

# XPS lineshape analysis of potassium coadsorbed with water on Ni(111)

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The line profiles of XP spectra of  $\text{H}_2\text{O}/\text{K}/\text{Ni}(111)$  were investigated for K submonolayer coverages. The K 2p spectra exhibit a strong alteration of lineshape with increasing water coverage. Without coadsorbed water a significant asymmetry was found which decreased rapidly and independently of the potassium precoverage with increasing water exposure up to  $\theta_{\text{H}_2\text{O}} = 0.7$ . The asymmetry observed in the K 2p spectra is assigned to a coupling of the potassium adatoms to the electronic structure of the nickel substrate. The coadsorption of water suppresses this mechanism via a loosening of the potassium–nickel coupling. Since the decrease of asymmetry is independent of the potassium coverage, it is concluded that this process is due to an adsorbate–substrate interaction between the water and the nickel substrate only. This contradicts models in which the coadsorption of water and potassium on metal substrates is manifested in hydration of the potassium adatoms.

## 1. Introduction

The adsorption of water with alkali metals on metal surfaces as a model system for investigating electro-chemical processes at a metal–electrolyte interface has been a topic of considerable interest in the past and is still the subject of many studies [1–7].

From XPS, UPS, LEED and TPD investigations is derived that the adsorption of alkali metals prior to water adsorption generally leads to a strengthening of the water–substrate bonding when water is adsorbed molecularly, or to a dissociation of the water molecules [3,4,6,7]. Since a stoichiometric amount of water molecules seems to be affected, it is sometimes concluded that adsorbing water tends to form a kind of hydration shell at each preadsorbed alkali atom [4,8]. In a TPD and UPS study of  $\text{H}_2\text{O}/\text{K}/\text{Ni}(111)$  is reported that dissociation occurs only when the potassium precoverage exceeds 0.14 [7].

Quantitative XPS measurements on the system  $\text{H}_2\text{O}/\text{K}/\text{Pt}(111)$  exhibit an onset in the decrease of K 2p intensity with increasing water coverage, which is interpreted as an indication of the formation of hydration shells [4]. The observed in-

crease of K 2p intensity with initial water adsorption is not discussed [4].

In this paper a detailed lineshape analysis of the K 2p spectra of the system  $\text{H}_2\text{O}/\text{K}/\text{Ni}(111)$  is presented. Since the asymmetry of the K 2p peaks exhibits strong alterations with increasing water coverage, increasing K 2p peak heights are simulated. A quantitative analysis of the behaviour of the asymmetry with increasing water coverage can provide additional information on the binding properties and should be considered when quantitative XPS is carried out.

## 2. Experimental

Experiments were carried out in a standard UHV chamber equipped with a spherical electron analyser (Kratos,  $r = 127$  mm), an X-ray source with Mg and Al anodes, a LEED system and devices for sample preparation. The pressure during the acquisition of the spectra was  $(1–2) \times 10^{-8}$  Pa. The analyser acceptance area on the sample was set to approximately  $3 \times 4$  mm<sup>2</sup> by means of electrostatic lenses in the entrance path

of the analyser. The pass energy was set to 40 eV in the K2p spectra and to 80 eV in the O 1s spectra, thus resulting in an overall resolution of 0.9 and 1.4 eV, respectively, including an excitation linewidth of 0.7 eV for MgK $\alpha$  and 0.8 eV for AlK $\alpha$ .

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 180 K and subsequent heating to certain temperatures at which the desired coverages are obtained.

Ultrapure water (Merck), which was further purified by cycles of freezing, pumping and thawing, was brought onto the sample surface at a temperature of 120 K using a differentially pumped doser system positioned at a distance of 25 mm from the sample. The area covered on the sample was approximately  $6 \times 5 \text{ nm}^2$ . Within the area analysed, the coverage does not vary more than 10%. Absolute coverage determination was performed using the O 1s peak area calibrated with respect to the O-p( $2 \times 2$ ) structure.

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

### 3. Results and discussion

O 1s spectra for a water coverage of 0.3 are shown in fig. 1 for the clean Ni(111) surface and for potassium precoverages of 0.13 and 0.25. 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. A second peak at the same binding energy of 533.2 eV as on the clean Ni(111) surface develops when the water coverage is increased. For even higher water coverages, when ice multilayers are formed, no saturation of this peak can be observed, only a slight shift towards higher binding energies due to the decrease of the core hole screening by the metal, so that this peak can be attributed to

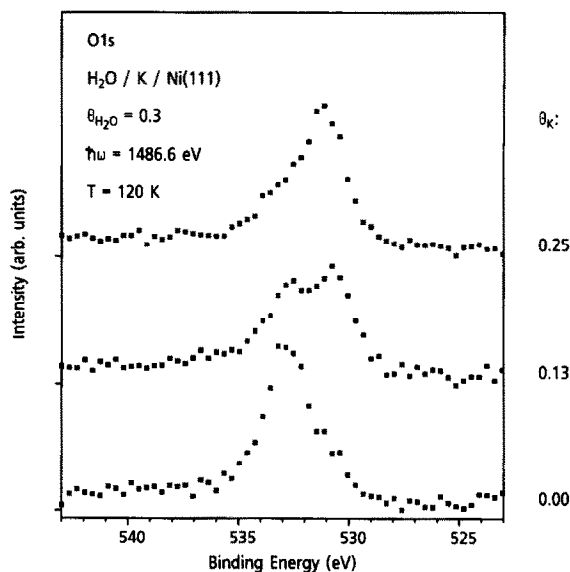


Fig. 1. O 1s spectra of 0.3 ML water adsorbed at 120 K on a clean (bottom curve) and on potassium precovered Ni(111) surfaces with potassium coverages of 0.13 (middle curve) and 0.25 (upper curve).

molecularly adsorbed water.

The first peak at 531.0 eV binding energy is visible even at low potassium coverages like 0.04. In the literature a peak at that binding energy is usually assigned to an adsorbed OH species [9–12]. Identifying this peak as originating from water dissociated upon adsorption implies that the critical potassium coverage, above which dissociation starts, has to be fixed to be less than 0.04, in contradiction to results from TPD and UPS investigations [7]. The fraction of water dissociated equals the potassium coverage, that is, one water molecule per potassium atom is dissociated, which agrees with studies in which alkali-induced dissociation is observed [3,4,6,7].

As there seems to be some ambiguity in identifying the O 1s peak at 531 eV binding energy with hydroxyl [9], another possible interpretation could be to discuss this peak as originating either from molecularly adsorbed first layer water for low potassium coverages or from dissociated hydroxyl species for higher potassium coverages.

In fig. 2, K 2p spectra are shown before (a) and after (b) water exposure for a potassium coverage of 0.25. The water coverage in curve (b) was 0.3. Drastic changes in lineshape can be observed.

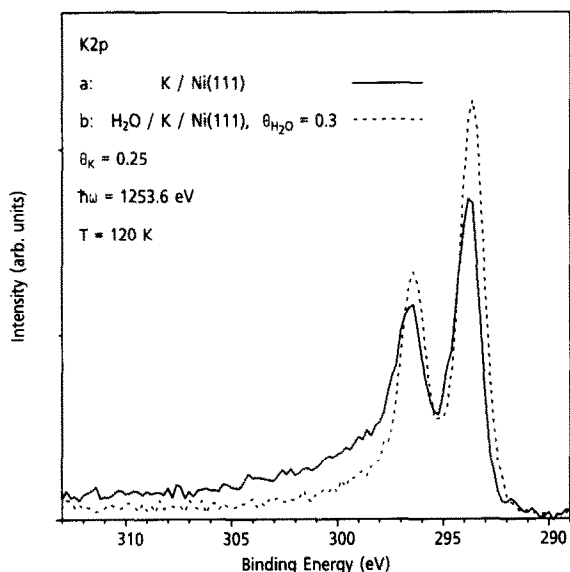


Fig. 2. Comparison of K2p spectra of 0.25 ML potassium on Ni(111) before (a, continuous line) and after adsorption of 0.3 ML water (b, dotted line) at 120 K.

The peak height of the K2p<sub>3/2</sub> peak increases by 60% with water coverage, and the ratio of the peak heights of K2p<sub>3/2</sub>/K2p<sub>1/2</sub> with respect to the subtracted constant background also increases. Curve (a) shows a clearly visible asymmetry in the tail towards lower kinetic energy, which is reduced when water is adsorbed.

To quantify the change in K2p lineshape, the peaks are fitted using Doniach–Sunjic lines, which are convoluted with a Gaussian contributing to the experimental resolution. Doublet Lorentz-peaks are used according to the doublet structure of the exciting MgK $\alpha$  radiation. The width of the Gaussian and the Lorentz-width of the Doniach–Sunjic line are kept constant for all fits, and the ratio of the K2p<sub>3/2</sub>/K2p<sub>1/2</sub> peak intensities is fixed to 2:1 according to the occupation numbers. A series of the fits performed is shown in fig. 3 for a potassium coverage of 0.25. Excellent agreement with the experimental data is achieved for all curves.

The obtained asymmetry parameters  $\alpha$  are depicted in fig. 4 for potassium precoverages of 0.09, 0.13 and 0.25, depending on the water cov-

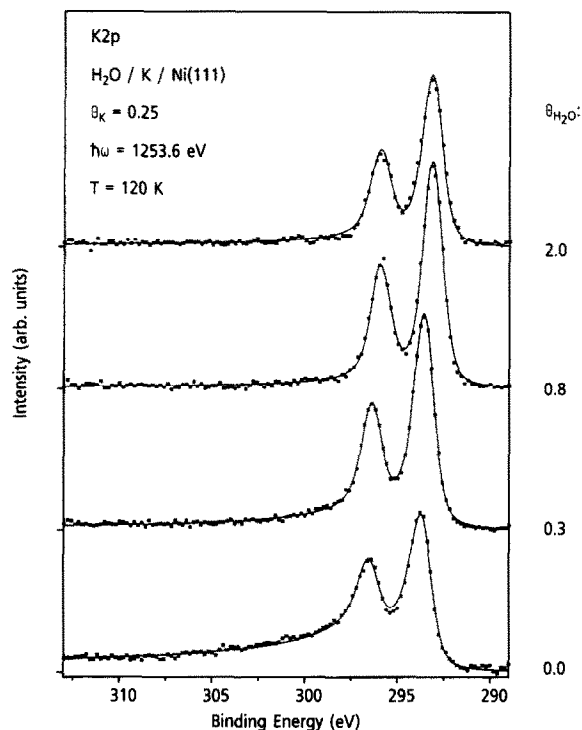


Fig. 3. Series of K2p spectra of 0.25 ML potassium adsorbed on Ni(111) with increasing water coverage at 120 K. The dots correspond to the experimental data, the continuous lines to a fit using Doniach–Sunjic lines (see text).

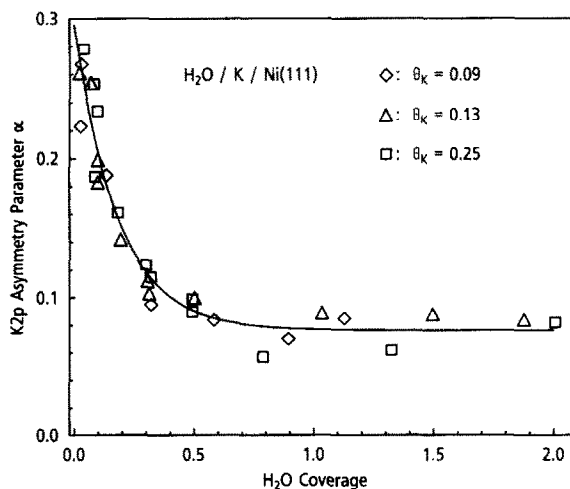


Fig. 4. Asymmetry parameter  $\alpha$  of the K2p lines obtained from the fits performed for water on the potassium precovered Ni(111) surface depending on the water coverage for potassium precoverages of 0.09, 0.13 and 0.25.

erage. A strong decrease of the line asymmetry with the initial water adsorption is observed, which is independent of the amount of potassium preadsorbed. A saturation value of  $\alpha = 0.08$  is reached when the water coverage exceeds 0.7.

In the formalism of Doniach and Sunjic the asymmetry observed in XP spectra is interpreted by the creation of low energy electron hole pairs at the Fermi edge in solids [13]. Thus the initial value of the asymmetry of 0.3 for the K 2p peaks of K/Ni(111) must be explained by a coupling of the potassium adatoms to the electronic structure of the nickel substrate [14]. Consequently, the rapid decrease of the value of the asymmetry parameter must correspond to a loosening of that coupling.

In a model in which each potassium atom is hydrated by a stoichiometric amount of water, the effect of the adsorbed water on the electronic properties of the potassium would depend on the amount of potassium adsorbed, i.e., for a higher potassium coverage, a higher water coverage would be needed to affect the above mentioned potassium–nickel coupling to the same extent. However, as can be seen from fig. 4, there is no such dependence on the potassium coverage.

This unexpected independence from potassium precoverage can be explained assuming a model in which the adsorbing water molecules establish a bond only to the metal substrate, which is the reason for the loosening of the potassium–nickel coupling. When the coupling of the potassium atoms to the metal, which leads to the asymmetry in the K 2p spectra, is weakened via the substrate coupling of the adsorbing water molecules, no dependence on the potassium coverage has to be expected.

A stochastic adsorption behaviour of the incoming water molecules, which would also explain the independence from the potassium coverage, can be ruled out considering the initial dissociation of the water molecules up to an amount equal to the potassium precoverage.

As pointed out, no hydration shells are built up by the water molecules in our model; the water is bound only to the substrate. The stoichiometric amount of water being dissociated can be explained by a kind of nearest neighbour in-

teraction between the water and the potassium adatoms.

Obviously the dissociated species changes the potassium–nickel coupling in the same way as the non-dissociated species.

The strong variation of the K 2p lineshape has to be taken into account when performing quantitative XPS. The choice of the integration limit can have a remarkable influence on the areas obtained. An upper integration limit of 303, 308 or 318 eV binding energy in the system considered leads to a decreasing, a constant or an increasing behaviour of the peak areas, respectively, with increasing initial water coverage. Integration results therefore have to be interpreted carefully.

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