CHEM6154 - Week 24 - Lecture 2: Common spin relaxation mechanisms

This lecture gives an overview of common liquid-state spin relaxation mechanisms. We will assume rotational modulation for all interaction anisotropies. Isotropic rotational diffusion approximation will be used throughout, and most derivations will be skipped.

**Dipole-dipole mechanism**

Stochastic modulation of magnetic dipole interaction is the most common relaxation mechanism in spin-$1/2$ systems. It stems from the inter-nuclear dipolar interaction, and arises because the interaction is direction-dependent and therefore modulated by rotational diffusion. The latter has a timescale of nanoseconds and usually has some spectral power density at NMR transition frequencies.

For two spins L and S, an arduous derivation along the lines of the previous lecture yields the following **longitudinal relaxation rates** as functions of distance $r$ and rotational correlation time $\tau_C$:

$$
\frac{1}{T_1^L} = \frac{1}{10 (4\pi)} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_L^2 \gamma_S^2 h^2}{r^6} \left( \frac{3\tau_C}{1 + \omega_L^2 \tau_C^2} + \frac{6\tau_C}{1 + (\omega_L + \omega_S)^2 \tau_C^2} + \frac{\tau_C}{1 + (\omega_L - \omega_S)^2 \tau_C^2} \right)
$$

$$
\frac{1}{T_1^L} = \frac{1}{10 (4\pi)} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_L^2 \gamma_S^2 h^2}{r^6} \left( \frac{3\tau_C}{1 + \omega_S^2 \tau_C^2} + \frac{6\tau_C}{1 + (\omega_S + \omega_L)^2 \tau_C^2} + \frac{\tau_C}{1 + (\omega_S - \omega_L)^2 \tau_C^2} \right)
$$

(1)

There are two important limiting cases. One is **extreme narrowing**, where $\omega_{L,S} \tau_C \ll 1$ and all denominators are equal to unity; this is often the case in non-viscous liquids:

$$
\frac{1}{T_1^L} = \frac{1}{T_1^T} = \frac{1}{10 (4\pi)} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_L^2 \gamma_S^2 h^2 \tau_C}{r^6}
$$

(2)

The other limit is encountered in ESR spectroscopy where the frequency of the electron is much greater than the frequency of the nucleus and so $\omega_E + \omega_N \approx \omega_E - \omega_N \approx \omega_E$, meaning that:

$$
\frac{1}{T_1^N} = \frac{1}{10 (4\pi)} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_N^2 \gamma_S^2 h^2}{r^6} \left( \frac{3\tau_C}{1 + \omega_N^2 \tau_C^2} + \frac{7\tau_C}{1 + \omega_E^2 \tau_C^2} \right)
$$

$$
\frac{1}{T_1^E} = \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_N^2 \gamma_S^2 h^2 \tau_C}{1 + \omega_N^2 \tau_C^2}
$$

(3)

The **transverse relaxation rates** are:

$$
\frac{1}{T_2^L} = \frac{1}{20 (4\pi)} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_L^2 \gamma_S^2 h^2}{r^6} \left( 4\tau_C + \frac{3\tau_C}{1 + \omega_L^2 \tau_C^2} + \frac{6\tau_C}{1 + (\omega_L + \omega_S)^2 \tau_C^2} + \frac{6\tau_C}{1 + (\omega_L - \omega_S)^2 \tau_C^2} + \frac{\tau_C}{1 + (\omega_L - \omega_S)^2 \tau_C^2} \right)
$$

$$
\frac{1}{T_2^L} = \frac{1}{20 (4\pi)} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_L^2 \gamma_S^2 h^2}{r^6} \left( 4\tau_C + \frac{3\tau_C}{1 + \omega_S^2 \tau_C^2} + \frac{6\tau_C}{1 + (\omega_S + \omega_L)^2 \tau_C^2} + \frac{6\tau_C}{1 + (\omega_S - \omega_L)^2 \tau_C^2} + \frac{\tau_C}{1 + (\omega_S - \omega_L)^2 \tau_C^2} \right)
$$

(4)

The key difference with the longitudinal rates is the presence of the rotational correlation time without a denominator in the round brackets. This means that, in the **slow motion limit** (opposite of extreme narrowing, $\omega_{L,S} \tau_C \gg 1$) the longitudinal relaxation times go to infinity, but the transverse relaxation times go to zero. In the extreme narrowing limit, longitudinal and transverse times are equal.
Figure 1. Longitudinal and transverse relaxation rates in typical homonuclear and heteronuclear spin systems, plotted as functions of magnet frequency and rotational correlation time.
Nuclear Overhauser effect

The dipolar mechanism can also move magnetisation between spins. This process is called nuclear Overhauser effect (NOE). Its rate depends on the sixth power of the distance:

\[
\sigma_{LS} = \frac{1}{10} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_s^2 \gamma_L^2 \hbar^2}{r^6} \left( \frac{\tau_c}{1 + (\omega_L - \omega_h)^2 \tau_c^2} \right) \left( 1 + (\omega_L + \omega_h)^2 \tau_c^2 \right)
\]

Unlike the relaxation rates (which are always positive), this expression can change sign: inter-proton NOE is negative for small molecules in non-viscous liquids and weak magnets, but becomes positive for large molecules in strong magnetic fields. Because of its distance dependence, NOE is a cornerstone of molecular structure determination using NMR spectroscopy.

Assuming a room temperature $^1$H-$^1$H spin system in a 600 MHz magnet with inter-nuclear distance of 1.03 Ångstrom and a rotational correlation time of 100 ps with proton magnetisation inverted at time zero, we get the following curves for the time dependence of the longitudinal magnetisation:

Several things in this figure are worth noting. Firstly, the room temperature equilibrium polarisation of $^{13}$C is approximately a factor of four smaller than that of protons, a consequence of the smaller magneto-gyric ratio. Secondly, an enhancement of $^{13}$C polarisation, by nearly a factor of three may be obtained via...
the Overhauser effect if the nearby proton is inverted. Thirdly, the inter-atomic distance and the rotational correlation time may be extracted by fitting.

**Chemical shift anisotropy mechanism**

Nuclear Zeeman interaction anisotropy – the orientation dependence of the spin energy level splitting in an external magnetic field – is another common cause of spin relaxation. Typical anisotropy of the proton chemical shift is a few ppm; in the case of $^{15}$N or $^{19}$F nuclei it can reach hundreds of ppm and play a major role in determining the relaxation behaviour. The rates are:

$$
\frac{1}{T_1} = \frac{2\Delta^2 \gamma^2 B^2}{15} \frac{\tau_c}{1 + \tau_c \omega_N^2}, \quad \frac{1}{T_2} = \frac{\Delta^2 \gamma^2 B^2}{45} \left( 4\tau_c + \frac{3\tau_c}{1 + \tau_c \omega_N^2} \right)
$$

where $\Delta^2$ is the squared anisotropy of the chemical shift tensor. The frequency-independent term in the brackets of the transverse relaxation rate is the chief cause of the sensitivity and line width problems that NMR spectroscopy encounters for large molecules. The chemical shielding anisotropy of $^{13}$C and $^{15}$N nuclei is of the order of 100 ppm, and for the molecules with rotational correlation times greater than about 50 ns the transverse relaxation becomes very fast, leading to intractably broad lines and magnetization losses during coherence transfer stages.