Elucidating Acid-base Behavior of Silica with *ab initio* Molecular Dynamics

by ***K. Leung, I.M.B. Nielsen, and L.J. Criscenti***

Motivation—Silanol (SiOH) groups on silica surfaces are readily deprotonated, leading to SiO^--lined water-silica interfaces ubiquitous in nanofluidics channels, biocompatible materials, and nanofabricated desalination membranes. For example, these negatively charged surfaces inside nanopores naturally repel chloride anions and can potentially remove salt from sea water. The silanol pK_a value determines its acidity, which in turn governs the surface charge at a given solution pH. A landmark surface-sensitive sum harmonic generation paper [Ong *et al*., Chem. Phys. Lett. (1992)] reveals two pK_a values: 4.5, similar to club soda, and a much less acidic 8.5 (Fig. 1a). The structural motifs associated with these pK_a's have been much speculated upon but never definitively determined.

Accomplishment—We take advantage of Sandia's massively parallel computer platforms, among the fastest in the world, and apply *ab initio* molecular dynamics (AIMD) methods with umbrella sampling to compute the pK_a of silanol groups on various crystalline surfaces. Our models include β-cristobalite (100) (unreconstructed, Fig. 2a, reconstructed, and also with a SiOH artificially replaced with SiH to break SiOH-SiOH hydrogen bonds), a $(H_3SiO)_3SiOH$ molecule, and a reconstructed quartz (0001) surface (Fig. 2b) – all immersed in liquid water. We find that most of the surface SiOH groups exhibit similar pK_a (median value ~8.4). Thus, contrary to assertions frequently made in the literature, varying the chemical connectivity (SiOH with its Si bonded to 2 versus 3 O-Si linkages) and hydrogen bonding network (whether surface silanol groups directly hydrogen bond to each other) do not yield SiOH groups that are more acidic by 4 pH units than the norm (Fig. 1b).

The lone exception is a reconstructed quartz (0001) surface. This model is designed to yield a low, 2.3 SiOH per nm^2 surface density, compared to the average experimental density of $4.6/nm^2$. This model is motivated by recent surface-sensitive vibrational spectroscopy measurements on silica and alumina, which suggest that the more acidic sites are associated with sparse hydroxyl density regions. This model quartz surface contains strained three member silica rings (Fig. 2b). Silanol groups residing on these rings exhibit a pK_a ~3 pH units lower than the median value for all other SiOH groups we have examined. *This is the only "strongly acidic" SiOH group we have found with our highly accurate and rigorous AIMD method.* Our study suggests that non-representative, strained, or defected regions on silica surfaces should be reexamined as the most promising source of low pK_a silanol groups.

Significance—As material interfaces shrink to nanometer sizes, e.g., in functionalized mesoporous silica membranes [Brinker, MRS Bulletin (2004)], novel behavior such as large shifts in silica pK_a may emerge. Our 2-year effort demonstrates that AIMD simulations conducted on Sandia's massively parallel computational platforms, with quantum chemistry input, can yield unique insights into long-standing interfacial acid-base problems. Our finding will motivate novel, nanoscale "litmus paper" experimental effort to verify the pK_a predictions. Going beyond flat interfaces, AIMD simulations will next be used investigate SiOH deprotonation inside silica nanopores, which is critical to desalination applications.

Partners: University of Ohio
Sponsors for various phases of this work include: Laboratory Directed Research & Development
Contact: Kevin Leung, Surface and Interface Sciences Department, Dept. 1114
Phone: (505) 844-1588, Fax: (505) 844-5470, Email: kleung@sandia.gov

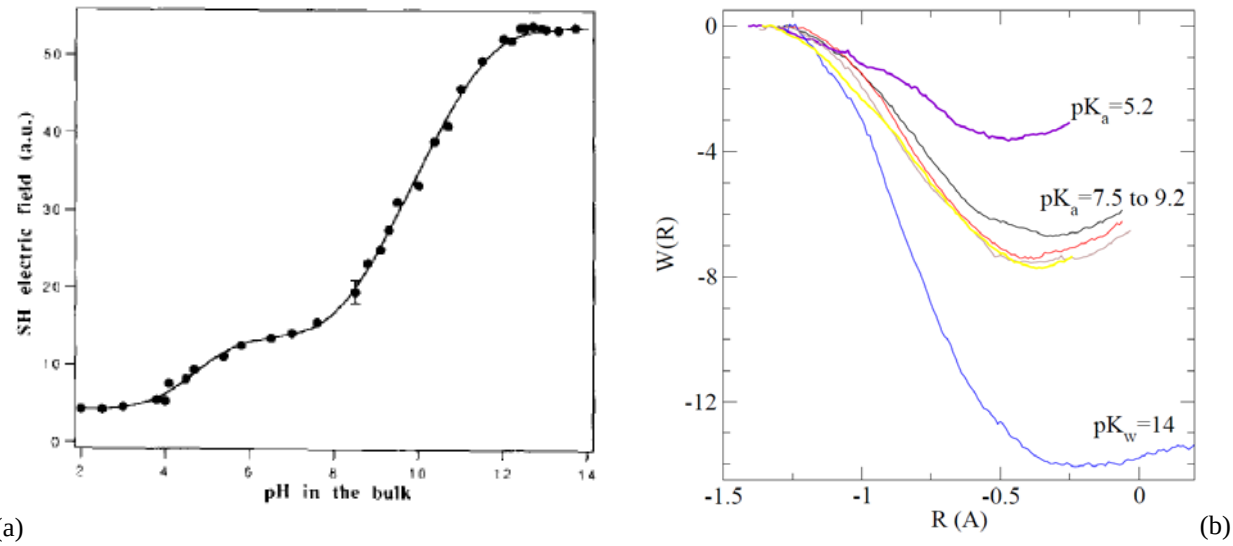

Figure 1. (a) Sum harmonic generation spectroscopy of silica surfaces, clearly indicating two pK_a values. (b) AIMD potential of mean force curves depicting the free energy changes associated with deprotonation of SiOH groups in different environments. Black & red: β-cristobalite (100); brown: reconstructed β-cristobalite (100); yellow: $(H_3Si)_3SiOH$; blue: water (reference system); violet: reconstructed quartz (0001), which alone exhibits a pK_a much lower than other silanol groups. Deprotonation proceeds in the negative "R" direction, and is almost complete at R=-1.4 A.

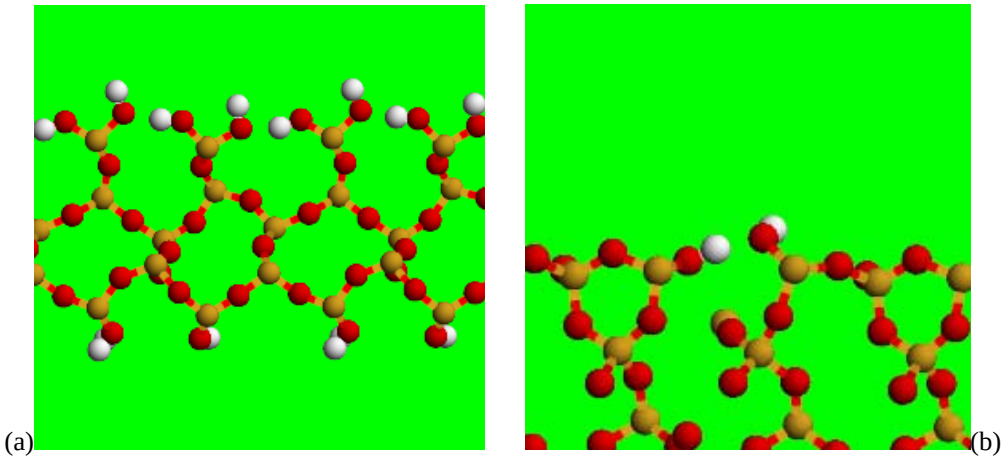

Figure 2. Side views of (a) β-cristobalite (100) surface, pK_a=7.5, 8.0 SiOH per nm^2; and (b) reconstructed quartz (0001) surface, pK_a=5.2, 2.3 SiOH per nm^2. Strained 3-member silica rings are clearly visible in the latter model. We stress that AIMD simulations are performed in the presence of liquid water at finite temperature; water molecules are omitted for clarity reasons.