Alkali Promotion of Metal Surfaces

A Surface Science Study of Potassium on Rhodium(111)

T.V.W. Janssens
Alkali Promotion of Metal Surfaces

A Surface Science Study of Potassium on Rhodium(111)

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof. dr. J.H. van Lint, voor een commissie aangewezen door het College van Dekanen in het openbaar te verdedigen op dinsdag 9 november om 16.00 uur

door

T.V.W. Janssens

geboren te Breda
The work described in this theses has been carried out at the Institute of Physical and Theoretical Chemistry at the University of Bonn (Germany) and at the Schuit Institute of Catalysis, Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology (the Netherlands). Financial support has been supplied by the Heinrich Hertz Stiftung and the Dutch Organization of Scientific Research (NWO, PGS 70-154).
Contents

1 Introduction 1

2 Preparation and Characterization of Potassium on the Rh(111) surface 9
   2.1 Introduction 9
   2.2 Experimental Methods 9
      2.2.1 Auger Electron Spectroscopy 10
      2.2.2 Low Energy Electron Diffraction 12
      2.2.3 Electron Energy Loss Spectroscopy 13
      2.2.4 Ultraviolet Photoelectron Spectroscopy 15
      2.2.5 Thermal Desorption Spectroscopy 17
   2.3 Sample Preparation 18
   2.4 Characterization of the Potassium Overlayer 23
   2.5 Conclusions 34

3 Photoemission of adsorbed Xenon, Krypton and Argon on Clean and Potassium Covered Rh(111) 37
   3.1 Introduction 37
   3.2 Photoemission of Adsorbed Noble Gases as a Local Work Function Probe 38
   3.3 Ultraviolet Photoemission of Adsorbed Noble Gases on Clean Rhodium(111) 41
   3.4 Adsorption of Xe, Kr and Ar on Potassium Covered Rh(111) 45
      3.4.1 Experimental and Analytical Procedures 45
      3.4.2 Determination of the Local Work Functions 50
   3.5 Final Remarks 69
   3.6 Conclusions 72

4 Calculations on the Electrostatic Potential on Potassium Promoted Rhodium(111) 75
   4.1 Introduction 75
   4.2 The Dipole Model 77
   4.3 Relation between Measured and Calculated Electrostatic Potential 88
   4.4 Quantum-Chemical Calculation of the Electrostatic Potential on Rhodium-Potassium Clusters 93
   4.5 Long Range Effect on Potassium Promoted Surfaces 105
   4.6 Conclusions 107
5  Heterogeneity of Oxygen-Potassium-Covered Rhodium(111):
Detection with Photoemission of Adsorbed Noble Gases  111

5.1 Introduction  111

5.2 Characterization of Adsorbed Oxygen on Clean and Potassium-Covered
Rhodium(111)  112

5.3 Influence of Potassium on Oxygen Adsorption on Rh and Other Transition
Metals  121

5.4 Photoemission of Adsorbed Noble Gases on Oxygen and Oxygen-Potassium
Layers on Rhodium(111)  123

5.5 Conclusions  134

6  Summary and Conclusions  137

Samenvatting  141

Publications  144

Dank  145

Curriculum Vitae  146
Introduction

Catalysts are widely used for the production of chemicals and have recently become more important for environmental purposes (e.g. automotive exhaust catalyst) as well. Small transition metal particles (Fe, Co, Ni, Ru, Rh, Pd, Pt) supported on oxidic materials (SiO$_2$, Al$_2$O$_3$, TiO$_2$) are well known catalysts. Many heterogeneous catalytic reaction involves three fundamental steps: The reactants first adsorb on the catalyst surface, then the reaction products are formed and finally the products desorb from the surface. An example of such a reaction is the hydrogenation of CO to hydrocarbons: First CO adsorbs and depending on the catalyst it may dissociate to adsorbed atomic carbon and oxygen. By reaction with hydrogen, hydrocarbons are formed on the surface, which finally desorb. Of course, the adsorption, reaction and desorption processes depend on the reactants, products and on the nature of the active material.

The activity and selectivity of a catalyst can be modified by applying additives to the active material. These additives are not necessarily catalysts themselves, but they can influence the course of the catalytic reaction. Such additives are called promoters. The ability of promoters to change the activity and selectivity of a catalyst makes them a useful tool for tuning catalysts. Generally, the role of promoters in a catalytic reaction is to suppress certain (unwanted) reaction pathways and to enhance the ones that lead to the desired reaction product.

Promoters can influence a catalytic reaction in different ways and can be classified in two main groups, viz. structural promoters and chemical promoters [1]. Structural promoters do not interact directly with the reactants or products, but they modify the active surface. Examples for such promoters are Fe and Zn ions on the Rh surface, that suppress the dissociation of CO [2]. For the dissociation of CO large surface ensembles are necessary [1-3] and the Fe or Zn reduces the size of the available ensembles. Other structural promoters stabilize certain surface phases. By example, Re stabilizes sulfur, which act as a site blocker on a Pt catalyst, used for formation of aromatics from alkanes [4,5]. Another example is Cs, which stabilizes chlorine on a silver catalyst, which in turn enhances the epoxidation of ethylene [6].

Chemical promoters directly influence reacting adsorbates on the surface. This can also take place in different ways. The promoter can directly interact with a precursor, which reacts with an activated species adsorbed elsewhere on the surface. Examples are the formation of acetates attached to a metal ion (Ti, Mn, Zr), which are precursors for C$_2$-oxygenates [2]. Another type of promoters are reducible oxides, e.g. V$_2$O$_5$, TiO$_2$ in the synthesis gas conversion. The valency of the V and Ti cations changes upon interaction with CO. The dissociation of CO is facilitated [1,2,7,8].

A third type of chemical promoter is adsorbed alkali on transition metal surfaces, which modifies the chemical bond between the atoms in an adsorbed molecule. This affects the activity.
of the catalyst as well as the product distribution. An example is Cs, which accelerates the water-gas shift reaction on a Cu(110) surface [9]. Alkali additives also increase the ammonia production over a Ru or Fe catalyst. The role of the alkali is to enhance the dissociation of nitrogen, which is the rate determining step in ammonia synthesis [10-12]. In the hydrogenation of CO to hydrocarbons, the dissociation of CO has become easier on a potassium promoted surface, which results in a higher selectivity for heavier and unsaturated hydrocarbons [13-17].

A large part of the knowledge about the properties of adsorbed alkali metals on transition metal surfaces comes from surface sensitive spectroscopic studies of model systems. Very often, the model systems are single crystal surfaces, which have a well defined structure. In this thesis a study of potassium adsorbed on a Rh(111) single crystal surface is presented. In this model system the Rh(111) surface represents the catalytically active surface; the adsorbed elementary potassium represents the promoter.

At low coverages, adsorption of alkali metal on transition metal surfaces is accompanied by an electron transfer from the adsorbate to the substrate, leading to electrostatic dipoles on the metal surface. This is seen in the rapid lowering of the work function when small amounts of alkali metal are adsorbed [16,18-22]. The dipole generates a local electrostatic field, close to the alkali cation. This is illustrated by calculations done by Lang et al. [12,23] for a single potassium atom adsorbed on an infinite jellium surface (Figure 1.1). Close to the potassium atom, the electrostatic potential (for an electron) is lowered upon potassium adsorption. This facilitates electron transfer from the metal surface to the adsorbates.

Holloway et al. have proposed a general concept for understanding how changes in local surface potential affect catalytic reactions [12]. They state that the direction of the local electrostatic field at the adsorption site of a molecule in combination with the electron donating or electron accepting character of the adsorbate determines whether the molecule is stabilized or destabilized by the promoter. The direction of the electrostatic field is determined by the type of promoter. An electropositive adsorbate (alkali metal) results in an electrostatic field

![Figure 1.1 Contour map of the electrostatic potential change with potassium adsorption on a jellium surface. The vertical line denotes the jellium edge. Near the potassium atom, the potential energy of an electron decreases. 1 Bohr = 0.529 Å. Reproduced from Lang, Holloway and Nørskov [23].](image-url)
Introduction

directed towards the surface, i.e. the potential energy of an electron decreases with increasing distance to the surface (Figure 1.2). In this case adsorbates with an electron accepting character (e.g. CO and N\textsubscript{2} in some cases) are stabilized and electron donating adsorbates (e.g. H\textsubscript{2}, alkenes) are destabilized. Reversely, for electronegative adsorbates (e.g. chlorine, sulfur or oxygen) the electrostatic potential increases going away from the surface (Figure 1.2). The electric field is directed away from the surface and the electron donating adsorbates are favored.

These effects are illustrated in Figure 1.3, for CO adsorbed on Ni. When the CO molecule is adsorbed next to a potassium atom, the energy distribution of the 2\pi\textsuperscript{*} orbital of the CO shifts partially below the Fermi level of the metal, due to the lower electrostatic potential at the CO adsorption site [24]. This potassium-induced shift of the CO 2\pi\textsuperscript{*}-level towards lower energy has been observed experimentally for CO on Pt(111) with inverse photoemission spectroscopy, which monitors the empty orbitals [25]. The population of the CO-2\pi\textsuperscript{*} level, antibonding for the carbon-oxygen bond, increases. The coadsorbed potassium stabilizes adsorbed CO [15,26-32] and enhances the dissociation of CO. This is illustrated in Figure 1.4, which displays the number of dissociated CO molecules per potassium atom on a potassium promoted Rh(111) surface. At low potassium coverage, the number of dissociated CO molecules per potassium atom increases rapidly and reaches the value of ~3 at 0.2 ML (~7 % with respect to the Rh surface atoms) potassium [15]. The decrease at higher potassium coverage may be due to both a less efficient dissociation and site blocking by the adsorbed potassium [33]. Only at low coverages, potassium acts as a promoter. Analogously, the dissociation of N\textsubscript{2} on iron is also enhanced, which results in the higher activity of potassium promoted catalysts for the ammonia synthesis.

When CO is adsorbed next to a sulfur atom, the energy distribution of the CO 2\pi\textsuperscript{*} level shifts away from the Fermi-level (Figure 1.3). Hence, the occupation of the 2\pi\textsuperscript{*}-level is lower. A higher infrared frequency for CO on a sulfur-covered surface, as compared to that of CO on the clean surface, is in agreement with a lower occupancy of the CO 2\pi\textsuperscript{*} orbital [34-36].

**Figure 1.2** Calculated electrostatic potential change upon potassium and sulfur adsorption on a jellium surface as a function of the distance to the jellium edge. The lateral distance to the adsorbed potassium or sulfur is 5 Bohr (2.65 Å). Reproduced from Lang, Holloway and Nørskov [23].
Adsorption of sulfur leads to a lower desorption temperature for CO [27,34,37-39]. Sulfur acts as a poison for CO dissociation.

In the hydrogenation of tetramethylethene, potassium suppresses the hydrogenation rate and therefore is a poison for this reaction, rather than a promoter [14] (Figure 1.5). In view of the model described above, the adsorption of both tetramethylethene and hydrogen are suppressed by the adsorbed potassium, as these are both electron donating adsorbates. Consequently, the surface concentrations of the reactants are lower on the potassium doped catalyst and hence the overall hydrogenation rate is also lower. This illustrates that the terms promoter and poison are strongly related to the reaction in question. Note that the model proposed by Holloway et al. treats the promoters and poisons in the same way.

*Figure 1.3* Calculated densities of states for a CO molecule in the gas phase and adsorbed on clean, potassium doped and sulfur doped Ni(100). The 5σ-level shifts to lower binding energy upon CO adsorption. Potassium adsorption leads to an energy decrease of the CO 2π*-level; with sulfur the energy of the CO 2π*-level increases. Reproduced from Wimmer, Fu and Freeman [24].

*Figure 1.4* The number of dissociated CO molecules per adsorbed potassium atom on the Rh(111) surface as a function of the potassium coverage. The dissociation of CO is most efficient at low potassium coverage. Reproduced from Somorjai and Garfunkel [15].
Introduction

Figure 1.5 Hydrogenation rate of 0.4% tetramethylethene in CO/H₂ as a function of the H₂/CO ratio on an iron catalyst. Potassium suppresses the hydrogenation activity of the catalyst. Reproduced from Dwyer [14].

So far, we have discussed the role of potassium in the catalytic reaction on the basis of data obtained from adsorbed elementary potassium. However, under real reaction conditions the potassium is present as an oxide, hydroxide or carbonate [9,11,12,16,22,40]. The actual chemical state of potassium under reaction conditions depends on the temperature and pressure in combination with the stability of the potassium compounds on the surface, the reactivity of the potassium towards the reactants and reaction products, and to a lesser extent on the catalyst preparation. In general, the potassium occurs as oxide or hydroxide with unknown stoichiometry. Calculations of the electrostatic potential in the vicinity of adsorbed potassium and oxygen suggest that the presence of oxygen does not entirely destroy the effect of potassium promotion. The range and magnitude of the effect of potassium is larger than that of oxygen (Figure 1.6) [12].

Scope of this thesis

The aim of this study is to determine experimentally the potassium-induced change in electrostatic potential around a potassium atom on a Rh(111) surface and to compare the results with theoretical calculations.

As suggested from Figure 1.4, the promoting action of potassium is most efficient at low potassium coverage. Therefore we focus on low potassium coverages, where the potassium is ionic. At low potassium coverages, the surface potential depends on the position with respect to potassium (Figure 1.1). With photoemission of adsorbed Xe, the surface potential at the Xe adsorption sites can be probed locally [41]. To obtain more detailed information on the electrostatic potential we use not only Xe, but also Kr and Ar as local surface potential probes. Because Kr and Ar are smaller, we vary the distance between the adsorbed potassium and the noble gas adsorption site. Thus, we get information about the magnitude and variation of the surface potential around an adsorbed potassium atom and about the range that is influenced by the adsorbed potassium. From a comparison with calculated electrostatic potentials we check
whether the experimentally obtained values can be understood with realistic physical parameters.

As stated above, the potassium is oxidized under catalytic conditions. Yet, the promoter effect seems to be governed by the potassium ion (Figure 1.6). The effect of oxygen on the local surface potential on a potassium covered Rh(111) surface is also examined by means of photoemission of adsorbed noble gases.

The organization of this thesis is as follows. First submonolayers of potassium on Rh(111) are characterized with surface sensitive spectroscopies, to obtain a general idea of the behavior of adsorbed elementary potassium on the Rh(111) surface. Chapter 3 deals with the experimental determination of the potassium-induced changes in the local surface potential by means of photoemission of adsorbed noble gases. The results are compared with calculations of the electrostatic potential in a hexagonally ordered network of dipoles and on small Rh/K clusters and the effects of the modified potential on adsorbed molecules is discussed (Chapter 4). In Chapter 5 photoemission of adsorbed noble gases is applied to layers of coadsorbed oxygen and potassium on Rh(111). Finally, we give the general conclusions in Chapter 6.

References

Introduction

2
Preparation and Characterization of Potassium on the Rhodium(111) Surface

2.1 Introduction

To study the promoter effect of potassium on transition metal catalysts we use surface sensitive spectroscopies on a model system. In the model system, the active component of the catalyst is represented by a Rh(111) single crystal surface. Adsorbed elementary potassium is used as a model for the promoter. Since the potassium itself is catalytically inactive, the surface concentration of potassium on the catalyst surface must be low. A high loading of potassium deactivates the catalyst, because it blocks too much of the catalytically active surface. Therefore, the properties of potassium at low coverages are important for understanding the promoter effect.

Generally, the work function of metal surfaces is significantly lowered by small amounts of adsorbed potassium, due to an electron transfer from the potassium atoms to the metal surface [1-6]. Hence, the potassium is ionic at low coverages. This ionic phase is important for the promoter effect. At high potassium coverages, the potassium becomes metallic.

To obtain a general idea of the different phases of potassium adsorbed on Rh(111), the pure potassium layers on Rh(111) at low and high potassium coverage are characterized, using surface sensitive spectroscopies (Section 2.4). First, the experimental methods and the spectroscopies that are used are shortly discussed (Sections 2.2 and 2.3).

2.2 Experimental Methods

The experiments are performed in an ultrahigh vacuum (UHV) system with a base pressure of $1 \times 10^{-10}$ Torr. The sample is a Rh single crystal with a [111] oriented surface of about 1 mm thick. It is mounted on a sample holder by two tungsten wires, pressed into grooves on the side faces of the crystal. This construction allows resistive heating of the sample to temperatures up to 1300 K. The sample can be cooled to 45 K by a closed-cycle He-refrigerator, which is connected to the sample holder via a copper string [7]. The sample temperature is measured with a NiCr-Ni thermocouple, spotwelded to the back of the crystal. The potassium is evaporated from a commercial getter source (SAES), mounted on an electrical feedthrough.
Chapter 2

The UHV-system is equipped with an ion gun for sample preparation. A cylindrical mirror analyzer (CMA) (Varian Model 981-2607) with an electron gun placed in the centre of the analyzer is used for Auger Electron Spectroscopy (AES) and Electron Energy Loss Spectroscopy (EELS). With this construction, we have normal incidence of the primary electrons. For Low Energy Electron Diffraction (LEED) a retarding field analyzer (VG 640 RVL) with a fluorescent screen is used. Ultraviolet Photoelectron Spectroscopy (UPS) is performed with a hemispherical energy analyzer (VG) and a helium-discharge lamp (VG) as photon source. The helium-lamp allows selection of two photon energies, \( \text{viz.} \) HeI-radiation (21.21 eV photon energy), obtained at about 0.1 Torr He-pressure in the discharge chamber, and HeII-radiation (40.8 eV photon energy), at a He-pressure of about 0.005 Torr. A quadrupole mass spectrometer (Balzers QME 112-2) is used for residual gas analysis and thermal desorption spectroscopy (TDS). In the next sections a brief review of these techniques is given.

2.2.1 Auger Electron Spectroscopy

From Auger electron spectroscopy (AES) one obtains qualitative and quantitative information about the composition of the surface region of the sample. Each element produces characteristic signals in the Auger spectrum. The intensity corresponds to the concentration of the element in the surface region.

In Auger electron spectroscopy one measures the kinetic energy of electrons emitted from the sample according to the Auger deexcitation process [8] (Figure 2.1). The first step in this process is the removal of an electron with binding energy \( E_1 \) out of the core shells of an atom, using either electrons, usually with an energy between 1 and 5 keV, or X-ray photons as excitation source. Such an excited atom fills the hole with an electron from a higher energy level \( E_2 \). The energy that is set free by this relaxation can be in the form of a (X-ray) photon or emission of a third electron from level \( E_3 \) with a certain kinetic energy. This electron is the Auger electron and its kinetic energy is measured. This kinetic energy can be approximated as:

\[
E_{\text{kin}} = E_1 - E_2 - E_3 - \epsilon - \phi
\]  

(2.1)

where \( E_n \) is the binding energy of the respective electron, with respect to the Fermi level of the sample; \( \epsilon \) accounts for relaxation effects, due to the presence of the core hole after ionization, and is in the order of a few eV; \( \phi \) is the work function of the sample. According to Eq. 2.1, the kinetic energy of the Auger electron is independent of the energy of the primary electrons (or photons), and depends on the binding energies of the electrons involved in the Auger process, which makes it element specific.

The intensity of the Auger signal depends on many factors, \( \text{viz.} \) sensitivities, concentration of the element in the surface region as a function of the depth, ionization cross sections, the probability of the Auger process to occur (Auger yield), the intensity of ionizing electrons (or photons plus secondary electrons), the cross section for ionization and an attenuation factor, accounting for the escape depth of the Auger electrons [8]. In addition, the Auger yield, the
Characterization of K on Rh(111)

Figure 2.1 The Auger deexcitation process. First a core electron is emitted either by photoionization or by electron impact. The atom relaxes by filling this hole with an electron from a higher level. The released energy is used for emission of a third electron, the Auger electron.

The number of ionizing electrons and the attenuation factor also depend on the chemical environment (matrix effects). The total number of ionizing electrons can be separated in two parts: The intensity of the primary electron beam and the contribution of the backscattered electrons, the latter being matrix dependent. The backscattered electrons may even lead to an enhanced Auger emission of an element compared to that of the free atom. Considering all effects mentioned above, the total intensity of the Auger signal is given by [8]:

\[
I_a = I_0 \cdot Q_a(E_p)[1 + \frac{1}{r_M(E_a, A)}] \int_0^z c_i(z) \exp \left( -\frac{z}{\lambda_M(E_a) \cos \theta} \right) dz
\]  

where \(I_0\) is the primary beam current, \(Q_a(E_p)\) is the cross section for Auger electron emission including both the ionization cross section and the Auger yield, \(E_p\) denotes the dependence on the energy of the primary electrons. The backscattering effect for Auger electrons with energy \(E_a\) of an element \(A\) in matrix \(M\) is accounted for by the factor \(r_M(E_a, A)\). The concentration of element \(i\) as a function of the depth in the sample is given by \(c_i(z)\). The exponential function describes the attenuation of Auger electrons of energy \(E_a\) in matrix \(M\) with a characteristic length ('mean free path'), \(\lambda_M\), escaping from depth \(z\). In electron-excited AES, the Auger peaks appear as small peaks on an intense background. Therefore the Auger spectra are often presented in a differentiated form, which makes the signals better visible.

We have used AES for checking the cleanliness of the sample (element determination) and for determination of the potassium coverage (intensity measurement). Since the potassium forms a thin layer on top of the rhodium surface, the concentration of potassium for \(z>0\) is zero and the integral in Eq. 2.2 may be replaced by the concentration of potassium. We see that the intensity of the potassium signal is proportional to the potassium coverage (=surface concentration). The absolute coverage is obtained by calibration to an independent measurement, in our case with LEED.
2.2.2 Low Energy Electron Diffraction

With LEED (Low Energy Electron Diffraction) one obtains information about the long range periodic structure of the surface [8] by diffraction of elastically scattered electrons.

In contrast to Auger electron spectroscopy, in the LEED experiment the information is obtained from the primary electrons, i.e. the electrons generated in the electron gun. Electrons with a well defined low energy (~100 eV) are scattered on the surface and the direction of the elastically scattered electrons is determined. The scattered electrons interfere with each other and produce a diffraction pattern. Constructive interference occurs only in those directions where the path difference of two waves equals an integer number of wavelengths. These directions are given by the Bragg relation:

\[ a(\sin \varphi_r - \sin \varphi_i) = n \lambda \]  

(2.3)

where \( a \) is the distance between the periodically ordered scatterers (lattice constant), \( \varphi_i \) is the angle of incidence and \( \varphi_r \), the diffraction angle. The order of the diffraction is indicated by \( n \). The wavelength of the incident electrons (\( \lambda \)) is given by the de Broglie relation:

\[ \lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE_{\text{kin}}}} \]  

(2.4)

where \( h \) is Planck's constant and \( p \) is the momentum of an incident electron, which can also be expressed in terms of the kinetic energy \( E_{\text{kin}} \) and the mass of an electron \( m \). The wavelength and thus the angle of constructive interference depend on the kinetic energy of the primary electrons. For normal incidence (\( \varphi_i = 0 \)) and after substitution of the constants Eq. 2.3 can be rewritten as:

\[ \sin \varphi_r = \frac{n}{a} \sqrt{\frac{150}{E}} \]  

(2.5)

with the electron energy \( E \) in eV and the lattice constant \( a \) in Å.

The use of electrons for the diffraction makes the technique surface sensitive. In order to observe a diffraction pattern one needs wavelengths in the order of the lattice constant of the sample, i.e. a few Å. Photons with wavelengths in this range are X-rays, which have high energy. Consequently, the mean free path of the photons is large and they penetrate deep in the sample. Electrons, however, have according to Eq. 2.4 a wavelength of about 1 Å at an energy of ~100 eV. The mean free path of electrons with this energy is just a few Ångström, and therefore electron diffraction is surface sensitive.

In the experiment the elastically scattered electrons are detected on a fluorescent screen. Inelastically scattered electrons are not detected by applying an appropriate retardation potential before detection. The direction of the constructively interfering electrons becomes visible as small spots. The distance between the spots of the undiffracted and the diffracted electrons...
Figure 2.2 The (2×1) and (√3×√3/R30°) adsorbate structure on a hexagonally ordered surface. The (2×1) structure contains one adsorbed particle per 2 substrate atoms, which corresponds to a coverage of 1/2. Analogously, the (√3×√3/R30°) structure corresponds to a coverage of 1/3.

is a measure of the refractive angle. A large lattice constant corresponds to small refraction angles and thus to small distances between the spots: The diffraction pattern represents the reciprocal lattice of the surface.

Periodically ordered adsorbates also produce LEED patterns. The characteristic distance that determines the adsorbate-induced diffraction is the regular distance between the adsorbed atoms. Because the information depth is larger than one layer, the pattern of the substrate remains visible. Consequently, the LEED pattern consists of both substrate correlated and adsorbate correlated spots ('superstructure'). This allows determination of the structure of the adsorbate layer. The diffraction pattern only yields information about the periodicity of the adsorbate structure; the positions of the adsorbates with respect to the surface atoms can not be determined from the diffraction pattern.

Adsorbate structures are often indicated as, e.g. (2×1) or (√3×√3/R30°). The notation (2×1) means, that the unit cell of the adsorbate structure is 2 substrate unit cells long and 1 wide (Figure 2.2, left). The edges of the (√3×√3/R30°) unit cell are a factor √3 larger than that of the substrate and are 30° rotated with respect to the surface structure (Figure 2.2, right). Coverages are obtained from the LEED patterns by counting the number of substrate atoms per adsorbed atom or molecule. For example, in the (2×1) structure shown in Figure 2.2, we have 2 substrate atoms per adsorbed atom or molecule and hence a coverage of 1/2. In analogy, we have a coverage of 1/3 for the (√3×√3/R30°) structure.

In this work LEED has been used for determination of the surface structures of potassium on the Rh(111) surface and for the calibration of the Auger intensities.

2.2.3 Electron Energy Loss Spectroscopy

Electrons are not only elastically scattered by the surface, but may also undergo inelastic scattering, leading to an energy loss of the electrons. These energy losses give information
about the electronic structure of the sample.

The energy loss is given by the difference between the energy of the primary electrons and the energy of the inelastically scattered electrons. Analogous to AES, the energy distribution of the electrons coming from the sample is measured. Peaks related with loss processes appear at a constant distance from the elastic peak, which has the highest kinetic energy in the spectrum, and usually is very intense. Since the position of the loss peaks in the spectrum depends on the primary energy, one can distinguish them from Auger peaks, which always appear at the same kinetic energy.

There are different processes leading to an energy loss of electrons, dependent on the primary energy. The first is the ionization of core electrons, which leads to an energy loss in the order of several hundred eV. Excitation of valence electrons into an unfilled level of the same band (intraband) or into another energy band (interband) may occur resulting in typical loss values of one to a few tens of eV [8,9]. Losses due to excitation of vibrations at the surface, e.g. adsorbed molecules on the surface, are in the meV range. Hence this application requires high resolution and is called High Resolution EELS (HREELS).

In this work EELS has been used to detect plasmon losses. A plasmon is a collective oscillation of the conduction electrons. It has a characteristic frequency, which corresponds to an energy $E_{pl}$, depending on the free electron density of the sample. Energy losses due to plasmon excitations typically are in the range from 1 to about 30 eV. When an electron excites more than one plasmon its energy loss is $\Delta E = nE_{pl}$, where $n$ is the number of excited plasmons (1,2,3,...). Consequently, plasmon losses are characterized by a series of equidistant peaks in the loss spectrum. Since a plasmon oscillation requires interaction between many free or loosely bound electrons, it is characteristic for metals. In this work the appearance of a potassium-induced plasmon loss has been used to determine the coverage at which the potassium becomes metallic.

Plasmons can be divided in two groups: Bulk plasmon waves, which are three dimensional in space and occur in the bulk of the sample, and surface plasmon waves, which do not extend in the direction perpendicular to the surface. The surface plasmons occur at interfaces where the dielectric constant changes. The ratio of the frequencies of the surface plasmon and bulk plasmon ($\omega_{surf}/\omega_{bulk}$) then is $\sqrt{1+\varepsilon'}$, where $\varepsilon'$ is the dielectric constant of the medium outside the solid. For vacuum $\varepsilon'=1$ and the ratio becomes $\sqrt{2}$ [8,9].

The EELS spectra have been taken with the same CMA and electron gun as the Auger spectra, but now the energy range around the energy of the primary electrons is detected. Although EELS can be done with different primary energies, which correspond to different information depths, we have only used a primary energy of $100 \pm 0.5$ eV. Note that for such experiments a monochromatic primary electron beam is required, contrary to AES, where the position of the peaks is independent of the primary energy.
2.2.4 Ultraviolet Photoelectron Spectroscopy

With photoelectron spectroscopy, electrons are emitted by photoemission, i.e. ionization with photons, and one determines the binding energy of the emitted electrons (Figure 2.3) [8]. The spectrum displays the number of emitted electrons as a function of the binding energy. When X-rays are used as excitation source, the spectroscopy is called XPS and information about the core electrons of the sample is obtained. In UPS, the excitation source is ultraviolet light and, due to the smaller photon energy, one obtains information about electrons with a low binding energy, which are mainly the valence electrons.

The binding energy of the electrons is largely determined by the orbital energy of the electron. This depends on the atom or molecule to which the orbital belongs, making the spectroscopy element specific. The binding energy of a given electron is also subject to variations (typically a few eV), caused by different chemical environments of the respective atom or molecule. Such shifts are called chemical shifts and play an important role in the identification of the chemical state of an atom in the surface region of the sample. Because these shifts are caused by a shift in the orbital energies before the photoemission process has taken place, these shifts are often referred to as initial state effects. They contain information about the orbital energies of the electrons before photoemission.

The existence of a hole after photoemission also affects the kinetic energy of the emitted electron. The ion left after photoemission is in an excited state rather than in its energetic ground state. The ion relaxes and, for slow ionization processes, when the ion reaches its ground state during the photoemission process, the outgoing electron picks up the relaxation energy ('adiabatic approximation'). This leads to a higher kinetic energy and, as a consequence, a lower binding energy in the spectrum. For solids this relaxation may be divided into an intra-atomic part and an extra-atomic part. The relaxation energy of the free atom is the intra-atomic part. The extra-atomic part arises from additional screening of the hole by the surrounding electrons in the solid. For fast ionization processes, the final state is not the ground state of the ion, and the outgoing electron gains less kinetic energy, which leads to 'shake up' and 'shake-off' peaks. Such effects, arising from the excited ion after photoemission, are often referred to as final state effects and may be important, when spectra of the same atom in different environments are compared.

UPS mainly yields information about the valence electrons in the surface region. This includes the valence electrons originating from adsorbates, thus giving information about adsorbed atoms or molecules. Principally, the UPS spectrum of an adsorbate reflects its atomic or molecular orbital structure. This offers also a possibility to identify the chemical state of an adsorbed species: The spectrum of molecular oxygen exists of 4 or 5 signals, whereas the spectrum of double charged atomic oxygen (O\(^2^+\)) has only one peak (Chapter 5). The UPS spectrum of adsorbed noble gases hardly changes upon adsorption. This indicates a very weak interaction with the substrate with preservation of the original electronic structure of the noble gas atoms. This property is used to measure the surface potentials on heterogeneous surfaces (Chapter 3).
The kinetic energy of the emitted electrons above the sample follows from energy conservation (Figure 2.3):

$$E_{\text{kin}} = \hbar \nu - E_B^F - \phi$$  \hspace{1cm} (2.6)

where $\hbar \nu$ is the photon energy and $E_B^F$ is the binding energy of an electron with respect to the Fermi-level and $\phi$ is the work function of the sample. The UPS spectrum shows the electron distribution as a function of the binding energy $E_B^F$.

The total width of a UPS spectrum is a measure for the work function of the sample. The lowest kinetic energy of an electron above the sample is given by $E_{\text{kin,min}} = 0$. The energy levels above the Fermi level are empty, and consequently, there is no emission from these levels. Therefore, the electrons with the highest kinetic energy ($E_{\text{kin,max}}$) have $E_B^F = 0$. Putting this in Eq. 2.6 yields:

$$E_{\text{kin,max}} = \hbar \nu - \phi$$ \hspace{1cm} (2.7)
$$E_{\text{kin,min}} = 0$$

Subtraction gives the width of the spectrum:

$$W = E_{\text{kin,max}} - E_{\text{kin,min}} = \hbar \nu - \phi$$  \hspace{1cm} (2.8)

which becomes after rearrangement:

$$\phi = \hbar \nu - W$$  \hspace{1cm} (2.9)

where $W$ is the total width of the spectrum. According to Eq. 2.9, the work function is found from subtraction of the width of the UPS spectrum from the photon energy, which has a known value. All work functions presented in this work have been determined with this method.

**Figure 2.3 Energy diagram for the photoionization process.** The kinetic energy of an emitted electron above the sample is determined by its binding energy, the work function of the sample and the photon energy. In the experiment, the binding energy with respect to the Fermi level is determined.
2.2.5 Thermal Desorption Spectroscopy

In contrast to all spectroscopies described above, thermal desorption spectroscopy is not an electron spectroscopy, but a kinetic experiment. The sample is covered with a certain amount of the adsorbate and heated according to a preset temperature program. Upon heating, the adsorbate desorbs. The desorption rate and sample temperature are recorded simultaneously. At sufficiently high pumping rates, the desorption rate becomes proportional to the partial pressure of the adsorbate in the vacuum (residual gas), which is measured with a mass spectrometer. Thus, the signal of the mass spectrometer (at the corresponding mass) is proportional to the desorption rate. The area of a desorption signal is a measure of the coverage.

The desorption rate is given by the Polanyi-Wigner equation:

\[ r = k \theta^n = v \theta^n \exp\left(-\frac{E}{RT}\right) \]  \hspace{1cm} (2.10)

where \( r \) is the desorption rate (s\(^{-1}\)), \( k \) is the rate constant, \( \theta \) is the coverage, \( n \) is the reaction order, \( v \) is the preexponential factor (s\(^{-1}\)), \( E \) is the activation energy for desorption (kJ/mol), \( R \) is the gas constant (8.3 * 10\(^{-2}\) kJ/K) and \( T \) is the temperature (K).

Several analysis procedures can be applied to extract the kinetic parameters, i.e. activation energy and preexponential factor and the order of the desorption reaction, from the desorption spectra [10-15]. The activation energy for desorption equals the adsorption energy for unactivated adsorption. The preexponential factor contains information about the mobility of the adsorbate on the surface.

TDS spectra are usually taken with different initial coverages. From such a series of spectra, one can recognize some characteristic patterns, which correspond to a different desorption behavior. For zeroth order desorption (\( n=0 \) in Eq. 2.10), the desorption rate is independent of the coverage. The leading edges of the spectra taken with different coverages coincide and are truly exponential. The tailing edges are very steep. For Ag on Ru(001) zeroth order desorption has been found [16]. Zeroth order desorption occurs, when the adsorbate forms islands on the surface. Islands are formed when there is a strong lateral attraction between the adsorbed particles, that dominates over the adsorbate-substrate interaction. The desorption rate is determined by the number of atoms at the edges of the islands. During desorption, this number hardly changes, whereas the islands themselves become smaller and thus the coverage decreases. As a result, the desorption rate is independent of the coverage.

In first order TDS spectra, the temperature of the maximum is independent of the initial coverage, when there are no lateral interactions between the adsorbed particles. First order desorption is observed for randomly desorbing molecules or atoms, e.g. Au desorption from Ru(001) [16].

When adsorbed atoms associate before desorption, e.g. desorption of oxygen from a Rh or Pd surface [17,18], we expect second order desorption. The maximum of the spectra moves to lower temperature with increasing coverage.
When an adsorbate has non-equivalent adsorption sites on the surface with significantly
different adsorption energies, the TDS spectrum of this adsorbate consists of several peaks.
The peak at the highest desorption temperature corresponds to the state with the highest adsorption
energy and hence is the most stable one. In this way TDS gives information of the number
of different adsorption states on the surface and an estimate of the adsorption energy. However,
one should take care in applying such quick interpretations. Very often a more precise analysis
and comparison of data obtained with other techniques is necessary to obtain more reliable
information.

We have used TDS as additional information for distinction of the first potassium layer
from the higher layers on Rh(111). The second layer has a lower desorption energy than the
first and hence will appear at a lower temperature.

2.3 Sample Preparation

Preparation of the Rh(111) surface.
The cleanliness of the Rh surface has been checked by AES, work function measurements
and UPS (HeI and HeII). Initially, contaminating carbon and sulfur were detected with AES.
Sulfur has been removed by 15 min. of Ar sputtering at room temperature (ion energy = 1 keV,
2μA sample current), followed by 15 min. annealing at 950 K. This leaves some carbon on
the surface, which has been removed by heating at 950 K in an atmosphere of 1x10^-7 Torr
O_2 and subsequent heating into vacuum to 1325 K [19-21]. After a few cycles, sulfur is not
detected any more, leaving only carbon contamination. To remove this carbon, the sample
is heated for 10 min. at 950 K in vacuum, directly followed by 10 min. heating in an atmosphere
of 1x10^-7 Torr oxygen and a short flash to ~1300 K. To maintain the cleanliness of the sample,
the latter procedure has been repeated daily.
The clean Rh(111) surface is characterized by the spectra shown in Figure 2.4. In the Auger
spectrum no carbon (272 eV) is detected; the work function of the clean surface is 5.60 ± 0.04 eV.
In the UPS spectra, we find a high intensity at the Fermi-level, which is characteristic of d-metals.
The HeI and HeII spectrum look different. In the HeI spectrum the secondary electrons, which
have a low kinetic energy, become visible at higher binding energy. In the HeII spectra emission
due to He satellite lines is seen at high binding energy. The different cross-section for Rh
with HeI or HeII radiation causes the somewhat different shape of the Rh valence band emission.

Preparation of the potassium layers.
The potassium has been deposited on the Rh(111) surface, mostly at low temperatures (~50 K),
by heating the potassium source. Different potassium coverages can be obtained by varying
the evaporation time or by desorbing potassium from multilayers. Variation of the evaporation
time is less favorable because the resulting potassium coverage and cleanliness of the overlayer
Figure 2.4 UPS and Auger spectra of clean Rh(111). The position of the carbon KVV Auger signal is indicated; this sample is practically carbon free.

depends on some experimental parameters such as sample position, emission current of the potassium source, base pressure, which are hard to reproduce. In addition, short evaporation times are required for low potassium coverages and therefore their relative errors, and hence the relative error in the coverage, are larger. A better method is to deposit a few monolayers of potassium on the surface. We have used an evaporation rate of approximately 1 ML/min
and evaporation times of about 4 minutes. Then the sample is heated with a heating rate of about 2 K/s to a certain temperature in the range 300-900 K and annealed for one minute at that temperature. The resulting potassium coverage depends on the annealing temperature, according to the curve in Figure 2.5. For reproducibility it is important that the temperature program is always the same in the preparation, which has been achieved with a computer controlled temperature controller. Another advantage of this method is that contaminating CO or water, which desorbs from the potassium source during the potassium evaporation, is removed from the surface, because the surface is heated after potassium deposition.

The cleanliness of the potassium covered surface has been checked by AES, UPS (with HeII radiation) and work function measurements (Figure 2.6). In the HeII-UPS spectra, the K-3p peak appears around 18 eV. At high potassium coverage, the high intensity at the Fermi-level, which is characteristic of d-metals, disappears, due to attenuation of the photoelectrons of the Rh surface. In the Auger spectrum, a small difference around 250 eV is observed for low potassium coverages. With thick potassium layers, the Rh-Auger signals are completely suppressed.

**Determination of the potassium coverage**

The absolute potassium coverage has been determined from the intensity (area) of the main potassium peak in the integrated AES spectrum at 252 eV ($A_K$) (Figure 2.6 and 2.7), taken with an excitation energy of 1500 eV. Differentially measured Auger spectra are first integrated numerically. The main potassium peak in the Auger spectrum overlaps with the Rh signal at 256 eV ($A_{Rh}$). To correct for this overlap we write for the intensity of peak A in Figure 2.7:

$$A = A_K + A_{Rh}$$  \hspace{1cm} (2.11)

Assuming that the ratio between the Rh Auger signal at 302 eV and that at 256 eV does not change with potassium adsorption, we can write for the Rh signal at 256 eV:
Figure 2.6 UPS and Auger spectra of potassium covered Rh(111) at low (left) and high (right) potassium coverage. At low potassium coverage, only the K-3p level appears in UPS. In the Auger spectrum a small difference occurs around 250 eV. When a thick potassium layer is adsorbed, the Rh emission is suppressed in both the Auger and the UPS spectrum.
Figure 2.7 Integrated Auger spectrum of clean and potassium covered Rh(111). The main Auger signal of potassium at 252 eV overlaps with the Rh Auger peak at 256 eV. The intensity of the potassium AES signal ($A_K$) is found after subtracting the Rh contribution in this peak ($A_{Rh}$).

\[ A_{Rh} = RB \]  
(2.12)

where $R = A_{Rh}/B$, i.e. the ratio of both the Rh signals as in pure Rh. Its value, obtained from AES spectra of clean Rh(111), is $0.59 \pm 0.04$. The Auger intensity for potassium becomes:

\[ A_K = A - RB \]  
(2.13)

We define the Auger intensity ratio as the relative contribution of the potassium to the total spectrum:

\[ I = \frac{A_K}{A_K + B_{Rh}} = \frac{A - RB}{A + (1 - R)B} \]  
(2.14)

where $A_K$ is the intensity of the pure potassium Auger signal; $A$ and $B$ are the total intensities of peaks A and B in the Auger spectrum. We assume that this value is proportional to the potassium coverage. This is true, when the total peak intensity of the potassium and Rh signals is constant for increasing potassium coverage, or, in other words, when the attenuation of the Rh signal due to the increasing potassium coverage equals the increase of the potassium signal. The Auger intensity ratio ($I$) has been calibrated using the LEED patterns. The intensity ratio at the coverages where the potassium induced (2x2) and the ($\sqrt{3}\times\sqrt{3}$/R30°) LEED-patterns are most intense are assigned to a potassium coverage of 0.25 and 0.33 respectively. Note that the coverages are given as an atomic ratio, i.e. the number of potassium atoms divided by the number of Rh surface atoms. The relative error in the coverage is large for low potassium coverages, due to the overlap of the potassium AES signal with a Rh signal.
2.4 Characterization of the Potassium Overlayer.

*Thermal Desorption Spectroscopy*

Figure 2.8 shows a series of thermal desorption spectra of potassium with different initial coverages. At potassium coverages below 0.5 the spectrum shows one very broad peak between 400 and 1000 K with low intensity (Inset B). At higher coverages new peaks around 340 K occur, attributed to the higher potassium layers. The two peaks around 340 K in the spectrum at $\theta_K = 1.0$ (K/Rh atomic ratio) are assigned to the second and higher layers of potassium. At higher potassium coverages the second layer is not resolved any more.

The intense narrow peak appearing at high potassium coverages has the typical zeroth order desorption behavior with the characteristic exponential leading edges (Inset A). This feature and the fact that the peak only occurs at high potassium coverages indicate multilayer desorption of potassium: In the higher potassium layers, the potassium forms islands.

The broad peak, only appearing at low potassium coverages, originates from the first potassium layer. The high desorption temperature of the first potassium layer indicates a strong interaction between this layer and the Rh(111) surface. A very broad TDS signal, corresponding to the first layer, followed by a sharp zeroth order TDS signal from multilayer desorption has also been found for sodium, potassium and cesium on Al [22], potassium on Si [23], potassium

![Figure 2.8 Thermal desorption spectrum of potassium on Rh(111) at various potassium coverages. Inset A: At high potassium coverage, the desorption rate becomes independent of the potassium coverage (zeroth order desorption). Inset B: The enlarged desorption curve for $\theta_K=0.4$. At this coverage the desorption curve is a broad peak with low intensity.](image-url)
on Pt [24], and potassium on Ru [25,26].

Zeroth order potassium desorption is only observed at coverages above 0.5. The desorption temperature is close to the melting point of potassium at 1 atm. (336 K) [27]. Therefore, it is attributed to the desorption of bulk potassium. Although the density of bulk potassium in the first layer has already been reached at a coverage of about 0.33, the desorption behavior indicates, at this coverage the potassium atoms have a stronger interaction with the rhodium substrate than they have in bulk potassium.

**Work function**
The development of the work function of the Rh(111) surface with increasing potassium coverage is typical for alkali metals on transition metal surfaces [1-6] (Figure 2.9). At low coverages (θ_K < 0.1) a strong and nearly linear decrease of the work function is observed. This indicates an electron transfer from the alkali-metal to the substrate. The alkali metal becomes positively charged, leading to dipoles on the surface, directed opposite to the surface dipole layer. Hence, the work function decreases.

Another interpretation of the strong decrease of the work function at low potassium coverages has been given by Aruga and Murata [3]. They propose a strong polarization of the potassium atoms without electron transfer, due to hybridization of the K-4s and the K-4p_z level. Wimmer et al. [28] describe the alkali-substrate bond by a polarized covalent bond involving the valence s-level of the potassium and the s,d-like surface states of the substrate. Note that in both the ionization and the polarization model the potassium valence electrons are situated in the substrate surface region, and both models involve an overlap between the substrate and adsorbate valence orbitals. According to Fisher et al. [29], the overlayer-substrate spacing for potassium on Ni(111) is 2.7 ± 0.1 Å, corresponding to a potassium radius of 1.46 ± 0.10 Å. This value is much closer to the tabulated radius of potassium ions (1.33 Å [30]) than to the covalent radius of metallic potassium (2.31 Å). In the polarization models the 4s-valence level of adsorbed potassium is still occupied, and a more covalent-like radius for adsorbed potassium can be expected. Hence, we prefer the ionization model above the polarization model.

The ionicity of the potassium atoms decreases with increasing coverage, due to the repulsion between the positively charged potassium atoms, resulting in a smaller dipole moment per potassium atom. This leads to a minimum in the work function of 1.8 eV around a coverage of 0.2, and even to a light increase of the work function.

At coverages above 0.5 the work function has reached the value for metallic potassium (2.45 ± 0.05 eV) and remains constant with increasing potassium coverage.

**Ultraviolet photoemission spectroscopy**
In the UPS spectrum (HeII radiation with photon energy 40.8 eV) of adsorbed potassium on the Rh(111) surface, an additional signal is observed with a binding energy of around 18 eV, corresponding to the K-3p level (Figure 2.6 and 2.10). At higher potassium coverages, changes at the Fermi edge of the spectrum are also observed which are due to both damping of the
Characterization of K on Rh(111)

Figure 2.9 Development of the work function of the Rh(111) surface with potassium coverage. At low coverages the work function decreases rapidly with increasing potassium coverage, due to electron transfer to the substrate. At higher potassium coverage less charge is transferred, leading to the minimum in the curve. In the multilayer region (> 0.5) the work function has the value corresponding to metallic potassium.

Rh-emission and the contribution of the K-4s level. The spectra in Figure 2.10 are arbitrarily normalized at 15.6 eV for comparison purposes. The intensity at this energy is assumed to be independent of the potassium coverage.

At low coverages ($\theta_k < 0.35$) a peak at 18.4 eV is detected, which shifts to lower binding energy (17.8 eV) with increasing coverage. The shift of the K-3p level to lower binding energy has also been observed with other systems [31-33]. The coverage range, in which this shift is observed, corresponds to the broad TDS signal and, therefore, to the first potassium layer. The K-3p shift to lower binding energy is consistent with a depolarization of the potassium layer, due to the shorter distance between the potassium atoms at high coverages.

At potassium coverages between 0.33 and 0.5, the K-3p signal becomes smaller and its position remains constant at 17.8 eV. The TDS spectra show, that at these coverages no multilayer desorption occurs and, therefore, this K-3p signal is correlated to the completion of the monolayer structure.

Above a potassium coverage of 0.5, a second peak at a binding energy of 18.6 eV appears,
Chapter 2

**Figure 2.10** The K-3p signal in HeII-UPS (photon energy 40.8 eV). At low potassium coverages this peak shifts gradually from 18.4 to 17.8 eV. In the intermediate coverage range the binding energy remains 17.8 eV. At high coverage, the binding energy is 18.6 eV, characteristic for metallic potassium. The lowest curve corresponds to $\theta_K = 0$; the step in this spectrum arises from emission from the Fermi-level, excited by a He-satellite line.

The same position as in thick potassium films. Upon heating to 400 K this peak disappears and the K-3p level shifts to 17.8 eV. This is in full agreement with the multilayer desorption peak around 340 K in TDS (Figure 2.8). Therefore we conclude, that the peak at 18.6 eV is characteristic of the K-3p levels of bulk metallic potassium. The higher K-3p binding energy for bulk potassium is not in agreement with a simple electrostatic model, which predicts a higher binding energy for the positively charged potassium atoms at low coverages. It seems, that the proximity of the Rh substrate to the first potassium layer influences the binding energy of the potassium electrons, either through screening of the core hole, as proposed by Neuber et al. [32], or by a electrostatic repulsion of the electrons in the surface, similar to the shifts observed for potassium salts [34]. In both viewpoints, potassium has no bulk properties at a coverage of 0.5; there is a significant influence of the Rh substrate on the adsorbed potassium.

The K-3p level the UPS spectra reveals three different phases of potassium with increasing coverage:

1) The K-3p signal gradually shifts from 18.4 eV at zero coverage to 17.8 eV at a coverage...
Characterization of K on Rh(111)

of 0.35. In this coverage range the potassium is ionic.
2) In the coverage range between 0.35 and 0.5 the K-3p signal remains at 17.8 eV.
3) At coverage above 0.5 a new K-3p signal appears at 18.6 eV, corresponding to metallic potassium.

**Low Energy Electron Diffraction**

When potassium is adsorbed on the Rh(111) surface, LEED patterns corresponding to a (2x2), a ($\sqrt{3}$x$\sqrt{3}$/R30$^\circ$) and a (2x2)-like surface structure are observed with increasing potassium coverage. The (2x2) structure at low potassium coverage is assigned to a potassium coverage of 0.25. The nearest neighbor distance of the potassium atoms is 5.38 Å. This is a more open structure, compared to bulk metallic potassium, which has a nearest neighbor distance of 4.61 Å.

At somewhat higher potassium coverage the ($\sqrt{3}$x$\sqrt{3}$/R30$^\circ$) pattern occurs. This structure of the potassium overlayer corresponds to a nearest neighbor distance of 4.66 Å between the potassium atoms, which is about the value for pure potassium (4.61 Å). However, the potassium density in this overlayer is 6% higher than in the (110) plane of metallic potassium, the most densely packed plane of the potassium bcc-crystal. This may seem contradictory, but the (110)-plane of potassium has a lower density than the hexagonally closed packed structure of the (111)-fcc crystal face. A compression of adsorbed alkali metal on Al [22], Ni [35] and Pt [36] surfaces has also been reported.

At a potassium coverage of 0.5, according the Auger calibration described earlier (Section 2.3), a (2x2)-like LEED pattern is observed. Probably this corresponds to a compressed potassium layer with potassium atoms in contact with the Rh atoms and in a higher lying plane.

![2x1 LEED](image_url)

**Figure 2.11** The 2x1 overlayer structure and the corresponding LEED-pattern. On the surface many domains and therefore all three possible orientations of this structure are present, resulting in a LEED pattern that looks like a 2x2 pattern. The solid dots indicate the diffraction pattern of the Rh(111) surface; the open dots are induced by the 2x1 adsorbate structure.
A (2×1) adsorbate structure on the (111) plane of a fcc-crystal gives the same LEED pattern as the (2×2) structure. In the (2×1) structure each atom in each second row of the substrate is covered by the adsorbate, giving the LEED-pattern given in Figure 2.11. This pattern can have three different orientations, 60° rotated with respect to each other. As there are several domains of ordered potassium, all three orientations will be seen simultaneously, resulting in a LEED pattern, which looks just like the (2×2)-pattern.

Such a (2×1) structure matches the potassium coverage of 0.5 found with AES. However, this requires a nearest neighbor distance of 2.69 Å between the potassium atoms on Rh(111) (Figure 2.11). Such a small radius is only possible with completely ionized potassium (ionic diameter of $K^+ = 2.66$ Å), which is very unlikely at such high coverages. A (2×2) structure with two inequivalent potassium atoms per unit cell allows a somewhat larger distance between the potassium atoms. We can put a potassium atom in the centre of the equilateral triangles.
that form the unit cell, when the diameter of the potassium particles is less than 3.10 Å. However, there is no reason why the potassium should occupy only one of the two available sites in the unit cell. Occupation of both sites results in a total potassium coverage of 0.75 (Figure 2.12), which is much larger than found by AES. In addition, the maximum diameter (3.10 Å) is still much lower than the diameter of potassium in the metallic phase (4.61 Å), suggesting that for this configuration the potassium must be ionic, which makes this configuration improbable.

When the extra potassium atoms are placed in a higher lying plane above the surface, a larger diameter of the potassium atoms is possible. Besides, due to this larger diameter, the second adsorption site in the unit cell we had before, is now automatically blocked when one of the two sites is occupied (Figure 2.13). This suggests that at a potassium coverage of 0.5 the potassium is not adsorbed in one plane, but at different heights from the surface. This potassium structure still can be compressed with respect to bulk metallic potassium. A reconstruction of the Rh surface is possible, but cannot be derived from our measurements.

As indicated in Figure 2.5, all LEED patterns appear below multilayer coverage. The sharp decrease of the Auger ratio at 340 K corresponds to the multilayer desorption in TDS. This suggests, that for the (2x2)-like structure all potassium atoms interact with the Rh surface. Probably, we have differently adsorbed potassium atoms: direct on the rhodium surface and between the previously adsorbed potassium. We do not resolve an additional TDS signal, which would be indicative for such and adsorption state, possibly due to the low intensity of the potassium desorption signal.

**Electron Energy Loss Spectroscopy**

Figure 2.14 shows a set of EELS spectra for clean and potassium covered Rh(111) at different coverages, taken with a primary energy of 100 eV. In the spectrum for clean Rh(111) four characteristic loss features at 8.0, 15.5, 23.5 and 32.5 eV are observed. The loss at 8.0 eV is attributed to the Rh-bulk-plasmon excitation. The other losses are observed at energies corresponding to multiple excitations (Section 2.2.3), but their relative energies are too small (and not adequately weighed) to be assigned to pure plasmon replicas. Therefore an overlap with interband transitions [9] is assumed.

With increasing potassium coverage to 0.5 an attenuation of these Rh features is observed together with a slight shift to lower loss energy (7.0 eV), correlated with the changed electronic structure due to the adsorbed potassium in the surface region: As the primary electrons have an energy of 100 eV, the information depth is limited. Simultaneously two new loss features at 20.5 and 29.0 eV appear due to the ionization of the K-3p and K-3s levels respectively. Up to a potassium coverage of 0.33, no evidence for a plasmon loss originating from potassium is observed. A first indication of an excitation in the low energy region (~3 eV) characteristic of metallic potassium is seen at a potassium coverage of 0.5 (knee). Only above this coverage a plasmon loss of 2.5 eV, indicative of metallic potassium [22], is detected.

The EELS experiment also reveals three different potassium phases:
1) At coverages below 0.33 only potassium induced loss features corresponding to the ionization
Figure 2.14 Electron energy loss spectra of the potassium covered Rh(111) surface at various coverages. At low potassium coverage, there is no indication of a potassium plasmon loss, indicating the non-metallic character of potassium. At a potassium coverage of 0.5, the first indication for a potassium plasmon loss is found (knee) which develops to a clear potassium induced plasmon loss at 2.5 eV at high coverages, indicating that only at coverages above 0.5, the adsorbed potassium is metallic.

of the K-3p and K-3s levels occur.

2) In the range between 0.33 and 0.5, a loss peak at 7.0 eV (shifted 1 eV downwards with respect to the loss for clean Rh(111)) is observed and its position remains constant with increasing potassium coverage up to 0.5. This indicates a change in the electronic structure of the substrate in the surface region. The plasmon loss characteristic of metallic potassium is not observed.

3) Above a potassium coverage of 0.5 a clear potassium induced plasmon loss structure at
2.5 eV is observed, indicating a metallic character of the potassium layer.

The EELS experiments show, that the metallic character of the adsorbed potassium layer only is found at coverages above 0.5. This coincides with the constant work function and with the binding energy transition of the K-3p level in UPS from 17.8 eV to 18.6 eV. At these coverages, also the multilayer desorption peak in TDS is seen: Only in the multilayer phase, the potassium has a metallic character.

**Auger Electron Spectroscopy**

The measured Auger signal is the sum of the contribution of the Auger electrons (pure Auger signal) and of the Auger electrons that have lost energy, like the primary electrons in the EELS experiment. In addition, the limited resolution of the spectrometer leads to a broadening of the measured signal.

The shape of the pure Auger signal is determined by the occupation of the electronic levels participating in the Auger deexcitation process. In particular, when valence levels of metals are involved, the shape of the Auger signal strongly depends on the energy distribution of the electrons in the valence band. The deconvolution of the measured Auger spectrum with an EELS spectrum results in an improved Auger lineshape. One considers the measured signal as the convolution of the pure Auger signal with the spectrometer response (= the signal of the spectrometer after a sharp pulsed input) and the loss processes, that an Auger electron undergoes. Assuming that these loss processes for an Auger electron are the same as for a primary electron, the EELS spectrum, taken with a primary energy equal to the energy of the Auger electron, describes the non-ideal behavior of the Auger electron. The limited resolution of the spectrometer (\(\Delta E/E = 0.5\%\)) is reflected in the width of the elastic peak.

The deconvolution is most easily calculated via the Fourier transforms of the spectra. The Fourier transform of the convolution of two functions equals the product of the Fourier transforms of these functions. Thus, the Fourier transform of the measured Auger spectrum is given by the product of Fourier transform of the pure Auger signal and Fourier transform of the EELS spectrum. Reversely, dividing the Fourier transform of the measured signal by the Fourier transform of the EELS spectrum results in the Fourier transform of the pure Auger signal. The deconvoluted Auger signal itself is found by backtransformation. For the numerical Fourier transformation the Fast Fourier Transform (FFT) algorithm has been used [37].

For lineshape analysis of the potassium (LMM) Auger signal at 250 eV the Auger spectra are taken with a primary energy of 1500 eV and a primary current of -1 \(\mu\text{A}\) in integrated mode in the energy range 200 - 320 eV. (The difference from the value in Section 2.3 (252 eV) arises from the different reference, here we refer to the maximum of the integrated signal, in Section 2.3 to the minimum of the differentiated signal). Appropriate background subtraction correcting for the contributions of secondary electrons has to be done for both the Auger and the EELS spectrum, because the FFT algorithm requires zero intensity at the start and end of the spectrum. Since the CMA allows no operation with a constant pass energy, the resolution deteriorates with increasing kinetic energy. Hence, the intensities of the signals become
proportional to the energy, which is corrected for by division each point of the spectrum by its energy. We have used an EELS spectrum taken at a primary energy of 250 eV, assuming a constant resolution (peak width) for the whole spectrum.

Figure 2.15 shows the Auger spectra after deconvolution with the EELS spectrum. From the difference spectrum we see that the measured Auger peaks are structurally deformed at the low energy side, which is correlated with loss processes.

At first sight it seems that the potassium signal shifts to lower energy with increasing coverage, but as already mentioned in Section 2.3 the potassium Auger signal overlaps with a Rh signal. For an accurate analysis of the lineshape of the potassium signal we have to decompose the signal in a Rh and potassium part and subtract the Rh part from the spectrum. Assuming that the lineshape of the Rh signal does not change with increasing coverage, we apply the same procedure as described in Section 2.3. After subtraction of the Rh contribution the position of the potassium signal remains constant at 250 eV (Figure 2.16, left).

Although in the potassium (LMM) signal the K-3p electrons are involved, we cannot resolve a development of the lineshape of the potassium (LMM) Auger signal correlated to the downward shift of the K-3p signal in UPS at low coverages. Nevertheless, some differences can be recognized between the lineshape at low and high coverage. At low coverage, the potassium signal shows two features around 232 eV and 250 eV. At a potassium coverage of ~1.5 (atomic K/Rh ratio), a small shoulder on the low energy side suggests the existence of two different potassium signals. This becomes clearer after differentiation. Figure 2.16 shows the differentiated signals at a potassium coverage of 0.15 (middle) and 1.5 (right). At the low potassium coverage, only two features are distinguished, whereas at high coverage, where the potassium has become
Characterization of K on Rh(111)

Figure 2.16 Deconvoluted Auger spectra of potassium on Rh(111) after subtraction of the Rh contribution (left). At a coverage of 0.15, only two potassium signals are detected (middle). Increasing the potassium coverage to 1.5 results in additional potassium signals at ~4 eV lower kinetic energy (right). This is most clearly seen in the differentiated spectra.

metallic, we see for both features a new signal at ~4 eV lower kinetic energy.

The lower kinetic energy for the Auger electron is qualitatively consistent with the higher binding energy of the K-3p level for metallic potassium. The kinetic energy of the Auger electron is given by Eq. 2.1. The values for $E_2$ and $E_3$ are related to the binding energy of the K-3p electrons, which has become larger according to UPS. Thus, the resulting kinetic energy of the Auger electron corresponding to the metallic phase of potassium is smaller.

Potassium in the first layer has another chemical environment compared to the metallic phase, giving rise to a chemical shift in Auger and UPS spectrum. For purely electrostatic effects, the shifts in Auger and UPS are equal. The energy difference between a photoemission signal and an Auger signal is the Auger parameter [38,39]. Since the photoemission signal and the Auger signal shift equally due to electrostatic effects, a changed Auger parameter indicates changes in the relaxation process. The difference between the shift in UPS (~0.8 eV kinetic energy) and Auger (~ -4 eV) is twice the difference in the extra-atomic final state relaxation. Assuming that the comparison with the HeII-UPS and the electron excited Auger is allowed, we estimate a change in the Auger parameter of -3.2 eV, corresponding to a change of -1.6 eV in the relaxation energy. The transition in the K-3p binding energy is explained by a less effective screening of the core holes in the metallic potassium phase. It supports the idea of a strong interaction of the first potassium layer with the Rh substrate, that is responsible for the more effective screening of the electron hole in the first potassium layer.
2.5 Conclusions

The properties of adsorbed potassium on Rh(111) depend on the potassium coverage. We find with TDS, work function measurements, UPS, EELS, AES three different phases of adsorbed potassium on Rh(111). For study of the promoter effect, however, only the low coverage range is relevant.

At potassium coverages below 0.2, the work function decreases nearly linearly from 5.60 eV to 1.80 eV, which indicates an electron transfer from the potassium to the Rh substrate, leading to potassium ions. In the coverage range between 0.2 to 0.33, a minimum in the work function is observed indicating a decrease in the extent of the electron transfer, due to the repulsive interaction between the positively charged potassium atoms. In this coverage range also a (2×2) and a (√3×√3/R30°) LEED pattern are observed. The UPS spectra show a gradual shift of the K-3p level from 18.4 eV to 17.8 eV, also correlated with the decreasing positive charge of the potassium atoms. We have no evidence for the existence of a bulk-like potassium phase, neither from EELS data nor from UPS data. TDS indicates, that at a potassium coverage of 0.33 all potassium interacts with the Rh surface.

At potassium coverages between 0.33 and 0.5 a surface structure transition occurs. In this coverage range a (2×2)-like LEED pattern develops, suggesting an increase of the adsorbate-substrate distance and an eventual compression of the potassium. The Rh plasmon energy has shifted from 8.0 eV to 7.0 eV and the position of the K-3p UPS-signal remains at 17.8 eV. These effects are attributed to a changed electronic structure in the surface region. The absence of the typical potassium plasmon loss and the K-3p UPS-signal at 18.6 eV indicate that the potassium is not metallic, although the density of bulk metallic potassium already has been reached at a coverage of 0.33. At this coverage, the rhodium influences all potassium atoms, as also can be inferred from the higher desorption temperature in TDS with respect to multilayer desorption.

At potassium coverages above 0.5, metallic potassium is identified. It is characterized by the multilayer desorption peak in TDS, a K-3p signal in UPS at 18.6 eV, the development of a potassium plasmon loss at 2.5 eV and a constant work function of 2.45 eV, which corresponds to the value for metallic potassium. In this coverage range the potassium Auger signals at 250 eV and 232 eV show a shoulder at the low binding energy side indicating that they are composed of at least two peaks. This shoulder is absent at low potassium coverages and is related to the higher binding energy of the K-3p level in UPS in the metallic potassium phase.
References

Chapter 2

Photoemission of Adsorbed Xenon, Krypton and Argon on Clean and Potassium-Covered Rhodium.

3.1 Introduction

The results of the previous chapter illustrate that the properties of adsorbed potassium at high coverages differ from that at low coverage. The application of potassium as promoter in catalysts requires a low potassium coverage. Therefore we now concentrate on the low coverage range. The strong work function decrease at low potassium coverages suggests an electron transfer from the potassium atoms to the Rh substrate (Sect. 2.3.2). Due to this electron transfer the potassium atoms on the surface become positively charged and the electrostatic potential on the surface is expected to be influenced locally around the adsorbed potassium atoms. Calculations of the electrostatic potential on an infinite jellium surface with a single potassium atom show such a local variation in the vicinity of the potassium atom (Chapter 1) [1-4]. This local variation of the surface potential is reflected in the local work function.

In analogy to the definition of the work function, we define the local work function as the energy needed to transfer an electron from the Fermi level to a given position just outside the surface [5]. Since the electrostatic potential on a potassium-covered surface varies locally in the vicinity of an adsorbed potassium atom, the local work function becomes dependent on the position, which is referred to in the term local. The position of adsorbed molecules is just outside the surface (~ 2 Å) and therefore the local work function is the effective work function experienced by adsorbates, such as the reactants of a catalytic reaction. The local work function is the energy needed to transfer an electron from the solid to a given adsorbate site and obviously is important for understanding promotion in catalysis.

The local work function can be determined experimentally by means of photoemission of adsorbed Xe (PAX) [5-9]. This method has been applied to the system K/Ru(001) [8], which is very similar to our K/Rh(111) system. When Xe was adsorbed on a Ru(001) surface covered with a few (< 5) at% of potassium, three Xe states were observed with UPS, attributed to Xe on bare Ru(001) patches, Xe on Ru next to a potassium atom and Xe on a potassium atom. From the difference in binding energy of the Xe-5p_{1/2} electrons at the three different sites, that arises from the different electrostatic potentials at the Xe adsorption sites
(Sect. 3.2), the local work function at the Ru sites next to a potassium atom appeared to be 0.57 eV lower than at the bare Ru sites. This indicates a potassium-induced lateral heterogeneity of the surface as a consequence of the short range electrostatic effect of the potassium adsorption.

With photoemission of adsorbed Xe, the local work function is probed at the Xe adsorption site. However, the distance between the potassium atom and the coadsorbed Xe is completely determined by its own radius and by the radius of potassium. The local work function is measured at a Xe specific distance from an adsorbed potassium atom and is averaged over the volume of a Xe atom. In this work not only Xe, but also the smaller Kr and Ar are used, allowing a variation of the distance between the potassium and the probe atom. Consequently, the local work function is probed at different distances from potassium and we get insight in the variation of the local work function in the vicinity of an adsorbed potassium atom. Since Kr and Ar are noble gases as well, the adsorption is of the same nature as that of Xe, suggesting that the same interpretation as for Xe can be applied to Kr and Ar as well. This is checked by adsorption of Xe, Kr and Ar on clean Rh(111).

In the next section the photoemission of adsorbed noble gases and the relation to the local surface potential is described by example of Xe. Then the adsorption of Xe, Kr and Ar on clean and potassium precovered Rh(111) are discussed according to this method, in order to determine the variation of the local work function in the vicinity of the adsorbed potassium atoms.

### 3.2 Photoemission of Adsorbed Noble Gases as a Local Work Function Probe

At sufficiently low temperatures (< 90 K) Xe can adsorb on a surface and the adsorbed species produces a signal in the photoemission spectrum. The measurement of the local work function with photoemission of adsorbed Xe is based on the experimental observation that the ionization energy of adsorbed Xe, i.e. the binding energy of the Xe electrons with respect to the vacuum level ($E_B^v$), is practically independent of the substrate [5]. In UPS, however, one measures the binding energy with respect to the Fermi-level of the substrate ($E_B^F$). These energies differ by the work function. Since the Xe atom only 'sees' its own adsorption site, it feels the work function at the adsorption site about 2 Å in front of the surface and we can write for the ionization energy ($E_B^v$):

$$ E_B^v = E_B^F + \varphi_{loc} \tag{3.1} $$

where the subscript "loc" reflects that the work function is measured locally.

With UPS, using HeI-UV light (21.21 eV photon energy), only the 5p electrons of Xe
can be detected. Due to the spin-orbit coupling, the UPS spectrum of adsorbed Xe consists of a doublet corresponding to the $5p_{1/2}$-state at the highest binding energy and the $5p_{3/2}$-state at 1.3 eV lower binding energy (Figure 3.1). For the determination of the local surface potentials, usually the $5p_{1/2}$-peak is used as reference, because its shape does not change significantly with increasing Xe coverage. The $5p_{3/2}$-peak may be split into the $m_\ell=1/2$ and $m_\ell=3/2$ components due to a lateral interaction between the adsorbed Xe atoms [10-12]. The absence of the splitting in the $5p_{3/2}$-peak is indicative of a weak lateral interaction between the Xe atoms.

The value for the ionization energy ($E^V_B$) of the Xe-$5p_{1/2}$ electrons is obtained by summation of the macroscopic work function of a homogeneous surface and the binding energy with respect to the Fermi-level, given by the UPS spectrum. On the homogeneous surface only equivalent Xe adsorption sites exist with a local work function that equals the macroscopic work function. In angle integrated photoemission, the ionization energy of Xe was found to be $12.3 \pm 0.15$ eV for at least 25 substrates [5], independent of their work function. This value may differ somewhat from the value found with an angle resolved measurement.

The substrate-independent ionization energy ($E^V_B$) of adsorbed Xe suggests a direct connection between the binding energy ($E_B^F$) of the Xe electrons, that is measured with UPS and the local work function on heterogeneous surfaces. Suppose we have a surface with two inequivalent Xe adsorption sites, having different local work functions. According to Eq. 3.1 the ionization energy of Xe at each site can be written as:
\[ E_{B,1}^V = E_{B,1}^F + \Phi_{loc,1} \]
\[ E_{B,2}^V = E_{B,2}^F + \Phi_{loc,2} \]  

(3.2)

Since \( E_B^V \) is the same for both Xe atoms, we find after subtraction:

\[ 0 = (E_{B,1}^F - E_{B,2}^F) + (\Phi_{loc,1} - \Phi_{loc,2}) \]
\[ \Delta E_B^F = -\Delta \Phi_{loc} \]  

(3.3)

We see, that, due to the constant ionization energy \( E_B^V \) for adsorbed Xe, a difference in local work function is directly reflected in the binding energy of the Xe electrons, and, reversely, a shift or splitting of the Xe signal can be explained in terms of a shift or difference in the local work function at the different Xe sites. The energy diagram in Figure 3.2 illustrates this property of adsorbed Xe.

The physical background to this behavior is the spatial size of the Xe atoms and the interaction between the adsorbed Xe and the metal surface. For Xe the radius is large enough to keep its electrons out of the surface dipole layer, so there is no influence of this dipole layer [5]. Since Kr and Ar are smaller, they may in contrast to Xe, experience the surface dipole layer. This question is dealt with in the next section.

The weak physisorptive bonding of Xe on the surface ensures that the electronic structure of adsorbed Xe is practically the same as for gaseous Xe, which is of course independent of the substrate. There is no significant orbital overlap between the adsorbed Xe atoms and the substrate.

Figure 3.2 Energy diagram of adsorbed Xe on sites with different work functions. Due to the constant ionization energy of adsorbed Xe \( E_B^V \), the difference in work function is reflected in the binding energy of the Xe electrons with respect to the Fermi level of the metal substrate \( E_B^F \). Reproduced from Wandelt [5].
The ionization energy of adsorbed Xe (12.3 eV) is 1.14 eV lower than the value for gaseous Xe (13.44 eV) [13]. This is ascribed to an extra-atomic relaxation effect for adsorbed Xe by the metal substrate. For adsorbed Xe, the hole in the Xe-ion is more efficiently screened than in gaseous Xe, due to the vicinity of the highly polarizable metal substrate. The electron escaping from the adsorbed Xe profits from this relaxation energy and its kinetic energy increases, which is converted to a lower binding energy in the UPS-spectrum. The image potential determines the extra-atomic relaxation energy, which is independent of the substrate.

The large variation in dipole moment for adsorbed Xe on various substrates (0.7 D on Pd(111), 0.6 D on Pd (100), 0.44 D on Pd(110) [14], 0.24 D on Al(111) [15], in the zero-coverage limit for Xe, and 0.24 D on Rh(111) (Sect.3.3), 0.13 D on Cu₃Pt(111) [16] and on Ni(100) [17] for a Xe monolayer) does not lead to large deviations in the measured ionization energy of adsorbed Xe: it remains within the error of 0.15 eV [5]. This suggests that the influence of the polarization of the Xe atom itself on the intra-atomic relaxation is insignificant. Consequently, the total relaxation for adsorbed Xe is completely determined by the extra-atomic relaxation, which is substrate independent.

On a heterogeneous surface - where different adsorption sites are available - the noble gases adsorb first on the most stable adsorption sites, i.e. the ones with the largest adsorption energy. When these sites are all occupied, adsorption takes place on the next stable site, if the temperature is low enough. Thus, the order of occurrence of the different adsorption states in the UPS spectra of noble gases with increasing coverage reflects the order of the stability (adsorption energy) for the different adsorption sites.

A complete monolayer of noble gas on the surface contains quantitative information about the distribution of the several noble gas adsorption sites with different local work functions on the surface. This requires a good separation of the first noble gas layer from the higher layers and therefore the adsorption energy for the first noble gas layer must be significantly higher than for the higher layers. When the difference in adsorption energy between the first and higher layers is small, the first and higher layers on the surface are formed simultaneously. This disturbs the spectrum of the first noble gas layer and makes a proper analysis of the first layer more complicated or even impossible.

### 3.3 Ultraviolet Photoemission of Adsorbed Noble Gases on Clean Rhodium(111).

**Ionization energies of adsorbed noble gases.**
The UPS spectra of adsorbed Xe, Kr and Ar (at 45 K) on freshly prepared Rh(111) are shown in Figure 3.3. The Rh background has been subtracted. The binding energy of the Xe-5p_{1/2} electrons is 6.70 eV and that of the 5p_{3/2} electrons is 5.40 eV with respect to the
Fermi-level of the Rh substrate. The spin-orbit splitting of 1.3 eV has been found earlier for adsorbed Xe [5-9,11] and gaseous Xe [13]. The fact that the spectra exhibit only one Xe-5p doublet up to large exposures (about 8 L) is an indication for the homogeneity of the Rh(111) surface. The new doublet appearing after higher exposures is accompanied by an intensity decrease of the former Xe signal and hence corresponds to Xe in the second layer.

The position of the Xe-5p$_{1/2}$ signal in the UPS spectrum at low Xe coverage and the macroscopic work function of the clean Rh(111) surface (5.60 eV) yield, according to Eq. 3.1, a Xe ionization energy of 12.30 eV, in full agreement with the value found on many other substrates [5]. At high Xe coverage, the binding energy of the Xe-5p$_{1/2}$ signal is 0.05-0.1 eV higher, due to small lateral interactions between the Xe atoms. The peak positions at the lowest possible coverage should be used for probing local work functions.

The position of the Xe-5p$_{1/2}$ signal is somewhat broader than the 5p$_{3/2}$-signal, but approximately symmetric up to a Xe coverage of 1 ML, indicating that the Xe does not form islands, but rather adsorbs randomly on the Rh(111) surface. The absence of Xe-induced LEED patterns for Xe on Rh(111) supports this conclusion. Contrary to this, adsorbed Xe on NiAl(110) [18] or Al(110) [19] forms islands. In these cases both a splitting of the 5p$_{3/2}$ peak in UPS and a Xe-induced LEED pattern are observed.

The Kr signal consists also of a doublet of two spin-orbit states, namely the 4p$_{3/2}$ and 4p$_{1/2}$ state with an energy difference of 0.68 eV (Figure 3.3, top right), close to the value for gaseous Kr (0.67 eV) [13] and for adsorbed Kr on Ni(110) (0.7 eV) [20]. Similar to the Xe spectra, no new Kr-doublet is observed before the second layer starts to grow, thus indicating that the Kr is adsorbed on a homogeneous surface. As a reference for the local work function measurements we take, in analogy with Xe, the maximum of the Kr-4p$_{1/2}$ signal at low Kr coverage (7.70 eV), corresponding to an ionization energy for Kr of 13.3 eV. For the measurement of local work functions with Kr, in the same way as with Xe, this ionization energy must be substrate independent. Unfortunately, only few data on adsorbed Kr are available. The ionization energy for Kr on Cu$_3$Pt(111) (work function: 5.30 eV), measured with the same apparatus, is also 13.3 eV [16], in good agreement with the concept of the substrate independent ionization energy. An ionization energy of 12.9 eV has been reported [20] for Kr on Ni(110), using angle resolved UPS, which may cause the somewhat different value from the one found with our angle integrated measurement (Sect. 3.2). It suggests, that Kr can also be used as a probe for the local work function.

Contrary to Xe and Kr, the UPS spectrum of adsorbed Ar on Rh(111) consists of a single peak (3p) that is slightly asymmetric on the high binding energy side (Figure 3.3, bottom left). For gaseous Ar the difference between the 3p$_{3/2}$ and 3p$_{1/2}$ peak is 0.18 eV [13]. Adsorption causes broadening of the signals and we are not able to resolve such a small spin-orbit splitting for the adsorbed species with our spectrometer. The uniform shape of the Ar signals is, like for Xe and Kr, an indication of a homogeneous surface. The second signal observed at higher coverages is only detected at Ar pressures above 10$^{-5}$ Torr and
corresponds to higher Ar layers, as can be inferred from the intensity decrease of the former signal as soon as it appears.

At low Ar coverages, the position of the maximum of the 3p signal is 8.70 eV, corresponding to an ionization energy of 14.3 eV. This value must be substrate independent for application of Ar as a local work function probe. For Ar on Ni(100) (work function: 5.30 eV) [17] and on Ni(110) [20] the same value has been reported, while for Ar on Ru(001) (work function: 5.65 eV) and on a monolayer of Cu on Ru(001) (work function: 4.95 eV) a value of 14.4 eV has been found [21], close to our value of 14.3 eV. This strongly suggests that the ionization energy truly is substrate independent, allowing the use of Ar as well for measurement of local work functions.

The substrate independent ionization energy for all three noble gases suggest, that the
Table 3.1 Ionization energies of gaseous [13] and adsorbed noble gases. The difference is the extra-atomic relaxation energy due to the presence of the metallic Rh surface.

<table>
<thead>
<tr>
<th></th>
<th>ionization energy</th>
<th>relaxation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gas</td>
<td>ads.</td>
</tr>
<tr>
<td>Xe-5p_{1/2}</td>
<td>13.4</td>
<td>12.3</td>
</tr>
<tr>
<td>Kr-4p_{1/2}</td>
<td>14.7</td>
<td>13.3</td>
</tr>
<tr>
<td>Ar-3p</td>
<td>15.8*</td>
<td>14.3</td>
</tr>
</tbody>
</table>

*referenced to the Ar 3p_{3/2} level of gaseous Ar.

surface dipole does not extend to the adsorption distances of the noble gases, or that the surface dipole contribution to the binding energy of the noble gas electrons is substrate independent.

For all three noble gases, we find a lower ionization energy for adsorbed atoms than for gas phase atoms. The difference equals the extra-atomic relaxation, arising from polarization of the metal substrate (Sect. 3.2). Table 3.1 summarizes the ionization energies for gaseous and adsorbed Xe, Kr and Ar and the extra-atomic relaxation energies for the adsorbed noble gases. In first approximation, the extra-atomic relaxation is determined by the image potential stabilization of the photoionized atom, which is inversely proportional to the distance to the surface. Hence, we expect for Xe the smallest relaxation energy and for Ar the largest, which is in agreement with the values we determined from our measurements.

Dipole moment of adsorbed noble gases

Upon noble gas adsorption, the macroscopic work function decreases, due to the induced dipole moment, or due to a charge transfer from the noble gases to the substrate, which are responsible for the physisorption [22, 23]. The average dipole moment of the adsorbed noble gas atoms can be calculated from the work function decrease for a complete noble gas

Table 3.2 The decrease in work function after adsorption of a full monolayer of Xe, Kr and Ar on clean Rh(111) and the calculated average dipole moments. The local electrostatic field is about the same for all three noble gases: The different dipole moments are therefore due to the different polarizabilities of the noble gases. The Van der Waals radii and polarizabilities are taken from [24].

<table>
<thead>
<tr>
<th></th>
<th>Δφ</th>
<th>r</th>
<th>N</th>
<th>$\bar{\mu}$</th>
<th>α</th>
<th>$E_{loc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>eV</td>
<td>Å</td>
<td>10^{14}</td>
<td>10^{-29}</td>
<td>10^{-24}</td>
<td>10^7 V/cm</td>
</tr>
<tr>
<td>Xe</td>
<td>0.54</td>
<td>2.2</td>
<td>5.96</td>
<td>8.01</td>
<td>0.24</td>
<td>4.0</td>
</tr>
<tr>
<td>Kr</td>
<td>0.47</td>
<td>2.0</td>
<td>7.22</td>
<td>5.76</td>
<td>0.17</td>
<td>2.5</td>
</tr>
<tr>
<td>Ar</td>
<td>0.33</td>
<td>1.9</td>
<td>8.00</td>
<td>3.87</td>
<td>0.11</td>
<td>1.6</td>
</tr>
</tbody>
</table>
monolayer. The Helmholtz equation relates the work function decrease and average dipole moment of the adsorbed particles:

\[
\bar{\mu} = \frac{\varepsilon_0 \Delta \varphi}{N}
\]  

(3.4)

where \(\bar{\mu}\) is the average dipole moment, \(\varepsilon_0\) is the dielectric constant in vacuum \((8.85 \times 10^{-14} \text{ C/V cm})\), \(\Delta \varphi\) is the induced potential difference of the dipole layer in Volt, which is numerically equal to the work function change in eV, and \(N\) is number of noble gas atoms per cm\(^2\). The number of atoms in a monolayer is estimated from the hexagonally closed packed structure. The radius of the atoms is given by the Van der Waals radius of the respective atoms [24]. The dipole moments of Xe, Kr and Ar on Rh(111) are given in Table 3.2.

From the dipole moments and the polarizabilities of the noble gas atoms, we can calculate the local electrostatic field, felt by the noble gas atoms (Table 3.2). The local field is given by:

\[
E_{\text{loc}} = \frac{\mu}{4\pi \varepsilon_0 \alpha}
\]  

(3.5)

where \(\alpha\) is the polarizability of the noble gases (cm\(^3\)) and \(\mu\) is the dipole moment (C cm). We see in Table 3.2, that the local field is about the same all three noble gases, suggesting that the polarization is caused by the image potential.

The measured work function decrease for a full monolayer of noble gas may also be influenced by a small charge transfer from the metal to the noble gas, as has been reported for Xe on Pd (6s-resonance model) [25]. This effect leads to a smaller decrease or an increase of the work function. In Table 3.2 we see that the work function decrease for Kr and Ar is smaller than for Xe, which we have explained with the smaller polarizability for Kr and Ar. When adsorption of Kr and Ar involves a larger electron transfer to the Kr-5s or Ar-4s level than for Xe to the Xe-6s level, the work function decrease can also be smaller with the same noble gas dipole moment. However, this is very unlikely, since the energy separation between the empty s-levels and the p-levels for Kr and Ar is larger than for Xe.

3.4 Adsorption of Xe, Kr and Ar on Potassium-Covered Rh(111).

3.4.1 Experimental and Analytical Procedures

For measurement of local work functions around adsorbed potassium atoms Xe, Kr and Ar were adsorbed on a potassium-covered surface and their UPS signals were recorded, using HeI-radiation. As discussed before, a heterogeneity in the local work function is reflected in
different positions for noble gas signals in the UPS spectrum. In this section we present noble gas adsorption measurements at three different potassium coverages. The potassium layers were prepared by annealing a thick potassium layer (Sect. 2.2.2) at 845 K, 755 K and 710 K respectively, resulting in potassium coverages of 2.7 at%, 4.1 at% and 5.0 at% (1 at% corresponds to 1 adsorbed potassium atom per 100 Rh surface atoms). The potassium coverage also results from the UPS spectra of adsorbed noble gases (Sect. 3.4.2).

Between the measurements the adsorbed noble gas and eventual contaminating water and carbon monoxide were desorbed by heating the sample to ~600 K. Since the potassium layers have been prepared by heating to higher temperatures, no potassium desorbs during this heating. This is confirmed by the work functions, that were measured immediately before each noble gas adsorption experiment (4.4 eV at $\theta_k = 2.7$ at%, 3.7 eV at...
UPS spectra (HeI-radiation, 21.21 eV photon energy) of adsorbed Xe and Kr on potassium covered Rh(111). Potassium coverage: 4.1 at%. Adsorption temperature of the noble gases: 45 K. The existence of more than one noble gas adsorption state at low coverages indicates a potassium-induced heterogeneity of the surface (see also Figure 3.4).

\[ \theta_K = 4.1 \text{ at\% and } 3.1 \text{ eV at } \theta_K = 5.0 \text{ at\%}. \] The difference with the value of the freshly prepared surface with potassium remained below 0.05 eV. At such low potassium coverages the work function is extremely sensitive to coverage changes (Sect. 2.3.2) and thus we can safely assume that the potassium coverage is not affected by heating to 600 K. This procedure ensured a constant potassium coverage in the measurements with the three noble gases.

Figures 3.4-3.6 show background-subtracted UPS spectra of Xe (top left), Kr (top right) and Ar (bottom left) adsorbed on potassium-covered Rh(111) with potassium coverages of 2.7 at\%, 4.1 at\% and 5.0 at\%, respectively. Compared to the spectra of the noble gases on clean Rh(111), additional peaks occur for all noble gases, which develop already after low exposures. This immediately indicates a potassium-induced lateral heterogeneity of the surface. In the Kr spectra the heterogeneity of the surface leads to an overlap of the different Kr signals. A precise interpretation of these spectra is given in the next section.

The analysis procedure.
The spectra in Figures 3.4-3.6 are the superposition of contributions of noble gas on different adsorption sites. A decomposition of the spectra into these contributions gives information about the distribution of the noble gas atoms over the different sites. Obviously, the spectrum of one monolayer noble gas gives quantitative information about the
distribution of the different sites over the whole surface.

The general procedure is to decompose a spectrum into subspectra, each representing a single noble gas adsorption state. The shape of such a subspectrum is known from the spectra of adsorbed noble gases on the clean surface (Sect. 3.3), where only one adsorption site exists.

Usually, a single Xe state is represented by 2 or 3 Lorentzian curves per Xe state [26], dependent on the splitting of the Xe5p312 signal. In this work mixed Gauss-Lorentz curves have been used as described by Fraser and Suzuki [27]. The analytical form of these curves contain a parameter (a) allowing a smooth change of the shape from purely Gaussian (a=0) to purely Lorentzian (a=1). In the decompositions presented in this work, this parameter is fixed to a=1/\sqrt{2}. This leaves three parameters per curve, viz. the peak height, the peak width

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig36.pdf}
\caption{UPS spectra (HeI radiation: 21.21 eV photon energy) of adsorbed Xe, Kr and Ar on potassium covered Rh(111). Potassium coverage: 5.0 at\%. Adsorption temperature of the noble gases: 45 K. (See also Figures 3.4 and 3.5).}
\end{figure}
and the position, like for the pure Lorentzian curves.

The decompositions were made starting with spectra of low Xe coverages and the result was used as an input for higher coverages. Since in case of clean Rh(111), the Xe-5p_{3/2} peak is approximately symmetric for all Xe coverages below one monolayer, we used in the decompositions only two curves for one Xe state, corresponding to the 5p_{1/2} and 5p_{3/2} state, with an energy separation of 1.3 eV and an intensity ratio of 1-1.5, the 5p_{3/2} having the highest intensity. The width of the 5p_{1/2} peak can be ~0.1 eV smaller than the that of the 5p_{3/2} peak. Ideally, increasing the Xe coverage only leads to an intensity increase of the Xe signals. However, small changes in binding energy and peak width (~0.05 eV), which have also been observed for Xe on the clean surface, are allowed. If the spectrum cannot be fitted satisfactorily with the given conditions, we assume a new adsorption state and add a new curve, with the characteristic form for Xe. A good method for detecting new adsorption states is to use the incremental difference spectra: a new state is recognized by the typical noble gas peak structure at a shifted position. With these restrictions reliable fits can be made.

The intensity (area) of a Xe signal is a measure of the relative abundance of the respective state. Because the 5p_{3/2} peak is more likely to change with increasing Xe coverage (Sect. 3.2), only the intensity of the 5p_{1/2} peak has been used to determine the relative abundance of the corresponding state. The 5p_{3/2} peak is merely used as a guideline for a correct decomposition of the 5p_{1/2} peak.

For Kr basically the same procedure has been used: the spectra obtained with clean Rh(111) yield the basic peak form corresponding to one adsorption state. This peak form is used to fit the measured spectra of the potassium-precovered surfaces. We start at low Kr coverages and use the result as input for the fits at higher Kr coverage. However, the fit of one adsorption state with two Gauss-Lorentz curves, as for Xe, does not work for the potassium-covered surfaces. The spin-orbit-splitting of the Kr signal overlaps with the potassium-induced splitting, which is difficult to resolve numerically. This situation is illustrated in the decomposition of a Kr spectrum (Figure 3.9), in which the centre maximum results from an overlap of the 4p_{1/2} of one state with the 4p_{3/2} of the other one. Only by keeping the intensity ratio of the 4p_{1/2} and 4p_{3/2} peak of a Kr state constant (known from the spectra of Kr on clean Rh(111)), a reliable decomposition of the spectra is possible. Therefore, we used experimental spectra representing a single Kr state, e.g. Kr on clean Rh(111), and fitted the position and intensity to the total Kr spectrum. New adsorption states are found from the incremental difference spectra. Obviously, the decomposition with experimental spectra is not very flexible with respect to the peak forms, but eventual differences in form can be accounted for by using different experimental spectra of a single Kr adsorption state. However, compared to the Xe spectra, where the mixed Gauss-Lorentz curves are used, the accuracy of the fits is less good.

Also for Ar experimental spectra, representing an appropriate single Ar adsorption state, are used, to avoid numerical problems. Now the problem is not the overlap of the different
Chapter 3

Ar adsorption states, but the overlap of the $3p_{1/2}$ and $3p_{3/2}$ peak of one adsorption state, which causes the slight asymmetry of the Ar signal (Figure 3.6). Because the Ar signal has only one maximum, the position of an Ar signal is easily determined from the maxima seen in the spectrum.

### 3.4.2 Determination of the Local Work Functions.

**Potassium coverage: 2.7 at%**.

The decomposition of the spectra in Figure 3.4 into single noble gas adsorption states, according to the procedure described in the previous section, yields positions and relative intensities of the noble gas signals.

The Xe-spectra consist of well resolved $5p_{1/2}$ and $5p_{3/2}$-peaks. Figure 3.7 shows the decomposition of the Xe spectra at different Xe coverages using the mixed Gauss-Lorentz curves. At low coverages only two Xe adsorption states are found. After larger Xe exposures, new Xe states are observed at higher binding energy. From a comparison of these spectra with the spectra obtained at higher potassium coverages and with the results from the K/Ru(001) surface [8], we can assign the Xe-$5p_{1/2}$-peak at 7.05 eV (labelled A in Figure 3.7) to the Xe on bare Rh patches (Xe/Rh), and the peak at 7.57 eV (B) to the Xe on the Rh surface next to a potassium atom (Xe/(K/Rh)). At higher Xe coverage the peaks corresponding to Xe on top of potassium (8.80 eV) (C) and Xe in the second layer (8.0 eV) develop. This order of the different adsorption states in the spectra is maintained through all potassium coverages and has also been found on the K/Ru(001) surface [8]. With increasing potassium coverage we see a decrease for Xe on bare Rh (A), which has the lowest binding energy, and an increase for Xe next to potassium (B) and Xe on top of potassium (C), confirming that (A) corresponds to the bare Rh sites. From the relative intensities it follows that (B) corresponds to Xe next to potassium, since there are more sites next to potassium than on top of potassium (C). In addition, the latter should occur at the highest binding energy, since the local work function on top of potassium is lower.

The development of the different states with increasing Xe exposure is shown in Figure 3.8. The dose corresponding to 1 ML Xe is determined by the strong intensity increase of the second layer peak and a damping of the first layer signals. After low Xe exposures, only the Xe/Rh state (A) and the Xe(K/Rh) state (B) are populated. Initially, a larger fraction of the adsorbed Xe is found on the next to potassium (B), indicating a slightly higher Xe adsorption energy at these sites. At higher Xe coverages the Xe on top of potassium (C) and the second and higher Xe layers are occupied, because they are less stable than Xe on Rh (A) and Xe next to potassium (B).

The decomposition of the Kr spectra, using experimental Kr spectra, is shown in Figure 3.9. After low Kr exposures, we see almost exclusively one Kr state with the Kr-$4p_{1/2}$-peak at 8.83 eV (B). When the Kr coverage is increased, new Kr states develop with the $4p_{1/2}$-peak at 8.12 eV (A) and at 9.1 eV (D).
Figure 3.7 Decomposition of the UPS spectra of adsorbed Xe on potassium covered Rh after various Xe exposures. Potassium coverage: 2.7 at%. The curves at the bottom (diff.) are the differences between the experimental (exp.) and fitted curves (fit). The different Xe-5p_{1/2} levels correspond to different adsorption sites for Xe: Xe on bare Rh (A), Xe next to potassium (B), and Xe on top of potassium (C).

The assignment of the different Kr states is made in analogy with the Xe spectra. The signal at the lowest binding energy (Kr-4p_{3/2} at 8.12 eV) is Kr on bare Rh (A). The 4p_{1/2} peak of this state is not resolved in the spectra because it overlaps with the 4p_{3/2} peak of the Kr(K/Rh) state. Its position is found by placing the Kr-4p_{3/2} peak of an experimental Kr spectrum on the Kr-4p_{3/2} peak of the Kr/Rh state, which is well resolved in the spectra. The other Kr signal that is detected at low Kr coverage (Kr-4p_{1/2} at 8.83 eV) (B) is assigned to
Kr next to potassium. This signal dominates at low coverages, indicating that Kr next to potassium has the highest adsorption energy, as is the case for Xe, too. The potassium-induced changes in local surface potential are evaluated on the basis of these two sites only. The signal at 9.1 eV is assigned to higher Kr layers and is discussed later.

The decomposition of the spectra of Ar on the same surface is illustrated in Figure 3.10. Initially, we see mainly one adsorption state with the maximum of the 3p-signal at 10.14 eV. A second maximum at lower binding energy (9.13 eV) is detected after higher Ar exposures. At 45 K the Ar layer saturates after 2 L exposure and only the two states mentioned above are seen in the spectra then. Above Ar pressures of $10^{-6}$ Torr new peaks appear at higher binding energy.

The assignment of the observed Ar peaks in the UPS spectra to adsorption sites is analogous to the Xe and Kr cases. The peak at the lowest binding energy is assigned to Ar on bare Rh (9.13 eV) (A). The other peak (10.14 eV) (B) corresponds to Ar next to potassium. The change in local surface potential at the Ar sites on the metal surface is found from these UPS signals.

Now we know the potassium-induced shifts of the noble gas signals in the UPS spectra and have correlated them to different adsorption sites. In order to determine the variation in local surface potential as a function of the distance from an adsorbed potassium atom, we have to locate the different adsorption sites on the surface. We need a model for the positions of the noble gas and potassium atoms on the potassium-covered Rh(111) surface.

The intensities of the signals in the spectrum for one monolayer noble gas reflect the relative abundance of the different adsorption sites on the surface [8]. On the basis of these

---

**Figure 3.8 Development of the relative intensities (in fraction of the total peak area) for the different Xe adsorption sites with increasing Xe exposure on Rh(111), covered with 2.7 at% potassium. The sites next to potassium and the sites on bare Rh are occupied simultaneously. After higher exposures, Xe also adsorbs on top of potassium. The intensity of Xe in the first layer decreases when the second layer develops.**
Figure 3.9 Decomposition of the UPS spectra of adsorbed Kr on potassium covered Rh after various Kr exposures, using experimental spectra of a single Kr adsorption state. Potassium coverage: 2.7 at%. The curves at the bottom (diff.) are the differences between experimental (exp.) and fitted curves (fit). The different Kr-4p levels correspond to different adsorption sites for Kr: Kr on bare Rh (A), Kr next to potassium (B), Kr on top of potassium (C), and Kr in higher layers (D).

data, we can construct a structure model for the potassium and coadsorbed noble gas (Figure 3.11) to obtain the distances between the noble gas adsorption sites and the potassium atoms. We also obtain an average distance between the potassium atoms, which immediately yields an estimate for the potassium coverage. For the construction of the structure models only the Xe data have been used, since the first Kr and Ar layer are not
Figure 3.10 Decomposition of the UPS spectra of adsorbed Ar on potassium covered Rh after various Ar exposures and under $10^{-7}$ Torr Ar pressure, using experimental Ar spectra of a single adsorption state. The curves at the bottom (diff.) are the difference between the experimental (exp.) and fitted curves (fit). Potassium coverage: 2.7 at%. The different Ar-3p levels correspond to different adsorption sites for Ar: Ar on bare Rh sites (A), and Ar next to potassium (B).

well resolved. Furthermore, we treat the Rh surface as a flat surface, thereby assuming that the surface does not reconstruct.

The decomposition of the spectrum of 1 ML Xe (7 L Xe, Figure 3.7, bottom right) gives the distribution of the Xe atoms over the different adsorption sites. We find 52 % for Xe on bare Rh (A), 40 % for Xe next to potassium (B) and 8 % for Xe on potassium (C). We see
Figure 3.11 Estimated adsorption geometry for Xe, Kr and Ar on potassium covered Rh(111). The mean distance between the potassium atoms is 16.1 Å, which corresponds to a potassium coverage of 2.7 at%.

Dark circles: potassium atoms.
Hatched circles: noble gas atoms next to potassium.
Dotted circles: noble gas atoms on bare Rh sites.
that the intensity ratio for Xe next to potassium (B) and Xe on top of potassium (C) is 5, suggesting a 5-fold coordination of Xe around the potassium atoms. This agrees well with the results obtained from Xe on K/Ru(001) [8].

The size of the adsorbed particles is given by the Van der Waals radii for the adsorbed noble gases (Table 3.2) and the ionic radius of potassium (1.33 Å) [24], thereby assuming completely ionized potassium atoms. The repulsive lateral interaction between the positively charged potassium atoms prevents formation of islands on the surface. Potassium is adsorbed as single atoms, distributed rather homogeneously over the surface. In the structure model we have assumed a fixed distance between the potassium atoms, which represents the mean distance in the experiment. Incorporation of potassium in the metal surface, as has been reported for potassium on Al(111) [28], seems improbable, since the bonding between the metal atoms in Rh is stronger than in Al, as can be deduced from the higher melting point for Rh (2239 K) compared to Al (933 K) [29].

By putting the Xe and potassium atoms on the surface according to the relative intensities from the spectra, we can construct a unit cell with 1 potassium atom, 5 Xe on the sites next to potassium (B) and 6 Xe atoms on bare Rh sites (A) (Figure 3.11, top). The position of the atoms allows a continuation of the unit cells over the whole surface. The ratios obtained from the structure model are in fair agreement with the experimental ratios (A:B:C = 6:5:1 in the structure model and 6.5:5:1 in the experiment), if we consider that the unit cell is an approximation, that allows only an integer number of Xe atoms. The distance between the potassium atoms in the model is 16.1 Å, corresponding to 4.32*10^{13} unit cells (potassium atoms) per cm². Division by the number of Rh-atoms per cm² (1.6*10^{15} cm⁻²) yields a potassium coverage of 2.7 at%.

For adsorption of Kr and Ar around potassium, we also assume a 5-fold coordination. As pointed out in Sect. 3.4.1, the measurements with Xe, Kr and Ar have been done with exactly the same potassium coverage. Consequently, we find the models for Kr and Ar directly by exchanging the Xe atoms for the smaller Kr and Ar atoms with a 5-fold coordination (Figure 3.11).

The distance between a noble gas adsorption site and the nearest potassium atom follows
from the geometry shown in Figure 3.12, which is taken from the structure model in Figure 3.11. Circle K represents the potassium atom, A and B are two noble gas atoms next to potassium, in 5-fold coordination positions, and C is a noble gas atom at a Rh site. Due to the 5-fold coordination of the noble gases around potassium, the angle $\alpha$ in Figure 3.12 is $36^\circ$. The distance AD is given by the radius of the noble gas atoms. Since the angles at D are all rectangular, the distance between the potassium atom and the neighboring noble gas atom is given by:

$$d = KA = \frac{r}{\sin 36^\circ} = 1.701 \times r$$  \hspace{1cm} (3.6)$$

where $r$ is the Van der Waals radius of the coadsorbed noble gas. Due to the 5-fold coordination the distance from the potassium atom to the site next to potassium does not depend on the radius of the potassium and is somewhat larger than the sum of the potassium radius and the Van der Waals radius of the noble gas.

The shortest possible distance to a bare Rh site is found by placing another noble gas atom in the hexagonal closed packed position to atoms A and B (Figure 3.12, circle C). Its distance to the potassium (KC) is found by addition of the lengths KD and DC and can be written as:

$$d = KD + DC = \frac{r}{\tan 36^\circ} + 2 \times r \cos 30^\circ = 3.108 \times r$$  \hspace{1cm} (3.7)$$

These equations yield the estimate for the distance between a potassium atom and the different noble gas adsorption sites.

As explained in Section 3.2 we interpret a shift of the noble gas signals in the UPS spectrum, due to the adsorbed potassium, as a potassium-induced change in local work function or local surface potential at the noble gas adsorption sites. This interpretation assumes, that the relaxations of the ionized noble gas atoms on the clean and potassium-covered surface are similar.

Table 3.3 lists the potassium-induced shifts of the noble gas signals in the UPS spectrum, associated with different adsorption sites, and the estimated distance from the

<table>
<thead>
<tr>
<th>Adsorption site</th>
<th>distance to K (Å)</th>
<th>UPS peak shift (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar(K/Rh)</td>
<td>3.23</td>
<td>1.44</td>
</tr>
<tr>
<td>Kr(K/Rh)</td>
<td>3.40</td>
<td>1.13</td>
</tr>
<tr>
<td>Xe(K/Rh)</td>
<td>3.74</td>
<td>0.87</td>
</tr>
<tr>
<td>Ar/Rh</td>
<td>5.90</td>
<td>0.43</td>
</tr>
<tr>
<td>Kr/Rh</td>
<td>6.23</td>
<td>0.42</td>
</tr>
<tr>
<td>Xe/Rh</td>
<td>6.83</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Table 3.3 Shifts of the noble gas signals in the UPS spectrum, which are attributed to changes in local surface potential at different distances from an adsorbed potassium covered Rh(111) surface. Potassium coverage: 2.7 at%. Reference is the position of the UPS signal of the adsorbed noble gas on clean Rh(111).
noble gas adsorption sites to the nearest potassium atom. Figure 3.13 is a graphic representation of these shifts, related to the different noble gas positions on the surface. At both sides a (positively charged) potassium atom is placed. The solid line is drawn as a guide to the eye. If we interpret the shifts in UPS as changes in local surface potential, the points indicate the local work function decrease at the positions between two potassium atoms. We see, that in the vicinity of an adsorbed potassium atom (< 4 Å) the potential changes rapidly (short range effect), whereas it becomes more or less constant at distances greater than about 5 Å. However, the peaks belonging to adsorbed noble gas on the bare Rh sites on the potassium-covered surface are found at ~0.4 eV higher binding energy, indicating that the bare Rh sites are also affected by the adsorbed potassium. It seems, that at this potassium coverage (2.7 at%) the potential further away from a potassium atom is still significantly lower (0.4 eV) than on the unpromoted surface, implying a long range effect of adsorbed potassium on the surface.

**Potassium coverage: 4.1 at%**.

We apply the same procedure as described above for the determination of the variation in
local surface potential around an adsorbed potassium atom at higher potassium coverages. The UPS spectra of Xe on the Rh(111) surface precovered with 4.1 at% potassium reveal at low Xe coverages two different adsorption states (Figure 3.14, top left). Analogous to the previous experiment, the Xe-5p_{1/2} signal with the lowest binding energy (7.31 eV) (A) corresponds to Xe on the bare Rh sites and the other one, with the Xe-5p_{1/2} peak at 7.85 eV (B), is assigned to Xe next to potassium atoms. After higher Xe exposures, the signals for...
Xe on top of potassium at 8.93 eV (C) and for Xe in the second layer are detected (Figure 3.14, top right).

The development of the Xe signals in the spectra with increasing Xe exposures is shown in Figure 3.14 (bottom). We see, that initially the Xe sites next to potassium (B) are occupied, indicating the higher adsorption energy for Xe on these sites. With increasing Xe exposure, we find a sequential occupation of the bare Rh sites (A), the sites on top of potassium (C) and the second layer. This order is the same as in the previous experiment. Compared to the experiment at 2.7 at% potassium, we now find more Xe next to potassium (B) and Xe on top of potassium (C) than Xe on bare Rh sites (A), in agreement with the assignment of the peaks. Again the second layer state is recognized from a strong growth at high Xe coverages and an attenuation of the former Xe signals.

The UPS signal of adsorbed Kr at low coverage also has two contributions. The Kr state at the lowest binding energy in the UPS spectrum (Kr-4p 1/2 at 8.42 eV) is assigned to Kr on the bare Rh sites (A) and the other one, at 9.03 eV, to Kr next to potassium (B) (Figure 3.15). At higher Kr coverages also Kr on top of potassium (10.14 eV) (C) and Kr in the second layer are detected. Spectra of adsorbed Ar on this surface are not available.

Like we did for θ_K = 2.7 at%, we derive an adsorption geometry for Xe on the basis of the spectra. The Kr model is constructed by replacing the Xe atoms for the smaller Kr atoms, leaving the potassium coverage unchanged. The relative intensities found by decomposing the spectrum of 1 ML Xe at θ_K = 4.1 at% are 16% for the Xe on bare Rh (A), 71% for the Xe next to potassium (B) and 13% for the Xe on top of potassium (C), which

---

**Figure 3.15** Decomposition of HeI-UPS spectra of Kr adsorbed on potassium covered Rh(111), using spectra representing a single Kr-adsorption state. Potassium coverage: 4.1 at%. Adsorption temperature Kr: 45 K. The positions of the different Kr adsorption states are labelled. A: Kr on bare Rh, B: Kr next to potassium, C: Kr on top of potassium.
Table 3.4  HeI-UPS peak shifts for adsorbed Xe and Kr on potassium covered Rh(111), referenced to the valence level binding energy of adsorbed Xe and Kr on clean Rh(111). Potassium coverage: 4.1 at%.

<table>
<thead>
<tr>
<th>Adsorption site</th>
<th>distance to K (Å)</th>
<th>UPS peak shift (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr(K/Rh)</td>
<td>3.40</td>
<td>1.33</td>
</tr>
<tr>
<td>Xe(K/Rh)</td>
<td>3.74</td>
<td>1.15</td>
</tr>
<tr>
<td>Kr/Rh</td>
<td>6.23</td>
<td>0.72</td>
</tr>
<tr>
<td>Xe/Rh</td>
<td>6.83</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Data for Ar at this potassium coverage are not available.
corresponds to a ratio $A:B:C$ of $1.2 : 5.6 : 1$. In the unit cell (Figure 3.16, top), which can be continued over the whole surface, this ratio is $2:5:1$. The distance between the potassium atoms is then $13.2 \, \text{Å}$, corresponding to a potassium coverage of $4.1 \, \text{at}\%$.

Due to the symmetry of the unit cell, we cannot construct a unit cell with only 1 Xe atom on a bare Rh site: We have to choose between 0 or 2. When we divide the unit cell into two identical triangles, the Xe atoms can be placed on bare Rh patches only when there is enough space in the centre of such a triangle between the Xe atoms on the sites next to potassium. But when there is space enough in one triangle to place a Xe atom, there automatically is space enough for a Xe atom in the other one. Since the intensity of the Xe/Rh signal in the spectra at monolayer coverage is rather high, the option with two Xe/Rh atoms per unit cell has been chosen.

After replacing the Xe atoms in the structure model by Kr atoms, we see that with Kr a higher relative intensity of the Kr/Rh state can be expected. This is qualitatively reflected in the spectra, where at higher Kr coverage (Figure 3.15, right) the relative intensities of the Kr on bare Rh (A) and next to potassium (B) are about the same, which is definitely not the case with the corresponding Xe spectra.

Table 3.4 gives the shifts of the noble gas peaks in the UPS spectra due to the adsorbed potassium. The distances of the adsorption sites to the nearest potassium atom is the same as in the previous experiment and hence can be calculated from Eqs. (3.6) and (3.7). The shortest distance between a potassium and Xe on bare Rh ($6.83 \, \text{Å}$) is larger than half the distance between the potassium atoms ($6.1 \, \text{Å}$). Since the unit cell has a hexagonal structure, the maximum distance is found when Xe is placed symmetrically between three potassium atoms and is given by $d_{K,K}/\sqrt{3}$ ($d_{K,K}$ is the distance between the potassium atoms in the structure model). In the present case the maximum distance is $7.62 \, \text{Å}$, which is larger than the distance between a Rh site and a potassium atom.
Figure 3.17 is a graphic representation of the potassium-induced shifts of the noble gas. UPS signals, as a function of the distance between potassium and noble gas. Again, we interpret this as the variation of the local surface potential between two potassium atoms. The local work function in the vicinity of potassium (<4 Å) is about 1-1.5 eV lower than on clean Rh and depends on the distance to the nearest potassium (short range effect). At the positions further away a constant local work function is found, ~0.7 eV lower than on clean Rh (long range effect). Apparently, the variation of the local surface potential has not changed qualitatively; both the short range effect and the long range effect have been reproduced.

**Potassium coverage**: 5.0 at%.

Figure 3.18 shows the decomposition of two Xe spectra (top) and the development of the different states with increasing Xe exposure (bottom). At low coverages only one Xe state is seen, contrary to the corresponding spectra at lower potassium coverages. The position of the $5p_{1/2}$ peak is 8.01 eV and it is attributed to Xe next to potassium (B). At high Xe coverage (~1 ML) a very small signal at 7.47 eV is observed accompanied by a shoulder at the low binding energy side of the $5p_{3/2}$ peak, which can be attributed to the Xe on bare Rh (A). The signal for Xe on potassium (C) at 9.17 eV is also seen at high Xe coverage. The Xe next to potassium dominates over a wide exposure range and the Xe on bare Rh (A) has almost disappeared (Figure 3.18 bottom). This is consistent with the higher potassium coverage, which leads to more adsorption sites next to potassium (B) and on top of potassium (C) at the expense of bare Rh sites (A).

In the spectrum of 7.5 L Xe a set of three Gauss-Lorentz curves has been used for Xe on the sites next to potassium (B) (Figure 3.18, top right). So far this splitting was neglected and is introduced here merely to resolve the Xe/Rh state (A) properly. It represents the splitting of the Xe-$5p_{3/2}$ signal (Sect. 3.4.1) [9-11,26].

The decomposition of the spectra of Kr on this surface is displayed in Figure 3.19. At very low Kr coverages, only one Kr signal, with the $4p_{1/2}$ at 9.27 eV (B), is detected and remains dominant after larger exposures. It is assigned to Kr next to potassium. At higher Kr coverage a new Kr signal appears at lower binding energy (Kr-$4p_{1/2}$ at 8.70 eV) (A), assigned to Kr at the bare Rh sites, analogous to the experiments described earlier. Due to the smaller radius of Kr, the relative intensity for Kr on bare Rh (A) is larger than for the corresponding Xe site, as can be deduced from the shoulder at the low binding energy side of the Kr signal. It represents the $4p_{3/2}$ peak for Kr on bare Rh (A). In addition, adsorption of Kr on the bare Rh sites is detected at rather low Kr coverages, whereas in the Xe case the corresponding state was only seen just before saturation of the monolayer. With high Kr exposures, also Kr on top of potassium (C) at 10.63 eV and in the second layer (10.04 eV) are detected. The local surface potential variation around potassium is evaluated from the signals for Kr on bare Rh (A) and for Kr next to potassium (B) only.

With Ar we also find two different states on this surface, attributed to Ar on bare Rh
(9.74 eV, A) and Ar next to potassium (10.40 eV, B). At low coverages almost exclusively sites next to potassium (B) are occupied. At higher Ar coverages larger amounts of Ar on bare Rh are detected (Figure 3.20), evidenced by the shoulder in the Ar signal. Its relative intensity is, like for Kr on bare Rh, higher for Xe on bare Rh, in agreement with the smaller radius of Ar. At Ar pressures above $10^{-6}$ Torr also two other Ar states are seen, assigned to Ar on top of potassium (11.9 eV) and Ar in higher layers (11.2 eV). Only the peaks for Ar
bare Rh and Ar next to potassium have been used for estimating the potassium-induced change in local surface potential.

The relative intensities of the different Xe adsorption states in the spectrum of 1 ML (7.5 L) Xe are 5% for the Xe on bare Rh (A), 80% for Xe next to potassium (B) and 15% for Xe on top of potassium (C) (ratio A:B:C = 0.3:5.3:1). As pointed out in the discussion of Figure 3.16, the number of Xe atoms on bare Rh sites in a unit cell cannot be 1, due to its symmetry. Since the intensity for Xe on bare Rh (A) is very low for this surface, we neglect it in the structure model. The low intensity is probably due to an inhomogeneous distribution of the potassium atoms over the surface. This causes domains with a locally higher potassium density, where is no space for Xe to adsorb on bare Rh, and domains with a somewhat lower potassium density, that leave just enough space for a Xe atom on bare Rh. Accordingly, the shift of this Xe signal in the UPS spectrum corresponds exclusively to domains with a lower potassium density than the mean value. Therefore it does not represent the situation for the actual potassium coverage and has not been used for the evaluation of local surface potentials.

Figure 3.21 displays the adsorption geometries of the noble gases at this potassium

![UPS](image-url)

**Figure 3.21** Decomposition of HeI-UPS spectra of adsorbed Kr on potassium covered Rh(111) after different Kr exposures. Potassium coverage: 5.0 at%. Adsorption temperature Kr: 45 K. The positions of the Kr-4p½ signals belonging to Kr on bare Rh (A) and Kr next to potassium (B) are indicated. The spectrum for Kr next to potassium (B) used in these fits has been derived from the experimental spectrum shown in the picture on the left and therefore the difference between experimental and fitted spectrum becomes zero for a larger part of the spectrum. The same spectrum has also been used in the decomposition of the spectrum shown in the picture on the right, where it leads to a larger difference between experimental and fitted spectrum.
coverage. In the model for Xe (top) we only have Xe next to potassium with a 5-fold coordination around the potassium atoms, as suggested from the monolayer spectrum. The geometries for Kr and Ar are found by replacing the Xe atoms for Kr and Ar, leaving the potassium structure intact. Since the spectra for Kr and Ar contain a significant signal for adsorption on bare Rh, there must be enough space for these atoms between the sites next to potassium. With a potassium coverage of 5 at%, there is no space for Xe on bare Rh, while adsorption of Kr and Ar on these sites is still possible. The distance between the potassium atoms then is 12.0 Å. The distances between the noble gas sites and the nearest potassium atom are not affected by the increased potassium coverage. Distances and shifts of the noble gas UPS signals, with respect to unpromoted Rh are given in Table 3.5.

Table 3.5 Hel-UPS peak shifts for adsorbed Xe, Kr and Ar on potassium covered Rh(111), referenced to the valence level binding energy of Xe, Kr and Ar adsorbed on clean Rh(111). Potassium coverage: 5.0 at%.

<table>
<thead>
<tr>
<th>Adsorption site</th>
<th>distance to K (Å)</th>
<th>UPS peak shift (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar(K/Rh)</td>
<td>3.23</td>
<td>1.70</td>
</tr>
<tr>
<td>Kr(K/Rh)</td>
<td>3.40</td>
<td>1.57</td>
</tr>
<tr>
<td>Xe(K/Rh)</td>
<td>3.74</td>
<td>1.31</td>
</tr>
<tr>
<td>Ar/Rh</td>
<td>5.90</td>
<td>1.04</td>
</tr>
<tr>
<td>Kr/Rh</td>
<td>6.23</td>
<td>1.00</td>
</tr>
<tr>
<td>Xe/Rh</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
Figure 3.21 Estimated adsorption geometry of Xe, Kr and Ar on potassium covered Rh(111). With a distance between the potassium atoms of 12.0 Å, corresponding to a potassium coverage of 5.0 at%, there is no room for Xe on bare Rh, while Kr and Ar still can be adsorbed on these sites, in agreement with the observed intensities in the UPS spectra.

The shifts of the noble gas UPS signals give the potassium-induced change in local surface potential, which varies between two potassium atoms as drawn in Figure 3.22. Again we find a strong and distance dependent lowering (1.3-1.7 eV) of the surface potential in the immediate vicinity of a potassium atom (<4 Å), as well as a rather constant lowering of ~1 eV further away (>5 Å). This is qualitatively the same result as obtained at lower potassium coverages.

Figure 3.23 summarizes the potassium-induced shifts of the noble gas UPS signals at the three potassium coverages. At all potassium coverages studied, all noble gas signals are shifted with respect to the clean Rh surface. This indicates, that on a potassium-promoted surface all adsorption sites available to the noble gas atoms - thus not only those immediately adjacent to a potassium atoms - but also those further away, are affected by the adsorbed potassium. If we interpret the curves in Figure 3.23 as changes in local surface potential at different distances from a potassium atom, we find for all potassium coverages a strong, distance dependent local surface potential decrease at distances below 4 Å from the potassium atoms (short range effect) and a weaker, but significant, distance independent potential decrease further away (>5 Å) (long range effect). The latter amounts to ~0.4 eV for a potassium coverage of 2.7 at% and to ~1.0 eV at 5 at% potassium coverage. At higher potassium coverage the influence of the next nearest potassium atoms on the local surface potential becomes more important, as the distance to these atoms decreases. The local surface potential is the result of the cumulative effect of the potassium atoms on the surface. Accordingly, the influence of the next nearest potassium atoms on the potential at the neighboring sites of potassium is smaller, but it certainly exists.
3.5 Final Remarks

Figure 3.23 reflects the change in local surface potential as a function of the distance to the nearest potassium atom. To estimate the distances between the noble gas adsorption sites and the potassium atoms, we have used adsorption geometries constructed according to the measured distribution of a complete monolayer Xe over the different adsorption sites. Note, that the exact adsorption geometry is not very critical. The distance between potassium and the noble gas sites next to potassium is approximately the sum of the radii of the potassium and noble gas atom, which also results from the 5-fold coordination of the noble gas atoms around potassium. Further away from potassium the potential has a constant value, indicated
by a uniform shift for Xe, Kr and Ar on the bare Rh sites. In addition, we find only one adsorption site for the noble gases on bare Rh sites, although the noble gas next to potassium leaves enough space for adsorption at different distances from the potassium. Apparently, all these sites are more or less equivalent with respect to the local surface potential. Consequently, the exact position of the noble gases on the Rh sites further away from a potassium atom is not important.

Since the local work function is a quantity that is defined along the trajectory of an escaping electron, it can have different values within atomic distances. The adsorbed noble gas atoms can sense a varying work function on their adsorption site and the value we measure is averaged over the volume of the noble gas atom. In first order approximation, i.e. for a constant or linearly varying work function over the atom, this average value equals the local work function at the centre of the noble gas atom. The results in Figure 3.23 suggest a varying surface potential close to the potassium atoms and a rather constant surface potential further away. Therefore, this approximation is better for the bare Rh sites than for the sites next to a potassium atom.

The distribution of the noble gas adsorption sites in the first noble gas layer can only be determined from the intensities of the noble gas UPS signals, when the first noble gas layer is occupied separately. Three dimensional growth of the noble gas layer disturbs the signals of the noble gas atoms in contact with the metal surface. For Kr on the potassium-covered (2.7 at%) Rh surface, we find a broadening at the high binding energy side of the Kr signal after 1.5 L Kr exposure (Figure 3.9). For this broadening a new Kr state (D, 9.10 eV) is assumed, tentatively attributed to Kr in the second layer, although the first Kr layer is not yet saturated: Additional Kr exposure leads to an increase of the signal of Kr on bare Rh (A). In contrast to Xe, the first and second Kr layer develop simultaneously (Figure 3.24) and therefore we do not have a spectrum of one monolayer Kr and an analysis of Kr over the different adsorption states, as for Xe, is impossible. The positions of the UPS signals for Kr on bare Rh and next to potassium, that have been used for evaluation of the local surface potential, originate from a spectrum at lower Kr coverage, which consists of these two contributions only (Figure 3.9, top left).

Due to the smaller Kr atoms, we might expect that not only Kr next to potassium, but also Kr in the second shell around potassium can be resolved from Kr on bare Rh, giving rise to the new adsorption state (D, 9.10 eV) after intermediate exposures. However, the position of the UPS signal for Kr in a second sphere is expected between that for Kr next to potassium (8.83 eV) and for Kr on bare Rh sites (8.12 eV), which is not the case. It is also very unlikely, that the signal at 8.83 eV (B) is Kr in the second sphere, because it is dominant at low Kr coverages. In addition no saturation of the signal at 9.1 eV has been observed, which contradicts the limited number of sites on the Rh surface. The adsorption state (D) is presumably not correlated with adsorption on the metal surface and therefore attributed to the second layer of Kr, which implies clustering of Kr on potassium-covered Rh, before saturation of the first layer.
The simultaneous occupation of the bare Rh sites and the second Kr layer also occurs at higher potassium coverages, but always after the sites next to potassium are all occupied (Figure 3.24). This suggests a significantly higher adsorption energy for Kr on the sites next to potassium and a small difference in adsorption energy for Kr on bare Rh and Kr in the second layer. The broadening of the signal for Kr in the second layer may be explained by a splitting of the Kr-4p\(_{3/2}\) peak due to a high Kr-Kr interaction, in analogy with Xe (Sect. 3.2).

The intensity for Ar next to potassium at potassium coverage 2.7 at% appears to be...
higher than for Ar on bare Rh, also after higher exposures. Therefore, also clustering of Ar on the potassium-covered Rh surface is assumed and the corresponding signals cannot be resolved. Consequently, the spectra for Ar in the first layer are also disturbed and to minimize the error in the local surface potential, the positions of the UPS peaks for Ar next to potassium and Ar on bare Rh have been determined at the lowest possible Ar coverage.

### 3.6 Conclusions

Clean and potassium-covered Rh(111) surfaces have been characterized by photoemission of adsorbed Xe, Kr and Ar. On the clean Rh(111) surface all three noble gases show only one adsorption state, indicative of a homogeneous surface. The energy difference between the valence $p_{1/2}$ and $p_{3/2}$ levels is 1.3 eV for adsorbed Xe and 0.68 eV for adsorbed Kr, the same values as for gas phase Xe and Kr. For gas phase Ar, the energy difference between the $3p_{1/2}$ and $3p_{3/2}$ is 0.18 eV. Due to broadening of the signals for adsorbed species, it has not been resolved. Only a slight asymmetry in the tailing edge of the Ar UPS peak is observed.

Adsorption of Xe, Kr or Ar on the clean Rh(111) surface results in a work function decrease. For one monolayer Xe the work function decrease is 0.54 eV, for 1 ML Kr 0.47 eV and for Ar 0.33 eV, corresponding to an average dipole moment for Xe of 0.24 D, for Kr of 0.17 D and for Ar of 0.11 D. The lower dipole moments for Kr and Ar compared to Xe agree well with the lower polarizability for Kr and Ar.

The ionization energies for the adsorbed species are 12.3 eV for the $5p_{1/2}$ level of Xe, 13.3 eV for the $4p_{1/2}$ level of Kr and 14.3 eV for the $3p$ level of Ar. The difference in ionization energy for gas phase and the adsorbed species is the relaxation energy, due to the vicinity of the metal surface for the adsorbed species. We find 1.1 eV for Xe, 1.4 eV for Kr and 1.5 eV for Ar. Measurements of the ionization energy for adsorbed noble gases on other substrates suggest a substrate independent ionization energy, which implies a substrate independent relaxation energy. Consequently, a change in binding energy of the noble gas levels can be interpreted as a change in local surface potential or local work function.

When Xe, Kr or Ar is adsorbed on a potassium precovered Rh(111) surface, few noble gas signals appear in the UPS spectrum. This immediately indicates different noble gas adsorption sites, viz. bare Rh sites, sites next to potassium and sites on top of potassium, and thus a potassium-induced heterogeneity of the surface.

The shift of the noble gas photoemission signals, referenced to the clean surface, have been interpreted as the potassium-induced change in local surface potential at the noble gas adsorption site. Since Xe, Kr and Ar have different sizes, the local surface potential is probed at different, noble gas specific distances from a potassium atom. These distances have been estimated from an adsorption geometry for the coadsorbed potassium and noble
gas, that can be constructed on the basis of the distribution of the Xe atoms over the different adsorption sites in a complete monolayer of Xe. This results in a 5-fold coordination of the noble gas atoms around potassium. Since for Kr and Ar on the potassium-covered surface cluster growth is suspected, we derived these adsorption geometries by replacing the Xe atoms by the smaller Kr and Ar atoms, which is allowed, since the experimental procedure guarantees a constant potassium coverage. The potassium coverage given in this chapter also results from these adsorption structures. However, these adsorption geometries are not critical at all, because the distance between a potassium atom and its neighboring noble gas site must be in the order of the sum of the radii of potassium and the respective noble gas. The potential at large distances turned out to be distance independent and hence the exact distance between a potassium and a bare Rh site is not important.

The shift of the noble gas signals, corresponding to the adsorption sites next to potassium, is different for Xe, Kr and Ar. We have interpreted this as a strong variation of the local surface potential within a radius of 4 Å around a positively charged potassium atom (short range effect). In contrast, the shifts corresponding to the adsorption sites further away (5-8 Å) are independent of the noble gas, but not zero. The local surface potential here is independent of the distance but significantly lower than for the clean Rh(111) surface (long range effect). This lowering is 0.4 eV at 2.7 at%, 0.7 eV at 4.1 at% and 1.0 eV at 5.0 at% potassium coverage. This coverage dependence indicates an increased influence of the next-nearest potassium atoms at higher potassium coverage.

Adsorption of potassium on Rh(111) results in a dominant lowering of the local work function on the noble gas adsorption sites next to a potassium atom and a smaller, but still significant lowering of the local work function on the rhodium sites further away, which is due to the cumulative effect of all potassium atoms on the surface.

References

16. U. Schneider, private communication.
4
Calculations on the Electrostatic Potential on Potassium Promoted Rhodium(111)

4.1 Introduction

In the previous chapter, we have demonstrated that potassium lowers the local work function at all adsorption sites on the surface. Close to a potassium atom (<4 Å), the local work function depends strongly on the distance to the nearest potassium atom. At larger distances (5-8 Å) the local work function becomes constant, but is still significantly lower than the value for unpromoted Rh(111). The potassium-induced change in local work function further away from the potassium decreases from -0.4 eV at 2.7 at% to -1.0 eV at 5.0 at% potassium coverage. This coverage dependence indicates an increased influence of the next nearest potassium atoms.

The lowering of the work function after potassium adsorption is the result of an electron transfer from the potassium atoms to the substrate. The positively charged potassium atoms produce an electrostatic field, which leads to a lowering of the surface potential for a test electron just in front of the surface. Accordingly, the change in energy of an electron escaping from the bulk of the solid to a given position just outside the solid becomes smaller. This corresponds to the decrease in local work function.

As described above, the potassium-induced change in local work function are due to changes in the electrostatic potential. In this chapter we compare calculated electrostatic potentials with the experimentally determined changes in local work function. The results of the calculations are used to check the validity of the local surface potential measurement with photoemission of adsorbed noble gases.

The calculation of the electrostatic potential is done at two levels. The first approach is the calculation of the electrostatic potential in a hexagonally ordered network of dipoles, consisting of positive and negative point charges. Secondly, the influence of an adsorbed potassium atom on the electrostatic potential close to a Rh cluster is calculated by a quantum-chemical calculation of the electronic structure of clusters consisting of Rh and potassium.

In the dipole model, each dipole represents a positively charged potassium atom with its image charge in the metal surface. The electrostatic potential between the dipoles is largely determined by the dipole moment, which is experimentally accessible by measurement of the work function (Chapter 3). It appears that the measured potential changes on the
potassium-covered Rh are in good agreement with the dipole model. In particular, the lowering of the surface potential further away from the potassium atoms, including the dependence on the potassium coverage (Figure 3.23), is very well described with the dipole model.

The electronic structure of potassium covered Rh can not be derived from the experiment. In the dipole model, we merely assume a charge transfer from the potassium atom to the Rh surface. To obtain more realistic charge distributions, the electronic structure and the influence of potassium on the electrostatic potential in the vicinity of Rh clusters is calculated with a quantum-chemical method. We will use a method based on the density functional theory. The Rh clusters studied contain ~10-15 atoms, which are hexagonally ordered, like in the Rh(111) surface. The influence of potassium on the electrostatic potential in the vicinity of the Rh surface is found from the difference in electrostatic potential close to a cluster containing potassium and Rh atoms and that of the same cluster without potassium.

The interpretation of Figure 3.23 in terms of changes in the local electrostatic potential at different positions on the surface implies that the potassium-induced shift of the noble gas signals is completely assigned to an initial state shift, i.e. a change of the orbital energy of the noble gas valence levels with respect to the Fermi-level of the substrate. The final state relaxation of the photoionized adsorbed noble gas atoms is assumed to be equal to the relaxation energy for adsorbed noble gases on clean Rh(111). A change in relaxation energy due to the presence of potassium can cause a difference between the local surface potential change and the shift of the UPS peak of adsorbed noble gases.

To estimate the importance of the relaxation energy in the measurements, we calculate the ionization energies for adsorbed Xe, Kr and Ar on a Rh cluster and a Rh/K cluster, also using density functional theory. When the presence of potassium does not influence the relaxation energy, the ionization energy of the adsorbed noble gas atom reflects the potassium-induced change in electrostatic potential.

This chapter is organized as follows. The calculations of the electrostatic potential in a hexagonally ordered network of dipoles is presented in Section 4.2. A discussion of the relation between the results of the dipole model and the experiment is given in Section 4.3. Section 4.4 deals with the calculation of the electrostatic potential on the Rh/K clusters and the calculation of the ionization energy for adsorbed noble gases. In Section 4.5, we discuss the effect adsorbed potassium on the adsorption of carbon-monoxide and nitrogen, in view of the measured change in local work function. We argue that the role of the lowered work function further away from the potassium atoms is important to understand the inhibition of nitrogen adsorption on some transition metal surfaces.
4.2 The Dipole Model

As pointed out above, the variation of the local surface potential is the result of a charge transfer from the potassium to the substrate, which produces dipoles on the surface. To investigate whether the electrostatic potentials caused by these dipoles result in the experimentally determined local work function changes, we model the potassium covered Rh surface with dipoles and calculate the electrostatic potential at different positions.

We take an infinite, hexagonally ordered two dimensional network of dipoles (Figure 4.1) as a model for the potassium covered surface. Each dipole corresponds to a positively charged potassium atom with its image charge and consists of a positive and a negative point charge. One dipole is placed in the origin. The distance from the charges (+Q and -Q) to the image plane is symbolized by \( d_z \); the separation of the positive and negative charge then becomes \( 2*d_z \). The distance between the dipoles \( (d_{Kk}) \) represents the average distance between the potassium atoms in the experiment (Figures 3.11, 3.16 and 3.21).

The total potential at a given point is found by addition of the contribution of each point charge to the potential at this point. The local work function is related to the potential energy of an electron just above the surface, which is the negative electrostatic potential. We will refer to it as 'the potential'. Then we write for the potential:

\[
-V(x,y,z) = \frac{Qe}{4\pi e} \sum_{(p,q)\in P} \left( \frac{1}{R_{neg}} - \frac{1}{R_{pos}} \right)
\]

(4.1)

Figure 4.1 Geometry of the hexagonally ordered dipole network. The distance between the dipoles \( (d_{Kk}) \) and the distance between the charges and the image plane \( (d_z) \) are indicated. The top view shows the positions of the dipoles in the plane parallel to the image plane; the side view shows the positions of the charges with respect to the image plane.
Chapter 4

where \( P \) is the set of points \((p_m, q_n)\) containing the \((x, y)\) coordinates of the dipole positions, \( Q \) is the nominal charge of the point charges in the dipoles, \( e \) is the elementary charge \((1.6 \times 10^{-19} \text{ C})\) and \( \varepsilon \) is the dielectric constant. \( R_{\text{neg}} \) and \( R_{\text{pos}} \) are the distances from the point \((x, y, z)\) to any negative or positive point charge in the dipole network. We calculate the sum starting from the contribution of the dipole in the origin and adding the contribution of the shells separately (Figure 4.1). When the contribution of a shell becomes less than a given constant (e.g. \(10^{-8}\)), we assume that the sum has converged.

The model contains several free parameters: The value of the point charges, the charge separation, the dielectric constant, the distance between the dipoles and the points \((x, y, z)\) where the potential is calculated. We discuss the effect of each parameter on the calculated potential separately.

**Charge** \((Q)\).

According to Eq. 4.1, the potential in the dipole network is proportional to the value of the point charges \((Q)\). This charge represents the amount of charge transferred from a single potassium atom to the substrate. When we assume that the positive charge is located on the potassium atoms at 3-fold adsorption sites and the negative charge in the first Rh layer, we estimate a value for \( Q \) of 0.75 from the measured dipole moment at low potassium coverage \((7.8 \text{ D}, \text{ see Section 4.3})\). This suggests that even at low potassium coverages the potassium is not necessarily fully ionized. However, one should note that this estimate is based upon an assumption about the location of the charges, which can not be derived from the work function measurement.

Figure 4.2 displays calculated potentials as a function of the distance to the nearest dipole at 2.5 \(\text{Å}\) above the image plane for several values for \( Q \). Obviously, the potential decrease becomes larger with increasing charge on the dipoles.

![Figure 4.2](image.png)

**Figure 4.2** Calculated electrostatic potential in a hexagonally ordered network of dipoles at 2.5 \(\text{Å}\) from the image plane for various point charge values. Distance between dipoles: 16.1 \(\text{Å}\); charge separation \((2d_z)\): 2 \(\text{Å}\).
Calculations on the Electrostatic Potential on K/Rh(111) 79

Figure 4.3 Calculated electrostatic potential in a hexagonally ordered network of dipoles at 2.5 Å from the image plane for various charge separations. Point charge value: 1; distance between dipoles: 16.1 Å.

Charge separation \((d_z)\).
The charge separation, \(2*d_z\), in the model, determines the distance from a given point to the point charges. Hence, it is implicitly expressed in the parameters \(R_{pos}\) and \(R_{neg}\). Figure 4.3 shows calculated potentials as a function of the distance to the nearest dipole for different values of \(d_z\). The calculated potentials decrease with increasing distance between the charges. In this example, the positive point charges move closer to our "test points" and the negative charges move away with increasing distance between the point charges. The contribution of the positive point charges becomes more important and a lower potential results. The dipole moment of the point charge dipoles is given by the product \(Q*2d_z\). Figure 4.4 displays calculated potentials at 2 Å from the image plane as a function of the distance to the nearest dipole, for various combinations of \(Q\) and \(d_z\) giving the same value for the dipole moment.

Figure 4.4 The electrostatic potential in a hexagonally ordered network of dipoles at 2 Å from the image plane for a dipole moment of 10 D, using different combinations of charge and charge separation. Distance between dipoles: 16.1 Å. A: \(Q=1.04, d_z=1\) Å; B: \(Q=0.69, d_z=1.5\) Å; \(Q=0.52, d_z=2\) Å.
(10.0 D). At 3.2 Å from a dipole the potential deviates from -1.20 V for Q=1.04 and dz=1 Å to -1.03 V for Q=0.52 and dz=2 Å. This deviation is smaller than 0.1 V at distances above 4 Å; closer to the dipoles it is in the order of 0.5 V. This indicates that we can calculate the electrostatic potential at distances above 3 Å from the dipole moment with reasonable accuracy, without knowing the exact positions of the charges and the amount of charge transferred to the surface. The accuracy of the potentials further away is better.

**Points (x,y,z).**

Using Eq. 4.1, we can calculate the potential at any point (x,y,z). We compare the calculated potential between 3 and 8 Å from the nearest dipole with the measured values. The

![Figure 4.5](image)

**Figure 4.5** Three dimensional representation of the electrostatic potential perpendicular to the image plane of a hexagonally ordered network of dipoles. The image plane is located at z=0. The point charges are placed at 1 Å from the image plane; the point charge value is 1.04, giving a dipole moment of 10 D. The distance between the dipoles is 16.1 Å. The potential at 3.2 Å (K/Rh site) and 6.4 Å (Rh site) from a dipole is indicated. Above 15 Å from the image plane, the electrostatic potential is homogeneous. A heterogeneous surface potential exists only close to the surface. Hence, an adsorbed molecule senses the position of the promoter atoms only when it is close to the surface. Further away, the molecules feel a homogenously lowered potential.
Calculations on the Electrostatic Potential on K/Rh(111)

Figure 4.6 Left: The potential at 3.2 Å (K/Rh site) and 6.4 Å from a dipole. Above 15 Å from the image plane the potential is the same on these sites. Its value corresponds to the macroscopic work function decrease. The vertical lines are drawn at 2.0 Å and 2.5 Å from the image plane, which is approximately the range in which Xe, Kr and Ar adsorb on the surface. Right: Contour plot of the electrostatic field parallel to the image plane. Close to the image plane it has values larger than 1 V/Å, indicating a heterogeneous potential. At distances above 15 Å it is less than 0.001 Å, which indicates that the variation in potential remains below 0.01 V in this region: The electrostatic potential is rather homogeneous (see also Figure 4.5).

The lateral electrostatic field is a measure of the heterogeneity of the surface potential. Close to the image plane, it can have values larger than 1 V/Å. Above 15 Å from the image plane it is always lower than $10^{-3}$ V/Å (Figure 4.6, right). This indicates that the variation of the electrostatic potential in the plane parallel to the image plane at 15 Å is more than 1000 times smaller than close to the image plane: The electrostatic potential has become homogeneous and corresponds to the macroscopic work function decrease. This indicates that close to the surface adsorbed molecules can sense the position of the promoter atoms. Further away, the molecules feel a homogeneous lower surface potential.
Dielectric constant ($\varepsilon$).

The electrostatic potential is inversely proportional to the (relative) dielectric constant (Eq. 4.1). Therefore, the effect of the dielectric constant is essentially the same as for the values of the point charges. In fact, the potential is not determined by the charges $Q$, but by the ratio $Q/\varepsilon_r$: The potentials for a relative dielectric constant $\varepsilon_r=2$ and charge $Q=1$ are the same as for $\varepsilon_r=1$ and $Q=0.5$.

The electrostatic potentials have been calculated for dipoles in vacuum with $\varepsilon_r=1$. However, in the metal the dielectric constant $\varepsilon_r$ has a higher value. As will be shown in the
next section, the potential on the vacuum side of the surface can still be described by a point charge dipole in the vacuum.

**Lateral distance between the dipoles.**
The lateral distance between the dipoles corresponds to the average distance between the potassium atoms on the surface, which is related to the potassium coverage. Like the charge separation, the distance between the dipoles is not expressed explicitly, but it determines the distances $R_{pos}$ and $R_{neg}$ in Eq. 4.1. Due to the reduced distance to the next nearest dipole, the potential decreases with increasing potassium coverage. Figure 4.7 shows this decrease at 3 Å from a dipole (K/Rh sites) and at 6 Å (Rh sites), as a function of the potassium coverage. This corresponds to the shift of all UPS signals of the adsorbed noble gases towards higher binding energy, which is larger at higher potassium coverages. The dipole model reproduces the dependence of the measured surface potentials on the potassium coverage.

**Fit of the measured changes in local work function with the dipole model.**
We find a good quantitative agreement with the experimentally estimated potassium-induced changes in potential at 2.5 Å above the image plane, approximately the position of the noble

![Figure 4.8](image_url)

**Figure 4.8** Electrostatic potential in a hexagonally ordered network of dipoles at 2.5 Å from the image plane for different dipole densities (solid lines). The distances between the dipoles are 16.1 Å, 13.2 Å and 12.0 Å for $\theta_K = 2.7\%$, 4.1% and 5.0% respectively, the same values as used in the structure models in Figures 3.11, 3.16 and 3.21. Assuming a dipole moment of 10 D, we obtain a good agreement between the calculated potentials and the experimentally estimated values for all potassium coverages (symbols).
Figure 4.9 Map of the calculated electrostatic potential at 2.5 Å above the symmetry plane in a hexagonally ordered network of dipoles located at 16.1 Å from each other, which corresponds to a potassium coverage of 2.7 at%, and a dipole moment of 10 D. The dipoles are placed at the minima. Note that the potential is lowered at every position on the surface. The equipotential lines for -1.05, -0.84, -0.63 and -0.42 V are indicated in the bottom plane. They are nearly circular close to a potassium atom, indicating that at these sites the potential is largely dominated by the nearest potassium atom. The equipotential line of, for example, -0.42 V has a clear hexagonal symmetry due to the influence of the dipoles further away.

gas atoms, using a dipole moment of 10 D in the model (Figure 4.8). Note that the potential at distances above 3 Å is largely determined by the dipole moment. The agreement between calculated and measured potentials indicates that we do not need long ranged changes in electronic structure to describe the observed local work function changes. The dipoles formed by a local change in electronic structure results in electrostatic potential changes over the whole surface in the correct order of magnitude.

The variation of the potential in the plane 2.5 Å above the image plane is visualized in Figure 4.9 for a potassium coverage of 2.7 at%, which corresponds to a lateral distance between the dipoles of 16.1 Å (Figure 4.8, top curve). The relevance of this picture for catalysis is, that it represents the variation of the effective work function that a molecule experiences, when it is adsorbed on a potassium-promoted surface.
Calculations on the Electrostatic Potential on K/Rh(111)

Figure 4.10 Geometry of the modified dipoles. To approximate the charge distribution in the metal surface, the negative charge is divided over several point charges that are located on a circle around the image position.

For low potassium coverages, the equipotential lines for a given distance to the image plane (z coordinate) are circular close to a dipole (Figure 4.9). Further away from the dipoles the equipotential lines become hexagonal, but here the potential hardly depends on the distance to the nearest dipole, in agreement with the experimental results (Figure 3.23). Therefore, the distance to the nearest dipole is sufficient to characterize the position belonging to a certain local surface potential.

Distribution of the negative charge.

In the model discussed so far, the negative image charge in the solid has been represented by a single point charge. However, calculations of the electron density for Li [2] and Na [1] on a jellium surface show that the electrons are distributed close to the surface in a range of a few Ångström. The positive charge, which is concentrated at the potassium atoms, is much more point charge-like.

To account for the distribution of the negative charge in the metal, we modify the dipole model by dividing the negative point charge into several point charges with charge $Q/N$ ($N$ is the number of negative charges) and place them symmetrically at a certain distance around the image position of the positive charge (Figure 4.10). To calculate the potential with these modified dipoles, Eq. 4.1 must be adjusted. For the negative charges, we introduce two new parameters, viz. the number of negative charges ($N$) and the distance between a negative charge and the image position ($r_{neg}$), which describes the spatial distribution of the negative charge in the solid. The contribution of the positive point charges to the potential is not changed.
By placing the negative charges symmetrically around the image position, the $z$ coordinates of the negative charges remain unchanged; only their $x$ and $y$ coordinates must be adjusted. The new $x$ and $y$ coordinates of the negative charges can be calculated by:

$$
\begin{align*}
x_k &= p + r_{neg} \cos (\varphi_0 + k\varphi_N) \\
y_k &= q + r_{neg} \sin (\varphi_0 + k\varphi_N)
\end{align*}
$$

(4.2)

where $x_k, y_k$ are the coordinates of the $k$th negative charge ($0<k<N$), $p$ and $q$ are the coordinates of the image point, $r_{neg}$ is the distance from the negative charges to the image point, $\varphi_0$ is the rotation angle between $(x_i,y_i)$ and the $x$-axis and $\varphi_N$ is the rotation angle between two negative charges, which is given by $360^\circ/N$. The value of one negative charge is given by $Q/N$. The contribution of one modified dipole to the electrostatic potential is:

$$
-V_{\text{one dipole}} = \frac{1}{4\pi \varepsilon} \sum_{k=1}^{N} \left( \frac{Qe}{NR_{neg,k}} \right) - \frac{Qe}{R_{pos}}
$$

(4.3)

where $R_{neg,k}$ is the distance to the $k$th negative point charge. Summation over all modified dipoles yields the total electrostatic potential:

$$
-V(x,y,z) = \frac{Qe}{4\pi \varepsilon} \sum_{(p,q)\in P} \left( \sum_{k=1}^{N} \frac{1}{NR_{neg,k}} - \frac{1}{R_{pos}} \right)
$$

(4.4)

This sum has also been calculated starting from the contribution of the dipole at the origin and adding the total contribution of the shells (Figure 4.1) separately, until the sum has converged.

The total dipole moment is found by vector addition of the contribution of each negative charge to the dipole moment. Compared to the simple dipoles, now the dipole moment has contributions in the plane parallel to the image plane. However, these contributions cancel due to the symmetry of the system (Figure 4.10). The total contribution perpendicular to the image plane is $N*Q*2d_z l/N = Q*2d_z$, the same result as for the simple dipoles.

Figure 4.11 shows calculated potentials as a function of the distance to the image plane, using the modified dipoles. The effect of the distribution of the negative charge on the

<table>
<thead>
<tr>
<th>number of neg. charges</th>
<th>K/Rh site (3.2 Å)</th>
<th>Rh site (6.4 Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-1.229</td>
<td>-0.434</td>
</tr>
<tr>
<td>6</td>
<td>-1.233</td>
<td>-0.435</td>
</tr>
<tr>
<td>60</td>
<td>-1.233</td>
<td>-0.435</td>
</tr>
</tbody>
</table>
Calculations on the Electrostatic Potential on K/Rh(111) potentials is limited. Only close to the negative charges, i.e. small lateral distance to the dipole, small charge separation and close to the image plane, the potential differs significantly from the potential calculated with simple dipoles (Figure 4.11, top left). When the distance to the negative charges is larger, the contribution to the potential hardly changes upon splitting the negative charge. At 2.5 Å distance from the image plane, which is approximately the position of the adsorbed noble gas atoms, the effect of the split negative charges on the potential is small (Figure 4.11). Therefore, the simple dipoles can be used to estimate the local work function changes at the noble gas adsorption sites.

Figure 4.11 Effect of the distribution of the negative charge on the electrostatic potential in a dipole network at 3.2 Å (K/Rh site, top) and 6.4 Å (Rh site, bottom) from a modified dipole. The negative charge is split in three point charges and is distributed on a circle with radius $r$ around the image position. The potential for dipoles containing only one negative charge is also indicated (dipole). Only close to the negative charge (small lateral distance and small $d_z$-value) the potential differs substantially from the potential obtained with ordinary dipoles.
Changing the number of charges hardly affects the calculated potential. The potential obtained with 3, 6 and 60 negative charges, keeping all other parameters constant differ less than 0.05 V (Table 4.1). In the modified dipole model, the size of the spatial distribution of the negative charge, expressed by \( r_{\text{neg}} \), is far more important than the number of negative charges.

Summarizing we can say that replacing the negative point charge by several point charges distributed in a certain range has only significant effect when the test point is close to a negative charge. The potential at 2.5 Å from the image plane at -3 Å from a dipole, which is relevant for the potential at the adsorption sites of the noble gases, is not very much affected by the split negative charge, and is well described by simple dipoles, which have only one negative point charge. In addition, the potentials further than 3 Å from a dipole are largely determined by the dipole moment. The effect of the charge distribution - the charge separation as well as the spatial distribution of the negative charge - is limited to the range very close to the dipole charges (<3 Å).

### 4.3 Relation between Measured and Calculated Electrostatic Potential

*Relation between measured dipole moment and point charge dipole moment.*

The dipole moment of the adsorbed potassium is experimentally accessible through work function measurements. The relation between the macroscopic work function and the dipole moment of an adsorbed particle at low coverages is given by the Helmholtz equation (see also Eq. 3.4):

\[
\overline{\mu} = \frac{-\Delta \varphi \, \varepsilon_0}{N_K}
\]

(4.5)

where \( \overline{\mu} \) is the average dipole moment per potassium atom, \( \varepsilon_0 \) is the dielectric constant in vacuum (\( 8.85 \times 10^{-14} \, \text{C/V cm} \)), \( -\Delta \varphi \) is the potassium induced potential change over the dipole layer in (V), which is numerically equal to the measured work function decrease in eV, and \( N_K \) is the number of potassium atoms per cm\(^2\), which is known from the potassium coverage. Table 4.2 summarizes the potassium coverages, number of potassium atoms per cm\(^2\), the measured work function decrease (Section 3.4.1), and the calculated dipole moment for adsorbed potassium. We find a dipole moment of 7.8 ± 0.5 D for potassium coverages below 5.0 at%. This value is of the same order of magnitude as for potassium on comparable substrates. Table 4.3 lists values for the dipole moment (\( \mu \)) of potassium on various substrates in the low coverage limit, according to Eq. 4.5.

To compare the dipole moment evaluated from the work function measurements using Eq. 4.5, we must realize that this equation relates a potential decrease with a dipole moment of a point charge dipole in the vacuum, by using \( \varepsilon_0 \) for the dielectric constant. This potential
Calculations on the Electrostatic Potential on K/Rh(111)

Table 4.2 The dipole moment per potassium atom, according to the Helmholtz equation. With the experimentally determined potassium-induced work function change and potassium coverage, we find a dipole moment of 7.8±0.5 D per adsorbed potassium atom.

<table>
<thead>
<tr>
<th>coverage</th>
<th>(N_K)</th>
<th>(\Delta \varphi)</th>
<th>dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>at%</td>
<td>cm(^2)</td>
<td>eV</td>
<td>C cm</td>
</tr>
<tr>
<td>2.7</td>
<td>4.32(\times)10(^{13})</td>
<td>1.2</td>
<td>2.5(\times)10(^{-27})</td>
</tr>
<tr>
<td>4.1</td>
<td>6.56(\times)10(^{13})</td>
<td>1.9</td>
<td>2.6(\times)10(^{-27})</td>
</tr>
<tr>
<td>5.0</td>
<td>8.00(\times)10(^{13})</td>
<td>2.5</td>
<td>2.8(\times)10(^{-27})</td>
</tr>
</tbody>
</table>

decrease is shown in Figure 4.12 (top curve) and can be calculated from (see also Eq. 4.5):

\[- \Delta \varphi = \frac{N \mu}{\varepsilon_0}\]  

(4.6)

where \(-\Delta \varphi\) is the potential decrease (V), \(N\) is the number of particles (cm\(^2\)) and \(\mu\) is the dipole moment (C cm). This dipole moment is given by \(Q \ast 2d\), where \(Q\) is the point charge value and \(d\) is the distance between the image plane and the point charges.

In the experimental situation, however, the negative charge is located in the metal, which has a dielectric constant \(\varepsilon_{\text{metal}} = \varepsilon_r \varepsilon_0\), with the relative dielectric constant \(\varepsilon_r \neq 1\). At the point

Table 4.3 Reported values for the dipole moment of adsorbed potassium on various substrates. Adsorbed potassium on a metal surface has a dipole moment in the order of 2-9 D, directed towards the surface. The dipole moments result from a charge transfer from the potassium atoms to the metal surface.

<table>
<thead>
<tr>
<th>Surface</th>
<th>dipole moment (D)*</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/Rh(111)</td>
<td>7.8</td>
<td>This work</td>
</tr>
<tr>
<td>K/Ni(100)</td>
<td>6.3</td>
<td>[3,4]</td>
</tr>
<tr>
<td>K/Ni(110)</td>
<td>2.7</td>
<td>[3,4]</td>
</tr>
<tr>
<td>K/Ni(111)</td>
<td>3.7</td>
<td>[5]</td>
</tr>
<tr>
<td>K/Ru(001)</td>
<td>7.9</td>
<td>[3]</td>
</tr>
<tr>
<td>K/Ru(1010)</td>
<td>7.1</td>
<td>[4]</td>
</tr>
<tr>
<td>K/Pt(111)</td>
<td>5.1</td>
<td>[4]</td>
</tr>
<tr>
<td>K/Al(100)</td>
<td>9.4</td>
<td>[3,4]</td>
</tr>
<tr>
<td>K/Fe(110)</td>
<td>2.3</td>
<td>[4]</td>
</tr>
<tr>
<td>K/Ta(110)</td>
<td>6.0</td>
<td>[3]</td>
</tr>
<tr>
<td>K/W(110)</td>
<td>6.5</td>
<td>[3]</td>
</tr>
<tr>
<td>K/W(110)</td>
<td>7.9</td>
<td>[3]</td>
</tr>
<tr>
<td>K/W(211)</td>
<td>6.8</td>
<td>[3]</td>
</tr>
<tr>
<td>K/W(100)</td>
<td>5.8</td>
<td>[3]</td>
</tr>
<tr>
<td>K/W(111)</td>
<td>4.3</td>
<td>[3]</td>
</tr>
</tbody>
</table>

* Values for \(\mu\), according to Eq. 4.1 are listed. In literature one often finds the double values (2\(\mu\)).
where the value of the dielectric constant changes, the slope of the curve in Figure 4.12 is reduced by a factor \( l/\varepsilon_r \). Assuming that this change takes place at the image plane of the dipoles [6], the total potential decrease is found from addition of the potential decreases on both sides of the image plane (Figure 4.12):

\[
-\Delta \varphi = \frac{N\mu}{2\varepsilon_r \varepsilon_0} + \frac{N\mu}{2\varepsilon_0}
\]

(4.7)

Since \( \varepsilon_r \) is large for metals, the first term reduces to 0 and the total potential decrease at the metal surface is given by the second term only, i.e. the potential decrease on the vacuum side. This can be rearranged to:

\[
\mu = \frac{-2 \Delta \varphi \varepsilon_0}{N}
\]

(4.8)

Comparing this result with Eq. 4.5, we see that the point charge dipole moment (in vacuum) is twice the experimentally determined dipole moment. This follows from the assumption of a large dielectric constant on the "metal-side" of the image plane and a dielectric constant equal to \( \varepsilon_0 \) on the vacuum-side. The high value for the dielectric constant in the metal is physically expressed as a charge accumulation in a certain range in the metal surface [1-3,6]. At the positions of the noble gas atoms, the effect of such a charge distribution on the potential is limited (Section 4.2).

According to this argumentation, the potential decrease on the vacuum side due to the potassium atoms with a measured dipole moment of 7.8 D is well described by a point charge dipole moment in vacuum of 15.6 D. The value of 10 D for the point charge dipole, which matches the experimentally estimated changes in surface potential, is lower than the value expected from the experiment. This suggests that the experimentally estimated potential changes are too low.

**Figure 4.12** The electrostatic potential along the surface dipoles for different values of the dielectric constant on the metal side of the image plane. For high values of the dielectric constant, the potential decrease is half of that in vacuum. Hence the potential decrease on the vacuum side of the metal surface is well described by a point charge dipole in vacuum, which has the double value of the experimentally determined dipole moment [6].
Calculations on the Electrostatic Potential on K/Rh(111)

Table 4.4 Comparison of the calculated electrostatic potential at the noble gas atom centre and the average potential over the noble gas atom at the different adsorption sites, according to the dipole model. The lateral distance between the noble gas atoms is the same as in the adsorption geometries in Figures 3.11, 3.16 and 3.21. The height (z) is determined on the basis of a 3-fold adsorption site of both the potassium and the noble gas atoms, using the Van der Waals radii for the noble gas atoms. Dipole moment per potassium atom: 10 D ($2d_z = 2.18 \, \text{Å}$, $Q=0.957$); potassium coverage 2.7 at%.

<table>
<thead>
<tr>
<th></th>
<th>K/Rh site</th>
<th>Rh site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>atom centre</td>
<td>atom averaged</td>
</tr>
<tr>
<td>Xe</td>
<td>-0.93</td>
<td>-0.84</td>
</tr>
<tr>
<td>Kr</td>
<td>-1.05</td>
<td>-0.95</td>
</tr>
<tr>
<td>Ar</td>
<td>-1.12</td>
<td>-1.01</td>
</tr>
</tbody>
</table>

Average potential over the volume of the noble gas atom.

The local surface potential probed by an adsorbed noble gas atom is an averaged value over the volume of the noble gas atom, weighed by the spatial distribution of the orbital that is ionized. We have approximated this averaged value as the potential at the centre of the noble gas atom. The deviation of the potential at the centre of a noble gas atom from the (unweighed) averaged value over the volume of the noble gas atom is an estimate of the error of this approximation. This can be calculated with the dipole model.

Assuming that the positively charged potassium atoms are adsorbed on a 3-fold adsorption site and the negative charge is located in the first Rh layer, we obtain a charge separation ($2d_z$) of 2.18 Å. To obtain a dipole moment of 10 D, which gives a good description of the experimental data, we need a charge $Q$ of 0.957. The size and position of the noble gas atoms are taken from the adsorption geometries given in Figures 3.11, 3.16 and 3.21. The distance from a noble gas atom to the image plane ($z$-coordinate) is estimated on the basis of a 3-fold adsorption site for the noble gases, assuming that no reconstruction of the Rh surface takes place.

Table 4.4 summarizes the potentials at the centre of the noble gas site and the atom-averaged potentials for the sites next to potassium and on bare Rh. The potential change at the centre of a noble gas atom next to a potassium atom at 2.7 at% potassium coverage is about 10% smaller than the atom averaged value. For the noble gas atoms on the Rh sites, the deviation is about 2%, in agreement with the smaller variation of the local surface potential further away from the potassium atoms. Assuming that the atom averaged value is a better approximation for the orbital averaged value, the values indicate that the potassium-induced change in potential at the centre of a noble gas atom is underestimated by the shifts of the noble gas photoemission signals. The error is larger for the sites close to the potassium...
The values presented here differ somewhat from the previously calculated potentials (Figure 4.8), since we used a different value for \(z\). Note that the calculated potentials at the Rh sites is about the same for Xe, Kr and Ar. The larger lowering of the potential due to the shorter distance to the nearest potassium atom (x-coordinate) for Kr and Ar, compared to Xe, is cancelled by the shorter distance to the surface (z-coordinate; Figure 4.6, left).

**Effect of relaxation**

As already mentioned in the introduction, the interpretation of Figure 3.23 in terms of changes in local work function implies that the extra-atomic relaxation energy of an adsorbed noble gas atom is the same on clean and potassium covered Rh(111). The extra-atomic relaxation energy for adsorbates on a metal surface is mainly determined by the image potential, which depends on the distance between noble gas atom and metal surface. Since this distance is the same on the clean and potassium covered Rh, the presence of potassium is not expected to influence the extra-atomic relaxation too much.

A method for detecting changes in extra-atomic relaxation energy experimentally is measurement of the Auger parameter (Section 2.3). The Auger parameter is the difference between the kinetic energy of an Auger electron and that of a photoelectron [7]. The kinetic energy of an Auger electron contains the relaxation energy of a doubly charged (2+) ion, whereas in the kinetic energy of the photoelectron the smaller relaxation of a singly charged (1+) ion is included. Therefore, a change in relaxation energy results in a change in the Auger parameter. The Auger parameter is not affected by electrostatic shifts of the Auger and photoemission signals, since they cancel by taking the difference. It appears that the change in Auger parameter is twice the extra-atomic relaxation [7].

Mullins *et al.* have measured the Auger parameter for adsorbed Xe on Ni(100) as a function of the potassium coverage, using the Xe-3d\(_5\)\(_2\) photoemission peak and the Xe(MNN) Auger peak [8]. The energy difference between these peaks Ni(100) is reduced from 40.4 eV for Xe on clean Ni(100) to 39.8 eV at a potassium coverage of 4\%. In this example the kinetic energy of the photoelectron is higher than that of the Auger electron. Hence, the smaller energy difference between the Auger and photoelectron for Xe on the potassium covered surface corresponds to a 0.3 eV larger relaxation energy. In the UPS spectrum, this is transformed to a 0.3 eV lower binding energy. Assuming that the result for Xe on potassium covered Ni is transferable to Rh, the potential changes on the potassium covered Rh surfaces are \(-0.3\) eV underestimated by the shift of the noble gas photoemission signals. Analogously, a difference in relaxation energy of 0.1 eV for Xe on clean Ru(001) and on a thick potassium layer on Ru(001) has been reported [9].

According to the discussion above, we have several indications, that the potassium induced changes in local work function at the noble gas adsorption sites are underestimated by the shifts of the UPS signals of adsorbed noble gases. First, the averaged potential change over the volume of a noble gas atom in a dipole network is smaller than the potential change
Calculations on the Electrostatic Potential on K/Rh(111)

at the centre of a noble gas atom. Secondly, measurement of the Auger parameter for Xe on clean and potassium covered Ni(100) suggests that the relaxation energy of the photoionized adsorbed noble gases is larger in the presence of potassium. This is consistent with a smaller dipole moment than expected from the experimental value to reproduce the experimental data.

4.4 Quantum-Chemical Calculation of the Electrostatic Potential on Rhodium-Potassium Clusters

Introduction
The actual charge distribution in the metal surface around a potassium atom remains undetermined in the calculation of the electrostatic potential in a hexagonally ordered network of dipoles (Section 4.2). However, above 3 Å from the nearest dipole the electrostatic potential is adequately described by the dipole moment. Closer to the dipoles, the position of the point charges and the distribution of the negative charge influence the calculated potential substantially.

By quantum-chemical computation of the electron distribution in clusters containing Rh and potassium atoms, we try to determine the electrostatic potential with a more realistic charge distribution than in the dipole model. The electron distribution in the clusters are calculated according to the density functional theory, using the ADF program [10] on an Alliant/FX2816 computer.

We use clusters with hexagonally ordered Rh atoms as a model for the Rh(111) surface. All clusters have at least a 3-fold rotation axis (C₃ᵥ-symmetry). The distance between the Rh atoms used in the calculations equals that of the Rh(111) surface, viz. 2.687 Å. Adsorbed potassium atoms are placed on top or on a 3-fold Rh site, with preservation of the cluster symmetry. In all calculations, a Rh-K distance of 2.674 Å has been used, i.e. the sum of the radius of Rh (1.344 Å) and of ionic potassium (1.33 Å). These are the same values as used in the adsorption geometries in the Figures 3.11, 3.16 and 3.21. The potassium-induced change in electrostatic potential is determined from the difference between the electrostatic potential on a Rh cluster with potassium and that on the same cluster without potassium.

We have calculated the potassium-induced change in electrostatic potential on various clusters, viz. Rh₇K, Rh₁₃K, Rh₁₂K₃, Rh₁₃K₃, Rh₁₆K₃, and two Rh₁₅K₃ clusters with a different geometry. On the larger clusters we can place 3 potassium atoms at about 10 Å from each other. This distance is somewhat smaller than for the highest potassium coverage in the experiments (12 Å). It appears that the potassium-induced change in electrostatic potential depends critically on the geometry of the cluster. The clusters that allow charge distribution around the potassium atom yield potentials that are closer to the experimental data.

To estimate the effect of the relaxation energy in the photoemission of adsorbed noble
gases, we calculate the ionization energies for adsorbed Xe, Kr and Ar on a Rh\textsubscript{15} and a Rh\textsubscript{15}K\textsubscript{3} cluster (Figure 4.15), using the same program. Unfortunately, the potassium-induced change in potential on this cluster is not in agreement with the experiment, due to the geometry of the cluster. However, the calculated ionization energy of the adsorbed noble gas atoms reflect the erroneous calculated potentials. This suggests that the presence of potassium does not affect the relaxation energy of the adsorbed noble gas atoms too much, in accordance with the assumption made in the interpretation of the noble gas UPS spectra.

Method
In the density functional theory, the electron density \( \rho(r) \), which is a function of the spatial coordinates, determines the ground state energy of the system. In other words, the ground state energy \( E[\rho] \) is a unique functional of the electron density \( \rho(r) \). This is expressed by the first theorem of Hohenberg and Kohn, saying that the external potential \( v(r) \) is uniquely defined by the electron density \( \rho(r) \), except for a trivial constant. The external potential is the total potential energy minus the electron-electron repulsion. Since the relation between electron density and ground state energy is unique, we can formulate a variational principle: The energy belonging to a trial density \( \rho \), \( E[\rho] \), is larger than or equal to the ground state energy \( E_0 \) (second Hohenberg-Kohn theorem). Minimization of the energy functional \( E[\rho] \) thus leads to the ground state energy. So we have to find the density \( \rho(r) \) that gives the lowest energy, with the restriction that \( \int \rho(r) \, dr = N \), the total number of electrons.

Kohn and Sham developed a method for finding the minimum energy iteratively [11]. They transformed the many electron problem to \( N \) non-interacting electrons in an effective potential \( v_{\text{eff}} \). The effective potential also depends on the electron density. One starts with a guessed electron density and calculates the effective potential. With this potential orbitals (the Kohn-Sham orbitals) are constructed, that result in a new density \( \rho(r) \). The energy of the ground state is found from the self-consistent solution for the electron density, \textit{i.e.} the orbitals constructed with an effective potential calculated from a electron density yield the same electron density.

This method is in principle exact, but one needs an explicit form for the exchange-correlation energy, which is unknown. The exchange-correlation energy contains the difference in kinetic energy between non-interacting and interacting electrons and the non-classical part of the electron-electron interaction. In the local density approximation (LDA), the exchange-correlation energy at position \( r \) is estimated by the exchange-correlation energy for a homogeneous electron gas with density \( \rho(r) \). Integration over \( r \) results in the total exchange-correlation energy. In our calculations, the expression proposed by Vosko, Wilk and Nusair has been used [11]. The reader is referred to Parr and Yang [11] for more information on the density functional theory.

The electrostatic potential at a given point \( r' \) is given by:
Calculations on the Electrostatic Potential on K/Rh(111)

Figure 4.13 Left: Geometry of the Rh$_7$K cluster. The central Rh atom is surrounded by 6 Rh atoms. The potassium is placed on top of the central Rh atom. Right: Electrostatic potential for on the Rh$_7$K-cluster in the plane perpendicular to the cluster through the dashed line. The curves give the potassium-induced change in potential as a function of the lateral distance to the potassium atom at various heights from the Rh plane.

\[ V(r') = \frac{1}{4\pi\varepsilon_0} \left( \sum_{i=1}^{N} \frac{Z_i}{|r'-r_i|} - \int \frac{\rho(r)}{|r'-r|} \, dr \right) \]  

where \( N \) is the number of atoms, \( Z_i \) the nuclear charge of the atom at position \( r_i \) and \( \rho(r) \) is the electron density.

A hexagonal cluster: Rh$_7$K

The Rh$_7$K cluster consists of a central Rh atom, that is surrounded by 6 Rh atoms in one plane and potassium atom on top of the central Rh atom (Figure 4.13). Adsorption of potassium on this Rh$_7$ cluster is accompanied by a charge transfer from the potassium atom to the Rh atoms, in agreement with the experiments and calculations of potassium on Cu clusters [12]. Figure 4.13 shows the potassium-induced electrostatic potential change on the Rh$_7$K cluster at different heights, in the plane perpendicular to the cluster along the x-axis. The heights (2.38 Å, 3.18 Å and 3.97 Å above the plane through the centre of the Rh atoms) include the heights where the noble gas atoms are adsorbed (2.85-3.24 Å for Ar, 2.96-3.34 Å for Kr and 3.18-3.54 Å for Xe). The potentials depicted in Figure 4.13 indicate the limits for the electrostatic potential change that would be detected by adsorbed noble gas atoms.

Very close to the potassium atom (<2.5 Å), the electrostatic potential decreases. However, at distances around 3 Å from the potassium atom, we find potential changes, that are much
smaller than the experimental values; at 2.38 Å from the Rh plane, we even find an increase in electrostatic potential. At this height, the contribution of the electrons to the potential dominates over the contribution of the positively charged potassium atom. This follows from the charge distribution in the cluster, which does not resemble that of the potassium-covered Rh surface. On the cluster, the charge transferred from the potassium can only be distributed over the 7 Rh atoms, which all correspond to the first Rh layer. To minimize the repulsion between the electrons, the charge accumulates at the edges of the cluster. A crude indication for the charge distribution in the cluster is the Mulliken charge of the Rh atoms after potassium adsorption: The potassium-induced change of the charge is -0.152 for the central Rh atom and -0.163 for each atom at the edge. These values indicate that 13% of the transferred charge remains on the central Rh atom; the rest accumulates at the edge of the cluster. This charge accumulation causes the high values for the electrostatic potential further away from the potassium atom. As this does not at all represent the situation in the experiment, the Rh$_7$K cluster is inappropriate to describe the electrostatic potential on potassium covered Rh(111).

A triangular cluster: Rh$_{15}$K
This Rh$_{15}$K cluster has a triangular form with 5 Rh atoms at one side. The potassium atom is placed in the 3-fold site in the centre of the cluster (Figure 4.14). On this cluster, the charge transferred to the Rh atoms upon potassium adsorption is also distributed in a large

![Figure 4.14](image)

**Figure 4.14** Left: Geometry of the Rh$_{15}$K cluster. Right: Potassium-induced change in electrostatic potentials on the Rh$_{15}$K cluster as a function of the lateral distance to the potassium atom at various heights from the Rh plane.
Calculations on the Electrostatic Potential on K/Rh(111)

Figure 4.15 Left: Geometry of the Rh$_{15}$K$_3$ cluster. The potassium atoms are adsorbed on top of the Rh atoms at the extremities of the triangle. Right: The potassium-induced changes in electrostatic potential at the Rh$_{15}$K$_3$ cluster at different heights from the Rh cluster. Due to the charge accumulation in the Rh atoms, the potential increases when potassium is adsorbed.

range around the potassium atom, although it remains more concentrated in the centre of the cluster: 53% is located on the Rh atoms in contact with the potassium atom. Only 8% of the charge is found at the extremities of the cluster.

The potassium-induced change in electrostatic potential is shown in Figure 4.14, at 2.38 Å, 3.18 Å and 3.97 Å above the Rh plane. Compared to the potential changes on the Rh$_7$K cluster, we find lower electrostatic potentials close to the potassium atom. The potential increase at 2.38 Å above the Rh plane, that we found on Rh$_7$K, is not reproduced. The potassium-induced potential changes on this cluster are closer to the experimental values than the changes found on the Rh$_7$K cluster.

More potassium atoms: Rh$_{15}$K$_3$

Due to the limited possibilities for distributing the transferred electrons, the clusters described above do not reproduce the experimentally estimated change in surface potential. An electron distribution, that is more similar to the experimental one, might be expected from the Rh$_{15}$K$_3$ cluster (Figure 4.15). In this cluster, a potassium atom is placed on top of the Rh atoms at the extremities. The distance between the potassium atoms is 10.75 Å. This corresponds to a potassium coverage of 6.2 at% for an infinite hexagonally ordered layer.

The potassium atoms in this Rh$_{15}$K$_3$ cluster donate electrons to the Rh atoms, which drives the electrons to the centre of the cluster, whereas the cluster itself pushes the electrons to the edges. We find 74% of the transferred charge on the Rh atoms beneath the potassium
atoms (A in Figure 4.15), 3% on the three central Rh atoms (B), 5% per atom on the Rh atoms next to the potassium site (C) and 12% on the atoms at half way distance between two potassium atoms (D). Compared to the previously discussed clusters, the electrons are more concentrated below the potassium atoms.

Figure 4.15 (right) shows the potassium-induced electrostatic potential changes on the Rh$_{15}$K$_3$ cluster for different heights between 2.65 and 3.70 Å along the x-axis (dashed line Figure 4.15). We find again a potential increase, which is even larger than on the clusters containing only one potassium atom. There are two contributions to this potential increase. First, more charge is transferred to the Rh atoms compared to the Rh$_7$K and Rh$_{15}$K cluster, since the Rh$_{15}$K$_3$ cluster contains three potassium atoms instead of one. The K/Rh ratio in the Rh$_{15}$K$_3$ cluster (0.2) is much higher than in the experiments (maximum: 0.05) and this cluster offers no possibility to locate electrons in the second Rh layer. The electrons accumulate at the Rh atoms between the potassium atoms. Therefore, the Rh atoms in the cluster become more negatively charged than the surface atoms in the experiment, which leads to an increase of the surface potential.

Secondly, the potassium atoms are placed at the extremities of the cluster and therefore the charge that is transferred to the Rh atoms can not be distributed around the potassium atom. This leads to an increased electron density in the centre of the cluster and hence in a higher electrostatic potential on the cluster. Better results can be expected, when the potassium atoms are surrounded by Rh atoms.

![Diagram of Rh$_{12}$K$_3$ cluster](image)

**Figure 4.16** Left: Geometry of the Rh$_{12}$K$_3$ cluster. The potassium atoms are placed on 3-fold sites at the extremities of a central triangle. Right: The potassium-induced change in electrostatic potential on the Rh$_{12}$K$_3$ cluster as a function of the lateral distance to the potassium atom on the left of the cluster at various heights from the Rh plane.
Increasing the potassium coordination: \( \text{Rh}_{12}K_3 \)

To avoid charge accumulation in the cluster, we have to change the geometry of the cluster in such manner, that the charge can be distributed around a potassium atom. Figure 4.16 depicts a \( \text{Rh}_{15}K_3 \) cluster with such a geometry. In this cluster, the potassium atoms are placed on 3-fold site just outside the edges of a central triangle, that consists of 6 Rh atoms. The distance between the potassium atoms is 8.06 Å, which corresponds to a potassium coverage of 11.1 at% in an infinite hexagonally ordered layer. In contrast to the \( \text{Rh}_{15}K_3 \) cluster, the electrons are also transferred to the Rh atoms at the edges, away from the centre of the cluster, thus reducing the electron density in the centre of the cluster: 12% of the transferred charge is located at the three central Rh atoms, the rest is distributed over the Rh atoms in contact with the potassium atoms.

Figure 4.16 (right) shows the potassium induced potential change on the \( \text{Rh}_{12}K_3 \) cluster along the \( x \)-axis (dashed line in Figure 4.16, left) of the cluster for different heights above the Rh plane between 2.65 Å and 3.70 Å. The potential change on the \( \text{Rh}_{12}K_3 \) cluster is much more like the experimental situation: Between 2.65 Å and 3.70 Å above the Rh plane, the potential further away from the potassium atoms is lowered due to the presence of potassium. Since the potassium atoms are better coordinated in this cluster, the electrons can be distributed around the potassium atoms. This results in a better description of the electrostatic potential on potassium covered Rh(111).

Some variations of \( \text{Rh}_{12}K_3 \): \( \text{Rh}_{15}K_3 \), \( \text{Rh}_{13}K_3 \) and \( \text{Rh}_{16}K_3 \).

Adsorption of potassium on the \( \text{Rh}_{12} \) cluster, which gives the \( \text{Rh}_{12}K_3 \) cluster, leads to a decrease of the electrostatic potential, in agreement with the experiment. The \( \text{Rh}_{12}K_3 \) cluster also allows a few variations in geometry. We can check how additional Rh atoms in the second layer influence the calculated potentials.

![Figure 4.17](image-url)
When we place Rh atoms beneath the potassium adsorption site in the Rh\textsubscript{12}K\textsubscript{3} cluster, we obtain a Rh\textsubscript{15}K\textsubscript{3} cluster, which we will denote as Rh\textsubscript{15}K\textsubscript{3} to distinguish it from the previously discussed Rh\textsubscript{15}K\textsubscript{3} cluster. The calculated potential on the Rh\textsubscript{15}K\textsubscript{3} cluster is shown in Figure 4.17. The potassium-induced change in potential is smaller on this cluster than on the Rh\textsubscript{12}K\textsubscript{3} cluster and is positive close to the Rh plane (<3 Å). This is caused by a larger charge transfer on the Rh\textsubscript{15}K\textsubscript{3} cluster: The Mulliken charge on the potassium atom is 1.49 in the Rh\textsubscript{15}K\textsubscript{3} cluster and 1.36 on the Rh\textsubscript{12}K\textsubscript{3} cluster. Due to this extra charge, all Rh atoms become more negatively charged, which causes the higher potential. The charge on the Rh atoms in the second layer is -0.05, which is 40% of the extra charge transferred to the Rh atoms, compared to the Rh\textsubscript{12} cluster. The remaining 60% is located in the surface atoms.

We can also put an extra Rh atom beneath the three central Rh atoms, which yields a Rh\textsubscript{13}K\textsubscript{3} cluster. In this cluster, the Rh atom in the second layer has no significant influence on the charge distribution and therefore the calculated electrostatic potential on this cluster (Figure 4.18, left part) is similar to that on the Rh\textsubscript{12}K\textsubscript{3} cluster (Figure 4.16).

The calculation of the potential on the clusters do not include the contribution of the potassium atoms further away. We can use the dipole model to estimate this contribution by subtracting the contribution of the dipoles that represent the three potassium atoms on the cluster from the total potential.

We assume that the negative charge is concentrated in the first Rh layer and the positive charge on a potassium atom adsorbed on a 3-fold site. Then we have a charge separation of 2.18 Å. Hence, the image plane of the dipoles is placed 1.09 Å above the Rh plane. The
Calculations on the Electrostatic Potential on K/Rh(111)

Distance between the dipoles is equal to the distance between the potassium atoms on the Rh$_{13}$K$_3$ cluster, viz. 8.06 Å. The potassium-induced change in the dipole moment perpendicular to the Rh$_{13}$K$_3$ cluster is 14.7 D. Assuming that this is the result of three dipoles at the position of the potassium atoms, we find a dipole moment of 4.9 D per potassium atom. This corresponds to 9.8 D for a point charge dipole in vacuum, assuming a high value...
for the dielectric constant in the metal phase. Thus, we have as input for the dipole model: 1.09 Å for \(d_1\), 8.06 Å for \(d_{kk}\), and a dipole moment of 9.8 D, which corresponds to a charge \(Q\) of 0.935 with the given value for the charge separation.

Figure 4.19 displays the contribution of the dipoles further away to the potential on the Rh\(_{13}\)K\(_3\) cluster as a function of the distance to the image plane. These contributions are almost independent of the lateral distance to the nearest dipole. When we add the potential on the Rh\(_{13}\)K\(_3\) cluster and the contribution of the dipoles further away, we obtain the potentials shown in Figure 4.18 (right). These potentials are considerably lower than the values without the dipole correction, but they do not reach the value of the potential in a hexagonally ordered network with this dipole density (-2 to -2.3 V), due to the more negatively charged Rh atoms.

By increasing the number of Rh atoms in the central triangle from 6 to 10, we get a Rh\(_{16}\)K\(_3\) cluster, with all Rh atoms in one plane (Figure 4.20, left). The distance between the potassium atoms is the same as on the triangular Rh\(_{15}\)K\(_3\) cluster, viz. 10.79 Å, corresponding to a potassium coverage of 6.2 at% for an infinite hexagonally ordered layer.

Figure 4.20 (right) shows the potassium induced potential changes along the x-axis on this cluster for different heights between 2.64 Å and 3.70 Å above the Rh plane. On this cluster we find a potassium induced potential increase at larger distances from the potassium atom. The Rh atoms surrounding the central Rh atom become negatively charged; they take 13% of the charge transferred to the Rh atoms. Since these atoms are located in the centre of the cluster, the potential further away from the potassium atoms increases with potassium adsorption. Compared to the Rh\(_{13}\)K\(_3\) cluster, which has the same distance between the potassium atoms, the potential increase is lower: In the Rh\(_{16}\)K\(_3\) cluster, the electrons are distributed around the potassium atoms.

**Applicability of K/Rh clusters to model potassium-covered Rh.**
The electron distribution in the K/Rh clusters differs from that of the potassium-promoted Rh surface, due to the limited size of the clusters. The Rh clusters contain only 4 or 5 Rh atoms per potassium atom, whereas the metal surface covered with 5% potassium contains 20 Rh atoms per potassium atom, the Rh atoms in the deeper layers not included. In agreement with the experimental observation, a charge transfer to the Rh atoms takes place when potassium is adsorbed on a Rh cluster. In a cluster, this charge is distributed over a smaller number of Rh atoms. The Rh atoms become more negatively charged, compared to the experiment, which leads to higher values for the potential. In addition, the contribution of the potassium atoms further away to the potential, which is in the order of 0.5-1.0 V, is not included in the cluster calculation. For these reasons, the calculated potentials at the clusters are higher than the experimentally estimated values. Correction for the contribution of the dipoles further away yields, of course, better values for the electrostatic potential.

The values for the potential depend critically on the geometry of the cluster. The direction of the electrostatic field perpendicular to the Rh plane is correct on all clusters: The
potential at larger distances from the cluster is lower. For clusters that allow distribution of the charge around the potassium atoms, the calculated potentials are closer to the experimentally estimated values. Therefore, such clusters are better models for potassium covered Rh(111).

Relaxation energy of ionized noble gas atoms on Rh\(_{15}K_3\).

The interpretation of the shifts of the UPS signals of adsorbed noble gases as changes in local work function implies that the presence of potassium does not affect the relaxation energy of the photoionized probe atoms. To check the validity of this assumption, we calculate the ionization energy of Xe, Kr and Ar adsorbed on the 3-fold site in the centre of the triangular Rh\(_{15}\) and Rh\(_{15}K_3\) cluster. Unfortunately, the potassium-induced change in surface potential on this cluster does not correspond to the experiment. Nevertheless, the ability of adsorbed noble gas atoms to detect surface potentials is independent of the actual value of the potential.

The ionization energy of the noble gas atom is given by the energy difference of the system containing an ionized noble gas atom and the same system with a neutral noble gas atom:

$$I = E_{n-1} - E_n = -\int_{n-1}^{n} \frac{\partial E(n)}{\partial n} \, dn$$  \hspace{1cm} (4.10)

where \(n\) denotes the number of electrons. An efficient method to calculate the ionization energy is to make use of the property, that the partial derivative of the energy to the occupation number equals the orbital energy of a Kohn-Sham orbital (Janak's theorem [11]). Then the ionization energy can also be written as:

$$I = -\int_{n-1}^{n} \epsilon(n) \, dn$$  \hspace{1cm} (4.11)

where \(\epsilon\) is the orbital energy from which the electron is removed. In first order approximation, this integral is equal to \(-\epsilon(n-\frac{1}{2}) \Delta n\). As \(\Delta n = 1\), this equals the orbital energy from which half an electron is removed. Therefore, we approximate the ionization energy of an adsorbed noble gas atom by removing half an electron from the noble gas valence level, and compute the new orbital energies in the cluster. The ionization energy is then given by the orbital energy of the partially ionized orbital. This is a very efficient way to calculate the ionization energies. Note that the ionization energy in the calculation is referenced to a fixed vacuum level, whereas in the experiments the Fermi-level of the substrate is fixed. Therefore, a change of the calculated ionization energy of an adsorbed noble gas atom has the same meaning as a shift of the noble gas signal in the UPS spectrum.

Table 4.5 summarizes the calculated ionization potentials for gaseous Xe, Kr and Ar and the same atoms adsorbed at the 3-fold site in the centre of the triangular Rh\(_{15}\) cluster.
Table 4.5 Calculated ionization energies for Xe, Kr and Ar in the gas phase and adsorbed on the Rh\textsubscript{15} cluster. The noble gas atoms are placed at the central 3-fold site of the cluster. The relaxation energy is the difference between the ionization energy of adsorbed and gaseous noble gases (See also Table 3.1).

<table>
<thead>
<tr>
<th>noble gas ionization energy</th>
<th>relaxation</th>
<th>gas phase</th>
<th>adsorbed on Rh\textsubscript{15}</th>
<th>(eV)</th>
<th>(eV)</th>
<th>(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe</td>
<td>-1.14</td>
<td>12.77</td>
<td>11.63</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kr</td>
<td>-1.56</td>
<td>14.59</td>
<td>13.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>-1.59</td>
<td>16.39</td>
<td>14.80</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Figure 4.15). The ionization energy of a noble gas atom adsorbed on the Rh\textsubscript{15} cluster is lower than the gas phase value. The difference between the ionization energy of gaseous and adsorbed noble gases is the extra-atomic relaxation energy. The calculated relaxation energies are close to the experimentally determined values (Table 3.1). The distance between the noble gas atom and the Rh atoms is not optimized, which may cause the small difference between the calculated relaxation energy for adsorbed Kr and Ar on the Rh\textsubscript{15} cluster.

The influence of potassium on the relaxation energy is estimated from a comparison of the difference in ionization energy for adsorbed Xe, Kr and Ar on the Rh\textsubscript{15} and the Rh\textsubscript{15}K\textsubscript{3} cluster with the value expected from the potassium-induced change in electrostatic potential.

Table 4.6 Calculated ionization potentials for Xe, Kr and Ar adsorbed on the Rh\textsubscript{15} and Rh\textsubscript{15}K\textsubscript{3} cluster. The noble gas atoms are placed in central 3-fold site of the clusters. The expected ionization energy differences are evaluated from the electrostatic potential at the noble gas atom centre and from the averaged potential over the z-axis of the noble gas atom. The calculated ionization energy deviates slightly from the value expected from the electrostatic potential on these clusters.

<table>
<thead>
<tr>
<th>calculated ionization energy of adsorbed noble gas</th>
<th>expected ionization energy change from electrostatic potential</th>
<th>deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>on Rh\textsubscript{15}</td>
<td>on Rh\textsubscript{15}K\textsubscript{3}</td>
<td>difference</td>
</tr>
<tr>
<td>(eV)</td>
<td>(eV)</td>
<td>(eV)</td>
</tr>
<tr>
<td>Xe 11.63</td>
<td>10.96</td>
<td>-0.67</td>
</tr>
<tr>
<td>Kr 13.03</td>
<td>12.33</td>
<td>-0.70</td>
</tr>
<tr>
<td>Ar 14.80</td>
<td>13.78</td>
<td>-1.02</td>
</tr>
</tbody>
</table>
Calculations on the Electrostatic Potential on K/Rh(111)

on the Rh$_{15}$K$_3$ cluster. As the potential close to the Rh$_{15}$ cluster increases upon potassium adsorption, we expect a lower ionization energy for a probe atom on this cluster compared to the Rh$_{15}$ cluster, in contrast to the experiments.

The spin-orbit coupling, which is observed in the experiments, is not included in the calculations. However, it is not affected by the presence of potassium: For all noble gas atoms on both the clean and potassium covered surfaces the spin-orbit splitting remains the same. In other words, each noble gas signal in the UPS spectrum can be used to estimate local surface potential changes.

The ionization energies of adsorbed Xe, Kr and Ar on the Rh$_{15}$ and the Rh$_{15}$K$_3$ cluster are given in Table 4.6. The lateral distance between the noble gas atom and the potassium atoms is 6.2 Å. The potassium-induced potential change at the centre of the noble gas atom and the potential change averaged over the z-axis in the noble gas atom sphere are also tabulated.

In agreement with the higher electrostatic potential close to the Rh$_{15}$K$_3$ cluster, the ionization energy for adsorbed Xe, Kr and Ar on this cluster is smaller compared to Rh$_{15}$. The difference between the potassium-induced potential increase and the expected ionization energy decrease from the change in electrostatic potential is also tabulated. These values suggest that the relaxation energy for the ionized noble gas atom is not very much affected by the presence of potassium. The potassium-induced change in ionization energy of adsorbed noble gas atoms is largely determined by a change in surface potential. However, small changes in relaxation energy (0-0.3 eV) due to the presence of potassium can not be excluded.

Since the presence of potassium on the Rh$_{15}$K$_3$ cluster leads to a lower potential, we expect that the ionization energy for adsorbed noble gas atoms on the Rh$_{15}$K$_3$ cluster are higher than when they are adsorbed on the Rh$_{15}$ cluster, like we have observed for potassium covered Rh(111). The presence of the dipoles further away causes a lower potential at the noble gas adsorption site. When an electron is removed from the same orbital with a changed potential, the ionization energy is changed by $q\cdot V$, where $V$ is the orbital-averaged potential. Thus, the ionization energies of adsorbed noble gas atoms on the Rh$_{15}$K$_3$ cluster will be 0.7-0.8 eV higher (Figure 4.19), due to the contribution of the surrounding dipoles to the potential.

4.5 Long Range Effect on Potassium Promoted Surfaces

Both the experimental data and calculated electrostatic potentials indicate that the lowering of the local work function on potassium-promoted Rh(111) is not confined to the sites adjacent to the potassium atoms. This indicates that all adsorbed particles on the surface are affected by the presence of the potassium atoms. Long range effects of potassium has also
been suggested from infrared spectra of adsorbed CO on promoted surfaces. Another example of a long range effect is the reported inhibition of nitrogen adsorption on potassium-promoted Ru(001) at rather low potassium coverage. These cases will be shortly discussed below.

**Carbon monoxide.**

Carbon monoxide binds to a metal surface by a chemisorptive bond of the $5\sigma$-orbital and backdonation from the metal to the $2\pi^*$-orbital. The lower local work function leads to a higher occupation of the $2\pi^*$ orbital. As this orbital is anti-bonding for the C-O bond, this bond is weakened and the energy barrier for CO dissociation is lowered [13-16]. In addition, the overlap between the $2\pi^*$ and the metal orbitals is larger in the case of bridged CO. Hence, the bridged position of CO is favored with a high occupation of the $2\pi^*$ orbital [17].

In vibrational spectroscopy, linearly bound CO has a frequency of about 2050 cm$^{-1}$ and bridged CO of about 1900 cm$^{-1}$. A transition from linearly to bridged CO is observed after potassium adsorption on Rh(111) [18] or Pt(111) [19,20], in agreement with the higher occupation of the $2\pi^*$ orbital. Bridged CO corresponds to the molecules on the sites adjacent to a potassium atom. The frequency of linearly bound CO, which is adsorbed on the sites further away from the potassium atoms, also decreases with increasing potassium coverage: 18 cm$^{-1}$ on Pt(111) at $\theta_K=0.05$ [20], 7 cm$^{-1}$ on Rh(111) at $\theta_K=0.03$, 28 cm$^{-1}$ on Rh(111) at $\theta_K=0.06$ [18], 45 cm$^{-1}$ on Ru(001) at $\theta_K=0.1$ [13,21], 16 cm$^{-1}$ on Ni(111) at $\theta_K=0.04$ [22]. Such frequency decreases may result either from dipole-dipole coupling between the CO molecules on the surface or from a higher occupation of the $2\pi^*$ orbital due the lowered local work function. The shifts of the photoemission signals of adsorbed noble gases indicate that on potassium-covered Rh(111) the local work function at the sites further away from a potassium is lowered with respect to unpromoted Rh(111). This suggests that a higher occupation of the $2\pi^*$ has a contribution to the decrease of the vibrational frequency.

**Nitrogen.**

For adsorption of nitrogen, which is isoelectronic with CO, the same mechanism as for CO can be assumed. However, the ability of the lowest unoccupied $\pi^*$ level to accept electrons is much less than for CO [4,23,24]. Adsorption of nitrogen on transition metals is governed by the $\sigma$-interaction. The interaction between nitrogen and potassium is repulsive. In the case of nitrogen on Fe, the backdonation to the $\pi^*$ orbital of nitrogen is similar to that of CO. Hence, the dissociation of nitrogen on Fe is facilitated by potassium. Potassium promoted iron is the catalyst for the production of ammonia, which requires dissociation of nitrogen [25].

According to DePaola et al., molecular nitrogen adsorption on Ru(001) is completely inhibited at potassium coverages above 8 at%, which indicates a minimum potassium-nitrogen interaction distance of 4.5 Å [23]. The electrostatic field perpendicular to the surface at 4.5 Å from a potassium atom is approximately 0.5 V/Å at 8 at% potassium coverage,
Calculations on the Electrostatic Potential on K/Rh(111) according to the dipole model. Close to the potassium atoms, this value has been reached for lower potassium coverages. Therefore, nitrogen adsorption at these sites is suppressed earlier and a preferential adsorption of molecular nitrogen far away from the potassium atoms results. Hence, the effect of potassium on the adsorption sites further away controls the adsorption of nitrogen on potassium-promoted Ru(001).

4.6 Conclusions

The heterogeneous surface potential on potassium covered Rh(111), which has been probed by means of photoemission of adsorbed noble gases (Chapter 3), can be described by the electrostatic potential of an infinite, hexagonally ordered network of dipoles. The dipole model shows that the heterogeneous surface potential exists only close to the surface. At distances above 15 Å from the dipole image plane, the lateral electrostatic field, and therefore the variation in surface potential, is about 1000 times smaller than at about 2 Å from the image plane.

For a dipole moment of 10 D we find a good quantitative agreement between the experimentally estimated potential change and the calculated electrostatic potential. The potential decrease, in particular that further away from the potassium atoms, depends on the potassium coverage, which is well reproduced by the dipole model. It confirms that the experimentally estimated potassium-induced changes in local work function result from a cumulative effect of all potassium atoms on the surface.

The shifts of the photoemission signals of noble gases adsorbed on potassium-promoted Rh(111) seem to underestimate the potassium-induced changes in potential. Measurements of the Auger parameter, which is sensitive to changes in relaxation energy, for Xe on potassium covered Ni(100) reported in literature suggest [7] that the relaxation energy for Xe increases ~0.3 eV, due to the presence of potassium. Since an increased relaxation energy is transformed to a lower binding energy in the UPS spectrum, the measured noble gas peak shifts are expected to be smaller than the actual potassium-induced change in local work function. The somewhat higher value for the electrostatic potential at the centre of a noble gas atom (~10% for the promoted sites and ~2% on the bare Rh sites) than the atom averaged potential also suggests a larger change in local work function than estimated experimentally. This is consistent with the lower dipole moment required in the dipole model than expected from the experiment to reproduce the measured changes in local work function.

The potential close to a potassium atom on a Rh/K cluster, which has been calculated on the basis of a quantum-chemical calculation of the electronic structure of the cluster, decreases upon potassium adsorption. However, the potential further away may increase. This is caused by the charge distribution in the cluster, that differs significantly from that of the
potassium-promoted Rh(111) surface, due to the limited number of Rh atoms in the cluster. The best model clusters are the ones that allow a charge distribution around the potassium atoms: Rh$_{12}$K$_3$, Rh$_{13}$K$_3$ and Rh$_{15}$K$_3$. On these clusters, the presence of potassium leads to a lower potential at larger distances from potassium around 3 Å from the Rh-plane, the typical distance between the centre of the Rh plane and a noble gas atom. This is qualitatively in agreement with the experimental data. On the Rh$_{16}$K$_3$ cluster, the potential increases in this region, but the increase is not as large as on the Rh$_{15}$K$_3$ cluster, which has the same distance between the potassium atoms.

The higher potential on the clusters, compared to the experiment and the values obtained with the dipole model, has two causes. First, the K/Rh ratio of the clusters is higher than that of the surface in the experiment (max. 0.05): The size of the clusters is limited to about 20 atoms, since the computation time increases rapidly with the number of valence electrons. Therefore, the Rh atoms in the cluster become more negatively charged, which causes the higher potential at larger distances from the potassium atoms. However, the direction of the electrostatic field perpendicular to the Rh plane is correct: The potential is lower for larger distances from the Rh plane. Secondly, the contribution of the dipoles further away is not included in the clusters. Including this contribution, estimated with the dipole model, we find a 0.5-1.0 V lower potential at the centre of the Rh$_{13}$K$_3$ cluster at about 3 Å above the Rh plane, thus giving more realistic results. This indicates that the contribution of the potassium atoms further away is significant.

The difference in calculated ionization energy for gaseous noble gas atoms and noble gas atoms adsorbed on the central 3-fold site of the Rh$_{15}$ cluster indicates an higher relaxation energy for the adsorbed species, which is in agreement with the experimental data.

The difference in ionization energy of adsorbed Xe, Kr and Ar on the Rh$_{15}$ and Rh$_{15}$K$_3$ cluster is largely determined by the potassium-induced change in electrostatic potential. The largest deviation from the value expected from the change in potential that we have found is 0.32 eV. This indicates that the effect of potassium on the relaxation of the adsorbed noble gases is limited.

References

   Vosko, Wilk and Nusair potential: Appendix E.
5

5.1 Introduction

The model system discussed so far consists of a Rh single crystal surface as a model for the active component of a catalyst, and potassium adsorbed on the surface representing the promoter. Adsorption of potassium on a Rh(111) surface leads to a heterogeneity of the local work function, thus modifying the environment of adsorbates on the surface.

In technical catalysts, the promoter is not pure potassium as in our model system discussed in Chapter 3. Usually, the potassium promoter is introduced as a solution of potassium salt, e.g. KNO₃, K₂CO₃, KOH, which is transformed to potassium oxide or potassium hydroxide with unknown stoichiometry during the catalyst preparation, independent of the initial potassium deposit [1-4]. In potassium promoted iron catalysts, which have been used for the ammonia synthesis or for Fischer-Tropsch synthesis of hydrocarbons, such potassium oxides or hydroxides have been found [5-7].

As pointed out in Chapter 3 the potassium-induced decrease of the surface potential, which is responsible for the promoter effect, is caused by an electron donation from the potassium atoms to the surface. This leads to formation of dipoles around the potassium atoms opposite to the surface dipole. This argumentation is based on experiments with pure potassium, and thus may not be valid for technical catalysts, where oxygen is present. In contrast to potassium, oxygen is an electron acceptor, and therefore adsorbed oxygen enhances electron transfer from the surface to the oxygen: The work function increases with oxygen adsorption. Thus the question arises whether on a surface covered with both oxygen and potassium a heterogeneous surface potential exists, similar to that of the surface covered with pure potassium. With photoemission of adsorbed noble gases, we are able to detect such a heterogeneous potential.

Calculations of the local electrostatic potential of adsorbed potassium and oxygen suggest that the heterogeneity of the surface is still determined by the potassium (Figure 1.6). The effect of the coadsorbed oxygen apparently is not strong enough to destroy the potassium-induced heterogeneity entirely.

The main goal of this chapter is to measure local work functions on a surface covered with both potassium and oxygen, in order to determine whether on these surfaces a
heterogeneity similar to that of potassium-covered Rh(111) exists and to estimate its magnitude. First the oxygen adsorption on the clean and potassium-covered Rh(111) surface is characterized by means of UPS and work function measurements (Section 5.2). For the formation of potassium oxide species on metal single crystal surfaces, the adsorption energy of oxygen on the metal substrate is important [3]. It determines whether oxygen prefers the metal sites or the potassium promoted sites. On noble metals, with a low affinity for oxygen, potassium stabilizes the adsorbed oxygen, whereas on metals like iron and nickel, a low potassium coverage hardly influences the oxygen. In these cases, only at high potassium coverages potassium oxides are formed [3]. In Section 5.3, we discuss the role of potassium for oxygen adsorption on Rh(111), compared to other metal substrates.

Section 5.4 describes the photoemission of adsorbed Xe, Kr and Ar on oxygen and oxygen-potassium-covered surfaces. If we detect more noble gas adsorption states on oxygen-potassium covered Rh(lll) than on oxygen covered Rh(lll), the heterogeneity of the oxygen-potassium surface exists. As in Chapter 3, we use the binding energy of the valence electrons of physically adsorbed noble gases, which is measured with UPS, to estimate the potassium-induced changes in local surface potential.

5.2 Characterization of Adsorbed Oxygen on Clean and Potassium-covered Rhodium(111).

Oxygen adsorption on clean rhodium(111) at 285 K.

After cleaning of the Rh(111) surface according to the procedure described in Section 2.2, the surface was exposed to different amounts of oxygen at 285 K and the UPS spectra were recorded, using HeII radiation (photon energy: 40.8 eV). To correct for intensity fluctuations of the He lamp, the spectra were normalized at a binding energy of 15.0 eV, assuming that the intensity at this point is independent of the oxygen coverage. Furthermore, the spectrum of clean Rh(lll) (also normalized) is subtracted as background. The resulting spectra are shown in Figure 5.1.

After oxygen adsorption on Rh(111), a single peak at 6.0 eV appears in the HeII-UPS spectrum. Adsorbed oxygen can be in the atomic or molecular state with charges varying between 0 and -2. In principle, the different oxygen species can be distinguished by UPS [8-14]. The single peak at 6.0 eV in the UP-spectrum is characteristic for the O^{2-}-ion, which is the only oxygen species giving a single peak in the UP spectrum [8,9,11].

In the low binding energy region of the spectrum, the interaction with oxygen is characterized by two minima at 0.0 eV and at 2.0 eV, due to attenuation and a change in the electronic structure of Rh, related to the adsorbed oxygen. The HeII-UPS spectrum of clean Rh(111) has a maximum at 2.3 eV, that has shifted to 2.7 eV after 10 L oxygen exposure (Figure 5.2). Together with the increased oxygen signal at 6 eV, this causes the intensity
Heterogeneity of Oxygen-Potassium-Covered Rh(111)

Figure 5.1 HeII-UPS difference spectra of adsorbed oxygen on clean Rh(111) after various oxygen exposures. Adsorption temperature: 285 K. The spectrum of clean Rh(111), without oxygen, has been subtracted.

increase at ~ 4 eV.

The shoulder in Figure 5.1 at ~ 8 eV and the small signal at ~ 11 eV are not always reproduced when oxygen is adsorbed (Figure 5.4). Therefore these peaks are believed to be due to some CO or water contamination. Adsorbed CO on Rh(111) produces two peaks in a HeII-UPS spectrum at ~ 8 eV and ~ 11 eV, of about equal intensity. Water can form hydroxyl groups on the surface. The HeII-spectrum of hydroxyl (OH) consists of two peaks with a spacing of ~ 3-4 eV in the regions 5-7 and 8-11 eV [15-17]. Therefore, the shoulder seen in Figure 5.1 at 7.8 eV and the small peak at 11 eV may also be due to formation of hydroxyl by dissociation of water from the residual gas.

Oxygen adsorption on potassium-covered Rh(111) at 285 K.

The same oxygen adsorption experiment as in Figure 5.1 has been done with a Rh(111) surface covered with ~5 at% potassium, corresponding to a mean distance of 12 Å between the adsorbed potassium atoms (Chapter 3). At this potassium coverage there is still a heterogeneity in the local work function, which has been determined by photoemission of adsorbed Xe, Kr and Ar. The potassium layer has been prepared in the same way as with the corresponding noble gas adsorption experiment, described in Section 3.4, i.e. by depositing a few layers of potassium on the surface, followed by 1 min. annealing at 710 K, using a
heating rate of ~2 K/s. The work function of the potassium-covered surface before oxygen adsorption is 2.94 eV. The work function of the surface used in the noble gas adsorption experiment with 5 at% potassium is 3.1 eV. Since the work function is very sensitive to the potassium coverage in this coverage region (Figure 2.7), the potassium coverage in this experiment is close to that in the noble gas experiment, viz. 5.0 at%.

The potassium-covered surface has been exposed to different amounts of oxygen and the HeII-UPS spectra are recorded. Figure 5.3 shows the normalized (at 15.0 eV), background subtracted spectra. The spectrum of the potassium-covered surface without oxygen is taken as background in this experiment, so the spectra show only the effect of oxygen adsorption.

After oxygen exposure a signal at 6.0 eV is seen, similar to the spectra from oxygen on clean Rh(111). Again the minima at the Fermi edge of the spectrum and at 2.0 eV are seen. With the potassium precovered surface the maximum at ~1 eV (Figure 5.3) may be more pronounced than with oxygen adsorption on clean Rh(111). However, this is not always reproduced (Figure 5.4), making an assignment to a potassium-induced effect doubtful.

In Figure 5.4 the difference between the (background subtracted) spectra for 10 L oxygen on clean and potassium-covered Rh(111) is displayed. It shows that, apart from the K-3p signal, there is no significant difference between these spectra.

The K-3p signal emerges in the HeII-UPS spectrum at ~18 eV (Figures 5.4 and 5.5) (Sections 2.2 and 2.3). Coadsorption of oxygen with potassium generally leads to a decrease of the binding energy of the K-3p electrons [2,17-22]. It can be explained by a point charge model: The presence of negatively charged particles close to the positively charged K⁺-particles leads to an extra repulsion of the potassium electrons. The extra attraction due to the eventually more positively charged potassium atoms is overcompensated [22].

Our data also suggest a decrease in binding energy of the K-3p level (Figure 5.5), with increasing oxygen coverage. However, since the K-3p signal overlaps with the emission of
the Fermi level at 17.1 eV and 17.6 eV, caused by He-satellite lines, a correct analysis of this shift becomes difficult. We know from the HeII-UPS spectrum that the signal at low binding energies is not only attenuated, but also shows a structural change with oxygen adsorption. The same structural changes will occur at these satellites, thus influencing the

Figure 5.3 HeII-UPS difference spectra of adsorbed oxygen on potassium covered Rh(111). Adsorption temperature: 285 K. Potassium coverage ~4 at%. The spectrum for potassium covered Rh(111) without oxygen has been subtracted.

Figure 5.4 Comparison of the oxygen induced HeII-UPS signal on clean and potassium covered Rh(111). There is no significant difference between the (background subtracted) spectra for oxygen on the clean and potassium covered surface at 285 K, except for the K-3p level around 18 eV.
total emission around the HeII-excited K-3p emission. However, after an oxygen exposure of 0.05 L oxygen the intensity at the Fermi level of the HeII spectrum has decreased, whereas the intensity at 17.6 eV and 17.1 eV increases (Figure 5.5). In addition, the intensity of the He-satellites is much smaller, and therefore the oxygen-induced changes in the spectrum caused by these satellite lines are expected to be smaller than the changes observed in the HeII-UPS spectrum. As we can see in Figure 5.5, the HeII-UPS signal below 1 eV binding energy is hardly affected by the small amount of adsorbed oxygen. Therefore the intensity increase at 17.6 eV can be attributed to a shift of the K-3p level with oxygen adsorption, thus indicating an interaction between the adsorbed oxygen and potassium.

Figure 5.6 shows the area of the oxygen-induced signal at ~6 eV as a function of the oxygen exposure for both clean and potassium-covered Rh(111). The area of the oxygen signal at 6 eV is assumed to be proportional to the oxygen coverage. The intensity measured after 10 L oxygen exposure to the clean and the potassium-covered surface was about the same and the mean value is defined as 1 ML. This suggests that in the presence of ~5 at% potassium, the UPS intensity of oxygen at saturation coverage is not substantially larger, but it is reached after lower exposures. This indicates a higher sticking probability of oxygen in the presence of potassium. The higher sticking probability is qualitatively in agreement with the lower work function of the potassium-covered surface. Figure 3.23 indicates, that at any point on the surface the work function is lowered after potassium adsorption. The electrons in the surface are more easily transferred to the adsorbate. This results in an enhanced dissociation of the oxygen molecules and a stronger interaction between the oxygen and the surface. The stronger interaction has also been observed in thermal desorption experiments from clean and potassium-covered Ru(0001) [23-24] and Pd(111) [25]. For the latter, both the amount of atomic oxygen and the desorption temperature are larger for the potassium covered surface after the same oxygen exposure. Note, that the potassium is not neces
for dissociative adsorption of oxygen on Rh(111) - oxygen adsorbs dissociatively on the clean Rh(111) surface as well - but the adsorption has become easier in the presence of potassium.

The oxygen-induced increase in work function is different for the clean and potassium-covered surface. Figure 5.7 displays the work function increase as a function of the oxygen coverage on clean and potassium-covered Rh(111). The reference is the work function of the surface without oxygen, i.e. the clean or potassium-covered surface. The oxygen coverage has been determined by the area of the oxygen signal in the UPS spectra. On both the clean and potassium-covered surface, the work function increases, which indicates oxygen

**Figure 5.6** The oxygen coverage on clean and potassium covered (θK ~5 at%) as a function of the oxygen dose at 285 K. The coverage has been determined by the area of the oxygen peak in the HeII-UPS spectrum at 6.0 eV, assuming a linear dependence between peak area and oxygen coverage. The saturation coverage has been defined as 1 monolayer.

**Figure 5.7** Oxygen induced work function change on clean and potassium covered (θK ~5 at%) Rh(111) at 285 K. The values are referenced to the respective surfaces without oxygen, i.e. the clean or potassium covered surface. The oxygen coverages are determined on the basis of the intensity of the oxygen signal in the HeII-UPS spectrum at 6 eV (see also Figure 5.6).
adsorption on the surface in both cases. The total oxygen-induced increase in work function of a saturated oxygen layer (10 L, Figure 5.6) is 0.78 eV for the clean Rh(111) and 1.35 eV for Rh(111) covered with 5 at% potassium. In Figure 5.7 we also see, that the difference exists already at low oxygen coverages; at higher coverage both lines are parallel. This agrees well with the increased charge transfer picture described above to explain the increased sticking coefficient. However, such a picture may be too simple to describe the work function increase, because it neglects the possibility of the formation of a surface compound resulting in a new (electronic) surface structure, that probably has a different work function.

We have seen that there is no qualitative difference between the HeII-UPS spectra of oxygen adsorbed on clean Rh(111) and Rh(111) covered with 5 at% potassium, apart from a shift of the K-3p signal. We can envisage three explanations. The first is a low cross section of the HeII radiation for an eventual potassium-oxide species, which would result in a very low intensity for such a species in the HeII-UPS spectrum. Another possibility is that the oxygen does not interact with the potassium and thus forms exactly the same species on both the clean and the potassium-covered surface. However, this is contradicted by the higher work function increase with oxygen adsorption on the potassium-covered surface and the shift of the K-3p level. Finally, it is also possible that there is an interaction between oxygen and potassium, but the resulting oxygen species is very much alike the species formed on clean Rh(111), which is not resolved in the HeII-UPS spectrum. The spectrum of atomic oxygen (O²⁻) adsorbed on different transition metal surfaces in a UP spectrum is mostly independent of the substrate, indicating that the electronic structure of this oxygen species is similar on many substrates [8].

Contrary to the adsorption of Xe, Kr and Ar, where at this potassium coverage a difference between the K/Rh sites and the Rh sites has been detected (Section 3.4), there is no detectable qualitative difference in the UP spectra between the oxygen species on clean and potassium-covered Rh. Since the intensity of the HeII signals of 1 ML of oxygen on clean and potassium-covered Rh(111) is about the same, we must have oxygen on both the bare Rh and the sites next to potassium that were observed for adsorbed noble gases. We conclude that the oxygen species formed is the same on all surface sites. It is identified as O²⁻ on the basis of the single signal in the UPS spectrum. The O²⁻-particles are positioned on the Rh surface between the potassium atoms.

Summarizing we can say that at 285 K oxygen adsorbs dissociatively on both clean and potassium-covered (θₖ = 5 at%) Rh(111). This species is characterized by the HeII-UPS signal at 6 eV and it is attributed to O²⁻ ions. At room temperature, oxygen forms a 2x1 surface structure [26-28] on clean Rh(111), with the oxygen atoms adsorbed in the 3-fold Rh-sites [29]. Although a qualitative difference in the oxygen signals between oxygen adsorbed on clean Rh(111) and on a surface precovered with 5 at% potassium is undetectable, there are indications of a different oxygen interaction with the potassium-covered surface. The most convincing argument for a different interaction is the much larger
work function increase with oxygen adsorption on a potassium precovered surface. Secondly, the K-3p signal shifts to lower binding energy. In addition, the sticking coefficient of oxygen is larger for the potassium-covered surface.

The larger work function increase with oxygen adsorption, the enhanced sticking probability of the oxygen on the potassium-covered surface and the shift of the K-3p level upon oxygen adsorption are all in agreement with an enhanced electron transfer from the surface to the oxygen due to the lower work function on the potassium-covered surface. The influence of the potassium atoms on the oxygen adsorption is indirect: The potassium modifies the Rh surface, leading to a different interaction of the oxygen with the potassium-covered surface, compared to clean Rh(111). Of course, the negatively charged oxygen atoms interact with the positively charged potassium atoms on the surface.

**Oxygen adsorption on clean and potassium-covered rhodium(111) at 50 K**

Since we want to determine the local surface potential on oxygen-potassium covered Rh(111) with photoemission of adsorbed noble gases, we first have to characterize the adsorbed oxygen on clean and potassium-covered Rh(111) at 50 K. Figure 5.8 shows the spectra of oxygen on Rh(111), adsorbed at 50 K. The main difference between adsorption at 285 K and 50 K is the occurrence of a molecular oxygen species at higher oxygen exposures (> 1.0 L), characterized by a series of five peaks with maxima at 4.5, 8.8, 10.3, 12.6 and 16.6 eV. The spacing between the peaks match that of gaseous oxygen (12.1, 16.1, 18.2, 20.3 and 24.5 eV [8,30,31]), thus indicating physisorbed oxygen molecules. The binding energies with respect to the vacuum level for physisorbed oxygen are 1.5±0.2 eV lower than the gas phase values, due to the extra-atomic relaxation by the Rh surface, similar to the case of physisorbed noble gases. Below oxygen exposures of 1.0 L no molecular oxygen species can be detected, so it seems impossible to get only molecular oxygen on a Rh(111) surface at 50 K. Annealing of the molecular oxygen layer to 135 K leads to a desorption of the physisorbed molecular oxygen, leaving only the same atomic oxygen as observed with adsorption at 285 K (Figure 5.8). In the spectrum for physisorbed oxygen on clean Rh(111) (Figure 5.8, bottom left), the signal at 6 eV, which is characteristic of atomic oxygen, is observed simultaneously with the spectrum for physisorbed oxygen.

On potassium-covered Rh(111), oxygen adsorption at low temperatures also leads to a molecular oxygen species after high oxygen exposures, characterized by four peaks at 6.2, 10.6, 12.2 and 14.5 eV. Compared to the molecular oxygen on the clean surface, the binding energy is 1.8±0.1 eV higher. This agrees well with the lower work function for the potassium-covered surface saturated with atomic oxygen (4.6 eV), compared to the clean Rh surface, saturated with atomic oxygen (6.3 eV). We do not resolve different adsorption sites for physisorbed oxygen.

When the surface is annealed at 120 K, the molecular oxygen desorbs, leaving the atomic oxygen species on the surface. The spectrum of the molecular oxygen species now overlaps with the spectrum of the atomic oxygen. The influence of the potassium on the atomic
oxygen adsorption is only detected in a larger work function increase on the potassium-covered surface (+1.14 eV, referenced to the potassium-covered surface without oxygen), compared to the clean surface (+0.7 eV), but no new oxygen species is detected with HeII-UPS on the potassium-covered surface (Figure 5.9). Furthermore, we find no qualitative difference between adsorbed atomic oxygen at 50 K and 285 K. The effect of the lower...
temperature is mainly the occurrence of additional physisorbed molecular oxygen after higher oxygen exposures on both the clean and the potassium-covered surface. The molecular oxygen does not affect the work function.

5.3 Influence of Potassium on Oxygen Adsorption on Rh and Other Transition Metals

Oxygen adsorbs dissociatively on many transition metal surfaces, even at low temperatures (~50 K), like in the present work for oxygen on Rh(111). On more noble metals, like Au, Pt, Ag, Cu and Pd, oxygen tends to adsorb molecularly at low temperatures (< 150 K) [8]. On these surfaces, the oxygen adsorption energy is rather low, compared to other metal surfaces. This indicates a weak interaction of oxygen with the metal and therefore the dissociation of the oxygen molecules is more difficult. Thermal desorption measurements of oxygen from Rh(111), Pt(111) and Pd(111) [25,32] illustrate this behavior. When oxygen is adsorbed on Pt(111) and Pd(111) at 100 K, a large amount of molecular oxygen is found, which desorbs around 150 K. The atomic oxygen desorbs around 800 K from these surfaces. On the Rh(111) surface, almost exclusively the atomic oxygen species is formed after oxygen adsorption at 100 K, which desorbs above 1100 K. At room temperature only the atomic oxygen exists; the molecular species has desorbed or dissociated.

The influence of coadsorbed potassium on the atomic oxygen (at low potassium coverages) depends on the affinity of the surface for oxygen: There is a competition of oxygen adsorption on the bare surface and oxygen adsorption on the potassium promoted
Table 5.1 Tabulated values for the oxygen-metal bond strength in diatomic molecules [34] for various metal atoms and activation energies for desorption of atomic oxygen from different metal surfaces. The bond strengths in diatomic molecules and the desorption energies indicate that the interaction of oxygen with Rh is intermediate, i.e. higher than with noble metals, e.g. Ag, Pd and Pt, but lower than for e.g. Fe, Ni and Ru.

<table>
<thead>
<tr>
<th>Bond strength</th>
<th>Desorption energy</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-O</td>
<td>213 ± 84</td>
<td>Pt(100)-hex</td>
</tr>
<tr>
<td>Pd-O</td>
<td>234 ± 29</td>
<td>Ag(110)</td>
</tr>
<tr>
<td>Cu-O</td>
<td>343 ± 63</td>
<td>Pt(111)</td>
</tr>
<tr>
<td>Pt-O</td>
<td>347 ± 34</td>
<td>Pd(111)</td>
</tr>
<tr>
<td>Rh-O</td>
<td>377 ± 63</td>
<td>Pd(100)</td>
</tr>
<tr>
<td>Ni-O</td>
<td>391.6 ± 3.8</td>
<td>Rh(111)</td>
</tr>
<tr>
<td>Fe-O</td>
<td>408.8 ± 1.3</td>
<td>Rh(110)</td>
</tr>
<tr>
<td>Ru-O</td>
<td>481 ± 3.8</td>
<td>Ru(001)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni(001)</td>
</tr>
</tbody>
</table>

sites. The most probable adsorption site is the one with the highest adsorption energy. Therefore, one can distinguish different cases of oxygen interaction with potassium promoted surfaces, on the basis of the adsorption energy of oxygen on the respective substrates [3].

The first group contains the substrates with a low adsorption energy for oxygen, which are the more noble metals (see above). Oxygen adsorbs mainly on the alkali metal promoted sites on such surfaces. For example, when oxygen is adsorbed on polycrystalline gold precovered with potassium, oxygen-potassium clusters are detected with SIMS, indicating that oxygen is adsorbed adjacent to potassium [33]. In this case, the oxygen-induced work function increase is larger than for the surface without potassium, which indicates an enlarged electron transfer from the surface to the oxygen, in accordance with the lower local work function at the promoted sites. For oxygen on potassium-covered Rh(111) we find a larger work function increase for low oxygen exposures (Figure 5.7). The sticking coefficient for oxygen is also enhanced by the coadsorbed potassium.

Substrates with a high adsorption energy for oxygen can compete with the alkali-oxygen bonding. An example is oxygen adsorption on Ru(001), which has an adsorption energy for oxygen of 400 kJ/mol [35]. At low alkali metal coverages, the sticking of oxygen is enhanced by the alkali metal, but the oxygen moves to the Ru to form Ru-O bonds. The initial change in work function with oxygen adsorption is the same for both the clean and potassium-covered surface (θK=5 at%) [3], in contrast to our observation for oxygen on potassium-covered Rh(111). In desorption experiments a critical alkali metal coverage and a critical oxygen coverage is needed to detect an alkali oxide species [24,37-39]. Other examples are the substrates that can form oxides, like Fe and Ni. On these substrates low
alkali metal coverages do not substantially affect the oxygen adsorption; formation of alkali metal oxides occurs only at high alkali metal coverages [23,40].

Our UPS data indicate that initially oxygen adsorbs dissociatively on both the clean and potassium-covered surface ($\theta_k = 5$ at%) at room temperature and at 50 K. This suggests a rather strong oxygen-Rh interaction: A weak interaction leads to a molecular oxygen species at low temperatures, as is the case for Au, Pt and Ag. On the other hand the oxygen coverage dependence of the work function supports the preferential occupation of the promoted sites on Rh(111), which is characteristic of a weaker oxygen substrate interaction. The preferential occupation of the promoted sites is also supported by the shift of the K-3p level after low oxygen coverages (Figure 5.5). Thus, the interaction of oxygen on Rh(111) is stronger than on Ag, Pd and Pt, but weaker than on Ru, Fe and Ni. The same classification arises from the measured value for the oxygen adsorption energy on Rh surfaces compared to other metal substrates and the tabulated values for the oxygen-metal atom bond strength in diatomic molecules (Table 5.1). The interaction of oxygen with Rh(111) apparently is strong enough to dissociate oxygen, but can not successfully compete with the alkali-oxygen bonding, like Ru, Fe or Ni.

### 5.4 Photoemission of Adsorbed Noble Gases on Oxygen and Oxygen-Potassium Layers on Rhodium(111)

In order to determine whether the oxygen-potassium-covered Rh(111) surface shows a heterogeneous surface potential similar to that of potassium-covered Rh(111), as suggested by Holloway *et al.* [41], we measured HeI photoemission spectra of adsorbed Xe, Kr and Ar

![Figure 5.10 Model surfaces for noble gas adsorption on mixed potassium-oxygen layers. The local surface potential is probed at the noble gas adsorption site. The left part shows the case with free metallic Rh, which is more relevant for catalysis. However, it is difficult to determine the exact amount of oxygen needed to produce this situation. The right part shows Xe on a saturated layer of atomic oxygen on potassium covered Rh, which is easier to produce.](image-url)
on oxygen and oxygen-potassium-covered Rh(111). For catalysis, the surface potential of the oxygen-potassium-covered surface, with all oxygen atoms placed adjacent to the potassium atoms (Figure 5.10, left) is the most important one. However, we did not succeed in preparing such a well defined oxygen-potassium-covered surface. Instead, we used a saturated layer of atomic oxygen on both the clean and the potassium-covered Rh(111) surface, on which the noble gases were adsorbed (Figure 5.10, right). The surface covered with oxygen, without potassium, is a reference for the oxygen-potassium-covered surface. In analogy with the experiments described in Chapter 3, a potassium-induced heterogeneity is recognized by additional noble gas photoemission signals on the oxygen-potassium-covered surface, compared to the surface without potassium. The position of the noble gas signals also gives an estimate of the local work function at the noble gas adsorption site.

**Figure 5.11** UPS spectra (*HeI*-radiation: 21.21 eV) of Xe, Kr and Ar on a saturated layer of atomic oxygen on Rh(111).
The oxygen covered Rh(111) surface is prepared by adsorbing 1.6 L oxygen at ~50 K, giving both atomic and molecular oxygen on the surface (Figure 5.8). The molecular oxygen is removed by heating to 135 K, which leaves a saturated layer of atomic oxygen on the surface. The HeI-UPS spectra adsorbed of Xe, Kr and Ar on this surface are shown in Figure 5.11. The shape of the noble gas signals is basically the same on clean Rh(111); the signals are only somewhat broader. The oxygen covered Rh surface is rather homogeneous, as can be inferred from the uniformity of the signals belonging to the first noble gas layer. After higher exposures the second noble gas layer is detected.

The position of the Xe-5p_{1/2}-level (5.67 eV) on the oxygen covered surface, with a work function of 6.52 eV, corresponds to an ionization energy of 12.2 eV for adsorbed Xe, in agreement with the previously determined value of 12.3 ± 0.15 eV on other substrates [42].
For the Kr-4p\textsubscript{1/2}-level (6.83 eV) we find, with a work function of 6.35 eV for the oxygen covered surface, a value of 13.2 eV for the ionization energy. The ionization energy for the Ar-3p level (7.96 eV, $\varphi_{\text{surf}} = 6.26$ eV) is 14.2 eV. These values are all close to the values found for the adsorbed noble gases on clean Rh(111).

The same experiment has been done on the oxygen-potassium-covered Rh(111) surface. Each noble gas was adsorbed on a freshly prepared oxygen-potassium overlayer. First the surface was covered with a few percent potassium by annealing a thick potassium layer at 755 K, like in the noble gas adsorption experiments on the surfaces without oxygen (Section 3.4). The potassium coverages were estimated from the work function of the potassium-covered surface without oxygen, which is 3.31 eV in the experiment with Xe, 3.52 eV in the experiment with Kr and 3.63 eV in the experiment with Ar. These values are close to that for 4.1 at% potassium on Rh(111) (3.4 eV, Section 3.4). Since the work function is very sensitive to the potassium coverage at low potassium coverages, we estimate a potassium coverage of about 4 at% in all experiments. The potassium-covered Rh(111) surface was exposed to 1.0 L oxygen at −50 K, which leads to formation of the molecular oxygen species. After annealing to 120 K, we obtain a surface that is covered with potassium and atomic oxygen only (Figure 5.8).

Figure 5.13 Hel-UPS spectra of adsorbed Xe on a saturated layer of atomic oxygen on Rh(111), without potassium (left) and with −4 at% potassium (right). The spectra are normalized to the maximum of the Xe-5p\textsubscript{1/2} peak. For low Xe coverages, the shape of the Xe peaks is preserved with increasing Xe coverage in absence of potassium. When potassium is present, the shape of the Xe signal changes in the same Xe coverage range, which indicates a heterogeneity of the surface. The features appearing after higher Xe exposures are assigned to the second Xe layer.
The HeI-UPS spectra of Xe, Kr and Ar adsorbed on the oxygen-potassium-covered surfaces are shown in Figure 5.12. In the spectra of Xe on the oxygen-potassium-covered surface, one does not see a new Xe-5p\(_{1/2}\) peak at once, as is the case on the potassium-covered surface with about the same potassium coverage (Figure 3.5). However, when the intensity of the 5p\(_{1/2}\)-peak of the spectra for different Xe coverages is normalized to the maximum of the 5p\(_{1/2}\)-peak, we see a shoulder at the low binding energy side of both the 5p\(_{1/2}\) and the 5p\(_{3/2}\)-signal (Figure 5.13). This becomes more obvious in the difference spectra:

**Figure 5.14** Decomposition of spectra of Xe on a saturated layer of atomic oxygen on Rh(111), precovered with ~4 at\% potassium. Xe adsorption temperature: 45 K. The positions of the Xe-5p\(_{1/2}\) peaks are labelled. A: Xe on O/Rh, B: Xe on O close to potassium, C: 2nd Xe layer.
In the difference between the spectra of 5 L Xe and 1 L Xe on oxygen in the absence of potassium, normalized to the maximum of the Xe-5p\textsubscript{1/2} peak, no significant difference is observed. The difference between the spectra of 7 L and 5 L Xe on oxygen covered Rh(111) corresponds to the formation of the second Xe layer. In contrast, the difference between the normalized spectra of 3 L Xe and 1 L Xe on the oxygen-potassium-covered surface clearly reveals a new Xe state, characterized by a positive difference at 6.81 eV and 5.3 eV. This indicates a heterogeneity of the surface potential on oxygen-potassium-covered Rh(111).

Figure 5.14 shows a few examples of the decomposition of the spectra of Xe on oxygen-potassium-covered Rh, according to the procedure described in Section 3.4.1, using the same Gauss-Lorentz curves. The intensity ratio of the two Xe-5p\textsubscript{1/2} signals (A:B ≈ 2:5) is comparable with the ratio found with 4.1 at% potassium without oxygen. Therefore we attribute the peak at 7.10 eV (B) to Xe on oxygen close to potassium and the peak at 6.81 eV (A) to the Xe on oxygen further away. The sites close to potassium (B) are populated first, which indicates a higher adsorption energy for Xe on these sites, compared to the sites further away (A), like for potassium-covered Rh(111) without oxygen. At higher Xe coverages a third peak (C) occurs at higher binding energy (7.70 eV), which is attributed to the Xe second layer. In the present experiment no adsorption state analogous to Xe on top of potassium, like on the surface without oxygen, has been resolved.

When Kr is used instead of Xe, we also find two noble gas photoemission signals belonging to the first layer, thus confirming the heterogeneity of the oxygen-potassium-

![Figure 5.15 Hel-UPS spectra of adsorbed Kr on a saturated layer of atomic oxygen on Rh(111), without potassium (left) and with ~4 at% potassium (right). The spectra are normalized to the maximum of the Kr-4p\textsubscript{1/2} peak. At low Kr coverages, the shape of the Kr signal changes significantly with increasing Kr coverage, when potassium is present. At high Kr coverages, the second Kr layer is detected.](image-url)
Figure 5.16 Decomposition of the spectra of Kr on a saturated layer of oxygen on Rh(111), precoversed with ~4 at% potassium, using the spectrum for 0.5 L Kr (top left). The positions of the Kr-4p_{3/2} are labelled. A: Kr on O/Rh, B: Kr on oxygen close to a potassium atom, C: 2nd Kr layer.

The existence of an additional adsorption state on the oxygen-potassium-covered surface of Kr is illustrated by the difference spectra, that are normalized to the maximum of the 4p_{3/2} signal. The difference between the normalized spectra of 3 L Kr and 0.6 L Kr on oxygen only has a positive difference at the low binding energy side of the 4p_{3/2} peak (Figure 5.15, left), that is caused by a small a broadening of this peak with increasing Kr coverage. Increasing the Kr exposure from 3 L to 4 L leads to the population of higher Kr layers. The difference between the normalized spectra for 2 L Kr and 0.5 L Kr on oxygen-potassium-covered Rh(111) shows two maxima, dissimilar to Kr on oxygen without
Figure 5.17 UPS spectra of Ar on a saturated layer of atomic oxygen on Rh(111), without potassium (left) and with ~4 at% potassium (right). The spectra are normalized to the maximum of the Ar-3p signal. In the absence of potassium, the shape of the Ar signal does not change significantly with increasing Ar coverage, until the second Ar layer develops. In the presence of potassium, the shape of the Ar signal changes with increasing Ar coverage before the second layer is detected, which is indicative for a second Ar adsorption site in the first Ar layer.

This strongly suggests an additional adsorption state for Kr (Figure 5.15, right).

The Kr spectra are decomposed with the spectrum of 0.3 L Kr on this surface as base function (Figure 5.16). At this Kr coverage, only one Kr state is seen. The first two Kr-signals appearing in the spectra series are attributed to Kr close to potassium (binding energy 4p_{1/2}-level: 8.10 eV) (B) and to Kr further away (7.66 eV) (A), in analogy to the experiment with Xe. Again the sites close to potassium are populated first, indicating a higher adsorption energy for Kr on these sites.

Figure 5.17 shows the normalized spectra for Ar on both the oxygen and the oxygen-potassium-covered surface. On the oxygen covered surface, we see no significant difference between the normalized spectra for 0.45 L Ar and 0.14 L Ar. At 50 K, the surface saturates at 1 L Ar exposure. The higher Ar layers, recognized by a UPS signal at higher binding energy, are only seen at Ar Pressures above 10^{-6} Torr at this temperature. On the oxygen-potassium-covered surface, the difference between the normalized spectra for 1 L and 0.3 L Ar clearly show the existence of a new Ar adsorption state at lower binding energy, again confirming the heterogeneity of the surface.

Figure 5.18 shows a few examples of the decomposition of the Ar spectra. The assignment of the adsorption states is made in analogy with the Xe and Kr results: The 3p-signal at 9.31 eV (B) is assigned to the Ar close to potassium and the peak at 8.8 eV (A) for
Heterogeneity of Oxygen-Potassium-Covered Rh(111)

Figure 5.18 Decomposition of the spectra of Ar on a saturated layer of atomic oxygen on Rh(111), precovered with ~4 at% potassium, using the spectrum for 0.2 L Ar (top left) as fit function. The positions of the Ar signals are labelled. A: Ar on O/Rh, B: Ar on oxygen, close to a potassium atom.

the Ar further away. Like for Xe and Kr, initially the sites close to potassium occupied by the Ar atoms.

The positions of the noble gas photoemission signals in the spectra are an estimate for the local work function at the respective noble gas adsorption site. To obtain a map of the local work functions as a function of the distance to the nearest potassium, we have to locate the noble gas adsorption sites on the surface. The adsorbed oxygen layer consists of O²⁻-ions, as evidenced by UPS. The radius of these ions on a Rh(100) surface is 0.78 ± 0.02 Å [28], in the same order of magnitude as the value of oxygen on Ni(100) (0.73 Å) and Cu(110)
(0.69-0.65 Å) [28]. The oxygen ions are much smaller than the adsorbed potassium atoms, which have an ionic radius of 1.33 Å. Both potassium and oxygen adsorb on the surface, as can be inferred from the effect of both adsorbates on the work function. Thus, the noble gas atoms still can "see" the potassium atoms like on the surface without oxygen (Figure 5.10, right). The intensity ratio for the Xe signals of one monolayer Xe (A:B = 2:5) on the oxygen-potassium-covered surface does not differ substantially from the ratio found on the surface without oxygen. Therefore, we assume the same adsorption geometry and lateral distances between the adsorbed noble gases and the potassium atoms as on the surface without oxygen (Figure 5.16). Table 5.2 summarizes the positions and the shifts of the noble gas signals on oxygen and oxygen-potassium-covered Rh(111), referenced to oxygen covered Rh(111) without potassium and clean Rh(111). A graph of the latter is shown in Figure 5.19, together with the curves obtained with potassium-covered Rh(111) without oxygen (Figure 3.23).

Because the oxygen-potassium-covered surface was renewed before each experiment, the potassium coverage was not exactly the same in the Xe, Kr and Ar experiment, as was the case with the experiments described in Chapter 3. Since the absolute values for the local work functions depend on the potassium coverage (Figure 3.23), the shifts of the noble gas signals are more scattered. This is in particular seen in the measured shifts for the noble gases further away from the potassium atoms, which we expect to be constant in analogy with the bare Rh patches on the surfaces without oxygen.

The shifts of the noble gas signals are interpreted as changes in local surface potential. Then, the overall picture is qualitatively the same as on the potassium-covered surfaces without oxygen, indicating that the coadsorbed oxygen does not completely destroy the

<table>
<thead>
<tr>
<th>Ads. site</th>
<th>$\Delta E_g^f$ on O/Rh</th>
<th>$\Delta E_g^f$ on O/K/Rh</th>
<th>distance to K ref. clean Rh</th>
<th>$\Delta E_g^f$ ref. O/Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar(O/K/Rh)</td>
<td>9.31</td>
<td>3.23</td>
<td>0.61</td>
<td>1.35</td>
</tr>
<tr>
<td>Kr(O/K/Rh)</td>
<td>8.10</td>
<td>3.40</td>
<td>0.40</td>
<td>1.27</td>
</tr>
<tr>
<td>Xe(O/K/Rh)</td>
<td>7.10</td>
<td>3.74</td>
<td>0.40</td>
<td>1.43</td>
</tr>
<tr>
<td>Ar(O/Rh)</td>
<td>7.96</td>
<td>5.90</td>
<td>0.10</td>
<td>0.85</td>
</tr>
<tr>
<td>Kr(O/Rh)</td>
<td>6.83</td>
<td>6.23</td>
<td>-0.04</td>
<td>0.83</td>
</tr>
<tr>
<td>Xe(O/Rh)</td>
<td>5.67</td>
<td>6.83</td>
<td>0.11</td>
<td>1.14</td>
</tr>
</tbody>
</table>
Heterogeneity of Oxygen-Potassium-Covered Rh(111) oxygen-potassium-covered surface reveals, that the potassium-induced heterogeneity of the surface is not completely destroyed by the coadsorbed oxygen. However, the difference between the shifts of the noble gas signals belonging to the sites close to potassium and the sites further away is smaller, as compared to the surface without oxygen. This suggests, that the difference in local surface potential at the sites adjacent to potassium and the sites further away is smaller in the case of oxygen-potassium-covered Rh(111). Apparently, the oxygen weakens the potassium-induced heterogeneity. The oxygen-induced increase in work function is also observed on the...
potassium-covered surface at all sites available for noble gas adsorption, which is in accordance with the electron acceptor character of oxygen.

5.5 Conclusions

Oxygen adsorbs dissociatively on the clean Rh(111) surface. The adsorbed atomic oxygen is characterized in HeII-UPS by a single peak at 6.0 eV, which is assigned to an O$_2^-$-species. When oxygen is adsorbed on a potassium-precovered surface at room temperature ($\theta_K \sim 5$ at%), the same oxygen species is detected with UPS. The work function increase with oxygen adsorption is larger on the potassium-covered surface, already after low oxygen exposures. Simultaneously, the K-3p level shifts from $-18.2$ eV to $-17.6$ eV. This indicates an interaction of the oxygen with the potassium on the surface. However, the resulting oxygen species is indistinguishable with HeII-UPS from that on the clean Rh surface; a specific potassium oxide or oxygen on potassium has not been detected. Therefore, we conclude that the oxygen-potassium-covered surface consists of atomic oxygen adsorbed on the Rh surface between the potassium atoms, with a preferential adsorption on the potassium promoted sites, as suggested from the changes in work function and the shift of the K-3p level. Due to the negative O$_2^-$-ions close to the potassium, the K-3p level shifts to lower binding energy.

On both clean and potassium-covered Rh(111), a molecular oxygen species is detected after oxygen exposures above 1 L at 50 K, which is recognized by a set of 4 or 5 peaks in the HeII-UPS spectrum. The separation between these peaks is the same as for gaseous oxygen, suggesting that the molecular species is physisorbed. After desorption of the molecular species at $-120$ K, the same atomic oxygen species as with adsorption at room temperature remains on the surface. We have no indication of any other oxygen species. After low exposures at 50 K oxygen also adsorbs dissociatively on the Rh surface between the potassium atoms.

Adsorption of Xe, Kr and Ar on the Rh(111) surface covered with a saturated layer of atomic oxygen shows no heterogeneity of the surface. The ionization potential of the noble gases, determined from the position of the noble gas peaks in the UPS spectrum and the work function of the sample, is $-0.1$ eV lower than the value found for the noble gases on clean Rh(111), which remains within the error limits reported for Xe [42]. This suggests applicability of the noble gases for local surface potential measurements on the oxygen covered surface as well.

When Xe, Kr and Ar are adsorbed on a saturated layer of atomic oxygen on Rh(111), precovered with approximately 4 at% potassium, a heterogeneity of the surface is found. When we interpret the shifts of the noble gas signals as changes in local surface potential and assume the same adsorption geometry for the noble gases as on the potassium-covered
surfaces without oxygen, we find a lower surface potential close to the potassium atoms than on the sites further away, similar to the potassium-covered surfaces without oxygen. However, compared to the surface with approximately the same potassium coverage without oxygen, the difference between the local surface potential close to the potassium atoms and the sites further away is lower in the presence of oxygen. Hence, we conclude that the potassium-induced heterogeneity is not destroyed by the oxygen, but that it is weakened.

References

Chapter 5

Summary and Conclusions

The main goal of this work is to investigate the effective potential that molecules, such as CO or N\textsubscript{2}, sense when they are adsorbed on a alkali-promoted metal surface. In this thesis, the potassium-induced change in surface potential on a Rh(111) surface at different locations has been determined experimentally and the results have been compared with theoretical calculations. The effective potential on a potassium-promoted metal surface is lower than on an unpromoted surface and depends on its position with respect to the potassium atoms. Hence, we speak of a local surface potential. This modified surface potential contributes to the promoter effect of potassium in catalytic reactions.

Potassium forms different phases on the Rh(111) surface, dependent on the coverage. As follows from measurements of the macroscopic work function, the potassium is ionic at low coverages (<0.2). Above a coverage of 0.5 the potassium is metallic. Increasing the coverage from 0.2 to 0.5 leads to a gradual depolarization of the potassium layer and formation of a transition phase between ionic and metallic potassium. For understanding the promoter effect in catalysis, the properties of the ionic phase at low coverages (<5 at%) is most important.

Photoemission of adsorbed noble gases is sensitive to changes of the local surface potential at the adsorption site of the noble gas atoms. Changes in local surface potential are reflected in the binding energy of the valence electrons of the adsorbed noble gases with respect to the Fermi level of the substrate. By using noble gases of different size (Xe, Kr and Ar) we have obtained information about the variation of the local surface potential in the vicinity of an adsorbed potassium atom. We find that between a potassium coverage of 2.7 at% and 5.0 at% all adsorption sites available for the noble gas atoms, both the ones adjacent to a potassium atom and those further away, are affected by the adsorbed potassium. The decrease in surface potential close to a potassium atom (<4 Å) is dominant and depends on the distance to the nearest potassium atom. Further away from the potassium atoms the surface potential is constant, but still significantly lower than the value for clean Rh(111): 0.4 eV at 2.7 at%, 0.7 eV at 4.1 at%, and 1.0 eV at 5.0 at% potassium coverage. The dependence on the potassium coverage indicates an increased influence of the next-nearest potassium atoms and is also noticeable in the decrease of the potential close to the potassium atoms. The surface potential is the result of the cumulative effect of all potassium atoms on the surface.

The potassium-induced changes in surface potential agree well with the electrostatic potential in a hexagonally ordered network of point charge dipoles, when we use a dipole moment of 10 D. This agreement indicates that a local change in electronic structure influences the potential at all available adsorption sites on a promoted surface. Another result of the dipole model is, that the heterogeneous electrostatic potential exists only close to the surface: At distances
further away (>10-15 Å), the potential is virtually homogeneous and corresponds to the potassium-induced decrease of the macroscopic work function.

If we assume that the relaxation energy of the adsorbed noble gases on potassium covered Rh(111) equals the value for the noble gases adsorbed on clean Rh(111), we can use adsorbed noble gases as a probe for the local surface potential, as mentioned above. Changes in relaxation energy due to the presence of potassium cause a difference between the potassium-induced shift of the photoemission signal and the change in local surface potential. An increase in relaxation energy, which has been reported for Xe on potassium-covered Ni, is transformed to a lower binding energy in the UPS spectrum. Then, the potassium-induced shifts of the photoemission signals are smaller than expected from the change in surface potential. This suggests that the changes in potential are underestimated by the shifts of the noble gas signals in the UPS spectrum. This is consistent with the dipole moment required in the dipole model to describe the experimentally determined changes in potential (10 D), which is smaller than expected from the experimental value for the dipole moment (15.6 D).

The influence of potassium on the surface potential has also been investigated by quantum-chemical calculation of the electronic structure of Rh-clusters and K/Rh-clusters. The potassium-induced change in potential on the K/Rh-clusters depends critically on the geometry of the clusters and may differ substantially from the experimental values. The potassium atoms on the K/Rh-clusters are positively charged, in agreement with the experiments. Hence, the electrostatic potential close to a potassium atom on the cluster is lowered upon potassium adsorption, like we found experimentally. However, the potential on the K/Rh-clusters is too high: The decrease of the potential is smaller than we have found experimentally and for some clusters, the potential further away from the potassium atoms increases after adsorption of potassium, which is not observed in the experiments. There are two reasons for the high values of the potential. First, the possibilities to distribute the transferred charge in the Rh clusters are limited. In addition, the K/Rh ratio in the clusters (~0.2) is higher than in the experiments (max. 0.05). Consequently, the Rh atoms in the cluster become more negatively charged than in the experiment, which leads to the higher values of the potential. Clusters that allow charge distribution around the potassium atoms give better results. Secondly, the potential on the clusters does not account for the contribution of the potassium atoms further away. When we include this contribution, estimated with the potential in a hexagonally ordered network of point charge dipoles for a potassium coverage of 11.1 at%, we find a total potential that is 0.5-1.0 V lower, which is more realistic. This indicates that the contribution of the potassium atoms further away to the potential is significant.

The effect of potassium on the relaxation energy of the photoionized noble gases has been investigated by calculating the ionization energy of adsorbed Xe, Kr and Ar on a triangular Rh₁₅ and a Rh₁₅K₃ cluster. The potential on the Rh₁₅ cluster increases upon potassium adsorption (see above). The ionization energy for a noble gas atom adsorbed on the Rh₁₅K₃ cluster is lower compared to the Rh₁₅ cluster and is close to the value expected from the potassium-induced change in potential. This indicates, that the influence of potassium on the relaxation energy
of the adsorbed noble gases is limited (max. \( \sim 0.3 \) eV).

In technical catalysts, the potassium-promoter is present in an oxidized form. To investigate whether the heterogeneity of the surface potential is similar to that of potassium-covered Rh(111), the effect of oxygen on potassium-covered Rh has also been studied with photoemission of adsorbed noble gases. Oxygen adsorbs atomically on clean or potassium-covered Rh(111) at 285 K and at 50 K. At 50 K also a physisorbed molecular oxygen species is found after higher oxygen exposures. On a Rh surface covered with 4 at\% potassium and saturated with oxygen, we have detected inequivalent adsorption sites for Xe, Kr and Ar, which indicates a heterogeneity of the surface potential. Comparison with the results obtained for adsorbed noble gases on 4 at\% potassium covered Rh(111) without oxygen indicates, that the heterogeneity on oxygen-potassium-covered Rh is qualitatively the same as on potassium-covered Rh without oxygen. However, the difference between the local work function on the sites adjacent to potassium and the sites further away is smaller than on potassium covered Rh without oxygen. Accordingly, the effect of potassium is not entirely destroyed by the coadsorbed oxygen, but it is weakened. This suggests, that the lower surface potential close to the potassium atoms also exists on the surface of a catalyst and thus influences the course of the reaction.
Samenvatting

Het voornaamste doel van dit werk is de effectieve potentiaal, die moleculen, zoals CO of N$_2$, voelen wanneer zij geadsorbeerd zijn op een alkali-gepromoteerd metaaloppervlak, te onderzoeken. In dit proefschrift is de door kalium veroorzaakte verandering van de oppervlaktepotentiaal op verschillende posities op een Rh(111) oppervlak experimenteel bepaald en de resultaten zijn vergeleken met theoretische berekeningen. De effectieve potentiaal op een kalium-gepromoteerd metaaloppervlak is lager dan op een ongepromoteerd oppervlak en hangt af van de positie ten opzichte van de kaliumatomen. Daarom spreken we van een lokale oppervlaktepotentiaal. De verandering in oppervlaktepotentiaal draagt bij aan het promotoreffect van kalium in katalytische reakties.

Kalium vormt verschillende fasen op het Rh(111) oppervlak, afhankelijk van de bedekking. Uit metingen van de macroscopische uittre-energie volgt dat het kalium als ion geadsorbeerd is bij lage bedekkingen (\(<0.2\)). Bij bedekkingen hoger dan 0.5 is het kalium metallisch. Verhogen van de bedekking van 0.2 tot 0.5 leidt tot een depolarisatie van de kalium-laag en de vorming van een overgangsfase tussen kalium-ionen en metallisch kalium. Om het promotoreffect in de katalyse te begrijpen zijn de eigenschappen van de kalium ionen bij lage bedekking (\(<5\) at\%) het belangrijkst.

Door middel van foto-emissie van geadsorbeerde edelgassen kan men veranderingen van de lokale oppervlaktepotentiaal op de plaats van de geadsorbeerde edelgasatomen detecteren. De veranderingen in lokale oppervlaktepotentiaal uiten zich als veranderingen in de bindingsenergie van de valentie-elektronen van de geadsorbeerde edelgasatomen ten opzichte van het Fermi-niveau van het substraat. Door edelgassen van verschillende grootte (Xe, Kr en Ar) te gebruiken hebben we informatie over de variatie van de lokale oppervlaktepotentiaal in de buurt van een geadsorbeerd kaliumatoom verkregen. We vinden dat tussen een kaliumbedekking van 2.7 at\% en 5 at\% alle voor edelgasadsorptie beschikbare plaatsen, d.w.z. zowel de plaatsen direct naast een kaliumatoom als de plaatsen verder weg, door het geadsorbeerde kalium worden beïnvloed. De verlaging van de potentiaal dicht bij een kaliumatoom (<4 Å) is overheersend en hangt af van de afstand tot het dichtstbijzijnde kaliumatoom. Op grotere afstand van de kaliumatomen is de oppervlaktepotentiaal constant, maar nog steeds belangrijk lager dan de waarde voor een schoon Rh(111) oppervlak: 0.4 eV bij een kaliumbedekking van 2.7 at\%, 0.7 eV bij 4.1 eV en 1.0 eV bij 5.0 at\%. De afhankelijkheid van de kaliumbedekking geeft een belangrijkere invloed van de overige kaliumatomen aan, hetgeen ook merkbaar is in de verlaging van de potentiaal dicht bij de kalium atomen. De oppervlaktepotentiaal is het resultaat van een cumulatief effect van alle kalium atomen op het oppervlak.

De door kalium veroorzaakte veranderingen in de oppervlaktepotentiaal komen goed overeen met de electrostatische potentiaal in een hexagonaal geordend netwerk van dipolen, bij een
dipoolmoment van 10 D. Deze overeenstemming laat zien dat een lokale verandering in de electroniche structuur de potentiaal op alle beschikbare adsorptieplaatsen op een gepromoteerd oppervlak beïnvloedt. Een ander resultaat van het dipool-model is, dat de heterogene electrostatische potentiaal alleen maar dicht bij het oppervlak bestaat: op iets grotere afstanden (>10-15 Å) is de potentiaal schijnbaar homogene en komt overeen met de verlaging van de macroscopische uittree-energie door de aanwezigheid van het kalium.

Als we aannemen dat de relaxatie-energie van de geadsorbeerde edelgassen op het met kalium bedekt Rh(111)-oppervlak gelijk is aan die van de geadsorbeerde edelgassen op schoon Rh(111), kunnen we foto- emissie van geadsorbeerde edelgassen gebruiken om de lokale oppervlaktpotentiaal te meten, zoals hierboven genoemd. Veranderingen in de relaxatie-energie ten gevolge van de aanwezigheid van het kalium veroorzaken een verschil tussen de verschuiving van het foto-emissie signaal en de verandering in lokale oppervlaktpotentiaal. Als de relaxatie energie toeneemt, zoals voor Xe op kalium-gepromoteerd Ni gevonden is, neemt de bindingsenergie, gemeten met UPS, af. In dat geval zijn de door kalium veroorzaakte verschuivingen van de foto-emissie pieken kleiner dan verwacht op grond van de verandering van de oppervlaktpotentiaal. Dit duidt erop, dat de veranderingen van de potentiaal onderschat worden door de verschuiving van de edelgaspieken in het UPS spectrum. Dit is consistent met het benodigde dipoolmoment om de experimenteel bepaalde veranderingen van de potentiaal te beschrijven (10 D), wat lager is dan op basis van de experimenteel gevonden waarde voor het dipoolmoment verwacht kan worden (15.6 D).

De invloed van kalium op de oppervlaktpotentiaal is ook onderzocht met behulp van quantum-chemische berekeningen van de electroniche structuur van Rh-clusters en K/Rh-clusters. De door het kalium veroorzaakte verandering van de potentiaal op de K/Rh-clusters hangt in belangrijke mate af van de geometrie van de clusters en kan aanzienlijk van de experimentele waarden afwijken. De kalium atomen in de K/Rh-clusters zijn positief geladen, in overeenstemming met de experimenten. Bijgevolg wordt de electrostatische potentiaal dicht bij een kalium atoom lager, zoals we in de experimenten reeds gezien hebben. Echter, de potentiaal op de K/Rh clusters is te hoog: de verlaging van de potentiaal is kleiner dan we experimenteel gevonden hebben en voor sommige clusters neemt de potentiaal op grotere afstand van een kalium atoom zelfs toe na kalium-adsorptie, in tegenstelling tot de experimenteel verkregen resultaten. Er zijn twee redenen voor de hoge waarden van de potentiaal. Ten eerste zijn de mogelijkheden om de overgedragen lading in het Rh cluster te verdelen beperkt. Bovendien is de K/Rh verhouding in de clusters (~0.2) hoger dan in de experimenten (max. 0.05). Als gevolg hiervan hebben de Rh-atomen in een cluster een grotere negatieve lading dan in het experiment, wat tot hogere waarden voor de potentiaal leidt. Clusters waarin de lading rondom het kalium-atoom verdeeld kan worden geven betere resultaten. Ten tweede is in de potentiaal op de clusters geen rekening gehouden met de bijdragen van de kalium-atomen verder weg op het oppervlak. Als we deze bijdrage, die geschat kan worden met de potentiaal in een hexagonaal geordend netwerk van dipolen voor een kalium bedekking van 11.1 at%, meenemen in de berekening, vinden we een totale potentiaal die 0.5-1.0 V lager is, wat realistischer is.
Dit laat zien, dat de kalium-atomen op grotere afstand belangrijk bijdragen in de potentiaal.

Het effect van kalium op de relaxatie-energie van de foton-geïoniseerde edelgassen is bestudeerd door de ionisatie-energie van geadsorbeerde Xe, Kr en Ar op een driehoekig Rh\textsubscript{15}-cluster en Rh\textsubscript{15}K\textsubscript{3}-cluster te berekenen. De potentiaal op het Rh\textsubscript{15}-cluster neemt toe na kalium adsorptie (zie boven). De ionisatie-energie van een geadsorbeerde edelgasatom op het Rh\textsubscript{15}K\textsubscript{3}-cluster is lager, in vergelijking met het Rh\textsubscript{15}-cluster en ligt dicht bij de waarde die we op basis van de verandering in potentiaal verwachten. Dit toont aan dat de invloed van het kalium op de relaxatie-energie van geadsorbeerde edelgassen beperkt is (max \(-0.3\) eV).

In technische katalysatoren is de kalium-promotor in een geoxideerde vorm aanwezig. Om na te gaan of de heterogeniteit van de oppervlaktepotentiaal op Rh(111), bedekt met kalium en zuurstof, vergelijkbaar is met die op Rh(111), met alleen kalium, is het effect van zuurstof op kalium-gepromoteerd Rh(111) met behulp van foto-emissie van geadsorbeerde edelgassen bestudeerd. Zuurstof adsorbeert atomair op zowel schoon als kalium-gepromoteerd Rh(111) bij 285 K en bij 50 K. Bij 50 K vinden we bij hoge zuurstofdoseringen ook moleculair gefysisorbeerd zuurstof. Op een Rh oppervlak, dat met 4 at\% kalium bedekt is en verzadigd met atomaire zuurstof, hebben we inequivalente adsorptieplaatsen voor Xe, Kr en Ar gevonden, hetgeen een heterogeniteit van de oppervlaktepotentiaal betekent. Vergelijking met de resultaten verkregen voor geadsorbeerde edelgassen op Rh, bedekt met 4 at\% kalium zonder zuurstof laat zien, dat de heterogeniteit op Rh, bedekt met kalium en zuurstof, kwalitatief hetzelfde is als op kalium-gepromoteerd Rh zonder zuurstof. Echter, het verschil in oppervlaktepotentiaal dicht bij de kaliumatomen en op grotere afstand van de kaliumatomen is kleiner dan op het kalium-gepromoteerde Rh oppervlak zonder zuurstof. Dus het effect van kalium wordt niet ongedaan gemaakt door het geadsorbeerde zuurstof, maar het is zwakker. Het is dus goed mogelijk dat, dat ook het oppervlak van een katalysator de oppervlaktepotentiaal in de nabijheid van de kaliumatomen lager is en zo het verloop van de reactie beïnvloedt.
Publications:

T.V.W. Janssens, K. Wandelt and J.W. Niemantsverdriet

*Long and Short Range Effects of Alkali Promoters on Metal Surfaces: K on Rh(111)*,
(Chapter 3 and 4)

T. Janssens, G.R. Castro, H. Busse, U. Schneider and K. Wandelt,

*Local Effects in the Interaction of Potassium with Rh(111)*,
(Chapter 3)

G.R. Castro, H. Busse, U. Schneider, T. Janssens and K. Wandelt,

*Geometric and Electronic Structure of Potassium on Rh(111)*,
(Chapter 2)

T.V.W. Janssens, G.R. Castro, J.W. Niemantsverdriet and K. Wandelt,

*Local Surface Potentials around Potassium Promoter Atoms on Rh(111) Measured with Photoemission of Adsorbed Xe, Kr and Ar.*
in preparation
(Chapter 3)

U. Schneider, G.R. Castro, H. Busse, T. Janssens, J. Wesemann and K. Wandelt,

*Xe adsorption on the Cu₅Pt(111) surface*,

G.R. Castro, U. Schneider, H. Busse, T. Janssens and K. Wandelt,

*The interaction of CO with the Cu₅Pt(111) surface*,

U. Schneider, G.R. Castro, H. Isern, T. Janssens and K. Wandelt,

*Xe adsorption on Al(110)*,

G. Mondio, F. Neri, M. Stöcker, T. Janssens, G.R. Castro and K. Wandelt,

*Surface chemical sensitivity of reflection electron energy loss spectra from metal surfaces*,
Dank

aan allen, die op een of andere wijze aan dit proefschrift hebben bijgedragen of mijn promotietijd aangename hebben gemaakt:

an allen, die irgendwie zu dieser Doktorarbeit beigetragen haben oder meine Promotionszeit angenehmer gemacht haben:

Curriculum Vitae

Stellingen

behorende bij het proefschrift
Alkali Promotion of Metal Surfaces:
A Surface Science Study of Potassium on Rhodium(111)
door T.V.W. Janssens

1. De bewering van Bonzel dat een kalium-promotor alleen de potentiaal in zijn directe omgeving verlaagt, zonder de potentiaal van de rest van het oppervlak te beïnvloeden, en dat dit in overeenstemming is met foto-emissie experimenten van Xe geadsorbeerd op kalium-gepromoteerde metaaloppervlakken, is onjuist.
Dit proefschrift.

2. Het gebruik van de term red-shift in infraroodspectroscopie dient vermeden te worden, omdat het hier niet een verandering van een waargenomen frequentie van licht betreft maar een verandering van een absorptiefrequentie die gerelateerd is aan een chemische binding, en het bovendien nog een verschuiving van het rode licht vandaan aangeeft, terwijl het een verschuiving in de richting van het rode licht suggereert.

3. De bewering dat door een puntlading geïnduceerde dipolen in dicht bij elkaar gelegen atomen gericht zijn op de puntlading is alleen waar als de atomen en de puntlading op één lijn liggen.


5. De aanwezigheid van gebrugd CO op een schoongemaakt Rh(100) oppervlak in ultra-hoog vacuüm bij lage CO bedekking, vastgesteld door een infrarood absorptie rond 1870 cm⁻¹, betekent dat het oppervlak niet goed schoongemaakt is.

6. Een mondelinge toezegging zonder getuigen is weliswaar rechtsgeldig, maar heeft verder geen enkele betekenis.

7. De aanwezigheid van signalen voor clusterionen in een SIMS spectrum duidt aan dat de samenstellende atomen van het cluster dicht bij elkaar op het oppervlak gezeten hebben, ongeacht of direkte emissie dan wel recombinatie van fragmenten heeft plaatsgevonden.

8. Het gebruik van steeds snellere computers en betere softwarepakketten voor de vervaardiging van figuren leidt tot steeds hogere kwaliteitseisen en niet tot een snellere produktie.

9. Het feit dat fysici en chemici nog steeds met elkaar bekvechten, bewijst dat ze elkaar niet kunnen missen.