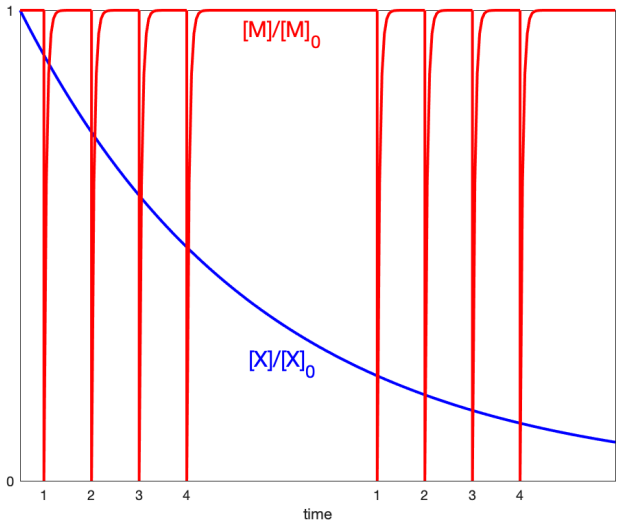
January 2025 NMR Topic of the Month: Kinetics and NMR II



I need a better signal-to-noise ratio, can I signal average a kinetics experiment?

Again, suppose you want to monitor a first order reaction by NMR. You are watching some species X with initial concentration $[X]_0$ decay over time ($[X] = [X]_0 exp[-\ kt]$). You have allowed for plenty of time between transients ($\Delta t \geq 7T_1$ for a $\frac{\pi}{2}$-pulse where T_1 is the longitudinal relaxation time) and can be assured that the decay of the signal (S) depends only on the rate of the reaction (k). However, you have decided to add multiple transients (four in the picture above) together to boost your signal-to-noise. This presents a complication to your analysis as it is unclear what time each NMR spectrum represents, because time did not pause for you to acquire the data.

What to do about the time and tide?

Under the conditions above, the signal (S) in the m^{th} evenly-spaced spectrum is:

$$S_m \sim [X]_0 exp\left\{-\ k\left[t_1 + (m\ -\ 1)\Delta\tau\right]\right\} \sum_{j=0}^{N-1} exp[-\ kj\Delta t]$$

Where t_1 is the start time of the first spectrum's first transient, $\Delta\tau$ is the time difference between two consecutive spectra's first transients (note: $\Delta\tau \geq N\Delta t$), N is the number of transients per spectrum, and Δt is the total time for each transient. All of these times and numbers are known, so you could fit this equation and get an accurate value for k…

But that's not what most people do. Most people "cheat" and assume the decay is linear across the transients and assign the average time (at the 2.5 positions in the picture above) to the amount of signal for each acquisition. Can this produce an accurate value for k? Yes, provided $N\Delta t$ is "small" so that the decay is (more-or-less) linear across the transients.

Can I acquire continuously ($\Delta\tau = N\Delta t$)?

If all of the conditions above are met and the decay curve is piecewise linear across the transients: yes you could. You could also acquire each transient separately ($N = 1$) and craft your signal averaging to better ensure linearity. But you need to be sure all the acquisition conditions are met, and note that 'could' is very different from 'should'.

References

1. NMR Topics of the Month from December of 2024 and the references therein cited.