

Supporting Information for:
Temperature-Dependent Nuclear Spin Relaxation Due to Paramagnetic Dopants Below 30
K: Relevance to DNP-Enhanced Magnetic Resonance Imaging

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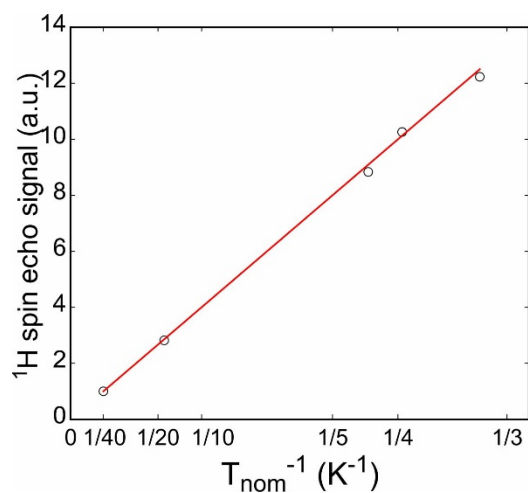


Figure S1: Experimental dependence of the ^1H NMR spin echo signal amplitude on the nominal cryostat temperature T_{nom} (circles). The fit with a linear dependence on $1/T_{\text{nom}}$ (red line) verifies that the actual sample temperature matches the nominal temperature down to 3.3 K. A glycerol/water sample containing 5 mM Dy^{3+} was used for these measurements.

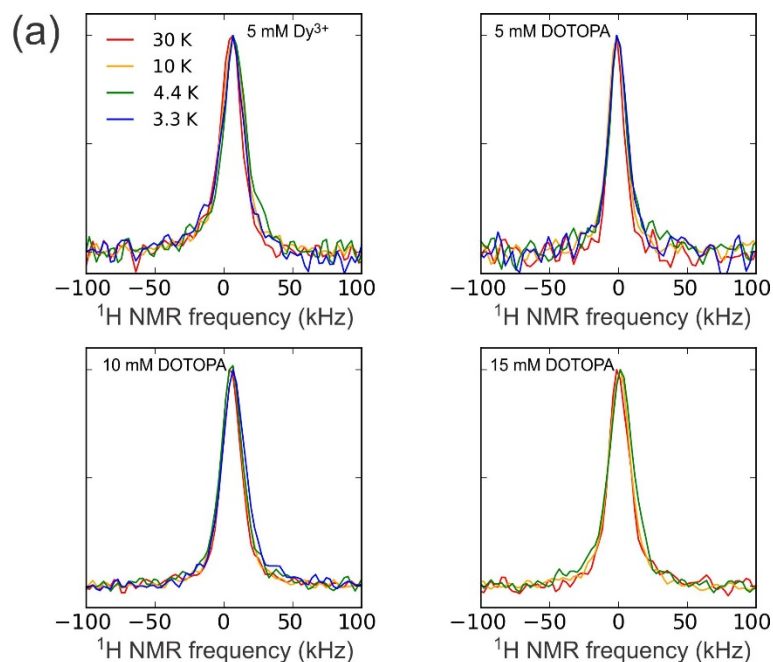


Figure S2: (a) ^1H NMR spectra of frozen glycerol/water solutions with 5 mM Dy^{3+} , 5 mM DOTOPA, 10 mM DOTOPA, and 15 mM DOTOPA at 30 K, 10 K, 4.4 K, and 3.3 K. (b) Table of ^1H NMR linewidths (full-width-at-half-maximum in kHz) in these spectra.

(b)

	5 mM Dy^{3+}	5 mM DOTOPA	10 mM DOTOPA	15 mM DOTOPA
30 K	15.8 ± 0.4	11.1 ± 0.4	14.2 ± 0.3	15.3 ± 0.4
10 K	17.5 ± 0.3	12.7 ± 0.4	15.1 ± 0.3	16.2 ± 0.3
4.4 K	17.8 ± 0.5	13.5 ± 0.5	16.5 ± 0.3	18.0 ± 0.4
3.3 K	18.4 ± 0.6	14.1 ± 0.6	17.2 ± 0.3	n.a.

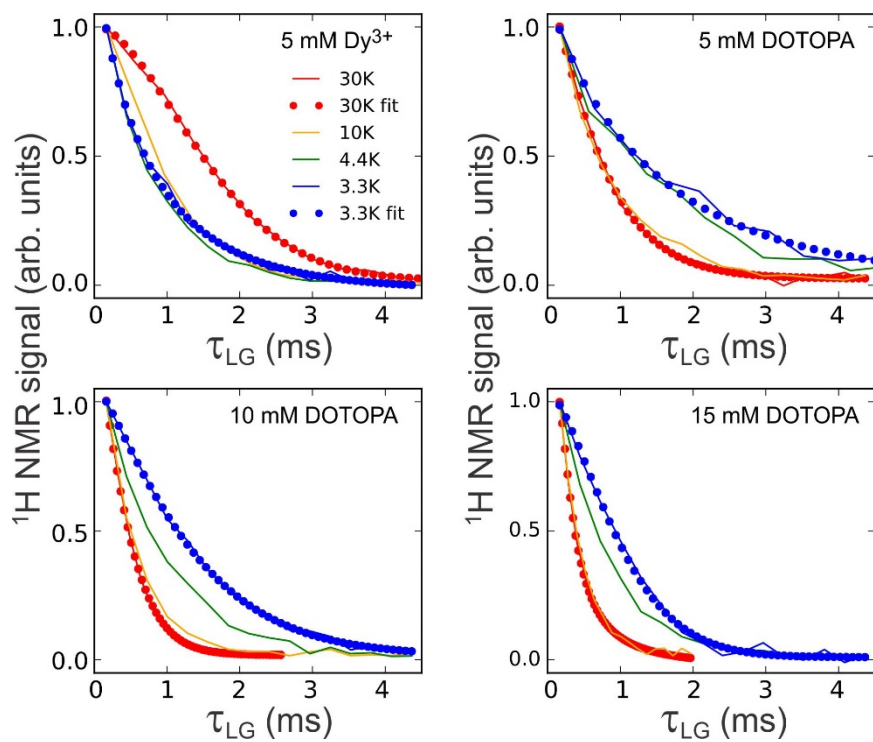


Figure S3: Experimental ^1H NMR signal decay curves as functions of τ_{LG} for the four samples at 30 K (red lines), 10 K (orange lines), 4.4 K (green lines), and 3.3 K (blue lines). Stretched-exponential fits (red and blue dots, for experimental data at 30 K and 3.3 K) were used to determine values of T_{2LG} , which are plotted in Fig. 3a.

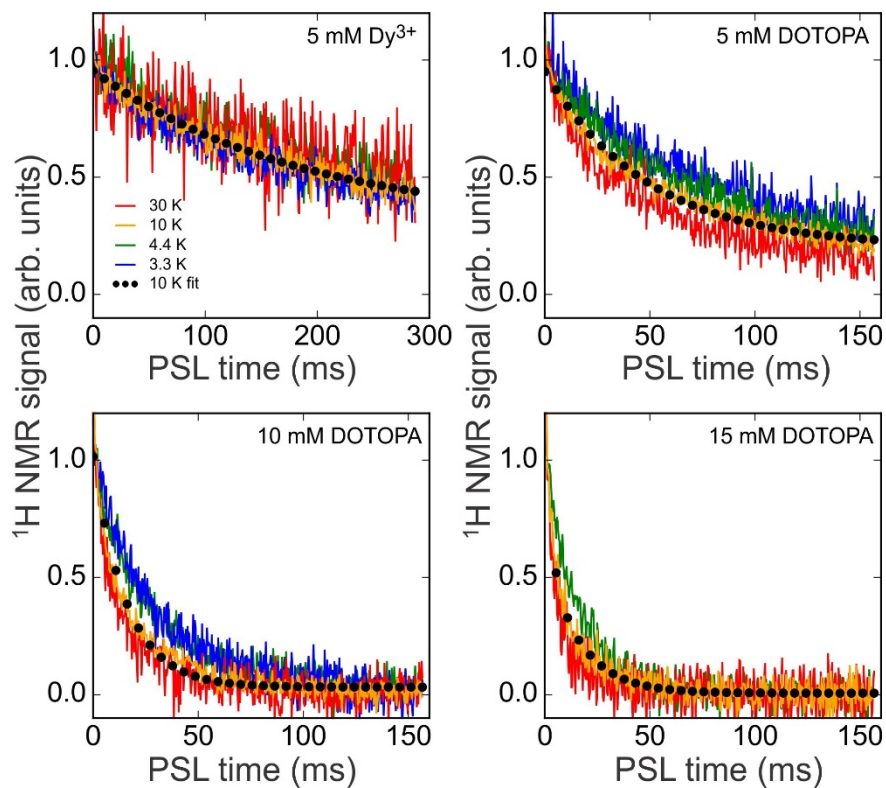


Figure S4: Experimental ^1H NMR signal decay curves under pulsed spin-locking for the four samples at 30 K (red lines), 10 K (orange lines), 4.4 K (green lines), and 3.3 K (blue lines). Single-exponential fits (black dots, for experimental data at 10 K) were used to determine values of T_{2PSL} , which are plotted in Fig. 3b.

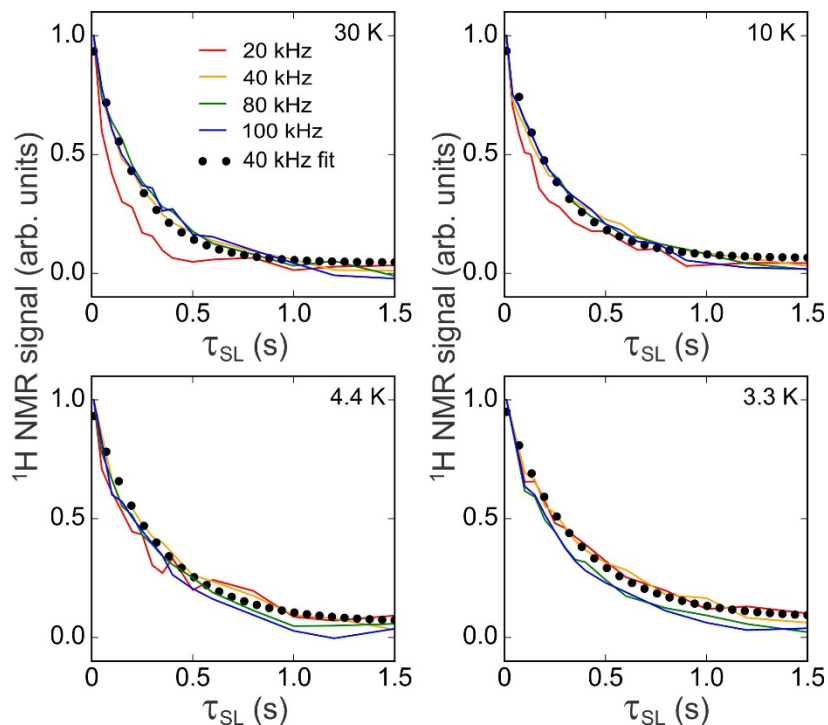


Figure S5: Experimental ^1H NMR signal decay curves as functions of τ_{SL} for the 5 mM DOTOPA sample at 30 K, 10 K, 4.4 K, and 3.3 K. Data are shown for CW spin-locking fields $\omega_1/2\pi = 20$ kHz (red lines), 40 kHz (orange lines), 80 kHz (green lines), and 100 kHz (blue lines). Stretched-exponential fits (black dots, for experimental data at $\omega_1/2\pi = 40$ kHz) were used to determine values of $T_{1\rho}$, which are plotted in Fig. 4b.

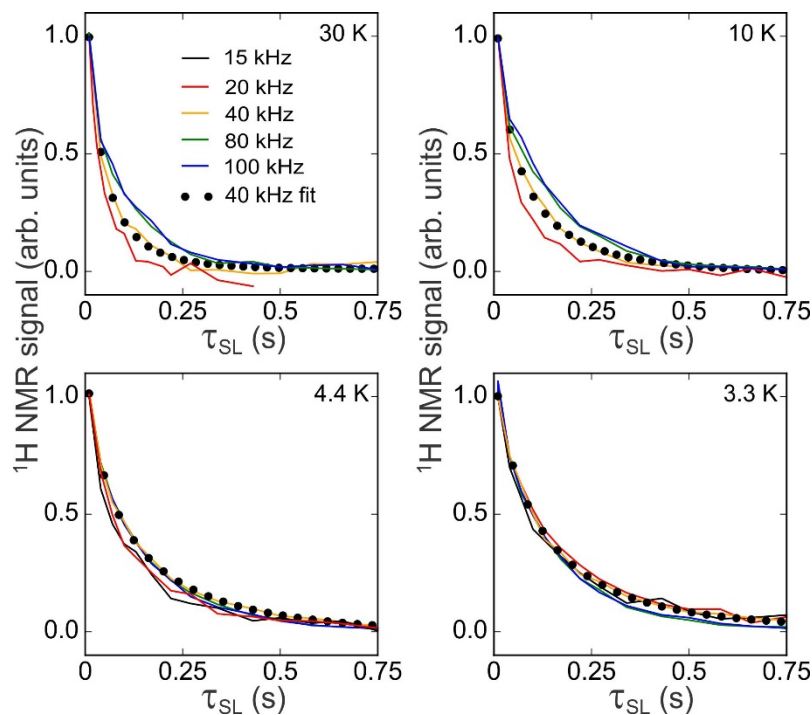


Figure S6: Same as Fig. S5, but for the 10 mM DOTOPA sample. $T_{1\rho}$ values are plotted in Fig. 4c.

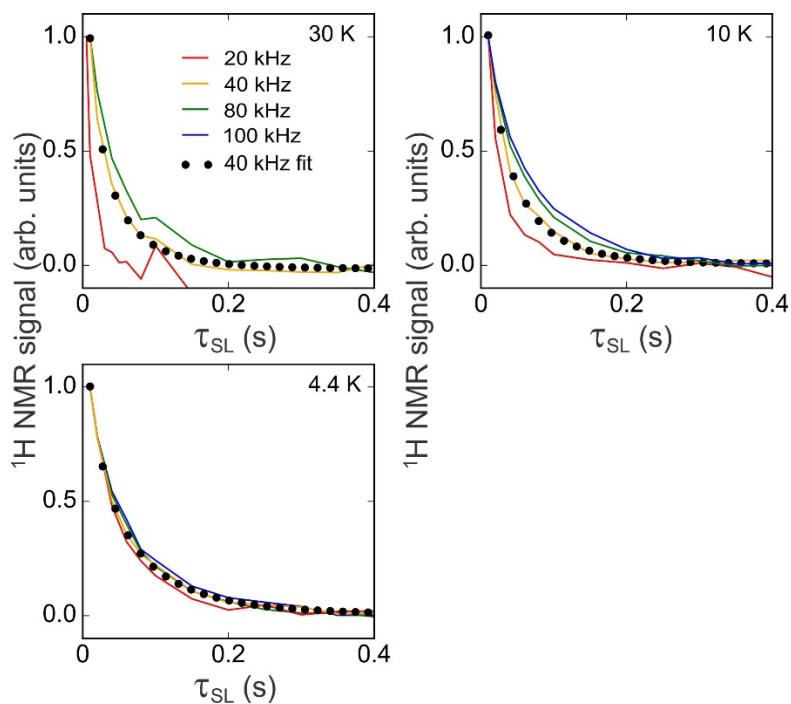


Figure S7: Same as Fig. S5, but for the 15 mM DOTOPA sample. $T_{1\rho}$ values are plotted in Fig. 4d.

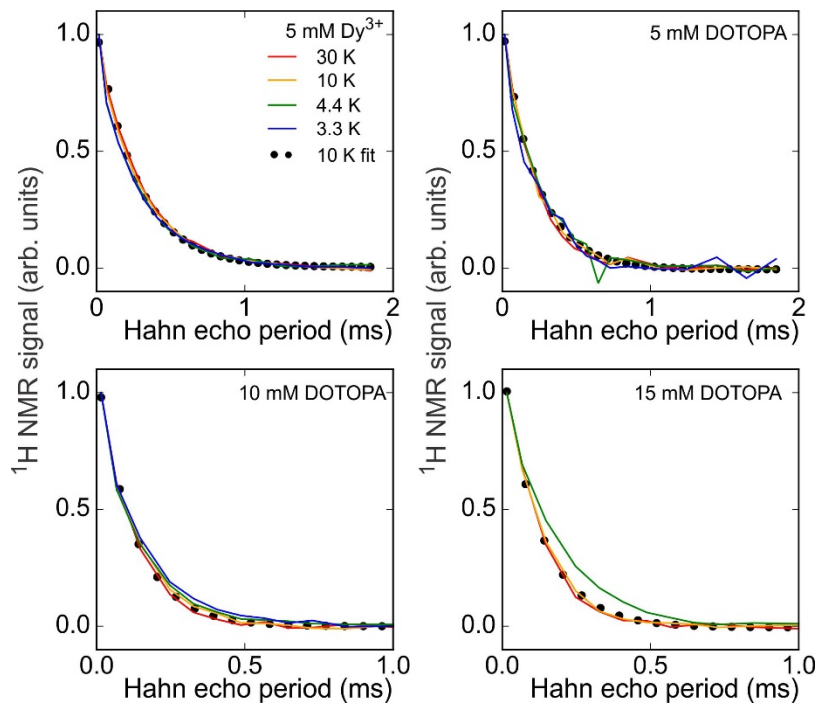


Fig. S8: Experimental ^1H NMR signal decay curves as functions of the Hahn echo period $2\tau_{echo}$ at 30 K (red lines), 10 K (orange lines), 4.4 K (green lines), and 3.3 K (blue lines). Single-exponential fits (black dots, for experimental data at 10 K) were used to determine values of T_2 . With 5 mM Dy^{3+} : $T_2 = 289 \pm 7 \mu\text{s}$, $279 \pm 9 \mu\text{s}$, $256 \pm 15 \mu\text{s}$, and $256 \pm 14 \mu\text{s}$ at 30 K, 10 K, 4.4 K, and 3.3 K, respectively. With 5 mM DOTOPA: $T_2 = 218 \pm 6 \mu\text{s}$, $227 \pm 7 \mu\text{s}$, $232 \pm 18 \mu\text{s}$, and $214 \pm 14 \mu\text{s}$ at 30 K, 10 K, 4.4 K, and 3.3 K, respectively. With 10 mM DOTOPA: $T_2 = 130 \pm 3 \mu\text{s}$, 136

$\pm 5 \mu\text{s}$, $137 \pm 6 \mu\text{s}$, and $147 \pm 7 \mu\text{s}$ at 30 K, 10 K, 4.4 K, and 3.3 K, respectively. With 15 mM DOTOPA: $T_2 = 137 \pm 4 \mu\text{s}$, $141 \pm 2 \mu\text{s}$, and $181 \pm 4 \mu\text{s}$ at 30 K, 10 K, and 4.4 K, respectively.

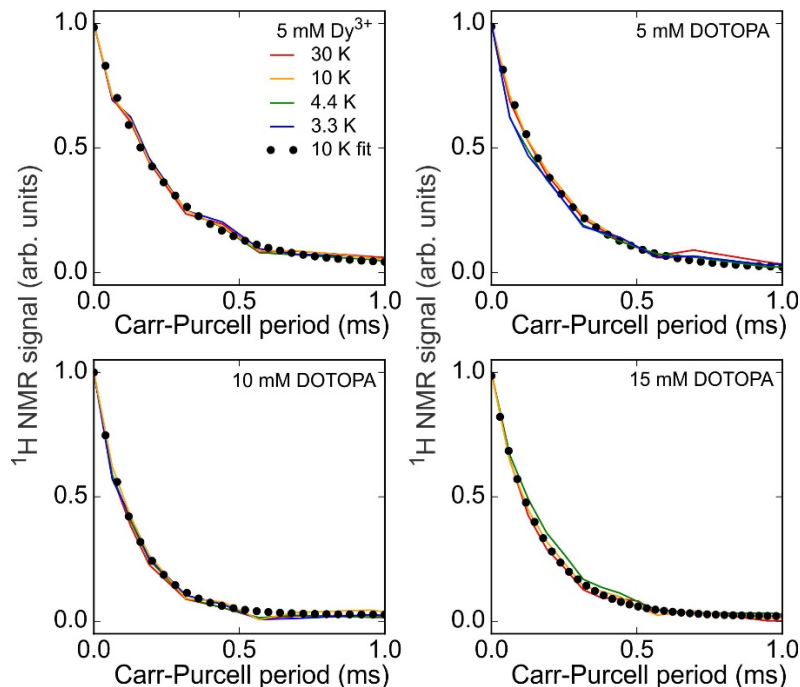


Fig. S9: Experimental ^1H NMR signal decay curves as functions of the Carr-Purcell echo train period $2N\tau_{echo}$, with $\tau_{echo} = 30 \mu\text{s}$, at 30 K (red lines), 10 K (orange lines), 4.4 K (green lines), and 3.3 K (blue lines). Single-exponential fits (black dots, for experimental data at 10 K) were used to determine values of T_2 . With 5 mM Dy^{3+} : $T_2 = 231 \pm 13 \mu\text{s}$, $236 \pm 13 \mu\text{s}$, $233 \pm 11 \mu\text{s}$, and $241 \pm 16 \mu\text{s}$ at 30 K, 10 K, 4.4 K, and 3.3 K, respectively. With 5 mM DOTOPA: $T_2 = 201 \pm 10 \mu\text{s}$, $207 \pm 5 \mu\text{s}$, $181 \pm 11 \mu\text{s}$, and $177 \pm 12 \mu\text{s}$ at 30 K, 10 K, 4.4 K, and 3.3 K, respectively. With 10 mM

DOTOPA: $T_2 = 127 \pm 3 \mu\text{s}$, $139 \pm 6 \mu\text{s}$, $132 \pm 4 \mu\text{s}$, and $134 \pm 7 \mu\text{s}$ at 30 K, 10 K, 4.4 K, and 3.3 K, respectively. With 15 mM DOTOPA: $T_2 = 154 \pm 5 \mu\text{s}$, $162 \pm 5 \mu\text{s}$, and $180 \pm 5 \mu\text{s}$ at 30 K, 10 K, and 4.4 K, respectively.

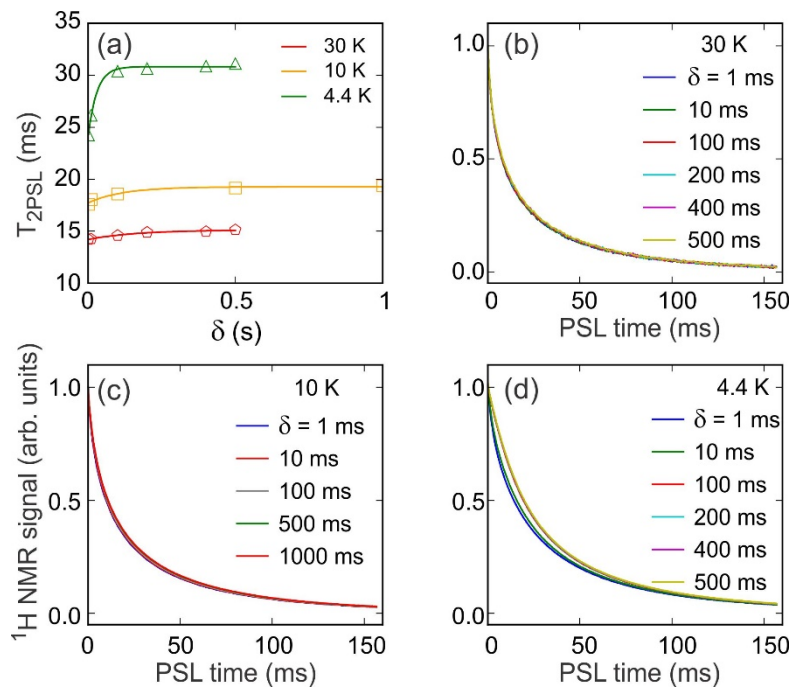


Figure S10: (a) Dependence of the experimentally determined T_{2PSL} value on the delay δ after switching microwaves off (see Fig. 1a) for measurements at 4.4 K (green triangles), 10 K (orange squares), and 30 K (red pentagons). The sample contained 10 mM DOTOPA. Color-coded lines are fits with the functional form $T_{2PSL} = T_a - T_b \exp(-\delta / \delta_0)$, which yield $\delta_0 = 30 \pm 6 \text{ ms}$, 120 ± 60 , and $170 \pm 50 \text{ ms}$ at 4.4 K, 10 K, and 30 K. (b,c,d) ^1H NMR signal decay curves used to determine T_{2PSL} values at 30 K, 10 K, and 4.4 K, respectively.

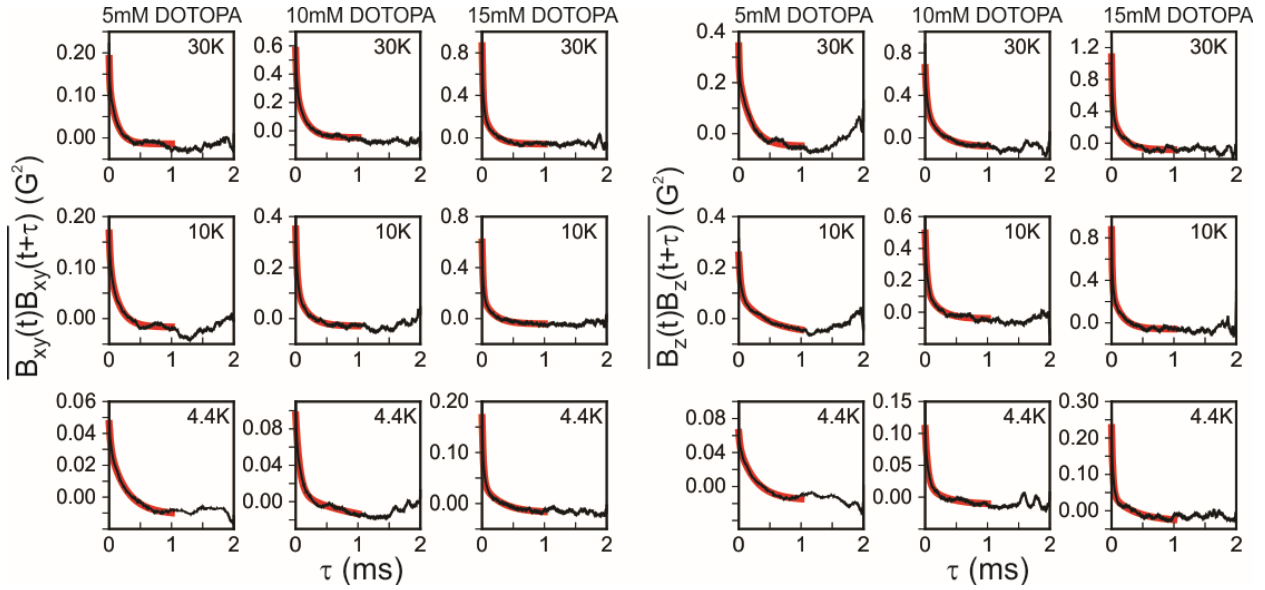


Figure S11: Autocorrelation functions $\overline{B_{xy}(t)B_{xy}(t+\tau)} = \frac{1}{2}[\overline{B_x(t)B_x(t+\tau)} + \overline{B_y(t)B_y(t+\tau)}]$ (left) and $\overline{B_z(t)B_z(t+\tau)}$ (right) from simulations of the electron spin dynamics in a system of thirty DOTOPA molecules in a cube with the indicated concentrations at the indicated temperatures. A 9.39 T magnetic field is applied along z . Autocorrelation functions (black lines) were averaged over 300 simulations for each condition, with a total period of 2ms in each simulation. Red curves are bi-exponential fits to the averaged autocorrelation functions up $\tau = 1$ ms. Best-fit parameters and corresponding nuclear spin relaxation times are given in Tables 1 and 2.

Derivation of expressions for nuclear spin relaxation rates

Theoretical approach

To derive expressions for the relaxation rates $1/T_{1\rho}$ and $1/T_{2LG}$, we use a standard method of second-order time-dependent perturbation theory to analyze the evolution of the nuclear spin density operator $\rho(t)$ under a Hamiltonian with the following form in the laboratory frame:

$$H(t) = \omega_0 S_z + 2\omega_1 S_x \cos \omega t + \boldsymbol{\varepsilon}(t) \cdot \mathbf{S} \quad (\text{S1})$$

Here ω_0 is the nuclear Larmor frequency, ω_1 and ω are the RF amplitude and frequency, and $\boldsymbol{\varepsilon}(t) = \gamma_H \mathbf{B}(t)$ is a vector representing the direction and magnitude of a randomly fluctuating magnetic field at the nucleus, produced by the magnetic moments of the surrounding electron spins. \mathbf{S} is the nuclear spin angular momentum vector. We assume that the three components of $\boldsymbol{\varepsilon}(t)$ satisfy

$$\overline{\varepsilon_\alpha(t)\varepsilon_\beta(t')} = \delta_{\alpha\beta} \overline{\varepsilon_\alpha(0)\varepsilon_\alpha(t-t')} \quad (\text{S2})$$

where the overbar indicates an ensemble average and $\alpha, \beta = x, y, z$. In other words, when averaged over the ensemble, the three fluctuating field components are not correlated with one another (*i.e.*, cross-correlation functions are zero) and the autocorrelation functions $\overline{\varepsilon_\alpha(t)\varepsilon_\alpha(t')}$ depend only on the difference between t and t' . Moreover, we assume that $\overline{\varepsilon_x(t)\varepsilon_x(t')} = \overline{\varepsilon_y(t)\varepsilon_y(t')} = f(t-t')$, because the positions and states of the electron spins are symmetric about z on average, and $\overline{\varepsilon_z(t)\varepsilon_z(t')} = g(t-t')$. We further assume that the ensemble average of $\boldsymbol{\varepsilon}(t)$ is zero at all times.

To apply second-order perturbation theory, we must first transform to a frame in which the first two terms in Eq. (S1) vanish. As shown below, such a transformation is accomplished by a series of rotations, with net rotation operator $R(t)$, resulting in a transformed Hamiltonian

$$\begin{aligned} \tilde{H}(t) &= R(t)[\boldsymbol{\varepsilon}(t) \cdot \mathbf{S}]R(t)^{-1} \\ &= \boldsymbol{\varepsilon}(t) \cdot (\tilde{S}_x(t), \tilde{S}_y(t), \tilde{S}_z(t)) \\ &= \tilde{\varepsilon}_x(t)S_x + \tilde{\varepsilon}_y(t)S_y + \tilde{\varepsilon}_z(t)S_z \end{aligned} \quad (\text{S3})$$

which determines the evolution in time of a transformed density operator $\tilde{\rho}(t) = R(t)\rho(t)R(t)^{-1}$ according to the Liouville equation $\frac{d\tilde{\rho}(t)}{dt} = -i[\tilde{H}(t), \tilde{\rho}(t)]$.

A second-order solution of the Liouville equation is

$$\tilde{\rho}(t) \approx \tilde{\rho}(0) - i \int_0^t dt' [\tilde{H}(t'), \tilde{\rho}(0)] - \int_0^t dt' \int_0^{t'} dt'' [\tilde{H}(t'), [\tilde{H}(t''), \tilde{\rho}(0)]] \quad (\text{S4})$$

Using the assumption that $\overline{\boldsymbol{\varepsilon}(t)} = 0$, and further assuming that all members of the ensemble have the same initial density operator, the ensemble average of Eq. (S4) becomes

$$\overline{\tilde{\rho}(t)} \approx \tilde{\rho}(0) - \int_0^t dt' \int_0^{t'} dt'' \overline{[\tilde{H}(t'), [\tilde{H}(t''), \tilde{\rho}(0)]]} \quad (\text{S5})$$

Since we are concerned with single-nuclear-spin systems, the density operator can be written as $\tilde{\rho}(t) = p_x(t)S_x + p_y(t)S_y + p_z(t)S_z$, where $\mathbf{p}(t)$ is a nuclear spin polarization vector. Then, using the standard commutation relations among angular momentum components, the double commutator in Eq. (S5) is

$$\begin{aligned} [\tilde{H}(t'), [\tilde{H}(t''), \tilde{\rho}(0)]] = & \left\{ -\tilde{\varepsilon}_y(t') [\tilde{\varepsilon}_x(t'') p_y(0) - \tilde{\varepsilon}_y(t'') p_x(0)] + \tilde{\varepsilon}_z(t') [\tilde{\varepsilon}_z(t'') p_x(0) - \tilde{\varepsilon}_x(t'') p_z(0)] \right\} S_x \\ & + \left\{ -\tilde{\varepsilon}_z(t') [\tilde{\varepsilon}_y(t'') p_z(0) - \tilde{\varepsilon}_z(t'') p_y(0)] + \tilde{\varepsilon}_x(t') [\tilde{\varepsilon}_x(t'') p_y(0) - \tilde{\varepsilon}_y(t'') p_x(0)] \right\} S_y \\ & + \left\{ -\tilde{\varepsilon}_x(t') [\tilde{\varepsilon}_z(t'') p_x(0) - \tilde{\varepsilon}_x(t'') p_z(0)] + \tilde{\varepsilon}_y(t') [\tilde{\varepsilon}_y(t'') p_z(0) - \tilde{\varepsilon}_z(t'') p_y(0)] \right\} S_z \end{aligned} \quad (\text{S6})$$

Eq. (S5) can then be written as an equation for the coefficients $p_a(t_0)$, where t_0 is the maximum time up to which the second-order expression in Eq. (S5) remains valid:

$$\begin{pmatrix} p_x(t_0) \\ p_y(t_0) \\ p_z(t_0) \end{pmatrix} = \begin{pmatrix} 1 - W_{xx} & -W_{xy} & -W_{xz} \\ -W_{yx} & 1 - W_{yy} & -W_{yz} \\ -W_{zx} & -W_{zy} & 1 - W_{zz} \end{pmatrix} \begin{pmatrix} p_x(0) \\ p_y(0) \\ p_z(0) \end{pmatrix} \quad (\text{S7})$$

Using the short-hand notation $\iint \overline{h_1 h_2} \equiv \int_0^{t_0} dt' \int_0^{t'} dt'' \overline{h_1(t') h_2(t'')}$, the matrix elements in Eq. (S7) are

$$\begin{aligned} W_{xx} &= \iint (\overline{\tilde{\varepsilon}_y \tilde{\varepsilon}_y} + \overline{\tilde{\varepsilon}_z \tilde{\varepsilon}_z}) & W_{xy} &= -\iint \overline{\tilde{\varepsilon}_y \tilde{\varepsilon}_x} & W_{xz} &= -\iint \overline{\tilde{\varepsilon}_z \tilde{\varepsilon}_x} \\ W_{yx} &= -\iint \overline{\tilde{\varepsilon}_x \tilde{\varepsilon}_y} & W_{yy} &= \iint (\overline{\tilde{\varepsilon}_z \tilde{\varepsilon}_z} + \overline{\tilde{\varepsilon}_x \tilde{\varepsilon}_x}) & W_{yz} &= -\iint \overline{\tilde{\varepsilon}_z \tilde{\varepsilon}_y} \\ W_{zx} &= -\iint \overline{\tilde{\varepsilon}_x \tilde{\varepsilon}_z} & W_{zy} &= -\iint \overline{\tilde{\varepsilon}_y \tilde{\varepsilon}_z} & W_{zz} &= \iint (\overline{\tilde{\varepsilon}_x \tilde{\varepsilon}_x} + \overline{\tilde{\varepsilon}_y \tilde{\varepsilon}_y}) \end{aligned} \quad (\text{S8})$$

Note that cross-correlations between the transformed field components (*i.e.*, quantities such as $\overline{\tilde{\varepsilon}_x(t') \tilde{\varepsilon}_y(t'')}$) are not necessarily zero, even though the cross-correlations are zero in the laboratory frame.

The next step in general is to replace the integrals with respect to t' and t'' with integrals over $\tau \equiv t' - t''$ and $u \equiv t' + t''$. Although correlation functions in the laboratory frame are assumed to be functions of τ alone, correlation functions in the transformed frame may involve products of functions of τ and functions of u (see below). In this case, it can be shown that

$\int_0^{t_0} dt' \int_0^{t'} dt'' h_1(\tau) h_2(u) = \frac{1}{2} \int_0^{t_0} d\tau h_1(\tau) \int_{\tau}^{2t_0 - \tau} du h_2(u)$. However, as shown below, terms that involve

functions of u make negligible contributions to Eq. (S7). The important terms, for which $h_2(u) = 1$, become $\int_0^{t_0} dt' \int_0^{t'} dt'' h_1(\tau) = \int_0^{t_0} d\tau h_1(\tau)(t_0 - \tau) \approx t_0 \int_0^\infty d\tau h_1(\tau)$, where the last approximation is legitimate when the correlation function $h_1(\tau)$ decays to zero with a characteristic correlation time τ_c that is much smaller than t_0 . Thus, the matrix elements in Eq. (S8) are approximately proportional to t_0 , as required if the evolution of the ensemble-averaged, transformed density operator is to be described by spin relaxation rates.

We then make the standard assumption that, for each member of the ensemble of nuclear spin systems, the fluctuating fields represented by $\tilde{\epsilon}(t)$ in the interval $[0, t_0]$ are completely uncorrelated with their values in the interval $[t_0, 2t_0]$, and the fluctuating fields in all subsequent intervals $[nt_0, (n+1)t_0]$ are also completely uncorrelated with one another. This assumption allows Eq. (S7) to be extended to

$$\begin{aligned} \begin{pmatrix} p_x(t) \\ p_y(t) \\ p_z(t) \end{pmatrix} &= \begin{pmatrix} p_x(Nt_0) \\ p_y(Nt_0) \\ p_z(Nt_0) \end{pmatrix} \\ &= \begin{pmatrix} 1 - t_0/T_{xx} & -t_0/T_{xy} & -t_0/T_{xz} \\ -t_0/T_{yx} & 1 - t_0/T_{yy} & -t_0/T_{yz} \\ -t_0/T_{zx} & -t_0/T_{zy} & 1 - t_0/T_{zz} \end{pmatrix} \begin{pmatrix} p_x((N-1)t_0) \\ p_y((N-1)t_0) \\ p_z((N-1)t_0) \end{pmatrix} \\ &= \begin{pmatrix} 1 - t_0/T_{xx} & -t_0/T_{xy} & -t_0/T_{xz} \\ -t_0/T_{yx} & 1 - t_0/T_{yy} & -t_0/T_{yz} \\ -t_0/T_{zx} & -t_0/T_{zy} & 1 - t_0/T_{zz} \end{pmatrix}^N \begin{pmatrix} p_x(0) \\ p_y(0) \\ p_z(0) \end{pmatrix} \end{aligned} \quad (\text{S8})$$

where $1/T_{\alpha\beta} \equiv W_{\alpha\beta}/t_0$. Subject to the assumptions discussed above, Eq. (S8) is valid for arbitrarily large values of $t = Nt_0$, while Eq. (S5) is valid only for $t \leq t_0$.

Off-diagonal matrix elements in Eqs. (S7) or (S8) produce small rotations of $\mathbf{p}(t)$, because $T_{\alpha\beta} = -T_{\beta\alpha}$ for $\alpha \neq \beta$. These rotations represent the well-known dynamic frequency shifts. Diagonal elements produce the decay of $\mathbf{p}(t)$ that corresponds to nuclear spin relaxation processes. If we ignore off-diagonal elements, Eq. (S8) becomes

$$\begin{aligned}
\begin{pmatrix} p_x(t) \\ p_y(t) \\ p_z(t) \end{pmatrix} &= \begin{pmatrix} 1-t_0/T_{xx} & 0 & 0 \\ 0 & 1-t_0/T_{yy} & 0 \\ 0 & 0 & 1-t_0/T_{zz} \end{pmatrix}^N \begin{pmatrix} p_x(0) \\ p_y(0) \\ p_z(0) \end{pmatrix} \\
&= \begin{pmatrix} \left(1-\frac{t}{NT_{xx}}\right)^N & 0 & 0 \\ 0 & \left(1-\frac{t}{NT_{yy}}\right)^N & 0 \\ 0 & 0 & \left(1-\frac{t}{NT_{zz}}\right)^N \end{pmatrix} \begin{pmatrix} p_x(0) \\ p_y(0) \\ p_z(0) \end{pmatrix} \\
&\approx \begin{pmatrix} \exp(-t/T_{xx})p_x(0) \\ \exp(-t/T_{yy})p_y(0) \\ \exp(-t/T_{zz})p_z(0) \end{pmatrix}
\end{aligned} \tag{S9}$$

using the fact that $\exp(-a) \approx (1 - a/N)^N$ if $a/N \ll 1$. Thus, we arrive at the final result that the quantities $T_{\alpha\alpha}$ are the desired spin relaxation times.

Expression for $T_{1\rho}$

To derive an expression for $T_{1\rho}$, we first transform to an intermediate frame that rotates around z at frequency $\omega = \omega_0$. The Hamiltonian in Eq. (S1) then becomes

$$H'(t) = \omega_1 S_x (1 + \cos 2\omega_0 t) - \omega_1 S_y \sin 2\omega_0 t + R_z(-\omega_0 t) [\boldsymbol{\varepsilon}(t) \cdot \mathbf{S}] R_z(\omega_0 t) \tag{S10}$$

with $R_z(\omega_0 t) = \exp(-iS_z \omega_0 t)$. After discarding terms that oscillate at $2\omega_0$, we then transform to a final frame that rotates around x at frequency ω_1 , in which the Hamiltonian is

$$\begin{aligned}
\tilde{H}(t) &= R_x(-\omega_1 t) R_z(-\omega_0 t) [\boldsymbol{\varepsilon}(t) \cdot \mathbf{S}] R_z(\omega_0 t) R_x(\omega_1 t) \\
&= \tilde{\boldsymbol{\varepsilon}}(t) \cdot \mathbf{S}
\end{aligned} \tag{S11}$$

with

$$\begin{aligned}
\tilde{\varepsilon}_x(t) &= \varepsilon_x(t) \cos \omega_0 t + \varepsilon_y(t) \sin \omega_0 t \\
\tilde{\varepsilon}_y(t) &= -\varepsilon_x(t) \sin \omega_0 t \cos \omega_1 t + \varepsilon_y(t) \cos \omega_0 t \cos \omega_1 t + \varepsilon_z(t) \sin \omega_1 t \\
\tilde{\varepsilon}_z(t) &= \varepsilon_x(t) \sin \omega_0 t \sin \omega_1 t - \varepsilon_y(t) \cos \omega_0 t \sin \omega_1 t + \varepsilon_z(t) \cos \omega_1 t
\end{aligned} \tag{S12}$$

$T_{1\rho}$ relaxation is determined by W_{xx} in Eq. (S7), because the spin-locking direction is x in the final frame. From Eqs. (S8) and (S12), using the assumptions regarding correlation functions that were stated at the beginning of this section, we have

$$\begin{aligned}
W_{xx} &= \int_0^{t_0} dt' \int_0^{t'} dt'' \overline{\varepsilon_x(t')\varepsilon_x(t'')} (\sin \omega_0 t' \sin \omega_0 t'' \cos \omega_1 t' \cos \omega_1 t'' + \sin \omega_0 t' \sin \omega_0 t'' \sin \omega_1 t' \sin \omega_1 t'') \\
&\quad + \int_0^{t_0} dt' \int_0^{t'} dt'' \overline{\varepsilon_y(t')\varepsilon_y(t'')} (\cos \omega_0 t' \cos \omega_0 t'' \cos \omega_1 t' \cos \omega_1 t'' + \cos \omega_0 t' \cos \omega_0 t'' \sin \omega_1 t' \sin \omega_1 t'') \\
&\quad + \int_0^{t_0} dt' \int_0^{t'} dt'' \overline{\varepsilon_z(t')\varepsilon_z(t'')} (\sin \omega_1 t' \sin \omega_1 t'' + \cos \omega_1 t' \cos \omega_1 t'') \\
&= \int_0^{t_0} dt' \int_0^{t'} dt'' f(t'-t'') (\sin \omega_0 t' \sin \omega_0 t'' \cos \omega_1 t' \cos \omega_1 t'' + \sin \omega_0 t' \sin \omega_0 t'' \sin \omega_1 t' \sin \omega_1 t'') \\
&\quad + \cos \omega_0 t' \cos \omega_0 t'' \cos \omega_1 t' \cos \omega_1 t'' + \cos \omega_0 t' \cos \omega_0 t'' \sin \omega_1 t' \sin \omega_1 t'') \\
&\quad + \int_0^{t_0} dt' \int_0^{t'} dt'' g(t'-t'') (\sin \omega_1 t' \sin \omega_1 t'' + \cos \omega_1 t' \cos \omega_1 t'') \\
&= \int_0^{t_0} dt' \int_0^{t'} dt'' f(t'-t'') \cos \omega_0(t'-t'') \cos \omega_1(t'-t'') + \int_0^{t_0} dt' \int_0^{t'} dt'' g(t'-t'') \cos \omega_1(t'-t'') \\
&= \int_0^{t_0} d\tau [f(\tau) \cos \omega_0 \tau \cos \omega_1 \tau + g(\tau) \cos \omega_1 \tau] (t - \tau) \\
&\approx t_0 \int_0^{\infty} d\tau [f(\tau) \cos \omega_0 \tau \cos \omega_1 \tau + g(\tau) \cos \omega_1 \tau]
\end{aligned} \tag{S13}$$

Then

$$1/T_{1\rho} = 1/T_{xx} = \int_0^{\infty} d\tau \left\{ \frac{f(\tau)}{2} [\cos(\omega_0 - \omega_1)\tau + \cos(\omega_0 + \omega_1)\tau] + g(\tau) \cos \omega_1 \tau \right\} \tag{S14}$$

Expression for T_{2LG}

To derive an expression for T_{2LG} , we first transform to an intermediate frame that rotates around z at frequency $\omega = \omega_0 - \Delta$, where $\Delta/2\pi$ is the Lee-Goldburg frequency offset. Ignoring rapidly oscillating terms, the Hamiltonian in this frame is

$$H'(t) = \Delta S_z + \omega_1 S_x + R_z(-\omega t) [\boldsymbol{\varepsilon}(t) \cdot \mathbf{S}] R_z(\omega t) \tag{S15}$$

We then transform to a second intermediate frame by applying a rotation about y by the magic angle $\theta_m = \cos^{-1}(1/\sqrt{3})$, obtaining

$$H''(t) = \omega_{LG} S_z + R_y(-\theta_m) R_z(-\omega t) [\boldsymbol{\varepsilon}(t) \cdot \mathbf{S}] R_z(\omega t) R_y(\theta_m) \tag{S16}$$

where $\omega_{LG} / 2\pi$ is the Lee-Goldburg effective field amplitude, with $\omega_1 = \sqrt{\frac{2}{3}}\omega_{LG}$ and $\Delta = \frac{1}{\sqrt{3}}\omega_{LG}$. We then transform to a final frame that rotates about z at frequency ω_{LG} , in which the Hamiltonian is

$$\begin{aligned}\tilde{H}(t) &= R_z(-\omega_{LG}t)R_y(-\theta_m)R_z(-\omega t)[\boldsymbol{\varepsilon}(t) \cdot \mathbf{S}]R_z(\omega t)R_y(\theta_m)R_z(\omega_{LG}t) \\ &= \tilde{\boldsymbol{\varepsilon}}(t) \cdot \mathbf{S}\end{aligned}\quad (\text{S17})$$

with

$$\begin{aligned}\tilde{\varepsilon}_x(t) &= \varepsilon_x(t)(\cos\theta_m \cos\omega_{LG}t \cos\omega t - \sin\omega_{LG}t \sin\omega t) \\ &\quad + \varepsilon_y(t)(\cos\theta_m \cos\omega_{LG}t \sin\omega t + \sin\omega_{LG}t \cos\omega t) + \varepsilon_z(t)\sin\theta_m \cos\omega_{LG}t \\ \tilde{\varepsilon}_y(t) &= -\varepsilon_x(t)(\cos\theta_m \sin\omega_{LG}t \cos\omega t + \cos\omega_{LG}t \sin\omega t) \\ &\quad - \varepsilon_y(t)(\cos\theta_m \sin\omega_{LG}t \sin\omega t - \cos\omega_{LG}t \cos\omega t) + \varepsilon_z(t)\sin\theta_m \sin\omega_{LG}t \\ \tilde{\varepsilon}_z(t) &= \varepsilon_x(t)\sin\theta_m \cos\omega t + \varepsilon_y(t)\sin\theta_m \sin\omega t + \varepsilon_z(t)\cos\theta_m\end{aligned}\quad (\text{S18})$$

T_{2LG} relaxation is determined by W_{xx} and W_{yy} in Eq. (S7). From Eqs. (S8) and (S18), we have

$$\begin{aligned}W_{xx} &= \int_0^{t_0} dt' \int_0^{t'} dt'' f(t'-t'') [\cos^2\theta_m \sin\omega_{LG}t' \sin\omega_{LG}t'' \cos\omega(t'-t'') + \sin^2\theta_m \cos\omega(t'-t'') \\ &\quad - \cos\theta_m \sin\omega_{LG}(t'-t'') \sin\omega(t'-t'') + \cos\omega_{LG}t' \cos\omega_{LG}t'' \cos\omega(t'-t'')] \\ &\quad + \int_0^{t_0} dt' \int_0^{t'} dt'' g(t'-t'') (\sin^2\theta_m \sin\omega_{LG}t' \sin\omega_{LG}t'' + \cos^2\theta_m) \\ W_{yy} &= \int_0^{t_0} dt' \int_0^{t'} dt'' f(t'-t'') [\cos^2\theta_m \cos\omega_{LG}t' \cos\omega_{LG}t'' \cos\omega(t'-t'') + \sin^2\theta_m \cos\omega(t'-t'') \\ &\quad - \cos\theta_m \sin\omega_{LG}(t'-t'') \sin\omega(t'-t'') + \sin\omega_{LG}t' \sin\omega_{LG}t'' \cos\omega(t'-t'')] \\ &\quad + \int_0^{t_0} dt' \int_0^{t'} dt'' g(t'-t'') (\sin^2\theta_m \cos\omega_{LG}t' \cos\omega_{LG}t'' + \cos^2\theta_m)\end{aligned}\quad (\text{S19})$$

Since $\cos\omega_{LG}t' \cos\omega_{LG}t'' = (\cos\omega_{LG}\tau + \cos\omega_{LG}u)/2$ and $\sin\omega_{LG}t' \sin\omega_{LG}t'' = (-\cos\omega_{LG}\tau + \cos\omega_{LG}u)/2$, the double integrals in Eq. (S19) contain terms of the form $\int_0^{t_0} dt' \int_0^{t'} dt'' f(\tau) \cos\omega\tau \cos\omega_{LG}u = \frac{1}{2} \int_0^{t_0} d\tau f(\tau) \cos\omega\tau \int_{\tau}^{2t_0-\tau} du \cos\omega_{LG}u = \frac{1}{2\omega_{LG}} \int_0^{t_0} d\tau f(\tau) \cos\omega\tau [\sin\omega_{LG}(2t_0-\tau) - \sin\omega_{LG}\tau]$. Unlike terms that do not depend on u , terms that contain $\cos\omega_{LG}u$ are not proportional to t_0 when $f(\tau)$ decays on the time scale of τ_c . These terms are therefore negligible, provided that $t_0 \gg 1/\omega_{LG}$.

Retaining only terms that do not depend on u , Eq. (S19) becomes

$$\begin{aligned}
W_{xx} &\approx t_0 \int_0^\infty d\tau f(\tau) \left[\sin^2 \theta_m \cos \omega \tau + \frac{(\cos \theta_m - 1)^2}{4} \cos(\omega_{LG} - \omega) \tau + \frac{(\cos \theta_m + 1)^2}{4} \cos(\omega_{LG} + \omega) \tau \right] \\
&\quad + t_0 \int_0^\infty d\tau g(\tau) \left(\cos^2 \theta_m + \frac{\sin^2 \theta_m}{2} \cos \omega_{LG} \tau \right) \\
&\approx W_{yy}
\end{aligned} \tag{S20}$$

Then

$$\begin{aligned}
1/T_{2LG} &= 1/T_{xx} \\
&= \frac{1}{3} \int_0^\infty d\tau \left\{ f(\tau) \left[2 \cos \omega \tau + \frac{(2 - \sqrt{3})}{2} \cos(\omega_{LG} - \omega) \tau + \frac{(2 + \sqrt{3})}{2} \cos(\omega_{LG} + \omega) \tau \right] \right. \\
&\quad \left. + g(\tau) (1 + \cos \omega_{LG} \tau) \right\}
\end{aligned} \tag{S21}$$

In terms of spectral density functions, defined by $J_{xy}(u) = 2 \int_0^\infty d\tau f(\tau) \cos u \tau$ and $J_z(u) = 2 \int_0^\infty d\tau g(\tau) \cos u \tau$, Eqs. (S14) and (S21) can be written as

$$1/T_{1\rho} = \frac{1}{4} [J_{xy}(\omega_0 - \omega) + J_{xy}(\omega_0 + \omega)] + \frac{1}{2} J_z(\omega_1) \tag{S22}$$

$$1/T_{2LG} = \frac{1}{3} J_{xy}(\omega) + \frac{(2 - \sqrt{3})}{12} J_{xy}(\omega_{LG} - \omega) + \frac{(2 + \sqrt{3})}{12} J_{xy}(\omega_{LG} + \omega) + \frac{1}{6} [J_z(0) + J_z(\omega_{LG})] \tag{S23}$$