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Structural paradox in submonolayer chlorine coverage on Au(111)V. V. Zheltov,¹ V. V. Cherkez,^{1,2,*} B. V. Andryushechkin,^{1,†} G. M. Zhidomirov,^{1,3} B. Kierren,²
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In this work, we present a combined low-temperature scanning tunneling microscopy (STM) and density functional theory (DFT) study of chlorine adsorption on Au(111) at low coverages. Our STM study of Cl/Au(111) system has shown that at submonolayer coverages ($\theta < 0.1$ ML) chlorine atoms form chainlike structures with abnormally short distances of 3.8 Å between them. Our DFT calculations have shown that chlorine atoms can interact with each other through distortion of the substrate and this indirect elastic interaction is strong enough to affect their arrangement in the chainlike structures.

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I. INTRODUCTION

Halogens are known to form a large variety of surface structures on metal surfaces [1]. Formation of a particular surface structure at certain temperature is always a result of a delicate balance between adsorbate-adsorbate and adsorbate-substrate interactions. For such electronegative adsorbates as halogens, repulsive dipole-dipole interactions are expected to play a major role in the surface structure formation. This repulsion has a natural tendency to lead to adatoms forming a hexagonal lattice, with a *period decreasing as coverage grows*. The densest commensurate lattice formed by halogens on all the fcc (111) metal surfaces studied is described as $(\sqrt{3} \times \sqrt{3})R30^\circ$ and corresponds to 0.33 monolayer (ML)[1].

Very little is known about submonolayer halogen coverage (<0.33 ML) due to lack of the structural studies because they have to be performed with low-temperature scanning tunneling microscopy. There is only one work by Nanayakkara *et al.* [2], in which authors demonstrated that taking into account long-range electronic interactions mediated by surface states makes it possible to explain arrangement of small two-dimensional (2D) $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands of bromine on Cu(111) at coverage lower than 0.33 ML.

In this paper, we report a case of a structural paradox that takes place in the Cl/Au(111) system: at submonolayer coverage (<0.02 ML), chlorine forms a chainlike structure with abnormally short interatomic distances 3.8 Å [if compared to lattice constant, 5.0 Å in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure]. The nature of this anomaly was found to be due to elastic interactions through the substrate lattice distortion (up to 19%).

Elastic interactions between adsorbed particles on surface have been studied for many years since the 1970s, mainly theoretically [3]. In the framework of the continuum approximation

of elasticity theory, Lau and Kohn [4] showed that the energy of elastic interactions decays as $1/r^3$. Elastic interactions were found to be attractive or repulsive depending on the substrate anisotropy [5]. The above-mentioned theories are generally only valid at large adsorbate distances, while at short and intermediate adsorbate distances, direct quantum-mechanical calculations are required. According to DFT calculations, the elastic part of the indirect interactions was found to be important at short adsorbate distances in a number of systems: Al/Al(111), Cu/Cu(111) [6], Ag/Ag(111) [7,8]. In all these systems, however, electronic interactions were found to be the dominant contributor to formation of surface structures.

Experimentally, the peculiarities of pair interactions between adatoms on metal surfaces have been studied with field-emission microscope for many years by Ehrlich *et al.* [9–13]. In particular, for systems characterized by weak dipole-dipole repulsion [metal heteropairs W-Pd and Re-Pd adsorbed on W(110)], the dominant role of elastic interactions at short distances was reported [10]. The elastic interactions at short adsorbate-adsorbate distances were also found to be important for the proper explanation of diffusion coefficients extracted from the STM experiments on the N/Fe(100) system [14,15]. However, according to the authors, the formation of the surface structures was determined by electronic interactions rather than elastic.

In this connection, the major role of elastic interactions in a system with a strong dipole-dipole repulsion [Cl/Au(111)] is of considerable importance.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

All experiments were carried out in a UHV setup containing LT-STM Omicron operating at 5–77 K. The Au(111) sample was prepared by repetitive circles of Ar⁺ bombardment at 1-keV ion energy and annealing up to 900 K. Introduction of Cl₂ gas (the partial pressure 1×10^{-10} Torr) on Au(111) was done using a fine leak piezo valve.

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The density-functional theory (DFT) calculations have been performed with the periodic plane-wave basis set code VASP 5.3 [16–19] and Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional [20]. All results have been obtained with projector-augmented-wave [21] potentials using a 400-eV plane-wave cutoff. The Au(111)-(1×1) substrate was modeled by a six-layer slab of a 6×6 unit cell with the top three layers allowed to relax and the bottom three layers remaining fixed in the bulk positions. We used a Monkhorst-Pack [22] k -point grid of 3×3×1 and 15-Å vacuum region between the slabs. The van der Waals corrected calculations were carried out using PBE functional with the semiempirical dispersion correction of Grimme [23] (PBE-D2). Scanning tunnel microscope (STM) images were simulated from the DFT results using the simple Tersoff-Hamann approximation [24] considering states between E_F and $E_F - 0.5$ eV.

III. RESULTS AND DISCUSSION

A. STM data

Figure 1(a) shows an atomic-resolution STM image of submonolayer (≈ 0.02 ML) coverage of chlorine on Au(111) obtained as a result of Cl_2 adsorption at 300 K. Chlorine atoms occupy positions exclusively in fcc domains of the herringbone reconstruction and form chainlike structures, as is seen in Fig. 1(a). The atomic structure is not the same along the chains. Three different regions can be found in the STM image in Fig. 1(a). Region I corresponds to the zigzag structure with nearest-neighbor distances of 3.8 and 4.6 Å. Chlorine atoms in regions II and III are separated by a distance of 5.0 Å and form straight one-dimensional chains and compact $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands, respectively.

A close-up STM image of regions I and III is shown in Fig. 1(b). The STM image was superimposed by a grid with nodes corresponding to positions of substrate gold atoms. We placed chlorine atoms forming $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands into threefold hollow sites taking into account that fcc sites had been found to be preferable in DFT calculations [25,26]. As a result, the positions of Cl atoms in the zigzag chain can be unambiguously identified to be fcc and bridge. Note that atoms in bridge positions are imaged in STM brighter than those in fcc positions. The measured corrugation between bridge and fcc sites is about $\delta z = 0.15$ – 0.20 Å. The zigzag chains appear to be of great interest because Cl-Cl distances in them are shorter than those (5.0 Å) in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase formed at 0.33 ML [25,27].

Thus, our STM data have revealed the formation of chlorine chains and abnormally short interatomic distances within the chains. Note also that at higher coverages (0.09 ML) the gold reconstruction disappears [28], leaving a foamlke structure on the surface, which consists of the same kind of chains as in Fig. 1. In this connection, we do not associate our findings with anisotropy caused by initial gold reconstruction Au(111)-(22 × $\sqrt{3}$) and use unreconstructed gold (111) surface in our DFT calculations.

B. DFT calculations

Previous DFT calculations performed for rather small $(\sqrt{3} \times \sqrt{3})R30^\circ$ [25] and (4×4) [26] unit cells determine

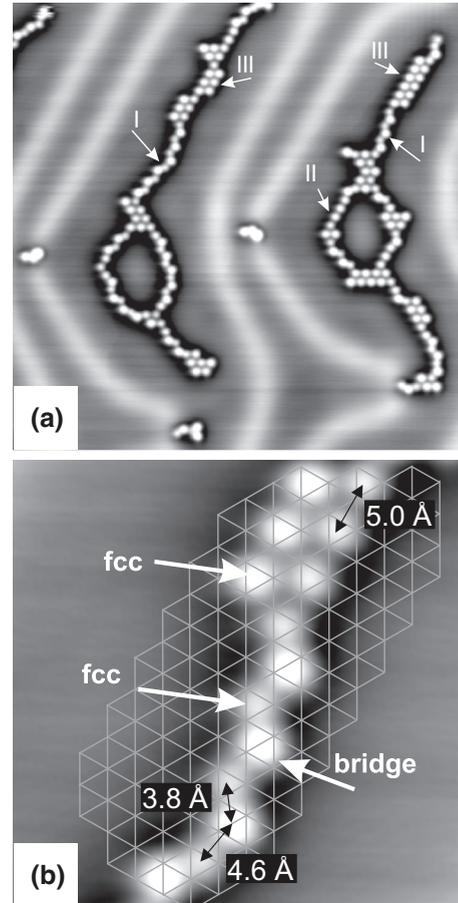


FIG. 1. (a) LT-STM image ($230 \times 230 \text{ \AA}^2$, $U_s = -1$ V, $I_t = 0.5$ nA, 5 K) of submonolayer (0.02 ML) chainlike structures formed by chlorine atoms on Au(111). Different local configurations are marked as I (zig-zag chain), II (linear chain), and III (compact $(\sqrt{3} \times \sqrt{3})R30^\circ$ configuration). (b) A close-up image of a single chain demonstrating that configuration I corresponds to the alternating fcc-bridge stacking of Cl atoms. A hexagonal grid of the Au(111)-(1×1) lattice was placed in a such way that atoms from configuration III appear to be in fcc threefold hollow positions.

the following ranking of adsorption energies of chlorine atoms in different adsorption sites on Au(111)-(1×1): $|E_{\text{fcc}}| > |E_{\text{hcp}}| > |E_{\text{bridge}}| > |E_{\text{top}}|$. In our PBE calculations on a (6×6) unit cell, the adsorption energies are ranked differently (see Table I): the fcc site remains more energetically favorable than the others, but the bridge is more favorable than the hcp. Calculated with PBE-D2, the gap between the bridge and the

TABLE I. Adsorption energies of a single chlorine atom on Au(111)-(1×1) calculated for the (6×6) unit cell.

Functional	fcc	E_{ads} (eV/atom) hcp	Bridge ^a
PBE	-0.950	-0.873	-0.885
PBE-D2	-1.075	-1.014	-1.035

^aNote that no local minimum was found in a bridge position (chlorine atom shifts into fcc position in the course of coordinates optimization). To obtain values of adsorption energies, x and y coordinates of chlorine atom were kept fixed.

	d, Å		E_{ads} , eV/atom	
	PBE	PBE-D2	PBE	PBE-D2
(a)	3.77	3.68	-0.943	-1.091
(b)	4.50	4.41	no local minimum	
(c)	5.05	4.88	-0.944	-1.079
(d)	5.92	5.77	-0.904	-1.027
(e)	6.80	6.65	-0.893	-1.030

FIG. 2. (Color online) Adsorption energies calculated for different configurations of two chlorine atoms on Au(111). The interatomic distances indicated for each configuration correspond to the calculated bulk values of gold crystal $a_{\text{PBE}} = 4.157 \text{ \AA}$ and $a_{\text{PBE-D2}} = 4.078 \text{ \AA}$ (the table bulk value of 4.0782 \AA [30]).

hcp is even larger. For smaller unit cells, the bridge position appears to be less preferable, in agreement with previous calculations. The substitutional adsorption was found to be strongly unfavorable [25,29].

In the next step, we calculated adsorption energies of two chlorine atoms placed at different distances (see Fig. 2). In PBE calculations, configurations fcc-bridge ($\approx 3.8 \text{ \AA}$) and fcc-fcc ($\approx 5.0 \text{ \AA}$) appear to be preferable, with very similar adsorption energies. For configuration fcc-hcp ($\approx 4.5 \text{ \AA}$), no local minimum was found: it transforms into configuration fcc-bridge in the course of coordinates optimization. The results of PBE calculations are in agreement with LT-STM data demonstrating coexistence of two structures at low chlorine coverage. For a pair of atoms, the adsorption energy at the interatomic distances $\approx 3.8 \text{ \AA}$ and $\approx 5.0 \text{ \AA}$ are almost the same, which is surprising, because a single chlorine atom prefers an fcc position to a bridge one (see Table I). PBE-D2 calculations show similar results, with the configuration fcc-bridge ($\approx 3.7 \text{ \AA}$) being even more preferable. Thus, our results indicate the presence of a *specific interaction* between chlorine atoms at short ($\approx 3.7\text{--}3.8 \text{ \AA}$) interatomic distances.

To determine the nature of this interaction, we used pair interaction energy (ΔE_{pair}) given by $\Delta E_{\text{pair}} = E_{S+a+b} - E_a - E_b + E_S$, where E_{S+a+b} is the total energy of a slab containing two chlorine adatoms; E_a , E_b are the total energies of a slab with one chlorine atom placed in positions a or b ; E_S is the total energy of a bare slab.

The total pair interaction energy calculated using PBE functional is shown in Fig. 3 as a function of the distance between chlorine adatoms on Au(111) (blue triangles). There is a noticeable attraction at a short distance of $\approx 3.8 \text{ \AA}$ (configuration fcc-bridge). The increase of the distance to $\approx 5.0 \text{ \AA}$ leads to a slight repulsion between chlorine atoms. At larger distances, the repulsion goes up, as is seen in Fig. 3. Similar results were obtained in PBE-D2 calculations (blue squares).

Although the attraction found at $\approx 3.7\text{--}3.8 \text{ \AA}$ explains the similarity of the adsorption energies for configurations (a) and (c) in Fig. 2, its origin is not clear. Indeed, the

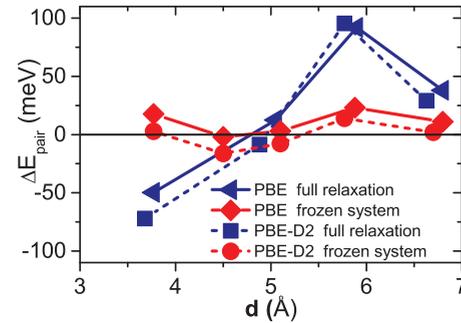


FIG. 3. (Color online) Total interaction energies (blue curves) and their electronic parts (red curves) shown as functions of the distance between two chlorine atoms adsorbed on Au(111)-(1×1). Solid and dashed curves correspond to calculations performed using PBE and PBE-D2 functionals, respectively. The electronic contribution was obtained by freezing the substrate.

dipole-dipole interaction is always repulsive and the Cl-Cl distance is too large for the direct interaction (since the bond length in molecular chlorine is equal to 1.99 \AA [31]). The helpful information was found in the results of coordinates optimization for atomic configurations listed in Fig. 2. Adsorption of chlorine seems to induce a significant distortion of gold atomic lattice. In particular, the change of gold-gold interatomic distances after adsorption of chlorine atoms can reach 19% (see Fig. 4). In this connection, we suggested that in the system in question, an important contribution to ΔE_{pair} could be given by an indirect interaction through the substrate distortion.

Distinguishing between electronic and elastic contributions to ΔE_{pair} is possible in DFT calculations [6,8]. To obtain the electronic contribution to ΔE_{pair} , atoms in the top layers of the bare slab were relaxed to their equilibrium positions, then these positions were kept frozen during further calculations of ΔE_{pair} . In this way, any elastic interaction was suppressed. The results of calculations with the PBE functional are presented in the plot by red diamonds (see Fig. 3). The local minimum at $\approx 3.8 \text{ \AA}$ is not there in a frozen substrate (one

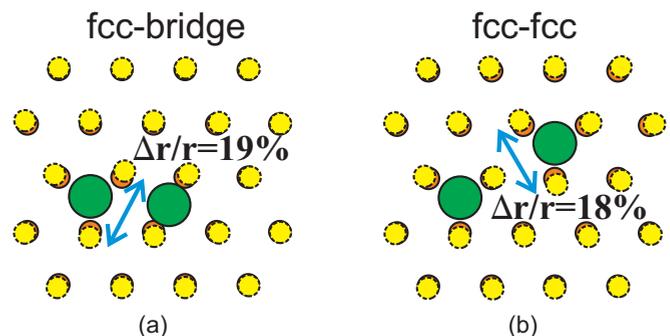


FIG. 4. (Color online) Model drawings corresponding to configurations fcc-bridge ($\approx 3.7\text{--}3.8 \text{ \AA}$) (a) and fcc-fcc ($\approx 4.9\text{--}5.0 \text{ \AA}$) (b). Positions of gold atoms in the upper layer before and after optimization of coordinates are shown by orange and yellow balls, respectively. Chlorine atoms are shown by green balls. The maximum values of the relative distortion of the Au(111)-(1×1) lattice are shown for both cases.

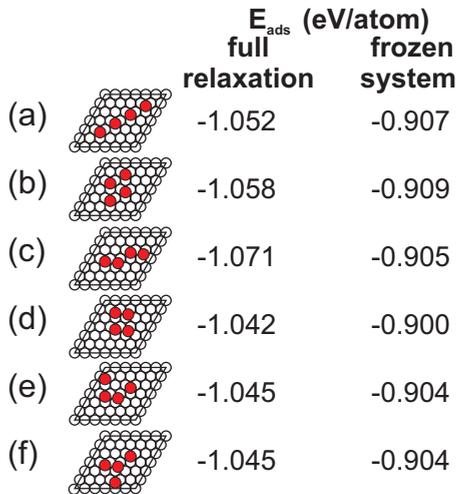


FIG. 5. (Color online) (a)–(f) Adsorption energies calculated using PBE-D2 functional for different configurations of four chlorine atoms on Au(111). Switching on a full optimization of coordinates resulted in different adsorption energies, with a zigzag geometry (c) being energetically preferable. Calculations for frozen system lead to the similar energy of adsorption for all shown configurations.

of the chlorine atoms shifts from bridge to hcp position). However, the calculations performed for fixed bridge positions of chlorine atoms show a slight repulsion at ≈ 3.8 Å. At ≈ 5.0 Å, no appreciable change in the interaction energy was found in the case of the frozen substrate. At distances larger than 5 Å, the repulsion appears to be several times smaller than that in the case of full relaxation. Note also that PBE-D2 calculations lead to quite a similar behavior of ΔE_{pair} (see red circles in Fig. 3). Therefore, the attraction at ≈ 3.7 – 3.8 Å found in the case of full relaxation is due to indirect interaction through the substrate lattice distortion (or elastic interaction).

We also analyzed the role of indirect elastic interactions in the formation of the chains. For this purpose, the adsorption energies were calculated for different configurations of four chlorine atoms on Au(111) (see Fig. 5). The calculations performed with full relaxation of atomic coordinates show that chains fcc-bridge–fcc-bridge with interatomic distances ≈ 3.8 and ≈ 4.6 Å are preferable [see Fig. 5(c)]. A compact structure with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ geometry [Fig. 5(b)] and a linear fcc-fcc structure [Fig. 5(a)] are slightly less preferable, with their adsorption energies being lower than those for the other geometries in Fig. 5. This result is in agreement with experimental data shown in Fig. 1. Calculations performed for a frozen system (atoms of the substrate were fixed at equilibrium positions of the bare slab and chlorine atoms were fixed at positions corresponding to single atom adsorption) do not show any preferable configuration of four chlorine atoms. Thus, the formation of the chainlike structures is also due to the presence of indirect elastic interactions.

C. STM image simulation and height positions of chlorine atoms

According to our PBE calculations, the height difference for chlorine atoms adsorbed in fcc and bridge sites is equal to 0.23 Å. We also simulated STM images for fcc-bridge and

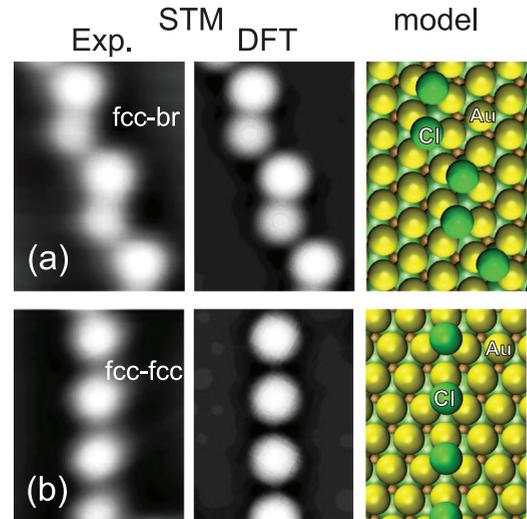


FIG. 6. (Color online) Tersoff-Hamann simulated STM images and corresponding structural models: (a) fcc-bridge chain; (b) fcc-fcc chain.

fcc-fcc chains of chlorine atoms using the simple Tersoff-Hamann approximation [24] (see Fig. 6). The height difference between fcc and bridge sites measured on the simulated STM image was found to be ≈ 0.20 Å in an agreement with the experiment (0.15–0.20 Å). Note also that we did not find any visible change in the fcc-bridge height difference depending on the bias voltage. Thus, we have demonstrated that in the case of the Cl/Au(111) system experimental STM images reflect the real-space geometry of chlorine atoms.

D. Reliability of computational results

In this section, we describe convergence of our computational results with respect to the unit-cell size and the thickness of the slab.

Figure 7 shows results of ΔE_{pair} calculations performed for different sizes of unit cell: 4×4 , 5×5 , 6×6 , and 7×7 (the equivalent k -point sampling was used). According to plots, a decrease of the size of the unit cell results in the disappearance of the attraction effect at 3.8 Å. Therefore, the agreement between calculations and experimental data can be achieved by taking a large unit cell $N \times N$ ($N > 5$). This fact should

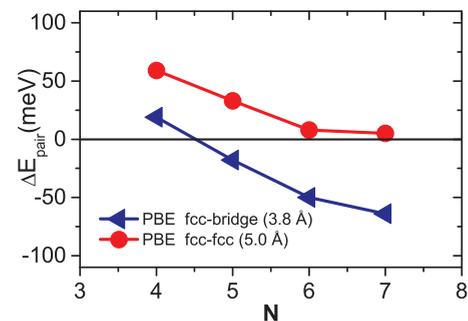


FIG. 7. (Color online) Total interaction energies between two chlorine atoms on Au(111)-(1×1) at distances 3.8 and 5.0 Å shown as functions of the unit cell size (N).

be kept in mind while carrying out calculations of the elastic contribution to the interaction energy at any surface.

Calculations performed with a four-layer slab (two relaxation layers) show no principal differences with respect to a six-layer slab [29]. This result is not surprising, since relaxation of gold lattice occurs mainly within the first atomic layer, leaving other layers almost unaffected.

IV. CONCLUSIONS

In summary, this work demonstrates experimentally and theoretically that indirect elastic interaction can play a dominant role in the formation of surface adsorbate structures at low coverage. For the Cl/Au(111) system, we have found that

this kind of interaction is responsible for both abnormally short Cl-Cl interatomic distances and the chains formation. These results are of general interest also for understanding of many other adsorbate systems that have not been studied in detail at low adsorbate coverage.

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- [1] E. I. Altman, in *Physics of Covered Solid Surfaces: Part I. Adsorbed Layers on Surfaces*, edited by H. P. Bonzel (Springer, Berlin, 2001), pp. 421–453.
- [2] S. U. Nanayakkara, E. C. H. Sykes, L. C. Fernández-Torres, M. M. Blake, and P. S. Weiss, *Phys. Rev. Lett.* **98**, 206108 (2007).
- [3] T. L. Einstein, *Handbook of Surface Science*, edited by W. N. Unertl (Elsevier, Amsterdam, 1996), Vol. 1, p. 577.
- [4] K. H. Lau and W. Kohn, *Surf. Sci.* **65**, 607 (1977).
- [5] A. M. Stoneham, *Solid State Commun.* **24**, 425 (1977).
- [6] A. Bogicevic, S. Ovesson, P. Hyldgaard, B. I. Lundqvist, H. Brune, and D. R. Jennison, *Phys. Rev. Lett.* **85**, 1910 (2000).
- [7] K. A. Fichtorn and M. Scheffler, *Phys. Rev. Lett.* **84**, 5371 (2000).
- [8] M. L. Merrick, W. Luo, and K. A. Fichtorn, *Prog. Surf. Sci.* **72**, 117 (2003).
- [9] G. Ehrlich and F. Watanabe, *Langmuir* **7**, 2555 (1991).
- [10] F. Watanabe and G. Ehrlich, *J. Chem. Phys.* **95**, 6075 (1991).
- [11] F. Watanabe and G. Ehrlich, *J. Chem. Phys.* **96**, 3191 (1992).
- [12] S. J. Koh and G. Ehrlich, *Phys. Rev. B* **60**, 5981 (1999).
- [13] S. J. Koh and G. Ehrlich, *Phys. Rev. Lett.* **87**, 106103 (2001).
- [14] L. Österlund, M. Ø. Pedersen, I. Stensgaard, E. Lægsgaard, and F. Besenbacher, *Phys. Rev. Lett.* **83**, 4812 (1999).
- [15] M. Ø. Pedersen, L. Österlund, J. J. Mortensen, M. Mavrikakis, L. B. Hansen, I. Stensgaard, E. Lægsgaard, J. K. Nørskov, and F. Besenbacher, *Phys. Rev. Lett.* **84**, 4898 (2000).
- [16] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
- [17] G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).
- [18] G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- [19] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [20] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [21] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [22] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [23] S. Grimme, *J. Comput. Chem.* **27**, 1787 (2006).
- [24] J. Tersoff and D. R. Hamann, *Phys. Rev. B* **31**, 805 (1985).
- [25] W. Gao, T. A. Baker, L. Zhou, D. S. Pinnaduwa, E. Kaxiras, and C. M. Friend, *J. Am. Chem. Soc.* **130**, 3560 (2008).
- [26] T. A. Baker, C. M. Friend, and E. Kaxiras, *J. Chem. Phys.* **129**, 104702 (2008).
- [27] B. V. Andryushechkin, V. V. Cherkez, E. V. Gladchenko, T. V. Pavlova, G. M. Zhidomirov, B. Kierren, C. Didiot, Y. Fagot-Revurat, D. Malterre, and K. N. Eltsov, *J. Phys. Chem. C* **117**, 24948 (2013).
- [28] V. Cerchez, Ph.D. thesis, Nancy-Université, 2011.
- [29] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.89.195425> for additional details of DFT calculations.
- [30] R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, London, 1963), Vol. 1.
- [31] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).
- [32] V. Sadovnichy, A. Tikhonravov, V. Voevodin, and V. Opanasenko, in *Contemporary High Performance Computing: From Petascale toward Exascale*, edited by J. S. Vetter (CRC, Boca Raton, 2013), pp. 283–307.