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First principles study of the structures, electronic states and stabilities of Al_nCu ($n=2$–7) clusters

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Abstract

Various structural possibilities for Al_nCu neutral isomers were investigated using B3LYP/6-31+G(d) methods. Our calculations predicted the existence of a number of previously unknown isomers. Al_nCu ($n=2$–7) neutral clusters favor to form cage-like structures. The Cu atom prefers to locate outside of cage-like structures in this series. Atomization energies per atom for Al_nCu ($n=2$–7) have the same trend as the binding energies per atom for Al_n ($n=3$–8) clusters. The stabilization energy reveals that Al_3Cu and Al_6Cu are the relatively most stable structures in the Al_nCu ($n=2$–7) clusters.

Keywords: AlnCu clusters; Geometric configuration; Stability

1. Introduction

The discovery of fullerenes [1] and metcars [2] has inspired theorists to consider other unusually stable aggregates (magic clusters) that might serve as building blocks for cluster-assembled materials. If such exotic materials could be formed, they might well exhibit unique electronic, magnetic, optical, mechanical, and catalytic properties, and these could potentially lead to technological uses. While several types of magic clusters have now been considered by theory and experiment [3–5], doped aluminum clusters recur repeatedly as especially promising candidates. These fall into two relatively distinct categories, Al_nX, where X is a non-metal dopant such as B, C, N, As, or S, and MAl_n, where M is a metal atom. The newly discovered Al_4^-, heterocyclic XAl_4^- (X=Li, Na, Cu) and XAl_3^- (X=Si, Ge, Sn and Pb) [6,7] clusters have been confirmed to exhibit characteristics of aromatics in both experiments and theory.

A large number of binary clusters of aluminum with some metallic elements, including Co, Cu, Li, Na, etc. have been produced by laser vaporization of various aluminum targets in high vacuum [6–13]. Of these systems, the binding energies of Al_nCu ($n=2$–15) anions have been measured using photoelectron spectroscopy [9] (PES). However, the laboratory spectroscopy has not yet been explained due to the lack of the information of their geometrical and electronic structures. Up to now no systemic study of geometries and relative stabilities has been reported for Al_nCu ($n=2$–7) neutral and anionic clusters except Al_4Cu^-. Hence, it is of interest to carry on an investigation on the aluminum–copper neutral and anionic clusters to improve our comprehension of the photoelectron spectroscopy [9] and reveal the influence of the heroatoms on the geometrical structures of aluminum clusters. In this work, we performed density functional calculations up to eight atoms at the standard B3LYP/6-31+G(d) level.

The rest of the paper is organized as follows. In Section 2, we give a brief description of the computational method used in this work. Results, discussion and stability will be presented in Section 3 for Al_nCu isomers. Finally, we will summarize our conclusions in Section 4.

2. Computational methods

Initial geometrical optimizations were performed at the B3LYP/6-31G(d) level without any symmetry constraints,

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except for those needed to maintain a particular geometry. These minimized Al_nCu ($n=2$–7) structures were further optimized using B3LYP/6-31+G(d) method. Frequency analyses were also performed at the final theoretical level to check whether the optimized structures are transition states or true minima on the potential energy surfaces of corresponding cluster. All calculations were carried out using the GAUSSIAN03 program [14].

3. Theoretical results

3.1. Geometry

One can estimate the accuracy of the calculations by comparing the results of calculations on dimmers for which experiments exist. For $Al_2(^3\Pi_u)$, $Cu_2(^1\Sigma_+^g)$ and $AlCu(^1\Sigma_g^+)$ dimer, their equilibrium separations calculated are 2.7642, 2.2722 and 2.4134 Å, respectively. A comparison of our bond lengths and experimental values [15–17] shows their differences are 2.3, 2.2 and 3.2%, respectively. Our theoretical prediction for the ground state of Al_4Cu^- is a square pyramid (C_{4v},$^1A_1$), which agrees with the theoretical prediction of the higher level of theory and experimental observations [6]. These agreements of the present results with the available data are encouraging for the application to larger clusters. In order to keep the length of this paper under control, we only discuss the geometries corresponding to the three low-lying energy states.

The energetically low-lying geometric sketches of Al_nCu clusters containing up to seven Al atoms are shown in Figs. 1–3, respectively. The 'bonds' are shown for internuclear separations less than 3.1 Å (Al–Al) and 2.7–Å (Al–Cu), respectively. The copper atoms have been pointed out in Figs. 1–3. Geometric parameters are listed in Table 1.

3.1.1. Al_2Cu

The energetically most favorable structure is a triangle Al–Cu–Al (C_{2v},$^2B_1$) 1(a) with the $1a_2^2 1a_1^2 1b_2^2 2a_1^2 1b_1^1$ valence electronic configuration, whose bond angle of Al–Cu–Al

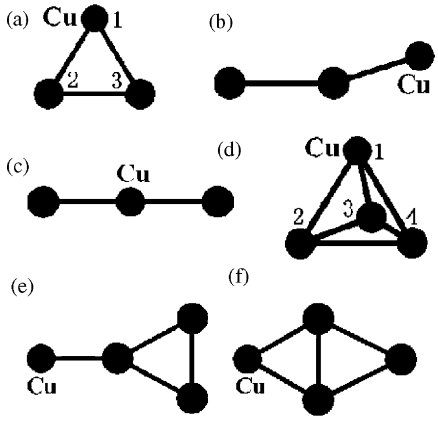

Fig. 1. Low-lying isomers of (a–c) Al_2Cu and (d–f) Al_3Cu clusters.

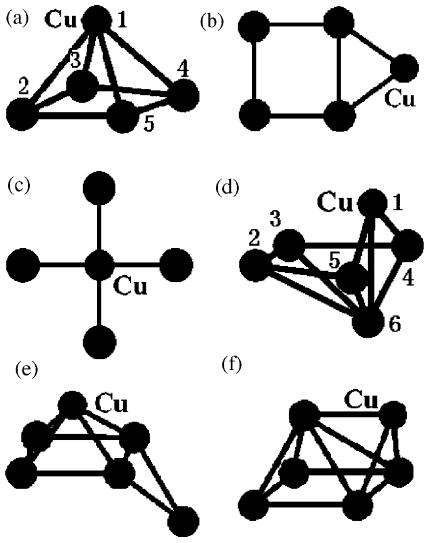

Fig. 2. Low-lying isomers of (a–c) Al_4Cu and (d–f) Al_5Cu clusters.

atoms is 62.94. This may be viewed as a substitution of an Al atom by a Cu atom in an Al_3 cluster [18]. This followed by a quasi-linear (C_s,$^2A'$) 1(b), lying 0.55 eV higher in energy. The linear ($D_{\infty h}$,$^4\Sigma$) 1(c), lying 1.88 eV higher in energy above the 1(a), has an imaginary bending mode frequency, which corresponds to a relative vibration of Cu atom along transverse direction that ultimately leads to forming the structure 1(a).

A comparison between neutral and anionic triangular species shows a little reduction of Al–Cu–Al bond angle and Cu–Al bond length in Al_2Cu^- (C_{2v},$^1A_1$). Additional electron occupies the anti-bonding lowest unoccupied

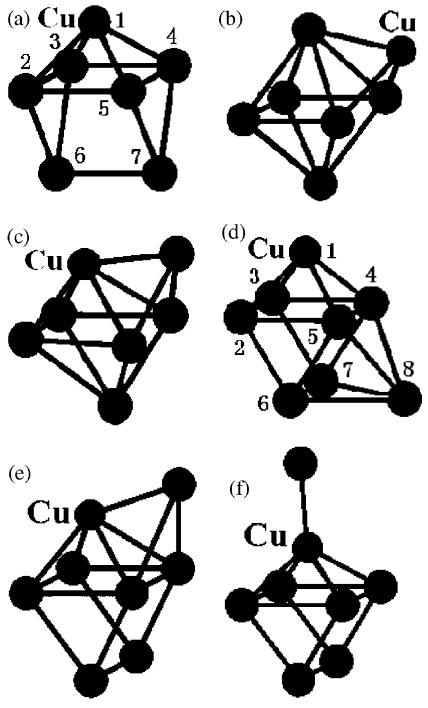

Fig. 3. Low-lying isomers of (a–c) Al_6Cu and (d–f) Al_7Cu clusters.