

Problem Set 5: Spectral-Density Functions

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:

$$\delta^{(IS)} = -2 \frac{\mu_0 \gamma_I \gamma_S \hbar}{4\pi r_{IS}^3} \quad (2)$$

Implement the calculations and plots in Matlab using the provided framework of the incomplete Matlab scripts:

- ex05_T1_1and2.m
- ex05_T1_3.m
- ex05_T2_1and2.m
- ex05_T2_3.m
- ex05_T2_4.m

Problem 1: T_1 Relaxation

The longitudinal auto-relaxation time of the S spin (^{15}N) is given by

$$\begin{aligned} \frac{1}{T_{1,S}} &= \Gamma_{S_z, S_z} \\ &= \left(\frac{\delta^{(IS)}}{4} \right)^2 [J(\omega_I - \omega_S) + 3J(\omega_S) + 6J(\omega_I + \omega_S)] + \frac{3}{4} (\omega_S \sigma_{zz}^{(S)})^2 J(\omega_S). \end{aligned} \quad (3)$$

1. Calculate $T_{1,S}$ as a function of the correlation time τ_c assuming that the chemical-shielding tensor is zero ($\sigma_{zz}^{(S)} = 0$ ppm). Generate a double-logarithmic plot of $T_{1,S}$ vs. $\omega_S \tau_c$ (where ω_S has a fixed value) for τ_c in the range from 10^{-12} to 10^{-5} s. Where do you observe a minimum of the $T_{1,S}$ time? Rationalize the position of the minimum by discussing the form of the spectral density function. Plot the relaxation rate constant $R_{1,S} = \frac{1}{T_{1,S}}$ in a semilogarithmic plot as a function of τ_c . In which range is the dipolar relaxation an effective relaxation mechanism?
2. Repeat the calculation of $T_{1,S}$ for chemical-shielding tensor values of $\sigma_{zz}^{(S)} = 50$ ppm and 150 ppm. What do you observe?
3. Calculate $T_{1,S}$ as a function of the static magnetic field B_0 between 1 and 30 T for correlation times of 10^{-12} , 10^{-10} and 10^{-8} s. Assume a chemical-shielding tensor of $\sigma_{zz}^{(S)} = 0$ ppm.
4. What will change when we consider a homonuclear spin pair with non-degenerate chemical shifts instead of the heteronuclear spin pair?

Hint: Where will we sample the spectral density function and how does its value depend on τ_c ?

Problem 2: T_2 Relaxation

The transverse auto-relaxation time of the S spin (^{15}N) is given by

$$\begin{aligned} \frac{1}{T_{2,S}} &= \Gamma_{S^+, S^+} \\ &= \frac{(\delta^{(IS)})^2}{32} [4J(0) + J(\omega_I - \omega_S) + 3J(\omega_S) + 6J(\omega_I) + 6J(\omega_I + \omega_S)] \\ &\quad + \frac{1}{2} (\omega_S \sigma_{zz}^{(S)})^2 J(0) + \frac{3}{8} (\omega_S \sigma_{zz}^{(S)})^2 J(\omega_S). \end{aligned} \quad (4)$$

1. Calculate $T_{2,S}$ as a function of the correlation time τ_c assuming that the chemical-shielding tensor is $\sigma_{zz}^{(S)} = 0$ ppm. Generate a double-logarithmic plot of $T_{2,S}$ vs. $\omega_S \tau_c$ (where ω_S has a fixed value) for τ_c in the range from 10^{-12} to 10^{-5} s. Rationalize why the $T_{2,S}$ relaxation time shows no minimum but decreases monotonically with increasing correlation time.

2. Repeat the calculation of $T_{2,S}$ for chemical-shielding tensor values of $\sigma_{zz}^{(S)} = 50$ ppm and 150 ppm. What do you observe?
3. Calculate $T_{2,S}$ as a function of the static magnetic field B_0 between 1 and 30 T for correlation times of 10^{-12} , 10^{-10} and 10^{-8} s. Assume a chemical-shielding tensor of $\sigma_{zz}^{(S)} = 0$ ppm.

If the longitudinal and the transverse relaxation times are known, the correlation time of the molecule can be determined as

$$\tau_c = \frac{1}{2} \sqrt{\frac{1}{\omega_S^2} \left(6 \frac{T_{1,S}}{T_{2,S}} - 7 \right)}. \quad (5)$$

4. Calculate the correlation time from the $T_{1,S}$ and $T_{2,S}$ values determined in 1.1 and 2.1 for a chemical-shielding tensor of $\sigma_{zz}^{(S)} = 0$ ppm. Plot the backcalculated correlation times against the input values used for τ_c . In which range of correlation times is Eq. (5) valid? Derive Eq. (5) from the analytical expressions for $T_{1,S}$ and $T_{2,S}$ given in Eqs. (3) and (4) considering the range of τ_c where Eq. (5) is valid.