

Periodic Density-Functional Calculations on Work-Function Change Induced by Adsorption of Halogens on Cu(111)

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Using periodic density-functional theory calculations, we address the work-function change induced by the adsorption of chlorine and iodine on Cu(111) which are shown to change the work function in opposite ways, contrary to what one may expect for these two electron acceptors. In contrast to previous studies, we demonstrate that substrate effects play only a minor role in work-function changes brought about by halogen adsorption on metals. Instead, polarization on the adsorbate not only explains the sign of the work-function change as a contributor to a positive surface dipole moment, but it is also the decisive factor in the dependence of adsorption-induced work-function changes on the coverage of halogens on metal surfaces.

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Work-function changes induced by adsorbates play an important role in many applications, for example, as a means to improve the performance of fluorescent lamp cathode surfaces [1,2], and also in electrochemistry, where specifically adsorbed ions directly influence the electrode potential through the induced work-function change [3,4]. Hence, adsorption-induced work-function changes $\Delta\phi$ belong to the properties of adsorbate systems which are routinely measured [5].

Among typical adsorbates, halogens are the chemical elements that have the strongest tendency to ionize by taking in an electron. Therefore it is rather likely that a halogen atom adsorbed on a metal surface acquires a negative charge that creates a local dipole with a dipole moment μ pointing into the bulk, which then increases the work function ϕ of the metal surface. While for many halogen on surface systems this picture indeed holds, it has also been observed that the adsorption of halogens reduces the work function of metal surfaces [6–9]. Likewise, the adsorption of the electronegative nitrogen on W(100) also leads to an anomalous decrease of the work function [10].

Explaining this paradox has since been the subject of theoretical work [11–15]. In general, it still has been found that these electronegative adsorbates are negatively charged. Two mechanisms have been invoked to explain this unexpected decrease in ϕ overcompensating the effect of the ionic bond between the adsorbate and the metal surface. Using cluster calculations to represent the metallic substrate, Bagus *et al.* related the work-function decrease for I/Cu(111) to the polarization in the metal substrate induced by the presence of the anionic adsorbate [14–16]. On the other hand, based on periodic density-functional theory (DFT) calculations, Michaelides *et al.* explained the nitrogen-induced work-function change on W(100) by a reduction in the surface overspill electron density into the vacuum [12].

Using periodic DFT calculations, we have now revisited the system I/Cu(111) and compared it to the system Cl/Cu(111). Unlike the previous studies, we propose that substrate effects play only a supporting role in the unexpected decrease in the work function. Comparing chlorine and iodine adsorption, we demonstrate through an explicit breakdown of the surface dipole into charge transfer and polarization components that it is rather the polarizability of the adsorbate that is directly linked to the sign of the work-function change.

An ideal metal surface is periodic in two of the three real-space dimensions, and so for several reasons it is more advantageous to use DFT implemented through periodic supercells over the cluster models used in previous studies. Adsorbate coverage is, for example, readily quantified here; the delocalized nature of the metallic states is better realized, and unphysical effects to the electron density distribution brought about by edges of finite clusters are avoided. It is also known that surface work functions can be calculated to within reasonable precision using periodic DFT.

This study also provides substantial improvements to previous models by firstly using a symmetric slab, which avoids errors brought about by dipoles on the reverse side of asymmetric slabs. The seven atomic layer-thick Cu slabs are separated by vacuum regions 25 Å wide. Metal substrate atoms were also allowed to relax, which can affect adsorption geometries and surface dipoles. Only the midmost three atomic layers of copper were fixed at bulk separation. Lastly, we have taken into account very low coverages in our calculations, demonstrating that it is necessary to go down to <0.1 ML to determine the location of the work-function minimum in I/Cu.

All calculations were carried out using the DFT code VASP [17]. Electron-electron exchange and correlation interactions within the generalized gradient approximation were included in the calculations using the PBE

functional [18]. The interaction between electrons and ions was described by the projector-augmented wave method [19] as implemented by Kresse and Joubert [20]. Electronic wave functions were expanded in terms of a discrete plane-wave basis set with kinetic energies of up to 300 eV. A $4 \times 4 \times 1$ mesh of special k points [21] was used to simplify Brillouin zone integration.

Geometry optimizations were terminated once the forces on relaxed halogen and copper atoms became less than 0.01 eV/Å. For the adsorbed halogen atoms at the lowest surface coverages, we found the adsorption on both the fcc and hcp threefold hollow sites of the surface to be most stable. We chose adsorption on threefold hollow sites for all surface coverages, consistent with the adsorption site choices of Bagus *et al.* [16].

Charge density differences were calculated using $\Delta\rho(\mathbf{r}) = \rho_{\text{Cu}+X}(\mathbf{r}) - [\rho_{\text{Cu}}(\mathbf{r}) + \rho_X(\mathbf{r})]$, where ρ_{Cu} , ρ_X , and $\rho_{\text{Cu}+X}$ are the charge density distributions of the copper surface, the halogen layer, and the conjugate system, respectively, across the volume of the supercell used. The symmetric slab used in our calculations makes it convenient to estimate the dipole moment normal to the surface (+ z) as a function of coverage by evaluating

$$\mu_N = \left[- \int \mathbf{r} \Delta\rho(\mathbf{r}) d^3r \right]_z = - \int_{\text{bulk}}^{\text{vac}} z \Delta\lambda_N(z) dz, \quad (1)$$

where the integration is limited to the half-cell volume ranging from the central layer of copper atoms of the slab up to the middle of the vacuum, and the negative sign is introduced because positive regions of $\Delta\rho(\mathbf{r})$ (charge buildup) are actually negatively charged. The one-dimensional charge density difference $\Delta\lambda_N(z)$ is $\Delta\rho(\mathbf{r})$ integrated over lateral coordinates x and y for each z plane.

Figure 1 shows the work function of Cu(111) as a function of halogen coverage. The presence of chlorine always increases the work function, qualitatively consistent with what one expects from a surface dipole created by a partial negative charge on the adsorbate [22]. The presence of iodine, however, decreases the work function of copper up to a coverage of 6/16 ML. Furthermore, a work-function minimum is seen, without subsurface

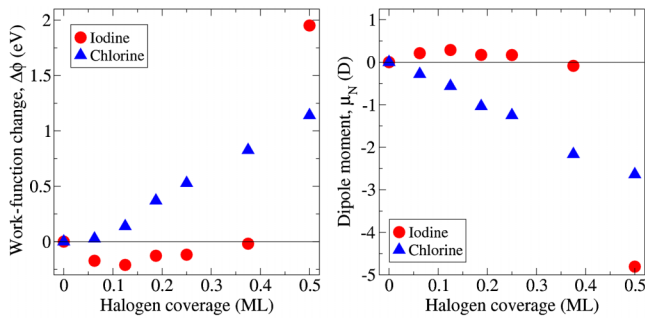


FIG. 1 (color online). Halogen coverage dependence of the change in the work function, $\Delta\phi$ (left), and the total surface dipole moment μ_N (right).

penetration of halogens or adsorption site effects that have been originally suggested as the causes of the observed work-function trends [7,9]. As the iodine coverage is increased to $\theta = 0.5$, the change in the work function of copper becomes positive, and reaches about 2 eV, exceeding that of Cl/Cu(111). The surface dipole moments associated with the adsorption of halogens at different coverages are shown in the right panel of Fig. 1. One can easily notice that this plot mirrors the work-function changes.

In order to understand these results, we first analyze in Fig. 2 the per-atom charge density difference $\Delta\lambda = \Delta\lambda_N/N$ in both systems, where N is the number of adsorbed halogen atoms on each face of the metal slab within the supercell. Furthermore, we define z_q as the position between the halogen and the copper surface in which $\Delta\lambda$ crosses from charge depletion to buildup. This choice of reference gives a hard upper bound for the amount of charge that is transferred from the substrate to the adsorbate.

Straightforward integration of $\Delta\lambda$ from z_q yields that the per-atom transfer of charge q from the substrate ranges from 0.09e at 1/16 ML to 0.14e at 6/16 ML Cl/Cu(111), and from 0.05e at 1/16 ML to 0.09e at 6/16 ML for

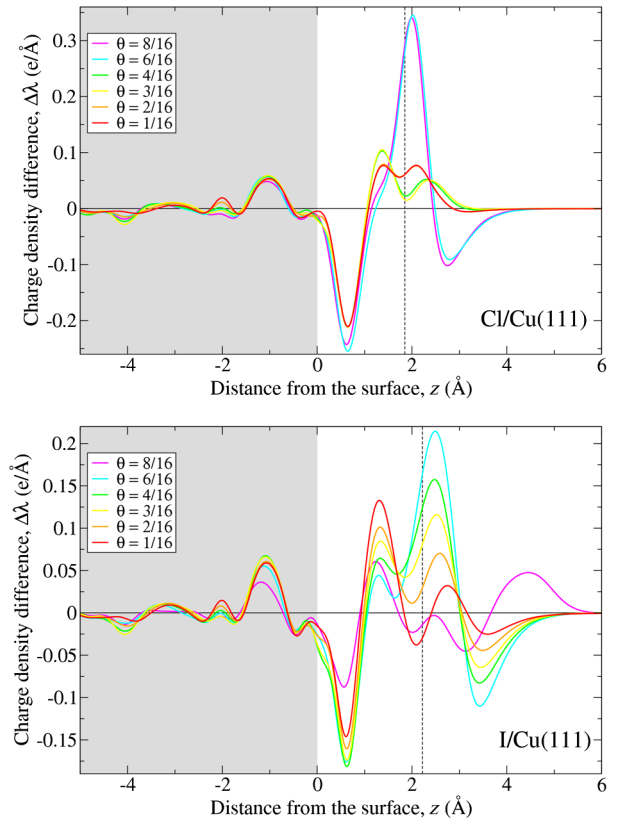


FIG. 2 (color online). Per-atom charge density difference $\Delta\lambda(z)$ for the adsorption of Cl and I on copper at different coverages. The subsurface is at $z < 0$. The vertical dashed lines indicate the approximate position of the halogen overlayers. Coverage values are expressed as fractions of a monolayer.

I/Cu(111). We find no evidence that the anomalous behavior of iodine on the Cu surface is due to a positive charge on the adatom. It was furthermore suggested in recent studies that the adsorbate-substrate distance takes an important role in determining the sign and magnitude of work-function changes [12,14,15]; yet iodine, which exhibits the anomalous behavior, adsorbs further away from the surface than chlorine by about 0.4 Å.

Note that the charge density difference profile in Fig. 2 exhibits a much stronger oscillatory structure for iodine than for chlorine. This can be easily understood considering the higher polarizability of iodine because of its larger size. This stronger electronic rearrangement of iodine is also visible in Fig. 3 where the charge density difference $\Delta\rho(\mathbf{r})$ of Cl/Cu(111) and I/Cu(111) is plotted for different coverages along a planar cut that passes through adjacent top, hcp, and fcc hollow sites. The stronger polarizability of iodine leads to a charge depletion region far from the surface that promotes a decrease in the work function. On the other hand, there is a considerable charge accumulation in the bonding regions, as both Figs. 2 and 3 demonstrate, which indicates the formation of a covalent bonding state between the Cu substrate and iodine [23]. Note that the charge rearrangement in the Cu substrate upon halogen adsorption is very similar for both considered halogens.

In order to further explain the trends found in Fig. 1, it is useful to analyze the per-adatom dipole moments $\mu = \mu_N/N$ in more detail and decouple contributions of charge transfer from polarization, $\mu = \mu_q + \mu_{\text{pol}}$, where μ_q is calculated using a simple model assuming charge transfer from the topmost Cu layer to the halogens, $\mu_q = -\bar{z}_X q$. Here, \bar{z}_X is the average position of the halogen adatoms from the Cu surface.

It is not possible to exactly break down μ_{pol} into substrate and adsorbate components since charge transfer is

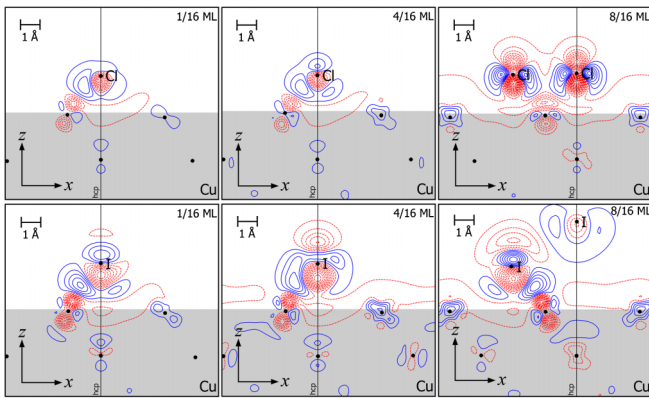


FIG. 3 (color online). Cross sections of charge density difference $\Delta\rho(\mathbf{r})$ at the surface at selected coverages. Upper (lower) panels are for Cl/Cu (I/Cu). Solid-blue (dashed-red) contours denote regions of charge buildup (depletion). An axis normal to the Cu surface and passing through the hcp hollow site is also included as a visual guide.

nonzero. However, it is useful to look at substrate trends through μ_S , which is calculated using Eq. (1) but with the integration done only up to the z coordinate that separates the substrate and the adsorbate into charge-neutral volumes in the supercell, and dividing by N .

Per-adatom dipole moments μ , together with μ_q , μ_{pol} , and μ_S , are plotted in Fig. 4. For Cl, $\mu(\theta)$ is not affected by the increased presence of Cl adatoms on the surface, leading to the linear increase in $\Delta\phi$. On the other hand, the work-function minimum for I/Cu is a natural consequence of the essentially linear decrease in μ with coverage for $\theta < 0.5$ ML.

As can be seen in Fig. 4, the terms μ_q and μ_{pol} have opposite signs, and the resulting sign of μ , and hence of $\Delta\phi$, depends on which term dominates. This corresponds to a model that is similar to that discussed by Shustorovich [8], albeit with one important difference: μ_{pol} here is not limited to only substrate polarization.

As far as Cl/Cu(111) is concerned, the fact that the per-adatom dipole moment μ is basically constant as a function of coverage does not imply that there is no inter-adsorbate interaction. At higher Cl coverages $\theta > 0.25$ there is an increase in the charge transfer, as already mentioned above and reflected in the change of the charge transfer term μ_q . Yet, this is compensated by a larger polarization caused by charge depletion far from the surface. Thus, the changes in μ_q and μ_{pol} effectively cancel each other, thereby leaving μ constant with coverage.

It has been suggested that polarization in the metal substrate induced by the presence of the iodine anion

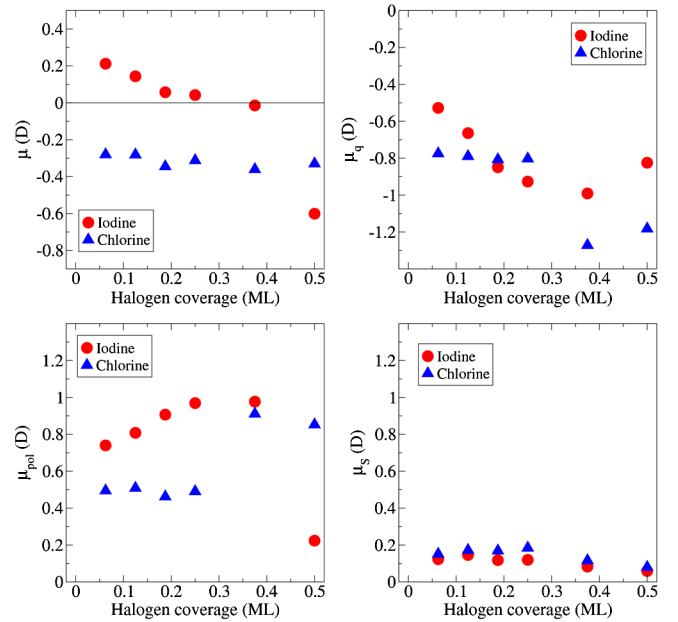


FIG. 4 (color online). Per-adatom dipole moment $\mu(\theta)$ together with the contributions μ_q , μ_{pol} , and μ_S as a function of halogen coverage. For the definitions of μ_q , μ_{pol} , and μ_S , see the text.

adsorbate becomes reduced with increasing coverage, explaining the increase in ϕ past the work-function minimum [15]. This is only very weakly observed here.

In contrast to Cl/Cu(111), for I/Cu(111) μ_{pol} increases already at low coverages as a function of coverage. However, this increase is overcompensated by the decrease in μ_q . Recall that the total surface dipole moment μ_N is obtained by multiplying $\mu(\theta)$ with the number N of adsorbates per unit cell. This leads to the initial decrease of the work function, but then the strong decrease of μ_q causes the nonmonotonic behavior of μ_N and thus the presence of the work-function minimum.

It is also difficult to explain the distinct work-function behaviors of chlorine and iodine by using μ_S alone, as the two halogens rearrange substrate electron density rather similarly. This fact is reflected in the change of the Cu d local density of states upon adsorption of the halogen atoms (not plotted). The presence of chlorine hardly changes the local density of states of the Cu atoms in the surface. Both the d -band center and the d -band width change by less than 120 meV. All the features of the d band remain, with just some peak heights modified.

The more covalent nature of iodine adsorption on Cu(111) leads to a larger shift of the Cu d band by up to 0.6 eV for an iodine coverage of 0.25. However, this shift is basically rigid, the d -band width is only changed by about 80 meV, and the features of the Cu d band are very similar to those of the chlorine-covered Cu(111) surface. Thus both in real space as well as in the density of states no strong charge rearrangement in the Cu substrate is seen upon iodine adsorption.

Finally, we address the jump in the work function of I/Cu(111) at $\theta = 0.5$. At the lower coverages, the adsorption distance of a halogen adatom from the Cu surface does not change significantly with coverage. More specifically, iodine adatoms stay about 2.26 Å from the surface, while chlorine is a little closer, at about 1.88 Å. The jump at $\theta = 0.5$ is caused by the formation of a second layer of iodine on the copper surface. The adatoms adsorbed on hcp hollow sites move up to a position 4.24 Å from the copper surface, while the iodine atoms adsorbed at fcc hollow sites stay 2.15 Å above the surface. A one-layer analogue for I/Cu(111) at $\theta = 0.5$ does exist, but is a metastable state higher in energy by about 0.5 eV/adatom. By forming the double layer, the nearest-neighbor distance is increased, reducing the Pauli repulsion between the iodine atoms. At this high coverage, I/Cu(111) has only half of the total number of iodine atoms directly interacting with copper. In order to stabilize this structure, there is a transfer of charge to the iodine atoms farther from the surface, leaving the two iodine layers in oppositely charged states. The resulting dipole layer leads to a drastic decrease in μ , and consequently, a large increase in the work function.

In conclusion, we show that the key factor in the anomalous work-function reduction of Cu(111) induced by iodine

adsorption is the strong polarizability of iodine. Together with supporting electronic rearrangement on the copper substrate, the polarization on iodine overcompensates the net charge transfer from the substrate to the adsorbed iodine atom. For higher coverages, the iodine-induced work-function change exhibits the expected increase. This nonmonotonic behavior of the work-function change as a function of iodine coverage is due to an increase in the charge transfer. Chlorine adsorption, on the other hand, causes the expected increase of the work function at all coverages since polarization effects play a less important role. The linear increase of the work function with increasing amounts of adsorbed chlorine is not an indication of the absence of adatom-adatom interactions, but is due to canceling effects of charge transfer and polarization.

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