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

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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 coupling constant consistent with the literature was chosen, C.Q=90 kHz.

We first tested the simplest possible model of motion: jumps among three tetrahedral sites around the O-Si bond at rate k\textsubscript{1} (first frame in Figure 1a of the main text, orange 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. \(^{5}\) A rate constant k\textsubscript{1} = 10^9 s\textsuperscript{-1} was used here since the motion is in the fast limit regime. A comparison of the 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 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 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\textsubscript{3v} axis in the second frame. We observe that the spectrum becomes narrower, as the quadrupolar 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 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 10^9 s\textsuperscript{-1} and 10^11 s\textsuperscript{-1}, but, as expected from the very narrow line width of the MAS resonances, reasonable results were only obtained when both motions are in the fast limit. In subsequent simulations the rate constants were fixed at k\textsubscript{1} = 3 \times 10^10 s\textsuperscript{-1} and k\textsubscript{2} = 10^10 s\textsuperscript{-1} for the first and second frame of motion, respectively. These rates were chosen because they give a simulated Zeeman relaxation rate in qualitative agreement with the observation that a 2 to 5 second relaxation delay is needed to obtain a fully recovered QE spectrum.\(^{3}\) 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.\(^{4}\) The best 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 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\textsubscript{3v} 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 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 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. 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\textsuperscript{-24} cm\textsuperscript{3} and 2.593 10\textsuperscript{-24} cm\textsuperscript{3} are found for atomic hydrogen and methane, respectively.\(^{5,6}\) Therefore, an orientation with the methyl groups pointing to the surface is expected to be more stable than an orientation where the deuteron is next to the surface. We thus investigated the effect of unequal populations (in the first 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 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, 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 appearance of a small, motionally induced asymmetry parameter.

In summary, the calculations show that the addition of a second frame of motion (describing the C3v axis orientation) leads to a significantly improved agreement compared to the 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 fast, three site jumps (k1 = 3 x 10^{10} s^{-1}) with unequal populations in the first frame (D:Me:Me = 1:4:4) and fast, (k2 = 10^{10} s^{-1}) small step (10° step size), nearest neighbour jumps on a 360° arc in the second frame (Figure A1d).

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 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 same (crystal-fixed) axes prior to performing the weighted average. Since the motional trajectories in the models considered here have symmetry lower than C3, the resulting quadrupole coupling tensors for each site are non-diagonal in the crystal fixed frame, and the motionally narrowed quadrupole coupling constant <Cq> and asymmetry parameter <η> are then found most simply by diagonalizing the average cartesian 3x3 tensor.

The results of this process are shown in Figure A2 as a function of arc length λ, for three different choices of populations populations in the first frame, p1 = (D:Me:Me) = 1:4:4. 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 <η> (Figure A2.B) arise because we have imposed the usual Haberlen conventions with regard to principal axis labels of the motionally averaged electric field gradient tensor, i.e., [HZZ] ≥ [HXX] ≥ [HYY], so that 0 ≤ η ≤ 1. We note in passing that EXPRESS handles these conventions automatically, and yields the same spectrum whether calculated for a single, “effective” site defined by given values of <Cq(λ)> and <η(λ)>, or directly in terms of fast jumps between the explicit orientations used to compute <Cq(λ)> and <η(λ)>.

Figure A1. Comparison between the experimental QE spectrum (in black) of [-SiDMc] 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 (first frame in Figure 1). The calculation was done with k1 = 10^{10} s^{-1} and a total of 10976 powder increments (simulation time 30 s). (b) Calculated spectrum obtained by considering 180° two site jumps (θ = 180°) around the Si-O bond (second frame in Figure 1), as well as jumps among three tetrahedral sites of the SiDMe2 group around the O-Si bond, modeled as in (a). The calculation was done with k1 = 3 x 10^{10} s^{-1}, k2 = 10^{9} 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 (θ = 0°, 10°, …) along an arc of 360° length for the second frame. The calculation was done with k1 = 3 x 10^{10} s^{-1}, k2 = 10^{9} 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 motional model as in (c) 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 (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 α1 = 0°, β1 = 74°, γ1 = 0°; 120°; 240° and α2 = 0°, β2 = 35°, γ2 = 145°.
Motionally averaged quadrupole coupling constants (A) and motionally induced asymmetry parameters (B), computed as a function of arc length, $\lambda$, for three different values of the site populations for SiD(CH$_3$)$_3$ 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 $<C_Q(\lambda)>$ and $<\eta(\lambda)>$, 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 spectrum of [-SiDMe$_2$] grafted on SBA, which is shown in blue in Figure A3. Evidently, line shapes computed 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 (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.

References