Supplementary Material (ESI) for PCCP

Supplementary information for *Ab initio simulation of proton spin diffusion*

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Content

In section A, we describe the product-operator basis set used to expand the density matrix, the rules for the evolution under the dipolar Hamiltonian, and the numerical integration scheme used to propagate the density matrix. In section B, we describe the experimental and simulated content of the matrices of proton spin diffusion (PSD) build-up curves. Section C contains the full list of dipolar couplings used for the simulation.

A. LCL simulation of polarisation transfer

1. *Picturing Liouville space*

In the solid state, the secular rotating-frame dipolar Hamiltonian for a system of N homonuclear spins I = 1/2 is:

$$H = \sum_{i>j} \frac{\mu_0 \gamma^2 \hbar}{4\pi r_{ij}^3} \frac{1}{2} \left(1 - 3\cos^2\theta_{ij}\right) \left(2 I_{iz} I_{jz} - \frac{1}{2}\left(I_{i+} I_{j-} + I_{i-} I_{j+}\right)\right), \qquad (1)$$

where $\vec{I_i}$ and $\vec{I_j}$ are nuclear spin operators, r_{ij} is the internuclear vector, θ_{ij} is the angle between the internuclear vector and the static magnetic field, and γ is the gyromagnetic ratio.

The density matrix σ that describes the spin system is considered here as a vector in Liouville space, and is expanded using a product-operator basis set:

$$\sigma(t) = \sum_{r=1}^{4^N} b_r(t) B_r, \qquad (2)$$

$$B_r = 2^{q_r - 1} \prod_{i=1}^{N} I_{i,r}, \qquad (3)$$

where the product is over all spins i, $I_{i,r} \in \{I_{iz}, I_{i+}/\sqrt{2}, I_{i-}/\sqrt{2}, E_i\}$, and q_r is the spin order for the product operator B_r, i.e., the number of single-spin operators $I_{i,r}$ different from the identity.

The time-evolution of the system under a Hamiltonian H is governed by the Liouville-von Neumann equation:

$$\frac{d\sigma}{dt} = L\sigma = -i[H, \sigma], \qquad (4)$$

where $L = -i[H, .]$ is the Liouvillian of the system. The action of the Liouvillian on any zero-quantum basis set operator can be calculated using a small set of evolution rules, reported in table I. These rules provide the connectivity between operators that can be used to “picture” the zero-quantum subspace.

TABLE I: Action of the dipolar Hamiltonian on zero-quantum product-operators. For each line, the product $LA = -i[H, A]$ is given for a one-spin or two-spin operator A.

$\cdot$	$\xrightarrow{H_{12}^D}$	$-i\omega_{12}^D($	$\cdot$	$+\frac{1}{2}($	$\cdot$	$))$
I_{1z}			0		$I_{1+}I_{2-} - I_{1-}I_{2+}$	
$I_{1+}/\sqrt{2}$			$\sqrt{2}I_{1+}I_{2z}$		$\sqrt{2}I_{1z}I_{2+}$	
$I_{1-}/\sqrt{2}$			$-\sqrt{2}I_{1-}I_{2z}$		$-\sqrt{2}I_{1z}I_{2-}$	
$\sqrt{2}I_{1z}I_{2+}$			$I_{2+}/\sqrt{2}$		$I_{1+}/\sqrt{2}$	
$\sqrt{2}I_{1z}I_{2-}$			$-I_{2-}/\sqrt{2}$		$-I_{1-}/\sqrt{2}$	
$I_{1+}I_{2-}$			0		$I_{1z} - I_{2z}$	

2. Numerical integration of the Liouville-von Neumman equation of motion

The density matrix σ after an evolution during τ under a time-dependent Liouvillian L can be written formally:

$$\sigma(\tau) = \hat{U}(\tau)\sigma(0) = T\exp\left(\int_0^\tau L(t)dt\right)\sigma(0), \tag{5}$$

where $\hat{U}(\tau)$ is the time-evolution superoperator. To calculate numerically $\sigma(\tau)$, a first approximation is made by considering that the Liouvillian is piece-wise time-independent during steps of duration Δt. Under this approximation, equation 5 becomes

$$\sigma(\tau) = \hat{U}(\tau)\sigma(0) \simeq \prod_{m=0}^{M-1} \exp\left(L(t_m)\Delta t\right)\sigma(0), \tag{6}$$

where $\tau = M\Delta t$ and $t_m = m\Delta t$. In order to calculate the density matrix at each step $\sigma(t_m) = \exp(L(t_{m-1})\Delta t)\sigma(t_{m-1})$ without storing explicitly the Liouvillian matrix and without performing matrix-vector multiplication, the Suzuki-Trotter (ST) algorithm is used to approximate the propagation over each timestep. In the ST algorithm, the Liouvillian is split into a sum of terms for which the time-evolution can be calculated analytically, and here a pair decomposition of the dipolar interaction was used

$$L = \sum_{i>j} L_{ij}, \tag{7}$$

where the sum is over pairs of spins and L_{ij} corresponds to the dipolar interaction between spins i and j. Using the rules given in table I, the action of L_{ij} can be calculated analytically in four dimensional subspaces. Increasingly complex decomposition of the propagator make it possible to obtain an increasing accuracy, and here a second-order scheme was employed

$$\exp\left(\sum_{i>j} L_{ij}\Delta t\right) = \left(\prod_{i=1}^{N}\prod_{j=1}^{i-1} \exp\left(L_{ij}\Delta t/2\right)\right)\left(\prod_{i=N}^{1}\prod_{j=i-1}^{1} \exp\left(L_{ij}\Delta t/2\right)\right) \tag{8}$$

where N is the total number of spins.

The actual implementation of this numerical integration scheme, in a code that we call Tourbillon, can be found in the ESI. For a simulation performed in a reduced Liouville space

X, the time evolution is formally driven by a Liouvillian L_X, where all the elements that would excite excluded coherences are set to zero. In the actual code, the evolution is simply not implemented in the subspaces involving coherences that are excluded from the reduced Liouville space.

B. Proton spin diffusion build-up curves

1. *Experimental*

Proton spin diffusion can be observed experimentally using the 2D pulse sequence in fig. 1 for a set of mixing times $\{\tau\}$. In the 2D spectrum a transfer of polarisation during the mixing time τ from spins observed at frequency ν_1 to spins observed at frequency ν_2 results in a cross peak at frequency coordinates (ν_1, ν_2). The peak volumes as a function of the mixing time τ, $P_{exp}(\nu_1, \nu_2, \tau)$, can be conveniently arranged in a $M \times M$ matrix, where M is the number of resolved peaks in the 1D spectrum, and are usually plotted as a $M \times M$ matrix of build-up curves.

Experimental proton spin diffusion data have been recorded for two powdered organic solids; the experimental details have already been reported in detail before.[1,2] β-L-aspartyl-L-alanine has been studied at a MAS frequency of 6.25 kHz and a ^{1}H Larmor frequency of 500 MHz, and thymol has been studied at a MAS frequency of 6.6 kHz and a ^{1}H Larmor frequency of 700 MHz.

2. *Simulated*

Under the assumption of a perfect pulse sequence, the volume of the (ν_1, ν_2) peak for a mixing time τ can be written:

$$P_{sim}(\nu_1, \nu_2, \tau) = \langle \sum_{j=1}^{N_2} I_{b_j z} | \hat{U}(\tau) | \sum_{i=1}^{N_1} I_{a_i z} \rangle \tag{9}$$

where the first and second summations are over groups of spins $\{a_i\}_{i=1,N_1}$ and $\{b_j\}_{j=1,N_2}$ that are observed at frequency ν_1 and ν_2 respectively, $\hat{U}(\tau)$ is the time-evolution superoperator for a mixing time τ. In the absence of unresolved or accidentally isochronous chemical sites, the spins observed at frequency ν_1 are equivalent, and the expression for the peak volume can be simplified to:

$$P_{sim}(\nu_1, \nu_2, \tau) = N_1 \langle \sum_{j=1}^{N_2} I_{b_j z} | \hat{U}(\tau) | I_{a_1 z} \rangle \tag{10}$$

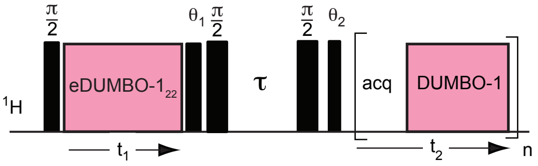

FIG. 1: Pulse sequence for the 2D PSD experiment.

where a_1 is any spin belonging to the group of equivalent spins observed at frequency ν_1. In consequence, the build-up curves are simulated by performing one independent calculation for each group of equivalent spins, with an initial density matrix that corresponds to a single polarised spin $\sigma(0) = I_{a_1 z}$, and observables that consists of the summed polarisations for groups of equivalent spins $\sum_j \langle I_{b_j z} \rangle / \| I_{1z} \|^2$. The resulting curves can be processed to take into account accidentally isochronous chemical sites and unresolved peaks, by simply summing over groups that correspond to a given peak in the 2D NMR spectra.

The explanation given above formally corresponds to the case of a single crystallite, but it can be extended to the case of powdered sample. Using the definitions introduced by Haeberlen, in the case of a single crystallite nuclei are equivalent for the PSD experiment if they are magnetically equivalent, while in the case of a powdered sample nuclei are equivalent if they are crystallographically equivalent. This property has to be taken into account to perform the minimum number of simulations necessary to obtain a full set of build-up curves.

For the systems studied here, proton positions were taken from single crystal X-ray diffraction data available from the Cambridge Structural Database[3] (entry code FUMTEM for β-L-aspartyl-L-alanine and IPMEPL for thymol).

3. Comparison

The experimental and simulated spin diffusion build-up curves are related by an overall normalisation factor

$$P_{exp}(\nu_1, \nu_2, \tau) = \xi P_{sim}(\nu_1, \nu_2, \tau), \tag{11}$$

where ξ depends on many experimental contributions that are not measured. In order to compare simulated and experimental data, ξ is determined from a least-squares fit between the calculated and experimental peak volumes. Separate values are obtained for each initial density matrix, i.e., for each line in the $M \times M$ matrix of build-up curves; these additional degrees of freedom makes it possible to account for some effects that are not included in the simulation, such as the non-ideality of the pulse sequence.

C. List of dipolar couplings

A system of N spins involves C_N^2 distinct dipolar couplings. For a single primitive unit cell, there are 1128 couplings for β-L-aspartyl-L-alanine and 3486 couplings for thymol. The full list of couplings, calculated using the minimum image convention to enforce periodic boundary conditions, is given in separate files.

1. β-L-aspartyl-L-alanine

See SI file fumtem_dipolar.txt

2. *Thymol*

See SI file ipmepl_dipolar.txt

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[1] B. Elena and L. Emsley, J. Am. Chem. Soc. **127**, 9140 (2005).

[2] E. Salager, R. S. Stein, C. J. Pickard, B. Elena, and L. Emsley, Phys. Chem. Chem. Phys. **11**, 2610 (2009).

[3] F. H. Allen, Acta Crystallogr., sect B **58**, 380 (2002).