7 Relaxation

When a nuclear spin system is outside of a magnetic field, the energy levels for the |α> and |β> spin states are degenerate. The probability for a spin to be in one or the other state (which don't really exist in the absence of the magnetic field) is equal. When the spin system is placed into a magnetic field, initially the energy levels are equally populated; the system is saturated and no magnetic moment exists. After a time characterized by an exponential decay constant

, the spin system comes to thermal equilibrium with a net excess population in the lower energy state. This equilibration requires "cooling" of the spin system by loss of energy to the surroundings. At NMR frequencies, the probability for a spontaneous transition between energy levels is essentially zero. The dominant mechanism for transitions between the energy levels is the presence of magnetic fields that fluctuate at the transition frequency. In the absence of a RF field, Brownian motion and Larmor precession are the only sources of fluctuating magnetic fields. The Larmor precession of a fixed, neighboring spin at frequency v gives rise to a fluctuating magnetic field ($e^{i2\pi vt} + e^{-i2\pi vt}$) at the proper frequency to induce a transition in the interacting spin. The component of the same circular polarization causes transitions between states. However, this mechanism only effects the interchange of energy between the two spins. A flip-up of one of the spins is concerted with a flip-down of the other and the total energy of the spin system remains constant. This spin-spin flip reduces the lifetime of a particular spin state and causes broadening of the transition but does not provide a mechanism of coupling the spin energy with the lattice. The efficiency of this flip-flop mechanism depends on the motional behavior of the neighboring spin. If the neighbor is static then the full force of the dipolar interaction is felt, however, motion of the neighbor causes an averaging of the dipolar field and a reduction in the efficiency of spin exchange. The higher the amplitude of low frequency motions, the more efficient the exchange.

In the absence of motion, the static Z component of a neighboring spin only effects the magnitude of the magnetic field felt at the nucleus. However, as the molecule tumbles randomly through thermal motion, neighboring magnetic dipoles become a source for fluctuating magnetic fields. If in these fluctuations there are frequency components of motion at the transition frequency, this becomes a mechanism for the interchange of spin energy with the thermal motions of the lattice. The amplitude of the spectral density of motion at the transition frequency, v, is proportional to the rate of relaxation. In contrast to the flip-flop mechanism, low frequency motion does not contribute to spin-lattice relaxation.

There is one, less apparent, contribution to relaxation through motion of the neighboring spin. The circularly polarized component that is opposite to the precessional direction of the relaxing nucleus can interact by having a component of motion that is twice the frequency of precession and opposite to the polarization of the neighbor. The apparent result of this motion is a circularly polarized magnetic field that has the same direction and frequency as the relaxing nucleus. Obviously, the frequency of this motion is two times the Larmor frequency.

All of these mechanisms shorten the lifetime of the spin states and cause broadening of the transition. The decay of the transition is related to the linewidth of the resonance and the rate is characterized by a relaxation constant $1/T_2$. The flip-flop mechanism is an entropic term an as such does not lead to a change in the energy state of the spin system. All of the other mechanisms listed above are related to the thermal motion of the lattice and cause a change in the total energy of the spin system.

The spectral density function of a system characterizes the amplitudes of the frequency components in the system. The area under the spectral density curve is a constant. If there is very slow motion, most of the spectral density is crowded near zero frequency. As discussed above, this leads to efficient flip-flops but little spin-lattice relaxation. As the motion becomes faster, the spectral density spreads out; higher frequencies obtain amplitude at the expense of the zero frequency amplitude. Spin-lattice relaxation becomes faster while spin-spin relaxation decreases. At a motional frequency that is equal to the Larmor precession frequency, spin-lattice relaxation becomes most efficient, since the spectral density components at that frequency are passing through a maximum amplitude. At very fast motion, the spectral density at the Larmor precession frequency has gone through a maximum and is decreasing with increasing frequency components. Spin-lattice relaxation in this region again becomes less efficient and spin-spin relaxation decreases even further with decreasing zero frequency components.

There are several other mechanisms for relaxation of spin systems which will only be mentioned. Chemical shift anisotropy causes relaxation as a fluctuating magnetic field is produced by the rotation of an anisotropic chemical shift tensor. This mechanism is most important for ^{13}C and ^{15}N among others. The relaxation rate is proportional to the square of the magnetic field. Scalar relaxation of the first kind is produced when the scalar coupling interaction between two spins is modulated by chemical exchange, i.e. the physical breaking of one of the bonds through which scalar coupling passes. Scalar relaxation of the second kind is similar to the other scalar relaxation mechanism except the time dependance of the coupling interaction involves the relaxation of one of a pair of scalar coupled partners. Mostly this is observed in systems containing quadrupolar nuclei or in systems with unpaired electrons. Spin-rotation relaxation couples the rotational degrees of freedom with the spin system. This is usually only important for very small, symmetric molecules. For nuclei that have spin quantum numbers that are greater than ½, the quadrupolar relaxation mechanism is usually dominant. This mechanism relies on an electric field gradient at the quadrupolar nucleus.

In most systems, scalar relaxation of the first kind along with chemical shift anisotropy are the major contributors to relaxation behind the dominant dipolar mechanism.

A nice compilation of relaxation equations and the appropriate physical constants used to calculate the rates can be found in Sudmeier et. al. *Concepts in Magnetic Resonance*, **2** 197-212 (1990).