Supporting Information

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SI Text

Supplementary Material A: Selective Dynamical Recoupling Driven by a High-Field J-Coupling. Assuming a system made up by two spin-1/2 qubits with zero average chemical shifts and a coupling among them, the total Hamiltonian of concern is (1)

$$H_t = \begin{pmatrix} \pi J/2 & 0 & 0 & 0 \\ 0 & \omega_o - \pi J/2 & \pi J & 0 \\ 0 & \pi J & -\omega_o - \pi J/2 & 0 \\ 0 & 0 & 0 & \pi J/2 \end{pmatrix}$$

where ω_o is the semidifference between the two-spins' chemical shifts and J is the spin-spin coupling. Focusing only on the zero-quantum subspace containing the off-diagonal elements, we have:

$$H_{\text{zero}} = \begin{pmatrix} \omega_o - \pi J/2 & \pi J \\ \pi J & -\omega_o - \pi J/2 \end{pmatrix}.$$

In a toggling reference frame (2) and over a cyclic RF perturbation of the form $\tau - \pi - 2\tau - \pi - \tau$ where ideal pulses are assumed, this Hamiltonian becomes

$$H_{\text{zero}}{}' = \begin{pmatrix} h(t)\cdot\omega_o - \pi J/2 & \pi J \\ \pi J & -ht(t)\cdot\omega_o - \pi J/2 \end{pmatrix}$$

where the $h(t)$ square-wave modulation introduced in Fig. 1, is a function that assumes a value of 1 for $0 < t < \tau$ and $3\tau < t < 4\tau$, and a value of -1 for $\tau < t < 3\tau$. It is possible to transform to an interaction frame where the chemical shift terms are accounted for using the following evolution operator

$$U_{CS} = \begin{pmatrix} \exp[-i\omega_o\phi(t)] & 0 \\ 0 & \exp[i\omega_o\phi(t)] \end{pmatrix}$$

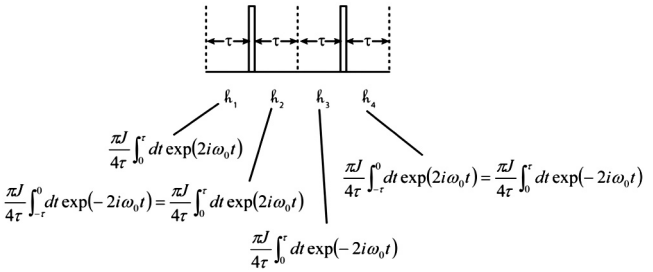
where $\phi(t) = \int_0^t h(t')dt'$. This leaves a Hamiltonian

$$H_{\text{zero}}{}''(t) = \begin{pmatrix} -\pi J/2 & \pi J \exp[2i\omega_o\phi(t)] \\ \pi J \exp[-2i\omega_o\phi(t)] & -\pi J/2 \end{pmatrix},$$

whose average to zero order is given by

$$\bar{H} = \frac{1}{T_c}\int_0^{T_c} H_{\text{zero}}{}''(t)dt$$

This average Hamiltonian can be found by breaking up the RF cycle into parts and calculating each element of the Hamiltonian matrix individually. For instance the following integrals:



yield the 1,2 matrix element of interest

$$\begin{aligned}\bar{h}_{1,2} &= \frac{\pi J}{4\tau}\int_0^{\tau} dt[2\exp(2i\omega_0 t) + 2\exp(-2i\omega_0 t)] \\ &= \frac{\pi J}{\tau}\int_0^{\tau} dt\cos(2\omega_0 t) = \frac{\pi J}{2\omega_0\tau}\sin(2\omega_0\tau),\end{aligned}$$

Likewise, the remainder of the average zero-quantum Hamiltonian

$$\bar{H} = \begin{pmatrix} -\pi J/2 & \pi Jk \\ \pi Jk & -\pi J/2 \end{pmatrix}$$

follows, where $k = \text{sinc}(2\omega_0\tau)$. As the toggling frame's final reference position coincides at the conclusion of each cycle with the original reference frame, it is unnecessary to transform back to the latter—all propagations will be carried out stroboscopically and at the end of such cycles. Returning back to the full 4×4 two-spin Hilbert space, the problem can then be cast as a need to diagonalize the average Hamiltonian:

$$\bar{H}_t = \begin{pmatrix} \pi J/2 & 0 & 0 & 0 \\ 0 & -\pi J/2 & \pi Jk & 0 \\ 0 & \pi Jk & -\pi J/2 & 0 \\ 0 & 0 & 0 & \pi J/2 \end{pmatrix},$$

which leads to the corresponding propagator

$$U_t = \begin{pmatrix} \exp(i\frac{\pi Jt}{2}) & 0 & 0 & 0 \\ 0 & \cos(\pi Jkt)\exp(-i\frac{\pi Jt}{2}) & i\sin(\pi Jkt)\exp(-i\frac{\pi Jt}{2}) & 0 \\ 0 & i\sin(\pi Jkt)\exp(-i\frac{\pi Jt}{2}) & \cos(\pi Jkt)\exp(-i\frac{\pi Jt}{2}) & 0 \\ 0 & 0 & 0 & \exp(i\frac{\pi Jt}{2}) \end{pmatrix}$$

If $\rho_0 = I_{1x} + I_{2x}$ then the observable response will be $\langle I_{1+}\rangle = Tr\{U_t^{-1}(I_{1x} + I_{2x})U_t \cdot I_{1+}\}$; an expression leading to $\langle I_{1+}\rangle \propto \cos[\pi Jt(1-k)]$. Such result agrees with that reported by Allerhand (3) and, more recently, by Kowalewski and coworkers (4).

To calculate from this derivation the observable NMR signal at the conclusion of an SDR sequence like that introduced in Fig. 1*E*, two propagators need to be considered: one for which the expression for k utilizes $\tau = x/2$ and $t = (N-1)x$, and another for which $t = TE - x(N-1)$ and $\tau = TE/2 - x(N-1)/2$ (TE being the overall time of the π-pulse train and N the number of pulses applied during this train). As these propagators commute, the overall evolution becomes $\langle I_{1+}\rangle = Tr\{U_2^{-1}U_1^{-1}(I_{1x} + I_{2x})U_1U_2 \cdot I_{1+}\}$ with $U_1 = U_t(t = x(N-1), \tau = x)$ and $U_2 = U_t(t = TE - x(N-1), \tau = t/2)$. This leads to

$$\begin{aligned}\langle I_{1+}\rangle = \cos\Big\{\pi J\cdot TE - \frac{\pi J}{\omega_o}[(N-1)\sin(\omega_o x) \\ + \sin(\omega_o(TE - x(N-1)))]\Big\}\end{aligned}$$

which is Eq. **4** in the paper and was used as the "analytical" prediction in Fig. 2.

Supplementary Material B: Selective Dynamical Recoupling Driven by Chemical Exchange. We next look at a spin-1/2 system that can exchange its environment at a rate κ, among two equally populated states possessing chemical shifts $\pm\omega_o$. As before, this ensemble will be subject to a sequence composed of $1 \leq i \leq N$ segments of duration $2\tau_i$ each, possessing an echoing π-pulse in their center and timed such that $\sum_{i=1}^{N} = TE/2$. Because of this pulsing a spin's phase will be refocused at the conclusion of each segment regardless of its environment—this, as long as no exchange has occurred during that segment. On the other hand, should a single exchange event happen during a segment i, the normalized magnetization amplitude would become

$$\langle I_+^i \rangle = \langle e^{i\Delta\Phi} \rangle_{+\omega_o \leftrightarrow -\omega_o}^{2\tau_i} = \frac{\sin(2\omega_o\tau_i)}{2\omega_o\tau_i}$$

For the slow, infrequent exchange regime where rates $\kappa < TE^{-1}$ that will here be assumed, the probability that such a single exchange has happened during a segment i is $\mathcal{P}_i(1) = \kappa 2\tau_i$. The probability that one single exchange has happened throughout the π-pulse train is then $\mathcal{P}(1) = \sum_{i=1}^{N} \mathcal{P}_i(1) = \kappa TE$, and the possibility of two or more spectral changes will be disregarded as too unlikely. This means that the probability of having a spin undergoing *zero* exchanges becomes $\mathcal{P}(0) = 1 - \kappa TE$; as in this latter, exchange-free case, the π-pulse train will entirely refocus the phases of the qubits, the resulting amplitude $\langle I_+ \rangle$ observed at the conclusion of the SDR train can be approximated as

$$\langle I_+ \rangle = \sum_{j=1}^{\infty} P(j)\langle I_{+,j} \rangle \approx P(0) \cdot 1 + \sum_{i=1}^{N} P_i(1)\langle I_+^i \rangle$$

From here one can find the first-order approximation to the resonance amplitude:

$$\langle I_+ \rangle \approx 1 - \kappa \cdot TE + \frac{\kappa}{\omega_o} \sum_{i=1}^{N} \sin(2\omega_o\tau_i),$$

which is the expression used to derive Eq. **5** in the main text.

It is interesting to reflect on three additional aspects of this scenario. A first issue to remark is that the $\langle I_+ \rangle$ equation just derived remains valid in cases where the two states are not equally populated, provided one takes $\kappa = 2(\kappa_{1\to 2} + \kappa_{2\to 1})\mathrm{Pop}_1\mathrm{Pop}_2$, where Pop_i is the population of state i and $\kappa_{i\to j}$ is the exchange rate between states i and j. As illustrated in Fig. S1 even in such cases chemical shift modulations can be measured on the major component's peak, that reveals the nature of its less-abundant exchange partner.

Also interesting to investigate is what would be the optimal pulse arrangement for minimizing the exchange-induced decay effects; i.e., the τ_i's that minimize the dynamics-induced decoherence that the "noise" (*i.e.*, the exchange) imparts on the qubit (i.e., the NMR amplitude). Given a number N of segments spanning a total echo time TE, one can use Euler-Lagrange methods to maximize such signal amplitude. Two domains result from these constraints. One arises when the average $\bar{\tau} = \frac{TE}{2N}$ is such that $\bar{\tau} \cdot \omega_o < \frac{\pi}{2} \Delta\bar{\tau} < \frac{\pi}{2}$. In this case the optimal solution to minimize the effect of the noise is a CPMG sequence where all τ_i are set equal to the average $\bar{\tau}$. This is to be expected, as for small ω_o's only linear frequency terms remain in the signal's amplitude and the problem reverts to the canonical DD domain. This contrasts with a second possible scenario, where the average $\bar{\tau}$ is such that $\bar{\tau} \cdot \omega_o > \frac{\pi}{2}$. In such cases, minimizing the signal's decay requires choosing the τ_i's in such a way as to set all $\sin(2\omega_o\tau_i)$ terms in Eq. **1** equal to 1. This can be achieved by setting the durations of certain segments to $\tau_j = \frac{(\frac{\pi}{2}+2\pi m+2\pi)}{\omega_o} > \bar{\tau}$ and the rest to $\tau_i = \frac{(\frac{\pi}{2}+2\pi m+2\pi)}{\Delta} > \bar{\tau}$, and by selecting the size of each group in such a way so as to keep the average τ as desired. Choosing in such fashion the sequence's timing according to ω_o, is something that has no parallel in any of the hitherto proposed DD methods.

A final interesting issue to consider concerns an exchange scenario where the dynamics can connect several $1 \leq k \leq M_{\mathrm{ex}}$ sites, each with population P_k and frequency ω_k, by a series of $\{\kappa_{k\to i}\}_{i\neq k}$ exchange rates. Like before we assume that this system is subject to N segments of duration $2\tau_i$ such $2\sum_{i=1}^{N} \tau_i = TE$, with an echo pulse in the middle of each segment and the infrequent jump condition $\kappa_{k\to i} \cdot TE \approx 1$ still valid. At the end of each segment the spins' evolution phases will be refocused unless there has been a state exchange during that segment. One can then calculate the average dephasing accumulated throughout the system and all segments, as

$$\langle I_+ \rangle = \sum_{i=1}^{M_{ex}} P_i \left(1 - TE \sum_{k\neq i}^{M_{\mathrm{ex}}} \kappa_{i\to k}\right)$$

Contribution of non-exchanged $k's$

$$+ \sum_{i=1}^{M_{\mathrm{ex}}} \sum_{k\neq i} \sum_{n=1}^{N} (P_i 2\kappa_{i\to k}\tau_n)\langle e^{i\Delta\Phi} \rangle_{\omega_i \leftrightarrow \omega_k}^{2\tau_n}$$

Contribution of all $i \to k$ exchanges

The microscopic detailed balance condition $P_k\kappa_{k\to i} = P_i\kappa_{i\to k}$ leads to:

$$\langle I_+ \rangle \approx 1 - TE \sum_{\substack{k=1 \\ k\neq i}}^{M_{\mathrm{ex}}} P_i\kappa_{i\to k} + 2 \sum_{\substack{i=1 \\ i\neq k}}^{M_{\mathrm{ex}}} \frac{P_i\kappa_{i\to k}}{\omega_i - \omega_k} \sum_{n=1}^{N} \sin\left[(\omega_i - \omega_k)\tau_n\right],$$

which is very similar to the result obtained earlier, only summed over all the possible site exchanges. On the basis of this modulation it follows that the behavior arising from site k from a SDR sequence like the one implemented in Fig. 3, leads to

$$\langle I_+^k \rangle \approx 1 - TE \sum_{\substack{i=1 \\ i\neq k}}^{M_{\mathrm{ex}}} P_i\kappa_{i\to k} + 2 \sum_{\substack{i=1 \\ i\neq k}}^{M_{\mathrm{ex}}} \frac{(N-1)P_i\kappa_{i\to k}}{\omega_i - \omega_k} \sin\left[(\omega_i - \omega_k)x\right]$$

This is once again a linear superposition, now involving *all* frequency differences connected by the exchange.

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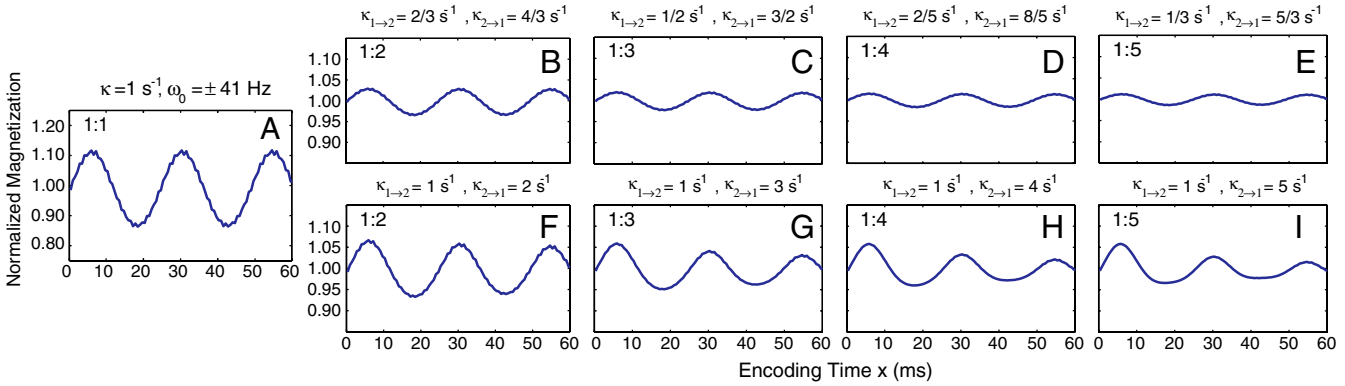

Fig. S1. Behavior expected upon applying selective dynamical recoupling to a two-site chemically exchanging system involving differing relative populations. Only the amplitude modulation expected for the resonance with the majority population component is plotted, and for all cases the $\pm\omega_o$ value was kept constant. The graphs show the progression as exchange shifts from (*A*) equally populations, to (*B–I*) sites populated with increasingly different ratios. All curves were calculated for an exchange train $TE = 1$ sec; (*B–E*) were calculated for a global $\kappa = 1$ sec^{-1} and normalized to an average signal intensity of unity for the major component; (*F–I*) repeat these calculations but for a constant $\kappa_{1\to2} = 1$ sec^{-1} forward rate of the process, and highlight the nearly constant sensitivity of the initial modulation despite the decreasing populations of the minority component.