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# Density functional study of atomic nitrogen and oxygen chemisorption on model clusters simulating the Cu and Ag (100) surfaces

J. Torras<sup>a,\*</sup>, M. Toscano<sup>b</sup>, J.M. Ricart<sup>a</sup>, N. Russo<sup>b</sup>

<sup>a</sup> *Departament de Química, Facultat de Química, Universitat Rovira i Virgili, Pça. Imperial Tàrraco 1, 43005 Tarragona, Spain*

<sup>b</sup> *Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata di Rende (CS), Italy*

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## Abstract

Density functional calculations which explicitly use the density gradient type nonlocal corrections to exchange and correlation are reported for the adsorption of atomic nitrogen and oxygen on the four-fold sites of (100) copper and silver surfaces simulated by Cu<sub>5</sub> and Ag<sub>5</sub> clusters. Binding energies, equilibrium distances and harmonic vibrational frequencies are in good agreement with the available experimental and high level theoretical data. An ionic contribution is found in the bonds between N and O and Cu and Ag clusters. Metal d orbitals are involved in the covalent part of the bond.

## 1. Introduction

Adsorption of atomic oxygen and nitrogen on copper surfaces has been the subject of several experimental [1–21] and theoretical [22–28] studies in view of its importance in heterogeneous catalysis and corrosion. From the experimental investigation it is well established that both N and O atoms chemisorb preferentially on the fourfold hollow site of the Cu(100) surface. The experimental equilibrium distances ( $R_e$ ) and vibrational frequencies are known for O and N on Cu(100) surface [3,7,8,20] while for O on Ag(100) there are only data for the vibrational frequency [12]. The binding energy (BE) for O on Cu(100) has been estimated from calori-

metric experiments [22]. To our knowledge, no experimental information is available for the adsorption of N on the Ag(100) surface. From a theoretical point of view, the nature of the interaction of O on the hollow chemisorption site of Cu(100) and Ag(100) surfaces has been investigated using the Hartree–Fock (HF) method by using the Cu<sub>5</sub> cluster in which four copper atoms simulate the first layer and one the second layer [24,25]. Clusters of increasing size have been used to test the influence of the cluster size on the physics of the chemisorption process [23,28]. Recently, HF and correlated Moller Plesset (MP2) methods have been employed for the investigation of N–Cu<sub>5</sub> and N–Ag<sub>5</sub> interactions [30].

The cluster model approach to surface chemistry provides a valuable and simple way to

\* Corresponding author.

study surface processes and the chemisorption bond. The usefulness of this approach relies on the fact that many properties of the adsorbate–surface system are rather local in nature and not very dependent on the cluster size. It has been shown that while structural parameters as equilibrium distances or vibrational frequencies or even the nature of the chemisorption bond are well described at the Hartree–Fock level of theory, important quantities as the binding energy are rather poor [29]. Then, it is necessary to include electronic correlation effects if quantitative results are desired. When using standard correlated calculations one of the important drawbacks is the huge amount of computer time necessary to deal with large clusters. Consequently, a different strategy which is being more and more employed is that of the density functional approach which, in principle, is able to account for the correlation energy at a cost which is comparable to that of Hartree–Fock calculation or just slightly above it. Therefore, it will be interesting to comparatively study some well defined cases at both levels of theory. In this work we have chosen to carry out such a study for the interaction of atomic nitrogen and oxygen on  $\text{Cu}_5$  and  $\text{Ag}_5$  clusters by means of Gaussian density functional theory. This theory has been previously employed for the study of many chemisorption phenomena proving that modern density functional theoretical approaches are powerful tools for a detailed and reliable treatment of ligand interactions with metallic surfaces [31–34].

## 2. Method

The linear combination of the Gaussian-type function local (nonlocal) spin density method [35] implemented in the deMon program [36] has been used for all the computations. The  $\text{Cu}_5$  and  $\text{Ag}_5$  cluster models are fixed in their bulk geometry and the position of adsorbed atoms has been optimised by using the BFPS algorithm [37]. The VWN local potential [38] has

been employed in conjunction with the gradient corrected Perdew and Wang [39] and Perdew [40] functionals. So, the total energy ( $E^{\text{NLSD}}$ ), taking into account the nonlocal corrections, is given as

$$E^{\text{NLSD}} = E^{\text{LSD}} + E_x^{\text{G}} + E_c^{\text{G}}$$

The first term is the energy obtained at local level while the other two represent the exchange and correlation nonlocal contributions. For copper and silver we have used a relativistic (mass–velocity and Darwin terms) extended ( $\text{Cu}^{+17}$  and  $\text{Ag}^{+17}$ ) model core potential which allows the explicit treatment of  $3p^6 3d^{10} 4s^1$  and  $4p^6 4d^{10} 4s^1$  valence electrons for Cu and Ag, respectively [41]. The (311/31/311) for Cu and (2211/2111/121) for Ag valence electron basis set have been employed with the corresponding (5, 5; 5, 5) and (3, 7; 3, 7) auxiliary basis set for copper and silver, respectively [42]. For nitrogen and oxygen the orbital basis (7111/411/1\*) [43] and the auxiliary sets (4, 4; 4, 4) [42] have been used.

Several calculations at the Hartree–Fock and MP2, or more properly open shell based MP2, levels have been carried out for O on  $\text{Ag}_5$ . We have used the nonempirical pseudopotentials of Durand and Barthelat [44,45] to represent the inner cores of Ag and O atoms dealing explicitly with the  $4d^{10} 5s^1$  and  $2s^2 2p^4$  valence electrons which were in turn described by using a [4s3p5d/2s1p2d] and [4s4p1d/2s2p1d] contracted GTO basis set, respectively. As in the DFT calculations, the cluster geometry has been fixed at the corresponding bulk values and the distance of the adsorbate to the surface has been optimised for each cluster. The vibrational frequencies have been calculated using the numerical second derivatives procedure assuming an infinite mass for the substrate.

The electronic structure of the  $\text{Cu}_5$  and  $\text{Ag}_5$  cluster models has been discussed in detail in the literature [25–30]. There are two low lying states which are a  $^4\text{A}_2$  arising from an  $e^2 a_1^1$  open-shell occupation and a  $^2\text{E}$  from an  $e^3$  electronic configuration. While the  $^4\text{A}_2$  is the

Hartree–Fock ground state the  ${}^2E$  state appears at lower energies if electronic correlation is explicitly considered, although the energy difference between them is rather small [25]. At the NLS D level of calculation the  ${}^2E$  is again the ground state. This state is lower by 9.2 kcal/mol ( $\text{Cu}_5$ ) and 11.5 kcal/mol ( $\text{Ag}_5$ ) with respect to  ${}^4A_2$ . Upon interaction with O (N), several electronic states are possible,  ${}^2E$  ( ${}^1A_1$ ) being the most stable ones, arising from  $a_1^1e^1$  ( $a_1^2$ ) electronic configurations.

### 3. Result and discussion

The NLS D equilibrium distances of oxygen and nitrogen on the copper and silver surface plane ( $R_d$ ), vibrational frequencies for the motion of the adsorbates perpendicularly to the surface ( $\nu_e$ ) and chemisorption energies BE are reported in Table 1 together with the available previous theoretical and experimental values. For oxygen adsorption on the  $\text{Cu}_5$  cluster, we found a  $R_e$  of 1.03 Å. The corresponding HF and MP2 distances are 0.90 and 0.92 Å, respectively [25], while SEXAFS measurement gives the oxygen atom located at 0.83 Å above the copper surface [20]. The NLS D data appears therefore slightly overestimated. For the corre-

sponding  $\nu_e$  we note that our DFT value (308  $\text{cm}^{-1}$ ) is very close to the corresponding MP2 one (323  $\text{cm}^{-1}$ ) [25]. For the binding energy, comparisons are possible with both previous theoretical [23,25,26,28] and experimental data [22]. As expected, the HF result is strongly underestimated, the interaction energy with respect to the neutral fragments for O and N on Ag are positive, meaning that the minimum is above the dissociation limit. This is not too surprising as it is well known that HF underestimates binding energies; this is specially true for adsorbates on metal surfaces [26–28]. The inclusion of correlation effects, even at the single reference MP2 level gives a value that is about 40 kcal/mol less than the lowest experimental reported value. The present NLS D value of 101 kcal/mol is closer to the experimental estimate.

In the case of the adsorption of O on silver we found an equilibrium distance that is 0.87 Å while the corresponding MP2 is 0.98 Å. The NLS D  $\nu_e$  is 225  $\text{cm}^{-1}$  while HF gives 304  $\text{cm}^{-1}$ . As in the case of the O– $\text{Cu}_5$  system, the HF frequency is overestimated. It should be stressed that the comparisons with experimental data are difficult because the results are very dependent on the coverage and surface reconstructions. For the BE the present NLS D calculations predicts a value of 80.7 kcal/mol. The

Table 1

NLS D values for the perpendicular equilibrium distance to the surface ( $R_e/\text{Å}$ ) and the distance from the adsorbate to its next neighbour surface metal atoms ( $R_{X-M}/\text{Å}$ ), binding energies (BE/kcal/mol) and equilibrium vibrational frequencies ( $\nu_e/\text{cm}^{-1}$ ) for oxygen and nitrogen adsorbed on  $\text{Cu}_5$  and  $\text{Ag}_5$  clusters

Method	O– $\text{Cu}_5$				O– $\text{Ag}_5$			
	BE	$R_e$	$R_{X-M}$	$\nu_e$	BE	$R_e$	$R_{X-M}$	$\nu_e$
HF	27.0 <sup>a</sup>	0.90 <sup>a</sup>	2.02 <sup>a</sup>	359 <sup>a</sup>	–7.8	0.96	2.25	298
MP2	76.2 <sup>a</sup>	0.92 <sup>a</sup>	2.03 <sup>a</sup>	323 <sup>a</sup>	40.4	0.98	2.26	275
DFT	101.0	1.03	2.08	308	80.7	0.87	2.21	225
Exp.	115–135 <sup>b</sup>	0.8 <sup>c</sup>	1.88 <sup>c</sup>	294 <sup>d</sup> –339 <sup>e</sup>	—	—	—	240 <sup>f</sup> –314 <sup>f</sup>
Method	N– $\text{Cu}_5$				N– $\text{Ag}_5$			
	BE	$R_e$	$R_{X-M}$	$\nu_e$	BE	$R_e$	$R_{X-M}$	$\nu_e$
HF <sup>g</sup>	–6.7	0.49	1.87	195	–63.2	0.96	2.25	270
MP2 <sup>g</sup>	95.0	0.32	1.83	244	46.6	0.96	2.25	171
DFT	93.0	0.48	1.87	308	64.9	0.60	2.12	258
Exp. <sup>h</sup>	—	0.4–0.6	—	320	—	—	—	—

<sup>a</sup> [25]; <sup>b</sup> [22]; <sup>c</sup> [3]; <sup>d</sup> [11]; <sup>e</sup> [8]; <sup>f</sup> [12]; <sup>g</sup> [30]; <sup>h</sup> [20].

Table 2

NLSD (HF) net charges from Mulliken population analysis for the adsorbate ( $q_x$ ) and the metal atoms ( $q_M$ ) of the surface layer

System	$q_x$	$q_M$ (1st layer)
O–Cu <sub>5</sub>	–0.61 (–0.98) <sup>a</sup>	0.15 (0.25)
O–Ag <sub>5</sub>	–0.80 (–1.02) <sup>a</sup>	0.33 (0.28)
N–Cu <sub>5</sub>	–1.07 (–1.03)	0.22 (0.24)
N–Ag <sub>5</sub>	–0.96 (–0.97)	0.29 (0.28)

<sup>a</sup> [29].

binding energy calculated at HF level suggests an unbonded situation (negative value of BE). A comparative analysis between the spectroscopic parameters for oxygen chemisorption on copper and silver reveals that the binding energy and consequently the vibrational frequency, decrease in going from copper to silver. This is in agreement with the periodic properties. In both cases, a charge transfer occurs from the metal to the adsorbate. The negative net charge values of oxygen atom adsorbed on Cu (–0.61) and on Ag (–0.80) together with the positive values of the first layer metallic centers (0.15 and 0.33 for Cu and Ag, respectively) confirm the existence of the charge transfer. Moreover, the charge transfer from the metal to the adsorbate is more pronounced for the O–Ag<sub>5</sub> system. Similar behaviour is obtained at HF level (see Table 2), but in this case the value of the oxygen net charge is larger. The presence of a significant net charge on the oxygen atom denotes a partial ionic character in the chemical bond formation. Mayer analysis evidences a bond order of 0.42 for each of the four O–first layer Cu interactions while the corresponding bond order between O and the second layer Cu atom is of only 0.05. In the case of the O adsorption on silver the bond order is 0.37 for the four O–first layer Ag atoms interactions. Also in this case the bond of the oxygen atom with the second layer silver is negligible. However, it should be stressed that Mulliken population analyses are often unreliable. In fact, previous results for O on Cu and Ag [26–28] and N on Cu and Ag [30] based on orbital projections and dipole moment curves show that the charge transfer is larger than the

one provided by the Mulliken method. The analysis of the composition of the chemical bond, shows that the d orbitals of copper and silver participate significantly to the bond formation. Similar results have been obtained through the constrained space orbital variation method in the framework of the HF theory [26–28].

The NLSD results for the interaction of nitrogen with Cu<sub>5</sub> cluster show that also in this case our spectroscopic constants are similar to those obtained from MP2 computations and from experimental measurements. In particular we mention that our BE is 93 kcal/mol, while the MP2 counterpart is 95 kcal/mol [13]. Good agreement with the experiment is found between the calculated NLSD vibrational frequency (308 cm<sup>–1</sup>) and the values reported by means high resolution electron energy loss spectroscopy (HREELS) of 320 cm<sup>–1</sup> [8] or by SEXAFS measurements analysed using the Einstein model in the quasiharmonic approximation (278 cm<sup>–1</sup>) [20]. With respect to the equilibrium distances it should be noted that while there is a slight dispersion for the perpendicular distance to the surface, the distances to the first layer Cu atoms are always very close. The present results are furthermore in agreement with the very recent results reported by Triguero et al. [46] for O and N on a Cu<sub>5</sub> cluster model using the modified coupled pair functional (MCPF) and density functional (DFT) methods and an extended all-electron basis set for Cu. They report an equilibrium distance of 0.98 Å for O and 0.36 Å for N and a binding energy of about 100 kcal/mol for both O and N atoms on Cu<sub>5</sub>. Because of the lack of previous experimental data, comparisons are not possible for the adsorption of nitrogen on Ag(100) surface. However there is the same tendency as in the case of oxygen, in going from copper to silver surface: the binding energy decreases and the equilibrium distance increases. We hope that our predictions on this interaction can stimulate future experimental and theoretical studies. From Table 2 it is seen that a significant charge transfer (higher than in the

case of oxygen adsorption) occurs from the first layer surface atoms to the adsorbed nitrogen. HF computations give almost the same values. The Mayer bond order for each of the four N–Cu and N–Ag interactions is 0.64 and 0.63, respectively. The interaction of nitrogen with the second layer Cu or Ag atom is negligible. The presence of a relevant contribution of the Cu and Ag d orbitals in the bond formation is confirmed also in these cases. Mulliken and Mayer analyses underline again the mixed ionic and covalent nature of the bond between nitrogen and copper and silver atoms.

#### 4. Conclusions

The results of the NLSD study on the interaction of oxygen and nitrogen on Cu<sub>5</sub> and Ag<sub>5</sub> clusters simulating the four-fold open site of Cu(100) and Ag(100) surfaces could be summarised as follows:

- the method employed coupled with extended Cu<sup>+17</sup> and Ag<sup>+17</sup> model core potentials is able to reproduce correctly the spectroscopic constants. Some minor deviation from other calculated and experimental parameters can be due to the minimal size of the used clusters.
- the bond between nitrogen and oxygen and both Cu<sub>5</sub> and Ag<sub>5</sub> clusters show significant ionic character.
- the participation of the metal d orbitals to the covalent part of the bond is not negligible.
- the second layer metal atom is important for a more realistic simulation of the surface, but does not participate to the chemical bond with the adsorbate.

The predicted spectroscopic and electronic properties for O–Ag(100) and N–Ag(100) systems can be considered realistic also in view of the general good agreement found between calculated and experimental properties in other well known adatom–surface interactions.

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