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Quantum Chemical Insights into the Dissociation of Nitric Acid on the Surface of Aqueous Electrolytes

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Recent experiments in our laboratory have shown that the probability of gaseous HNO₃ deprotonation on the surface of water is dramatically enhanced by anions. Herein, we report a quantum chemical study of how a HNO₃ molecule transfers its proton upon approaching water clusters containing or not a chloride ion. We find that HNO₃ always binds to the outermost water molecules both via donating and accepting hydrogen-bonds, but the free energy barrier for subsequent proton transfer into the clusters is greatly reduced in the presence of Cl[−]. As the dissociation of HNO₃ embedded in water clusters is barrierless, we infer that interfacial proton transfer to water is hindered by

the cost of creating a cavity for NO₃[−]. Our findings suggest that nearby anions catalyze HNO₃ dissociation by preorganizing interfacial water and drawing the proton—away from the incipient [H⁺---NO₃[−]] close ion-pairs generated at the interface. This catalytic mechanism would operate in the 1 mM Cl[−] range (1 Cl[−] in $\sim 5.5 \times 10^4$ water molecules) covered by our experiments if weakly adsorbed HNO₃ were able to explore extended surface domains before desorbing or diffusing (undissociated) into bulk water. © 2012 Wiley Periodicals, Inc.

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How gas-phase nitric acid reacts on environmental aqueous surfaces has important implications in atmospheric chemistry. Nitrate (rather than nitric acid) is a sink for the nitrogen oxides polluting urban air, whence it is removed via wet or dry deposition. The stratospheric clouds produced by condensation of gaseous nitric acid play a key role in the Antarctic ‘ozone hole’ by recycling active chlorine.^[1–4] Thus, the issue of whether nitric acid, a strong acid in bulk water, dissociates on the surface of airborne ice, aerosol, and water particles has recently received much attention, both experimentally and theoretically. However, most reports on the relevant HNO₃ interactions with water in gas–liquid encounters are mainly theoretical.^[5–7] Experimental studies on this issue have focused on the extent of dissociation of dissolved HNO₃(aq) at the air–water interface.^[8,9] A few reports explored the dissociation of HNO₃(g) on wet salts^[10,11] and other solids.^[10,12] The more realistic case in which HNO₃(g) collides with the surface of dilute (<1 mM) electrolytes have received less attention. It has been predicted that HNO₃(g) could dissociate yielding contact ion pairs on discrete ($n \geq 4$) water clusters.^[2,13,14] Accurate theoretical descriptions of the air–water interface, however, remain a challenge.^[15–17] ‘Surface-specific’ spectroscopies do provide information on interfacial structures whose identities, however, are subject to interpretational ambiguities.^[18] Some reports predicted a kinetic barrier toward HNO₃ dissociation at the air–water interface,^[6,7,19–23] whereas others did not.^[8,17] Previous experiments involving the interaction of HNO₃(g) on wet salts, as surrogates of marine aerosols, have provided evidence of NO₃[−] formation.^[10,24] Thus, our understanding of the fate of gaseous nitric acid at aqueous surfaces remains unclear. In this article we reinvestigate these issues, focusing on the dissociation of HNO₃(g) on the surface of dilute electrolyte solu-

tions. We ask whether HNO₃(g) dissociates upon colliding with the surfaces of (i) neat water and (ii) aqueous electrolytes.

Before describing our computational model, we summarize the phenomenon of ion-partitioning at aqueous interfaces. It has been shown by a variety of experimental^[25–29] and theoretical^[26,27,30,31] methods that ions, especially large monovalent anions, tend to partition to the air–water interface. Although the forces driving this phenomenon are not fully understood,^[32,33] it can be safely assumed that a fraction of dissolved Cl[−] is present at the aerial interface of aqueous NaCl solutions. Herein, we investigate using quantum mechanics (QM) whether those interfacial ions participate in the dissociation of HNO₃(g) molecules during collisions with the surface of water. We use density functional theory (DFT) at the B3LYP level to analyze interfacial (iif) dissociation of nitric acid on model surfaces of pure water and aqueous electrolyte.

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Computational Methods

We carried out DFT calculations using the B3LYP functional shown to provide an accurate description of small clusters of water.^[34] Application of a hybrid density functional-like B3LYP to describe gas–water interactions may be computationally inexpensive and quite insightful, but has limitations.^[35] The thermochemistry and ground state structures of chemical species are well-captured by DFT calculations, but their ability to predict kinetic barriers for chemical reactions has been argued.^[36–38] However, recent calculations based on the B3LYP functional produced transition state energies and structures for a series of organic reactions in good agreement with experimental data.^[38] In a previous report, we evaluated binding energies of water clusters, W_n , (range $n = 2–8, 20$) along with hydration and neutralization energies using DFT functionals (B3LYP, X3LYP, M06, M06-2X, and M06-L), and compared them against high-level theory (CCSD(T)/aug-cc-p VDZ level). We found that the results of B3LYP calculations were in excellent agreement with high-level theory, with and without the basis set superposition error correction.^[34] Moreover, our experimental results validate these predictions and will appear elsewhere.^[23] Here, we used the 6-31G**basis set for H, C, N, and O,^[39] and the 6-311G**++ basis for Cl^- .^[40] Geometries were minimized and transition states were calculated for proton transfer processes between $\text{HNO}_3(\text{g})$ and model water/electrolyte surface. After geometry optimization, the electronic energy E_{elec} was evaluated with the 6-311G**++ basis on all atoms. The Hessians at these geometries were used to determine that the minima and transition states led to 0 and 1 imaginary frequency, respectively. The vibrational frequencies from the Hessians were also used to provide zero point energies, and the vibrational contributions to enthalpies and entropies. The free energies of nitric acid and nitrate at 1 atm were calculated using statistical mechanics for ideal gases.

Results and Discussion

We used a water decamer, W_{10} , to obtain an understanding of the effects (Supporting Information Fig. S1). To test for limitations in the W_{10} cluster, we repeated the calculations for a W_{20} cluster, which could provide a more accurate molecular framework to investigate local gas–water interactions. We used the energy optimized cluster of 20 water molecules, W_{20} , composed of overlapping 10-membered planes to represent the air–water interface. Several low-energy W_{20} cluster structures lie within a 1.0 kcal mol^{−1} free energy range. The structure chosen here is amongst the lowest energy ones.^[41,42] We found that the results obtained for W_{20} and W_{10} clusters are in close agreement. Thus, we consider that our W_{20} model is adequate to capture the interfacial chemistry of our system. In fact, our theoretical results for $\text{HNO}_3(\text{g})$ dissociation at the surface of pure water are qualitatively consistent with a large body of experimental and theoretical work.^[6,7,19,21–23,43] More specifically, we confirmed the following observations:

1. A HNO_3 molecule forms two weak H-bonds with the surface of W_{20} . At 298 K the resulting adduct (A) has a lower en-

thalpy $\Delta H^0 = -4.7$ kcal mol^{−1} and a higher free energy $\Delta G^0 = 4.0$ kcal mol^{−1} (because of translational and rotational entropy losses) than the reactants. Thus, our calculations predict a weakly bound, mobile HNO_3 moiety on the surface (Fig. 1A).

2. The transition state for transferring a proton from the adduct state, A, to the cluster interior leaving a NO_3^- outside is at $\Delta H^\ddagger = 5.4$ kcal mol^{−1} and $\Delta G^\ddagger = 10.3$ kcal mol^{−1} above the reactants (hereafter at $\Delta H^0 \equiv 0$, $\Delta G^0 \equiv 0$ kcal mol^{−1}). The product state is at $\Delta G^0 = 11.5$ kcal mol^{−1} and $\Delta H^0 = 3.8$ kcal mol^{−1} above reactants (Fig. 1A).

3. A neutral HNO_3 molecule initially placed inside W_{10} dissociates spontaneously. This finding is consistent with previous Car-Parrinello molecular dynamics calculations using the BLYP functional and a Gaussian valence basis set.^[6,44]

By using the same methodology, similar trends were predicted for $\text{HNO}_3(\text{g})$ interacting with smaller W_{10} cluster (Supporting Information Fig. S1). Our calculations predict a low probability for $\text{HNO}_3(\text{g})$ dissociation in collisions with the surface of pure water, which is qualitatively consistent with and accounts for the $\gamma \sim 0.1 < 1$ uptake coefficient reported by Vandoren and coworkers.^[45]

To represent an air-electrolyte interface, we optimized the $(\text{Cl}^-W_{20})^-$ adduct produced by adding a Cl^- to the optimized W_{20} cluster. Since our motivation is to find a mechanism that explains our experimental results on ~ 1 mM NaCl solutions, we consider that the inclusion of a Na^+ counterion within a W_{20} cluster would be unrealistic, since this would correspond to 2.8 M NaCl solution. In 1 mM solutions, counterions are separated by distances much larger than those accessible by our QM calculations. We find that the Cl^- is stabilized at the surface of W_{20} by accepting five H-bonds from surrounding water molecules. This is in agreement with previous experimental^[25–29] and theoretical^[27,30,31,35] work on anion-fractionation. To confirm, we optimized several structures comprising a Cl^- embedded into water clusters ranging from W_{10} , W_{15} , W_{16} , to W_{20} . (Supporting Information Fig. S2). For $W_{20}\text{Cl}^-$ the most stable geometry was chosen for studying proton transfer from $\text{HNO}_3(\text{g})$. We also considered a W_{10} cluster containing a Na^+ and found that it prefers to stay inside (Supporting Information Fig. S3). The fact that Cl^- accumulates at the surface of W_{20} implies that the potential of the surface becomes more amenable for proton transfer from HNO_3 . There is experimental evidence that addition of electrolytes does increase the negative potential at air–water interfaces.^[25]

Figure 1B shows the free energy and enthalpy landscapes for dissociation of nitric acid on $(W_{20}\text{Cl})^-$ at 298 K. In contrast to pure water case shown in Figure 1A, we observe that:

1. Gas-phase HNO_3 forms stronger H-bonds with the surface of water. The adduct A is more stable than the reactants by $\Delta G^0 = -5.6$ kcal mol^{−1} and $\Delta H^0 = -16.2$ kcal mol^{−1},

2. The free energy and enthalpy barriers for transferring a proton to $W_{20}\text{Cl}^-$ are reduced dramatically relative to the pure water case above^[6]: $\Delta G^\ddagger = 4.5$ kcal mol^{−1} and $\Delta H^\ddagger = 0.6$

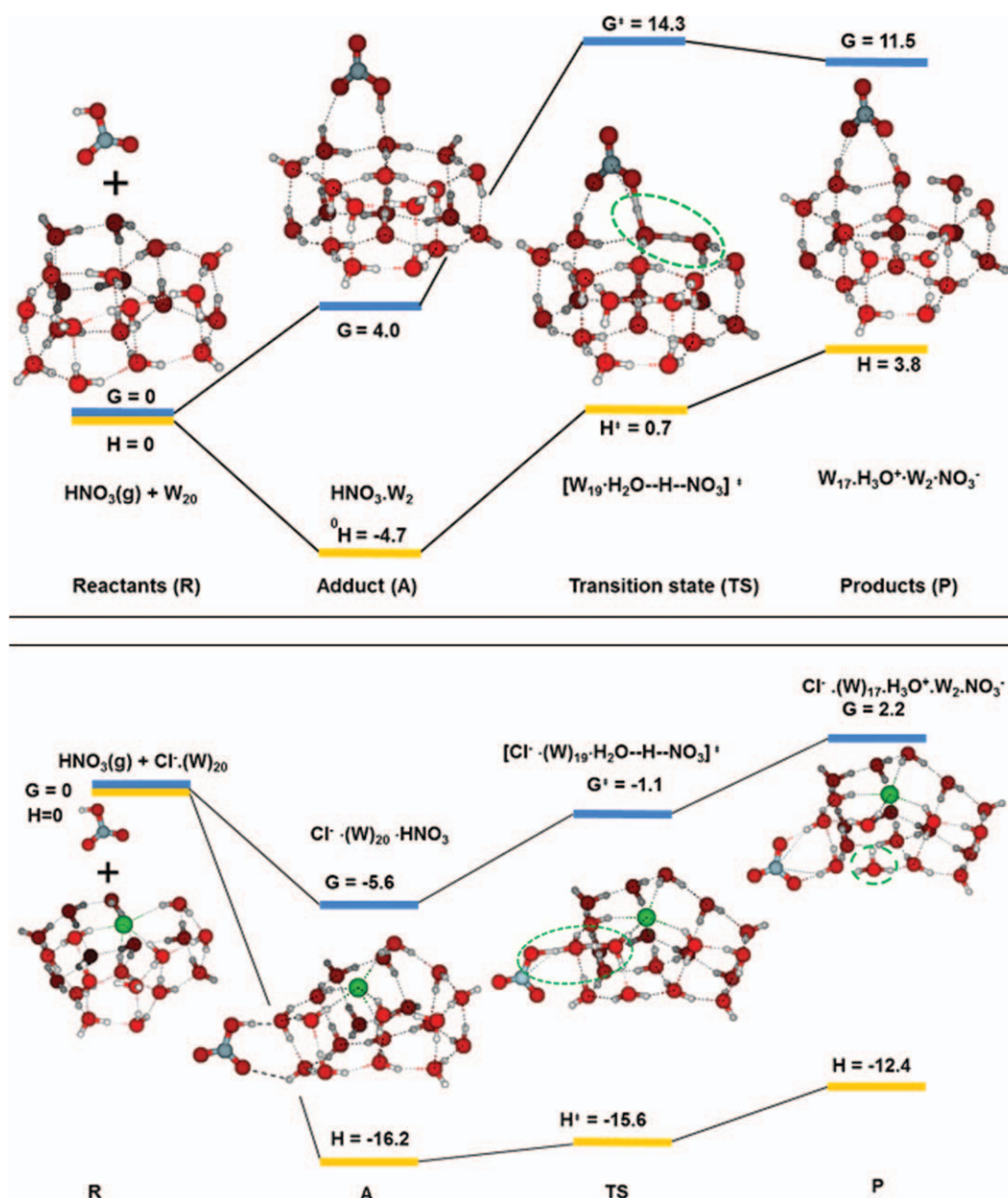


Figure 1. Calculated Gibbs free energies (G^0) and enthalpies (H^0) of reactants, adducts, transition states, and products of optimized water clusters in contact with nitric acid in the absence (A) and in the presence (B) of interfacial chloride. Concerted proton transfer process highlighted. Energies in kcal mol⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

kcal mol⁻¹. The free energy and enthalpy of the product state after proton transfer were found to be $\Delta G^0 = 2.2$ kcal mol⁻¹ higher and $\Delta H^0 = -12.4$ kcal mol⁻¹ below than the corresponding values for the reactants. It should be pointed out that the electronic energy of the TS configuration is higher than that of product by 0.17 kcal mol⁻¹, but the addition of zero-point energy corrections and temperature effects nearly equalize their free energies, thereby rendering the reverse ion recombination a diffusionally controlled process, as expected.

By increasing the size of the water cluster, we anticipate that enhanced solvation of NO_3^- ion should further stabilize the products. However, we expect that calculations on much larger clusters will still reflect significant anion effects on HNO_3

dissociation at the surface of water. Indeed, recent experiments show that dissociation of $\text{HNO}_3(\text{g})$ at air–water interface is minimal, but there is a dramatic enhancement on 1 mM NaCl solutions.^[23] From these results we envision the process of nitric acid dissociation on aqueous electrolyte surface as follows:

1. A gas phase HNO_3 molecule collides with the surface of dilute aqueous electrolyte solution at sites that may be, on average, far removed from dissolved Cl^- . It sticks to the surface by forming H-bonds with $\Delta H^0 = -4.7$ kcal mol⁻¹.
2. This weakly H-bonded HNO_3 then diffuses across the surface for a few nanoseconds eventually approaching a Cl^- ,

whereby it falls into a deeper potential well followed by rapid proton transfer to nearby waters. Or,

3. The surface bound HNO_3 desorbs back into the gas-phase.

4. Alternatively the HNO_3 could diffuse undissociated into the bulk liquid where it will dissociate spontaneously as suggested by previous calculations^[6,44] and confirmed herein.

What is the origin of the barrier for dissociating gas-phase HNO_3 on the surface of pure water, and how does interfacial Cl^- catalyze this reaction? The answer depends critically on the solvation status of interfacial NO_3^- . There have been extensive theoretical and experimental investigations of dissolved NO_3^- at air–water interface, but it is not entirely clear whether NO_3^- resides at the interface or in the bulk.^[5,46–48] We consider that the size of NO_3^- , which is incompatible with the tetrahedral network of water, in conjunction with the cohesiveness of water conspire against direct incorporation of NO_3^- into bulk water. Thus, after HNO_3 transfers its proton to W_{20} producing an interfacial close ion pair, further inward proton displacements will both entail moderate stabilization via enhanced H_3O^+ hydration and a large electrostatic destabilization, unless NO_3^- follows in concert behind. For the aqueous electrolyte case, interfacial chloride ion attenuates the electrostatic bias on hydronium, H_3O^+ , imposed by NO_3^- , thereby reducing the barrier. Furthermore, we find that in the presence of Cl^- the H-bonded adduct is structurally similar to the TS associated with proton transfer, thereby requiring minimal rearrangement of solvent coordinates during PT (Supporting Information Section 1 and Fig. S4 contain more analysis).

Summarizing, QM calculations on small water clusters are able to account for the fact that interfacial anions catalyze interfacial proton transfer between nitric acid and the surface of water. Our calculations on pure water case confirm presence of a kinetic barrier and predict that the equilibrium position of NO_3^- after proton transfer is at the surface. The transition state involves a concerted proton transfer through two intervening waters to the final location of the H_3O^+ . This is similar to formation of a solvent separated ion pair, as suggested by Hynes and coworkers.^[44] For the aqueous electrolyte case, interfacial chloride ion attenuates the electrostatic bias on hydronium, H_3O^+ , generated by NO_3^- , thereby reducing the barrier. Further, we find that in case of interfacial Cl^- the H-bonded interfacial adduct is structurally similar to the TS suggesting minimal rearrangement of solvent coordinates during PT (Supporting Information Section 1 and Fig. S4 contains more analysis). Although, our model deals with high effective halide concentrations (2.8 M), we argue that the predicted catalytic effects would persist at lower concentrations because a HNO_3 weakly hydrogen-bound to water should be able to diffuse along its surface until it encounters a halide ion in competition with desorption to the gas-phase. Further, enrichment of anions at air–water interface may significantly enhance anion populations at aqueous surface relative to the bulk solution. We expect that similar catalytic effects from other inert


anions, including Br^- , I^- , and small organic carboxylates such as oxalate and formate. This finding may have important implications across atmospheric chemistry and biology.

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Keywords: nitric acid dissociation • proton transfers at aqueous interfaces • electrostatic preorganization • interfacial anions • air–water interface

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 Additional Supporting Information may be found in the online version of this article.

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