Supporting Information for ‘Inversion of Hyperpolarized $^{13}$C NMRSignals Through Cross-Correlated Cross-Relaxation in Dissolution DNP Experiments’

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Figure S1. Simulations of methyl group relaxation starting from -1:-0.01:3 ($^1$H:$^13$C:Z:A-E) order for individual carbon transitions. As indicated in each panel, different relaxation mechanisms were neglected in the simulations. Obviously, a lack of DD relaxation leads to only very weak transfer from the $^1$H nuclei to the $^{13}$C nucleus.

Figure S2. Influence of the A-E imbalance on the $^1$H-$^{13}$C CCR starting from -1:-0.01:x ($^1$H:$^{13}$C:Z:A-E), the value for x is shown at the top of each panel.
Figure S3. Representation of the polarization used to simulate the methyl $^{13}$C time traces in the main text.

Figure S4. Simulated methyl $^1$H longitudinal relaxation time at various magnetic fields switches starting from 6.7 T and considering DD, CSA, DDCSA and rnd mechanisms, but no paramagnetic relaxation enhancement.

Simulations of CH$_3$ and CH$_2$ Relaxation.

The signal evolutions (main text Fig. 3 and 4, SI Fig. S1 and S2) were simulated using a modified version of SpinDynamica notebook of reference 1 and runs with Mathematica 12.0 and SpinDynamica 3.5.0.

The relaxation superoperator $\Gamma$ was generated using Redfield’s theory of relaxation by dipolar coupling (DD), chemical shift anisotropy (CSA) and random field fluctuations (rnd):

$$\Gamma = \Gamma_{DD} - DD + \Gamma_{CSA} - CSA + \Gamma_{DD} - CSA + \Gamma_{rnd} - rnd$$  \hspace{1cm} (S1)

For the first three terms we modeled the systems as rigid rotors using the following formula:
\[ \Gamma_{\ldots} = \sum_{\iota} \xi_{\iota} \xi_{\iota} \sum_{m} = -\frac{\tau_{\ldots}}{2\tau_{\ldots} + m^2 \tau_{\ldots}} D_{0,m}(\Omega_{\ldots}) D_{0,m}(\Omega_{\ldots}) \sum_{m} = -2 (-1)^m \left[ T_{\ldots}^{m}, T_{\ldots}^{m} \right] \]  

(S2)

Where \( \iota \) and \( \iota' \) indices refer either to the atoms involved in case of CSA, or the pair of atoms in case of DD interaction, \( \tau_{\ldots} \) is the correlation time, \( \tau_{\ldots} \) is the rotation time, \( D_{0,m}(\Omega_{\ldots}) \) are the angle between the interaction and the molecular frame, \( T_{\ldots}^{m} \) are the irreducible spherical tensors, and \( \xi_{\iota} \) are the interaction coefficients. Note that the DD-CSA term in eq. S1 accounts for DD-CSA cross-correlated cross relaxation, while the DD-DD and CSA-CSA terms account for both cross-correlated as well as auto-relaxation.

The term accounting for random field fluctuations is given by:

\[ \Gamma_{\ldots} - \Gamma_{\ldots} = \sum_{\iota} -B_{\iota} B_{\iota} \tau_{\ldots} \sum_{m} = -1 (-1)^m \left[ T_{\ldots}^{m}, T_{\ldots}^{m} \right] \]  

(S3)

Where \( B_{\iota} \) indicates the statistical random field fluctuation at the position of the spin. We considered all the fluctuation correlated for each couple \( \iota, \iota' \). We considered a fluctuation of 30000\( \pi \) 1/s for the proton and 22000\( \pi \) 1/s for carbons.

The relaxation behavior of the spin system was then computed by solving the master equation in Liouville space (see Bengs et al.):

\[ \frac{d}{dt} \rho(t) = \mathcal{L}(t) \rho(t) \]

Where \( \rho \) is the density matrix and \( \mathcal{L} \) the Liouvillian.

The time traces of Fig. S2 were calculated by selectively removing a term from eq. S1.

The simulation parameter used are:

|    | \( \tau_{\ldots} \) | \( \tau_{\ldots} \) | \( \delta \) CSA \( ^1H \) | \( \delta \) CSA \( ^13C \) |
|----|-----------------|-----------------|------------------|------------------|
| CH3 | 14 ps           | 1.4 ps          | 5 ppm            | 34 ppm           |
| CH2 | 5.0 ps          | 2.0 ps          | 6 ppm            | 60 ppm           |

where \( \delta \) is the anisotropy parameter according to the Haeberlen-Mehring-Spiess formalism. To solve the master equation, the relaxation superoperator was combined with a time-independent Hamiltonian to create the Liouville superoperator, as suggested by Dumez et al. Dipolar interactions were calculated using a CH bond length of 110 pm and assuming tetrahedral configurations around the central carbons. All further details can be found in the commented simulation codes below.

### SpinDynamica Code for CH3 group

This code was adapted from Dumez et al. Details about the spin physics behind the simulations can be found therein and in the associated Supporting Information. For the code used here, comments are shown in green, headlines in blue. The comments and headlines guide the reader step-by-step through the code.

Needs["SpinDynamica"]
Setting System
SetSpinSystem[{{1,1/2},{2,1/2},{3,1/2},{4,1/2}}]; (* 4 Spin \(\frac{1}{2}\) particles *)
IsotopicType[1|2|3] = 1; (* 3 Protons *)
IsotopicType[4] = 13; (* 1 Carbon nucleus *)

Geometry
rCH = 1 1.1 10^-10; (* CH bond length in m *)
aCH = 1*70.5Degree; (* CH bind angle time 0.5 *)
hCH = rCH*Cos[aCH];
hHH = 3/2 Sqrt[rCH^2-hCH^2];
rHH = hHH/Sin[60 Degree];
coordinates = {{-(1/3)hHH,1/2 rHH,hCH},{-(1/3)hHH,-(1/2)rHH,hCH},{2/3 hHH,0,hCH},{0,0,0}}; (* atom coordiantes *)
RR[j_,k_]:=Distance[coordinates[[j]],coordinates[[k]]] (* atom-to-atom distances *)

Hamiltonian
Hparams := {ωCSH->2 Pi 0,ωCSC->2 Pi 0,JCH-> 127,JHH-> 0} (* Hamiltonian parameters, rotating frame Larmor frequencies and J-coupling constants *)
HCS = ωCSH Sum[opI[i,"z"],{i,1,3}]+ωCSC opI[4,"z"]; (* nuclear Zeeman *)
HJCH = 2 Pi JCH opI[4,"z"]. opI[{1,2,3},"z"]; (* CH J-coupling *)
HJHH = 2 Pi JHH opI[1].opI[2]+opI[1].opI[3]+opI[2].opI[3]; (* HH J-coupling *)
H = HCS+HJCH+HJHH; (* total Hamiltonian *)

Basis Set
SetBasis[ZeemanBasis[]];
A symmetry basis Kets (* Setup Basis Kets in the symmetrized Basis, irreducible representation A *)
KetsAα={BasisKets[][[1]],Sqrt[1/3](BasisKets[][[2]]+BasisKets[][[3]]+BasisKets[][[5]]),Sqrt[1/3](BasisKets[][[7]]+BasisKets[][[6]]+BasisKets[][[4]]),BasisKets[][[8]]};
KetsAβ={BasisKets[][[9]],Sqrt[1/3](BasisKets[][[10]]+BasisKets[][[11]]+BasisKets[][[13]]),Sqrt[1/3](BasisKets[][[15]]+BasisKets[][[14]]+BasisKets[][[12]]),BasisKets[][[16]]};

E symmetry basis Kets (* Setup Basis Kets in the symmetrized Basis, irreducible representation E *)
KetsEα={Sqrt[1/3](BasisKets[][[2]]+Exp[I 2π/3]BasisKets[][[1]]+Exp[-I 2π/3]BasisKets[][[3]]),Sqrt[1/3](BasisKets[][[4]]+Exp[-I 2π/3]BasisKets[][[7]]+Exp[I 2π/3]BasisKets[][[6]]),Sqrt[1/3](BasisKets[][[13]]+Exp[-I 2π/3]BasisKets[][[10]]+Exp[I 2π/3]BasisKets[][[11]]),Sqrt[1/3](BasisKets[][[5]]+Exp[I 2π/3]BasisKets[][[2]]+Exp[-I 2π/3]BasisKets[][[3]]),Sqrt[1/3](BasisKets[][[4]]+Exp[I 2π/3]BasisKets[][[7]]+Exp[-I 2π/3]BasisKets[][[6]]),Sqrt[1/3](BasisKets[][[13]]+Exp[I 2π/3]BasisKets[][[10]]+Exp[-I 2π/3]BasisKets[][[11]]),Sqrt[1/3](BasisKets[][[5]]+Exp[-I 2π/3]BasisKets[][[2]]+Exp[I 2π/3]BasisKets[][[3]]),Sqrt[1/3](BasisKets[][[15]]+BasisKets[][[14]]+BasisKets[][[12]]),BasisKets[][[16]]};
Symmetrized basis Kets (* Combine A and E *)
SymmetrizedBasisKets=Join[KetsAα,KetsAβ,KetsEα,KetsEβ,KetsEβ];
DefineBasis[SymmetrizedBasis, SymmetrizedBasisKets, CheckBasis -> True];

Relaxation Superoperator
SetOperatorBasis[ShiftAndZOperatorBasis[]]

Interactions
\( \omega_0H = \text{LarmorFrequency}[1, B_0]; \) (* compute proton Larmor Frequency *)
\( \omega_0C=\text{LarmorFrequency}[13, B_0]; \) (* compute carbon Larmor Frequency *)
\( \omega_{DD}[i,j] := \text{DirectDipolarCoupling}[\text{IsotopicType}[i], \text{IsotopicType}[j], RR[i,j]]; \) (* Dipolar Coupling *)
\( \Omega_{DDPR}[i,j] := \text{AxesToEuler}[	ext{AxisSystem}[\text{coordinates}[[i]]], \text{AxisSystem}[-ez]]; \) (* Angles for Wigner Matrix *)
\( \omega_{CSA}[i] := \text{LarmorFrequency}[	ext{IsotopicType}[i], B_0] \times \text{CSA}[i] 10^{-6}; \) (* CSA contribution *)
\( \Omega_{CSAPR}[4] := \{0, 0, 0\}; \) (* Coordinate system centered around 13C *)
\( \Omega_{CSAPR}[i] := \Omega_{DDPR}[i, 4]; \)

DD relaxation
\( \Gamma_{DD}[i,j,k,l] := \frac{6}{5} \omega_{DD}[i,j] \omega_{DD}[k,l] \left( \sum (\tau_C \tau_R)/(\tau_R + m_1^2 \tau_C) \right) \)
\( \text{WignerD}[2,0,m_1][\Omega_{DDPR}[i,j]] \text{Conjugate}[\text{WignerD}[2,0,m_1][\Omega_{DDPR}[k,l]], \{m_1,-2,2\}] \sum (-1)^m \text{DoubleCommutationSuperoperator}[\text{opT}[i,j,k,l], \text{opT}[i,j,-k,-l]] \) (* Solving the double commutator formalism *)
\( \Gamma_{DD} = \text{Superoperator}[\sum \Gamma_{DD}[i,j,k,l]]; \) (* Sum up relaxation superoperator for dipolar relaxation *)

CSA relaxation
\( \text{constCSA} = \sqrt{3/8}; \)
\( \text{opTC}[i,m] := \text{NullOperator}[]; \)
\( \text{opTC}[i,0] := \text{Sqrt}[8/3] \text{opI}[i, "z"]; \) (* Iz operators *)
\( \text{opTC}[i,1] := \text{opI}[i, "+"]; \) (* positive ladder operators *)
\( \text{opTC}[i,-1] := \text{opI}[i, "-"]; \) (* negative ladder operators *)
\( \Gamma_{CSA}[i,k,l] := (-1/5) \text{constCSA}^2 \omega_{CSA}[i] \omega_{CSA}[k,l] \left( \sum (\tau_C \tau_R)/(\tau_R + m_1^2 \tau_C) \right) \)
\( \text{WignerD}[2,0,m_1][\text{CSAPR}[i]] \text{Conjugate}[\text{WignerD}[2,0,m_1][\text{CSAPR}[k,l]], \{m_1,-2,2\}] \sum (-1)^m \text{DoubleCommutationSuperoperator}[\text{opTC}[i,m], \text{opTC}[k,l], \text{opTC}[k,m], \{m,-1,1\}] \) (* Solving the double commutator formalism *)
\( \Gamma_{CSA} = \text{Superoperator}[\sum \Gamma_{CSA}[i,j,k,l]]; \) (* Sum up relaxation superoperator for CSA relaxation *)
**DD/CSA relaxation**

\[ \Gamma_{DDCSA}(i,j,k) := -\frac{(\text{const}_{CSA}\sqrt{6})}{5}\omega_{DD}(i,j)\omega_{CSA}(k)\sum\left(\frac{\tau_C\tau_R}{\tau_R + m_1^2\tau_C}\right) WignerD(2,0,m_1)[\Omega_{DDP}(i,j)]\text{Conjugate}[WignerD(2,0,m_1)[\Omega_{CSAP}(k)],\{m_1,-2,2\}]\sum(-1)^m\text{DoubleCommutationSuperoperator}[opT[i,j,m],opTCSA[k,-m]] + \sum(-1)^m\text{DoubleCommutationSuperoperator}[opTCSA[k,m],opT[i,j,2-m]],\{m,-1,1\}]\]  (* Solving the double commutator formalism *)

\[ \Gamma_{DDCSA} = \text{Superoperator}\left[\sum\Gamma_{DDCSA}(i,j,k),\{i,1,3\},\{j,i+1,4\},\{k,1,4\}\right]; \]  (* Sum up relaxation superoperator for DD/CSA relaxation *)

**Correlated random-field relaxation**

\[ \Gamma_{rand}(i,j) := -\tau_C\text{Br}(i)\text{Br}(j)\sum(-1)^m\text{DoubleCommutationSuperoperator}[opT[i,1,m],opT[j,1,-m]],\{m,-1,1\}]\]  (* Solving the double commutator formalism *)

\[ \Gamma_{rand} = \text{Superoperator}\left[\sum\Gamma_{rand}(i,j),\{i,1,4\},\{j,1,4\}\right]; \]  (* Sum up relaxation superoperator for random field relaxation *)

**Total relaxation superoperator**

\[ \Gamma_{tot} = \text{Superoperator}\left[\Gamma_{DD}+\Gamma_{DDCSA}+\Gamma_{CSA}+\Gamma_{rand}\right]; \]  (* sum up total relaxation superoperator *)

\[ \Gamma_{totsec} = \text{Secularize}[\Gamma_{tot},\{\{1,2,3\},\{4\}\}]; \]  (* secularize relaxation superoperator *)

**Initial state and observables**

**A initial state**

\[ \text{SpinThreeHalvesInitialState} = \text{Operator}[\text{SparseArray}@\text{DiagonalMatrix}[\text{Join}[\text{Table}[1/8,\{8\}],\text{Table}[0,\{8\}]]],\text{SymmetrizedBasis}]; \]  (* spin state for a “perfect” A-E imbalance with overpopulated A states *)

**Single-transition operators, 13C**

\[ \text{opSTA1z} = \text{SingleTransitionOperator}[[\{1,5\}d,\text{SymmetrizedBasis}]]; \]  (* compute single transition operator between levels 1 and 5 in the symmetrized basis, see above *)

\[ \text{opSTA2z} = \text{SingleTransitionOperator}[[\{2,6\},\text{SymmetrizedBasis}]]; \]

\[ \text{opSTA3z} = \text{SingleTransitionOperator}[[\{3,7\},\text{SymmetrizedBasis}]]; \]

\[ \text{opSTA4z} = \text{SingleTransitionOperator}[[\{4,8\},\text{SymmetrizedBasis}]]; \]

\[ \text{opSTEa1z} = \text{SingleTransitionOperator}[[\{9,11\},\text{SymmetrizedBasis}]]; \]

\[ \text{opSTEa2z} = \text{SingleTransitionOperator}[[\{10,12\},\text{SymmetrizedBasis}]]; \]

\[ \text{opSTeb1z} = \text{SingleTransitionOperator}[[\{13,15\},\text{SymmetrizedBasis}]]; \]

\[ \text{opSTeb2z} = \text{SingleTransitionOperator}[[\{14,16\},\text{SymmetrizedBasis}]]; \]

**Single-transition operators, 1H**

\[ \text{opST1H1} = \text{opT}[[\{1,2,3\}]]; \]

\[ \text{opST1H2} = \text{opT}[[\{1,2,3\}]]; \]
Trajectories

peak1op = opSTA1z; (* Observable for peak 1 of the methyl quartet *)
peak2op=1/3 (opSTA2z+opSTea1z+opSTeb1z); (* Observable for peak 2 of the methyl quartet *)
peak3op=1/3 (opSTA3z+opSTea2z+opSTeb2z); (* Observable for peak 3 of the methyl quartet *)
peak4op=opSTA4z; (* Observable for peak 4 of the methyl quartet *)
relaxparams ={τC-> 1.4 10^-11, τR-> 0.14 10^-11, B0->11,7, δCSA[1|2|3]->5, δCSA[4]->34, BrH-> 2 Pi 15 10^3, BrC-> 2 Pi 11 10^3, κHH-> 1, κCH-> 1}; (* relaxation parameters for all four mechanisms *)
Lsop=CombineGenerators[Γtotsec/.relaxparams, H/.Hparams]; (* combine Hamiltonian and relaxation superoperator to create the Liouvillian *)
dLsop2 = NDiagonalize[Lsop]; (* diagonalize Liouvillian *)

{peak1fun,peak2fun,peak3fun,peak4fun,ST1H1fun,ST2H2fun}=Trajectory[SpinThreeHalvesInitialState +op[1,"z"]+op[2,"z"]+op[3,"z"]+0.01*op[4,"z"])->
{peak1op,peak2op,peak3op,peak4op,opST1H1,opST1H2},{dLsop2,4000}]; (* Compute evolution of the spin system using the SpinDynamica routine *)

13C plot

Plot[{10Re@peak1fun[t],10Re@peak2fun[t],10Re@peak3fun[t],10Re@peak4fun[t]},{t,0,400},PlotRange->Full] (* now plot *)

1H plot

Plot[{Re@ST1H1fun[t],Re@ST2H2fun[t]},{t,0,400},PlotRange->Full] (* now plot *)

Spin Dynamica Code for CH2 group

Needs["SpinDynamica"]

Setting System

SetSpinSystem[{{1,1/2},{2,1/2},{3,1/2}}]; (* 3 Spin ½ particles *)
IsotopicType[1|2] = 1; (* 2 Protons *)
IsotopicType[3] = 13; (* 1 Carbon nucleus *)

Geometry

rCH = 1.1 10^-10; (* CH bond length in m *)
aCH = 1*70.5Degree; (* CH bind angle time 0.5 *)
coordinates = {{rCH Cos[aCH],rCH Sin[aCH],0},{rCH Cos[aCH],-rCH Sin[aCH],0},{0,0,0}}; (* atom coordinate *)
RR[j_,k_,]:=Distance[coordinates[[j]],coordinates[[k]]] (* atom-to-atom distances *)
Hamiltonian

\[ H_{\text{params}} = \{\omega_{CSH} \rightarrow 2\, \text{Pi} 0, \omega_{CSC} \rightarrow 2\, \text{Pi} 0, J_{CH} \rightarrow 127, J_{HH} \rightarrow 0\} \] (* Hamiltonian parameters, rotating frame Larmor frequencies and J-coupling constants *)

\[ H_{CS} = \omega_{CSH} \sum_{i \in \{1,2\}} opl[i, "z"] + \omega_{CSC} opl[3, "z"] \] (* nuclear Zeeman *)

\[ H_{JCH} = 2\, \text{Pi} \, J_{CH} \, opl[3, "z"] \, opl[\{1,2\}, "z"] \] (* CH J-coupling *)

\[ H_{JHH} = 2\, \text{Pi} \, J_{HH} \, (opl[1] \cdot opl[2]) \] (* HH J-coupling *)

\[ H = H_{CS} + H_{JCH} + H_{JHH} \] (* total Hamiltonian *)

Basis Set

SetBasis[ZeemanBasis[]];

T basis Kets (* Setup Basis Kets in the symmetrized Basis, triplet states *)

\[ \text{Kets}_{T\alpha} = \{\text{BasisKets}[[1]], \sqrt{1/2}(\text{BasisKets}[[3]] + \text{BasisKets}[[2]]), \text{BasisKets}[[4]]\} \]

\[ \text{Kets}_{T\beta} = \{\text{BasisKets}[[5]], \sqrt{1/2}(\text{BasisKets}[[7]] + \text{BasisKets}[[6]]), \text{BasisKets}[[8]]\} \]

S basis Kets (* Setup Basis Kets in the symmetrized Basis, singlet states *)

\[ \text{Kets}_{S\alpha} = \{\sqrt{1/2}(\text{BasisKets}[[3]] - \text{BasisKets}[[2]]\} \]

\[ \text{Kets}_{S\beta} = \{\sqrt{1/2}(\text{BasisKets}[[7]] - \text{BasisKets}[[6]]\} \]

Symmetrized basis Kets

SymmetrizedBasisKets = Join[\text{Kets}_{T\alpha}, \text{Kets}_{T\beta}, \text{Kets}_{S\alpha}, \text{Kets}_{S\beta}]; (* Combine T and S *)

Relaxation Superoperator

SetOperatorBasis[ShiftAndZOperatorBasis[]]

Interactions

\[ \omega_{OH} = \text{LarmorFrequency}[1, B0]; \] (* compute proton Larmor Frequency *)

\[ \omega_{OC} = \text{LarmorFrequency}[13, B0]; \] (* compute carbon Larmor Frequency *)

\[ \omega_{DD}[i, j] = \text{DirectDipolarCoupling}[\text{IsotopicType}[i], \text{IsotopicType}[j], \text{RR}[i, j]]; \] (* Dipolar Coupling *)

\[ \Omega_{DDPR}[i, k] = \text{AxesToEuler}[\text{AxisSystem}[\text{coordinates}[k] - \text{coordinates}[i]], \text{AxisSystem}[\text{-ez}]]; \] (* Angles for Wigner Matrix *)

\[ \omega_{CSA}[i] = \text{LarmorFrequency}[\text{IsotopicType}[i], B0] \times 10^{-6}; \] (* CSA contribution *)

\[ \Omega_{CSAPR}[3] = \{0, 0, 0\}; \] (* Coordinate system centered around 13C *)

\[ \Omega_{CSAPR}[i] = \Omega_{DDPR}[i, 3]; \]

DD relaxation

\[ \Gamma_{DDterm}(i, j | k, l) = -(6/5)\omega_{DD}[i, j] \, \omega_{DD}[k, l] \, \text{Sum}[\{\tau_C \, \tau_R \, \tau_R + m1^2 \, \tau_C\} / \text{WignerD}[2, 0, m1] \, \text{WignerD}[2, 0, m1] \, \text{Conjugate}[\text{WignerD}[2, 0, m1] \, \text{WignerD}[k, l)]] \, \text{Sum}[\{-1 \}^m \text{DoubleCommutationSuperoperator}[\text{opT}[i, j, [2, m]], \text{opT}[k, l, [2, -m]]] \, \text{opT}[i, j, [2, -m]]] \] (* Solving the double commutator formalism *)
\[ \Gamma_{DD} = \text{Superoperator}[\text{Sum}[\Gamma_{DDterm}[i,j],[k,l]],\{i,1,2\},\{j,i+1,3\},\{k,1,2\},\{l,k+1,3\}] ; \] (* Sum up relaxation superoperator for dipolar relaxation *)

**CSA relaxation**

\[
\begin{align*}
\text{constCSA} &= \sqrt{\frac{3}{8}}; \\
\text{opTCSA}[i_,m_] &= \text{NullOperator}[]; \\
\text{opTCSA}[i_,0] &= \sqrt{\frac{8}{3}}\text{opI}[i,"z"]; \quad (* Iz operators *) \\
\text{opTCSA}[i_,1] &= -\text{opI}[i,"+"]; \quad (* positive ladder operators *) \\
\text{opTCSA}[i_,-1] &= \text{opI}[i,"-"]; \quad (* negative ladder operators *) \\
\Gamma_{CSAterm}[i_,k_] &= -(1/5) \text{constCSA}^2 \omega_{CSA}[i] \omega_{CSA}[k] \left[ \text{Sum}[\tau_C \tau_R, \tau_R + m_1^2 \tau_C] \right] \\
&\quad \times \text{WignerD}[2,\{0,m_1\}] \text{Conjugate}[\text{WignerD}[2,\{0,m_1\}]], \{m_1,-2,2\}] \text{Sum}[-1]^m \text{DoubleCommutationSuperoperator}[\text{opTCSA}[i,m],\text{opTCSA}[k,-m]],\{m,-1,1\}] \right) ; \quad (* Solving the double commutator formalism *) \\
\Gamma_{CSA} &= \text{Superoperator}[\text{Sum}[\Gamma_{CSAterm}[i,j],[i,1,3],[j,1,3]]] ; \quad (* Sum up relaxation superoperator for CSA relaxation *) \\
\end{align*}
\]

**DD/CSA relaxation**

\[
\begin{align*}
\Gamma_{DDCSAterm}[i_,j_,k_] &= -(1/5) \text{constCSA}^2 \omega_{CSA}[i] \omega_{CSA}[k] \left[ \text{Sum}[\tau_C \tau_R, \tau_R + m_1^2 \tau_C] \right] \\
&\quad \times \text{WignerD}[2,\{0,m_1\}] \text{Conjugate}[\text{WignerD}[2,\{0,m_1\}]], \{m_1,-2,2\}] \text{Sum}[-1]^m \text{DoubleCommutationSuperoperator}[\text{opT}[i,j],[2,m]],\text{opTCSA}[k,-m]],\{m,-1,1\}] + \text{Sum}[\tau_C \tau_R, \tau_R + m_1^2 \tau_C] \right] \\
&\quad \times \text{WignerD}[2,\{0,m_1\}] \text{Conjugate}[\text{WignerD}[2,\{0,m_1\}]], \{m_1,-2,2\}] \text{Sum}[-1]^m \text{DoubleCommutationSuperoperator}[\text{opTCSA}[k,m],\text{opT}[i,j],[2,-m]],\{m,-1,1\}] \right) \right) ; \quad (* Solving the double commutator formalism *) \\
\Gamma_{DDCSA} &= \text{Superoperator}[\text{Sum}[\Gamma_{DDCSAterm}[i,j],[i,1,2],[j,i+1,3],[k,1,3]]] ; \quad (* Sum up relaxation superoperator for DD/CSA relaxation *) \\
\end{align*}
\]

**Correlated random-field relaxation**

\[
\begin{align*}
\text{Br}[1|2] &= \text{BrH} ; \quad (* random field fluctuations experiences by protons *) \\
\text{Br}[3] &= \text{BrC} ; \quad (* random field fluctuations experiences by the carbon nucleus *) \\
\Gamma_{randterm}[i_,j_] &= \tau_C \text{Br}[i] \text{Br}[j] \text{Sum}[-1]^m \text{DoubleCommutationSuperoperator}[\text{opT}[i,\{1,m\}],\text{opT}[j,\{1,-m\}],\{m,-1,1\}] ; \quad (* Solving the double commutator formalism *) \\
\Gamma_{rand} &= \text{Superoperator}[\text{Sum}[\Gamma_{randterm}[i,j],[i,1,2],[j,i+1,3],[k,1,3]]] ; (* Sum up relaxation superoperator for random field relaxation *) \\
\end{align*}
\]

**Total relaxation superoperator**

\[
\Gamma_{tot} = \text{Superoperator}[\Gamma_{DD} + \Gamma_{DDCSA} + \Gamma_{CSA} + \Gamma_{rand}] ; \quad (* sum up total relaxation superoperator *) \\
\Gamma_{totsec} &= \text{Secularize}[\Gamma_{tot},\{(1,2),\{3\}\}] ; \quad (* secularize relaxation superoperator *) \\
\]

**Initial state and observables**
T initial state
SpinInitialState = Operator[SparseArray@DiagonalMatrix[Join[Table[1/6, {6}], Table[0, {2}]]], Symmetrize dBasis]; (* spin state for a “perfect” T-S imbalance with overpopulated T states *)

Single-transition operators, 13C
opSTT1z = SingleTransitionOperator[{1, 4}, SymmetrizedBasis, "z"]; (* compute single transition operator between levels 1 and 4 in the symmetrized basis, see above *)

opSTT2z = SingleTransitionOperator[{2, 5}, SymmetrizedBasis, "z"];
opSTT3z = SingleTransitionOperator[{3, 6}, SymmetrizedBasis, "z"];
opSTSz = SingleTransitionOperator[{7, 8}, SymmetrizedBasis, "z"];

Single-transition operators, 1H
opST1H1 = opI[{1, 2}, "z"] . opI[3, "α"];
opST1H2 = opI[{1, 2}, "z"] . opI[3, "β"];

Trajectories
peak1op = opSTT1z; (* Observable for peak 1 of the methylene triplet *)
peak2op = 1/2 (opSTT2z + opSTSz); (* Observable for peak 2 of the methylene triplet *)
peak3op = opSTT3z; (* Observable for peak 3 of the methylene triplet *)

relaxparams = {τC -> 5.0 10^-12, τR -> 2.0 10^-12, B0 -> 11.7, δCSA[1|2|3] -> 6, δCSA[4] -> 60, BrH -> 2 Pi 15 10^3, BrC -> 2 Pi 11 10^3}; (* relaxation parameters for all four mechanisms *)
Lsop = CombineGenerators[Γtotsec /. relaxparams, H /. Hparams]; (* combine Hamiltonian and relaxation superoperator to create the Liouvillian *)
dLsop = NDiagonalize[Lsop]; (* diagonalize Liouvillian *)

{peak1fun, peak2fun, peak3fun, ST1H1fun, ST2H2fun} = Trajectory[{0.5*SpinInitialState + opI[1, "z"] + opI[2, "z"] + 0.01*opI[3, "z"]}, {peak1op, peak2op, peak3op, opST1H1, opST1H2}, {dLsop, 200}]; (* Compute evolution of the spin system using the SpinDynamica routine *)

13C plot
Plot[{1000 Re@peak1fun[t], 1000 Re@peak2fun[t], 1000 Re@peak3fun[t]}, {t, 0, 100}, PlotRange -> Full] (* now plot *)

1H plot
Plot[{1000 Re@ST1H1fun[t], 1000 Re@ST2H2fun[t]}, {t, 0, 100}] (* now plot *)

Solvent Paramagnetic Relaxation Enhancement (sPRE) Calculations.
The calculations (main text Fig. 7) were carried out as outlined in reference 4. In brief, the longitudinal sPRE rate $\Gamma_1$ was calculated as

$$\Gamma_1 = \frac{2}{15}K^2S(S+1)J_{\text{approx}}(\omega)$$  \hspace{1cm} (S4a)

$$K = \frac{\mu_0}{4\pi}\frac{1}{\gamma}g$$  \hspace{1cm} (S4b)

Where $\gamma$ is the gyromagnetic ratio, $g$ the g-factor, $S$ the electron spin, $\omega$ the nuclear Larmor frequency, $\beta_m$ the Bohr magneton, $\mu_0$ the vacuum permeability, and $J_{\text{approx}}(\omega)$ the spectral density function:

$$J_{\text{approx}}(\omega) = \frac{J(0)}{1 + a\omega^2 + b\omega}$$  \hspace{1cm} (S5)

$$\langle r^{-5} \rangle_{\text{norm}} = \frac{J(0)}{n_\epsilon\tau_c}$$  \hspace{1cm} (S6)

Where $r$ is the average distance between the electrons and the nucleus, $n_\epsilon$ the electron concentration (0.36 mM) and $\tau_c$ the correlation time. For the calculations shown in the main text, the parameters $a$ and $b$ where chosen to be $7 \times 10^{-10}$ and $6 \times 10^{-6}$, to match the results of reference. $\tau_c$ was set to $1 \times 10^{-12}$ s and the average distance $<r>$ to 20 nm. However, it should be noted that $<r>$ and $\tau_c$ are correlated parameters and that various combinations can lead to similar results. Hence, the values given here have to be considered with caution.

References

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