

# Chlorine interaction with defects on the Au(111) surface: A first-principles theoretical investigation

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Chlorine is an important element in promoting oxidation on noble metal surfaces. Here, we report a comprehensive theoretical study of chlorine interaction with defects on the Au(111) surface, using density functional theory calculations and periodic slabs to model the surface. We find that chlorine binds preferentially on steps, vacancies, and gold adatoms. The increase in binding energy per chlorine atom, compared to binding on the flat, defect-free surface, is 0.29 eV when the chlorine atom is on top of a gold adatom, 0.38 eV when it is at the edge of a step, and 0.19 eV when it is next to a single surface vacancy. An extensive study of chlorine interaction with different numbers of surface gold vacancies revealed that chlorine interacts the strongest with three vacancies. © 2008 American Institute of Physics. [DOI: 10.1063/1.2975329]

## I. INTRODUCTION

Gold has recently become important as a catalytic material.<sup>1–3</sup> Supported gold nanoparticles can be used to catalyze many reactions including the reduction of NO<sub>x</sub> by hydrocarbons,<sup>4,5</sup> the oxidation of CH<sub>4</sub>,<sup>6,7</sup> CO<sup>8</sup> and propene,<sup>9</sup> and the epoxidation of propene.<sup>10</sup> Chlorine increases the selectivity of certain heterogeneous reactions including ethylene epoxidation on Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Ref. 11) and olefin partial oxidation on Au(111) (Ref. 12) by dispersing and redistributing surface oxygen.<sup>13</sup> Despite these indications, the details of how chlorine and oxygen coadsorb on the surface and the role that this plays in oxidation is not understood. This issue is actually one of broader interest. Namely, finding the active site of a heterogeneous catalyst is crucial in understanding how the catalyst can be effective and how it might be improved.<sup>14</sup> The active site is closely related to stable and metastable positions of a reactant on a surface, like chlorine on Au(111), whose adsorption is often the first step in a corrosion or catalytic reaction cycle.

The rich chemistry and physics between the interaction of chlorine and gold also makes this an important system from a fundamental viewpoint. Gold (III) chloride is used as homogeneous catalyst for a number of important organic reactions including intramolecular cyclizations and cross-cycloisomerization reactions.<sup>15,16</sup> Chlorine is used as a lixiviant for gold<sup>17</sup> and the chlorine adsorption on the Au(111) electrode has been studied electrochemically.<sup>18</sup> Chlorine also plays an important role in the contact between gold and semiconductor electrodes.<sup>19</sup> The adsorption of chlorine on Au(111) is dynamical in nature, involving many different structures and types of Cl bonding to Au.<sup>20,21</sup> Depending on Cl coverage, it involves initial release of gold atoms from the

herringbone reconstruction, a chemisorbed overlayer, and further release of gold atoms to form a gold chloride.<sup>22</sup>

Potential binding sites of chlorine on a gold surface include flat terrace sites and different types of defect sites. Defects and undercoordinated gold atoms are especially important to understand in catalysis, since these sites are thought to be more reactive and are often the active sites on a surface. For example, step edge sites of MoS<sub>2</sub> nanoparticles were found to be the active site for electrochemical H<sub>2</sub> evolution.<sup>23</sup> Undercoordinated Au atoms could be possible sites for binding or even dissociation of O<sub>2</sub> for CO oxidation on Au nanoparticles.<sup>24–26</sup> Using scanning tunneling microscopy (STM), Biener *et al.*<sup>27</sup> showed that small AuS clusters preferentially nucleated at defect sites upon the adsorption of sulfur on Au(111). Chlorine, an electronegative species such as sulfur and oxygen, may exhibit the same properties: the relevant stable and metastable chlorine positions could be on a step, an island, a terrace, or at the interface between a nanoparticle and the metal-oxide support.<sup>28</sup>

In this work, we report a set of comprehensive calculations based on density functional theory (DFT) for the adsorption of chlorine on a Au(111) surface. Specifically, we investigate the interaction of chlorine with defects on this surface including a gold adatom, a step edge, and terrace vacancies. By comparing the adsorption energy of Cl on various sites on the defective surfaces, we found that Cl binds to all three of these defects stronger than it binds to the flat, defect-free Au(111) surface.

## II. CALCULATIONAL DETAILS

The DFT results were obtained using the VASP code<sup>29</sup> with the generalized gradient approximation (GGA)-PW91 (Ref. 30) functional to describe electron exchange and correlation. Ultrasoft pseudopotentials are employed with the default plane-wave cutoff (219.471 eV) taken from the GGA

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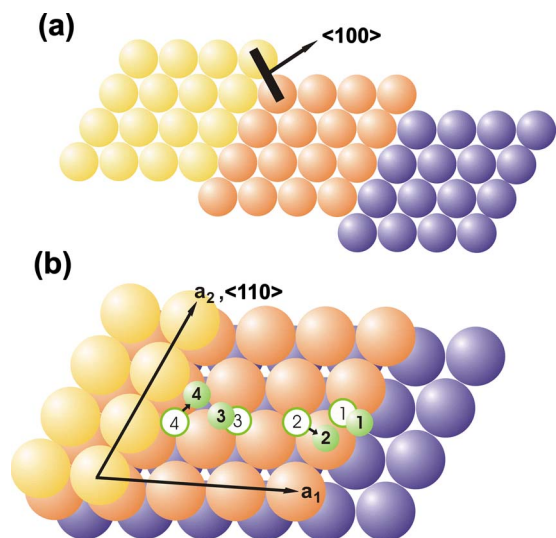


FIG. 1. (Color online) The model of the stepped  $\langle 110 \rangle / \{100\}$  Au(533) surface employed in the calculations: (a) side view of the slab with each unit cell shown in a different color; (b) top view of stepped surface. Each unit cell contains four (111) layers and is offset to create a step. Yellow circles are the gold atoms that make up the upper step, orange circles represent the terrace, and purple circles are the layer of the lower step. White circles represent initial starting positions and solid green circles the final positions of the chlorine atom after relaxation. The vector normal to the plane of the step edge,  $\langle 100 \rangle$ , is shown in (a) and the lattice unit cell vectors  $a_1$  and  $a_2$  are shown in (b).

ultrasoft-pseudopotential database<sup>31,32</sup> and a  $7 \times 7 \times 1$   $k$ -point sampling was used. A high number of  $k$ -points were necessary to accurately describe the stepped surface. The surface was modeled by a slab consisting of four layers in the (111) direction, with a  $4 \times 4$  primitive unit cell in the lateral directions; only the two uppermost layers of the slab were allowed to relax, with the rest fixed at the ideal bulk positions. By changing computational parameters (such as reciprocal-space sampling or slab thickness) we found small changes in relative energies; from these, we estimate that energy differences, on which all physical conclusions are based, include error bars no greater than 0.1 eV, small enough to not affect any of the conclusions we draw. The bulk positions were taken from the calculated lattice constant of 4.17 Å which is in good agreement with the experimental value 4.08 Å.<sup>33</sup> Spin-polarized calculations were also performed for the entire adsorption system, but had no substantial effect on the results.

To study the interaction of chlorine with defects, three different Au(111) substrates were considered: a stepped surface,  $\langle 110 \rangle / \{100\}$  Au(533), where  $\langle 110 \rangle$  is the direction along the step edge and  $\{100\}$  is the plane of the step edge, a surface containing a single gold adatom, and a surface containing vacancies. In all of the calculations a single chlorine atom was adsorbed on the surface, corresponding to a  $\frac{1}{16}$  ML (monolayer) coverage. The stepped surface consisted of the (111) terraces with each unit cell offset to create a step, shown in Fig. 1(a), the adatom surface had an additional gold adatom sitting on a threefold site on the top layer of gold, and the vacancy surface had gold atoms removed from the top layer of the gold substrate; the number of removed gold atoms ranged from 1 to 13.

### III. RESULTS AND DISCUSSION

The reference configuration in this work is the adsorption of atomic chlorine on the flat, defect-free Au(111) surface. The adsorption energy was calculated for three different sites: on top of a gold atom (coordination number, CN=1), on the bridge site (CN=2), and on a threefold site (CN=3). The adsorption energy is defined relative to the chemical potential of  $\text{Cl}_2$  gas:

$$E_{\text{ads}}(\text{Cl}) = - \left[ E(\text{Au/Cl}) - E(\text{Au}) - \frac{1}{2} E(\text{Cl}_2) \right],$$

where  $E(\text{Au/Cl})$  is the total energy of a gold substrate with the chlorine atom adsorbed,  $E(\text{Au})$  is the energy of the gold substrate, and  $E(\text{Cl}_2)$  is the energy of a  $\text{Cl}_2$  molecule. The clean  $(1 \times 1)$  Au(111) surface is a good reference point for two reasons: first, the experimentally observed herringbone reconstruction of the clean Au(111) surface is lifted upon initial chlorine adsorption, and second, the difference in surface energy between the ideal  $(1 \times 1)$  surface and the surface with the herringbone reconstruction is actually quite small,  $\sim 0.02$  eV per surface Au atom.<sup>34</sup> In this definition, a positive value for the adsorption energy means that the structure with the adsorbed Cl atom on the Au surface is energetically preferred over the bare surface plus Cl in molecular form far from the surface. The calculated bond length and binding energy for the  $\text{Cl}_2$  molecule using the PW91 functional are 2.02 Å and 2.68 eV, respectively; the corresponding experimental values are 1.99 Å and 2.51 eV;<sup>33</sup> these values calculated with the RPBE functional are 2.00 Å and 2.54 eV.<sup>35</sup>

Chlorine adsorbed on the threefold site was found to be the most stable, with an adsorption energy of  $E_{\text{ads}} = 0.99$  eV, followed by adsorption to the bridge site with  $E_{\text{ads}} = 0.94$  eV, and on the top site with  $E_{\text{ads}} = 0.78$  eV. Previous DFT calculations also found the threefold site to be the preferred binding site of chlorine on Au(111), with nearly the same Au–Cl distance and an adsorption energy at  $\frac{1}{2}$  ML coverage that was 0.48 eV lower than our value.<sup>36</sup> Since the adsorption energy of chlorine decreases with increasing coverage, and our adsorption energy was calculated at  $\frac{1}{16}$  ML coverage, we considered this to be reasonable agreement. All of the adsorption energies are positive, agreeing with the experimental observation that chlorine dissociation occurs on the Au(111) surface. The Au–Cl bond length increases with increasing CN, being 2.41 Å on the top site, 2.59 Å on the bridge site, and 2.66 Å on the threefold site. These distances are all slightly longer than the Au–Cl distances found in bulk gold (III) chloride. The crystal of bulk chloride contains planar  $\text{Au}_2\text{Cl}_6$  molecules in a herringbone arrangement. The experimental bond distance for chlorine bonded to one gold atom and two gold atoms is 2.23 and 2.33 Å, respectively.<sup>37</sup>

The first gold defect used to test the adsorption of chlorine was a single gold adatom on the unreconstructed Au(111) surface. Gold adatoms can play an important role on the Au(111) surface, especially when considering the initial adsorption on a clean surface. The clean Au(111) surface reconstructs in the so-called herringbone pattern, resulting in an excess of 4.5% Au atoms on the top layer compared to the bulk (111) plane.<sup>38–40</sup> The presence of several adsorbed molecules lifts the reconstruction, thus releasing gold adatoms

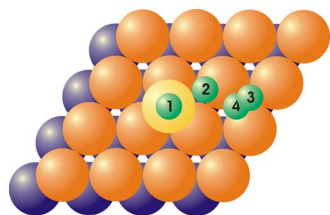


FIG. 2. (Color online) Chlorine adsorption sites on the Au(111) surface with a Au adatom. Orange circles represent the top layer of the gold, the yellow circle is the gold adatom, and smaller numbered green circles indicate the relaxed chlorine positions.

onto the surface;<sup>27,41,42</sup> making it is reasonable to use the unreconstructed surface as a reference point. Figure 2 shows multiple locations for the adsorption of chlorine on the Au(111) surface with a gold adatom present. Many different configurations were tested; the ones shown in Fig. 2 are final configurations after the system was relaxed, each position being a local minimum on the potential energy surface. For configurations 1 (chlorine bound on top of the gold adatom) and 2 (chlorine bound to both the adatom and a gold atom on the substrate) the adsorption energy is 1.28 and 1.18 eV, respectively, which is 0.29 and 0.18 eV higher (stronger adsorption) than chlorine on a threefold site on the defect-free surface. The increase in the strength in binding can be seen in the bond length, for example, the  $\text{Au}_{\text{adatom}}\text{-Cl}$  bond distance for configuration 1 is 2.30 Å, which is 0.11 Å shorter than Cl on top of a Au atom on the defect-free surface.

The interaction between the Au adatom and the Cl is short range, on the order of  $< \sim 4$  Å, since placing the chlorine away from the gold adatom had no significant effect on the adsorption energy compared to that of the defect-free surface. For example, in configuration 4 the adsorption energy is 0.92 eV, nearly the same as the adsorption energy found for chlorine on a bridge site of the defect-free surface. The same is true for configuration 3 whose adsorption energy is 0.93 eV, essentially the same as the adsorption energy for Cl on the hcp threefold site on a defect-free surface, 0.94 eV. Therefore, there appears to be no long-range effect of the gold adatom on Cl adsorption. Similar short range effects have been observed for the coadsorption of CO and O on Pt(111) (Ref. 43) and for CO and S on Rh(111).<sup>44</sup>

There are two important implications of these results. First, since the adsorption of chlorine is stronger to a gold adatom than any site on a flat (111) surface, even the threefold site on the terrace, the initial chlorine atoms that are deposited on the surface will interact with adatoms that are present on the surface. Second, the presence of chlorine will lower the energy cost to create a gold adatom on the surface. The energy cost required to create an adatom is defined as

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

where  $E(\text{Au}_{\text{surface+adatom}})$  is the total energy for the gold substrate with the Au adatom adsorbed on a threefold site,  $E(\text{Au}_{\text{atom in bulk}})$  is the energy of a gold atom in the bulk crystal, and  $E(\text{Au}_{\text{surface}})$  is the energy of the gold substrate with a clean, defect-free surface. The energy cost to create a gold adatom without chlorine present is 0.61 eV while the

energy cost with chlorine adsorbed on top of a gold adatom is 0.21 eV.

The second gold substrate investigated was the Au(533) stepped surface. The adsorption energy of chlorine was tested at various different sites. The starting and ending points of the geometry relaxation are shown in Fig. 1(b), illustrating that chlorine prefers to interact with both the edge of a step and ledge of a step where the terrace meets the upper edge. Chlorine atoms relax away from the terrace either moving toward the edge of the step or toward the ledge depending on their starting location. The adsorption energies for the four configurations, shown in Fig. 1(b) are 1.37, 0.97, 0.80, and 0.99 eV, in order. The configuration with the highest adsorption energy is the one with chlorine at the edge of the step, “hanging” over the step and coordinated to two gold atoms. The binding energy for chlorine at the edge of the step is 0.38 eV higher than that of a defect-free surface. The Au–Cl distance at the step edge is 2.50 Å, 0.09 Å shorter than the Au–Cl distance for Cl on a bridge site of the defect-free surface. Chlorine prefers to bind on a step edge, consistent with the general trend that atoms bind more strongly to step edges;<sup>45</sup> for example, atomic oxygen (an electronegative species such as Cl) also prefers to bind on a step of a Au(111) surface.<sup>46,47</sup> Upon the adsorption of chlorine at 300 K in experiments, dynamic STM images show serrated step edges, indicating an etching or migration of atoms at the step edge, which is in agreement with our calculations that chlorine shows a strong preference for these sites.

Experiments show that upon the adsorption of chlorine on Au(111), pits of atomic height begin to form on the surface.<sup>22</sup> It is unclear, however, if Cl is interacting or adsorbed near these pits on the surface. To investigate this phenomenon and, at the same time, test another type of surface defect as potential Cl attractor, the adsorption of chlorine was tested on a surface that contained gold vacancies. These vacancies are created by removing atoms from the top layer of the gold substrate and the adsorption energy was calculated for Cl residing at a threefold site. The results are shown in Fig. 3. Much like the other defect surfaces, the adsorption energy of chlorine is higher on a surface containing gold vacancies than on the clean, defect-free surface. The effect of the vacancy is greater when the gold atom removed is coordinated with two of the gold atoms to which the chlorine atom is bound. The adsorption energy also increases as the number of vacancies increases but only up to three vacancies. With more than three vacancies, the adsorption energy slowly starts to decrease. There is a clear interaction between the chlorine atom and the vacancy since in many of the configurations the chlorine relaxes toward the vacancy. For example, in a configuration containing one vacancy (the gold atom labeled C in Fig. 3 having been removed), the chlorine is shifted toward the vacancy site with the shortest Au–Cl distance being 2.61 Å and the next two Au–Cl distances being 2.68 and 2.77 Å. With three vacancies, the chlorine sits in the middle of a threefold site with a shortest Au–Cl distance of 2.60 Å, which is 0.06 Å shorter than the Au–Cl distance on a defect-free surface, indicating a stronger interaction.

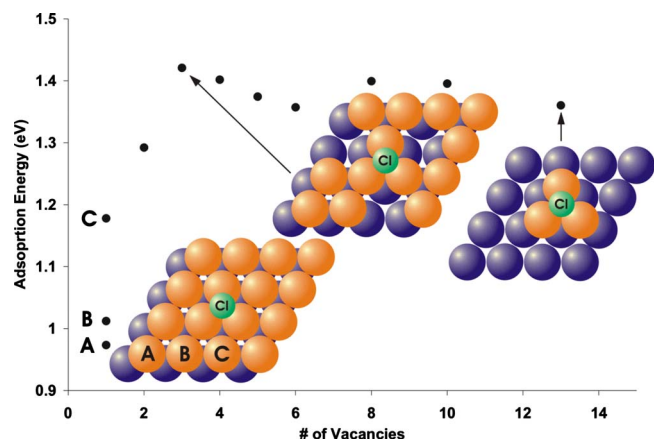


FIG. 3. (Color online) Adsorption energy of atomic chlorine as a function of number of vacancies on Au(111). Orange circles represent the top layer of gold and purple circles the second layer of gold. With only one vacancy there are three different configurations we considered: the gold atom removed to create the vacancy and the corresponding energy value are labeled A, B, and C. The optimal structure (with highest absorption energy) corresponds to three gold vacancies and the chlorine atom at the threefold site on top of the remaining top-layer gold atoms, shown in the middle configuration. The structure with the highest number of vacancies (13) and its energy are shown on the right.

The results from each type of defect illustrate how the adsorption of chlorine can contribute to the release of gold atoms from the surface. Generally, strongly electronegative adsorbates can release gold from the surface, some examples on Au(111) being  $\text{NO}_2$ ,<sup>48</sup> S,<sup>49</sup>  $\text{CH}_3\text{SH}$ ,<sup>50,51</sup> and O.<sup>52,53</sup> In fact, recent experimental work showed that at higher coverages of chlorine it is energetically favorable to incorporate gold atoms in the adsorbate adlayer.<sup>22</sup> The release of gold from the substrate upon adsorption is the result of either (or both) of two processes occurring: (a) the adsorbate interacts favorably with the gold atoms released, or (b) the adsorbate interacts favorably with a vacancy that is left behind after the gold atom is released. In the case of Cl on Au(111), our calculations show that chlorine stabilizes both adatoms and vacancies, suggesting that this is the driving force for the Au atom release that is observed experimentally at higher coverages.

Finally, we will use charge difference density plots to elucidate the bonding of Cl to different defect surfaces. Figure 4(a) is the charge difference plot for the preferred adsorption site of chlorine on the vacancy surface, the bridge site adjacent to the vacancy. The plot is the difference in the electron density for the adsorbed system and the gold substrate with the gold atoms frozen in the positions from the adsorbed system. The figure shows this difference in the plane through the top layer of gold. There is a large negative region of charge in the middle of the plot corresponding to the location of the vacancy. When the vacancy is created, charge density is removed from what appears to be  $d$  orbitals around each neighboring gold atom and accumulates on the edge of the vacancy. A vacancy created without the adsorption of chlorine results in the symmetric accumulation of charge around the vacancy (results not shown). The adsorption of chlorine creates a slightly asymmetric charge redistribution, with more charge facing the vacancy on the side opposite to the chlorine adsorption site. The adsorbed chlo-

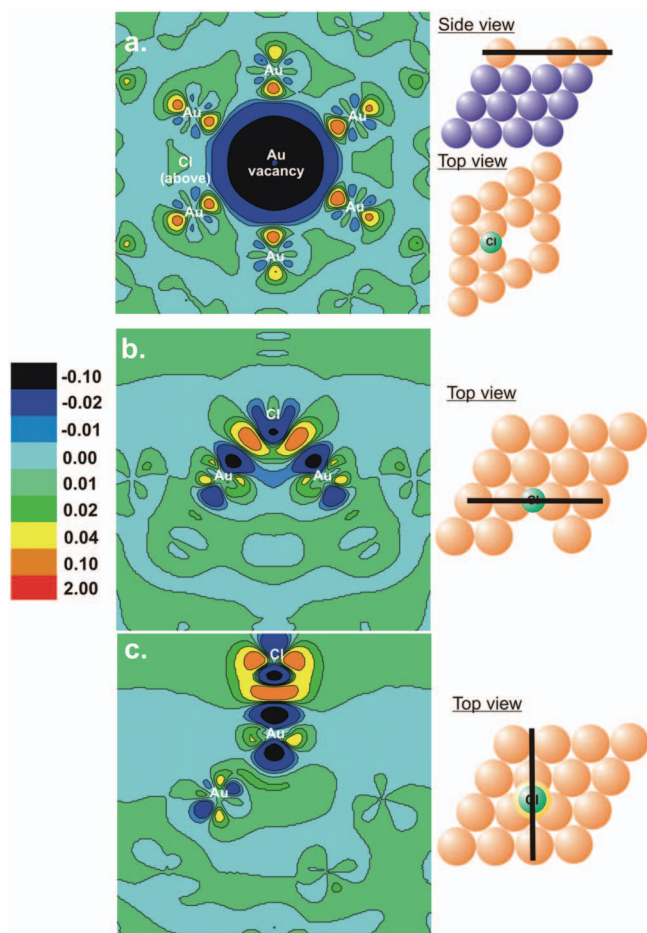


FIG. 4. (Color) Charge difference plots for (a), (b) chlorine bound next to a gold vacancy and (c) chlorine bound on top of a gold adatom. Structural figures on the side of each plot indicate the atomic arrangements; the black line in each case indicates the plane on which the charge difference is plotted. Each plot corresponds to an area of  $100 \text{ \AA}^2$ .

rine must polarize charge density in and around the vacancy to create this asymmetry. Interestingly, the adsorption of chlorine not only affects the charge density of the gold atoms to which it is coordinated but also gold atoms much farther away; for example, atoms on the other side of the vacancy which are nearly two lattice constants away ( $\sim 6 \text{ \AA}$ ). This effect is more pronounced on the surface with vacancies compared to the ideal surface.

Figures 4(b) and 4(c) illustrate the bonding of chlorine on the vacancy and adatom gold surface. In these plots the charge of the frozen gold substrate and free Cl atom is subtracted from the charge of the total adsorbed system including the substrate. A large localization of charge directly between the chlorine and gold atoms is evident in both cases, suggesting a strong covalent interaction. The amount of charge is much greater and localized than on the clean surface. Figure 4(c) also illustrates that a small amount of electron density is added between the gold adatom and the first layer of the gold. This may help stabilize the gold adatom and strengthen its interaction with the top layer of gold. This effect, combined with the stronger covalent interaction, leads to the stronger binding of chlorine to the gold surfaces with vacancies or adatoms.

#### IV. CONCLUSIONS

Our extensive set of DFT calculations show that atomic chlorine favorably interacts with defects on a gold surface. The adsorption of chlorine is stronger for a chlorine atom interacting with gold adatoms, steps, and vacancies. We expect that for a process that involves chlorine, the active sites on gold surfaces, such as those of a supported gold nanoparticle, will be near the defects (adatoms, steps, and vacancies) rather than sites on the flat terraces. These results also shed some light onto the interaction of chlorine with surface defects and the experimentally observed release of gold atoms upon the adsorption of chlorine. This mechanism may also be related to the effect of chlorine on the selectivity of olefin partial oxidation on Au(111), and other similar catalytic systems.<sup>54–56</sup>

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