



# Chemisorption of NCO on Cu(100): A density functional theory study

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Received 18 April 2005; accepted for publication 28 September 2005

Available online 21 October 2005

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## Abstract

The isocyanate group adsorption on sites of different coordination of Cu(100) was theoretically studied considering the cluster approach. The site of four-fold symmetry is the most favored. When NCO adsorbs on Cu, it charges negatively. This electron transfer from the substrate is greater for the site of lowest coordination. The projected DOS curves for the most important valence molecular orbitals of isocyanate group indicate a strong mixing between its  $2\pi$  orbital and  $3d_{xz}$  and  $3d_{yz}$  AOs of Cu. The predicted asymmetric mode at  $2187\text{ cm}^{-1}$  for NCO adsorbed on the hollow site agrees very well with the experimental observed values of  $2162\text{--}65\text{ cm}^{-1}$ .

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*Keywords:* DFT; NCO adsorption; Cluster model; Cu(100)

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## 1. Introduction

Catalytic converter is a component of the vehicle exhaust system used to transform gases like NO, CO and hydrocarbons to  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The oxygen atoms necessary for the CO oxidation to  $\text{CO}_2$  come from  $\text{O}_2$  cleavage or from NO reduction. For this reason, the  $\text{NO} + \text{CO}$  reaction has been extensively studied in the past [1–8].

Infrared spectroscopy measurements revealed that during the reaction between NO and CO on supported metal catalysts the isocyanate (NCO) species is formed. Moreover, NCO can be the source for the formation of HCN and  $\text{C}_2\text{N}_2$ , dangerous gases which can also act as catalyst poisons [9]. In these catalysts, NCO is formed on the metal and then migrates onto the support where it can accumulate in great amount yielding an intense infrared absorption band due to the asymmetric stretching mode [1,2,10]. Although the NCO was considered in general as a spectator species, very recently some experimental studies suggest that it

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could act as an intermediate in the production of  $\text{N}_2\text{O}$  or  $\text{N}_2$  [6,7,11].

It was established that the NCO on Cu is more stable than on Pt, Rh and Ru in metal supported catalysts. On the latter systems, no NCO was detected above 300 K due to its decomposition or migration to the support. Conversely, it disappears completely above 473 K on supported Cu catalysts [10].

Researchers have studied the adsorption of NCO over well-defined metal faces in order to understand the behavior of this species over different metals. As it is not possible to produce NCO over pure metals via  $\text{NO} + \text{CO}$  reaction at low pressures, it was tried to circumvent this problem by adsorbing isocyanic acid (HNCO). For instance, Gorte and Schmidt studied the adsorption of HNCO on clean Pt(111) [12]. They found that it is molecularly adsorbed at very low temperatures and it decomposes at 250 K to form CO and atomic N without forming a stable isocyanate species. Similar results were obtained by Solymosi and Kiss on Pt(110) [13]. HNCO adsorbs molecularly on Rh(111) at 95 K and begins to dissociate already at 150 K [14]. Preadsorbed oxygen on Rh(111) enhances the NCO stability region at least by 60 K [15]. The NCO formation was observed on Ru(001) by the reaction of CO with coadsorbed nitrogen atoms [16]. The dissociation of NCO starts at around 290 K on this surface. On the other hand, HNCO interacts in a very different way on the (111) and (100) faces of Cu. Solymosi and Kiss found that HNCO does not adsorb at 300 K on Cu(111) but readily reacts with preadsorbed oxygen to give surface NCO [17]. The authors proposed a mechanism in which the H atom of the isocyanic acid interacts with an adsorbed O atom, yielding a hydroxyl and an isocyanate species on adjacent adsorption sites. The formed NCO was stable up to 400 K. More recently, Celio et al. investigated NCO adsorption on Cu(100) from thermal decomposition of HNCO at 300 K and from the reaction of cyanogens ( $\text{C}_2\text{N}_2$ ) with preadsorbed oxygen [18]. The NCO obtained from both methods was stable on this surface up to 500 K.

Very recently, the interaction of NCO on a  $\text{Cu}_{14}$  cluster was studied from a theoretical point of view

using DFT and a Gaussian basis set [19]. The calculations indicate that among different configurations analyzed the adsorption via the N atom is the most favored and that the bonding with the surface is mainly ionic.

The cluster model is an important theoretical tool for studying chemisorption and reactions on metal surfaces, particularly to attain a reliable modeling of these surface processes at very low coverages. It was established that whereas some aspects of the adsorbate–substrate interaction, such as the adsorbate geometry and frequencies, are rather cluster size independent, other aspects, such as the adsorption energy are clearly size dependent [20]. However, some authors realized that there are clusters which present certain requirements at the outermost electronic states, in terms of energy and symmetry, and give appropriate adsorption energies [21,22]. In the study of the interaction between an adsorbate molecule and a cluster representing a surface, a general criterion is to achieve a stabilization of the adsorption energy by increasing the size of the cluster. Furthermore, in large clusters it would be expected a higher probability for mono-electronic levels to present adequate symmetry and energy to form a bond with the adsorbate [23].

Then, as the NCO on Cu surfaces is more stable than on those of Pt, Rh and Ru, metals usually used on supported catalysts, we consider of great interest to study the interaction of NCO on Cu(100) from a theoretical point of view.

## 2. Computational method and cluster model

Our calculations were performed within the density functional theory (DFT) approach, by using the ADF (Amsterdam Density Functional) package [24]. Geometry optimizations and frequency calculations were run using the local density approximation (LDA) with the Vosko–Wilk–Nusair functional. Generalized gradient (GGA) corrections are applied self-consistently through the Becke–Perdew (B88-P86) formulas [25,26].

A triple- $\zeta$  plus polarization Slater-type basis set was used for all the atoms. The inner cores of copper (1s2s2p3s3p), as well as oxygen, nitrogen and

carbon (1s), were treated by the frozen-core approximation.

Because of the fact that the models for the Cu surface attempt to simulate an extended nonmagnetic metal, we proceeded to use the minimal multiplicity for the different clusters. Taking into account that the isolated NCO species has 15 valence electrons (with the electronic configuration:  $4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4 7\sigma^2 2\pi^3$ ) and that each Cu atom adds 11 valence electrons, the NCO/Cu(100) system will present an open or closed shell electronic configuration depending on the number of copper atoms in the cluster. Then, if the substrate has an even number of atoms, the system will have multiplicity two, but if the number is odd, it will have multiplicity one. For the sake of comparison, the calculations of the geometrical optimization and energies were also made considering the multiplicity of the ground state. Thus, the calculations were carried out using two different criteria, choosing (i) minimal multiplicities (MM) and (ii) ground states (GS) of the clusters. The GS for different systems were obtained exploring four spin states.

Experimental and theoretical works have established that NCO adsorbs linearly and perpendicular to the surface bonded via the N atom [16,19,27]. Thus, in the calculations the NCO was constrained to lie in this geometry. The N-surface, N–C and C–O distances were optimized to get the minimal total energy. Taking into account the well-known influence of cluster size on molecular adsorption properties, two series of metallic clusters with an increasing number of atoms were considered. The first series (for top and hollow adsorption sites) has the  $C_{4v}$  symmetry and the second one (for bridge site) has the  $C_{2v}$  symmetry. The corresponding clusters are named writing in parenthesis the amount of atoms in the first and in the second layers. Then, in the first series, for on-top sites, we have: Cu<sub>13</sub>(9,4), Cu<sub>21</sub>(9,12), Cu<sub>25</sub>(13,12), Cu<sub>33</sub>(21,12) Cu<sub>37</sub>(21,16), Cu<sub>45</sub>(21,24). For hollow sites we have the same clusters, but inverting the order of the layers. Finally in the second series, for bridge adsorption, the clusters are: Cu<sub>12</sub>(6,6), Cu<sub>18</sub>(12,6), Cu<sub>24</sub>(16,8), Cu<sub>32</sub>(20,12), Cu<sub>36</sub>(20,16), Cu<sub>46</sub>(26,20). In Fig. 1, Cu<sub>37</sub>(21,16), Cu<sub>36</sub>(20,16) and Cu<sub>37</sub>(16,21) are displayed. Moreover, in order to test that the calculations performed on two layer

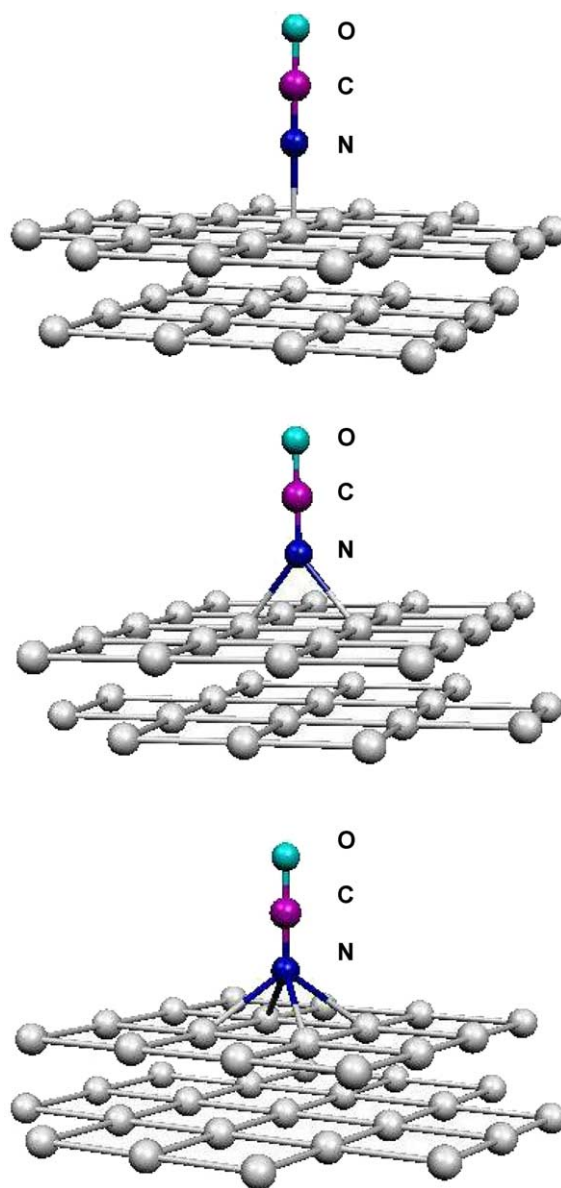


Fig. 1. Schematic view of NCO adsorption on Cu(100). For on-top geometry a cluster with 37 atoms of copper was used (top panel). For bridge geometry a cluster with 36 atoms was used (middle panel). For hollow geometry a cluster with 37 atoms was used (bottom panel).

clusters are reliable, some other calculations have been performed with three layer clusters: Cu<sub>46</sub>(21,16,9), Cu<sub>49</sub>(16,21,12) and Cu<sub>48</sub>(20,16,12) for on-top, hollow and bridge adsorption sites respectively.

How representative are all these clusters of an actual Cu surface? To clarify that question the ionization potentials (IP) for these clusters have been calculated from total energy differences for the  $M_n \rightarrow M_n^+ + e^-$  process and their values displayed in Fig. 2 in the case of the minimal multiplicity. Notice that the capability to give an electron is generally higher for clusters with an even number of atoms in comparison with clusters composed by an odd number of atoms. The IP decreases as the number of atoms in the clusters increases, approaching an IP of nearly 5.4 eV. This value is in reasonable agreement with the work function calculated for a three layer slab of (100) normal orientation for which a value of 4.9 eV was obtained using the linear augmented plane wave method [28]. Looking at Fig. 3, we could conclude that a two-layer cluster of greater than 35 atoms is enough to study the adsorption of NCO. However, taking into account that for Cu the delocalized s-p valence electrons are relevant to describe adequately the interaction with an adsorbed molecule, the border effects could be significant and a study of the adsorption energy by increasing the size of the cluster must be performed.

The atomic net charges were calculated following the Mülliken and Hirshfeld schemes. It is well-known that the widely used Mülliken analysis is

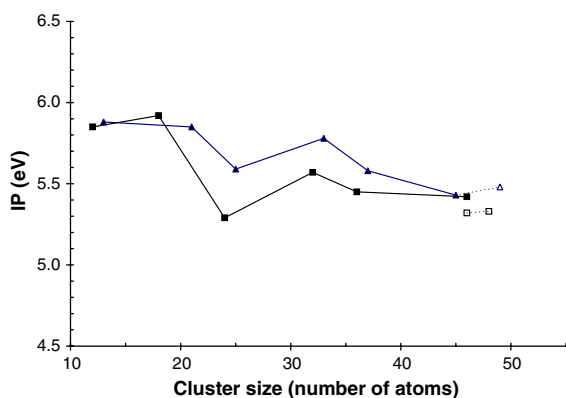


Fig. 2. Ionization potential (IP) values as a function of the cluster size for the first series of copper clusters with an odd number of atoms ( $\blacktriangle$ ): Cu<sub>13</sub>, Cu<sub>21</sub>, Cu<sub>25</sub>, Cu<sub>33</sub>, Cu<sub>37</sub>, Cu<sub>45</sub> and for the second series with an even number ( $\blacksquare$ ): Cu<sub>12</sub>, Cu<sub>18</sub>, Cu<sub>24</sub>, Cu<sub>32</sub>, Cu<sub>36</sub>, Cu<sub>46</sub>. Furthermore, the IP values for Cu<sub>46</sub>(21, 16, 9), Cu<sub>48</sub>(20, 16, 12) and Cu<sub>49</sub>(16, 21, 12) are included (empty symbols).

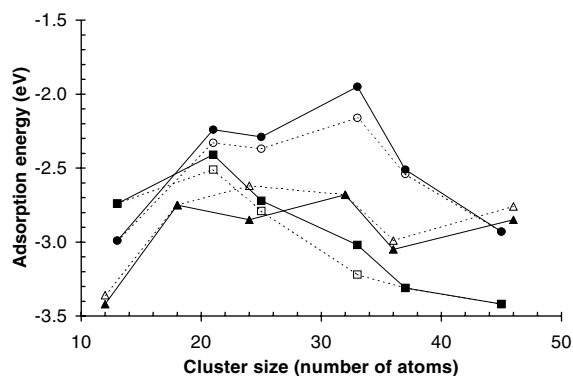


Fig. 3. Adsorption energy expressed as a function of the number of atoms composing the metallic cluster. The circles correspond to on-top sites, the triangles to bridge sites and the squares to hollow sites of Cu(100) surface. The full black symbols and solid connecting line corresponds to the minimal multiplicity (MM) criterion, the blank symbols and dashed connecting line to the ground state (GS) criterion.

rather arbitrary in the procedure of charge partitioning [29]. For this reason, we prefer to compare the Mülliken charges with a more realistic approach, like that of Hirshfeld [30]. As basis sets of triple- $\zeta$  plus polarization quality were used, basis set superposition error (BSSE) corrections for adsorption energies should be negligible. In fact, a systematic study using different basis sets performed by Rosa et al. indicates that the error is about 0.05 eV for this basis [31].

The electronic structure of the adsorbate/metal bond was analyzed using density of states (DOS) and projected density of states (PDOS) curves. They have been computed by applying a 0.25 eV Lorentzian broadening to the eigenvalues of the clusters.

### 3. Results and discussion

#### 3.1. Geometry of adsorption sites

In Tables 1–3, the different equilibrium interatomic distances and adsorption energies corresponding to NCO adsorbed on mono-coordinated, di-coordinated and tetra-coordinated sites of Cu(100) are reported for the clusters described in the last section, respectively. For this calcula-

Table 1  
On-top NCO adsorption on Cu(100)

Cluster	$d_{\text{N-Cu}}$	$d_{\text{N-C}}$	$d_{\text{C-O}}$	$E_{\text{ads}}$
Cu <sub>13</sub> (9, 4)	1.897	1.204	1.200	-2.99
Cu <sub>21</sub> (9, 12)	1.949	1.207	1.201	-2.24
Cu <sub>25</sub> (13, 12)	1.945	1.207	1.200	-2.29
Cu <sub>33</sub> (21, 12)	1.949	1.206	1.200	-1.95
Cu <sub>37</sub> (21, 16)	1.926	1.204	1.200	-2.51
Cu <sub>45</sub> (21, 24)	1.897	1.207	1.196	-2.93
Cu <sub>46</sub> (21, 16, 9)	1.926 <sup>a</sup>	1.204 <sup>a</sup>	1.200 <sup>a</sup>	-2.73

Interatomic N–Cu, N–C and C–O distances (in Å) and adsorption energies (in eV) for the different clusters considering the minimal multiplicity criterion. The Cu atom is the nearest to the N atom.

<sup>a</sup> Geometry as for Cu<sub>37</sub>.

Table 2  
Bridge NCO adsorption on Cu(100)

Cluster	$d_{\text{N-Cu}}$	$d_{\text{N-C}}$	$d_{\text{C-O}}$	$E_{\text{ads}}$
Cu <sub>12</sub> (6, 6)	2.033	1.216	1.190	-3.42
Cu <sub>18</sub> (12, 6)	2.037	1.215	1.190	-2.75
Cu <sub>24</sub> (16, 8)	2.103	1.221	1.190	-2.85
Cu <sub>32</sub> (20, 12)	2.058	1.217	1.191	-2.68
Cu <sub>36</sub> (20, 16)	2.051	1.212	1.193	-3.05
Cu <sub>46</sub> (26, 20)	2.047	1.215	1.190	-2.85
Cu <sub>48</sub> (20, 16, 12)	2.051 <sup>a</sup>	1.212 <sup>a</sup>	1.193 <sup>a</sup>	-3.02

Interatomic N–Cu, N–C and C–O distances (in Å) and adsorption energies (in eV) for the different clusters considering the minimal multiplicity criterion. The Cu atom is the nearest to the N atom.

<sup>a</sup> Geometry as for Cu<sub>36</sub>.

Table 3  
Hollow NCO adsorption on Cu(100)

Cluster	$d_{\text{N-Cu}}$	$d_{\text{N-C}}$	$d_{\text{C-O}}$	$E_{\text{ads}}$
Cu <sub>13</sub> (4, 9)	2.338	1.232	1.184	-2.74
Cu <sub>21</sub> (12, 9)	2.239	1.234	1.181	-2.41
Cu <sub>25</sub> (12, 13)	2.231	1.230	1.184	-2.72
Cu <sub>33</sub> (12, 21)	2.233	1.226	1.183	-3.02
Cu <sub>37</sub> (16, 21)	2.226	1.227	1.182	-3.31
Cu <sub>45</sub> (24, 21)	2.228	1.229	1.182	-3.42
Cu <sub>49</sub> (16, 21, 12)	2.226 <sup>a</sup>	1.227 <sup>a</sup>	1.182 <sup>a</sup>	-3.23

Interatomic N–Cu, N–C and C–O distances (in Å) and adsorption energies (in eV) for the different clusters considering the minimal multiplicity criterion. The Cu atom is the nearest to the N atom.

<sup>a</sup> Geometry as for Cu<sub>37</sub>.

tion, the MM criterion has been applied. Results obtained with the GS criterion differ at most 0.005 Å from the MM ones.

Looking at first column of Tables 1–3 we deduce that the influence of the cluster size on the distance between nitrogen and its nearest copper atom is not completely negligible. The values for this distance differ at most by 2.7% for the mono-coordinated, 3.4% for the di-coordinated and 5.0% for the tetra-coordinated sites. This observation is also true for the N–C and C–O distances of isocyanate group (see second and third columns of Tables 1–3) which differ up to ~0.7%. If we consider now the dependence of these interatomic distances on the type of adsorption site, we note that the N–Cu distance increases noticeably as a function of the coordination number: ~1.93 Å (on-top), ~2.05 Å (bridge) and ~2.25 Å (hollow). An analogous but less marked trend was obtained for the N–C distance, with mean values of 1.21 Å (on-top), 1.22 Å (bridge) and 1.23 Å (hollow). Conversely, the C–O distance decreases as a function of the coordination number: 1.20 Å (on-top), 1.19 Å (bridge) and 1.18 Å (hollow). The reason for this behavior will be given in Section 3.

Unfortunately, there are no experimental values for these distances on NCO adsorbed over transition metal surfaces. Nevertheless, Yang and Whitten [27] studied theoretically the adsorption of isocyanate group on Ni(100) arriving at the conclusion that the N–Ni distance increases in the following order: 1.97 Å, 2.19 Å and 2.36 Å, for mono-, di- and tetra-coordinated sites, respectively, while the N–C and the C–O distances present nearly the same values for the three sites ( $d_{\text{N-C}} = 1.20$  Å and  $d_{\text{C-O}} = 1.22$ – $1.23$  Å). We underline the fact that N–Ni distances obtained by these authors are 0.04–0.15 Å larger than our results for N–Cu distances.

If we consider the interatomic distances for the free isocyanic group ( $d_{\text{N-C}} = 1.230$  Å and  $d_{\text{C-O}} = 1.194$  Å), we observe that the N–C distance shortens up to ~2% (on-top site), while the C–O distance undergoes lower modifications, stretching by 0.6% (on-top site) or shortening by 1% (hollow site).

### 3.2. Adsorption site preference

Looking at the adsorption energy values in the last column in Tables 1–3, we notice that they



change markedly when the number of atoms in the cluster increases. However, the  $E_{\text{ads}}$  values do not show the same site preference when they are calculated for a similar size of the cluster. If we constrain the analysis for only one kind of site we appreciate an oscillatory behavior. This is a well-known physical property of small metallic clusters [21] which is related to the quantum mechanics of nanoscopic systems. This fact cannot be avoided and may yield limitations in the study of the interaction of molecules with metallic surfaces. When a chemisorptive interaction is present, generally an intermediate cluster size could be sufficient to that purpose. If it is not the case, some embedding technique or bigger clusters for which the oscillations are diminished can be used.

In order to appreciate these oscillations, the different adsorption energies of Tables 1–3 have been displayed in Fig. 3. The adsorption energy values corresponding to the GS criterion have also been reported in this figure. For the smaller clusters with less than 25 atoms, an unambiguously defined more favored site cannot be found. Indeed, for  $\text{Cu}_{12}$  and  $\text{Cu}_{13}$ , the site adsorption preference is bridge > on-top > hollow while for  $\text{Cu}_{24}$  and  $\text{Cu}_{25}$  the order is bridge > hollow > on-top. Regarding the larger clusters with more than 25 atoms, the adsorption energy for the bridge site shows a fluctuation of 0.2 eV around a mean of  $-2.8$  eV. On the other hand, for the on-top site, the fluctuation reaches to 0.5 eV around a mean of  $-2.5$  eV and for the hollow site the adsorption energy decreases continuously covering an interval of 0.7 eV. The last two sites show an adsorption energy difference between them of almost 0.5 eV, never crossing. For the largest clusters, bridge and on-top sites show a small competition, giving very similar adsorption energy values. An asymptotic limit seems to be attained where the hollow site is the more favored. This result is in agreement with many theoretical and experimental investigations which show that open-shell adsorbates prefer high coordination sites [32–35].

To verify the consistency of results obtained with the two layer clusters, the adsorption energies of NCO on the three layer clusters have been calculated. They are reported in Tables 1–3. For these cases, the NCO adsorption geometry was taken

from the parameters obtained with two layers results, taking into account the minor effect of cluster size on the geometry of isocyanate group. Indeed, going from  $\text{Cu}_{37}$  to  $\text{Cu}_{45}$  the Cu–N distance for on-top site modifies by  $0.03 \text{ \AA}$  or less. It is remarkable that the corresponding  $E_{\text{ads}}$  values are close to the results above commented obtained with the two layer clusters, thus maintaining the site preference sequence: hollow > bridge > on-top.

Comparing in Fig. 3 the results obtained with the MM and GS criteria we notice that both approaches give essentially the same adsorption energy values. The larger discrepancy, which is of nearly 0.2 eV, is observed for  $\text{Cu}_{24}$  and  $\text{Cu}_{33}$ . As a consequence, either of the two criteria is equally valid when Cu clusters are used to represent extended surfaces.

### 3.3. Electronic structure

In order to attain a deeper understanding of the adsorption process of NCO on different sites of (100) face of copper, the electronic structure for this system has been analyzed. For that purpose, the  $\text{Cu}_{36}$  and  $\text{Cu}_{37}$  clusters have been used, the first for the bridge site and the second for the on-top and hollow sites. These clusters are not the largest studied but they retained the general trends differentiating the adsorption sites and at the same time, they can be used with a reasonable computational cost. Table 4 summarizes the atomic net charges using the Mülliken and the Hirshfeld population analyses. Both showed that the NCO charge increases when it is adsorbed on copper, being this tendency more evident as the coordination site decreases. For all the cases, even for free NCO, the charge is accumulated on N and O atoms yielding the C atom positively charged. Although the magnitudes of the atomic charges calculated from the Mülliken analysis are higher than those obtained from that of Hirshfeld, the general qualitative trend as a function of the coordination site is similar.

The variation in dipole moment along the surface normal with respect to the surface-NCO distance was also calculated. The values for the first derivative of the dipole moment,  $d\mu/dR$ , are

Table 4

Mülliken and Hirshfeld net atomic charges (in electron units) of NCO molecule adsorbed on Cu(100) considering Cu<sub>36</sub> (bridge site) and Cu<sub>37</sub> (on-top and hollow sites) clusters

	Mülliken net charge				Hirshfeld net charge			
	Free	On-top	Bridge	Hollow	Free	On-top	Bridge	Hollow
N	-0.285	-0.317	-0.401	-0.526	-0.128	-0.316	-0.302	-0.272
C	0.685	0.483	0.580	0.720	0.212	0.131	0.154	0.185
O	-0.400	-0.555	-0.536	-0.491	-0.084	-0.248	-0.224	-0.178
NCO	0	-0.389	-0.357	-0.297	0	-0.433	-0.372	-0.265

-0.62, -0.76 and -0.85 a.u. for hollow, bridge and on-top sites, respectively. Notice that this negative slope indicates an electronic transfer from the metal to the isocyanate group, in agreement with the above mentioned electronic population results. The values obtained by Yang and Whitten at ab initio CI level on Ni(100) are also negative but higher (-1.07, -1.35 and -1.37 a.u. for hollow, bridge and on-top sites, respectively) [27].

The last observation can also be analyzed considering the values of IP for the larger clusters (as a measure of the copper work function) and the chemical potential for the adsorbate (see Ref. [36]). While for the greater copper clusters the IP value is near 5.4 eV, the chemical potential value for NCO is 8.37 eV. Then, considering the arguments from Ref. [36], there is a net ability of Cu to transfer its valence electron charge to NCO predicting the formation of a NCO<sup>δ-</sup> species.

There is an interesting relationship between the net charge of NCO, the shortening of N–C bond and the elongation of C–O bond. Indeed, if we go from the hollow site to the on-top site, the negative charge of the NCO increases by nearly 0.10e<sup>-</sup> while the N–C distance lowers in 0.02 Å and the C–O distances rises in 0.02 Å. It is noteworthy that this relationship is an intrinsic property of NCO as a group. In Fig. 4, the N–C and C–O distances have been displayed as a function of the negative fractional charge at free NCO. Notice the monotonic and opposite behavior between both distances as a function of NCO electronic charge. This behavior can be understood considering the 2π filling. This molecular orbital undergoes the major change when the isocyanate group gains electronic charge (see Table 6). An inspection of atomic coefficients of the 2π MO shows that it is

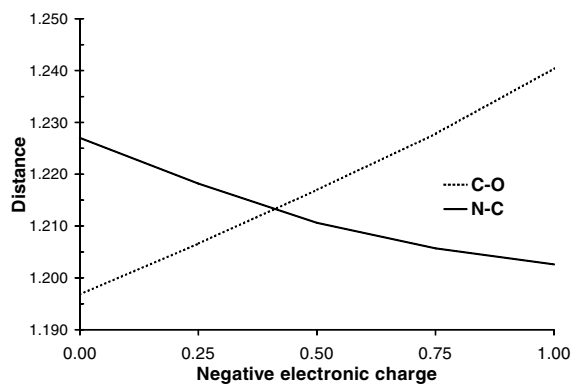


Fig. 4. Interatomic N–C and C–O distances (in Å) represented as a function of net molecular NCO charge (in electron units) for free NCO molecule.

characterized by a bonding interaction between N and C, and an antibonding interaction between C and O. Hence, the filling of this MO produces an enhancement of N–C bond and a weakening of C–O bond, with the concomitant influence on the interatomic distances.

The C–O bond strength can be studied employing the overlap population (OP) concept. Looking at Table 5, we observe that the OP (CO) increases

Table 5

Overlap populations of N–Cu, N–C and C–O bonds for NCO molecule adsorbed on Cu(100) considering Cu<sub>36</sub> (bridge site) and Cu<sub>37</sub> (on-top and hollow sites) clusters

	Free	On-top	Bridge	Hollow
N–Cu	–	0.221	0.116	0.073
N–C	0.675	0.699	0.730	0.645
C–O	0.525	0.501	0.536	0.563

The Cu atom is the nearest to the N atom.

as the coordination number increases, in agreement with the C–O shortening as was mentioned in Section 2. Regarding the N–C bond, its OP for hollow sites is  $\sim 10\%$  lower than that for on-top or bridge sites. If we want to compare the bond strength between N and their nearest copper atoms for different coordination numbers, a multiplying factor of four must be included for the hollow site, and a factor of two for the bridge site. In this way, we have the sequence  $0.22 < 0.23 < 0.29$  for on-top, bridge and hollow respectively. This result is in agreement with the adsorption energy values reported in Tables 1–3 and displayed in Fig. 3. It is also interesting to remember that the Shustorovich bond order conservation theory [37] establishes that the overlap population must be shared between the different bonds as it is approximately the case in our calculations.

On the other hand, the electronic structure for this system can also be studied considering the concept of projected density of states (PDOS) for the most important valence molecular orbitals of NCO. In Fig. 5, the corresponding PDOS for  $7\sigma$ ,  $2\pi$  and  $3\pi$  molecular orbitals of NCO adsorbed on the different possible adsorption sites of

Cu(100) have been displayed. In the same figure, the values of energy levels for the free molecule have been indicated. We notice that all the NCO molecular orbitals undergo a certain degree of coupling with the Cu orbitals. Nevertheless, their role in chemical bonding is remarkably different. Thus, the NCO molecular orbitals that participate more actively in the chemical bonding are the  $7\sigma$  and  $2\pi$  ones. Both orbitals are mainly composed by N atomic orbitals. Indeed, in  $7\sigma$  orbital N( $p_z$ ) and N(s) participate with about 50% and 30%, respectively. The  $2\pi$  one is fundamentally N( $p_{x,y}$ ) (nearly 60%). The  $3\pi$  orbital which is the LUMO of NCO (with a major participation of C( $p_{x,y}$ ) orbitals,  $\sim 60\%$ ) shows a minimal coupling with the Cu orbitals below the Fermi level.

If the mean positions of these MOs are compared, we observe that they become less stable with respect to the free molecule as the coordination number decreases. This is a simple consequence of the greater negative electronic charge retained by the NCO molecule as it adsorbs on sites of lower coordination (see Table 4). Then, the inter-electronic repulsion becomes larger and the molecular orbitals destabilize.

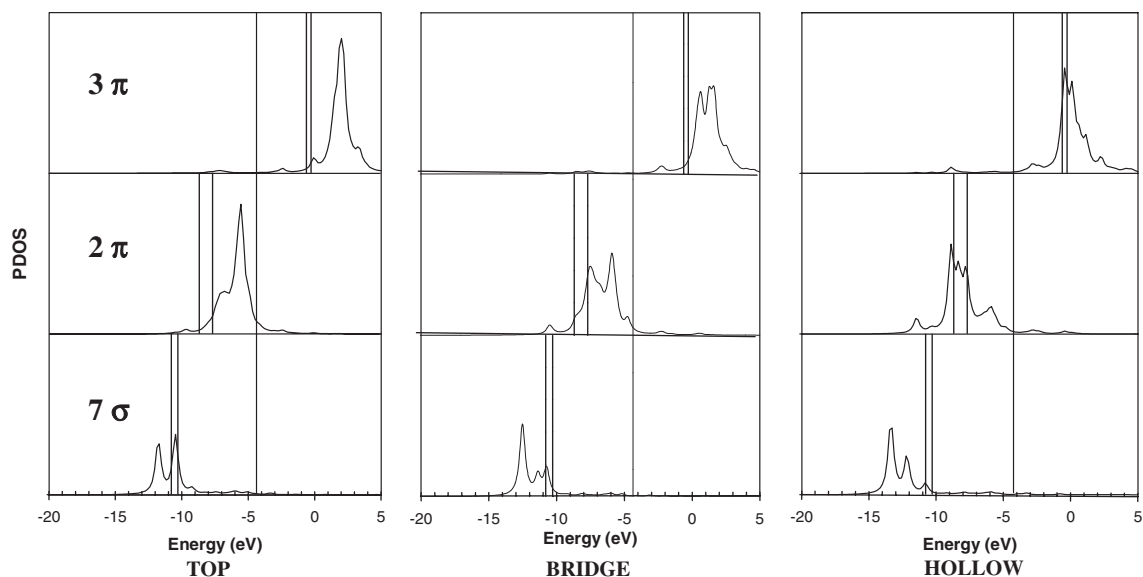


Fig. 5. Projected DOS of  $3\pi$  (top panel),  $2\pi$  (middle panel) and  $7\sigma$  (bottom panel) molecular orbitals for NCO adsorbed on on-top, bridge and hollow sites of Cu(100) (from left to right). The common vertical line indicates the position of Fermi energy level; the other vertical lines show the positions of  $7\sigma$ ,  $2\pi$  and  $3\pi$  molecular orbitals for free NCO.



Regarding now the role played by the surface Cu orbitals, we have focused the analysis on the two extreme possible cases: the tetra-coordinated (hollow) and mono-coordinated (on-top) ones. In Fig. 6, the PDOS for  $7\sigma$ ,  $2\pi$  and  $3\pi$  molecular orbitals of NCO are compared with those of Cu orbitals for NCO adsorbed on the hollow site. In Fig. 7, the same procedure was followed with the

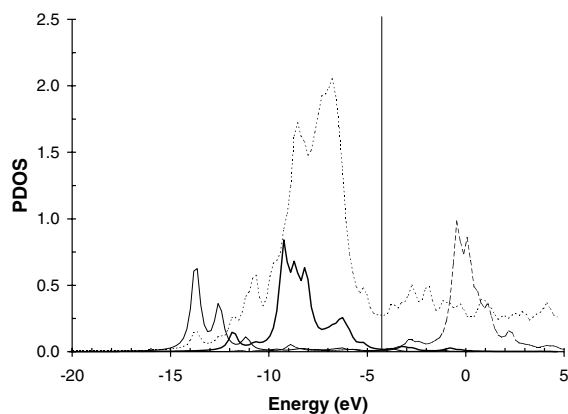


Fig. 6. Projected DOS of  $7\sigma$  (thin solid line),  $2\pi$  (bold solid line) and  $3\pi$  (dashed line) molecular orbitals for NCO adsorbed on the hollow site of Cu(100) displayed together with the projected DOS of surface copper atoms directly linked to NCO (thin dotted line). The thin vertical line shows the position of Fermi energy level.

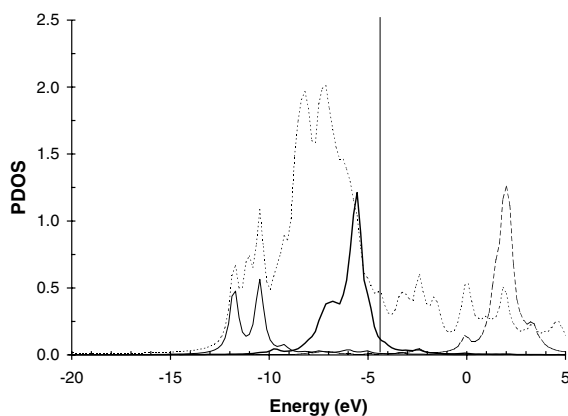


Fig. 7. Projected DOS of  $7\sigma$  (thin solid line),  $2\pi$  (bold solid line) and  $3\pi$  (dashed line) molecular orbitals for NCO adsorbed on the on-top site of Cu(100) displayed together with the projected DOS of the surface copper atom directly linked to NCO (thin dotted line). The thin vertical line shows the position of Fermi energy level.

NCO adsorbed on-top site. Further information is obtained integrating these molecular orbitals up to the Fermi level. The corresponding molecular orbital populations are reported in Table 6. Looking at Fig. 6 (hollow site), the straight correspondence between the  $2\pi$  band of NCO and the lower part of the Cu band is noteworthy, while the  $7\sigma$  MO of NCO has some mixing with these Cu orbitals. Looking now at Fig. 7 (on-top site), we notice that the  $2\pi$  band of NCO mixes with the upper part of the Cu band; nevertheless, it is narrower than in the case of the hollow site. The  $7\sigma$  MO of NCO couples with the bottom part of the Cu band.

Looking at the populations for  $2\pi$  and  $7\sigma$  MOs, we observe negligible or at most small differences between hollow and on-top geometries. Hence, how do we establish which orbitals are the responsible of the Cu–NCO chemical interactions? The  $2\pi$  MO of NCO, which is mainly due to the contributions of  $p_x$  and  $p_y$  orbitals of N and O, mixes more strongly with  $3d_{xz}$  and  $3d_{yz}$  AOs of Cu at hollow site than with the same AOs of Cu at on-top. As in other similar situations (see Ref. [38]), the energy interval between bonding and antibonding levels should become smaller in the second case and therefore the antibonding  $2\pi$ -metal combinations would be lower in energy and more easily to be occupied.

Table 6

Molecular orbital (MO) populations for NCO molecule adsorbed on Cu(100) considering  $\text{Cu}_{36}$  (bridge site) and  $\text{Cu}_{37}$  (on-top and hollow sites) clusters

MO	Free	On-top	Bridge	Hollow
$1\pi$	4.0	3.8674	3.8458	3.8092
$2\pi$	3.0	3.6877	3.6715	3.6254
$3\pi$	0.0	0.1460	0.1810	0.2448
Total $\pi$	7.0	7.7010	7.6982	7.6794
$4\sigma$	2.0	1.9243	1.9046	1.8630
$5\sigma$	2.0	1.9417	1.9275	1.9040
$6\sigma$	2.0	1.9387	1.9275	1.9086
$7\sigma$	2.0	1.8717	1.8427	1.8151
$8\sigma$	0.0	0.0555	0.0714	0.0948
Total $\sigma$	8.0	7.7320	7.6738	7.5855
Total $\pi + \sigma$	15.0	15.433	15.372	15.265

The values have been renormalized in order to attain the Hirshfeld atomic net values of Table 4.

### 3.4. Vibrational frequencies

The adsorbed NCO species shows two normal modes in infrared spectra. One, very intensive, is the  $\nu_{\text{asym}}$  with a frequency near 2160–2200  $\text{cm}^{-1}$ , and the other the  $\nu_{\text{sym}}$  with a frequency near 1200–1300  $\text{cm}^{-1}$ . The calculated values for  $\nu_{\text{asym}}$  and  $\nu_{\text{sym}}$  obtained when NCO is adsorbed on hollow site of  $\text{Cu}_{37}$  cluster are 2187  $\text{cm}^{-1}$  and 1280  $\text{cm}^{-1}$ , respectively. The results for  $\nu_{\text{asym}}$  are in excellent agreement with those reported by Celio et al. [18] in an IR experimental study for NCO adsorbed on Cu(100) at low NCO coverage. These authors found a value of 2165  $\text{cm}^{-1}$  for  $\nu_{\text{asym}}$  when NCO was produced from thermal decomposition of HNCO on Cu(100) and a value of 2162  $\text{cm}^{-1}$  for NCO obtained by reacting  $\text{C}_2\text{N}_2$  and preadsorbed oxygen on this same surface. Regarding the values for  $\nu_{\text{sym}}$ , the only experimental result corresponds to high NCO coverages. Nevertheless, if we consider that the NCO–NCO coupling produces analogous vibrational shifts for both normal modes, we arrive at a  $\nu_{\text{sym}}$  value of 1283  $\text{cm}^{-1}$ , which is in very good agreement with our result of 1280  $\text{cm}^{-1}$  for NCO on hollow site.

The computational cost for calculating the vibrational frequencies for adsorbed NCO is high. In order to study comparatively the variation of these frequencies with the coordination number of adsorption site, we decided to restrict the comparison of calculated frequencies to the use of relatively small clusters, having between 10 and 15 Cu atoms. The justification for such a methodology is that frequencies depend smoothly on the cluster size, as it was demonstrated in other ab initio calculations [20]. In fact, our results of calculated frequencies of  $\nu_{\text{asym}}$  for the hollow site differ within  $\pm 20 \text{ cm}^{-1}$  around a mean of 2160  $\text{cm}^{-1}$ . The results obtained for both  $\nu_{\text{asym}}$  and  $\nu_{\text{sym}}$  are reported in Table 7. Notice that both frequencies are decreasing functions of the coordination number.

An important consequence of comparing our theoretical values of NCO normal modes frequencies with the experimental ones is that we can affirm that the most favored adsorption site is that of higher coordination number. This is in agreement with our predicted adsorption site preference based only on energetic arguments.

Table 7

Frequencies (in  $\text{cm}^{-1}$ ) of asymmetric and symmetric normal modes for NCO adsorbed on Cu(100)

	On-top	Bridge	Hollow	Hollow	Experiment	
	$\text{Cu}_{13}$	$\text{Cu}_{12}$	$\text{Cu}_{13}$	$\text{Cu}_{37}$	$\theta \approx 0$	$\theta \gg 0^a$
$\nu_{\text{asym}}$	2237	2206	2153	2187	2163	2201
$\nu_{\text{sym}}$	1335	1310	1256	1280	–	1321

The experimental values are from Ref. [18].

<sup>a</sup> For 85 L HNCO exposure.

## 4. Conclusions

The main conclusions of this work can be summarized as follows:

A DFT study of the problem of isocyanate group adsorption on the (100) face of copper based on the cluster approach was presented. For that purpose, a careful analysis of the influence of cluster size on the chemisorptive properties of NCO was performed.

Our results show that whereas the N–C, C–O and N–metal distances are rather independent on the cluster size, the adsorption energy on different possible sites of Cu(100) shows an oscillatory dependence. The site of four-fold symmetry is the most favored. The N–Cu distance elongates as the coordination number of the site increases. At the same time, the N–C distance also elongates but the opposite trend was obtained for the C–O distance. This behavior can be understood considering the  $2\pi$  filling. This MO is characterized by a bonding interaction between N and C and an antibonding interaction between C and O. Hence, the filling of this MO produces an enhancement of N–C bond and a weakening of C–O bond.

When NCO adsorbs on Cu, it charges negatively. The electron transfer from the substrate is greater for the on-top adsorption site than for the hollow one.

The total overlap population of nitrogen with the nearest copper atoms increases as the coordination number of the site increases, in correspondence with the larger values in the magnitude of the adsorption energy.

The projected DOS curves for the most important valence molecular orbitals of isocyanate group indicate a strong mixing between its  $2\pi$

orbital and  $3d_{xz}$  and  $3d_{yz}$  AOs of Cu. The greater binding of NCO to the metallic site of four-fold symmetry in comparison with the one-fold symmetry can be explained in terms of bonding–antibonding arguments. Taking into account that when NCO links to the on-top site the  $2\pi$ – $3d$  antibonding combinations become much more occupied than on the hollow site, the NCO–metal coupling results less important in the former case.

The isocyanate group has two sufficiently intense normal modes to be detected in an infrared spectrum. The predicted asymmetric mode at  $2187\text{ cm}^{-1}$  for NCO adsorbed on the hollow site agrees very well with the experimental observed values of  $2162\text{--}65\text{ cm}^{-1}$ . Both asymmetric and symmetric modes diminish their frequency values as the coordination number of the site increases.

### Acknowledgements

G.R.G. and N.J.C. acknowledge the financial support of Universidad Nacional del Sur. R.M.F. and N.J.C. also acknowledge the financial support of CONICET of Argentina.

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