Relaxation times and steady state

Following a perturbation (rf pulses), the magnetization returns to equilibrium. This is called longitudinal relaxation. The longitudinal relaxation constant is called $T_1$. See also page 15 of chapter 3 by James Keeler.

$T_1$ relaxation can be measured by the inversion-recovery experiment: $180^\circ - t - 90^\circ -$ acquisition. For short $t$ delays, the signal is negative. For increasingly longer $t$ delays, the signal becomes less negative, zero, positive and, for $t$ delays longer than five times $T_1$, positive and as large as it would have been in the absence of the $180^\circ$ pulse. Mathematically:

$$M_z(t) = M_z(0) \left[ 1 - 2 \exp(-t/T_1) \right]$$

$T_2$ relaxation is also called transverse relaxation. It describes the exponential loss of transverse magnetization generated, e.g., by a $90^\circ$ pulse. Mathematically:

$$M_{tr}(t) = M_{tr}(0) \exp(-t/T_2)$$

For a singlet, transverse relaxation can be measured by a spin-echo sequence: $90^\circ - t - 180^\circ - t -$ acquisition. The longer the delay $t$, the less magnetization remains.

$T_2$ relaxation arises from differences in precession frequencies of spins in different molecules (defocusing of magnetization vectors that were aligned immediately after the excitation pulse).
Precession frequencies differ, because the effective magnetic field at the site of a nuclear spin depends on the orientation of the molecule in the magnetic field (as the electrons in the bonds shield some of the external field from the spin). Brownian motion leads to fast reorientation of small molecules, i.e. the averaging between different effective Larmor frequencies is very efficient. Large molecules tumble slowly in solution, so that small differences in Larmor frequencies have time to build up phase differences. Therefore, $R_2$ relaxation rates ($R_2 = 1/T_2$) are fast for large molecules. This is unfortunate, as the full line width at half-height of a Lorentzian is

$$\text{FWHH} = R_2/\pi$$

Big molecules have not only more signals but also broader signals!

$T_1$ relaxation is caused by “magnetic noise” generated by the tumbling of the molecule in solution. The transverse components of the magnetic field variations act like small-flip-angle pulses which help to bring the magnetization of the solute back to equilibrium, provided the variations occur with the Larmor frequency. If a molecule is small, it tumble quickly and easily generates magnetic noise components in the high MHz range. If a molecule tumbles slowly, there is very little magnetic noise at high frequencies and the $T_1$ relaxation becomes slower.

The tumbling rate of a molecule is described by the rotational correlation time $\tau_c$ which is the time constant for exponential loss of memory of the orientation of the molecule at time $t$ compared to its orientation at (an arbitrarily chosen) time zero:
$\exp(-t/\tau_c)$

For small molecules (short rotational correlation time $\tau_c$), $T_1$ and $T_2$ relaxation times are virtually the same. For molecules of high molecular weight (long rotational correlation time $\tau_c$), $T_2$ is always shorter than $T_1$.

\[ W \]

transverse

longitudinal

Comparison of the longitudinal and transverse relaxation rate constants as a function of the correlation time for the fixed Larmor frequency. The longitudinal rate constant shows a maximum, but the transverse rate constant simply goes on increasing.

Relaxation rates are the inverse of the relaxation times.

**Steady state**

Following a scan, the magnetization must relax back to $z$-magnetization prior to the next scan. As a rule of thumb one needs to wait $5* T_1$ to restore almost complete equilibrium magnetization. For best signal-to-noise and to save time in 2D experiments, one would only wait $1* T_1$, accepting steady-state magnetization rather than equilibrium magnetization. In this situation, the peak intensities depend on the $T_1$ relaxation rates.

For best signal-to-noise in a 1D NMR spectrum, one can also use a smaller excitation flip angle than 90° (the so-called Ernst angle) combined with a recovery delay well shorter than $5* T_1$.

**Exercises:**

1) Why can’t one use the spin-echo sequence for measuring $T_2$ relaxation of a multiplet?
2) The signal of a compound goes through zero in an inversion-recovery experiment for $t = 0.5$ s. How long is $T_1$?
3) Why does the inversion-recovery sequence work equally well for singlets and multiplets?
4) Following a 90° excitation pulse, how long does one need to wait to recover 99% of the equilibrium magnetization?
5) Based on the considerations above, would you expect broader or narrower NMR signals for a macromolecule in the earth magnetic field (as opposed to a conventional NMR spectrometer)?