Measurement of Spin-Lattice Relaxation Time (T_1)

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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 (Figure1.)

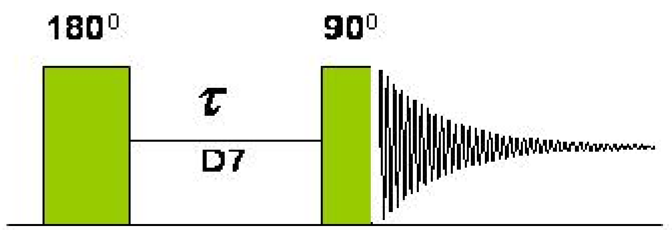

Figure 1. The pulse sequence to measure spin-lattice relaxation time. The D7 delay corresponds to time τ .

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.

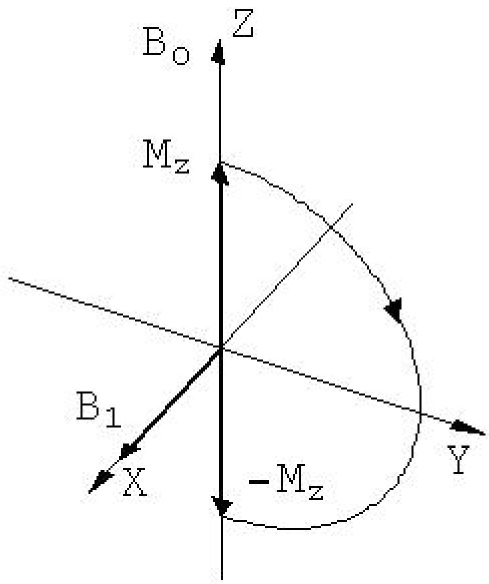

Figure 2. The inverted magnetization M_z after 180^0 pulse.

The spin-lattice relaxation makes the magnetization M_z increase (Figure 3) during τ interval from -M_0 throughout zero until it is back to original value $M_z = M_0$.

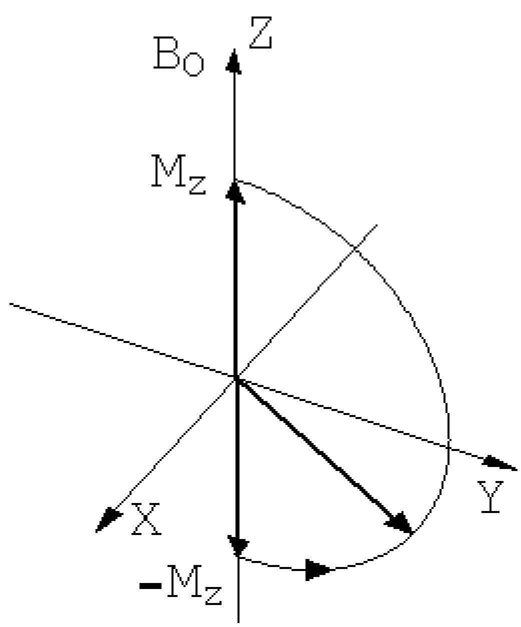

Figure 3. Magnetization M_z relaxes back to the original position after 180^0 pulse.

One can find the value of M_z at any time of τ using the following formula:

$$M_z = M_0(1 - 2e^{-\frac{\tau}{T_1}}) \qquad (1)$$

If at some time τ following the 180^0 pulse, the 90^0 pulse is applied M_z is rotated around the X axis and will then lie somewhere along the Y axis. If the time τ 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.

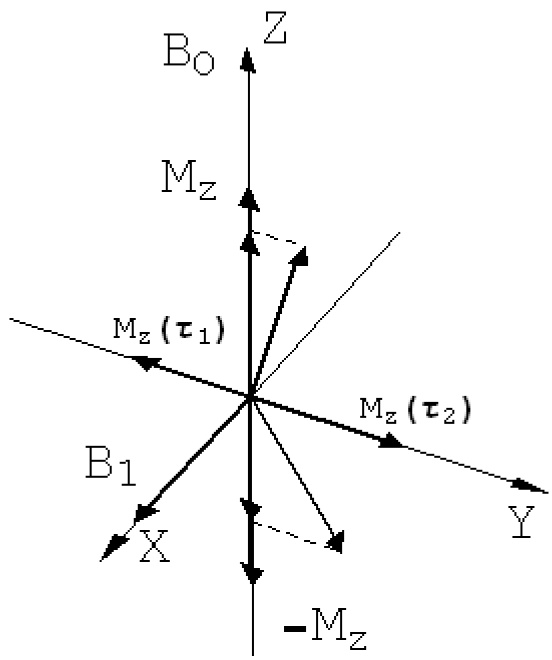

Figure 4. The magnetization M_z is transferred to Y axis by 90^0 pulse, negative $M_z(\tau_1)$ and positive $M_z(\tau_2)$

Finding T_1 involves measurements of the signal amplitude for several different τ intervals. Such magnitudes of amplitudes are depicted on Figure 5.

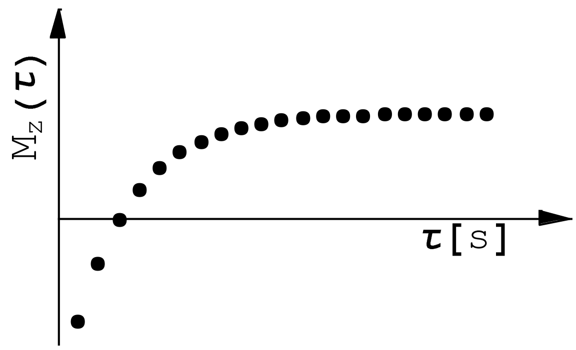

Figure 5. Spin-lattice magnetization recovery according to measurements.

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:

$$T_1 = \frac{\tau_{null}}{\ln 2} \qquad (2)$$

Again, it needs to be stressed that this a rough estimate.

To run this experiment one needs to calibrate the 90^0 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 τ. After τ_{null} is found T_1 is calculated.

Further reading

1. A. Abragam, “Principles of Nuclear Magnetism”, Oxford University Press1961
2. M. H. Levitt “Spin Dynamics” ,Wiley & Son 2001
3. Jurkiewicz A. and Maciel G.E., ANALYTICAL CHEMISTRY Volume: 67 Issue: 13 Pages: 2188-2194 Published: JUL 1 1995

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