

Analysis of parahydrogen polarized spin systems in low magnetic fields

Supplementary Information

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Appendix A: Derivation of the three-spin density matrix

The Liouville-von-Neumann equation describes the temporal evolution of the spin state characterized by the time dependent density matrix $\rho_{I_1 I_2 S}(t)$ under the influence of the Hamiltonian $\mathcal{H}^{I_1 I_2 S}$. The time dependent density matrix $\rho_{I_1 I_2 S}(t)$ contains all spin operators which can be generated by $\mathcal{H}^{I_1 I_2 S}$ acting on the initial singlet state ρ_p . If non-detectable spin states are neglected the resulting system consists of six coupled linear differential equations characterized by the coefficients $a(t)$, $b(t)$, ... $f(t)$. The general time dependent form is

$$\begin{aligned} \rho_{I_1 I_2 S}(t) = & I_{1z} I_{2z} + a(t) \cdot ZQ_x + 2 \cdot b(t) \cdot ZQ_y S_z + c(t) \cdot (I_{1z} - I_{2z}) S_z \\ & + 2 \cdot d(t) \cdot ZQ_x S_z + e(t) \cdot ZQ_y + \frac{1}{2} f(t) (I_{1z} - I_{2z}). \end{aligned}$$

Introducing $\Delta J = J_{1S} - J_{2S}$ and $\Delta\omega = \omega_1 - \omega_2$ the system of six linear, coupled differentials becomes

$$\begin{aligned} \frac{\partial a(t)}{\partial t} &= \pi \Delta J b(t) + \Delta\omega e(t) \\ \frac{\partial b(t)}{\partial t} &= 2\pi J_{12} c(t) - \pi \Delta J a(t) - \Delta\omega d(t) \\ \frac{\partial c(t)}{\partial t} &= -2\pi J_{12} b(t) \\ \frac{\partial d(t)}{\partial t} &= \pi \Delta J e(t) + \Delta\omega b(t) \\ \frac{\partial e(t)}{\partial t} &= 2\pi J_{12} f(t) - \pi \Delta J d(t) - \Delta\omega a(t) \\ \frac{\partial f(t)}{\partial t} &= -2\pi J_{12} e(t). \end{aligned}$$

The boundary condition is that the initial state of the system $\rho_{I_1 I_2 S}(t = 0)$ has to correspond to the singlet state ρ_p of parahydrogen. Solving these equations one obtains the general form of $\rho_{I_1 I_2 S}(t)$. The symmetry breaking process of the initial singlet state occurs continuously over a time period τ . The coefficients are oscillating with frequencies $2\pi J_{12} \sqrt{1 + x_+^2}$ and $2\pi J_{12} \sqrt{1 + x_-^2}$ where $x_- = y - x$ and $x_+ = y + x$.

The steady state solution of the density matrix $\overline{\rho_{I_1 I_2 S}}$ is obtained by the time averaged coefficients \bar{a} ... \bar{f} . If we assume that $\tau^{-1} \ll 2\pi J_{12} \sqrt{1 + x_+^2}$, \bar{b} and \bar{e} will be equal to zero. The limiting cases

$$\begin{aligned} \lim_{\Delta\omega_{12} \rightarrow 0} \overline{\rho_{I_1 I_2 S}} &= I_{1z} I_{2z} + \frac{1}{1 + y^2} ZQ_x + \frac{y}{1 + y^2} (I_{1z} - I_{2z}) S_z \\ \lim_{\Delta J \rightarrow 0} \overline{\rho_{I_1 I_2 S}} &= I_{1z} I_{2z} + \frac{1}{1 + x^2} ZQ_x + \frac{x}{2(1 + x^2)} (I_{1z} - I_{2z}) \end{aligned}$$

agree with the known forms in case there is either no chemical shift difference between nuclei I_1 I_2 or no heteronuclear J -coupling term.

Appendix B: Energy Eigenvalues, transition frequencies and bandwidth

Introducing $v_0^* = v_0(1 + (\delta_1 + \delta_2)/2)$ the energy eigenvalues of the two-spin system Hamiltonian $\mathcal{H}_{I_1 I_2}$ are given by

$$\begin{aligned} E_1 &= h \left(-v_0^* + \frac{J}{4} \right) \\ E_2 &= h \left(-\frac{1}{2} \sqrt{J^2 + (\delta v)^2} - \frac{J}{4} \right) \\ E_3 &= h \left(\frac{1}{2} \sqrt{J^2 + (\delta v)^2} - \frac{J}{4} \right) \\ E_4 &= h \left(v_0^* + \frac{J}{4} \right). \end{aligned}$$

Note that the frequency difference $E_4 - E_1 = h \Delta v_D$ defines the spectral width of the spectrum and therefore the minimum bandwidth of the amplifier. This is used for the analytical description of the SNR.

The four corresponding eigenstates can be expressed in the Zeeman basis set ($|\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle, |\beta\beta\rangle$) using the mixing angle $\phi = \frac{1}{2} \arctan(x^{-1})$.

$$\begin{aligned} \varphi_1 &= (0,0,0,1) \\ \varphi_2 &= (0, \cos \phi, -\sin \phi, 0) \\ \varphi_3 &= (0, \sin \phi, \cos \phi, 0) \\ \varphi_4 &= (1,0,0,0) \end{aligned}$$

The transition frequencies between the eigenstates can be expressed in a Taylor series as a function of x assuming the inverse weak coupling limit ($\delta v < J$). Truncation after the 4th order yields

$$\begin{aligned} v_1 &= \frac{E_2 - E_1}{h} \approx v_0^* - J \left(1 + \frac{1}{4} x^2 - \frac{1}{16} x^4 \right) \\ v_2 &= \frac{E_4 - E_3}{h} \approx v_0^* - \frac{1}{4} x^2 + \frac{1}{16} x^4 \\ v_3 &= \frac{E_3 - E_1}{h} \approx v_0^* + \frac{1}{4} x^2 - \frac{1}{16} x^4 \\ v_4 &= \frac{E_4 - E_2}{h} \approx v_0^* + J \left(1 + \frac{1}{4} x^2 - \frac{1}{16} x^4 \right). \end{aligned}$$

These equations define the non-linear splitting.

Appendix C: Line Amplitudes for thermal and parahydrogen induced polarization

If a two-spin system is subjected to a $\pi/2$ x -pulse spin components will be aligned to the y -axis of a coordinate frame rotating at the Larmor frequency. The observable magnetization is given by

$$\langle I_{1y} + I_{2y} \rangle = \text{Tr} \left[(I_{1y} + I_{2y}) \cdot e^{-\frac{i}{\hbar} \mathcal{H}^{I_1 I_2} t} \cdot \rho_{init} \cdot e^{\frac{i}{\hbar} \mathcal{H}^{I_1 I_2} t} \right].$$

ρ_{init} defines the type of polarization which is either a thermally or a parahydrogen polarized spin state. For convenience a unitary transformation can be performed to change into the eigenbasis of the Hamiltonian $\mathcal{H}^{I_1 I_2}$. The unitary matrix U is composed of the four orthonormal eigenvectors in the Zeeman basis

$$U = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos \phi & -\sin \phi & 0 \\ 0 & \sin \phi & \cos \phi & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

The corresponding expression for the Hamiltonian describing the time evolution consists of the diagonal matrix $\lambda = \text{diag}\{E_1, E_2, E_3, E_4\}$ including the eigenvalues of $\mathcal{H}^{I_1 I_2}$.

$$e^{\frac{i}{\hbar}\lambda t} = U^{-1} \cdot e^{\frac{i}{\hbar}\mathcal{H}^{I_1 I_2} t} \cdot U$$

If the sample is thermally prepolarized the initial density matrix ρ_{init}^{Boltz} in the high temperature approximation after a $\pi/2$ x -pulse is

$$\rho_{init}^{Boltz} = \beta(I_{1y} + I_{2y}).$$

With β as defined by Eq. (4). Using these expressions and assuming $\beta = 1$ the characteristic amplitudes A_i^{Boltz} of transitions for thermally polarized systems become

$$A_1^{Boltz} = A_4^{Boltz} = \frac{1}{4} - \frac{1}{4\sqrt{1+x^2}}$$

$$A_2^{Boltz} = A_3^{Boltz} = \frac{1}{4} + \frac{1}{4\sqrt{1+x^2}}.$$

For PHIP with $\pi/2$ and $\pi/4$ excitation pulses the amplitudes are given by

$$A_1^{\frac{\pi}{2}PHIP} = A_2^{\frac{\pi}{2}PHIP} = -A_3^{\frac{\pi}{2}PHIP} = -A_4^{\frac{\pi}{2}PHIP} = \frac{x^2}{4(1+x^2)^{3/2}}$$

$$A_1^{\frac{\pi}{4}PHIP} = -A_4^{\frac{\pi}{4}PHIP} = \frac{x^2(-1 - \sqrt{2} + \sqrt{1+x^2})}{8(1+x^2)^{3/2}}$$

$$A_2^{\frac{\pi}{4}PHIP} = -A_3^{\frac{\pi}{4}PHIP} = \frac{x^2(1 + \sqrt{2} + \sqrt{1+x^2})}{8(1+x^2)^{3/2}}.$$

These expressions define the sum $\sum_i |A_i|$ in Eq. (20). The amplitudes are the analytic description of line amplitudes expected in PHIP spectra which are shown in Fig. 2b. Irrespective of the applied excitation pulse the transition lines ν_2 and ν_3 have an opposite sign of and the same magnitude of amplitudes. This explains the boundaries of the integral $\mathcal{S}_{\nu_{23}}$ in Eq. (18), as for reasons of symmetry only the part of a Lorentz shaped peak which overlaps with the other peak of opposite sign leads to area cancelation.

Appendix D: Signal to Noise model

For a coil detected NMR signal with a constant polarization P_n the SNR limited by the Johnson noise ($\sqrt{4kTR_s \Delta\nu_D}$) using the detection bandwidth $\Delta\nu_D = J_{12} (1 + \sqrt{1+x^2})$ (see appendix A) can be defined as

$$SNR = \alpha \frac{B_0 \cdot P_n}{\sqrt{4kTR_s \Delta\nu_D}} \sum_i |A_i|.$$

For the two-spin system investigated in this article we require at least $\Delta\nu_D \geq \nu_4 - \nu_1$. From appendix C we get

$$\sum_{i=1}^4 |A_i^{\frac{\pi}{2}PHIP}| = \frac{x^2}{(1+x^2)^{3/2}}$$

$$\sum_{i=1}^4 |A_i^{\frac{\pi}{4}PHIP}| = \frac{x^2}{4(1+x^2)} \text{ for } x > \sqrt{2(1+\sqrt{2})}$$

$$= \frac{(1+\sqrt{2})x^2}{4(1+x^2)^{3/2}} \text{ for } x < \sqrt{2(1+\sqrt{2})}.$$