

Chlorine Adsorption on Au(111): Chlorine Overlayer or Surface Chloride?

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Abstract: We report the first scanning tunneling microscope (STM) investigation, combined with density functional theory calculations, to resolve controversy regarding the bonding and structure of chlorine adsorbed on Au(111). STM experiments are carried out at 120 K to overcome instability caused by mobile species upon chlorine adsorption at room temperature. Chlorine adsorption initially lifts the herringbone reconstruction. At low coverages (<0.33 ML), chlorine binds to the top of Au(111)-(1 \times 1) surface and leads to formation of an overlayer with $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure at 0.33 ML. At higher coverages, packing chlorine into an overlayer structure is no longer favored. Gold atoms incorporate into a complex superlattice of a Au–Cl surface compound.

Introduction

Chlorine adsorption on gold has been considered as an important gas–solid interaction system,^{1–4} especially with recent studies on Au catalysis where both gold and chlorine are often involved.^{5,6} For example, gold is found to be especially active toward catalytic oxidation of mercury by chlorine⁵ and has shown potential commercial applications in environmental mercury removal.⁷ However, the role of gold, especially how gold interacts with Cl and Hg, is still unclear.⁵ Gold is also an active catalyst in olefin partial oxidation.^{8,9} Recent studies on Au(111) show that chlorine can disperse and redistribute surface oxygen and hence increases the reaction selectivity.^{6,10} Although this dispersion effect has been clearly revealed, the structure of chlorine and oxygen coadsorbed on gold is still unclear.¹⁰ To answer these fundamental questions that are raised during development of gold toward practical applications, it is crucial to first elucidate the adsorption and structure of chlorine on gold.

Furthermore, previous studies of chlorine adsorption on Au have generated debate about the bonding and structure of the

overlayer. Spencer and Lambert¹ reported that a lower-temperature Cl₂ desorption peak at ~ 650 K would start to develop in temperature-programmed reaction only after a higher-temperature peak at ~ 800 K saturated, suggesting a tightly bound layer formed first. They proposed that gold chloride (AuCl₃), possibly multiple layers, directly forms upon chlorine adsorption on Au(111). Kastanas and Koel² subsequently studied chlorine adsorption on Au(111) over a wider temperature range and observed a $(\sqrt{3} \times \sqrt{3})R30^\circ$ low-energy electron diffraction (LEED) pattern at temperatures below 230 K. Furthermore, they did not detect a Cl 2p binding energy shift in X-ray photoelectron spectroscopy (XPS) as a function of increasing chlorine coverage. Since there is no evidence of chloride formation, they concluded that only a chemisorbed chlorine overlayer was present. They also proposed an overlayer structure, where chlorine is bound to the top of Au(111)-(1 \times 1) surface, based on the $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity in LEED pattern, which corresponded to a coverage of 1.33 monolayers (ML) of Cl. With the obvious inconsistency in two studies, the nature of Cl–Au interaction and the structure of Cl on Au(111) remain unsolved.¹¹

In this article, we report the first scanning tunneling microscope (STM) studies of Cl₂ adsorption on Au(111). The STM work in combination with density functional theory (DFT) calculations and XPS are used to demonstrate that chlorine interaction with Au(111) is a dynamic process involving multiple stages at different chlorine coverages. Initially at low Cl

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coverage (below 0.33 ML), Au atoms are released from the herringbone reconstruction to relieve surface stress. Continuous chlorine adsorption leads Cl atoms to bind on top of a Au-(111)-(1 × 1) layer, ultimately leading to the Au(111)-(√3 × √3)R30°-Cl overlayer at 0.33 ML coverage. At higher coverage, more Au atoms are removed from the surface and a surface chloride compound that contains Au atoms forms. Interestingly, the charge on the chemisorbed Cl is similar to the gold (III) chloride, based on our theoretical results, accounting for the absence of a Cl 2p binding energy shift. Our study demonstrates the delicate balance between charge transfer and formation of a compound overlayer on the surface. We place our studies of Cl on Au(111) in a more general context.

Methods

Experimental Section. Experiments were carried out in a two-chamber ultrahigh vacuum (UHV) system with a base pressure of 2×10^{-10} Torr. The Au single crystal with (111) orientation was cleaned in a preparation chamber by repeated Ar⁺ ion sputtering and annealing to 900 K. Auger electron spectroscopy (AES) and LEED confirmed that the surface was clean and the herringbone reconstruction was present. Temperature-programmed desorption (TPD) experiments were also carried out in the preparation chamber, with heating rate ~ 10 K/s. Chlorine (Matheson Tri Gas Inc., research grade) was background dosed through a leak valve attached to the preparation chamber.

The STM images were acquired in the second UHV chamber using a commercial, variable-temperature STM (RHK Technology, Inc.). The scanner was calibrated using atomically resolved images of the clean Au(111) surface and the Au(111) step height for the lateral and vertical directions, respectively. In this article, all STM images were collected with the bias voltage of +0.3 V (sample biased, empty states) and a tunneling current of 1 nA.

The X-ray photoelectron spectra were obtained in a separate UHV system equipped with LEED, quadrupole mass spectrometer (Balzers), a dual anode X-ray source (Perkin-Elmer 04-548), and a hemispherical energy analyzer (SPECS EA-10-plus). Core-level spectra were excited 1253.6 eV Mg K α_1 , α_2 radiation. To quantify the coverages using intensities measured in XPS, the Shirley background was subtracted.¹² Sulfur-covered Au(111) is prepared by exposing Au to 1×10^{-5} Torr SO₂ for 30 min at 300 K, followed by flashing the sample to 550 K.^{13,14} A split ($\sqrt{3} \times \sqrt{3}$)R30° LEED pattern was observed after this procedure, which corresponds to a sulfur coverage of 0.28 ML.^{13,15} The split spots signify that there are three equivalent domains on the surface.

Computational Details. The DFT results were obtained with the VASP code¹⁶ using the GGA-PW91 functional¹⁷ to model electron exchange and correlation. Ultrasoft pseudopotentials were used with the default plane-wave cutoffs for different elements taken from the GGA ultrasoft pseudopotential database.¹⁸ Calculations were done with a 12-layer slab of a ($\sqrt{3} \times \sqrt{3}$)R30° unit cell of Au(111), with the bottom six layers remaining fixed in their bulk positions and the top six layers allowed to relax. A large vacuum region between the slabs of ~ 20 Å was used to ensure that the dipole created by the chlorine adsorption did not artificially interact in neighboring unit cells. A Monkhorst-Pack Γ -centered $6 \times 6 \times 1$ *k*-point sampling was used. Spin-polarized calculations were used to test each set of data and were found to have no significant effect on the energy comparisons.

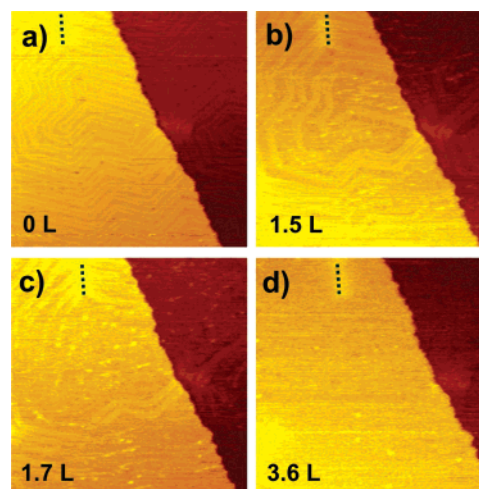


Figure 1. STM images recorded during Cl adsorption on Au(111), all from the same area of 150×150 nm². The dashed line marks a screw dislocation as a position reference. Cl₂ pressure is 4×10^{-9} Torr. Cl₂ dosing and STM imaging are at 120 K.

Results and Discussions

Experimental Results. At room temperature, chlorine adsorption on Au(111) causes corrosion and formation of mobile species (Supporting Information). To overcome the instability induced by mobile species, STM experiments were carried out at 120 K. Clean Au(111) reconstructs to the so-called herringbone structure, such that the surface contains $\sim 4\%$ more atoms than the same plane in the bulk. The strain created by the mismatch between the top layer and the underlying bulk is minimized by the zigzag arrangement of soliton walls¹⁹ (Figure 1a).

Adsorption of Cl₂ leads to the obvious disturbance and partial disappearance of the herringbone structure (Figure 1b,c). The surface reconstruction is lifted, and excess Au atoms on the surface layer are ejected, as indicated by the particles observed in the images. Because the surface temperature is low in these data, the Au released from the herringbone has limited mobility; thus, some particles are formed on the terraces. When the Cl₂ dosage reaches 3.6 L, no soliton wall can be observed using STM (Figure 1d). Previous LEED studies also showed that, upon dosing chlorine, Au(111) reconstruction spots disappeared and only sharp (1 × 1) spots were observed.^{1,2} The reversal of the herringbone reconstruction and ejection of Au atoms from the surface also occurs upon oxygen,²⁰ sulfur,^{13,20} NO₂,²¹ and styrene²² adsorption on Au(111). The strong charge transfer between gold and electronegative species presumably serves as the driving force for this process; however, the nature of the structures formed in these various cases depends on the specific surface–adsorbate interaction.

Accurate determination of the chlorine coverage is essential for further understanding the structures formed on Au(111). By measuring AES and XPS signal intensities, Kastanas and Koel used oxygen adsorption on platinum as the reference to derive

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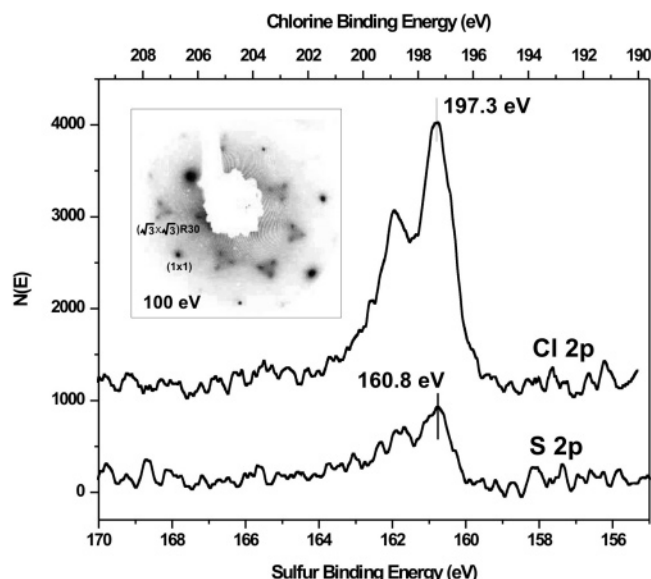


Figure 2. Inset shows LEED pattern obtained on Au(111) after exposing to 5×10^{-5} Torr SO_2 for 30 min at 300 K, followed by flashing sample to 500 K. After LEED, sulfur 2p XPS is obtained. Chlorine 2p spectrum is obtained after dosing 5×10^{-8} Torr Cl_2 at 300 K to saturation. The Cl and S spectra are plotted on shifted energy scales so as to overlap for the convenience of comparing intensities.

oxygen and further chlorine coverages on Au(111).² This method introduced several variables that resulted in a large discrepancy between their coverage estimates (2.9 and 0.8 ML) obtained from AES and XPS, respectively.

Herein, we use sulfur on Au(111) as a reference to determine the Cl coverage using intensities measured using XPS. Previous studies precisely determined the coverage of specific ordered structures of S on Au(111) using radioactive tracer techniques employing ^{35}S .^{14,23} Since no chlorine diffusion into the bulk is observed on Au(111),^{1,2} the chlorine coverage can be quantified with XPS using the split $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ LEED pattern (inset, Figure 2) for sulfur ($\theta_{\text{S}} \approx 0.3$ ML) on Au(111) as a standard. The corresponding sulfur 2p spectrum and Cl 2p spectrum at the saturated Cl coverage are plotted in Figure 2. The integrated areas under the spectra are first normalized to the Au 4f peaks and then divided by the corresponding sensitivity factors of Cl and S (0.48 and 0.35, respectively).²⁴ The ratio of chlorine to sulfur intensity is measured to be 3.2:1. Because the sulfur coverage is known as ~ 0.3 ML, the saturation Cl coverage on Au(111) is therefore ~ 1 ML.

To further obtain structural information of chlorine on Au(111), Cl_2 was first dosed at 300 K and STM images were collected at 120 K. The chlorine coverage was estimated by comparing the area under the Cl_2 desorption trace relative to that of saturation coverage. When the chlorine coverage reaches ~ 0.33 ML, STM images in Figure 3a and the corresponding zoom-in image in Figure 3b show a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ structure, which is consistent with the observed LEED pattern (inset of Figure 3a). It is also noticed that, with varying bias voltages from +0.3 to -2 V, there is no distinguishable contrast change observed in STM. Previous studies have also shown that chlorine adsorption on most fcc (111) surfaces form $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$

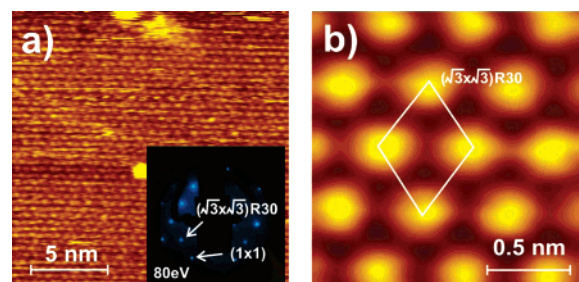


Figure 3. (a) STM images recorded at ~ 0.3 ML chlorine on Au(111). (b) Zoom-in image of (a), showing a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ atomic arrangement. Inset in (a) shows LEED pattern of the surface. Cl_2 is dosed at 300 K. STM imaging and LEED are carried out at 120 K.

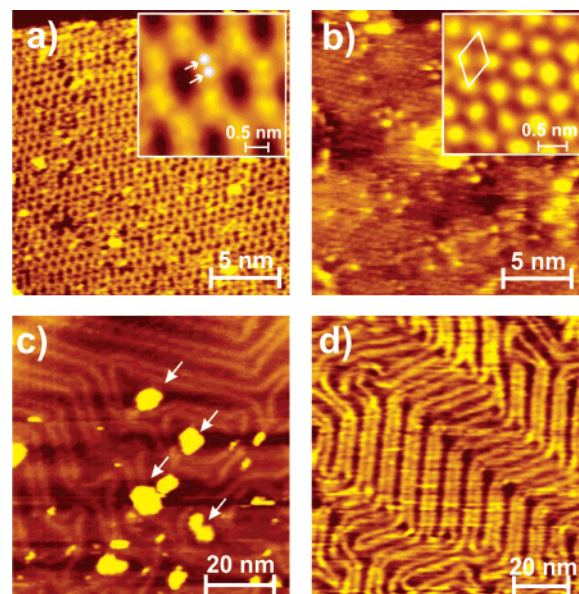


Figure 4. STM images of (a) ~ 0.8 ML chlorine on Au(111) showing the honeycomb structure. The inset shows that each unit in the hexagon adopts a dimer structure. (b) Flashing (a) to 750 K. (c) Annealing (a) at 750 K for 1 min. (d) Annealing (a) at 750 K for 5 min. Cl_2 is dosed at 300 K. All STM images were collected at 120 K.

structure at coverage of 0.33 ML, and it is often attributed to Cl located at threefold hollow sites.¹¹

Upon further dosing of chlorine at 300 K to 0.8 ML and imaging at 120 K, the surface transforms into a “honeycomb” structure, as shown in Figure 4a. The inset of Figure 4a shows a closeup of this “honeycomb” structure. It is observed that each honeycomb hexagon is composed of six units, and each unit adopts a dimer structure. Indeed, gold chloride is found to exist as dimers in both solid and gas phases.^{25–27} Therefore, this structural similarity implies that, at this high chlorine coverage, Au atoms incorporate into the adsorbate layer and form surface compound.

We unequivocally demonstrate that gold atoms from the surface are incorporated into the Cl structure at high coverage by the observed change in surface morphology upon desorption of a fraction of the Cl from the surface. As reported previously,^{1,2} Cl_2 evolves from Au(111) with a broad peak centered at ~ 640

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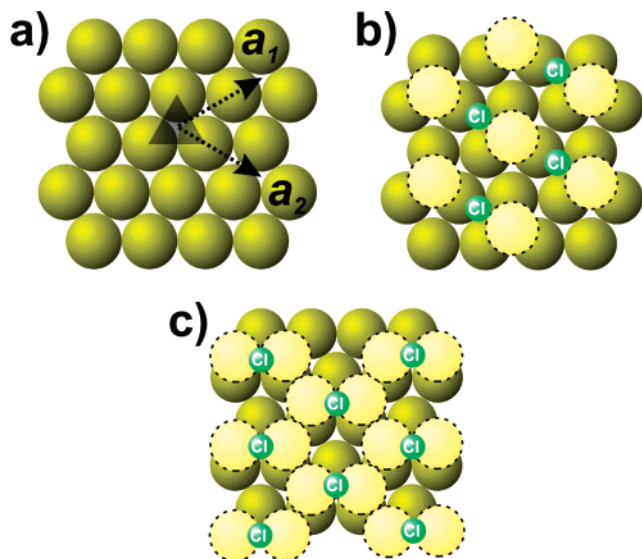


Figure 5. Different configurations to test Cl adsorption on Au(111) with DFT. (a) Clean $(\sqrt{3} \times \sqrt{3})R30^\circ$ Au(111) surface with the unit cell and lattice vectors a_1 and a_2 . (b) 0.33 ML Cl on the “side” of the 0.33 ML Au adatoms. (c) 0.33 ML Cl on “bridge sites” of the 0.67 ML Au adatoms. The dark large circles represent the underlying gold, whereas the lighter large circles represent Au adatoms, and the small green circles are chlorine atoms.

K and a high-temperature peak at ~ 790 K (Figure S2, Supporting Information). By flashing the “honeycomb” structure to 750 K using a heating rate similar to the TPD experiments, only ~ 0.16 ML chlorine is left on the surface, as estimated from TPD (Supporting Information). At this stage, STM images obtained at 120 K show patches of $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and disordered particles (Figure 4b). Longer annealing at 750 K for 1 min desorbs all the chlorine. At this stage, both particles and partially re-formed soliton walls can be observed (Figure 4c). These particles have Au(111) single atomic height and cover $\sim 6\%$ of the surface area; therefore, these particles must include Au atoms derived from the bulk structure, *not* just the excess atoms that would be incorporated into the herringbone. Notably, in the STM image, the herringbone structure is already partially manifested, so that the total amount of Au originally associated with the Au–Cl surface compound is greater than 6%. After the sample is annealed at 750 K for 5 min, all Cl is removed from the surface; the particles disappear (Figure 4d) and the characteristic herringbone structure re-forms, further indicating that gold is released from a complex during chlorine desorption. No Au desorption was detected in any of our desorption experiments, indicating that the Au released remains on the surface. Therefore, the STM results at different annealing stages demonstrate that, at coverages above 0.33 ML, Au atoms incorporate into the adsorbate layer to form a surface compound.

Density Functional Theory Calculations. Experimentally, we have unambiguous evidence that Au atoms incorporate into a chloride structure at high coverage (>0.33 ML), but no evidence for Au incorporation into $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. Below 0.33 ML, Au initially released from the herringbone reconstruction mainly appears to migrate to step edges and incorporate into a (1×1) Au structure under the Cl overlayer. DFT calculations were used to test possible structures for the 0.33 ML Cl on Au(111) and to test model systems that

Table 1. Energies Calculated Using the PW91 Functional for 0.33 ML Cl Bound to Three Different Surfaces: Clean Au(111), Au(111) with 0.33, and 0.67 ML Au Adatoms

surface	site	energy (eV)
Au(111)	top	−0.65
	bridge	−0.87
	hcp	−0.88
	fcc	−0.91
Au(111)+0.33 ML Au adatom	top	−0.43
	side	−0.47
	bridge	−0.81
Au(111)+0.67 ML Au adatom	bridge	−0.81
	vacancy	−0.24

incorporate Au adatoms so as to gain physical insight into the driving forces for this phenomenon.

The adsorption of chlorine is tested on three different Au(111) substrates: clean Au(111)- (1×1) surface and surfaces covered with 0.33 and 0.67 ML of Au adatoms (Figure 5). We restrict ourselves to only testing structures with $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell, according to periodicity observed in both LEED and STM at 0.33 ML Cl coverage (Figure 5a). One layer in the unit cell only contains three gold atoms; therefore, 0.33 and 0.67 ML of adatoms represent all the possible substrates that could result in gold incorporation upon the adsorption of chlorine.

We calculate the energies of Cl bound to the Au using the Au(111)- (1×1) surface as a reference to evaluate the *relative* stability of the various structures tested. The energies for the chlorine adsorbed system are defined relative to the breaking of a Cl–Cl bond and the cost required to create adatoms on the surface in the relevant cases:

$$E(\text{Cl}) = E(\text{Cl}/\text{Au}) - \frac{1}{2}E(\text{Cl}_2) + E_{\text{Au cost}} - E(\text{Au})$$

where $E(\text{Cl}/\text{Au})$ is the total electronic energy of a chlorine bound on the gold substrate, $E(\text{Au})$ is the energy of the Au(111)- (1×1) substrate, $E(\text{Cl}_2)$ is the energy of Cl_2 molecule, and $E_{\text{Au cost}}$ is the energy for creating n gold adatoms, which is defined as:

$$E_{\text{Au cost}} = E(\text{Au}_{\text{surface+adatom}}) - nE(\text{Au}_{\text{atom in bulk}}) - E(\text{Au})$$

where $E(\text{Au}_{\text{surface+adatom}})$ is the total energy of the Au(111) substrate with the adatom, and $E(\text{Au}_{\text{atom in bulk}})$ is the energy of a gold atom in the bulk. This energy cost was calculated for 0.33 and 0.67 ML of adatoms on the top layer of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell and found to be 0.75 and 0.65 eV, respectively. The calculated bond length and binding energy for Cl_2 using the PW91 functional was found to be 2.02 Å and 2.68 eV, respectively, where the experimental values are 1.99 Å and 2.48 eV.²⁸ These values were also previously calculated using the RPBE functional and found to be 2.00 Å and 2.54 eV.²⁹

On Au(111)- (1×1) , the binding of a single chlorine (0.33 ML coverage) was tested at four different sites: top, bridge, and the hcp and fcc threefold sites (Table 1). The threefold hollow sites are found to be the lowest in energy, and a very small advantage in energy was found for the adsorption of chlorine at an fcc site. The very small energy differences between the fcc, hcp, and bridge site (0.04 eV) indicate a very small energy barrier for chlorine migration on Au(111) surface.

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Previous DFT calculations also found the threefold site to be the preferred binding site for chlorine on Au(111), with nearly the same Au–Cl distance and an adsorption energy at 0.5 ML coverage that was 0.40 eV higher in energy (due to increased repulsive interactions at higher coverage) than our value.⁴ The adsorption of Cl on Ag(111) also prefers the threefold site and is slightly stronger than the Au–Cl interaction ($E_{\text{ads}} = -1.63$ eV at 0.33 ML coverage).³⁰ The bond enthalpy of diatomic AuCl is -3.56 eV.³¹

In previous studies of chlorine structure on Au(111), Kastanas and Koel suggested a model in which 1.33 ML chlorine are packed on Au(111) surface to form a flat overlayer.² Our coverage calibration ruled out this model.¹¹ Nevertheless, we also tested this model with DFT by first allowing all degrees of freedom of the chlorine atoms to relax on a flat($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ unit cell of Au. However, it was found that the chlorine did not remain bound on a flat surface. The Cl atoms were then constrained in the z -direction (perpendicular to the surface), and the energy was found for different distances from the surface. Using the PW91 functional, no energy gain is found for packing this many chlorine atoms on the surface. Therefore, a coverage of 1.33 ML Cl overlayer on a flat Au (1×1) surface, as proposed by Kastanas and Koel,² is unfavorable.

With an additional 0.33 ML Au adatoms located on threefold sites of Au(111), the adsorption of 0.33 ML Cl was tested on various sites on the surface of the ($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ unit cell of Au(111)-(1×1). Chlorine bound on the side of an adatom resulted in the lowest energy (Figure 5b). It was found that the binding of Cl on both top and the side of an adatom is stronger than that of chlorine on Au(111)-(1×1) surface as overlayer. But this stronger interaction cannot compensate for the cost of creating the adatom covered surface (0.75 eV), and Au incorporation would result in a higher total energy than the chlorine overlayer (Table 1).

When the surface contains 0.67 ML Au adatoms (equivalently, 0.33 ML of vacancies), the energy cost of creating this surface is 0.65 eV. The adsorption of chlorine was tested on various sites on the substrate, and the energy was the lowest for chlorine on a bridge site coordinated to two gold adatoms (Figure 5c). Chlorine bonded in the vacancy is found to be much higher in energy than the bridge site. Similar to the previous case, the energy gain for adsorbing chlorine to adatoms is not enough to compensate the energy cost of creating adatoms (Table 1). Therefore, the DFT calculations indicate that gold atoms are *not* incorporated into ($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ structure at 0.33 ML Cl coverage.

In the above discussions, “overlayer” and “chloride” are mainly referred to the geometric arrangement of adsorbed Cl atoms. However, this definition may not be accurate to describe, from an electronic point of view, the nature of Cl–Au bonding. Upon the adsorption of 0.33 ML chlorine overlayer, we found the charge on the chlorine atom was -0.33 . In fact, gold (III) chloride (Au_2Cl_6) adopts a planer dimer structure.^{25,26} The experimental (calculated) bond distance for chlorine bonded to one gold atom and two gold atoms in the dimer is 2.23 \AA (2.30 \AA) and 2.33 \AA (2.39 \AA), respectively. The charge for bridge Cl

(bonded to two Au atoms) was found to be -0.33 , whereas the charge found for terminal Cl (bonded to one Au atom) was -0.22 (Supporting Information). Compared with that of the Au-(III) chloride compound, the similar charge of Cl in 0.33 ML Cl overlayer suggests a significant charge transfer from the gold substrate to the chlorine atom.^{32–34}

The fact that the charge on the Cl in the overlayer is similar to the gold (III) chloride indicates chloride-like bonding even without Au adatom incorporation. This may be responsible for the contradictory interpretations of spectroscopic results to discriminate chemisorbed Cl and chloride on Au(111).^{1,2} For example, the absence of a Cl 2p binding energy shift with coverage change,² therefore, cannot conclusively rule out the possibility of chloride formation. Indeed, a small increase (~ 0.4 eV) in Cl 2p binding energy from coverage of 0.26 ML to saturation is observed in our XPS data (Figure S3, Supporting Information). But because of the very small binding energy shift and limited instrument resolution, we do not attempt to assign specific chlorine species. In this case, synchrotron-based high-resolution XPS may be able to provide more valuable information.³⁵ On the other hand, the strong interaction between gold and chlorine in the overlayer also suggests that the overlayer formation can cause large electronic disturbance to the Au(111) substrate. One needs to be cautious in halogen adsorption studies because models in which substrate is treated as an undisturbed surface can be oversimplified. We are currently trying to address this point using additional DFT studies.

Conclusions

Our results reveal a dynamic process of chlorine adsorption on Au(111). Chlorine initially lifts the herringbone reconstruction. At low coverages (< 0.33 ML), chlorine binds to the top of Au(111)-(1×1) surface and leads to formation of an overlayer with ($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ structure at 0.33 ML. At higher coverages, gold atoms are removed from Au(111)-(1×1) and form a complex superlattice of a Au–Cl surface compound.

The picture of chlorine interaction with gold revealed by STM studies can provide insight into the mechanism of surface reactions.³ However, important questions still remain in this system: What is the microscopic mechanism of transformation from chlorine overlayer to surface compound? What is the structure of surface gold chloride? Halogenation is a complex process that involves multiple mechanistic aspects, as indicated by tremendous studies and continuing effort on other transition-metal surfaces. Moreover, the gold chloride structure has been considered as a challenge in both experimental and theoretical studies.^{36,37} Therefore, we believe our results will initiate further studies on this system.

Acknowledgment. This work was supported primarily NSF-CHE Grant No. 0545335 with additional support from the Materials Research Science and Engineering Center of the National Science Foundation under NSF Award No. DMR-

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0213805. T.A.B. thanks the support of the NSF through a graduate fellowship. Extremely valuable discussions with Dr. J. Haubrich and Prof. R. J. Madix are also acknowledged.

Supporting Information Available: STM result of chlorine-covered Au(111) surface, details of chlorine coverage evaluation,

chlorine TPD from Au(111), XPS of chlorine on Au(111), calculation details of charge on chlorine, and test with other exchange-correlation functionals in DFT. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA077989A