Role of hydrogen bond lifetimes on auto-dissociation of water molecules and proton transport in bulk water and water at silica glass surfaces

Describing the atomistic mechanism regarding proton transport (PT) in different scenarios can be used to differentiate the effects of the apparently incompatible experimental results of slow reorientation time of hydrogen bonding at an interface, which should reduce proton transport, with the enhanced proton transport seen in electrochemical studies of wet mesoporous silica. Importantly, understanding the role of auto-dissociation of the water molecule in different environments and role of the hydrogen bond lifetimes in relation to PT to separate the resulting ions (H_3O^+ and OH^-) plays the dominant role in electrochemical measurements of pH in neat water. Similarly, understanding interface-induced dissociation of water requires an understanding of the role of the interface on molecular reorientations and proton transfer.

Interfaces with water slow hydrogen-bond reorientation times [1], which would affect proton transport, but electrochemical studies find enhanced proton transport in wet mesoporous amorphous silica[2, 3, 4, 5]. Delineating these competing behaviors involving an energetically and structurally heterogeneous silica surface (see fig. 1) with multiple types of bonding environments for interactions with water requires reactive and accurate large scale – long time simulations. Professor Garofalini's lab has developed the reactive MG multi-body potential for molecular dynamics simulations that matches many bulk water properties[6] and when transferred to studying water-silica surfaces [7, 8], water confined in nanopores[9, 10, 11], proton transfer in bulk water [12, 13], and hydrogen-bond lifetimes in bulk water[14] and at the water/silica interface[15] matches experimental and ab-initio data for those scenarios. However, Garofalini's simulations cover many tens of thousands of atoms and long times that are unavailable to ab-initio calculations and more fine-tuned than experimental data. Application to such diverse scenarios indicates that the MG potential is robust, accurate, and transferable.

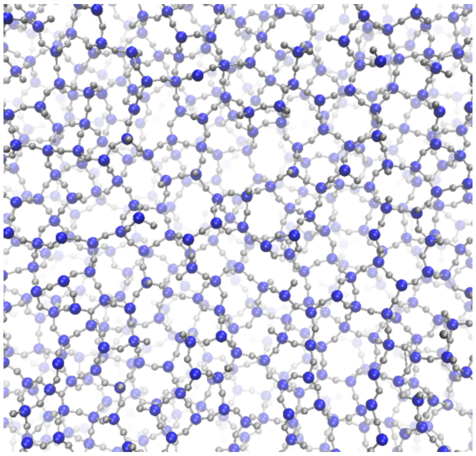
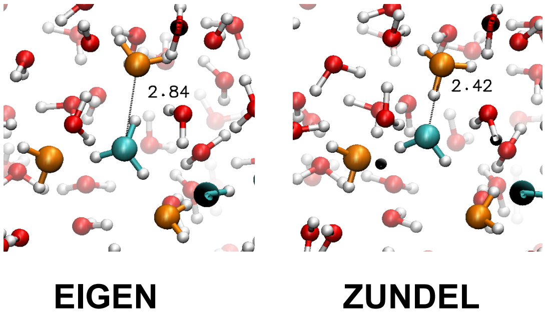


Fig. 1: Top view silica surface: heterogeneity in ring structure, requiring large size simulations to account for this.



For example, regarding PT after formation of the H_3O^+ ion in bulk water, the common explanation is the Eigen-Zundel-Eigen (EZE) mechanism in which the H_3O^+ ion has 3 hydrogen bonds to first shell waters (the Eigen complex) and normal O-O spacings (fluctuating near 2.8Å), followed by a rearrangement in which the H_3O^+ ion has a single close bond to only one neighboring water molecule (the Zundel complex), at which point the excess proton is transferred to the neighboring H_2O molecule, creating a new H_3O^+ ion and a new Eigen complex. Consistent with ab-initio calculations, our simulations show such an EZE process and

PT when the 2 oxygens in the Zundel complex decreases to a short distance of 2.42Å during a simulation, as shown in figure 2 (numbers indicate O-O spacing).

Consistent with the implications of proton transfer shown in figure 2, potential of mean force calculations by his group showed a free energy barrier to proton transport when the O-O spacing between the oxygens in the Zundel complex was 2.4Å is consistent with that observed in quantum calculations, with an appropriate increase in the barrier with increasing O-O spacing, again similar to quantum calculations.

The use of large numbers of atoms in the simulations enables better statistical data than found in ab-initio calculations, providing closer relevance to real systems.

Additional details can be found in the Publications tab on the web-site: glass.rutgers.edu from our references below.

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