

Problem Set 6: Coupled Relaxation Modes

In this problem set we will try to investigate the behaviour of longitudinal and transverse relaxation in a simple two-spin system. We assume an isolated heteronuclear ^{15}N - ^1H spin pair attached to a rigid molecule that undergoes isotropic rotational tumbling with a correlation time τ_c . The spectral density function for isotropic rotational tumbling is given by

$$J(\omega) = \frac{2}{5} \frac{\tau_c}{1 + (\omega\tau_c)^2}. \quad (1)$$

We will look at the relaxation properties of the ^{15}N atom due to the dipolar coupling to the proton as well as the axially symmetric CSA tensor of the nitrogen atom. Unless noted otherwise, we assume a static magnetic field of $B_0 = 14.1 \text{ T}$ and an internuclear distance of 1.1 \AA .

Useful constants:

$$\begin{aligned} \gamma_{\text{H}} &= 26.75 \cdot 10^7 \text{ rad s}^{-1} \text{ T}^{-1} \\ \gamma_{\text{N}} &= -2.712 \cdot 10^7 \text{ rad s}^{-1} \text{ T}^{-1} \\ \hbar &= 1.05457 \cdot 10^{-34} \text{ J s rad}^{-1} \\ \mu_0 &= 4\pi \cdot 10^{-7} \text{ V s A}^{-1} \text{ m}^{-1} \end{aligned}$$

Definition of the anisotropy of the dipolar coupling tensor:

$$\begin{aligned} \delta^{(IS)} &= -2 \frac{\mu_0 \gamma_I \gamma_S \hbar}{4\pi r_{IS}^3} \\ \delta^{(S)} &= \omega_S \sigma_{zz}^{(S)} \\ \delta^{(I)} &= \omega_I \sigma_{zz}^{(I)} \end{aligned}$$

Problem 1: Coupled Relaxation Modes

If we look at longitudinal relaxation in a heteronuclear two-spin system, we find that all three relaxation modes are coupled and can be described by a system of coupled differential equations

$$\frac{d}{dt} \begin{bmatrix} \langle I_z \rangle(t) \\ \langle S_z \rangle(t) \\ \langle I_z S_z \rangle(t) \end{bmatrix} = - \begin{bmatrix} \Gamma_{I_z, I_z} & \Gamma_{S_z, I_z} & \Gamma_{2I_z S_z, I_z} \\ \Gamma_{S_z, I_z} & \Gamma_{S_z, S_z} & \Gamma_{2I_z S_z, S_z} \\ \Gamma_{2I_z S_z, I_z} & \Gamma_{2I_z S_z, S_z} & \Gamma_{2I_z S_z, 2I_z S_z} \end{bmatrix} \begin{bmatrix} \langle I_z \rangle(t) - \langle I_z \rangle_{\text{eq}} \\ \langle S_z \rangle(t) - \langle S_z \rangle_{\text{eq}} \\ \langle I_z S_z \rangle(t) - \langle I_z S_z \rangle_{\text{eq}} \end{bmatrix} \quad (2)$$

If we neglect cross-correlated cross relaxation, the system simplifies into two blocks

$$\frac{d}{dt} \begin{bmatrix} \langle I_z \rangle(t) \\ \langle S_z \rangle(t) \\ \langle I_z S_z \rangle(t) \end{bmatrix} = - \begin{bmatrix} \Gamma_{I_z, I_z} & \Gamma_{S_z, I_z} & 0 \\ \Gamma_{S_z, I_z} & \Gamma_{S_z, S_z} & 0 \\ 0 & 0 & \Gamma_{2I_z S_z, 2I_z S_z} \end{bmatrix} \begin{bmatrix} \langle I_z \rangle(t) - \langle I_z \rangle_{\text{eq}} \\ \langle S_z \rangle(t) - \langle S_z \rangle_{\text{eq}} \\ \langle I_z S_z \rangle(t) - \langle I_z S_z \rangle_{\text{eq}} \end{bmatrix} \quad (3)$$

The four relevant relaxation-rate constants are given

$$\Gamma_{I_z, I_z} = \left(\frac{\delta^{(\text{IS})}}{4} \right)^2 [J(\omega_I - \omega_S) + 3J(\omega_I) + 6J(\omega_I + \omega_S)] + \frac{3}{4} (\delta^{(I)})^2 J(\omega_I) \quad (4)$$

$$\Gamma_{S_z, S_z} = \left(\frac{\delta^{(\text{IS})}}{4} \right)^2 [J(\omega_I - \omega_S) + 3J(\omega_S) + 6J(\omega_I + \omega_S)] + \frac{3}{4} (\delta^{(S)})^2 J(\omega_S) \quad (5)$$

$$\Gamma_{2I_z S_z, 2I_z S_z} = \left(\frac{\delta^{(\text{IS})}}{4} \right)^2 [3J(\omega_I) + 3J(\omega_S)] + \frac{3}{4} (\delta^{(I)})^2 J(\omega_I) + \frac{3}{4} (\delta^{(S)})^2 J(\omega_S) \quad (6)$$

$$\Gamma_{S_z, I_z} = \left(\frac{\delta^{(\text{IS})}}{4} \right)^2 [-J(\omega_I - \omega_S) + 6J(\omega_I + \omega_S)] \quad (7)$$

$$\Gamma_{2I_z S_z, I_z} = \frac{6}{8} (\delta^{(\text{IS})} \delta^{(I)})^2 J(\omega_I) \quad (8)$$

$$\Gamma_{2I_z S_z, S_z} = \frac{6}{8} (\delta^{(\text{IS})} \delta^{(S)})^2 J(\omega_S) \quad (9)$$

There are many ways how one can solve the following problems in MATLAB or similar packages. One can either use a solver for the system of equations or one can calculate the relaxation matrix and calculate the solution via the matrix exponent. The various ways are fully equivalent.

1. Calculate the time evolution of the S_z magnetization (^{15}N spin) after a 180° inversion pulse, i.e., for an initial condition $\sigma_0 = -S_z$ by solving the differential equation [1.8] assuming isotropic rotational tumbling at correlation times $\tau_c = 10^{-8}$ and 10^{-10}s . Assume that both chemical-shielding tensor are $\sigma_{zz}^{(I)} = \sigma_{zz}^{(S)} = 0$ ppm and that cross-correlated cross relaxation can be neglected. Compare the curve with a mono-exponential buildup towards thermal equilibrium with a time constant of T_{1S} . Discuss the results.
2. To get an estimate of the influence of cross-correlated cross relaxation and the chemical-shielding tensor on the longitudinal relaxation, we examine different scenarios. Calculate the evolution of the S_z magnetization including the cross-correlated cross relaxation once with and once without the chemical shield tensors $\sigma_{zz}^{(I)} = \sigma_{zz}^{(S)} = 100$ ppm. Compare the results with curves from the previous calculation in subtask 1. Discuss the results.

3. If we saturate the protons by applying on-resonance cw irradiation on the I spin during the relaxation delay, the system of differential equations is modified. We can assume that $\langle I_z \rangle(t) = 0$. Calculate the time evolution of the S_z magnetization after a 180° inversion pulse under these conditions analytically. What is now the rate constant with which the system relaxes towards the steady-state equilibrium value.
4. The same experiment, i.e., saturation of the I spin is the so-called steady-state NOE experiment. Calculate analytically the steady-state value of the NOE. What is the signal enhancement generated by the NOE? Calculate the signal enhancement numerically as a function of the correlation time assuming that the chemical-shielding tensor is $\sigma_{zz}^{(S)} = 0$ ppm.