



Fluorine adsorption on transition metal surfaces – A DFT study

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Abstract: Based on density functional theory calculations, the adsorption of fluorine was investigated on a) Cu(111), Au(111), Pd(111) and Pt(111) surfaces, b) on Pd monolayer surfaces over Cu(111), Au(111) and Pt(111) surfaces and c) on the surfaces of Pd(111) monocrystals with an inserted metal monolayer (M = Cu, Au or Pt) underneath the first Pd surface layer. The results evidenced that the adsorption did not cause significant changes of the structural parameters of metallic substrate. The strongest adsorption, amounting to –4.49 eV, was calculated in the case of the Cu(111) surface. The Cu(111) and Au(111) surface atoms interact with F adatoms exclusively by the mediation of the *sp*-band, while the surface atoms of Pt and Pd-based surfaces interact with F adatoms additionally by the mediation of the *d*-band. In the case of Pt(111) and Pd_{ML}/M(111) surfaces, the binding energies correlated with the *d*-band center positions, which indicated a significant contribution of covalent interaction. These results confirmed that the nature of surface interaction of highly electronegative F atom with metallic surfaces depends significantly on the nature of the metal substrate.

Keywords: Fluorine, adsorption, electronic structure, adsorption trends

INTRODUCTION

Adsorption of halogen atoms and halide ions on metallic surfaces presents important questions in different fields, which have particular importance in electrochemistry. Namely, it is well known that adsorption of ions can significantly affect the properties of metal/solution interfaces and determine electrochemical behavior of a given electrode material.^{1,2} The active debate in the scientific community on the nature of adsorbed halogens has lasted since the very beginning of investigations of halogen–metal interactions. Some experiments indicated that the nature of the bond depended on the nature of the halogen atom. For example,

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Huemann *et al.*³ concluded that Cl–Cu(100) and I–Cu(100) interaction are prevalently ionic and covalent, respectively.

According to a review by Koper,⁴ the first topic of electrochemical importance investigated by *ab initio* calculations was the adsorption of halides on metallic surfaces. Special care in this sense was paid to the strength of the interaction, the preferred geometry and the effects of solvent and electric field, being important parameters of all metal–solution interfaces. Some of the first Hartree–Fock calculations for Ag,⁵ Hg^{6,7} and Cu⁸ substrates indicated a large ionicity of the adsorbed halogen. The theoretically established trends in halide adsorption on metallic substrates were found to oppose the experimental results, which was explained by the absence of a solvent,⁹ but its inclusion did not resolve the problem.¹⁰ The theoretical approach can enable the investigation of charge-neutral systems (corresponding to the adsorption of halogen atom) or negatively charged systems (corresponding to the adsorption of halide ions), however, Sellers *et al.*¹¹ proposed that a simple thermodynamic cycle could be used to convert the binding energy of adsorbed halogen to the binding energy of halide ion and *vice versa*. Moreover, trends in binding energies of halide ions and halogen atoms were often found to be identical.⁴ Migani and Illas¹² performed a systematic study based on the density functional theory (DFT) and provided data regarding the structure and bonding of halogen atoms on low-index transition metal surfaces. According to the aforementioned work, surfaces with higher work function are associated with more covalent bonding of halogen atoms.

In a previous work,¹³ the adsorption of Cl, Br and I on transition metal surfaces and Pd-monolayer surfaces, having particular importance in electrocatalysis, were investigated.^{1,14} The adsorption on the three-fold adsorption sites was found to be the strongest for all the surfaces, and adsorption energies decreased with increasing size of the halogen atom. For the case of the Pd-monolayer surface, it was demonstrated that the energy of adsorption of halogen atoms could be correlated to the position of the *d*-band of the surface atoms. The provided data enabled the rationalization of the experimentally observed effects of chloride ion adsorption on the catalytic activity of a Pd-monolayer over Pt(111) towards the oxygen reduction reaction. The present work is a continuation of the previously reported studies.¹³ The herein derived calculations evidenced that the metallic substrates investigated in this work provide a possibility to separate the effects of the electronic structure and the work function on the strength of the adsorption of halogen atoms. As there is a debate on the nature of halogen–metal bonds, the extreme case of fluorine, being the most electronegative element in the Periodic Table of Elements, was investigated. Moreover, it was investigated how the electronic structure of a metallic substrate affects the adsorption strength.

CALCULATION DETAILS

DFT calculations were performed using the PWscf code of the Quantum ESPRESSO distribution.¹⁵ The Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was used.¹⁶ Marzari–Vanderbilt cold smearing¹⁷ with a broadening of 0.02 Ry was used to augment convergence. The kinetic energy cutoff was 32 Ry. The equilibrium lattice parameter (a_0) of Cu, Au, Pd and Pt were obtained by optimization of the respective bulk unit cell and were found to be 3.63, 4.17, 4.00 and 4.01 Å, respectively. The calculated lattice parameters agree well with the experimentally determined ones.¹³ Damped dynamics¹⁸ was used for structural relaxation. The geometrical optimization was allowed to run until the forces on the atoms became less than 0.02 eV Å⁻¹. The work function (Φ) was calculated using the equation:

$$\Phi = V(+\infty) - E_F \quad (1)$$

where $V(+\infty)$ is the electrostatic potential in the middle of the vacuum region, and E_F denotes the Fermi energy of the slab. The d -band density of states was determined by projection of the plane waves onto spherical harmonic orbitals. Löwdin population analysis¹⁹ was used to determine the population of the d -states of the investigated transition metal surfaces.

Halogen adsorption was modeled using hexagonal (2×2) cell for the (111) oriented surfaces, with three metal layers in the slab. The given model corresponds to a surface coverage of 0.25 ML. The metal atoms were placed in their fully relaxed positions, obtained by structural relaxation of the clean surfaces. The first irreducible Brillouin zone was sampled using Monkhorst–Pack²⁰ scheme set to $4 \times 4 \times 1$. The applicability of this slab model to describe correctly the electronic structure of surfaces was confirmed by a number of tests involving thicker metal slabs. In addition, a number of previously published studies demonstrated that this simple model is applicable for the description of atomic and molecular adsorbates.^{13,21} Fluorine atoms were placed on one side of the slab, and the structural relaxation was allowed for adatoms as well as for the first surface layer only. Binding energies (E_{F-M}) were calculated using the following equation:

$$E_{F-M} = E_{\text{slab+fluorine}} - (E_{\text{slab}} + E_{\text{fluorine}}) \quad (2)$$

where $E_{\text{slab+Fluorine}}$, E_{slab} and E_F are the total energy of the slab with an adsorbed fluorine atom, the total energy of the metal slab and the total energy of an isolated fluorine atom, respectively. Although having a minor effect on the adsorption energetics, relaxation was taken into account in order to unveil the details regarding the local adsorption equilibrium geometry.

RESULTS AND DISCUSSION

The metallic surfaces investigated in this work as the substrates for fluorine adsorption were densely packed (111) surfaces of Cu, Au, Pd and Pt. In addition, Pd monolayers over Cu(111), Pt(111) and Au(111), denoted as Pd_{ML}/M(111), were investigated. Surface models consisted of two M layers (M = Cu, Pt or Au) over which a Pd monolayer was placed in a homoepitaxial manner with a lattice parameter matching the one of a host metal M. Furthermore, “sandwich” structures, where a single Cu, Au or Pt layer was inserted under the first surface layer of the Pd(111) surface, were also investigated. These were denoted hereafter as M_{UND}Pd(111) surfaces. In this case, the surface models consisted of three metal

layers in total, with M layer inserted within two Pd layers. Lattice constant in these three cases matched the one of Pd. The combination of these metallic surfaces presents a suitable set of model systems to investigate the effects of the work function and electronic structure on fluorine adsorption on metallic surfaces. Namely, clean M(111) surfaces (M = Pd, Pt, Cu or Au) distinguish themselves by different population of *d*-states as well as electronic structure, described through *d*-band center position ($E_{d\text{-band}}$), and work function (Table I).

TABLE I. The electronic properties of the studied surfaces: *d*-band center ($E_{d\text{-band}}$), population of *d*-states (*d*) and calculated work function (Φ). Reprinted¹³ with permission by Elsevier

Surface	$E_{d\text{-band}} / \text{eV}$	<i>d</i> / electrons	Φ / eV
Pd(111)	-1.71	9.29	5.26
Pt(111)	-2.13	8.97	5.97
Cu(111)	-2.53	9.69	4.72
Au(111)	-3.17	9.67	5.34
Pd _{ML} /Pt(111)	-1.80	9.28	5.28
Pd _{ML} /Cu(111)	-2.42	9.21	5.28
Pd _{ML} /Au(111)	-1.37	9.27	5.29
Pt _{UND} Pd(111)	-1.81	9.19	5.28
Cu _{UND} Pd(111)	-1.76	9.29	5.25
Au _{UND} Pd(111)	-1.63	9.28	5.40

Among the investigated surfaces, the Cu and Au ones have low-lying filled *d*-states while the Pd and Pt ones have partially filled *d*-states, which enable direct interaction with adsorbed F atoms (Fig. 1). Moreover, the differences of

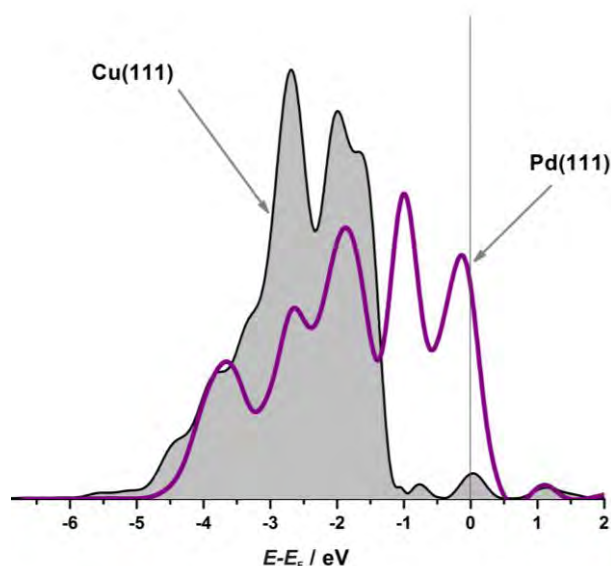


Fig. 1. Projected density of *d*-states (PDOS) for Cu(111) and Pd(111) surface. Thin vertical line indicates the position of the Fermi level.

the work function are up to 1.25 eV, enabling investigation of the role of this quantity on fluorine adsorption. By comparing these quantities for the Pd_{ML}/M(111) and M_{UND}Pd(111) surfaces, it could be seen that the population of *d*-states is almost independent of the nature of metal M (M = Cu, Au or Pt). Moreover, the calculated work functions for all these surfaces are mutually similar.¹³ However, these surfaces can be discriminated based on the position of the *d*-band center, which is tuned by the ligand effect²² (for M_{UND}Pd(111) surface) or simultaneously by the ligand and strain effect²² (for Pd_{ML}/M(111) surfaces). Hence, these surfaces could be used to analyze the effects of electronic structure on the adsorption of fluorine, while the effects of *d*-band population and work function are eliminated.

In continuation, an analysis of adsorption of F on the investigated surfaces was performed. As the adsorption could induce structural changes of the metallic substrate, first the adsorption geometry was characterized in terms of the vertical distance of the F adatom from the surface ($z(\text{F-M})$) and by the vertical displacement of surface metal atoms from their neighbors (ΔM) caused by the adsorption of F (Fig. 2).

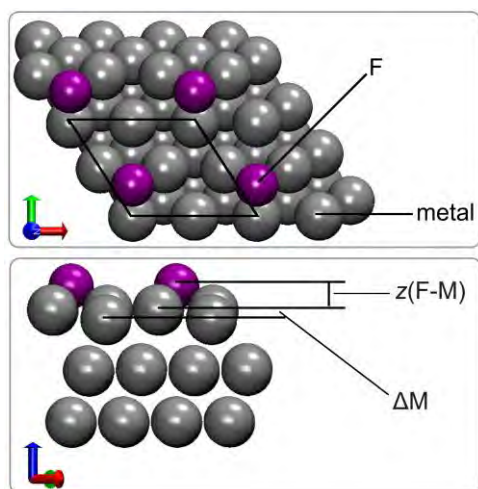


Fig. 2. Top view of a slab model used to investigate fluorine adsorption with designated surface unit cell used in calculations (top) and a side view of a three-layer slab with adsorbed fluorine accompanied by a designation of the quantities used to characterize the adsorption geometry (bottom).

Among the investigated M(111) surfaces, the Cu(111) surface displayed the strongest F adsorption, then followed Pd(111), Pt(111) and Au(111) surfaces (Table II). This trend is in fair agreement with the one reported by Migani and Illas,¹² although in the present study, somewhat more exothermic adsorption was found. With the exception of Pt(111), where top adsorption site was identified as the preferential one, three-coordinated fcc sites were found to be preferential for F adsorption. The vertical distances of adsorbed F atoms ($z(\text{F-M})$) on the investigated surfaces were found to be correlated with the lattice parameters, and

all adsorption sites follow this trend. On the other hand, the displacements of surface atoms were rather small, without an obvious trend and do not exceed 4 % of a_0 . This stimulates the conclusion that the adsorption geometry is predominantly determined by the relative differences in the atomic radii of the substrate and adsorbate, while the interaction of F adatom does not disturb significantly the substrate structure. The obtained adsorption geometries fit well to those reported previously.¹²

TABLE II. Description of F adsorption geometry and calculated binding energies on M(111) surfaces (M = Pd, Pt, Cu or Au)

Surface	Adsorption site	$\Delta(M) / \text{Å}$	$z(\text{F-M}) / \text{Å}$	$E_{\text{F-M}} / \text{eV}$
Pd(111)	fcc	0.03	1.60	-3.84
	hcp	0.04	1.63	-3.76
	top	0.04	1.99	-3.62
	bridge	0.04	1.68	-3.78
Pt(111)	fcc	0.02	1.69	-3.32
	hcp	0.02	1.75	-3.20
	top	0.15	1.98	-3.62
	bridge	0.11	1.72	-3.37
Cu(111)	fcc	0.07	1.50	-4.49
	hcp	0.07	1.52	-4.47
	top	0.04	1.85	-4.05
	bridge	0.07	1.56	-4.41
Au(111)	fcc	0.03	1.74	-3.29
	hcp	0.01	1.75	-3.29
	top	0.01	2.09	-3.13
	bridge	0.03	1.80	-3.27

When calculated binding energies of F are compared with binding energies of Cl, Br and I reported previously,¹³ it can be seen that F adsorbs more strongly than the other halogens, confirming that the strength of halogen adsorption decreases along the group of Periodic Table of Elements from top to bottom. This corresponds with the work of Migani and Illas¹¹ for the (111) and (100) surfaces of fcc metals, but it does not hold for the least densely packed (110) surface.

A much more interesting situation was found in the case of Pd_{ML}/M(111) and M_{UND}Pd(111) surfaces, where only the d -band center positions differ mutually, while the populations of d -states and the work functions do not. The previously mentioned observations regarding the adsorption geometries also hold here: the changes of the substrate structure are rather subtle, and vertical distance of F adatom from the surface can be linked to the 2D lattice constant of the substrate (Table III). However, the binding energy, ranging between -3.43 eV (Pd_{ML}/Cu(111) surface) to -3.91 eV (Pd_{ML}/Au(111)), indicated clearly that the d -band structure of the surface atoms played a significant role. Moreover, the effect of surface strain, introduced by changes in the lattice constant of the under-

lying metal in the case of Pd_{ML}/M(111) surfaces, was much more pronounced than the ligand effect, being operative for M_{UND}Pd(111) surfaces (Table III). This clearly indicates that even for highly electronegative adatom such as Fluorine, covalent interaction plays an important role and that the nature of the metal–fluorine bond is not purely ionic.

TABLE III. Description of F adsorption geometry and calculated binding energies on Pd_{ML}/M(111) and M_{UND}Pd(111) surfaces (M = Pt, Cu or Au)

Surface	Adsorption site	$\Delta(M) / \text{\AA}$	$z(\text{F-M}) / \text{\AA}$	$E_{\text{F-M}} / \text{eV}$
Pd _{ML} /Pt(111)	fcc	0.03	1.57	-3.86
	hcp	0.05	1.63	-3.74
	top	0.04	1.99	-3.62
	bridge	0.04	1.66	-3.77
Pd _{ML} /Cu(111)	fcc	0.02	1.80	-3.43
	hcp	-0.04	1.82	-3.39
	top	-0.15	2.07	-3.25
	bridge	-0.04	1.85	-3.39
Pd _{ML} /Au(111)	fcc	0.02	1.49	-3.91
	hcp	0.02	1.53	-3.78
	top	0.03	2.00	-3.48
	bridge	0.03	1.61	-3.77
Pt _{UND} Pd(111)	fcc	0.03	1.61	-3.87
	hcp	0.04	1.65	-3.78
	top	0.06	1.99	-3.67
	bridge	0.05	1.69	-3.81
Cu _{UND} Pd(111)	fcc	0.02	1.60	-3.70
	hcp	0.04	1.63	-3.61
	top	0.03	2.00	-3.43
	bridge	0.04	1.68	-3.62
Au _{UND} Pd(111)	fcc	0.02	1.58	-3.68
	hcp	0.03	1.61	-3.61
	top	0.02	1.99	-3.48
	bridge	0.03	1.67	-3.62

To backup these conclusions further, attention was turned to the work of Hammer and Nørskov,²³ who established a linear correlation between the position of the *d*-band center and the energy of adsorption, which actually assumed a covalent substrate–adsorbate interaction. Such a relationship was demonstrated previously for Cl, Br and I adsorption, when the slope of the $E_{\text{F-M}}$ vs. $E_{d\text{-band}}$ line was approximately the same for all three halogen adatoms, which was ascribed to the valence orbitals of the adatom having the same electronic structure. The continuation of previous work¹³ is clearly depicted in Fig. 3, which demonstrates the same linearity between $E_{\text{F-M}}$ and the $E_{d\text{-band}}$. However, it appears that the binding energy of fluorine is somewhat less sensitive to the

modification of electronic structure, possibly due to higher electronegativity compared to other halogen atoms and increased contribution of an ionic interaction.

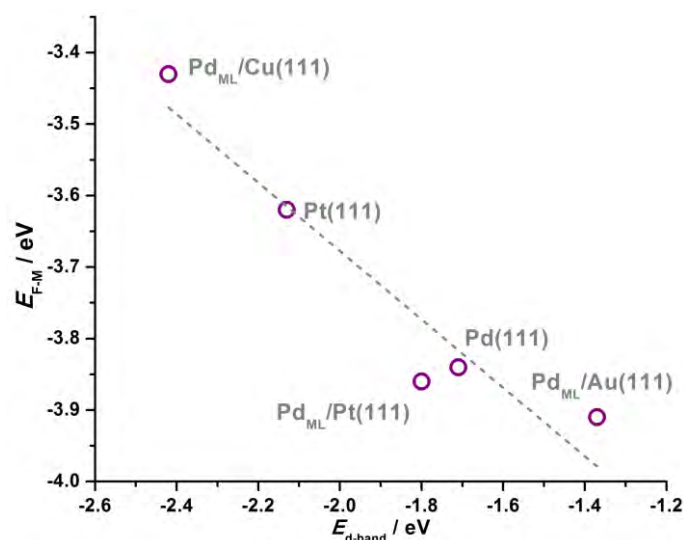


Fig. 3. Correlation between the fluorine binding energy (E_{F-M}) and the d -band center position ($E_{d\text{-band}}$). The linear fit is presented by the dashed line.

The states responsible for the interaction between the F adatom and the substrate can be identified by comparison of substrate projected densities of states prior to and after the adsorption, as introduced by Liu *et al.*²⁴. The analysis was performed in such a way that the projected density of states, in this particular case the projected d -band density of states, for a clean metallic surface and the corresponding counterpart with adsorbed F are subtracted. In this way, one may perceive a redistribution of electronic states due to interaction between the adsorbate and substrate and identify the states responsible for the interaction. In the case of Cu(111), the d -states become redistributed, positive parts of Δ PDOS are located below the Fermi energy, indicating that all the bonding and anti-bonding states arising from d - p interactions are filled (Fig. 4). Similarly, the formation of bonding and anti-bonding states upon adsorption of Cl on Cu(111) was previously observed in the same energy window by Peljhan and Kokalj.²⁵ Complete filling of bonding and anti-bonding states suppressed strong covalent bonding, but the interaction was considered to be not purely an ionic one.²⁵ This holds also for the case of an Au(111) surface, the d -band of which is located at lower values compared that of a Cu(111) surface (see the value of $E_{d\text{-band}}$, Table I). These conclusions fit to the completely filled low-lying d -band of Cu and Au and to the finding of Koper and van Saten,²⁶ who highlighted that the strength of the interaction of halogen p -states decreased when the d -band of the substrate atoms

shifted towards lower energies. However, it could also be fitted to the results of Hammer and Nørskov,²³ which explains the weaker F–Au interaction, compared to F–Cu interaction, by a more prominent Pauli repulsion. The performed population analysis confirmed the transfer of charge to the F adatom for all the studied metallic surfaces, but in the case of Cu and Au surfaces, the charge originated from the conduction *sp*-band, with the *d*-population remaining almost the same as for clean surfaces. In the cases of Pt(111) and Pd-monolayer surfaces, the *d*-states were significantly redistributed both above and below the Fermi level (Fig. 4), which indicated a higher contribution of covalent bonding in the interaction in comparison to the Cu and Au surfaces. In the case of Pt(111) and Pd-based surfaces, the charge transfer to F adatom was mainly from *d*-states although *sp*-states also contributed to some extent. It is also important to note that the charge redistribution was limited to the adsorption site only, *i.e.*, it did not extend to the surface atoms not in contact with an F adatom.

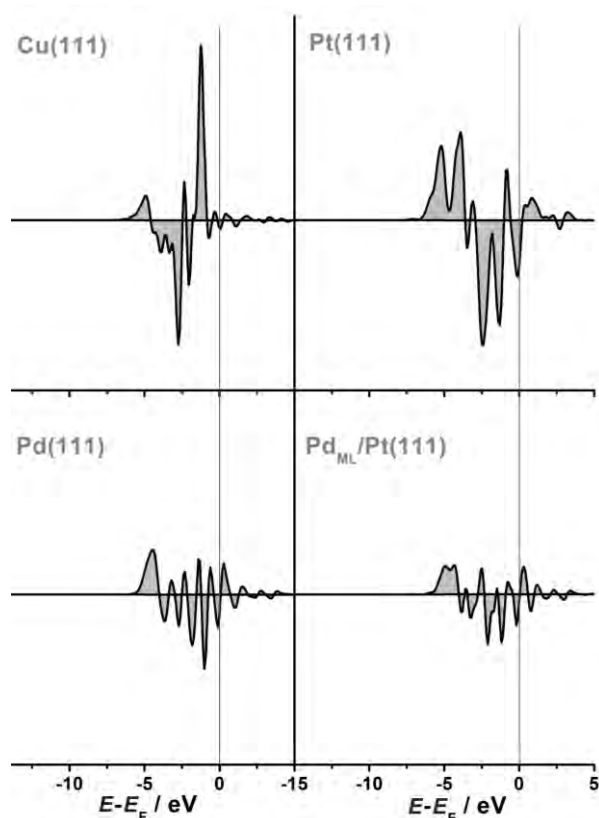


Fig. 4. Δ PDOS analysis of the modification of the *d*-band electronic structure of Cu(111) (top left), Pt(111) (top right), Pd(111) (bottom left) and Pd_{ML}/Pt(111) (bottom right) surface upon adsorption of fluorine. Pale vertical lines indicate the position of the Fermi levels.

CONCLUSIONS

In this contribution, fluorine adsorption was investigated on Cu(111), Au(111), Pd(111) and Pt(111) surfaces, as well as Pd monolayer surfaces involving Pd monolayers on Cu(111), Au(111) and Pt(111) surfaces and “sandwich” structures, denoted as $M_{\text{UND}}\text{Pd}(111)$. The selection of the analyzed substrates was made in such a way that the effects of electronic structure and work function on fluorine adsorption could be mutually discriminated. It was observed that fluorine adsorption did not result in significant structural changes of the metallic substrate. Among the investigated surfaces, F adsorbs most strongly on the Cu(111) surface with $E_{\text{F-M}}$ amounting to -4.49 eV. In the case of Pt and $\text{Pd}_{\text{ML}}/\text{M}(111)$ surfaces, it was found that binding energies scale with the d -band center position, which is characteristic for a significant contribution of covalent interaction. Cu(111) and Au(111) interact with F adatom through the sp -band, while Pt and Pd-based surfaces interact through the d -band too. The obtained results indicate that the nature of interaction of the highly electronegative F atom with metallic surfaces depended significantly on the nature of the metal, making possible to tailor the adsorption characteristics of metallic surface solely through modification of the d -band structure, while the population of the d -states and work function can be kept approximately constant. In spite of its large electronegativity, it can be concluded that the F–metal interaction is not purely ionic.

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ИЗВОД

АДСОРПЦИЈА ФЛУОРА НА ПОВРШИНАМА ПРЕЛАЗНИХ МЕТАЛА – DFT СТУДИЈА

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На бази теорије функционала густине испитивана је адсорпција флуора на површинама а) Cu(111), Au(111), Pd(111) и Pt(111), б) на монослојевима Pd преко површина монокристала Cu(111), Au(111) и Pt(111) и с) на површинама монокристала Pd(111) са убаченим монослојевима метала М (М = Cu, Au или Pt) одмах испод првог Pd слоја. Нису нађене значајне промене структурних параметара метала подлоге после адсорпције. Највећа енергија везе од $-4,91$ eV нађена је у случају површине Cu(111). Површински атоми Cu(111) и Au(111) интерагују са адатомом флуора посредством sp -траке, док површински атоми Pt и Pd интерагују и посредством d -траке. У случају Pt и површина типа $\text{Pd}_{\text{ML}}/\text{M}(111)$, уочено је да се енергије везе корелишу са положајем центра d -траке, што је индикација значајног доприноса ковалентне интеракције приликом адсорпције. Добијени резултати указују да природа интеракције изразито електронегативног флуора са металним површинама зависи значајно од природе метала.

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