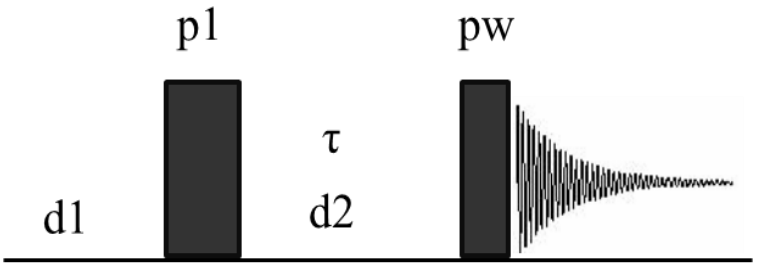
Measuring Spin-lattice Relaxation Time (T_1)

IU NMR Facility-March, 2014

Spin-lattice relaxation (T_1) also known as longitudinal relaxation is the mechanism by which excited magnetization returns to equilibrium on the z-axis. Inversion recovery pulse sequence (Figure 1), is the mostly widely used experiment for measuring T_1. Compared to other methods, this experiment is robust and relatively tolerant to imperfect pulse width calibration; however, it is recommended that one performs pulse width (pw90) calibration before running T_1 experiment.



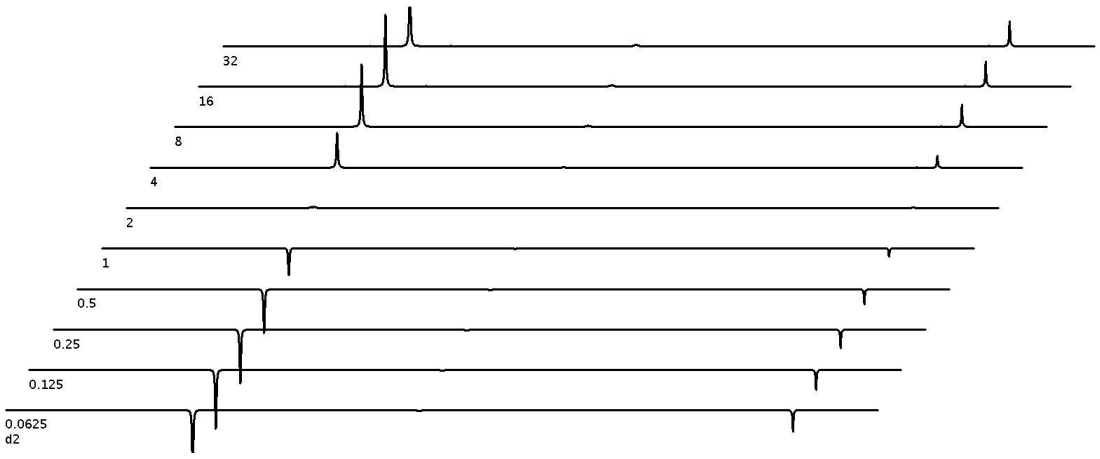
The d1 delay in the pulse sequence should be set to ~5 * the longest T_1 of interest in the molecule; this requires that one has to estimate the T_1. Setting the d1 too short will give shorter T_1's than the "actual" values; whereas too long d1 will result in longer experiment time. The d2 delay (tau) is arrayed; thus a series of spectra are collected with different tau values. The data is then fit to an exponential recovery curve to get the T_1 values.

Step by Step Procedure for Running T_1 Experiment on our Instruments

1. In VnmrJ click on the Experiment tab and choose the nuclei of interest, e.g. Proton. From your calibrated pw90 (see instructions on pw90 calibration), enter the correct pw90 (e.g. pw90=10).
2. Enter the macro **T1setup**. Answer the questions that appear by entering the minimum expected T_1, the maximum expected T_1 and the experiment time in hours.
   You may run a quick experiment in order to know the approximate T_1 values. Once the approximate T_1 values are known, you can then run an experiment that will give more accurate T_1's.
3. Set the appropriate receiver gain (gain). This should be set from a quick (nt=1) PROTON spectrum with a 90^o pulse angle. Remember the "autogain" option is not available for arrayed experiments.
4. Start the experiment by typing au, ga, go or by clicking on acquire.

Processing T_1 Experiment

1. Type **wft** to Fourier transform the data.
2. Display the last spectrum which has all the peaks almost fully recovered by typing **ds(#)**, where # is the spectrum number, and phase the spectrum.
   Note: *If you had 10 values of d2 arrayed, you will have 10 spectra. To see all the spectra, set wc=200 and sc=50 and type* ***wft dssa dssl('value').*** *This will display the spectra in the format shown in the example below.*



3. Set a threshold for the desired peaks. Type **dll** (**d**isplay **l**ine **l**isting) to display a list of the peaks to be used for the fit. The list can be seen in the Text Output panel under the Process tab
4. Type **fp** (**f**ind **p**eaks). This command will find the peak intensities of the selected peaks in all the spectra. To get the intensities of say lines 5 and 6 in the line listing, type fp(5,6).
5. Type **t1** or **t1s** to fit the data; the results will be displayed in the Text Output panel of the Process tab. The **t1** command gives more detailed information about the fitting whilst the **t1s** command gives a shorter output of the T_1 values and the error associated with each value. See example of an output of the **t1s** command below.

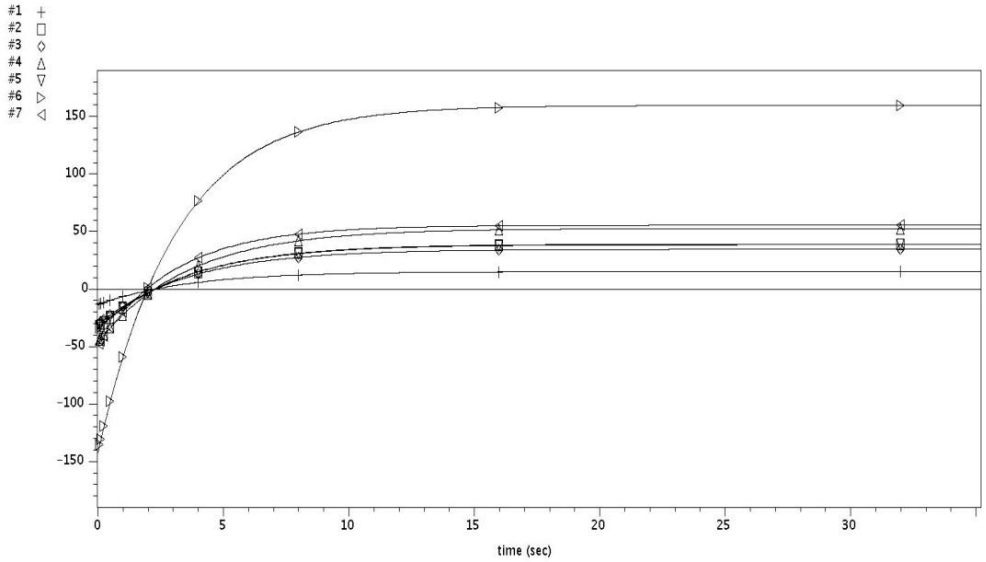
Index	freq(ppm)	intensity
1	7.25443	15.5051
2	7.23563	39.2769
3	7.21732	34.8624
4	7.16288	52.9271

Exponential data analysis:

Peak	T1	error
1	3.573	0.007605
2	3.586	0.005975
3	3.582	0.01006
4	3.592	0.007492

Optional Steps

6. To see how good the data fitting on the exponential recovery curve is, type **expl** and enter. To see only one curve type **expl**(#), where # is the number you want to display.



NOTE: *To delete a data point from the data use for the fitting, use the **dels(#)** command (**del**ete **s**pectrum). The **dels** command deletes the spectra selected from the file fp.out (the output of fp). After typing **fp**, type **dels**(#), where # is the number of the selected spectrum you want to remove, e.g. dels(4) will delete spectrum number 4 and dels(5,9) will delete spectra 5 and 9. The deleted spectra can be restored by rerunning the fp command.*

7. The curves can be plotted (paper copy) by typing **pexpl page**.
8. To print the T_1 values, type **printon t1s printoff** or **printon t1 printoff.** Once again using **printon t1 printoff** will print the detailed fitting for each peak which you probably don't need. Therefore use **printon t1s printoff** which will only print the T_1 values and the error associated with each value.

Some Things to Consider when Measuring T_1

1. Concentration of sample, T_1 values depends on concentration.
2. The choice of solvent. For the same sample, using different solvents will give different T_1's.
3. The temperature at which the measurement is done. Changing the temperature will change the T_1 values.

4. Dissolved oxygen which is paramagnetic will reduce T_1. Performing about 3 cycles of freeze-pump-thaw will give more accurate T_1 values. The freeze-pump-thaw is especially invaluable if experiments like NOESY and ROESY are to be performed.
5. Relaxation is magnetic field dependent. For the same sample, the T_1 obtained from i500 will be different from that obtained from i400.