Relaxation Measurements
**Two Relaxation Mechanisms**

T₁: **Spin-lattice** or **longitudinal relaxation** is the average lifetime of the nuclei in the higher spin state.

T₂: **Spin-spin** or **transverse relaxation** corresponds to a de-coherence of the transverse nuclear spin magnetization.
Spin-Lattice Relaxation Time or $T_1$

- Any factor which slows molecular motion (e.g. increasing solution viscosity, aggregation, or rigidifying the molecule) shortens the spin-lattice relaxation time.
- A short $T_1$ favors sensitivity but too short can result in line broadening and degradation of resolution since $T_2$ cannot be longer than $T_1$.
- 3 principal magnetic interactions that contribute to $T_1$ relaxation of spin $\frac{1}{2}$ nuclei:
  - Dipole-dipole interaction - the nucleus experiences a fluctuating field due to the motions of neighboring dipoles, unpaired electrons, or other nuclei.
  - Chemical shift anisotropy - chemical shielding of the nucleus is a function of molecular orientation with respect to $B_0$ field direction.
  - Spin rotation interaction – small magnetic fields are induced at the nucleus as a molecule reorients; this field fluctuates because the motions are not uniform but proceed by a series of small jumps.
- Small amounts of paramagnetic substances speed up relaxation.
- Inversion recovery experiment measures $T_1$. 
$T_1$ Measurement: Inversion Recovery

**Parameters to note & Optimize**

- To change the value of the delay, $d7$, a variable delay list must be created.
- In the acquisition parameters a VDLIST can be generated which contains values that typically cover a time range which extends past the expected $T_1$ value.

\[ I_z = I_0(1-2\exp(-d7/T_1)) \]

\[ \ln(I_0-I_z) = \ln(2I_0)-d7/T_1 \]

\[ T_{null} = T_1*\ln2 \]
Spin-Spin Relaxation Time or $T_2$

- $T_1 = T_2$ when molecular tumbling is fast compared with the Larmor frequency; this is the condition for small molecules.
- Mechanisms of spin-spin relaxation:
  - Chemical exchange
  - Scalar spin-spin coupling if modulated at a ‘suitable rate’; these are detectable when a $^1\text{H}$ is coupled to a quadrupolar nuclei such as $^{14}\text{N}$, $^{35}\text{Cl}$, or $^{37}\text{Cl}$
- In a frozen sample, line broadening increases as the result of static dipole-dipole interactions.
- $T^*_2$ describes the magnetization ($M_\gamma$) decay resulting from $B_0$ inhomogeneity.
$T_2$ Measurement: CPMG Experiment

;cpmg1d
;1D experiment with T2 filter using Carr-Purcell-Meiboom-Gill sequence

"p2=p1*2"
"d11=30m"

1 ze
2 30m
d1
p1 ph1
3 d20
p2 ph2
d20
10 to 3 times l4
go=2 ph31
30m mc #0 to 2 F0(zd)
exit

ph1=0 0 2 2 1 1 3 3
ph2=1 3 1 3 0 2 0 2
ph31=0 0 2 2 1 1 3 3

; d20: fixed echo time to allow elimination of J-mod. effects
; d20 should be $<< 1/J$, but $(50 * P2)$ $[1-2 \text{ msec}]$
;l4: loop for T2 filter $[4 - 20]$
$T_1$ & $T_2$ Relaxation Analysis

1. First popup select “FID”, second popup enter a value of “1”
2. This will process all slices based on the first slice.

- Select “Manual Integration” and integrate regions of interest.
- Once regions are selected, save integrals to the relaxation module through the “Save Region as…” icon (see below).
$T_1$ & $T_2$ Relaxation Analysis

- Will extract integrals and plot for fitting.
- Calculates relaxation parameter for single site. Click for all sites.

Relaxation Report

$I(t)=I(0)+P\cdot\exp(-t/T_1)$

8 points for Peak 1, Peak Point at 2.714 ppm

Results Comp. 1

$I(0) = -1.488e+000$
$P = 2.335e+000$
$T_1 = 5.186s$
$\text{SD} = 1.790e-002$

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