Solvation and Reaction of Ammonia in Molecularly Thin Water Films

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ABSTRACT: Determining the interaction and solvation structure of molecules with solvents near a surface is of fundamental importance for understanding electro- and photochemical processes. Here we used scanning tunneling microscopy (STM) to investigate the adsorption and solvation structure of ammonia on water monolayers on Pt(111). We found that at low coverage NH₃ binds preferentially to H₂O molecules that are slightly elevated from the surface and weakly bound to the metal. Density functional theory (DFT) calculations showed that as the NH₃ molecule descends onto the water adlayer a high-lying water molecule reorients with zero energy barrier to expose a dangling OH ligand to H-bond NH₃. We also found that NH₃ prefers to bind to the metal substrate when water only partially covers the surface, indicating that NH₃ is more strongly attracted to the metal than to H₂O. In addition to this solvation interaction, a proton transfer reaction occurs as revealed by reflection–absorption infrared spectroscopy (RAIRS), leading to the formation of ammonium ions (NH₄⁺) in addition to molecularly adsorbed NH₃.

INTRODUCTION

Because of the economic importance of corrosion, industrial catalysis, and electrochemistry, the interplay of hydrogen bonding and water–metal interactions has been studied extensively.¹–³ As a result of such efforts, the first wetting layer on many metals at cryogenic temperatures was found to have no dangling H bonds⁴,⁵ and thus, potentially, to behave hydrophobically; water monolayers on Pt(111) are a representative example.⁶ The hydrogen atoms in the first wetting layer either form H-bonds to neighboring molecules or point toward the surface.⁴,⁶–⁸ Growth of metastable multilayer water films that preserve an H-down orientation of water has been proposed to occur on Pt(111), resulting in the formation of “ferroelectric ice.”⁹ The growth of entropically favorable proton-disordered ice requires rotating some of the molecules in the first layer to expose dangling H atoms.¹⁰,¹¹ In addition to energetic effects, kinetic hindrance of such molecular reorientation has been invoked as the reason for the hydrophobic character of water monolayer films.¹²,¹³ In previous work, the adsorption of CO and N₂ at 20 K was found to flip some H-down water molecules into an H-up configuration on Pt(111),¹³ implying that the flipping energy barrier is low.

On the more reactive Ru(0001) surface, known to dissociate H₂O at temperatures as low as 138 K,¹⁴ low-energy sputtering (LES), reactive ion scattering (RIS), and reflection–absorption infrared spectroscopy (RAIRS) showed that the H₂O monolayer is acidic enough to protonate NH₃ to form NH₄⁺.¹⁵,¹⁶ However, owing to the spatially averaging nature of the techniques used in these experiments, no information could be obtained on the structure and spatial distribution of the products formed.

The present study, which is part of an effort to understand solvation phenomena, provides the first real-space images of molecular adsorption on a water monolayer and the initial adsorption sites, which correspond to slightly lifted molecules. Through DFT calculations we discovered that on Pt(111) the adsorption causes such water molecules to rotate and expose an H atom to form a hydrogen bond with the incoming NH₃. Most notably, such a process proceeds without an energy barrier. Further, we have found that ammonia bonds more strongly to Pt than to H₂O and thus segregates from water. This preference of adsorption on the metal is in contrast with the intimately mixed structures on Cu(110) predicted by DFT calculations,¹⁷ a behavior that we attribute to attraction between NH₃ and the unfilled d-bands of Pt.

METHODS

Scanning tunneling microscopy (STM) experiments were performed in a home-built low-temperature microscope described elsewhere.¹⁸ A Pt(111) single crystal (Princeton Scientific) was mounted in an ultrahigh vacuum (UHV) chamber with a base pressure of <7 × 10⁻¹¹ mbar and cleaned by argon ion sputtering at 1 kV followed by annealing to 1300 K and heating in 5 × 10⁻⁷ mbar oxygen at 1200 K for 15
min to remove carbon contaminations. A final annealing step to 1200 K in UHV removed residual oxygen from the surface. Auger electron spectroscopy and STM confirmed that the surface had less than 1% of defects and impurities and consisted of (111) terraces with an average width of >100 nm. Water (Sigma-Aldrich, deuterium depleted, <1 ppm D$_2$O) was purified by freeze, pump, and thaw cycles prior to being dosed onto the cooled sample through a directional dosing tube. The sample temperature and time were adjusted to obtain different water structures. Islands of a ($\sqrt{37} \times \sqrt{37}$)R25.3° structure and a complete ($\sqrt{39} \times \sqrt{39}$)R16.1° water film were formed by different exposures at 140 K, while a ($\sqrt{3} \times \sqrt{3}$)R30° water layer was formed by depositing H$_2$O at 77 K and annealing the surface to 140 K. A clean Pt(111) surface was recovered after annealing to 160 K for 20 min, indicating that the water structures consist of intact H$_2$O molecules and do not contain hydroxyl species. Ammonia (Sigma-Aldrich, 99.99%) was deposited through another directional dosing tube at sample temperatures of 5 and 77 K. Heating the sample to 350 K desorbed ammonia to recover the clean Pt(111) surface.

Reflection–absorption infrared spectroscopy (RAIRS) measurements were performed in a multipurpose UHV surface analysis chamber equipped with instrumentation for LEIS, RIS, and temperature-programmed desorption (TPD), with a background pressure of <2 $\times$ 10$^{-10}$ mbar. The experiment was performed in a grazing angle (84°) reflection geometry, with linearly p-polarized infrared (IR) light in a Fourier transform IR instrument (PerkinElmer) equipped with a mercury–cadmium telluride detector. In this arrangement, RAIRS detects vibrations with the transition dipole moment perpendicular to the surface. All RAIR spectra were averaged 256 times at a spectral resolution of 4 cm$^{-1}$ and measured at a temperature of 90 K. The water layer was prepared by vapor deposition at 140 K, conditions known to produce ($\sqrt{37} \times \sqrt{37}$)R25.3° and ($\sqrt{39} \times \sqrt{39}$)R16.1° water films depending on exposure. The surface coverage of water and ammonia on Pt(111) was estimated from TPD experiments.

We generated DFT results using the projector augmented wave (PAW) version of the VASP, plane-wave DFT code. Electronic exchange-correlation effects were treated in the Perdew–Burke–Ernzerhof (PBE) version of the generalized gradient approximation. We modeled the metal substrate as a three-layer Pt(111) slab, fixing its lowest layer atoms at theoretical bulk Pt positions (PBE lattice constant = 3.97 Å, compared to experiment = 3.92 Å).

A perfect ($\sqrt{37} \times \sqrt{37}$)R25.3° H$_2$O layer was initially adsorbed on the uppermost Pt layer and an NH$_3$ molecule situated with its symmetry axis normal to the slab. Its H atoms were set higher than its N atom, which was 5.6 Å directly above the O atom of a high-lying, H-down water molecule. In the final state of the sticking calculation, the NH$_3$ had accepted an H bond from the underlying host H$_2$O molecule, whose free OH ligand had flipped up to bind the NH$_3$. In the final state, the N atom was located 2.77 Å away from the O atom, and the system had gained an adsorption energy of about 0.42 eV.

We took pains to cancel unphysical fields associated with adsorption on the upper Pt surface only. The accuracy of the cancellation requires a sufficiently wide vacuum region (19.2 Å) between each slab with its upper-layer adsorbates and the bottom of its periodic neighbor slab. Thus, we set the distance between the NH$_3$ molecule and the bottom of the periodic image slab above it to about 13.6 Å.

To estimate the NH$_3$ sticking barrier, we used the Climbing Image Nudged Elastic Band Method (CINEB) with five images spaced along the sticking path (minimum energy path, MEP). Michailides, Alavi, and King have found, for an idealized first layer of water on Ru(0001), that rotation of a water molecule in its H–O–H plane is the low-energy mode for replacing a downward-pointing free OH by an upward-pointing one. We assumed the same would hold here. This assumption was amply validated by our discovery, discussed further below, that the OH flip then proceeds with no barrier at all.

We conducted initial calculations using a gamma-point-only surface Brillouin zone (SBZ) sample and a plane-wave cutoff equal to 400 eV. We then checked the quality of the results by redoing the calculations with the SBZ sample increased to 3 $\times$ 3 or the plane-wave cutoff raised to 756 eV. Because the changes associated with these improvements were small, we assumed they are additive.

**RESULTS AND DISCUSSION**

**First Water Layer on Pt(111).** On Pt(111), water adsorbs intact and forms three ordered monolayer (ML) structures, representative images of which are shown in Figure 1. The energetically most stable structure is a ($\sqrt{37} \times \sqrt{37}$)R25.3° arrangement of pentagons, hexagons, and heptagons (hereafter termed R37 structure) exhibiting a Moiré-like pattern as shown in Figure 1a. DFT calculations showed that all molecules in this structure adsorb either flat-lying or with a hydrogen bond oriented perpendicular to the surface. This can be seen in the RAIRS spectrum shown in Figure 1b, where the H-flip vibration is evident. The NH$_3$ molecule is shown in Figure 1c, with its adsorption energy of 0.42 eV.
atom pointing toward the substrate. Water molecules bonded close to the surface, through a Pt–O bond, appear darker in STM images (tip closer to the surface), while molecules not in registry with the substrate are slightly lifted off the surface and appear brighter in the image (tip farther away from the surface). As the coverage is increased the surface rearranges to form a (√3 × √3)R30° structure (R3 structure), which is a slightly denser arrangement of pentagons, hexagons, and heptagons. The R3 structure also consists of flat-lying and of H-down-oriented molecules and typically includes one second layer water molecule per unit cell, which exposes a dangling H atom. The first layer again appears as a Moiré of closely bonded (dark) and lifted (bright) molecules in STM, on top of which additional H2O molecules form a regular array of bright spots (cf. Figure 1b).3

In addition to these two energetically favored structures, water can form a (√3 × √3)R30° structure (R3 structure), which is 0.1 eV/molecule less stable than the R37 structure.5 Mixed water–hydroxyl films, formed by coadsorption of H2O and O atoms6 or by electron injection after prolonged scanning in an STM experiment,7 were reported to exhibit (√3 × √3)R30° geometry. In the present case, however, the clean substrate was recovered after annealing to 160 K, indicating that the H2O molecules were intact,8 forming an array of hexagons resembling a flattened bilayer of the basal plane of hexagonal Ih ice. In our STM images, some of the hexagons in the R3 phase exhibit a dark center (cf. Figure 1c). In previous experiments on Ru(0001), a similar phenomenon was observed, which could be explained as a result of hydrogen atoms being trapped inside the water hexagon.14 Since H2 is a common contaminant in a vacuum chamber, we propose H atoms trapped in the center of the water hexagon as the stabilizing agent of the R3 structure. In addition, we observe narrow regions separating water hexagons that appear brighter. In analogy with the R37 and R39 H2O structures, we assume the brighter regions contain water molecules that are slightly lifted off the surface. To the best of our knowledge, such a buckled structure has not been reported previously.

**Adsorption of Ammonia on a Fully Water-Covered Surface.** To study the interaction of ammonia with water, we first adsorbed NH3 on a surface fully covered by a water layer, either in the R39 or the R3 structure. Figure 2a shows a high-resolution STM image recorded after adsorption of ammonia on the R39 water monolayer, revealing two new species. First, we observe that some of the bright bumps of the second layer water molecules are replaced by even brighter protrusions. The second layer water molecules in this structure were shown to exhibit a dangling H atom,9 suggesting that ammonia can H-bond to such a molecule or displace it to form a hydrogen bond with first layer molecules. Second, some of the water hexagons commensurate with the substrate (located in the darker areas) show a new species in their center, imaged as a protrusion inside the dark triangles.

To identify the species observed in STM chemically, we performed RAIRS experiments of ammonia on 1.2 ML water, i.e., on a complete first and partial second layer, shown in panel I of Figure 3. Before ammonia adsorption, the pure water spectrum shows the expected O–H stretch (∼3390 cm⁻¹) and scissors (∼1630 cm⁻¹) modes of water. The appearance of a dangling OH peak at 3710 cm⁻¹ in the spectrum for pure water is in line with the presence of second layer water molecules in the R39 structure that expose dangling H atoms.8,13 Upon ammonia adsorption (cf. Figure 3b) the intensity of the dangling OH band decreases, also in line with the STM observation that ammonia bonds to the dangling H of the second layer water molecules to form an O–H···N bond. At the same time, two strong bands at ∼1110 and ∼1470 cm⁻¹ and a weaker one at ∼1250 cm⁻¹ appear, which can be assigned to the ν4 (umbrella) mode of NH3 adsorbed on water.8,13 The ν4...
 Adsorption of Ammonia on a Partially Water-Covered Surface. Having studied the adsorption of ammonia on a full water layer, we coadsorbed ammonia with a partial water monolayer to investigate the effect of the Pt(111) substrate. Figure 4a shows a representative STM image obtained after dosing ammonia onto a submonolayer water film in the R3 phase. We observe substantial segregation of the two species, with water-forming monolayer islands (imaged as bright regions) and ammonia molecules adsorbed preferentially on areas of bare Pt (bright protrusions on the dark background). Two different species can be distinguished in the bare substrate regions, appearing as protrusions of different height (brightness), which correspond to NH$_3$ monomers and dimers, as previously observed on Ru(0001). As on Ru, the dimers could be dissociated into monomers by applying a 2 V pulse with the tip. On the R3 water islands (cf. Figure 4c), very few bright protrusions are observed, suggesting that ammonia moves off the water islands and onto the substrate.

We can understand the formation of separate H$_2$O and NH$_3$ domains by considering bond strengths. The interaction of NH$_3$ and H$_2$O is based on hydrogen bonding, while the molecule–substrate interaction is covalent. In the bulk, the molecules can reorient easily to optimize the H-bond network, forming intimately mixed crystal structures. On a metal surface, however, the molecules cannot reorient freely, and adsorption structures are thus determined by the interplay of adsorbate–substrate and interadsorbate bond strengths. For H$_2$O/Pt(111), the interactions are of similar strength, whereas for NH$_3$/Pt(111), the adsorbate–substrate interaction dominates. Thus, water grows in crystalline films on Pt(111), while ammonia forms irregular assemblies of molecules bonded to Pt through the N atom. The hydrogen bond strength in water is typically 26 kJ/mol, while for bulk NH$_3$, it is only ~11 kJ/mol. Moreover, amounting to 23 kJ/mol, the O–H···N bond is stronger than both the N–H···N and N–H···O (11 kJ/mol) bonds, implying that it is preferable for NH$_3$ to bond to H–O through the N atom.

To investigate the interaction of ammonia with a water layer known to expose no dangling H atoms, we deposited NH$_3$ onto R37 water islands at 5 K (cf. Figure 4b). Such low-temperature experiments not only limit adsorbate mobility but also provide important information about the energy barrier involved in the NH$_3$ adsorption process. As $k_B T$ is only 0.4 meV at 5 K, where $k_B$ is the Boltzmann constant, observing a rotation from H-down to H-up water similar to that proposed on R3 water suggests a very low activation barrier. Figure 4d shows a high-resolution image recorded shortly after ammonia deposition. The Moiré structure of the R37 water structure is still clearly visible, but the lifted regions are covered in streaks and bright spots, confirming that NH$_3$ adsorption occurs even at 5 K. The streaky appearance suggests that molecules are moving under the tip. Since the streaks only appear on top of brightly imaged water regions, we infer that the mobile species bond to H$_2$O molecules that are weakly bonded to the substrate, analogous to our observation on the R3 water film. After prolonged scanning, the mobile species largely disappear, and the structure of the underlying water layer becomes visible, as in Figure 4e. These observations indicate that some molecules move off the water layer and onto the Pt substrate where they can bind more strongly, likely through the interaction with the STM tip. In addition, we observe occasional bright bumps, one of the same height as the streaks, and also a brighter kind, suggesting that two species are present.
To determine whether the protrusions observed in STM are due to ammonia or ammonium species, we conducted RAIRS measurements of a partially water-covered Pt(111) surface (0.7 ML) before and after NH$_3$ adsorption, shown in panel II of Figure 3. The growth conditions employed here (cf. Methods) imply the presence of an R37 water layer. The conspicuous absence of a free O−H stretch band at ~3710 cm$^{-1}$, characteristic of dangling OH groups, indicates that the clean R37 water layer exposes no unsaturated H atoms. Adsorption of ammonia onto this surface results in vibrational features for NH$_3$ on H$_2$O at 1110 cm$^{-1}$, NH$_4^+$ at the Pt−H$_2$O interface at 1250 cm$^{-1}$, and NH$_4^+$ at 1470 cm$^{-1}$. RAIRS thus suggests that, in addition to H-bonding NH$_3$, the water provides protons to form ammonium ions. As the N−H···O bond is weaker than the O−H···O bond, NH$_4^+$ is likely the more mobile species on H$_2$O than NH$_3$ and can thus move off the H$_2$O islands onto bare Pt under the STM tip, where it can decompose into NH$_3$ and H.$^{16}$

**Atomic-Scale Details of the NH$_3$ Adsorption Process.**

Our STM measurements show that NH$_3$ only bonds to regions in an R3 and R37 water film where H$_2$O molecules are lifted off the surface and thus weakly bonded to the metal, suggesting that an H$_2$O reorients to accommodate the NH$_3$ adsorbate. Since NH$_3$ bonds to the second layer water molecules that expose a dangling H in the R39 structure, it is likely that a weakly bonded H$_2$O in the R3 or R37 film can rotate to provide an H pointing to the NH$_3$ and form an H bond. This effect is observed even at 5 K, the energy barrier for the process must be low. To investigate the adsorption process and the energetics involved, we performed density functional theory (DFT) calculations, using the climbing image nudged elastic band method. Previous such calculations for a hypothetical, pure H$_2$O R3 structure showed barriers for water flipping, of 0.1 eV on Pt(111)$^{32}$ and 0.3 eV on Ru(0001).$^{31}$ Compared to thermal energies of $k_B T = 6.6$ meV at 77 K and 0.4 meV at 5 K, these values are too high to explain how NH$_3$ sticking can occur.

Here, we calculated the sticking barrier for the R37 structure, but unlike in the barrier estimates of refs 44 and 31, the molecule descending onto the water layer was present in our calculations. With the NH$_3$ molecule included, rotation of an H$_2$O in its H−O−H plane does not begin simply by breaking an H-bond in the water layer. Instead, a new H-bond is forming between the incoming NH$_3$ and the OH ligand rotating out of the water layer. This is what makes the barrier small: new bonds form as old ones break. High barriers occur in the absence of an adsorbing molecule because the energy of breaking the H-bond is not compensated by new bond formation. The results of our CINEB optimization of the minimum energy trajectory are shown in Figure 5. Note that there is no adsorption barrier, a result we found to be robust against improving the SBZ sample from 1 × 1 to 3 × 3 or increasing the plane-wave basis cutoff from 400 to 756 eV.

**CONCLUSIONS**

In conclusion, our investigation of the interaction of two different H-bonding molecules, NH$_3$ and H$_2$O, on a Pt substrate provides important information on the molecular level details of the solvation and reaction process of ammonia by water. We found that the ammonia adsorption process involves the rotation of an H-down molecule into an H-up configuration and proceeds without an energy barrier. The solvation structure in that case consists of a single water molecule donating an H bond to the ammonia molecule (HOH···NH$_3$). This distorts the local environment of the “solvating” molecule, which now does not point its H to the Pt surface atoms. On a partially water-covered surface, ammonia prefers to bond to the Pt substrate rather than to water, resulting in the formation of largely separate water and ammonia domains on the Pt(111) substrate. We also learned from RAIRS that in addition to solvated NH$_3$, NH$_4^+$ ions are formed as a result of proton transfer from H$_2$O to NH$_3$. Our experiments show that ammonia flags the molecular sites where water molecules can rotate to expose dangling H bonds and which are necessary to initiate bulk ice growth.

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**Notes**

The authors declare no competing financial interest.

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