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Ab Initio Calculations

Water Dissociation in the Presence of Metal Ions**

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Metal-ion solution chemistry is of fundamental importance and has practical implications in a wide variety of chemical, biological, and environmental processes.[1] In particular, events such as water dissociation play a central role in determining solution pH value and chemical reactivity. Though there are many studies of metal-ion solutions, all have focused on the structure of the solvated metal ion. Herein, water dissociation, hydroxylation of metal ions, and proton transfer in aqueous solutions of metal ions are studied by ab initio molecular dynamics simulations coupled with sampling techniques.

The quest for understanding the behavior of the proton in water has a long history. In 1806, Grotthuss[2] introduced the notion of "structural diffusion" for which the detailed "Grotthuss mechanism" has only recently been demonstrated to involve the motion of a proton in water along a network of hydrogen bonds. Important aspects of this mechanism include the structures and energetics of the hydrated proton. In the mid-20th century, Eigen proposed a $H_9O_4^+$ complex[3] in which a hydronium ion is bound to three water molecules, and Zundel proposed a $H_5O_2^+$ complex[4] in which a proton is bound to two water molecules. These concepts dominate our modern understanding of the proton in water.

A mechanism is presented for water dissociation in the presence of Cr^{3+} and Fe^{3+} derived from Car–Parrinello molecular dynamics (CPMD) simulations with transition path sampling (TPS). These techniques provide unprecedented insight into dynamical events that are difficult to observe experimentally.

The initial trajectories used in TPS were obtained from CPMD simulations. We observe a slightly elongated O–H bond (over 1.1 Å; Figure 1 A) in the first solvation shell. In the following 80 fs (TPS calculations), the proton moves and leaves the transition-metal ion hydroxylated (Figure 1 B). Once the proton moves beyond the first shell, Zundel and Eigen complex formation may be observed. Within 30 fs of the proton moving to the second shell (Figure 1 C), hydrogen-bond fluctuations lead to the formation of a $H_5O_2^+$ (Zundel) complex. In the following 50 fs, a $H_9O_4^+$ (Eigen) complex forms through proton transfer between the second and third shells (Figure 1 D). No immediate return path to the undissociated state of water is observed once the water ions form and are separated by the breaking of the chain-like hydrogen bonds as previously observed.[5] The system rapidly interconverts between Eigen and Zundel complexes as has been observed in simulations of a proton in water.[6–8]

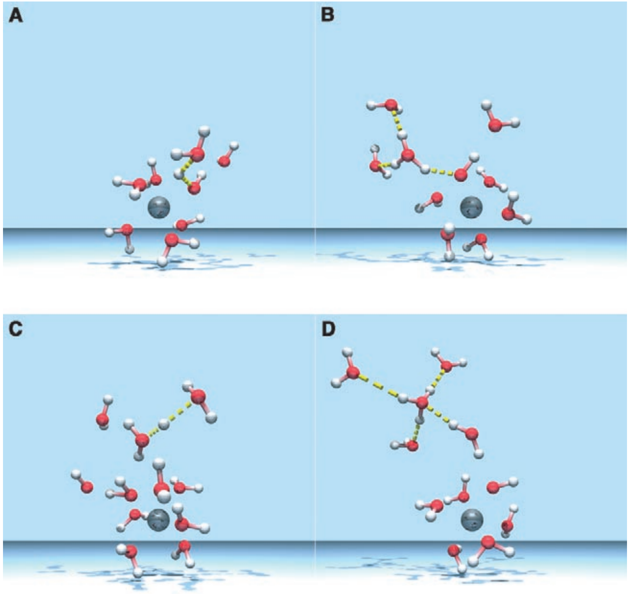

Figure 1. Illustration of proton transfer around metal ions from CPMD/TPS simulations (gray metal, red O, white H, H-bonds given by yellow dashed lines). A) $t=6$ fs, B) $t=80$ fs, C) $t=110$ fs, D) $t=160$ fs.

The Zundel complex forms in the second shell (1.5 Å closer to the metal ion), and the Eigen complex forms between the second and thirds shells. Geometric parameters of the Zundel (H^+–O bond lengths of 1.16 Å and 1.19 Å and an O–O separation of 2.2 Å) and Eigen complexes (H^+–O bond length of 1.59 Å and an O–O separation of 2.61 Å) are similar for solutions of Fe^{3+} and Cr^{3+} ions. The asymmetric binding of the proton within the Zundel complex has been found in theoretical[9,10,24] and experimental[11] studies. Furthermore, the O–O distances are 0.6 Å ($H_5O_2^+$) and 0.2 Å ($H_9O_4^+$) shorter than for the water dimer.[12] The H^+–O bond lengths of the Zundel and Eigen complexes differ from those of pure water by 1–3%.[10]

In Figure 2, the free-energy changes for proton transfer between Zundel and Eigen complexes in the vicinity of Cr^{3+} and Fe^{3+} ions are presented. The plots show minima for

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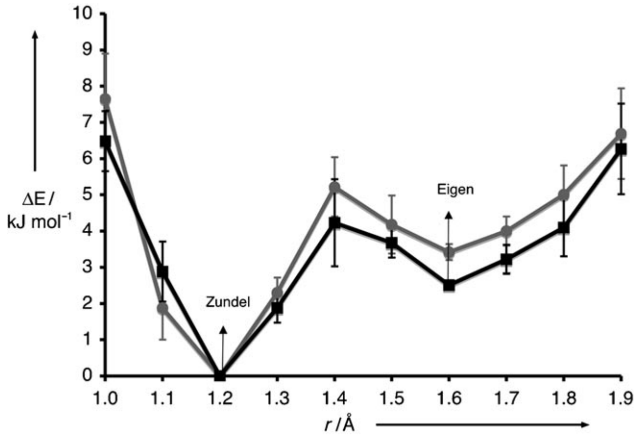

Figure 2. Free-energy change associated with proton transfer for Cr^{3+} (gray) and Fe^{3+} (black) at different $H^+{-}OH_2$ distances *r*, calculated by umbrella sampling. Error bars were calculated by averaging over TPS path ensembles.

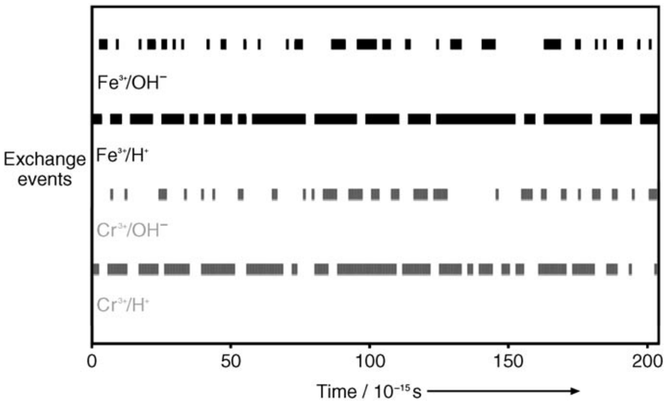

Figure 3. Exchange events involving H^+ and OH^- ions around Cr^{3+} (gray) and Fe^{3+} (black). The presence of a solid bar illustrates an exchange event taking place at the indicated time.

proton transfer located at $H^+{-}OH_2$ distances of 1.2 Å ($H_5O_2^+$) and 1.6 Å ($H_9O_4^+$). The energy differences indicate that formation of $H_5O_2^+$ is slightly preferred over $H_9O_4^+$. This preference might change with different numbers of water molecules and different methods used in simulations.

The present results do not show large deviations from previous experimental and theoretical studies of protons.[6–11] IR measurements confirm the existence of the Zundel complex.[13] Direct observation of the Eigen complex was reported recently using femtosecond pump–probe spectroscopy.[14] We observe both water complexes in the vicinity of Fe^{3+} and Cr^{3+} ions, as seen in previous theoretical studies of protons in water.[24]

The predicted distances between the metal ion and the first-shell O atom for Al^{3+} (1.92 Å), Cr^{3+} (2.05 Å), and Fe^{3+} (1.99 Å) show agreement within 0.2 % of diffraction spectroscopy measurements.[15] The first-shell coordination number is six in all cases, but the second-shell coordination number varies from 8 to 14 around the Al^{3+} ion and from 11 to 14 around the Cr^{3+} and Fe^{3+} ions. These results are indistinguishable from reported experimental observations.[15,16] Differences are seen in comparison to pure water: the first-to-second-shell O–O distance is 0.2–0.3 Å shorter and the second-shell H-O-H angle is 3–4 % larger around the metal ions than in pure water, in agreement with neutron diffraction studies of crystalline hydrates.[17] A water molecule is coordinated to the Eigen complex (Figure 1 D).

The average hydroxylation number (1.7 for Cr^{3+} and 2.1 for Fe^{3+}) is directly related to the pH value of the solution. These results predict a lower pH value for a Fe^{3+} solution than for a Cr^{3+} solution. Hydrolysis constants and pKa values support this result,[18] predicting that the hydrated Fe^{3+} ion should become hydroxylated more easily than the Cr^{3+} ion.

The mobility of the H^+ ion is of central importance in acid–base chemistry. A quantitative description of ion mobility in exchange events involving H^+ and OH^- ions obtained from the present study is illustrated in Figure 3. For both Fe^{3+} and Cr^{3+} ions, the movement of a proton between adjacent pairs of hydrogen-bonded water molecules is more frequent than for the analogous event involving OH^- ions, consistent with previous studies.[10,19,20]

The present findings do not imply that proton transfer does not occur in solutions of Al^{3+} ions but indicate that water dissociates in the vicinity of Cr^{3+} and Fe^{3+} ions. These results further suggest that electrostatic effects alone do not fully account for water dissociation.

The different behavior of Al^{3+} may be rationalized by noting that it has no filled d orbitals and has an ionic radius roughly 15 % smaller than Cr^{3+} and Fe^{3+}.[21] One study using ^{17}O NMR spectroscopy indicates that Fe^{3+} has a stronger effect on water cluster size than would be anticipated based solely on ionic radius differences.[22] Oxygen 1s X-ray absorption spectra display extra pre-edge features for Cr^{3+} and Fe^{3+} that are absent for Al^{3+}, which has been interpreted to indicate mixing between water orbitals and d shells on Cr^{3+} and Fe^{3+} ions.[23]

In conclusion, we characterize water dissociation in the vicinity of Cr^{3+} and Fe^{3+} ions using CPMD simulations with TPS as well as the resulting Zundel and Eigen proton complexes.

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