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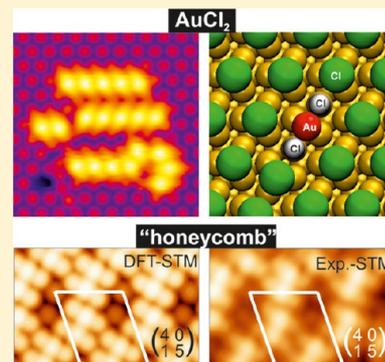
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Self-Organization of Gold Chloride Molecules on Au(111) Surface

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S Supporting Information

ABSTRACT: Adsorption of molecular chlorine on Au(111) has been studied with a low-temperature (5 K) scanning tunneling microscope in combination with density functional theory calculations. The formation of AuCl₂ quasi-molecules was detected at chlorine coverage exceeding 0.33 ML. The self-organization of the AuCl₂ species into the ordered “honeycomb” structure was clearly demonstrated for coverages close to saturation.



■ INTRODUCTION

Surface chemistry of gold interacting with active gases attracts a lot of interest because of potential applications in catalysis.^{1,2} Indeed, recently Deng and Freind³ demonstrated the activity of gold catalyst in the reaction of alkene epoxidation. The presence of chlorine atoms on a surface was found to increase drastically the selectivity of the reaction.⁴ To look into the reaction mechanism, one must know the atomic structure of the surface at each stage of the reaction. To date, the number of papers on molecular chlorine adsorption onto gold monocrystalline surfaces is limited and an understanding of the atomic structure has not been achieved. The first detailed study of Cl₂ interaction with Au(111) surface in ultrahigh vacuum (UHV) conditions was performed by Spencer and Lambert⁵ who detected two different chemical states in thermodesorption (TD) spectra. At the beginning of adsorption, a high-temperature peak at 815 K starts growing. A low-temperature peak at 670 K appears after saturation of the high-temperature peak. The fragmentation of low- and high-temperature peaks is different. Kastanas and Koel⁶ performed a detailed Auger electron spectroscopy (AES), TDS, and low-energy electron diffraction (LEED) study of molecular chlorine adsorption on Au(111) in a wide temperature range of 100–400 K. They confirmed the presence of two peaks in TD spectra and

reported the ordering of the chlorine overlayer and the formation of the dense ($\sqrt{3} \times \sqrt{3}$)R30° structure corresponding to a Cl coverage of 1.33 monolayer (ML).⁶ Recently, Gao et al.⁷ studied chlorine structures on Au(111) with STM, LEED and DFT techniques. They have established that chlorine adsorption results in the formation of a ($\sqrt{3} \times \sqrt{3}$)R30° chlorine lattice with one chlorine atom per unit mesh. They also performed DFT calculations and found that chlorine atoms occupy fcc positions.⁷ The STM examination of the saturated chlorine coverage revealed a complex “honeycomb” structure consisting of dimers that Gao et al. thought were associated with gold chloride species.

However, two important questions remain in the Cl–Au(111) system: What is the structure and chemical composition of surface gold chloride? How does the chlorine monolayer transform into a surface compound? In our study, we propose an answer to these important questions using a low-temperature scanning tunneling microscope (LT-STM) in combination with DFT calculations.

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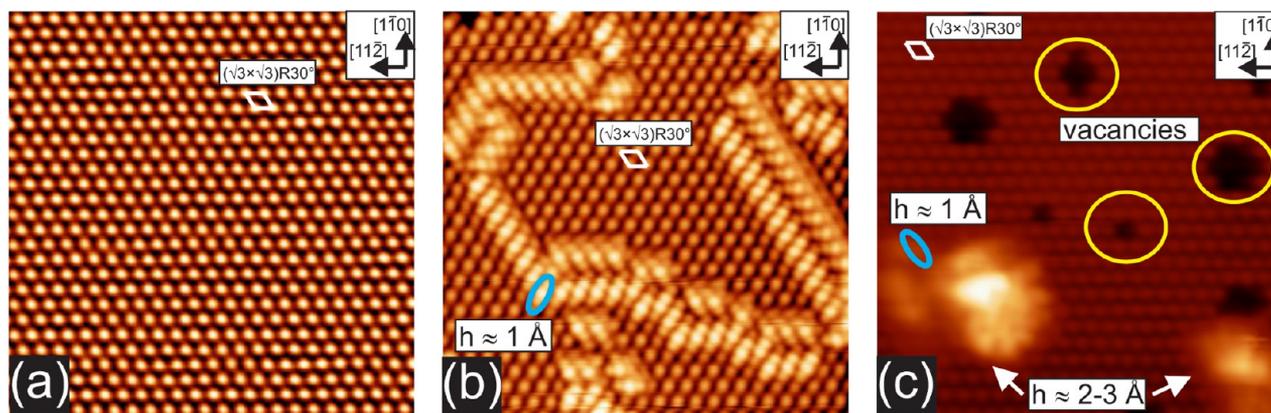


Figure 1. STM images ($120 \times 120 \text{ \AA}^2$; $T = 5 \text{ K}$) of the Au(111) surface chlorinated at 130 K demonstrating a simple commensurate $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure (chlorine dosing time $t_{\text{Cl}_2} = 153 \text{ s}$) (a) and appearance of numerous oval-shaped objects ($t_{\text{Cl}_2} = 168 \text{ s}$) (b). (c) STM image of the surface obtained from (b) by annealing at 300 K.

METHODS

Experimental Section. All experiments were carried out in a UHV setup containing an LT-STM Omicron instrument operating at 5–77 K and LEED optics. The pressure of the residual gases in the chamber during experiments was better than 5×10^{-11} Torr.

The gold (111) sample was prepared by repetitive cycles of Ar^+ bombardment (1 keV) and annealing up to 900 K. Chlorine introduction on Au(111) was done at 130 K using a fine leak piezo-valve connected with a capillary placed 20 mm from the sample face. The chlorine partial pressure in the chamber was fixed at 1×10^{-10} Torr.

Computational Details. All DFT calculations were carried out using the Vienna ab initio simulation package^{8–11} employing the projector augmented wave method¹² and PBE-GGA (Perdew–Burke–Ernzerhof) functional.¹³ A plane-wave cutoff energy of 400 eV was applied. The gold (111) substrate was modeled by a four-layer slab. During structure optimizations, the two top layers of Au atoms as well as the overlayer atoms were allowed to relax while the bottom two layers of Au were held fixed. A vacuum layer with a thickness of 15 Å was inserted between two neighboring slabs. The integration of Brillouin zone was done using Monkhorst–Pack¹⁴ k-point mesh ($2 \times 2 \times 1$) for the $(3\sqrt{3} \times 6\sqrt{3})R30^\circ$ unit cell used for a AuCl_2 modeling and $(5 \times 5 \times 1)$ for the $\begin{pmatrix} 4 & 0 \\ 1 & 5 \end{pmatrix}$ cell of the honeycomb structure. STM images were simulated from the DFT results using the simple Tersoff–Hamann approximation¹⁵ considering states between E_F and $E_F - 0.5 \text{ eV}$.

RESULTS AND DISCUSSION

Experimental Results. Adsorption of Cl_2 on Au(111) at 130 K leads to the lifting of the herringbone reconstruction and to the formation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ adsorbate structure ($\theta = 0.33 \text{ ML}$) with one Cl atom per unit mesh, as shown in Figure 1a. This observation is in agreement with data by Kastanas and Koel⁶ and Gao et al.⁷

A small increase in chlorine coverage above 0.33 ML (keeping the sample temperature at 130 K) drastically changes the structure of the surface (see Figure 1b). LT-STM image in Figure 1b indicates the appearance of numerous bright, oval objects. The length of the object measured in the STM image was 5.5–6.0 Å, while its height was in the range of 0.8–1.0 Å

irrespective of the bias voltage (at least in the range from -1 to $+1 \text{ V}$).

The distance between centers of the neighboring objects in the line corresponds to the nearest-neighbor distance in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure (5 Å). Linear structures are usually coupled with 10 Å between the couples, as is clearly seen in Figure 1b. Increasing the temperature to 300 K leads to a local change in the surface morphology. According to the STM image in Figure 1c, the agglomeration of objects into 3D islands (with height greater than 3 Å) occurs, leaving vacancy islands in the chlorine layer.

The fragment of the atomic-resolution STM image of a single object is shown in Figure 2a. Each object consists of three

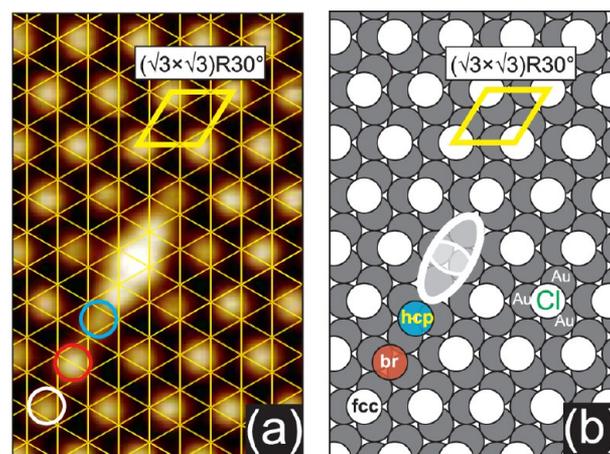


Figure 2. Close up of the isolated object surrounded by the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure ($\theta > 0.33 \text{ ML}$). (a) STM image $U_s = 0.2 \text{ V}$, $I_t = 0.4 \text{ nA}$, 5 K; (b) atomic model. Blue, red, and white colors mark hcp, bridge, and fcc positions of chlorine atoms on Au(111), respectively. Gold atoms from the upper substrate layer are shown in gray.

protrusions, with the central maximum being the brightest. To determine adsorption sites of the oval-shaped objects, a hexagonal grid with nodes corresponding to the positions of substrate atoms in the Au(111)- (1×1) lattice was drawn on the STM image in Figure 2. Atoms belonging to the undisturbed $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice were placed in fcc 3-fold hollow positions, in accordance with DFT calculations.⁷ As a result, the central protrusion of the object appears to be in a

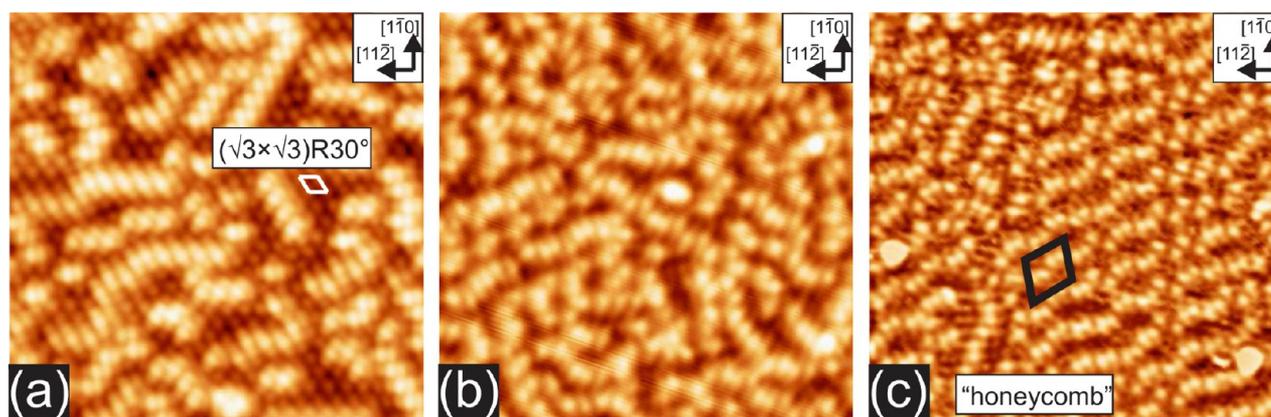


Figure 3. STM images ($120 \times 120 \text{ \AA}^2$; $T = 5 \text{ K}$) of the Au(111) surface chlorinated at 130 K demonstrating a compression of the chlorine overlayer into a honeycomb structure: (a) coexistence of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and chainlike structure ($t_{\text{Cl}_2} = 303 \text{ s}$), (b) disappearance of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ and the formation of dense chains of objects ($t_{\text{Cl}_2} = 373 \text{ s}$), and (c) the formation of the honeycomb structure ($t_{\text{Cl}_2} = 640 \text{ s}$).

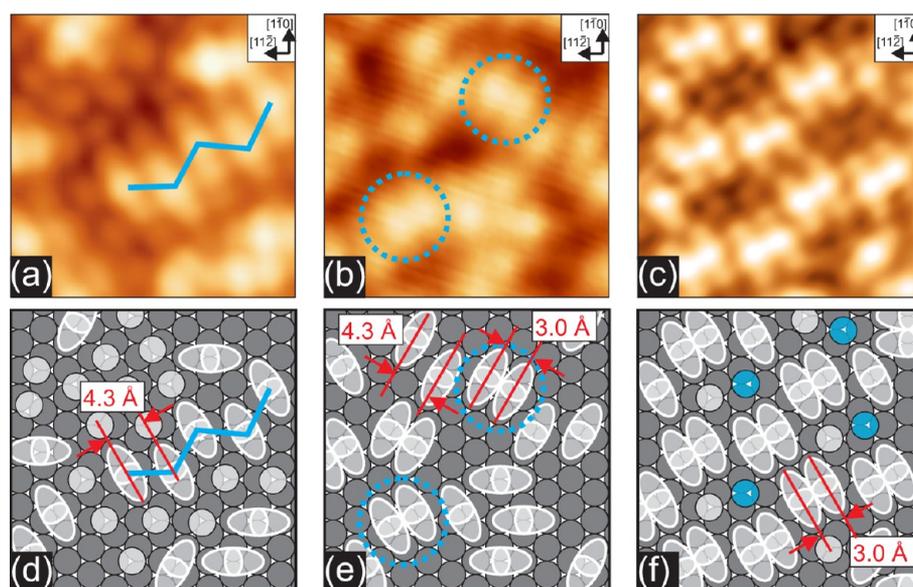


Figure 4. STM close-ups and models of the new stacking observed as chlorine coverage increases on Au(111): (a,d) zigzag chain, (b,e) dimer formation, and (c,f) arrangement in a honeycomb lattice.

bridge position, as seen in Figure 2a. The other two maxima in the object are situated close to on-top positions. According to Figure 2a, the formation of the object leads to the distortion of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice. Two chlorine atoms near the low end of the object are appreciably shifted to hcp and bridge positions. Such a distortion means that new objects are placed directly on the metal surface and are incorporated into the chlorine monolayer.

Further chlorine adsorption leads to the increase of the density of the objects on the surface (see Figure 3a,b) and to the substantial decrease of the areas of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains. At the coverage close to saturation, the ordering of the objects into the 2D superstructure occurs, as seen in Figure 3c. This structure resembles the honeycomb structure previously reported by Gao et al.⁷

Figure 4 presents highly magnified STM images and corresponding model drawings for the same coverages shown in Figure 3. According to Figure 4a,d, the increase of chlorine dosing leads first to a new zigzag stacking of objects. Although the local distance between their centers remains 5 Å, the

reorientation of the chains in the $\langle 110 \rangle$ direction results in a denser packing with a 4.3 Å separation, as seen in Figure 4d.

Further chlorine dosing leads to the formation of dimers of these objects (see Figure 4b). Now, the objects within the chain are distributed more densely. The structural model of dense chains with dimers is presented in Figure 4e. The distance between objects in the dimer measured in the STM image appears to be $3.0 \pm 0.1 \text{ \AA}$, which is close to the lattice constant of Au(111) (2.9 Å).

The STM image in Figure 4c shows a high-resolution fragment of the honeycomb structure from Figure 3c. In our model shown in Figure 4f, the honeycomb structure consists of zigzag chains of dimers aligned in the $\langle 110 \rangle$ direction with a period of 14.7 Å (five lattice constants of Au(111) surface unit cell) and couples of chemisorbed chlorine atoms in positions close to fcc and hcp. Adjacent rows are shifted with respect to each other by a half-period. The “small” distance between dimers in two rows is equal to 7.7 Å and the “large” distance is 12.6 Å. Thus, we experimentally demonstrated that the

honeycomb structure reported by Gao et al.⁷ is formed as a result of the self-organization of separate oval-shaped objects.

Now we turn to an analysis of a possible chemical composition of the oval-shaped objects. According to Figure 1, the nucleation of the oval-shaped objects starts at coverage exceeding 0.33 ML. Therefore, after the completion of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ layer at least one additional chlorine atom is required to build a new object. The STM image of the surface heated to 300 K (Figure 1c) demonstrates 3D agglomerates of objects and vacancy islands in the chlorine layer. This observation indicates that one more (the second) chlorine atom used for the object construction comes from the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice. Therefore, each oval-shaped object consists of at least two chlorine atoms. Taking into account that gold atoms in the honeycomb structure are incorporated in the chlorine layer,⁷ each oval-shaped object may be considered as a surface chloride molecule (of the unknown composition) containing at least one gold and two chlorine atoms. The source of gold atoms is likely the step edge. This statement is supported by an atomic resolution STM image of the step edge (see Supporting Information) demonstrating an enhanced concentration of the objects and distortion of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice of chlorine.

Density Functional Theory Calculations. Gold is known to form two stable compounds with chlorine: AuCl and AuCl₃. Gold monochloride consists of $-\text{Au}-\text{Cl}-\text{Au}-\text{Cl}-$ chains.¹⁷ Gold trichloride exists always as Au₂Cl₆ molecules which form a molecular crystal in the solid state.^{18–20} Because each oval-shaped object contains at least two chlorine atoms, the AuCl model was excluded from our DFT analysis.

At first, we suggested that oval-shaped object could be AuCl₃ or Au₂Cl₆. The starting and optimized models of AuCl₃ surrounded by a chlorine monolayer are shown in the left-hand part of Figure 5a. After the optimization of coordinates, the central chlorine atom from AuCl₃ appears to be 3 Å higher than the surrounding chlorine atoms from the $(\sqrt{3} \times \sqrt{3})R30^\circ$ monolayer. As a result, the AuCl₃ molecule appears as a bright protrusion with a height of about 4 Å in the simulated STM image (Figure 5a). This value is not consistent

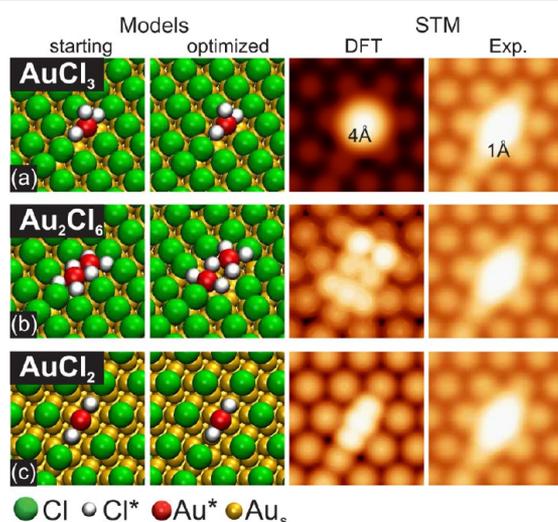


Figure 5. Structural models of AuCl₃ (a), Au₂Cl₆ (b), and AuCl₂ (c) molecules on Au(111) surrounded by a $(\sqrt{3} \times \sqrt{3})R30^\circ$ chlorine monolayer. Theoretically calculated STM images are shown in comparison with the theoretical STM image.

with the experimentally measured height of the objects (0.8–1.0 Å). We also tried to incorporate the AuCl₃ molecule in the vacancy in the upper gold layer. However, the optimization of coordinates in this case resulted in significant changes in the positions of the neighboring atoms and the rotation of the AuCl₃ molecule, which of course are not in agreement with experimental data.

Results of the testing of the planar Au₂Cl₆ molecule are demonstrated in Figure 5b. Optimization of coordinates splits the Au₂Cl₆ molecule into two pieces. One gold atom shifts between two chlorine atoms, the other gold atom (keeping 4-fold coordination with chlorine atoms) rises appreciably over the monolayer chlorine atoms (by 1.5 Å). As a result, the calculated STM image does not correspond to the experimental one, as seen in Figure 5b.

Thus, models based on AuCl₃ and Au₂Cl₆ do not correspond to our experimental STM images.

The next candidate is a quasi-molecule: AuCl₂. The starting and optimized models of AuCl₂ on Au(111) are shown in Figure 5c. In the starting configuration, the gold atom occupies a bridge position with respect to substrate gold atoms, and two chlorine atoms appear to be in on-top positions. During optimization of coordinates, no appreciable changes in the geometry of the AuCl₂ molecule were detected with the exception of a little shortening of the Au–Cl distance. Experimental and simulated STM images are in agreement, as seen in Figure 5c.

To provide additional thermodynamic characterization of the models preserving their initial geometry (AuCl₂ and AuCl₃), the surface formation energies per unit cell (see Supporting Information) were calculated. As a result, we found that AuCl₂ is more energetically favorable than AuCl₃ by 37 meV.

We also tested models with two quasi-molecules AuCl₂ arranged in linear chains or dimers (Figure 4) and in both cases found good correspondence of simulated and experimental STM images (Figure 6).

Now, we turn to the DFT analysis of the honeycomb structure. We used a simple model from Figure 4f to construct a starting model of the honeycomb structure described by the oblique unit cell $\begin{pmatrix} 4 & 0 \\ 1 & 5 \end{pmatrix}$. In the model, the unit cell contains two dimers (AuCl₂)₂ and two chemisorbed chlorine atoms in

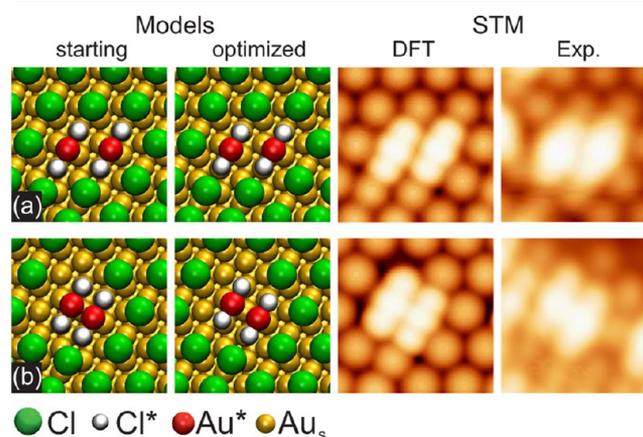


Figure 6. Structural models and theoretical and experimental STM images of differently packed pairs of AuCl₂ quasi-molecules on Au(111) surrounded by the $(\sqrt{3} \times \sqrt{3})R30^\circ$ chlorine monolayer corresponding to low (a) and high (b) coverage.

fcc and hcp positions, respectively. Chlorine atoms from AuCl_2 occupy approximately on-top positions. Figure 7a shows an

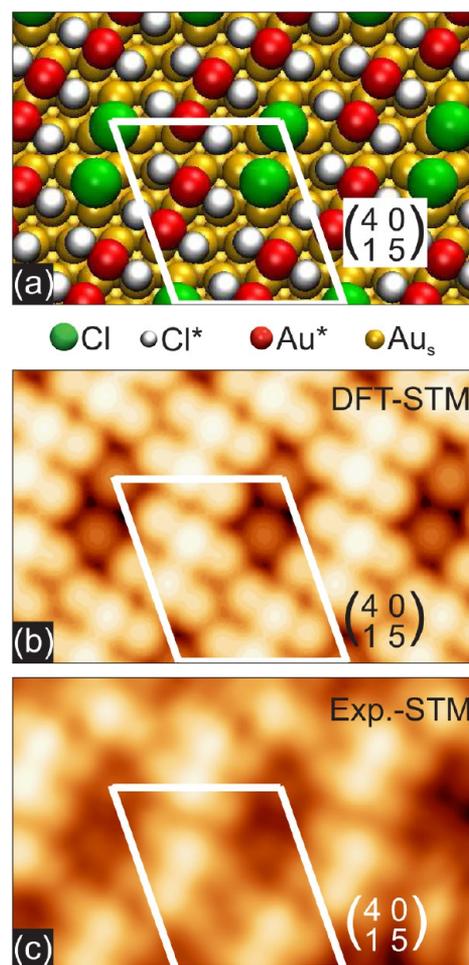


Figure 7. DFT-optimized model of the honeycomb structure (a) shown together with the theoretical (b) and experimental (c) STM images. The unit cell is indicated.

optimized model of the honeycomb structure. Optimization of coordinates resulted only in the slight contraction of Au–Cl distances within the AuCl_2 quasi-molecules. Simulated and experimental STM images of the honeycomb structure (shown in Figure 7b and 7c, respectively) are in good agreement.

Note also that the honeycomb structure corresponds to a Cl coverage of 0.5 ML, as is seen in Figure 7. In ref 7, a larger value ~ 0.8 ML was reported based on XPS measurements. The difference in the coverage may be explained by the different conditions of chlorine adsorption. In our case, we adsorbed chlorine at 130 K and measured at 5 K, whereas Gao et al.⁷ adsorbed Cl_2 at 300 K. According to the STM image in Figure 1c, the 3D agglomeration of AuCl_2 can occur at room temperature. Therefore, the thickness of chloride coverage prepared at 300 K may be larger than that in the case of low-temperature chlorine adsorption.

It is also of interest to discuss interatomic distances in the quasi-molecule AuCl_2 and compare them with those in $(\text{AuCl}_3)_2$. The interatomic distances for a single quasi-molecule AuCl_2 , two quasi-molecules AuCl_2 from a linear chain, dimer $(\text{AuCl}_2)_2$, and a honeycomb structure are shown in Table 1.

Table 1. Principal Interatomic Distances in AuCl_2 -Based Structures on Au(111)

	interatomic distance (Å)			
	single quasi-molecule AuCl_2 (Figure 5c)	two quasi-molecules AuCl_2 (Figure 6a)	dimer $(\text{AuCl}_2)_2$ (Figure 6b)	pseudo honeycomb (Figure 7)
Au^*-Cl^*	2.30	2.30	2.31	2.31
Au^*-Au^*	–	5.10	3.56	3.49
Cl^*-Au_s	2.65	2.65	2.67	2.66
Au^*-Au_s	2.94	2.94	2.97	2.96
Au^*-Cl	4.82	4.80	4.58	5.31

Although these structures correspond to a different packing density of the quasi-molecules, the distance between the chlorine and gold atoms (Au^*-Cl^*) is equal to ≈ 2.3 Å for all calculated configurations. This value is close to the distances between gold and chlorine atoms in the dimer $(\text{AuCl}_3)_2$ (2.24, 2.34 Å).^{18–20} The distance between the chlorine atom in AuCl_2 and the nearest gold atom from the substrate (Cl^*-Au_s) is slightly larger (2.65, 2.67 Å). The distances between gold atoms (Au^*-Au^*) in the dimers $(\text{AuCl}_2)_2$ and in the honeycomb structure equaled 3.49 and 3.56 Å, respectively, and roughly correspond to the Au–Au distance in $(\text{AuCl}_3)_2$ (3.42 Å).

Thus, we conclude that interatomic distances within the AuCl_2 quasi-molecule are not influenced by the structure and density of surrounding atoms.

Now, we would like to address the charge state of atoms in a honeycomb structure. We applied Bader's analysis¹⁶ to obtain the distribution of charges on chlorine and gold atoms. The results are shown in Figure 8. The charges on all chlorine atoms

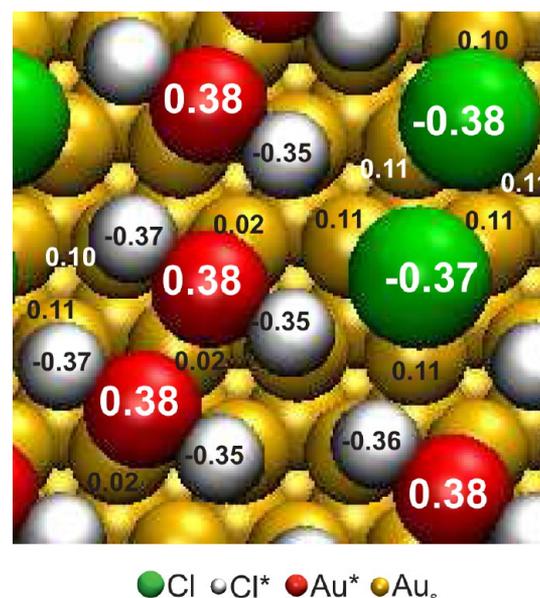


Figure 8. Results of Bader's analysis of the honeycomb structure. Charges on Cl and Au atoms are indicated.

appear to be nearly the same. In particular, the charges of chlorine atoms in AuCl_2 are equal to -0.37 and -0.35 , while charges on chlorine atoms chemisorbed on Au(111) are equal to -0.37 and -0.38 . These charge values are in agreement with ones reported by Gao et al.⁷ for chemisorbed chlorine on Au(111) and for a free molecule Au_2Cl_6 . What is more interesting is the charge distribution on gold atoms. According

to our calculations, the charge on a gold adatom from AuCl₂ occupying a bridge position is +0.38. Two gold atoms neighboring the adatom have almost no charge (+0.02), while other gold atoms from the upper Au(111) plane are slightly charged ($\approx +0.1$). For comparison, we calculated charges on gold adatoms (placed in 3-fold and bridge positions) and gold atoms from the upper Au(111) layer in the absence of chlorine. In both cases, the charge on the adatom (+0.07) appears to be much less than that in the case of AuCl₂ on Au(111). Thus, we have shown that AuCl₂ species could be considered to be quasi-molecules because the state of gold atoms is clearly different from the state of atoms in the upper Au(111) layer.

We can also discuss the absence of the chemical shift of Cl 2p XPS line for low- and high- chlorine coverages on Au(111).^{5–7} The charges on chlorine atoms in the chemisorbed, quasi-molecular (AuCl₂) and chloride (Au₂Cl₆)⁷ states were found to be very close to each other. At the same time, the large charge on a gold atom in AuCl₂ can induce a significant shift of the gold XPS line. Unfortunately, the contribution of gold adatoms to the total XPS signal is quite low, which makes it difficult to detect such a chemical shift.

Another point is the way the molecules bond on Au(111). In our system, the Cl₂ molecule splits into separate Cl atoms that in turn form a quasi-molecular structure (Cl–Au–Cl) using a gold adatom. Maksimovich et al.²¹ reported that organosulfur molecules adsorbed on Au(111) split into two parts and form quasi-molecular structures with gold adatoms occupying bridge positions. In this connection, the bonding of the split molecules via a gold adatom seems to be a peculiarity of the adsorption on the Au(111) surface.

CONCLUSION

Thus, we have established that after formation of the ($\sqrt{3} \times \sqrt{3}$)R30° chlorine monolayer on Au(111), the nucleation of surface chloride quasi-molecules AuCl₂ takes place. As the coverage increases, the number of the AuCl₂ quasi-molecules increases, leading to their self-organization into the $\begin{pmatrix} 4 & 0 \\ 1 & 5 \end{pmatrix}$ honeycomb structure. It was found that each ring of the honeycomb structure consists of six (AuCl₂)₂ dimers. Two chlorine atoms are placed inside the ring and occupy fcc and hcp 3-fold positions.

In summary, it is of great interest to make a bridge between details of atomic structures obtained in our paper and the promotion role of chlorine in the reaction of the styrene epoxidation.⁴ This point will be addressed in our future LT-STM research of the coadsorption of styrene, chlorine, and oxygen on Au(111).

ASSOCIATED CONTENT

Supporting Information

STM image of the step edge on chlorine-covered Au(111) surface and details of the surface formation energy calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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