

# 1 **Work function change of platinum electrodes induced by halide ad-** 2 **sorption**

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## 8 **Abstract**

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

## 19 **Keywords**

20 density functional theory, ionicity, polarizability, surface dipole, work function

## 21 **Introduction**

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

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

46 We have now extended this previous study by considering the adsorption of fluorine, chlorine,  
47 bromine and iodine on Pt(111) in order to check whether the findings for halogen adsorption on

48 Cu(111) are also valid for the technologically important electrode material platinum. It has been  
49 already observed experimentally [18-20] as well as theoretically [11,13,17] that the adsorption  
50 of chlorine, bromine and iodine on Pt(111) leads to an unexpected decrease of the work function.  
51 Based on calculations for several adsorbates on tungsten surfaces, Leung, Kao and Su pointed out  
52 that it is possible to relate the electronegativity scale to the direction of the charge transfer but not  
53 necessarily to the induced work function change. The problem of the unexpected work function  
54 decrease was also tackled by Michaelides et al. [8] for a system of nitrogen adsorbed on a tungsten  
55 (100) surface. They showed that the work function decrease depends strongly on the length of the  
56 chemisorption bond. If the adatom is located close to the surface, it is in the region of the overspill  
57 electron density of the metal. This leads to an area of electron depletion far from the surface, and  
58 in combination with an electron buildup in the area around the adsorbed ion, to a work function  
59 decrease.

60 In this paper we present a detailed study of the halogen-induced work function change on Pt(111)  
61 as a function of the halogen coverage which has still been missing. We will show that the observed  
62 work function decrease upon chlorine, bromine and iodine adsorption on Pt(111) at low cover-  
63 age can be explained by the strong polarization of the adsorbed halogen atoms, as in the case of  
64 I/Cu(111) [9]. We contrast these results with findings obtained for fluorine adsorption on calcium  
65 where an adsorption-induced work function decrease is also observed. However, due to the particu-  
66 lar geometric conditions in this system, the spillout mechanism [8,21] is operative.

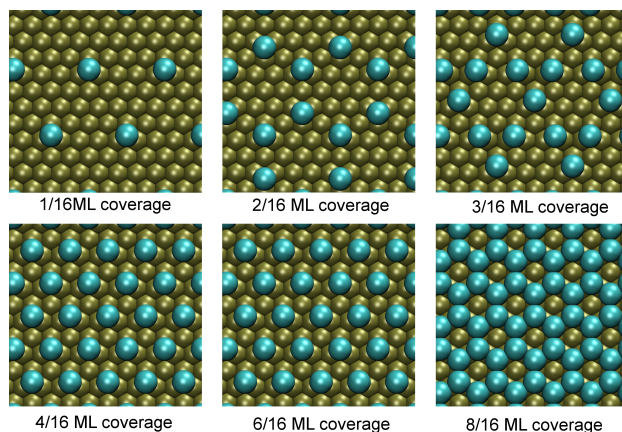
## 67 **Methods**

68 For the following calculations the periodic density functional theory (DFT) program Vienna Ab  
69 initio Simulation Package (VASP) was used. The exchange and correlation energy was calculated  
70 using the generalized gradient approximation (GGA) within the PBE functional, developed by  
71 Perdew, Burke and Ernzerhof [22]. To describe the ionic cores of the atoms, we used the projected  
72 augmented wave potentials (PAW) constructed by Kresse and Joubert [23]. The electronic wave  
73 functions were expanded in a plane wave basis set up to an energy cutoff of 400 eV. For the calcu-

74 lations, a periodic slab with a thickness of 7 atomic layers and  $4 \times 4$  lateral periodicity was cho-  
75 sen. All calculations were done using a symmetric setup of the slab, i.e., the halogen atoms were  
76 adsorbed on both sides of the slab, the middle three layers of the slab were kept fixed and the out-  
77 ermost two layers of both sides of the slab together with the adatoms were relaxed. Thus no dipole  
78 correction was necessary in order to derive the work function of the surface terminations. The unit  
79 cell was computed with a gamma-centered  $4 \times 4 \times 1$   $k$ -point mesh.

80 The optimized lattice constant for platinum was found to be  $a = 3.98 \text{ \AA}$ , which is only 1.48% larger  
81 than the standard experimental value [24]. The halogens iodine, bromine and chlorine adsorb for  
82 low coverages most stably at the fcc threefold-hollowsite position on a platinum (111) surface.

83 Since the hcp threefold-hollow position is also quite stable, the halogens were ordered in symmet-  
84 ric patterns on the surface with the highest possible nearest neighbor distance to other adsorbed  
85 atoms in hcp and fcc positions. The threefold-hollow adsorption positions are considered as the  
86 most probable adsorption sites for halogens on metals [9,10,14,25]. In this manner, six different  
87 coverages – 1/16 ML, 2/16 ML, 3/16 ML, 4/16 ML, 6/16 ML and 8/16 ML – were created, which  
88 are illustrated in Fig. 1. The structures of iodine, bromine and chlorine were relaxed completely.



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

89 Interestingly enough, fluorine atoms adsorb more stably at the on-top position on platinum. At this  
90 position, the average distance to the topmost surface layer is larger than on the threefold-hollow  
91 sites. Since we are interested in getting trends among the halogen atoms in order to understand

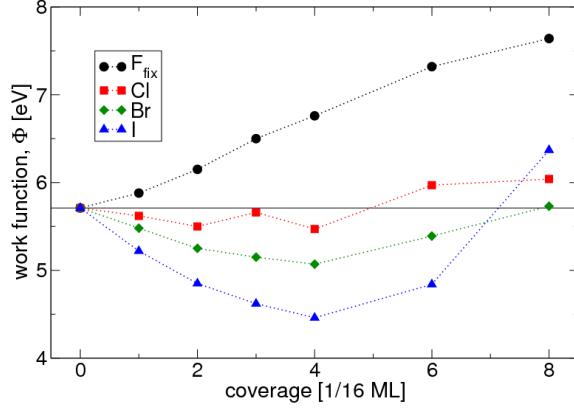
92 and predict adsorption processes, we kept the fluorine in the threefold-hollow site positions, but  
93 allowed for vertical relaxation, allowing a better comparison with the results for the chlorine,  
94 bromine and iodine adsorption structures.

## 95 **Results and Discussion**

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

101 Figure 2 shows the work function of halogen-covered Pt(111) as a function of halogen coverage.  
102 For clean Pt(111), the calculations yield a value of 5.71 eV. Various experimental measurements in  
103 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-  
104 32]. The presence of fluorine on Pt(111) always increases the work function, qualitatively consis-  
105 tent with what one expects from a dipole involving a negative charge on the adsorbate. The adsorp-  
106 tion of chlorine, bromine or iodine on a platinum (111) surface reduces the work function at low  
107 coverages. While the trend reverses at 0.25 ML,  $\Delta\Phi$  only becomes positive at the half-monolayer  
108 coverage. The experimental trends [18-20] as well as theoretical values by Migani et al. [10] agree  
109 with the calculated results.

110 Aside from the sign of the work function change, the dependence of  $\Delta\Phi$  on halogen coverage is  
111 another aspect that needs to be clarified. In a simple model, one may completely neglect the in-  
112 teraction between the adsorbates. In this case, a linear trend  $\Delta\Phi(\theta) \propto -\theta\Delta\mu$  would be expected,  
113 where  $\theta$  is the surface coverage and  $\Delta\mu$  is the change in the surface dipole moment brought about  
114 by the adsorption of a halogen atom. Obviously, this model is applicable only at low coverages in  
115 Fig. 2. In a more advanced model, the electrostatic interaction between adjacent dipoles is taken  
116 into account by assuming that the mutual repulsion of the dipoles leads to a decrease in the polarity  
117 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.

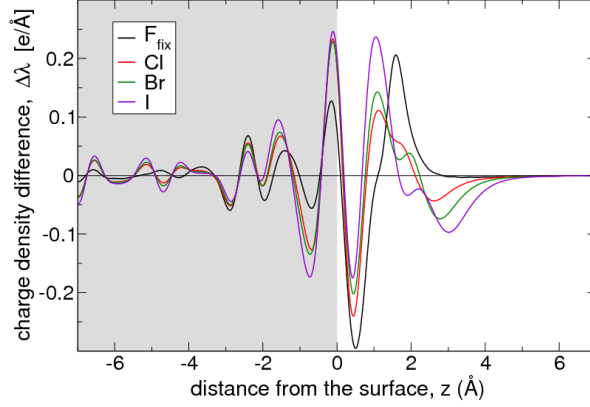
118  $\Delta\Phi$  at high coverages. However, this does not explain the observed non-monotonic behavior of the  
 119 work function change and so a more comprehensive explanation is needed.

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

$$125 \quad \Delta\Phi = -\frac{e}{\epsilon_0}(\mu_z - \mu_{z,0}) = -\frac{e}{\epsilon_0}\Delta\mu, \quad (1)$$

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

131 The surface dipole moment changes when the electron density close to the surface becomes redis-  
 132 tributed upon bond formation. This redistribution is most straightforwardly described through the  
 133 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  $z < 0$ .

134 ing system with the sum of electron density of the non-interacting metal slab and halogen layer at  
 135 the same atomic positions,  $\rho_{\text{diff}} = \rho_{\text{Hal+Pt}} - (\rho_{\text{Hal}} + \rho_{\text{Pt}})$ . The electron density difference profile  
 136  $\Delta\lambda(z)$  along the  $z$  direction corresponds to the lateral sum of the electron density difference in the  $x$   
 137 and  $y$  directions,

$$138 \quad \Delta\lambda = \frac{1}{N} \iint_{\text{cell}} \rho_{\text{diff}} dx dy, \quad (2)$$

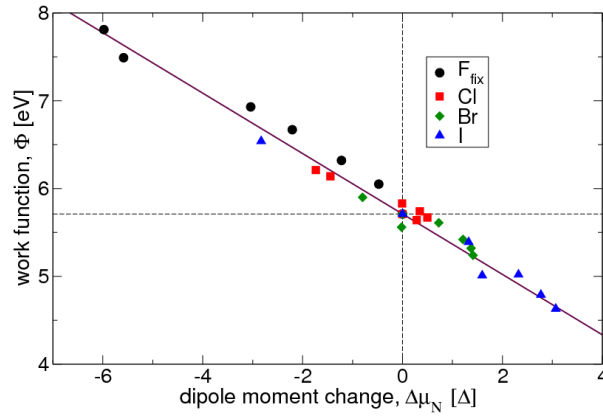
139 where  $N$  is the number of halogen atoms adsorbed on one side of the slab per unit cell. The  $\Delta\lambda$   
 140 profiles for the 1/16 ML coverages of the four halogens are shown in Fig. 3. The shape of the dia-  
 141 grams for the higher coverages look similar. The profiles illustrate how the electron density is reor-  
 142 ganized along the  $z$  direction when the adatoms adsorb. The gray area on the left hand side denotes  
 143 the metal slab. The topmost metal atoms are centered at  $z = 0 \text{ \AA}$ . The electron density difference  
 144 profile shows a significant electron depletion far from the surface for the case of chlorine, bromine  
 145 and iodine, followed by an electron buildup close to the surface, and oscillations in the metal. In  
 146 the case of fluorine, there is just an electron buildup around the fluorine atom, followed by oscilla-  
 147 tions into the bulk. This electron buildup around the fluorine atom indicates an ionic state. Fluorine  
 148 is partially constrained to remain at the threefold-hollow sites, where the average distance from the  
 149 center of the adsorbates to the topmost surface layer is smaller than for fluorine adsorbed at the on-

150 top position. Calculations for F atoms at the most stable adsorption site may give slightly different  
 151 results in charge transfer and dipole moments.

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

$$157 \quad \Delta\mu_N = - \int_{\text{bulk}}^{\text{vac}} z \Delta\lambda_N(z) dz \quad (3)$$

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



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

163 Since  $\Delta\lambda$  of the fluorine-covered platinum slab shows for all coverages the structure of an electron  
 164 buildup far from the surface, followed by an electron depletion close to the surface, the dipole mo-  
 165 ment on each face of the slab becomes more negative as a function of coverage, consistent with a



166 work function increase. For the other three halogens, the electron density difference profile looks  
167 more complicated. There is an electron depletion far from the surface, followed by an electron  
168 buildup. This structure is sufficiently strong to invert the dipole moment, so that  $\Delta\mu_N$  changes sign  
169 as a function of the coverage.

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

## 181 **Coverage trends**

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

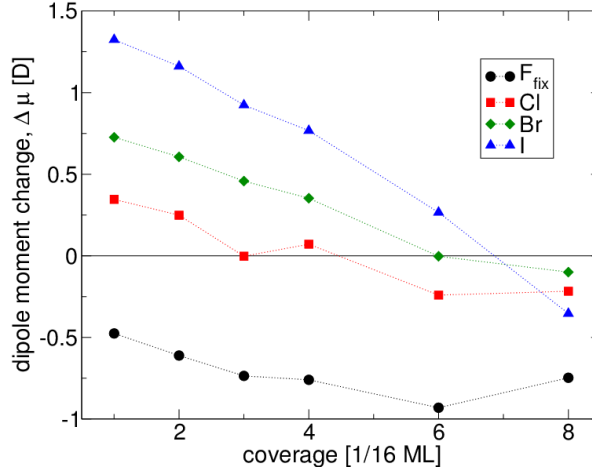
188 The work function minimum has also been explained through the differences in site occupancies as  
189 halogen coverage increases. Subsurface penetration followed by surface adsorption was one of the  
190 possibilities considered in explaining the work function minimum for chlorine on platinum [18],  
191 based on the assumption that subsurface penetration and surface adsorption lead to opposite dipole

192 moments on the surface. In contrast, for iodine on platinum, an adsorption site effect was sug-  
193 gested under the assumption that threefold-site adsorption decreases the work function, while  
194 adding iodine to top sites increases it [20]. As coverage increases, more top sites get occupied by  
195 iodine, leading to the increase in  $\Phi$  beyond the minimum. Still, the surface work function change  
196 remained negative over the entire coverage range used.

197 A more recent computational study has shown that the adsorption of isolated iodine atoms at the  
198 hollow or top sites both lead to  $\Delta\Phi < 0$ , although the decrease in the work function is larger for  
199 iodine adsorption at the hollow site [17]. Another perspective to explaining the work function min-  
200 imum was proposed: through changes in the polarization of the metal substrate. The authors found  
201 that polarization in the platinum substrate induced by the presence of the iodine anion adsorbate  
202 becomes reduced with increasing coverage, hence explaining the non-monotonic behavior in  $\Delta\Phi$ .  
203 While changing site occupancy with increasing coverage can and will lead to observable changes  
204 in the work function, in this study we focus on work function changes that are caused by effects  
205 that are primarily electronic in nature, i.e. which are not due to changes in the adsorption or ab-  
206 sorption site. Hence a deeper analysis of charge transfer, internal redistribution of charge in the  
207 metal substrate, and redistribution of charge on the halogen adatoms is needed. To analyze surface  
208 dipole moments in detail, we use the total surface dipole moment per unit cell normalized to the  
209 number of adatoms to define the dipole moment change created per adsorbed atom,

$$210 \quad \Delta\mu = \frac{\Delta\mu_N}{N}. \quad (4)$$

211 The normalized dipole moments are shown in Fig. 5. The plots are nowhere flat, suggesting the  
212 presence of considerable neighboring adatom interactions even at the lowest coverages. There is  
213 also a clear tendency for the dipole moment induced by the adsorption of a single halogen atom to  
214 be reduced as the concentration of adatoms increases on the Pt surface. Note that the 0.5 ML cover-  
215 age of iodine is so closely packed that the repulsion of the electron shells induces a two-layer struc-  
216 ture of the adsorbate layer. Every second iodine atom became a part of a second adsorbate layer,  
217 which is positioned at around  $1.7 \text{ \AA}$  farther from the surface than the first layer of iodine atoms.



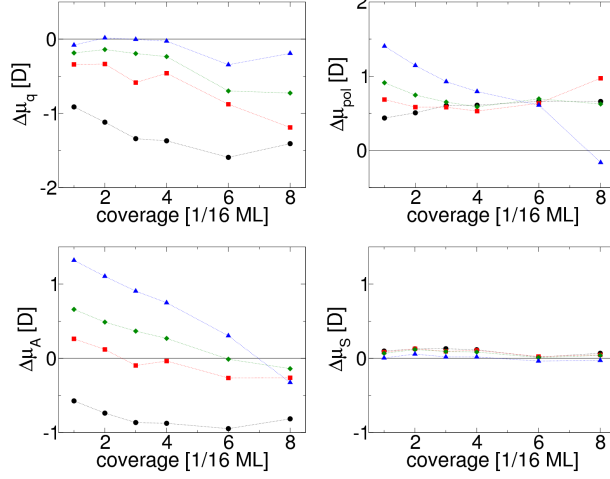
**Figure 5:** Calculated normalized dipole moment as a function of coverage of fluorine, chlorine, bromine and iodine on Pt(111).

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

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

$$230 \quad \Delta\mu_q = -\bar{z}_X \int_{z_q}^{\text{vac}} \Delta\lambda(z) dz, \quad (5)$$

231 where  $\bar{z}_X$  is the average distance of the halogen adatoms from the metal surface. We combine all  
 232 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.

233 tion effects in the metal and adlayer. The combination of both contributions leads to the total dipole  
 234 moment change,

$$235 \quad \Delta\mu = \Delta\mu_q + \Delta\mu_{\text{pol}}. \quad (6)$$

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

242 Results also suggest that higher surface concentrations of adatoms decrease the dipole moment  
 243 change per adatom through mutual depolarization. This effect is most pronounced for iodine, as  
 244 well as for low-coverage adsorption of bromine and chlorine, but not for fluorine because of the  
 245 low polarizability of small atoms. Besides the repulsion of the dipoles, the electron shells of ad-  
 246 sorbed atoms at higher coverages start to repel.

247 Another interesting question concerns the importance of the electron density oscillations in the  
 248 subsurface, as shown in Fig. 3. It might be speculated that these oscillations could be responsible  
 249 for the significant polarization part  $\Delta\mu_{\text{pol}}$  of the total dipole moment  $\Delta\mu$ . To answer this question,  
 250 we have divided  $\Delta\lambda$  into two parts: one representing the dipole moment change due to polarization  
 251 in the adsorbate layer and the other part representing the dipole moment change due to polarization  
 252 in the substrate,

$$253 \quad \Delta\mu = \Delta\mu_A + \Delta\mu_S. \quad (7)$$

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

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

$$260 \quad \int_{z_0}^{\text{vac}} \Delta\lambda(z) dz = 0 \quad (8)$$

261 For this choice, the analogous integral on the metal side is also zero due to the overall charge neu-  
 262 trality of the supercell. It is then possible to estimate the surface dipole moment  $\mu_S$  and the adsor-  
 263 bate dipole moment  $\mu_A$  using

$$264 \quad \Delta\mu_S = \int_{\text{bulk}}^{z_0} z\Delta\lambda(z) dz \quad (9)$$

265 and

$$266 \quad \Delta\mu_A = \int_{z_0}^{\text{vac}} z\Delta\lambda(z) dz. \quad (10)$$

267 We briefly summarize the difference in the integration limits  $z_q$  and  $z_0$  of eq. 5 and eq. 9, respec-  
268 tively: these equations have the purpose of dividing the unit cell into two parts, but it is not clear  
269 where exactly the adatom ends and where the platinum begins or vice versa. The two integration  
270 limits mark special points in the graph of  $\Delta\lambda$ . The border  $z_q$  divides the unit cell at the point of  
271 maximum charge on the adatom, in contrast to  $z_0$  which divides at the point of zero charge on the  
272 adatom.

273 The adsorbate and the substrate dipole moments plotted in Fig. 6 c and d, respectively, indicate that  
274 the influence of the metal substrate dipole moment change  $\Delta\mu_S$  to the total dipole moment change  
275  $\Delta\mu$  is minor compared with the impact of adsorbate polarization  $\Delta\mu_A$ , which affects the total dipole  
276 moment change quite dramatically. This also means that our analysis does not support the view  
277 [17] that substrate polarization plays an important role in explaining the halogen-induced work  
278 function decrease.

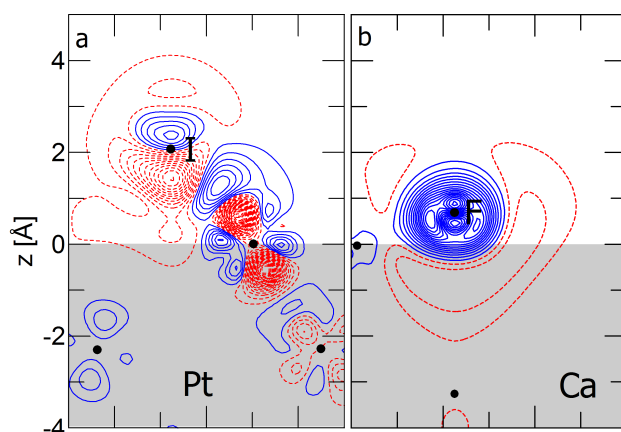
279 Additionally, it is noticeable that the decrease in the total dipole moment change for the case of io-  
280 dine and chlorine at around 0.25 ML is much more significant on platinum compared with the total  
281 dipole moment change of copper [9]. The work function of copper is about 1 eV smaller,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

## 285 **Fluorine on calcium**

286 We have shown that the strong polarizability of large atoms such as iodine leads to a considerable  
287 charge buildup in the adatom-surface bonding regions, which is consistent with covalent bonding,  
288 and an accompanying electron depletion region far from the surface which creates a net dipole on  
289 the adatom that in turn promotes a decrease in the work function. Here we show that the adsorption  
290 of fluorine can also decrease the work function of a metal surface, namely calcium, but through a  
291 different mechanism. Calcium is considered to be an attractive electrode material in electrochem-  
292 ical energy storage because of its low electronegativity, earth abundance, and low cost [34]. Flu-

293 orine adsorbs stably at a threefold hollow site on calcium, which is an fcc metal with a calculated  
 294 lattice constant that is 39% larger than that of platinum. At its equilibrium adsorption position, flu-  
 295 orine is only 0.73 Å from the topmost layer of Ca atoms. In contrast, iodine adsorbs 2.07 Å from  
 296 the platinum surface.

297 In Fig. 7, we contrast two systems in which halogen adsorption decreases the work function of the  
 298 metal substrate. The left panel shows iodine adsorption on Pt(111) at a coverage of 1/9 ML; the  
 299 right panel shows fluorine adsorption on Ca(111) at a coverage of 1/4 ML. This yields similar ab-  
 300 solute coverages per area for the two systems given the stark difference between the lattice con-  
 301 stants of Pt and Ca. At these adsorption coverages, iodine reduces the platinum work function by  
 302 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<sup>3</sup>. The region of the metal slab is shaded gray as a visual aid.

303 Figure 7 shows that halogen adsorption can create a surface dipole that reduces the work function  
 304 in two very distinct mechanisms: adatom polarization and spillout depletion. Iodine on platinum  
 305 is characterized by negligible charge transfer, covalent bonding, and polarization on the adatom.  
 306 There is no evidence for a dominantly ionic bond for I/Pt(111) reported in ref. [17]. Fluorine ad-  
 307 sorption on calcium on the other hand is characterized by a large charge transfer to the adatom with  
 308 negligible polarization, creating a system comprised of a negative ion enveloped by electron deple-  
 309 tion. Since fluorine is adsorbed very close to the surface, it is embedded within the electron spillout

310 region of calcium. The depletion of electron density in the spillout region not only reduces the ef-  
311 fect of the strongly negative fluorine on the net dipole, but even overcompensates it, resulting in a  
312 work function decrease.

## 313 **Conclusions**

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

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

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

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