Supporting Information

I. $^{13}CH_2D$ groups:

Relaxation of L_1 and L_2 due to intra-methyl H-H interactions:

$$\frac{d}{dt}\begin{bmatrix} L_1 \\ L_2 \end{bmatrix} = -k_{\mathrm{HH}}\left\{ J_{HH}(0)\begin{bmatrix} 3/8 & 0 \\ 0 & 3/8 \end{bmatrix} + J_{HH}(\omega_H)\begin{bmatrix} 3/8 & 1/4 \\ 1/4 & 3/8 \end{bmatrix} + J_{HH}(2\omega_H)\begin{bmatrix} 1/4 & 0 \\ 0 & 1/4 \end{bmatrix} \right\}\begin{bmatrix} L_1 \\ L_2 \end{bmatrix}$$

Relaxation of L_1 and L_2 due to interaction with external protons:

$$\frac{d}{dt}\begin{bmatrix} L_1 \\ L_2 \end{bmatrix} = -k_{\mathrm{HH_{EXT}}}\left\{ J_{EXT}(0)\begin{bmatrix} 7 & -2 \\ -2 & 7 \end{bmatrix} + J_{EXT}(\omega_H)\begin{bmatrix} 15 & -6 \\ -6 & 15 \end{bmatrix} + J_{EXT}(2\omega_H)\begin{bmatrix} 18 & -12 \\ -12 & 18 \end{bmatrix} \right\}\begin{bmatrix} L_1 \\ L_2 \end{bmatrix}$$

Relaxation of L_1 and L_2 due to intra-methyl C-H/H-H cross-correlated interactions:

$$\frac{d}{dt}\begin{bmatrix} L_1 \\ L_2 \end{bmatrix} = -k_{\mathrm{CH/HH}}\left\{ J_{CH/HH}(0)\begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix} + J_{CH/HH}(\omega_H)\begin{bmatrix} 1/4 & 0 \\ 0 & -1/4 \end{bmatrix} \right\}\begin{bmatrix} L_1 \\ L_2 \end{bmatrix}$$

Relaxation of L_1 and L_2 due to intra-methyl C-H interactions (auto-correlated terms):

$$\frac{d}{dt}\begin{bmatrix} L_1 \\ L_2 \end{bmatrix} = -k_{\mathrm{CH}}\left\{ \begin{array}{l} J_{CH}(0)\begin{bmatrix} 1/6 & 0 \\ 0 & 1/6 \end{bmatrix} + J_{CH}(\omega_C)\begin{bmatrix} 1/4 & 0 \\ 0 & 1/4 \end{bmatrix} + J_{CH}(\omega_H)\begin{bmatrix} 1/4 & -1/8 \\ -1/8 & 1/4 \end{bmatrix} \\ +J_{CH}(\omega_H-\omega_C)\begin{bmatrix} 1/24 & 0 \\ 0 & 1/24 \end{bmatrix} + J_{CH}(\omega_H+\omega_C)\begin{bmatrix} 1/4 & 0 \\ 0 & 1/4 \end{bmatrix} \end{array} \right\}\begin{bmatrix} L_1 \\ L_2 \end{bmatrix}$$

Relaxation of L_1 and L_2 due to intra-methyl C-H/C-H cross-correlated interactions:

$$\frac{d}{dt}\begin{bmatrix} L_1 \\ L_2 \end{bmatrix} = -k_{\mathrm{CH}}\left\{ J^x_{CH}(\omega_H)\begin{bmatrix} 1/8 & -1/8 \\ -1/8 & 1/8 \end{bmatrix} + J^x_{CH}(\omega_H-\omega_C)\begin{bmatrix} 1/24 & 0 \\ 0 & -1/24 \end{bmatrix} + J^x_{CH}(\omega_H+\omega_C)\begin{bmatrix} -1/4 & 0 \\ 0 & 1/4 \end{bmatrix} \right\}\begin{bmatrix} L_1 \\ L_2 \end{bmatrix}$$

In the above, $L_1 = |\beta\rangle|2\rangle\langle\beta|\langle 3| + |\alpha\rangle|1\rangle\langle\alpha|\langle 2|$ and $L_2 = |\beta\rangle|1\rangle\langle\beta|\langle 2| + |\alpha\rangle|2\rangle\langle\alpha|\langle 3|$ (see Fig. 1a for definitions of eigenvectors in the $^{13}CH_2(D)$ spin-system). $R^F_{2,\mathrm{H}}$ - $R^S_{2,\mathrm{H}}$ is calculated as the difference between relaxation rates of L_1 and L_2.

II. $^{13}CH_3$ groups:

Relaxation of L_1, L_2, L_3, L_4 due to intra-methyl H-H interactions (auto-correlations):

$$\frac{d}{dt}\begin{bmatrix} L_1-L_3 \\ L_2 \\ L_1+L_3 \\ L_4 \end{bmatrix} = -k_{\mathrm{HH}}\left\{ J_{HH}(0)\begin{bmatrix} 3/4 & 0 & 0 & 0 \\ 0 & 3/4 & 0 & 0 \\ 0 & 0 & 3/4 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + J_{HH}(\omega_H)\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 1/4 & \sqrt{2}/4 \\ 0 & 1/4 & 1 & -\sqrt{2}/4 \\ 0 & \sqrt{2}/4 & -\sqrt{2}/4 & 3/4 \end{bmatrix} + J_{HH}(2\omega_H)\begin{bmatrix} 3/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \\ 0 & 0 & 1/2 & 0 \\ 0 & 0 & 0 & 1/2 \end{bmatrix} \right\}\begin{bmatrix} L_1-L_3 \\ L_2 \\ L_1+L_3 \\ L_4 \end{bmatrix}$$

Relaxation of L_1, L_2, L_3, L_4 due to intra-methyl H-H cross-correlated interactions:

$$\frac{d}{dt}\begin{bmatrix} L_1 - L_3 \\ L_2 \\ L_1 + L_3 \\ L_4 \end{bmatrix} = -k_{\mathrm{HH}} \left\{ J^x_{HH}(0) \begin{bmatrix} 3/4 & 0 & 0 & 0 \\ 0 & -3/4 & 0 & 0 \\ 0 & 0 & 3/4 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + J^x_{HH}(\omega_H) \begin{bmatrix} 1/2 & 0 & 0 & 0 \\ 0 & 0 & -1/4 & \sqrt{2}/4 \\ 0 & -1/4 & 1/2 & \sqrt{2}/4 \\ 0 & \sqrt{2}/4 & \sqrt{2}/4 & -1/4 \end{bmatrix} + J^x_{HH}(2\omega_H) \begin{bmatrix} 3/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & \sqrt{2}/2 \\ 0 & 0 & -1/2 & 0 \\ 0 & \sqrt{2}/2 & 0 & 0 \end{bmatrix} \right\} \begin{bmatrix} L_1 - L_3 \\ L_2 \\ L_1 + L_3 \\ L_4 \end{bmatrix}$$

Relaxation of L_1, L_2, L_3, L_4 due to interactions with external protons:

$$\frac{d}{dt}\begin{bmatrix} L_1 - L_3 \\ L_2 \\ L_1 + L_3 \\ L_4 \end{bmatrix} = -k_{\mathrm{HH_{EXT}}} \left\{ J_{EXT}(0) \begin{bmatrix} 9 & 0 & 0 & 0 \\ 0 & 9 & -4 & 2\sqrt{2} \\ 0 & -4 & 9 & -2\sqrt{2} \\ 0 & 2\sqrt{2} & -2\sqrt{2} & 7 \end{bmatrix} + J_{EXT}(\omega_H) \begin{bmatrix} 21 & 0 & 0 & 0 \\ 0 & 21 & -12 & 6\sqrt{2} \\ 0 & -12 & 21 & -6\sqrt{2} \\ 0 & 6\sqrt{2} & -6\sqrt{2} & 15 \end{bmatrix} + J_{EXT}(2\omega_H) \begin{bmatrix} 30 & 0 & 0 & 0 \\ 0 & 30 & -24 & 12\sqrt{2} \\ 0 & -24 & 30 & -12\sqrt{2} \\ 0 & 12\sqrt{2} & -12\sqrt{2} & 18 \end{bmatrix} \right\} \begin{bmatrix} L_1 - L_3 \\ L_2 \\ L_1 + L_3 \\ L_4 \end{bmatrix}$$

Relaxation of L_1, L_2, L_3, L_4 due to intra-methyl C-H auto-correlated interactions:

$$\frac{d}{dt}\begin{bmatrix} L_1 - L_3 \\ L_2 \\ L_1 + L_3 \\ L_4 \end{bmatrix} = -k_{\mathrm{CH}} \left\{ \begin{array}{l} J_{CH}(0) \begin{bmatrix} 1/6 & 0 & 0 & 0 \\ 0 & 1/6 & 0 & 0 \\ 0 & 0 & 1/6 & 0 \\ 0 & 0 & 0 & 1/2 \end{bmatrix} + J_{CH}(\omega_C) \begin{bmatrix} 1/4 & 0 & 0 & 0 \\ 0 & 1/4 & 0 & 0 \\ 0 & 0 & 1/4 & 0 \\ 0 & 0 & 0 & 3/4 \end{bmatrix} + J_{CH}(\omega_H) \begin{bmatrix} 3/8 & 0 & 0 & 0 \\ 0 & 3/8 & -1/4 & 0 \\ 0 & -1/4 & 3/8 & 0 \\ 0 & 0 & 0 & 3/8 \end{bmatrix} \\ + J_{CH}(\omega_H + \omega_C) \begin{bmatrix} 3/4 & 0 & 0 & 0 \\ 0 & 3/4 & -1/2 & 0 \\ 0 & -1/2 & 3/4 & 0 \\ 0 & 0 & 0 & 3/4 \end{bmatrix} + J_{CH}(\omega_H - \omega_C) \begin{bmatrix} 1/8 & 0 & 0 & 0 \\ 0 & 1/8 & -1/12 & 0 \\ 0 & -1/12 & 1/8 & 0 \\ 0 & 0 & 0 & 1/8 \end{bmatrix} \end{array} \right\} \begin{bmatrix} L_1 - L_3 \\ L_2 \\ L_1 + L_3 \\ L_4 \end{bmatrix}$$

Relaxation of L_1, L_2, L_3, L_4 due to intra-methyl C-H/C-H cross-correlated interactions:

$$\frac{d}{dt}\begin{bmatrix} L_1 - L_3 \\ L_2 \\ L_1 + L_3 \\ L_4 \end{bmatrix} = -k_{\mathrm{CH}} \left\{ \begin{array}{l} J^x_{CH}(0) \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1/3 \end{bmatrix} + J^x_{CH}(\omega_C) \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1/2 \end{bmatrix} + J^x_{CH}(\omega_H) \begin{bmatrix} 1/4 & 0 & 0 & 0 \\ 0 & 1/4 & -1/4 & \sqrt{2}/4 \\ 0 & -1/4 & 1/4 & -\sqrt{2}/4 \\ 0 & \sqrt{2}/4 & -\sqrt{2}/4 & 0 \end{bmatrix} \\ + J^x_{CH}(\omega_H + \omega_C) \begin{bmatrix} 1/2 & 0 & 0 & 0 \\ 0 & 1/2 & -1/2 & \sqrt{2}/2 \\ 0 & -1/2 & 1/2 & -\sqrt{2}/2 \\ 0 & \sqrt{2}/2 & -\sqrt{2}/2 & 0 \end{bmatrix} + J^x_{CH}(\omega_H - \omega_C) \begin{bmatrix} 1/12 & 0 & 0 & 0 \\ 0 & 1/12 & -1/12 & \sqrt{2}/12 \\ 0 & -1/12 & 1/12 & -\sqrt{2}/12 \\ 0 & \sqrt{2}/12 & -\sqrt{2}/12 & 0 \end{bmatrix} \end{array} \right\} \begin{bmatrix} L_1 - L_3 \\ L_2 \\ L_1 + L_3 \\ L_4 \end{bmatrix}$$

where

$$k_{\mathrm{HH}} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{6\hbar^2\gamma_{\mathrm{H}}^4}{r_{\mathrm{HH}}^6};\ k_{\mathrm{HH_{EXT}}} = \left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{1}{4}\right) \frac{\hbar^2\gamma_{\mathrm{H}}^4}{r_{\mathrm{HH_{EXT}}}^6};\ k_{\mathrm{CH/HH}} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{6\hbar^2\gamma_{\mathrm{H}}^3\gamma_{\mathrm{C}}}{r_{\mathrm{HH}}^3 r_{\mathrm{CH}}^3};\ k_{\mathrm{CH}} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{6\hbar^2\gamma_{\mathrm{H}}^2\gamma_{\mathrm{C}}^2}{r_{\mathrm{CH}}^6};$$

γ_k is the gyromagnetic ratio of spin k, r_{kl} is the distance between spins k and l, μ_0 is the vacuum permeability constant.

In the above, L_1, L_2, L_3, L_4 are defined as in the main text (see Fig.1b for definitions of eigenvectors in the (^{13}C)H_3 spin-system):

$$L_1 - L_3 = \sqrt{3}(|3\rangle\langle 4| - |1\rangle\langle 2|)$$
$$L_1 + L_3 = \sqrt{3}(|3\rangle\langle 4| + |1\rangle\langle 2|)$$
$$L_2 = (2|2\rangle\langle 3| + |5\rangle\langle 6| + |7\rangle\langle 8|)$$
$$L_4 = \sqrt{2}(|2\rangle\langle 3| - |5\rangle\langle 6| - |7\rangle\langle 8|)$$

The form of the spectral density function, $J(\omega)$, used for all numerical simulations described in the text is as follows,

$$J_{\mu\nu}(\omega) = \frac{1}{5}\left\{ S_{axis}^2 S_{axis,\mu} S_{axis,\nu} \frac{\tau_C}{1+(\omega\tau_C)^2} + \left[P_2(\cos\theta_{\mu,\nu}) - S_{axis}^2 S_{axis,\mu} S_{axis,\nu} \right] \frac{\tau_e}{1+(\omega\tau_e)^2} \right\}$$

where μ and ν index the interactions ($\mu = \nu$ and $\mu \neq \nu$ for auto- and cross-correlated spectral density functions, respectively; above, the cross-correlated spectral density functions for C-H/C-H and H-H/H-H interactions are labeled with superscript x); S_{axis} is the generalized order parameter of the methyl three-fold axis; $P_2(x) = \frac{1}{2}(3x^2 - 1)$, and $\theta_{axis,a}$ is the angle between the methyl symmetry axis and vector a that connects a pair of spins; $S_{axis,a} = P_2(\theta_{axis,a})$; τ_C is the rotational correlation time of global molecular reorientation; $1/\tau_e = 1/\tau_f + 1/\tau_C$, where τ_f is the correlation time of (fast) local motions. For external interactions the following simplified form of the spectral density was assumed:

$$J_{EXT}(\omega) = \frac{1}{5}\left\{ \frac{\tau_C}{1+(\omega\tau_C)^2} \right\}$$

where all the symbols are defined above. $R^F_{2,H}$ - $R^S_{2,H}$ is calculated as the difference between relaxation rates of $L_1 + L_3$ (the scheme of Figure 4b, top) and L_2 or between relaxation rates of L_1 - L_3 (the scheme of Figure 4b, bottom) and L_2.