Chemistry Research Journal, 2018, 3(2):22-25

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Density functional theory study of Cu_4N and Cu_8N clusters

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Abstract Cu_4N and Cu_8N clusters are investigated using density functional theory methods. Optimized geometries are obtained using the conjugate gradient scheme and three symmetries were obtained T_d C_{4v} and C_{3v} for Cu_4N and Cu_8N respectively, employing the Martin-troullier pseudopotential. Also, in this article, the densities of state and charge transfer were investigated. It seems that for both clusters, the charge was transferred to 2p orbital of nitrogen atom with good agreement the available results.

Keywords Density functional theory, clusters, geometries, charge transfer

Introduction

Copper nitride forms the most accessible member of the family of noble metal nitrides and attracted much attention from researchers on experimental aspects. In experimental view, the facile decomposition of this compound, though absolutely troublesome for film growth practitioners, promises many innovative applications such as fabrication of optical storage devices [1–3] and microscopic metal links [4,5].

In other research areas, metallic clusters having a few nitrogen atom in the nitride form are also relevant for catalytic purposes [6,7,8,9]. Recently [10], a series of nitrogen-bearing copper clusters anions have been synthesized and characterized. All those clusters play important roles in the catalytic processes.

On computational side, there are not theoretical works done to simulate different physical properties. Recently, there is a new work done by J.G. Han *et al* [11] studying the electronic and geometry configurations of $Cu_nN^{0,\pm 1}$ (n=1-4). This paper constitutes a unique reference for CuN clusters investigation.

The present paper involves with a computational study of Cu_4N and Cu_8N clusters using DFT framework. It includes the determination of clusters equilibrium geometries and the calculation of their total energy, natural and Mulliken electronic configuration and density of states.

Computational method

Our calculations were performed using the SIESTA (12-14) package, which implement DFT with the pseudopotential approximation and a basis set of linear combination of atomic orbital. We used the generalized gradient approximation (GGA) for the exchange-correlation functional parameterized by Perdew, Burke and Ernzerhof [15]. The pseudopotentials were constructed using the Troullier and Martin scheme [16] to describe the valence electron interaction with the atomic core.

The atomic-orbital basis set employed throughout was a split-valence double zeta polarized basis for copper atom (Cu) and simple zeta for nitrogen (N).The charge density was calculated in a regular real-space grid with a cutoff energy of 120 Ry. Structural optimisations were performed for all configuration using the conjugate gradient (CG)

algorithm until the residual forces were smaller than 0.04 eV/Å. We used periodic boundary conditions and a supercell greater than 20^3 Å to make sure that there was no additional interaction between image clusters.

Results and Discussion

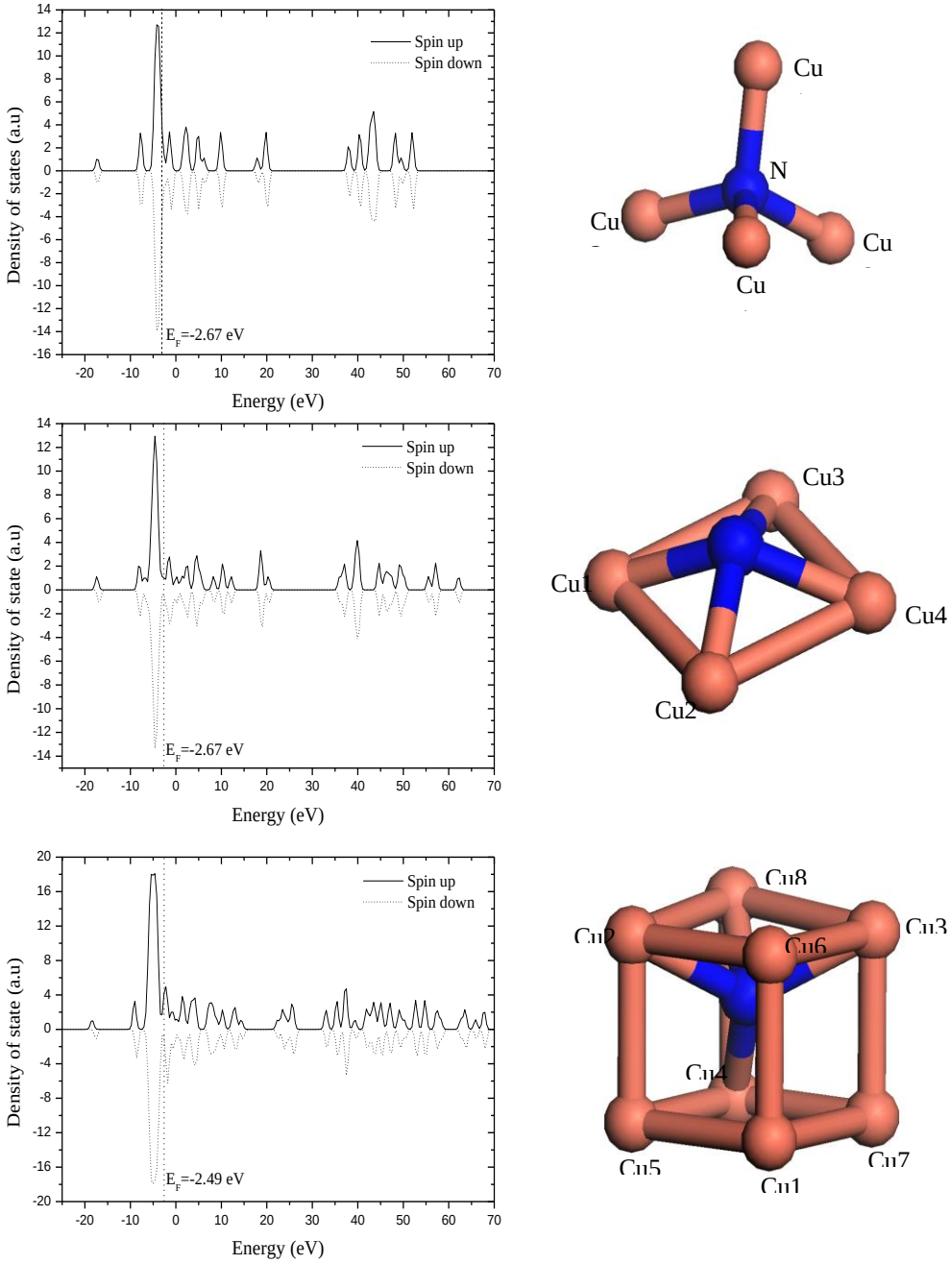

Figure 1: Density of states and optimized geometries of Cu4N and Cu8N clusters

On figure 1, right side the optimized geometry configuration of Cu_4N and Cu_8N clusters were represented. The two Different structures of Cu_4N exhibit two different symmetries, T_d and C_{4v}. The N atom in both cases is bonded to the four Cu atoms via sp3 hybridization. In T_d cluster, the N-Cu bond lengths are 1.870 and 1.877Å, in excellent

agreement with values obtained by J.G. Han *et al* [11]. Elsewhere, C_{4v} cluster optimization gave three different N-Cu bond lengths: 1.950, 1.952 and 1.954 Å, slightly longer than those of the first cluster. The four Cu-Cu bonds equal to 2.556 and form equilateral pyramidal base. The total energies (in eV) were mentioned on table 1. We see that C_{4v} cluster is more stable than its T_d counterpart.

Cu8N adopts the C_{3v} symmetry. The N atom is bonded to four Cu atoms. The bound length values are obtained: 2.001 and 1829 Å (see table 01). Cu atoms are bonded forming an irregular cube with mean three length sides: 2.444, 2.433 and 2.612 Å. The total energy equals -10038.59 eV. Comparatively with total energies of the first clusters (Cu_4N), Cu_8N cluster seems to be more stable.

Table 1: Geometry, symmetry, interatomic distances, total energy and fermi level of the Cu_nN(n=4,8) clusters (s.o.s.p: Second-Order Saddle Point).

Cluster	Symmetry	N-Cu1-8 (Å)	Cu-Cu (Å)	E_t(eV)	E_F (eV)
Cu4N	T_d	1.877		-5153.286300	-2.677
		1.870			
		1.870	s.o.s.p		
		1.870			
Cu4N-1	C_{4v}	1.950	2.556	-5153.712460	-2.678
		1.952			
		1.952			
		1.954			
Cu8N	C_{3v}	s.o.s.p	2.444	-10038.594674	-2.492
		2.001	2.433		
		2.001	2.612		
		2.001			
		s.o.s.p			
		s.o.s.p			
		s.o.s.p			
		1.829			

Also on figure 01, the densities of states were represented. T_d and C_{4v} clusters reveal the same shape of densities. The fermi levels are located at -2.677 and 2.678 eV, respectively. The most intense peak which represent in its major party the d orbital contribution of Cu atoms, locates below Fermi level line.

Calculated Mulliken and natural orbital population analysis charges along with orbital electron configurations are listed in table 2. It is important to note that orbital population analysis provide more accurate description for the charge distribution in a cluster than the Mulliken population analysis.

In T_d Cu_4N cluster, the natural orbital charges of the N and Cu atoms are 0.691, -0.168 and -0.170 respectively. In this molecule a global charge transfer occurs following this way: the electrons originally localized on 2s of N and 4s and 3d of Cu atoms have been transferred to 2p orbital of nitrogen atom and 4p of copper atoms. The occupation value of 2p is 3.969. This value is not reached in C_{4v} Cu_4N clusters. It equals 3.781 and those of 4p are more important (0.291). This situation can be explained by the fact that in C_{4v} cluster, Cu atoms are bonded and the Cu-Cu bound length is smaller that in T_d one. The same global results are reported by J.G. Han *et al* [11].

For Cu8N cluster, the natural orbital population for N and Cu atoms are 0.579, 0.031,-0.12, -0.028 and -0.170 respectively (see table 2).

The same transfer charge phenomenon is seen but less strongly. The nitrogen 2p orbital population takes 3.801 and the 4p orbital were populated respectively by 0.363, 0.388, 0.348 and 0.336 electron charges. These four values seem to be the most important compared to Cu_4N clusters and interpreted by the great number of Cu-Cu bonds.

Table 2: Mulliken and natural orbital population analysis charges, and natural orbital electronic configuration of Cu_nN (n=4,8) clusters.

Cluster configuration	Symmetry	Atom	Mulliken	Natural	Orbital electronic
Cu4N	T_d	N	0.014	0.691	$2s^{1.722}2p^{3.969}$
		Cu1	0.246	- 0.168	$4s^{0.841}3d^{9.748}4p^{0.243}$
		Cu(2-4)	0.247	- 0.170	$4s^{0.839}3d^{9.748}4p^{0.243}$
Cu4N-1	C_{4v}	N	0.371	0.577	$2s^{1.796}2p^{3.781}$
		Cu1	0.156	-0.145	$4s^{0.836}3d^{9.728}4p^{0.291}$
		Cu(2,3)	0.158	-0.140	$4s^{0.837}3d^{9.731}4p^{0.292}$
		Cu(4)	0.158	-0.139	$4s^{0.839}3d^{9.731}4p^{0.291}$
Cu8N	C_{3v}	N	0.699	0.579	$2s^{1.778}2p^{3.801}$
		Cu1	0.489	0.031	$4s^{0.948}3d^{9.720}4p^{0.363}$
		Cu2,3,4	0.205	-0.121	$4s^{0.775}3d^{9.716}4p^{0.388}$
		Cu5,6,7	0.156	-0.028	$4s^{0.892}3d^{9.732}4p^{0.348}$
		Cu8	0.058	-0.170	$4s^{0.804}3d^{9.690}4p^{0.336}$

Conclusion

This paper is devoted to study Cu_4N and Cu_8N clusters. Cu_4N cluster exhibits two symmetries: T_d and C_{4v}. N-Cu bonds length in T_d molecule is shorter than in C_{4v}. Both clusters exhibit he same fermi level. Cu_8N molecule reveals two different N-Cu distances: 2.001, 1.829 and show a C_{3v} symmetry. Total energies demonstrate that Cu_8N is more stable than Cu_4N ones. Also, charge transfer is mainly occurred to 3d and 4p orbital of Cu atom in good agreement with previous works.

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