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Theoretical study of adsorption of Cu, Ag, and Au on the NaCl(100) surface

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The adsorption of noble metal atoms (Cu, Ag, and Au) on the NaCl(100) surface has been studied by means of an embedded cluster approach. We use different models for the surface in order to study the convergence of the properties participating in the bonding. The use of a suitable embedding and the lack of participation of the sodium 3*s* orbitals allows for reliable results with small clusters. Adsorption energies and metal-surface distances are calculated by using *ab initio* Hartree-Fock calculations and including the correlation energy at the second order of perturbation theory. An effective core potential approximation, which includes relativistic mass-velocity corrections for silver and gold, is used for the inner electrons of the metal. Corrections for the basis set superposition error are considered as well. The metal atoms are preferentially adsorbed on the top of cationic sites. The interaction energy is small ($\approx$0.1 eV) and the distances long ($>$3 Å) for all models considered. Adsorption has no noticeable chemical contributions. This is explained by resorting to the electronic structure of metal and surface. Most of the binding energy is due to electrostatic and dispersion forces.

I. INTRODUCTION

Understanding the nature of bonding between metal atoms and insulating surfaces is of great importance in fields such as heterogeneous catalysis, microelectronics, the antithermic and anticorrosion coating industry, metallic coating for optical devices, etc. This explains why numerous studies have been carried out on this question, either at a macroscopic level (measurement of wetting angles, adhesion energies, shear strengths, etc.) or, more recently, at a microscopic level (spectroscopic methods, low-energy ion scattering, electronic tunneling, or force microscopies).[1]

An increasing number of studies are being devoted to the first stages of deposition of metallic atoms and to the determination of growth modes of clusters, many of them on oxide surfaces. The most relevant questions in this respect concern (i) characteristics of the chemical bond formed between the adsorbed metal atom and the ionic surface and (ii) discrimination between cluster (Volmer-Weber) or bidimensional growth (Stranski-Krastanov or Franck Van der Merwe).[2] Although the analysis of core level photoemission peaks, low-energy electron losses, Auger parameters, low-energy ion scattering, or electron microscopy have recently provided information on those systems, there remains considerable controversy in the literature.[2–12]

Several theoretical works have been done to simulate the adsorption of single metal atoms on ionic surfaces.[13–16] For oxide surfaces, these studies highlight the formation of metal–oxygen bonding and antibonding states, the latter being completely filled in the case of noble metals (Cu, Ag); otherwise only partly filled. Thus the interactions are considered to be mainly of a chemical nature. This is a reasonable assumption for relatively reactive surfaces such as those of many metal oxides. However, other ionic surfaces, such as NaCl(100), are known to be highly stable and the nature of the metal-NaCl(100) bond is not so clear. Focusing attention on the Au-NaCl(100) system, different theoretical approaches have been used. Yanagihara and Yamaguchi considered the physisorption of a gold atom over the stepped NaCl(100) surface.[17] They found that the most stable site for physisorption corresponds to a gold atom over a Na^+ terrace site. The binding energy (0.7 eV) is in excellent agreement with the measured desorption energy of Au from this surface. Other electrostatic treatments have been done by Chan *et al.*[18] and Bambakidis.[19] Classical kinematical theories in which the atom-surface interactions are described thermodynamically and/or statistically have also been reported.[20–27]

A different point of view of this system was given by Fuwa *et al.*,[28] who included chemical interactions. They reported local density approximation calculations of the electronic structure of a single gold atom situated atop a sodium site in a $Na_{17}Cl_{17}$ cluster. This calculation shows that there is a negligible interaction of the adsorbate with the underlying sodium ion. However, a true chemical bond is supposed to form between the Au $5d_{z^2-r^2}$ orbital and $3p_z$ orbitals on the four nearest-neighbor Cl^- ions.

No further theoretical studies on this system exist in the literature. However, recent developments in embedding methods for nonempirical quantum-mechanical calculations of local phenomena,[29–31] development of computer technology, as well as modern techniques of analysis and sample preparation of well-defined surfaces of insulating ionic crystals[32] encourage the theoretical revision of this system.

In the present paper, the bonding of single noble metal atoms (Cu, Ag, and Au) to the ideal NaCl(100) surface is studied by means of quantum-chemical methods. One of the aims is the introduction of all the important effects involved in the interaction between metal atom and ionic surface. The local nature of the possible metal-surface bonds enables the use of the finite cluster approach. The classical electrostatic and quantum contributions from the rest of the system, not included in the cluster, are introduced by means of a nonempirical embedding model potential approach.[29,30] Another important factor to consider is the relativistic effects due to the high speeds of the inner electrons in the gold atom (60% of the light speed for the 1*s* electrons).[33] Although this effect is considerably larger for the core electrons, since they are subjected to larger nuclear charges, they manifest themselves in

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the valence space significantly enough to introduce substantial alterations in chemical bonding and physical properties of heavy atoms. It is well known that the $6s$ orbital of the gold atom contracts substantially because of a relativistic effect called the mass-velocity correction. This correction will be considered here through an effective core potential approach.[34]

In this paper, besides the inclusion of the important effects governing the metal/NaCl(100) interaction, the intention is to obtain some information on the nature of bonding. Thus the electrostatic/covalent nature of the interaction in analyzed. Several relevant properties of the fragments (electric field at the surface and energy levels of the molecular orbitals) are analyzed as well.

The main conclusion from our results is that the bonding of Cu, Ag, and Au to the NaCl(100) ideal surface is mainly electrostatic and rather weak, without appreciable covalent contribution.

The paper is arranged as follows. First, a brief summary of the methods and computational details is given in Sec. II. In Sec. III the properties of the isolated fragments, surface, and metal atoms, are reported. Properties taking part in covalent (symmetry and energy of the molecular orbitals) as well as electrostatic (electric field at the surface) interactions are given. The binding energies and distances for different cluster models are reported in Sec. IV. This will permit us to check the adequacy of the models used. Basis set superposition errors (BSSE) and correlation energies are also reported. The different contributions to the binding energy are analyzed in Sec. V by means of the constrained orbital variation (CSOV) method.[35–37] Finally, the main conclusions from these results are summarized in Sec. VI.

II. METHOD AND COMPUTATIONAL DETAILS

Due to the local nature of the metal–ionic surface interaction, a finite cluster approach can be used to model the Cu,Ag,Au/NaCl(100) system. This procedure has been shown to be reliable in describing adsorption over ionic surfaces if a proper embedding method is used.[37]

In this work, compact model potentials (CMP) and point charges array are used for the embedding. Theoretical details of the CMPs are given elsewhere;[29–31,38] here only a brief explanation of the method is given in order to comment on the main approximations involved.

The first point to discuss is the cluster choice. Once this is done, the wave function of the system Φ is written as a product of cluster Φ_{clus} and environment Φ_{env} subsystem wave functions

$$\Phi = M\hat{A}\Phi_{\text{clus}}\Phi_{\text{env}},$$

where M is a normalization constant and $\hat{A}$ is an operator which antisymmetrizes the product with respect to exchange of electrons between the cluster and its environment. This equation is a good approximation when there is no charge transfer between subsystems.

The second approximation concerns the description of the environment. If the cluster contains the nuclei and electrons responsible for the local phenomenon to be described, the environment can be viewed as a frozen spectator, thus, Φ_{env} can be fixed.

The next point is the description of the cluster, that is, the obtention of a good Φ_{clus}. This is done variationally and including cluster-environment orthogonality constraints. This procedure leads to an effective cluster Hamiltonian, in which the cluster-environment interactions are introduced through simple operators, the compact model potentials. For ionic environment the total potential is written as single ionic contributions, each one being

$$\hat{V}^{\text{CMP}} = \hat{V}^{\text{CMP}}_{\text{S.R.}} + q/r,$$

where the second term on the right-hand side is the long-range potential due to the ionic charge q and the first term is a short-range potential which accounts for the finite size of the ions, exchange interactions, and cluster-ion orthogonality.

Summarizing, the approximations done are cluster-environment separability and the frozen description of the environment. The interactions included are the intracluster contributions considered in Φ_{clus} as well as cluster-environment quantum and classical interactions.

In this work, Hartree-Fock description of the cluster will be adopted. The open shell systems are treated with unrestricted Hartree-Fock (UHF) wave functions. This method allows for the treatment of unpaired electrons and introduces spin polarization effects. In order to account for the electron correlation effects, the Moller-Plesset second-order perturbational correction to the UHF energy (UMP2) has been calculated.

The orbitals corresponding to the cluster are built from a basis set of Gaussian type orbitals. For Na^+ and Cl^- we use basis sets given by Huzinaga for the ions.[39] Additional orbitals to describe the $3s$ orbital of sodium and d polarization orbitals for chloride are also used. The final basis sets are $[10s4p/6s2p]$ for Na^+ and $[10s5pd/4s2pd]$ for Cl^-. The inner electrons of the metal atoms are described through the compact effective potentials approach of Stevens *et al.*[34] This allows for the treatment of the metal atoms as 19 electron systems ([core] $ns^2\ np^6\ nd^{10}\ (n+1)s^1$). Mass-velocity and Darwing relativistic effects for silver and gold are considered in this approach. The valence basis set for metals is a triple zeta one and includes the $(n+1)p$ empty atomic orbitals.[34] The resulting basis sets are $[8s8p6d/4s4p3d]$ for copper $[8s8p5d/4s4p3d]$ for silver, and $[7s7p5d/4s4p3d]$ for gold.

The ions of the environment are described by restricted Hartree–Fock wave functions (RHF). The atomic orbital basis sets are the same as those for the ions in the cluster. For the obtention of the short-range operator the use of a basis set is also necessary. The uncontracted atomic orbitals basis set is used to obtain the CMPs representative of the Na^+ and Cl^- ions. The charges appearing in the long-range potential are the respective ionic formal charges. The Na^+ and Cl^- RHF wave functions and, consequently, the CMPs obtained from them, are generated in calculations where the ions are embedded within the bulk NaCl crystal or at their perfect NaCl(100) surface sites. It has been shown that the use of CMPs obtained for bulk ions to represent surface ions gives results different from the use of CMPs obtained for the description of ions at the surface.[38]

The experimental Na-Cl distance is used in all the calculations. The (100) surface is considered to be ideal and no

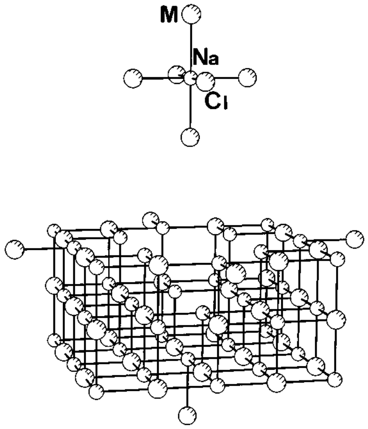

FIG. 1. Cluster $MNaCl_5^{4-}$ used to model adsorption on Na^+ site.

rumpling has been taken into account. Preliminary test calculations showed that the inclusion of such rumpling does not modify the results with respect to adsorption over an ideal surface.

An array of 13×13×4 environment ions is used for the embedding. Such an array converges with respect to the electric field and its derivatives at the surface when the ions are represented by point charges.[38] From these 676 ions, the 74 neighbors closest to the cluster are introduced as CMPs. The rest of the ions do not contribute with any short-range potential to the total potential at the adsorption site and, consequently, they are described by means of point charges which contribute to the Madelung potential.

Two kinds of model cluster are used. The first one consists of the central ion, where the metal atom is adsorbed, plus the surrounding five nearest neighbors. This results in $MNaCl_5^{4-}$ and $MClNa_5^{4+}$ models for adsorption on cation and anion, respectively. These clusters have C_{4v} symmetry (see Figs. 1 and 2). The $MNa_{14}Cl_5^{9+}$ cluster has also been used in order to include the possibility of delocalization of the band formed by superposition of sodium $3s$ atomic orbitals (see Fig. 3). In this case the 13 cations added are represented in a minimal STO-3G basis set, which includes $1S$, $2S$, $2P$, and $3S$ atomic orbitals. As will be shown in the next section, the use of larger clusters is not necessary because of the rapid convergence of electric properties and molecular orbital energies with the cluster size.

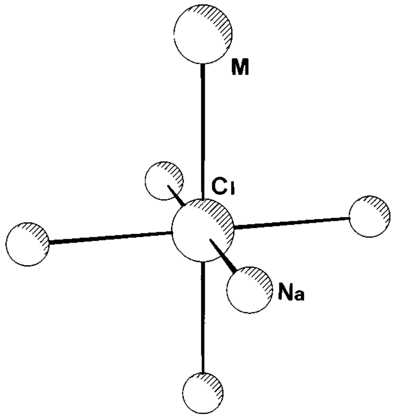

FIG. 2. Cluster $MClNa_5^{4+}$ used to model adsorption on Cl^- site.

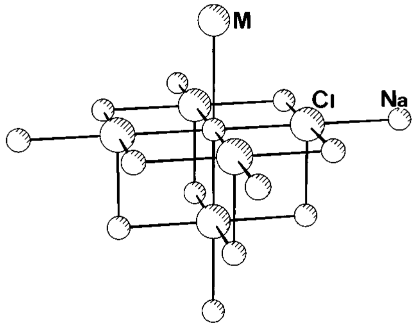

FIG. 3. Cluster $MNa_{14}Cl_5^{9+}$ used to model adsorption on Na^+ site. This cluster also allows for the delocalization of the $3S_{Na}$ surface orbitals.

All the calculations reported here were done with a locally modified version of the Gamess program.[40]

III. PROPERTIES OF FREE ATOMS AND SURFACE MODEL

In this section the properties of noninteracting fragments, free metal atoms, and surface clusters will be described. In order to understand the possible electrostatic contribution to the bonding when using $NaCl_5^{4-}$ or $Na_{14}Cl_5^{9+}$ clusters, plus corresponding embedding for the surface, we will first look at the electrostatic potential, electric field, and first derivative of the electric field at the surface on the Na^+ site for both models. Figure 4 shows that, although the electrostatic potential [Fig. 4(a)] due to both models being slightly different ($\approx$0.05 Hartree/e^-) at the distances considered here (5–10.5 Bohr), the shapes of both functions are quite similar, leading, thus, to almost the same electric fields [Fig. 4(b)] and electric field derivatives [Figs. 4(c) and 4(d)]. Since the electrostatic interaction of the metal atom with the surface will mainly consist of electric field-induced dipole and electric field derivatives-induced quadrupole moments, one expects that the classical contributions to the bonding are quite similar for both surface models.

Energy and symmetry of the molecular orbitals of the fragments determine the possible covalent contributions to the M/NaCl(100) bonding. Figure 5 shows the energy levels of the relevant MOs. The surface MOs, which likely participate in the bonding, are those representing the filled bands formed from the p_x, p_y, p_x AOs of the Cl^- ions as well as those corresponding to the empty band of $3s_{Na}$ character. The former orbitals are responsible for the donor properties of the surface. The MOs resulting from the mixture of p_x Cl^- AOs correspond to the A_1 symmetry of the C_{4v} point group of the $NaCl_5^{4-}$ and $Na_{14}Cl_5^{9+}$ clusters; thus this orbital is able to interact with the empty np_x AO of the metal atoms. In the same way, p_x and p_y orbitals of Cl^- of the surface may interact with np_x and np_y AOs of the atoms (E symmetry). However, the large energy gap between surface p orbitals and empty p AOs of the metal, always larger than 11 eV (see Table IA), leads one to think that this interaction is weak.

As shown in Table IB, the energy gap between the singly

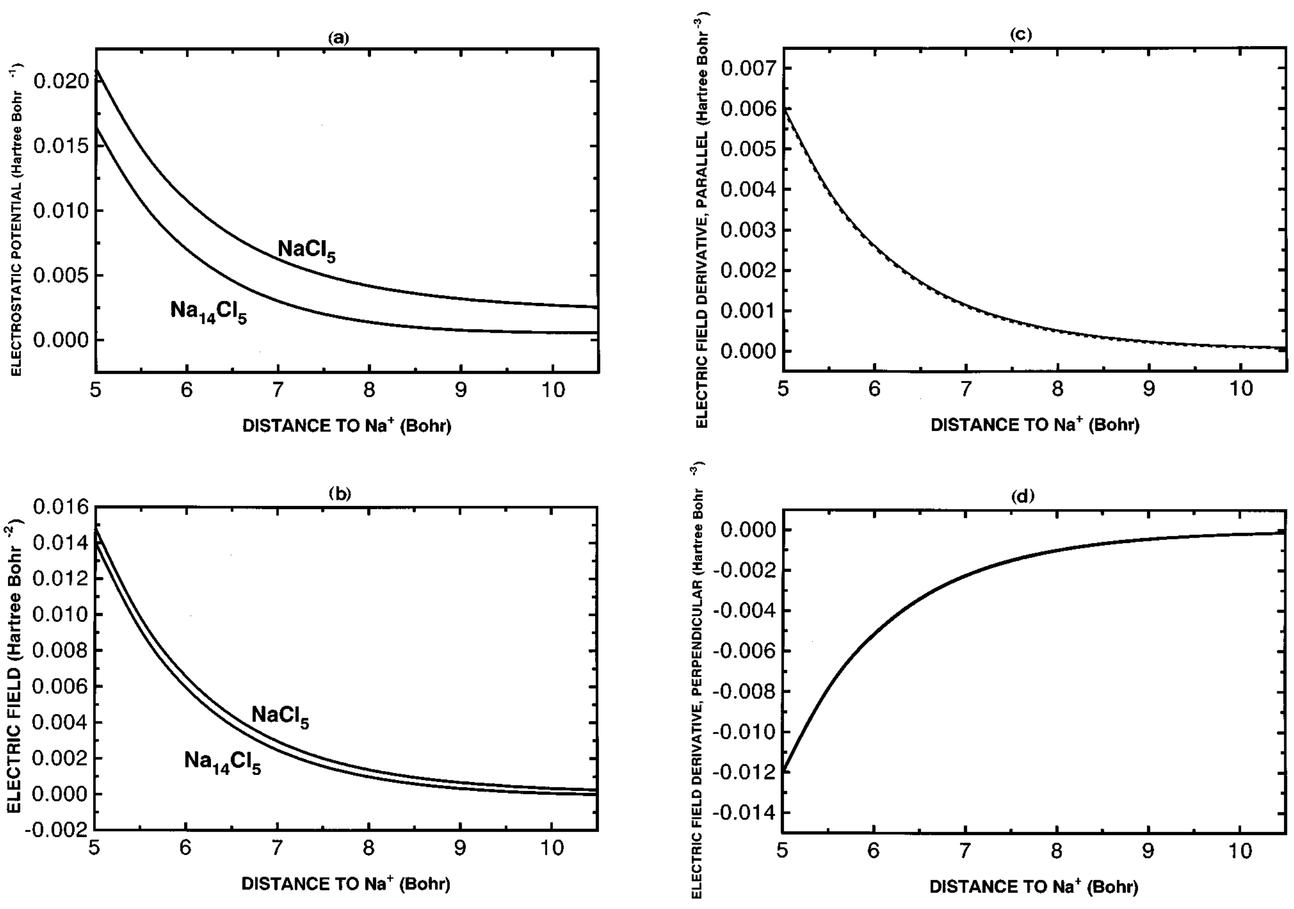

FIG. 4. (a) Electrostatic potential, (b) electric field, and (c), (d) electric field derivatives over Na^+ site for $NaCl_5{}^{4-}$ and $Na_{14}Cl_5{}^{9+}$ surface models. Contributions from embedding (model potentials+point charges array) are included.

occupied ns AO of the metal and the p_z Cl^- AOs, between 3.6 and 5.3 eV depending on the metal and the surface model, is not as large as the p–p gap. This suggests a possible covalent contribution of two orbitals and three electrons. The fact that the gap for gold is smaller than for silver is attributed to the stabilization of the valence orbitals due to the mass-velocity correction.

In regard to the possible charge transfer from the metal atom to the surface, the relevant interaction is the possible mixing between the singly occupied ns metal orbital and the $3s$ orbitals of Na, both with A_1 symmetry. However, the energy difference between those levels is large (larger than 9 eV, see Table IC) and this interaction is not likely to happen.

It is not worth considering other orbital interactions even when there is a small energy difference between orbitals of the surface and the metal atom. For example, the metal d orbitals are close in energy to the surface p orbitals but the resulting bonding and antibonding states are completely full, giving rise to a zero net interaction. However, this last contribution may be important for other metal atoms with d levels not completely occupied.

An interesting point is the difference between energy levels for $NaCl_5{}^{4-}$ and $Na_{14}Cl_5{}^{9+}$ clusters. As can be seen in Fig. 2, the p surface orbitals are almost at the same energy for both models. It has been tested that "unfreezing" more Cl^- ions by including them in the cluster does not modify this result. In fact, it is known that the p states in this kind of system are highly localized.[41] On the contrary, the localized/delocalized nature of the empty surface s band is not so clear[42] and, in fact, the $3s$ sodium level lowers by 1.9 eV when going from $NaCl_5{}^{4-}$ to $Na_{14}Cl_5{}^{9+}$. The inclusion of more cations in the cluster does not decrease the energy of the $3s$ AOs further; thus the enlargement of the cluster does not reduce the $3s_{\mathrm{Na}}$-ns_{M} energy gap. Therefore, clusters larger than $Na_{14}Cl_5{}^{9+}$ will not be considered.

IV. BINDING ENERGIES AND DISTANCES

The first question concerning the adsorption of metal atoms on the NaCl(100) surface is the existence of a preferential adsorption site. In principle, we have considered adsorption on both cationic and anionic sites. As can be seen in Table II, adsorption on the anionic site, $MClNa_5{}^{4+}$ cluster, is rather weak (around 0.05 eV) and the metal–chloride distances are long. Correcting for the BSSE (UHF+BSSE column in Table II) results in the disappearance of bonding. Thus the metal atoms are not bonded over anionic positions. On the contrary, there is adsorption on cationic positions for the three metals considered here and all the models analyzed. However, in all cases, the interaction is weak. The adsorption energies (0.141, 0.121, and 0.252 eV for Cu, Ag, and Au respectively) and distances (3.840, 3.998, and 3.729 Å) follow the trend Au>Cu>Ag. Binding energies and distances are in rather good agreement for $MNaCl_5{}^{4-}$ and $MNa_{14}Cl_5{}^{9+}$ clusters. This means that the larger stabilization of the sodium $3s$ orbitals obtained for the second cluster does not

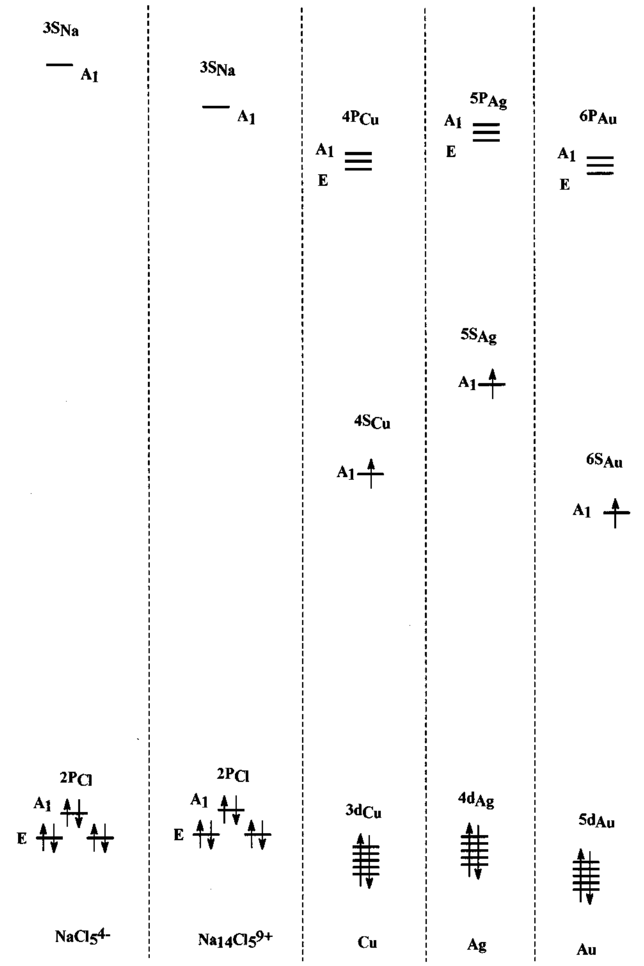

FIG. 5. Energy level and symmetry of orbitals of the metal atoms (Cu, Ag, and Au) and surface models ($NaCl_5^{4-}$ and $Na_{14}Cl_5^{9+}$).

TABLE I. Energy gaps between surface and metal orbitals. (A) *p* orbitals of Cl to empty metal *p* orbitals. (B) *p* orbitals of Cl to metal singly occupied *ns* orbital. (C) Metal singly occupied *ns* orbital to sodium 3*s* orbital. All the quantities are given in eV.

	$NaCl_5^{4-}$	$Na_{14}Cl_5^{9+}$
IA		
Cu	13.1	11.5
Ag	13.3	13.1
Au	13.3	13.2
IB		
Cu	4.9	4.8
Ag	5.3	5.1
Au	3.8	3.6
IC		
Cu	11.5	9.5
Ag	11.1	9.2
Au	12.6	10.7

result in stronger adsorption. As will be shown in the next section, this is due to the fact that charge transfer from the metal to the surface does not occur in an appreciable extent. Thus it is not necessary to go beyond the $MNaCl_5^{4-}$ cluster in order to adequately describe the M/NaCl(100) interaction.

The BSSE has been corrected by using the counterpoise method.[43] This leads to enlargement of metal–cation distances (3.873, 4.332, and 4.067 Å for Cu, Ag, and Au) and still smaller binding energies (0.064, 0.061, and 0.063 eV for Cu, Ag, and Au)

In order to explore contributions of the correlation to the description of adsorption, the MP2 correction to the UHF energy (UMP2 column in Table II) is given for the $MNaCl_5^{4-}$ model. The effect of the correlation before correcting the BSSE is the strengthening of the binding. The M-Na^+ distances are shortened by almost 1 Å for Cu and Ag and around 0.5 Å for gold. The binding energies are larger by 0.2 eV than in the UHF result. The removal of the BSSE (UMP2+BSSE column in Table II) is, again, an important correction. The distances increase by 0.449 Å for Cu, 0.915 Å for Ag, and 0.379 Å for Au, binding energies decrease substantially by 0.089, 0.080, and 0.096 eV for Cu, Ag, and Au, respectively.

We have to remark that the clusters used in this work are highly charged and this means that the embedding field is quite important to the stability of the system and the energy zero of the substrate. To show this effect we have done UHF

TABLE II. Binding energies (eV) and metal-Na^+ distances (Å) for different models and calculations. $MNaCl_5^{4-}$ and $MNa_{14}Cl_5^{9+}$ clusters are used for the adsorption over the Na^+ site. $MClNa_5^{4+}$ cluster models the adsorption on Cl^- site. UHF: unrestriced Hartree–Fock calculation without BSSE correction. UHF +BSSE: UHF calculation plus BSSE correction using the counterpoise method. UMP2: UHF plus second-order perturbational correction for the correlation energy. UMP2+BSSE: UMP2 calculation plus counterpoise correction.

		UHF		UHF+BSSE	UMP2	UMP2+BSSE	UHF	UHF+BSSE
		$MNaCl_5$	$MNa_{14}Cl_5$	$MNaCl_5$	$MNaCl_5$	$MNaCl_5$	$MClNa_5$	$MClNa_5$
Cu	r_0	3.840	3.600	3.873	2.984	3.433	3.476	⋯
	D	0.141	0.168	0.064	0.376	0.089	0.057	0.000
Ag	r_0	3.998	3.725	4.332	3.092	4.007	3.733	⋯
	D	0.121	0.148	0.061	0.348	0.080	0.056	0.000
Au	r_0	3.729	3.361	4.067	3.224	3.603	3.925	⋯
	D	0.252	0.220	0.063	0.376	0.096	0.055	0.000

TABLE III. CSOV decomposition of the adsorption energy of Cu, Ag, and Au over NaCl(100). The metal-Na^{+} distance is fixed at 7.5 Bohr. Cluster $\mathrm{MNaCl}_5{}^{4-}$ is used. The wave function is of the ROHF type. All the energies are given in eV. The different contributions to the adsorption energy are given from steps 1 to 7. The total interaction energy is given in the last row. See text for details on the meaning of the different contributions.

Step	Cu	Ag	Au
1. frozen core	0.063	0.062	0.065
2. pol. M	0.004	0.004	0.004
3. CT $M\rightarrow$Surf.	0.002	0.004	0.003
4. Pol. $\mathrm{NaCl}_5{}^{4-}$	0.003	0.003	0.002
5. CT Surf.$\rightarrow M$	0.048	0.045	0.057
6. Mix. open–closed shells	0.006	0.006	0.004
7. Full SCF	0.000	0.000	0.000
Total binding energy	0.126	0.124	0.135

calculations of the interaction of Cu with each end of the NaCl molecule assuming linear geometries. We find that there is no Cu⋯NaCl attractive interaction. On the contrary, the binding energy for the NaCl⋯Cu configuration is 0.212 eV, the Cl–Cu distance being 2.641 Å. Those results contrast to the preference of adsorption at the Na^{+} site at the surface and show that the embedding effects, and consequently the choice of the cluster must influence largely the adsorption energy. This suggests that the preferential adsorption may be due to the use of different clusters for the cationic or anionic bonding sites. We have investigated this idea by calculating the binding energy of Cu to the anionic position of the $\mathrm{NaCl}_5{}^{4-}$ embedded cluster. An UHF calculation with Cu–Cl distance fixed at 3.5 Å gives a binding energy of 0.029 eV. This value is quite similar to the 0.057 eV obtained with the $\mathrm{ClNa}_5{}^{4+}$ cluster. Moreover, correcting for the BSSE results in zero binding energy. Therefore, the preference for adsorption on cationic position at the surface is a real physical effect and not an artifact of the model.

V. DECOMPOSITION OF THE INTERACTION ENERGY

The different contributions to the interaction energy arising from electrostatic, polarization, and charge transfer effects have been analyzed by means of the CSOV procedure[35–37] for the $\mathrm{MNaCl}_5{}^{4-}$ model. In this case we have adopted a restricted open shell Hartree-Fock description. This calculation gives results completely equivalent to those given by the UHF method for the adsorption. The metal-Na^{+} distance is fixed to 7.5 Bohr for the three metals.

In the CSOV method the SCF calculation is carried out in several steps, each one associated to a given physical effect. The starting point is the construction of an initial wave function by superposition of the two interacting units, the $\mathrm{NaCl}_5{}^{4-}$ embedded cluster plus the free-metal atom. At this stage (step 1 in Table III) the interaction energy contains purely electrostatic and Pauli repulsion contributions. This accounts for 0.06 eV of the adsorption energy. Although this quantity is small it represents 50% of the total binding energy. In step 2 orbitals of the metal atom vary in response to the presence of the surface. This polarization stabilizes the system by reducing the Pauli repulsion between the initially frozen electron densities. In our system, this metal atom polarization represents an unimportant effect, favoring the interaction in ≈0.004 eV. In the third step, the mixing between occupied orbitals in the metal and empty orbitals at the surface is allowed; thus, the possible chemical bonding due to charge donation from the metal to the substrate takes place. The energetic contribution of this effect is quite small, 0.002 eV for Cu, 0.004 eV for Ag, and 0.003 eV for Au. This means that there is no charge transfer to the $3S_{\mathrm{Na}}$ band at the surface. The polarization of the $\mathrm{NaCl}_5{}^{4-}$ cluster in response to the presence of the metal atom is introduced in step 4. This is, again, an extremely small effect, accounting for ≈0.003 eV of the binding energy. In step 5, charge donation from the surface to the metal atom is allowed by the mixing of occupied orbitals in the cluster, mainly $2p_{\mathrm{Cl}}$ orbitals, with the empty orbitals of the metal atom. This contributes in 0.048, 0.045, and 0.057 eV for Cu, Ag, and Au, respectively. However, the large $2p_{\mathrm{Cl}}$–p_{M} energy gap (larger than 10 eV) and the large metal-surface distance suggests that this is not a true physical effect. This contribution is best attributed to the BSSE. In fact, the differences between BSSE corrected and uncorrected binding energies for the NaCl_5^{4-} cluster, given in Table II, are rather similar to step 5 in Table III. The mixture between open- and closed-shell orbitals takes place in step 6. This allows for the interaction between the singly occupied s orbital of the metal and the $2p$ band of the surface. However, the ns_{M}–$3p_{\mathrm{Cl}}$ gap (4–5 eV) and the large distance prevent this interaction from being an important bonding mechanism. At the final step, full SCF, the $\mathrm{MNaCl}_5{}^{4-}$ cluster wave function is allowed to optimize without restrictions. This does not introduce any contribution to the adsorption energy, which means that all the important effects are included up to step 6.

As an example of adsorption on the anionic position, we have decomposed the binding energy of the Cu–$\mathrm{ClNa}_5{}^{4+}$ model. In order to compare with the results shown above, the Cu–Cl distance has been fixed to 7.5 Bohr and the ROHF wave function has been calculated. The main contribution given by the CSOV decomposition is the charge transfer from the surface to metal, 0.038 eV, which is 74% of the total binding energy, 0.051 eV. For the same reasons then for M–$\mathrm{NaCl}_5{}^{4-}$, we attribute this charge transfer energy to the BSSE. The other steps are quite small contributions to the total energy: 0.002-eV frozen core, 0.003-eV Cu polarization, 0.002-eV charge transfer from Cu to the surface, 0.001-eV polarization of $\mathrm{ClNa}_5{}^{4+}$, and 0.005-eV mixture between open- and closed-shell orbitals.

The analysis above clearly indicates that there are no significant chemical contributions to the Cu,Ag,Au/NaCl(100) interaction. 50% of the binding energy is explained by physical interactions, in which no charge transfer between atom and surface happens.

VI. SUMMARY AND CONCLUSIONS

This work deals with the theoretical approach to the interaction of noble metal atoms (Cu, Ag, and Au) with the ideal NaCl(100) surface by means of an *ab initio* embedded cluster method. Compact model potentials and point charges array are used for the embedding. The former accounts for shape and finite size of the environment ions as well as quantum effects (exchange and orthogonality). The latter introduces the Madelung potential at the surface. Two different cluster models have been used. In the simplest one, the ion over which the adsorption occurs and its five nearest neighbors are included. A larger cluster, including up to 14 cations surrounding the adsorption site is also used. Both clusters give identical results for the adsorption because of their similar electrostatic and covalent properties. The only difference between them is the relative stabilization of the $3s$ orbital of Na in the larger cluster.

We have found that adsorption takes place preferentially on Na^+ sites. No stabilization was found for the metal on anionic positions.

At the cationic sites the adsorption is weak, with binding energies in the order of 0.1 eV and metal–surface distances larger that 3 Å in all cases. The main contributions to the bonding are of electrostatic and dispersive characters. No appreciable chemical contribution to the adsorption was found. This can be attributed to several factors. First, the energy gap between surface and metal empty and full orbitals is large. The smallest gap, larger than 3 eV, occurs for the ns singly occupied metal orbital and the p orbitals of Cl. For the rest of the orbital interactions the gaps are of the order of 10 eV. Second, the Pauli repulsion between closed shells of metal atom and surface ions does not allow for the approach of the atom to the surface, resulting in small orbital overlapping.

Adsorption of other metal atoms, with valence d orbitals not completely full, would likely lead to stronger adsorption because of the reduction of the Pauli repulsion and, moreover, the possibility of bonding contributions by mixing between surface p band and metal d orbitals. In our case, the $nd^{10}\ ns^1$ configuration of the metal does not allow for this bonding mechanism. This conclusion agrees with studies about the growth of ultrathin metal films on ionic surfaces.[43] In these studies it was found that metals such as Cr $(3d^5 4s^1)$ and Fe $(3d^6 4s^2)$ interact strongly with the $TiO_2(110)$ surface at the initial stages of deposition, following a layer growth model. In contrast, chemical interaction between Cu and the ionic surface has not been found and the metal grows in the Volmer-Weber (3-D island) model. Moreover, the ability of the metal film to wet an oxide substrate correlates directly with the reactivity of the metal towards oxygen. In our scheme, the interaction of the surface band of chloride p character with the valence d shell of the metal determines the strength of the adsorption. This agrees with the experimental observation on the metal–oxygen bond, which plays the role of the metal–Cl bond in our system. It is likely that a net bonding interaction between p band and d atomic orbitals leads, concomitantly, to a more active participation of the metal s valence orbital in the interaction because of a shorter metal–surface distance.

Besides the nature of the metal, the considerations above bring up questions concerning the nature of the surface. When going from NaCl(100) to metal oxide surfaces, such as MgO(100), the p surface orbitals rise in energy (increase of 2.8 eV according to preliminary calculations). This may favor the interaction with singly occupied orbitals of the metal or, contrarily, Pauli repulsion may hold the metal–surface distance large enough so as to avoid orbital overlapping. Another interesting point is the role of surface defects, such as steps and kinks. For example Pacchioni *et al.* found that the adsorption of CO over MgO is stronger at the corner (0.5–0.83 eV) and edge (0.33–0.49 eV) than at the surface (0.23–0.32 eV) sites. Moreover, the CSOV decomposition shows that this effect is due to electrostatic interactions and Pauli repulsion.[45]

Another conclusion is that the three atoms, Cu, Ag, and Au, adsorb in a rather similar way. The similarity is even greater between Cu and Au. This is due to the relativistic (mass-velocity) effects for gold, which result in shorter metal-Na^+ distance for gold than for silver.

From the values of adsorption energies reported here and the values of the energy of metal-metal bond found in the literature (approximately 2 eV for Cu_2, 1.6 eV for Ag_2, 2.3 eV for Au_2, 3.3 eV for Cu_3, 2.2 eV for Ag_3, and 3.5 eV for Au_3)[46] one can conclude that the growth mode of Cu, Ag, or Au on NaCl(100) surface at the initial stages must follow the Volmer-Weber model; although, of course, the adsorption at defective sites, probably stronger, must be considered.

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[1] M. Rühle, A. G. Evans, M. F. Ashby, and J. P. Hirt, *Metal Ceramic Interfaces*, Acta Scr. Met. Proc. Series 4 (Pergamon, New York, 1990).

[2] L. C. Dufour and M. Perderau, in *Surfaces and Interfaces of Ceramic Materials*, Vol. 173 of *NATO Advanced Studies Institute, Series E: Applied Sciences*, edited by L. C. Dufour, C. Monty, and G. Petot-Ervans (NATO, Meudon, France 1990), p. 419.

[3] J. W. He and P. J. Møller, Surf. Sci. **180**, 411 (1987).

[4] T. Conard, J. M. Vohs, P. A. Thiry, and R. Caudano, Surf. Interface Anal. **16**, 446 (1990).

[5] U. Diebolt, J. M. Pan, and T. E. Madey, Phys. Rev. B **47**, 3868 (1993).

[6] P. J. Møller and M. C. Wu, Surf. Sci. **224**, 265 (1989).

[7] M. C. Wu and P. J. Møller, Surf. Sci. **224**, 250 (1989).

[8] U. Diebolt, J. M. Pan, and T. E. Madey, Surf. Sci. **287**, 896 (1993).

[9] J. Deng, D. Wang, X. Wei, R. Zhai, and H. Wang, Surf. Sci. **249**, 213 (1991).

[10] K. Tamura, M. Kudo, M. Owari, and Y. Nihei, Chem. Lett. **1986**, 1921.

[11] D. N. Belton, Y. M. Sun, and J. M. White, J. Phys. Chem. **88**, 1690 (1984); **88**, 5172 (1984).

[12] C. Goyennex, and C. R. Henry, J. Electron Spectrosc. Relat. Phenom. **61**, 65 (1992).

[13] K. H. Jhonson and S. V. Pepper, J. Appl. Phys. **53**, 6634 (1982).

[14] A. B. Anderson, C. Ravimohan, and S. P. Mehandru, Surf. Sci. **183**, 438 (1987).

[15] K. H. Jhonson, A. C. Balazs, and H. J. Kolari, Surf. Sci. **72**, 733 (1978).

[16] J. A. Horsley, J. Am. Ceram. Soc. **101**, 2870 (1979).

[17] T. Yanagihara and H. Yamaguchi, Jpn. J. Appl. Phys. **23**, 529 (1984).

[18] E. M. Chan, M. J. Buckingham, and J. L. Robins, Surf. Sci. **67**, 285 (1977).

[19] G. Bambakidis, Thin Solid Films **55**, 55 (1978).

[20] G. Zinsmeister, Thin Solid Films **2**, 497 (1968).

[21] T. Johanesson and B. Persson, Phys. Scr. **2**, 309 (1970).

[22] V. N. E. Robinson and J. L. Robins, Thin Solid Films **20**, 155 (1974).

[23] M. J. Stowell, Thin Solid Films **21**, 91 (1974).

[24] C. J. Rossouw, I. A. Kotze, and C. A. O. Henning, Thin Solid Films **29**, 71 (1975).

[25] J. A. Venables, Thin Solid Films **32**, 135 (1976).

[26] A. Puskeppel and M. Harsdorff, Thin Solid Films **35**, 99 (1976).

[27] A. Howie and L. D. Marks, Philos. Mag. **49**, 95 (1984).

[28] K. Fuwa, K. Fujima, H. Adachi, and T. Osaka, Surf. Sci. **148**, L659 (1984).

[29] J. A. Mejías, Ph.D. thesis, Universidad de Sevilla, 1994.

[30] J. A. Mejías and J. F. Sanz, J. Chem. Phys. **102**, 327 (1995).

[31] J. A. Mejías, J. Oviedo, and J. F. Sanz, Chem. Phys. **191**, 133 (1995).

[32] *Adsorption on Ordered Surfaces of Ionic Solids and Thin Films*, edited by H. J. Freund and E. Umbach (Springer-Verlag, Berlin, 1993).

[33] K. Balasubramanian, J. Phys. Chem. **93**, 6585 (1989).

[34] W. J. Stevens, M. Krauss, H. Basch, and P. G. Jasien, Can. J. Chem. **70**, 612 (1992).

[35] P. S. Bagus, K. Hermann, and C. W. Bauschlicher, Jr., J. Chem. Phys. **80**, 4378 (1984).

[36] P. S. Bagus, K. Hermann, and C. W. Bauschlicher, Jr., J. Chem. Phys. **81**, 1966 (1984).

[37] P. S. Bagus and F. Illas, J. Chem. Phys. **96**, 8962 (1992).

[38] J. A. Mejías, A. Marquez, J. Fernández-Sanz, M. Fernández-García, J. M. Ricart, C. Sousa, and F. Illas, Surf. Sci. **327**, 59 (1995).

[39] *Gaussian Basis Sets for Molecular Calculations*, edited by S. Huzinaga, Physical Science Data 16 (Elsevier, Amsterdam, 1984).

[40] M. W. Schmidt, K. K. Baltridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jeusen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).

[41] P. S. Bagus, F. Illas, and C. Sousa, J. Chem. Phys. **100**, 2943 (1994).

[42] There is evidence of the delocalized nature of the $3S$ band in the bulk MgO. See Ref. 41.

[43] S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).

[44] See paper by Th. E. Madey, U. Diebold, and J.-M. Pan, in *Adsorption on Ordered Surfaces of Ionic Solids and Thin Films* (Ref. 32), p. 147 and references therein.

[45] See the paper by G. Pacchioni and P. S. Bagus in *Adsorption on Ordered Surfaces of Ionic Solids and Thin Films* (Ref. 32), p. 181.

[46] From the atomization energies compiled in Ref. 33. The exact values depend on the method of calculation, for example, a MRSDCI calculation gives 3.3 eV for Au_3 and the experimental value is 3.8 eV. An average value of 3.5 eV is given here. Those values are reported to show that the metal–metal bonding is ten times stronger than the metal–surface interaction energy.