Electronic properties of gold on Mo(110): d → s,p charge redistribution and valence band shifts

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Received 9 December 1994; accepted for publication 6 March 1995

Abstract

The interaction between Au atoms and Mo(110) has been investigated using photoelectron spectroscopy and ab initio self-consistent field calculations. The formation of Au–Mo bonds induces shifts toward higher binding energy (0.3–0.7 eV) in the core levels and valence d band of gold. This is accompanied by an important redistribution of charge, in which Au loses 5d electrons and gains (6s,6p) electrons. The positive binding-energy shifts in the Au 4f levels and 5d band reflect the effects of a Mo-induced reduction in the Au 5d electron population.

Keywords: Ab-initio quantum chemical methods and calculations; Atom–solid interactions; Gold; Metal–metal interfaces; Molybdenum; Thermal desorption spectroscopy; X-ray photoelectron spectroscopy

1. Introduction

In recent years, the study of the electronic properties of Cu, Ni and Pd atoms supported on surfaces of early-transition metals has been the subject of many works [1–20]. For these admetals, the results of X-ray photoelectron spectroscopy (XPS) show core levels that are shifted toward higher binding energy with respect to those in pure Cu, Ni or Pd [1–4,14,19]. These electronic perturbations are accompanied by an admetal-induced reduction in the work function of the metal substrate [6–9,12,18,19]. The results of XPS and the work-function measurements suggest that electrons move from the Cu, Ni or Pd adatoms toward the substrates [1,2,10,13,20]. Self-consistent field (SCF) calculations have shown that the net charge transfer in these bimetallic systems is small [20,21]. For the Pd adatoms, bimetallic bonding induces a d → s,p rehybridization that produces a redistribution of charge, in which 4d electrons "move" from the Pd center into the region around the bimetallic bond [20]. This redistribution of d electrons contributes to a positive binding-energy shift in the Pd core levels [1b,16], and diminishes the ability of the metal to adsorb CO [2,20,22]. The electronic perturbations observed for the Pd overlayers are similar to those seen in bulk alloys [20,23], where results of photoemission and L-edge XANES (X-ray absorption near-edge structure) experiments show that bimetallic bonding induces an increase in the binding energy of the core levels and valence band of Pd with a reduction in the Pd(4d) electron population [23].

In the present work, we examine the electronic properties of Au atoms supported on Mo(110) using...
photoelectron spectroscopy and ab-initio SCF calculations. It is worthwhile to compare the behavior of the Au adlayers with that reported previously for the Cu, Ni and Pd overlayers [1,2,13,20]; since Au has an electron affinity (223 kJ mol\(^{-1}\) [24]) much larger than that of Cu (118 kJ mol\(^{-1}\) [24]), Ni (156 kJ mol\(^{-1}\) [24]) or Pd (98 kJ mol\(^{-1}\) [24]). Our results indicate that, in spite of a net Mo → Au charge transfer, the 4f levels and 5d band of Au shift to higher binding energy on the Mo(110) surface. The shifts in the core levels and valence band of Au reflect changes in the Au(5d) electron population. It is shown that the magnitude of the electronic perturbations in supported Au depends strongly on the fraction of empty states in the valence band of the metal substrate.

2. Experimental and theoretical methods

2.1. Photoemission measurements

The experiments were carried out in an ultrahigh-vacuum system (base pressure < 4 × 10\(^{-10}\) Torr) equipped with a quadrupole mass spectrometer for thermal desorption mass spectroscopy (TDS) and a hemispherical electron-energy analyzer with multichannel detection for photoemission studies. The photoemission spectra were acquired using a Mg K\(\alpha\) X-ray source. Binding energies were calibrated using the Au 4f\(_{7/2}\) and Mo 3d\(_{5/2}\) peaks of the pure metals, which were set at 83.9 and 227.9 eV, respectively [25].

The Mo(110) crystal was mounted in a manipulator capable of resistive heating to 1550 K and liquid-nitrogen cooling to 80 K. An electron beam assembly provided capabilities for heating to 2400 K. The Mo(110) surface was cleaned following standard procedures [4,10]. Gold deposition was performed by resistively heating a loop-shaped Ta wire wrapped with an ultrapure Au thin foil. The Au coverages were determined by TDS area analysis [26–29]. These coverages are reported with respect to the number of Mo(110) surface atoms (1.43 × 10\(^{15}\) atoms/cm\(^2\)). One Au adatom per substrate surface atom corresponds to \(\theta_{Au} = 1\) monolayer (ML).

2.2. Molecular orbital calculations

The electronic properties of several gold molybdenum clusters were investigated at the ab-initio SCF level. The molecular orbital (MO) calculations were performed using the HONDO program [30]. The non-empirical effective core potentials (ECPs) of Hay and Wadt [31] were used to describe the inner shells of Mo and Au. These ECPs are able to reproduce the results of ab-initio all-electron Hartree-Fock SCF calculations. Mass—velocity and relativistic effects are incorporated into the ECPs [31]. The 5s, 5p and 4d atomic orbitals of Mo were explicitly treated by a basis set of three s, three p, and four d primitive Gaussian-type orbitals [31] contracted to two s, one p and two d (3s3p4d/2s1p2d). To describe the 6s, 6p and 5d atomic orbitals of Au, we used the Gaussian basis set employed in our previous study for the adsorption of gold on aluminum (3s3p4d/2s1p2d) [20].

The charges and orbital populations reported in this work were calculated by a Mulliken population analysis [32]. Due to the limitations of this type of analysis [33], the charges must be considered only in qualitative terms.

3. Results and discussion

The interaction between gold and Mo(110) has been previously investigated using TDS, low-energy electron diffraction (LEED), work-function measurements and Auger electron spectroscopy (AES) [27–29,34,35]. In the Au/Mo(110) system, there is no alloying of the metals. The first monolayer of gold grows two-dimensionally on top of Mo(110), displaying lattice structures that are different from the lattice of the Mo substrate or the (111) face of bulk Au [27].

Fig. 1a shows valence photoemission spectra taken after depositing Au on Mo(110) at 350–380 K. A comparison of the spectra for clean Mo(110), bottom one, and a thick Au multilayer (\(\theta_{Au} > 20\) ML), top one, indicates that the cross section for the Au 5d band is much larger than that for the Mo 4d band. This fact allows the monitoring of the Au 5d\(_{3/2}\) and 5d\(_{5/2}\) signals on top of a background produced by electron emissions from the Mo 4d band. The unique
features of the Au overlayers are more clearly depicted in the difference spectra of Fig. 1b. The substraction of the Mo 4d signal was done taking into consideration the attenuation induced by the Au overlayer on the Mo features [7,36]. During the substraction, the base line of the Au/Mo(110) and Mo(110) spectra was not modified. The trends observed in Figs. 1a and 1b for the Au peaks are identical.

In Fig. 1, a Au\textsubscript{0.39}/Mo(110) system exhibits Au 5d\textsubscript{3/2} and 5d\textsubscript{5/2} peaks centered at binding energies of ~ 6 and 4 eV, respectively. An increase in the Au coverage from 0.39 to 0.93 ML produces an enhancement in the intensity of the Au 5d\textsubscript{3/2} and 5d\textsubscript{5/2} features without inducing significant changes in their positions. The position observed for the 5d\textsubscript{3/2} peak of Mo-bonded Au is close to that seen for the 5d\textsubscript{3/2} peak of bulk Au. In contrast, the 5d\textsubscript{5/2} features of Mo-bonded Au appear shifted toward higher binding energy (~ 0.7 eV) with respect to those of bulk Au. In Au alloys, the 5/2-component of the Au 5d band is more sensitive to changes in the nature of the metal–metal bond than the 3/2-component [36,38–41]. For the Au atoms supported on Mo(110), the 5d\textsubscript{3/2}–5d\textsubscript{5/2} energy separation (a property that reflects the strength of the Au–Au interactions and the number of Au nearest neighbors surrounding a Au atom [36,38–41]) is ~ 2 eV. This value is in between those found for atomic (~ 1.5 eV [42]) and bulk metallic Au (~ 2.7 eV).

Previous photoemission studies for a Au monolayer on Ru(001) revealed the existence of interface states at ~ 1.5 eV below the Fermi level [36]. For a Cu monolayer on Ru(001), interface states have been detected at 3.6 and 1.5 eV [43]. On the other hand, photoemission experiments for the deposition of Au or Cu on early-transition metals (Au/Nb(110) [44], Cu/Nb(110) [6] and Cu/W(110) [5]) have not shown the presence of interface states in this type of bimetallic system. The XPS results in Fig. 1 do not show extra features between 0 and 2 eV that would provide a clear indication for the existence of interface states in the Au/Mo(110) system. All the photoemission features can be attributed to pure Mo or Au.

Fig. 2 displays Au 4f spectra acquired after dosing
Au to Mo(110) at 350–380 K. An increase in the Au coverage from 0.20 to 0.93 ML produces only very minor changes in the position of the Au 4f$_{7/2}$ level, which is always close to the value of 83.9 eV found for a thick Au multilayer ($\theta_{Au} > 20$ ML). The lack of a shift in the admetal core levels at submonolayer coverages has been seen before in photoemission studies for Au, Ag and Cu overlayers on Ru(001) [38,45,46]; the phenomenon indicates the formation of large two-dimensional islands of the admetal on top of the substrate [45–48]. For Au(100) and Au(111), the atoms in the surface layer exhibit 4f$_{7/2}$ binding energies that are ~0.35 eV smaller than that of the bulk atoms [49,50]. The formation of bonds between Au and Mo shifts the 4f$_{7/2}$ level of the Au surface atoms toward higher binding energy, close to the 4f$_{7/2}$ position for bulk Au.

In order to obtain a better understanding of the interactions between Au and Mo(110) at an atomic orbital level, we investigated the adsorption of a Au atom on a hollow site of a Mo$_9$ cluster (see cluster I in Fig. 3), using ab-initio SCF calculations. Strictly speaking, the Au/Mo$_9$ system is a good model for the Au/Mo(110) surface only at the limit of small Au coverages, when the admetal ↔ admetal interactions are negligible. However, this is not a serious problem, since the TDS [27–29] and photoemission results for Au/Mo(110) indicate that the Au ↔ Au interactions are weaker than the Au ↔ Mo interactions, and the qualitative trends in the TDS [27–29] and XPS spectra do not change with Au coverage. In the Au/Mo$_9$ cluster, the Mo–Mo distances and Mo–Mo–Mo bond angles were set equal to those in bulk Mo [51]. The Au–Mo bond lengths were optimized at the ab-initio SCF level, obtaining Au–Mo nearest-neighbor distances of 2.77 Å for the ground state of the cluster. This value is somewhat smaller than the sum of the metallic radii of Mo (1.40 Å [51]) and Au (1.44 Å [51]). The electronic properties of the Au/Mo$_9$ cluster were compared to those of a Au/Au$_9$ cluster that models the adsorption of Au on a hollow site of Au(111) (see cluster II in Fig. 3). In the homonuclear Au cluster, the geometry was set equal to that seen in bulk Au [51].

In Table 1 are listed the calculated charge and orbital populations for Au in Au/Mo$_9$. The charge

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<th>Atomic orbital populations for Au adatoms (electrons)</th>
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See Ref. [64].

a From Ref. [20].
transfer in the Mo–Au bond is small. The ab-initio calculations indicate that Au is a net electron acceptor on Mo(110). For Au on Mo(110) [27] or other early-transition metals (Nb(110) [44], W(110) [8] and poly-crystalline Re [52]), a net substrate → Au charge transfer leads to an increase in the work function of the metal surface. Atomic Au has a 5d\textsuperscript{10}6s\textsuperscript{1} electronic configuration. The formation of Au–Au bonds induces a weak Au(5d) → Au(6s,6p) rehybridization [53,54]. A gold atom bonded to Mo shows a significant reduction in the electron population of the 5d orbitals and an increase in the population of the (6s,6p) orbitals. This is a consequence of inter- and intra-atomic electron transfers: Au(5d) → Mo(4d,5s), Mo(4d,5s) → Au(6s,6p) and Au(5d) → Au(6s,6p). In previous studies for bulk alloys, it has been shown that Au can act as a 5d-electron donor and a (6s,6p)-electron acceptor when forming intermetallic compounds [39,41,55–58]. Au L\textsubscript{II,III}-edge XANES experiments indicate a net loss of electrons from the Au(5d) orbitals upon the formation of AuTi and AuTa alloys [39,58].

Fig. 4 displays the energy range covered by the occupied 5d orbitals of a Au atom supported on Mo\textsubscript{n} and Au\textsubscript{n} clusters. A change from a Au to a Mo substrate is accompanied by a large decrease in the width of the 5d "band" of the Au adatom and a shift of the band centroid toward deeper energy. Identical trends are observed in the photoemission results displayed in Fig. 1. Our MO calculations did not include effects of final-state relaxation present in photo-emission processes. This fact makes impossible a quantitative comparison with the XPS results. Nevertheless, after examining the MO calculations, we can conclude that the shifts observed in the photoemission experiments for the Au/Mo(110) surfaces come in part from changes in the initial state of the system.

The positive Au 4f and 5d binding-energy shifts found after depositing Au on Mo(110) cannot be explained on the basis of the net charge transfer within the Au–Mo bond. In principle, an increase in the number of electrons on Au should produce shifts in its core and valence levels with a sign opposite to that seen in the experiments [59]. In the Au/Mo(110) surfaces, the effects of increasing the Au(6s,6p) populations are overcome by a reduction in the Au(5d) population. In general, the core levels and valence d band of Au are much more sensitive to variations in the population of the 5d orbitals than to changes in the occupancy of the 6s and 6p orbitals [20,39,41,55–58]. The 5d orbitals are more compact than the 6s or 6p orbitals and exhibit larger Coulomb interactions with the Au core electrons [57,60]. For example, in the case of atomic Au, a 5d\textsuperscript{10}6s\textsuperscript{1} → 5d\textsuperscript{9}6s\textsuperscript{2} rehybridization increases the stability of the Au 4f and 5d levels by 4.7 and 3.8 eV, respectively [60].

Fig. 5a compares the binding-energy shift observed for the 5/2-component of the Au 5d band on Mo(110) (from Fig. 1) with shifts seen when the noble metal is in contact with Al(100) [20,61], poly-crystalline Ti [20,62], Nb(110) [44], Ru(001) [37] and Pt(100) [63]. In all these systems, bimetallic bonding induces shifts toward higher binding energy in the 5/2-component and centroid of the Au 5d band. In general, the magnitude of the electronic perturbations in supported Au increases when the
fraction of empty states in the valence bands of the metal substrate rises. An identical trend is observed in MO calculations for the adsorption of an Au atom on Al$_9$ [20], Mo$_9$, Pt$_9$ [64] and Au$_9$ clusters (see Fig. 4).

In Table 1 are listed the calculated charges for an Au atom deposited on Mo, Pt and Al substrates. For the deposition of Au on Pt, a net Au → substrate charge transfer leads to a decrease in the work function of the Pt surface [63]. This behavior is opposite to that seen for Au/Mo, where there is a net substrate → Au charge transfer and an increase in the work function of the Mo surface [27]. However, Au atoms bonded to Pt and Mo surfaces exhibit shifts in their 5d band toward higher binding energy.

Fig. 5b shows the calculated Au 5d populations for the Au/X$_9$ clusters (X = Al, Mo, Pt or Au). By comparing the qualitative trends in Figs. 4 and 5, one can see a correlation between the reduction in the Au 5d population and the positive binding-energy shifts in the Au 5d band. A decrease in the Au 5d population reduces electron–electron repulsion within this d shell, increasing its stability. The behavior seen for the Au adatoms is similar to that seen for Au in bulk compounds [57]. Linear-augmented Slater-type orbital (LASTO) calculations for binary alloys containing Au and a 5d-transition metal show a decrease in the Au(5d) electron population when the fraction of empty states in the valence bands of the transition metal increases [57]. The trends in Fig. 5b can be understood in terms of a simple model based on orbital mixing [1,4]. Hybridization of the electron-rich 5d band of Au with the electron-poor valence bands of Al or an early-transition metal leads to a loss of Au(5d) character in the occupied states of the system. The smaller the occupancy in the valence bands of the substrate, the larger the reduction in the 5d population of the Au adatoms.

The electronic perturbations observed in Fig. 5 for the Au overlayers on Al and early-transition metals are similar to those found for Pd [20], Ni [1,2], Cu [21] and Pt [66] overlayers. In this type of bimetallic systems, the admetals exhibit shifts toward higher binding energy in the core levels and valence d band with a reduction in the valence d population. The magnitude of these electronic perturbations depends strongly on the occupancy of the valence bands of the metal substrate [1,2,20,21,66].

4. Conclusions

Gold atoms bonded to Mo(110) exhibit 4f levels and a 5d band shifted toward higher binding energy with respect to those of pure Au. These shifts reflect a reduction in the Au(5d) electron population.

Acknowledgements

This work was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the US Department of Energy, Office of Basic Energy Sciences, Chemical Science Division.
References

to model the adsorption of Au on a fcc hollow site of Pt(111)
[21]. The Pt–Pt distances were set equal to 2.77 Å, as in bulk
Pt [51]. The Au–Pt bond lengths in the Au/Pt<sub>c</sub> cluster were
optimized at the ab-initio SCF level, considering several
possible electronic states with different orbital occupancies
and spin multiplicities. For the ground state, the calculations
yielded Au–Pt bond distances of 2.74 Å. This value is close
to the sum of the corresponding metallic radii: Au + Pt = 2.83
Å [51], and to bond lengths reported for bulk platinum gold
alloys [65].

[65] M. Hansen, Constitution of Binary Alloys, 2nd ed. (Mc-
4279.