Water–Solid Interfaces

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Acidic Water Monolayer on Ruthenium(0001)**

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The ubiquity of water in natural environments makes the interaction of water with solid surfaces an important subject of study in a wide variety of scientific disciplines and technologies.[1] One of the most intensively investigated systems for the interaction of water with metal surfaces is water on Ru(0001), which has become a test system for our understanding of this scientific field.[1,2] Numerous experimental[2a–o] and theoretical studies[2h,p–x] conducted during the past decade have greatly improved our understanding of the structure and dynamics of water adsorption on Ru(0001). These studies have reached the consensus[1c] that water adsorption leads to the formation of an intact molecular-water layer on the surface at low temperature (less than about 155 K). As the surface is heated, H_2O partially dissociates to form a mixed $OH + H_2O + H$ adsorption layer, in competition with desorption of H_2O. On the other hand, D_2O does not dissociate on the surface and desorbs intact due to a kinetic isotope effect. Despite the wealth of theoretical and experimental research on this system, there are still many open questions, in particular concerning the acid–base properties of adsorbed water. This information is fundamentally important to heterogeneous catalysis, corrosion, and electrochemistry because it determines the proton transfer and acid–base characteristics of the water–solid interface. Therefore, it is highly desirable to investigate these properties for adsorbed water using a systematic surface science approach; this could be one way to unravel the intricacies of the acid–base chemistry at water–solid interfaces. In the present work, we study the proton-transfer ability of water molecules adsorbed on a Ru(0001) surface by using surface spectroscopic measurements and ammonia adsorption experiments. The study shows that the first monolayer of water is much more acidic than bulk water, with the ability to spontaneously transfer a proton to an ammonia molecule.

We prepared a water layer on Ru(0001) in ultrahigh vacuum (UHV) by the adsorption of H_2O vapor at 140 K to a monolayer saturation coverage, a condition that is known to produce an intact molecular-water layer on the surface.[1c] Then, NH_3 was adsorbed onto the H_2O monolayer surface for a small coverage [0.04 ML; 1 ML = 1.14×10^{15} molecules cm^{-2} corresponding to the monolayer density of water on Ru(0001)]. The NH_3 molecules served as a probe for the surface acidity. Figure 1 shows the results of low-energy sputtering (LES) and reactive-ion scattering (RIS) measurements for the H_2O monolayer before and after the adsorption of NH_3.

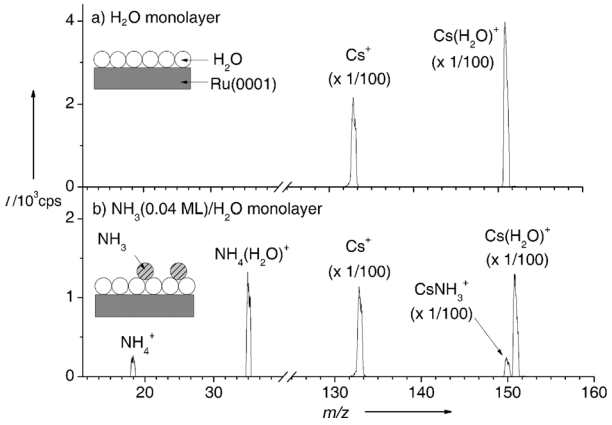

Figure 1. LES and RIS mass spectra of positive ions obtained from a) H_2O monolayer formed on Ru(0001) at 140 K, and b) after NH_3 adsorption (ca. 0.04 ML) on surface at 80 K. The LES and RIS measurements were conducted at 80 K with a Cs^+ beam energy of 25 eV.

The RIS and LES methods measure neutral and ionic species, respectively, on the surface.[3] For a layer of pure H_2O, spectrum a in Figure 1 shows the RIS signal of CsH_2O^+ (m/z = 151 amu/charge), which was produced by the pickup of surface H_2O molecules by scattering Cs^+ projectiles. The peak of elastically scattered Cs^+ ions appeared at $m/z = 133$. After NH_3 adsorption (spectrum b in Figure 1), a $CsNH_3^+$ ($m/z = 150$) signal appeared with a small intensity, indicating the presence of neutral NH_3 adsorbates on the surface. In addition, LES signals appeared for NH_4^+ ($m/z = 18$) and $NH_4(H_2O)^+$ ($m/z = 36$), indicating the presence of NH_4^+ and its hydrated species. These ammonium signals indicated that protons were transferred from the water monolayer to NH_3 adsorbates to form NH_4^+.

In additional experiments, we observed that the ammonium signals exhibited the following features. First, the NH_4^+ and $NH_4(H_2O)^+$ signals did not appear when NH_3 was adsorbed onto a multilayer ice film grown on Ru(0001).[4] This result showed that the first water monolayer was the proton donor to NH_3. Second, in order to check if the ammonium signals originated from preformed ions on the surface, we measured the appearance threshold of the NH_4^+ signal as a function of Cs^+ impact energy for the water monolayer (where the NH_4^+ was formed by proton transfer) and for the multilayer ice film (where only neutral NH_3 was present). The two surfaces showed well-distinguished characteristics for the threshold energy and intensity of NH_4^+ emission. The NH_4^+ signal from the water monolayer exhibited a lower threshold energy (20–25 eV) and stronger intensity than that from the multilayer film, which is characteristic for the low-energy sputtering of preformed NH_4^+ species.[4] On the other hand, on the multilayer ice film,

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an NH_4^+ signal appeared only at a high energy (> 35 eV) and with a very weak intensity, as a result of the secondary ionization of neutral NH_3 adsorbates.[4] These observations further support that NH_4^+ is formed by proton transfer from the water monolayer to NH_3.

The proton transfer was also examined using reflection absorption infrared spectroscopy (RAIRS). The results obtained from an H_2O monolayer on Ru(0001) before and after NH_3 adsorption are compared in the RAIR spectra a and b (Figure 2), respectively. The spectrum from a clean H_2O monolayer shows the IR absorption features characteristic of an intact molecular layer;[2e] these are the bands at

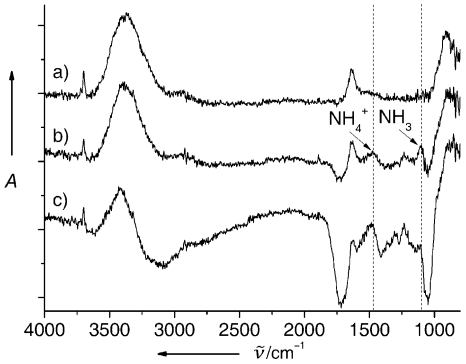

Figure 2. RAIR spectrum of a) H_2O monolayer formed on Ru(0001) at 90 K, and b) after NH_3 adsorption on the H_2O monolayer for coverage of ca. 0.2 ML at 80 K. c) RAIR spectrum obtained after co-deposition of HCl (ca. 0.1 ML) and NH_3 (ca. 0.2 ML) on the H_2O monolayer at 80 K. The amount of NH_3 adsorbate used for the RAIRS experiment was higher than that for the LES and RIS studies, owing to the low sensitivity of RAIRS.

$\approx 900\ cm^{-1}$ (H_2O librational mode), $\approx 1630\ cm^{-1}$ (scissors), $\approx 3390\ cm^{-1}$ (O–H stretch), and $3680\ cm^{-1}$ (dangling O–H stretch). Upon adsorption of NH_3 on the H_2O surface, spectrum b in Figure 2 shows new bands at $\approx 1100\ cm^{-1}$ and $\approx 1470\ cm^{-1}$, corresponding to the ν_2 band of NH_3 on the H_2O surface,[5] and the ν_4 band of NH_4^+,[5,6] respectively. A weaker band at $\approx 1230\ cm^{-1}$ is attributed to NH_3 molecules that are adsorbed on a Ru surface with additional H-bonding to neighboring water molecules.[5] These features indicate the coexistence of NH_3 and NH_4^+ on the surface, in agreement with the LES and RIS results shown in Figure 1. To confirm the assignment of the NH_4^+ vibrational band, we externally provided NH_4^+ to the sample by co-adsorption of NH_3 and HCl on an H_2O monolayer, which generated NH_4^+ through HCl ionization and the subsequent acid–base reaction of H_3O^+ and NH_3.[4,6b] In spectrum c (Figure 2), the externally added NH_4^+ produced an IR band at $\approx 1470\ cm^{-1}$, basically at the same position as that of NH_4^+ produced by proton transfer from H_2O monolayer (see Figure 2b), alongside complex alterations in the spectral region of 1000–1700 cm^{-1} as a result of the interactions of HCl and NH_3 with water.[6b] The NH_4^+ feature at $\approx 1470\ cm^{-1}$ did not appear when NH_3 was adsorbed on a thick (60 ML) ice film, which confirmed the non-occurrence of the proton-transfer reaction on a thick ice film as observed in the LES experiments.

Recent studies involving H_2O adsorption on Ru(0001)[1c,2a–j,o–t,7] have shown that an intact H_2O monolayer (A2 phase) is formed upon adsorption of H_2O to a monolayer saturation at low temperature (less than about 155 K), but that H_2O partially dissociates at higher temperatures to form a mixed OH + H_2O + H adsorption layer (A1 phase). The exact molecular structure and hydrogen-bonding geometry of these phases have not yet been fully resolved.[1c] We examined whether molecular water or its dissociated species are responsible for the observed proton transfer to NH_3. Because the A1 and A2 phases are formed in different temperature regions, we investigated the NH_4^+ signal intensity as a function of the surface temperature by performing temperature-programmed LES (TPLES) experiments. Figure 3 shows the result of the TPLES study for the NH_4^+ signal from an H_2O monolayer with adsorbed NH_3. The temperature-dependent

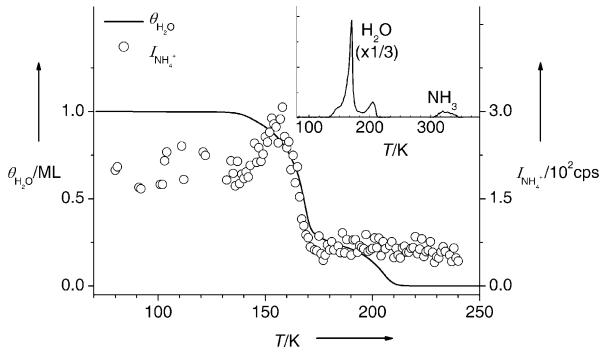

Figure 3. Variation in NH_4^+ signal intensity (I) in TPLES experiment, and H_2O coverage (θ) as functions of temperature. The inset shows TPD measurements of H_2O and NH_3 from the sample. An H_2O monolayer was formed at 140 K, and NH_3 was absorbed for a coverage of 0.04 ML at 70 K. The temperature-ramping rate was 1 $K\,s^{-1}$ in both the TPD and TPLES experiments.

variation in the NH_4^+ signal intensity is shown overlapped with the temperature dependency of the H_2O surface coverage. The latter was obtained by integrating the temperature-programmed desorption (TPD) curve of H_2O (inset in Figure 3), which was measured from a saturated water monolayer with NH_3 adsorbates (ca. 0.04 ML). The intensity profile of the NH_4^+ signal shows that it decreased by about 80 % as the surface temperature was increased across the 155–170 K region. Notably, this decrease in the NH_4^+ signal occurred concurrently with a decrease in the water coverage in this region. It has been reported[2a,b,e–g] that water desorption in this region occurs exclusively from the intact H_2O layer (A2 phase). The correlation between the NH_4^+ intensity and the surface area of the A2 phase provides a clue that the molecular-water species donates a proton to NH_3.

Heating the sample above 170 K removes the A2 phase from the surface and leaves only the A1 phase, or a mixed layer of OH, H_2O, and H species.[2a,b,e–g,l] In this region, the NH_4^+ signal intensity was low, but it maintained a constant level during a TPLES scan until it ended at 240 K. Note that the A1 phase disappeared from the surface at ≈ 210 K. NH_3 adsorbates remained on the surface up to ≈ 350 K as observed

in TPD experiments (see inset in Figure 3). The continual appearance of the low-intensity NH_4^+ signal in the 170–240 K region, unaffected by the removal of the A1 phase from the surface, indicates that the $OH + H_2O + H$ adsorption layer does not contribute to the NH_4^+ signal. We suspect that the NH_4^+ signal at $T > 170$ K was produced by the secondary ionization of neutral NH_3 adsorbates during the Cs^+ impact. At such low water coverage, a large portion of NH_3 molecules were probably attached directly to the metal surface. These NH_3 molecules may diffuse on the surface at high temperature and form self-solvated ammonium clusters, which may increase the yield of secondary NH_4^+ emission. Hydrogen atoms remaining on the surface at up to ≈ 350 K after H_2O dissociation[2b] may also contribute to the secondary NH_4^+ emission. Atomic hydrogen impurities were absent from the original Ru surface, which was cleaned by heating at 1500 K. The self-solvation of NH_3 was very unlikely to occur on the A2 monolayer surface at low temperature. Therefore, we can exclude the possibility of secondary NH_4^+ emission associated with these phenomena on the A2 surface at $T < 155$ K.

Additional experiments were performed to better understand the proton-transfer reaction from H_2O to NH_3. First, we examined how the surface coverage of H_2O influenced the proton transfer. We covered a Ru(0001) substrate with different amounts of H_2O at 80 K, and then adsorbed a fixed amount (0.04 ML) of NH_3 onto it. The NH_4^+ signal from the surface was measured by LES as a function of the water coverage. According to previous discoveries,[2h,m] water grows initially in form of isolated small clusters on Ru(0001) at this temperature, and an increase in water exposure increases the density of clusters rather than their size.[2m] The aggregation of water clusters into extended, ordered hydrogen-bonded islands occurs only at substantially high coverage.[2h,m] We observed that an NH_4^+ signal appeared with appreciable intensity from the surface with adsorbed NH_3 and H_2O only when the H_2O coverage exceeded approximately 0.3 ML. The NH_4^+ signal intensity increased with increasing water coverage up to a monolayer, but then decreased upon the formation of a multilayer. These observations agree with the interpretation that the first water monolayer is the proton donor. Furthermore, they indicate that the formation of water monolayer domains with a continuous H-bonded structure is important for the proton transfer, because the NH_4^+ signal appeared only above a certain threshold of water coverage. On the other hand, the proton transfer was inefficient when only small water clusters existed on the surface without forming an extended structure, nor on the partially dissociated A1 surface on which water and hydroxy species formed clusters with varying H_2O:OH ratios.[2a,b,e–g,l] In the LES spectrum (Figure 1), the $NH_4(H_2O)^+$ signal appeared stronger than the NH_4^+ signal. The strong signal of hydrated ammonium hints that the proton transfer is mediated by H-bonded water molecules that bridge the proton donor and acceptor separated from each other (Grotthuss mechanism).[8]

To estimate the acid strength of the water molecules, we titrated an H_2O monolayer (A2 phase) with increasing amounts of NH_3, and monitored the resulting change in the NH_4^+ signal intensity in LES measurements. This study showed that NH_4^+ population increased with increasing NH_3 coverage, and that $\theta(NH_4^+) \approx \theta(NH_3)$ was reached at $\theta(NH_3) \approx 0.02$ ML. That is, approximately half of the NH_3 adsorbates were converted to NH_4^+ at this coverage. For comparison, the protonation equilibrium constant of ammonia in liquid water at room temperature is only 1.8×10^{-5}. A coverage of 0.04 ML NH_3 on water monolayer is numerically equivalent to a bulk concentration of approximately 2 M NH_3 in aqueous solution, and this solution would contain a ratio of NH_4^+:NH_3 in the order of 3×10^{-3}:1. Obviously, the 1:1 ratio on the water monolayer is very high, which indicates that the monolayer has unusually strong acidity compared to bulk water. It is questionable, however, whether such high acidity implies that the water molecules in the monolayer are actually self-ionized to the hydronium and hydroxide states to a large extent. Our LES and RAIRS measurements did not detect a H_3O^+ signal in the H_2O monolayer, opposing the idea of extensive ionization of monolayer water in the absence of ammonia adsorbates.

Although the experimental observations described above provide clear evidence that the water monolayer has increased acidity, it will require further research to fully understand the mechanism of the proton transfer that is at work. From the limited clues available at present, it can be imagined that an NH_3 adsorbate extracts a proton from a water molecular assembly with an extended H-bond network, leading to a state such as $OH^-(H_2O)_nNH_4^+$. The kinetic barrier of this proton transfer is expected to be lower than that of H–OH dissociation on a Ru surface, owing to the tunneling nature of the former. Indeed, the proton transfer was observed to be facile, even at low temperature (less than about 155 K; Figure 3), at which water dissociation was prohibited. The proton transfer can be driven by the proton affinity of NH_3 as well as the stabilization energies of OH^- and NH_4^+ in the molecular system. For a small water cluster in gas phase, a similar proton-transfer reaction may be thermodynamically uphill and thus not possible. In the present system, however, the extended H-bonding network in the water monolayer and the bonding with a metal surface may provide the extra stabilization to make up the energy deficit.

In summary, this study demonstrated that the acidity of adsorbed water can be studied using the adsorption of probe molecules and spectroscopic measurements in UHV conditions. The first monolayer of water on Ru(0001) is anomalously acidic. The evidence for this statement includes the formation of NH_4^+ by the proton transfer from water to adsorbed NH_3, which was detected by LES and RAIRS. TPLES and TPD experiments showed that protons are released from the water molecules in an intact H_2O monolayer, rather than from the OH, H_2O, and H species in a mixed monolayer. This finding is somewhat surprising because it contrasts with the preconception in water surface chemistry that the surface-catalyzed dissociation of water into H and OH may lead to a pathway for hydronium and hydroxide formation. Further, our result suggests that the acidity of water is increased by the formation of an extended H-bond network in the water monolayer. The effect of a metal substrate on the electronic structure of adsorbed water[1a] may also be important, but this effect alone cannot account for the unique increase in the acidity of an intact water monolayer,

which does not occur for a mixed H_2O–OH layer or small water clusters. In future studies, it will be interesting to investigate whether similar effects appear on other metal surfaces. Interestingly, studies of the work function for thick ice films growing on Pt(111) have shown that the growing ice surface is positively charged, suggesting a substantial degree of water ionization at the ice/Pt interface buried under the ice film.[9] We anticipate that diverse probe molecules and spectroscopic methods will to be used to explore the acid–base properties of water monolayer in further detail, as well as theoretical investigation of the proton-transfer mechanism in the monolayer. Such studies would advance the understanding of the chemical properties of water layers beyond the limits of traditional study of water-adsorption structure.

Experimental Section

The experiment was carried out in a UHV surface analysis chamber[3a] equipped with instrumentation for LES, RIS, RAIRS, and TPD. H_2O was adsorbed on a Ru(0001) crystal maintained at a specified temperature between 60–150 K by back-filling the UHV chamber with H_2O vapor at a partial pressure of around 1×10^{-8} Torr. NH_3 and HCl vapors were introduced into the chamber using separate leak valves and guided close to the sample surface through tube dosers. The coverage of H_2O, NH_3, and HCl on the sample surface was estimated using TPD measurements.

The chemical species present on the surface were analyzed using RIS, LES, and RAIRS. In RIS and LES, a Cs^+ beam from a low-energy ion gun (Kimball Physics) collided with the sample surface, typically at an incident energy of 25 eV, unless mentioned otherwise, and the ions emitted from the surface were detected by a quadrupole mass spectrometer (Extrel) with its ionizer filament switched off. In RIS, the *neutral* species (X) on the surface are picked up by scattering Cs^+ projectiles to form Cs^+-neutral clusters (CsX^+). In LES, preformed ionic species (Y^+) on the surface are ejected upon Cs^+ impact. Thus, the RIS and LES signals revealed the identities of the neutral (X) and ionic species (Y^+) on the surface, respectively. The mechanisms of the RIS and LES processes on surfaces have been explained previously.[3] The incident flux of a Cs^+ beam was kept low ($\approx1\times10^{11}$ ions cm^{-2} s^{-1}) so as to minimize the surface contamination by the Cs^+ beam. Whenever necessary, fresh samples were prepared for the kinetic measurements to reduce the accumulated Cs^+ beam dosage. The RAIRS experiment was performed with a typical geometry used for in situ surface analysis,[2c,10] viz., a grazing reflection angle of 84°, a resolution of 4 cm^{-1}, and unpolarized light from a commercial Fourier-transform infrared spectrometer (PerkinElmer Spectrum 100).

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