Main Idea: Spin-Lattice and Spin-Spin Relaxation Mechanisms

There are two primary relaxation types for spins in an NMR system. The first, and longer, of the two is spin-lattice relaxation; it is also frequently referred to as T1 or longitudinal relaxation. This relaxation refers to the “resetting” of spins to the vertical direction, or restoration of the Boltzmann equilibrium. The predominant mechanism for spin-lattice relaxation is the loss of spin energy due to interactions with molecules in the lattice — that is to say, most of spin-lattice relaxation occurs because of loss of energy to the surrounding environment. As energy is lost, the protons’ spins will return to the lowest-energy state, causing them to re-align with the magnetic field. Spin-lattice relaxation can also occur due to motion in the lattice causing slight changes in the local magnetic field, nullifying some of the x- and y-components of the spin processions. In paramagnetic substances, unpaired electrons can have a similar effect on the magnetic field, and in systems where spin is greater than one half, electric fields can effect T1 relaxation as well.

Spin-spin relaxation, also known as T2 or transverse relaxation, refers to the “spreading out” of precessing spins along the xy-plane. This is predominately caused by interactions between aligned spins pushing one another away, resulting in a reduction of the net xy-planar alignment. It can also result from inhomogeneities in the magnetic field. The mechanisms which cause spin-lattice relaxation can also result in transverse relaxation. This is referred to as the effective T2; while the interactions causing relaxation are between the spin and the lattice, they are affecting the relaxation in the xy-plane, and we cannot differentiate them from spin-spin interactions while they are occurring. Additionally, as the spins are aligning in the vertical direction, they are coming closer together, increasing spin-spin interactions. It is therefore impossible to have T1 relaxation without also having an effective T2 relaxation, although it is possible to have T2 relaxation without having T1 relaxation. This also results in T2 always being less than or equal to T1.

Methodology: Delay Time Between Pulses

Our experiment relied on spin echo pulse sequences, meaning that we sent two separate pulses through the material with a delay time between them, wait, and then repeat this process. Controlling the amount of time between these two pulses allows us to control how much relaxation can occur between them. Relaxation begins after the first pulse — if it is a 180° pulse, we will predominantly see longitudinal relaxation, while if it is a 90° pulse, we will see more transverse relaxation. For our sequences with a 180° then 90° pulse, we see that the magnetization increases with this increase of our delay time τ proportionally to *T1*, following the equation

$$M_z = M_0(1 - 2e^{-\frac{\tau}{T1}}).$$

Conversely, a sequence with a 90° then 180° pulse will see an exponential decrease in magnetization with increasing τ proportional to *T2*:

$$M_z = M_0 e^{-\frac{2\tau}{T2}}.$$

But why is this the case? Because of our setup, we are only able to receive a signal when the spins are in line with the detector, which is at a right angle with the magnetic field, so this is where we are measuring magnetization. When we start with a 180° pulse, the spins skip this part over and begin spin-lattice relaxation back to the Boltzmann equilibrium. If we gave it enough time, the system's spins would eventually line up with the detector on their way back to this equilibrium, giving us a reading that should be equal to the maximum magnetization. However, before this can happen, we provide a 90° pulse, flipping the system to the plane of the detector.

Here, we get a reading that is less than the maximum possible voltage (proportional to the z-directional magnetization) because at least some of the spin magnetization is in the xy-plane. If we were to immediately pulse 180° then 90° (so, if we were to make τ zero), we would see all magnetization opposite the maximum. If we provide a 90° pulse, then a 180° pulse we see almost the opposite effect; we will see two readings, the second of which is smaller the longer we allow relaxation. This second reading would be zero if we had an infinitely large τ (if we didn't provide a second pulse), and would be as large as possible if we immediately went from 90° to 180° (which would essentially be the same as only providing the 180° pulse).

Data: Period Between Sequences

In order to get clear data between spin echo pulse sequences, we need to allow the system to relax. If we start a new sequence following too closely after the one before it, the system will have a "memory" of the prior sequence, interfering with our data. Providing another pulse before relaxation is complete extends the sequence. In fact, this is how we take our data; we follow one pulse with another before relaxation is complete. It is therefore crucial that we allow the system to finish relaxing between pulse sequences; otherwise, we would be taking a completely different set of data to analyze. So, we know that our delay time will have to be at least as long as the relaxation time being measured. However, to set our period to this would require us to precisely and accurately know the relaxation times before we measure them. Therefore, we need to be able to account for some level of uncertainty by overestimating the required period. Even if we have measurements from an experiment with the same equipment, we can't know for certain that the relaxation times will be exactly the same as they were before because any changes in the magnetic field's strength, its homogeneity, or the temperature within the magnet can change the relaxation times. Most importantly, however, the spins don't all move together perfectly; they, as quantum-mechanical states, follow a probabilistic distribution. So, while there is no way to guarantee that all of the spins are in a certain position unless we have infinite time, we want to pick a time where we can state with relative certainty that the spins should all have reset to align with the field. Another way to think about this is with the formulae above showing that the relaxation follows exponential decay patterns. We would need an infinite amount of time to guarantee that every single spin was re-aligned with the magnetic field. However, after a certain point, the equation predicts that we will see all but a fraction of a spin reset; since a single spin must be in one state or another, we can assume at this point that the magnetization has reset completely. Therefore, we use a period around ten times the relaxation time.

Works Cited

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