

CHEM6154 - Week 24 - Lecture 2: Common relaxation mechanisms in NMR

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.

1. Chemical shift anisotropy relaxation mechanism

Nuclear chemical shielding anisotropy – and the resulting orientation dependence of the spin energy level splitting in an external magnetic field – is a common mechanism of spin relaxation in liquids. Note that there is a difference between chemical *shielding* and chemical *shift*.

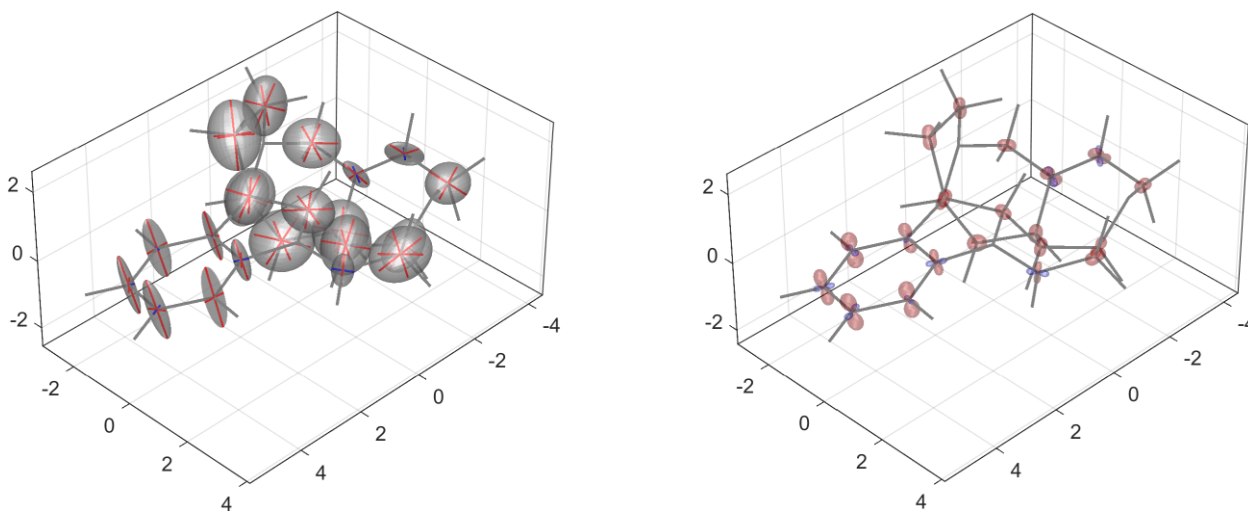


Figure 1. Schematic diagrams of ^{13}C chemical shielding tensors in strychnine. Axis ticks are in Ångström. **(Left)** Ellipsoid plots: three principal directions of the ellipsoid are aligned with the shielding tensor eigenvectors, and the three sizes are proportional to the corresponding eigenvalues. **(Right)** Spherical harmonic plots: a more nuanced representation that uses group theory to precisely map the directional features of each shielding tensor.

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. When molecular orientation changes randomly as a result of Brownian motion in a liquid, relaxation theory yields:

$$\frac{1}{T_1} = \frac{2\Delta_{\text{CSA}}^2 \omega_{\text{N}}^2}{15} \frac{\tau_{\text{C}}}{1 + \tau_{\text{C}}^2 \omega_{\text{N}}^2}, \quad \frac{1}{T_2} = \frac{\Delta_{\text{CSA}}^2 \omega_{\text{N}}^2}{45} \left(4\tau_{\text{C}} + \frac{3\tau_{\text{C}}}{1 + \tau_{\text{C}}^2 \omega_{\text{N}}^2} \right) \quad (1)$$

where Δ_{CSA}^2 is the squared anisotropy of the chemical shift tensor (remember that *ppm* denotes a $\times 10^{-6}$ multiplier), τ_{C} is the rotational correlation time (around 100 ps for strychnine in chloroform), and ω_{N} is the nuclear Zeeman frequency. The following limits are pertinent:

1. Fast motion limit: $\omega_{\text{N}}\tau_{\text{C}} \ll 1$. The relaxation rates become:

$$\frac{1}{T_1} = \frac{2\Delta_{\text{CSA}}^2 \omega_{\text{N}}^2 \tau_{\text{C}}}{15}, \quad \frac{1}{T_2} = \frac{\Delta_{\text{CSA}}^2 \omega_{\text{N}}^2 \tau_{\text{C}}}{5} \quad (2)$$

Both rates are linear functions of the rotational correlation time – lines get narrower and the longitudinal relaxation slows down for smaller molecules and less viscous liquids.

2. Slow motion limit: $\omega_{\text{N}}\tau_{\text{C}} \gg 1$. The relaxation rates become:

$$\frac{1}{T_1} = \frac{2\Delta_{\text{CSA}}^2}{15\tau_C}, \quad \frac{1}{T_2} = \frac{4\Delta_{\text{CSA}}^2\omega_N^2\tau_C}{45} \quad (3)$$

Lines get broader and the longitudinal relaxation slows down for larger molecules and more viscous liquids. This is the chief cause of the sensitivity and line width problems that NMR spectroscopy encounters for large molecules: the chemical shift anisotropy of ^{13}C and ^{15}N nuclei is of the order of 100 ppm – for molecules with rotational correlation times greater than about 50 ns, the transverse relaxation becomes very fast, leading to intractably broad lines.

2. Dipole-dipole relaxation mechanism

Rotational modulation of magnetic dipole-dipole interaction is another common relaxation mechanism in liquid state NMR systems. It arises because dipole-dipole interaction is direction-dependent and therefore modulated by rotational diffusion. The latter has a timescale of picoseconds (small molecules in non-viscous liquids) to nanoseconds (proteins in water).

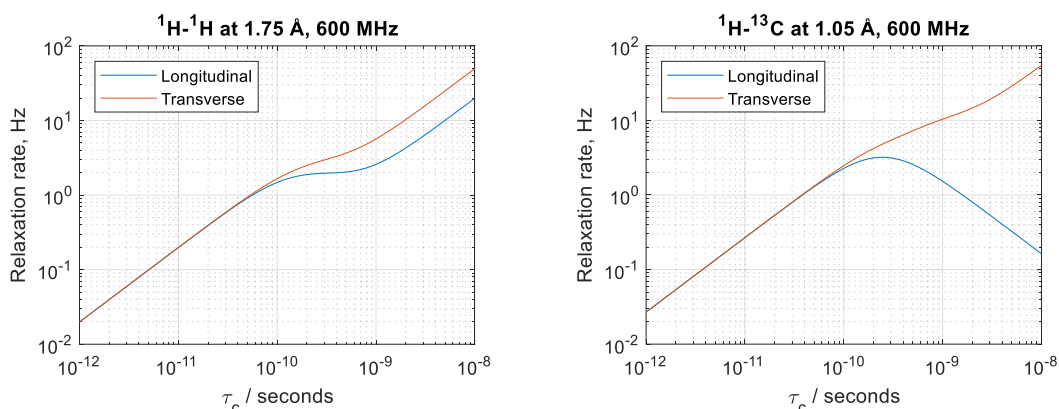


Figure 2. Longitudinal and transverse relaxation rates in typical homonuclear and heteronuclear spin systems in a typical NMR magnet, plotted as functions of rotational correlation time.

For two spin-1/2 particles 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 τ_C :

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

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

Labels are swapped for the rates pertaining to the S spin. There are four important limiting cases:

1. **Fast motion limit** (aka “extreme narrowing”), where $\omega_{L,S}\tau_C \ll 1$ and all denominators are therefore equal to unity; this holds for small molecules in non-viscous liquids:

$$\frac{1}{T_1^L} = \frac{1}{T_1^S} = \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_L^2 \gamma_S^2 \hbar^2 \tau_C}{r^6} \quad (5)$$

Both rates are linear functions of the rotational correlation time – lines get narrower and the longitudinal relaxation slows down for smaller molecules and less viscous liquids (Figure 2, right edges of both the homonuclear and the heteronuclear diagram).

2. Slow motion limit (aka “extreme broadening”) in the homonuclear case, where $\omega_{L,S}\tau_C \gg 1$ and the difference between ω_L and ω_S is of the order of parts per million. The relaxation rates become:

$$\frac{1}{T_1^L} = \frac{1}{10} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_L^2 \gamma_S^2 \hbar^2 \tau_C}{r^6}, \quad \frac{1}{T_2^L} = \frac{1}{4} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_L^2 \gamma_S^2 \hbar^2 \tau_C}{r^6} \quad (6)$$

and therefore lines get broader and the longitudinal relaxation accelerates for larger molecules and more viscous liquids (Figure 2, right edge of the left diagram).

3. Slow motion limit (aka “extreme broadening”) in the heteronuclear case, where $\omega_{L,S}\tau_C \gg 1$ and the difference between ω_L and ω_S is of the order of $\omega_{L,S}$ themselves. The relaxation rates become:

$$\frac{1}{T_1^L} = \frac{1}{10} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_L^2 \gamma_S^2 \hbar^2}{r^6 \tau_C} \left(\frac{3}{\omega_L^2} + \frac{6}{(\omega_L + \omega_S)^2} + \frac{1}{(\omega_L - \omega_S)^2} \right) \quad (7)$$

$$\frac{1}{T_2^L} = \frac{1}{5} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_L^2 \gamma_S^2 \hbar^2 \tau_C}{r^6}$$

and therefore lines get broader and the longitudinal relaxation slows down for larger molecules and more viscous liquids (Figure 2, right edge of the right diagram).

4. Electron-nuclear limit, when one of the two spins is an electron and therefore $\omega_E \gg \omega_N$. This means that $\omega_E + \omega_N \approx \omega_E - \omega_N \approx \omega_E$. Longitudinal relaxation rates become:

$$\frac{1}{T_1^N} = \frac{1}{10} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_N^2 \gamma_E^2 \hbar^2}{r^6} \left(\frac{3\tau_C}{1 + \omega_N^2 \tau_C^2} + \frac{7\tau_C}{1 + \omega_E^2 \tau_C^2} \right) \quad (8)$$

$$\frac{1}{T_1^E} = \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_N^2 \gamma_E^2 \hbar^2}{r^6} \frac{\tau_C}{1 + \omega_E^2 \tau_C^2}$$

and similarly for the transverse relaxation rates. This limit is encountered in EPR and paramagnetic NMR spectroscopy.