

2.5: Effects of Tip Angle in Quantitative NMR Experiments

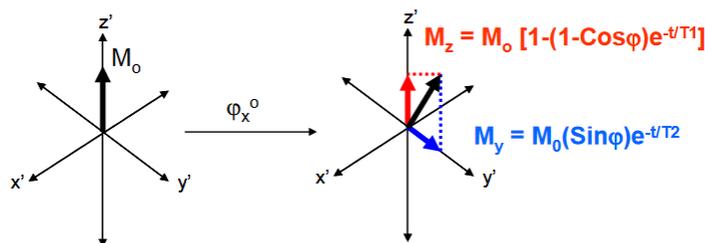
In experiments where the goal is qualitative analysis, it is not necessary to acquire the spectra in a manner that produces fully relaxed spectra. In this case, one can use the Ernst Angle relationship to calculate the tip angle that will maximize S/N for a given repetition time.¹ In such experiments, it is typically most efficient to eliminate the relaxation delay and use a repetition time equivalent to the acquisition period. Typically the acquisition time is set to allow the FID to decay to noise. This is often approximated by setting the acquisition time to about $3 \times T_2^*$, which will allow the magnetization to decay by 95% of its initial value.

$$\text{Ernst Angle Relationship: } \cos \vartheta = e^{-\frac{T_r}{T_1}} \quad (2.5.1)$$

In the Ernst angle equation, ϕ is the tip angle, T_r is the repetition time and T_1 is the spin-lattice relaxation time of the resonance of interest. For example, with a repetition time of 3 sec and a T_1 relaxation time of 5 sec, we calculate an Ernst angle of 56.7° . While this repetition time and tip angle maximizes S/N, it will not give us integrals that can be interpreted quantitatively in a straight forward way. It is possible to correct for incomplete T_1 relaxation, however this introduces greater error in the result and is not always practical, since analytic solutions.

Where quantitative integrals are desired there is generally not that great of time savings by using a tip angle less than 90° . To see why, let's look at a concrete example. Assume that for an analyte resonance with a T_1 relaxation time of 5 sec, we have to coadd 100 FIDs to achieve a S/N of 250:1 using a 90° pulse. In this experiment, the shortest repetition time we should use is $5 \times T_1$, or 25 sec, which will allow the magnetization to relax to 99% of its initial value. This means that it would take 2500 sec (or 0.694 hr) to complete this experiment.

What would happen if we used a shorter tip angle? By using a smaller tip angle, the magnetization will take less time to recover following the pulse however we will also detect less intensity following the pulse.



The intensity of the magnetization following a pulse, M_y , can be described by the equation below, where M_0 is the intensity of the fully relaxed magnetization, t is the time following the pulse, for a tip angle of ϕ , and T_2^* is the apparent spin-spin relaxation time.

$$M_y = M_0 \sin \vartheta e^{-\frac{t}{T_2^*}} \quad (2.5.2)$$

Immediately following the pulse, $t = 0$. For a 56.7° tip angle, M_y would be $0.836 M_0$ immediately following the pulse. This means that we would have 83.6% of the signal that we would have achieved with a 90° pulse. However, unlike a 90° pulse, the value of M_z is not zero immediately following a 56.7° pulse. In general, the value of M_z following a pulse with a tip angle, ϕ , can be described by the equation below, where t is the time following the pulse, for a tip angle of ϕ , and T_1 is the apparent spin-lattice relaxation time.²

$$M_z = M_0 [1 - (1 - \cos \vartheta) e^{-\frac{t}{T_1}}] \quad (2.5.3)$$

This means that immediately following a 56.7° pulse, $t = 0$ and the value of M_z , governed by $\cos \phi$ is already $0.549 \times M_0$. Since we want to acquire fully relaxed spectra, the question is how long will we have to wait until $M_z = 0.99 \times M_0$ if the T_1 relaxation time is 5 sec? Substitution into the equation above we calculate that $t = 19.04$ sec. This is a significant time savings over the 25 sec we would have to wait for T_1 relaxation if a 90° pulse were used. However, using a 56.7° pulse we have generated only 83.6% of the signal we had if a 90° pulse had been used. Since we gain S/N as the square root of the number of FID's coadded we would have to acquire 1.43 times as many FIDs as we did with a 90° pulse to obtain the desired S/N of 250:1. Therefore, the total experiment time using a 56.7° pulse would be $19.04 \text{ sec} \times 143$ or 2723 sec or 0.756 hr, a slightly longer total acquisition time than was required

using a 90° pulse. For this reason, most NMR spectroscopists simply use a 90° pulse and with a repetition time of at least $5 \times T_1$ for quantitative NMR experiments.

References

1. R. R. Ernst and W. A. Anderson “Application of Fourier Transform Spectroscopy to Magnetic Resonance” *Rev. Sci. Inst.* (1966) **37**:93-102.
2. D. L. Rabenstein “Sensitivity Enhancement by Signal Averaging in Pulsed/Fourier Transform NMR Spectroscopy” *J. Chem. Ed.* (1984) **61**:909-913.

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