

Bruker T_1 Measurements

Background

T_1 is the longitudinal (or spin-lattice) relaxation time, and is the decay constant for the recovery of the z component of the nuclear spin magnetization to equilibrium.

Empirical Setup

Sample Preparation

Samples need to be of proper concentration and volume - do not short the samples in either way. Samples should also be fully solvated, degassed, and in properly rated tubes.

Pulse-Acquire

A necessary first step in a T_1 experiment is to acquire and evaluate the sample's zg or zgig experiment¹. You want to use the full $\pi/2$ pulse, as one aspect of the resulting spectrum you are evaluating is the quantity of signal. Remember, you need to be able to follow the signal accurately as it passes through a null, so you need to be able to judge how many scans are required to clearly see the signal of interest.

You also need to be confident that your system is in a stable pseudo equilibrium between scans. Although it is traditional to do so, it is not required that you wait until the system has fully returned to thermal equilibrium. Just make sure that use enough dummy scans (ds) or long enough relaxation time (d1) so that doubling the number of scans (ns) produces twice the signal.

The next concern to address is the transmitter offset. In general, you want to place the transmitter offset (o1p) halfway between the two most extreme (highest and lowest) shifts of interest. There are exceptions to this rule; for example, if the two most extreme shifts are very different you may have to run the entire T_1 experiment with different transmitter offsets. The reason being that the bandwidth of the π pulse and $\pi/2$ pulse are not the same, so if they signals are far away from the transmitter offset you will see artifacts².

Finally, be sure you are not truncating your signal of interest and feel free to adjust your spectral width and other acquisition parameters to taste/need. (For example, the decoupler offset should be reasonably correct; that is, generally centered between the relevant resonances).

T_1 Experiment

There are two choices for the T_1 experiment that parallel the pulse-acquire experiment, namely t1ir and t1irig¹. There are two parameter sets already saved off that can help with this: H1_t1ir_TAMU and C13_t1irig_TAMU. It is more tricky than you might suspect to just copy the pulse-acquire experiment and convert it to the T_1 experiment, so we recommend that you start with one of these parameter sets. But make sure to carry all the parameters from the pulse-acquire setup over to the relaxation experiment.

These experiments acquire the data as a stacked series of 1D data sets; in other words, the second dimension is not a Fourier transform dimension. The reason the data is acquired in this fashion is that it allows for the entire ensemble to be

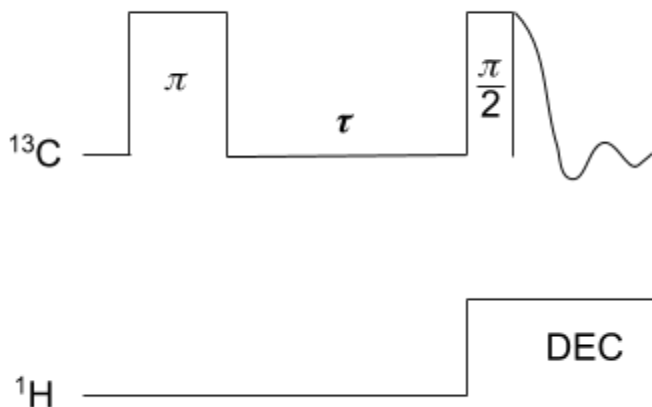
¹ For completeness there are zgpg and t1irpg experiments, but they are not recommended. Decoupling during the relaxation delay (d1) and inversion recovery delay (vd) is unnecessary as everything of interest during these delays commutes with I_z and spin diffusion is not significant in liquid samples.

² You could imagine trying a composite or shaped pulse, but these just do not work well.

processed and fit at once with exactly the same parameters. However, you may want to run individual τ points, which can be done with a corresponding 1D experiment (eg: t1ir1d) or by using a vclist with the single entry.

The pulse sequence used to determine T_1 values is called inversion-recovery. A pulse diagram of the t1irig sequence is shown in Figure 1 below for ^{13}C and ^1H , the t1ir is the same except there is no decoupling on a second nucleus. In the t1irig experiment, following the relaxation delay (d1), a π pulse (p2) is applied to the spins to be measured, which puts the magnetization along the -z axis. The spin system is then allowed to relax from -z to +z over the delay τ (vd, set with vclist), which is varied to produce the relaxation curve. Finally, a $\pi/2$ pulse (p1) is used to flip the magnetization into the transverse plane for detection under decoupling during t_2 (aq), after which the decoupler is turned off.

Figure 1: Inverse-Gated Decoupled T_1 Experiment



A critical step in properly determining a T_1 inversion-recovery measurement is to run the experiment with a appropriate series of values for the τ delay. These values are stored in a single column text file that is located in directory /opt/topspin3.6.1/exp/stan/nmr/lists/vd. The safest way is to create this text file from within TopSpin using an edlist command (or from the Edit button next to the vclist entry of the AcquiPars tab) where you may create and edit your own text file lists. Be sure that your list is assigned as the vclist (set in the AcquiPars tab), and that the number of entries in the list is set as the TD(F1). When constructing the list arrange the delay from least to greatest, and remember this is an exponential decay (so use more small delays than large ones).

To accomplish the full phase cycle these experiments require a number of scans (ns) to be a multiple of 8, but lower powers of 2 are common. It is recommended that you not use an ns of 1 though, as the two step phase cycle on the π pulse is a good idea. Furthermore, the pulse program notes that the number of dummy scans (ds) should be 4, which isn't a bad idea but *may* not be strictly necessary.

Basic T_1 Experiments

It's not a bad idea to first do a quick measurement. Create a vclist with the goal of reaching the signal's null, rather than continuing on to full recovery. Once you know the null time, divide that by $\ln 2$ and you're close to the T_1 time. And for many purposes, that's good enough! But at the very least you now have a good starting point for creating a new vclist, as the system will be 99% relaxed at 5 times T_1 and you can fill out the exponential from there. The more expansive vclist can then be properly fit, and a good T_1 time determined. For example, suppose you are looking for a maximum T_1 time of 1.00 seconds using a total of 10 points, a suitable vclist (entries in seconds) would be 0.001, 0.003, 0.007, 0.017, 0.044, 0.113, 0.292, 0.753, 1.941, 5.000.

Quantitative T_1 Experiments

Normally, T_1 experiments do not have to be done quantitatively, but they can be made so. Never try to do the quantitative experiment first, as you really need to have some idea what the T_1 is before spending the time. Both the maximum τ and $d1$ delays should be set to at least 7 times the T_1 (99.9% relaxed) of the longest decay constant to be determined. Plan on spending time calibrating pulses and analyzing small spectral windows.

Pitfalls

For better and worse, T_1 times are sensitive to many conditions, so it is important to control as much of the experimental setup as you can. Temperature regulation is a must, and T_1 variation with temperature is often used in characterizations. Sample purity is key, even trace contaminants can vitiate an otherwise perfect experiment.

Processing

As the 1D data sets are completed, you may check the experiment's progress by transforming the F2 dimension using the `xf2` command. To see a particular result in the `vdlist`, use the `rser #` command - where `#` is the number of the entry you'd like to see. The `rser #` command will display the designated entry in a new window.

When the data has been fully collected, use the `rser` command to read in the last spectrum. Properly phase the spectrum, as you would any other 1D data set (with positive peaks), but then make sure to tap the "save for nD" button before tapping the "return and save phased spectrum" button.

Next go ahead and integrate that same last spectrum, just as you normally would. However, when you go to save the integrations tap the "Save region as..." button and select "Export Regions to Relaxation Module and .ret."

Next go to the Analyze tab's Dynamics drop box and choose "T1T2 (t1t2)", which will open up the fitting interface. Tap the "Calculate fit for all peaks" button and a brief report of the T_1 fit for each region will be displayed, along with the fit curve for each region. You may switch which region is displayed by tapping the "+" and "-" buttons, and be sure to tap the "Show full spectrum, reset intensity scale [.all]" button to see the entirety of the data fit. The other button of interest is the "Show Report" button, which provides the fitting parameters - including the integral values at each point.

The Bruker software fits the relaxation data to an equation of the form $I(t) = I(0) + P \exp[-t/T_1]$, and the report does provide the values determined by the fit and a standard deviation. However, this equation is not universally preferred, but if you would like the data fit to a different model take the raw integral values out of the report for your analysis.