

## **Supporting Information**

### **Influence of Strong Confinement on the Structure and Dynamics of Liquids: A Study of the Clay/Water Interface Exploiting $^2\text{H}$ NMR Spectroscopy and Spin-Locking Relaxometry**

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## 1. Time Evolution of the Coherences

The time evolution of the various coherences is described by the master equation<sup>1-3</sup> in the framework of Redfield's theory<sup>1-3</sup>:

$$\frac{d\sigma^*}{dt} = -i [H_S^*, \sigma^*] + f(\sigma^*) \quad (\text{S1})$$

As indicated by the asterisk, all calculations are performed in the Larmor frequency rotating frame. The first contribution to the master equation describes the influence of the static Hamiltonian  $H_S^*$  that includes the residual static quadrupolar Hamiltonian:  $H_{QS}^* = \sqrt{2/3} \omega_Q T_{20}^{IR}$  and the Hamiltonian corresponding to the radio frequency pulse:  $H_{1S}^* = I_x \omega_1 = \sqrt{2} \omega_1 T_{11}^{IR}(a)$ . The second contribution to the master equation  $f(\sigma^*)$  describes the contribution from the fluctuating components of the Hamiltonians  $H_F^*(t)$  monitoring the relaxation of the coherences<sup>1-4</sup>:

$$f(\sigma^*) = -\int_0^t \left\langle \left[ H_F^*(t), \left[ e^{-iH_S^* \tau} H_F^*(t-\tau) e^{iH_S^* \tau}, \sigma^*(t) \right] \right] \right\rangle d\tau \quad (\text{S2})$$

The decorrelation of the quadrupolar and heteronuclear dipolar couplings, responsible for the NMR relaxation of water molecules confined within dense clay sediments, occurs at a time-scale of  $10^{-4}$  s, *i.e.* shorter than the time evolution of the various coherences (typically  $10^{-3}$  s). As a consequence, the upper time-limit of the integration displayed in equation S2 may be set equal to infinity. This is a major limitation, restricting the use of Redfield theory for analyzing NMR relaxation measurements of confined fluids. As displayed in Equation 3 in the article, an increase of the size of the confining media by one order of magnitude, thus leading to micrometric interfacial domains, will enhance the correlation time of the magnetic

couplings of the diffusing probes by two orders of magnitude, invalidating the above mentioned approximation.

Neglecting the contributions from the NMR relaxation mechanism, the master equation (Eq S1) may be written for the above mentioned basis set of spin  $I = 1$  nuclei<sup>4</sup>:

$$\frac{d}{dt} \begin{pmatrix} T_{20}^{IR} \\ T_{11}^{IR}(a) \\ T_{21}^{IR}(s) \\ T_{22}^{IR}(s) \\ T_{10}^{IR} \\ T_{11}^{IR}(s) \\ T_{21}^{IR}(a) \\ T_{22}^{IR}(a) \end{pmatrix} = i \begin{pmatrix} 0 & 0 & -\sqrt{3} \omega_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \omega_Q & 0 & 0 & 0 & 0 & 0 \\ -\sqrt{3} \omega_1 & \omega_Q & 0 & -\omega_1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\omega_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\omega_1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\omega_1 & 0 & \omega_Q & 0 \\ 0 & 0 & 0 & 0 & 0 & \omega_Q & 0 & -\omega_1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\omega_1 \end{pmatrix} \begin{pmatrix} T_{20}^{IR} \\ T_{11}^{IR}(a) \\ T_{21}^{IR}(s) \\ T_{22}^{IR}(s) \\ T_{10}^{IR} \\ T_{11}^{IR}(s) \\ T_{21}^{IR}(a) \\ T_{22}^{IR}(a) \end{pmatrix} \quad (\text{S3})$$

As illustrated by the matrix form of Eq. S3, the time evolution of the various coherences under the influence of the static Hamiltonians splits in two independent sub-sets<sup>4</sup>:

$$e^{iH_s^* \tau} T_{20}^{IR} e^{-iH_s^* \tau} = \sqrt{3} \omega_1 \omega_Q \frac{1 - \cos(k_1 \tau)}{k_1^2} T_{11}^{IR}(a) + \frac{\omega_Q^2 + \omega_1^2 (1 + 3 \cos(k_1 \tau))}{k_1^2} T_{20}^{IR} \\ - i \sqrt{3} \omega_1 \frac{\sin(k_1 \tau)}{k_1} T_{21}^{IR}(s) + \sqrt{3} \omega_1^2 \frac{\cos(k_1 \tau) - 1}{k_1^2} T_{22}^{IR}(s) \quad (\text{S4a})$$

$$e^{iH_s^* \tau} T_{11}^{IR}(a) e^{-iH_s^* \tau} = \frac{\omega_Q^2 \cos(k_1 \tau) + 4 \omega_1^2}{k_1^2} T_{11}^{IR}(a) + \sqrt{3} \omega_1 \omega_Q \frac{1 - \cos(k_1 \tau)}{k_1^2} T_{20}^{IR} \\ + i \omega_Q \frac{\sin(k_1 \tau)}{k_1} T_{21}^{IR}(s) + \omega_1 \omega_Q \frac{1 - \cos(k_1 \tau)}{k_1^2} T_{22}^{IR}(s) \quad (\text{S4b})$$

$$e^{iH_s^* \tau} T_{21}^{IR}(s) e^{-iH_s^* \tau} = i \omega_Q \frac{\sin(k_1 \tau)}{k_1} T_{11}^{IR}(a) - i \sqrt{3} \omega_1 \frac{\sin(k_1 \tau)}{k_1} T_{20}^{IR} \\ + \cos(k_1 \tau) T_{21}^{IR}(s) - i \omega_1 \frac{\sin(k_1 \tau)}{k_1} T_{22}^{IR}(s) \quad (\text{S4c})$$

$$\begin{aligned}
e^{iH_s^* \tau} T_{22}^{IR}(s) e^{-iH_s^* \tau} &= \omega_1 \omega_Q \frac{1 - \cos(k_1 \tau)}{k_1^2} T_{11}^{IR}(a) + \sqrt{3} \omega_1^2 \frac{\cos(k_1 \tau) - 1}{k_1^2} T_{20}^{IR} \\
&\quad - i \omega_1 \frac{\sin(k_1 \tau)}{k_1} T_{21}^{IR}(s) + \frac{k_1^2 - \omega_1^2 (1 - \cos(k_1 \tau))}{k_1^2} T_{22}^{IR}(s)
\end{aligned} \tag{S4d}$$

for the first set of coherences  $\{ T_{20}^{IR}, T_{11}^{IR}(a), T_{21}^{IR}(s), T_{22}^{IR}(s) \}$  and

$$\begin{aligned}
e^{iH_s^* \tau} T_{10}^{IR} e^{-iH_s^* \tau} &= \frac{k_2 \cos(k_3 \tau) + k_3 \cos(k_2 \tau)}{k_1} T_{10}^{IR} - i \omega_1 \frac{\sin(k_3 \tau) + \sin(k_2 \tau)}{k_1} T_{11}^{IR}(s) \\
&\quad + \omega_1 \frac{\cos(k_3 \tau) - \cos(k_2 \tau)}{k_1} T_{21}^{IR}(a) - i \frac{k_2 \sin(k_3 \tau) - k_3 \sin(k_2 \tau)}{k_1} T_{22}^{IR}(a)
\end{aligned} \tag{S5a}$$

$$\begin{aligned}
e^{iH_s^* \tau} T_{11}^{IR}(s) e^{-iH_s^* \tau} &= -i \omega_1 \frac{\sin(k_3 \tau) + \sin(k_2 \tau)}{k_1} T_{10}^{IR} + \frac{k_2 \cos(k_2 \tau) + k_3 \cos(k_3 \tau)}{k_1} T_{11}^{IR}(s) \\
&\quad + i \frac{k_2 \sin(k_2 \tau) - k_3 \sin(k_3 \tau)}{k_1} T_{21}^{IR}(a) + \omega_1 \frac{\cos(k_3 \tau) - \cos(k_2 \tau)}{k_1} T_{22}^{IR}(a)
\end{aligned} \tag{S5b}$$

$$\begin{aligned}
e^{iH_s^* \tau} T_{21}^{IR}(a) e^{-iH_s^* \tau} &= \omega_1 \frac{\cos(k_3 \tau) - \cos(k_2 \tau)}{k_1} T_{10}^{IR} + i \frac{k_2 \sin(k_2 \tau) - k_3 \sin(k_3 \tau)}{k_1} T_{11}^{IR}(s) \\
&\quad + \frac{k_2 \cos(k_2 \tau) + k_3 \cos(k_3 \tau)}{k_1} T_{21}^{IR}(a) - i \omega_1 \frac{\sin(k_3 \tau) + \sin(k_2 \tau)}{k_1} T_{22}^{IR}(a)
\end{aligned} \tag{S5c}$$

$$\begin{aligned}
e^{iH_s^* \tau} T_{22}^{IR}(a) e^{-iH_s^* \tau} &= -i \frac{k_2 \sin(k_3 \tau) - k_3 \sin(k_2 \tau)}{k_1} T_{10}^{IR} + \omega_1 \frac{\cos(k_3 \tau) - \cos(k_2 \tau)}{k_1} T_{11}^{IR}(s) \\
&\quad - i \omega_1 \frac{\sin(k_3 \tau) + \sin(k_2 \tau)}{k_1} T_{21}^{IR}(a) + \frac{k_2 \cos(k_3 \tau) + k_3 \cos(k_2 \tau)}{k_1} T_{22}^{IR}(a)
\end{aligned} \tag{S5d}$$

for the second set of coherences  $\{ T_{10}^{IR}, T_{11}^{IR}(s), T_{21}^{IR}(a), T_{22}^{IR}(a) \}$ . In these equations, the characteristic angular velocities<sup>4</sup>  $\{ k_1, k_2, k_3 \}$  are defined by:

$$k_1 = \sqrt{\omega_Q^2 + 4\omega_1^2} \tag{S6a}$$

$$k_2 = \frac{\omega_Q + \sqrt{\omega_Q^2 + 4\omega_1^2}}{2} \tag{S6b}$$

$$k_3 = \frac{\sqrt{\omega_Q^2 + 4\omega_1^2} - \omega_Q}{2} \quad (\text{S6c})$$

The set of Eqs S4-S6 was used to optimize of transfer of coherences implied in our multi-quanta filtering of NMR spectroscopy and multi-quanta NMR relaxation measurements.

## 2. Quadrupolar Relaxation

In bulk water, quadrupolar coupling is the main mechanism responsible for the relaxation of heavy water<sup>1-4</sup>:

$$H_Q(t) = C_Q \sum_{m=-2}^2 (-1)^m T_{2,m}^Q F_{2,-m}^Q(t) \quad (\text{S7a})$$

where the quadrupolar coupling constant, defined by:

$$C_Q = \sqrt{\frac{3}{8}} \frac{e^2 q Q}{\hbar I (2I - 1)} \quad (\text{S7b})$$

is equal to  $\sqrt{2/3} \times \pi \times 210$  kHz for deuterium in bulk heavy water<sup>5</sup>. The spin operators describing quadrupolar coupling are related to the second order coherences ( $T_{2m}^{IR}$  for  $m \in \{0, 1, 2\}$ ):

$$T_{2,0}^Q = \frac{1}{\sqrt{6}} (3I_z^2 - I(I+1)) = T_{20}^{IR} \quad (\text{S7c})$$

$$T_{2,\pm 1}^Q = \mp \frac{1}{2} (I_z I_{\pm} + I_{\pm} I_z) = \frac{1}{\sqrt{2}} (T_{21}^{IR}(s) \mp T_{21}^{IR}(a)) \quad (\text{S7d})$$

$$\text{and } T_{2,\pm 2}^Q = \frac{1}{2} I_{\pm}^2 = \frac{1}{\sqrt{2}} (T_{22}^{IR}(s) \mp T_{22}^{IR}(a)) \quad (\text{S7e})$$

The functions  $F_{2,m}^Q(t)$  in Eq. S7a are the second order spherical harmonics<sup>6</sup> describing the reorientation of the  $OD$  director in the static magnetic field  $\mathbf{B}_0$ . Since the electrostatic field gradient felt by the deuterium nucleus in heavy water is directed along the  $OD$  bond, the functions  $F_{2,m}^Q(t)$  are related to the two Euler angles  $(\theta^{LW}, \phi^{LW})$ :

$$F_{2,0}^Q(t) = Y_{2,0}(\theta^{LW}(t)) = \frac{3 \cos^2 \theta^{LW}(t) - 1}{2} \quad (\text{S7f})$$

$$F_{2,\pm 1}^Q(t) = Y_{2,\pm 1}(\theta^{LW}(t), \phi^{LW}(t)) = (\pm 1) \sqrt{\frac{3}{8}} \sin 2\theta^{LW}(t) e^{\mp i \phi^{LW}(t)} \quad (\text{S7g})$$

$$F_{2,\pm 2}^Q(t) = Y_{2,\pm 2}(\theta^{LW}(t), \phi^{LW}(t)) = \sqrt{\frac{3}{8}} \sin^2 \theta^{LW}(t) e^{\mp 2i \phi^{LW}(t)} \quad (\text{S7h})$$

By using the master equation (see Eqs S1 and S2), one easily derives the contribution of the quadrupolar relaxation mechanism to the time evolution of the coherences:

$$\frac{d}{dt} \begin{pmatrix} T_{20}^{IR} \\ T_{11}^{IR}(a) \\ T_{21}^{IR}(s) \\ T_{22}^{IR}(s) \\ T_{10}^{IR} \\ T_{11}^{IR}(s) \\ T_{21}^{IR}(a) \\ T_{22}^{IR}(a) \end{pmatrix} = -\text{diag}(A^Q, B^Q, C^Q, D^Q, E^Q, B^Q, C^Q, D^Q) \cdot \begin{pmatrix} T_{20}^{IR} \\ T_{11}^{IR}(a) \\ T_{21}^{IR}(s) \\ T_{22}^{IR}(s) \\ T_{10}^{IR} \\ T_{11}^{IR}(s) \\ T_{21}^{IR}(a) \\ T_{22}^{IR}(a) \end{pmatrix} \quad (\text{S8})$$

with  $A^Q = 3J_1^Q(\omega_0)$

$$B^Q = \frac{3}{2}J_0^Q(0) + \frac{5}{2}J_1^Q(\omega_0) + J_2^Q(2\omega_0)$$

$$C^Q = \frac{3}{2}J_0^Q(0) + \frac{1}{2}J_1^Q(\omega_0) + J_2^Q(2\omega_0)$$

$$D^Q = J_1^Q(\omega_0) + 2J_2^Q(2\omega_0)$$

$$E^Q = J_1^Q(\omega_0) + 4J_2^Q(2\omega_0)$$

The so-called spectral densities ( $J_m^Q(m\omega_0)$ ) used in Eq. S8 are the Fourier transform of the autocorrelation functions  $G_m^Q(\tau)$  describing the loss of memory of the fluctuating part of the quadrupolar coupling:

$$J_m^Q(m\omega_0) = (-1)^m C_Q^2 \int_0^\infty \left( F_{2,-m}^Q(0) - \langle F_{2,-m}^Q \rangle \right) \left( F_{2,m}^Q(\tau) - \langle F_{2,m}^Q \rangle \right) e^{im\omega_0\tau} d\tau \quad (\text{S9})$$

### 3. Hetero-Nuclear Dipolar Relaxation

Because of the presence of fluorine embedded in the clay network of the synthetic clay, the hetero-nuclear dipolar coupling may also contribute significantly to the NMR relaxation of the confined heavy water. The corresponding Hamiltonian<sup>6,7</sup> is defined by:

$$H_D(t) = C_D \sum_{m=-2}^2 (-1)^m \frac{T_{2,m}^D F_{2,-m}^D(t)}{r_{IS}^3(t)} \quad (\text{S10a})$$

where the dipolar coupling constant is given by:

$$C_D = -\frac{\mu_0}{4\pi} \sqrt{6} \gamma_I \gamma_S \hbar \quad (\text{S10b})$$

and the spin operators become:

$$T_{20}^D = \frac{1}{\sqrt{6}} \left( 2I_z S_z - \frac{1}{2}(I_+ S_- + I_- S_+) \right) = \frac{1}{\sqrt{6}} \left( 2\sqrt{2} T_{10}^{IR} S_z + \frac{1}{2} [T_{11}^{IR}(s)(S_- - S_+) - T_{11}^{IR}(a)(S_- + S_+)] \right) \quad (\text{S10c})$$

$$T_{2\pm 1}^D = \mp \frac{1}{2} (I_z S_{\pm} + I_{\pm} S_z) = \mp \frac{1}{\sqrt{2}} (T_{10}^{IR} S_{\pm} \mp [T_{11}^{IR}(s) \mp T_{11}^{IR}(a)] S_z) \quad (\text{S10d})$$

$$T_{2\pm 2}^D = \frac{1}{2} I_{\pm} S_{\mp} = \mp \frac{1}{\sqrt{2}} (T_{11}^{IR}(s) \mp T_{11}^{IR}(a)) S_{\mp} \quad (\text{S10e})$$

where  $S_{\alpha}$  stems for the various components of the fluor spin.

The functions  $F_{2,m}^D(t)$  in Eq. S10a are the same as in Eq. S7a but they now describe the reorientation of the vector joining the two coupled spins (noted  $\vec{r}_{IS}(t)$ ) by reference with the static magnetic field  $\mathbf{B}_0$ . In addition to that angular dependency, the dipolar Hamiltonian is also very sensitive to the diffusion of the probe through the variation of the separation between the coupled spins (*cf.* the term  $r_{IS}^{-3}(t)$  in Eq. S10a). The contribution from the hetero-nuclear dipolar coupling to the master equation (see Eqs S1 and S2) may also be written in a matrix form<sup>8</sup>:

$$\frac{d}{dt} \begin{pmatrix} T_{20}^{IR} \\ T_{11}^{IR}(a) \\ T_{21}^{IR}(s) \\ T_{22}^{IR}(s) \\ T_{10}^{IR} \\ T_{11}^{IR}(s) \\ T_{21}^{IR}(a) \\ T_{22}^{IR}(a) \end{pmatrix} = -\text{diag}(A^D, B^D, C^D, D^D, E^D, B^D, C^D, D^D) \cdot \begin{pmatrix} T_{20}^{IR} \\ T_{11}^{IR}(a) \\ T_{21}^{IR}(s) \\ T_{22}^{IR}(s) \\ T_{10}^{IR} \\ T_{11}^{IR}(s) \\ T_{21}^{IR}(a) \\ T_{22}^{IR}(a) \end{pmatrix} \quad (\text{S11})$$



with  $A^D = \frac{1}{3} J_0^D(\omega_0 - \omega_s) + J_1^D(\omega_0) + 2 J_2^D(\omega_0 + \omega_s)$

$$B^D = \frac{2}{9} J_0^D(0) + \frac{1}{18} J_0^D(\omega_0 - \omega_s) + \frac{1}{6} J_1^D(\omega_0) + \frac{1}{3} J_1^D(\omega_s) + \frac{1}{3} J_2^D(\omega_0 + \omega_s)$$

$$C^D = \frac{2}{9} J_0^D(0) + \frac{5}{18} J_0^D(\omega_0 - \omega_s) + \frac{5}{6} J_1^D(\omega_0) + \frac{1}{3} J_1^D(\omega_s) + \frac{5}{3} J_2^D(\omega_0 + \omega_s)$$

$$D^D = \frac{8}{9} J_0^D(0) + \frac{1}{9} J_0^D(\omega_0 - \omega_s) + \frac{1}{3} J_1^D(\omega_0) + \frac{4}{3} J_1^D(\omega_s) + \frac{2}{3} J_2^D(\omega_0 + \omega_s)$$

$$E^D = \frac{1}{9} J_0^D(\omega_0 - \omega_s) + \frac{1}{3} J_1^D(\omega_0) + \frac{2}{3} J_2^D(\omega_0 + \omega_s)$$

The corresponding spectral densities are:

$$J_m^D(\omega) = (-1)^m N_s S(S+1) C_D^2 \int_0^\infty \left( \frac{F_{2,-m}^D(0)}{r_{IS}^3(0)} - \left\langle \frac{F_{2,-m}^D}{r_{IS}^3} \right\rangle \right) \left( \frac{F_{2,m}^D(\tau)}{r_{IS}^3(\tau)} - \left\langle \frac{F_{2,m}^D}{r_{IS}^3} \right\rangle \right) e^{im\omega_0\tau} d\tau \quad (\text{S12})$$

where  $N_s$  is the average number of fluorine spin coupled to each deuterium nucleus.

#### 4. Contributions to the Spin-Locking Relaxation Rate

The relaxation of the coherences during the spin-locking experiments is again described by the master Equations S1-S2. In this study, we focus only on the  $m = 0$  contribution of Eq. S2, since the  $m = \pm 1$  and  $m = \pm 2$  components are only slightly modified<sup>4</sup> by the irradiation field whose angular velocity  $\omega_1$  is negligible compared to the resonance angular velocity  $\omega_0$ . For the quadrupolar coupling, the corresponding  $m = 0$  component is given by:

$$f_{m=0}^{\mathcal{Q}}(\sigma^*) = -C_{\mathcal{Q}}^2 \int_0^{\infty} \left( F_{20}^{\mathcal{Q}}(t) - \langle F_{20}^{\mathcal{Q}}(t) \rangle \right) \left( F_{20}^{\mathcal{Q}}(t-\tau) - \langle F_{20}^{\mathcal{Q}}(t) \rangle \right) \left[ T_{20}^{IR}, \left[ e^{-iH_s^* \tau} T_{20}^{IR+} e^{iH_s^* \tau}, \sigma^* \right] \right] d\tau \quad (\text{S13})$$

The time evolution of the  $T_{20}^{IR}$  coherence under the influence of the static residual quadrupolar coupling and the locking irradiation is described by the  $e^{-iH_s^* \tau} T_{20}^{IR+} e^{iH_s^* \tau}$  term in the double commutator of Eq. S13. As described by Eq. S4a, the quadrupolar contributions to spin-locking relaxation measurement probes the spectral density  $J_0^{\mathcal{Q}}(\omega)$  at the angular velocity  $k_1$  defined in Eq. S6a in addition to the angular velocity  $\omega=0$  which is already probed by the relaxation rates of the  $T_{11}^{IR}(a,s)$  and  $T_{21}^{IR}(a,s)$  coherences (see the  $B^{\mathcal{Q}}$  and  $C^{\mathcal{Q}}$  terms in Eq. S8). Thanks to the completeness of the basis set, the quadrupolar contribution to the time evolution of the coherences described by the the master equation<sup>4</sup> (see Eqs S1, S2 and S13) may also be written in a matrix form:

$$\frac{d}{dt} \begin{pmatrix} T_{20}^{IR} \\ T_{11}^{IR}(a) \\ T_{21}^{IR}(s) \\ T_{22}^{IR}(s) \\ T_{10}^{IR} \\ T_{11}^{IR}(s) \\ T_{21}^{IR}(a) \\ T_{22}^{IR}(a) \end{pmatrix} = - \begin{pmatrix} A^{\mathcal{Q}} & -\sqrt{3}K^{\mathcal{Q}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & B^{\mathcal{Q}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & C^{\mathcal{Q}} & 0 & 0 & 0 & 0 & 0 \\ 0 & -K^{\mathcal{Q}} & 0 & D^{\mathcal{Q}} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & E^{\mathcal{Q}} & 0 & -K^{\mathcal{Q}} & 0 \\ 0 & 0 & 0 & 0 & 0 & L^{\mathcal{Q}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & M^{\mathcal{Q}} & 0 \\ 0 & 0 & 0 & 0 & 0 & -K^{\mathcal{Q}} & 0 & D^{\mathcal{Q}} \end{pmatrix} \begin{pmatrix} T_{20}^{IR} \\ T_{11}^{IR}(a) \\ T_{21}^{IR}(s) \\ T_{22}^{IR}(s) \\ T_{10}^{IR} \\ T_{11}^{IR}(s) \\ T_{21}^{IR}(a) \\ T_{22}^{IR}(a) \end{pmatrix} \quad (\text{S14})$$

with  $A^{\mathcal{Q}} = 3J_1^{\mathcal{Q}}(\omega_0)$

$$B^{\mathcal{Q}} = \frac{3\omega_{\mathcal{Q}}^2 J_0^{\mathcal{Q}}(0) + 4\omega_1^2 J_0^{\mathcal{Q}}(k_1)}{2k_1^2} + \frac{5}{2} J_1^{\mathcal{Q}}(\omega_0) + J_2^{\mathcal{Q}}(2\omega_0)$$

$$C^{\varrho} = \frac{3\omega_{\varrho}^2 J_0^{\varrho}(0) + 4\omega_1^2 J_0^{\varrho}(k_1)}{2k_1^2} + \frac{1}{2} J_1^{\varrho}(\omega_0) + J_2^{\varrho}(2\omega_0)$$

$$D^{\varrho} = J_1^{\varrho}(\omega_0) + 2J_2^{\varrho}(2\omega_0)$$

$$E^{\varrho} = J_1^{\varrho}(\omega_0) + 4J_2^{\varrho}(2\omega_0)$$

$$L^{\varrho} = \frac{3}{2} \frac{\omega_{\varrho}^2 J_0^{\varrho}(0) + 2\omega_1^2 (J_0^{\varrho}(0) + J_0^{\varrho}(k_1))}{k_1^2} + \frac{5}{2} J_1^{\varrho}(\omega_0) + J_2^{\varrho}(2\omega_0)$$

$$M^{\varrho} = \frac{3\omega_{\varrho}^2 J_0^{\varrho}(0) + 2\omega_1^2 (J_0^{\varrho}(0) + J_0^{\varrho}(k_1))}{2k_1^2} + \frac{1}{2} J_1^{\varrho}(\omega_0) + J_2^{\varrho}(2\omega_0)$$

$$K^{\varrho} = \frac{3\omega_1 \omega_{\varrho} (J_0^{\varrho}(0) - J_0^{\varrho}(k_1))}{2k_1^2}$$

In the same manner, the  $m = 0$  contribution of the hetero-nuclear dipolar coupling is given by:

$$f_{m=0}^D(\sigma^*) = -\frac{4}{9} C_D^2 N_S S(S+1) \int_0^{\infty} \left( \frac{F_{20}^D(t)}{r_{IS}^3(t)} - \left\langle \frac{F_{20}^D}{r_{IS}^3} \right\rangle \right) \left( \frac{F_{20}^D(t-\tau)}{r_{IS}^3(t-\tau)} - \left\langle \frac{F_{20}^D}{r_{IS}^3} \right\rangle \right) [T_{10}^{IR}, [e^{-iH_S^* \tau} T_{10}^{IR+} e^{iH_S^* \tau}, \sigma^*]] d\tau \quad (\text{S15})$$

The time evolution of the  $T_{10}^{IR}$  coherence under the influence of the static residual quadrupolar coupling and the locking irradiation is described now by the  $e^{-iH_S^* \tau} T_{10}^{IR+} e^{iH_S^* \tau}$  term in the double commutator of Eq. S15. As described now by Eq. S5a, the dipolar contribution to spin-locking relaxation measurement probes the spectral density  $J_0^D(\omega)$  at the angular velocities  $k_2$  and  $k_3$  defined in Eqs S6b and S6c respectively. A matrix formulation of the

hetero-nuclear dipolar relaxation mechanism to the master equation (see Eqs S1, S2 and S15)

may be written<sup>9</sup>:

$$\frac{d}{dt} \begin{pmatrix} T_{20}^{IR} \\ T_{11}^{IR}(a) \\ T_{21}^{IR}(s) \\ T_{22}^{IR}(s) \\ T_{10}^{IR} \\ T_{11}^{IR}(s) \\ T_{21}^{IR}(a) \\ T_{22}^{IR}(a) \end{pmatrix} = - \begin{pmatrix} A^Q & -\sqrt{3}K^Q & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & B^Q & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & C^Q & 0 & 0 & 0 & 0 & 0 \\ 0 & -K^Q & 0 & D^Q & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & E^Q & 0 & -K^Q & 0 \\ 0 & 0 & 0 & 0 & 0 & L^Q & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & M^Q & 0 \\ 0 & 0 & 0 & 0 & 0 & -K^Q & 0 & D^Q \end{pmatrix} \begin{pmatrix} T_{20}^{IR} \\ T_{11}^{IR}(a) \\ T_{21}^{IR}(s) \\ T_{22}^{IR}(s) \\ T_{10}^{IR} \\ T_{11}^{IR}(s) \\ T_{21}^{IR}(a) \\ T_{22}^{IR}(a) \end{pmatrix} \quad (\text{S16})$$

$$\text{with } A^D = \frac{1}{3} J_0^D(\omega_0 - \omega_s) + J_1^D(\omega_0) + 2J_2^D(\omega_0 + \omega_s)$$

$$B^D = \frac{2(k_2 J_0^D(k_3) + k_3 J_0^D(k_2))}{9k_1} + \frac{1}{18} J_0^D(\omega_0 - \omega_s) + \frac{1}{6} J_1^D(\omega_0) + \frac{1}{3} J_1^D(\omega_s) + \frac{1}{3} J_2^D(\omega_0 + \omega_s)$$

$$C^D = \frac{2(k_2 J_0^D(k_3) + k_3 J_0^D(k_2))}{9k_1} + \frac{5}{18} J_0^D(\omega_0 - \omega_s) + \frac{5}{6} J_1^D(\omega_0) + \frac{1}{3} J_1^D(\omega_s) + \frac{5}{3} J_2^D(\omega_0 + \omega_s)$$

$$D^D = \frac{8}{9} J_0^D(0) + \frac{1}{9} J_0^D(\omega_0 - \omega_s) + \frac{1}{3} J_1^D(\omega_0) + \frac{4}{3} J_1^D(\omega_s) + \frac{2}{3} J_2^D(\omega_0 + \omega_s)$$

$$E^D = \frac{1}{9} J_0^D(\omega_0 - \omega_s) + \frac{1}{3} J_1^D(\omega_0) + \frac{2}{3} J_2^D(\omega_0 + \omega_s)$$

$$L^D = \frac{2(k_2 J_0^D(k_3) + k_3 J_0^D(k_2))}{9k_1} + \frac{1}{18} J_0^D(\omega_0 - \omega_s) + \frac{1}{6} J_1^D(\omega_0) + \frac{1}{3} J_1^D(\omega_s) + \frac{1}{3} J_2^D(\omega_0 + \omega_s)$$

$$M^D = \frac{2(k_2 J_0^D(k_3) + k_3 J_0^D(k_2))}{9k_1} + \frac{5}{18} J_0^D(\omega_0 - \omega_s) + \frac{5}{6} J_1^D(\omega_0) + \frac{1}{3} J_1^D(\omega_s) + \frac{5}{3} J_2^D(\omega_0 + \omega_s)$$

$$K^D = \frac{2\omega_1(J_0^D(k_3) - J_0^D(k_2))}{9k_1}$$

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