J. Phys. Chem. A **2005,** *109,* 7815−7821 **7815**

Theoretical Study of the Interaction of Molecular Oxygen with Copper Clusters

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Received: April 29, 2005; In Final Form: June 21, 2005

A new method based on frontier orbital theory has been used to investigate the binding site of molecular oxygen to neutral and anion copper clusters. It has been shown that one can make useful predictions of the binding sites based on the knowledge of the donor local reactivity of the cluster using the condensed Fukui function, f_{Ff}^{-}. In this way, it was found that Cu_3, Cu_5, and Cu_5^- have the highest reactivity toward molecular oxygen.

Introduction

The very unique electronic and structural properties of metal clusters have made them a research subject of great importance in different areas such as catalysis, nanomaterials, composite materials, etc. This has promoted active research on the structure and reactivity of metals clusters from the experimental[1−4] and theoretical points of view.[5−8]

The properties of small metal clusters are different from those of the atoms and may show both similarities and differences to their bulk counterpart. For clusters with a small number of atoms, their physical and chemical properties may be quite sensitive to the addition or removal of one atom. To understand and to predict properties of atomic clusters, it is necessary to further our knowledge, from both theoretical and experimental points of view, particulary about the evolution of the cluster properties as a function of cluster size. Some information is now available concerning the spectroscopy, structure, and reactivity of transition-metal clusters.[4,9,10] However, this knowledge raises as many questions as answers and much is yet to be learned.

The electronic structure of transition-metal clusters is particularly complicated because their atoms include both localized nd ($n = 3, 4, 5$) electrons and delocalized ($n + 1$)s valence electrons. The electronic configuration of the noble metals Cu, Ag, and Au is characterized by a closed d shell and a single s valence electron (Cu:Ar$(3d)^{10}(4s)^1$, Ag:Kr$(4d)^{10}(5s)^1$, Au:Xe$(5d)^{10}(6s)^1$). In view of this characteristic, clusters of those noble metals are expected to exhibit certain similarities to simple alkali-metal clusters. Also, large clusters of these metals have isolated electronic bands, which reflect that the number of low-lying electronic states is small. This behavior is different for other transition-metal clusters, such as Ni, which has many low-lying electronic states.[11]

The electronic structure and size of the clusters play a determining role in their chemical reactivity. For this reason, in the last few decades, the influence of size and charge state of the noble-metal clusters on their chemical reactivity[12−17] has been extensively studied. For example, Lee and Ervin[4] found that the Cu_n^- clusters with even n (odd valence electron) are reactive toward oxygen, while those with odd n are less reactive or unreactive; a similar tendency was observed for gold anion clusters. On the other hand, Riley and co-workers[10] observed that neutral copper clusters reacted with O_2 but that the clusters with closed shells were particularly unreactive. Whetten et al.[18] found that neutral Au_n clusters with an odd number of electrons (odd n) bind O_2 more strongly than those with an even number of electrons (even n).

The above-described research has been carried out to understand the dependence of cluster reactivity with its size and charge state, but very little has been done on the prediction of the active site of clusters. One of such investigations was done by Gordon et al.[19] who proposed a set of simple rules, based on frontier orbital theory, to predict the binding site of propene to Au clusters and to estimate the strength of the bond propene−Au. They[20] also showed that those rules apply to almost all neutral, positive, and negative silver clusters in their interaction with propene. The a priori knowledge of the reactivity tendency can save a substantial amount of computational time.

The goal of the present work is (a) to study the chemical reactivity of neutral and negatively charged copper clusters toward molecular oxygen, (b) to determine the size−reactivity relationship, and (c) to provide a method that can be used to make useful predictions related to the active site. It will be shown that the use of a recently developed variant of the condensed Fukui function allows us to predict the site of the cluster where the molecular oxygen will be bonded.

Theoretical Background

In this section, we review briefly some of the more important points of the Fukui function, which makes it relevant to the investigation of the chemical reactivity in this work. For more detailed discussions the reader is referred to available reviews.[21,22]

In Fukui's concepts of frontier orbitals,[23] the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, are of vital importance to the modern chemical reactivity theory. They were initially introduced in the context

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10.1021/jp052245+ CCC: $30.25

of Hartree−Fock theory. However, they have found a deeper theoretical framework in the context of density functional theory[24] thanks to the Parr and Yang[25] definition of the Fukui function as

$$f(\vec{r}) = \left[\frac{\delta\mu}{\delta v(\vec{r})}\right]_N \tag{1}$$

where μ is the electronic chemical potential and $v(\vec{r})$ is the external potential. The functional derivative must be taken at a constant number of electrons N. It has been shown[25] that, in a first approximation, the Fukui function is equal to the square of the respective frontier orbital, the HOMO when the derivative is taken from the left, f^-, and the LUMO when the derivative is taken from the right, f^+. Moreover, in the Kohn−Sham scheme, one can define the Kohn−Sham Fukui function as[26]

$$f(\vec{r}) = \left[\frac{\delta\mu}{\delta v_{\mathrm{ks}}(\vec{r})}\right]_N \tag{2}$$

where $v_{\mathrm{ks}}(\vec{r})$ is the effective Kohn−Sham potential. The importance of this new definition is that this derivative is exactly equal to the respective frontier orbital. Hence, in the Kohn−Sham scheme

$$f^{\alpha}(\vec{r}) = |\phi^{\alpha}(\vec{r})|^2 \tag{3}$$

where ϕ^{α} is the frontier orbital (α = HOMO or LUMO), is an exact equation, and the so defined Fukui function is a positive definite function which normalizes to unity.[21,22,27] Therefore, in this work, the last equation has been used to calculate the Fukui function.

From a practical point of view, it is easier to work with the condensed version of the Fukui function, and there are various forms to do it. However, the condensed Fukui function based on some population analysis[27] introduces two problems. One is that the values can be negative,[27,29] which complicates the interpretation, and the other is that the results are highly dependent on the basis set.[29]

One way to avoid the use of any population analysis method is to do a numerical integration of the Fukui function over an a priori defined region of the space Ω_{k}. Hence, the whole space is divided into various regions $\{\Omega_{\mathrm{k}}\}$, and the condensed Fukui function in region k will be

$$f_{\mathrm{k}}^{\alpha} = \int_{\Omega_{\mathrm{k}}} f_{\mathrm{k}}^{\alpha}(\vec{r})\,\mathrm{d}\vec{r} \tag{4}$$

In a previous work[30] it has been shown that a partition of the space according to the topological analysis of the Fukui function itself yields good results. It has been shown that the Fukui function presents basins associated to one atom and, in some cases, basins associated to a bond. The last characteristic is not present in almost all other methodologies to condense the Fukui function.[21,22] Note also that, in general, the Fukui function yields only information about the intramolecular site selectivity. It does contain information about the intramolecular reactivity or about the bond forming process. For the first point, the softness should be used and for the second one, the HOMO. Recently, an interesting extension using the concept of a reactive orbital has been proposed.[31]

In this work, the calculations were carried out at the density functional theory (DFT/BLYP) level. For copper, the effective core potential of the Los Alamos National Laboratory (LANL) set[32] together with the double-ξ type basis set (LANL2DZ) were used. To improve the performance of the pseudopotential the basis set was augmented with s, p, and d diffuse functions. For oxygen atoms the basis set was augmented with s and p diffuse functions. One test of the validity of the chosen geometry of the system is the prediction of the vertical detachment energy (VDE). Hence we calculated for each of the anion clusters the VDE in a single run by using the electron propagator calculation of the outer valence Green's function approximation (OVGF).[33,34] All calculations were performed using the Gaussian-98 programs,[35] without any symmetry constraints. The condensed Fukui function was evaluated using a modified version of the program Top-Mod.[36]

TABLE 1: Comparison of Bond Lengths (in Å), Frequencies (cm^{-1}), and Dissociation Energies (in eV) between the Calculated and the Experimental Data (in parentheses) of the Ground State of Cu_2 (neutral and anionic) Clusters

structures	bond lengths	frequencies	*Do*
Cu_2	2.257(2.22)[a]	263.2(265.0)[a]	2.1(2.08)[b]
Cu_2^-	2.38(2.35)[a]	196.3(210 ± 15)[a]	1.7(1.64 ± 0.15)[c]

[a] From ref 3. [b] From ref 40. [c] From ref 41.

Results and Discussions

A. Bare Copper Clusters. The electronic structure of transition-metal clusters is very complicated, and a reliable study from the first principles is computationally rather demanding. Currently, the density functional theory techniques, combined with relativistic effective core potentials, seem to be the most practicable tool to deal with these metal clusters. To calibrate the reliability of this approach, we calculated spectroscopic parameters of Cu_2 and its anion using the BLYP functional. Table 1 shows that the calculated results are in good agreement with experimental values.[3,37,38] The most stable structures located by BLYP for neutral, anion, and cation copper clusters are displayed in Figure 1. Vibrational frequency analysis shows that all structures are stable on potential energy surfaces. The ground-state geometry of the neutral Cu_n (n = 1−6) is planar, similar to the corresponding alkali and Au clusters. Also the charged small Cu clusters have planar ground-state geometries with the exception of the cation pentamer and the anion hexamer, which are trigonal bipyramidal and square bypiramidal, respectively. For Cu_7 clusters, cation, neutral, and anion, we found that the most stable structures are three-dimensional structures and the geometry is independent of the cluster charge. Jahn Teller distortions, which reduce the energy of the system, are responsible for the geometric changes in Cu_3^-, Cu_5^+, and Cu_6^- with respect to the neutral ones. The calculated geometric parameters (see Figure 1), electronic state, and symmetry are in agreement with both experimental and theoretical studies.[38−46] In general, the bond lengths of the neutral clusters are shorter than the corresponding bond in the cation and anion cluster.

Analysis of the variation of the binding energies with the size of the neutral clusters is presented in Table 2. The binding energies (*Do*) have been calculated as $Do = (E(\mathrm{Cu}_n) - nE(\mathrm{Cu}))$. The results, in eV, are compared in Table 2 with the experimental values. Experimental data of the binding energies of the neutral cluster were derived from the dissociation energy data of anionic clusters from the threshold collision induced dissociation experiments (TCID).[39] The inset shows that our calculated binding energies are in good agreement with the experimental data. On the other hand, note that *Do* increases rapidly with the size of the clusters.

The results obtained for the vertical (cation and anion have the neutral geometry) ionization potentials (IP) and electron affinity (EA) as well as the adiabatic (optimal geometries for

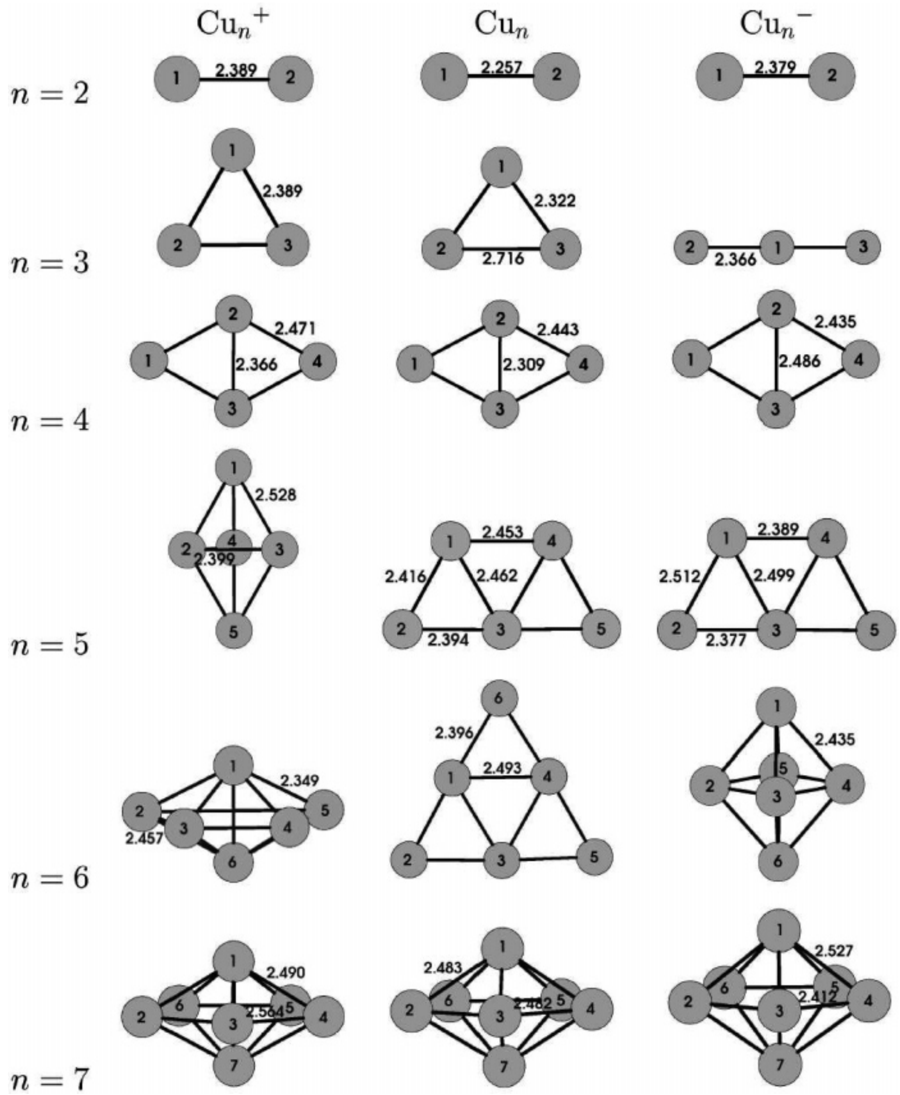

Figure 1. Optimized ground-state geometries of cationic, neutral, and anionic copper clusters. Indicated distances in angstroms.

TABLE 2: Binding Energy (*Do*) in eV of Cu_n^- ($n = 1-7$) Clusters in Their Calculated Ground States and Experimental Data

Do	Cu	Cu_2	Cu_3	Cu_4	Cu_5	Cu_6	Cu_7
calculated		2.14	3.23	5.58	7.5	10.08	12.11
experimental		2.04	3.19	5.91	7.76	10.32	12.98

neutral, cation, and anion) IP and EA are shown in Figure 2. The difference between the vertical and adiabatic IP and EA is greater in the cases were a structural change is involved. The data shows that the evolution of the electronic properties of the clusters follows even−odd alternations. This behavior is in agreement with the experimental and theoretical studies.[3,9,47] The even−odd alternation in IP and EA has been explained based on the electronic cluster structures. In the case of clusters with an even number of atoms, all electrons are paired, giving a closed shell electronic structure and spin pairing, with the highest energy gap as can be seen presented in Figure 2c. In contrast, all odd-numbered clusters have a very small band gap with the HOMO occupied by a single electron. Therefore, it is much more difficult to ionize the even-numbered clusters than the odd ones but much easier to attach an electron to the odd clusters than the even ones.

Similar tendency is observed for the VDE for Cu_n^- ($n = 1$, 2, 3, 4, 5, and 7) clusters, presented in Figure 3a which are in good agreement with experimental values.[9]

Figures 2c and 3b show the behavior of the energy gap for the neutral and anionic clusters obtained using the frontier orbital energies, gap $= (E_H - E_L)$ while E_H and E_L are the energies of the HOMO and the LUMO, respectively. The energy gap can be seen as a charge transfer. Therefore, we expect the cluster with even n to present maximum values of energy gap, and these systems are not able to transfer an electron to other systems. On the other hand, we observed the same patterns as in IP and EA vs cluster size and even−odd alternations due to the same reason discussed above.

B. Interaction of Copper Clusters with Molecular Oxygen. It has been proposed in the literature[10] that oxygen binding to a copper cluster involves electron donation from the HOMO of the cluster to the LUMO of oxygen molecule. For this reason, to predict the localization of the binding site in the clusters we have evaluated the local donor reactivity of the neutral and anion copper clusters using the condensed Fukui function, f_{Ff}^{-}, in regions associated with the basins of the frontier orbital. These results are shown in the Figures 4 and 5. The numbers in the figures are the f_{Ff}^{-} values. In each cluster, the regions of higher values of f_{Ff}^{-} are assigned as active regions for the reaction with oxygen, and the region of lower values of the f_{Ff}^{-} are assigned as inactive regions. For example, for the neutral Cu_4, atoms 1 and 4 in f_{Ff}^{-} represented in Figure 4 are active regions and 2 and 3 are inactive regions.

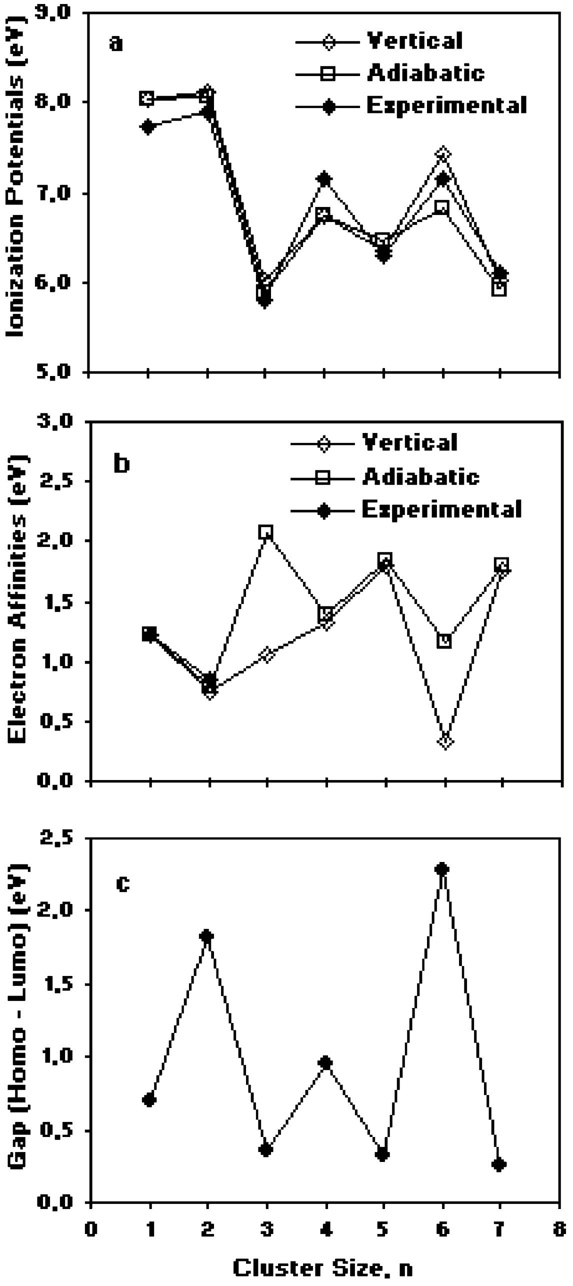

Figure 2. (a) Calculated ionization potential (IP) of Cu_n clusters, (b) electron affinity (EA), and (c) gap (HOMO−LUMO).

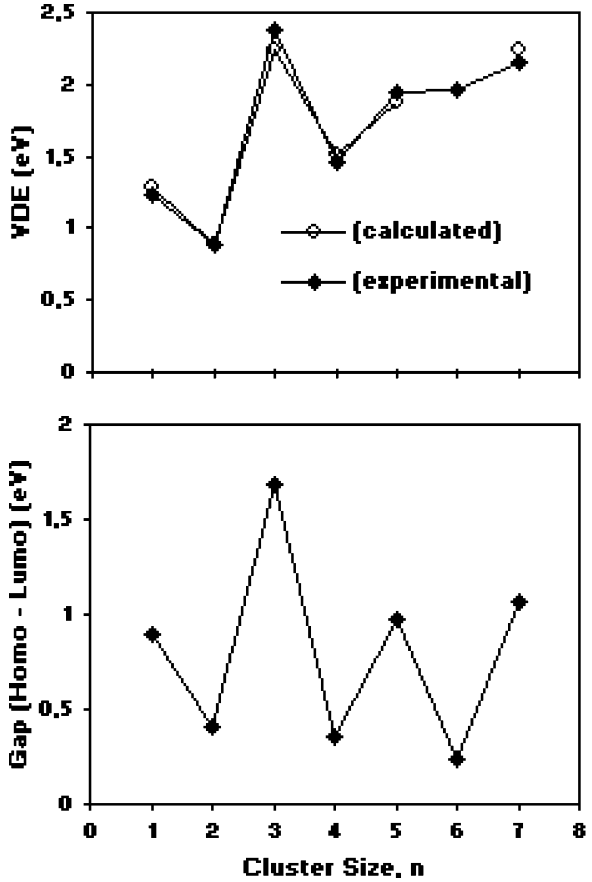

Figure 3. (a) Calculated vertical detachment energies (VDE) of Cu_n^- clusters and (b) gap (HOMO−LUMO).

TABLE 3: Calculated Energies for Interaction of O_2 with Cu_n ($n = 1-7$) Clusters

structures	$E_b(O_2)$ (eV)	R_{O-O} (Å)	ω (cm^{-1})	ground state
2	0.57	1.439	905.0	$^3A_2$
3a	2.39	1.435	913.0	$^2A_2$
3b	1.72	1.383	1028.0	$^2A''$
3c	1.93	1.428	971.4	$^2A_2$
4a	1.0	1.362	1073.2	$^3A''$
4b	0.46	1.337	1131.0	^3A
5a	2.30	1.449	898.5	$^2A''$
5b	1.23	1.365	1069.7	$^2A''$
6	0.47	1.335	1111.3	$^3A_2$
7	1.38	1.381	1024.0	^2A

To evaluate the accuracy of the method, we used a large number of initial positions of the oxygen molecule and determined their minima. We report here those corresponding to the lowest energy. We calculated the binding energies of the oxygen molecule to Cu_n and Cu_n^- and the length of the O−O bond and determined the spin state having the lowest energy. The results for neutral copper clusters are shown in Table 3 and Figure 6, and the results for the anion copper cluster are shown in Table 4 and Figure 7. The binding energies of molecular oxygen to the copper clusters were determined from $E_b = E(Cu_n) + E(O_2) - E(Cu_nO_2)$, the oxygen molecule in the triplet state. The binding energies of the oxygen molecules to the negatively charged copper clusters were determined in the same way.

It is encouraging to see that the condensed Fukui function is able to predict the site where the oxygen molecule prefers to bind. The most favorable oxygen cluster interaction always occurs at the site where the Fukui function present the highest value. The only possible exception is the interaction of O_2 with Cu_4^-, because in this case there is a drastic change in the geometry of the cluster which goes from a rhombus planar geometry to a tetrahedron.

Tables 3 and 4 show the following trend: Clusters with an odd number of electrons adsorb O_2 more strongly than those with an even number of electrons. The O−O bond is longer when the molecule is bound to a cluster having an odd number of electrons than when it is bound to a cluster with an even number of electrons. For neutral clusters, the binding energy to oxygen, $E_b(O_2)$, is predicted to exhibit strong odd−even oscillations, with the value of $E_b(O_2)$ being 1.0−1.8 eV higher for odd-numbered clusters. The stronger binding in the odd-numbered cluster is accompanied by activation of the O−O bond length to about 1.4 Å; also the O−O bond elongation leads to a drastic lowering of the O−O frequency, involving charge transfer to the empty $2\pi^*$ orbitals. For anion clusters, we found that the aforementioned even−odd relationship of the O_2 adsorption is much less pronounced than that for the neutral

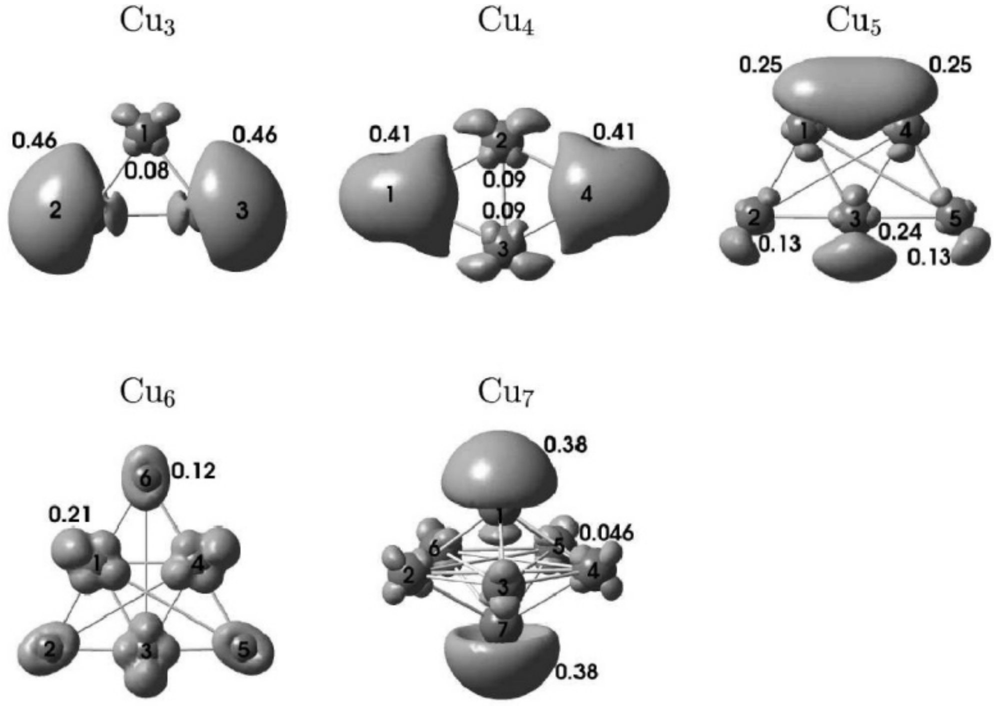

Figure 4. Donor Fukui function f^-_{Ff} of the neutral clusters.

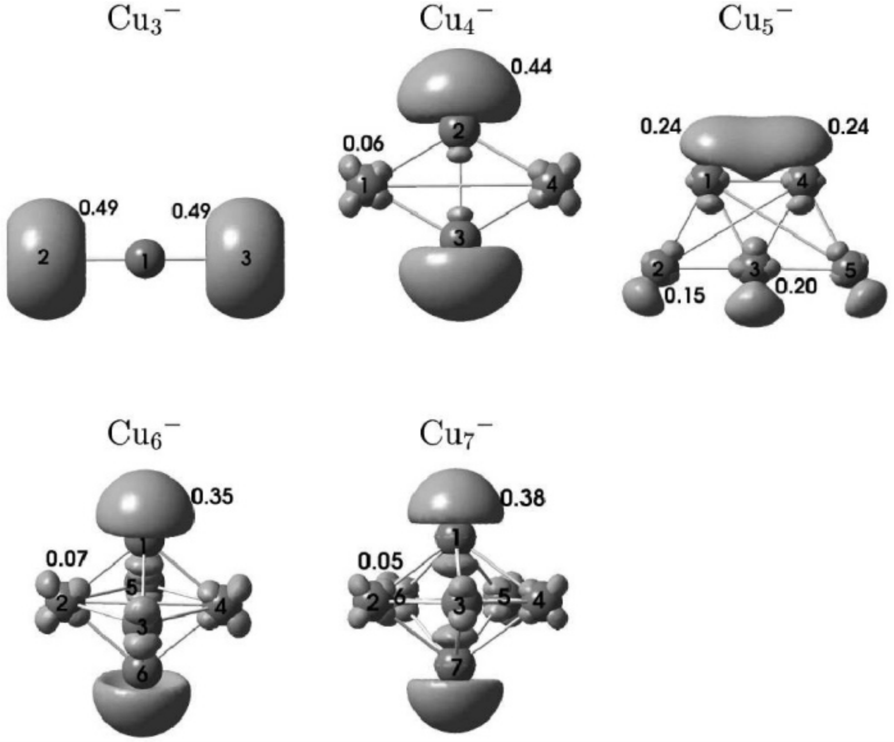

Figure 5. Donor Fukui function f^-_{Ff} of the anion clusters.

copper cluster (see Figure 8.). Not only even-numbered but also odd-numbered Cu anions exhibit significantly high reactivities toward O_2 adsorption.Our results show a very good agreement with the experimental data.[4] For example, oxygen does not bind to the cluster Cu_3^-, because it has a high band gap value (Figure 3c), which is similar to the behavior found for the Au_3^- oxygen interaction.[48] The even/odd tendency for the reaction of the neutral copper cluster with molecular oxygen may be understood in terms of the frontier orbitals of the clusters and molecular oxygen. The degenerate $2\pi^*$ antibonding orbitals of oxygen each have an unpaired electron. Oxidative addition to the cluster requires interaction of an O_2 π^* orbital with the HOMO of the cluster. In the case of odd n clusters, the HOMO has an unpaired electron. Pairing this electron with the unpaired electron in an O_2 π^* orbital in the bonding combination of the two orbitals results in an attractive interaction. For even n clusters, the HOMO is doubly occupied, and the interaction with O_2 π^* is much less attractive because the additional electron must be placed in the antibonding orbital of the complex. As a result, the even clusters either are completely unreactive or else require a costly electron promotion in the cluster before reaction can occur. It is known that the reactions of neutral copper clusters

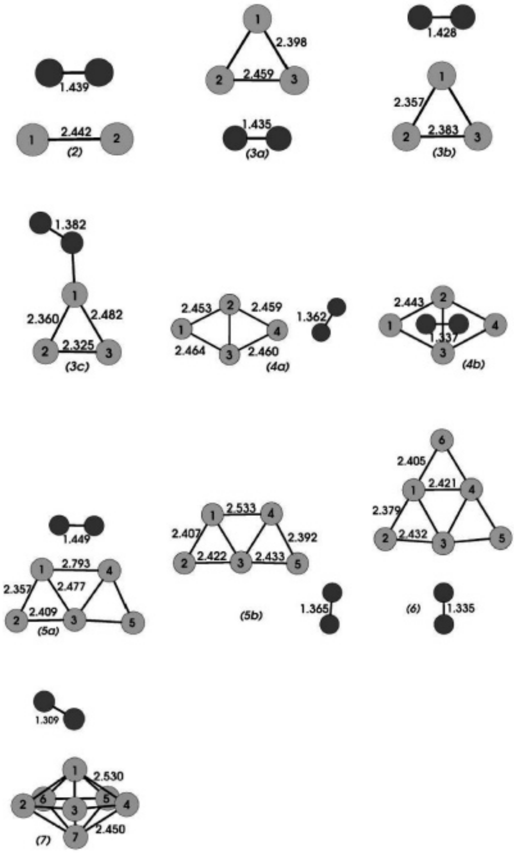

Figure 6. Optimized structures of Cu_nO_2, ($n = 1-7$). The bond lengths are given in angstroms.

TABLE 4: Calculated Energies for Interaction of O_2 with Cu_n^- ($n = 1-7$) Clusters

structures	$E_b(O_2)$ (eV)	R_{O-O} (Å)	ω (cm^{-1})	ground state
2	1.6	1.594	635.2	$^2A'$
3	−2.23	1.398	986.1	$^3A''$
4a	1.88	1.556	679.2	^2A
4b	1.82	1.443	930.9	$^2A'$
4c	1.29	1.536	790.8	$^2A_1$
5a	2.40	1.584	657.1	^1A
5b	1.70	1.398	994.03	$^3A''$
6	1.78	1.369	991.4	$^2A''$
7	1.34	1.393	993.9	^3A

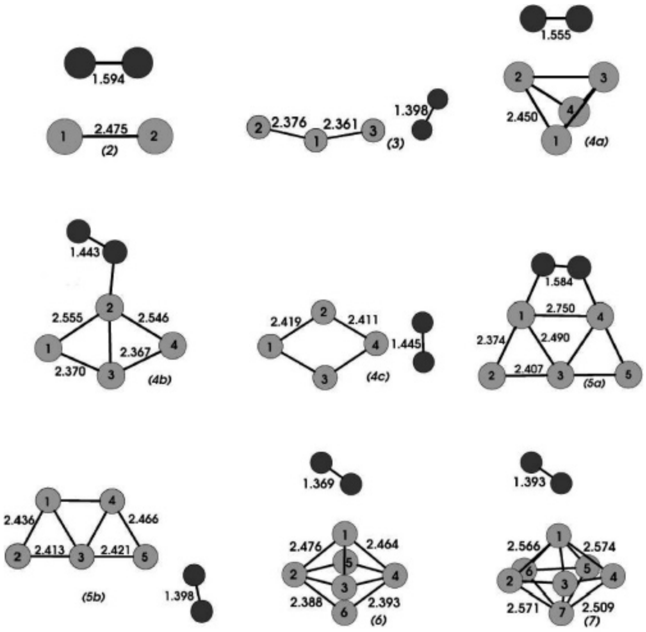

Figure 7. Optimized structures of $Cu_n^-O_2$, ($n = 1-7$). The bond lengths are given in angstroms.

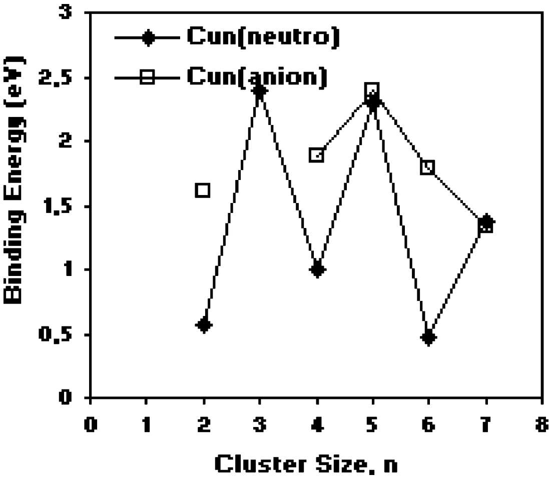

Figure 8. Binding energy of an oxygen molecule to copper clusters neutral and anions.

with odd n occur by dissociative chemisorption promoted by electron transfer from the metal cluster to the O_2 π^* orbital, which weakens the O−O bond. The electron transfer is promoted by low cluster ionization potentials for neutral clusters.

It can be concluded from binding energies presented in Tables 3 and 4 that in the case of several different stable binding configurations for O_2 on Cu_n and Cu_n^- the condensed Fukui function, f^-_{Ff}, suggests the better binding site.

In general, the oxygen adsorption changes substantially the structure of the cluster. This geometry change may be understood qualitatively as evidence that the O_2 molecule acts as a charge acceptor.

Concluding Remarks

In the reaction of molecular oxygen with copper clusters, dramatic even/odd alternations in reactivity were observed. These variations in reactivity can be understood by examining the molecular orbitals involved in the reactions. Molecular oxygen interacts with the HOMO orbital of the cluster through the unpaired electron in an O_2 π^* antibonding orbital. This interaction is attractive for odd n clusters with an unpaired electron in the HOMO but is unfavorable for even n numbered clusters.

It has been shown that the recently proposed condensation of the Fukui function is able to predict the site where the oxygen molecule prefers to bind. The most favorable oxygen cluster interaction always occurs at the site where the Fukui function presents the highest value.

Acknowledgment. The authors acknowledge the financial support received from the University of Antioquia under the project Sostenibilidad 2005. E.F. thanks COLCIENCIAS and University of Antioquia for her Ph.D. scholarship. Part of this work has been supported through the Millenium Nucleus for Applied Quantum Mechanics and Computational Chemistry, project P02-004-F, and Fondecyt grant 1050294.

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