

Electronic Supporting Information (ESI) for the paper

Singlet-triplet conversion in molecular hydrogen and its role in parahydrogen induced polarization

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1. Model of singlet-triplet conversion in H₂

To implement the model for singlet-triplet conversion we numerically solved the equations for σ_f and σ_b given in the main article.

In this model, we first specify the Hamiltonians

$$\hat{H}_f = 0, \quad \hat{H}_b = \frac{1}{2}\delta\omega\{\hat{I}_{1z} - \hat{I}_{2z}\}$$

Thus, we neglect any spin evolution in the free form of H₂ and consider only a single term in \hat{H}_b , which originates from the frequency difference of the two protons in the bound form. After that, we go to the Liouville space and specify σ_f and σ_b as column vectors with 16 elements (corresponding to a two-spin system). In this representation, $\hat{H}_{f,b}$ are written as superoperators, which are 16×16 matrices, whereas the relaxation superoperators are also matrices $\hat{\Gamma}_{f,b}$. To specify all elements of $\hat{\Gamma}_{f,b}$ we use the model of partly correlated fluctuating local fields, $B^{(1)}(t)$ and $B^{(2)}(t)$, experienced by the two spins. This means, that we use the same method as before^{1,2} but averaging of the local fields is performed using the following expressions (here $g(\tau)$ is the auto-correlation function of the process):

$$\langle B_i^{(1)}(t)B_j^{(1)}(t+\tau) \rangle = \langle B^2 \rangle \delta_{ij}g(\tau),$$

$$\langle B_i^{(2)}(t)B_j^{(2)}(t+\tau) \rangle = \langle B^2 \rangle \delta_{ij}g(\tau),$$

$$\langle B_i^{(1)}(t)B_j^{(2)}(t+\tau) \rangle = C \times \langle B^2 \rangle \delta_{ij}g(\tau)$$

Hence, different components are non-correlated while the amplitudes and auto-correlation functions of the two fields are the same. The parameter $\langle B^2 \rangle$ determines the effective relaxation rate in the system in the free or bound form, T_1^f and T_1^b . Specifically, in the limiting narrowing case, each T_1 -value is related to $\langle B^2 \rangle$ as follows: $T_1^{-1} = 2\tau_c \langle B^2 \rangle$, where τ_c is the motional correlation time. Hereafter, all products of the field components are expressed via $1/T_1$, omitting all unnecessary coefficients. The coefficient C defines the degree, to which the two fields are correlated: $C = 0$ means independent correlations and $C = 1$ means complete correlation. Here, we use C approaching unity, meaning that the singlet-triplet relaxation transitions are much slower than the relaxation transitions in the triplet manifold. We take $C = 0.9$ in order to keep singlet-triplet transitions operative (for $C = 1$ singlet-triplet relaxation is turned off).

To solve numerically the set of equations

$$\begin{cases} \frac{d}{dt}\sigma_f = -i[\hat{H}_f, \sigma_f] - \hat{\Gamma}_f \sigma_f - k_{as}\sigma_f + k_{dis}\sigma_b \\ \frac{d}{dt}\sigma_b = -i[\hat{H}_b, \sigma_b] - \hat{\Gamma}_b \sigma_b - k_{dis}\sigma_b + k_{as}\sigma_f \end{cases}$$

we proceed as follows. First, we compose a vector made out of σ_f and σ_b :

$$\sigma = \begin{pmatrix} \sigma_f \\ \sigma_b \end{pmatrix}$$

and, second, rewrite the system in one equation:

$$\frac{d}{dt}\sigma = \hat{A}\sigma, \quad \text{where} \quad \hat{A} = \begin{pmatrix} -i\hat{H}_f - \hat{\Gamma}_f - k_{as}\hat{\mathbb{1}} & k_{dis}\hat{\mathbb{1}} \\ k_{as}\hat{\mathbb{1}} & -i\hat{H}_b - \hat{\Gamma}_b - k_{dis}\hat{\mathbb{1}} \end{pmatrix}$$

Here $\hat{\mathbb{1}}$ is the unity 16×16 matrix. Using this equation, we can compute the σ -vector at any instant of time:

$$\sigma(t) = \exp[\hat{A}t]\sigma(0)$$

Knowing σ , we can calculate any parameter of interest, e.g., the populations of the spin states of H₂.

Parameters used in the calculations are:

- ✓ exchange reaction rates: $k_{as} = 6 \text{ s}^{-1}$, $k_{dis} = 60 \text{ s}^{-1}$
- ✓ relaxation times $T_1^f = 3 \text{ s}$, $T_1^b = 1 \text{ s}$, $C = 0.99$
- ✓ the value of $\delta\omega/2\pi$ was varied

2. Optimization of experimental parameters

The dependence of the signal enhancement in the SLIC-SABRE scheme is shown in **Figure 1S**. The optimal timing is given by $t_d = 500$ ms, $t_{cw} = 39$ ms, which was used in all experiments.

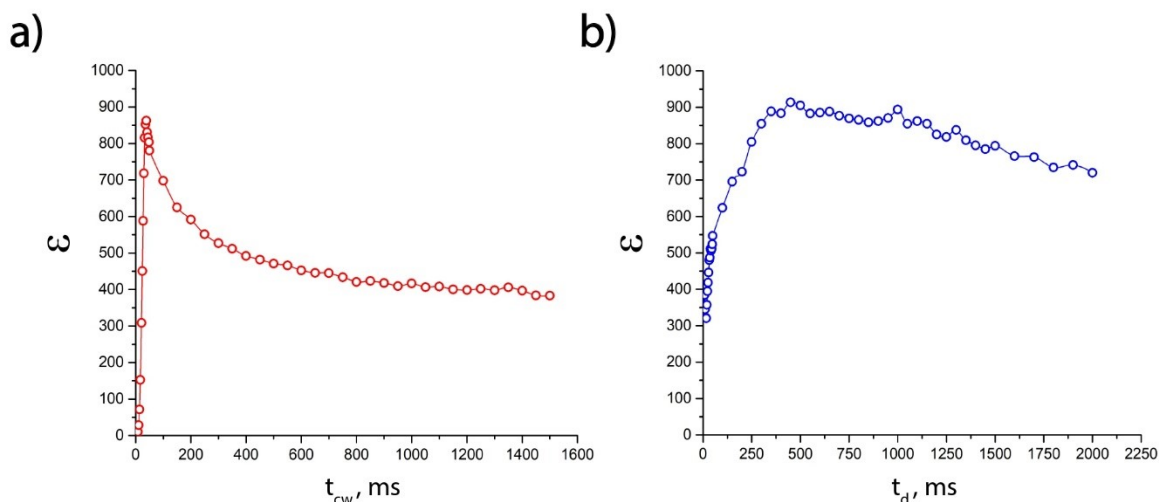


Figure 1S. Dependence of the ^{15}N signal enhancement (a) on the duration t_{cw} of the CW pulse (with $t_d = 250$ ms) and (b) on the delay between polarization transfer cycles t_d (with $t_{cw} = 39$ ms.). The experiments were performed with $[S] = 60$ mM and $[C] = 9.5$ mM. SLIC-SABRE parameters were set as follows: $\omega_1/2\pi = 10$ Hz, offset $\Delta/2\pi = -14$ Hz, number of repetitions $n = 50$.

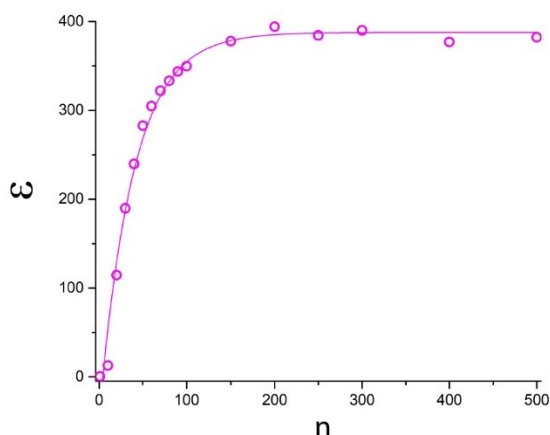


Figure 2S. Dependence of the ^{15}N signal enhancement on the number of polarization cycles n . The experiments were performed using the SLIC-SABRE method with 192 mM of the substrate (containing 10% of ^{15}N nuclei). SLIC-SABRE parameters were set as follows: $\omega_1/2\pi = 10$ Hz, offset $\Delta/2\pi = -14$ Hz, $t_d = 500$ ms, $t_{cw} = 39$ ms.

The resulting NMR enhancement also strongly depends on the number of repetitions of the polarization transfer cycle. The n -dependence of the signal enhancement in the SLIC-SABRE scheme is shown in **Figure 2S**. The signal increases with n , showing that it is usually sufficient to have $n = 50$ cycles. All experiments reported in the main article have been done with 50 repetitions.

References

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