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Abstract

A theoretical study was carried out on the adsorption of carbon monoxide on small Cu_n ($n \leqslant 8$) clusters and its comparison with the adsorption of oxygen using density functional methods. The study of the CO–copper system is important for understanding the mechanism of synthesis of organic substances catalyzed by copper. Adsorption energies from 9.3 to 27.9 kcal/mol were found, which represented values very similar to those calculated for the adsorption of molecular oxygen in a previous study. Nevertheless, the reactivity of the CO molecule is independent of even–odd alternation with respect to the number of atoms of copper in the cluster, a result in contrast with previous results on the reactivity of the molecular oxygen with the same copper clusters. The CO molecule is adsorbed on a top site (1-fold coordination) approaches perpendicularly to the adsorption site, presenting a high degree of symmetry in the adsorption system. A high degree of symmetry of the adsorption system was also found for the adsorption of oxygen, both atomic and molecular, in previous studies. This showed that symmetry could be an important factor to consider for describing the adsorption process of elemental gases on copper clusters.
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Keywords: Copper cluster; CO adsorption; Quantum chemical calculations

1. Introduction

In recent decades metal clusters have received particular attention both on the theoretical and experimental level due to their potential application in catalytic processes and electronic materials [1–3]. Clusters containing from as little as a few to several thousand atoms have been studied to determine the evolution of bulk matter properties from atomic properties [4]. In addition, basic properties of metal clusters are believed to be an important link in understanding the fundamental mechanism of catalysis and other chemical transformations [5,6]. Only recently has the adsorption of gases on clusters of noble and transition metals begun to be studied [7–13]. Oxygen and carbon monoxide are two of the most important gases which participate in important catalytic processes in heterogeneous

phase, with the study of clusters being relevant for clarifying important, but currently poorly understood aspects such as reactivity and selectivity of specific chemical products [2,14–17]. Several experimental and theoretical studies have recently been produced in relation to bare copper clusters with different size and charge as well as the CO–copper cluster system, with emphasis on the study of structural and electronic properties, and reactivity [18–24]. The related studies on the reactivity of CO with copper clusters have shown that is strongly dependent on the size of the cluster, with some studies also showing a certain dependence on the even–odd alternation in function of the number of atoms in the copper cluster [22–24]. This latter behavior was also observed for the adsorption of molecular oxygen on copper clusters [25,26]. On the other hand, it was found that copper clusters with more than 20 atoms showed little reactivity towards CO [22]. These studies also showed that small clusters had greater reactivity and could be good candidates for use as potential catalysts. It was

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also established that CO acted mainly as an electro-donor, although it was possible that there was also back-donation from the copper cluster towards the $2\pi^*$ orbital of the CO molecule [24].

The goal of the present work is to study the adsorption of carbon monoxide on neutral Cu_n ($n \leqslant 8$) clusters and compare this with the oxygen adsorption on the same type of cluster, as recently reported [26,27], using functional density methods. The analysis of energetic stability, and both structural and electronic properties with regard to CO adsorption, is highly relevant for the understanding of important aspects of reactivity in relation to copper clusters.

2. Methodology and computational details

Energy and electronic properties have been calculated by solving the Kohn–Sham equations in an atomic basis set formed by Gaussian functions. The calculations have been done using the B3LYP [28–31] exchange correlation functional, which is of the hybrid type. It consists of a careful mixing of Hartree–Fock exchange, calculated with Kohn–Sham orbitals, and the B88 exchange functional [29] plus the LYP correlation functional [31]. The use of B3LYP functional has been used in previous calculations with good agreement with experimental data [21,26,27]. For the copper atoms the Stuttgart pseudopotential [32] with the corresponding basis set has been used. The pseudopotential replaces 10 core electrons thus 19 valence electrons are considered. For carbon and oxygen atoms in the CO molecule the 6-311G* basis set [33–35] has been used. The calculated bond length and bond energy for gas phase of CO are 1.127 Å and 11.02 eV, respectively, in good agreement with experimental values of 1.128 Å and 11.24 eV [36]. The natural bond order (NBO) population analysis [37,38] was used for the discussion of results. Initial geometries of Cu_n clusters were those optimized in a previous work [21]. The interaction of the CO molecule with copper clusters was fully optimized without symmetry restrictions in different adsorption sites and orientations on the copper cluster. Top, bridge and threefold hollow type sites are possible to identify in the copper cluster. All the calculations have been done using the Gaussian 98 program [39].

The binding energy for the Cu_nCO system was calculated as

$$E_b = E(Cu_nCO) - nE(Cu) - E(C) - E(O); \quad n \leq 1 - 8 \tag{1}$$

and the adsorption energy for the optimum process as

$$E_{ad} = E(Cu_nCO) - E(Cu_n) - E(CO); \qquad n \leq 1 - 8 \tag{2}$$

being $E(Cu_nCO)$, $E(Cu_n)$, $E(CO)$, $E(Cu)$, $E(C)$ and $E(O)$ the energies of CO–copper cluster, bare copper cluster, CO molecule, copper atom, carbon atom and oxygen atom, respectively. Eqs. (1) and (2) are the same ones used to cal-

culate the binding and adsorption energies in the adsorption of atomic and molecular oxygen in previous works [26,27] and that it will allow us the comparison with these systems.

3. Results and discussion

3.1. Geometries

Fig. 1 shows the optimal geometrical structures of the CO–copper cluster systems, with the corresponding geometrical parameters. When comparing these structures with those reported for the bare copper clusters in a previous study [21] we can observe that the interaction between the CO molecule with each copper cluster only weakly modifies the geometry of the cluster. Generally, distortions are observed in the local environment, that is, in the region of adsorption of the CO molecule. This same behavior was reported for the oxygen adsorption, both atomic and molecular, in recently published studies [26,27]. The average Cu—Cu distance in Cu_nCO and in bare copper clusters is plotted in Fig. 2. In this figure we can clearly observe that the CO adsorption does not produce a significant change in the Cu—Cu distance, with the finding of a stretching of only 0.01–0.06 Å. The Cu_3 cluster undergoes the greatest change which tends to be more symmetrical, in which it goes from being an isosceles triangle to one which is equilateral, a process which shortens the Cu—Cu distance due to the interaction with the CO molecule. This last effect was also observed for the oxygen adsorption both at the atomic and molecular levels in previous studies [26,27]. The CO interaction affects all the copper clusters equally, not showed an even–odd alternation with respect to the number of atoms in the copper cluster, as was observed for the oxygen adsorption [26,27]. Beginning with Cu_n having $n > 6$, no effect is observed on the geometry of the cluster, which suggests that in a very large copper cluster the distortions occurring with the CO adsorption are negligible. Also, it is observed that the adsorption is produced on a top site (1-fold coordination), with the CO molecule, in general, approaches perpendicularly to the adsorption site, and with CO interacting with the copper cluster by means of the carbon atom. This same orientation was observed experimentally in the CO adsorption on the Cu(100) surface [40], finding that this is adsorbed perpendicularly to the surface on a top site with a CO—Cu(100) surface distance of 1.92 Å and a C—O distance of 1.13 Å, very similar to the values found in our calculations. The adsorbed C—O distance varied between 0.002 and 0.008 Å suggesting that it underwent a very weak distortion of about 7% longer than the C—O distance in the gas phase (1.127 Å). Finally, we can observe in Fig. 1 that the CO adsorption produces Cu_nCO systems with a high degree of symmetry: $C_{\infty v}$ Cu_2CO, C_{2v} for Cu_3CO, Cu_4CO and Cu_6CO, C_{5v} for Cu_7CO and C_s for CuCO, Cu_5CO and Cu_8CO. This same behavior was observed for the oxygen adsorption [26,27], indicating that the conservation of a
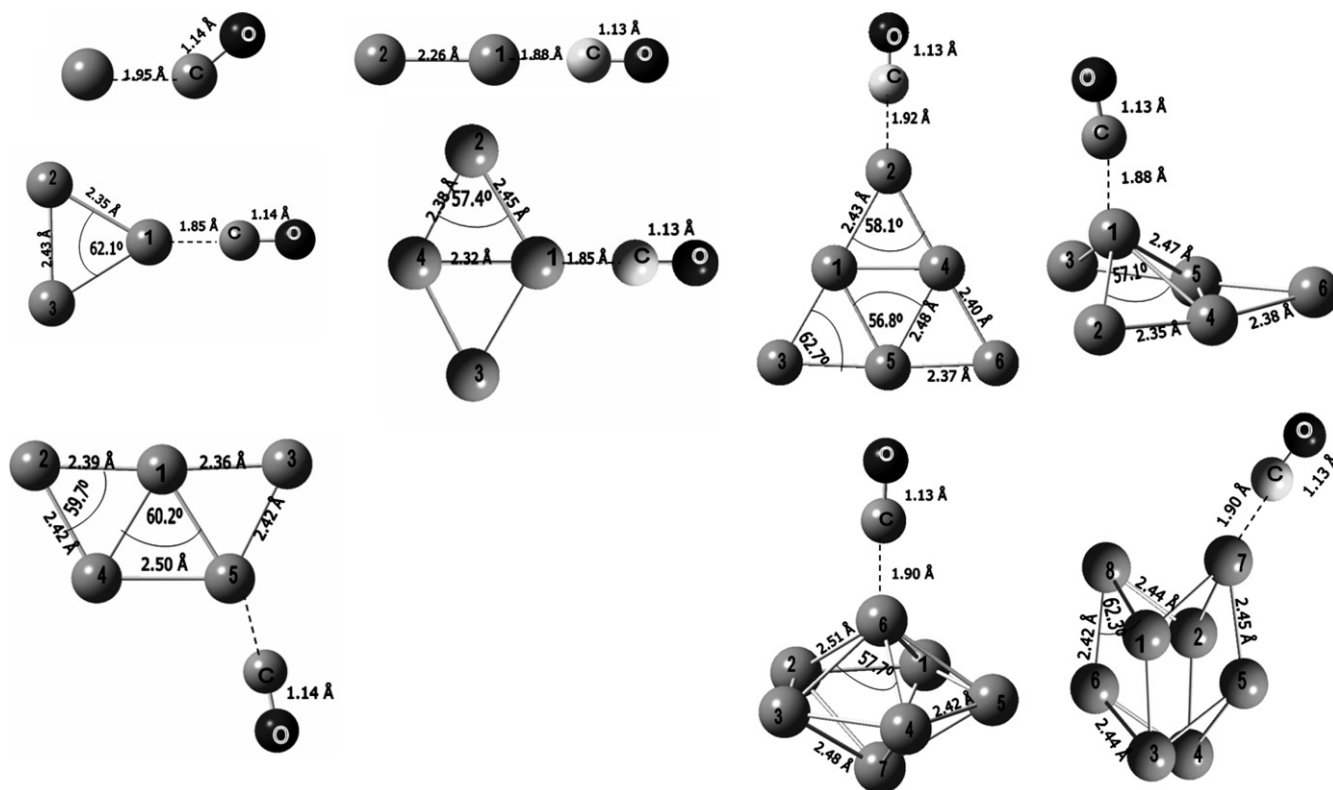
Fig. 1. Geometrical structures of neutral Cu_nCO systems.
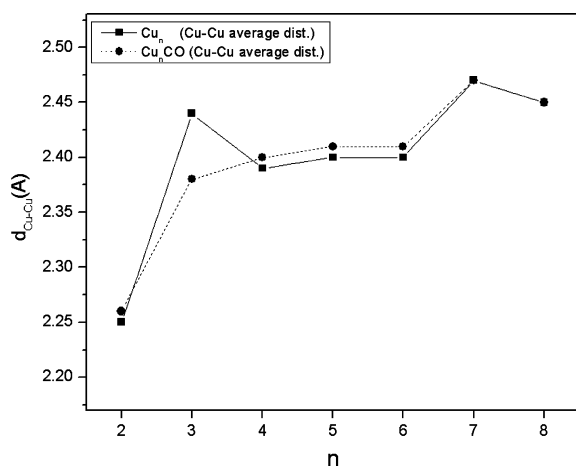
Fig. 2. Cu—Cu average distances for Cu_n clusters and Cu_nCO systems.

high degree of geometrical symmetry could be an important factor to consider for describing the process of adsorption of gases on copper clusters.

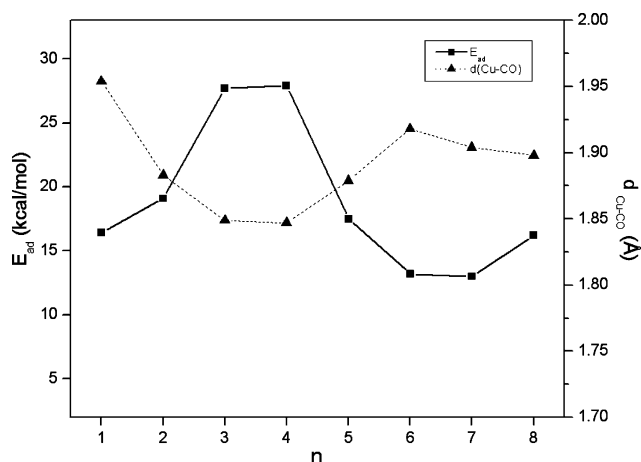### 3.2. Energies and electronic properties

The binding energy per atom, adsorption energy, LUMO–HOMO gap and other properties for Cu_nCO systems are summarized in Table 1. First, the binding energy per atom is shown in Fig. 3. As can be seen, the binding energy decreases progressively with the increase in the number of copper atoms to $n = 6$. Beginning at $n > 6$ the binding energy becomes constant, and as expected for a copper cluster with a high n value, the interaction of CO would not significantly affect the stability of the cluster. Second, the adsorption energy has values from 9.3 to 27.9 kcal/mol, being maximum for the Cu_3CO and Cu_4CO systems. These values are very similar to those found for the adsorption of molecular oxygen in a previous study [26]. Nevertheless, for the Cu_nCO systems no dependence is observed of the adsorption energy with the even–odd alternation, as was observed for the Cu_nO_2 systems [26], suggesting that the CO adsorption is less selective to the electronic properties of the copper cluster. The adsorption energy and the Cu_n—CO distance for the Cu_nCO systems are showed in Fig. 4. In this figure we can observe that there is good correlation between these properties, where the greater the adsorption energy, the less is the Cu_n—CO distance. In Fig. 5 we can also observe a good behavior when comparing the values of the adsorption energy with the Cu_n—CO bonding frequency, observing in this case that the greater the adsorption energy, the greater is the bonding frequency. The values of charge transfer suggest a mechanism to favor of back-donation, that is, charge transfer from the copper cluster to the CO molecule. Thus, this can be explained on the basis of cluster studies [24] and of surfaces [40] supposing that the CO behaves as a charge acceptor, the charge is transferred from the copper cluster to the empty $2\pi^*$ orbital of CO molecule; however, the charge transfer destabilizes this orbital, appearing as a
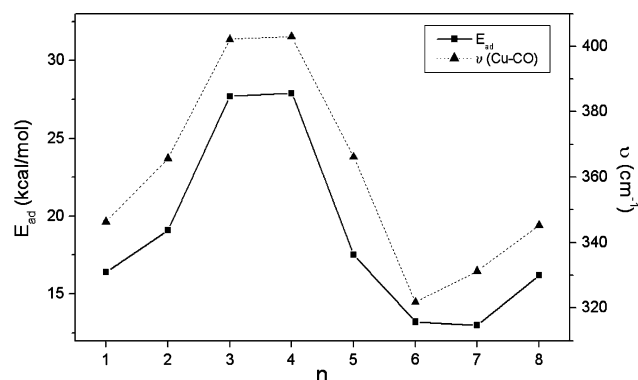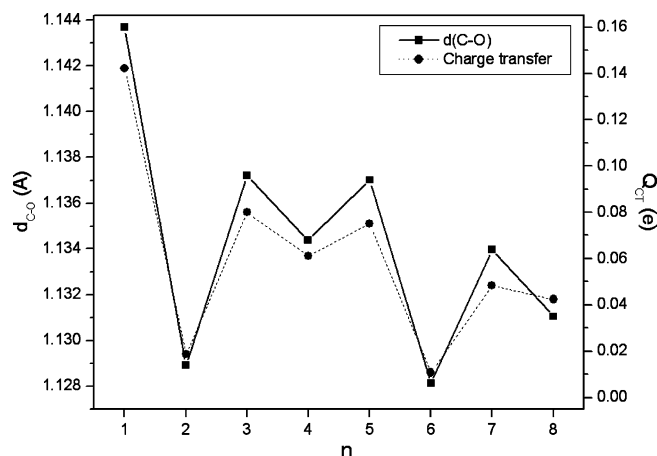
Table 1
Binding energies (E_b), adsorption energies (E_{ad}), gap between frontier orbitals, LUMO–HOMO (ΔE_{L-H}), C—O bond (R(C—O)), Cu_n—CO bond (R(Cu_n—CO), C—O stretching frequency (ν(C—O)), Cu_n—CO stretching frequency (ν(Cu_n—CO)) and electronic ground state, doing $n = 1$–8 and $w = n + 2$ for Cu_nCO adsorption systems

	E_b/w (eV)	E_{ad} (kcal/mol)	ΔE_{L-H} (eV)	R(C—O) (Å)	R(Cu_n—CO) (Å)	ν(C—O) (cm^{-1})	ν(Cu_n—CO) (cm^{-1})	Ground state
CuCO	3.82	16.4	2.07	1.142	1.954	2045.6	346.4	^{2}A′
Cu$_2$CO	3.43	19.1	3.03	1.129	1.883	2187.8	365.8	^{1}A′
Cu$_3$CO	3.00	27.7	1.46	1.136	1.849	2118.1	402.3	^{2}B$_2$
Cu$_4$CO	2.85	27.9	2.87	1.134	1.847	2146.2	341.5	^{1}A′
Cu$_5$CO	2.63	17.5	1.38	1.135	1.879	2118.2	366.2	–
Cu$_6$CO	2.57	13.2	2.55	1.129	1.918	2185.9	321.5	^{1}A$_1$
Cu$_7$CO	2.47	13.0	1.37	1.132	1.904	2146.7	331.4	^{2}A$_1$
Cu$_8$CO	2.47	16.2	2.45	1.132	1.898	2152.9	345.3	^{1}A′
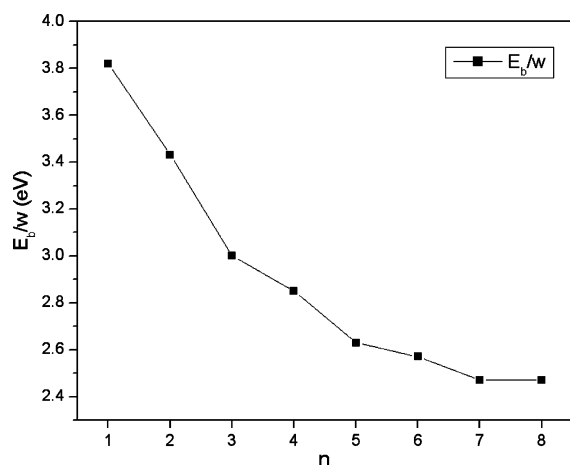
Fig. 3. Binding energy per atom for Cu_nCO systems with $w = n + 2$.

Fig. 5. Adsorption energy and Cu—CO stretching frequency for Cu_nCO systems.

Fig. 4. Adsorption energy and Cu—CO bond distance for Cu_nCO systems.

Fig. 6. C—O bond distance and charge transfer for Cu_nCO systems.

lengthening of the CO bond, which is a behavior clearly observed in Fig. 6, where a greater charge transfer produces a lengthening in the C—O distance. In Fig. 7 the C—O distance is compared with the C—O stretching frequency. In this figure we can observe that an increase in the C—O distance produces a decrease in the C—O frequency, which another result confirming the suggestion is made above. Nevertheless to conserve the energetic

stability in the system, the molecule of CO delivers a charge by means of an σ orbital to the Cu cluster, producing a shortening of the Cu_n—CO distance, as also observed in our calculations (see Fig. 4). The effects of charge transfer, either as the donor or through back-donation, suggests the occurrence here of chemisorption, which is manifested in all the Cu_nCO systems. The process of chemisorption was also observed for the adsorption of both atomic [27] and molecular [26] oxygen. Fig. 8 displays the energy of adsorption and the dipolar moment. It is interesting to observe that systems which demonstrates greater adsorption energy
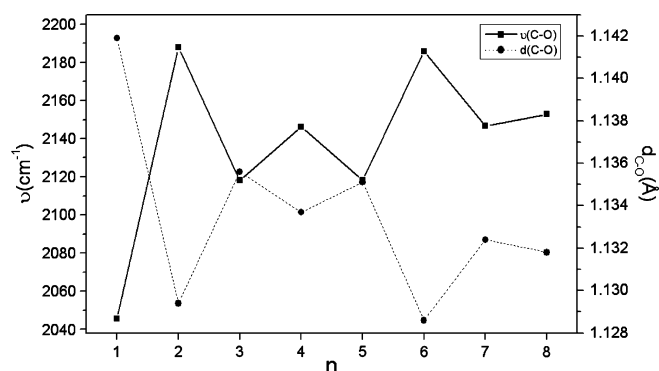
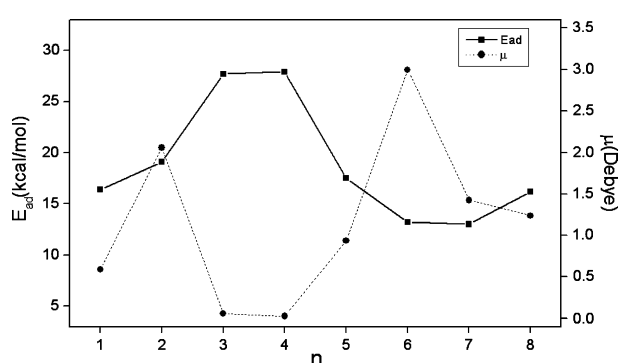Fig. 7. C—O bond distance and stretching frequency for the adsorbed CO molecule.

Fig. 8. Adsorption energy and dipole moment (μ) for Cu_nCO systems.

show a lower dipolar moment. This result suggests that the adsorption system that produces a lower degree of polarization (charge separation) produces a more effective interaction of the CO molecule with the copper cluster. The preceding could be regulated by back-donation effect. Also, we found that a non-planar structure is also possible for the Cu_6CO system which is less stable and only 1.3 kcal/mol with respect to a planar structure (see Fig. 1). Thus we believe that both structures are possible. Nevertheless, the symmetry of non-planar structure (C_s) is less than of the planar (C_{2v}), suggesting that a planar structure would be favored to present greater symmetry of the adsorption system.

A theoretical study for the adsorption of carbon monoxide on copper clusters has recently reported data which are in contrast with our calculations [24], but similar to the results of another study reported by Cao et al. [23]. In relation to the first study, our results suggest: (1) that calculations show stability for CuCO, similar to that found by Poater et al. [24]. This latter result is in contrast with our results reported for the adsorption of molecular oxygen where no stability for CuO_2 was found [26]. (2) In relation to Cu_5CO, this study [24] predicts a trigonal bipyramidal structure type, in contrast with our calculations, where we found a planar structure. (3) For Cu_7CO an interaction is predicted for the CO by the C_5 plane of the copper cluster, while our calculations predict high interaction through the axial position of greater symmetry, which is an interac-

tion similar to that found in the study by Cao et al. in the same system [23]. Finally, (4) in reference to the Cu_nCO systems, adsorption energies are reported which are of greater magnitude than those predicted by our calculations, but of the same order as those calculated by Cao et al. [23]. Nevertheless, our calculations predict that the greater energy of adsorption will be found in the Cu_3CO and Cu_4CO systems, similarly to those found by Poater et al. [24], but different than the results of Cao et al. [23], where they found a greater adsorption energy for Cu_5CO.

It is of interest to analyze the nature of CO adsorption on copper clusters with respect to the physical parameters or reactivity, and establish some type of correlation that allows us to describe and predict the behavior of the adsorption process. First, we analyzed the gap, since this gap is a measure of the relative chemical reacting to the molecular hardness [41]. Fig. 9 shows the LUMO–HOMO gap for the Cu_nCO systems with respect to the number of atoms in the copper cluster. For $n > 2$ this figure shows that the gap is maintained almost constant at 1.40 eV for odd numbers of copper atoms in the clusters, in contrast, in clusters with even numbers of copper atoms there are always high values, tending to decrease as the number of copper atoms increases. This same behavior is observed for bare copper clusters [21], indicating that the properties of the copper clusters are weakly modified with interaction with CO. Fig. 10 shows the difference in gaps between Cu_nCO and Cu_n and the charge transfer. Again we observe that the copper clusters with odd n are maintained almost constant (≈ 0 for gap difference), that is, they have values very similar to those of the bare copper clusters, and the copper clusters with an even n tend to decrease in an alternate form as n increases. This confirms previous results, and that the properties of the copper clusters are weakly modified by the CO adsorption, showing a natural tendency of copper clusters with very large n to have properties which are almost not observed to be altered. As the n increases, the reactivity of the CO molecule is lower, with a tendency toward a constant value for the adsorption energy. In addition, in Fig. 10 we can observe that there
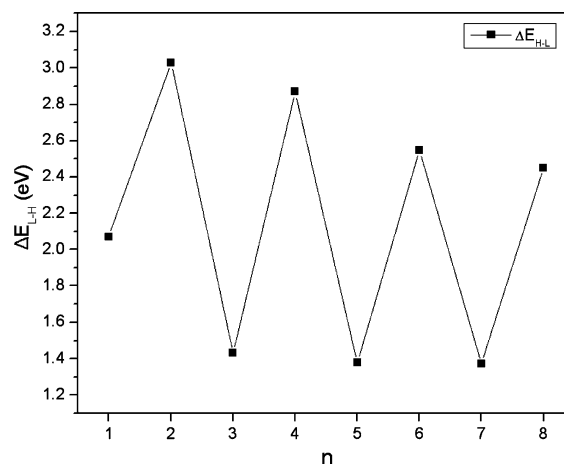

Fig. 9. Gap between frontier orbitals, LUMO–HOMO (ΔE_{H-L}).
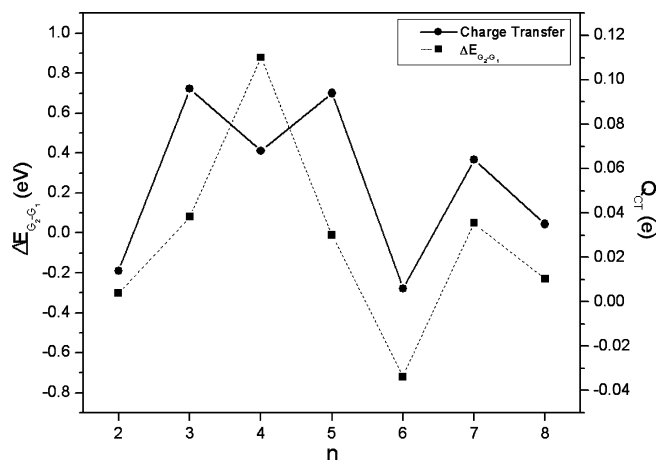
Fig. 10. Adsorption energy and difference of gaps $\Delta E_{G_2-G_1} = G_2(Cu_nCO) - G_1(Cu_n); G_m = E_{LUMO} - E_{HOMO}; m = 1, 2$.

is a good behavior between the difference in gaps and the charge transfer where it is observed that clusters with odd number of copper atoms in general show high charge transfer than copper clusters with an even number of copper atoms, but the charge transfer of both types of clusters decrease as number of copper atoms increases, which is another result that demonstrates that reactivity toward the CO molecule decreases with the size of the copper cluster.

3.3. Comparison between the Cu_nCO and Cu_nO_2 systems

We have recently reported a theoretical study of the adsorption of molecular oxygen on the same copper clusters as mentioned above [26]. In this section we will present a more detailed analysis in establishing the similarities and differences between these two systems. First, for CuCO system an effective interaction is found, result that it is in contrast with oxygen interaction where no stability for CuO_2 was found. The latter result suggests that the back-donation mechanism is acting to stabilize CuCO system. Second, the adsorption of CO and O_2 weakly modifies the geometry of the copper clusters, which denotes the interaction is not very strong, tending to preserve the geometry of the different copper clusters. The distortions are even weaker in the case of Cu_nCO systems than for Cu_nO_2 systems, but in both systems these distortions are preferentially observed in the region of molecular adsorption. Third, the general reactivity of CO is similar to that of O_2 with the exception of the Cu_5O_2 system, which shows higher reactivity, and where the adsorption energy is 40% greater in comparison with the Cu_4CO system which shows the highest reactivity of the Cu_nCO systems. On the other hand, for Cu_6O_2 a very small adsorption energy was found and the results seen to indicate stabilization by interactions of the van der Waals type. This last result is in contrast with Cu_6CO system where a strong interaction was found. As Cu_6 cluster has an electronic configuration of closed

shell and therefore, in general, to exhibit a low reactivity toward adsorbates [22]. Thus, the reactivity observed in Cu_6CO is due to the action of the back-donation mechanism. Fourth, as mentioned above, the reactivity of CO is independent of the even–odd alternation with respect to the number of atoms in the copper cluster, only showing preference for simple coordination sites (1-fold coordination). In contrast, O_2 shows reactivity for highly coordinated sites in the copper clusters (2- and 3-fold coordination). Fifth, the CO adsorption approaches perpendicular to the adsorption site, in contrast to O_2 which is preferentially adsorbed in parallel to the copper cluster. Sixth, the adsorption of O_2 produces a significant effective charge transfer from the copper cluster to the O_2 molecule, where in contrast, the adsorption of CO only produces a weak effective charge transfer. Nevertheless the latter factor is explained by the process of back-donation acting in the Cu_nCO systems, a mechanism for which was explained above. Due to the presence of charge transfer in both systems, the adsorption will be produced by chemisorption process. Seventh, it has been mentioned that the bond energy per atom (cohesion energy) of Cu_nCO systems in general decreases to $n < 6$ and is practically constant for systems with $n \geqslant 6$. The behavior for the Cu_nO_2 systems is different, where it was found more likely to be constant for all these systems. This shows that the Cu_nO_2 systems are comparatively more stable than the Cu_nCO systems to $n < 6$. For systems with $n \geqslant 6$ the behavior both for systems with CO and O_2 is similar, tending to be less reactive. The latter factor is verified when analyzing the adsorption energy, which has lower values when starting with the copper cluster having $n \geqslant 6$ when comparing adsorption of both molecules. Reactivity in the Cu_nO_2 systems is fundamentally related to the capacity of charge transfer from the copper cluster to the O_2 molecule, in contrast, for the Cu_nCO systems, it appears that the back-donation effect plays an important role in reactivity. Finally, both adsorption systems (Cu_nO_2 and Cu_nCO) show a high degree of symmetry in relation to adsorption, which makes it appear that, may be another important factor to be considered besides the electronic and energetic effects. This aspect was also found for the adsorption of atomic oxygen as recently reported [27].

4. Concluding remarks

The adsorption of carbon monoxide on copper clusters was studied recently, and its properties were analyzed and compared with those found for the adsorption of molecular oxygen on the same clusters as reported in a previous study [26]. It was found that the reactivity of CO was similar to that of O_2 on copper clusters, but CO is less selective in relation to the electronic structure of the copper clusters. With CO, no dependence was found with respect to the even–odd alternation in relation to the number of copper atoms in the cluster, as found in the case of O_2 adsorption. The CO molecule is adsorbed at simple

adsorption sites (1-fold coordination), perpendicular to the adsorption site, and is a process which occurs in a way that high symmetry is maintained in the adsorption system. The high degree of symmetry was also found for the adsorption of atomic [27] and molecular oxygen [26], which suggests that symmetry, may be another aspect which needs to be considered in the process of adsorption of gases on copper clusters. The presence of charge transfer indicates that the adsorption process is one of chemisorption, where the process of back-donation plays an important role in the stabilization of the Cu_nCO systems.

Acknowledgements

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