Maximum anti-phase transfer between hermitian operators:

Consider the evolution for the heteronuclear IS spin system as defined in the text. Let the source operator \( \sigma(0) = 2I_zS_x \) and the target operator \( F = I_y \). Then, the maximal theoretical efficiency of polarization transfer \( b_{\text{theo}}(t) \) is

\[
b_{\text{theo}}(t) = \| \text{Tr}[F^\dagger U(t) \sigma(0) U^\dagger(t)] \| = \sin(\pi J_{\text{IS}} t) \quad (1S)
\]

for the transfer time \( t \leq 1/(2J_{\text{IS}}) \) and \( 1 \) for \( t > 1/(2J_{\text{IS}}) \).

Let \( \sigma \) denote the subspace spanned by the orthonormal basis \( \{2I_zS_y, 2I_zS_x, 2I_zS_z\} \) and \( i \) denote the subspace spanned by the orthonormal basis \( \{I_x, I_y, I_z\} \). We represent the starting operator \( \sigma(0) \) and the target operator \( F^\dagger \) as a column vector \( p = [1,0,0]^T \) in \( s \) and \( i \), respectively. All the theorems and lemmas are referred to Reiss et al. (Reiss et al., 2002).

We prove that the Eq. (1S) is applicable individually for \( 2I_zS_i \to I_j \), \( 2I_yS_i \to I_j \), \( 2I_xS_i \to I_j \) transfers, where \( i,j = x,y,z \), which enables generalization to the \( 2I_kS_i \to I_j \) transfer, where \( k,i,j = x,y,z \). Let \( L(a_1,a_2,a_3) = \exp[-i\frac{\pi}{2}J_{\text{IS}}(a_1I_xS_x + a_2I_yS_y + a_3I_zS_z)] \), which will be simplified to \( L \). From Theorem 2 any experimentally achievable unitary propagator can be represented by the product \( U_F = Q_1LQ_2 \), where \( Q_{1,2} \) represent arbitrary unitary transformations by rf-hamiltonians. Using circular permutation rule under trace operator Eq. (3S) can be rewritten as

\[
b_{\text{theo}}(t) = \| \text{Tr}[Q_1^\dagger F^\dagger Q_1 L Q_2 \sigma(0) Q_2^\dagger L^\dagger] \|. \quad (2S)
\]

It’s sufficient to restrict \( Q_1 \) to operators acting in \( i \) subspace (since \( F \) commutes with the spin \( S \) operators) and \( Q_2 \) to operators acting in \( s \) subspace (since we consider three subspaces \( s \) spawned by the \( I_zS_i, I_yS_i \) and \( I_xS_i \) operators, \( i = x,y,z \), individually). The action \( \sigma(0) \to Q_2 \sigma(0) Q_2^\dagger \) can then be represented as \( p \to Vp \), where \( V \) is a orthogonal matrix.

Let \( P_i \) denote the projection on the subspace \( i \) yielding:
\[ P(L 2I_x S_i L^\dagger) = \cos(\pi J_{IS} a_3)\sin(\pi J_{IS} a_2) I_y, \]
\[ P(L 2I_y S_i L^\dagger) = -\cos(\pi J_{IS} a_3)\sin(\pi J_{IS} a_1) I_x, \]
\[ P(L 2I_z S_i L^\dagger) = 0 I_z. \]

The action \( \sigma(0) \rightarrow P_1 [ L Q_2 \sigma(0) Q_2^\dagger L^\dagger ] \) can then be represented as \( p \rightarrow \Sigma Vp \), where \( \Sigma \) is a square diagonal matrix, \( \Sigma = \text{diag}(\cos(\pi J_{IS} a_3)\sin(\pi J_{IS} a_2), \cos(\pi J_{IS} a_3)\sin(\pi J_{IS} a_1), 0) \).

Therefore Eq. (2S) can be rewritten as

\[ b_{\text{theo}}(t) = \|p^\dagger K^\dagger \Sigma Vp\| \quad (3S) \]

where \( K \) and \( V \) are real orthogonal matrices and the negative sign of the second projection is absorbed into \( K \) or \( V \) matrices. We can select \( a_{1,2,3} \) such that \( \cos(\pi J_{IS} a_3)\sin(\pi J_{IS} a_2) \geq \cos(\pi J_{IS} a_3)\sin(\pi J_{IS} a_1) \geq 0 \). As a consequence of Lemma 1 the maximum of Eq. (3S) is \( |\cos(\pi J_{IS} a_3)\sin(\pi J_{IS} a_2)| \). From the property of the sine and cosine functions it can be seen that we maximize the above expression if \( |a_i| \leq 1/(2J_{IS}) \), \( i = 1, 2 \). In that case we have to maximize \( f(a_1, a_2, a_3) = \cos(\pi J_{IS} a_3)\sin(\pi J_{IS} a_2) \) under a restraint that \( a_1 + a_2 + a_3 = T \), where \( T \) is the maximal time available for the evolution of the IS spin system. By setting \( a_1 = a_3 = 0 \) and \( a_2 = T \) we obtain the Eq. (1S). For \( t = 1/(2J_{IS}) \) the maximum achievable transfer is one. Because \( \sigma(0) \) and \( F \) are normalized, this is the maximum possible transfer between these operators. For \( t > 1/(2J_{IS}) \) the extra time can be spent by evolution under the refocusing pulse resulting in the same maximum transfer amplitude. The same maximum efficiency is achieved for \( 2I_x S_i \rightarrow I_j \) and \( 2I_y S_i \rightarrow I_j \) transfers, thus completing the proof.
Figure S1 Contour plots of \([\textsuperscript{15}N,\textsuperscript{1}H]-\text{COCAINE}\) of uniformly \(\textsuperscript{15}N\)-labeled ubiquitin in 95\% H\(_2\)O/5\% D\(_2\)O at 25 °C, pH = 7.3, measured at the \(\textsuperscript{1}H\) frequency of 600 MHz. Water magnetization is suppressed by a WATERGATE sequence (Piotto et al., 1992) before the acquisition. (A) In-phase and (B) antiphase doublet components of the COCAINE spectrum were obtained using the experimental scheme in Fig. 1. (C) Downfield and (D) upfield doublet components of the COCAINE spectrum were obtained by (C) adding and (D) subtracting the in-phase and antiphase spectra, respectively. Note that downfield component spectra need to be transposed along \(\textsuperscript{15}N\) dimension due to the negative and positive \(\textsuperscript{15}N\) frequency encoded on the downfield and upfield \(\textsuperscript{1}H\) doublet components, respectively. Solid and dotted contours represent positive and negative intensities, respectively. The residue are also given by numbers and the downfield component of doublets are marked with *. 
Spectral representation of the signals in \[\text{\textsuperscript{13}C,\textsuperscript{13}C}\]-COSY:

For the generic three linearly coupled spin system C1\text{--}C2 (highlighted in bold is the spin which chemical shift is detected):

\[
\text{Signal}_{C1C2}(\omega_{C1}, J_{C1C2}) = \\
(4 \exp(-i\omega/J_{C1C2}) \pi^2 J_{C1C2}^2 ((\exp(i\omega/J_{C1C2}) - \cos(\omega_{C1}/J_{C1C2})) (3\omega^2 - 4\pi^2 J_{C1C2} + \omega_{C1}^2) \omega_{C1} - \\
i\omega \sin(\omega_{C1}/J_{C1C2}) (\omega^2 - 4\pi^2 J_{C1C2} + 3 \omega_{C1}^2)) / ((\omega^2 - \omega_{C1}^2)((\omega^2 - 4\pi^2 J_{C1C2}^2)^2 - 2 (\omega^2 + \\
4\pi^2 J_{C1C2}^2 \omega_{C1}^2 + \omega_{C1}^4)))
\]

(4.1S)

For the generic three linearly coupled spin system C1\text{--}C2\text{--}C3 with $\kappa = J_{C2C3}/J_{C1C2}$.

\[
\text{Signal}_{C1C2C3}(\omega_{C2}, J_{C2C3}, \kappa) = \\
(2 \exp(-i\omega/J_{C1C2}) \pi J_{C1C2} (\omega^6 \sin(\pi \kappa) \sin(\omega_{C2}/J_{C1C2}) - 2 \exp(i\omega/J_{C1C2}) \pi \kappa J_{C1C2} \omega_{C2} (-3\omega^4 + \pi^4 (-4 + \kappa^2) J_{C1C2}^4 + 2\omega^2 \omega_{C2}^2 + \omega_{C2}^4 + 2\pi^2 (4 + \kappa^2) J_{C1C2}^2 (\omega^2 - \omega_{C2}^2)) + 2 \cos(\omega_{C2}/J_{C1C2}) \omega_{C2} (\pi \kappa \cos(\pi \kappa)) \\
(\kappa^2 - \pi^4 (-4 + \kappa^2) J_{C1C2}^4 + 2\omega^2 \omega_{C2}^2 + \omega_{C2}^4 + 2\pi^2 (4 + \kappa^2) J_{C1C2}^2 (\omega^2 - \omega_{C2}^2)) - i\omega \sin(\pi \kappa) \\
(-\pi^4 (-4 + \kappa^2) J_{C1C2}^4 + (\omega^2 - \omega_{C2}^2)^2 + 2\pi^2 (-4 + \kappa^2) J_{C1C2}^2 (\omega^2 + \omega_{C2}^2)) + \\
\sin(\omega_{C2}/J_{C1C2}) (-2i \pi \kappa \omega \cos(\pi \kappa) J_{C1C2} (\omega^4 + \pi^4 (-4 + \kappa^2) J_{C1C2}^4 + 2\omega^2 \omega_{C2}^2 - 3 \omega_{C2}^4 + \\
2\pi^2 (4 + \kappa^2) J_{C1C2}^2 (\omega^2 - \omega_{C2}^2)) + \sin(\pi \kappa) (\pi^6 (-4 + \kappa^2) J_{C1C2}^6 \omega^4 \omega_{C2}^2 - \omega_{C2}^2 + \omega_{C2}^4 + \omega_{C2}^6 \\
- \pi^4 (-48 + 8 \kappa^2 + \kappa^4) J_{C1C2}^4 (\omega^2 + \omega_{C2}^2)) + \pi^2 J_{C1C2}^2 (-12 + \kappa^2) \omega^4 + 2 (-4 + 5 \kappa^2) \omega^2 \\
\omega_{C2}^2 - (12 + \kappa^2) \omega_{C2}^2)))) / ((\omega - \pi (-2 + \kappa) J_{C1C2} - \omega_{C2}) (\omega + \pi (-2 + \kappa) J_{C1C2} - \omega_{C2}) (\omega \\
- \pi (2 + \kappa) J_{C1C2} - \omega_{C2}) (\omega - \pi (-2 + \kappa) J_{C1C2} + \omega_{C2}) (\omega + \pi (-2 + \kappa) J_{C1C2} + \omega_{C2}) (\omega \\
+ \pi (2 + \kappa) J_{C1C2} + \omega_{C2}) (\omega^2 - (-\pi (2 + \kappa) J_{C1C2} + \omega_{C2})^2))
\]

(4.2S)
Thus, for the $\text{C'} \rightarrow \text{C}^{\alpha}$ and $\text{C}^{\alpha} \rightarrow \text{C}^{\beta}$ magnetization pathways the amplitudes of the corresponding cross-peak in the absolute value spectrum are given by Eq. (5.1S) and Eq. (5.2S), respectively.

$$\text{Signal}_{\text{C'} \rightarrow \text{C}^{\alpha}}(\omega_{\text{C}}, \omega_{\text{C}^{\alpha}}) = \text{Signal}_{\text{C}^{\alpha} \rightarrow \text{C}^{\beta}}(\omega_{\text{C}}, J_{\text{C}^{\alpha} \text{C}^{\alpha}})^*$$

$$\text{Signal}_{\text{C}^{\alpha} \rightarrow \text{C}^{\beta}}(\omega_{\text{C}^{\alpha}}, \omega_{\text{C}^{\beta}}) = \text{Signal}_{\text{C}^{\alpha} \rightarrow \text{C}^{\beta}}(\omega_{\text{C}^{\beta}}, J_{\text{C}^{\alpha} \text{C}^{\alpha}}, \kappa = J_{\text{C}^{\alpha} \text{C}^{\beta}} / J_{\text{C}^{\alpha} \text{C}^{\beta}})$$

Reference