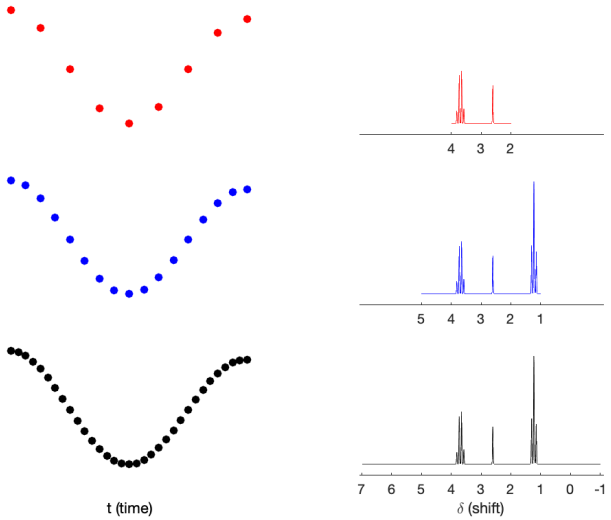
December 2023 NMR Topic of the Month: Time & Frequency



What is the relationship between the data acquired and spectrum analyzed?

Modern NMR spectrometers collect a discrete number of data points evenly distributed throughout the acquisition time. These points are then filtered and adjusted before being (fast) Fourier transformed to produce the frequency spectrum. One of the characteristics of the frequency spectrum is its spectral width: that is, how wide a frequency range is covered in the spectrum. This spectral width is important to adjust so that the spectrum (properly) shows the information required for the experiment. The spectral width is uniquely determined by the spacing between the collected data points (called the dwell time). Specifically, larger spectral widths require more closely spaced data points, and vice versa.

In the cartoon above there are three mock ^{1}H NMR experiments on (very dry) ethanol: (the very start of) each experiment's acquired (time) data points are shown on the left, and the resulting spectra are shown on the right. The red experiment was acquired with too small a spectral width to show all the signals. The blue experiment was acquired with just enough spectral width and would suffice, though it might be best to adjust the center (carrier or offset) frequency. The black experiment was acquired with more than enough spectral width, which is preferable to too little but should be avoided in great excess. Notice how the spacing between the acquired (time) data points is reduced as the spectral width increases, so increased dwell time means a smaller frequency space.

When is this really important?

This fact is particularly important when you adjust the spectral width of an experiment. On a Bruker instrument, the software will keep the total number of points acquired constant as the spectral width is changed; which, by necessity, means the acquisition time is changed. If you only reduce the spectral width and acquire for longer you may introduce unnecessary noise or even be in danger of running the decoupler for too long. If you only increase the spectral width and acquire for a shorter time you may sabotage your resolution or even exceed a safe duty cycle. Instead, be sure to adjust your acquisition time after you have set your spectral width. On a Varian instrument, the software will keep the total time constant and adjust the number of acquired points as the spectral width is changed, so it is still necessary to evaluate whether or not the data is being acquired properly.

References

1. Pulse Fourier transform NMR: R.R. Ernst and W.A. Anderson, *Rev. Sci. Instrum.* **37**, 93 (1966).
2. E. Fukushima, and S.B.W. Roeder, *Experimental Pulse NMR: A Nuts and Bolts Approach [Section 1.D.2]*, Addison-Wesley, Ontario (1981).
3. J.C. Hoch and A.S. Stern, *NMR Data Processing [Chapters 2 & 3],* Wiley-Liss, New York (1996).
4. E.O. Brigham, *The Fast Fourier Transform*, Prentice-Hill, New Jersey (1974).