# Jigsaw 1D

1. *In a $^{1}$H NMR spectrum of $CHCl_3$ at natural abundance, can we observe the heteronuclear $^{1}$H-$^{13}$C J-coupling? Why or why not?*

Almost all $CHCl_3$ molecules contain $^{12}$C (about 99% naturally), while only about 1% contain $^{13}$C. However, since only about 1% of the molecules contain $^{13}$C, this doublet is extremely weak and is usually hidden under the main singlet from the $^{12}$C–H signal. **Singlet from the 1H. 12C has spin 0 and it is not NMR active!**

In theory, the $^{1}$H–$^{13}$C coupling could be observed if no broadband decoupling is applied, but in practice its signal is very small due to the low natural abundance of $^{13}$C.

2. *When we acquire an NMR spectrum for a given amount of sample, what can we do to improve the signal-to-noise ratio?*

To improve the signal-to-noise ratio for a given amount of sample, we can use time averaging. The NMR experiment is repeated many times and the resulting FIDs are summed and averaged. Nevertheless, it has to be noted that because of some noise, the improvement is on the order of $\sqrt{N}$. **, Where N is the number of experiments.**

To answer this issue, we can use a cryoprobe or cooled detection system. Indeed, cooling the detection circuit reduces thermal noise from the resistance of the coils.
This way, the signal strength from the sample remains the same, the noise decreases significantly and the signal-to-noise ratio improves.

Another way to improve the signal-to-noise ratio is to increase the magnetic field strength : the NMR signal becomes stronger at higher magnetic fields because the population difference between spin states increases with the field strength.

3. *Why does broadband decoupling eliminate multiplets in 13C spectra?*

The broadband decoupling sets all of the $^{1}$H–$^{13}$C couplings to zero by rapidly flipping the proton spins. So, the multiplets become singlets, one for each unique carbon.

4. *Why are 13C spectra usually recorded with decoupling?*

13C spectra are often recorded with decoupling for a few reasons. Thanks to the decoupling, the number of peaks corresponds directly to the number of chemically non-equivalent carbons in our sample, hence no multiplets can be observed and only singlets can be seen. The signal to noise ratio is also improved as the intensities appear as singlets. In addition, this method also makes the assignment of chemical shifts easier.

# Jigsaw D :

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1: In a 1H NMR spectrum of CHCl3 at natural abundance, can we observe the heteronuclear 1H-13C J-coupling? Why or why not?

The only hydrogen atom in the molecule is bonded to a single carbon atom. This carbon can be present as either its most abundant isotope, carbon-12 (approximately 98.9%), or as carbon-13 (approximately 1.1%). Carbon-12 has a nuclear spin of 0, so it does not couple with the proton, resulting in a single signal on the $^{1}$H NMR spectrum. By contrast, carbon-13 has a nuclear spin of ½, which allows $^{1}$H–$^{13}$C scalar coupling, leading to a doublet in the proton signal. However, because only about 1.1% of the molecules contain carbon-13, this doublet is extremely weak compared to the dominant singlet arising from carbon-12. Consequently, although the $^{1}$H–$^{13}$C J-coupling is physically present, it is not visible in a conventional proton NMR spectrum.

2: When we acquire an NMR spectrum for a given amount of sample, what can we do to improve the signal-to-noise ratio?

The best way to improve signal to noise ratio (SNR) is by taking more measurements because as we do more of them, SNR improves by a factor of $\sqrt{n}.$ , **Where n is the number of experiments.** We can also get stronger magnets (or fields). This will reduce the time of acquisition of the signal, meaning we can make more measurements. Furthermore, we can use digital smoothing filters (such as Fourrier filters). Finally, with a specific amount of compound, we can use less deuterated solvent, which will increase the compound concentration and thus the signal

3: Why does broadband decoupling eliminate multiplets in 13C spectra?

During broadband decoupling, the strong radiofrequency field causes the spins of the $^{1}$H nuclei to change so fast, that the $^{13}$C nucleus experiences it as a continuous change. Since the J-coupling interaction depends on the change of the spin states and given that the net spin change is experienced as zero, there is no constant coupling to split the $^{13}$C resonance. Hence, the signal becomes a singlet.

4: Why are 13C spectra usually recorded with decoupling?

First of all, it simplifies the spectrum by removing the coupling between $^{13}$C and attached $^{1}$H nuclei, so each carbon gives a single sharp peak instead of multiplets. **Then, it increases the signal intensity, in fact, proton decoupling produces a Nuclear Overhauser Effect, which boosts the $^{13}$C signal strength. (not seen in theory...)** Finally, it eases the interpretation, one peak per carbon environment makes chemical shift assignment straightforward. So, to summarize, $^{13}$C spectra are decoupled to get stronger, simpler, and easier-to-read signals.