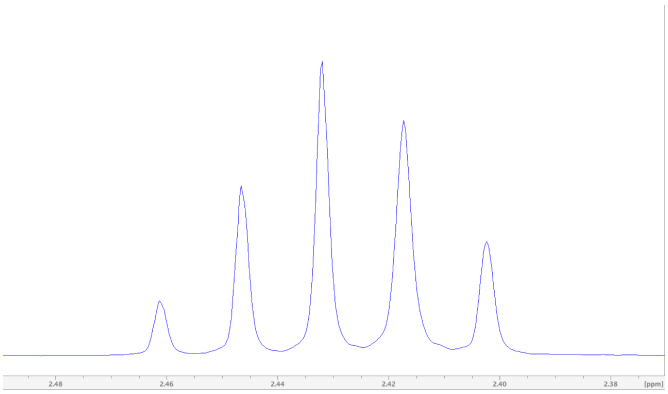
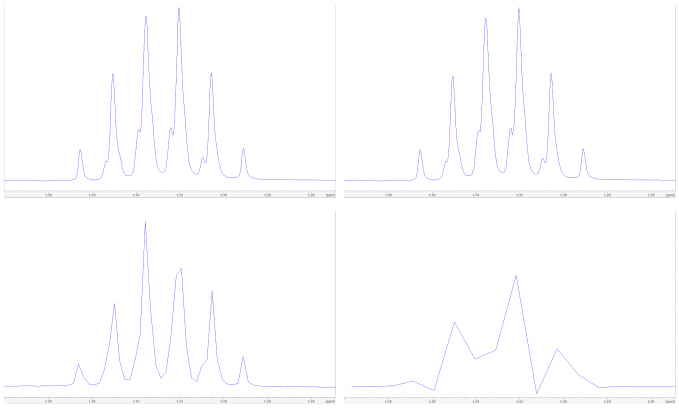
January 2024 NMR Topic of the Month: Resolution

3-heptanone ^{1}H at 2,4 spectrum



3-heptanone ^{1}H at 6 spectrum (SI = 64k, 32k, 8k, & 2k)



What does resolution mean in NMR?

Being able to resolve signals in NMR means those signals are separated in frequency to the degree that they are fully independently distinguishable.

Consider the signals above and on the left. Pictured there is a zoomed in portion of a ^{1}H NMR centered at 6 ppm with a spectral width of 20 ppm from a FID size of 64k using one zero-fill and no apodization. This region of the spectrum features the signals from the methylenes of 3-heptanone in the 2 and 4 positions. Notice that the lines are nicely shaped and sharp, but it is not casually apparent which lines are associated with which position. On this same NMR system there is nothing that can be done about this situation with a 1D experiment. In the HSQC experiment the two methylenes do separate, but no amount of acquiring (in number of scans or FID length) or manipulating (filtering, predicting, etc.) will further distinguish these peaks in the 1D. This is an example of a well-shimmed, properly acquired spectrum with ambiguous resolution of these protons. (Yes, by determining the peak ratios of ⅛:⅓:7/12:⅔:¼ one can unambiguously assign which signals are associated with which site, but a more general solution is to do the 2D experiment(s)).

Now consider the four sets of signals above on the right. Here again is the exact same spectrum as on the left, except that the region of interest is around the methylene in the 6 position and the size of the FID is varied as indicated. Notice that as the number of points is reduced it becomes impossible to discern the multiple peaks in the signal. Adding additional points beyond 64k will not help with the resolution either, as evidenced by how similar the results from 64k and 32k appear. Here the resolution is limited by the linewidths of the peaks and the choice of acquisition time.

What are the take-home messages?

First, resolution is the ability to distinguish between signals on the frequency axis. Properly, resolution has absolutely nothing to do with the intensity of the spectrum. Second, the resolution is determined by how broad the signals are (from relaxation, shimming, filtering, etc.) and how long those signals are observed during acquisition. Third, overlapping signals in a 1D spectrum may be separable using higher-dimensional experiments.

References

1. R.R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions [Chapters 2, 6, & 7]*, Oxford Science Publications, New York (1987).
2. R. Freeman, *Spin Choreography. Basic Steps in High Resolution NMR*, Spektrum, Oxford (1997).
3. J. Cavanagh, W.J. Fairbrother, A.G. Palmer III, and N.J. Skelton, *Protein NMR Spectroscopy. Principles and Practice [Chapter 3]*, Academic Press, San Diego (1996).