



Acid-base dissociation mechanisms and energetics at the silica–water interface: An activationless process



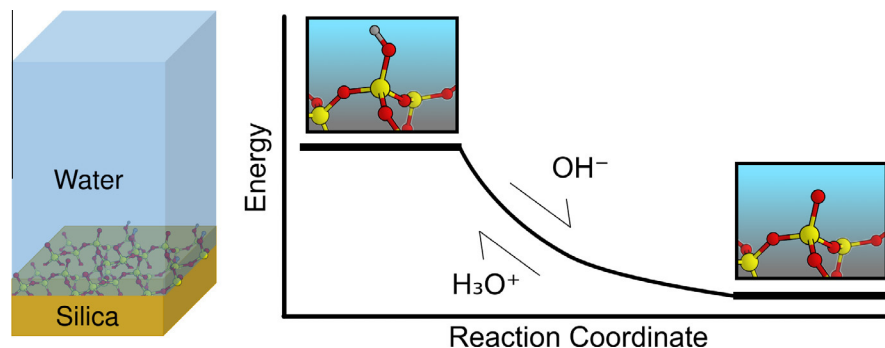
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GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Silanol groups at the silica–water interface determine not only the surface charge, but also have an important role in the binding of ions and biomolecules. As the pH is increased above pH 2, the silica surface develops a net negative charge primarily due to deprotonation of the silanol group. An improved understanding of the energetics and mechanisms of this fundamentally important process would further understanding of the relevant dynamics.

Simulations: Density Functional Theory *ab initio* molecular dynamics and geometry optimisations were used to investigate the mechanisms of surface neutralisation and charging in the presence of OH^- and H_3O^+ respectively. This charging mechanism has received little attention in the literature.

Findings: The protonation or deprotonation of isolated silanols in the presence of H_3O^+ or OH^- , respectively, was shown to be a highly rapid, exothermic reaction with no significant activation energy. This process occurred via a concerted motion of the protons through ‘water wires’. Geometry optimisations of large water clusters at the silica surface demonstrated proton transfer to the surface occurring via the rarely discussed ‘proton holes’ mechanism. This indicates that surface protonation is possible even when the hydronium ion is distant (at least 4 water molecules separation) from the surface.

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Abbreviations: DFT, Density Functional Theory; AIMD, *ab initio* molecular dynamics; SCM, Surface Complexation Model; FET, Field Effect Transistor; MP2, Second Order Møller–Plesset; NC-PP, norm-conserving pseudopotential.

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1. Introduction

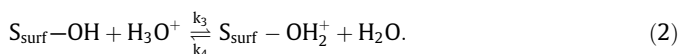
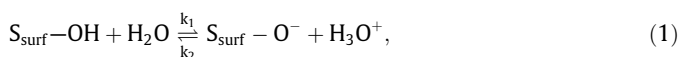
Silica and water represent two of the most abundant chemical systems, and therefore it is unsurprising that understanding the interface between them is relevant to a wide variety of systems. Surface charging is fundamental to a range of phenomena such

as dissolution rates [1–3] and the surface adsorption of ions and molecules [4,5]. Chemical reactions of reactive silanol groups (Si–OH) with H⁺/OH[−] are thought to be the primary surface charging mechanism for silica [6], with electrolyte effects having a measurable but less significant effect [7].

1.1. Oxide surface charging

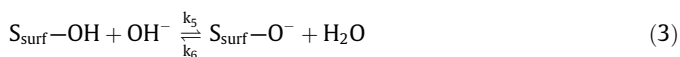
One of the most popular approaches to modelling surface proton reactions has been Surface Complexation Models (SCM). One such example is the 2-pK model which assumes that the surface state can be modelled as two consecutive protonation reactions, the equilibrium constants of which are often obtained empirically from acid-base titration data [8,9]. This methodology has the advantage of being highly generalisable, but neglects any direct information obtained about the oxide–water interfacial structure and dynamics obtained experimentally or via simulation. While the thermodynamic description of the 2-pK model is suitable for describing certain processes such as ion complexation and surface dissolution [8,10], it provides little insight into the atomic-scale interactions which are present at water–surface interfaces and are required to understand many dynamic interfacial processes, such as double layer formation, solvent structure, surface-charging kinetics and non-equilibrium interfacial processes.

As the pH is increased above 2 ± 1, the silica surface becomes increasingly negatively charged [11]. Silicon surface atoms (S_{surf}) are present as a neutral oxide that can dissociate or protonate according to the following chemical equilibria:



X-ray photoelectron spectroscopy measurements have shown that significant quantities of Si–OH₂⁺ are only present at extremely low pH (~2 or lower) [12]. High level *ab initio* calculations have demonstrated the chemical instability of this species in neutral water, supporting the notion that at conditions relevant to most applications (pH 2–14) this species is an insignificant component of the surface composition [13]. Given this observation, Borkovec explained how the 2-pK model should be interpreted as reactions between a pair of neighbouring ionizable groups, as opposed to a single site as has often been assumed [14].

Although the 2-pK model can be used to describe the average surface charge from a system-scale perspective by considering only the reaction with hydronium ions, the surface at an atomistic scale presents a far more complex environment in which Eq. (2) is competing with the analogous hydroxyl reaction shown in Eq. (3).



1.2. Charge transport in pure water

Given the chemical similarity between proton transfer of water–water proton transfers and of silanol–water proton transfers, the mechanism of proton transport in pure water is relevant. In pure water, solvated hydronium ions are transported via the Grotthuss mechanism [15] which involves interconversion between the symmetric Zundel cation H₅O₂⁺ and the triply-hydrogen bonded Eigen cation H₉O₄⁺ [16,17]. The rate limiting step for proton transfer is believed to be the reorientation of water molecules, which necessarily involves breaking hydrogen bonds [16]. The concerted motion of protons along a chain of water molecules

is sometimes referred to as a ‘water wire’. Solvated hydroxide ions are thought to have a different mechanism for transport than hydronium ions and correspondingly demonstrate a lower ionic mobility [18]. This mechanism has been suggested to involve interconversion between the square planar H₉O₅[−] anion and the tetrahedral H₇O₄[−] anion, with the rate limiting step being the formation of the latter [16,19,20].

1.3. Modelling the silica–water interface

With regard to the silica–water interface, both *ab initio* and classical molecular modelling have been used to describe atomistic surface charge. Many classical forcefields capable of representing negative charges have been developed, the majority of which require *a priori* knowledge of the surface charge, treating surface charges as predefined and fixed throughout the simulation [21–30]. In order to study time-varying surface charge using molecular dynamics, a force field must be used which can allow bond breaking and formation. Such a forcefield is usually referred to as reactive or dissociative. The reactive force field of Rustad et al. incorporated water dissociation and led to a fully hydroxylated surface with no surface charge [31], but was not designed to accurately represent surface charging and only considered a short time-frame of 10 ps. The dissociative force field of Mahadevan and Garofalini [32] was used to study formation of silanols and transfer of protons at the surface, similarly, the Hybrid-QM/MM study of Du et al. [33] was used to model formation of silanols at the surface, however none of these models were designed to investigate protonation/deprotonation dynamics of surface silanols and do not discuss this aspect of their model. The reactive forcefield ‘reaxFF’, developed by Goddard et al. [34] and applied by Fogarty et al. [35], was utilised to study the silica–water interface. Their 600 ps dynamics implied that a fully hydroxylated surface was produced from a freshly cleaved slab after approximately 250 ps, the concentration of silanolate groups at the surface was not explicitly stated.

Ab initio molecular dynamics (AIMD) studies based on periodic Density Functional Theory (DFT) have investigated protonation/deprotonation involving hydronium ions in order to calculate pK_a values [13,36,37] and in order to investigate dissolution mechanisms involving hydronium ions [32,38,39]. DFT has shown that hydronium ions can facilitate transfer of negative charge across the surface via the Grotthuss mechanism [13]. Mahadevan and Garofalini have noted that hydronium ions are important in short lived proton transfer processes at the surface [32], which has been supported by experimental observations [40–42].

Reaction of hydronium ions with silanolate groups at the silica–water interface has been shown by Leung et al. to have no barrier along the reaction coordinate based on Potential of Mean Force calculations [13,36]. In agreement with this result, Liu et al. have shown that there is no energetic barrier to acid dissociation of orthosilicic acid (Si(OH)₄) [36]. In contrast to silanol acid dissociation reactions, the counterpart basic reaction shown in Eq. (3) has received much less attention within the literature using *ab initio* methods for silica surfaces.

It has long been known that the dynamics and energetics of hydroxyl-based proton transfer in pure water differs from hydronium-based proton transfers [16], and therefore Eq. (3) must be considered separately from hydronium reactions (Eq. (2)) for an accurate representation of atomic interfacial proton transfer reactions. The hydroxyl transfer reaction shown in Eq. (3) has received little attention with respect to *ab initio* studies, one of the key exceptions being the work of Xiao and Lasaga who have investigated this reaction as a possible precursor to silica dissolution [43]. Xiao and Lasaga used SiH₃OH and (HO)₃Si–O–Si(OH)₃ cluster models for the silica surface at the HF/6-31G* level (for

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