A semiempirical quantum approach to possible structures of copper electrodeposits at submonolayer and monolayer levels on Pt(100) and Pt(111) clusters

M.B. López, G.L. Estiú, E.A. Castro and A.J. Arvia

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Sucursal 4, Casilla de Correo 16, (1900) La Plata, Argentina

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The development and reconstruction of surface structures formed by underpotential deposition (UPD) of Cu atoms on Pt(100) and Pt(111) clusters are approached through extended Hückel molecular orbital (EHMO) calculations applied to a statistical Cu atom deposition. These results allow us to obtain a qualitative description of the different stable configurations of Cu atoms on the Pt cluster surfaces in terms of the corresponding binding energies.

1. Introduction

The underpotential deposition (UPD) of atoms on a foreign metal substrate changes its electronic and structural characteristics, a fact which is interesting from the standpoint of heterogeneous catalysis including electrocatalysis [1–5]. The UPD of a foreign metal on noble metal electrodes has been extensively investigated [1,4,9–12], particularly in relation to its influence on the electro-oxidation of small molecules such as CO on Pt in acid solutions [4]. It should be noted that the complex structure of the electrochemical interface depends on both the electrode material and its structure, and the constituents of the solution in contact with the electrode. Accordingly, an electrochemical adsorbate–substrate system becomes more complex than the corresponding metal/gas system.

On the other hand, the knowledge of bimetallic structures at submonolayer and monolayer ranges provides new insights for those processes leading to surface reconstruction of the substrate (6–8). Thus, the UPD of Cu on Pt produces a bimetallic Pt_NCu_L system in contact with an aqueous electrochemical environment, a process

which implies potential and crystalline face dependent interactions between Cu and Pt atoms. Although for such a bimetallic system no definite vertical reconstruction has been concluded from either voltammetric [12] or optical [10,11] data, it appears that metastable bimetallic structures are initially produced and changed into other more stable ones. This type of surface reconstruction which is feasible when the interaction energy among substrate and UPD layer atoms becomes comparable to the interaction energy among atoms at the proper UPD metal layer, can be statistically described as a phase transition [13–16]. As a first approach foreign metal UPD on a metal substrate can be compared to a gas phase adsorption process influenced by the magnetization of the substrate [17,18]. In this case, M_S , the magnetization saturation of the system, can be approximately expressed as an excess of S , the spin of electrons in the metal [18]:

$$M_S \cong S^\uparrow - S^\downarrow, \quad (1)$$

where the arrows denote the spin directions. Accordingly, the adsorption of the foreign atom can be related to changes in the spin distribution of surface atoms. Therefore, the change in magneti-

zation can be regarded as the driving force leading to surface rearrangements at adsorbate–substrate domains. This type of process becomes extremely important in dealing with adsorbates such as the open-shell–high-electron-number transition metals.

Magnetization changes are usually described within a statistical framework, although this approach is rather limited for a quantitative description of structural characteristics of metal deposits, it allows one to envisage the microscopic mechanism of metal surface restructuring.

The present work refers to a molecular orbital calculation related to Cu UPD on Pt(100) and Pt(111) under different applied electric potentials to determine as a first approach the stability of the different structures emerging after a certain number of UPD Cu atoms has been accumulated on the Pt single crystal surface. The extended Hückel molecular orbital (EHMO) data presented in this work qualitatively accounts for the structural modifications of UPD Cu deposits on Pt which have been experimentally determined [19], and provides an explanation for the driving force operating the surface rearrangement at the Cu submonolayer level. The results derived from EHMO calculations are limited to establish only qualitative trends related to the influence of the structural parameters on the stability of different surface atom configurations. Accordingly, the MO interpretations of those calculations have only a qualitative predictive capacity.

2. Calculation procedure

For the EHMO method used in this work [20], one electron orbital attractive energies and core–core interatomic repulsive interactions are considered [21]. The off-diagonal energy matrix term, H_{ij} is multiplied by an $\exp(-0.13R_{ab})$ term to allow the interaction energy to decrease as R_{ab} increases. In this way it is possible to correct the long tailed diatomic dissociation curve resulting from standard EHMO methods.

The attractive component energy matrix elements are:

$$H_{ii}^{aa} = -(\text{VSIP})_i^a, \quad (2)$$

$$H_{ij}^{aa} = 0, \quad (3)$$

$$H_{ij}^{ab} = 1.125(H_{ii}^{aa} + H_{jj}^{bb})S_{ij}^{ab} \exp(-0.13R_{ab}), \quad (4)$$

where i and j denote atomic orbitals, and a and b correspond to different atoms. VSIP stands for the valence state ionization potential; S_{ij} is the overlap integral involving orbital i on center a , and orbital j on center b ; R_{ab} is the internuclear distance between centers a and b . The VSIP's are experimentally based [22,23] and valence orbitals are of the Slater's form with exponents based on SCF calculations [24–27].

Initially Cu atoms occupy the most reactive sites on Pt. At the electrochemical interface the

Table 1
Atomic parameters used in the calculation

Atom	System	s			p			d					
		<i>n</i>	ζ	VSIP (eV)	<i>n</i>	ζ	VSIP (eV)	<i>n</i>	ξ_1	VSIP (eV)	<i>C</i> ₁	<i>C</i> ₂	ξ_2
Pt	(A)	6	2.550	−8.96	6	2.250	−4.92	5	6.013	−9.56	0.6567	0.5715	2.390
	(B)	6	2.850	−10.95	6	2.550	−6.91	5	6.313	−11.55	0.6567	0.5715	2.420
	(C)	6	2.850	−11.35	6	2.550	−7.31	5	6.013	−11.95	0.6567	0.5715	2.420
Cu	(A)	4	1.850	−7.77	4	1.550	−3.98	3	5.950	−11.96	0.5589	0.5878	2.100
	(B)	4	2.150	−9.58	4	1.850	−5.79	3	6.250	−12.50	0.5589	0.5878	2.600
	(C)	4	2.150	−9.58	4	1.850	−5.79	3	6.250	−12.50	0.5589	0.5878	2.600

(A) Pt_NCu_L system (metal vacuum).

(B) Pt_NCu_L in aqueous media.

(C) Pt_NCu_L in aqueous media and UPD conditions.

n = principal quantum number for s and p orbitals, ζ = Slater orbital exponent, VSIP = valence state ionization potential, C_1 and C_2 are linear coefficients.

simultaneous interaction of Cu atoms, water molecules and Pt sites defines an adsorption ensemble characterized by a specific VSIP value. The latter is related to the equilibrium potential of the system. The VSIP value results when the charge transfer at the equilibrium distance of each internuclear bond is close to that predicted by the electronegativity difference of the diatomic bond resulting from Pauling's ionicity relationship [28]. Values assembled in table 1 define the zero potential conditions (reference potential) of the system.

The application of an electric potential can be simulated by either decreasing or increasing the VSIP's (table 1) for either positive or negative Pt surface charging, respectively. Various semiempirical approaches for the band shift caused by electric charging have been used for describing several electrochemical systems [29–33] including surface dopant effects [33,34]. According to one of them VSIP changes of ± 1.0 eV can be arbitrarily correlated to ± 1.0 V changes in the reference potential. Correspondingly, as the standard equilibrium potential of the Cu/Cu²⁺ electrode is $E^0(\text{Cu}/\text{Cu}^{2+}) = 0.34$ V (versus the standard hydrogen electrode), for attaining Cu UPD conditions the Fermi level of Pt has been set 0.4 eV above the reference potential.

Our metal atom clusters are high spin, meaning each d-band molecular orbital is occupied by at least one electron. Thus, while lower levels are doubly occupied, some other ones are singly occupied. The result is that the clusters have spin magnetic moments approximating bulk values. Bulk superimposable Pt_N clusters, *N* being equal to 25 for the Pt(100) and 24 for Pt(111), respectively (fig. 1), are used to model the Pt surfaces. The clusters are geometrically built up with the Pt–Pt bond length constant at 0.277 nm. The latter which has been used in previous calculations [29] agrees with the Pt–Pt interatomic distance in bulk Pt.

From the standpoint of the calculation procedure the initial growth of Cu deposit on Pt single crystals can be described, in principle, as an equilibrium adsorption process on a surface where all Pt atoms are represented by the [(Xe)4f¹⁴5d¹⁰] electronic structure.

Fig. 1. Schemes of atom surface layers describing [Pt(111)]₂₄ and [Pt(100)]₂₅.

Different types of adsorption sites can be defined on the surface of Pt single crystal structures, namely, top, bridge, and hollow sites. The latter are considered as equivalent and undistinguishable sites where Cu atom adsorption takes place. This situation remains until either a Cu₃ or a Cu₄ hollow site is formed. In this case two distinguishable and non-equivalent adsorption sites compete for the attachment of the incoming Cu atom.

The unpaired spin electronic configuration of Cu atoms [(Ar)3d¹⁰4s¹] is that of a fermionic system. Therefore, all adsorbed Cu fermions at the first adsorbate layer can be similarly oriented. No adsorbate–substrate spin pairing is possible when Cu atoms adsorb on Pt[(Xe)4f¹⁴5d¹⁰] atoms. For *L*, the number of Cu atoms adsorbed, a multiplicity $m = L + 1$ characterizes the first adsorbed layer. Hence, the high multiplicity of the Cu atom overlayer pushes the electronic spin of the incoming Cu atom in a direction opposite to that defining the first layer. Furthermore, when Cu atom aggregate structures are being formed on the Pt surface, they can reconstruct to a new one through spin pairing leading to a decrease in the total energy (fig. 2).

The preceding approach can be extended to the UPD of Cu at the electrochemical interface under the simplest assumption that the presence of water molecules modifies uniformly the surface energy characteristics of both Pt and Cu atoms. For the growth of the Cu overlayer on Pt a

Fig. 2. Scheme of a 2D atom monolayer rearrangement leading to a minimum energy spin configuration. (a) $L = 10 = 7^{\uparrow} + 3^{\downarrow}$, (b) $L = 10 = 5^{\uparrow} + 5^{\downarrow}$.

statistical model based upon molecular orbital calculations can be advanced, as the latter allows one to evaluate the stability of several Pt_NCu_L surface structures for different applied electric potentials.

3. Results and interpretation

For both $[\text{Pt}(111)]_{24}$ and $[\text{Pt}(100)]_{25}$ surfaces with N Pt atoms at the interacting surface, $\text{BE}(L)$, the Pt–Cu binding energy in the Pt_NCu_L surface system, decreases according to CN, the coordination number of the adsorption site (table 2), Cu atom deposition is, in principle, favored on Pt sites with the highest CN values, i.e., the site properties become important for defining the stability of the adsorbate structure. As previously discussed [35,36] the latter is also slightly influenced by underlying Pt atoms. However, it is possible to overcome this drawback by considering a sufficiently large monolayer Pt surface for modeling the adsorption of several Cu atoms.

The Cu monolayer on Pt is built up through the successive addition of Cu atoms, and correspondingly, the $\text{BE}(L)$'s for Cu atoms on either $[\text{Pt}(111)]_{24}$ or $[\text{Pt}(100)]_{25}$ decrease as L increases. Thus, when the Cu atom coverage becomes suffi-

Fig. 3. Structures resulting from the sequential attachment of 16 Cu atoms (numbered and dashed circles) on $[\text{Pt}(111)]_{24}$. The possible Cu atom rearrangement has been calculated at 0.4 V. ● spin down; ● spin up.

ciently large to make $\text{BE}(L)$ smaller than $\text{BE}(\text{Cu–Cu})$, the Cu–Cu atom binding energy, the second Cu atom layer starts to grow.

Although preferred Cu atom adsorption always takes place on higher CN sites regardless the number of Cu atoms previously adsorbed, the Cu monolayer growth also implies the appearance of different Cu-adsorption sites. For each value of L , however, the $\text{BE}(L)$ value depends on the substrate structure. Thus, the value of $\text{BE}(L)$ for CN = 4 on $[\text{Pt}(100)]_{25}$ is greater than the value of $\text{BE}(L)$ for CN = 3 on $[\text{Pt}(111)]_{24}$. This difference is reflected through the structure of Cu adsorbed layers. Thus, for $[\text{Pt}(100)]_{25}$ the higher the $\text{BE}(L)$ value the greater the trend of Cu atoms to occupy $N = 4$ sites. Conversely, for $[\text{Pt}(111)]_{24}$, as soon as a Cu_3 site has been formed Pt_3 and Cu_3 sites are competing for the adsorption of Cu(4) (tables 3 and 4).

The stabilization energy of different Cu adsorbate structures resulting when the second Cu layer starts to grow at 0.4 V is assembled in table 3. Accordingly, the first and the second Cu atom

Table 2
 $\text{BE}(L)$ values for Cu(1) on Pt(100) and Pt(111) surface sites as a function of the applied electric potential for $N = 4$ [35]

Adsorption site	$\text{BE}(L)$ (eV)					
	– 0.6 V		0.4 V		1 V	
	Pt(100)	Pt(111)	Pt(100)	Pt(111)	Pt(100)	Pt(111)
Top	0.978	0.706	1.657	1.297	2.921	2.623
Bridge	1.342	0.826	1.962	1.468	3.216	2.835
Hollow	1.728	1.049	2.256	1.653	3.629	3.032

Table 3

BE(*L*) values for Cu atom surface structures on [Pt(111)]₂₄ hollow sites according to the sequential attachment numbers shown in fig. 3

Cu atom <i>L</i>	Electrode potential					
	− 0.6 V		0.4 V		1.0 V	
	BE(<i>L</i>) (eV)	ΔBE(<i>L</i>) (eV)	BE(<i>L</i>) (eV)	ΔBE(<i>L</i>) (eV)	BE(<i>L</i>) (eV)	ΔBE(<i>L</i>) (eV)
1	1.435		2.044		3.323	
2	1.436	−0.22	1.993	−0.17	3.053	−0.27
3	1.424	0.00	1.914	−0.05	2.881	−0.13
4	1.758	0.47	1.980	0.09	2.803	0.02
5	1.360		1.910		2.737	
6	1.318		1.877		2.658	
7	1.986	0.67	2.216	0.35	2.745	0.26
8	0.556		0.93		1.447	
9	1.964	0.90	2.231	0.77	2.963	0.78
10	1.314		1.53		2.168	
11	1.137		1.485		2.089	
12	2.040	1.00	2.429	1.04	2.841	
13	1.073		1.392		2.012	
14	1.024		1.373		1.851	
15	2.196	1.13	2.428	1.14	2.938	1.15
16	1.046		1.304		1.777	
1 + 2 + 3	4.296		5.852		9.256	
5 + 6 + 7	4.665		5.997		8.141	
1 + 2	2.871		4.037		6.375	
8 + 9	2.530		2.395		4.410	

ΔBE(*L*) values correspond to the Cu atom binding energy difference in the first and in the second Cu atom layer. Positive values indicate that the adsorption on the second layer is favored.

Table 4

BE(*L*) values for Cu atom surface structures on [Pt(100)]₂₅ hollow sites according to the sequential attachment numbers shown in figs. 5a–5c; ΔBE(*L*) is defined in table 3

Cu atom <i>L</i>	Electrode potential					
	− 0.6 V		0.4 V		1.0 V	
	BE(<i>L</i>) (eV)	ΔBE(<i>L</i>) (eV)	BE(<i>L</i>) (eV)	ΔBE(<i>L</i>) (eV)	BE(<i>L</i>) (eV)	ΔBE(<i>L</i>) (eV)
1	2.460		2.580		3.367	
2	1.920		2.530		3.230	
3	1.880		2.490		3.210	
4	2.380		2.430		3.100	
5	1.770	−0.60	2.380	−0.32	3.050	−0.35
6	1.620	−0.52	2.350	−0.25	2.890	−0.21
7	1.100	1.26	2.060	−0.04	2.676	−0.01
8	1.630		2.118	0.11	1.447	0.12
9	1.180		1.110		2.550	
10	2.530	1.59	2.400		2.100	
11	1.170		1.660	1.31	1.890	
12	2.730	1.79	2.460	1.07	2.940	1.09
13	1.160		1.550		1.860	
14	2.760	1.84	2.640		1.850	0.07
15	2.050		1.230		2.770	

layer can grow simultaneously on $[\text{Pt}(111)]_{24}$ leading to distinguishable bimetallic structures of similar energies (fig. 3), involving Cu atom aggregates of different sizes interacting with the substrate. In this case there is no univocal sequence for Cu atom adsorption. For L smaller than or equal to the number of Cu atoms constituting the Cu monolayer, the attachment of the following Cu atoms leads to a heterogeneous surface consisting of Cu aggregates and bare Pt domains.

The subsequent location of Cu(5) on a site adjacent to a Cu_4 pyramidal cluster cannot be directly determined by comparing the corresponding $\text{BE}(L)$ value to that of Cu(1) adsorption on bare $[\text{Pt}(111)]_{24}$ (table 3). However, a stable structure can be achieved by attaching three Cu atoms at sites adjacent to the Cu_4 pyramidal cluster yielding a unique seven Cu atoms aggregate. This type of structure on $[\text{Pt}(111)]_{24}$ is comparatively more stable than that consisting of two separate Cu_4 and Cu_3 clusters (table 3).

A similar calculation can be extended to the adsorption sequences Cu(1) and Cu(2), and Cu(8) and Cu(9) on $[\text{Pt}(111)]_{24}$ (fig. 3). In this case the most favorable site for the adsorption of Cu(8) is one far from that occupied by Cu(7) in the bilayer structure. Because of the fact that Cu clusters of different sizes can be simultaneously formed on $[\text{Pt}(111)]_{24}$ the Cu_5 -based adsorption structures appear as the most likely ones.

Applied electric potentials which are set positive with respect to $E^0(\text{Cu}/\text{Cu}^{2+})$ tend to stabilize the Cu monolayer domains. Otherwise, as the applied potential approaches $E^0(\text{Cu}/\text{Cu}^{2+})$, 2D to 3D changes at the Cu monolayer leading to the lowest energy Cu adsorbate structures are favored through the rearrangement of electronic spins of Cu atoms (table 3). Therefore, the most stable structure implies the minimization of the total electronic spin (fig. 4).

The adsorption of Cu(5) on a Cu_4 hollow site formed on $[\text{Pt}(100)]_{25}$ does not require the cancellation of unpaired spins as it is the case of a Cu_3 hollow site on $[\text{Pt}(111)]_{24}$. Structures almost similarly stable are achieved when either the Cu monolayer or a Pt–Cu bilayer structure is grown on $[\text{Pt}(100)]_{25}$ (fig. 5). In this case, nearly a similar decrease in $\text{BE}(L)$ is attained by reorienting the

Fig. 4. Scheme of a Cu atom monolayer structure on $[\text{Pt}(111)]_{24}$ surface. (a) Parallel spin Cu atoms arrangement, $E = -5055.41$ eV, (b) antiparallel spin Cu atoms arrangement, $E = -5066.87$ eV. E denotes the total energy of the Cu atom monolayer. $\bullet$ spin down, $\circ$ spin up.

electronic spins of adsorbed Cu atoms (fig. 6). Incidentally, it should be noted that for $[\text{Pt}(100)]_{25}$ the Cu monolayer is formed easier than for $[\text{Pt}(111)]_{24}$. This fact can explain why Pt bare areas, probably constituted by Pt(111) domains, remain on polycrystalline Pt during Cu UPD [12].

Fig. 5. Surface Cu atom (numbered and dashed circles) structures resulting on $[\text{Pt}(100)]_{25}$ at different applied electric potentials. (a) 0.4 V, (b) 1.0 V, (c) -0.6 V. The numbers indicate the Cu atom attachment sequence. Possible Cu surface atom rearrangements are indicated. $\bullet$ spin down, $\circ$ spin up.

Fig. 6. Scheme of a Cu atom monolayer structure on [Pt(100)]₂₅ surface. (a) Parallel spin Cu atoms arrangement, $E = -4778.52$ eV, (b) antiparallel spin Cu atoms arrangement, $E = -4787.18$ eV. E denotes the total energy of the Cu atom monolayer. ● spin down, ○ spin up.

The application of a positive electric potential to [Pt(100)]₂₅ also changes the BE(Cu–Cu) in the direction of increasing the Cu monolayer formation (table 4) as for [Pt(111)]₂₄. Otherwise, the application of a negative electric potential to [Pt(100)]₂₅ turns out the growth of the Pt–Cu bilayer structure easier than on [Pt(111)]₂₄. Accordingly, a different Cu atom attachment sequence has to be considered.

4. Comparison with experimental data

There is experimental evidence [12] that Cu UPD on Pt electrodes in acid solutions implies the spontaneous and reversible formation of 3D Cu aggregates either just before or immediately after the completion of the Cu monolayer. The relaxation of 2D Cu domains yields 3D Cu aggregates at the substrate surface simultaneously with the appearance of bare Pt domains. The latter are revealed through the H-atom electrosorption process [12]. On the other hand, by setting the potential more negative than $E^0(\text{Cu}/\text{Cu}^{2+})$ the formation of a 3D phase Cu atom overlayer is favored. Therefore, the Pt–Cu bimetallic structures and BE(L) values resulting through the present calculations agree with the conclusions derived from electrochemical data.

Calculated data also show that the relaxation of the UPD Cu layer is facilitated on Pt(111) (fig. 6) as it also occurs on Pt(100), although for the latter, the spin reorganization is further assisted through the proper 2D initial Cu structures.

The applied electric potential modifies the relative BE(L) values of both 3D and 2D aggregates on both [Pt(111)]₂₄ and [Pt(100)]₂₅. Thus, at a sufficiently high positive potential the lower energy metal orbitals involved in the adsorption process favor the growth of Cu aggregates with several Cu atoms, but from the electrochemical standpoint this situation is counterbalanced by the most favorable ionization process of Cu atoms.

On the other hand, for applied electric potentials lower than $E^0(\text{Cu}/\text{Cu}^{2+})$ the formation of highly stable bilayer structures takes place. In this case, the spontaneous rearrangement of the Cu structures at the monolayer level is accomplished on both [Pt(111)]₂₄ and [Pt(100)]₂₅.

5. Molecular orbital interpretation

The electronic configuration of Cu implies that the adsorption of Cu(1) on both [Pt(111)]₂₄ and [Pt(100)]₂₅ results in a reactive submonolayer with an unpaired electronic spin. The same situation arises for the adsorption of a single Cu atom on the stable Cu monolayer itself.

Otherwise, on [Pt(111)]₂₄ for $L = 3$, different submonolayer configurations can be produced which are characterized by either $(L - 1)$ or $(L + 1)$ unpaired spins (fig. 7) offering at least two possible substrate structures after the adsorption of Cu(4). These examples show how the second Cu atom layer growth implies the appearance of the lowest energy surface structures. However, when adjacent Pt hollow sites are completely occupied by Cu atoms, the lowest energy configuration is attained through a reorganization of the Cu monolayer (fig. 7). In this case the greatest adsorbate stability corresponds to those configurations involving the lowest multiplicity due to the filling of the higher energy levels, driving the evolution of the system towards the mutual cancellation of spins.

On the other hand, on [Pt(100)]₂₅ for $L = 4$ configurations characterized by $(L - 1)$ and $(L + 1)$ unpaired spins resulting from the adsorption of Cu(5) on either the second or the first adsorbate layer. The energy values resulting in this case are about 50 percent lower than that resulting for

Fig. 7. Diagram of energy levels characterizing different electronic configurations associated with Cu aggregates on $[\text{Pt}(111)]_{24}$.

$[\text{Pt}(111)]_{24}$. Unfortunately, as the energy values of both adsorbate configurations are very close, it remains uncertain whether the second Cu atom layer starts to grow either before or after the Cu monolayer structure becomes stable.

6. Discussion

The preceding analysis indicates that orientation of the unpaired spins of Cu atoms plays an important role in determining the lowest energy configuration for the Cu atom overlayers on Pt single crystal structures.

Let us consider that Pt adsorption sites at well defined crystallographic faces are characterized by a closed shell structure (fig. 2). For $[\text{Pt}(111)]_{24}$ the Cu(1) adsorption leads to a Pt_3Cu adsorbate ensemble, the latter appearing as an adsorption site itself. Further incorporation of Cu atoms lead to two kinds of adsorption sites, namely Cu_3 site with a multiplicity $m = 4$ (three parallel electron spins), and Pt_3 site defined by the close shell Pt atoms. These two kinds of sites which are considered as mutually independent, are competing for Cu(4) adsorption. When the latter occurs at a Cu_3 site, an adsorbate structure with $m = 3$ is

produced, resulting from 2 parallel and 2 antiparallel electron spins. Otherwise, when Cu(4) adsorption takes place on a Pt_3 site, an adsorbate structure with $m = 5$ results from four parallel electron spins of adsorbed Cu atoms. The stability of these systems (fig. 7) increases by filling progressively the lower energy orbitals. Correspondingly, the total energy of the system decreases according to m .

On the other hand, for $[\text{Pt}(100)]_{25}$ when either a Cu_7 ensemble at UPD or a Cu_6 ensemble at OPD (over potential deposition) has been formed (table 4), two kinds of adsorption sites are present, namely a Cu_4 site with $m = 5$ (four parallel electron spins), and a Pt_4 site defined by close shell Pt atoms. These sites are competing for either Cu(8) or Cu(7), respectively. For the UPD-built Cu_7 ensemble the adsorption of a Cu atom at a Cu_4 site leads to an adsorbate structure with $m = 7$ (six parallel and two antiparallel electron spins). Otherwise, Cu adsorption at sites adjacent to a Pt_4 -site increases m to 9 (eight parallel electron spins of adsorbed Cu atoms).

Furthermore, when sites adjacent to Cu aggregates are occupied by Cu atoms with parallel electronic spins, the assumption that adsorption sites are equivalent and mutually independent ones, is no longer valid because of the strong interactions among adsorbed particles at distinguishable surface domains. In this case, the initial structure of Cu atom aggregate turns into a new one of lower energy produced through electron spin pairing. Accordingly, the multiplicity of the adsorbate ensemble appears again as the driving force for the Cu overlayer rearrangement. The mechanism of this process can be considered as a phase transition involving a magnetization change as the driving force assisting the reordering of the adsorbate-substrate domains. The qualitative evaluation of this possibility, however, is beyond the abilities of the EHMO calculations [37,38].

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References

- [1] N. Furuya and M. Shibata, *J. Electroanal. Chem.* 266 (1989) 461.
- [2] M. Shibata and N. Furuya, *J. Electroanal. Chem.* 269 (1989) 217.
- [3] M. Shibata, N. Furuya, M. Watanabe and S. Motoo, *J. Electroanal. Chem.* 263 (1989) 97.
- [4] J. Clavilier, A. Fernández Vega, J.M. Feliú and A. Aldaz, *J. Electroanal. Chem.* 258 (1989) 89.
- [5] I.T.E. Fonseca, A.C. Marin and D. Pletcher, *J. Electroanal. Chem.* 218 (1987) 327.
- [6] E. Schmidt and H. Siegenthaler, *J. Electroanal. Chem.* 150 (1983) 59.
- [7] A. Bewick and B. Thomas, *J. Electroanal. Chem.* 85 (1977) 320.
- [8] A. Bewick and B. Thomas, *J. Electroanal. Chem.* 84 (1977) 127.
- [9] B.S. Parajón Costa, C. Canullo, D. Vásquez Moll, R.C. Salvarezza, M.C. Giordano and A.J. Arvia, *J. Electroanal. Chem.* 244 (1988) 261.
- [10] D.M. Kolb and R. Kötz, *Surf. Sci.* 64 (1977) 698.
- [11] D.M. Kolb, A. Kötz and K. Yamamoto, *Surf. Sci.* 87 (1979) 20.
- [12] D. Margheritis, R.C. Salvarezza, M.C. Giordano and A.J. Arvia, *J. Electroanal. Chem.* 229 (1987) 327.
- [13] R. Kubo, *Statistical Mechanics*, 1st ed. (North-Holland, Amsterdam, 1965) pp. 302–312.
- [14] R.K. Pathria, *Statistical Mechanics* (Pergamon, Oxford, 1986) p. 87.
- [15] L.E. Reichl, *A Modern Course in Statistical Physics* (Oxford Press, Oxford, 1980) pp. 106–120, 280–297.
- [16] A.B. Anderson, *J. Chem. Phys.* 6 (1975) 1185.
- [17] P.W. Selwood, *Chemisorption and Magnetization* (Academic Press, New York, 1975).
- [18] R. Fournier and D.R. Salahub, *Surf. Sci.* 238 (1990) 330; F. Raatz and D.R. Salahub, *Surf. Sci.* 176 (1986) 219; D.R. Salahub and F. Raatz, *Int. J. Quantum Chem. Symp.* 18 (1984) 173; R. Fournier and D.R. Salahub, *Int. J. Quantum Chem.* 29 (1986) 1077.
- [19] R.J. Nichols, D.M. Kolb and R.J. Behm, *J. Electroanal. Chem.* 313 (1991) 109.
- [20] J. Howell, A. Rossi, D. Wallance, K. Haraki and R. Hoffmann, *FORTICON 8*, Program No. 344, ECPE (Cornell University Press, Ithaca, 1977).
- [21] G.L. Estiú, S.A. Maluendes, *Z. Phys. Chem. (Leipzig)* 271 (1990) 846.
- [22] W. Lotz, *J. Opt. Soc. Am.* 60 (1970) 206.
- [23] C.E. Moore, *Atomic Energy Levels*, NBS circular 467, National Bureau of Standards (US Government Printing Office, Washington, DC, 1958) pp. 115–123.
- [24] E. Clementi and D.L. Raimondi, *J. Chem. Phys.* 38 (1963) 2686.
- [25] E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, 14 (1974) 427.
- [26] J.W. Richardson, W.C. Nieuwpoort, R.R. Powell and W.F. Edgell, *J. Chem. Phys.* 36 (1962) 1057.
- [27] H. Basch and H.B. Gray, *Theor. Chim. Acta* 4 (1966) 367.
- [28] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell University Press, Ithaca, NY, 1960) p. 45.
- [29] G.L. Estiú, S.A. Maluendes, E.A. Castro and A.J. Arvia, *J. Phys. Chem.* 92 (1988) 2512.
- [30] G.L. Estiú, S.A. Maluendes, E.A. Castro and A.J. Arvia, submitted.
- [31] G.L. Estiú, S.A. Maluendes, E.A. Castro and A.J. Arvia, *J. Electroanal. Chem.*, submitted.
- [32] A.B. Anderson and D.P. Onwood, *Surf. Sci.* 154 (1985) L261.
- [33] A.B. Anderson and M.K. Awad, *J. Am. Chem. Soc.* 107 (1985) 7854.
- [34] N.K. Ray and A.B. Anderson, *Surf. Sci.* 125 (1983) 803.
- [35] M.B. López, G.L. Estiú, E.A. Castro and A.J. Arvia, *J. Mol. Struct. (THEOCHEM)* 210 (1990) 353.
- [36] M.B. López, G.L. Estiú, E.A. Castro and A.J. Arvia, *J. Mol. Struct. (THEOCHEM)* 210 (1990) 365.
- [37] F. Pilar, *Elementary Quantum Chemistry* (McGraw-Hill, New York, 1968) pp. 584–644.
- [38] H.S. Green and C.A. Hurst, *Order–Disorder Phenomena*, *Monographs in Statistical Physics and Thermodynamics* (Wiley, London, 1964) pp. 123–136.