Density Functional Calculation of the Structure and Electronic Properties of Cu_nO_n ($n=1-4$) Clusters

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Abstract. We have performed *ab initio* Monte Carlo simulated annealing simulations and density functional theory calculations to study the structures and stabilities of copper oxide clusters, Cu_nO_n ($n=1-4$). We determined the lowest energy structures of neutral, positive and negatively charged copper oxide clusters using the B3LYP/LANL2DZ model chemistry. The geometries are found to undergo a structural change from two- to three-dimensions when $n = 4$ in the neutral clusters. We have investigated the size dependence of selected electronic properties of the binding energies, second differences of the energy, ionization potentials, electron affinities, and HOMO-LUMO gaps. We also have investigated fragmentation channels and charge distributions.

Keywords: Density functional theory, copper oxide clusters.

1 Introduction

Studies of clusters help understand the evolution of properties from isolated atoms to bulk matter as well as to probe the details of solvation. Recently, it has been found that metal oxide clusters contribute to health hazards [1, 2, 3, 4]. The high speed collision of clusters with solid surfaces can give rise to short-lived species at extreme temperature and pressures. It has been shown that these impact-heated clusters provide an environment in which chemical reactions can be induced. Energetic cluster impact also has the potential for technological application in the formation of particularly dense and coherent metal and semiconductor thin films. Metal oxide clusters formed during combustion react with many organic compounds. [5, 6] The practical uses of metal clusters are well known and include catalysis, nanomaterials, and composite materials.

Experimental [7, 8, 9, 10] and computational [11, 12, 13, 14] studies exist for some small copper oxide clusters (1-2 copper atoms.) Three isomers have been suggested as possible structures for CuO_2 [15]: bent CuOO (bent, C_s), linear OCuO , and C_{2v} OCuO . Evidence has been found both the bent CuOO [16, 17, 18, 19] and the linear OCuO [15, 20, 21]. Vibrational frequencies have been calculated [20] for CuO_3 , OCuO_2^- , and $\text{Cu}(\text{O}_3)^-$. Recently, the structures of CuO_4 , CuO_5 [22] and neutral and negatively charged CuO_6 [23] were determined using plane-wave density functional theory. In addition, Cu_2O_x ($x=1-4$) have been studied using

anion photoelectron spectroscopy and density functional calculations [24, 25]. In this paper, we investigate the electronic and geometric structures of neutral and charged copper oxide clusters $((\text{CuO})_n, n=1-4)$.

2 Method of Calculation

2.1 *Ab Initio* Monte Carlo Simulation

The study of atomic and molecular clusters is hindered by the existence of multiple isomers for a given size cluster. Without an *a priori* knowledge of the global energy minima, the use of computer simulation methods, such as simulated annealing, often allow the location of global minima. For this reason, we performed *ab initio* simulated annealing Monte Carlo (MC) simulations (using Gaussian 03 and homegrown scripts) [26] to locate stable geometric structures for these clusters. The simulations used multiple starting geometries for each cluster size. The temperature was decreased from 2000 K to 300 K over a period of up to 500 MC steps. We used the B3LYP (Becke's 3-parameter exchange functional with Lee-Yang-Parr correlation energy functional) [27, 28, 29] version of DFT to calculate the energy.

2.2 Basis Sets

We evaluated several basis sets as candidates for our studies. These were 6-31G** [30, 31, 32], 6-31++G** [33, 30, 34, 35, 36, 37], 6-311G** [36, 38, 39, 40], 6-311++G** [35, 41], LANL2DZ [42, 43, 44], and DGDZVP [45, 46]. MC simulations were followed by standard geometry optimization using [47]. Calculations found the lowest energy clusters for Cu_2O_n ($n = 1 - 4$) shown in Fig. 1. For Cu_2O_3 and Cu_2O_4 , different isomers were found depending on basis set (Cu_2O_3 -a: 6-31G**; Cu_2O_3 -b: 6-31++G**, 6-311G**, 6-311++G**, LANL2DZ and DGDZVP; Cu_2O_4 -a: 6-31++G**, 6-311++G**, LANL2DZ and DGDZVP; Cu_2O_4 -b: 6-31G** and 6-311G** .) Experimental data of electron affinities of Cu_2O to Cu_2O_4 clusters is available [48]. A comparison of calculated and measured electron affinities are shown in Table 1. The best agreement with experimental data is found with the LANL2DZ basis set, which is therefore used in the remainder of this work.

Table 1. Electron affinity comparing basis sets with experimental data

	Electron Affinities (eV)					
	6-31G**	6-31++G**	6-311G**	6-311++G**	LANL2DZ	DGDZVP
Cu_2O	0.94	1.27	0.14	1.24	1.15	1.15
Cu_2O_2	1.41	2.33	0.89	1.76	2.41	2.24
Cu_2O_3	2.35	2.65	1.67	3.09	3.25	3.08
Cu_2O_4	3.26	3.34	2.75	3.35	3.54	3.31

EXP [48]

Fig. 1. Lowest energy clusters for Cu_2O_n , $n = 1 - 4$. Different basis sets give different lowest energy isomers for $n = 3$ and 4 (Cu_2O_3 -a: 6-31G**;
 Cu_2O_3 -b: 6-31++G**, 6-311G**, 6-311++G**, LANL2DZ and DGDZVP; Cu_2O_4 -a: 6-31++G**, 6-311++G**, LANL2DZ and DGDZVP; Cu_2O_4 -b: 6-31G** and 6-311G**) (see Table 1 for details.) White atoms are coppers and black atoms are oxygens.

3 Results and Discussion

3.1 Geometric Structure

The optimized structures of neutral, positive and negatively charged $(\text{CuO})_n$ clusters with $n=1-4$ are shown in Fig. 2. The low-lying spin states (i.e., singlet, doublet, triplet, and quartet) of a given cluster were considered in the calculations. Every neutral copper oxide cluster, $(\text{CuO})_n$, can be made from $\text{Cu}_{n-1}\text{O}_{n-1}$ cluster by attaching a Cu-O molecule to the side of $\text{Cu}_{n-1}\text{O}_{n-1}$ cluster.

In CuO, the Cu-O distances are 1.76Å(cation), 1.76Å(neutral) and 1.74Å(anion). Our calculated value of neutral Cu-O distance is in good agreement experimental value of 1.73 Å. [49] The spin states of optimized structures

Fig. 2. Optimized structures of neutral, positively, and negatively charged $(\text{CuO})_n$ clusters with $n=1-4$. White atoms are coppers and black atoms are oxygens.

are doublet, singlet and singlet for the neutral, cation and anion clusters, respectively. The structure of the lowest energy Cu_2O_2 cluster is rhombus in our simulations and calculations. The spin states of optimized structures are singlet, doublet, and doublet for the neutral, cation and anion clusters, respectively. Wang et al. [24] and Dai et al. [25] have suggested minimum energy structures for Cu_2O_2 . Wang, et. al., suggest the structure is a rhombus while Dai, et. al, suggest the structure is linear or near linear. The Cu-O bond length of Cu_2O_2 structure found by Wang et al. is 1.78Å and the angle of Cu-O-Cu of Cu_2O_2 structure is 80°. Our Cu-O bond lengths are 2.01Å(cation), 1.86Å(neutral) and 1.92Å(anion) and average angle Cu-O-Cu of Cu_2O_2 structure is 81.2°. The Cu-O-Cu bond angles are 135°(cation), 82°(neutral), and 75°(anion). Cu_3O_3 clusters have nearly planar structures. The neutral cluster is a quartet while the charged clusters have triplet ground states. The average Cu-O-Cu bond angles are 121.8°(cation), 98.1°(neutral), and 94.2°(anion). The Cu-O-Cu bond angles are smaller than the O-Cu-O bond angles while the CuO are shorter than found in the Cu_2O_2 clusters. Our Cu-O bond lengths are 1.89Å(cation), 1.90Å(neutral) and 1.85Å(anion). The Cu_4O_4 cluster is the first nonplanar structure found for Cu_nO_n and consists of 2 copper atoms above and below the plane of a Cu_2O_4 unit. A similar structure is found for the cation cluster, while the anion cluster is planar. The spin states of optimized structures are triplet (neutral) and doublet (cation and anion.) Our Cu-O bond lengths are 1.92Å(cation), 1.94Å(neutral) and 1.81Å(anion).

3.2 Binding Energies, Ionization Potential, Electron Affinities

The binding energies per atom have been calculated from

$$E_b = [n E(\text{Cu}) + n E(\text{O}) - E(\text{Cu}_n\text{O}_n)] / 2n \quad (1)$$

Table 2. Bond lengths (Å) of Cu-O in $(\text{CuO})_n$ (n=1-4) clusters

Clusters		d_{1-2}			
CuO	CuO	$d_{1-2}=1.81$			
	CuO^+	$d_{1-2}=1.76$			
	CuO^-	$d_{1-2}=1.74$			
Cu_2O_2	Cu_2O_2	$d_{1-3}=1.86$	$d_{1-4}=1.86$	$d_{2-3}=1.86$	$d_{2-4}=1.86$
	Cu_2O_2^+	$d_{1-3}=2.01$	$d_{1-4}=2.01$	$d_{2-3}=2.01$	$d_{2-4}=2.01$
	Cu_2O_2^-	$d_{1-3}=1.92$	$d_{1-4}=1.92$	$d_{2-3}=1.92$	$d_{2-4}=1.92$
Cu_3O_3	Cu_3O_3	$d_{1-4}=1.83$	$d_{1-6}=2.06$	$d_{2-4}=1.81$	$d_{2-5}=1.83$
	Cu_3O_3^+	$d_{1-4}=1.75$	$d_{1-6}=1.77$	$d_{2-4}=1.78$	$d_{2-5}=2.13$
	Cu_3O_3^-	$d_{1-4}=1.84$	$d_{1-6}=1.85$	$d_{2-4}=1.85$	$d_{2-5}=1.85$
Cu_4O_4	Cu_4O_4	$d_{1-5}=1.96$	$d_{1-6}=1.97$	$d_{2-6}=1.88$	$d_{2-7}=1.93$
		$d_{3-5}=1.88$	$d_{3-8}=1.93$	$d_{4-5}=1.97$	$d_{4-6}=1.96$
	Cu_4O_4^+	$d_{1-5}=1.94$	$d_{1-6}=1.93$	$d_{2-6}=1.88$	$d_{2-7}=1.94$
		$d_{3-5}=1.87$	$d_{3-8}=1.93$	$d_{4-5}=1.92$	$d_{4-6}=1.95$
	Cu_4O_4^-	$d_{1-5}=1.81$	$d_{1-8}=1.81$	$d_{2-5}=1.80$	$d_{2-6}=1.79$
		$d_{3-6}=1.81$	$d_{3-7}=1.83$	$d_{4-7}=1.80$	$d_{4-8}=1.80$

Table 3. Spin states, ionization energies (IE), electron affinities (EA), and binding energies (E_b) for Cu_nO_n , $n = 1 - 4$. Energies are in electron volts and are calculated using the B3LYP/LANL2DZ model chemistry.

	Spin State	IE	EA	E_b
CuO	doublet			
CuO^+	singlet	12.25	1.35	1.22
CuO^-	singlet			
Cu_2O_2	singlet			
Cu_2O_2^+	doublet	8.24	2.35	1.85
Cu_2O_2^-	doublet			
Cu_3O_3	quartet			
Cu_3O_3^+	triplet	9.36	3.65	2.19
Cu_3O_3^-	triplet			
Cu_4O_4	triplet			
Cu_4O_4^+	doublet	8.37	3.40	2.35
Cu_4O_4^-	doublet			

Figure 3 shows the binding energy per atom, E_b , as a function of number of copper atoms in the cluster. There is a rapid increase from a binding energy of 1.24 eV ($n = 1$) to 2.22 eV ($n = 3$.) The $n = 4$ cluster has a similar binding energy to the $n = 3$ cluster, though not close to the bulk work function of >5 eV. Thus studies of larger clusters are necessary to more closely examine the size evolution of the properties of these clusters.

Fig. 3. Binding energies of neutral $(\text{CuO})_n$ clusters with $n=1-4$

Fig. 4. Calculated adiabatic ionization potential and electron affinities of $(\text{CuO})_n$ clusters with $n=1-4$

Fig. 5. Calculated HOMO-LUMO gap of $(\text{CuO})_n$ clusters with $n=1-4$

Table 4. Fragmentation channels of $(\text{CuO})_n$ clusters with $n=1-4$. Energies are in kcal/mol.

	ΔE
$(\text{CuO})_2 \rightarrow \text{CuO} + \text{CuO}$	57.91
$(\text{CuO})_3 \rightarrow \text{Cu}_2\text{O}_2 + \text{CuO}$	75.90
$(\text{CuO})_4 \rightarrow \text{Cu}_3\text{O}_3 + \text{CuO}$	75.56
$\rightarrow \text{Cu}_2\text{O}_2 + \text{Cu}_2\text{O}_2$	93.55

Fig. 4 shows the adiabatic ionization potentials ($\text{IP}(\text{X}_n)=\text{E}(\text{X}_n^+)-\text{E}(\text{X}_n)$) and electron affinities ($\text{EA}(\text{X}_n)=\text{E}(\text{X}_n)-\text{E}(\text{X}_n^-)$). These properties display the even-odd oscillation often seen in clusters. The HOMO-LUMO gaps in these clusters are shown in Fig. 5.

3.3 Fragmentation Channels

We have also calculated the fragmentation energies of $(\text{CuO})_n$ ($n=1-4$) clusters for various dissociation pathways. The fragmentation channels of $(\text{CuO})_n$ clusters are shown in Table 4. The fragmentation energy of Cu_2O_2 cluster requires the least amount of energy to fragment and the lowest energy pathway for all clusters is to lose a single CuO group.

4 Conclusions

The electronic and structural properties of small copper oxide clusters have been studied using density functional theory and several basis sets. Comparison with existing experimental work demonstrated that the LANL2DZ basis set is in best agreement and therefore was used study study Cu_nO_n clusters. It was found that the clusters are planar for up to $n = 3$ and then become nonplanar. Ionization energies, electron affinities, and binding energies demonstrate some oscillations with cluster size, as is typical for clusters. Larger clusters must be studied in order to explore the approach to bulk properties.

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