**ARTICLE TYPE** 

## Motional Heterogeneity in Single-Site Silica Supported Species Revealed by Deuteron NMR.

Julia Gath,<sup>9</sup> Gina L. Hoaston,<sup>b</sup> Robert L. Vold,<sup>c</sup> Romain Berthoud, <sup>d</sup> Christophe Copéret,<sup>d</sup> Mary Grellier, <sup>e</sup> Sylviane Sabo-Etienne, <sup>e</sup> Anne Lesage, <sup>a</sup> and Lyndon Emsley<sup>a</sup>

SUPPLEMENTARY INFORMATION

## **Motional Models**

- In order to reproduce the quadrupolar echo spectrum shown in the main text, Figure 2, many numerical calculations were performed with different motional models. For all calculations, a chemically intuitive tetrahedral geometry was assumed at the silicon atom, and a value of the quadrupolar 15 coupling constant consistent with the literature was chosen,
- $C_0 = 90 \text{ kHz.}^1$

We first tested the simplest possible model of motion: jumps among three tetrahedral sites around the O-Si bond at rate k1 (first frame in Figure 1a of the main text, orange 20 arrow). This is not the same as free (zero potential energy barrier) rotation around this bond, although free rotation and three site jumps give the same fast-limit QE and MAS line shapes.<sup>2</sup> A rate constant  $k_1 = 10^9 \text{ s}^{-1}$  was used here since the motion is in the fast limit regime. A comparison of the

25 experimental and calculated QE spectra is shown Figure A1a. Despite the poor S/N ratio of the experimental spectrum, it is obvious that this simple motional description is incorrect. The calculated spectrum is much too broad (80 kHz), compared to the experimental one (40 kHz) and the simulated spectrum has

30 a pronounced dip in the middle and pronounced shoulders, which are not consistent with the experimental spectrum.

A second motional frame was then introduced into the calculations, to account for possible motion of the 3-fold jump axis (z-axis of the first frame) (blue arrow on the structure of

- 35 Figure 1a in the main text) Large angle (180°) two site jumps were first considered for this second frame. The calculated QE spectrum is shown in red Figure A1b for fast two site jumps (180°) of the C<sub>3v</sub> axis in the second frame. We observe that the spectrum becomes narrower, as the quadrupolar
- 40 interaction is further reduced by motion in the second frame. Moreover, it is encouraging that the central dip and pronounced shoulders disappear. However, the calculated spectrum does not agree with the experimental one. The QE line shape is known to be very sensitive to the two site jump
- 45 angle so this parameter was varied from 60° to 180°, but no better agreement with the experimental spectrum could be found. The rate constants for both frames were also varied between 10<sup>0</sup> s<sup>-1</sup> and 10<sup>11</sup> s<sup>-1</sup>, but, as expected from the very narrow line width of the MAS resonances, reasonable results
- 50 were only obtained when both motions are in the fast limit. In subsequent simulations the rate constants were fixed at  $k_1 = 3$ x  $10^{10}$  s<sup>-1</sup> and  $k_2 = 10^{10}$  s<sup>-1</sup> for the first and second frame of motion, respectively. These rates were chosen because they give a simulated Zeeman relaxation rate in qualitative
- 55 agreement with the observation that a 2 to 5 second relaxation

delay is needed to obtain a fully recovered QE spectrum.<sup>3</sup> Finally, calculations were made for different values of the Si-O-Si bond angle, which was varied between 135° and 155°, consistent with values reported in the literature.<sup>4</sup> The best 60 agreement between the calculated and experimental spectra were found for an angle of 145° and so this value was kept constant and used in all subsequent calculations.

Since large step two site motion in the second frame does not reproduce the experimental data we explored an 65 alternative motional model. The fast, three site jumps (first frame) are kept the same, but in the second frame we consider the motion of the O-Si C<sub>3v</sub> axis to be fast, small step, nearest neighbour jumps along an arc of limited length. The populations of the different sites along the arc were taken to 70 be equally probable. This is intended to mimic constrained diffusional motion along the arc. Simulation results for an arc of angle 360°, modelled using 10° jumps (corresponding to 37 sites), are shown in Figure A1c. We observe that the width of the line is still much too narrow, and that the overall line 75 shape once again resembles a standard powder pattern with pronounced shoulders and a deep dip in the middle. There is still no agreement with experiment.

So far, the three orientations in the first frame (rotation about the 0-Si bond) have been considered to be equiprobable.

80 However, this is not necessarily a valid assumption. The interactions between the complex and the surface are essentially van-der-Waals interactions, whose strength can be estimated from the polarizabilities of the interacting groups. In the literature, polarizability values of 0.667 10<sup>-24</sup> cm<sup>3</sup> and 85 2.593 10<sup>-24</sup> cm<sup>3</sup> are found for atomic hydrogen and methane, respectively.<sup>5,6</sup> Therefore, an orientation with the methyl groups pointing to the surface is expected to more stable than an orientation where the deuteron is next to the surface. We thus investigated the effect of unequal populations (in the first 90 frame) on the calculated deuteron static QE line shape. For the case of a large angle two-site (180°) jump around the Si-O bond in the second frame, calculations were performed with population ratios ranging from D:Me:Me = 1:3:3 to 1:10:10 in the first frame of motion (data not shown). A ratio of 95 D:Me:Me = 1:4:4 was found to give the best agreement between the calculated and experimental spectra recorded at 293 K (Figure A1d). The same calculation was done for fast small step, nearest neighbour jumps on a 360° arc with 10° step size (Figure 3(e)). The effect on the lineshape is drastic, 100 especially for the large angle jump (Figure 3(d)), where the deuteron line shape becomes much wider than the one calculated with equal populations (Figure 3(b)). However, while the line width at half height matches reasonably well,

the overall shape is quite different. For the fast rotation in the second frame (Figure 3(e)), the impact of unequal populations is obviously not so important, the calculated spectrum being qualitatively similar to the one of Figure 3 (c), except for the <sup>5</sup> appearance of a small, motionally induced asymetry parameter.

In summary, the calculations show that the addition of a second frame of motion (describing the  $C_{3v}$  axis orientation) leads to a significantly improved agreement compared to the

- <sup>10</sup> simplest one-frame model. However, despite a plethora of adjustable parameters in the calculations (rate constants, jump angles, relative populations, Si-O-Si bond angle), no simulation could be found with any single parameter set that adequately matches the QE spectrum. The best final model is <sup>15</sup> fast, three site jumps ( $k_1 = 3 \times 10^{10} \text{ s}^{-1}$ ) with unequal
- populations in the first frame (D:Me:Me = 1:4:4) and fast, ( $k_2 = 10^{10} \text{ s}^{-1}$ ) small step (10° step size), nearest neighbour jumps on a 360° arc in the second frame (Figure A1d).



**Figure A1.** Comparison between the experimental QE spectrum (in black) of [-SiDMe<sub>2</sub>] grafted on SBA from figure 2(a) with different calculated spectra (in red). (a) Calculated spectrum obtained by considering jumps among three tetrahedral sites around the O-Si bond 25 (first frame in Figure 1). The calculation was done with  $k_1 = 10^9 \text{ s}^{-1}$  and a total of 10976 powder increments (simulation time 30 s). (b) Calculated spectrum obtained by considering 180° two site jumps ( $\theta = 180^\circ$ ) around

the Si-O bond (second frame in Figure 1), as well as jumps among three tetrahedral sites of the SiDMe<sub>2</sub> group around the O-Si bond, modeled as <sup>30</sup> in (a). The calculation was done with  $k_1 = 3 \times 10^{10} \text{ s}^{-1}$ ,  $k_2 = 10^{10} \text{ s}^{-1}$ , and a total of 28657 powder increments, (simulation time 4.5 min). (c)

Calculated spectrum obtained by considering fast jumps among three tetrahedral sites around the O-Si bond for the first frame as in (a) and (b), and fast, small step, nearest neighbour jumps ( $\theta = 0^{\circ}, 10^{\circ}, ...$ ) along an <sup>35</sup> arc of 360° length for the second frame. The calculation was done with  $k_1 = 3 \times 10^{10} \text{ s}^{-1}$ ,  $k_2 = 10^{10} \text{ s}^{-1}$ , and a total of 28657 powder increments

(simulation time 50 min). (d) Same motional model as in (b) but with different populations for the three sites of the first frame according to D:Me:Me = 1:4:4. All other parameters are the same as in (b). (e) Same 40 motional model as in (c) but with different populations for the three sites

as in total index as in (c) but with directile populations for the three sites of the first frame according to D:Me:Me = 1:4:4. All other parameters are the same as in (c). For all the calculations shown here, tetrahedral geometry was assumed around the silicon atom and the Si-O-Si bond angle was set to 145°, corresponding to Euler angles of  $\alpha_1 = 0^\circ$ ,  $\beta_1 = 74^\circ$ , 45  $\gamma_1 = 0^\circ$ ;120°;240° and  $\alpha_2 = 0^\circ$ ,  $\beta_2 = 35^\circ$ ,  $\gamma_2 = 145^\circ$ .

## **Parameter Distributions**

Since all motions are in the fast limit, the line shapes generated using EXPRESS to integrate the stochastic Liouville equation for jumps among multiple sites along a <sup>50</sup> given trajectory can be equally well computed by solving the simpler equations for a single site, in which the quadrupole tensor is defined as the population-weighted average of quadrupole coupling tensors for each site. Of course, it is necessary to express the quadrupole tensor for each site in the 55 same (crystal-fixed) axes prior to performing the weighted average. Since the motional trajectories in the models considered here have symmetry lower than C<sub>3</sub>, the resulting quadrupole coupling tensors for each site are non-diagonal in the crystal fixed frame, and the motionally narrowed  $_{\rm 60}$  quadrupole coupling constant  ${<}C_Q{>}$  and asymmetry parameter  $<\eta>$  are then found most simply by diagonalizing the average cartesian 3x3 tensor.

The results of this process are shown in Figure A2 as function of arc length  $\lambda$ , for three diffeent choices of populations populations in the first frame, p1= (D:Me:Me). As expected, the motionally averaged quadrupole coupling constant (Figure A2.A) decreases strongly with increasing arc length. The unusual "cusps" in the computed values of  $\langle \eta \rangle$ (Figure A2.B) arise because we have imposed the usual 70 Haberlen conventions with regard to prinicipal axis labels of the motionally averaged electric field gradient tensor, i.e.,  $|q_{ZZ}| \ge |q_{XX}| \ge |q_{YY}|$ , so that  $0 \le \eta \le 1$ . We note in passing that EXPRESS handles these conventions automatically, and yields the same spectrum whether calculated for a single, 75 "effective" site defined by given values of  $\langle C_Q(\lambda) \rangle$  and  $\langle \eta(\lambda) \rangle$ , or directly in terms of *fast* jumps between the explicit orientations used to compute  $\langle C_O(\lambda) \rangle$  and  $\langle \eta(\lambda) \rangle$ .



**Figure A2 :** Motionally averaged quadrupole coupling constants (A) and motionally induced asymetry parameters (B), computed as a function of arc length,  $\lambda$ , for three different values of the site populations for  $s SiD(CH_3)$  in frame 1. Green : (1 :1 :1); Red : (1 :4 :4) and Black : (1 :8 :8).

Figure A3 shows the final line QCPMG line shapes, computed as sums of line shapes for  $\langle C_Q(\lambda) \rangle$  and  $\langle \eta(\lambda) \rangle$ , weighted according to a beta distribution of  $\lambda$  with  $\alpha = 1.1$ and  $\beta = 6.8$ . These were found by methods described in the main text to yield the best fit to the 187 K experimental QCPMG spectrrum of [-SiDMe<sub>2</sub>] grafted on SBA, which is shown in blue in Figure A3. Evidently, line shapes computed

- <sup>15</sup> for equal populations (green) cannot reproduce the experimental data because, according to Figure A2B, no values of arc length produce a large enough average asymmetry parameter to "fill in" the center of the spectrum. However, line shapes computed for frame 1 populations
- <sup>20</sup> ~(1:3:3) or greater are quite similar, and it is unlikely that the actual values of these populations can be determined with great precision.



- **Figure A3:** (a) <sup>2</sup>H QCPMG spectrum recorded on [-SiDMe<sub>2</sub>] grafted on <sup>25</sup> SBA at 187 K (in blue). (b), (c) and (d) are the calculated spectra fitting the best with the experimental one for various population ratio of the three sites jumps motion around the O-Si bond. Similar distributions of arc length were obtained in (b) and (c), see Table 2 of the main text.
- <sup>30</sup> <sup>a</sup> Université de Lyon, CNRS / ENS Lyon / UCB Lyon 1, Centre de RMN à Très Hauts Champs, 5 rue de la Doua, 69100 Villeurbanne, France. Fax: +33 4 78 89 67 61; Tel: +33 4 26.23.38.92; Email: Lyndon.Emsley@enslyon.fr.

<sup>b</sup>Department of Physics, College of William and Mary, P.O. Box 8795, 35 Williamsburg, VA 23187-8795, USA

<sup>c</sup>Department of Applied Science, College of William and Mary, P.O. Box 8795, Williamsburg, VA 23187-8795, USA <sup>d</sup>Université de Lyon, Institut de Chimie de Lyon, (CNRS – Université Lyon 1 – ESCPE Lyon), C2P2 Equipe LCOMS, ESCPE Lyon, 43 boulevard du

 40 11 Novembre, 69616 Villeurbanne Cedex, France
<sup>e</sup>Laboratoire de Chimie de Coordination, 205, route de Narbonne 31077 - Toulouse cedex 04, France
ξ Present address: Physical Chemistry, ETH Zürich ,Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland

## 45 **References**

55

- 1. R. Ader and L. A., Molec. Phys., 1974, 27, 1113-1115.
- 2. D. A. Torchia and A. Szabo, J. Magn. Res., 1982, 49, 107-121.
- 3. R. L. Vold and G. L. Hoatson, J. Magn. Res., 2009, 198, 57-72.
- 50 4. X. Solans-Monfort, J.-S. Filhol, C. Copéret and O. Eisenstein, New. J. Chem, 2006, **30**, 842-850.
- 5. T. K. Bose, J. S. Sochanski and R. H. Cole, *J. Chem. Phys.*, 1972, **57**, 3592.
- 6. T. M. Miller and B. Bederson, Adv. At. Mol. Phys., 1977, 13, 1.