



Probing the geometric structures and bonding mechanisms of Cu–I hybrid clusters: $\text{Cu}_4\text{I}_4^{-/0}$

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ABSTRACT

We present a theoretical investigation on the geometric structures and bonding mechanisms in $\text{Cu}_4\text{I}_4^{-/0}$ clusters using density functional theory calculations. Different density functional methods (B3LYP, PBE, and BPW91) assign the relative energies to these isomers. The results showed that $\text{Cu}_4\text{I}_4^{-}$ anion has a C_{2h} symmetric planar structure with the four I atoms surrounding the Cu_4 rhombic framework, whereas Cu_4I_4 neutral adopts D_{2d} symmetric V-shaped structure. Bond length, Wiberg bond order, and molecular orbital analyses suggest that the Cu–I interactions in $\text{Cu}_4\text{I}_4^{-/0}$ are weak. Interestingly, $\text{Cu}_4\text{I}_4^{-}$ anion exhibits significant aromaticity.

1. Introduction

Luminescent materials based on Aggregation-Induced Emission (AIE) phenomenon have attracted considerable attentions in the past decades because of their unique light-emitting behaviors at the aggregated solid states [1–3]. To date, numerous investigations have been devoted to exploring new types of AIE luminescent materials, such as hydrocarbon AIE, heteroatom-containing AIE, macromolecular AIE, and metal-complex AIE luminescent materials [4–7]. Particularly, noble metal Au(I), Pt(II), Ag(I), and Ir(III) complexes with AIE effect have been investigated extensively [8–12]. Nevertheless, the corresponding uniform nanoparticles of most of metal-complex AIE luminescent materials were hard to be obtained due to their retained bulk solid states, resulting in significantly restricting their further applications as luminescent inks.

Cu–I based hybrid clusters have been extensively studied due to their excellent photoluminescent properties for optoelectronic applications [13,14]. Luminescent inorganic-organic Cu–I cluster based hybrids are considered as attractive candidates for synthesizing low cost and high quality luminescent AIE inks because the copper and iodine are non-toxic and abundant elements in comparison to noble metals. Recently, a series of Cu–I clusters based highly luminescent hybrids have been synthesized by facile solution routes [15,16], but no AIE phenomenon has been observed. Very recently, Chen et al. [17] have synthesized the highly luminescent inks by using the cubic Cu_4I_4 cluster as core in microemulsion droplets, which exhibit great potentials and superiority in practical applications including anti-fake

patterns, solid phosphor coatings, and light emitting layers in LEDs. However, the microscopic bonding mechanisms in Cu_4I_4 core have not been revealed. In this work, we investigated the geometric structures and bonding mechanisms in isolated $\text{Cu}_4\text{I}_4^{-/0}$ clusters using density functional theory calculations. Different density functional methods (B3LYP, PBE, and BPW91) assign the relative energies to these isomers [18,19]. The results showed that $\text{Cu}_4\text{I}_4^{-}$ anion has a C_{2h} symmetric planar structure with the four I atoms surrounding the Cu_4 rhombic framework and exhibits significant aromaticity, while Cu_4I_4 neutral adopts D_{2d} symmetric V-shaped structure.

2. Theoretical methods

Full structural optimizations and frequency analyses of $\text{Cu}_4\text{I}_4^{-}$ anion and its neutral counterpart were carried out employing density functional theory (DFT) with the Beck's three-parameter and Lee–Yang–Parr's gradient-corrected correlation hybrid functional (B3LYP) [20,21], as implemented in the Gaussian 09 program package [22]. The exchange-correlation potential and effective core pseudopotential LanL2DZdp basis set [23] was used for the I atoms and the Pople's all-electron 6-311+G(d, P) basis set [23] was used for the Cu atoms. Due to the Cu atom is early transition metal, the Pople's all-electron 6-311+G(d, P) basis set is adequate to represent the electronic wave function in the density-functional theory¹ in order to turn the partial differential equations of the model into algebraic equations suitable for efficient implementation, which is widely used in the theoretical calculations for cluster containing Cu atom [24–26]. As for the I

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¹ https://en.wikipedia.org/wiki/Density_functional_theory.

atom, the exchange-correlation potential and effective core pseudopotential LanL2DZdp basis set can accurately describe the electronic wave function in the density-functional theory and also save a lot of computer storage and computing time, which is also used in the theoretical calculations for cluster containing I atom [27]. No symmetry constraint was imposed during the geometry optimizations for both anionic and neutral clusters. The swarm-intelligence-based CALYPSO structure prediction software [28] was used to search the initial structures for both anionic and neutral Cu_4I_4 clusters. Harmonic vibrational frequency analyses were performed to verify that the optimized structures are the true minima on the potential energy surfaces. Generalized gradient approximation in the Perdew-Burke-Ernzerhof (PBE) functional [29] and BPW91 functional [30] were tested for the results obtained from B3LYP functional being independent with the functional. The theoretical vertical detachment energies (VDEs) were calculated as the energy differences between the neutrals and anions both at the geometries of anionic species, whereas the theoretical adiabatic detachment energies (ADEs) were calculated as the energy differences between the neutrals and anions with the neutrals relaxed to the nearest local minima using the geometries of the corresponding anions as initial structures. Natural population analysis (NPA) was performed to gain insight into the charge distributions of $\text{Cu}_4\text{I}_4^{-/0}$ within the Natural Bond Orbital (NBO) version 3.1 programs [31–38], as implemented in the Gaussian 09 program package. To further probe the bonding properties of Cu–I hybrid clusters, we used the Multiwfn program (3.41 package) [39] to analyze the orbital compositions of the most stable isomer of Cu_4I_4^- by using natural atomic orbital method.

3. Theoretical results and discussion

The typical low-lying isomers of Cu_4I_4^- anion are presented in Fig. 1. The relative energies (ΔE) of low-lying isomers and their theoretical VDEs and ADEs are also summarized in Fig. 1. In addition, the photoelectron spectrum of the lowest-lying isomer of Cu_4I_4^- anion is simulated based on the generalized Koopmans' theorem (GKT) [40,41] and is displayed in Fig. 2. In the DOS spectra, each transition is treated equally in the simulations. The typical low-lying isomers of Cu_4I_4 neutral are presented in Fig. 3, along with their ΔE .

Cu_4I_4^- . As shown in Fig. 1, the global minimum of Cu_4I_4^- , isomer A, is a C_{2h} symmetric planar structure with the four I atoms surrounding the Cu_4 rhombic framework. The bonding Cu–I distances are 2.57 and 2.73 Å, and Cu–Cu bond length is 2.52 Å. The bond angles of Cu–Cu–Cu, Cu–I–Cu, and Cu–Cu–I are 116.1°, 56.6°, and 58.3°, respectively. The calculated VDE and ADE of isomer A are 2.98 and 2.24 eV, respectively. As shown in Fig. 2, the simulated photoelectron spectrum of isomer A has a relatively weak peak at 2.98 eV, two high-intensity overlapping peaks centered at 4.08 eV, and another weak peak at 4.16 eV. The simulated spectrum shows that the peaks at higher EBE region are more congested than those at lower EBE region, more likely

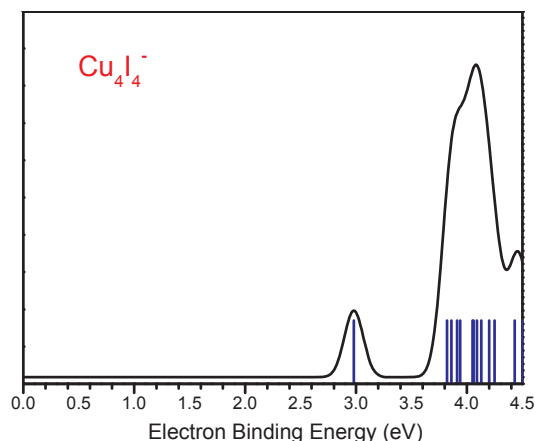


Fig. 2. The simulated photoelectron spectrum of the lowest-lying isomer of Cu_4I_4^- . Simulated spectrum was obtained by fitting the distribution of the transition lines with the unit area Gaussian functions of 0.20 eV full widths at half-maximum. The vertical lines in blue are the calculated vertical detachment energies for Cu_4I_4^- .

due to the electron detachments of Cu_4I_4^- are easier and electronic transitions are more intensive at higher EBE region in terms of Frank-Condon overlapping factor. The other isomers of Cu_4I_4^- , isomers B and C, are higher in energy than isomer A by 0.46 and 0.63 eV, respectively, calculated at the B3LYP level. Isomer B is a C_{3v} symmetric Cu_4 tetrahedral structure with the I atoms capping the edge or apex of Cu_4 framework. Isomer C has a similar structure with isomer B. It is worth noting that isomer A is also the global minimum for Cu_4I_4^- anion calculated at the PBE and BPW91 levels and the calculated relative energy orders between the three isomers are consistent at different levels of theory.

Cu_4I_4 . As shown in Fig. 3, the global minimum of Cu_4I_4 neutral (A') is a D_{2d} symmetric V-shaped structure (composed of two Cu_2I_3 five-membered rings sharing with an I–I bond) with the bonding Cu–I distance of 2.52 Å. The bond angles of Cu–I–Cu and I–Cu–I are 70.6° and 117.0°, respectively. Isomers B' and C' are higher in energy than isomer A' by 0.47 and 0.78 eV, respectively, calculated at the B3LYP level. Isomer B' is a C_{3v} symmetric pyramid-shaped structure. Isomer C' is a T_d symmetric cubic structure, which is very similar with the cubic Cu_4I_4 core in microemulsion droplets reported in the literature [17]. We would like to point out that isomer A' is also the lowest-lying structure for Cu_4I_4 neutral at the PBE and BPW91 levels and the calculated relative energy orders between the three isomers are also consistent at different levels of theory. Also, we found that the calculated relative energy orders of three isomers for Cu_4I_4 neutral calculated at the B3LYP level are slightly overestimate than those calculated at the PBE and BPW91 levels.

The lowest-lying isomers of Cu_4I_4^- anion and Cu_4I_4 neutral adopt different structures, which is very common that molecules or clusters have varied structures at different charge states. The variation of geometric structures at different charge states can be understood from three points of view. Firstly, the added electron will affect the electron-electron interactions and electron-atomic nucleus interactions, therefore, changes the potential of the Schrodinger equation and the wave function of the molecule, and further affect the potential energy surface and equilibrium structures of the molecule. Secondly, the addition of electron will change the charge distributions, hence, affects the Coulomb interactions between different atoms. Thirdly, the electron might be added to a bonding molecular orbital or a nonbonding molecular orbital. Depending on the orbital it stays, it will affect the bond formation in a molecule or cluster. In summary, the excess electron has obvious effect on the structures of Cu_4I_4^- anion and Cu_4I_4 neutral.

The Cu–I bond lengths in Cu_4I_4^- anion are 2.57 and 2.73 Å, which are longer than the Cu–I bond length of 2.46 Å in the CuI diatomic

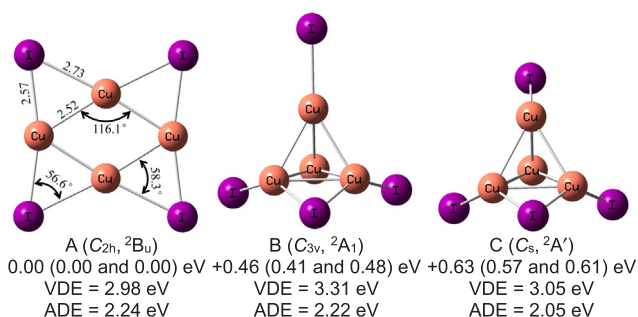


Fig. 1. Typical low-lying isomers of Cu_4I_4^- anion as well as their relative energies, ADEs, and VDEs obtained at the B3LYP level. The relative energies in parentheses are calculated at the PBE and BPW91 levels. The bond lengths are given in angstrom.

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