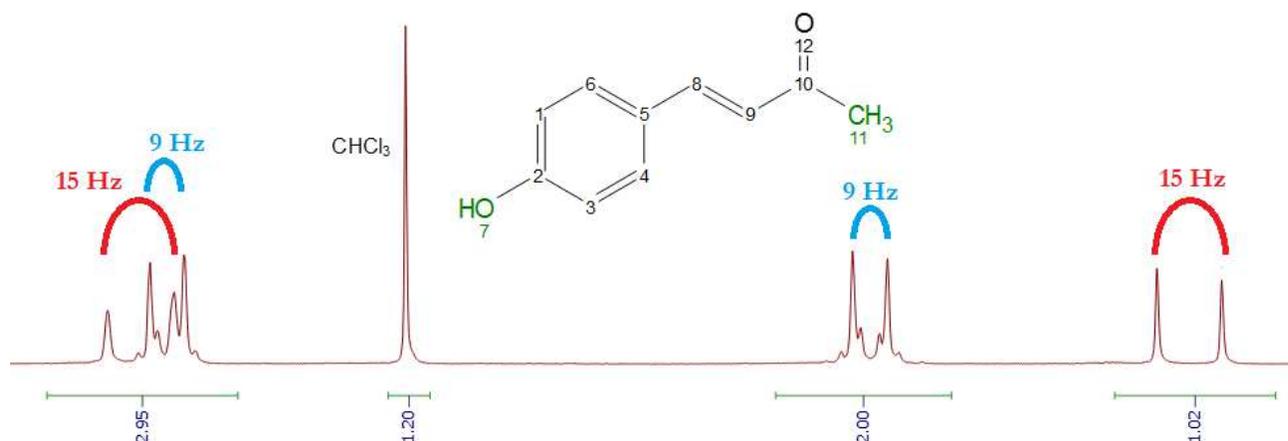


Figure 1-11: An NMR spectrum with two different pairs of leaning peaks.

The multiplet tool in MestreNova might not work immediately for analyzing overlapping multiplets like this. Instead, you should follow the instructions at <http://resources.mestrelab.com/resolving-overlapped-multiplets/> to deal with them.