Theoretical study of chlorine adsorption on the Ag(111) surface

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We study the adsorption of chlorine on the Ag(111) surface with full potential gradient corrected density functional calculations. When considering a $\sqrt{3} \times \sqrt{3} R30^\circ$ pattern, we find that the fcc hollow is the most favorable adsorption site. We obtain an Ag-Cl bond length of 2.62 Å which is intermediate between two controversial experimental results. We discuss the differences of core level energies and densities of states for the different adsorption sites. We find the Cl-Ag interaction to be more consistent with an ionic, rather than covalent, picture of the bonding. In addition, we compute energetics and related properties of Ag bulk and the clean Ag surface, comparing the local density approximation and the generalized gradient approximation.

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I. INTRODUCTION

The study of halogen adsorption on metal surfaces has become a very interesting field in surface science. Important questions such as adsorption geometries and energetics have been addressed in experimental studies. The adsorption of chlorine on the Ag(111) surface has been studied by various groups and with different techniques including low energy electron diffraction (LEED),¹⁻⁵ surface extended x-ray absorption fine structure (SEXAFS),^{6,5} Auger spectroscopy,¹⁻³ thermal desorption,^{1,3} measurements of adsorption isobars and isotherms,⁷ work function measurements,¹ and scanning tunneling microscopy.^{4,8}

However, there is still an ongoing discussion about the correct interpretation of the experiments. Various explanations of observed adsorption patterns have been proposed, and the bond length has been measured twice with significantly different results.^{6,5}

We recently presented a theoretical study of chlorine adsorption on the Cu(111) surface⁹ and we are therefore confident that simulation can shed some light on the difficult question of chlorine adsorption. As a test of our computational method, we performed additionally calculations on Ag bulk and clean surfaces. These are presented in Sec. II. The question of chlorine adsorption is discussed in Sec. III.

II. Ag BULK AND CLEAN SURFACES

A. Computational parameters

We used a local basis set formalism where the basis functions are Gaussian type orbitals centered at the atoms as implemented in the code CRYSTAL.¹⁰ In order to examine the effect of various treatments of electron exchange and correlation, we have used the local density approximation (LDA) with Dirac-Slater exchange¹¹ and the Perdew-Zunger correlation functional,¹² the gradient corrected exchange and correlation functional of Perdew and Wang (GGA-PW),¹³ and the gradient corrected functional of Perdew, Burke, and Ernzerhof (GGA-PBE).¹⁴

For silver, we used a relativistic pseudopotential with corresponding basis set.¹⁵ For the calculation on the free atom, we used the original basis set. For the calculation on the solid and surfaces, we kept the inner exponents ($[2s1p1d]$) fixed and reoptimized the outermost exponents within the GGA-PW approximation. Values of $0.63/a_0^2$ (with the Bohr radius a_0) and $0.11/a_0^2$ for the s exponents, $0.23/a_0^2$ for the p exponent and $0.18/a_0^2$ for the d exponent were obtained (the most diffuse s exponent could not be optimized and was kept fixed at a value of $0.11/a_0^2$ to avoid numerical instabilities). This resulted as a whole in a $[4s3p2d]$ basis set. The Cl basis set is $[5s4p1d]$, as used in our recent study of Cl adsorption on Cu(111).⁹

The density functional potential was fitted with an auxiliary basis set, which consisted, for both Ag and Cl, of 12 s and p functions with exponents taken to be a geometrical sequence from $0.1/a_0^2$ to $2000/a_0^2$. For Cl five d functions with exponents in the range $0.8/a_0^2$ to $100/a_0^2$ were employed, and for Ag eight d and f functions from $0.1/a_0^2$ to $100/a_0^2$.

We used a Pack-Monkhorst net of shrinking factor 16 for Brillouin zone sampling, which resulted in 145 irreducible $\vec{k}$ points for the bulk, 45 for the clean (100) surface, 81 for the clean (110) surface, 30 for the clean (111) surface, and 30 or 73 for the system Cl/Ag(111), depending on the adsorption site [30 for hcp and 73 for fcc, bridge and atop sites—an explanation of the sites is given in Sec. III; see also Fig. 1 (Ref. 16)]. A smearing temperature of $0.03E_h$ was applied to the Fermi function ($E_h = 27.2114$ eV). This approach has been shown to give stable results for lithium bulk and surfaces¹⁷ as well as for the study of Cl on the Cu(111) surface.⁹

B. Properties of bulk Ag and clean Ag surfaces

Results for cohesive properties of bulk Ag are in excellent agreement with those published in the literature (Table I). The tendency of the LDA to overbind results in a short lattice constant, too high bulk modulus, and too high binding

FIG. 1. The structures considered for Cl, adsorbed on the Ag(111) surface at one-third coverage, in a $\sqrt{3} \times \sqrt{3} R30^\circ$ unit cell. When Cl is adsorbed in a fcc hollow, it rests above a Ag atom in the third layer (upper left) while in the hcp hollow it is above an atom in the second layer (upper right). The atop position is Cl adsorbed vertically above a surface atom (lower left). In the bridge position it is vertically above the middle of two surface atoms (lower right). The x direction is horizontal in the plane, the y direction is vertical, and the z direction points out of the plane of the page.

energy. The GGA improves the binding energy and bulk modulus; the deviation of the lattice constant is similar to that in the LDA (with opposite sign, however).

Surface formation energies (in E_h per surface atom) of the clean, unrelaxed surfaces are displayed in Table II. The surfaces were modeled with a finite number of Ag layers (typically from one to seven); this model was *not* periodically repeated in space. The surface energy was found to be stable from three layers onward. The bulk energy was computed with the same computational parameters (basis set, shrinking factors, smearing temperature).

TABLE I. The ground state properties of bulk Ag.

Method	a (Å)	E_{coh} (units of E_h)	B (GPa)
LDA	3.98	0.129	165
GGA-PW, GGA-PBE	4.10	0.088	113
LDA ^a	3.95–4.01		137–163
LDA ^b	4.00		139
GGA-PW ^a	4.12–4.14		93–98
GGA-PW ^b	4.17		84.8
Experiment	4.03 ^b	0.109 ^c	102 ^b

^aReference 23.

^bReference 24.

^cReference 25.

TABLE II. The surface energy (E_h per surface atom) of the low index silver surfaces.

Surface	LDA	GGA-PW, GGA-PBE	Ref. 18 (GGA-PBE)
(100)	0.033	0.023	0.024
(110)	0.050	0.033	0.035
(111)	0.026	0.017	0.020

LDA binding energies are approximately 50% higher than those obtained with gradient corrected functionals, which is higher than found in a previous study.¹⁸ The GGA-PW and GGA-PBE methods turned out to give practically identical results in all cases that are in excellent agreement with those in the literature.¹⁸

III. Cl ON THE Ag(111) SURFACE

The adsorption of Cl on the Ag(111) surface has been investigated by several research groups. Still, there is no agreement on adsorption patterns, coverages, preferred sites, and bond lengths. In the first study with LEED and Auger spectroscopy,² a $\sqrt{3} \times \sqrt{3} R30^\circ$ pattern at low chlorine coverage and a (3×3) pattern at higher coverage were observed. In a second study, a $\sqrt{3} \times \sqrt{3} R30^\circ$ pattern at a coverage of 1/3 and a (10×10) pattern at a coverage of 0.49 were found.¹ Within an Arrhenius model, the binding energy was determined to be $0.080E_h$ per Cl_2 . A similar energy was found in another experiment,⁷ but the LEED pattern was interpreted as an epitaxial AgCl layer. A $\sqrt{3} \times \sqrt{3} R30^\circ$ pattern at a coverage close to 1 was found in Ref. 3. Scanning tunneling microscopy experiments have been interpreted as a parallel double row structure, where Cl atoms occupy bridge and threefold hollow sites,⁸ or as a (17×17) overlayer at saturation.⁴

A structural determination with SEXAFS gave a Ag-Cl bond length of 2.70 ± 0.02 Å at a nominal coverage of 1/3 of a monolayer and 2.70 ± 0.01 Å at a nominal coverage of 2/3 of a monolayer.⁶ Cl was found to adsorb in threefold hollow sites in a $\sqrt{3} \times \sqrt{3} R30^\circ$ pattern; for the higher coverage a vacancy honeycomb structure was proposed. This determination has been questioned in a recent article where a bond length of 2.48 ± 0.04 Å has been deduced from SEXAFS measurements for a nominal coverage of 1/3 of a monolayer.⁵ In this study an order-disorder transition was found at 195 K, below which a $\sqrt{3} \times \sqrt{3} R30^\circ$ pattern at a coverage of 1/3 of a monolayer was identified in LEED measurements; this pattern was found to vanish above the transition temperature. In addition, a (13×13) overlayer was identified at a coverage of 0.37. The bond length of 2.48 Å was found to fit better with other bond lengths of chlorine adsorbates on $3d$ and $4d$ fcc metals. Therefore, it was suggested that previous experiments should be reinterpreted. A variation of the bond length with coverage was found neither for Cl on Ag(111),⁶ nor for the similar system of I on Rh(111).¹⁹

These experimental observations therefore pose an interesting problem for simulation studies. In our calculations, we

TABLE III. Adsorption of Cl on the Ag(111) surface, GGA-PW results. δ_{1-2} is the change in interlayer spacing between first and second silver layers relative to the bulk value, $d_{\text{Cl-Ag top layer}}$ is the interlayer distance between the Cl layer and the top Ag layer, $d_{\text{Cl-Ag NN}}$ is the distance between Cl and the nearest neighbor Ag. The adsorption energy is the difference $E_{\text{Cl at Ag(111)}} - E_{\text{Ag(111)}} - E_{\text{Cl}}$. n is the number of silver layers in the slab.

n	$d_{\text{Cl-Ag top layer}}$ (Å)	δ_{1-2} (Å)	$d_{\text{Cl-Ag NN}}$ (Å)	$E_{\text{adsorption}}$ (units of E_h per Cl atom)
fcc site				
3	2.01	-0.043	2.62	-0.11164
4	2.01	-0.039	2.62	-0.11173
hcp site				
3	2.01	-0.042	2.62	-0.11068
4	2.02	-0.036	2.62	-0.11129
Bridge site				
3	2.08	-0.040	2.54	-0.10878
Atop site				
3	2.38	-0.034	2.38	-0.09460

modeled the adsorption of Cl on Ag(111) as a slab periodic in two dimensions but with a finite thickness of three or four layers of silver. This was found to be sufficiently thick to obtain stable results for the surface energy of the clean Ag(111) surface. The slab was covered by a layer of chlorine corresponding to a coverage of one-third of a monolayer, in a $\sqrt{3} \times \sqrt{3} R30^\circ$ pattern. Cl was adsorbed in four different sites: the atop site on top of a silver atom in the top layer, the bridge site in the middle of two Ag atoms in the top layer, and hcp (and fcc) hollows where the chlorine is in threefold hollow sites with a silver atom in the second (third) layer under the chlorine atom (see Fig. 1). In the following, all the calculations were performed at the GGA-PW level, if not explicitly stated otherwise.

The results of these calculations are summarized in Table III. First, it turns out that the threefold hollow sites are lowest in energy, with the bridge site being about $0.003E_h$ higher and the atop site $0.017E_h$ higher in energy. This picture is quite similar to that of chlorine adsorption on the Cu(111) surface.⁹ As the threefold sites are nearly degenerate in energy, we considered an improved model with four silver layers to investigate the dependence of the results on the number of layers. It turns out that the fcc hollow stays lower in energy, although the energy difference is reduced from $0.001E_h$ (three layers) to only $0.0004E_h$ (four layers). There-

TABLE IV. Adsorption of Cl on the Ag(111) surface, LDA results. The notation is the same as in Table III.

Site	$d_{\text{Cl-Ag top layer}}$ (Å)	δ_{1-2} (Å)	$d_{\text{Cl-Ag NN}}$ (Å)	$E_{\text{adsorption}}$ (units of E_h per Cl atom)
fcc	1.96	-0.052	2.55	-0.13653
hcp	1.96	-0.046	2.55	-0.13422
bridge	2.03	-0.052	2.47	-0.13297
atop	2.33	-0.047	2.33	-0.11487

fore, a fully reliable prediction of the adsorption site cannot be made as more layers might still change this picture. The total adsorption energy is $0.111E_h$ per chlorine atom. We computed a dissociation energy $D_0^0 = 0.099E_h$, vibrational constant $\omega_e = 520 \text{ cm}^{-1}$, and internuclear distance $r_e = 2.05 \text{ Å}$ for the chlorine dimer in reasonable agreement with experiment ($D_0^0 = 0.091E_h$, $\omega_e = 560 \text{ cm}^{-1}$, $r_e = 1.99 \text{ Å}$).²⁰ Therefore, our binding energy corresponds to $0.123E_h$ per Cl_2 when computed with respect to the Cl_2 molecule, using our computed binding energy for the chlorine dimer. This is higher than that deduced from thermal desorption experiments¹ ($0.080E_h$) and measurements of adsorption isobars and isotherms⁷ ($\sim 0.088E_h$ for the heat of adsorption of Cl_2). However, the first experimental value depends on an empirical prefactor assumed in the Arrhenius model and was questioned in Ref. 1; the authors stated that it should be higher as D_0^0 of the Cl_2 molecule because desorption as atomic Cl was observed.

Another important aspect is the adsorption geometry. We allowed the top silver layer to relax vertically and a slight inward relaxation by about 0.04 Å was found for all adsorption sites. The Ag-Cl bond length was determined to be 2.62 Å for the threefold hollow sites, 2.54 Å for the bridge site, and 2.38 Å for the atop site. Tests on the four-layer slab demonstrated that these bond lengths are stable with respect to the number of layers. Other tests, such as varying the outermost diffuse exponents in the basis set or applying a smaller smearing temperature, were performed, and it turned out that the bond length was also stable with respect to these parameters; the variation was of the order of $\pm 0.02 \text{ Å}$. Therefore, we can conclude that the computed bond length is not highly sensitive to computational details. The remaining approximation in our simulations is the choice of the exchange-correlation functional. The effects of this choice were examined by recomputing the surface properties within the LDA (Table IV). The LDA gives the same preference of adsorption sites and a similar energy splitting. The adsorption energies are $(20-25)mE_h$ higher than those computed using the GGA-PW, and the bond lengths are shorter by $0.05-0.07 \text{ Å}$. The bond length computed with our model (2.62 Å in GGA-PW, 2.55 Å in LDA) is intermediate between those in two controversial experiments [2.48 Å (Ref. 5) and 2.70 Å (Ref. 6)]; therefore we cannot support either experiment over the other.

Combining our data for Cl on Ag(111) and Cl on Cu(111), we can comment on the effective radius of the Cl adsorbate, under the assumption that both the chlorine adsorbate and the copper and silver surfaces are made of hard spheres. For the fcc site and Cl on Cu, a bond length of 2.40 Å was obtained. If we subtract the atomic radius of copper of $3.63/2\sqrt{2} \text{ Å}$, then we obtain a radius for Cl of 1.12 Å . For Cl on Ag, we obtain a radius of $2.62 - 4.10/2\sqrt{2} \text{ Å} = 1.17 \text{ Å}$. This radius for Cl is intermediate between the atomic (0.99 Å) and ionic (Cl^- ; 1.81 Å).²¹ The bond lengths predicted here and previously computed for the Cu(111)-($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ -Cl surface give a consistent picture of the radius of the adsorbed Cl^- ion.

TABLE V. Charge and position of $3s$ eigenvalue for Cl on different adsorption sites.

Site	Charge (units of $ e $)	$3s$ level relative to E_{Fermi} (units of E_h)
Cl on Ag		
fcc	-0.198	-0.563
hcp	-0.204	-0.562
bridge	-0.218	-0.555
atop	-0.252	-0.532
Cl on Cu		
fcc	-0.207	-0.578

The Mulliken population analysis gave a slight charge transfer of $0.2e$ to $0.25|e|$ to the chlorine atom, increasing in the order $\text{fcc} \sim \text{hcp} < \text{bridge} < \text{atop}$; of course, one has to keep in mind that the error associated with this number is larger in the case of metals with diffuse basis functions because the diffuse Cl basis functions can be used to partially describe Ag states, and vice versa. Still, it is very interesting to compare the charge transfer with the position of the Cl $3s$ eigenvalue (Table V). If we assume that intra-atomic interactions dominate the core eigenvalues of the Cl atom, then the position of the Cl $3s$ eigenvalue provides a measure of the atomic charge: the more negatively charged the Cl ion, the lower the binding energy of the core eigenvalue. As this is related to the observable core level shift, it can provide an experimental mechanism for distinguishing adsorption sites. We observe this correlation in our results for different adsorption sites (Table V), but we find that this correlation is not retained when comparing Cl adsorption on Cu to that on Ag. The $3s$ eigenvalue is at lower binding energy for Cl on the Ag surface despite the Cl charge being lower in magnitude than that of Cl on the Cu surface. This could be due to errors in the Mulliken charge estimates, which are more reliable within a consistent set of basis sets.

The position of the Cl levels is visible in the Mulliken projected densities of states (Figs. 2, 3, and 4). First, we projected the density of states on the chlorine orbitals (Fig. 2). The $3s$ level moves as described to higher energies (corresponding to lower binding energies) with higher Mulliken orbital populations. For all adsorption sites, the valence band contribution consists of a broad background from $\sim -0.2E_h$ to $\sim -0.08E_h$, which contains contributions from Cl $3p_x, p_y$ and $3p_z$. The peak at $\sim -0.1E_h$ is due to $3p_x$ and $3p_y$ contributions in all cases; there is no distinct peak from $3p_z$ contributions. The $3p_x$ peak and $3p_y$ peak are virtually identical in the case of fcc, hcp, or atop adsorption sites; for the bridge site the p_y peak carries more weight than the p_x peak (Fig. 3). These findings are consistent with orbital projected Mulliken charges (Table VI), which are highest for p_x and p_y in the case of fcc, hcp, and atop sites. For the bridge site, the p_y population is higher than p_x and again higher than p_z —note that, in our choice of geometry, for the bridge site, the Cl $3p_x$ orbital overlaps more with the silver atoms in the top layer than the Cl $3p_y$ orbital (see Fig. 1). We can therefore conclude that in all sites the charge trans-

FIG. 2. Projected density of states for Cl on Ag(111) and different adsorption sites. The part of the density of states that is due to the Cl basis functions is shown in this projection. The Fermi energy is fixed at $0 E_h$.

ferred to the Cl atom occupies those orbitals that have lowest overlap with the silver atoms. This is consistent with an ionic rather than covalent picture of the bonding. We note that these orbitals may be separately observed by exploiting the polarization dependence of angle resolved photoemission.²² When comparing the chlorine adsorption on silver with the chlorine adsorption on copper (Fig. 4), we find that the bandwidth of the $3p$ states is similar; as mentioned earlier the $3s$ peak is at slightly higher energy for Cl on Ag than for Cl on Cu, although the charge is a bit smaller in magnitude ($-0.207|e|$ for copper vs $-0.198|e|$ for silver). The peak

FIG. 3. Projected density of states for Cl on Ag(111), bridge site. The density of states is shown, projected on the Cl basis functions (p_x, p_y , and p_z). The Fermi energy is fixed at $0 E_h$.

FIG. 4. Projected density of states for Cl on Cu(111) and Cl on Ag(111), fcc hollow. The part of the density of states that is due to the Cl basis functions is shown in this projection. The Fermi energy is fixed at $0 E_h$.

structure is different from Cl on Ag(111) as we find one additional peak for Cl $3p_z$; the two other peaks carry equal weight from Cl $3p_x$ and Cl $3p_y$. As in the case of silver, the Cl $3p_x$ and $3p_y$ orbitals carry slightly more charge than Cl $3p_z$.

Finally, in Figs. 5 and 6, we display the total charge density of Cl adsorbed in the fcc hollow site and the charge density difference. The plane was chosen in such a way that the center of the chlorine atom, the center of one of the nearest neighbor silver atoms (at a distance of $2.62 \text{ \AA}$), and the centers of two more silver atoms (at a distance of $3.91 \text{ \AA}$) lie in the same plane. The charge density difference has been obtained by subtracting the charge densities of a clean Ag slab [with the geometry of the system $\text{Ag}(111) - (\sqrt{3} \times \sqrt{3})R30^\circ\text{-Cl}$] and a layer of chlorine atoms from the charge density of the system after the chlorine adsorption. We find no evidence of bond formation in the charge density plots so that these plots support the idea of an ionic binding mechanism. Further evidence of an ionic bonding is the very small overlap population of $\sim 0.01|e|$ between Cl and the nearest silver atom.

TABLE VI. Orbital projected Cl charge, in units of $|e|$, on different adsorption sites.

Site	p_x	p_y	p_z
Cl on Ag			
fcc	-3.794	-3.794	-3.629
hcp	-3.795	-3.795	-3.636
bridge	-3.766	-3.840	-3.628
atop	-3.822	-3.822	-3.605
Cl on Cu			
fcc	-3.802	-3.802	-3.598

FIG. 5. Total charge density for Cl on Ag(111), fcc hollow, from 0.01 to 0.09 a.u. in steps of 0.01.

IV. SUMMARY

We have studied the adsorption of chlorine on the Ag(111) surface using density functional theory calculations in which we have paid close attention to numerical accuracy. The fcc hollow site was found to be the preferred adsorption site, slightly lower in energy than the hcp site. The adsorption energy is computed to be $0.111 E_h$ per atom with respect to free Cl atoms or $0.123 E_h$ per Cl_2 molecule.

The computed Ag-Cl distance of $2.62 \text{ \AA}$ at the GGA-PW level (or $2.55 \text{ \AA}$ at the LDA level) is intermediate between two controversial values deduced from experiment. The bond length is consistent with that computed for Cl on Cu, which would indicate an effective radius of the Cl adsorbate of $\sim 1.15 \text{ \AA}$. For the different adsorption sites of Cl on Ag(111), we find that the charge on chlorine is consistent with the relative position of the Cl $3s$ level, i.e., the higher the charge on Cl, the lower the binding energy of the $3s$ level. This might be valuable in the interpretation of core level shift observations. From projected densities of states, we conclude that the chlorine charge is larger in those orbitals that are most separated from silver, which means that the character of the bond tends towards ionic rather than covalent.

FIG. 6. Difference in charge density [i.e., charge Cl on Ag(111) - charge of clean Ag(111) - charge of a layer of Cl atoms] for Cl on Ag(111), fcc hollow, from -0.007 to 0.009 in steps of 0.001 a.u. Excess negative charge is displayed with long dashed lines, excess positive charge with solid lines, and zero difference with short dashed lines.

lent. In our choice of geometry, the chlorine $3p_x$ and $3p_y$ orbitals have a slightly higher occupation than the chlorine $3p_z$ orbital for the threefold hollow sites, which might also be observable in photoemission experiments.

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