TD Cargèse 2013 – 1h30

Decoupling in solid state NMR

GDP/TC

Exercice 1 – Some insight into CW decoupling

1- NMR Interactions in solids

Consider a two-spin system (S-I) under CW decoupling applied on the I channel. Write the corresponding Hamiltonian in the rotating frame (using Cartesian operators) including

- Isotropic chemical shift $\omega_{S/I}^{iso}$
- Chemical shift anisotropy $\omega_{S/I}^{ani}$
- Dipolar interaction ω_{SI}^{dip}
- Indirect (J) interaction
- CW RF field strength ω_1 along the x axis

Until specified otherwise, we assume that there is no sample spinning (i.e. $\frac{\omega_R}{2\pi} = 0$).

In the following the part of the Hamiltonian describing the interactions will be denoted $\mathcal{H}_0$ and the CW irradiation on the I-channel will be denoted $\mathcal{H}_1$.

2- Spins rotation under RF field

We want to calculate the effect of the CW RF irradiation on the internal Hamiltonian $\mathcal{H}_0$. For that we first need to rewrite the Hamiltonian into the "interaction frame" defined by the CW irradiation.

Give a reason for doing so?

Write down the transformation of the operators I_x, I_y and I_z in the frame rotating around the x axis at ω_1 . Calculate the full Hamiltonian in the (RF) interaction frame (noted $\mathcal{H}_0{}'$).

3- AHT for a 2-spin system

3.1 In the interaction frame defined above the Hamiltonian of the system $\mathcal{H}_0{}'$ is periodic of period $\tau_c = \frac{2\pi}{\omega_1}$.

Show that we only need to know the short time evolution of the system over one cycle τ_c, i.e. $U_0(\tau_c) = \hat{T}exp\left(-i\int_0^{\tau_c} dt'\mathcal{H}_0{}'(t')\right)$, to describe the state of the system at any integer multiple of the cycle time.

3.2 By definition, the effective Hamiltonian of the system over a cycle time τ_c can be written:

$U_0(\tau_c) = exp(-i\bar{H}\tau_c)$

And the average Hamiltonian over a cycle τ_c can be calculated using the Magnus expansion. Using the formulae below, derive an average Hamiltonian (to the second order) in the interaction frame over the cycle time τ_c.

Magnus Expansion:

$$\bar{\mathcal{H}}^{(1)} = \frac{1}{\tau_c}\int_0^{\tau_c} \mathcal{H}_0{}'(t)dt$$

$$\bar{\mathcal{H}}^{(2)} = \frac{-i}{2\tau_c}\int_0^{\tau_c} dt_2 \int_0^{t_2} dt_1 \left[\mathcal{H}_0{}'(t_2), \mathcal{H}_0{}'(t_1)\right]$$

Discuss the effect of the CW irradiation.

4- CW decoupling under MAS

4.1 In the following, we now consider that the sample is spinning at the magic angle with a MAS frequency $\omega_R/2\pi$. The CSA and heteronuclear dipolar tensors will be written as periodic function of the MAS frequency ω_R : $\omega_{SI}^{dip} = \sum_{\substack{k=-2 \\ k\neq 0}}^{2} \omega_{SI}^{(k)}\, e^{-ik\omega_R t}$ and $\omega_{S/I}^{CSA} = \sum_{\substack{k=-2 \\ k\neq 0}}^{2} \omega_{S/I}^{(k)}\, e^{-ik\omega_R t}$.

What is the effective Hamiltonian obtained assuming perfect MAS averaging and no RF irradiation applied? What is the ideal Hamiltonian for a perfect heteronuclear decoupling?

4.2 The Hamiltonian in the interaction frame derived ealier ($\mathcal{H}_0{}'$) contains a second time-dependency through the rotation of the sample. The application of AHT requires that one can find a unique period (or frequency modulation). In order to simplify this 2-frequency dependent problem, we assume that ω_1 and ω_R are commensurate, i.e. $\omega_1 = \frac{p}{q}\omega_R = \alpha\omega_R$ with (p,q) integer numbers.

Calculate the effective Hamiltonian to the second order as a function of α.

Discuss the special cases where $\alpha = 1, 2$.

4.3 Rewrite the previous result in the limit of very strong CW irradiation ($\alpha \to \infty$). Comment the relative importance of the various terms and compare this result to the one obtained in the static case.

5- Why TPPM works better? Ref. Bennett et al., JCP, 1995

5.1 Let us consider now a RF decoupling scheme called Two Pulse Phase Modulation (TPPM). In this case the RF field amplitude is constant equal to $\omega_1$and the phase alternates between $\phi = \varphi_0$ and $\phi = -\varphi_0$ with a cycle time equal to τ_c (corresponding to a modulation frequency $\omega_c/2\pi$):

Write the RF irradiation on the I-channel.

5.2 Such irradiation scheme can be decomposed into two components along the x- and y-axis. The x-component is typically much larger than the y-component and equivalent to a (constant) CW irradiation along the x-axis. The y-component is smaller in amplitude ($\varphi_0 \ll 1$) and oscillates between two values with a period τ_c. In order to simplify the problem we will "truncate" the full TPPM irradiation with respect to its main component (i.e. x-axis) Show that the Y-component of the TPPM sequence can produce a second averaging step if $\omega_c = \omega_1 \; cos\, \varphi_0$. Write the corresponding effective field (to the lowest order in the Magnus expansion) in the interaction frame defined by the x-component.

5.3 Using the results from questions 1 and 3, discuss the effect of this second component on the residual heteronuclear terms.