Measuring ^{1}H T_1 Values in IconNMR

updated: 1 June 2022 (cgf)

Summary

Knowledge of spin-lattice relaxation times, T_1, is important many experiments in NMR:

a) **Quantitative assays** and **analyses of reaction kinetics** require having accurate knowledge of relaxation times. In particular the *longest T_1 of all protons of interest* must be known to properly optimize acquisition parameters and avoid systematic errors.

b) All **NOESY** and **ROESY** experiments require at least semi-quantitative knowledge of proton T_1 values for proper setup and interpretation.

c) **All NMR experiments** require qualitative knowledge of the *longest T_1 of the nuclei of interest* to properly setup repetition rates, typically equal to **d1+aq**.

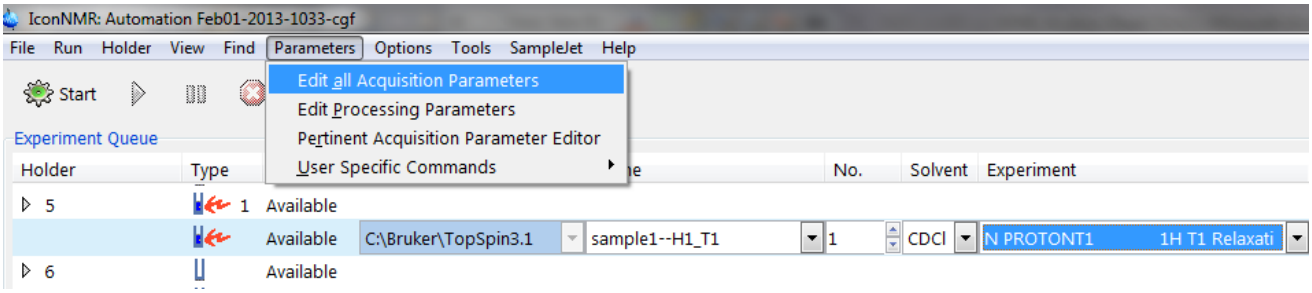
T_1 values accurate enough for b) and c) above can be obtained by an inversion-recovery null-crossing measurement. These were performed with regularity on our Varian spectrometers, with the array function in vnmr making such measurements straightforward. Similar procedures can be done in TopSpin (although to be honest, not in as easy a manner), as detailed in a companion document:

http://www.chem.wisc.edu/~cic/nmr/Guides/Ba3vug/AV3_1H-T1null.pdf

In this document, a simple method for obtaining *quantitative* T_1 values using IconNMR is presented.

A. IconNMR's Inversion-Recovery Experiment – Setup and Acquisition:

1. In IconNMR, ADD the **H1_T1invrec.UW** experiment.
2. In the main menu, select PARAMETERS → EDIT ALL ACQUISITION PARAMETERS



3. IconNMR will switch you into the ACQUPARS panel in TopSpin; you will see ALL parameters. Press ⎍ or type **ased↵** to reduce the list to a reduced set (see Figure 1 next page).
4. Check the VDLIST by clicking … and if not already set, select **t1uwchem** from the SOURCE = /home/topspin3.1/uwchem/lists/pp (in the upper right dropdown). Click Set selected item in editor then Close at the lower right. The list can be viewed and edited using the E button.
5. The list of delays is a good one for typical organic compounds under normal atmosphere. See NMR staff for more assistance if you are working with very small compounds, paramagnetism, or samples sealed under inert atmospheres. Otherwise the default list should work ok.
6. The # of values in VDLIST must equal TD[F1] (see Fig 1). On the command line, use **TD↵** .

Figure 1: **A**ll ACQUPARS parameters.

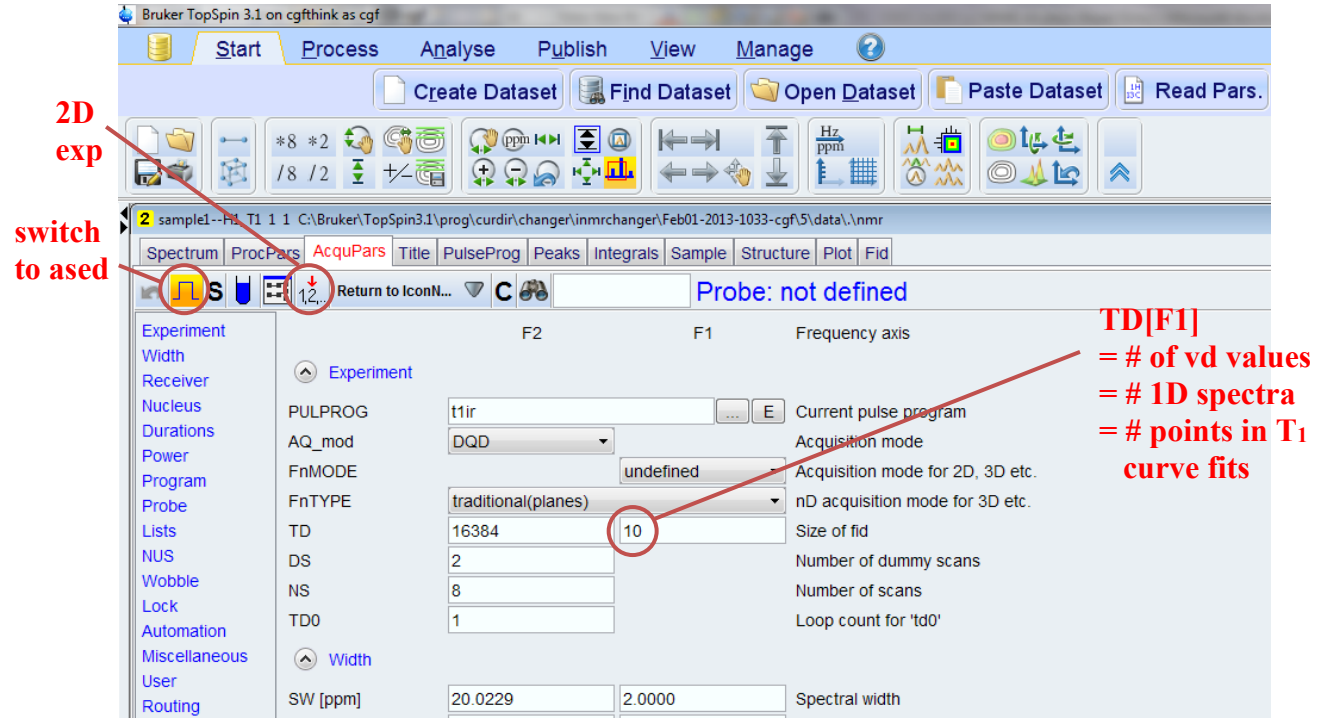
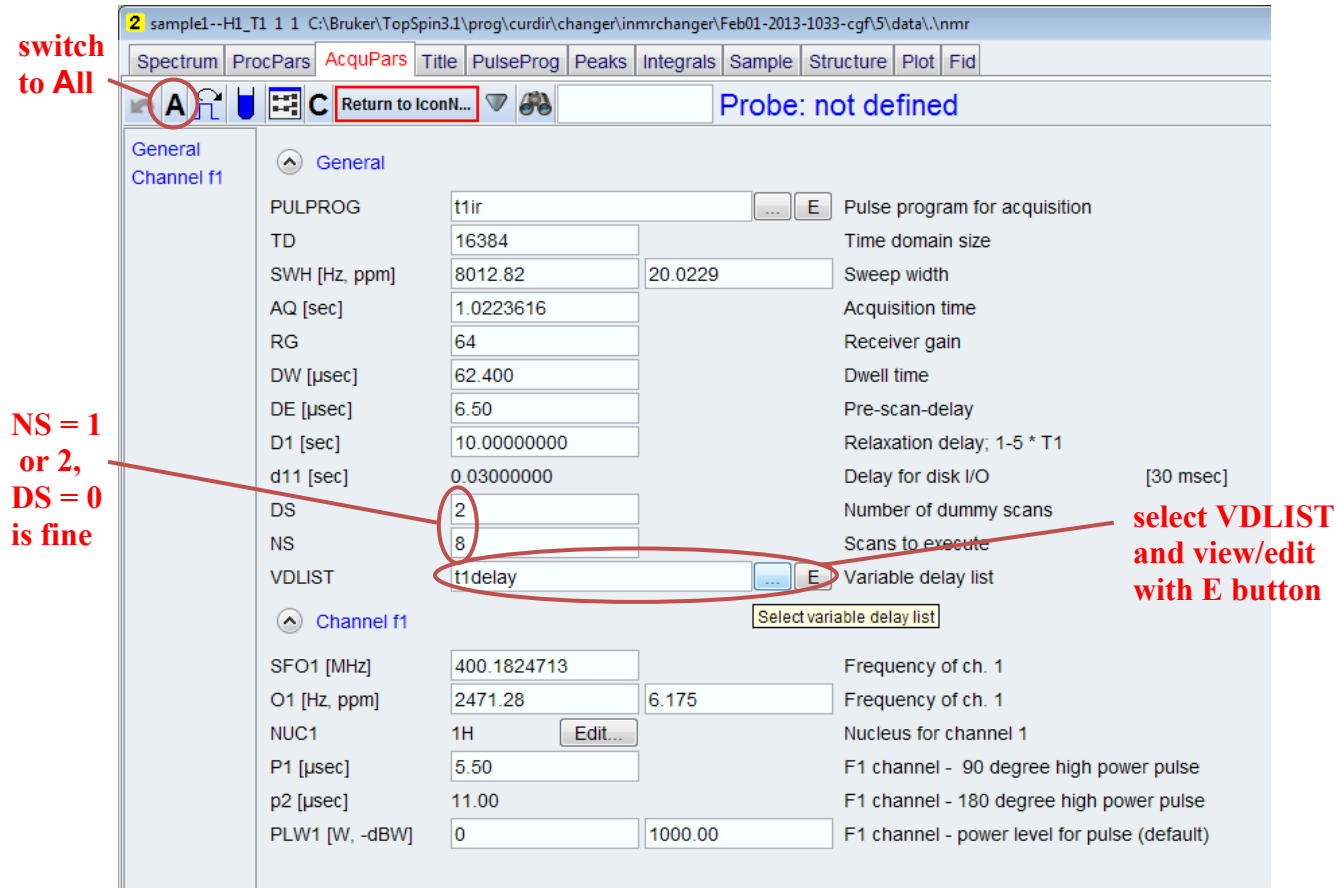


Figure 2: or **ased** reduced ACQU parameters.



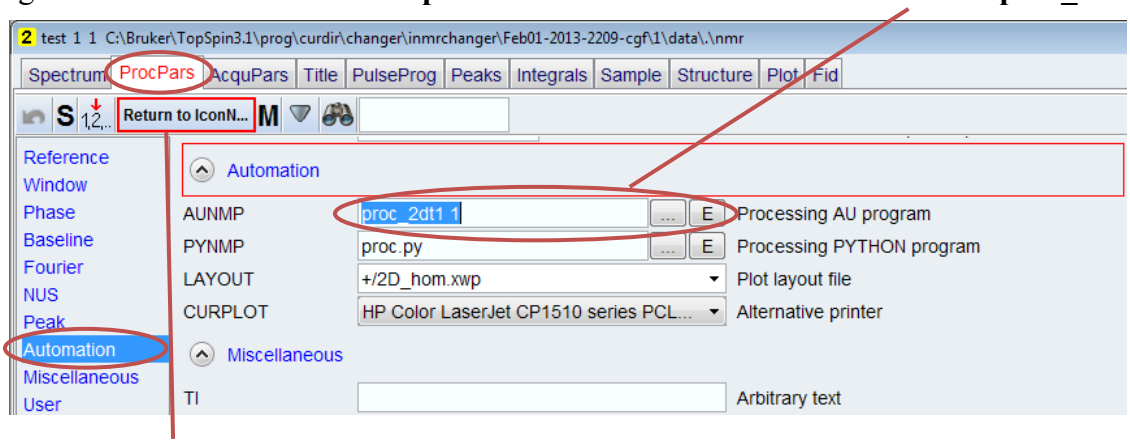
7. **D1** = 15 sec is the default. This value is too small for some compounds, and will need to be made longer when quantitative T_1 values are needed. If

   D1+AQ ≤ 5×T1 [for nuclei of interest; i.e., ignore TMS or other solvent peaks]

   is found to be true in the analysis (see below), then the results are at best qualitative. The experiment would need to be rerun to obtain accurate results. When D1+AQ ≤ 3×T_1 the experiment should be rerun. For the most accurate results, using D1+AQ = 10×T_1 is recommended, as is randomizing the VDLIST values, and including 3 or more duplicates of the longest VD value.

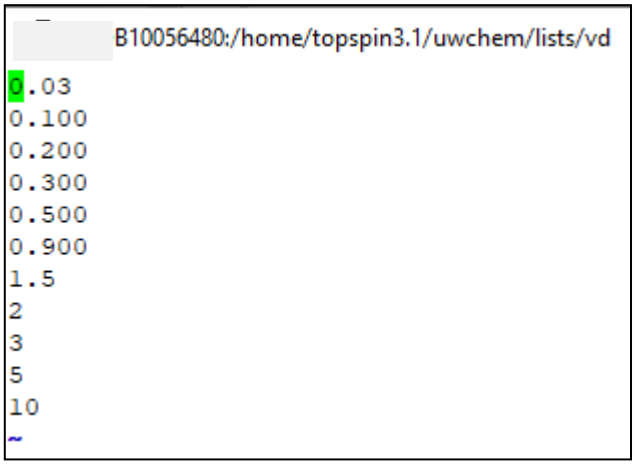
8. Although the **t1ir** pulse sequences recommend **NS**=8×i and **DS**=4, **NS**=1 or 2 and **DS**=0 will work fine on our spectrometers (assuming your sample is at sufficient concentration).

9. Optional: IconNMR will perform an automated analysis of the data. You can check the processing set by clicking on the PROCPARS tab, then on the AUTOMATION link in the left-hand navigation bar. Make sure that a **<space>1** is at the end of the **AUNMP** name: **proc_2dt1** .



10. Click on the RETURN TO ICONNMR tab, and SUBMIT the experiment.

Figure 3: The default VDlist (in **t1uwchem**). **TD1**=11 **D1**=15 are other important default values.



B. Processing and Analysis of T_1 data:

1. If **AUNMP** is set correctly (as described in step 9 above), TopSpin will automatically process the data. Setup and results can be found in the following text files:

   <datasetname>/10/vdlist ; contains the vdlist delay values
   <datasetname>/10/pdata/1/dt1t2.txt ; contains a brief summary of the T_1 values
   <datasetname>/10/pdata/1/ct1t2.txt ; contains a detailed summary of the T_1 values

   The automated processing is somewhat problematic, especially ascertaining which multiplet regions are solute peaks, rather than impurities and solvent. The required information can be obtained, especially on very pure and relative simple compounds. Otherwise, manual workup (MNova!) and processing will likely be preferred.

2. *MestreNova*: Working up the data for visually inspection is (mostly) straightforward.

   a) Some trouble occurs when importing raw data. Suppose the data folder name in TopSpin is:

      e.g., **D1404180938_sucrose_1HT1 10 1**

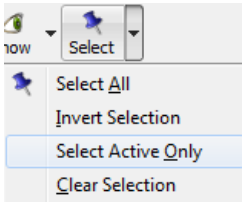
      If you drag the **D1404180938_sucrose_1HT1/10** folder into MNova, it identifies that the dataset is pseudo-2D (i.e., comprised of a series of 1D spectra) and auto-processes it, including performing an autophase. On my (cgf) computer, the phases of individual spectra get jumbled by somewhat random 180° changes, and these are a pain to fix.

      Recommended: drag the processed data folder in:

      i.e., **D1404180938_sucrose_1HT1/10/pdata/1**

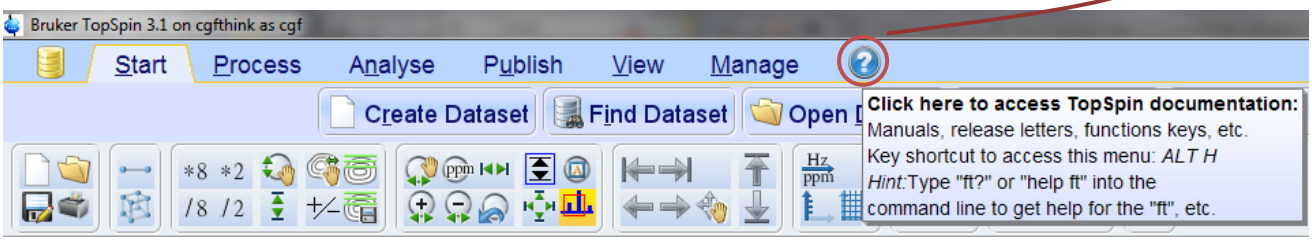
      The phasing from TopSpin will then be used in MNova, and will (likely) be correct.

   b) To phase individual spectra in the stack, use the **Stacked Spectra** table view . Pin the spectrum you want to work on by checking the box under the pin icon or choose **Select → Select Active Only**.

   c) You should be able to visually observe where the nulls occur. The d7 delays for each spectrum will be listed in the **Stacked Spectra** table under the T/G column. $\mathbf{T_1 = 1.4 \times d7_{null}}$.

3. *Manual workup using TopSpin*: Bruker provides a good set of instructions in Chapter 8.2.4 of their "1D and 2D Step-by-Step – Advanced" manual, which can be accessed in TopSpin3.x by clicking the help button.:

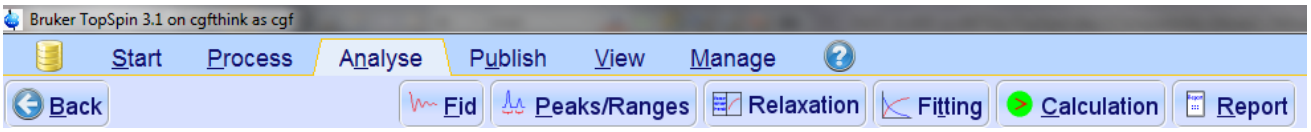


A brief summary of the steps (use the TopSpin guide initially, but then this will likely suffice):

a) **rser 10** (last fid) → **ef** → manually phase **.ph** → store to 2D by clicking →

b) return to the 2d experiment by clicking and transfer with **xf2**

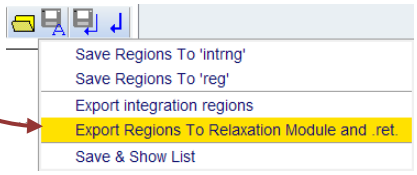
c) enter relaxation analysis with Analyse → T1/T2 which give the following menu:



d) click Fid → SPECTRUM → enter last fid # (10) → OK

e) click Peaks/Ranges → MANUAL INTEGRATION → OK

f) integrate all interesting multiplets/peaks → then



g) click Relaxation → OK to RELAXATION PARAMETERS

h) click Fitting → CLOSE → OK

i) click Calculation → CLOSE →

j) note the BRIEF REPORT, or look at the full report by clicking Report