First-Principle Study of Adsorption and Desorption of Chlorine on Cu(111) Surface. Does Chlorine or Copper Chloride Desorb?

Tatiana V. Pavlova, Boris V. Andryushechkin, and Georgy M. Zhidomirov

1Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, Russia
2G.K.Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia

First-principle density-functional calculations have been applied to study the interaction of molecular chlorine with the (111) plane of copper. Using transition-state search method, we considered the elementary processes (Cl₂ dissociation, adsorption, diffusion, association and desorption) on the chlorinated Cu(111) surface. A systematic study of possible desorption pathways has been carried out for different species (Cl, Cl₂, CuCl, CuCl₂, and Cu) at various chlorine coverage. As a result, we concluded that chlorine monolayer irrespective of the coverage desorbs in the form of CuCl molecules from step edges.

I. INTRODUCTION

The adsorption of chlorine on Cu(111) has been a subject of extensive experimental studies since the 1970s. In the first work, Goddard and Lambert studied the Cl/Cu(111) system with temperature programmed desorption (TPD), Auger electron spectroscopy (AES), work function measurements and low-energy electron diffraction (LEED). According to TPD and AES spectra obtained in Ref.1, only one chemical state (chemisorbed chlorine) has been identified on the Cu(111) surface. In addition, TPD experiments showed that chlorine atoms were the only desorption products. Eltsov et al. considered the Cl₂ adsorption on Cu(111) in the temperature range of 150-300 K and detected two chemical states on the chlorinated Cu(111) surface: chemisorbed chlorine and copper (I) chloride. Both states were clearly visible in TPD and AES spectra. Analysis of desorption products reveals that the chlorine phase desorbs in the form of CuCl₃ trimers, whereas chemisorbed chlorine desorbs as CuCl molecules. Formation of two chemical states has been also confirmed in the work by Walter et al.

First structural studies of chemisorbed chlorine phases on Cu(111) have been performed with LEED. Goddard and Lambert found that the (√3 × √3)R30° structure developed at chlorine coverage of 0.33 ML is replaced by several complex diffraction patterns containing the 6-spot triangles around the √3 positions at higher coverages. Similar diffraction patterns were also reported in Refs.4,11. These patterns have been explained in Refs.4,11 by diffraction on the uniformly compressed hexagonal lattices of chlorine rotated by 30 degrees with respect to basic directions of Cu(111). Note that in the early scanning tunneling microscopy (STM) study this model has been confirmed. However in 2000, the model of the uniform compression was revised in the STM works by Andryushechkin et al. Compression of the chlorine lattice on Cu(111) was found to be uniaxial and non-uniform. According to Refs.14,15, the increase of chlorine coverage above 0.33 ML leads to the commensurate-incommensurate (C-I) phase transition via formation of striped super heavy domain walls.

The local geometry of Cl atoms on Cu(111) has been studied experimentally7,10,12 using surface extended X-ray absorption fine structure (SEXAFS), photoelectron diffraction and x-ray standing waves techniques7,10. As a result, chlorine atoms were found to be adsorbed in fcc hollow sites.

Recently, new results were obtained for the submonolayer chlorine coverage (< 0.33 ML) on Cu(111). Measurements performed with low temperature scanning tunneling microscopy (LT-STM) showed that chlorine tends to form chain-like structures at the submonolayer stage of adsorption. In the case of single atomic chains, chlorine atoms can alternately occupy fcc-hcp positions corresponding to interatomic distances of 3.9 Å being smaller than those (4.4 Å) in the (√3 × √3)R30° structure. Indirect electronic interaction was found to be responsible for abnormally short Cl-Cl interatomic distances in the chains.

First-principle calculations have been performed for the Cl/Cu(111) system in a number of works. In the first computational work, Doll and Harrison studied the (√3 × √3)R30° structure formed by chlorine atoms on Cu(111) and concluded that fcc hollow sites are preferable. Migani et al. reported a systematic study of all halogens on several metal surfaces. For the Cl/Cu(111) system, the authors considered two supercells ((√3 × √3)R30° and (3 × 3)) and confirmed principal conclusions of the paper by Doll and Harrison. Chlorine adsorption on Cu(111) was examined in the recent study by Roman and Gross, in which the experimentally observed monotonic increase of the work function with chlorine coverage has been supported by density-functional theory (DFT) calculations.

The most detailed work on the chlorine adsorption on the (111) plane of copper was published by Peljhan and Kokalj. Authors suggested several structural models of the chlorine layer corresponding to coverages in the range of 1/16 – 1 ML and analyzed their stability. One of conclusions of the paper is that only one (√3 × √3)R30° structure appears to be stable. However, the authors cited only articles describing models of the uniform compression and did not take into account STM data by Andryushechkin et al. demonstrating the formation of the uniaxially compressed domain-wall.
phases at coverages exceeding 1/3 ML. Another problem that can be found in the paper by Peljhan and Kokal\cite{2062} concerns the process of the chlorine desorption from the Cu(111) surface. Using the work of Goddard and Lambert\cite{2063} as a reference, the authors reproduced the atomic chlorine desorption in their calculations. However, they did not take into account desorption in the form of CuCl molecules reported in Ref\cite{2064}. Note that the CuCl desorption was also reported by Nakakura et al.\cite{2065} in the case of the Cl/Cu(100) system. In this connection, further computational studies are required to clarify the situation with desorption products.

In this paper, we present a systematic computational study of the molecular chlorine adsorption on the Cu(111) surface. We tried to describe theoretically not only all chlorine structures detected in the STM experiments\cite{2066,2067,2068} but to examine several defect structures and test their stability. In addition, first-principle calculations have been performed for all stages of the Cu(111) chlorination: dissociation of the Cl₂ molecule, adsorption of chlorine atoms, diffusion of copper and chlorine atoms across the surface, association and desorption of reaction products. As a result, all the contradictions between experimental and theoretical description of the chlorine monolayer desorption from Cu(111) have been ruled out.

II. THEORETICAL METHOD

The calculations were performed within the framework of DFT using the Vienna ab-initio simulation package (VASP)\cite{2062,2063} employing the projector augmented wave method\cite{2064}. The generalized gradient approximation with the exchange-correlation functional form of Perdew–Burke–Ernzerhof (PBE) was applied\cite{2065}. The valence electron eigenfunctions are expanded in a plane-wave basis set with an energy cutoff of 400 eV and Fermi smearing of 0.2 eV. The equilibrium lattice parameter of bulk copper was calculated to be 3.64 Å, in agreement with the experimental value of 3.61 Å\cite{2066}. The Cu(111) surface was represented by a four-layer slab separated by a vacuum gap with a thickness ≈ 18 Å. The bottom two layers were fixed at bulk positions while positions of atoms in the remaining copper and chlorine layers were allowed to relax. Steps were modeled as a part of the fifth Cu(111) layer. Reciprocal cell integrations were performed using (7×7×1), (5×5×1), and (2×12×1) Monkhorst–Pack k-point grids for the (4×4), (6×6), and (12×2) surface supercells, respectively. Non-spin-polarized DFT method was used for all calculations. Spin-polarized calculations were performed for some systems (among them single atom under the surface) to study the impact of this effect on the results. We have examined that non-spin-polarized full energies agree with spin-polarized ones within the accuracy of our calculations.

The reaction barriers were evaluated using the nudged elastic band (NEB) method\cite{2067} implemented into VASP. Calculations of minimal energy paths (MEP) and activation barriers on potential energy surface (PES) were carried out with a spring constant of 5 eV/Å². A smaller k-point grid was employed at MEP evaluation in order to reduce the computational cost.

The adsorption energy of chlorine on Cu(111) was calculated according to the formula

\[ E_{\text{ads}} = \frac{E_{\text{Cu/Cu}\{111\}} - E_{\text{Cu}\{111\}} - E_{\text{Cl}_2}}{N_{\text{Cl}}} \],

(1)

where \( E_{\text{Cu/Cu}\{111\}} \), \( E_{\text{Cu}\{111\}} \), and \( E_{\text{Cl}_2} \) are the total energy of adsorption system, clean Cu(111), and gaseous Cl₂ in vacuum, respectively; \( N_{\text{Cl}} \) is a number of Cl atoms adsorbed on copper surface.

To determine the thermodynamically stable configurations of chlorine on the Cu(111) surface, we calculate the surface free energy per surface area \( A \),

\[ \gamma = \frac{\Delta G - N_{\text{Cu}}\mu_{\text{Cu}} - N_{\text{Cl}}\mu_{\text{Cl}}}{A} \],

(2)

where \( G \) is the Gibbs free energy, \( N_{\text{Cu}} \) is a number of Cu adatoms. Since the chemical potential of chlorine in gas phase (\( \mu_{\text{Cl}} \)) is supposed usually to keep the main temperature and pressure dependence\cite{2068}, only the total energies have been left in \( G \), \( \Delta G = E_{\text{Cu/Cu}\{111\}} - E_{\text{Cu}\{111\}} \). The chemical potential of copper (\( \mu_{\text{Cu}} \)) is assumed to be equal to the total energy of a copper atom in a bulk, \( E_{\text{Cu}} \). Since defects (step edges and adatoms) have been generated on surface before chlorine adsorption, we can put \( N_{\text{Cu}} = 0 \) and account Cu adatoms in total energy calculations (\( E_{\text{Cu}\{111\}} \)) assuming Cu(111) as a clean surface with defects. Now \( \gamma \) can be rewritten in terms of \( E_{\text{ads}} \):

\[ \gamma = \rho \theta (E_{\text{ads}} - \Delta \mu_{\text{Cl}}) \],

(3)

where \( \Delta \mu_{\text{Cl}} = \mu_{\text{Cl}} - E_{\text{Cl}_2}/2 \), \( \rho \) is a number of copper atoms per surface area \( A \), \( \rho = 0.175 \text{ Å}^{-2} \), \( \theta \) is chlorine coverage in ML (1 ML is defined as a density of surface atoms).

The desorption energy of a specie X (X = Cl, Cl₂, CuCl, CuCl₂, Cu) from the chlorinated Cu(111) surface is defined as

\[ E_{\text{des}} = E_{\text{fin}} + E_X - E_{\text{Cl/Cu}\{111\}} \],

(4)

where \( E_{\text{fin}} \), \( E_X \), and \( E_{\text{Cl/Cu}\{111\}} \) are the total energies of the final surface after desorption, gaseous product X in vacuum, and initial metal surface with adsorbate, respectively.

To put a link to the experiment, we estimated positions of thermodesorption peaks using the values of desorption energies obtained in our calculations. Usually, the Polanyi–Wigner equation is used to describe thermal desorption process:

\[ r_{\text{des}} = k \theta^\alpha, \quad k = \nu \exp\left\{-\frac{E_{\text{des}}}{k_B T}\right\}, \]

(5)
where \( r_{\text{des}} \) is the desorption rate, \( n \) is the order of the desorption kinetics, \( k_B \) is the Boltzmann constant, \( \nu \) is a frequency factor \( (\approx 10^{13} \text{s}^{-1}) \). For the zero-order, first-order, and second-order kinetics the dependence of \( \theta^{(n)} \) on initial adsorbate coverage \( (\theta) \) and desorption time \( (t) \) is determined as (see, for example, Ref. 30)

\[
\theta^{(0)} = \theta (1 - kt/\theta),
\]

\[
\theta^{(1)} = \theta \exp(-kt),
\]

\[
\theta^{(2)} = \theta (1 + k\theta t)^{-1},
\]

where \( T = T_0 + \beta t \), \( \beta \) is the heating rate, \( T_0 \) is the initial substrate temperature. The temperature \( T_m \) corresponding to peak of the desorption rate can be found from the following condition:

\[
\frac{d r_{\text{des}}}{dT} \bigg|_{T=T_m} = 0.
\]

III. RESULTS AND DISCUSSION

A. Dissociation of Cl\(_2\) Molecule

The dissociation of molecule above metal surface may be sensitive to its position and orientation with respect to the substrate plane (see Ref. 31). In this connection, we considered both parallel and perpendicular initial orientations of the Cl\(_2\) molecule with respect to the Cu(111) plane. The minimal energy path was evaluated between initial and final states shown in Fig. 1.

For both orientations, the initial states were taken as minimum height positions above the surface, in which the optimization of coordinates would not lead to changes in the distance between Cl\(_2\) molecule and Cu(111). Note that we were not able to use positions of the molecule close to the surface as the initial states due to its fast dissociation into a pair of separate atoms during the optimization of coordinates. The minimal distance between the lowest Cl atom in the molecule and the plane of Cu surface atoms was estimated to be 3.6 Å and 6.3 Å for parallel and perpendicular molecule orientations, respectively. The calculated Cl\(_2\) bond length in the initial state is equal to 1.99 Å that agrees with the calculated value for the isolated chlorine molecule and with the experimental value of 1.987 Å\(^{32}\). According to recent DFT calculations of pair adsorption of chlorine on the Cu(111) surface\(^{16}\), the configuration fcc–hcp with a separation of 3.9 Å is favorable. That was a reason to take it as the final configuration in the dissociation process.

Calculations predict no energy barrier for the Cl\(_2\) dissociation during the adsorption in both orientations\(^{11}\). This result is in line with previous DFT calculations of the chlorine dissociation on Cu(111)\(^{20}\) performed only for the parallel orientation.

For the perpendicular molecule orientation, we found a stable state (reaction coordinate 6 in \( \Box \)) corresponding to the adsorption energy of \(-0.566 \text{ eV} \) per Cl atom \( (E_{\text{ads}} = 0 \text{ eV} \) for the initial state and \( E_{\text{ads}} = -1.826 \text{ eV} \) for the final one). Since MEP has the stable state, we performed two NEB-calculations: before (reaction coordinates 1–6 in \( \Box \)) and after (reaction coordinates 6–11 in \( \Box \)) the stable state. In this state, the first Cl atom is placed above the second one occupying the fcc position. During adsorption, the Cl–Cl bond distance increases by 0.65 Å and becomes equal to 2.64 Å. Note, that similar state (Cl–Cl distance of 2.34 Å) has been predicted for the case of the Cl\(_2\) adsorption on Ag(111) in Ref. 33.
B. Adsorption

In this section, we present a computational study of several surface structures formed by chlorine on the Cu(111) surface. We focused mainly on the structures that have been reported in the experimental STM studies.\[14-16\] In addition, we considered the adsorption on the step edges and near the copper adatom.

At the first stage, we analyzed the adsorption of the single chlorine atom on Cu(111). For the \((4 \times 4)\) unit cell, we calculated adsorption energies for the Cl adsorption in fcc, hcp, bridge and top sites (see 2a). The fcc position was found to be favorable \((E_{\text{ads}} = -1.831 \text{ eV})\), in agreement with results of experiments\[7-10,12\] and previous calculations\[16,20\].

Adsorption of the single chlorine atom was considered also near the copper adatom placed in the fcc position on Cu(111) (2b). According to calculations performed with the \((4 \times 4)\) unit cell, the position on the top of the adatom \((E_{\text{ads}} = -1.810 \text{ eV})\) is less favorable than the positions near the adatom \((E_{\text{ads}} = -1.877 \text{ eV})\) and the fcc position on the terrace. For the optimized structure (2b, 5), the distance between the adsorbed chlorine atom and the copper adatom is equal to 2.21 Å. This value appears to be less than the bond length between the Cl atom and the nearest Cu surface atom (2.42 Å).

2c shows the model drawing and adsorption energies for the single chlorine atom adsorption on the step edges. We consider two types of steps on the (111) facet aligned parallel to \(\langle 111 \rangle\) and \(\langle 112 \rangle\) directions (unit cell \(6 \times 6\), coverage \(\theta = 0.03 \text{ ML}\)). For both types of steps, the favorable position of the Cl atom is the threefold hollow site between two copper atoms from the upper terrace and one copper atom from the lower terrace (see 2c). According to calculations, chlorine appears to be more strongly bound on the \(\langle 111 \rangle\) step \((E_{\text{ads}} = -2.126 \text{ eV})\) than on the \(\langle 112 \rangle\) one \((E_{\text{ads}} = -2.076 \text{ eV})\). It is noteworthy that both values of adsorption energy are significantly larger than those for chlorine adsorption on terraces and near adatoms. Thus, we can conclude that the step edges are the most attractive sites for chlorine adsorption on the Cu(111) surface.

2d shows the case of the pair adsorption of chlorine atoms on Cu(111). Calculations performed within the \((4 \times 4)\) unit cell (coverage \(\theta = 0.12 \text{ ML}\)) show that the fcc–hcp configuration (3.9 Å) is slightly preferable in comparison with the fcc–fcc one (4.4 Å). This conclusion is in line with results of the recent PBE-D2 study,\[16\], in which this difference was found to be more pronounced.

We also considered the adsorption of two chlorine atoms near the copper adatom on Cu(111). The DFT optimized structure corresponds to the linear geometry, in which the copper adatom and chlorine atoms occupy bridge and on top positions, respectively (see 2e). Therefore, the adsorption of two chlorine atoms near the surface adatom is more favorable \((E_{\text{ads}} = -1.953 \text{ eV})\) than the adsorption of two separate chlorine atoms on the Cu(111) terrace \((E_{\text{ads}} = -1.826 \text{ eV})\). Since the distances between Cl atoms and the Cu adatom (2.16 Å) appear to be less than those between Cl atoms and the underlying copper atoms from the upper substrate layer (2.38 Å), we can consider the Cl-Cu-Cl configuration as a quasi-molecule CuCl\(_2\). It is noteworthy that the arrangement of the CuCl\(_2\) quasi-molecule on the Cu(111) surface is very similar to the case of the AuCl\(_2\) quasi-molecules observed in the Cl/Au(111) system.\[34\]
According to STM experiments\textsuperscript{14,15}, chlorine forms on the Cu(111) surface a simple \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure at 0.33 ML. In this phase, all Cl atoms occupy equivalent fcc sites as seen from \textsuperscript{2}. The adsorption energy of chlorine in the \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure was found to be equal to \(-1.789\) eV.

Further chlorine dosing above 0.33 ML gives rise to the uniaxial compression of the chlorine lattice\textsuperscript{14,15} via formation of the striped super-heavy domain walls. At the final point of compression, the chlorine lattice is described by the \((12\times\sqrt{3})R30^\circ\) unit cell\textsuperscript{12,14}. Results of our calculations (optimized model and energy of adsorption) are presented in \textsuperscript{2f}. Some chlorine atoms were found to occupy exactly fcc adsorption sites, while others — positions located between fcc and bridge sites. This structure is energetically less favorable \((E_{\text{ads}} = -1.697\) eV\) in comparison with the \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure since only some of Cl atoms are adsorbed into the optimal fcc sites. According to calculations, the nearest-neighbor Cl–Cl distances are varied in the range of 3.5 \(\text{Å} - 4.0\) \(\text{Å}\). Taking into account the proximity of these values to the van der Waals diameter of chlorine (3.6 \(\text{Å}\)), one can conclude that further compression of the chlorine lattice on Cu(111) is unfavorable.

Summarizing the results shown in \textsuperscript{2} we conclude that chlorine first adsorbs on the step edges (the maximal value of adsorption energy). Although, there are no LT-STM images demonstrating the presence of chlorine atoms near copper adatoms on the Cu(111) surface, such configuration can exist at elevated temperatures. Energies of adsorption for single and pair of chlorine atoms on the Cu(111) terraces appear to be very close to each other. For complete monolayers characterized by both hexagonal \((\sqrt{3} \times \sqrt{3})R30^\circ\) and quasi-hexagonal \((12\times\sqrt{3})R30^\circ\) lattices, the energies of adsorption was found to be considerably lower than those for the case of single and pair adsorption.

C. Thermodynamical Stability of Surface Structures

To make a link between calculated adsorption structures with those observed in the experiment, the surface free energy \((\gamma)\) was evaluated as a function of the Cl chemical potential \(\Delta\mu_{\text{Cl}}\) by \textsuperscript{3}. The thermodynamically most stable structure at given \(\Delta\mu_{\text{Cl}}\) corresponds to the lowest energy line in \textsuperscript{3}. The horizontal line at \(\gamma = 0\) represents the clean surface.

The clean copper surface is the most stable at the chemical potential smaller than the lowest adsorption energy for chlorine on Cu(111), \(\Delta\mu_{\text{Cl}} < -2.13\) eV. Chlorine at step edges is the most stable configuration from \(\Delta\mu_{\text{Cl}} = -2.13\) eV and until these sites become completely filled.

On terraces, Cl atoms in CuCl\(_2\) quasi-molecules and near Cu adatoms are most thermodynamically stable at \(\Delta\mu_{\text{Cl}} > -1.95\) eV and \(\Delta\mu_{\text{Cl}} > -1.88\) eV, respectively, and till adatoms are present on the surface. Single Cl atoms are stable in a tiny range \(-1.83\) eV < \(\Delta\mu_{\text{Cl}} < -1.82\) eV. At \(-1.82\) eV < \(\Delta\mu_{\text{Cl}} < -1.77\) eV, chains are thermodynamically preferred.

The \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure is stable in the range of \(-1.77\) eV < \(\Delta\mu_{\text{Cl}} < -1.33\) eV. Increase of the chlorine chemical potential above \(\Delta\mu_{\text{Cl}} = -1.33\) eV leads to the \((12\times\sqrt{3})R30^\circ\) structure, which is stable up to \(\Delta\mu_{\text{Cl}} = -0.83\) eV, i.e. to the CuCl bulk formation energy.

D. Diffusion

Diffusion of chlorine and copper atoms on the Cu(111) surface may effect on the kinetics of the adsorbate layer transformation and on the rearrangement of copper atoms on terraces and steps edges. In the present work, we used the NEB calculations to study the mobility of Cl and Cu atoms on both perfect and defective Cu(111) surfaces.

According to our calculations, the minimal energy paths (MEP) passes through the bridge site playing a role of the transition state. The energy barrier for the fcc–hcp migration of the Cl atom is equal to the difference between adsorption energies of chlorine in fcc and bridge sites. The height of the energy barrier was evaluated as 0.08 eV, in agreement with earlier computations\textsuperscript{20}, in which this value was reported to be less than 0.1 eV.

The height of the energy barrier for the fcc–hcp copper
adatom hopping on the terrace was found to be equal to 0.05 eV (taking into account that MEP is the same as for the Cl atom diffusion). The estimated barrier height for the direct Cu atom movement from the step edge to the terrace is equal to 1.27 eV [4]. In the other scenario, the copper atom can migrate to the terrace through a kink site of the step. The transition of Cu from the step edge to the kink site requires the activation energy of 0.90 eV, and from kink site to the terrace — 0.63 eV [4]. It means that at energies higher than 0.90 eV, copper atoms can migrate along step edges inducing a change in their shape.

E. Association & Desorption

To investigate the desorption of chlorine from the Cu(111) surface, we calculated activation energies for probable desorption products: Cl, Cl$_2$, CuCl, CuCl$_2$, and Cu. According to the transition state theory, MEP for the dissociative adsorption is the same as for the associative desorption.

Since the Cl$_2$ molecule dissociates above Cu(111) without any activation barrier, the associative desorption of molecular chlorine also has no additional barrier. Therefore, the energy barrier of the associative Cl$_2$ desorption is determined only by the energy difference between the initial and finite states and could be calculated by [4].

We carried out the NEB-calculations of CuCl and CuCl$_2$ molecules adsorption on Cu(111). As initial states for MEP calculation, we considered the perpendicular orientation of these molecules with respect to the substrate plane. The calculated Cl-Cu distance in the initial state of the CuCl molecule is equal to 2.04 Å. In the initial configuration of the CuCl$_2$ molecule, the Cl-Cu and Cl-Cl distances were found to be 2.05 Å and 4.11 Å, respectively. Note that structural parameters of the both molecules in the initial state above the Cu(111) surface agrees well with the calculated values for the isolated molecules in vacuum. In the final states, the molecules stay on the surface (see [2] and [4]) and the bonds are slightly stretched. According to our calculations, CuCl and CuCl$_2$ molecules adsorb on Cu(111) without any activation barrier. The same conclusion was made in Ref. [35], wherein the desorption of the on-top adsorbed chlorine atom together with the underlying copper atom from the substrate has been considered.

Table summarizes the desorption energies for probable desorption products from the chlorinated Cu(111) surface. Calculations have been performed for both perfect and defective surfaces. The structural model of defective surface contains two types of steps (aligned parallel to (111) or (112) directions) with several adsorption sites. However, we present here only the lowest energy configuration.

Next, we analyze desorption processes for each species depending on the chlorine coverage.

a. Cl desorption. As expected, the energy required to break bonds between chlorine and surface copper atoms decreases as chlorine atoms start to occupy less favorable adsorption sites (see [4]). Moreover, at any coverage the atomic desorption of chlorine from step edges is less favorable than that from the perfect surface.

b. Cl$_2$ desorption. The Cl$_2$ desorption demonstrates qualitatively very similar behavior as the atomic Cl desorption. According to our calculations, the desorption of the Cl$_2$ molecule from the (12$\sqrt{3}$×$\sqrt{3}$R30$^\circ$) structure (3.29 eV) is easier than that of other structures (($\sqrt{3}$×$\sqrt{3}$)R30$^\circ$ — 3.59 eV, two individual atoms in fcc–hcp sites — 3.64 eV, step edge — 4.14 eV). Thus, in the desorption process, chlorine is released first from less favorable adsorption sites populated only at high coverage (0.42 ML).

c. CuCl desorption. The easiest way for the CuCl desorption is to remove the Cl atom together with the Cu adatom (2.18 eV). The activation barrier for the CuCl desorption from the step edges appears to be higher (2.59 eV for the coverage of 0.42 ML, 3.02 eV for 0.33 ML, and 2.92 eV for 0.03 ML). The desorption of the CuCl molecule from the Cu(111) terrace is less favorable. Indeed, the activation barrier of the CuCl desorption is equal to 3.14 eV for the coverage of 0.42 ML, 3.66 eV for the coverage of 0.33 ML, and 3.71 eV for the coverage of 0.06 ML. The CuCl desorption energy is defined mainly by the number of the nearest Cu atoms: the less
Table I: Desorption energies (in eV) calculated for probable desorption products from the chlorinated Cu(111) surface

| $\theta$, ML | desorption sites       | specie    | $E_{\text{des}}$, eV |
|--------------|------------------------|-----------|----------------------|
| 0            | adatom                 | Cu        | 2.69                 |
|              | step edge              | Cu        | 3.42                 |
|              | terrace                | Cu        | 4.47                 |
| 0.03         | step edge              | CuCl      | 2.92                 |
|              | step edge              | Cl        | 3.58                 |
|              | step edge              | CuCl$_2$  | 3.66                 |
|              | step edge              | Cl$_2$    | 4.14                 |
| 0.06 –       | Cl with Cu adatom      | CuCl      | 2.18                 |
| 0.12         | CuCl$_2$ quasi-molecule| CuCl$_2$  | 2.60                 |
|              | fcc site               | Cl        | 3.33                 |
|              | chain (fcc–hcp)        | Cl$_2$    | 3.64                 |
|              | Cl from fcc and Cu from terrace | CuCl | 3.71                 |
| 0.33         | step edge              | CuCl      | 3.02                 |
|              | ($\sqrt{3} \times \sqrt{3})R30^\circ$ | Cl | 3.30                 |
|              | step edge              | CuCl$_2$  | 3.41                 |
|              | step edge              | Cl        | 3.57                 |
|              | ($\sqrt{3} \times \sqrt{3})R30^\circ$ | Cl$_2$ | 3.59                 |
|              | Cl from ($\sqrt{3} \times \sqrt{3})R30^\circ$ and Cu from terrace | CuCl | 3.66                 |
| 0.42         | step edge              | CuCl      | 2.59                 |
|              | ($12 \times \sqrt{3}-R30^\circ$) | Cl | 3.03                 |
|              | Cl from ($12 \times \sqrt{3}-R30^\circ$) and Cu from terrace | CuCl | 3.14                 |
|              | step edge              | Cl        | 3.20                 |
|              | ($12 \times \sqrt{3}-R30^\circ$) | Cl$_2$ | 3.29                 |
|              | step edge              | CuCl$_2$  | 3.37                 |

nearest-neighbors Cu are around the CuCl molecule, the less energy is required to break Cu–Cu bonds.

d. CuCl$_2$ desorption. Using analogy with the CuCl desorption, we believe that the easiest way to desorb CuCl$_2$ is to remove two chlorine atom together with the copper adatom or with the copper atom from the step edge. That is why, we did not consider the possible extraction of the copper atom from the upper Cu(111) plane. According to our calculations, the CuCl$_2$ desorption barrier appears to be higher than that for the desorption of the CuCl molecule (see [5]).

e. Cu desorption. According to our calculations, the activation energy of the desorption of copper atoms from the Cu(111) surface increases in the series: adatoms, step edges, and first surface layer (see [6] at zero chlorine coverage). As in the case of the CuCl desorption, the less number of copper atoms in the first coordination sphere, the easier Cu atom can be removed. Our calculations show that copper sublimation starts at 2.69 eV (adatoms removal). This energy considerably exceeds the activation energy of copper atoms diffusion from step edges to the terrace (1.27 eV). Therefore, the desorption mechanism via adatoms removal seems to be plausible.

Thus, analysis of our computational results obtained for desorption of Cl, Cl$_2$, CuCl, and CuCl$_2$, shows that copper (I) chloride has the lowest barrier height at all coverages up to 0.42 ML. For the better recognition, we present our data on the plot showing the dependence of the desorption energy on the chlorine coverage [6]. In [5] we presented only the minimal desorption energy for each specie for the given coverage. Since there is no experimental evidence of Cu adatom presence at chlorine coverage 1/3 ML, corresponded to the starting coverage in desorption experiments, desorption of CuCl and CuCl$_2$ molecules from adatoms is not shown in [5].

Now we can describe the desorption mechanism as following. The desorption of chlorine takes place in the form of CuCl molecules at any coverage. Desorption preferably occurs from the step edges (minimal barrier for desorption). Since the chlorine adsorption on the step edges is energetically more favorable than the adsorption on the terrace, the chlorine population at the step edges is recovered continuously as a result of fast (energy barrier is equal to 0.08 eV) diffusion of chlorine atoms from the terrace.

These conclusions are in line with thermodesorption data published in the work by Eltsov et al. [5], in which the desorption of chlorine monolayer was found to take place in the form of CuCl molecules in the temperature range of 700-850 K (peak maximum $\approx$800 K). Taking into account that in our calculations the CuCl desorption corresponds to minimal activation energy (2.59 – 2.92 eV at $\theta = (0.42 – 0.03)$ ML) with respect to other probable desorption products (Cl, Cl$_2$, CuCl$_2$), we can make a
rough estimation of the position of the CuCl desorption peak. Using experimental conditions taken from work by Eltsov et al. (θ = 0.42 ML, β = 2 K/s, T₀ = 160 K), we obtained values 840 K and 859 K for first-order and second-order desorption for E_	ext{des} = 2.59 eV, respectively. Thus, a good agreement with experimental data has been achieved.

In their work, Goddard and Lambert reported atomic chlorine as the only desorption product. The reported activation energy of desorption was estimated as 236 kJ/mol (2.45 eV) that is close to our data for the CuCl desorption from steps but not with atomic chlorine desorption. In our belief, the contradiction can be solved if assume that in the experiments by Goddard and Lambert the sensitivity of the mass-spectrometer was likely not enough to detect CuCl species.

Figure 5: Minimal desorption energies for Cl, Cl₂, CuCl₂, and CuCl shown as functions of chlorine coverage. The lines connecting the points are guides to the eye.

IV. CONCLUSIONS

We have computationally studied the reaction of molecular chlorine with both clean and defective Cu(111) surfaces. It was found that the Cu(111) surface has a strong catalytic effect on the Cl₂ dissociation leading to the elimination of the activation barrier at both perpendicular and parallel orientations of the molecule axis. Copper and chlorine atoms have negligibly small diffusion barriers on Cu(111) allowing the transformation of the surface phases at E > 0.1 eV. Step edges are more stable and can be modified at higher activation energies (E > 0.9 eV).

The most energetically favorable desorption sites for chlorine are step edges. In this positions, the Cl atom is attached to two Cu atoms from the upper terrace and occupies position directly above one Cu atom from the low terrace.

Chlorine desorption from the Cu(111) surface takes place in the form of CuCl molecules. The CuCl species desorb first from step edges (at θ < 0.42 ML). After each event of the CuCl desorption, the population of chlorine atoms at the step edges is recovered continuously as a result of fast diffusion of chlorine atoms from the terrace.

V. ACKNOWLEDGEMENTS

Authors are grateful to K.N. Eltsov for ideas and helpful discussions. The reported study was supported by RFBR, research project 15-02-99607. We thank the Joint Supercomputer Center of RAS and the Supercomputing Center of Lomonosov Moscow State University for the use of their computational facilities.

* Electronic address: pavlova@kapella.gpi.ru

1 Goddard, P. J.; Lambert, R. M. Adsorption-desorption Properties and Surface Structural Chemistry of Chlorine on Cu (111) and Ag (111). Surf. Sci. 1977, 67, 180–194.

2 Westphal, D.; Goldmann, A. Chlorine Adsorption on Copper. I. Photoemission from Cu(OOl) and Cu(lll) Substrates. Surf. Sci. 1983, 131, 92–112.

3 Westphal, D.; Goldmann, A. Chlorine Adsorption on Copper. II. Photoemission from Cu(OOl)c(2 × 2)-Cl and Cu(lll)(√3 × √3)R30°-Cl. Surf. Sci. 1983, 131, 113–138.

4 Walter, W. K.; Jones, R. G. Chlorine Adsorption on Cu(111): Low-temperature Adsorption, Electron-stimulated Desorption and Chloride Formation. J. Phys.: Condens. Matter 1989, 1, SB201–SB202.

5 Eltsov, K. N.; Zueva, G. Y.; Klimov, A. N.; Martynov, V. V.; Prakhov, A. M. Reversible Coverage-dependent Cu+Cl₄ads → CuCl Transition on Cu(lll)/Cl₂ Surface. Surf. Sci. 1991, 251/252, 753–758.

6 Motai, K.; Hashizume, T.; Lu, H.; Jeon, D.; Sakurai, T.; Pickering, H. W. STM of the Cu(111)(1 × 1) Surface and its Exposure to Chlorine and Sulfur. Appl. Surf. Sci. 1993, 67, 246–251.

7 Crapper, M. D.; Riley, C. E.; Sweeney, P. J. J.; McConville, C. F.; Woodruff, D. P.; Jones, R.G. Complete Adsorption Site Information for Cl on Cu(111) Using X-Ray Absorption Fine Structure and Photoelectron Diffraction. Europhys. Lett. 1986, 2, 857–861.

8 Crapper, M. D.; Riley, C. E.; Sweeney, P. J. J.; McConville, C. F.; Woodruff, D. P.; Jones, R.G. Investigation of the Cu(111)(√3 × √3)R30°-Cl Structure Using SEXAFS and Photoelectron Diffraction. Surf. Sci. 1987, 182, 213–230.

9 Woodruff, D. P.; Seymour, D. L.; McConville, C. F.; Riley, C. E.; Crapper, M. D.; Prince, N. P.; Jones, R. G. Simple X-ray Standing-wave Technique and its Application to the Investigation of the Cu(111)(√3 × √3)R30°-Cl Structure. Phys. Rev. Lett. 1987, 58, 1460–1462.

10 Woodruff, D. P.; Seymour, D. L.; McConville, C. F.; Riley, C. E.; Crapper, M. D.; Prince, N. P.; Jones, R. G. A Simple X-ray Standing-wave Technique for Surface Structure Determination — Theory and an Application. Surf. Sci.
Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. Phys. Rev. B 1996, 54, 11169–11186.

Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. Phys. Rev. B 1999, 59, 1758–1775.

Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.

Kittel, C. Introduction to Solid State Physics; John Wiley & Sons, Inc.: New York, 2005.

Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin Zone Integrations. Phys. Rev. B 1976, 13, 5188–5192.

Jonsson, H.; Mills, G.; Jacobsen, K. W. Classical and Quantum Dynamics in Condensed Phase Simulations; World Scientific: Singapore, 1998.

Reuter, K.; Scheffler, M. Composition, Structure, and Stability of RuO$_2$(110) as a Function of Oxygen Pressure. Phys. Rev. B 2001, 65, 035406.

Oura, K.; Lifshits, V. G.; Saranin, A. A.; Zotov, A. V.; Katayama, M. Surface Science. An Introduction; Springer-Verlag: Berlin, 2003.

Hammer, B.; Scheffler, M.; Jacobsen, K. W.; Norskov, J. K. Multidimensional Potential Energy Surface for H2 Dissociation over Cu(111). Phys. Rev. Lett. 1994, 73, 1400–1403.

Doll, K.; Harrison, N. M. Theoretical Study of Chlorine Adsorption on the Ag(111) Surface. Phys. Rev. B 2001, 63, 165410.

Gava, P.; Kolaj, A.; Giroucoli, S.; Baroni, S. Adsorption of Chlorine on Ag(111): No Subsurface Cl at Low Coverage. Phys. Rev. B 2008, 78, 165419.

Andryushechkin, B. V.; Cherkez, V. V.; Gladchenko, E. V.; Pavlova, T. V.; Zhidomirov, G. M.; Kierren, B.; Didiot, C.; Fagot-Revurat, Y.; Malterre, D.; Eltsov, K. N. Chlorine Adsorption on Cu(111) Revisited: LT-STM and DFT Study. Surf. Sci. 2015, 659, 7–12.

Doll, K.; Harrison, N. M. Chlorine Adsorption on the Cu(111) Surface. Chem. Phys. Lett. 2000, 317, 282–289.

Migani, A.; Illas, F. A Systematic Study of the Structure and Bonding of Halogens on Low-Index Transition Metal Surfaces. J. Phys. Chem. B 2006, 110, 11894–11906.

Roman, T.; Gross, A. Periodic Density-Functional Calculations on Work-Function Change Induced by Adsorption of Halogens on Cu(111). Phys. Rev. Lett. 2013, 110, 156804.

Peljhan, S.; Kolaj, A. Adsorption of Chlorine on Cu(111): A Density-Functional Theory Study. J. Phys. Chem. C 2009, 113, 14363–14376.

Nakakura, C. Y.; Phanse, V. M.; Altman, E. I. Comparison of the Interaction of Cl$_2$ and Br$_2$ with Cu(100). Surf. Sci. 1997, 370, L149–L157.

Kresse, G.; Hafner, J. Ab initio Molecular Dynamics for Liquid Metals. Phys. Rev. B 1993, 47, 558–561.

Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for...