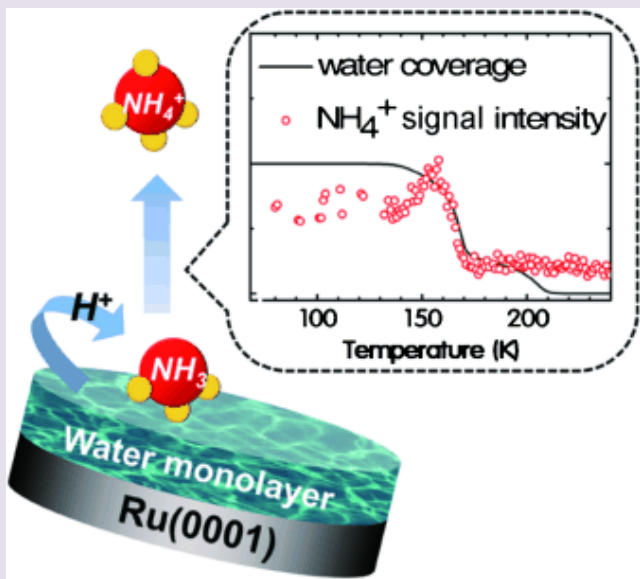


# Acidic Water Monolayer on Ruthenium(0001)

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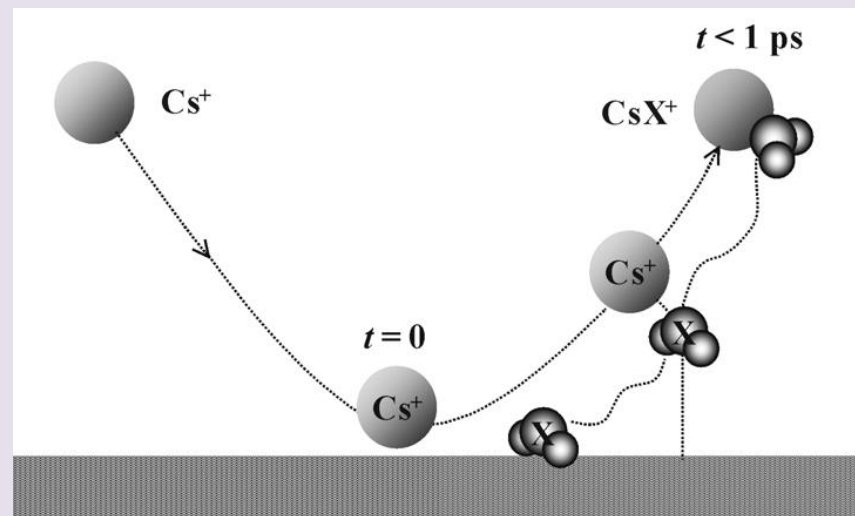
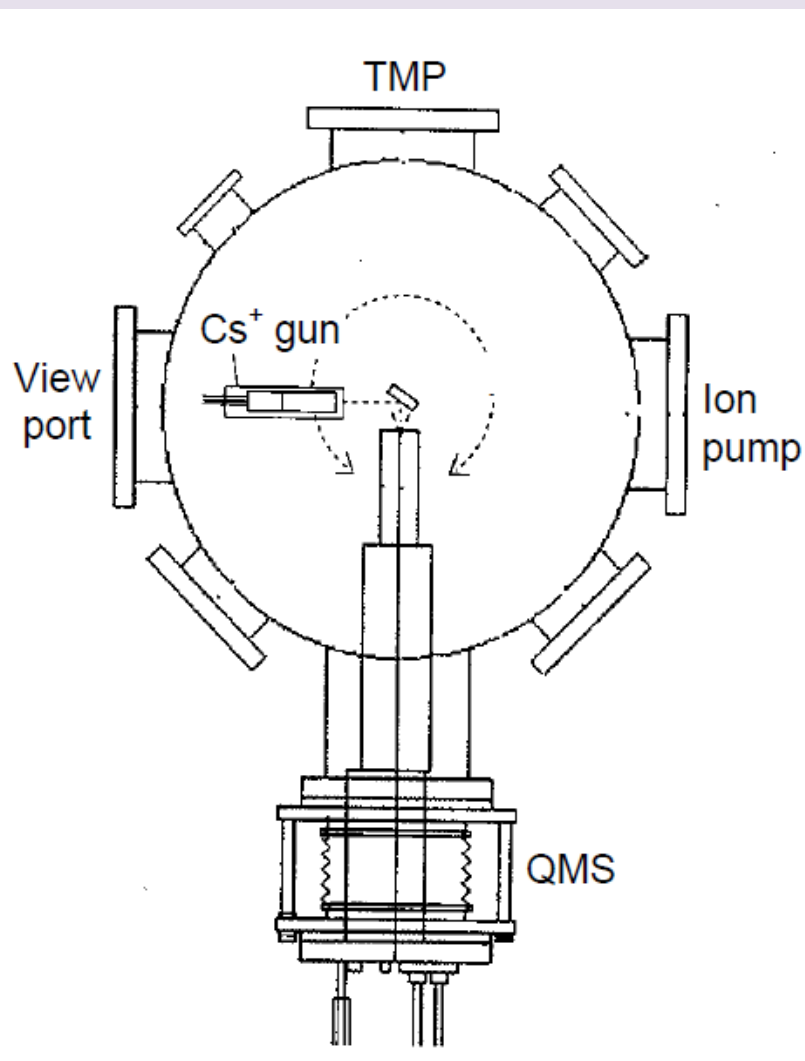
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# Introduction

- The omnipresence of water in natural environment makes the interaction of **water with solid surfaces** as an important field of study.
- One of the **most intensively investigated systems** for the interaction of water with metal surfaces is **water on Ru(0001)** and has become a test system for our understanding of this scientific field.
- Different studies have shown that water adsorption on Ru(0001) leads to the **formation of an intact molecular water layer** on the surface at low temperature ( $< 155$  K) and as the surface is heated,  $\text{H}_2\text{O}$  partially **dissociates to form a mixed  $\text{OH}+\text{H}_2\text{O}+\text{H}$**  adsorption layer, in competition with desorption of  $\text{H}_2\text{O}$ .

- On the other hand,  $D_2O$  does not dissociate on the surface and desorbs intact due to a kinetic isotope effect.
- But there are still many open questions, in particular concerning the acid–base properties of adsorbed water as this information is fundamentally important to heterogeneous catalysis, corrosion, and electrochemistry as it determines the proton transfer and acid–base characteristics of the water–solid interface.
- In the present work, they studied 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.

# Experimental Section

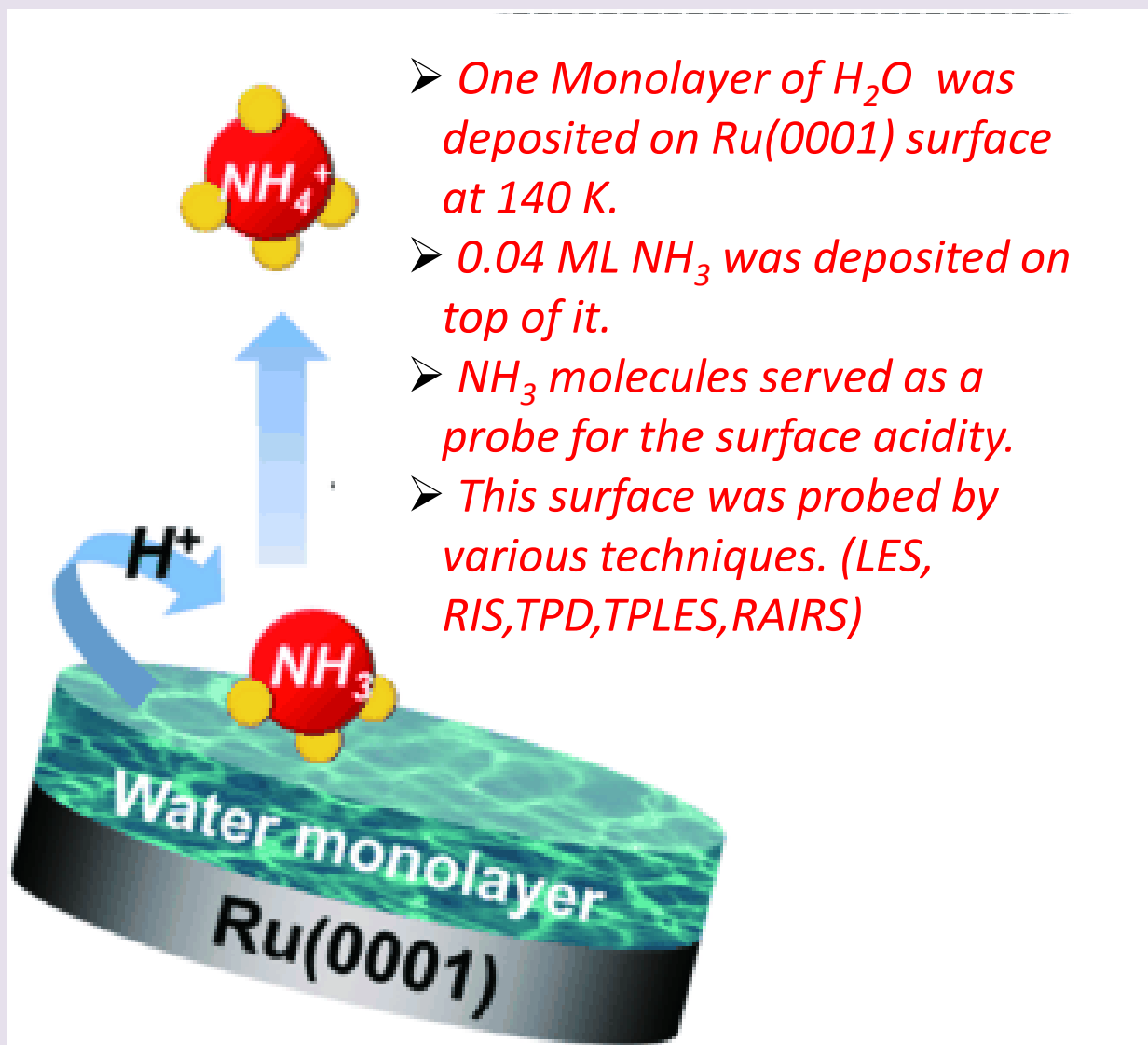


H. Kang, Bull. Korean Chem. Soc. 2011, 32, 389–398.

H. Kang, Acc. Chem. Res. 2005, 38, 893–900.

**Low energy sputtering (LES)**- ionic species detection.  
**Reactive-ion scattering (RIS)**- neutral species detection.  
**Temperature programmed LES (TPLES)**  
**Temperature programmed desorption (TPD)**  
**Reflection Absorption IR Spectroscopy (RAIRS)**

# Results and Discussion



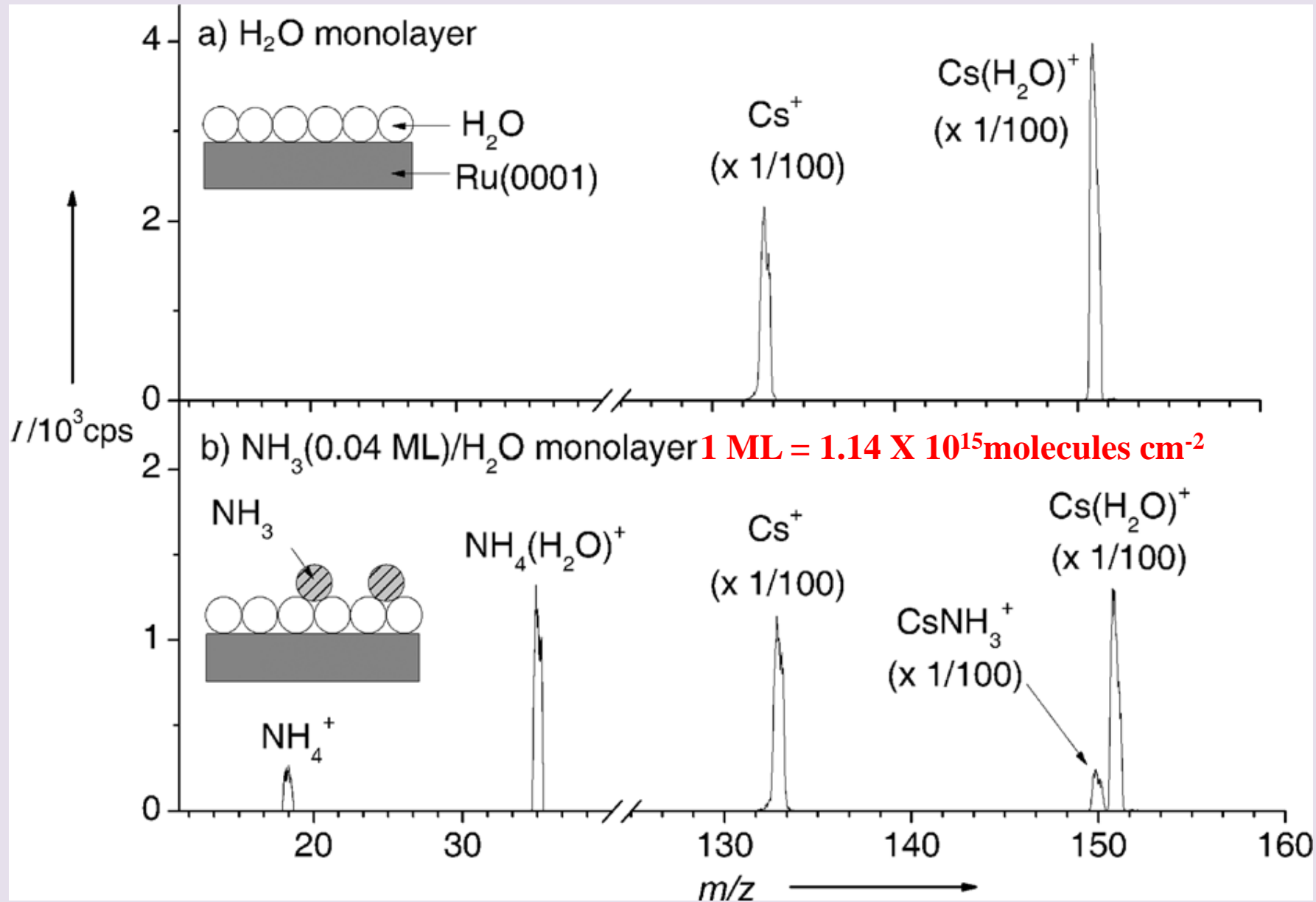
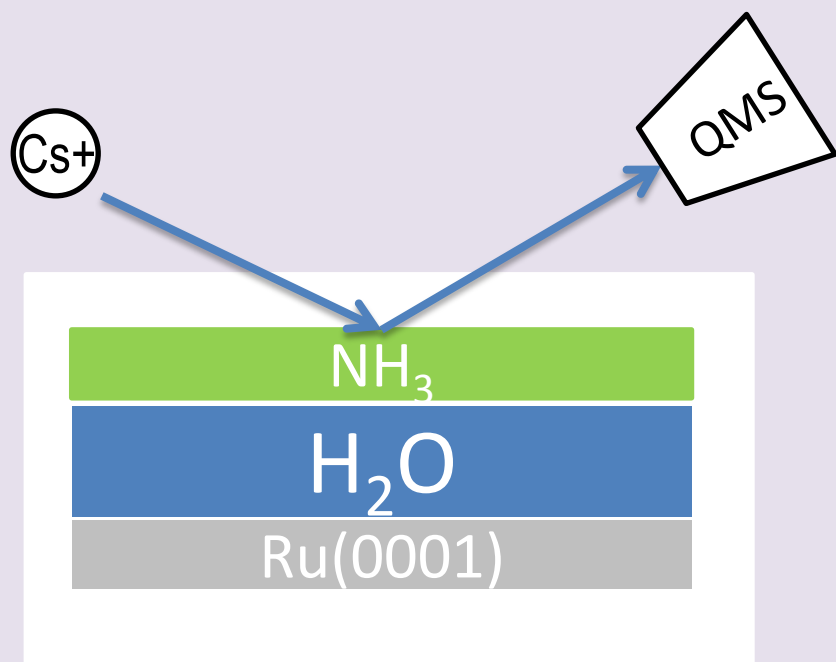


Figure 1. LES and RIS mass spectra of positive ions obtained from a) H<sub>2</sub>O monolayer formed on Ru(0001) at 140 K, and b) after NH<sub>3</sub> adsorption (0.04 ML) on surface at 80 K. The LES and RIS measurements were conducted at 80 K with a Cs<sup>+</sup> beam energy of 25 eV.



- ✓ NH<sub>4</sub><sup>+</sup> and NH<sub>4</sub>(H<sub>2</sub>O)<sup>+</sup> signals **did not appear** when NH<sub>3</sub> was adsorbed onto a **multilayer ice film** grown on Ru(0001).
- ✓ The NH<sub>4</sub><sup>+</sup> 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<sub>4</sub><sup>+</sup> species.

- ✓ For **multilayer ice** film, NH<sub>4</sub><sup>+</sup> 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<sub>3</sub> adsorbates.

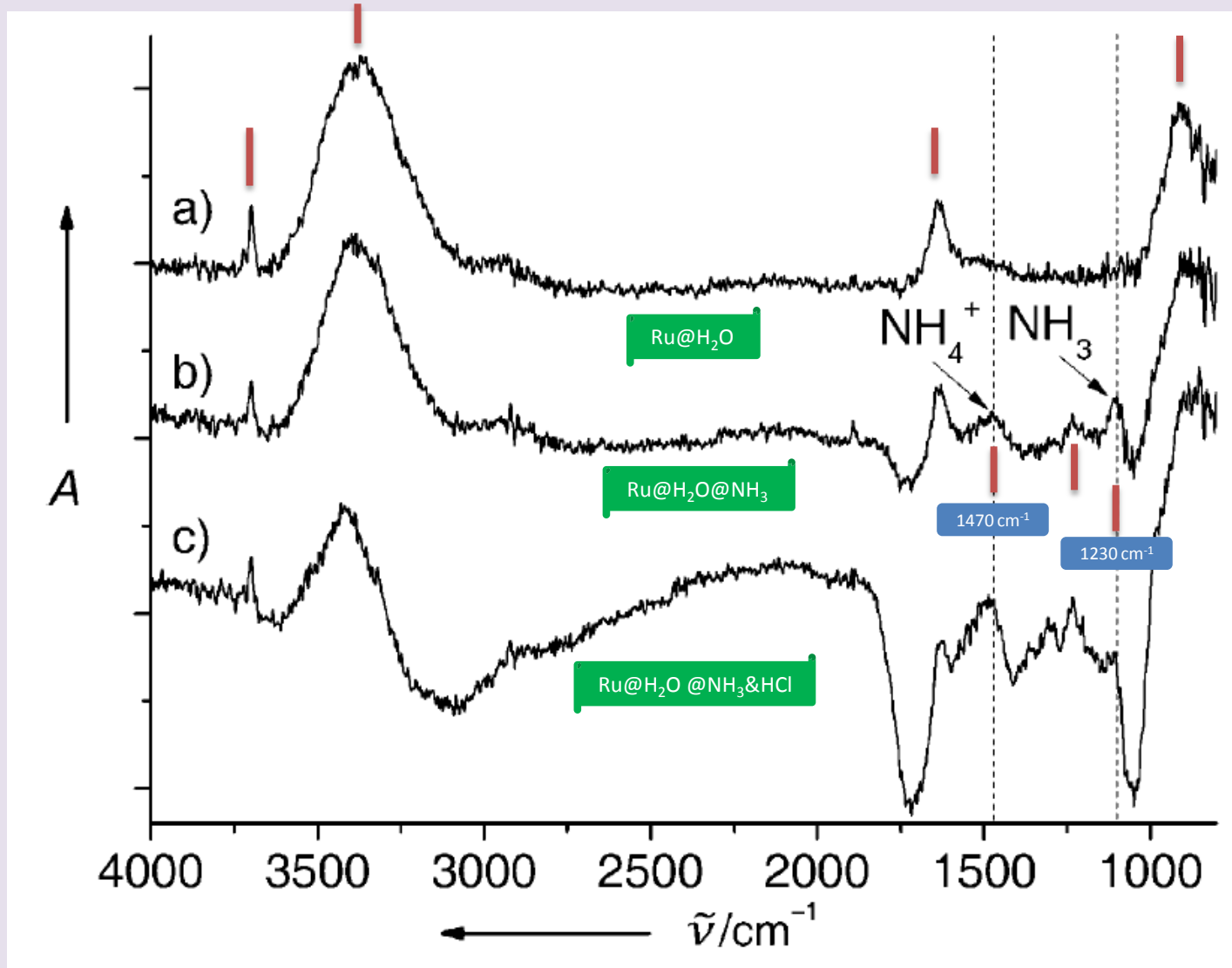


Figure 2. RAIR spectrum of a)  $\text{H}_2\text{O}$  monolayer formed on Ru(0001) at 90 K, and b) after  $\text{NH}_3$  adsorption on the  $\text{H}_2\text{O}$  monolayer for coverage of ca. 0.2 ML at 80 K. c) RAIR spectrum obtained after co-deposition of HCl (ca. 0.1 ML) and  $\text{NH}_3$  (ca. 0.2 ML) on the  $\text{H}_2\text{O}$  monolayer at 80 K. The amount of  $\text{NH}_3$  adsorbate used for the RAIRS experiment was higher than that for the LES and RIS studies, owing to the low sensitivity of RAIRS.



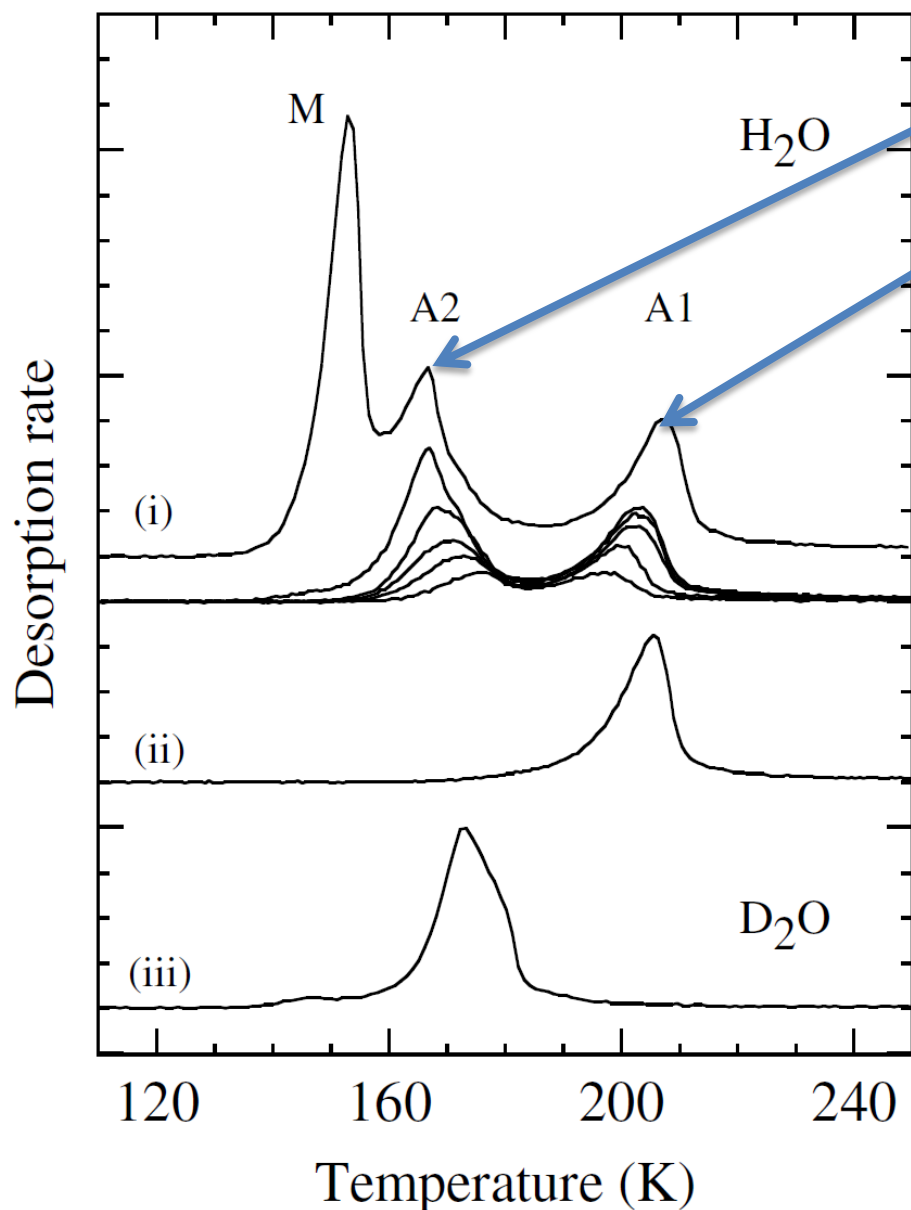


Figure 3. Thermal desorption of water from Ru(0001) taken at a heating rate of 1 K/s. H<sub>2</sub>O desorption following: (i) dosing at 138 K (1.65 ML, top trace) and at 145 K (coverages up to 0.75 ML, lower traces); (ii) H<sub>2</sub>O adsorbed at 166 K; (iii) desorption of 0.75 ML D<sub>2</sub>O dosed at 145 K.

**C. Clay et.al. Chem. Phys. Lett. 2004, 388, 89–93.**

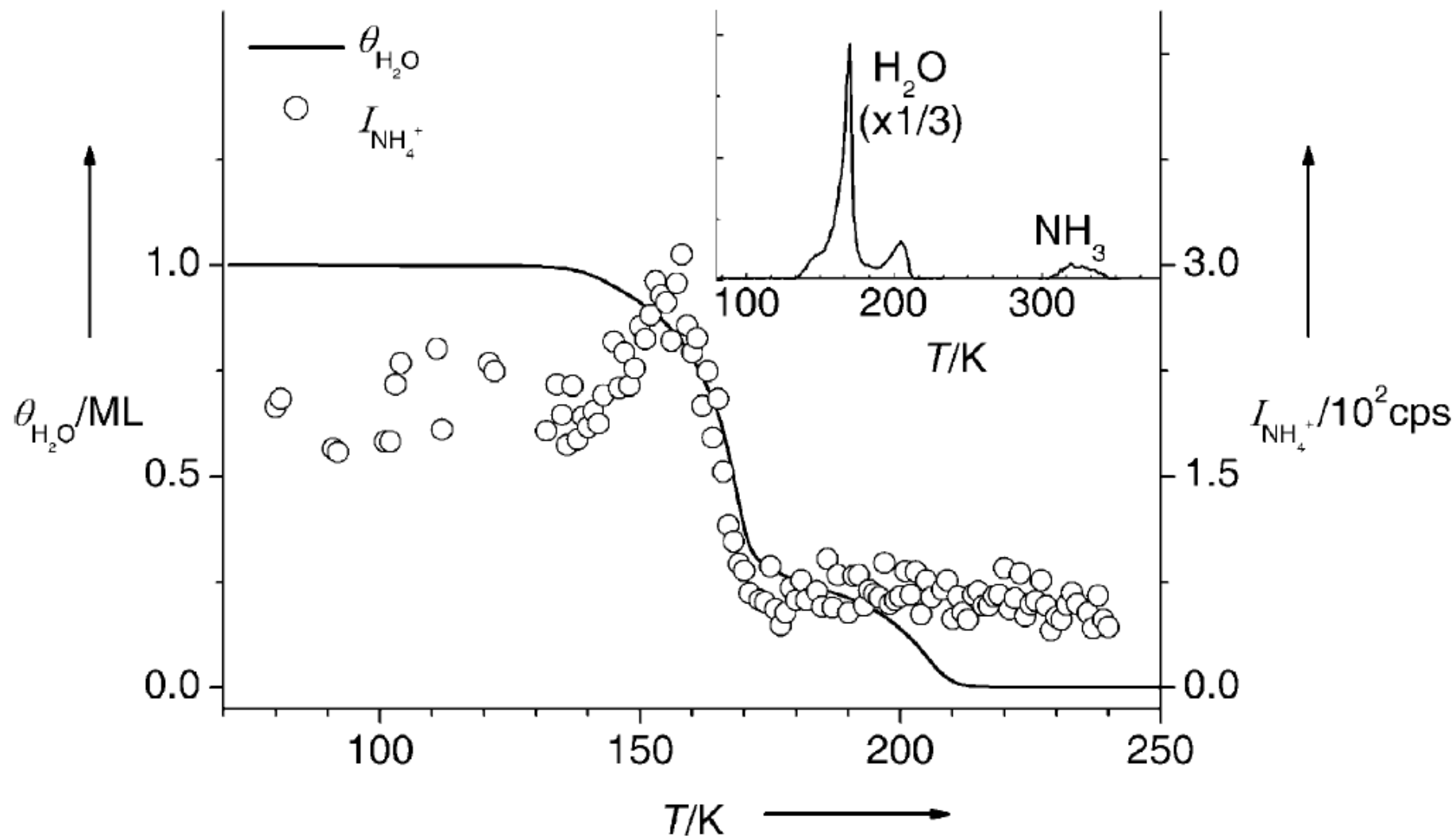
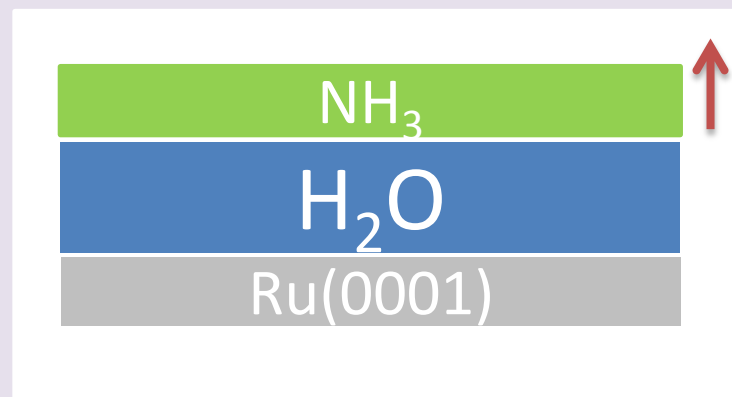
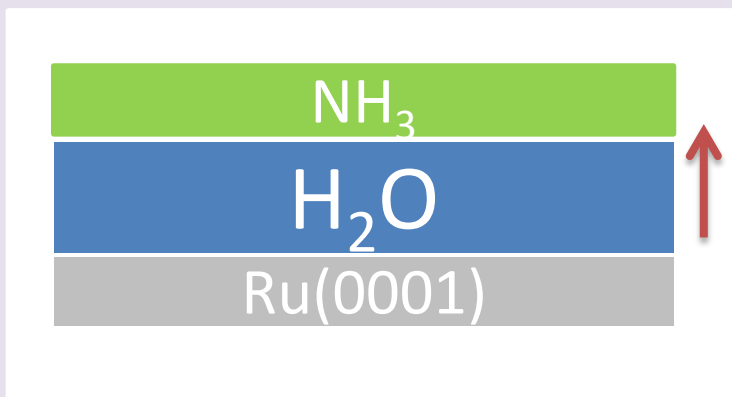


Figure 3. Variation in  $\text{NH}_4^+$  signal intensity ( $I$ ) in TPLES experiment, and  $\text{H}_2\text{O}$  coverage ( $\theta$ ) as functions of temperature. The inset shows TPD measurements of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  from the sample. An  $\text{H}_2\text{O}$  monolayer was formed at 140 K, and  $\text{NH}_3$  was absorbed for a coverage of 0.04 ML at 70 K. The temperature-ramping rate was  $1 \text{ K s}^{-1}$  in both the TPD and TPLES experiments.



✓  $\text{NH}_4^+$  signal appeared with appreciable intensity from the surface with adsorbed  $\text{NH}_3$  and  $\text{H}_2\text{O}$  only when the  $\text{H}_2\text{O}$  coverage exceeded approximately **0.3 ML**.

✓ The  $\text{NH}_4^+$  signal intensity increased with increasing water coverage up to a monolayer, but then decreased upon the formation of a multilayer.

✓ This shows that water monolayer with a continuous **Hydrogen bonded structure is important** for the proton transfer to occur, as the  $\text{NH}_4^+$  signal appeared only above a certain threshold of water coverage.

✓ This study showed that  $\text{NH}_4^+$  population increased **with increasing  $\text{NH}_3$  coverage**, and that  **$\theta(\text{NH}_4^+) = \theta(\text{NH}_3)$  was reached at  $\theta(\text{NH}_3) = 0.02 \text{ ML}$** . That is, approximately half of the  $\text{NH}_3$  adsorbates were converted to  $\text{NH}_4^+$  at this coverage.

✓ For comparison, the protonation equilibrium constant of ammonia in liquid water at room temperature is only  $1.8 \times 10^{-5}$ . A coverage of  $0.04 \text{ ML}$   $\text{NH}_3$  on water monolayer is numerically equivalent to a bulk concentration of approximately  $2 \text{ M}$   $\text{NH}_3$  in aqueous solution, and this solution would contain a ratio of  $\text{NH}_4^+:\text{NH}_3$  in the order of  $3 \times 10^3:1$ . and here it is  $1:1$  ratio is found.

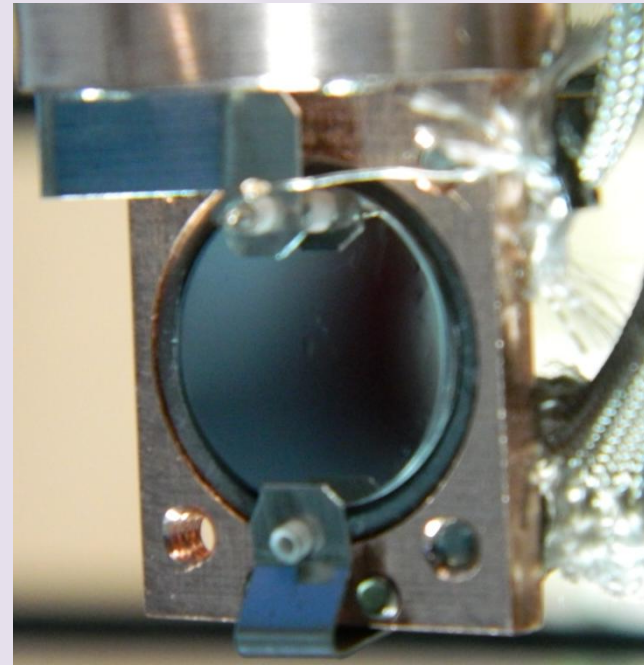
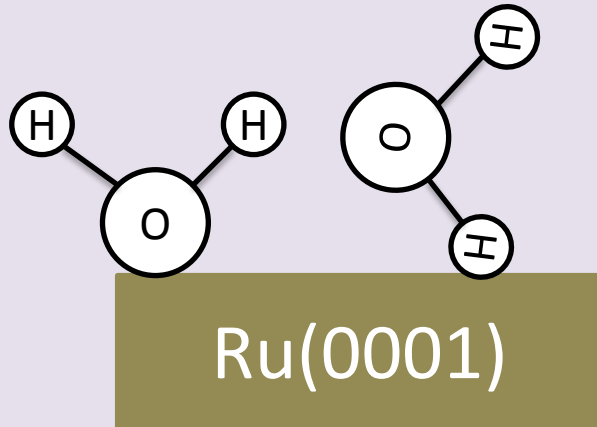
**So the water monolayer has unusually strong acidity compared to bulk water.**

## Conclusions

- 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  $\text{NH}_4^+$  by the proton transfer from water to adsorbed  $\text{NH}_3$ , which was detected by LES and RAIRS.
- TPLES and TPD experiments showed that protons are released from the water molecules in an intact  $\text{H}_2\text{O}$  monolayer, rather than from the  $\text{OH}$ ,  $\text{H}_2\text{O}$ , and  $\text{H}$  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.
- This result also 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 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<sub>2</sub>O-OH layer or small water clusters.

## *Future perspective*



- ❖ **Reactive ion collision** on a single monolayer of ice → **H abstraction** may be easy.
- ❖ H abstraction followed by **diffusion** can be tried and if this is possible we can make **surface acidic**.

*Thank you all...*

The text "Thank you all..." is written in a vibrant red, three-dimensional cursive font. Each letter has a slight shadow, giving it a 3D appearance. Below the text, there is a simple, thick red arc that starts under the 'T' and ends under the 'l'.