

## Coupling Revisited: Coupling Constants, Decoupled Carbon Spectra, and Coupled Carbon Spectra

Normally, carbon spectra are run “decoupled.” As the data are collected at the carbon frequency (100 MHz on the Avance 400), the hydrogen nuclei are irradiated over a range of frequencies centered at 400 MHz. This stops the splitting of the C-13 peaks by hydrogen. In the absence of irradiation, nuclear spins do not change during the collection of an FID (i.e. a spin  $+1/2$  nucleus does not flip to spin  $-1/2$ ). No splitting occurs during irradiation because the  $^1\text{H}$  nuclei to “flip” their spins more rapidly than the FID is collected and the  $^{13}\text{C}$  nucleus experiences an average zero spin.

Decoupling is used for several reasons: 1) Since  $^{13}\text{C}$  is only *ca.* 1% abundant, splitting the peaks requires many more scans to observe the signals above the noise, 2) the inherent sensitivity of  $^{13}\text{C}$  is much lower than  $^1\text{H}$  (i.e. the same number of atoms give signals that are smaller), and 3) the carbon peaks of carbons attached to hydrogen are amplified by a factor of up to three when the hydrogen nuclei are decoupled (called the [Nuclear Overhauser Effect](#)). The combination of these factors makes decoupled carbon spectra much easier to collect.

In this experiment, obtain three spectra of ethylbenzene (EtPh):

1. *A standard H-1 spectrum.* In addition to the normal summary table also calculate the three bond H-H coupling constant,  $^3J_{\text{HH}}$ , by measuring the distance between two adjacent peaks in a doublet, triplet, or quartet and then converting the ppm to Hz. This calculation can be done by setting the ratio of ppm to  $10^6 =$  the coupling (in Hz) to the total frequency of the instrument (in Hz ( $400 \times 10^6$  for the Avance NMR)). Your value should be greater than 2 Hz and less than 50 Hz if calculated correctly.
2. *A standard C-13 spectrum.* Collect a standard  $^{13}\text{C}$  NMR using the 13CPD32 parameter set. Print it out (because the next thing you do will do is destroy the spectrum).
3. *A coupled spectrum.* Click on the command line and type “PLW2 0” and hit enter. Repeat with “PLW12 0” and “PLW13 0”. Click on the “Go” button to collect a spectrum. Alternatively, you may click on the AcquisPar tab, which is next to the Spectrum tab. On the next line down are a series of icons, one of which will say “Force Parse of Pulse Program” when you hover over it. The icon is towards the left side. When you click on it, scroll to the bottom of the page and you will see PLW2, PLW12, and PLW13. In the first column of boxes, change the values to zero. Then Click go.
4. Collect a  $^{13}\text{C}$  NMR spectrum with **just 1 scan**. To do this, set up a standard (coupled)  $^{13}\text{C}$  experiment, but before you start the run, type “NS 1” on the command line. Alternatively, you can type “NS” there and a dialog box will open where you can enter 1. You don’t need that spectrum now, but will use it later this semester when we discuss signal-to-noise. Since it’s already in the instrument, it will save you time later. You will need the spectrum from #2 above for the same lab.

### Write-up

- i) Make a summary table of this including a column for the coupled information. Be sure to indicate on your coupled carbon spectrum the group giving the peak and explain the multiplicity obtained.

- ii) Comment on the relative noise you see between your spectra. (i.e. the height of the peaks relative to the amount of noise in the baseline). In particular, in light of what is said above, explain in your own words why any one of the effects lowers the relative noise.
- iii) Calculate the single bond C-H coupling constant,  $^1J_{CH}$ , from one of your coupled peaks. Your value should be greater than 50 Hz and less than 400 Hz if calculated correctly.
- iv) If you expand the print window on the ethyl triplet/quartet peaks, you should see something interesting (called "long range coupling"). The three triplet peaks will each be split into a quartet and the four quartet peaks will each be split into a triplet. Pick 1 splitting from each of 3 or 4 of the multiplets and calculate the coupling constant. Comment on why the splitting occurs and why the splitting you calculate here is so much smaller than that measured in point (iii).
- v) Answer questions 1-5 for **ethanol, CH<sub>3</sub>CH<sub>2</sub>OH**. (You can print the page, write the answers in the left margin, and turn it in with your spectra.

### Homework

1. The C-13 coupled spectrum will show a \_\_\_\_\_ for the CH<sub>2</sub> (methylene group).  
 A) singlet      B) doublet      C) triplet      D) quartet      E) multiplet
2. In the proton spectrum, from the highest chemical shift to the lowest, integration of the peaks will be:  
 A) 1,2,3      B) 1, 1, 1      C) 3, 2, 1      D) 0, 4, 3      E) 2, 3, 1
3. In the proton spectrum, the peaks from highest to lowest chemical shift will be:  
 A) singlet, doublet, triplet      C) singlet, triplet, quartet      E) quartet, triplet singlet  
 B) singlet, quartet, triplet      D) triplet, quartet doublet
4. In the coupled carbon spectrum, the peaks from highest to lowest chemical shift will be:  
 A) singlet, doublet, triplet      C) triplet, quartet      E) quartet, triplet, singlet  
 B) singlet, singlet      D) triplet, quartet, doublet
5. The normal (decoupled) carbon-13 spectrum will consist of \_\_\_\_\_ different peaks.  
 A) 1      B) 2      C) 3      D) 6      E) more than 6
6. On a 60 MHz instrument, 0.50 ppm in the proton spectrum corresponds to \_\_\_\_\_ Hz. On the same instrument C-13 is run at a frequency of 15 MHz. On its spectrum, 0.50 ppm corresponds to \_\_\_\_\_ Hz.  
 A) 60, 15      B) 15, 15      C) 7.5, 7.5      D) 7.5, 30      E) 30, 7.5