Halide adsorption on close-packed metal electrodes

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Two mechanisms have been cited as the reason for unexpected work function decrease upon adsorption of electronegative adatoms: electron spillout depletion [Michaelides *et al., Phys. Rev. Lett.*, 2003, **90**, 246103] and polarization on the adatom [Roman *et al., Phys. Rev. Lett.*, 2013, **110**, 156804]. We attempt to bridge the two pictures in this work. Work function changes due to the adsorption of halides on (111) surfaces of fcc metals (Ca, Sr, Ni, Pd, Pt, Cu, Ag, Au, Al and Pb) were studied using periodic density functional theory. The two mechanisms were found to be clearly independent of each other because of the opposite factors that lead to the work function decrease, and are therefore easy to distinguish. A more general picture of interpreting bond ionicity based on observed work function changes is discussed.

1 Introduction

Electrochemical processes typically occur at the interface between an electron conductor, the electrode, and ion conductor, the electrolyte[1]. Therefore the structure of the electrode/electrolyte interface is of strong interest in electrochemistry. At this interface, an electric double layer is formed, consisting of an electronic charge on the electrode and a corresponding ionic counter charge in the electrolyte. Of particular importance is the adsorption of anions on metal electrodes[2,3]. Often they adsorb specifically, i.e., they form chemical bonds with the metal surface. These adsorbed anions not only affect the chemical properties of electrodes[4], but in general they also change the work function of the electrode, which is directly related to the electrode potential[5].

As a part of a systematic effort to model electrode/electrolyte interfaces from first-principles[6–9], we have recently addressed the work function change induced by the adsorption of halides on Cu(111)[10] and on Pt(111) and Ca(111)[11]. Cu and Pt are metals well-studied in electrochemistry[12,13], whereas calcium is considered to be an attractive electrode material in electrochemical energy storage because of its low electronegativity, earth abundance, and low cost[14]. The equilibrium coverage of halides as a function of the electrode potential using a simple thermodynamic model was also investigated[15,16].

An adsorbed halogen layer is expected to produce an observable increase in the work function Φ of the metal surface since electrons, in leaving the metal surface, will have to pass through the resulting interface dipole layer comprised of a positively-charged metal substrate and a negatively-charged halogen layer. However, it has already been observed experimentally[17–19] as well as theoretically[20–22] that the adsorption of chlorine, bromine and iodine on metal surfaces leads to an unexpected decrease of the work function.

In our previous work[10,11], we have identified two different mechanisms that can explain the unexpected negative work function change if a halogen is adsorbed at a metal substrate: polarization of the adatom[10], and reduction in the surface spillout electron density[11,23]. On the former mechanism, the strong polarizability of large atoms like iodine leads to a considerable charge accumulation in the adatom–surface bonding regions, consistent with covalent bonding, and an accompanying charge depletion region far from the surface. This creates a dipole on the adatom that in turn promotes a decrease in the work function. Fluorine adsorption on calcium, on the other hand, is characterized by a large charge transfer to the adatom with negligible polarization, creating a system comprised of a negative ion enveloped by electron depletion. Since fluorine is adsorbed very close (ca. 0.7 Å) to the surface, it is embedded within the electron spillout region of calcium. The depletion of electron density in the spillout region not only reduces the effect of the negatively-charged fluorine on the overall dipole, but overcompensates it, resulting in a work function decrease.

A complete picture of the factors leading to a decrease in the work function is however still missing. It is for instance not clear as to which particular circumstances would make one specific mechanism dominant, or perhaps in which situations would these two independent mechanisms contribute on equal footing to the decrease in the work function. In the present study we have therefore extended our previous work by systematically studying the adsorption properties of halogens at (111) surfaces of several fcc metals (Ca, Sr, Ni, Pd, Pt, Cu,

Ag, Au, Al, Pb). We will show that halogen atoms can lower the work function on most of the considered metals, and we will discuss the mechanisms leading to this still unexpected work function decrease.

2   Computational details

Periodic DFT calculations that employ the exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE)[24] were done using the Vienna ab initio simulation package (VASP)[25]. Electron-core interactions were accounted for by the projector augmented wave method[26,27]. The electronic one-particle wave functions were expanded in a plane-wave basis set up to an energy cutoff of 500 eV. The metal substrates were represented by slabs of seven atomic layers, of which the inner three layers were kept fixed in the bulk position during geometry optimizations while the rest of the system was allowed to relax. Halogen atoms were placed symmetrically at both sides of the slab.

For these systems, it is possible to quantify work function changes brought about by adatoms through two methods: straightforwardly from the local potential of electrons, and from the dipole moment (multiplied by a factor $-e/\varepsilon_0$) based on changes in electronic density. We already showed and discussed in detail that these two methods lead to in principle identical findings[11]. In this study we use only the former, in which the work function is obtained from the difference between the Fermi energy and the average local potential of electrons in the vacuum, where the potential does not change anymore with increasing distance from the surface.

The coverage has a strong impact on the work function change[10,11]. Since the various fcc metals studied span a broad range of lattice constants, the absolute coverage (adatoms per unit area) and not the relative coverage per surface atom has to be similar in order to allow a fair comparison among the different substrates. The coverages used within this study are shown in Table 1. For the integration over the first Brillouin zone we used a mesh of $5 \times 5 \times 1$ special k-points[28] with a Methfessel-Paxton smearing[29] of 0.1 eV.

3   Results and discussion

The differences in the energies between fcc and hcp hollow site-adsorption of halogens on fcc metals are shown in Fig. 1. Aluminum is not included here because of its unique preference for top-site adsorption. The top position is also the most stable for the case of F/Pt(111). Halogens mostly favor fcc hollow site adsorption on the transition metals, whereas adsorption on the hcp hollow site is more favored on the alkaline earth metals. The copper group of coinage metals (Cu, Ag, Au) shows the least absolute difference between fcc and hcp
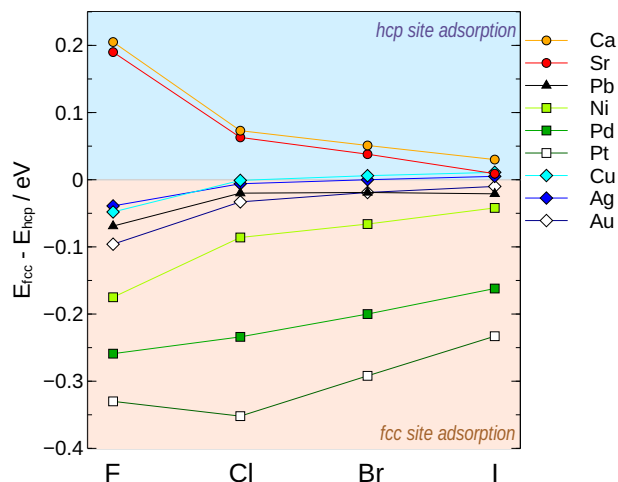

Fig. 1 Relative stability of fcc-site adsorption compared with hcp-site adsorption.

adsorption, which implies that the occupancy of hcp and fcc sites are similarly probable. The energetic difference between the adsorption energies on the two threefold-hollow sites decreases with increasing adatom size, i.e. fluorine discriminates between the hcp and fcc sites more strongly than iodine. Also, the figure shows that fcc metals with higher work functions generally have more stable fcc-site adsorption of halogens. There is no simple explanation for these trends.

Adsorption energies of halogen atoms with respect to the free halogen molecule are shown in Fig. 2. Most metals interact strongly with F and weaker with Cl, Br and the least with I. However, Pd, Pt and Au do not follow this trend, which can be rationalized as a transition from predominantly ionic bonding to predominantly covalent bonding. Surfaces with low work functions such as Ca and Sr easily transfer electronic charge

Table 1 Computed lattice constants a, work function Φ of the clean (111) surface, and halogen relative and absolute coverages (Θ_{rel} and Θ_{abs}, respectively) on (111) surfaces of fcc metals used in this study

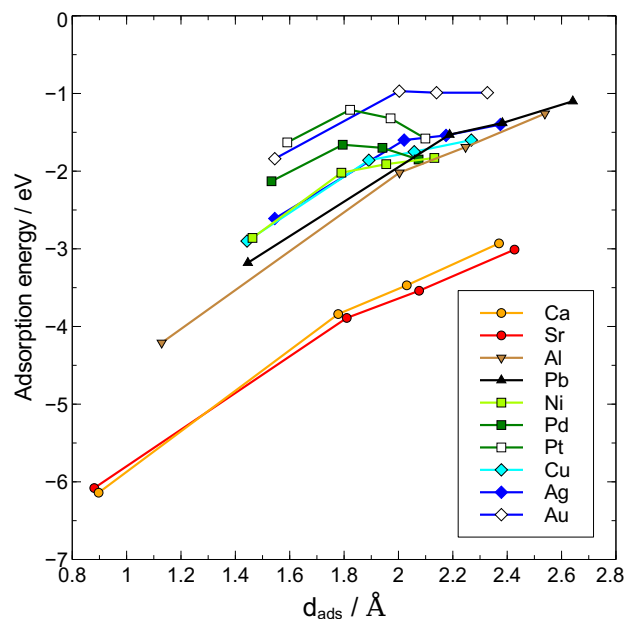|	a (Å)	Φ (eV)	Θ_{rel} (ML)	Θ_{abs} (1/Å^2)
Ni	3.524	5.03	1/9	2.067×10^{-2}
Cu	3.636	4.77	1/9	1.941×10^{-2}
Pd	3.964	5.23	1/9	1.633×10^{-2}
Pt	3.978	5.71	1/9	1.622×10^{-2}
Al	4.051	4.04	1/9	1.564×10^{-2}
Ag	4.164	4.35	1/9	1.480×10^{-2}
Au	4.174	5.07	1/9	1.473×10^{-2}
Pb	5.040	3.69	1/4	2.273×10^{-2}
Ca	5.531	2.96	1/4	1.887×10^{-2}
Sr	6.030	2.59	1/4	1.588×10^{-2}

Fig. 2 Adsorption energies of halogens on the (111) surface of different fcc metals as a function of the adsorption distance of the halogen to the surface. The four data points shown for each substrate correspond to the adsorption of F (smallest adsorption distances), Cl, Br and I (with increasing adsorption distance, respectively).

Fig. 3 Work function changes due to the adsorption of halogens on the (111) surface of different fcc metals as a function of the adsorption distance. The four data points shown for each substrate correspond to the adsorption of F (smallest adsorption distances), Cl, Br and I (with increasing adsorption distance, respectively).

to electronegative adsorbates such as halogen atoms, resulting in a more ionic bonding situation. Hence the more electronegative (i.e., smaller) halogen atoms exhibit the strongest bonding. On the other hand, surfaces such as Pt, Pd and Au which have large work functions exhibit a smaller charge transfer to electronegative adsorbates so that the bonding becomes mostly covalent in nature, as we already showed[10,11]. And here the more polarizable (i.e., larger) halogen atoms then bind most strongly.

In Fig. 3 the work function changes due to the adsorption of halogen atoms on different fcc metal surfaces is shown as a function of the adsorption distance d_{ads} of the halogen atom to the surface. From the knowledge that halogens mostly prefer fcc-site adsorption, we have used the fcc adsorption site for all metals in order to calculate comparable work function changes. We note that adsorption on a substrate with a larger lattice constant does not necessarily mean that the adatom will adsorb more closely to the surface. This is visible for iodine adsorption on Ca, Sr and Pb, in contrast to Pt, Pd and Ni. Strong covalent bonding on the nickel group of elements leads to this trend.

We find rather short adsorption distances for a fluorine atom adsorbing on Ca(111), Sr(111) and Al(111). The work function change in these systems is negative due to a reduction
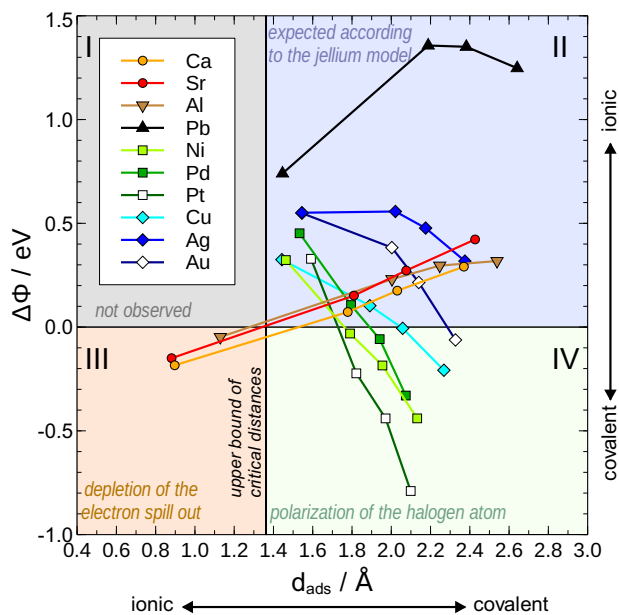
of the electron spillout of the metal. On the other hand, the larger adsorption distances of Cl, Br and I lead to the expected increase of the work function, in accordance with the jellium model. They adsorb at distances that are larger than a certain critical distance that determines whether a negative work function change due to a reduction of the electron spillout occurs. The critical distance is the distance at which the work function change is zero in Fig. 4. The metal atoms were fixed at the structure of the clean surface in these calculations. This figure excludes the work function change curve on nickel because of challenges in correctly describing spin-polarized electronic structure off the adsorption energy minimum.

Depending on the nature of the metallic substrate, a weaker or stronger polarization of the halogen atom occurs. On surfaces with low work functions (i.e., alkaline earth metals), the work function change increases with increasing adatom size because a larger halogen-metal separation increases the magnitude of the dipole moment associated with the negative charge on the halogen and positive charge on the surface. On the other hand, for surfaces with large work functions (i.e., transition metals), the work function decreases with increasing adatom size because larger atoms have lower electronegativities and are more polarizable. Now while the work function change increases monotonously for halogens adsorbed on
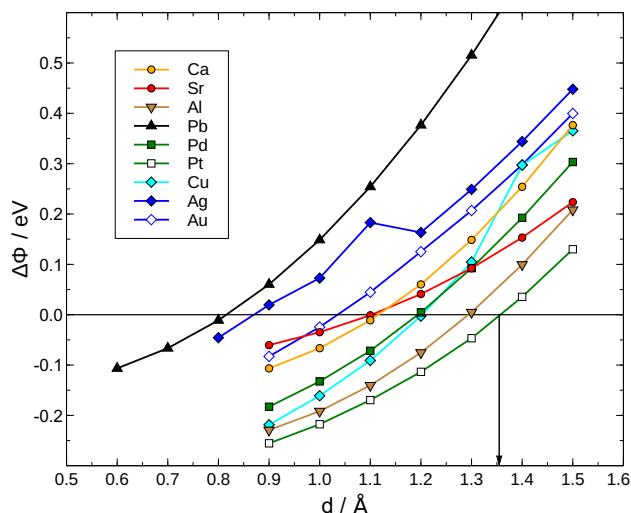
Fig. 4 Determination of the critical distance: it is defined as the distance of a fluorine atom to the surface at which the work function of the metal surface does not change due to the presence of the adatoms. The upper bound of critical distances is indicated by the arrow.

Ca(111), and decreases monotonously on Pt(111), there is a kink in the plot of work function change for halogens adsorbed on Pb(111): while the adsorption of Cl leads to a larger work function change than the adsorption of F, the adsorption of I induces a lower work function change than Cl. Such a trend can be interpreted as the result of the two opposing mechanisms acting on an equal footing.

Based on an analysis of how the electron distribution rearranges because of the adsorption, a correlation between the observed change in the work function, the adsorption distance, and the bonding mechanism is summarized through Fig. 3. Systems that fall under quadrants II and III of Fig. 3 show dominantly ionic bonding, while all dominantly covalent systems lie in quadrant IV.

The adsorption of iodine decreases the work function of clean Pt by 0.79 eV, while chlorine increases the work function of Pb(111) by 1.36 eV. This contrast emphasizes how starkly different the effects of halogen adsorption are on the work function of metals. The adsorption of iodine on platinum yields the largest decrease in the work function because Pt has the largest work function among the fcc metals considered, and I has the lowest electronegativity. Ionic bonding is hence weak. Calcium on the other hand has the lowest work function, and F has the highest electronegativity among the halogens, and so one can expect that the adsorption of fluorine on calcium should give the strongest work function increase. This is however not seen due to the fact that F adsorbs within the metal's electron spillout region. The work function of Pb

is lower compared with the transition metals, and Cl has a high electronegativity. Thus one can expect the Cl-Pb bond to have a strong ionic character. The Cl-Pb bond is much longer compared to the F-Ca bond, and so the adatom is outside the spillout region of Pb. This therefore leads to a large work function increase.

Furthermore, a more strongly charged atom that is adsorbed/absorbed into a metal induces a stronger screening charge surrounding it. It is then no surprise that fluorine, the most electronegative element, adsorbs on calcium with an accompanying electron density depletion region envelope[11]. Together with their small sizes, this explains why the electronegative second row elements have been observed to create anomalous surface dipole moments[23,30] upon adsorption onto metals.

Finally, Fig. 5 shows the dependence of the work function changes on the electronic properties of the various metal surfaces: the work function changes due to the adsorption of I on different fcc metal surfaces are plotted versus the work function of the bare metals. The trend is obvious. The higher the work function of the bare metal, the lower the work function change. For transition metals, the adsorption of I leads to a decrease of the work function. The exception is Ag, due the high charge transfer to iodine, given the low work function of silver. A similar dependence has been reported by Migani *et al.*[21]: they looked at the halogen charge transfer as a function of the work function of the metal. They observed that the higher the work function, the less charge transfer takes place. This also means that the higher the work function, the less ionic and the more covalent is the bond. Additionally, it can be said that the more covalent the metal-halogen bond, the stronger the polarization of the halogen atom. Finally, a stronger polarization leads to a more negative work function change.

4 Conclusions

We have discussed the role of the substrate in promoting a decrease in the work function upon halogen adsorption, governed by two mechanisms: electron spillout depletion associated with ionic interaction, and polarization on the adatom associated with covalent bonding. These two mechanisms are clearly independent of each other because of the opposite factors that lead to the work function decrease. With the exception of adsorption on Pb and Ag, we have shown that halogen adsorption can decrease the work function on (111) faces of fcc metals.

The two mechanisms are well-distinguishable. A work function decrease due to electron spillout depletion is favored for (1) small adatoms, which adsorb more closely to the metal surface, are more strongly charged, and are less polarizable, and (2) substrates with small work functions, which promote a more ionic and less covalent character to the adsorption in-
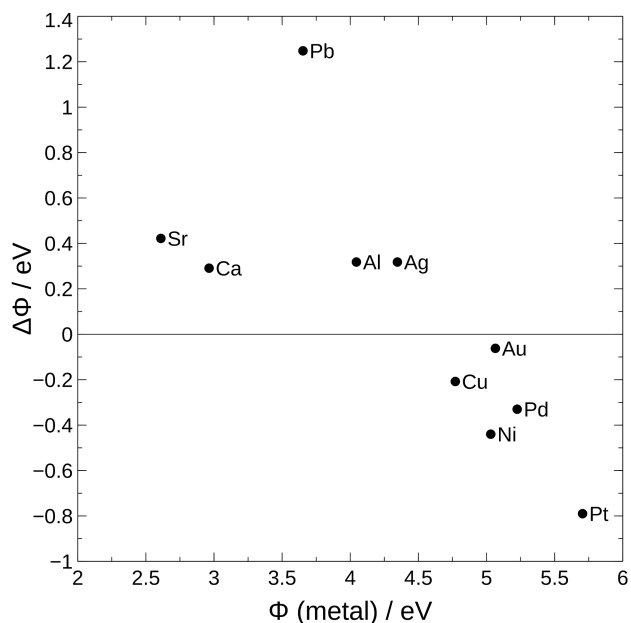
Fig. 5 The polarization mechanism: the work function change due to the adsorption of I on different metal substrates is plotted against the work function of the respective metal.

teraction. Consequently, a decrease in the work function due to adatom polarization is seen more for large adatoms and substrates with large work functions. The fact that iodine adsorption does not decrease the work function of calcium, as well as fluorine on platinum, suggest that both conditions have to be met. The stark difference between the two mechanisms suggest that a system in which both of them operate together to decrease the work function of the metal may not exist.

Acknowledgments

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