



Supporting Information

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Water Dissociation in the Presence of Metal Ions

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In this work, we show that the fluctuations driving water dissociation around metal ions involve the motion of many atoms, and the driving force for water dissociation (meaning here that dissociation takes place through the breaking of chain-like hydrogen bonds and we have not observed a path which leads immediately back to the undissociated state of water) is due to the collective coordinates studied by CPMD simulations and TPS calculations.

We have performed isothermal-isobaric ensemble CPMD simulations of Fe-water, Cr-water, and Al-water systems each with one metal ions and 64 D₂O molecules in periodic cubic boxes of 12.7, 12.6, and 12.4 Å, respectively, corresponding to a water density of 1 g cm⁻³. The electronic structure of valence electrons was described by DFT, using the PBE functional and Hamann pseudopotentials for water and Troullier-Martin pseudopotentials for the metal ions with a cutoff value of 140 Ry. The valence electronic wave function were expanded in plane waves, and their interactions with nuclei and the core electrons were described through generalized norm-conserving Hamann pseudopotentials. The nonlocal part of the pseudopotentials were modified to a completely separable form as suggested by Kleinmann and Bylander.^[1,2] Since the original Hamann pseudopotential requires a high cutoff energy for oxygen, a softer potential that was constructed by Bylaska and co-workers by increasing the core radii has been used.^[3,4] Details about the pseudopotentials can be found in References 1-4. These simulations for 30 ps (after 10 ps equilibration) enabled us to validate the method we have used by comparison to experimental results for Fe-water, Cr-water, and Al-water systems. Simulations with a NPT ensemble were performed at 300 K and

0.1 MPa pressure using a Nosé-Hoover thermostat. A time step of 0.1 fs was used for the simulations. Long-range interactions were treated with the Ewald mesh method.

According to these simulations, the average metal ion to oxygen distances in the second shell are about 0.2 Å shorter in the vicinity of both Cr³⁺ and Fe³⁺ in comparison to those around Al³⁺ (Table 1). However, the hydrogen-bond distances between the first and neighboring second shell water molecules are 0.2 Å longer in the vicinity of Al³⁺ than those around Cr³⁺ and Fe³⁺ (Table 1). In addition, the second shell water H-O-H angle opening is slightly larger in the vicinity of Cr³⁺ and Fe³⁺ than the analogous water angles in the presence of Al³⁺ (Table 1). The first shell coordination number of water is six around the Al³⁺, Cr³⁺, and Fe³⁺ ions. The calculated metal-oxygen radial distribution functions at room temperature are shown in Figure 1. These results show agreement with the time averaged values presented in Table 1 and with previous experimental and theoretical results. These results indicate that the chosen method yields values in agreement with experimental data for these metal ions in aqueous solution. Some structural results indicate that Cr³⁺ and Fe³⁺ have a different impact on liquid water than on Al³⁺. However, differences in the nature of liquid water around these metal ions are not clear from these analyses. These results are in general agreement with spectroscopic measurements and previous theoretical studies.^[5-10]

Bond breaking and bond formation processes usually involve the crossing of large energy barriers that separate reactant states from product states. In CPMD simulations where inter-atomic forces are determined by solving the electronic structure problem, total simulation times (such as our CPMD simulation time of 30 ps) do not exceed dozens of picoseconds and do not capture the studies of rare events. Transition path sampling (TPS) simulations allow a thorough study of rare events such as water dissociation in the presence of metal ions.^[11-13] In contrast to other methods, transition path sampling does not require any prior knowledge of the mechanism. TPS simulations were performed on initial trajectories taken from CPMD simulations. The transition path ensemble was defined using the dynamical path probability that is based on the idea that the time evolution of a system is continuous and it is convenient to discretize time and represent trajectories by an ordered sequence of states. Thus, consecutive states are separated by Δt ($t=\text{time}$).^[13] Trajectories along the transition pathways are generated from our initial configurations by shooting steps in a manner that the simulation ensemble is conserved.^[14] Microcanonical ensemble CPMD simulations were performed to ensure conservation of energy. To generate the

trajectories, we applied momentum changes (conserving the total and angular momentum) while we kept the coordinates constant. The momentum-modified trajectories were then propagated in both directions of time. For this purpose, we used the reaction descriptor (proton and oxygen distance) as a quantitative property for the identification of transition pathways that go from the neutral state of water molecules to charge separated water molecules. The chosen simulated transition configurations were chosen for further determination of more transition pathway trajectories. These trajectories led to a manifold of dynamical pathways and each of these pathways described a possible transition pathway for water dissociation around metal ions.

In this work, the shooting steps for generating new trajectories were applied in alternating order in the reactant and product state regimes to avoid slow convergence. The trajectories were calculated by deterministic dynamics, applying dynamical propagation to a phase space of CPMD trajectories using momentum rescaling.^[11,13] The transition states are characterized by an equal probability (a configuration of [r,p] of a given path) to reach each stable state. In this work, we used 60 trial paths per time step. For determining the shifting moves, we applied the algorithm used for deterministic dynamics. This means in a forward shift of length δt , the new trajectory was generated by integrating the equations of motion along with the Lagrangian of Car and Parrinello for $\delta t / \Delta t$.

The combination of CPMD and TPS simulations were accomplished by selecting the time slice from existing path and then the corresponding momentum was changed according to the rules described above and in Ref 13. The modified phase space point was supplied to the simulation program. A forward shot was determined by momentum rescaling. The CPMD program then integrated the equations of motion to produce the trajectories. We then proceeded with the backward part of the shooting move as described above. When the newly generated backward trajectory segment was computed by the path sampling module, the momenta along this segment were inverted such that they pointed forward along the path. The shooting move was completed by accepting the move if it was in the right region; otherwise, we rejected it. A summary of this algorithm is given in Ref. 13.

The time propagation describing the mechanism presented in Figure 1 was calculated by averaging the sampling of these transitions. The exchange events and average hydroxylation number might play an important role in acid/base reactions and in solutions in general and clearly should be considered in

mechanistic studies of such processes. In this work, the number of deprotonated water molecules was calculated by determining the average number of hydroxyl groups (deprotonated water molecules in the first shell) during time dependent microcanonical simulations involving 60 trial pathways per time step for each metal-water system studied in this work and then taking these trajectories and simulating for 5 ps. Furthermore, we have predicted the free energy change using the umbrella sampling method of calculating the potential mean force using dynamics.^[13]

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Al ³⁺		Cr ³⁺		Fe ³⁺	
R _{Al-O2} /Å	4.12±0.06	R _{Cr-O2} /Å	3.91±0.03	R _{Fe-O2} /Å	3.96±0.04
R _{O2-H2} /Å	0.98±0.02	R _{O2-H2} /Å	0.98±0.01	R _{O2-H2} /Å	0.99±0.01
R _{O1-O2} /Å	2.72±0.03	R _{O1-O2} /Å	2.63±0.03	R _{O1-O2} /Å	2.64±0.02
R _{HB} /Å	1.95±0.02	R _{HB}	1.65±0.04	R _{HB}	1.63±0.05

Table 1. Average structural properties for Al-water, Cr-water, and Fe-water systems from Car-Parrinello molecular dynamics simulations. HB denotes the hydrogen bond distance between first and second shell water molecules. The error was calculated by the time dependent standard deviation method.

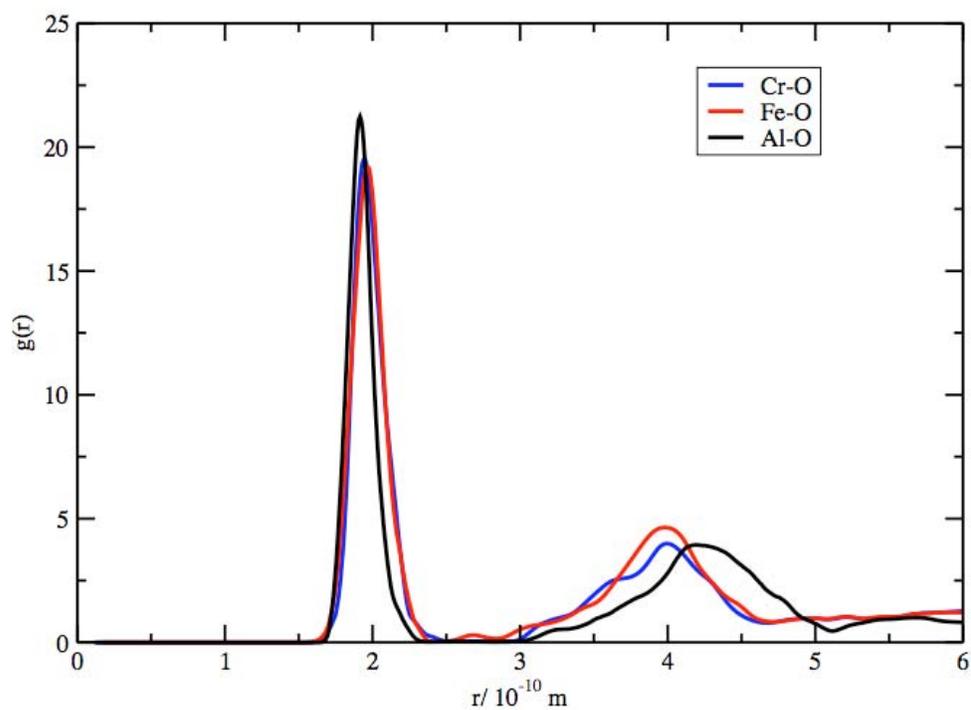


Figure 1. Metal-oxygen radial distribution functions determined from NPT ensemble CPMD simulations. Cr-O (blue curve), Fe-O (red curve), and Al-O (black curve).