Elucidating the bimodal acid-base behavior of the water-silica interface from first principles

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(Dated: February 1, 2010)

Understanding the acid-base behavior of silica surfaces is critical for many nanoscience and bio-nano interface applications. Silanol groups (SiOH) on silica surfaces exhibit two acidity constants—one as acidic as vinegar—but their structural basis remains controversial. The atomic details of the more acidic silanol site govern not just the overall surface charge density at near neutral solution pH, but also how ions and bio-molecules interact with and bind to silica immersed in water. Using ab initio molecular dynamics simulations and multiple representative crystalline silica surfaces, we determine the deprotonation free energies of silanol groups with different structural motifs. We show that previously proposed motifs related to chemical connectivity or inter-silanol hydrogen bonds do not yield high acidity. Instead, a plausible candidate for $pK_a=4.5$ silanol groups may be found in locally strained or defected regions with sparse silanol coverage. In the process, irreversible ring-opening reactions of strained silica trimer rings in contact with liquid water are observed.

INTRODUCTION

Deprotonation of silanol (SiOH) groups at water-silica interfaces is one of the most common and important, yet intriguing, interfacial chemical reactions. Silica (SiO$_2$) is a major component of rocks and lines the channels of many nanofluidic devices. Deprotonation governs dissolution rates, affects lipid binding to silica nanostructures, creates negative surface charges that can be tuned with moderate changes in solution pH to perform desalination and ion gating, and may even hinder extraction of positively charged crude oil. The acidities of surface silanol groups have been assigned to different chemical connectivities or inter-silanol hydrogen bonding. In accordance with the literature, we differentiate SiOH groups according to whether they are directly hydrogen bond to other SiOH groups or only part of 2 Si-O-Si (“Q$_2$,” Fig. 1b); whether the 4-coordinated Si atom of the SiOH group is part of 3 covalent Si-O-Si- linkages (“Q$_3$,” Fig. 1c), or only part of 2 Si-O-Si (“Q$_2$,” Fig. 1d). It has been suggested that the ratio of H-bonded to isolated SiOH groups is about 1 to 4, similar to the relative occurrence of pK$_a$=4.5 and 8.5; thus pK$_a$=4.5 has been ascribed to isolated silanol groups. SFVS experiments on α-quartz reached similar conclusions and further suggested that the low-acidity silanol groups reside in regions with strong water-water hydrogen bonds. A titration study on silica gel (amorphous silica) and X-ray photoelectron spectroscopy measurements on quartz also independently demonstrated the existence of SiOH groups with pK$_a$ between 4 and 5.5. Such qualitative agreement on different forms of silica is expected because liquid water is known to react with even crystalline silica to form an amorphous layer. These measurements suggest that the earlier, single pK$_a$=6.8 reported in amorphous silica titration experiments may reflect a composite of two types of SiOH.

The acidities of surface silanol groups have been assigned to different chemical connectivities or inter-silanol hydrogen bonding. In accordance with the literature, we differentiate SiOH groups according to whether they are directly hydrogen bond to other SiOH (“H-bonded,” Fig. 1d), or are not so hydrogen-bonded (“isolated,” Fig. 1b); whether the 4-coordinated Si atom of the SiOH is part of 3 covalent Si-O-Si- linkages (“Q$_3$,” Fig. 1c), or only part of 2 Si-O-Si (“Q$_2$,” Fig. 1d). In 1992, Ong et al. demonstrated that 19% of silanol groups on fused silica surfaces exhibit a pK$_a$ of 4.5, about the same as vinegar (acetic acid), while 81% exhibit pK$_a$=8.5. SFVS experiments on α-quartz reached similar conclusions and further suggested that the low-acidity silanol groups reside in regions with strong water-water hydrogen bonds.
FIG. 1: (a)-(d) Four types of SiOH groups discussed in this work. (a) Hydrogen-bonded; (b) isolated; (c) Q^2; (d) Q^2. Oxygen, silicon, and hydrogen atoms are colored in yellow, red, and white, respectively.

AIMD simulations have successfully reproduced the pK_a value. Given the absence of well-defined water-crystalline silica interfaces, and the fact that the precise atomic structure of amorphous silica surfaces is unknown, we examine six distinct, representative silanol environments. These include hydroxylated β-cristobalite (100) surface (Fig. 2a), hydroxylated β-cristobalite (100) with one SiOH removed (Fig. 2b), reconstructed β-cristobalite (100) surface (Fig. 2c), a molecular system (Fig. 2d), and two distinct SiOH on reconstructed quartz (0001) (Fig. 2e). They represent the SiOH motifs proposed to be responsible for pK_a=4.5 or 8.5 in the literature (Figs. 1a-d).

FIG. 2: The heterogeneous SiOH environments examined in this work. (a) Hydroxylated β-cristobalite (100) surface. The SiOH groups have σ_{SiOH} ~ 8 nm^{-2}, are Q^2 and H-bonded, pK_a=7.6 ± 0.3. (b) Hydroxylated β-cristobalite (100) surface with one SiOH group replaced with a SiH to break the chain of hydrogen bonds. The tagged (deep blue) SiOH (Q^2 and isolated) exhibits pK_a=8.9±0.3. (c) Reconstructed β-cristobalite (100) surface, σ_{SiOH} ~ 4 nm^{-2}, Q^3 and isolated; pK_a=8.1±0.5 (6 layers of water) and 7.0±0.4 (4 layers). (d) The structure in panel (c) comes from removing atoms shown here in blue, and attaching the resulting undercoordinated Si and O atoms. Panels (a)-(d) represent ~1.5 simulation cells in the lateral direction. (e) (H_3SiO)_3SiOH, which is Q^3 and isolated, exhibits pK_a=7.9±0.5. (f) Top half of a reconstructed quartz (0001) surface model containing cyclic silica trimers (Si-O)_3, σ_{SiOH} ~ 2.3 nm^{-2}, Q^3 and H-bonded; one SiOH resides on a trimer ring (pK_a=5.1±0.3), the other does not (pK_a=3.8±0.4 and pK_a=4.8±0.4 depending on whether a nearby trimer ring breaks; see text). Si, O, and H atoms are in yellow, red, and white, respectively. (b) and (e) are finite-temperature AIMD snapshots, with water molecules omitted for clarity, while (a), (c), and (f) are shown at T=0 K.

COMPUTATIONAL METHODS

AIMD simulations apply the Perdew-Burke-Ernzehof (PBE) functional and the Vienna Atomic Simulation Package (VASP). A 400 eV energy cutoff, Γ-
point sampling of the Brillouin zone, deuterium mass for all protons, and a 0.375 fs time step at each Born-Oppenheimer dynamics time step. The trajectories are thermostat at T=425 K; elevated temperature is needed to represent liquid water properties when the PBE functional is applied and quantum nuclear effects are neglected, which is the case herein (SI, Sec. S1). Four to six umbrella sampling windows of 20 ps production trajectory length each are used per pK_a calculation on hydroxylated β-cristobalite (100) (Figs. 2a,b) and reconstructed β-cristobalite (Fig. 2c) surfaces. These periodically replicated simulation cells measure 10.17 × 10.17 × 26 Å^3. Their lateral dimensions are commensurate with simulation cells often used for AIMD studies of pure water structure or ion hydration. This is one of the reasons we have focused on the (100) rather than the (111) surface of β-cristobalite, which actually has a σ_{SiOH} similar to that of amorphous silica. The more computationally costly reconstructed quartz (0001) system has a cell size of 10.0 × 17.32 × 24 Å^3, and 12 to 18 ps trajectories are used per window. For each crystalline silica simulation cell, we always start from crystal slab structures optimized at zero temperature using Density Functional Theory (DFT) and the PBE functional. Next we switch to the CHARMM SiO_2 force field and the SPC/E model for water. The number of water molecules occupying the simulation cell is determined using these force fields, the Grand Canonical Monte Carlo (GCMC) technique, and the Towhee code. With this approach, the spaces between hydroxylated and reconstructed β-cristobalite surfaces are filled with 58 and 63 water molecules, respectively, which amount to roughly six layers of water, while the reconstructed quartz simulation cell contains about 63 (about 4 layers of) water molecules. The (H_2SiO)_3SiOH pK_a calculation utilizes a (12.42 Å)^3 cell with 57 H_2O and 20 ps sampling trajectories. Finally, to check system size dependences, umbrella sampling simulations for a smaller reconstructed β-cristobalite (100) simulation cell, 20 Å in the z-direction and containing 44 (4 layers of) water molecules, are also conducted for at least 10 ps per window.

pK_a has been reported for molecules in liquid water using the AIMD technique. It is related to the standard state deprotonation free energy ΔG(0) via −log_{10} exp(−βΔG(0)), where β is 1/k_BT and

\[ ΔG(0) = -k_BT \ln \left\{ C_0 \int_0^{R_{cut}} dR \ A(R) \ \exp[-\beta W(R)] \right\}. \]

Here C_0 denotes 1.0 M concentration, R is the reaction coordinate, A(R) is a phase space factor to be discussed below, R_{cut} is the cutoff distance delimiting the reaction and product valleys in the free energy landscape, and W(R) is the potential of mean force which provides the information needed to compute the free energy of deprotonation. Regardless of the reaction coordinate used, W(R) generally do not exhibit turning points in the deprotonated region, and R_{cut} can be taken as the onset of the plateau where W(R) → 0.

The umbrella sampling method is used to compute the W(R) associated with SiOH deprotonation. A four-atom reaction coordinate R (Fig. 3a) is found to work best under our simulation conditions. It controls what we call the “wandering proton” problem. We label the first, second and third neighbor H_2O molecules of the SiO^− oxygen (green sphere) shown in Figs. d “water 1” (O depicted red), “2” (blue), and “3” (pink). When R ∼ −0.4 Å (Fig. 3b), the SiOH bond is intact. As R decreases to ∼ −1.1 Å (Fig. 3c), the SiOH proton is transferred to a “water 1” which has been hydrogen-bonded to the SiOH group, yielding a SiO^−-H_3O^+ contact ion pair. As R further decreases (Fig. 3d), a proton originally residing on “water 1” is now transferred to a second water molecule (“water 2”), creating a water-separated SiO^−/H_3O^+ pair, at which point the deprotonation reaction is almost complete. This analysis appears consistent with insights from a transition path sampling AIMD simulation as follows. The Fig. 3a configuration, with the excess proton and the SiO^− separated by two hydrogen bonds, form a possible free energy dividing surface between the intact and the deprotonated acid species, provided that the electric polarization between the two states, arising from the surrounding water molecules, has sufficient time to equilibrate. Our simulation conditions allow such equilibration, and the excess proton is indeed observed to diffuse away if R fluctuates to regions significantly more negative than ∼ −1.4 Å. Umbrella potentials of the type (A/2)(R−R_o)^2 are used to sample the reaction coordinate R. Just as significantly, they ensure that R > −1.4 Å and control the extent of proton transfer from “water 1” to all possible “water 2,” so that at most a water-separated ion-pair is obtained. Otherwise, if the excess proton is several hydrogen bonds removed from the SiO^− (say if it spends a significant amount of time on “water 3” via proton transfer from “water 2”), it can start to diffuse (“wander”) through the simulation cell via the Grotthuss mechanism at O(1) ps time scale per proton transfer. With tens of H_2O molecules in the simulation cell and 10-20 ps trajectories, once the excess H^+ leaves the second hydration shell of the SiO^− it does not return, and equilibrium sampling is not achieved. This “wandering” likely arises because the higher temperature and longer umbrella sampling trajectories than are generally used in the AIMD literature facilitate diffusion of the excess proton away from the SiO^−. Other deprotonation reaction coordinates used in the literature are discussed in the SI (Sec. S2). They are found to give rise to wandering excess protons under our simulation conditions. As long as equilibrium sampling is achieved, the deprotonation free energy cost should not depend on the choice of coordinate.
To apply Eq. 1, we use a method similar to Ref. 8 finding the most probable optimal O\textsubscript{(water 1)}-H\textsuperscript{+} hydrogen bond distance \(r_{O-H}\) at each \(R\), thus locally converting \(W(R)\) to \(W(r_{O-H})\); performing a spline fit to the resulting \(W(r_{O-H})\); and integrating over \(r_{O-H}\) with a \(4\pi r^2\) volume element, which takes the place of the phase space factor \(A(R)\) in Eq. 1. Equation 1 assumes that the entropic factors such as rotations of the reactant and products about the O-H axis are adequately sampled in the AIMD trajectories; otherwise additional constraints and entropic factors are introduced.\[51, 52\] SI Sec. S2 shows that such constraints do not affect water autoionization free energies, partly because the variation in \(r_{O-H}\) needed to complete the deprotonation reaction is relatively small. Furthermore, we always reference predicted silanol p\(K_a\) to that of water autoionization\[9\] computed using the same reaction coordinate and elevated temperature. This minimizes systematic error arising from the simulation protocol (SI Sec. S2), and phase space contributions approximately cancel out.

The metadynamics technique,\[53–55\] a promising and powerful alternative to umbrella sampling, has been applied to calculate dissociation free energies on surfaces\[37\] and acid-base reactions of small molecules.\[10\] This method, not yet implemented in VASP, can potentially be used for efficient comparative study of p\(K_a\) on other material surfaces after it has been adapted to deal with the wandering proton problem.

Gas-phase, high-level \textit{ab initio} calculations are performed to check and correct chemical bonding energies predicted with the PBE functional used in the AIMD simulations. The Gaussian03 program suite is applied.\[56\] The pertinent sample chemical reaction is

\[
\text{Si(OH)}_4 + \text{H}_2\text{O} \cdots \text{OH}^- \rightarrow \text{Si(OH)}_3\text{O}^- \cdots \text{H}_2\text{O} + \text{H}_2\text{O}
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Geometries are optimized, and harmonic vibrational frequencies computed, with density functional theory using the B3LYP method\[57, 58\] and the 6-311++G\((d, p)\) basis set. At the B3LYP geometries, energies are computed with the coupled-cluster singles and doubles method including a perturbative correction for triple substitutions, CCSD(T),\[59\] using the aug-cc-pVDZ basis set. Basis set incompleteness corrections are added to the CCSD(T) energies. Finally, zero-point vibrational energies computed from the B3LYP/6-311++G\((d, p)\) frequencies are added. Using this protocol, the high-level \textit{ab initio} calculation yields a reaction energy of -30.51 kcal/mol.

FIG. 3: (a) The 4-atom reaction coordinate \(R\), illustrated for silicic acid in water but is similar for all silanol containing species. Panels (b)-(d) are snapshots from AIMD deprotonation simulations, with outershell H\textsubscript{2}O molecules removed for clarity reasons. As deprotonation proceeds, \(R\) progresses from intact SiO-H (\(R \sim -0.4\) Å, panel (b)) to SiO\textsuperscript{-}H\textsubscript{2}O\textsuperscript{+} contact ion pair (\(R \sim -1.0\) Å, panel (c)) and then, via a Grotthuss proton transfer, to a solvent-separated SiO\textsuperscript{-}/H\textsubscript{2}O\textsuperscript{+} pair (\(R \sim -1.32\) Å, panel (d)). Yellow, red, white, and green spheres represent Si, O, H, and the “O-” atoms, respectively. Additionally, the water O atoms which are second and third nearest neighbor to the SiO\textsuperscript{-} oxygen are colored blue and pink, respectively. p\(K_a\) predictions for silicic acid will be reported in a future publication.

**RESULTS**

Hydroxylated \(\beta\)-cristobalite (100): chemically homogeneous SiOH. We first show that our simulation protocol predicts reproducible p\(K_a\) for chemically equivalent SiOH
groups on the hydroxylated β-cristobalite (100) surface (Fig. 2b). This well-studied model crystalline surface exhibits $\sigma_{\text{SiOH}}=8 \text{ nm}^{-2}$, larger than the experimental value of $4.6 \text{ nm}^{-2}$ for amorphous silica. At zero-temperature, it features two types of Q$^2$ silanol groups: alternating hydrogen bond donors and acceptors arranged in chains (Fig. 2b) not found in small molecules. This feature is dynamically preserved in our finite-temperature, aqueous-phase simulations (SI Sec. S4).

Figure 4 shows that two chemically equivalent, hydrogen bond-accepting SiOH groups on this surface are predicted to exhibit deprotonation $W(R)$ within 0.5 kcal/mol of each other. At large negative values of the reaction coordinate $R$, the deprotonated SiO$^-\equiv$ is stabilized with three hydrogen bonds (i.e., $N_w=3$, Figs. 4b and 4c). At $R > \sim< 0.8 \text{ Å}$, the SiO-H bond is only partially broken, $N_w < 3$, and the local $W(R)$ is not sensitive to the slight difference in $N_w$ in the two simulations that arises from statistical noise. These observations appear consistent with a recent two-dimensional potential of mean force analysis of formic acid deprotonation. Accounting for zero-point energy, correcting the AIMD functional with more accurate quantum chemistry methods, and referencing Eq. 1 to the water autoionization constant $k_{w}=14.8$, we estimate $k_{a}$ values of 7.5 and 7.7, close to the less acidic $k_{a}$ value reported by Ong et al. The standard deviation is 0.3 pH unit. Multiple deprotonation on this surface is discussed in SI Sec. S5.

**Heterogeneity:** Isolated, H-bonded, Q$,q$, and Q$^3$ SiOH all exhibit $k_{a}>7$. We next show that, contrary to previous hypotheses, isolated, H-bonded, Q$,q$, and Q$^3$ silanol groups all exhibit $k_{a}>7$. We first create an isolated silanol group by replacing a hydrogen bond donating SiOH group on the hydroxylated β-cristobalite (100) surface with a SiH so that its neighboring SiOH group is no longer H-bonded (Fig. 2b). Figure 5 shows that this isolated SiOH exhibits $k_{a}=8.9\pm0.3$, and is less acidic by 1.2-1.4 pH unit than when the SiOH hydrogen donor is present (Fig. 2b). This is entropically reasonable because a hydrogen bond-donating SiOH partner stabilizes the neighboring SiO$^-$ alongside two water molecules, while three water molecules are required for an isolated SiO$^-$. AIMD correctly accounts for this effect because it models H$_2$O and SiOH on the same dynamical footing and because water-water and water-silanol hydrogen bond energies are similar. Hydroxyls on oxides with more ionic character than SiO$_2$ form stronger hydrogen bonds, and indeed the relative abundance of interhydroxyl hydrogen bonding may partially be responsible for the crystal facet-dependent acidity of α-Al$_2$O$_3$. This will be the subject of future, comparative studies.

To compare Q$^2$ and Q$^3$ silanol groups, we reconstruct the hydroxylated β-cristobalite (100) surface by condensing every other pair of H-bonded SiOH groups into a SiOH and a H$_2$O molecule (Fig. 2d). This involves the elimination of a hydrogen-bond donating OH group plus the proton on its adjacent, hydrogen-bond accepting SiOH (Fig. 2d). The resulting undercoordinated Si and O atoms are joined together to form a covalent bond, in the process pulling apart the remaining H-bonded SiOH pairs so they are now isolated from one another. A similar structural motif has been considered in the literature. This surface has $\sigma_{\text{SiOH}}=4 \text{ nm}^{-2}$, with all SiOH groups being Q$^3$, isolated, and residing on silica rings containing at least 5 Si atoms. Such rings should be unstrained, unlike 3-member (Si-O)$_3$ rings discussed below. The pK$_a$ is found to be $8.1\pm0.5$ (Fig. 5).

We also consider a (SiH)$_3$SiOH molecule featuring an isolated, Q$^3$ SiOH group (Fig. 2f), which exhibits a comparable pK$_a=7.9\pm0.5$. Thus, in general, Q$^2$ and Q$^3$ silanol groups do not exhibit pK$_a$ values that differ by 4 pH units as previously proposed. Over the range 4 nm$^{-2} \leq \sigma_{\text{SiOH}} \leq 8 \text{ nm}^{-2}$, the precise value of $\sigma_{\text{SiOH}}$ has little effect on pK$_a$.

To some extent, all our crystalline silica models are nano-slits with thin water slabs confined between the surfaces. As the water content decreases, the dielectric solvation of SiO$^-\equiv$ and H$^+$ species should decrease, while intact SiOH groups should be weakly affected. Thus one expects a lower acidity and a higher pK$_a$ in strongly nano-confined aqueous media. To examine confinement effects, a pK$_a$ calculation is performed for a smaller reconstructed β-cristobalite (100) simulation cell, 20 Å in the $z$-direction, containing 4 layers of water. This system actually yields a lower pK$_a=7.0\pm0.4$—but is lower only by 1.1 pH units (dashed brown line in Fig. 5). It is possible the unexpected pK$_a$ decrease between the 6- and 4-water layer models arises from anomalies in the hydrogen bonding network not apparent from visual inspection of water configurations. The water density is also affected by the confinement. In the 4-layer model, all water molecules are at most two layers away from the crystalline silica surfaces, and AIMD conducted with GCMC-predicted water content is found to yield a second layer H$_2$O density that is 18% above 1.0 g/cc. However, this is unlikely to change the dielectric response sufficiently to lower the pK$_a$ by 1 unit. Assuming one can apply the Born hydration formula for excess proton hydration in this heterogeneous medium, $\Delta G_{\text{hyd}} \sim X(1-1/\epsilon_o)$ where $X \approx -264 \text{ kcal/mol}$ for the proton. If the 6-layers of water have $\epsilon_o=80$, the 4-layer system must exhibit $\epsilon_o=140$ to make hydration more favorable by 1 pH unit when in fact confinement generally reduces the dielectric constant of water. In any case, the discrepancy in pK$_a$ is actually within two standard deviations and may simply arise from statistical uncertainties. This test suggests that confinement effects are not large for the slit pore geometry down to about 1 nm slit widths. Therefore our reported pK$_a$ for 6-water layer systems should be good approximations of pristine crystalline silica sur-
Having considered $\sigma_{\text{SiOH}}=8$ and 4 nm$^{-2}$, we examine an even lower SiOH surface density. A recent experimental study has attached crystal violet dyes to deprotonated silanol groups. Based on the flat, 120 nm$^2$ surface area of the dye molecule, it is proposed that strong acidity is correlated with local SiOH surface density $\sigma_{\text{SiOH}} < 0.83$ nm$^{-2}$.[22] In our DFT calculations, the optimal geometry of crystal violet when covalently bonded to $\text{(HO)}_3\text{Si}^-$ is not flat but is substantially distorted. However, this suggestion of low SiOH surface density being associated with the more acidic SiOH appears consistent with other experimental and theoretical observations discussed below.

Since most cuts through crystalline forms of silica yield surfaces with substantial hydroxylation,[69] we investigate a reconstructed, completely dehydroxylated quartz (0001) model, featuring (Si-O)$_3$ trimer rings, predicted to be metastable in vacuum.[71] 2.3 SiOH groups per square-nanometer are re-introduced by removing two surface Si atoms and performing further reconstruction and hydroxylation to keep all atoms fully coordinated. This yields two types of silanol groups which are hydrogen-bonded to each other; one member of the pair resides on a cyclic trimer while the other does not (Fig. 2f). Regions devoid of SiOH and dominated by siloxane (Si-O-Si) bridges are hydrophobic, and this model surface may therefore be consistent with hydroxyl groups in hydrophobic pores reported to be unusually acidic on other oxides.[72] We conduct one deprotonation umbrella sampling simulation of a silanol group residing on a cyclic trimer (Fig. 4, solid violet curve), and two simulations where the SiOH does not reside on a trimer (dashed and dot-dashed violet). Figure 5 indeed shows that these SiOH groups exhibit $pK_a \sim 5.1 \pm 0.3$, $4.8 \pm 0.4$, and $3.8 \pm 0.4$, respectively — close to the experimental value of 4.5. More significantly, their average $pK_a$ are separated from the median of all other SiOH groups previously examined in this work by 3.4 pH units.

Unlike cyclic silica tetramers or larger Si-O rings, cyclic silica trimers are strained.[1, 71, 72] At zero temperature, in the absence of water, the Si atom of the SiOH group residing on a silica trimer ring exhibit Si-O-Si angles of 137.5°, 130.4°, and 120.0°. For the SiOH group not residing on a silica trimer, the angles are 154.9°, 131.8°, and 147.8°. A few of these angles deviate substantially from the ideal, unstrained Si-O-Si value of approximately 145°. This likely accounts for the low $pK_a$ computed for these SiOH groups. Other trimer rings not decorated with SiOH are also strained, and the slow spatial decay of their surface strain fields[73] may also contribute to the high acidity of SiOH group not residing on them.

Within hours in moist air,[1, 71, 72] cyclic trimer-containing surfaces are known to incorporate water and break open to reduce strain and increase the local $\sigma_{\text{SiOH}}$. At the water-reconstructed quartz interface, during un-
brella sampling deprotonation of the SiOH group residing on a 3-member ring (Fig. 2), we indeed observe a water molecule forming a transient bond with another Si atom on a Si-O trimer 6 Å away from the tagged SiO⁻ within picoseconds (Fig. 2b). The resulting 5-coordinated Si has been observed in simulations[71, 76, 77] and found to be the intermediate in the trimer ring-opening mechanism on wet silica amorphous surfaces in reactive force field and molecular orbital calculations.[76, 78] Our AIMD trajectories show that this mechanism remains operative at explicit liquid water-silica interfaces; proton hopping via the Grothuss mechanism occurs readily, enabling the H₂O adsorbed on the surface Si to lose a proton to bulk water, forming a new SiOH group within ~10 ps (Fig. 2). Then, in 2 of the 4 sampling windows, a Si-O bond on the now 5-coordinated Si breaks to open the OH-incorporated (Si-O)₃ ring and irreversibly introduce another new SiOH (Fig. 3). Our trajectories thus differ from a recent molecular dynamics study of the liquid water-reconstructed quartz interface, where the adsorbed water molecule, not described by a reactive force field, ultimately desorbs from the 5-coordinated surface Si atom without inducing chemical reactions.[71]

These irreversible side reactions prevent strict equilibrium sampling needed for W(R) calculations. Fortunately, for the SiOH residing on a cyclic trimer (Fig. 3), analysis of the pre- and post ring-breaking statistics reveals that the nearby chemical reaction has little effect on its pKₜ. We further analyze trimer ring-opening effects on the pKₜ of another SiOH group, this one not residing on a surface 3-member ring. A H₂O incorporation reaction also occurs in the neighborhood of this tagged SiOH (Fig. 4). We split the sampling windows into two groups: (A) those without irreversible hydrolysis of a nearby silica ring (Fig. 4a); and (B) those with trimer ring breaking and formation of two new SiOH groups (Fig. 4b). Then two complete sets of sampling windows spanning the entire deprotonation pathway are spawned from these seed windows, yielding two pKₜ: case A, pKₜ=3.8 (Fig. 5 dashed violet curve); and case B, pKₜ=4.8 (Fig. 5 dot-dashed violet). The results show that H₂O incorporation and a single ring-breaking event nearby does appear increase the pKₜ of the tagged SiOH not residing on a trimer ring. However, the increase is only 1.0 pH unit, almost within statistical uncertainties. In case (A), the three Si-O-Si angles on the silica trimer ring average to 121.1°, 134.0°, and 132.2° along the trajectory; the first refers to the angle where both Si are below the silica surface (“buried”). In case (B), this angle linking the buried Si atoms relaxes significantly to 140.5°. The second angle, which involves the surface Si and a buried Si, remains almost unchanged at 136.0°. (The third linkage is destroyed during ring opening.) Si atoms which no longer participate in strained Si-O-Si linkages should be more stable against H₂O attack.

From these considerations, we conclude that, despite interference from H₂O incorporation reactions, there remains a statistically significant difference in the pKₜ’s on this surface, and the pKₜ’s ranging from 7.0 to 8.9 for all other silanol groups investigated before (Fig. 5). This finding suggests that strain, low local silanol surface density, hydrophobicity, and low pKₜ are correlated on amorphous silica surfaces. Indeed, atomistic model surfaces with low local pKₜ regions almost always exhibit 3-member rings.[70, 76, 79] These regions may be in dynamic equilibrium with solvated silica fragments in solution, constantly being dissolved/hydrolyzed and reconstituted when dissolved fragments re-nucleate on hydroxylated regions.[71, 80, 82] The dynamic equilibrium has recently been demonstrated in Monte Carlo simulations[81] using a reactive silica force field.[83]

We have only observed one ring-opening reaction on each surface. The limited AIMD trajectory length does not conclusively allow us to predict how many trimer rings persist at the liquid water-amorphous silica interface as a function of time. Therefore we do not definitively assign this structure to the observed pKₜ=4.5 SiOH group, and instead pose it as a challenge to experi-
FIG. 6: Water incorporation onto reconstructed quartz. (a) Initial equilibrated snapshot of SiO\(^{-}\) H\(^{+}\) contact ion pair on the reconstructed quartz (0001) surface where the SiO\(^{-}\) resides on a 3-member ring (truncated in this figure). The tagged SiO\(^{-}\) oxygen is in deep blue; its H-bond SiOH donor is out of the frame. All other Si, O, and H atoms are in yellow, red, and white, respectively. (b) Snapshot after \(\sim 3\) ps. To the left of the SiO\(^{-}\), a water molecule (light blue) has attached itself to a Si atom on another silica trimer ring, which is unhydroxylated. That Si becomes 5-coordinated. (c) This water molecule loses a proton to bulk water; one of the Si-O bonds not on the trimer ring becomes stretched. This is reversible as long as another SiOH is not created. (d) In another sampling window for this SiOH, the trimer ring breaks open instead, forming a new SiOH after extracting a proton from water.

mental work, including single molecule spectroscopy,\(^84\) to determine whether they are sufficiently abundant over time to account for the 19\% of all silanol groups shown to exhibit high acidity.\(^{16,17}\) We also point out that, while cyclic silica trimers are well known to react with moist air, other popular crystalline silica model surfaces should also be hydrolytically unstable.\(^21\) Thus, the hydroxylated \(\alpha\)-quartz (0001) and \(\beta\)-cristobalite (100) surfaces, with \(\sigma_{\text{SiOH}} \sim 9\) and 8 nm\(^{-2}\) respectively, are often used as models to study the interface between liquid water and generic silica solids in classical MD simulations. However, if these simulations permit chemical reactions over long enough times, we speculate that some of the SiOH groups on such surfaces may also react with water\(^22\)\(^,\)\(^51\) in a way to reduce the silanol surface density towards the amorphous silica \(\sigma_{\text{SiOH}}=4.6\) nm\(^{-2}\) observed in experiments.\(^2,30\)

Discussions AIMD-based potential of mean force calculations simulations have been demonstrated to yield reproducible pK\(_a\) for chemically equivalent silanol groups.

The statistical uncertainties of our simulation protocol are estimated to be about 0.3-0.5 pH unit, consistent with explicit calculations on two chemically equivalent SiOH. Therefore these simulations should reliably distinguish relative pK\(_a\) of heterogeneous SiOH groups 4 pH units apart. Resolving hydroxyl pK\(_a\) on other surfaces may remain a challenge if the acidities are less widely separated.

Our pK\(_a\) calculations suggest that comparative studies between SiO\(_2\) and other material surfaces will be extremely interesting. One intriguing candidate surface is a quartz surface densely functionalized with carboxylic acid groups. To our knowledge, this is the only other material surface which clearly exhibits bimodal pK\(_a\) behavior.\(^83\) Other candidates are the different facets of crystalline alumina, which may feature several pK\(_a\)'s unresolved into distinct, measurable components.\(^72,86,87\) Structural motifs such as chemical connectivity and inter-hydroxyl hydrogen bonding have also been invoked to explain the pK\(_a\) in these systems; as mentioned in the text, inter-hydroxyl hydrogen bonding may affect the pK\(_a\) of the more ionic Al\(_2\)O\(_3\) surfaces more strongly than on any form of silica surfaces. See SI, Sec. S6, for more details on these material systems. Finally, SFVG spectra\(^17\) and time-dependent acid-base phenomena on quartz\(^88\) can also be investigated in the future.

CONCLUSIONS

In this paper, we have performed AIMD pK\(_a\) calculations on five representative crystalline silica surfaces plus
a molecular system exhibiting different silanol (SiOH) structural motifs. From the results, we have conclusively shown that the more acidic of the two pK\textsubscript{a} observed in experiments cannot, as previously proposed,\cite{22-29} be explained by the existence of silanol groups with certain chemical connectivities or inter-silanol hydrogen bonding. In fact, we find pK\textsubscript{a} \sim 4.5 silanol groups only on strained surfaces with sparse silanol coverage. While our demonstration of the existence of such low pK\textsubscript{a} SiOH groups is necessarily somewhat speculative, this study highlights the role of defected regions as the most promising candidate to explain the elusive bimodal acid-base behavior of silica surfaces.\cite{16,18} Assigning structural motifs to the more strongly acidic SiOH groups is particularly crucial in non-reactive force field-based modeling of silica nanofluidic channels, where the preferentially deprotonated SiOH sites at neutral pH have to be assigned in a static way.\cite{12,23,69,67,89,90} In the process of studying the acid-base behavior, we also observe irreversible, water-assisted ring-opening reactions of strained silica trimer rings in contact with liquid water. The reaction was previously studied on wet silica surfaces;\cite{76,76,78} our AIMD simulations demonstrate that a similar mechanism is operative at liquid water-silica interfaces.

Acknowledgement

We thank Ron Shen, Steven Garofalini, Susan Rempe, Jeff Brinker, Dave Tallant, Ying-Bing Jiang, and Franz Geiger for discussions. This work was supported by the Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy. LJC acknowledged support from the U.S. DOE Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences.

Supporting Information Available

Further information are provided regarding details of the AIMD simulations, justification for the reaction coordinate used, quantum chemistry calculations (including all energies and optimized geometries), the dynamics of hydrogen bond fluctuations on silica surfaces, proton exchange due to multiple deprotonation, and a brief overview of acid-base behavior in alumina and carboxylate acid functionalized surfaces. This information is available free of charge via the Internet at http://pubs.acs.org/
