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Nature of the *ns*-derived states for an isolated alkali atom on a surface

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Abstract

It has recently been shown (for K/graphite) that experimental core level spectroscopy data for adsorbed Ar combined with calculations is a most valuable tool in order to obtain information about the alkali-derived unoccupied density-of-states [A. Sandell et al., Phys. Rev. Lett. 78 (1997) 4994]. We present experimental results for Ar on various metallic substrates and discuss them in terms of adsorption properties of an isolated K adatom. We find a clear tendency for increased 4s–substrate mixing as the substrate work function decreases, in accordance with a simple extension of the Gurney model. It is also shown that core level spectroscopy data for Ar coadsorbed with K can be used to investigate the effects on the 4s resonance of increasing K coverage. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Alkali metals; Chemisorption; Single crystal surfaces; Soft X-ray photoelectron spectroscopy; Surface electronic phenomena

1. Introduction

Alkali metals adsorbed on solid surfaces have been heavily studied within the field of surface science. This is partly because of the technical importance of such systems, e.g. in promoted catalytic reactions, but it has also served as a touchstone for our understanding of the most fundamental properties of the adsorption process [1]. Since the alkali metal–substrate bond is assumed to be largely determined by the interaction between the alkali *ns* level and the outermost

valence levels of the substrate, this chemisorption system has been regarded as a relatively simple prototype case.

Nonetheless, the debate concerning the most fundamental properties of the alkali chemisorption bond is still lively. This is especially the case for the situation where the alkali coverage on the surface is extremely low. A central issue is whether the bonding of an essentially isolated alkali atom on a surface can be considered ‘ionic’ or ‘covalent’ [2–7]. This involves a controversy over whether there is charge transfer from the alkali atom to the substrate or not. In order to assess these problems, detailed information about the electronic structure of the alkali–substrate complex is most desirable.

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A qualitative model of alkali bonding to metal surfaces in the single-adatom limit was presented by Gurney [8] and later quantified by Lang and Williams for a jellium substrate [9]. In this picture, the valence ns and np states of the alkali atom are broadened into resonances upon adsorption. If the ns resonance is located above the Fermi level, the bonding is ionic, whereas in the case of pure covalent bonding the ns resonance straddles E_F and is essentially half-filled. This corresponds to a chemical picture in which the substrate work function plays the role of the electron affinity of an electron acceptor, and the alkali ionization potential locates its valence level relative to vacuum zero. The calculations showed that for Li/Al, although the center of gravity of the ns resonance is located above E_F , its tail is slightly occupied, indicating a partially covalent bonding. Most of the more recent theoretical efforts support this model in the sense that the center of the ns resonance is expected to occur 1–3 eV above the Fermi level at low coverages. However, there are considerable disagreements concerning the possible transfer of alkali charge to the substrate.

Experimental studies using electron energy loss spectroscopy (EELS) and inverse photoemission spectroscopy (IPES) have shown the existence of an alkali-induced state typically 2–3 eV above the Fermi level at low coverages [2,10–13]. However, this state has commonly been associated with alkali np states rather than ns states. The ns resonance has generally been assumed to be positioned within 1 eV from E_F . Two-photon photoemission (2PPE) experiments reveal an alkali-derived feature 2–3 eV above E_F but the interpretations of this state differ: in one study [K/Ag(100)] [14], it was identified as the ns resonance; whereas in the other, it was attributed to an np -derived state [15]. However, in the latter case some doubts were raised about the assignment, since no feature corresponding to the ns resonance could be observed below the presumed np peak. Recently, an investigation of photoinduced desorption of K from graphite was presented [16]. With this technique, a position of the 4s level 2.4 eV above E_F could be estimated. Furthermore, in an attempt to tackle the charge transfer problem, a detailed lineshape analysis of the alkali core level photoemission

spectra has been performed, leading to the interpretation that the ns charge is still located in the vicinity of the alkali atom [17].

A major drawback of the experimental approaches mentioned above is the low signal-to-background ratio for the adsorbate-induced features when approaching zero coverage. This makes the positioning of the ns resonance uncertain and also precludes observation of finer details in the unoccupied density-of-states (DOS), such as the long tail down to E_F predicted by theory. In order to circumvent this problem, we have recently developed an alternative approach with which the unoccupied alkali-derived DOS in the low coverage limit can be determined in more detail [18]. The method, based on a combination of experimental core level spectroscopy data and calculations, was demonstrated for the K/graphite system. It was shown that core excitation and decay spectra of adsorbed Ar combined with calculations can be applied to obtain a consistent picture of the local unoccupied states for an isolated K atom on graphite. We found that the K 4s resonance is located 2.7 eV above E_F with an adsorption-induced hybridization width of the order of 0.1 eV.

In this paper, we present experimental core level spectroscopy data for adsorbed Ar on various metallic substrates and discuss the results in terms of adsorption properties of an isolated K adatom. A clear qualitative trend supporting the pivotal role of the substrate work function is found, and with the use of the detailed treatment in our previous paper, the uncertainties in the results can be discussed. It is furthermore our hope that this experimental data set will stimulate future theoretical efforts in order to obtain a more complete picture.

2. Experimental

The experiments were performed at Beamline 22 at the National Synchrotron Facility MAX I in Lund, Sweden. The experimental set-up consists of a modified Zeiss SX 700 monochromator, a large hemispherical electron analyzer of Scienta-type for photoemission studies and a channeltron with a retarding grid for X-ray absorption spectro-

scopy (XAS) measurements via detection of secondary electrons [19]. The photon energy resolution was 0.15 eV (0.30 eV for Ar+K/graphite) and the electron energy resolution 0.3 eV. Photon energies were calibrated by measuring a given spectral feature using both first and second order light at the same monochromator setting, such that the difference is the photon energy. XA spectra were measured in partial Auger yield mode. The samples Pt(111), Au(110), Cu(100), Ag(110) and highly oriented pyrolytic graphite (HOPG) were cooled to less than 25 K. The Ar monolayers were prepared by formation of multilayers followed by desorption until only one Ar $2p_{3/2}$ component was observed in the photoemission spectrum. For Ar/Au(110), the monolayer was found to consist of more than one type of Ar due to the (2×1) surface reconstruction. In this case, Ar was desorbed until only one component remained, leading to a submonolayer coverage. The coverage of preadsorbed K on the graphite surface in the Ar+K coadsorption experiment was about 0.1 ML, corresponding to a dispersed phase [7].

3. Results and discussion

This part of the paper is organized in the following way. We will first introduce the technique with which the local unoccupied DOS of an isolated adsorbed alkali atom can be determined by going through the recently obtained experimental and theoretical results for K/graphite [18]. This includes a discussion about the factors that have to be considered and the uncertainties with this type of approach. We will then proceed with a brief discussion about the effects of increasing the K coverage on graphite and finally apply the technique in order to systematically study the properties of an isolated K atom on various metallic substrates.

3.1. The method: an isolated K atom on graphite

Our novel approach in its complete form requires experimental measurements as well as theoretical calculations. The experimental part makes use of the fact that the valence electron

distribution of Ar with a core hole is similar to that of K (the $Z+1$ approximation). The $Z+1$ approximation functions very well as we use it here; the limitations come when the outer valence electronic configuration can deviate, as e.g. in the case of Be, which has no 2p electrons in the core region [20]. To verify this, calculations have been performed for both Ar with a core hole and ground state K on graphite and the differences are negligible [18,21]. Thus, by applying core level electron spectroscopy on adsorbed Ar, the properties of ground state K *in Ar geometry* are probed. This gives us a clear benchmark for the calculations. In the final step, calculations are performed after making corrections for the differences in adsorption geometry between Ar and K. We will now show in more detail how this is done and what kind of information the method yields. The system that will be discussed is K/graphite.

The photon energy needed for the Ar $2p_{3/2} \rightarrow 4s$ excitation measured by XAS and the binding energy (BE) of the Ar $2p_{3/2}$ peak measured by X-ray photoemission (XPS) gives the energy relationship between a neutral core-excited ($2p_{3/2}^{-1}4s^1$) and a core ionized ($2p_{3/2}^{-1}$) Ar atom on the surface. This energy relationship for 1 ML Ar/graphite is illustrated in Fig. 1 on a relative energy scale where zero represents the $2p_{3/2}$ BE relative to the graphite Fermi level. Since the first peak observed in the XA spectrum, i.e. the Ar 4s resonance, has a positive energy on this scale it can be concluded that an ionic configuration is energetically favorable.

Furthermore, the XPS BE can be envisaged as the Fermi level in the XA spectrum [22–24]. This implies that for 1 ML Ar/graphite, there is an empty 4s resonance well above E_F . If we then consider that the features observed in XAS reflect the DOS of the core-excited state [23] and apply the $Z+1$ approximation, we can from Fig. 1 infer that the 4s resonance for a K-like Ar atom on graphite is situated at $E_F + 2.1$ eV. However, this ‘quasi-potassium’ atom is not directly comparable to an isolated K atom. Adjusting for effects caused by the surrounding Ar atoms leads to a decrease in the XPS–XAS energy difference by 0.5 eV [25,26] (this was also verified by us in a measurement of the Ar 2p spectrum for 0.06 ML

Fig. 1. (a) Ar $2p_{3/2} \rightarrow 4s$ XAS spectrum for 1 ML Ar/graphite. This spectrum illustrates the local unoccupied states for a K-like adatom at the adsorption distance of Ar and embedded in an Ar layer. The zero point, given by the corresponding XPS BE for the $2p_{3/2}$ level, represents the Fermi level of the system (see text). (b) Ar $2p_{3/2} \rightarrow 4s$ XAS spectrum for 0.2 ML Ar+0.1 ML K/graphite. This spectrum illustrates the local unoccupied states for a K-like adatom at the adsorption distance of Ar in close proximity to a K atom, i.e. a situation resembling a K dimer. The zero point, given by the corresponding XPS BE for the $2p_{3/2}$ level, represents the Fermi level of the system (see text).

Ar/graphite). That is, the position of the 4s resonance for an isolated K-like atom adsorbed on graphite in Ar geometry is estimated to be 1.6 eV above E_F .

The results of the first-principles calculations are shown in Fig. 2 (for details concerning the theoretical treatment, see Refs. [18,21]). These were performed for a K atom positioned 2.6 and 3.2 Å above the graphite surface, corresponding to the experimentally determined bond distances of K and Ar, respectively. The theoretical value of the 4s position for K at Ar distance is

Fig. 2. Calculated DOS for K adsorbed on graphite at two different adsorption distances, with E_F at 0.0. The experimental results are represented by a Lorentzian with FWHM 0.05 eV (see text).

$E_F + 1.7$ eV, which reproduces the experiment very well.

Further experimental information can be gained from core hole decay spectra. The XPS and XAS final states have finite lifetimes after which they decay primarily through electron emission. The two types of decay (denoted Auger and autoionization decay, respectively) are very different for physisorbed atoms (like Ar/graphite). However, charge transfer to or from the substrate may take place during the lifetime of the core hole, leading to the appearance of a decay spectrum consisting of an Auger part and an autoionization part [27]. That this process takes place for Ar/graphite is demonstrated in Fig. 3: the figure shows the autoionization spectrum recorded at the photon energy corresponding to the Ar $2p_{3/2} \rightarrow 4s$ excitation (dotted). This spectrum also contains an Auger part (full line). Thus, we can conclude that the $2p_{3/2}^{-1}4s^1$ state generated by the XA process may

Fig. 3. (a) Ar $2p_{3/2}$ autoionization (dotted) and Auger spectra (line) for 1 ML Ar/graphite. Features due to decay from $2p_{1/2}$ excited states have been subtracted from the Auger part. The presence of Auger features in the autoionization spectrum is evidence for transfer of the 4s electron from the core-excited, K-like Ar atom to the substrate. The charge transfer rate (τ_{CT}) has an estimated relative uncertainty of 10–15%. (b) Ar $2p_{3/2}$ autoionization spectrum for 0.2 ML Ar+0.1 ML K/graphite. This spectrum is identical to the gas phase case, meaning that the 4s electron remains on the core-excited, K-like Ar atom during the lifetime of the core hole, i.e. no charge transfer takes place.

decay to the energetically more favorable ionic $2p_{3/2}^{-1}$ state prior to the core hole decay, i.e. the 4s electron is transferred to the substrate. The different processes are schematically illustrated in Fig. 4. Using a simple model, in which the charge transfer rate (τ_{CT}) and the Auger rate governed by the core hole lifetime (τ_F) are exponential, a characteristic charge transfer time can be derived from the relative intensities of the two spectral parts and the lifetime of the Ar $2p_{3/2}$ hole [18,24]. Note that τ_F does not depend on whether the 4s electron is present or not since the decay processes only

involve the 3s and 3p levels. The charge transfer time is furthermore related to an interaction width (via Heisenberg's uncertainty principle), which in this case can be viewed as a measure of the 4s–substrate hybridization width. In this case, we obtain a charge transfer time of 1.3×10^{-14} s, corresponding to a hybridization width of 0.05 eV. If we return to the calculations for K at Ar distance, we again find good agreement: the widths of the individual features are 0.05–0.1 eV. We can therefore conclude that one can, via experimental measurements combined with calculations, accurately determine the *position* and the *adsorption induced hybridization width* of the 4s level for an isolated K atom at the Ar distance. The last step is to calculate the effects of changing to the proper K distance. As shown in Fig. 2, this results in an upward shift, and slightly increased widths, of the features. Thus, the best theoretical description of the 4s level for K/graphite in the dilute limit places it 2.7 above E_F with a K/graphite hybridization width of about 0.1 eV. These numbers are close to the recently obtained values for less than 0.3 ML of K on graphite using photodesorption: 2.4 eV above E_F and a width of about 0.15 eV [16]. Returning to the fundamental question of ionicity vs. covalency, the facts that the 4s resonance is situated above the Fermi level and is very narrow strongly suggest that the bonding of dispersed K on graphite is largely ionic, thereby confirming previous results [28–30]. It is important to stress that the DOS probed in this measurement is that part which has weight directly on the adatom core. This essentially eliminates the theoretical quandary of choosing an integration volume.

3.2. Coadsorption of Ar and K on graphite: simulation of a K dimer

Adsorption of small amounts of K on graphite is thus expected to lead to a dispersed phase with a largely ionic adsorbate–substrate bond [7,28–30]. As a next step, we have investigated Ar coadsorbed with dispersed K on graphite. Ar 2p photoemission spectra for two different doses of Ar on a graphite surface precovered with 0.1 ML K shows that one species strongly dominates at an Ar coverage of about 1/5 of a monolayer. After

Fig. 4. Illustration of the different non-radiative core hole decay channels for a system with the possibility for a charge transfer process during the lifetime of the core hole. This case illustrates the situation where the Ar $2p_{3/2} \rightarrow 4s$ resonance energy is greater than the Ar $2p_{3/2}$ XPS binding energy.

increasing the coverage to 0.3 ML, a second type of Ar appears, characterized by a lower binding energy. Previous results on Ar+K/Rh(111) provide us with an answer to this behavior [31]: the high BE component is associated with Ar adsorbed in sites adjacent to the K atoms whereas the low BE component is associated with Ar adsorbed further away from the K atoms. From this it follows that adsorption of ≤ 0.2 ML Ar yields a rather well-defined situation in which the Ar atoms are situated close to the K atoms. It is such a situation that will be considered in the following discussion.

A neighboring K atom on the graphite surface causes the Ar 2p photoemission BE to increase 2.8 eV as compared to 1 ML Ar/graphite. However, the position of the 4s resonance as measured by XAS is not affected in the same way; it only displays a downward shift of 0.3 eV as compared to the pure Ar monolayer, which can be explained by a reduced spatial confinement effect of the 4s orbital due to the low Ar coverage. Thus, in Fig. 1 it can be seen that the 4s resonance is now 0.7 eV *below* the core ionization energy.

The reversed energy relationship between the

core ionized state and the neutral core-excited state has a strong influence on the core hole decay spectrum. This is because the relaxation of the core-excited state to the core ionized state via transfer of the 4s electron to the substrate prior to the core hole decay is no longer energetically favorable. That this indeed is the case is illustrated in Fig. 3; the autoionization spectrum recorded at the Ar $2p_{3/2} \rightarrow 4s$ excitation energy is now lacking Auger features and is identical to the autoionization spectrum observed for free Ar, i.e. the 4s electron remains on the Ar atom [32].

If we then again interpret the core level spectroscopy results for Ar in terms of the behavior for adsorbed K, we find that the two situations, Ar and Ar+K on the surface, in principle illustrate how the 4s resonance is affected by increasing K coverage, although it should be noted that the situation of core-excited Ar adjacent to K is geometrically not identical to an adsorbed K dimer. In the low coverage limit, the K atoms display properties which are ionic according to the Gurney model, i.e. the 4s level is situated well above E_F . For larger amounts of K on the surface, the 4s level is degenerate with occupied states of the

substrate. The autoionization results show that for isolated K the 4s electron is transferred to the substrate, whereas for two K ions in close proximity on graphite, autoionization confirms that the lowest energy configuration entails an increased probability for localization of the 4s electron on the K atom, i.e. a ‘metallization’ of the overlayer. This is consistent with other studies [7,33], and gives the added insight that only two atoms in close proximity are required to initiate the metallization.

3.3. Adsorption of an isolated K atom on metallic substrates

We will now address the issue of isolated alkali atoms on metallic substrates, using the same experimental approach as for K/graphite. Fig. 5 shows Ar $2p_{3/2} \rightarrow 4s$ XA spectra for four different metallic substrates displayed on an XPS binding energy-referenced energy scale (see Section 3.1). The coverage is 1 ML in all cases except on Au(110) (see Section 2). Unfortunately, due to the low Ar coverage and the high background, it was not possible to record a presentable XA spectrum for Ar/Au(110), so the 4s resonance centroid is merely indicated with a line.

We find a clear trend in Fig. 5: the 4s resonance moves gradually closer to zero ($=E_F$) in the substrate order Pt–Au–Cu–Ag. Moreover, variations in the 4s lineshape can be observed in the XA spectra. Most obvious is the appearance of a tail extending down to E_F for Ar/Ag(110), but the tendency of an asymmetry on the low energy side can be observed for Ar on Cu(100) and Pt(111) as well (see also Ref. [24] for more details on Ar/Pt).

The corresponding core hole decay spectra recorded at the Ar $2p_{3/2} \rightarrow 4s$ excitation energy are presented in Fig. 6. We observe Auger parts due to charge transfer in all four situations, as expected from the XAS–XPS energy relationships, but the Auger features are much more pronounced than for 1 ML Ar/graphite. Previous results for Ar on metallic surfaces [Ru(0001), Pt(111) and Gd(0001)] show evidence for transfer of the Ar 4s electron to the substrate upon creation of a core hole and it has been ascribed to the alkali-like

Fig. 5. Ar $2p_{3/2} \rightarrow 4s$ XA spectra for 1 ML Ar on Pt(111), Cu(100) and Ag(110). The Ar coverage on Au(110) is below 1 ML. These spectra illustrate the local unoccupied states for a K-like adatom at the adsorption distance of Ar and, for all cases except on Au(110), embedded in an Ar layer. The energy scale is aligned to the zero point, given by the corresponding XPS BE for the $2p_{3/2}$ level, which represents the Fermi level of the system (see text). Both the 4s position and lineshape show a strong substrate dependence.

nature of the core excited rare gas atom [34–36]. The charge transfer effect from physisorbed argon atoms to a metallic substrate for varying adsorbate–substrate coupling (achieved by the introduction of Xe spacer layers) has furthermore been the subject of a very recent study [37].

Fig. 6. Ar $2p_{3/2}$ autoionization (dotted) and Auger spectra (line) for Ar on the four different metallic substrates. Features due to decay from $2p_{1/2}$ excited states have been subtracted from the Auger part. The presence of Auger features in the autoionization spectra show that transfer of the 4s electron from the core-excited, K-like Ar atom to the substrate occur in all cases but with varying rates. The charge transfer rates (τ_{CT}) have estimated relative uncertainties of 10–15% for Ar/Pt(111) and Ar/Au(110) and 60% for Ar/Cu(100) and Ar/Ag(110).

However, no systematic study comparable to the one presented in Figs. 5 and 6 has been undertaken before, and it is interesting to note that the charge transfer rate is strongly dependent on the substrate. It increases in the order Pt–Au–Cu–Ag, i.e. it is correlated with the shift of the 4s resonance observed in the XA spectra. Thus, profound changes in the 4s–substrate interaction take place which are strongly substrate-dependent. Since these effects are probed via creation of a core hole on the Ar atom, we will from now on discuss the effects in terms of adsorbed K and, since our quasi-potassium atom is situated in the position of adsorbed Ar, it will henceforth be denoted ‘K’.

The effects observed in Figs. 5 and 6 are readily explained in terms of variations in the mixing of the 4s orbital with the substrate levels close to E_F . Since the adatomic level, ‘K’ 4s, is situated well above E_F , we expect that new hybrid states extending primarily down to E_F appear as the degree of mixing increases, thereby explaining the tails observed in Fig. 5. The increased 4s–substrate hybridization strength furthermore entails an increased ability for transfer of the 4s electron to the substrate as confirmed by the core hole decay spectroscopy results. If we return to the fundamental question regarding ‘ionicity’ and ‘covalency’, these findings can be interpreted as an increased degree of covalency in the ‘K’ 4s–substrate bond in the substrate order Pt–Au–Cu–Ag, but it is noteworthy that the main part of the 4s resonance always lies above E_F .

The observed substrate dependence can be understood using the Gurney model: the work function for these metals decreases in the order Pt–Au–Cu–Ag {the following work function values have been obtained previously: $\phi[\text{Pt}(111)] = 6.4$ eV [38], $\phi[\text{Au}(110)] = 5.37$ eV [39], $\phi[\text{Cu}(100)] = 4.59$ eV [40] and $\phi[\text{Ag}(110)] = 4.42$ eV [41]}. Thus the ‘K’ 4s resonance should approach E_F from above in this model. Chemically speaking, elements with a large difference in electronegativity form ionic bonds whereas covalent bonds are formed if the difference is small. Since the work function is related to electronegativity, the probability for formation of a covalent bond is highest between strongly electropositive K and the substrate with the lowest work function,

Ag(110). The observation of the 4s resonance clearly above E_F , with a tendency of a tail extending down to E_F (especially evident for 'K'/Ag) is in good agreement with models for alkali adsorption presented by Gurney, Newns, Lang-Williams, Gunnarsson et al. and Scheffler et al. [6,8,9,42,43].

This leads us to the question of how our results can be applied in order to understand 'real' K adsorption systems. Following the same procedure as for 'K'/graphite, the first step is to correct the XAS–XPS relationship for effects caused by surrounding Ar atoms. For 'K' on Pt(111), Cu(100) and Ag(110), where the Ar coverage is 1 ML, the 4s resonance should be shifted in the same manner as on graphite, i.e. about 0.5 eV closer to E_F . The adjustment for 'K'/Au(110) is harder to estimate, due to the difficulties in determining the exact coverage. Nevertheless, we can conclude that the effects due to neighboring Ar atoms do not significantly alter the *trend* in the 4s resonance position depending on substrate.

The remaining part is to estimate the changes due to differences in the adsorption geometry between Ar and K. This can be done by theoretical calculations and, as previously mentioned, the experimental results for quasi-potassium provide an excellent benchmark for the theoretical treatment. In our study of K/graphite, the calculations showed that the adsorption distance was the most important parameter and the correction from 3.2 Å down to 2.6 Å resulted in an upward shift of the 4s resonance by 1.1 eV (see Section 3.1 and Refs. [18,21]). Thus, the shift of the 4s resonance induced by the decreased adsorbate–substrate distance is in this case in the direction opposite to the shift due to the surrounding Ar atoms. Regarding the shape of the 4s resonance, the K/graphite study showed that the correction in bond distance resulted in only a slight broadening of the 4s-derived states.

Of the metallic substrates used in this study, information about adsorption distances for both Ar and K are found only for Pt(111) and Cu(100). Also in these cases K is found to adsorb more closely to the substrate: the Ar–Pt(111) distance is calculated to be 3.2 Å [44] whereas electron diffraction yields a K–Pt(111) distance of about 2.8 Å [45]. For Cu(100), a calculated Ar–Cu

distance of 2.56 Å is found [46], whereas an electron diffraction study of K/Cu(100) gives a distance of 2.25 Å [47]. In passing we note that the decreased adsorbate–substrate distances when going from Pt to Cu are most probably a result of the stronger interaction in the latter case, which is well in line with our findings.

Since the nature of the *ns*–substrate bonding is strongly dependent on the DOS of the metal, a more definite determination of location and shape of the *ns* resonance requires complementary theoretical results. Still, based on existing information it is possible to speculate about the effects on the 4s-derived states when decreasing the adsorbate–substrate distance. The valence of the transition metals consists of a d-band and an sp-band and we will for simplicity assume that the alkali *ns*–Me d and *ns*–Me sp interactions can be considered separately. In order to estimate the effects on the *ns* resonance due to the *ns*–Me sp interaction which appear when the alkali–substrate distance is decreased, theoretical results for alkali/jellium can be used [42]. It was found that changing the distance by 2 a.u. gives no major shift in the position of the *ns* resonance maximum, only a slight broadening when approaching the surface. When considering the interaction between the alkali *ns* resonance and the Me d-band, these levels are well separated in energy. Perturbation theory then gives that an increased hybridization, which is expected in the case of a decreased adsorbate–substrate distance, should lead to an increased splitting of the *ns* and d-levels, i.e. the *ns* level shifts away from E_F .

Based on this argumentation, we suppose that changing the adsorbate–substrate distance of the 'K' atom to the distance of 'real' K induces the same type of changes in the 4s-derived density of states for K on transition metal substrates as for K/graphite, i.e. a slight upward shift of the 4s resonance maximum accompanied by a broadening of the 4s-derived features. Thus, the 4s resonance positions for the 'real' K adsorption systems should not be closer to E_F than what is found in Fig. 5. This implies that the location of the 4s resonance is generally more in line with the 2PPE results than with the IPES interpretations. The calculations needed to estimate the magnitude of

distance-dependent changes for the different substrates are not available. Nevertheless, we suggest that it is likely that the substrate-dependent trend in the formation of hybrid states between the 4s peak and E_F observed for the metallic substrates will not change drastically when the K atom is situated a little bit closer to the surface.

Although the 'K' adsorption systems may have somewhat different properties than expected for adsorption of 'real' K, we would like to discuss some further details concerning the 4s–substrate bonding which can be derived from the present data. As mentioned above, an increased alkali 4s–substrate mixing should give rise to states between E_F and the 4s peak. We observe strong trends, but we cannot discuss properties like charge transfer in absolute terms. However, we can learn something about the character of the 4s-derived states. For 'K'/graphite, the 4s electron is transferred to the substrate, but the coupling is very weak. For 'K'/Ag(110), the states between the 4s peak and the Fermi level are clearly visible in the XA spectrum. Since the intensity of an XA peak is strongly dependent on the overlap between the core hole and the state to which the electron is excited, this means that states degenerate with the substrate levels are located on the adsorbate. Consequently, the screening of the adsorbate provided by the substrate is expected to be more efficient. This can be seen in Fig. 6, where the energy separation between the doubly-ionized Auger states and the singly-ionized autoionization states decreases in the substrate order Pt–Au–Cu–Ag.

Further information about the character of the 4s states can be found in recently published results for Ar/Pt(111) [24]. The charge transfer process was here investigated in detail at excitation energies around the 4s resonance. It was found that the charge transfer rate increases in the energy regime between the 4s resonance and the Fermi level. This can be taken as evidence for an increased substrate character of the states close to E_F .

4. Conclusions

We have recently demonstrated (for K/graphite) that experimental core level spectroscopy data for

adsorbed Ar combined with calculations can be employed to obtain information about the alkali-derived unoccupied density-of-states [18]. Here, we have presented experimental results for Ar on various metallic substrates and discussed the data in terms of adsorption properties of an isolated K adatom. Using the detailed treatment of the K/graphite system, we are able to roughly estimate the uncertainties with the use of core-excited and core-ionized Ar in order to simulate an isolated K adatom. We find a clear tendency for increased 4s–substrate mixing as the substrate work function decreases, in accordance with the Gurney model. The substrate character of the 4s-derived states increases for energies closer to the Fermi level. Using graphite as substrate, we also show that core level spectroscopy data for Ar coadsorbed with K can be used to investigate the effects on the 4s resonance of increasing K coverage.

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