

# Supplementary information for *Master-equation approach to the description of proton-driven spin diffusion from crystal geometry using simulated zero-quantum lineshapes*

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## A. Supplementary PDS D build-up curves

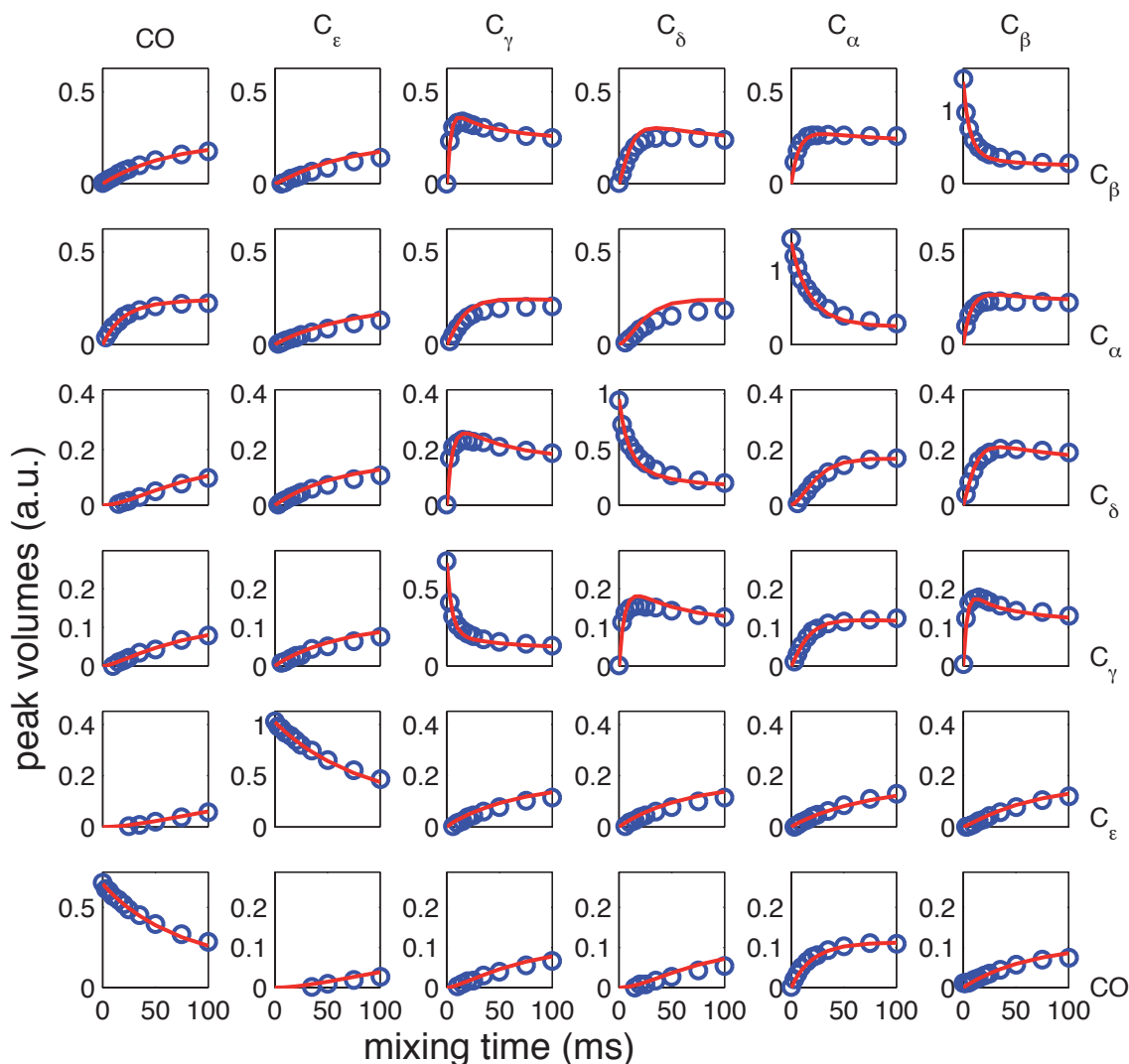


FIG. 1. PDS D build-up curves recorded for a polycrystalline sample of L-histidine.H<sub>2</sub>O.HCl with 15 kHz MAS. Experimental measurements (blue) and curves calculated with a kinetic model (red) are shown. Experimental curves were obtained by integrating peak volumes in a series of 2D PDS D experiments. The rates used in the kinetic model were determined from the experimental curves using a least-error matrix analysis.

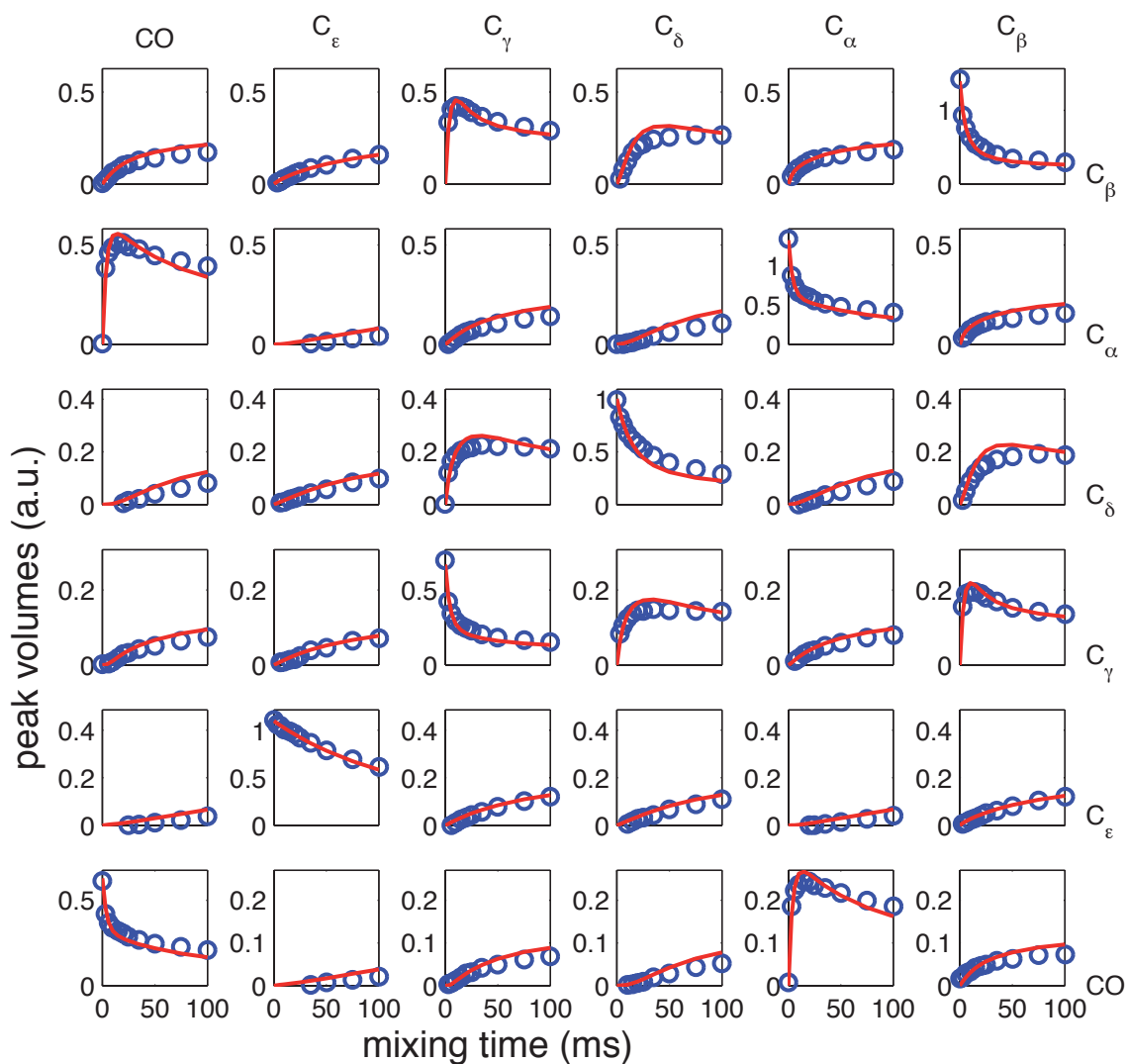


FIG. 2. PDSB build-up curves recorded for a polycrystalline sample of L-histidine.H<sub>2</sub>O.HCl with 20 kHz MAS. Experimental measurements (blue) and curves calculated with a kinetic model (red) are shown. Experimental curves were obtained by integrating peak volumes in a series of 2D PDSB experiments. The rates used in the kinetic model were determined from the experimental curves using a least-error matrix analysis.

## B. Rate-matrix analysis of polarisation transfer

### 1. Time evolution of experimental observables

In a master-equation approach to the description of polarisation transfer for a system of  $N$  homonuclear spins, the time evolution of the polarisations is described by:

$$\frac{d}{dt}\mathbf{M} = \mathbf{KM}. \quad (1)$$

$\mathbf{M}$  is a vector of coefficients of the carbon polarisations  $\{M_i\}$ , and  $[\mathbf{K}]_{ij}$ , hereafter noted  $k_{ij}$  is the rate of transfer from spin  $j$  to spin  $i$ .

For a system containing groups of equivalent spins, it is useful to introduce the summed polarisations  $M'_p$  for groups of equivalent spins

$$M'_p = \sum_{i=1}^{N_p} M_{a_i}, \quad (2)$$

where  $p$  denotes a group of  $N_p$  equivalent spins, and the sum is over all spins  $\{a_i\}$  in the group. Using this set of variables, the rate matrix becomes block-diagonal, and only the block involving the summed polarisations has to be taken into account. The other variables, the detailed expression of which is irrelevant, can be dropped from the description. The kinetic model then simplifies to

$$\frac{d}{dt}\mathbf{M}' = \mathbf{K}'\mathbf{M}', \quad (3)$$

where

$$k'_{pq} = \frac{1}{N_p} \sum_{i=1}^{N_p} \sum_{j=1}^{N_q} k_{a_i b_j}. \quad (4)$$

This simplification would not be possible for groups that include non-equivalent spins, as discussed by Robyr *et al.* in Ref. 1. Equation 4 can be simplified by considering the fact that, because the spins in a given group are equivalent, the sum  $\sum_{j=1}^{N_q} k_{a_i b_j}$  is identical for all values of  $i$  :

$$k'_{pq} = \sum_{j=1}^{N_q} k_{a_1 b_j}. \quad (5)$$

For proton-driven spin diffusion in polycrystalline solids under magic-angle spinning, nuclear spins are equivalent if they are crystallographically equivalent according to the definition introduced by Haeberlen, i.e., if the nuclei are related by a symmetry operation of the crystal. There are as many groups of equivalent spins as there are spins in the asymmetric unit, and the sums over all spins in a group are sums over asymmetric units. In consequence, for a system where all the carbons in the asymmetric unit are resolved in the experimental spectra, Eq. 3 describes the time evolution of the peak volumes in a PDS experiment.

### 2. PDS rates and effective dipolar couplings

In proton-driven spin diffusion, the rate of transfer between two carbons  $i$  and  $j$  can, under certain conditions, be written:

$$k_{ij} = \kappa\omega_{ij}^2 F[G_{ij}(\nu)], \quad (6)$$

where  $\omega_{ij}$  is the dipolar coupling between spins  $i$  and  $j$ ,  $F[G_{ij}(\nu)]$  is a function of the zero-quantum lineshape for the pair  $ij$ , and  $\kappa$  is a geometrical factor. Combining Eq. 5 and 6, the rate of transfer between groups of crystallographically equivalent spins can be written:

$$k'_{pq} = \kappa \sum_{j=1}^{N_q} \omega_{a_1 b_j}^2 F[G_{a_1 b_j}(\nu)]. \quad (7)$$

If the zero-quantum lineshapes are approximated by convolutions of single-quantum lineshapes,<sup>2</sup> then, as all the spins in the group  $q$  are equivalent, the term  $F[G_{a_1 b_j}(\nu)]$  becomes identical for all spin pairs  $(a_1, b_j)$ , regardless of the value of  $j$ . Equation 7 can then be factored as,

$$k'_{pq} = \kappa \omega_{pq,\text{eff}}^2 F[G_{a_1 b_1}(\nu)], \quad (8)$$

where

$$\omega_{pq,\text{eff}}^2 = \sum_{j=1}^{N_q} \omega_{a_1 b_j}^2. \quad (9)$$

The quantity  $\omega_{pq,\text{eff}}$ , sometimes called “effective dipolar coupling”, is straightforward to calculate for a given crystal structure. It can be noted that the cost of the calculation of  $k'_{pq}$  is greatly reduced when Eq. 8 is used. The term  $F[G_{a_1 b_1}(\nu)]$ , which is costly to calculate, only has to be evaluated once for each pair of groups of equivalent spins, and not once for each pair of spins.

### C. Convergence of single-quantum lineshapes

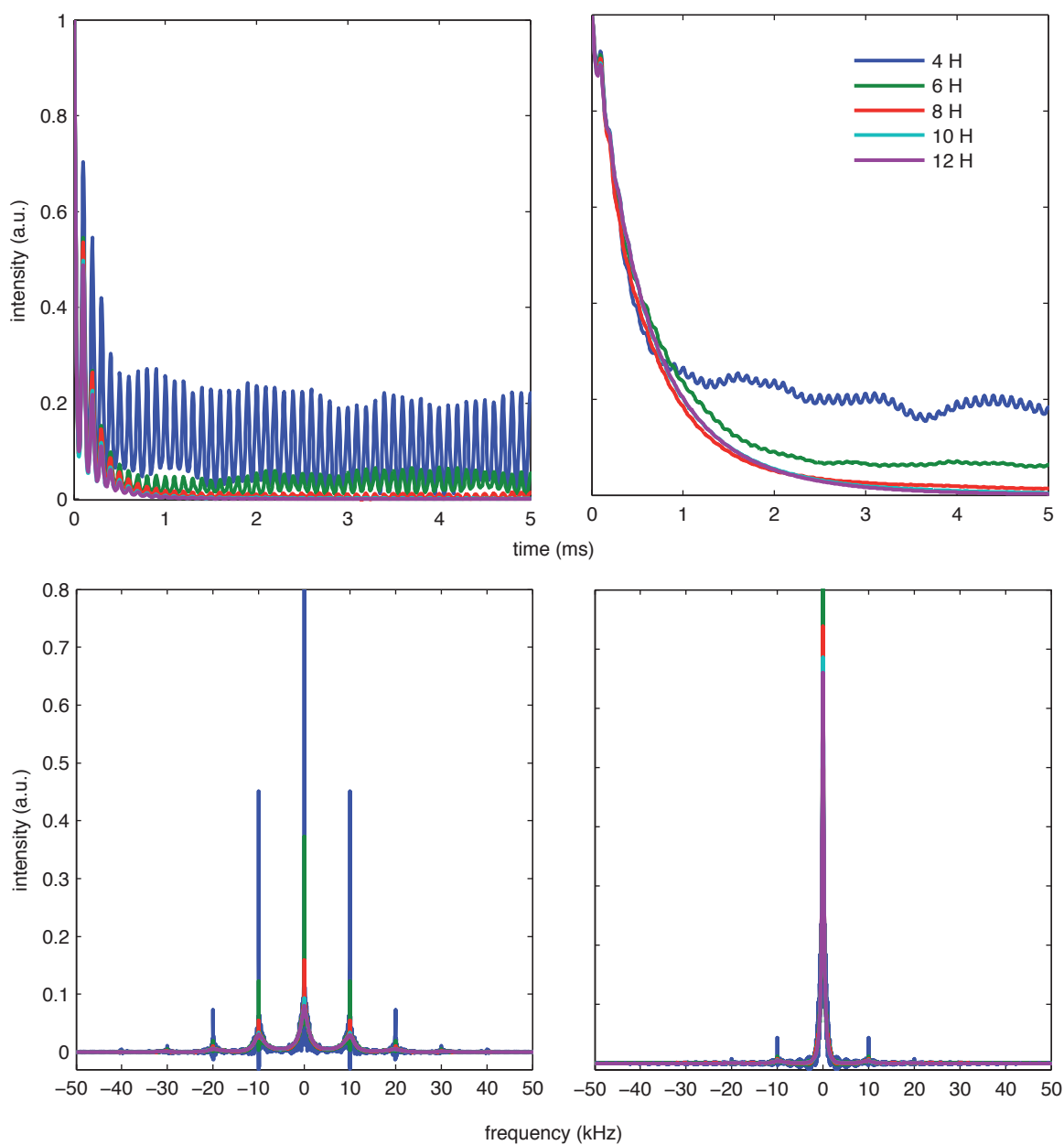


FIG. 3. Examples of simulated powder-averaged carbon single-quantum free-induction decays and lineshapes with 10 kHz MAS. Curves are shown for the  $C_\alpha$  (left) and the  $C_\gamma$  (right) of L-histidine. $H_2O.HCl$ . In each simulation, the system consisted of a single carbon and of the  $N$  protons that are the closest to this carbon. A ZCW set of 144 orientations was used for the simulation.

- <sup>1</sup> P. Robyr, M. Tomaselli, J. Straka, C. Grobispiano, U. W. Suter, B. H. Meier, and R. R. Ernst, *Mol. Phys.*, **84**, 995 (1995).
- <sup>2</sup> M. Ernst and B. H. Meier, in *Solid State NMR of Polymers*, edited by I. Ando and T. Asakura (Elsevier, Amsterdam, 1998) pp. 83–120.