

Week 5

Measuring Spin Effects

5.1 NMR Relaxation

- 3/4:
- While we're acquiring our fid, neighboring protons' magnetic fields interact with each other.
 - While we're RF pulsing, the instrument's magnetism is far stronger. But when we stop RF pulsing and collect, the protons can interact with each other.
 - We want to be at equilibrium in the z -axis every time we pulse the system.
 - Thus, relaxation time must be $\geq t_1$.
 - If the acquisition time and relaxation delay do not add up to the right amount, the spins could be upside down when we pulse, and then the signals (positive and negative) will add to 0.
 - t_1 effect: Spin-lattice relaxation, which is in the direction of the magnetic field.
 - t_2 effect: Spin-spin relaxation, which is perpendicular to the direction of the magnetic field.
 - It is t_2 relaxation causes the fid to decay away!
 - If our spins were coherent forever (if they stayed knocked over forever), we would get a constant signal (instead of a decayed one) when we turn the RF off.
 - t_2 value: The reciprocal of the FWHM (width of a peak at the middle) in hertz. Hence, shorter t_2 's mean broader lines.
 - Acquisition time should be double the t_2 .
 - Small molecules have t_2 's in the range of a quarter of a second to 1 second.
 - t_2 's much smaller for bigger molecules (e.g., polymers, proteins, etc.)
 - Analogous protons on different molecules are in slightly different magnetic environments due to variations in the neighboring protons' magnetism.
 - The longer the FID, the sharper the signal.
 - We more often use 30° or 45° pulses in ^1H NMR because it's much faster for the signal to recover to equilibrium.
 - However, we do not get maximal signal in these cases.
 - By trigonometry, 30° gives us 50% of the maximum signal and 45° gives us 71% of the signal, which is a good compromise.
 - Note that since ^{13}C t_1 's are longer, we usually only go to 30° .
 - Lengthening $d1$ (the relaxation delay) from a tenth of a second to 10 seconds causes almost no difference in sensitivity/resolution. For some protons, it does, though.

- DMSO-d6 samples tend to relax relatively fast compared to CDCl₃ or MeOD samples.
- Goes over spin echos as t_2 -filtering techniques.
- Using NMR to detect exchange broadening.
- Good drug molecules have “compositional or chemical heterogeneity.” I.e., they can be in multiple ionization states, labile protons, etc. This tends to increase the probability that it will go from the source all the way that it should.