

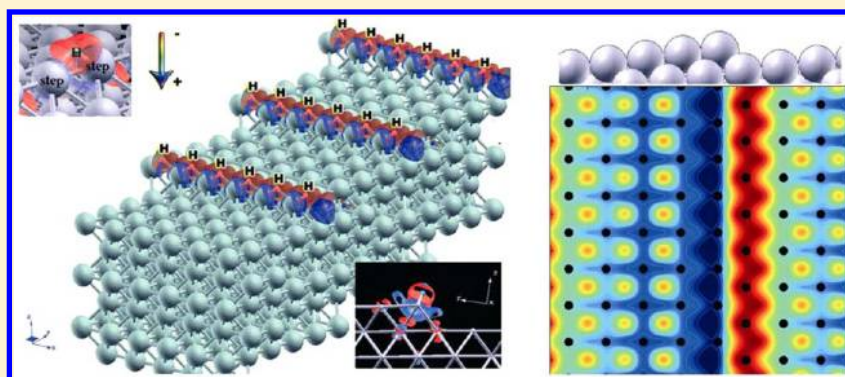
Electronic Anisotropy at Vicinal Ag(11*n*) Surfaces: Work Function Changes Induced by Steps and Hydrogen Adsorption

Maria F. Juárez[‡] and Elizabeth Santos^{*†‡}

[†]Facultad de Matemática, Astronomía y Física, Instituto de Física Enrique Gaviola (IFEG-CONICET), Universidad Nacional de Córdoba, 5000 Córdoba, Argentina

[‡]Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

S Supporting Information



ABSTRACT: We have systematically analyzed both the electrical dipole originated by the presence of steps and that produced by the H–Ag bond at different sites of the vicinal Ag(11*n*) surfaces. We have considered both basal planes as reference systems. We have taken into account relaxation, coverage, and structural effects. An anisotropy of the electronic properties has been found along the terraces between steps. Long-range interactions and localization effects have been identified.

INTRODUCTION

Hydrogen–metal interactions is one of the most investigated topics in surface science. A classical review by Christmann¹ summarizes the most important aspect of hydrogen adsorption. More recently, Ferrin et al.² have given a broad outline of the research done on this topic focusing mainly on single-crystal surfaces. As pointed out by Gross in a perspective paper,³ the interaction of hydrogen with metal surfaces is as relevant as ever and will continue to be interesting and important. These interactions play an important role in a variety of practical problems, such as corrosion, hydrogen storage, hydrogenation processes, electrosynthesis, heterogeneous catalysis, and electrocatalysis. Particularly, we are interested in the hydrogen evolution and oxidation reactions, which are important reactions in fuel cells.^{4–7} They are inner-sphere reactions, with rates varying by about 6 orders of magnitude on various electrodes.⁸

The interaction of hydrogen with metal surfaces is of fundamental interest to theoreticians. In principle, hydrogen is the prototype of a simple adsorbate. Nevertheless, the phenomena involved in its interactions with the substrates are not simple but show a strong dependence on the specific metal, crystallographic orientation, surface coverage, etc. We can distinguish three groups of metallic substrates: first, transition metals such as Pt or Ir, where molecular hydrogen dissociates spontaneously and the oxidation reaction occurs very fast and

as a consequence is difficult to investigate; second, sp metals such as Hg and Cd, which are practically inactive and therefore less interesting; finally, coin metals such as Au, Ag, and Cu, where dissociation is activated and the electrochemical oxidation reaction is not too fast to be investigated in detail over a large range of overpotentials. Concerning the latter three metals, in the case of Cu it is very difficult to obtain a clean, reproducible surface. The surface of Au reconstructs very easily, and hence, it is inappropriate to analyze structural effects. Thus, Ag surfaces appear as the ideal substrates to understand metal–hydrogen interactions. Because of the differences in electronic properties, the binding energy of H–Ag is lower than that corresponding to transition metals, but once hydrogen has adsorbed, the properties should be quite similar to those of the transition-metal system, as asserted by Lee and Plummer.⁹ Interesting are experiments where hot electrons are injected in the range of 0–2.5 eV above the Fermi level of silver, causing hydrogen evolution at electrode potentials more positive than those needed in common electrochemistry.^{10,11} The understanding of these phenomena, which open a new field of future applications, requires a detailed comprehension of H–Ag interactions.

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Surface adatoms and vacancies with low coordination, islands and steps, behave rather differently compared to flat surfaces, and usually they are more active. A systematic study of the reactivity of nanostructures requires a precise control of the number of superficial defects. Using stepped surfaces is an effective method to achieve this aim; therefore, they are frequently chosen as model objects.¹² Thus, the interaction of hydrogen with stepped surfaces is an important topic to be explored.

An extremely sensitive probe of chemisorption is the adsorbate-induced work function changes. This property is directly related to the charge transfer process between the reactant and metal, allowing the characterization of bond polarity.¹³ As a first approximation, the sign of the change of the work function gives information on whether the adsorbate is positively ($\Delta\Phi < 0$) or negatively ($\Delta\Phi > 0$) polarized. Yanagisawa et al. have given an interesting discussion about the origin of this interfacial dipole.¹⁴ For hydrogen adsorption on clean, flat surfaces, quite often an increase of the work function occurs, with few exceptions. The frequently observed increase indicates a net flow of electron from the metal to the hydrogen (usually less than $0.1 e_0$). Thus, the resulting dipole after adsorption is quite small, suggesting an almost covalent bond. In the simplest cases, a linear relationship between coverage and changes of work function is found, and this is a good approach to determine the amount of adsorbed species. When the hydrogen adsorption induces relaxation of the metal atoms involved in the bond, or reconstruction phenomena take place, additional surface charge rearrangements occur, which also contribute to the change of the work function. In these cases, an analysis becomes more complicated. So far, there have not been any systematic investigations for different systems of the effect of coverage on the work function. Christmann¹ shows a compilation of results for different systems. Although a broad variety of experimental data are available, there is still a lack of understanding, because it is difficult to separate structural and electronic effects. In the case of stepped surfaces, the electronic and energetic heterogeneity is still larger. The presence of steps and defects can also induce changes in the work function of clean surfaces due to the Smoluchowski effect.¹⁵ In an electrochemical environment, an interesting correlation exists between the potential of zero charge (E_{pzc}) and the work function.^{8,12,13,16,17} Therefore, in the absence of specific adsorption of anions, the change ΔE_{pzc} can also be expressed, to a good approximation, in terms of the dipole moment per step atom p_z .¹⁷

In this study, we perform a theoretical approach to analyze the different factors affecting the work function of vicinal surfaces of Ag(11*n*). Work function changes are global values containing both electronic and structural changes. As mentioned above, it is impossible from experimental measurements to separate these contributions. An advantage of theoretical calculations is that, using appropriate conditions, it becomes possible. We have previously applied this strategy to distinguish between geometrical and chemical effects in monolayers of a foreign metal deposited on different substrates by using artificial lattice constants.¹⁸

Since the sites of the terraces and the sites of the steps of Ag(11*n*) surfaces are the same as those in the planar (100) and (111) surfaces, respectively, we shall consider both basal planes as reference systems. We shall systematically analyze the electrical dipole originated by the presence of steps and that produced by the H–Ag bond at different sites. We shall take

into account relaxation and structural effects. The present work is an extension of another work, where the focus is in the energetics and electronics of Ag–H bonds.¹⁹

■ COMPUTATIONAL METHODS

Periodic density functional theory (DFT) calculations based on plane waves have been performed as implemented in the DACAPO code.²⁰ Ultrasoft pseudopotentials²¹ were used to describe the electron–ion interactions for all atomic species. The wave functions and charge densities were expanded by plane-wave basis sets with cutoffs of 350 and 600 eV, respectively. The Perdew–Burke–Ernzerhof (PBE) formulation²² has been employed for the exchange and correlation functionals.

Silver surfaces have been modeled using periodically repeated slabs with a vacuum layer of 10 Å between them. In constructing the slabs, we used $a_0 = 4.142$ Å for the lattice constant, which compares very well with the experimental value of 4.09 Å.²³ Planar (100) and (111) surfaces have been described using (2×2) and (3×3) supercells with five metal layers.

Monatomic steps have been modeled by the vicinal Ag(11*n*) surfaces (*n* is an odd integer), which have (100)-oriented terraces and (111)-oriented steps. Their unit cells contain $m = (n + 1)/2$ silver atoms exposed in the surface and two of them located in the step. (1×1) and (2×1) supercells, containing $5m$ metal layers, were used to study the vicinal surfaces.¹⁹

Brillouin-zone (BZ) integrations were performed with the $8 \times 8 \times 1$ Monkhorst–Pack²⁴ mesh corresponding to the (1×1) unit cell of the (100) surface. H atoms were adsorbed on one side of the slab; therefore, and to compensate the work function difference between two sides of the slab, we employed the dipole correction.²⁵

In the geometry optimization of slabs, all the adsorbate atoms and the 2 or the $2m$ topmost metal layers were allowed to relax in planar or vicinal surfaces, respectively.

The work function Φ was calculated using the expression⁸

$$\Phi = \varphi(\infty) - E_F \quad (1)$$

where φ corresponds to the electrostatic potential and E_F to the Fermi level energy. There are various phenomena that can induce changes in the work function of a metal, such as the creation of defects (steps, adatoms, vacancies)²⁶ or the adsorption of species.²⁷ In a first approach, we neglect depolarization effects and exchange–correlation (XC) terms. The latter contribution can be important for a local work function, usually defined at distances close to the surface,²⁸ but these terms are usually 1 order of magnitude lower for work functions defined as a global property.²⁹ Therefore, the mathematical expression for the work function change can be approximated by the Helmholtz equation:

$$\Delta\Phi = \frac{q_e n_s}{\epsilon_0} \Delta p_z \quad (2)$$

where q_e is the elemental charge and ϵ_0 the electrical permeability in a vacuum, n_s is the density of defects or the concentration of adsorbates at the surface which originate the changes in the surface dipole, and Δp_z is the normal components of the dipole moment changes. Here, it is assumed that the potential in the interior of the metal remains unchanged.³⁰ In our case, we shall consider two different sources of this change: the presence of steps and the adsorption

of hydrogen. The reference state will be the planar surface in the first case, whereas for the adsorption of hydrogen, we shall take the same surface (planar or vicinal) in the absence of the hydrogen atoms. The dipole caused by the formation of an adsorbate–metal bond has three main contributions: the chemical effect induced by a partial charge transfer between the adlayer and the metal surface, the change in the intrinsic metal surface dipole because of the modification of the metal electron density tail induced by the presence of the adsorbate, and the changes induced by the metal in the intrinsic dipole of the adsorbate. Obviously, these effects are hard to separate from each other. The hydrogen atom itself does not have any dipole moment; therefore, the resulting dipole just arises from the formation of the H–Ag bond.

We have used two different ways to calculate the work function shifts, a direct and an indirect method. The direct method consists of calculating the difference between the work functions of the modified and the unmodified systems, calculated separately through eq 1. The second method is related to the calculation of the dipole moment changes Δp_z induced by the modification of the surface (in our case the presence of steps or the adsorption of hydrogen) and is given by the general approach used by Michaelides et al.:^{28,29,31,32}

$$\Delta p_z = \int_{-a}^{-a+z_0/2} z \Delta \rho(z) dz \quad (3)$$

Here z is the coordinate perpendicular to the surface plane, $z_0/2$ is half the length of the unit cell in the z direction, and a is the distance from the center of the slab to the top of the surface layer. $\Delta \rho(z)$ is the electronic charge density difference at z , averaged over the xy plane in the unit cell region:

$$\Delta \rho(z) = \int_{\text{unit cell}} \Delta \rho(x, y, z) dx dy \quad (4)$$

With this definition, a positive (negative) value of Δp_z indicates a dipole oriented to the vacuum (surface) side, and its presence produces a decrease (increase) of the work function. Further details on the calculation of the charge density difference will be given in the corresponding sections.

RESULTS AND DISCUSSION

Effect of Hydrogen Adsorption on the Work Function of the Ag(111) and Ag(100) Surfaces. Table 1 shows the work function of the bare and H-covered surfaces for different adsorption sites. The values corresponding to the dipole created between the H atom and the silver surface are also shown. The calculated work functions of the bare surfaces using eq 1 are 4.25 and 4.48 eV for the Ag(100) and Ag(111) bare surfaces, respectively. These values are very close to the

Table 1. Work Function and Surface Dipole Moment for Silver Surfaces Covered by Hydrogen ($\theta = 0.25$, 2×2 Cell) at Different Adsorption Sites

site	Ag(100)		Ag(111)	
	$\Phi_0 = 2.248$ eV	$\Phi_0 = 4.475$ eV	$\Delta\Phi$ /eV	Δp_z /e Å
hollow	−0.03	+0.005		
fcc			0.08	−0.013
hcp			0.07	−0.012
top	0.78	−0.148	0.48	−0.078
bridge	0.29	−0.056		

experimental data. Effectively, Chelvayohan and Mee have reported a value of 4.22 ± 0.02 eV for Ag(100) and a value of 4.46 ± 0.02 eV for Ag(111), when the surface is adequately treated to eliminate sulfur traces coming from the bulk.³³ These values also compare very well with previous calculations.^{2,33,34}

The changes produced in the work function by adsorption of hydrogen strongly depend on the local bonding geometry. Here, we show results for configurations corresponding not necessarily to global minima of energy but to local minima of energy. A thermodynamic study of chemisorption is the topic of another paper.¹⁹

In most of the cases, an increase of the work function is observed, due to the fact that the H–Ag bond produces a dipole pointing from the H atom to the surface. Such an increase of the work function is expected, since the electronegativity of hydrogen is higher than that of metals. In almost all cases studied, the silver surface gives electrons to the H atom; therefore, hydrogen becomes slightly negatively charged, and the work function increases.

In a 4-fold hollow site, the electron density can spread out wider than in other cases; therefore, hydrogen adsorbed on this site produces changes in the work function that are lower than those on bridge (brd) or top positions. Moreover, the changes corresponding to the 4-fold-hollow site show an opposite sign. Similar behavior is observed by the adsorption of hydrogen on either fcc or hcp sites of the Ag(111) surface. Here, the work function slightly increases. Larger changes occur when hydrogen adsorbs on the top position. Anyway, this is not an energetically favorable site.^{2,19,35} Within the uncertainty of DFT, Ferrin et al. have obtained values similar to our calculations for the hydrogen adsorption on fcc-Ag(111) and on brd-Ag(100) ($\Delta\Phi = 0.11$ and 0.32 eV, respectively).² To the best of our knowledge, there are no experimental data for changes in the work function by hydrogen adsorption on Ag(100) surfaces. Lee and Plummer⁹ have measured a hydrogen-induced work function change of $\Delta\Phi = +0.32$ eV for a coverage of about $\theta = 0.5$ at the Ag(111) surface. This value decreases to $\Delta\Phi = +0.18$ eV for a coverage similar to our conditions of $\theta = 0.25$. The high-resolution electron energy loss (HREEL) spectra indicate that the binding site is a 3-fold hollow site and reveal appreciable H–H lateral interactions. The authors claim that this is an uncharacteristically large value for a close-packed surface and assign this result to surface structural changes. Effectively, they confirm the induced reconstruction by low-energy electron diffraction (LEED) studies. Zhou et al. reported a decrease in the work function of the Ag(111) surface ($\Delta\Phi = -0.17$ eV) exposed to saturation atomic deuterium.³⁶ An increase of $\Delta\Phi = +0.22$ eV was measured for a metastable hydrogen saturation coverage on the Ag(110) surface by Sprunger and Plummer.³⁷

To obtain a better understanding of the electronic effects on the H–Ag interactions, we shall estimate how much charge is actually transferred to (from) the hydrogen atom.

We have compared three different methods to calculate the charge accumulated or depleted during the adsorption: Bader analysis (method 1), which is an intuitive method to calculate the charge enclosed around an atom,^{38–41} and Löwdin population analysis (method 2), which uses a transformation of all the atomic orbitals to an orthogonal basis that automatically restricts the number of electrons in each transformed atomic orbital to the correct range.^{42,43} These two methodologies are well-known techniques, and they are

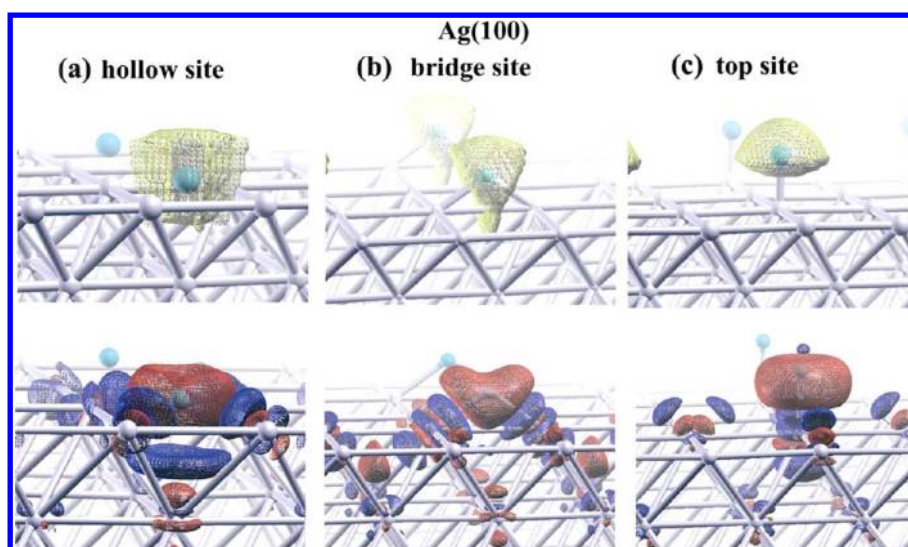


Figure 1. Redistribution of charge after adsorption of hydrogen at different sites of the Ag(100) surface ($\theta = 0.25$). Upper panel: view of the Bader surface around the hydrogen atom. The values obtained for the integration over the Bader volumes are given in Figure 3. Bottom panel: charge differences obtained from eq 5. Red and blue colors correspond to electron accumulation and depletion, respectively. The $0.0015 \text{ e } \text{Å}^{-3}$ isosurface has been plotted with the XCRYSDEN package.⁴⁵

not going to be explained here. Both methods can lead to results quite unreasonable if diffuse basis functions lacking pronounced atomic character are present.⁴⁴

Figure 1 (upper panel) shows the 3D plots of the Bader surfaces around the adsorbed hydrogen atom at the three different sites, i.e., hollow, bridge, and top, of Ag(100) surfaces. The calculated accumulated charges obtained by integration of the electronic density over these Bader regions were 0.23 electron for both hollow and bridge sites and 0.20 electron for the top site. The corresponding values obtained by the Löwdin method yield 0.21, 0.20, and 0.14 electron, respectively. Similar values were obtained with both methods for the fcc, hcp, and top sites of the Ag(111) surface (for more numerical details, see S1-Table in the Supporting Information). In any case, the flow of charge from the metal to the adsorbed hydrogen is quite small. Experimentally, for the system H/Ni(111) a charge transfer of less than 0.1 electron was inferred on the basis of an LEED structure determination.¹ In the case of silver, the values of charges and of the dipole moments clearly indicate the covalent character of the H–Ag bond.

Another description of electronic redistribution can be obtained by a precise analysis of charge differences. We have also calculated electron density changes induced by the adsorption of hydrogen, according to the following expression:

$$\Delta\rho_{\text{Ag}}^{\text{H}} = \rho_{\text{Ag slab} + \text{H}} - \rho_{\text{Ag slab}} - \rho_{\text{H}} \quad (5)$$

where ρ_{H} and $\rho_{\text{Ag slab}}$ were calculated using the same coordinates as in the system when the hydrogen is adsorbed. As an example, Figure 1 (bottom panel) shows the 3D plots of the electron density difference obtained when hydrogen adsorbs in three different sites, i.e., hollow, bridge, and top, of Ag(100) surfaces.

Here it becomes clear that the change in the surface dipole is due to the accumulation of electronic charge on the H side and the depletion on the surface, as expected from the modifications observed in the work function. However, it is also evident that the redistribution of electronic charge shows a complicated pattern with accumulation–depletion oscillations. Not only do these fluctuations occur around the surface silver

atoms participating in the bond, but the silver atoms of the second layer are also affected. When hydrogen adsorbs on a hollow site, because of the shorter distance to the surface, the charge split-up is much less evident, explaining the low change observed in the work function.

We can also use these results for the charge difference to estimate the charge transferred to the adsorbed hydrogen atom (method 3). Therefore, in a second step the density differences were integrated in the xy plane of the unit cell. The resulting linear charge densities are plotted in Figure 2 as a function of the z coordinate perpendicular to the surface. From these results it is also evident that a net electronic accumulation around the H atom occurs for all the adsorption configurations ($\Delta\rho(z) \geq 0$ around z_{H} positions). The maxima almost coincide with the position of the hydrogen atom. For H-top, $\Delta\rho_{\text{max}}$ is more pronounced than that for H-bridge and for the latter more than for H-hollow. Near the first layer of silver, strong oscillations of the electronic charge are observed. The second layer of silver still shows some electronic rearrangement, but farther than the second metal layer the perturbation in the electronic density is negligible. Finally, and to obtain the total charge on the H atom, the area under the accumulation region was calculated. The values obtained with this procedure were mostly much lower than those obtained from the Bader or Löwdin method, with the exception of the top positions. From Figure 1c it is clear that the separation of charge is stronger in the latter case. In the other cases, the electronic distribution around H atoms is not spherical, and there is a continuous oscillation of the charge between the H atom and the surface, which results in missing contributions from some regions, while others are overcounted. The hydrogen atom for hollow, fcc, and hcp sites is very close to the first metal layer. In these cases, it is difficult to separate the charge corresponding to one atom from the charge of the rest of the surface; therefore, there is this discrepancy with the results obtained with the other methods. Actually, the charge is not an observable and would depend on the attribution of electronic density to atoms. To explore the origins of the inconsistent values obtained with the third method, we have “tuned” the electronic attribution using boxes

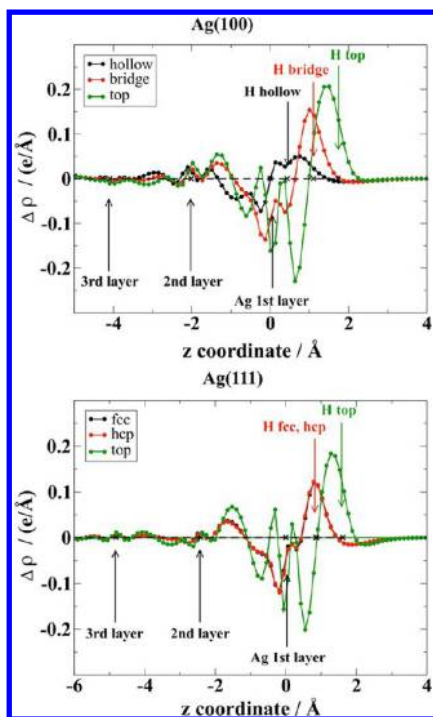


Figure 2. Linear charge densities of H-covered Ag(100) (top) and Ag(111) (bottom) surfaces obtained by integrating the electron density differences $\Delta\rho$ (see eq 4) over the xy plane. Positive values correspond to an increase in electron density. The positions of the three top layers of silver and of the H atom are also indicated.

of different sizes and geometries, instead of the unit cell for the integration limits of the charge average. Figure 3 shows the results obtained with these different boxes in comparison with the values of the Bader method. A strong dependence on the box sizes is obtained, as expected. All the curves go through a maximum since, up to a given distance from the position of the hydrogen atom, the depletion of charge on the metal atoms contributes to the decrease.

Obviously, it is fictitious to represent the behavior of the systems through ideal dipoles with a well-defined charge split; the charge difference plots of Figure 1 show the typical alternation of charge appearing in a covalent bond. While dipole moments can be obtained from the analysis of charge differences with a good precision, the method frequently fails to get the right charge at a given atom of the system.

The foregoing discussion was for a given constant coverage ($\theta = 0.25$) of hydrogen. Further below, we shall analyze the

effect of coverage on the work function changes, which can deliver us more complete information about the H–Ag bond. We shall take the hydrogen adsorption on the Ag(100) surface as a test system. Taking into account the polarity of this bond, and neglecting any lateral interactions, according to eq 2, a linear increase of the work function is expected. However, this ideal behavior is only found in a limited number of H–metal systems, and usually only at low coverages. A variety of complex $\Delta\Phi$ – θ relations have been found, including reversal of the sign, a maximum at certain coverage, and a monotonic decrease. In some cases, such as the three low-index faces of Fe, a variation of opposite signs for $\Delta\Phi$ on the various crystal faces⁴⁶ is observed.

Figure 4a shows the changes induced in the work function of Ag(100) surfaces after adsorption of hydrogen on hollow sites at different coverages. The work function values were calculated by the difference between the electrostatic potential and the Fermi level according to eq 1, taking the clean surface as a reference. At first glance, it seems to be an almost linear relation obeying eq 2, but with the opposite polarity that should be expected. Also the fact that different structural configurations of the hydrogen overlayer give the same changes should indicate the absence of mutual interactions between adsorbates, such as depolarization effects or structural changes. However, a more careful analysis reveals a more complex situation. First, the sign of the change $\Delta\Phi$ at the lowest coverage ($\theta = 1/9$) is positive, while it is negative for all the other overlayers. Second, the coverage dependence shows a deviation from the linear behavior, revealing a larger apparent dipole moment for higher coverages, instead of a depolarization effect.

These results reveal that the simple picture of an electro-negative adsorbate increasing the work function as a consequence of charge transfer from the substrate to it is in this case not valid. We need to consider different factors that determine the fine details of the charge redistribution, which play a role in this behavior: structural rearrangements of the upper layers of silver, bond distance to the surface of adsorbed hydrogen, and the extension of the spillout of the metallic electronic states.

This behavior is very similar to that observed for the adsorption of hydrogen on Pt(111) surfaces.^{47,48} Effectively, Christmann et al. have found an overproportional decrease of $\Delta\Phi$ with coverage (exponent of 1.33). To distinguish whether the Helmholtz eq 2 is no longer valid, or a real change of the dipole moment occurs, we have also calculated the dipole moment with eq 3 from electron density differences, $\Delta\rho$. The corresponding planar averaged charge density changes are

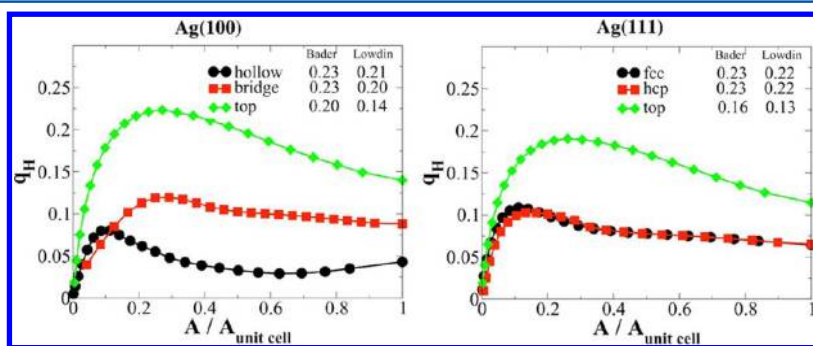


Figure 3. Electronic charge around the hydrogen atom adsorbed at different sites on the Ag(100) surface (left) and Ag(111) surface (right) obtained by method 3 (see the text). The corresponding values given by Bader and Löwdin analysis are given in the insets.

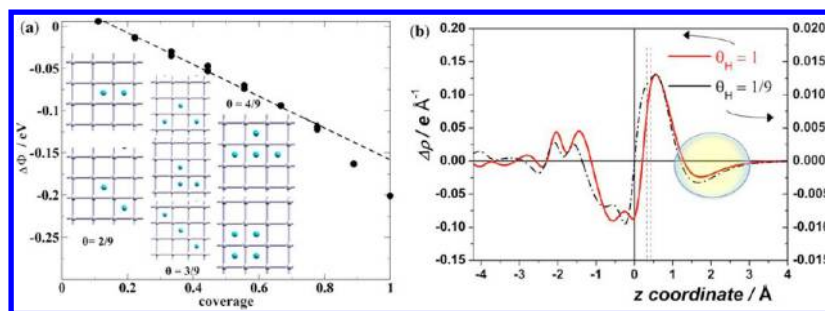


Figure 4. (a) Changes in the work function $\Delta\Phi$ of the metal surface Ag(100) after H adsorption on hollow sites at different coverages (calculated by eq 1). The different points at the same coverage correspond to different possible structural configurations,¹⁹ as shown in the inset. The dashed line is only a guide for the eyes. (b) Planar averaged charge density change upon H adsorption at the minimum and maximum coverages (black and red lines, respectively) as a function of the z coordinate perpendicular to the surface. The vertical solid line indicates the position of the upper layer of Ag, and the dashed lines indicate the equilibrium position of hydrogen. The circle shows the electronic depletion in the outer tail region.

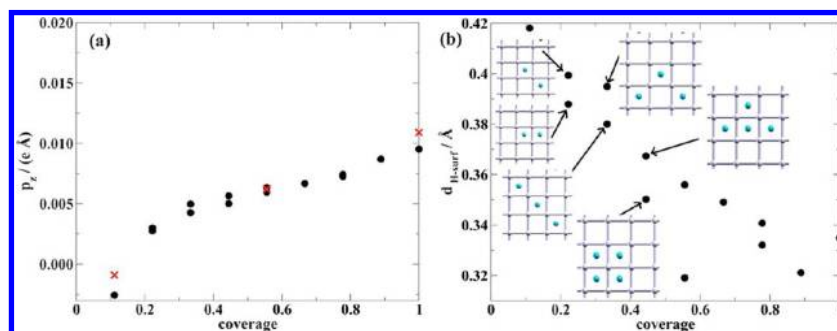


Figure 5. (a) Dipole moments created between H atoms and the silver (100) surface after H adsorption. Dipole moments were calculated from the work function shifts (obtained with eq 1). The red times signs correspond to the values calculated from electron density differences (eqs 4 and 5). (b) Distances from the H atom to the silver surface for the different geometric configurations.

shown in Figure 4b for the lowest and highest coverages (first and last points of Figure 4a, respectively). Figure 5a shows the dipole calculated from the work function changes using eq 2 in comparison with that obtained directly from the charge differences using eq 3. The almost good agreement between both methods demonstrates that the dipole is not constant and instead it continuously changes with coverage.

A reasonable explanation can be found if other parameters are simultaneously analyzed. Figure 5b shows the equilibrium distance between the H atom and the silver surface as a function of coverage. According to these results, an increase in the H coverage on the surface reduces the distance between the H atoms and the metal. Obviously, a concerted rearrangement of the adsorbed hydrogen occurs, which decreases the distance to the surface such that the repulsion is minimized and the adsorption energy remains constant. This situation is only possible up to a coverage of 0.5. At higher values, the rearrangements cannot compensate the repulsion and the energy of adsorption starts to increase.¹⁹

According to these results, an increase in the H coverage on the surface reduces the distance between the H atoms and the metal (Figure 5b) and lowers the work function of the surface (Figure 4). These two facts are not unrelated. The lowering in the work function indicates that there is an increase in the charge transferred from the surface to H atoms that reduces the electron density around the metal surface and weakens the H–Ag bonds.

Therefore, to keep the bond order, the distance between them is shortened. The decrease in the electron density not only involves the H–Ag bonds, but also slightly reduces the bond order between the metal layers. When H adsorbs, the

silver atoms in the surface are more coordinated than those of a bare surface. Therefore, the atoms in the first layer move away from the atoms in the second layer, and in fully H covered surfaces, the distance between the first and second layers is 7% larger than at low coverages. In the case of low coverage, each metal atom is coordinated to only one single adsorbate atom. When the coverage increases, a bonding competition mechanism takes place⁴⁹ since metal atoms must bond with more than a single adatom. The metal atom participating in more than one adsorbate–metal bond can also enable electron delocalization as can be clearly inferred from the analysis of charge difference plots and the density of states shown in Figure 6. At very low coverage ($\theta = 1/9$), the hydrogen atom only interacts with the four silver atoms of the hollow adsorption site (Figure 6a). When the coverage of hydrogen increases ($\theta = 5/9$), some silver atoms simultaneously form bonds with adjacent adsorbates. In Figure 6b, for example, we can observe that one silver atom participates in the bond with four different hydrogen atoms at the same time. At the highest coverage ($\theta = 1$), the adsorbed hydrogen atoms are “swimming” in a continuous “sea” of charge (see Figure 6c). Thus, individual bonds cannot be further distinguished when the surface is covered by a monolayer. The participation of not only d but also sp states of silver is clear from Figure 6d. Effectively, an overlap between sp and d states (mainly d_{xy}) of silver with $1s$ states of hydrogen is evident in the energy range between -8 and -6.5 eV (bonding states) and around -2 eV (antibonding states). Direct dipole–dipole interactions between neighboring atoms, which could produce depolarization effects, can be neglected, since the hydrogen Bohr radius is much smaller than the lattice constant of the substrate.

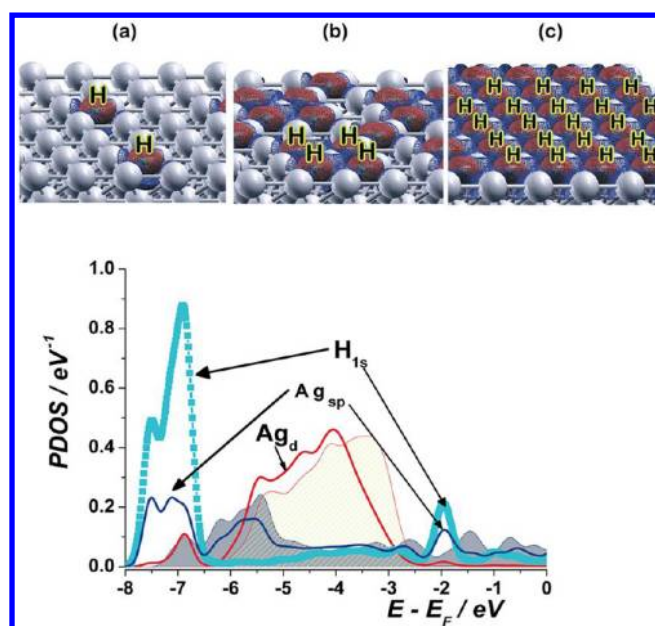


Figure 6. Upper panel: charge difference plots for the adsorption of hydrogen at the hollow site of Ag(100) at different coverages, (a) $\theta = 1/9$, (b) $\theta = 5/9$, (c) $\theta = 1$. Bottom panel: density of states for the adsorption of hydrogen at hollow sites projected onto the 1s states of hydrogen (cyan closed squares), d states (red line), and sp states (blue line) of silver atoms of the hollow sites. The corresponding sp states (gray shaded area) and d states (yellow shaded area) of surface silver atoms free of hydrogen are also included.

Certainly, the silver atoms screen the hydrogen atoms from one another, since the latter are almost “immersed” in the hollow sites. In this case, only the operation of indirect repulsive long-range interactions (“through-bond”) between adsorbed hydrogen may come into play.^{49,50} Especially sp states, which extend further than d states, could promote these interactions through electron delocalization. The d band of Ag is generated by the fully occupied 4d orbitals, which are more spatially contracted and therefore account for the formation of localized bonds. The sp electrons, on the other hand, are much more mobile and can easily move away from the bonded metal atom toward neighboring atoms, facilitating the indirect interactions. This complex interplay between different electronic states has been addressed for the water–metal interactions⁵¹ and also for hydrogen adsorption on nanostructures of Pd–Au.¹⁸ Because of the increase in electron density between the bonds, an enhancement of the dipole moment is produced at higher coverage of H.

Previous theoretical approaches based on DFT calculations^{14,27,30–32} have clarified the subtle effects of charge redistribution on the sign of the dipole resulting after adsorption of either simple atoms or complex adsorbates.

For example, it is interesting to compare our results with those obtained by Michaelides et al. for the work function change induced by nitrogen adsorption on W(100).³¹ They have explained the anomalous behavior that the work function decreases despite the electronegativity of N adatoms. They have found that the slight electronic charge depletion at distances farther from the surface strongly contributes to the observed work function decrease. Although small compared to the electron accumulation layer nearer the surface, it is sufficiently far from the surface to determine the sign of the dipole. We have to recall that the dipole is weighted by the

distance from the center of the slab. In our case, Figure 4b also shows such electronic depletion at about 1.5 Å (see the circle in Figure 4b). If we neglect this contribution, setting the upper integration limit in eq 3 to 1.25 Å, a dipole of $-3.8 \times 10^{-2} \text{ e \AA}$ is obtained for the fully H covered surface, instead of the value of $+1.1 \times 10^{-2} \text{ e \AA}$ corresponding to the last point in Figure 5a. Similar to the N adsorbate, H adsorbed at the hollow site is located below the electron spillout density of silver. Metallic electronic states extending out into the vacuum before adsorption become depopulated. At higher hydrogen coverages, this effect is enhanced because of the shorter H–Ag bond distances. When hydrogen adsorbs at top or bridge sites, the hydrogen atoms are much farther from the surface, and this effect is not observed (see Figure 2). In the latter cases the work function increases upon adsorption, since the net dipole is pointing downward.

Work Function of Vicinal Ag(11n) Surfaces. Creating a step from a planar surface not only requires an amount of energy but also produces a change in the work function of the surface. Interesting experiments using cylindrical or hemispherical single crystals deliver maps of the work function dependence on the surface orientation.⁵² Studies of the work function of vicinal stepped surfaces of a variety of metals have shown that linear reductions of the work function with increasing step density are observed near low-index surfaces. At higher step densities, step–step interactions cause mutual depolarization, and deviation of the linearity behavior occurs. Anisotropy maps have also been obtained by modeling the work function of stepped metallic surfaces.^{53,54}

A qualitative explanation, supported by the jellium model,^{55,56} is the well-known Smoluchowski effect.¹⁵ The charge modulation caused by the smooth contour of the electron density in response to the sharp potential contour of the ion cores of the atoms at the step leads to electron accumulation at the bottom and to an electron depletion at the top of the step. This rearrangement of the electronic density in the step edges creates a dipole moment. These dipoles are oriented outward, in the direction opposite that of the dipoles due to the adsorption of hydrogen.

However, the real cause of this dipole is the change in the bonding between the atoms at the steps and the substrate, which can be followed by measuring the charge density difference produced by formation of the step^{25,56} and carefully analyzing the density of states. The rearrangement of the electronic density has been calculated as²⁵

$$\Delta\rho_{\text{Ag}(11n)}^n = \rho_{\text{Ag}(11n)}^n - \rho_{\text{Ag}(11n)}^{n-1} - \rho_{\text{Ag}} \quad (6)$$

where $\rho_{\text{Ag}(11n)}^n$, $\rho_{\text{Ag}(11n)}^{n-1}$, and ρ_{Ag} are the electronic densities of the vicinal (11n) surface, of the same surface without the atom at the step edge, and of the single silver atom, respectively.

Figure 7 shows the charge density change on the (119) surface, where red and blue colors correspond to an increase and decrease of electronic charge, respectively.

In the outer region above the atom at the step, the electronic charge is reduced, and this charge is shifted to the region between the step atom and its neighbors. According to these results, there is a depletion of electronic density at the step, and therefore, the dipole moment is pointing outward, as expected. Consequently, a decrease of the work function occurs. Increasing the density of steps in the surface will decrease the work function further.

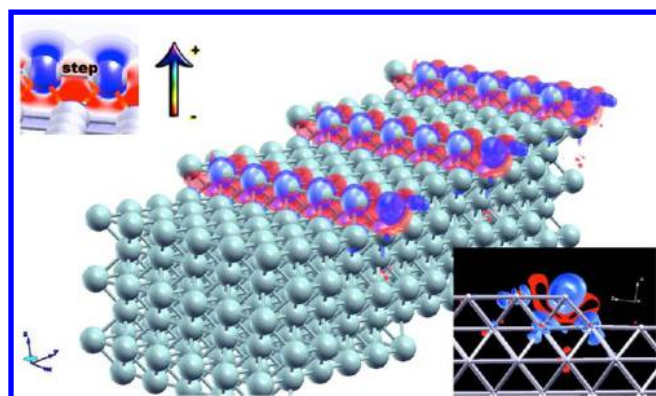


Figure 7. Side-top views of the charge density difference $\Delta\rho$ for the Ag(119) vicinal surface (the Ag(100) surface has been taken as a reference). Red and blue contours correspond to the accumulation and depletion of electron density, respectively. The $0.0015 \text{ e } \text{\AA}^{-3}$ isosurface has been plotted. Upper inset: projection onto the plane perpendicular to the step. Lower inset: side view of the step.

Here is also interesting to see the interplay between the different orbitals of the atoms near the step. There are previous attempts based on the jellium model^{55,56} to analyze the effect of the presence of steps on the density of states. However, this model is limited to sp metals where the electrons are considered as a sea of negative charge without any structure.

The dipole moment changes Δp_z induced by the step were obtained by using eq 3. The changes in the work function were calculated using eq 2 and are shown in Figure 8 as a function of

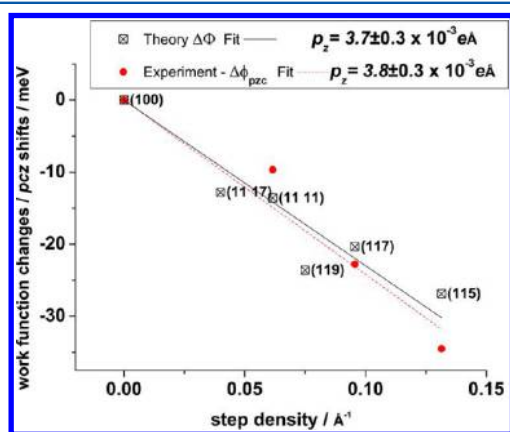


Figure 8. Work function changes as a function of the step density. Comparison between theoretical values (\times inside \square) and values calculated from experimental values of the potential of zero charge (\bullet) (experimental data taken from ref 58).

the step density for Ag(11*n*) with $n = 5, 7, 9, 11,$ and 17 . In the same figure are included experimental results obtained for the shift of the potential of zero charge (ΔE_{pzc}) on stepped silver electrodes. In an electrochemical environment, the potential of zero charge and the work function are directly related,^{8,13,17,57–59} and in the absence of specific adsorption of anions the change ΔE_{pzc} can also be expressed in terms of the changes in the surface dipole moment per step atom, Δp_z :

$$\Delta E_{\text{pzc}} = -\frac{\Delta p_z}{\epsilon_0 a_{\parallel} L} \quad (7)$$

where $L \propto N^{-1}$ is the distance between steps, which is proportional to the inverse of the step density N , and a_{\parallel} is the atom length unit along the step edge. The dipole moments of step atoms are not necessarily the same in a vacuum and in an electrochemical environment. The arrangement of the dipolar water molecules around the step atoms^{59,60} or the specific adsorption of anions may cause either a reduction or an enhancement of the dipole moment. However, theoretical and experimental results obtained from the shift of the potential of zero charge (ΔE_{pzc}) in stepped silver electrodes⁵⁸ agree surprisingly well. There is a linear relation between the work function (and also ΔE_{pzc}) and the density of steps. From the slope a dipole moment equal to $0.0038 \text{ e } \text{\AA}$ is obtained, confirming the validity of eq 7. Small discrepancies between the experimental values and our results could be due to the great difficulty in the numerical integration of the small electron density differences. These values for the dipole of the steps are about an order of magnitude lower than those obtained with STM for monatomic steps of Cu and Au.⁶¹ Nevertheless, a monatomic row is still less coordinated than a semi-infinite step.

Work Function of Vicinal Ag(11*n*) Surfaces Covered by Hydrogen.

There are two groups of sites for the hydrogen adsorption:¹⁹ terrace and step sites. The terrace sites are the same as in the planar (100) surface: hollow and bridge sites. However, because of the presence of the step, the symmetry in the bridge and hollow sites is broken. Therefore, the sites in the terrace are different, and they can be distinguished according to their distances from the step. We also have to differentiate between the bridge sites parallel (brd-p) and perpendicular (brd-s) to the steps.

The sites placed in the step are similar to those in the Ag(111) flat surface: bridge, fcc, and hcp. The less coordinated atoms in the surface are located in the upper part of the step, whereas the most coordinated ones are in the bottom of the same step. This difference makes the three sites in the step different; bridge and hcp sites are the less coordinated silver atoms, while the fcc site in the bottom of the step is more coordinated.

An examination of the adsorption energy values¹⁹ suggests a localized character of the bond between H atoms and vicinal silver surfaces. The bonds between the surface and the H atoms are quite independent of the index of the surface. According to our results, the dispersion of the distance values for the same sites is below 3%, even for different vicinal surfaces.

Dipole moments and work functions have been calculated. The dipole moments were obtained from the changes in the work function using eq 2 and the charge density difference calculated from eq 5. As an example, Figure 9 shows the charge density difference for the Ag(119) surface when the steps are covered by hydrogen at bridge sites, which is the most favorable site.¹⁹ From the pictures, it is clear that the H atom increases its electronic density, whereas the surrounding silver atoms lose electrons, similar to the flat surfaces discussed above. In this case, it is expected that the dipole points to the surface. When hydrogen adsorbs on other sites, the electronic rearrangement can be different, as observed from Figure 10, where plots similar to those of Figure 9 are shown for different sites. Larger bond distances correspond to H adsorbed on step sites, and lower values are obtained for adsorption on hollow positions. The lowest dipoles result when hydrogen adsorbs at fcc (Figure 10a) and hollow (Figure 10c) sites. In the case of the hollow site near the step (Figure 10c), the dipole is similar to that

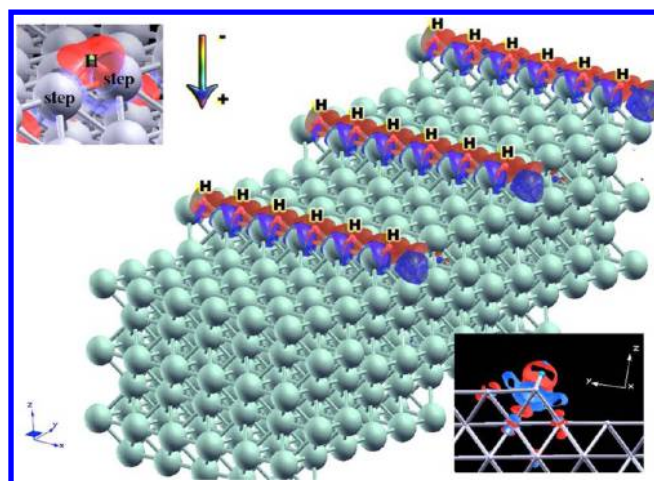


Figure 9. Side-top view of the charge density difference $\Delta\rho$ for Ag(119) covered by hydrogen at bridge sites of the step. Red and blue contours correspond to accumulation and depletion of electrons, respectively. The isosurface corresponds to $0.0015 \text{ e } \text{\AA}^{-3}$ (the bare surface has been taken as a reference). Upper inset: projection onto the plane perpendicular to the step. Lower inset: side view.

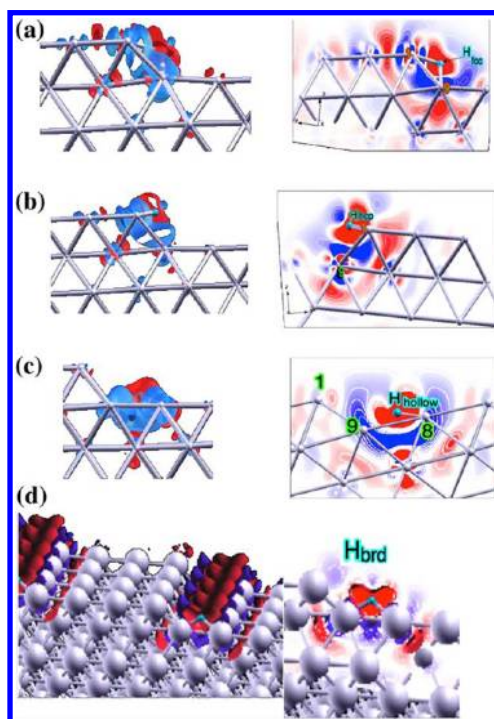


Figure 10. Side views of isosurfaces (left, $0.0015 \text{ e } \text{\AA}^{-3}$) and projections onto the plane perpendicular to the step (right) for the adsorption of hydrogen at different sites on Ag(119). Bridge (d) and hollow (c) sites correspond to the terrace, whereas fcc (a) and hcp (b) sites correspond to the step. Red and blue contours correspond to accumulation and depletion of electrons, respectively.

obtained for the hollow site of the flat Ag(100) surface. The behavior is different for the fcc and hcp sites. While in the case of Ag(111) surfaces the adsorption of hydrogen at fcc site produces a dipole of $-0.013 \text{ e } \text{\AA}$, the value obtained at the step in the (115) vicinal surface is practically zero ($-0.003 \text{ e } \text{\AA}$). The other vicinal surfaces show a value similar to that of Ag(111). All the stepped surfaces display some more negative dipoles for the hydrogen adsorption at the hcp site.

According to eq 2, the only significant part of the dipole that contributes to shifting the work function is the perpendicular component to the terrace. Due to the fact that H on the fcc site is nearly parallel to the terrace, the resultant component p_z is rather small for the (115) surface. The tilting of the H–Ag bond is particularly large for this surface in comparison with the other ones having larger terraces; therefore, the dipole component normal to the surface is diminished. In the case of the dipole produced by the adsorption at the hcp site of the step, the H–Ag bond rises more straight up than for the adsorption at the fcc site (compare Figure 10a,b). Additionally, electronic effects due to the charge redistribution at the step and the decrease of the coordination determine the larger difference in comparison with the adsorption at a similar site of the flat (111) surface.

However, a more detailed analysis reveals subtle variations in the dipole moments, which can be ascribed to the electronic anisotropy of the system.

Following an interpolation procedure, we have built 2D surfaces mapping the dipoles created at vicinal Ag surfaces after hydrogen adsorption. For the construction of these plots, we have considered sites where hydrogen is adsorbed with a local minimum of energy and their coordinates fully relaxed. In all the cases the lowest coverage has been considered (1 H atom/unit cell) to avoid interaction effects. We have disregarded the top sites because of the considerable difficulty to get any optimized geometries. Moreover, these sites do not correspond to any local minimum of energy, but to a transition state.¹⁹ Similarly, the hollow site near the upper part of the step also corresponds to a transition state and has been disregarded.

Figure 11 shows, as examples, the maps for these vicinal surfaces in comparison with the (100) orientation. These figures prove that, in addition to the anisotropy observed for different crystal orientations,^{53,54} there is also an intrinsic refined anisotropy for a given surface. In general, for sufficiently large terraces, different surfaces have the same dipoles for the same sites. Adsorption at hollow sites produces a dipole slightly positive or near zero. The dipoles corresponding to sites at the upper part of the step are clearly more negative than those of sites at the terraces. More interesting is the behavior of the dipole originated by hydrogen adsorption on the terraces. A continuous gradient of the dipoles between the sites on the terraces close to the upper part of one step and the bottom part of the next step is clearly observed. This tendency is shown by the adsorption at either bridge site, parallel and perpendicular to the step. The dipoles are more negative than those corresponding to the sites of the flat (100) surface. The difference is more marked close to the top of the step (see the Supporting Information for more details). Also the surface with the wider terraces (1 1 17) shows this anisotropy, indicating a long-range effect (compared with the (100) surface). We have observed an anisotropy in the adsorption energy¹⁹ for the different sites of the terraces, although the tendency is different. In the latter case the adsorption energy increases at the terrace sites near either the upper or the bottom part of the steps (see the Supporting Information). Nevertheless, both these effects could be a consequence of electronic delocalization mainly mediated by the sp states, as we have discussed in a section above.

Finally, we have calculated the work function changes and the corresponding dipole moments created after H adsorption on silver (115) surfaces at different coverages. We have followed the two procedures described in the previous section.

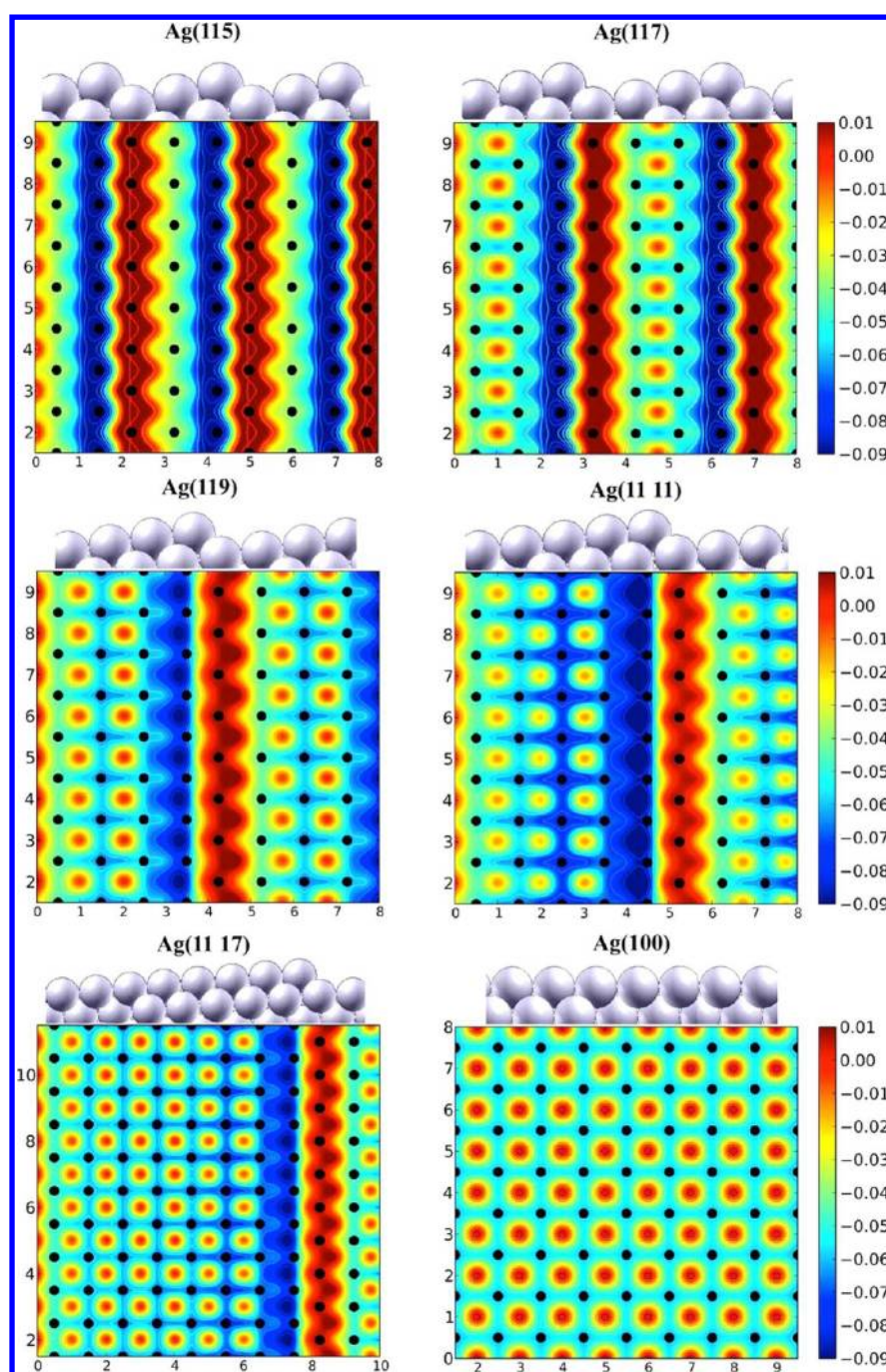


Figure 11. Top view of the 2D surfaces showing the dipole moment created after the adsorption of one H atom on planar (100) and vicinal ($11n$) silver surfaces. A side view of the clean surfaces has also been included. All dipole moments are given in e Å. See the text for more details on the calculations.

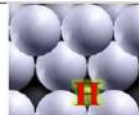

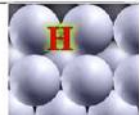




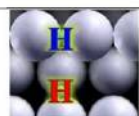
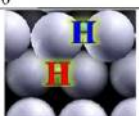
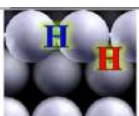
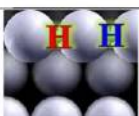
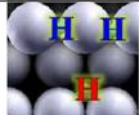
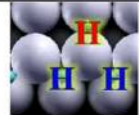
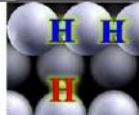
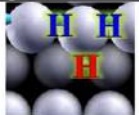
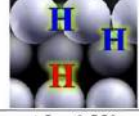

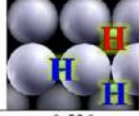
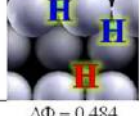
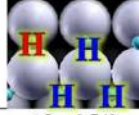
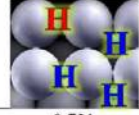
Unlike the preceding case, we found important differences between the dipole moments obtained using both methods. These discrepancies are quite reasonable considering the increasing interactions between neighbors and the difficulties in making a proper integration of the electron density (eq 3).

Table 2 shows work function changes calculated from the electrostatic potential. The dipole moments were obtained using eq 2, and they correspond to the average value in a unit cell ($A_{\text{unit cell}} = 22.29 \text{ \AA}$). There are different bonds between the H atoms and the surface; however, the dipole moments were calculated for the whole surface, not for a particular bond or region of the surface.

Despite of the different coverages, the dipole moment seems to be a local property, only slightly influenced by the surrounding atoms in the surface. According to our results, in a low-coverage regime the adsorption of H atoms on different sites will only produce the addition of all dipole moments. Therefore, the resulting dipole moment per H atom is the average of the dipole moments.

However, adding more H atoms ($\theta \geq 3/6$) to the sites near the step produces a distortion in the bonds located on the step, which modifies the corresponding dipole moments. Nevertheless, H adsorption around H-covered steps improves the adsorption.¹⁹ Interaction between H adsorbed on the bottom

Table 2. Optimized Geometries, $\Delta\Phi^a$ and p_z^b for Several Coverages of H on the Ag(115) Surface

Terrace sites			Step sites		
$\theta=1/6$					
					
$\Delta\Phi = -0.006$	0.080	0.165	0.016	0.370	0.099
$p_z = 0.143$	-1.98	-4.08	-0.402	-9.12	-2.43
					
$\Delta\Phi = 0.222$					
$p_z = -5.48$					
$\theta=2/6$					
					
$\Delta\Phi = 0.469$			0.353	0.481	0.726
$p_z = -5.79$			-4.35	-5.93	-8.95
$\theta=3/6$					
					
$\Delta\Phi = 0.746$	0.376	0.832	0.445		
$p_z = -6.13$	-3.09	-6.84	-3.66		
					
$\Delta\Phi = 0.550$	0.670	0.526			
$p_z = -4.52$	-5.51	-4.32			
					
$\Delta\Phi = 0.484$					
$p_z = -3.98$					
$\theta=4/6$					
					
$\Delta\Phi = 0.743$	0.721				
$p_z = -4.58$	-4.44				

^aWork functions were obtained by using eq 1. The $\Delta\Phi$ values have been calculated as the difference between the work functions of the H-covered and the clean (115) surfaces. All $\Delta\Phi$ values are in electronvolts. ^bDipole moments reported correspond to the averaged value for all the H bonds in the surface. All p_z values are in 10^{-2} e Å.

of the step with bonds on the upper part of the step also significantly reduces the work function. Despite the differences observed for the various geometrical configurations, a general trend of increasing work function with coverage can be inferred (see Figure 12).

CONCLUSIONS

The dipole moment induced by the presence of steps has been calculated, and a very good agreement with experimental data has been obtained. An almost linear correlation between the induced changes in the work function and the density of steps has been found.

The adsorption of hydrogen also produces changes in the work function, mostly due to a dipole moment oriented inward to the surface. However, depending on the adsorption site, complicated electronic charge redistributions take place.

Interesting, a continuous gradient of these dipoles uprising upon the adsorption of hydrogen between the sites at the terraces near the upper part of one step and the bottom part of the next step has been found. This effect is still noticeable for surfaces with wide terraces. This anisotropy indicates a long-range effect. The dipoles produced by the adsorption of hydrogen on sites near the bottom of the step are slightly less negative than those when hydrogen adsorbs on sites near the upper part. Also the symmetry between bridge sites parallel and

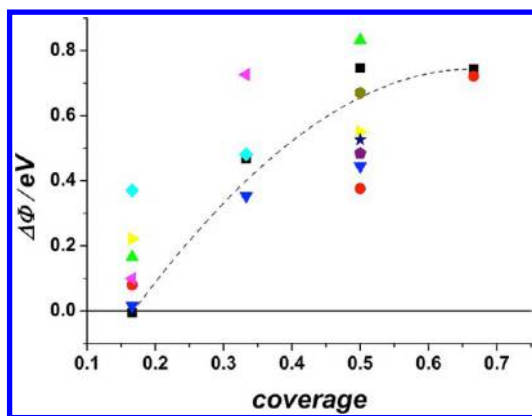


Figure 12. Hydrogen adsorption induced change in the work function of Ag(115) for different coverages. The symbols represent the geometrical configurations of Table 2. The dashed line is only a guide for the eye.

perpendicular to the step is broken, and as consequence, different dipole moments are given.

Despite the different coverages, the dipole moment seems to be a local property, only slightly influenced by the surrounding atoms in the surface. Nevertheless, adding more H atoms to the sites near the step produces a distortion in the bonds located on the step, which modifies the corresponding dipole moments.

■ ASSOCIATED CONTENT

📄 Supporting Information

(S1) Table listing the charge on H atoms adsorbed on planar Ag surfaces, (S2) figure showing the adsorption energy for hydrogen at different sites on the Ag(1 1 17) terrace and step, (S3) figure showing the dipole moments for hydrogen adsorption at different sites on the Ag(1 1 17) terrace and step, and (S4) figure showing the dependence on the surface orientation of the dipole moments. This material is available free of charge via the Internet at <http://pubs.acs.org>

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: esantos@uni-ulm.de.

Author Contributions

Both authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

DFT, density functional theory; PBE, Perdew–Burke–Ernzerhof; LEED, low-energy electron diffraction; STM, scanning tunneling microscopy

■ REFERENCES

(1) Christmann, K. Interaction of hydrogen with solid surfaces. *Surf. Sci. Rep.* **1981**, *9*, 1–163.

(2) Ferrin, P.; Kandoi, S.; Nilekar, A. U.; Mavrikakis, M. Hydrogen adsorption, absorption and diffusion on and in transition metal surfaces: A DFT study. *Surf. Sci.* **2012**, *606*, 679–689.

(3) Groß, A. Hydrogen on metal surfaces: Forever young. *Surf. Sci.* **2012**, *606*, 690–691.

(4) Santos, E.; Lundin, A.; Pötting, K.; Quaino, P.; Schmickler, W. Model for the electrocatalysis of hydrogen evolution. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, *79*, 235436.

(5) Santos, E.; Lundin, A.; Pötting, K.; Quaino, P.; Schmickler, W. Hydrogen evolution and oxidation—a prototype for an electrocatalytic reaction. *J. Solid State Electrochem.* **2009**, *13*, 1101–1109.

(6) Santos, E.; Pötting, K.; Schmickler, W. On the catalysis of the hydrogen oxidation. *Faraday Discuss.* **2009**, *140*, 209–218.

(7) Santos, E.; Quaino, P.; Schmickler, W. Theory of electrocatalysis: hydrogen evolution and more. *Phys. Chem. Chem. Phys.* **2012**, *14*, 11224–11233.

(8) Schmickler, W.; Santos, E. *Interfacial Electrochemistry*; Springer Verlag GmbH: Heidelberg, Germany, 2010.

(9) Lee, G.; Plummer, E. W. Interaction of hydrogen with the Ag(111) surface. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1995**, *51*, 7250–7261.

(10) Diesing, D.; Winkes, H.; Otto, A. Time resolved investigation of the hydrogen evolution reaction on Ag(111), Ag(100), smooth polycrystalline, and activated polycrystalline silver surfaces. *Phys. Status Solidi A* **1997**, *159*, 243–254.

(11) Diesing, D.; Kritzler, G.; Stermann, M.; Nolting, D.; Otto, A. Metal/insulator/metal junctions for electrochemical surface science. *J. Solid State Electrochem.* **2003**, *7*, 389–415.

(12) Feliú, J. M.; Herrero, E.; Climent, V. In *Catalysis in Electrochemistry: From Fundamentals to Strategies for Fuel Cell Development*; Santos, E., Schmickler, W., Eds.; Wiley: Hoboken, NJ, 2011; Chapter 4.

(13) Ibach, H. *Physics of Surfaces and Interfaces*; Springer Verlag GmbH: Berlin, Germany, 2006.

(14) Yanagisawa, S.; Lee, K.; Morikawa, Y. First-principles theoretical study of Alq₃/Al interfaces: Origin of the interfacial dipole. *J. Chem. Phys.* **2008**, *128*, 244704.

(15) Smoluchowski, R. Anisotropy of the electronic work function of metals. *Phys. Rev.* **1941**, *60*, 661–674.

(16) Trasatti, S. In *Advances in Electrochemistry and Electrochemical Engineering*; Gerischer, H., Tobias, C. W., Eds.; Wiley Interscience: New York, 1977; Vol. 10.

(17) Giesen, M.; Beltramo, G. In *Catalysis in Electrochemistry: From Fundamentals to Strategies for Fuel Cell Development*; Santos, E., Schmickler, W., Eds.; Wiley: Hoboken, NJ, 2011; Chapter 3.

(18) Santos, E.; Quaino, P.; Schmickler, W. On the electrocatalysis of nanostructures: Monolayers of a foreign atom (Pd) on different substrates M(111). *Electrochim. Acta* **2010**, *55*, 4346–4352.

(19) Juárez, M. F.; Santos, E. Manuscript in preparation.

(20) <http://www.fysik.dtu.dk/campos> (accessed Oct 2007).

(21) Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1990**, *41*, 7892–7895.

(22) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(23) Liu, L.; Bassett, W. A. Compression of Ag and phase transformation of NaCl. *J. Appl. Phys.* **1973**, *44*, 1475–1479.

(24) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B: Solid State* **1976**, *13*, 5188–5192.

(25) Bengtsson, L. Dipole correction for surface supercell calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 12301–12304.

(26) Müller, J. E.; Ibach, H. Migration of point defects at charged Cu, Ag, and Au (100) surfaces. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *74*, 085408–1–085408–10.

(27) Wang, L.-L.; Cheng, H.-P. Density functional study of the adsorption of a C60 monolayer on Ag(111) and Au(111) surfaces. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *69*, 165417–1–165417–12.

- (28) Merrick, I.; Inglesfield, J. E.; Attard, G. A. Local work function and induced screening effects at stepped Pd surfaces. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *71*, 085407–1–085407–9.
- (29) Mamatkulov, M.; Filhol, J.-S. An ab initio study of electrochemical vs. electromechanical properties: the case of CO adsorbed on a Pt(111) surface. *Phys. Chem. Chem. Phys.* **2011**, *13*, 7675–7684.
- (30) Leung, T. C.; Kao, C. L.; Su, W. S.; Feng, Y. J.; Chan, C. T. Relationship between surface dipole, work function and charge transfer: Some exceptions to an established rule. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *68*, 195408–1–195408–12.
- (31) Michaelides, A.; Hu, P.; Lee, H.; Alavi, A.; King, D. A. Resolution of an ancient surface science anomaly: Work function change induced by N adsorption on W{100}. *Phys. Rev. Lett.* **2003**, *90*, 246103.
- (32) Wang, L.-L.; Cheng, H.-P. Rotation, translation, charge transfer, and electronic structure of C60 on Cu(111) surface. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *69*, 045404–1–045404–7.
- (33) Chelvayohan, M.; Mee, C. H. B. Work function measurements on (110), (100) and (111) surfaces of silver. *J. Phys. C: Solid State Phys.* **1982**, *15*, 2305–2312.
- (34) Bocquet, M. L.; Rappe, A. M.; Dai, H. L. A density functional theory study of adsorbate-induced work function change and binding energy: Olefins on Ag(111). *Mol. Phys.* **2005**, *103*, 883–890.
- (35) Wang, Y.; Wang, W.; Fan, K.; Deng, J. Structural and electronic properties of silver surfaces: Ab initio pseudopotential density functional study. *Surf. Sci.* **2001**, *490*, 125–132.
- (36) Zhou, X. L.; White, J. M.; Koel, B. E. Chemisorption of atomic hydrogen on clean and Cl-covered Ag(111). *Surf. Sci.* **1989**, *218*, 201–210.
- (37) Sprunger, P. T.; Plummer, E. W. Interaction of hydrogen with the Ag(110) surface. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, *48*, 14436–14446.
- (38) Bader, R. F. W.; Henneker, W. H.; Cade, P. E. Molecular charge distributions and chemical binding. *J. Chem. Phys.* **1967**, *46*, 3341–3363.
- (39) Bader, R. F. W.; Cade, P. E.; Beddall, P. M. Partitioning and characterization of molecular charge distributions. *J. Am. Chem. Soc.* **1971**, *93*, 3095–3107.
- (40) Henkelman, G.; Arnaldsson, A.; Jónsson, H. *Comput. Mater. Sci.* **2006**, *36*, 354–360.
- (41) Gudmundsdóttir, S.; Tang, W.; Henkelman, G.; Jónsson, H.; Skúlason, E. *J. Chem. Phys.* **2012**, *137*, 164705–164714.
- (42) Löwdin, P. O. On the non-orthogonality problem connected with the use of atomic wave functions in the theory of molecules and crystals. *J. Chem. Phys.* **1950**, *18*, 365–375.
- (43) Löwdin, P. O. On the nonorthogonality problem. *Adv. Quantum Chem.* **1970**, *5*, 185–199.
- (44) Bruhn, G.; Davidson, E. R.; Mayer, I.; Clark, A. E. Löwdin population analysis with and without rotational invariance. *Int. J. Quantum Chem.* **2006**, *106*, 2065–2072.
- (45) Kokalj, A. Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale. *Comput. Mater. Sci.* **2003**, *28*, 155–168; XCrySDen. A new program for displaying crystalline structures and electron densities. *J. Mol. Graphics Modell.* **1999**, *17*, 176–179; code available from <http://www.xcrysden.org/> (accessed Oct 2010).
- (46) Boszo, F.; Ertl, G.; Grunze, M.; Weiss, M. Chemisorption of hydrogen on iron surfaces. *Appl. Surf. Sci.* **1977**, *1*, 103–119.
- (47) Christmann, K.; Ertl, G.; Pignet, T. Adsorption of hydrogen on a Pt(111) surface. *Surf. Sci.* **1976**, *54*, 365–392.
- (48) Christmann, K.; Ertl, G. Interaction of hydrogen with Pt(111): The role of atomic steps. *Surf. Sci.* **1976**, *60*, 365–384.
- (49) *Metal–Surface Reaction Energetics. Theory and Applications to Heterogeneous Catalysis, Chemisorption, and Surface Diffusion*; Shustorovich, E., Ed.; VCH: New York, 1991.
- (50) Grimley, T. B.; Torrini, M. The interaction between two hydrogen atoms adsorbed on (100) tungsten. *J. Phys. C: Solid State Phys.* **1973**, *6*, 868–872.
- (51) Schiros, T.; Takahashi, O.; Andersson, K. J.; Öström, H.; Pettersson, L. G. M.; Nilsson, A.; Ogasawara, H. J. The role of substrate electrons in the wetting of a metal surface. *Chem. Phys.* **2010**, *132*, 094701–094709.
- (52) Besocke, K.; Krahl-Urban, B.; Wagner, H. Dipole moments associated with edge atoms; a comparative study on stepped Pt, Au and W surfaces. *Surf. Sci.* **1977**, *68*, 39–46.
- (53) Fall, C. J.; Binggeli, N.; Baldereschi, A. Theoretical maps of work-function anisotropies. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2001**, *65*, 045401–1–045401–6.
- (54) Fall, C. J.; Binggeli, N.; Baldereschi, A. Work functions and surface charges at metallic facet edges. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2002**, *66*, 075405–1–075405–10.
- (55) Thompson, M. D.; Huntington, H. B. Adatom binding at the surface ledges of a jellium metal. *Surf. Sci.* **1982**, *116*, 522–538.
- (56) Ishida, H.; Liebsch, A. Calculation of the electronic structure of stepped metal surfaces. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *46*, 7153–7156.
- (57) Beltramo, G. L.; Ibach, H.; Giesen, M. A novel approach to measure the step line tension and the step dipole moment on vicinal Au(0 0 1) electrodes. *Surf. Sci.* **2007**, *601*, 1876–1885.
- (58) Beltramo, G. L.; Ibach, H.; Linke, U.; Giesen, M. Determination of the step dipole moment and the step line tension on Ag(0 0 1) electrodes. *Electrochim. Acta* **2008**, *53*, 6818–6823.
- (59) Beltramo, G.; Giesen, M.; Ibach, H. Anomalous Helmholtz-capacitance on stepped surfaces of silver and gold. *Electrochim. Acta* **2009**, *54*, 4305–4311.
- (60) Lin, X.; Gross, A. First-principles study of the water structure on flat and stepped gold surfaces. *Surf. Sci.* **2012**, *606*, 886–891.
- (61) Jia, J. F.; Inoue, K.; Hasegawa, Y.; Yang, W. S.; Sakurai, T. Variation of the local work function at steps on metal surfaces studied with STM. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *58*, 1193–1196.