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Effect of adsorbed potassium on the electrostatic potential on Rh clusters in relation with photoemission of adsorbed noble gases

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A locally lowered surface potential develops around potassium atoms on a transition metal surface. These potentials are accessible experimentally by measuring the ultraviolet photoemission spectra of adsorbed noble gases. We determine the potassium-induced change in electrostatic potential on K/Rh clusters on the basis of calculated electronic structures using density functional theory. It appears that the calculated potentials depend critically on the geometry of the cluster and may differ substantially from the experimentally observed values. Clusters that allow a substantial charge redistribution around the potassium atoms give the best results. Another improvement is obtained from adding the contribution of potassium atoms further away from the potential. We also present theoretical evidence that the potassium-induced change in ionization energy of Xe, Kr, and Ar on a Rh_{15}K_3 cluster is mainly determined by the change in electrostatic potential. This provides support for the use of photoemission of adsorbed noble gases as a probe for changes in local surface potential induced by adsorbed species.

I. INTRODUCTION

The promoter effect of potassium on transition metal catalysts involves a local lowering of the surface potential around the potassium atoms.¹ (The potential refers to the potential energy of an electron, which has the opposite sign compared to the usual convention used in electrostatics.) At low coverage, potassium becomes positively charged when adsorbed on a metal surface, which is responsible for the lower surface potential.²⁻⁸ Experimental evidence that the promoter effect of potassium is predominantly a local one comes from surface science studies of adsorbates, such as CO or N_2 , on metal single crystal surfaces, precovered with small amounts of potassium.⁹⁻¹⁶ Photoemission of physisorbed noble gases is of particular interest because the binding energy shift of the adsorbate is a direct probe for the potential at different sites on the surface.¹⁷⁻²⁰ In this way, we have found a dominant lowering of the surface potential of $\sim 1-1.5$ eV on sites next to potassium atoms, while at sites further away the surface potential becomes practically constant, but still significantly, i.e., 0.5–1 eV, depending on potassium coverage—lower than on unpromoted Rh(111), see Fig. 1(a). The fact that the surface potential, as probed by the noble gas atoms, depends on the potassium coverage, forms strong evidence that it results from a cumulative effect of all potassium atoms on the surface. The observed changes in potential agree very well with the electrostatic potential in an infinite, hexagonally ordered network of point charge dipoles, confirming the cumulative effect of the potassium atoms.^{19,20} However, by calculating the surface potential using point charge dipoles, the actual charge distribution in the surface region remains undetermined. Therefore, we determine the potassium-induced change in potential on the basis of calculated electronic structures of K/Rh clusters.

Several theoretical calculations on alkali-promoted metal surfaces have been published.^{1,21-24} These investigations, however, all dealt with the effect of a single alkali atom. In this work we used density functional theory to calculate the

electron distribution in several clusters consisting of rhodium and three potassium adatoms. We determine the potassium-induced change in surface potential from the difference between the electrostatic potential on a K/Rh cluster and that on the same cluster without potassium in order to simulate the potassium-induced change in surface potential on the Rh(111) surface.

Probing the potassium-induced change in potential on a metal surface with photoemission of adsorbed noble gases presupposes that the extra-atomic relaxation energy of the photoionized noble gas atoms, due to the presence of the metal surface, is not affected by the adsorbed potassium. As this extra-atomic relaxation energy is mainly determined by the distance between the noble gas atom and the surface, which does not change upon adsorption of potassium, a substantial change in extra-atomic relaxation energy is not expected. In this paper we also show that the potassium-induced change in ionization energy of adsorbed Xe, Kr, and Ar on a Rh cluster indeed monitors the change in electrostatic potential, indicating that the interpretation of potassium-induced changes in binding energy in photoemission of adsorbed noble gases as changes in local surface potential is permitted.

II. METHOD

To calculate the electronic structure of the clusters, we have performed nonrelativistic, unrestricted density functional calculations in the local density approximation (LDA). We have used the Amsterdam density functional program (ADF) developed by Baerends and co-workers, which gives a solution of the Kohn–Sham equations.²⁵⁻²⁷ For the exchange-correlation energy the Vosko–Wilk–Nussair potential²⁸ has been used. The molecular orbitals are represented by linear combinations of atomic Slater-type orbitals. In the calculations, only the valence levels of the atoms are used (4s and 4d for Rh, 3p and 4s for K, 5s and 5p for Xe, 4s and 4p for Kr, and 3s and 3p for Ar); the core levels are kept frozen.

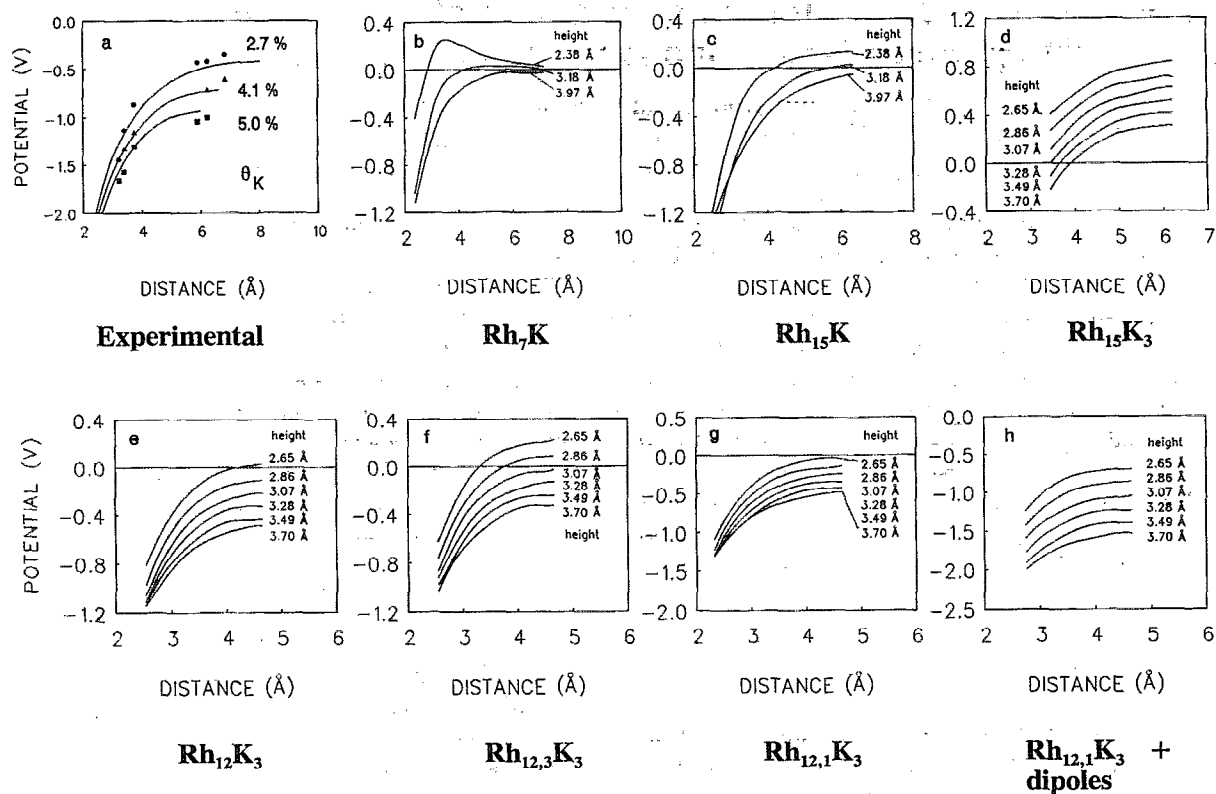


FIG. 1. Potassium-induced changes in electrostatic potential. (a) Symbols: experimental values obtained from photoemission of adsorbed Xe, Kr, and Ar on potassium-covered Rh(111) at three different coverages. Solid lines: calculated potential of a hexagonally ordered network of point-charge dipoles, from Refs. 19 and 20. (b)–(g) Potassium-induced changes in potential on the K/Rh clusters shown in Fig. 1 at the indicated heights above the rhodium plane. (h) Data from (g), corrected for the contribution of the potassium atoms further away, estimated by adding the potential due to a hexagonally ordered network of point-charge dipoles outside the cluster.

Since we want to compare the potassium-induced change in electrostatic potential on a Rh cluster with that on the Rh(111) surface, we calculate the electronic structure of clusters with hexagonally ordered Rh atoms. The geometries of the clusters that are studied are shown in Fig. 2. In all clusters, the distance between the Rh atoms is 2.687 \AA , the same as on the Rh(111) surface. The adsorbed potassium atoms are placed on top (Rh_7K and Rh_{15}K_3) or on a threefold Rh site (Rh_{15}K , Rh_{12}K_3 , $\text{Rh}_{12,3}\text{K}_3$, and $\text{Rh}_{12,1}\text{K}_3$), with preservation of the cluster symmetry. The distance between a potassium atom and a Rh atom is 2.674 \AA , i.e., the sum of the radius of a Rh atom (1.344 \AA) and that of ionic potassium (1.33 \AA).²⁹ No further optimization of the geometry has been performed.

On the Rh_{15}K_3 cluster, the distance between the potassium atoms is 10.75 \AA , which corresponds to a potassium coverage of 6.2 at. % in an infinite, hexagonally ordered layer. For the Rh_{12}K_3 , $\text{Rh}_{12,3}\text{K}_3$, and $\text{Rh}_{12,1}\text{K}_3$ cluster, this distance is 8.06 \AA , corresponding to a coverage of 11.1 at. %. Note that these distances are smaller than in the experiments reported in Refs. 19 and 20, where the highest potassium coverage was 5 at. %, corresponding to 12.0 \AA between the potassium atoms.

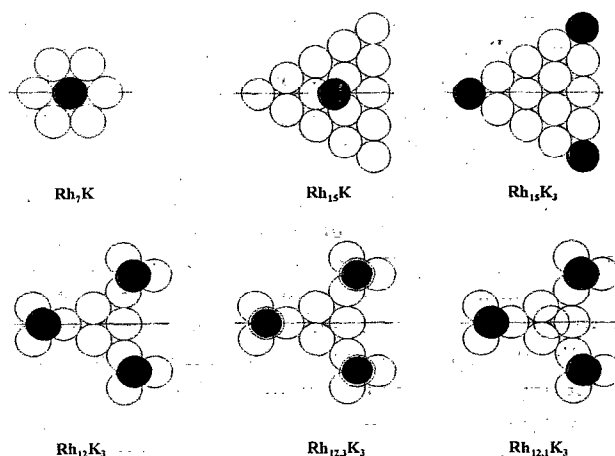


FIG. 2. Geometries of the K/Rh clusters used in this study. The black circles indicate the potassium atoms on the cluster; the dashed circles represent rhodium atoms in the second layer of the cluster.

III. RESULTS AND DISCUSSION

A. Potassium-induced changes in electrostatic potential on the K/Rh clusters

Figure 1(a) summarizes the experimentally determined potassium-induced changes in surface potential on Rh(111). The solid lines represent the potentials in a hexagonally ordered network of dipoles.²⁰ Figures 1(b)–1(g) show the changes in potential on the K/Rh clusters shown in Fig. 2, as a function of the distance to the potassium atom along the x axis of a cluster (indicated by the dashed lines in Fig. 2) at different heights above the Rh plane. The heights indicated in Fig. 1 include the positions of the noble gas atoms above the Rh plane, which are between 2.85 and 3.24 Å for Ar, between 2.96 and 3.34 Å for Kr, and between 3.18 and 3.54 Å for Xe. These ranges include positions from the threefold to the on-top site, as derived from the van der Waals radii of the noble gas atoms (1.9 Å for Ar, 2.0 Å for Kr, and 2.2 Å for Xe).²⁹ Therefore, the potentials shown in Fig. 1 cover the potential range that would be detected by the noble gases on the clusters.

On all clusters studied, we find that the potential decreases steeply towards the potassium atoms, in agreement with the experimental data [Fig. 1(a)]. However, the potential further away from the potassium is significantly higher than observed in the experiment, though the distances between the potassium atoms on the clusters is smaller. There are two reasons for these high values of the potential. First, the charge distribution in the clusters differs from that of the semi-infinite K/Rh(111) system. Second, the contribution of the potassium atoms beyond those present in the cluster is not included. We discuss both factors separately in the following.

1. Charge distribution

In all clusters, we find positively charged potassium atoms, as indicated by their positive Mulliken charge. This points to a transfer of charge from potassium to rhodium atoms, in qualitative agreement with experiments.³⁰ Although Mulliken charges on the atoms may be unreliable, they give a useful qualitative indication of the charge distribution in the clusters and we will use them for this purpose.

The charge transferred to the rhodium in the cluster is necessarily distributed over a limited number of atoms. Consequently, the geometry of the cluster strongly influences the calculated potentials, as illustrated in Figs. 1(b)–1(g). The electrons tend to accumulate at the edge of the cluster in order to minimize the repulsion. Consequently, we find for instance in the Rh₇K cluster that 87% of the transferred charge is located at the six rhodium atoms at the edge. This causes the high potentials and the increase in potential at 2.38 Å above the rhodium plane as shown in Fig. 1(b). Such a charge distribution is unrealistic and hence the Rh₇K cluster is unsuitable for describing the surface potential of the potassium-covered Rh(111) surface.

In the Rh₁₅K cluster, the transferred charge remains more concentrated in the center of the cluster: 53% is located on the Rh atoms in contact with the potassium atom, while only 8% is found at the extremities. Accordingly, the changes

in potential are lower than on Rh₇K and closer to the experimental values, see Fig. 1(c).

In the Rh₁₅K₃ cluster, the potassium atoms at the extremities donate electrons to the rhodium atoms. This drives the electrons to the center of the cluster, whereas the cluster itself pushes the electrons to the edges. In this cluster we find 74% of the charge on the Rh atoms beneath the potassium atoms, 3% on the three central Rh atoms, 10% on the Rh atoms next to the potassium site, and 12% on the atoms at halfway distance between two potassium atoms. Compared to the Rh₇K and Rh₁₅K, the charge remains more concentrated below the potassium atoms.

The potentials on the Rh₁₅K₃ cluster, however, are even larger than on the Rh₇K and Rh₁₅K cluster, see Fig. 1(d). This is caused by the larger number of potassium atoms—three instead of one—and the lacking possibility to distribute the electrons around the potassium atom. Hence, more charge is transferred to the Rh atoms, which accumulates at the center of the cluster. Better results are expected when the potassium atoms are surrounded by rhodium atoms. Note, however, that although the absolute values of the potential are too high, the variation of the potential across the surface is of the same order of magnitude as that in the experiment.

A cluster that allows the transferred charge to be distributed around the potassium is the Rh₁₂K₃ cluster in Fig. 2. In this cluster we find only 12% of the transferred charge on the three central Rh atoms. The potassium-induced changes in potential on this cluster are closer to the experimental values, due to the better coordination of the potassium atoms. Between 2.65 and 3.70 Å above the rhodium plane we find a decrease in potential [Fig. 1(e)], in agreement with the experiment.

The Rh_{12,3}K₃ and Rh_{12,1}K₃ clusters are variations of the Rh₁₂K₃ cluster. In the Rh_{12,3}K₃ cluster, three extra rhodium atoms have been placed in the hexagonally closed packed position beneath the atoms in contact with potassium atoms. Compared to Rh₁₂K₃, the potassium-induced change in potential is smaller, however, and becomes even positive at distances below 3 Å above the surface, see Fig. 1(f). This is due to a larger charge transfer from potassium, giving a higher negative charge on the rhodium atoms. The change in potential on the Rh_{12,1}K₃ cluster, which has one extra atom beneath the three central rhodium atoms, is rather similar to that of Rh₁₂K₃, as Fig. 1(g) indicates. Thus, among the clusters considered in this paper, Rh₁₂K₃, Rh_{12,3}K₃, and Rh_{12,1}K₃ clusters appear to give the best reproduction of the experimentally determined surface potential on potassium-promoted Rh(111). Note however, that the variation in potential across the surface can also satisfactorily be simulated with the Rh₁₅K₃ cluster, which has the advantage that the distance between the potassium atoms corresponds better to the K/Rh(111) systems for which experimental data are available.

2. Contribution of potassium atoms further away

The second reason why the potentials on the cluster are higher than the experimentally observed potentials is that the contribution of the potassium atoms further away is not included in the cluster calculation. To estimate this contribu-

TABLE I. Calculated ionization energies (in eV) for Xe, Kr, and Ar in the gas phase and adsorbed on the Rh₁₅ and Rh₁₅K₃ cluster. The effect of potassium on the ionization energy for adsorbed Xe, Kr, and Ar is largely determined by the potassium-induced change in electrostatic potential on the cluster.

	Calculated ionization energy			Extra-atomic relaxation energy		K-induced change on Rh ₁₅ K ₃	Expected from change in potential		Difference	
	Gas phase	On Rh ₁₅	On Rh ₁₅ K ₃	Calc.	Expt. ^a		Atom center	z axis averaged	Atom center	z axis averaged
Xe	12.77	11.63	10.96	-1.14	-1.1	-0.67	-0.50	-0.58	-0.17	-0.09
Kr	14.59	13.03	12.33	-1.56	-1.4	-0.70	-0.61	-0.66	-0.09	-0.04
Ar	16.39	14.80	13.78	-1.59	-1.5	-1.02	-0.66	-0.70	-0.36	-0.32

^aSee Refs. 19 and 20.

tion we calculate the potential in a hexagonally ordered network of dipoles as in Ref. 20, from which we subtract the contribution of the three dipoles representing the potassium atoms on the cluster. For calculating the potential in the dipole network, we assume that the image plane of the dipoles is placed 1.09 Å above the Rh plane, which corresponds to the threefold adsorption site for potassium. The lateral distance between the dipoles, 8.06 Å, is the same as between the potassium atoms on the cluster. The dipole moment is evaluated from the potassium-induced change in dipole moment perpendicular to the Rh₁₃K₃ cluster, which is 14.7 D. Assuming that this is the result of the three dipoles at the potassium atoms, we find a dipole moment of 4.9 D per potassium atom. As explained by Aruga and Murata,⁴ we need to use the double value (9.8 D for the point-charge dipoles in the dipole network to obtain an adequate description of the surface potential. By adding the contribution of the dipoles further away, which amounts to between -0.7 and -0.9 V at the sites where noble gas atoms adsorb, to the potential on the Rh₁₂K₃ cluster [Fig. 1(g)], we obtain the results of Fig. 1(h). These potentials are considerably lower, and closer to the experimental data than the values without the dipole contribution, but they do not quite reach the value of the potential in a hexagonally ordered network with this dipole density (-2 to -2.3 V), due to the negative charge on the rhodium atoms.

B. The relaxation energy of ionized noble gas atoms on the K/Rh(111) surface

The interpretation of binding energy shifts in photoemission spectra of adsorbed noble gases in terms of changes in surface potential only, neglects the possible effects of adsorbed potassium on the final state relaxation energy of the noble gases. To check the validity of this assumption, we calculate the ionization energy of Xe, Kr, and Ar adsorbed on the threefold site in the center of the Rh₁₅ and Rh₁₅K₃ cluster. Although the actual values of the potassium-induced changes in surface potential on this cluster do not correspond to the experiment, the variation in these values across the surface is well reproduced. This is in fact sufficient, as the ability of adsorbed noble gas atoms to detect differences in the surface potential on different adsorption sites is independent of the actual value of the potential.

The ionization energy of the noble gas atom corresponds to the energy difference of the system containing an ionized

noble gas atom and the same system with a neutral noble gas atom. An efficient method to calculate the ionization energy is to use 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),³¹ which is obtained from the density functional calculation. Then, the ionization energy (I) is written as

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

where E is the energy of the system as a function of the occupation number n and ϵ is the energy of the orbital from which the electron is removed. In first-order approximation, the last integral in Eq. (1) equals $-\epsilon(n - \frac{1}{2}) \Delta n$. As $\Delta n = 1$, the ionization energy equals the energy of an orbital from which half an electron has been removed. Therefore, we approximate the ionization energy of an adsorbed noble gas atom by calculating the orbital energy of a valence level in which half an electron is missing. It should be noted that the ionization energy in the calculation is referenced to a fixed vacuum level, whereas in the experiments it is the Fermi level of the substrate that 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 a photoemission spectrum.

Table I summarizes the calculated ionization potentials of gaseous Xe, Kr, and Ar and of the same atoms adsorbed at the threefold site in the center of the Rh₁₅ and Rh₁₅K₃ clusters. The distance between the noble gas and the rhodium atoms has been derived from the van der Waals radii and has not been optimized in the calculations. The lateral distance between the noble gas atom and the potassium atoms on Rh₁₅K₃ is 6.2 Å, which corresponds to a bare rhodium site on potassium-covered Rh(111).^{19,20}

As expected, the ionization energy of a noble gas atom adsorbed on the Rh₁₅ cluster is lower than in the gas phase, the difference being the extra-atomic relaxation energy, due to the presence of the rhodium atoms. The calculated relaxation energies agree well with the experimentally determined values (Table I).^{19,20} Upon adsorption of a noble gas atom, the degeneracy of its p orbitals is lifted: the p_x and p_y orbitals are oriented parallel to the surface plane while the p_z orbital has a perpendicular orientation. However, due to the weak interaction between the physisorbed noble gas and the

rhodium atoms, the differences in ionization energy between the p_x or p_y and the p_z valence orbitals of adsorbed Xe, Kr, or Ar are in the order of 0.05 eV only.

The influence of potassium on the relaxation energy has been estimated by comparing the difference in ionization energy of Xe, Kr, and Ar adsorbed on the Rh_{15} and $Rh_{15}K_3$ clusters with the value expected from the potassium-induced change in electrostatic potential on the $Rh_{15}K_3$ cluster. 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 Rh(111) surfaces the spin-orbit splitting remains the same.^{19,20}

The ionization energies of adsorbed Xe, Kr, and Ar on the Rh_{15} and the $Rh_{15}K_3$ cluster are also given in Table I. The potassium-induced potential change at the center of the noble gas atom and the potential change averaged over the z axis in the noble gas atom sphere, which is a better estimate for the potential probed by the noble gas atom, are also tabulated. As expected from 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 than on Rh_{15} . All values are smaller than expected from the change in electrostatic potential (Table I). However, the difference is 0.3 eV at most, indicating that the relaxation energy of the ionized noble gases at 6.2 Å from the potassium is hardly affected by the presence of potassium. Relaxation shifts of a few tenths of an eV have also been reported for Xe on Ni(100), precovered with a small amount of potassium (<5 at. %).³²

The calculations thus suggest that the potassium-induced change in ionization energy of adsorbed noble gas atoms is predominantly determined by a change in surface potential. Therefore, photoemission of adsorbed noble gases on potassium-covered Rh(111) yields a good estimate for the local surface potentials, at least for the sites ~6 Å away from the potassium atoms. The small increase in relaxation energy gives a slightly lower binding energy in the photoemission spectrum than expected from the changes in surface potential only. Therefore, the real changes in surface potential on the potassium-covered Rh(111) may be somewhat larger than indicated in Fig. 1(a).

C. Conclusions

To check whether the potential on a K/Rh cluster can serve as a model for the surface potential on potassium-promoted Rh(111) surfaces, we have calculated the electrostatic potential on the basis of a density functional calculation of the electronic structure of several clusters. The geometry of the clusters strongly influences the effect of potassium on the calculated electrostatic potential. For all geometries studied, we find that close to a potassium atom the potential decreases upon potassium adsorption. The potential further away may increase—in contrast to the experimental data—due to the charge distribution in the cluster, that differs significantly from that of the potassium-promoted Rh(111). The best model clusters are the ones that allow a charge distribution around the potassium atoms: $Rh_{12}K_3$, $Rh_{12,3}K_3$, and $Rh_{12,1}K_3$. On these clusters, the presence of potassium leads to a lower potential at larger distances from potassium

around 3 Å from the rhodium plane, the typical distance between the center of the rhodium plane and a noble gas atom, which is in qualitative agreement with the experimental data. The variation in the electrostatic potential across the surface, however, is also satisfactorily reproduced by the $Rh_{15}K_3$ cluster, which offers the inherent advantage that the K–K distances are more representative for the experimental situation.

On all K/Rh clusters studied, we find higher values for the potential than we might expect from the experimental data. One reason for this is the high K/Rh ratio of the clusters (~0.2) as compared to the highest potassium coverage for which experimental data are available (K/Rh=0.05).^{19,20} This leads to a higher negative charge on the rhodium atoms of the cluster. A second reason is that the clusters contain three potassium atoms only and that potassium atoms further away do not contribute to the potential, as they do in the experiment. Including this contribution as estimated from the potential in a hexagonally ordered network of point-charge dipoles, we find potentials that are 0.7–0.9 V lower at the adsorption site of a noble gas atom. These values are more realistic for the surface potential on potassium-covered Rh(111).

The ionization energies of adsorbed Xe, Kr, and Ar decrease upon adsorption on the Rh_{15} cluster, due to the extra-atomic relaxation energy of atoms adsorbed on a metal. Calculations of the ionization energy of adsorbed Xe, Kr, and Ar on Rh_{15} and $Rh_{15}K_3$ indicate that the potassium-induced change in ionization energy for a noble gas atom is predominantly determined by the change in electrostatic potential, though a small increase (<0.3 eV) in relaxation energy cannot be excluded. This confirms that the interpretation of a potassium-induced change in the binding energy of a noble gas signal in photoemission spectroscopy as a change in local surface potential is permitted, although the actual changes in electrostatic potential may be slightly underestimated due to the small potassium-induced increase in relaxation energy of the photoionized noble gases.

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