Work function change of platinum electrodes induced by halide adsorption

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Abstract

The properties of a halogen-covered platinum (111) surface have been studied using density functional theory (DFT) as halides are often present at electrochemical electrode/electrolyte interfaces. We focused in particular on the halogen-induced work function change as a function of coverage of fluorine, chlorine, bromine and iodine. For electronegative adsorbates, an adsorption-induced increase of the work function is usually expected, yet we find a work function decrease for Cl, Br and I which is most prominent at a coverage of approximately 0.25 ML. This coverage-dependent behavior can be explained through a combination of charge transfer and polarization effects on the adsorbate layer. The results are contrasted to the adsorption of fluorine on calcium, a system in which a decrease in the work function is also observed despite involving large charge transfer to the halogen adatom.

Keywords
density functional theory, ionicity, polarizability, surface dipole, work function
Introduction

In electrochemistry, processes at the interface between an electron conductor, the electrode, and an ion conductor, the electrolyte, are studied [1]. In order to be charge neutral, the electrolyte contains equal amounts of anions and cations. In aqueous electrolytes, protons acting as cations are always present [2] whereas halides are often chosen as anions. The contact of a particular solvent with an electrode surface can lead to a rather complex situation at the electrode surface [3,4]. The characteristics of the solvent affects processes like adsorption and desorption significantly. Because of the strong interaction of halogen atoms with metal electrodes, the metal electrodes typically become halogen-covered through specific adsorption. These adsorbed anions are not only part of the electrochemical double layer, in general they also change the work function of the electrode which is directly related to the electrode potential [5]. Furthermore, they also affect the chemical properties of electrodes [6].

In spite of the importance of the specific adsorption of anions in electrochemistry, atomistic details of the role of anions in surface electrochemistry are still poorly understood [7]. Here, surface science studies focusing on the change of the properties of metal surfaces upon halide adsorption can help to elucidate the role of anionic specific adsorption at electrode/electrolyte interfaces, in particular with respect to the adsorption-induced work function change. It is known that the work function is strongly influenced by the adsorption of ions, which can lead to both an increase and a decrease of the work function [8-17]. In a previous study, we have addressed the adsorption of iodine and chlorine on Cu(111) [9] using periodic density functional theory (DFT) calculations. Whereas chlorine causes the expected work function increase upon adsorption of an electronegative adsorbate, iodine leads to a surprising work function decrease for coverages up to approximately 0.4 ML. Analyzing the underlying electronic structure, we were able to show that this behavior can be explained through a combination of charge transfer and polarization effects of the adsorbate layer.

We have now extended this previous study by considering the adsorption of fluorine, chlorine, bromine and iodine on Pt(111) in order to check whether the findings for halogen adsorption on
Cu(111) are also valid for the technologically important electrode material platinum. It has been already observed experimentally [18-20] as well as theoretically [11,13,17] that the adsorption of chlorine, bromine and iodine on Pt(111) leads to an unexpected decrease of the work function. Based on calculations for several adsorbates on tungsten surfaces, Leung, Kao and Su pointed out that it is possible to relate the electronegativity scale to the direction of the charge transfer but not necessarily to the induced work function change. The problem of the unexpected work function decrease was also tackled by Michaelides et al. [8] for a system of nitrogen adsorbed on a tungsten (100) surface. They showed that the work function decrease depends strongly on the length of the chemisorption bond. If the adatom is located close to the surface, it is in the region of the overspill electron density of the metal. This leads to an area of electron depletion far from the surface, and in combination with an electron buildup in the area around the adsorbed ion, to a work function decrease. In this paper we present a detailed study of the halogen-induced work function change on Pt(111) as a function of the halogen coverage which has still been missing. We will show that the observed work function decrease upon chlorine, bromine and iodine adsorption on Pt(111) at low coverage can be explained by the strong polarization of the adsorbed halogen atoms, as in the case of I/Cu(111) [9]. We contrast these results with findings obtained for fluorine adsorption on calcium where an adsorption-induced work function decrease is also observed. However, due to the particular geometric conditions in this system, the spillout mechanism [8,21] is operative.

Methods
For the following calculations the periodic density functional theory (DFT) program Vienna Ab initio Simulation Package (VASP) was used. The exchange and correlation energy was calculated using the generalized gradient approximation (GGA) within the PBE functional, developed by Perdew, Burke and Ernzerhof [22]. To describe the ionic cores of the atoms, we used the projected augmented wave potentials (PAW) constructed by Kresse and Joubert [23]. The electronic wave functions were expanded in a plane wave basis set up to an energy cutoff of 400 eV. For the calcu-
lations, a periodic slab with a thickness of 7 atomic layers and $4 \times 4$ lateral periodicity was chosen. All calculations were done using a symmetric setup of the slab, i.e., the halogen atoms were adsorbed on both sides of the slab, the middle three layers of the slab were kept fixed and the outermost two layers of both sides of the slab together with the adatoms were relaxed. Thus no dipole correction was necessary in order to derive the work function of the surface terminations. The unit cell was computed with a gamma-centered $4 \times 4 \times 1$ $k$-point mesh.

The optimized lattice constant for platinum was found to be $a = 3.98 \text{ Å}$, which is only 1.48% larger than the standard experimental value [24]. The halogens iodine, bromine and chlorine adsorb for low coverages most stably at the fcc threefold-hollowsite position on a platinum (111) surface. Since the hcp threefold-hollow position is also quite stable, the halogens were ordered in symmetric patterns on the surface with the highest possible nearest neighbor distance to other adsorbed atoms in hcp and fcc positions. The threefold-hollow adsorption positions are considered as the most probable adsorption sites for halogens on metals [9,10,14,25]. In this manner, six different coverages – 1/16 ML, 2/16 ML, 3/16 ML, 4/16 ML, 6/16 ML and 8/16 ML – were created, which are illustrated in Fig. 1. The structures of iodine, bromine and chlorine were relaxed completely.

![Image](image.png)

**Figure 1:** The figures show the relaxed structures of different coverages of chlorine on a Pt(111) surface.

Interestingly enough, fluorine atoms adsorb more stably at the on-top position on platinum. At this position, the average distance to the topmost surface layer is larger than on the threefold-hollow sites. Since we are interested in getting trends among the halogen atoms in order to understand
and predict adsorption processes, we kept the fluorine in the threefold-hollow site positions, but
allowed for vertical relaxation, allowing a better comparison with the results for the chlorine,
bromine and iodine adsorption structures.

Results and Discussion

Of central importance for this particular work is the determination of the work function change as
a function of the halogen coverage. In periodic slab calculations, the work function is given by the
difference between the Fermi energy and the value of the one-electron potential in the vacuum. The
vacuum is reached when the potential does not change anymore with increasing distance from the
surface.

Figure 2 shows the work function of halogen-covered Pt(111) as a function of halogen coverage.
For clean Pt(111), the calculations yield a value of 5.71 eV. Various experimental measurements in
the last decades do not agree well with each other. They are in the range of 5.6 eV to 6.1 eV [20,26-
32]. The presence of fluorine on Pt(111) always increases the work function, qualitatively consis-
tent with what one expects from a dipole involving a negative charge on the adsorbate. The adsorp-
tion of chlorine, bromine or iodine on a platinum (111) surface reduces the work function at low
coverages. While the trend reverses at 0.25 ML, $\Delta \Phi$ only becomes positive at the half-monolayer
coverage. The experimental trends [18-20] as well as theoretical values by Migani et al. [10] agree
with the calculated results.

Aside from the sign of the work function change, the dependence of $\Delta \Phi$ on halogen coverage is
another aspect that needs to be clarified. In a simple model, one may completely neglect the in-
teraction between the adsorbates. In this case, a linear trend $\Delta \Phi(\theta) \propto -\theta \Delta \mu$ would be expected,
where $\theta$ is the surface coverage and $\Delta \mu$ is the change in the surface dipole moment brought about
by the adsorption of a halogen atom. Obviously, this model is applicable only at low coverages in
Fig. 2. In a more advanced model, the electrostatic interaction between adjacent dipoles is taken
into account by assuming that the mutual repulsion of the dipoles leads to a decrease in the polarity
of the halogen-metal bond. The term $\Delta \mu$ thus becomes coverage-dependent, causing a saturation of
Figure 2: Calculated work function change vs. coverage for the adsorption of fluorine, chlorine, bromine and iodine on Pt(111). The high value for the 0.5 ML calculation of iodine is due to a double layer structure of the adsorbates, caused by the larger size of iodine atoms.

ΔΦ at high coverages. However, this does not explain the observed non-monotonic behavior of the work function change and so a more comprehensive explanation is needed.

In general, an adsorbate layer that involves charge transfer in the adsorption reaction can produce an observable change in the work function of the metal surface since electrons, in leaving the metal surface, will have to pass through the resulting interface dipole layer. Depending on the orientation of the dipole, this can either make removing electrons easier, or harder. More precisely, the connection between work function change and surface dipole moment change is given by

\[
\Delta \Phi = -\frac{e}{\varepsilon_0}(\mu_z - \mu_{z,0}) = -\frac{e}{\varepsilon_0} \Delta \mu, \tag{1}
\]

where \(\mu_{z,0}\) is the surface-normal dipole moment per unit area of the clean surface, \(\mu_z\) is the surface-normal dipole moment per unit area for the adsorbate-covered surface. A positive value of \(\mu\) has traditionally been assigned to a dipole pointing away from the bulk, that leads to a decrease of the work function (\(\Delta \Phi < 0\)). Conversely, a negative \(\mu\) points into the bulk and increases the work function (\(\Delta \Phi > 0\)).

The surface dipole moment changes when the electron density close to the surface becomes redistributed upon bond formation. This redistribution is most straightforwardly described through the electron density difference which is given by the difference of the electron density of the interact-
Figure 3: Charge density difference $\Delta \lambda(z)$ for fluorine, chlorine, bromine and iodine adsorption on Pt(111) at the fcc hollow position for a coverage of 1/16 ML. The subsurface region corresponds to the gray-shaded area at $z < 0$.

The electron density difference profile $\Delta \lambda(z)$ along the $z$ direction corresponds to the lateral sum of the electron density difference in the $x$ and $y$ directions,

$$\Delta \lambda = \frac{1}{N} \int \int_{\text{cell}} \rho_{\text{diff}} \, dx \, dy,$$

(2)

where $N$ is the number of halogen atoms adsorbed on one side of the slab per unit cell. The $\Delta \lambda$ profiles for the 1/16 ML coverages of the four halogens are shown in Fig. 3. The shape of the diagrams for the higher coverages look similar. The profiles illustrate how the electron density is reorganized along the $z$ direction when the adatoms adsorb. The gray area on the left hand side denotes the metal slab. The topmost metal atoms are centered at $z = 0$ Å. The electron density difference profile shows a significant electron depletion far from the surface for the case of chlorine, bromine and iodine, followed by an electron buildup close to the surface, and oscillations in the metal. In the case of fluorine, there is just an electron buildup around the fluorine atom, followed by oscillations into the bulk. This electron buildup around the fluorine atom indicates an ionic state. Fluorine is partially constrained to remain at the threefold-hollow sites, where the average distance from the center of the adsorbates to the topmost surface layer is smaller than for fluorine adsorbed at the on-
top position. Calculations for F atoms at the most stable adsorption site may give slightly different results in charge transfer and dipole moments.

In the next step, the resulting surface dipole moment change $\Delta \mu_N$ can be determined by analyzing $\Delta \lambda$, as in Ref. [9] for the adsorption of iodine and chlorine on Cu(111). The $N$ indicates that this is the total surface dipole moment of $N$ atoms adsorbed at the unit cell. The dipole moment change due to the adsorption process can be calculated by integration of $\Delta \lambda_N(z) = N\Delta \lambda(z)$ along the $z$ direction, perpendicular to the surface,

$$
\Delta \mu_N = - \int_{\text{vac}}^{\text{bulk}} z \Delta \lambda_N(z) \, dz
$$

where the negative sign is introduced because positive regions of $\Delta \lambda_N$ (i.e., electron buildup) are in fact negatively charged. The integration runs from the central layer of the platinum slab to the middle of the vacuum. Figure 4 shows the good correlation between the calculated work function and the dipole moment derived from the charge distribution, verifying the assumptions underlying eq. 3.

**Figure 4:** Calculated work function versus dipole moment. The solid line corresponds to the expectation according to eq. 1.

Since $\Delta \lambda$ of the fluorine-covered platinum slab shows for all coverages the structure of an electron buildup far from the surface, followed by an electron depletion close to the surface, the dipole moment on each face of the slab becomes more negative as a function of coverage, consistent with a
work function increase. For the other three halogens, the electron density difference profile looks more complicated. There is an electron depletion far from the surface, followed by an electron buildup. This structure is sufficiently strong to invert the dipole moment, so that $\Delta \mu_N$ changes sign as a function of the coverage.

It has been suggested that adsorbates which are located rather close to a surface can decrease the electron spillout at the surface. This can cause unexpected work function changes, such as the work function decrease observed for N on the W (100) surface [8] or the small dipole moment for O on Al(111) [21]. However, the area of electron depletion for chlorine, bromine and iodine is approximately 2.5-4 Å away from the center of the topmost platinum atoms, far beyond the region of a sizable electron spillout for the uncovered surface. This electron density shift rather corresponds to a redistribution of the electron density in the adatom layer which can be associated with a covalent character of the chemisorption bond. This rearrangement is particularly strong for the adsorption of iodine and slightly weaker for bromine and chlorine. The covalent character of the halogen chemisorption bond has been discussed before, for example for the adsorption of Cl on Au [14] or I on Cu [9]. Fluorine, on the other hand, tends to adsorb mainly ionically on the Pt(111) surface.

**Coverage trends**

Our calculations confirm the experimental observations [18-20] of a work function minimum as a function of halogen coverage. Several mechanisms have been proposed to explain its occurrence. For cationic adsorbates, the subsequent increase of $\Phi$ beyond the work function minimum was attributed to a reduction of the ionicity of the cationic adsorbate [33]. This explanation, however, does not apply to the halogen adsorption considered here as we still find no indication of cationic adsorption.

The work function minimum has also been explained through the differences in site occupancies as halogen coverage increases. Subsurface penetration followed by surface adsorption was one of the possibilities considered in explaining the work function minimum for chlorine on platinum [18], based on the assumption that subsurface penetration and surface adsorption lead to opposite dipole
moments on the surface. In contrast, for iodine on platinum, an adsorption site effect was sug-
gested under the assumption that threefold-site adsorption decreases the work function, while
adding iodine to top sites increases it [20]. As coverage increases, more top sites get occupied by
iodine, leading to the increase in $\Phi$ beyond the minimum. Still, the surface work function change
remained negative over the entire coverage range used.

A more recent computational study has shown that the adsorption of isolated iodine atoms at the
hollow or top sites both lead to $\Delta \Phi < 0$, although the decrease in the work function is larger for
iodine adsorption at the hollow site [17]. Another perspective to explaining the work function min-
imum was proposed: through changes in the polarization of the metal substrate. The authors found
that polarization in the platinum substrate induced by the presence of the iodine anion adsorbate
becomes reduced with increasing coverage, hence explaining the non-monotonic behavior in $\Delta \Phi$.

While changing site occupancy with increasing coverage can and will lead to observable changes
in the work function, in this study we focus on work function changes that are caused by effects
that are primarily electronic in nature, i.e. which are not due to changes in the adsorption or ab-
sorption site. Hence a deeper analysis of charge transfer, internal redistribution of charge in the
metal substrate, and redistribution of charge on the halogen adatoms is needed. To analyze surface
dipole moments in detail, we use the total surface dipole moment per unit cell normalized to the
number of adatoms to define the dipole moment change created per adsorbed atom,

$$\Delta \mu = \frac{\Delta \mu_N}{N}. \quad (4)$$

The normalized dipole moments are shown in Fig. 5. The plots are nowhere flat, suggesting the
presence of considerable neighboring adatom interactions even at the lowest coverages. There is
also a clear tendency for the dipole moment induced by the adsorption of a single halogen atom to
be reduced as the concentration of adatoms increases on the Pt surface. Note that the 0.5 ML cover-
age of iodine is so closely packed that the repulsion of the electron shells induces a two-layer struc-
ture of the adsorbate layer. Every second iodine atom became a part of a second adsorbate layer,
which is positioned at around 1.7 Å farther from the surface than the first layer of iodine atoms.
Figure 5: Calculated normalized dipole moment as a function of coverage of fluorine, chlorine, bromine and iodine on Pt(111).

Looking at charge transfer as a function of coverage is useful to understanding the negative slopes of $\Delta \mu$ for halogen adsorption. Quantifying charge transfer between atoms however always involves a more or less ambivalent choice as far as associating electron density to a particular atom is concerned. We have therefore considered two limits: a maximum charge transfer picture, and a zero-charge transfer picture of halogen adsorption on platinum.

The maximum charge transfer is obtained by assuming that the complete electron buildup between an adatom and the surface is always counted to the adsorbate. In practice, this is done by determining the plane $z = z_q$ between the metal and the adatom that maximizes the area under $\Delta \lambda(z)$ at the halogen side. The charge transfer from the metal surface to the adatoms gives rise to a dipole moment change $\Delta \mu_q$. Using a simple model that assumes charge transfer from the topmost Pt layer to the halogen adlayer, the contribution of electron transfer to the surface dipole moment can be quantified,

$$\Delta \mu_q = -\bar{z}_X \int_{z_q}^{\text{vac}} \Delta \lambda(z) \, dz,$$

where $\bar{z}_X$ is the average distance of the halogen adatoms from the metal surface. We combine all other parts contributing to the total dipole moment in the term $\Delta \mu_{\text{pol}}$, because it involves polariza-
Figure 6: Contributions to the total dipole moment change $\Delta \mu$ coverage according to eq. 6 and eq. 7 as a function of halogen. The term $\Delta \mu_q$ describes the purely charge transfer induced dipole moment and $\Delta \mu_{\text{pol}}$ the polarization induced dipole moment; $\Delta \mu_A$ shows the effect of the adsorbate layer on the total dipole moment and $\Delta \mu_S$ indicates substrate effects. The color code denoting the different halogen atoms is the same as used in the previous figures.

These contributions are plotted in Fig. 6 a and b, respectively. The effect of charge transfer $\Delta \mu_q$ to the surface dipole is nearly zero for iodine. For fluorine, however, charge transfer plays a significant role that can be expected since it is more electronegative than the other halogens, as also reported by Migani et al. [10]. Moreover, the negative dipole moment change for F adsorption decreases even more with increasing coverage, which is due to the fact that the adsorption distance and charge transfer to the F adatoms increase with increasing coverage.

Results also suggest that higher surface concentrations of adatoms decrease the dipole moment change per adatom through mutual depolarization. This effect is most pronounced for iodine, as well as for low-coverage adsorption of bromine and chlorine, but not for fluorine because of the low polarizability of small atoms. Besides the repulsion of the dipoles, the electron shells of adsorbed atoms at higher coverages start to repel.
Another interesting question concerns the importance of the electron density oscillations in the subsurface, as shown in Fig. 3. It might be speculated that these oscillations could be responsible for the significant polarization part $\Delta \mu_{\text{pol}}$ of the total dipole moment $\Delta \mu$. To answer this question, we have divided $\Delta \lambda$ into two parts: one representing the dipole moment change due to polarization in the adsorbate layer and the other part representing the dipole moment change due to polarization in the substrate,

$$\Delta \mu = \Delta \mu_A + \Delta \mu_S. \quad (7)$$

This zero-charge transfer picture for breaking down polarization is especially effective for iodine adsorption on platinum.

Such a division between pure substrate and adsorbate contributions is again an arbitrary choice. In order to obtain trends, the integration was started from the point $z_0$, where the unit cell is divided exactly into the charge neutral part of the adlayer and the charge neutral part of the platinum slab, defined by the condition

$$\int_{z_0}^{\text{vac}} \Delta \lambda(z) \, dz = 0 \quad (8)$$

For this choice, the analogous integral on the metal side is also zero due to the overall charge neutrality of the supercell. It is then possible to estimate the surface dipole moment $\mu_S$ and the adsorbate dipole moment $\mu_A$ using

$$\Delta \mu_S = \int_{\text{bulk}}^{z_0} z \Delta \lambda(z) \, dz \quad (9)$$

and

$$\Delta \mu_A = \int_{z_0}^{\text{vac}} z \Delta \lambda(z) \, dz. \quad (10)$$
We briefly summarize the difference in the integration limits \( z_q \) and \( z_0 \) of eq. 5 and eq. 9, respectively: these equations have the purpose of dividing the unit cell into two parts, but it is not clear where exactly the adatom ends and where the platinum begins or vice versa. The two integration limits mark special points in the graph of \( \Delta \lambda \). The border \( z_q \) divides the unit cell at the point of maximum charge on the adatom, in contrast to \( z_0 \) which divides at the point of zero charge on the adatom.

The adsorbate and the substrate dipole moments plotted in Fig. 6 c and d, respectively, indicate that the influence of the metal substrate dipole moment change \( \Delta \mu_S \) to the total dipole moment change \( \Delta \mu \) is minor compared with the impact of adsorbate polarization \( \Delta \mu_A \), which affects the total dipole moment change quite dramatically. This also means that our analysis does not support the view [17] that substrate polarization plays an important role in explaining the halogen-induced work function decrease.

Additionally, it is noticeable that the decrease in the total dipole moment change for the case of iodine and chlorine at around 0.25 ML is much more significant on platinum compared with the total dipole moment change of copper [9]. The work function of copper is about 1 eV smaller, thus the charge transfer should be larger on copper than for the platinum system. The results of the present study confirm this. Hence the polarization effect which decreases the work function has a much stronger impact to the total surface dipole moment \( \Delta \mu \) in the case of halogen adsorption on Pt.

**Fluorine on calcium**

We have shown that the strong polarizability of large atoms such as iodine leads to a considerable charge buildup in the adatom-surface bonding regions, which is consistent with covalent bonding, and an accompanying electron depletion region far from the surface which creates a net dipole on the adatom that in turn promotes a decrease in the work function. Here we show that the adsorption of fluorine can also decrease the work function of a metal surface, namely calcium, but through a different mechanism. Calcium is considered to be an attractive electrode material in electrochemical energy storage because of its low electronegativity, earth abundance, and low cost [34]. Flu-
orine adsorbs stably at a threefold hollow site on calcium, which is an fcc metal with a calculated lattice constant that is 39% larger than that of platinum. At its equilibrium adsorption position, fluorine is only 0.73 Å from the topmost layer of Ca atoms. In contrast, iodine adsors 2.07 Å from the platinum surface.

In Fig. 7, we contrast two systems in which halogen adsorption decreases the work function of the metal substrate. The left panel shows iodine adsorption on Pt(111) at a coverage of 1/9 ML; the right panel shows fluorine adsorption on Ca(111) at a coverage of 1/4 ML. This yields similar absolute coverages per area for the two systems given the stark difference between the lattice constants of Pt and Ca. At these adsorption coverages, iodine reduces the platinum work function by 0.79 eV, while fluorine reduces the calcium work function by 0.20 eV.

**Figure 7:** Cross sections of electron density difference $\rho_{\text{diff}}(\mathbf{r})$ at the surface. Solid-blue (dashed-red) contours denote regions of electron buildup (depletion). The interval between contours of constant electron density is 0.01 electrons/Å$^3$. The region of the metal slab is shaded gray as a visual aid.

Figure 7 shows that halogen adsorption can create a surface dipole that reduces the work function in two very distinct mechanisms: adatom polarization and spillout depletion. Iodine on platinum is characterized by negligible charge transfer, covalent bonding, and polarization on the adatom. There is no evidence for a dominantly ionic bond for I/Pt(111) reported in ref. [17]. 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 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 strongly negative fluorine on the net dipole, but even overcompensates it, resulting in a work function decrease.

Conclusions

The work function change induced by halogen adsorption on Pt(111) as a function of coverage was studied by electronic structure calculations. In general, because of their electronegativity, the adsorption of halogens is associated with a charge transfer from the metal substrate to the adsorbate layer. In the case of fluorine adsorption, this leads to the expected increase in the work function. However, for chlorine, bromine and iodine adsorption on Pt(111), the charge transfer effect is over-compensated by a significant polarization of the adsorbate, causing a work function decrease. The decreasing dipole moment change per adatom as with adsorption coverage leads to a maximum in the total surface dipole moment and a minimum in the work function at a coverage of approximately 0.25 ML. Mutual depolarization within the adsorbate layer contributes to the eventual work function increase.

The anomalous work function change on platinum is large because of the high work function of clean platinum, which favors only a small electron transfer to the halogen adatoms compared with other metals. Therefore, polarization effects that reverse the dipole moment attributed to charge transfer are more pronounced than on metals with smaller work functions such as copper.

Furthermore, we showed that fluorine adsorption can also lead to an anomalous work function decrease, but through a different mechanism. On calcium, fluorine is adsorbed close to the surface because of the large spacing between the calcium atoms. This causes a depletion of the electron density in the spillout region, resulting in a work function decrease.

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