Measurement of Spin-Lattice Relaxation Time ($T_1$)

Dr. Antoni Jurkiewicz, Department of Chemistry University of Chicago

Spin lattice-relaxation process $T_1$ plays a critical role in achieving correct quantitation of NMR spectra both in liquid and solid state NMR experiments [1, 2, 3]. Thus, appropriate magnetization recovery time (D1) between scans needs to be set up carefully and fulfill condition: $D1 \geq 5T_1$ when $90^0$ excitation pulses is applied. Generally, the knowledge of accurate $T_1$ is necessary to perform NMR experiments in accurate and efficient way. The measurement of $T_1$ in case of $^1$H NMR experiments is most often easy and quick to perform. In case of $^{13}$C spectroscopy because of low sensitivity the experiment is much more time consuming and sometimes prohibitively long. In solid state NMR spectroscopy the spin-lattice measurement might be additionally complicated by nonlinear cross-polarization spin dynamics [3] therefore, more difficult to perform.

The most often used pulse sequence to measure spin-lattice relaxation time is the $180^0 - \tau - 90^0$ sequence (Figure 1.)

![Figure 1. The pulse sequence to measure spin-lattice relaxation time. The D7 delay corresponds to time $\tau$.](image)

It is known also as the inversion recovery $T_1$ measurements. At the time $\tau = 0$ the $180^0$ pulse inverts the magnetization vector $M_z$. After this the magnetization $M_z$ lies along the negative z axis and $M_z = -M_z$. Fig.2.
The spin-lattice relaxation makes the magnetization $M_z$ increase (Figure 3) during $\tau$ interval from $-M_0$ throughout zero until it is back to original value $M_z = M_0$.
One can find the value of $M_z$ at any time of $\tau$ using the following formula:

$$M_z = M_0 \left(1 - 2e^{-\frac{\tau}{T_1}}\right)$$  \hspace{1cm} (1)

If at some time $\tau$ following the 180° pulse, the 90° pulse is applied, $M_z$ is rotated around the X axis and will then lie somewhere along the Y axis. If the time $\tau$ separating two following passages is short compared with $T_1$, the two NMR signals have the same sign, and opposite sign when $\tau > T_1$ Fig.4.

Figure 4. The magnetization $M_z$ is transferred to Y axis by 90° pulse, negative $M_z(\tau_1)$ and positive $M_z(\tau_2)$

Finding $T_1$ involves measurements of the signal amplitude for several different $\tau$ intervals. Such magnitudes of amplitudes are depicted on Figure 5.
Performing the curve fitting according to formula (1) will give $T_1$. It is known that formula (1) does not always describe correctly the magnetization recovery (this depends on molecular structure and dynamics), so the person performing the experiment needs to decide if the modified formula should be applied instead.

To protect quantitation and correct timing for most of the two-dimensional experiments on a daily basis, there is no need to run the time consuming full size $T_1$ measurements. Instead the so called “null” method proves useful. In this method the time $\tau = \tau_{null}$ for which $M_z = 0$, and signal disappeared needs to be found. The $T_1$ can be estimated using the following formula:

$$T_1 = \frac{\tau_{null}}{\ln 2}$$

(2)

Again, it needs to be stressed that this a rough estimate.
To run this experiment one needs to calibrate the 90° pulse (since the inversion recovery method is sensitive to pulse accuracy) and call the experiment: e.g. “rpar H1T1null.BBI”. The D7 delay in the Bruker software has a meaning of $\tau$. After $\tau_{null}$ is found $T_1$ is calculated.

Further reading

1. A. Abragam, “Principles of Nuclear Magnetism”, Oxford University Press 1961