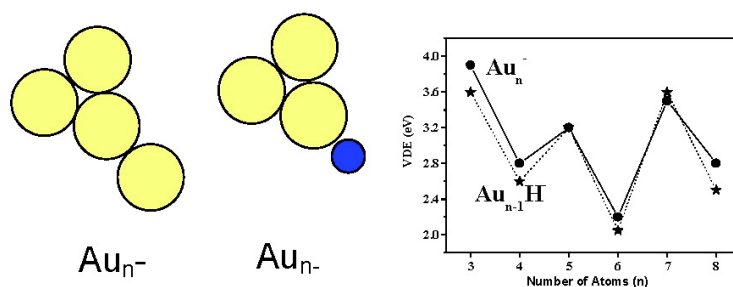Article

Anomalous Behavior of Atomic Hydrogen Interacting with Gold Clusters

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Replacement of Au by H does not change electronic and geometric structures.

"Metallic" behaviour of H

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Anomalous Behavior of Atomic Hydrogen Interacting with Gold Clusters

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Abstract: The change in the electronic structure of Au_n^- clusters induced by the exchange of an Au atom by hydrogen is studied using photoelectron spectroscopy. Au anion clusters react with one hydrogen atom but not with molecular hydrogen. The spectra of Au_n^- and $Au_{n-1}H^-$ clusters show almost identical features for $n > 2$ suggesting that hydrogen behaves as a protonated species by contributing one electron to the valence pool of the Au_n^- cluster. This behavior is in sharp contrast to that of the commonly understood electronic structure of hydrogen in metals; namely, it attracts an electron from the conduction band of the metal and remains in an "anionic" form or forms covalent bonding. We discuss the influence of the unique electronic structure of H on the unusual catalytic behavior of Au clusters.

1. Introduction

Most of the materials present on the earth contain hydrogen atoms. Obviously, an understanding of the bonding of hydrogen with other elements is one of the most fundamental problems in chemistry, biology, and physics. Hydrogen shows a similar valence orbital structure to those of the alkali (Li, Na, K, Rb, Cs) and coinage (Cu, Ag, Au) atoms. Yet its properties are very different from these metals. For example, H atoms combine to form H_2 gas under ambient conditions and become an insulating liquid at cryogenic temperatures. Alkali and coinage metal atoms, in contrast, form metallic crystalline phases. In bulk metals or on metal surfaces, hydrogen molecules usually dissociate and bind atomically. The hydrogen atom generally draws electrons from the conduction band and remains in an "anionic" form, resulting in the H induced density of states lying several electronvolts below the Fermi energy.[1-3] For late transition metals such as Au, Cu, and Ag, dissociation of H_2 shows relatively large activation barriers, and metal-H bonding involves negligibly small charge transfers.[4-6] At higher pressure conditions, metal hydrides can form.[7] In contrast, alkali metals are generally strong electron donors on metal surfaces.[8]

Previous studies have shown that metal clusters can readily bind with molecular hydrogen even though it does not form a stable hydride phase in the same system.[9] Chemisorption reactivity of metal clusters toward hydrogen adsorption depends strongly on the size and composition of the clusters and can vary over several orders of magnitude in a small size range.[9] However, detailed studies on electronic structures of H on metal clusters are few,[10,11] and therefore, no generally accepted picture for the electronic structures of H on metal clusters is established. Formation of a covalent bond between H and Al_{13}^- was found in theoretical studies.[12] For Li_nH clusters, one electron from the Li valence orbital is localized on H; in other words, H is anionic.[13] It is worth mentioning that the hydrogen-cluster interaction is an important issue in heterogeneous catalysis. For example, clusters consisting of Au, which is inert in the bulk from, are active toward various reactions, in which hydrogen plays an important role (e.g., propylene epoxidation).[14] Studies of the interactions between hydrogen and Au clusters are essential to unveil the origin of the unusual chemical activities of Au, which is currently one of the most extensively studied subjects in heterogeneous catalysis and surface chemistry. It is important to mention that, recently, gas-phase Au anion clusters were shown to be suitable model systems to shed light on reaction mechanisms of Au-based catalysis.[15,16]

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The properties of clusters of "simple" metals such as Na or Au depend strongly on the number of valence electrons.[17] For example, clusters with 2, 8, 18... electrons are magic; that is, they are stable and chemically inert. These properties can be explained by the electronic shell model,[17] in which the delocalized "conduction" electrons occupy shells in an almost spherical potential. Magic clusters with high stabilities have the closed shell configurations. These electronic shells can be observed directly using photoelectron spectroscopy.[18,19] The electronic shell model is found to be valid for clusters of many different metals[20] like the alkali metals (Na, K, Rb, Cs),[17] the coinage metals (Cu, Ag, Au),[18,19,21,22] group II and III metals (e.g., Mg, Al)[23] and bimetallic clusters such as Au_nNa_m.[20,24−27]

The shell closing (or 18 electron rule for organometallic compounds) also plays a pivotal role in the adsorbate-cluster systems or organometallic compounds.[28−32] For example, the observations that $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$ are more stable than other carbonyl compounds can be explained in terms of closed shell configuration, taking into account that CO provides two electrons into the electronic shells of metals.[29] It is noteworthy that, in inorganic or cluster compounds, CO often acts as a strong electron donor.[28,29,31,32] Consequently, coadsorption of CO and other electron-withdrawing adsorbates such as oxygen can become cooperative rather than competitive on small metal clusters, which is different from the results on metal single-crystal surfaces.[33] Note that a strong metal−CO bonding is a consequence of the withdrawal of electrons from the metal surface via the π-back-donation.[34] A question may be raised if other adsorbates such as H which are known to exist in the anionic state or form covalent bonding on transition metal surfaces can also act as a strong electron donor in the cluster compounds.

The shell orbitals form by superposition of atomic s and p orbitals, for example, in the case of Au, the 6s and 6p orbitals. Valence d orbitals are more localized and will be neglected for further discussion.[18,19] Size dependent variations of structures and properties are mainly caused by the strong dependence of the (s,p)-derived density of states on the number of contributing atomic orbitals. This is especially valid for alkali clusters and clusters of the coinage metals such as Au.

Here, we examine the changes in the electronic structure induced by adsorption of a single H atom on Au clusters. Previously, the reactivity of hydrogen adsorption was found to be sensitive to the electronic structures of metal clusters.[35,36] For small Au clusters, for example, cation and neutral clusters allow chemisorption of hydrogen molecules, whereas the anion clusters do not.[35,36] Geometric structures of an H atom attached to the small Au clusters have been tackled by theoretical studies.[10] However, electronic structures of H on Au cluster are still unveiled. On Au bulk surfaces, a few studies of H chemisorption are carried out. For molecular hydrogen, no chemisorption is observed and only physisorption occurs,[4,37] but atomic hydrogen is chemisorbed readily.[5,38,39] For many transition metals including Cu, Ag, and Au, H chemisorption results in the appearance of an additional feature in the band structure which is assigned to covalent metal−H bond formation.[6] Based on this result, one may expect that hydrogen should form a covalent bond with Au anion clusters. On the other hand, Au atoms have a larger electron affinity compared to that of hydrogen, and thus Au clusters may behave differently toward H than bulk Au does. Our photoelectron experiment on Au_nH^- clusters shows that hydrogen behaves like a monovalent metal atom, donating an electron to the valence pool of the Au clusters.

2. Experimental Details

We studied structures of mass-selected Au_n^- and $Au_{n-1}H^-$ using photoelectron spectroscopy. The experimental set up has been described in detail elsewhere.[40] Au_n^- anions are produced with a pulsed arc cluster ion source and mass selected using a time-of-flight spectrometer (mass resolution $m/\Delta m = 400$). H_2 was inserted into the extender tube. A considerable amount of molecular hydrogen is dissociated in the electric arc generating H atoms.[12] At these conditions Au_nH^- clusters are observed with intensities sufficient for spectroscopy. The temperature of the clusters is estimated to be about room temperature. A selected bunch is irradiated by a ultraviolet (UV) laser pulse (photon energy = 4.66 eV), and the kinetic energies of the detached electrons are measured using a "magnetic-bottle"-type time-of-flight electron spectrometer with an energy resolution of about 2%. For larger Au clusters with $n > 3$, the mass resolution is not sufficient to separate Au_n^- and Au_nH^- clusters, and these spectra have been obtained by subtraction of spectra recorded with and without H supply. Chemisorption of H_2 on Au clusters is predicted to be endothermic,[41] and we do not observe $Au_nH_m^-$ clusters with $m > 1$.

3. Results

In Figure 1, photoelectron spectra of Au^-, AuH^-, Au_2^-, and Au_2H^- are compared. In the spectrum of Au^- (Figure 1a), two peaks are observed (A, B) and the position of the first peak A at 2.3 eV corresponds to the electron affinity (= detachment energy).[42] Peak B of Au^- corresponds to the transition from

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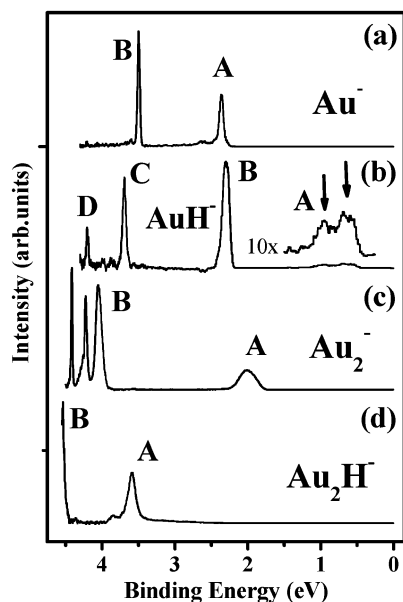(42) Handschuh, H.; Ganteför, G.; Bechthold, P. S.; Eberhardt, W. *J. Chem. Phys.* **1994**, *100*, 7093−7100.

Figure 1. Photoelectron spectra of Au_1^- (a), AuH^- (b), Au_2^- (c), and Au_2H^- (d). The photon energy is 4.66 eV. For the discussion of the marked features, see text.

the anionic electron ground state to the neutral quintet ($^2D_{5/2}$) state.[42] H chemisorption induces a large change in the spectrum of AuH^-, and four features are observed (see peaks A–D in Figure 1b). The appearance of feature A at a low binding energy (BE) indicates a strong decrease of the vertical detachment energy (VDE) down to 0.6 ± 0.2 eV with respect to the bare Au atom. This feature exhibits a vibrational fine structure (arrows) corresponding to a vibrational frequency of 2400 ± 200 cm^{-1} which can be assigned to the Au–H stretching.[43–45]

To complement the experimental work and gain an understanding on the electronic structure of hydrogen, we have calculated the geometry and total energies of neutral and anionic AuH cluster and compared these to Au_2 using density functional theory and generalized gradient approximation for exchange and correlation potential. The atomic orbitals were represented by Gaussian basis. We have used the Stuttgart Relativistic Small Core ECP basis set (commonly referred to as RSC basis)[46] for Au and 6-311++G basis for H available in the Gaussian 98 code for our computations.[47] This choice yields the ionization potential and the electron affinity of Au to be 9.46 and 2.33 eV, respectively. These agree well with the corresponding experimental values of 9.22 and 2.31 eV. The ground state of the AuH^- cluster is found be a spin doublet with a bond length of 1.64 Å. The vertical detachment energies from the doublet anion to the singlet and triplet states of the neutral AuH having the geometry of the anion lie at 0.84 and 3.78 eV, respectively. These results are consistent with peaks A and C in Figure 1b. Peak B in Figure 1b could not be assigned based on the theoretical calculations. Since one ends up with the ultimate ground state of each spin state in our calculations, peak B should most likely result from the excitation from anionic doublet

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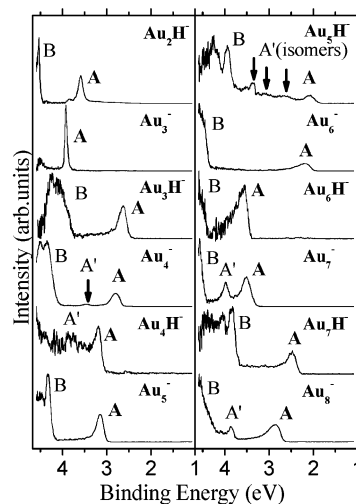(47) Frisch, M.; et al. *Gaussian 98*; Gaussian Inc.: Pittsburgh, PA, 1998.

Figure 2. Photoelectron spectra of Au_nH^- and Au_n^- clusters (photon energy = 4.66 eV). The spectra of clusters with the same total number of atoms exhibit a surprising similarity. For the discussion of the marked features, see text.

ground state to the one of nonground-state singlet of neutrals. The neutral AuH dimer has a bond length of 1.52 Å, a binding energy of 3.10 eV, and a vibrational frequency of 2278 cm^{-1}, which are in line with experimental values of 3.32 eV and 2305 cm^{-1}. Mulliken analysis reveals that the charge on the H atom in neutral AuH is +0.13. In the metallic host, this is around −0.5. In the AuH^- cluster, the charge on H is +0.2 and that on Au amounts to −1.2. Thus the added electron in AuH^- prefers to reside on the Au atom rather than on the H atom. This arises due to the large electron affinity of Au which is 2.3 eV.

Figure 1 parts c and d illustrate the change induced by H chemisorption for Au_2^-. In the spectrum of bare Au_2^- (Figure 1c), peak A at low BE is observed corresponding to a VDE of 2.0 eV.[42,48] H-chemisorption induces a strong increase of the VDE up to 3.6 ± 0.1 eV (peak A in Figure 1d). The energy positions of peaks A and B in Figure 1c correspond to the calculated VDEs (2.13 and 3.86 eV) resulting from the transition from the doublet state of the Au_2^- to the singlet and triplet state of the neutral counterpart. The calculated binding energy and bond length of Au_2 of 1.06 eV and 2.56 Å are also consistent with the experimental values of 1.15 eV and 2.47 Å, respectively.

For the dimers, the exchange of an Au atom by an H atom results in a considerable change of the spectra. However, these differences almost vanish for the larger species. Figure 2 displays spectra of Au_n^- and $Au_{n-1}H^-$ clusters for $n = 3-8$. A first inspection suggests that the spectra of the $Au_{n-1}H^-$ clusters are similar to those of the respective Au_n^- clusters. Linear Au_3^- has a high VDE (feature A at 3.9 eV),[42] and a relatively high VDE is also observed for Au_2H^- (feature A at 3.6 eV). Following the even/odd alternation, the VDE is relatively low for Au_4^- (2.8 eV) as it is for Au_3H^- (2.6 eV). The spectra of the four-atom clusters are very similar except for the small differences in BE of the d-orbital emission (features marked B[22]).

For the five-atom clusters, the VDEs are again similar (peaks marked A), but the spectrum of Au_4H^- looks different compared

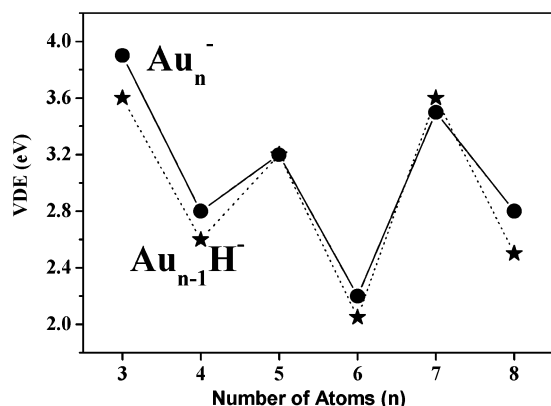(48) Ho, J.; Ervin, K. M.; Lineberger, W. C. *J. Chem. Phys.* **1990**, *93*, 6987–7002.

Figure 3. Comparison of the vertical detachment energies (VDEs) of the bare Au_n^- (circles) and reacted $Au_{n-1}H^-$ (stars) clusters as extracted from the photoelectron spectra. The absolute uncertainty of the VDE is ± 0.1 eV.

to that of Au_5^-. Like in the other spectra, a distinct peak (A) appears at low BE, but at higher BE a continuous signal with weak superimposed maxima (marked A′) is visible. A similar behavior is observed for the six-atom clusters. The main features A and B are at comparable BEs for Au_6^- and Au_5H^-, but in the spectrum of Au_5H^- there are several additional weak peaks (marked A′, arrows). We assign these weak features to different, less abundant isomers. Such isomers are known to exist for bare Au_n^- cluster anions.[49,50] In the spectrum of Au_4^-, a weak feature (A′) is visible, which is assigned to an almost degenerate isomer of the tetramer anion.[49,50] The topic of different coexisting isomers of Au_nH^- clusters and their formation has been addressed in a recent paper.[10]

The main peaks (A,B) are very similar for the four-atom clusters, Au_3H^- and Au_4^-, and for the six-atom clusters, Au_5H^- and Au_6^-. For the larger clusters displayed in Figure 2, the even/odd alternation continues and the shell closing expected at eight electrons (Au_7^-, Au_6H^-) manifests itself by a relatively high VDE. For these larger clusters ($n = 7, 8$), the similarity between the spectra of the $Au_{n-1}H^-$ and Au_n^- clusters is again obvious, if we tentatively assign weak additional peaks (marked A′) to different isomers. In Figure 3, the VDEs are plotted for the $Au_{n-1}H^-$ and Au_n^- clusters supporting the similarity of the electronic structures of these clusters. The electronic structure of these alloy clusters is determined by the number of delocalized electrons and this number is not changed, if a Au atom is replaced by a monovalent atom. Here, H acts like an alkali or a coinage metal atom.

4. Discussion

For Figure 1, at a first glance no systematic trends of H chemisorption can be extracted. In one case, the VDE increases by 1.7 eV, and in the other, a decrease by 1.6 eV is observed upon H-chemisorption. However, a comparison of the spectrum of Au_2^- (Figure 1c) with that of AuH^- (Figure 1b) might shed some light on the chemisorption mechanism. The spectrum of the bare dimer can be understood in terms of bond formation by the interaction of the two 6s orbitals forming a bonding σ and an antibonding σ^* orbital.[42,48] The additional electron in the anionic state occupies the antibonding σ^* orbital and gives rise to the appearance of peak A (Figure 1c) at low BE. The

antibonding character of this orbital is reduced by strong s/p hybridization and relativistic effects compared to Ag_2^- and Cu_2^-.

The spectrum of AuH (Figure 1b) can be discussed in terms of the interaction of the H 1s orbital located at 13.6 eV (far beyond the range of our experiment) and the Au 6s orbital. Again, bonding σ and antibonding σ^* orbitals are formed, and the additional electron occupies the antibonding σ^* orbital. Removal of this antibonding electron gives rise to excitations into various vibrational states explaining the observed fine structure (arrows in Figure 1b). The low BE of this orbital corresponds to an increased bonding−antibonding splitting caused by the shorter bond length of Au−H compared to that of Au−Au[43−45] and a higher binding energy of the AuH molecule as discussed above. In addition, s−p-hybridization and relativistic effects are weaker and do not stabilize the antibonding orbital as in the case of Au_2^-.

For a number of Au atoms (n) higher than 3, electronic structures of Au_n^- and $Au_{n-1}H^-$ were shown to be similar (Figure 2). One may assume that the geometries of $Au_{n-1}H^-$ and Au_n^- are also similar, since there is a strong coupling between geometric and electronic structures. This assumption can be confirmed by comparison with calculations, in which energetics and geometric structures of Au_nH^- were studied, even though electronic structures of these compounds were not tackled.[10] The case with the most pronounced similarity of the photoelectron spectra is $n = 4$: the spectra of Au_4^- and Au_3H^-. For Au_4^-, theory predicts a planar structure with a base triangle of three Au atoms and a fourth atom attached at the apex of the triangle.[49,50] The same structure has been calculated for Au_3H^- with the H replacing the top Au atom with a slightly shorter bond length.[10] For the cases of Au_6^- and Au_5H^-, the calculated geometries are very similar too: Au_6^- has a planar triangular structure,[49,50] and Au_5H^-, a similar structure with the H atom replacing a corner Au atom.[10] Accordingly, for the two sizes ($n = 4, 6$), the geometries of the bare and hydrogenated cluster anions are similar as are the photoelectron spectra. It is important to note that these calculations were performed for many different isomers.[10] Among many isomers, the structures mentioned above correspond to the clusters with the highest concentrations in our experiments. For more details, please see ref 10.

In our photoelectron spectra, we observe the uppermost occupied orbitals of the cluster valence band. This binding energy regime is dominated by the (s,p)-derived density of states, and these states can be viewed as a superposition of 6s and 6p orbitals of the Au atoms in the cluster. If one atom is removed, the hole manifold of states is changed as proven by the pronounced size dependence of the spectra of the bare Au_n^- clusters. The manifold of s/p-derived orbitals remains almost unchanged upon replacement of an Au atom by another atom, only when the new atom contributes to the manifold of states in a manner similar to how an Au atom does, resulting in no changes in electronic and geometric structures.

Since we only observe the uppermost occupied orbitals, changes might be occurring for s/p-derived orbitals at higher binding energies, especially for the lowest molecular orbital of the conduction "band". In preliminary calculations, indeed a strong disturbance of the molecular orbital of Au_5H^- (with respect to Au_6^-) has been found.[51] The lowest molecular orbital

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in the conduction "band" is shifted toward a higher binding energy and localized close to the H atom adsorption site. However, already the orbitals next higher in energy are very similar in shape and symmetry for Au_5H^- and Au_6^-.[51]

Only the dimers seem to be different (Figure 1b,c). The difference has been explained by the increased bonding−antibonding splitting of the σ-orbitals in Au−H, which is a consequence of the high BE of the H 1s orbital. In the larger species, most likely the same thing happens: the BE of the "lower edge of the conduction band" is higher for an $Au_{n-1}H^-$ cluster compared to an Au_n^- cluster due to the contribution of the H 1s orbital. Correspondingly, the most antibonding orbital ("upper edge of the conduction band") has a symmetrically increased BE analogous to the dimer case. However, in all larger clusters, this antibonding orbital is not occupied and the effect is not visible in our experiment. All the s/p-derived orbitals between the most bonding and the most antibonding orbital remain almost unchanged, if an Au atom is replaced by an H atom. If the Au atom is simply removed, these orbitals change dramatically. Therefore, H contributes like a metal atom to most delocalized orbitals in a Au cluster.

Previously, CO was shown to be a two-electron donor on coinage metal clusters.[28,29,31,32] One of the important consequences of this result is that coadsorption of CO with other electron-accepting adsorbates such as oxygen can be noncompetitive but cooperative.[33] Our result shows that, on Au clusters, H provides an electron to the valence electron pool of Au clusters, which can result in cooperative adsorption between H and oxygen, analogous to the case of CO and O_2 coadsorption on Au anion clusters. This can be closely related to the high activities of Au clusters toward various reactions in which H adsorption in involved. For the partial oxidation of propylene in H_2 and O_2 environments, hydroperoxide (H_2O_2) is believed to be an important reaction intermediate.[14] To maximize the yield of hydroperoxide, the rates of the $H + O_2 \rightarrow HOO$ and $H + O_2H \rightarrow HOOH$ reactions should be enhanced. On Pt-group metals, hydrogen adsorption lowers the rate of oxygen adsorption, or vice versa, most likely because H is an electron acceptor like oxygen, leading to the competitive adsorption of both reagents.[52] Consequently, the HOOH formation involves a high activation barrier. On Au clusters, HOOH formation can be facilitated as a consequence of the cooperative adsorption of H and O_2. It is worth mentioning that Au clusters do not react with H_2 but only react with H, implying that, in real catalysis, dissociation of hydrogen occurs on defects of oxide support materials, and the atomic H can then diffuse onto the Au particles. Alternatively, H_2 only dissociate in the presence of the precovered oxygen on Au nanoclusters.

5. Conclusion

We presented photoelectron spectra of bare Au_n^- and $Au_{n-1}H^-$ clusters. The spectra of the clusters with the same total number of atoms exhibit a surprising similarity. The replacement of an Au atom by an H atom induces minor electronic and geometric structural changes as it would be expected for a monovalent metal atom. Therefore, our data indicate that single hydrogen atoms in the environment of an Au cluster behave like metal atoms.

(52) Mitsui, T.; Rose, M. K.; Fomin, E.; Ogletree, D. F.; Salmeron, M. *Surf. Sci.* **2002**, *511*, 259−266.