13. ^1H Spin-Lattice Relaxation, T_1

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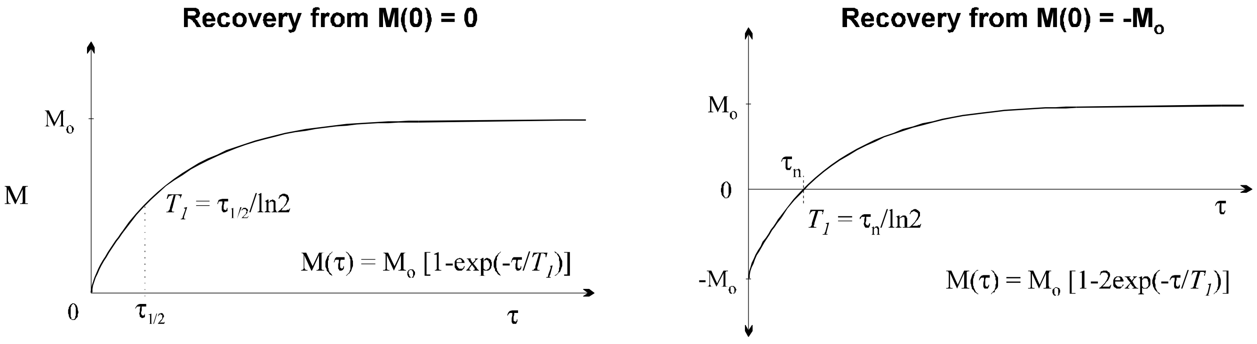
I. Discussion

Spin-lattice relaxation is nominally an exponential process, and becomes important for any quantitative, exchange, or cross-relaxation type of experiment such as NOE. The relaxation from zero magnetization and from an inversion pulse are both shown in the figure below.



T1-RECV.CDR

Often a quick determination of the T_1 is sufficient; for most liquids, use the rapid, inversion-recovery method in Section II below. This method involves finding τ_n for the ^1H of interest. For more accurate determinations, use the procedure described in Section IV.

II. Rapid Determination of T_1 by Inversion Recovery Null Method

(good for any sample—e.g. any liquid—but is semi-quantitative at best)

- Obtain a reasonable quality ^1H spectrum. Locate protons of interest for visual observation.
- 180° and 90° pulse lengths must be reasonably accurate. If your sample is highly polar (e.g., ionic water solution), you must calibrate beforehand. Otherwise, if tuned correctly, prior calibrations can be used.
- Decrease SI and TD (keep SI=TD) to 8k if possible.
- Set AI=1 (answer Y to REINITIALIZATION?), NS=1.
- Reacquire fid with **ZG**, **EF**, and phase manually in EP.
- **AS T1NULL.AU**

  P2=16 µs (180° pulse length; see calibration sheet on wall)

  VD VDLIST.001
    1 0.01 s (to start with)
    2 EN (or **[**)

  RD = 0
  PW = 8 µs (90° pulse width)

DE (set by spectrometer)
NS = 1
DS = 0

- **NE = 1**
- **AU** <ret> (or equivalently AU T1NULL.AU<ret>)
- VD=0.01 should give large negative peaks. Lengthen VD until proton peaks of interest are nulled (slightly shorter VD should give negative peaks; slightly longer should give positive peaks). For the nulled $\underline{VD}_n$, $T_1 \cong \underline{VD}_n/\ln 2 = \underline{VD}_n * 1.44$.
- Find $\underline{VD}_n$ for other protons of interest.

III. Rapid, approximate measurement of T_1 by Repetition-Rate method

(only for samples where $T_2 << T_1$, e.g. solids *[but not for nominal liquids; see previous section]*)

1. if present, **RJ H1REPRAT.005** or **.010** (for 5mm or 10mm probes, respectively), or:

   set **NS** = 1, **DS** = 0, **RD** = 0, **SW** = 20ppm (10000 on AM500, 7200 on AM360), **SI** = 16K, **AQ** = 0.1s, and **PW** = 90° pulse length (see calibration sheet next to spectrometer; or recalibrate 90° - see section xxx)
2. set **O1** close to, or on peak of most interest (use **EP**, set cursor on peak and enter **O1** then **M**)
3. check **RG** (I like to reduce TD = 1k to see beginning of FID clearly, with RD set to compensate for shorter AQ), then wait at least $5T_1$;
4. set absolute intensity mode by typing **AI**, answer **Y** if queried REINITIALIZE?
5. **ZG**, then **EF**, go into **EP**, and **P**; after good phasing type **M** and **<RET>** out of **EP**
6. adjust vertical scaling so 2<(height of peak of interest)<4 divisions; note height and scaling
7. set **DS** = 8, and **RD** so that RD+AQ ~ $T_1/2$
8. **ZG**, then **EFP**
9. adjust **RD** until height of peak of interest is half height noted in step 6 (i.e. same height with scaling doubled)
10. $T_1 \cong (AQ+RD)/\ln 2$

IV. Quantitative measurement of T_1 by Inversion Recovery Method

A. Comments

- A reasonable estimate of T_1 must be known to correctly setup: use the Inversion Recovery Null Method (Section II).
- 180° and 90° pulse lengths must be accurate. If your sample is highly polar (e.g., ionic water solution), you must calibrate beforehand. Otherwise, if tuned correctly, prior calibrations can be used.
- For precise measurements, use D1 = 10 T_1; D1 = 5 T_1 will provide reasonable values if experimental times get long. The number of VD values can also be decreased to lessen experimental times ≅ NS*NE*(2*D1)*(second # in VC list)

B. Acquisition Set-up

1. setup normally as for high-resolution ^1H spectra; make sure RG is set correctly (not too big!), and NS = 8
2. set-up two lists used by the automation routine: a VC (variable counter) list, and a VD (variable delay) list

i) enter the variable delay editor by typing: **VD<RET>**

- use the default name VDLIST.001, or enter a unique name you can recall later
- enter the delays; Table I giving a reasonable grouping
- enter a number followed by S, M or U for seconds, milliseconds, or microseconds
- end the list by entering **ESC**

Table I. A reasonable grouping of VD delays for Inversion-Recovery T_1 sequence, where T_1^r is the T_1 estimate (usually from repetition-rate experiment.

$0.01T_1^r$	$0.5T_1^r$
$10T_1^r$	$10T_1^r$
$2T_1^r$	$5T_1^r$
$0.3T_1^r$	$0.1T_1^r$
$10T_1^r$	$0.01T_1^r$
$0.7T_1^r$	$1.4T_1^r$
$1.0T_1^r$	$10T_1^r$

ii) enter the variable counter list editor by typing: **VC<RET>**

- use the default name VCLIST.001, or enter a unique name you can recall later
- the first line must contain the number of delays in the VD list = NE
- the second line contains the number of complete cycles of NS and VD to do; for ^1H T_1 = 1
- end the list by entering **ESC**

3. start automation setup for the inversion-recovery sequence: **AS INVREC.AU**

i) change values for the VC list, or enter **<CNTL>-L** to list

ii) **D1** = $10T_1^r$

iii) **P2** = **2*PW**, where PW = 90° pulse length (see calibration sheet next to spectrometer, or recalibrate using procedure in section xxx)

iv) **RD** = 0, **DE** set by computer, **NS** = 8 (or multiple of), **DS** = 0

v) **NE** = number of delays in VD list

4. experiment time ≅ NS*NE*(2*D1)*(second # in VC list)
5. start automation routine: **AU<RET><RET>**; enter unique filename with *no* suffix

C. T_1 Analysis

1. Transfer data to data station using Lightnet (can use wildcard), or enter other session
2. check **NE** = size VD list
3. set **AI** = 1, Y if asks REINITIALIZE?
4. **RE** filename.002 (assuming .002 has longest VD), do **EF**, then **EP**, **P**, and when good phase, **M**
5. do all FT's by running automation routine: **AU FT.AU**

   enter filename of T_1 set, then new name of FT'd spectra (e.g., T1SET and T1SETF)
6. if want plot, go through DPO (Y to both axes, N to parameter list, Y is want TI), CX=CY=10 to 20, MAXY = 10 to 20
7. go into EP, set cursor on top of peak of interest and enter **T**, then **<RET>** to accept T1PTS as filename

   go to next peak of interest and enter **T** (*no* <RET>); repeat for all peaks of interest
8. enter T_1 routine: **T1<RET>**
   - i) enter **PD**, N to integrals list, N to VD list, Y to EP list
   - ii) when see display, enter **CT1** to calculate T_1
   - iii) enter **PLTD** to plot (can change TI and DPO prior to plot)
   - iv) enter **NXTP** to go to next peak
   - v) enter **QUIT** to exit T_1 routine