

Equilibrium determination of H₂O desorption kinetic parameters of H₂O/K/Ni(111)

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Equilibrium measurements in a dynamic equilibrium of adsorption and desorption were performed to obtain coverage-dependent kinetic parameters of water desorption from K/Ni(111) with K coverages in the submonolayer regime. A H₂O particle beam was employed which enabled beam fluxes up to $8 \times 10^{19} \text{ m}^{-2} \text{ s}^{-1}$ while the water equilibrium coverage in the temperature range from 155 to 175 K was determined using x-ray photoelectron spectroscopy (XPS). On the clean sample water desorbs with two different sets of desorption kinetic parameters, for water coverages below 0.42 monolayers (ML) a desorption energy of $(52 \pm 3) \text{ kJ/mol}$ and a pre-exponential factor of $10^{16 \pm 1} \text{ s}^{-1}$ were found, whereas for higher coverages values of $E_{\gamma} = (38.6 \pm 0.3) \text{ kJ/mol}$ and $\nu_{\gamma} = 8 \times 10^{12 \pm 0.1} \text{ s}^{-1}$, characteristic for desorption from ice multilayers, were determined. The effect of preadsorbed K manifested itself in a dissociation of one H₂O molecule per K atom to OH and H and in the presence of a more strongly bound molecular water species. No K induced changes of the desorption kinetics of the further adsorbed water could be observed for $\Theta_{\text{K}} \leq 0.15 \text{ ML}$, and the water coverage of 0.42 monolayers, at which the icelike state is initially observed, also remains unchanged. This implies that the structure of the first layer of adsorbed water is similar for potassium precoverages lower than 0.15 ML.

INTRODUCTION

The coadsorption of water with alkali metals on single crystal surfaces as a model system for the investigation of elementary reaction steps of electrochemical processes at a metal–electrolyte interface has received considerable interest during the last decade and is still the subject of many studies.^{1–8} Due to the difficulties of *in situ* investigation only few data are available to the electrochemists. Useful information for the exploration of the relevant processes can be the kinetic parameters of water adsorption on alkali-precovered metal surfaces. In spite of the great number of publications on water adsorption studies, only little reliable and coverage dependent kinetic data are recently available. This fact may be due to the difficulties in the evaluation of kinetic data from temperature programmed desorption (TPD) spectra,⁹ one of the most frequently employed techniques for the determination of desorption kinetics.

In this paper we present equilibrium measurements of the kinetic parameters of water desorption from pure and potassium-precovered Ni(111) surfaces. Since all available evidence indicates that the adsorption of water on metal surfaces is not activated, the sticking coefficient can be assumed to be unity. This is in agreement with our own adsorption experiments on Ni(111) at temperatures at which desorption is negligible. Determining thus the coverage which adjusts itself in a dynamic equilibrium of adsorption and desorption at various temperatures, one obtains from an Arrhenius plot directly the coverage-dependent kinetic parameters, desorption energy and pre-exponential factor.

In the following section a water particle beam device

will be presented, which allows water partial pressures at the sample surface up to $2 \times 10^{-3} \text{ Pa}$ while an x-ray photoelectron spectroscopy (XPS) acquisition is running. Using that device it is possible to perform equilibrium measurements of water adsorption in the temperature range of 155–175 K. In Sec. II results of the equilibrium measurements are presented, together with results from XPS and TPD investigations. Section III will then be dedicated to the interpretation and discussion of the results; a short summary will be given in the last paragraph.

EXPERIMENT

Experiments were carried out in a standard ultrahigh vacuum (UHV) chamber equipped with a spherical electron analyzer (Kratos, $r = 127 \text{ mm}$), an x-ray source with Mg and Al anodes, a low-energy electron diffraction (LEED) system and devices for standard sample preparation. The analyzer acceptance area on the sample was set to approximately $3 \times 4 \text{ mm}^2$ by means of electrostatic lenses in the entrance path of the analyzer. The pass energy was set to 80 eV, thus resulting in an overall resolution of 1.4 eV, including the linewidth of the exciting Al-K _{α} radiation.

The sample (diameter 12 mm) was prepared using standard techniques, and the quality of the surface was checked routinely by XPS and LEED.

Potassium was evaporated from a commercial SAES-Getters filament, which was carefully degassed prior to operation. No contamination could be detected on the sample. The potassium layers were prepared by evaporating higher coverages at $T = 180 \text{ K}$ and subsequent heating to certain temperatures at which the desired coverages were obtained.

Figure 1 shows the water particle beam device used for dosing water onto the sample surface. It consists of a differentially pumped doser system, whose outer tube is pumped

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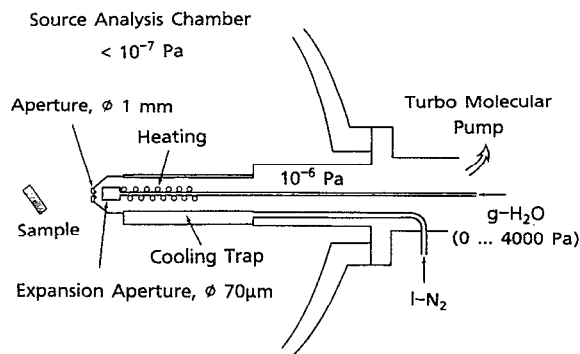


FIG. 1. Schematic drawing of the water particle beam device used for the equilibrium measurements.

by a turbomolecular pump in connection with a concentrically arranged cooling trap for liquid nitrogen operation, achieving very efficient pumping of water. Ultrapure water was used, which was further purified by cycles of freezing, pumping, and thawing. Water vapor in the pressure range of 0–4000 Pa is expanded through an aperture of 70 μm diam at the end of the inner tube. This aperture was heated to 380 K during the measurements with a tantalum filament to prevent the formation of ice at the aperture. The part of the beam not directed onto the sample is cut off by a second aperture of 1 mm diameter positioned at a distance of 20 mm from the sample. The incident angle of the water beam on the surface was 55° to the surface normal; the distance between the two apertures and the distance to the sample are adjustable and were set to give a covered area on the sample of approximately $6 \times 5 \text{ mm}^2$. Within the area analyzed, the coverage does not vary more than 10%. A water partial pressure up to 2×10^{-3} Pa at the sample surface is obtained in that configuration while the overall pressure in the analysis chamber does not exceed 10^{-7} Pa. Between two successive operations of the water beam device, the pressure was always below 2×10^{-8} Pa.

Absolute coverage determination was performed using the O 1s and K 2p peak areas calibrated with respect to the LEED O- $p(2 \times 2)$ and K- $p(2 \times 2)$ structures, respectively. Coverages are given normalized to the surface atom number. For the equilibrium measurements the analyzer was fixed to a binding energy of 533.2 eV, and the count rate at that energy for different water coverages calibrated vs the O 1s peak area.

The H₂O beam intensity was calibrated with respect to the water pressure before expansion by time dependent water uptake curves at 100 K sample temperature, assuming a constant sticking coefficient of $S = 1$. In the given configuration the intensity-pressure ratio was found to be $(1.11 \pm 0.05) \times 10^{-3} \text{ ML}/(\text{s Pa})$ for the Ni(111) surface.

The sample temperature was measured with a Ni/NiCr thermocouple and could be kept constant within 0.25 K during the measurements.

Equilibrium curves of the water coverage versus the incident water beam intensity were taken at various temperatures in the range of 155–175 K, stopping the water beam

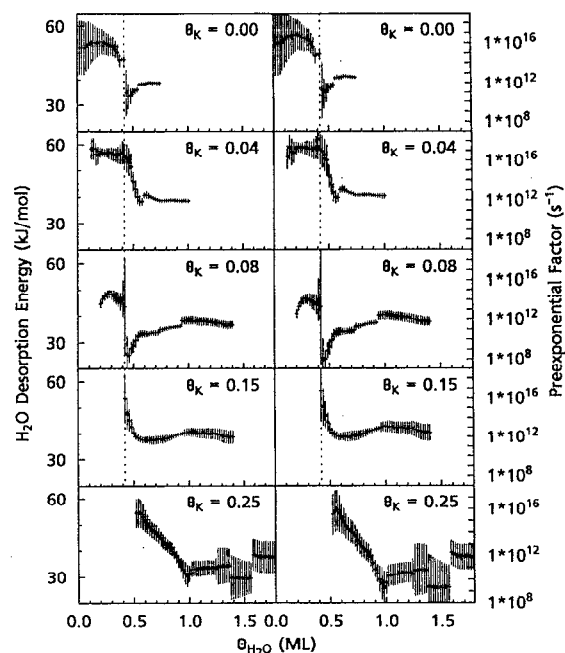


FIG. 2. Apparent H₂O desorption kinetic parameters depending on water coverage for clean and potassium precovered Ni(111) surfaces with potassium coverages of 0.04, 0.08, 0.15, and 0.25, obtained from equilibrium measurements. Left, desorption energy; right, pre-exponential factor.

flux after the acquisition of each single data point and allowing the adsorbed water to desorb. The equilibrium water coverage $\Theta_{\text{H}_2\text{O}}$ which adjusts itself at a given water flux j onto the sample is then depicted over j , thus determining the desorption rate k_{des} via $k_{\text{des}} = j \cdot S$ for each water coverage. The time needed for the uptake of the equilibrium curve at one temperature did not exceed a quarter of an hour, with total water doses at the sample surface between 300 and 1300 L, depending on temperature, where $1 \text{ L} = 10^{-4} \text{ Pa s}$.

RESULTS

Results from equilibrium measurements are shown in Fig. 2 for water desorption from pure Ni(111) and for four different potassium precoverages. On the left and right-hand side of the figure the apparent desorption energy $E(\Theta)$ and the apparent pre-exponential factor $\nu(\Theta)$ are depicted over the water coverage, respectively. These curves were obtained from the measured equilibrium curves under the assumption of an Arrhenius expression for the desorption rate and a first order desorption, $k_{\text{des}} = \Theta \cdot \nu(\Theta) \cdot \exp[-E(\Theta)/kT]$. To illustrate this procedure, in Fig. 3 are some sample Arrhenius plots reproduced for the clean surface with $\Theta_{\text{H}_2\text{O}} = 0.1, 0.3, 0.4,$ and 0.6 ML . On the clean sample two adsorption states with different desorption parameters can be seen: the first at water coverages below 0.42 ML, exhibiting a desorption energy of $(52 \pm 3) \text{ kJ/mol}$ and a pre-exponential factor of $10^{16 \pm 1} \text{ s}^{-1}$, and the second at higher water coverages with values of $(38.6 \pm 0.3) \text{ kJ/mol}$ and $8 \times 10^{12 \pm 0.1} \text{ s}^{-1}$, the latter characteristic for desorption from an icelike state. The values of the

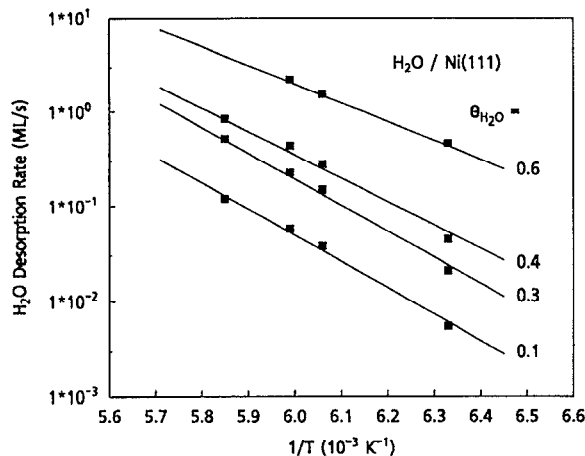


FIG. 3. Arrhenius plot of the H₂O desorption rate derived from equilibrium measurements at temperatures between 158 and 171 K on the clean Ni(111) surface.

apparent kinetic parameters of both states are independent of the water coverage within the experimental error.

Predosing potassium, a certain amount of water, which is adsorbed first, is bound more strongly and does not desorb fast enough to be accessible to the performed equilibrium measurements. This amount is indicated by the onset of the kinetic parameter curves of Fig. 2 at nonzero water coverages. For potassium coverages up to 0.15 ML two water adsorption states can be seen with kinetic parameters similar to the ones observed on the clean sample. The water coverage at which in each case the desorption from the icelike state starts, 0.42 ML, is the same for the clean sample and for the potassium coverages ≤ 0.15 ML, indicated by the dotted line in Fig. 2.

At $\Theta_{\text{K}}=0.25$ the curves of the kinetic parameters start at a water coverage of 0.5 ML with values of (55 ± 6) kJ/mol and $5 \times 10^{15 \pm 1.5}$ s⁻¹ for the desorption energy and the pre-exponential factor, respectively. Increasing the water coverage, these values decrease continuously down to $\Theta_{\text{H}_2\text{O}} = 1.0$ ML, where they reach the values of ice multilayers. The curves of the desorption energy vs $\Theta_{\text{H}_2\text{O}}$ on the left-hand side in Fig. 2 have a shape similar to that of the logarithmic preexponential factor vs $\Theta_{\text{H}_2\text{O}}$ on the right-hand side.

Information about the more strongly bound water can be extracted from XPS and TPD measurements. O 1s spectra for a water coverage of 0.3 ML at 120 K are shown in Fig. 4 for the clean Ni(111) surface and for potassium precoverages of 0.13 and 0.25 ML. Without preadsorbed potassium only one peak at a binding energy of 533.2 eV is observed. With increasing potassium precoverage, initial water adsorption leads to a peak at 531.0 eV binding energy, which saturates at a coverage approximately equal to the potassium coverage. This peak, in Fig. 4 denoted by α , is attributed to an adsorbed OH species, in agreement with other publications.¹⁰⁻¹³ Further adsorption of water leads to the same peak at 533.2 eV binding energy as on the clean Ni(111) surface, which is assigned to molecularly adsorbed water. Preadsorption of potassium thus leads to the dissociation of

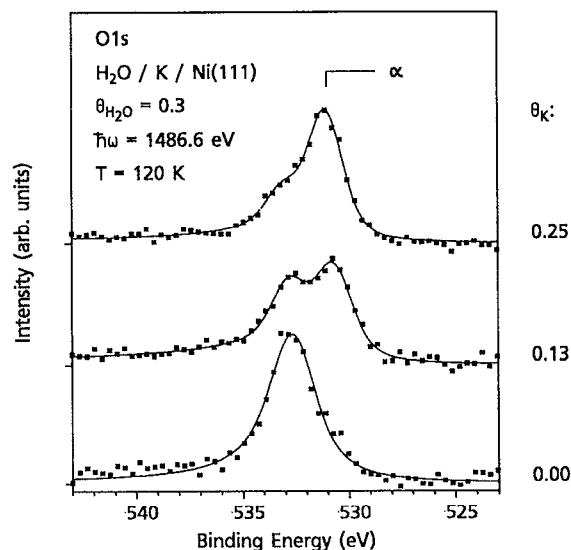


FIG. 4. O 1s spectra of 0.3 ML water adsorbed at 120 K on a clean (bottom curve) and on potassium precovered Ni(111) surfaces with potassium coverages of 0.13 (middle curve) and 0.25 (upper curve). The index α corresponds to the nomenclature used in the text and labels dissociatively adsorbed water; the continuous lines are a guide to the eye.

one H₂O molecule per potassium atom. This effect was observed even at the lowest potassium precoverage under investigation, $\Theta_{\text{K}}=0.04$ ML.¹⁴ Appreciable thermal desorption of the OH species occurred only at temperatures where the potassium atoms also start to desorb, so that desorption kinetics of that species, which we will refer to with α , are not accessible.

The whole amount of water which is not accessible in the equilibrium measurements thus consists of two different water species, the dissociated OH species and a more strongly bound molecular species, whose desorption can be observed with TPD. Figure 5 shows a series of TPD spectra of the desorption of approximately 1.4 ML water at various potassium precoverages. From the pure sample water desorbs in a two-peak structure. The two peaks are named γ and δ in Fig. 5 and are assigned to first layer and multilayer water, respectively, according to literature.^{4,15,16} An additional peak originating from a transition layer, as it was found by Pachc *et al.*,¹⁷ was not resolved in our spectra.

Upon predosing potassium, the intensity of the γ peak is attenuated and a broad desorption feature observed at higher temperatures, which we call β . The mean desorption temperature of this peak increases from 190 K at $\Theta_{\text{K}}=0.04$ ML to 265 K at $\Theta_{\text{K}}=0.25$ ML. This temperature shift and the structure of the peak indicate a complex desorption behavior of the β species. Using the peak areas of the respective XP spectra taken after heating the sample to the γ desorption temperature, the maximum coverage of this species was found to be twice the potassium coverage at $\Theta_{\text{K}}=0.04$ ML, decreasing to approximately 1.5 times at $\Theta_{\text{K}}=0.15$ ML.

DISCUSSION

From XP spectra we found evidence for water dissociation on the potassium precovered Ni(111) surface. The criti-

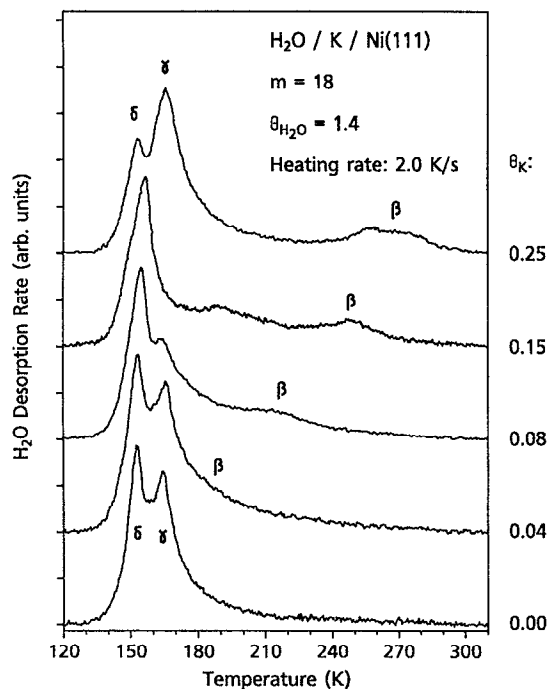


FIG. 5. Thermal desorption spectra of 1.4 ML water adsorbed on the clean Ni(111) surface and for potassium precoverages of 0.04, 0.08, 0.15, and 0.25. The indices β , γ , and δ correspond to the nomenclature used in the text.

cal potassium coverage, that is the coverage which is necessary to dissociate water on the nickel surface, is found to be less than 0.04 ML. This contradicts the result of Bornemann *et al.*, who found a critical potassium coverage of $\Theta_K=0.14$ ML from TPD and UP spectra.⁴ This discrepancy may be due to a possible recombination of OH and H at low potassium coverages during thermal desorption. Such a recombination could take place at higher temperatures for higher potassium coverages, so that it would not be included in an evaluation of TPD peak areas.

The β -peak observed in TPD spectra arises due to the presence of coadsorbed potassium and has been found previously by Bornemann *et al.*⁴ This desorption peak is assigned to a more strongly bound molecular water species on the potassium precovered surface. The saturation coverage of this species is $\Theta_\beta=2\Theta_K$ for low potassium coverages. Together with the maximum coverage of the dissociated species the total coverage of water influenced by potassium amounts to three times the potassium coverage. This value agrees with that reported by Bornemann *et al.* for more strongly bound molecular water at low potassium coverages.⁴

The position of the β TPD peak shifts distinctly depending on the potassium precoverage. This behavior and the large width of the desorption peak direct to a complex desorption mechanism, where the water is either initially adsorbed in different adsorption states or runs through different states during the desorption. A strong repulsive interaction would also explain the large width of the β TPD peak. However, the desorption mechanism cannot be discussed completely by the present experiments only.

A simple qualitative interpretation of the desorption behavior, though, can be given by the assumption that the strength of the interaction of β -H₂O and potassium depends on the number of water molecules surrounding the potassium atom, in such a way that this attractive interaction increases during water desorption. Since higher potassium precoverages increase the number of interaction partners for the water molecules, the β -H₂O desorbs at higher temperatures in TPD spectra with increasing potassium density.

For the γ species, a constant desorption energy of (52 ± 3) kJ/mol and a pre-exponential factor of $1\times 10^{16\pm 1}$ s⁻¹ were found, independent of potassium precoverage. These values are in general agreement with the values of Pache *et al.* of (57 ± 5) kJ/mol and $\nu=10^{17\pm 1}$ s⁻¹, obtained from TPD measurements at the clean Ni(111) surface for small water coverages.¹⁷

The sum of the saturation coverages of the α , β , and γ species is constant as long as the potassium precoverage will not exceed 0.15 ML. The entire coverage of these three species of $\Theta_\alpha+\Theta_\beta+\Theta_\gamma=0.42$ ML equals the monolayer coverage found for water on the clean Ni(111) surface, where $\Theta_\gamma=0.42$ ML. For $\Theta_K=0.15$ ML the maximum coverage of the β -H₂O is $\Theta_\beta=0.27$ ML. At this potassium precoverage, the first water layer of 0.42 ML will build up from the α and β species only. As the saturation coverage of the first layer is independent of the potassium precoverage, the maximum coverage of β -H₂O is limited for $\Theta_K>0.15$ by the number of free adsorption sites in the first layer. Since the number of dissociatively adsorbed water molecules equals the number of preadsorbed potassium atoms, the coverage of the initial water layer would rise over 0.42 ML if a constant ratio of Θ_β/Θ_K is assumed. It should be mentioned that the potassium coverage of 0.15 ML coincides more or less with the critical potassium coverage for water dissociation of 0.14 ML found by Bornemann *et al.*⁴

Recently we have shown that on K/Ni(111) OH and H₂O compete for the free adsorption sites on the nickel surface and that this behavior does not depend on the amount of preadsorbed potassium.¹⁴ These results are supported by the equilibrium measurements; the desorption parameters of the water species denoted by γ do not depend on the potassium precoverage as is expected for a water-substrate bonding unaffected by coadsorbed atoms.

From this and the constant first-layer coverage of 0.42 ML we conclude that due to the presence of adsorbed OH (α species) and the more strongly bound molecular water (β species) the number of possible adsorption sites for the γ species decreases. This agrees with the conception that both, the water and the OH radical, adsorb with the oxygen atom bound to the nickel surface.¹⁴ Due to this blocking of γ -H₂O adsorption sites by the α and β species, the saturation coverages of which depend on the potassium precoverage, the γ saturation coverage decreases with increasing potassium coverage. This coincides with the fact that in TPD spectra at a potassium coverage of 0.15 ML no γ peak is visible.

A new TPD peak at 165 K, denoted as well by γ because of the similar peak position, arises for potassium precoverages higher than 0.15 ML. This peak is assigned to water adsorption in the second layer on top of the first, α and β

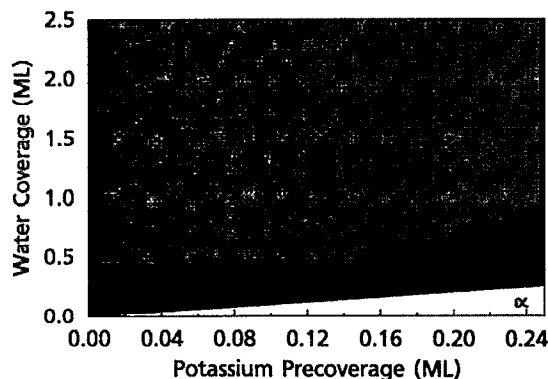


FIG. 6. Population of different states of adsorbed water of H₂O/K/Ni(111). α , water dissociated to OH upon adsorption; β , more strongly bound molecular water; γ , monolayer water; δ , water exhibiting multilayer desorption parameters.

water containing layer. The kinetic parameters of this “new” γ species differ from those that have been obtained for the γ species at low potassium coverages. While the latter show kinetic parameters not depending on water coverage, the kinetic parameters for water desorption from the second layer do, indicating repulsive lateral interaction of the second-layer γ -H₂O, e.g., electrostatic repulsion between water molecules. Since this H₂O species is present only when the adsorption sites in the first layer are completely occupied, its formation must be related either to the potassium–water interaction which is not saturated by the amount of water adsorbed in the first layer, or to a changed adsorption geometry induced by the missing γ -H₂O in the first layer.

After the adsorption sites for γ -H₂O are completely occupied, the formation of H₂O multilayers (δ species) is observed. The desorption energy of 38.6 kJ/mol and the pre-exponential factor of $8 \times 10^{12} \text{ s}^{-1}$ of this species are in good agreement with the results obtained by He and Norton employing isothermal desorption.¹⁸

The change of kinetic parameters from those of the γ species to those of the δ species with increasing water coverage produces the prominent feature observed in Fig. 2. As there is a change in desorption energy as well as in the pre-exponential factor, the curves show a compensational behavior. The desorption energy and the pre-exponential factor are the result of a mixture of different adsorbed water species. For low water coverages the δ -state is unoccupied and the desorption parameters of the γ species ($E_b = 52 \text{ kJ/mol}$, $\nu = 10^{16} \text{ s}^{-1}$) are observed. At high H₂O coverages the δ -state is completely occupied and the γ -H₂O is covered, so that the parameters of δ -H₂O ($E_b = 38.6 \text{ kJ/mol}$, $\nu = 8 \times 10^{12} \text{ s}^{-1}$) can be measured. In the coverage range in which the δ -state is partially occupied, the kinetic parameters are the result of a mixing of γ - and δ -states. Thus the functional forms of the desorption energy and the logarithm of the pre-exponential factor vs $\Theta_{\text{H}_2\text{O}}$ exhibit the similarity observed in Fig. 2.

The different species of adsorbed water found on K/Ni(111) can be summarized in a figure similar to a phase diagram, as it is depicted in Fig. 6. Depending on potassium precoverage and total water coverage, the various coverages

of the different species can be obtained from this figure. The peak intensities of the thermal desorption spectra of Fig. 5, for example, can be predicted using Fig. 6 and considering the respective water coverages for the various potassium precoverages below a horizontal line at $\Theta_{\text{H}_2\text{O}} = 1.4$.

CONCLUSIONS

As has been demonstrated, combining surface science techniques with an UHV compatible permanently operating water supply provides a method for investigating the kinetic properties of water adsorption in a dynamic equilibrium of adsorption and desorption. Supplementary experiments (e.g., TPD and XPS) can give additional information about the different adsorption states.

For the system H₂O/K/Ni(111) we found a dissociation of one water molecule per preadsorbed potassium atom to OH (α species) even at the lowest potassium coverage under investigation ($\Theta_K = 0.04 \text{ ML}$). This dissociated species desorbs only at temperatures where the potassium also starts to desorb. A further amount of molecularly adsorbed water is more strongly bound in the presence of preadsorbed potassium (β species). Since the desorption kinetic parameters of this species depend strongly on the water coverage, they are not derivable from equilibrium measurements. Increasing the water coverage, water desorbs from a state with desorption kinetic properties not affected by potassium [γ species, $E = (52 \pm 3) \text{ kJ/mol}$ and $\nu = 10^{16 \pm 1} \text{ s}^{-1}$]. The maximum coverage of these three species (α, β, γ) together is 0.42 ML, independent of potassium coverage up to $\Theta_K = 0.15 \text{ ML}$. From that it is concluded that the first layer of water consists of these three species and that its structure remains mainly unchanged by preadsorbed potassium.

At higher water coverages desorption from an icelike state with a desorption energy of $(38.6 \pm 0.3) \text{ kJ/mol}$ and a pre-exponential factor of $8 \times 10^{12 \pm 0.1} \text{ s}^{-1}$ can be observed.

The desorption kinetic parameters of the γ and δ species are directly accessible from equilibrium measurements with high accuracy.

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