Communication

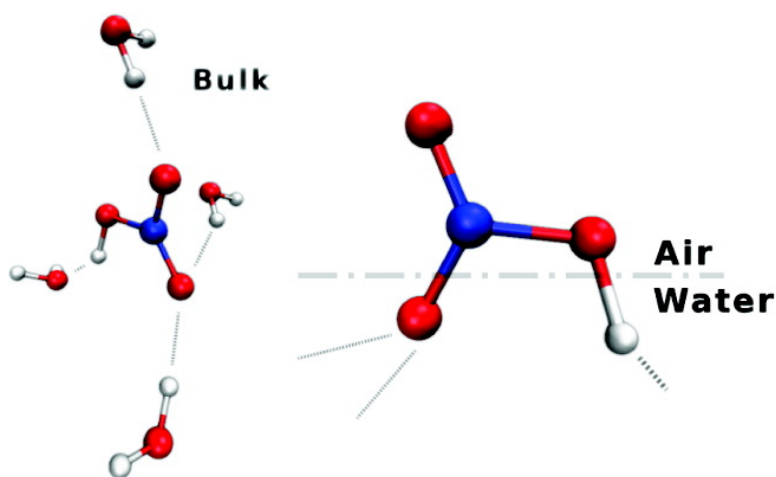# At the Water's Edge: Nitric Acid as a Weak Acid

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At the Water's Edge: Nitric Acid as a Weak Acid

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Nitric acid plays a key role in many important heterogeneous chemical reactions in our upper and lower atmosphere.[1] At the surface of aerosols and cloud droplets, it has the opportunity to inflict its highly reactive nature on a host of organic and inorganic species.[2] But how applicable is our knowledge of nitric acid in solution to predicting its behavior at an aqueous surface? In this paper, we report the distinctly different behavior of nitric acid on a water surface relative to its bonding and acidic behavior in bulk water. We find through molecular dynamics calculations that nitric acid orients and bonds to a water surface in a way that reduces its ability to be a strong dissociating acid. Altered hydrogen bonding to surface water molecules plays a key role in this molecular behavior. The results throw into question how we should think about the reactivity of nitric acid on aqueous surfaces if we rely on models solely derived from its behavior in bulk.

Recent computational[3,4] and experimental[5−10] studies have suggested that molecular nitric acid and nitrate anion can be found at or below an aqueous surface, but there were uncertainties from these as to the bonding and orientation of the molecular form. We confirm by simulation the altered bonding of surface nitric acid. In these simulations, nitric acid molecules were introduced to the surface in the two different orientations shown in Figure 1: with the molecular plane perpendicular and the other parallel to the surface. We investigated the nitric acid's molecular orientation (defined by the tilt angle between the vector normal to the molecular plane of the nitric acid containing the three NO bonds and the interface normal), HNO_3 coordination to solvating water molecules, OH bond and NO bond lengths, and the acid distances to solvating water molecules. Comparison was carried out of the behavior of the nitric acid at the surface and in the bulk solution.

Ab initio molecular dynamics simulations were performed using density functional theory (DFT)[11] with the help of the QUICKSTEP package.[12] Energies and forces corresponding to the system Born−Oppenheimer surface were calculated for each MD step using the atom-pseudo potentials of the Goedecker, Teter, and Hutter type,[13] the exchange-correlation functional of Becke, Lee, Yang, and Parr (BLYP),[14] and a Gaussian valence basis set of double-ζ quality augmented by one set of polarization functions (DZVP). A simulation time step of 1.0 fs was used. A starting point was a periodic box with 64 water molecules. To simulate the bulk solution, two water molecules were replaced by an acid molecule. To generate the surface model, two-dimensional periodic boundaries were set for the *x* and *y* axes of the water box. The resulting infinite slab model includes two open surfaces interfacing with the vacuum. An acid molecule was placed above one of them. Two "extreme" initial configurations were tested for the acid, with the molecular plane either parallel or perpendicular to the liquid surface, as shown

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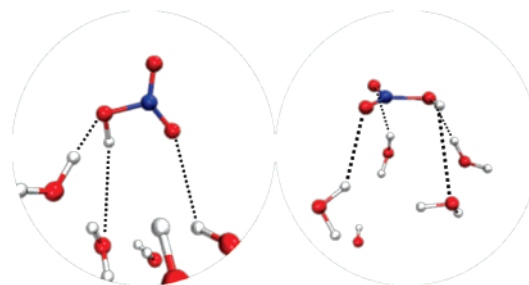‡ The Hebrew University.
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Figure 1. Snapshot of the initial configurations of surface nitric acid molecules that were used in the surface trajectories. In one trajectory, the nitric acid molecular plane containing the three NO bonds was initially placed perpendicular to the surface (left) and the second trajectory (right) with its molecular plane initially parallel to the water surface plane.
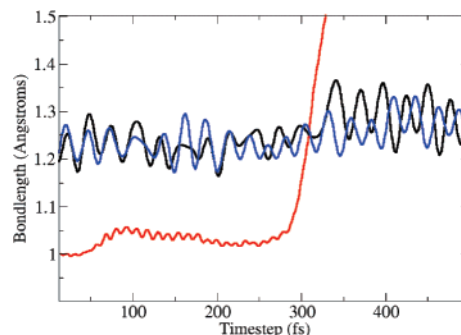

Figure 2. Trajectories of the acid OH bond length (red), and the two unprotonated NO bonds (blue and black) during the dissociation event in the bulk model. The point of dissociation occurs after 500 fs of equilibration and ~300 fs of data collection when the hydrogen is equidistant from the O-atoms of the acid and the acceptor water molecule (1.3 Å). Dissociation of bulk nitric acid increases the N−O bond lengths.

in Figure 1 (trajectories I and II). The initial configurations were minimized, and the systems were equilibrated for 0.5 ps. The two slab systems were then subjected to NVE simulations for a further 20 ps. The bulk system was simulated for 25 ps. The atomic position data were collected at every step.

The simulations show that dissociation of the nitric acid in the bulk solution happens very readily just after the equilibration period, consistent with its known high degree of acidity. As shown in Figure 2, HNO_3 initially placed in the interior of the slab dissociates within 800 fs of simulation time as evidenced by the abrupt lengthening and dissociation of the OH bond, co-incident with the dissociation is the lengthening of the two unprotonated NO bonds. Prior to dissociation, the acid molecule forms two strong H-bonds through the oxygens (primarily the NO_2 moiety) and one to water via the proton, with a total of three strong H-bonds. In contrast, a single nitric acid molecule placed on the surface of a neat water slab did not dissociate over the full simulation time and typically formed
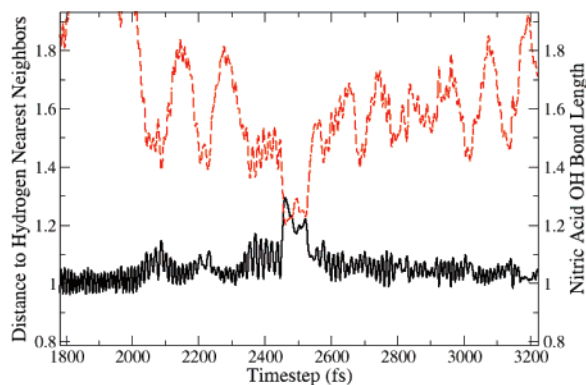
Figure 3. Several times during trajectory II the OH bond length increases above 1.3 Å. These excursions of the proton typically last approximately 50 fs, during which the proton is equidistant to the O-atoms of acid and neighboring water. Shown are the distances from the proton to the nearest water oxygen (dashed red line) and the nitric acid OH bond length (solid black line). Lower frequency oscillations correspond to intermolecular vibration of the solvating water molecule.

one strong H-bond to the water phase through the proton and occasionally a second strong bond via NO (see Supporting Information).

In trajectory I, one NO bond is pointing into the vacuum, and the NOH moiety and second NO bond are both directed into the aqueous phase. The molecular tilt angle oscillates about 90°, with amplitude of 62° to either side. The three NO bonds have distinctly different characteristics. The NO pointing toward the vacuum phase shows no interaction with surface water molecules and consequently is the shortest of the three NO bonds at 1.21 Å. The submerged NO (1.24 Å) interacts weakly with water, with O···H distance distribution peaking at 2.24 Å. The H-bond of acid hydrogen to water oxygen appears relatively strong, with H···O distance peaking at 1.87 Å (as compared to 1.74 Å for water−water bonds). The protonated NO bond is longer than the unprotonated ones at 1.51 Å, and the oxygen is only weakly H-bonded <25% of the trajectory. The OH bond length remained at 1.01 Å. Although the surface acid forms H-bonds to the water phase, the solvation is insufficient to induce ionization. Past computational studies indicate that only fully solvated HNO_3 molecules in the bulk dissociate to ions.[15−17]

In trajectory II, the acid molecule oscillates close to the tilt angle of 0° with the surface normal but occasionally flips on the surface. The NO_2 moiety is weakly H-bonded to water for ∼60% of the trajectory. The N−O lengths were similar (1.22−1.23 Å) to the perpendicular configuration, but the protonated N−O was slightly shorter at 1.43 Å. One observes several ultrafast incipient ionization events. The typical OH bond length was 1.01 Å, but during these approximately 50 fs excursions, the proton moves away to a distance of over 1.3 Å from the acid oxygen. It oscillates near an equidistant position with respect to a neighboring water oxygen without fully dissociating. Figure 3 shows a section of the surface molecule trajectory during one of these proton excursions. This behavior is indicative of a very strong H-bond through the proton.

These calculated results are consistent with a VSF study by this group,[10] in that the surface molecule was found to bind strongly to a single water through the acid proton to form the monohydrate species. However, these calculations show varying degrees of weak bonding to the NO_2 that may not be observed experimentally through frequency shifts.

The implications of these results are wide ranging. The molecular nature of nitric acid at a water surface makes it more readily available for reactions with its ambient surroundings. However, this exposure also brings with it a dramatic change in its chemical propensity to dissociate. As the appreciation for the importance of heterogeneous surface reactions in the atmosphere and our environment continues to grow, so does our need to evaluate predictive models of such surface reactions that might be based on either gas phase or condensed phase reaction conditions.

Supporting Information Available: Further simulation and analysis details are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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