SP$^3$-Hybridization Feature of Ag$_4$ Superatom in Superatomic Molecules$^*$

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Analogous to atoms, superatoms can be used as building blocks to compose molecules and materials. To demonstrate this idea, the possibility of using tetrahedral Ag$_4$ cluster to form a series of superatomic molecules Ag$_4$X$_4$ (X=H, Li, Na, K, Cu, Ag, Au and F, Cl, Br) is discussed. Based on the super valence bond model, a tetrahedral Ag$_4$ cluster can be viewed as a 4-electron superatom, which can mimic a sp$^3$ hybridization C atom. By comparison of the representative superatomic molecules Ag$_4$X$_4$ (X=Au, Cl) with the corresponding simple molecules CX$_4$ (X=H, Cl), the similarities in terms of chemical bonding patterns and molecular orbitals (MOs) are conspicuous. Energy calculations predict that the Ag$_4$ superatom can bind with all the involved ligands. Furthermore, the stabilities of superatomic molecules are enhanced by the large gaps of the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO gaps) and high aromaticity. Our studies may find applications in assembling materials with superatoms.

Key words: Superatom, Magic numbers, Super valence bond, Binding energy, Aromaticity

I. INTRODUCTION

Atomic clusters with magic numbers have attracted considerable attention in recent years [1−6]. The great interest arises due to the pioneer work of Knight and co-workers, where a model of superatom is proposed to understand the mass spectra of sodium atomic clusters ($N=2−100$) [7]. Originally, superatom was defined as a unified atom which could mimic some features of atoms. With the development of the cluster science, the concept of superatom was modified. Especially after Khanna and Jena designed stable superatoms Al$_{12}$Si and Al$_{12}$C [5], many theoretical and experimental studies were emerging on superatoms, for example, the superatom of Al$_{13}$ was found to be similar to a halogen atom [3, 6, 8, 9]. Finally, an extended concept was suggested by Castleman and Khanna, where the superatom was termed not only displaying some properties of a single atom, but also a motif with new features [8, 9].

The stabilities of superatoms can be explained by the jellium model [10−12], which is often used to investigate clusters with weakly bound valence electrons. In such a model, the motions of valence electrons are assumed in a uniform potential, which is originated from the average effects of atomic nuclei and inner electrons. There are extensive potentials, such as square well potentials, simple three dimensional harmonic oscillator potentials, or potentials with intermediate shapes [13]. For the widely used square well potential, the electronic levels of metal clusters are $1S^2|1P^6|1D^{10}|2S^21F^{14}|2P^61G^{18}|2D^{10}3S^21H^{22}|⋯$, with S-P-D-F-G-H characterizing angular momentum quantum numbers, where the resulting magic numbers are 2, 8, 18, 20, 34, 40, 58, 68, 90, ⋯.

Jellium model is powerful in dealing with clusters of spherical symmetry, while when the clusters are non-spherical, it will be no longer reasonable enough. In order to solve such issues, our group proposed a super valence bond (SVB) model [14], of which the shell closures of superatoms were obtained by sharing valence pairs and nuclei with superatoms or ligands. According to this model, a Li$_4$ cluster can mimic a simple molecule CH$_4$, which gives a good explanation of the small peak $N=8$ in the mass spectra of sodium clusters. The SVB model has also been applied successfully to many other systems, where the spherical jellium model is not suitable [14−17].

In our previous studies, we have indicated the similarities of Li clusters (such as Li$_{14}$, Li$_{19}$, and Li$_8$) with simple molecules (such as F$_2$, N$_2$, and CH$_4$) in terms of the electronic shells and bonding patterns [14]. Herein we will use a tetrahedral Ag$_4$ to demonstrate the univer-

$^*$Dedicated to Professor Qing-shi Zhu on the occasion of his 70th birthday.

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sality of superatoms in forming superatomic molecules. Based on the jellium model, the electronic sequence of Ag₄ is 1S¹1P², where the effective valence electrons are from 5s¹ rather than the filled 4d¹⁰ shell. The open shell Ag₄ superatom in molecular state obtains closed shell by SP³ hybridization with four ligands. Firstly, we will illustrate the similarities of Ag₄ superatom with sp³ hybridization C atom by comparing their molecular orbital (MO) contours and chemical bonding patterns. Secondly, the differences between superatomic and planar configurations of the same composition will be analyzed. Finally, the stabilities of representative superatomic molecules are studied from the aspects of energies, aromaticity and HOMO-LUMO (H-L) gaps which are the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

II. COMPUTATIONAL DETAILS

The structures are optimized at the density functional theory (DFT) level using the TPSS functional [18]. We take a moderate basis set, LanL2dz for Au/Ag atoms and 6-31G* for the ligand atoms [19, 20]. MO analysis is based on the same basis set as it produces a small variation of MO [21]. For energy calculations relatively large basis sets, def2-tzvp and 6-311+G*, are used to describe Au/Ag atoms and the ligand atoms, respectively [22]. All the DFT calculations are completed on Gaussian 09 package [23].

III. RESULTS AND DISCUSSION

A. Models

In this work, we mainly focus on two models of Ag₄X₄ as shown in Fig.1. The first one is with T₄ symmetry. The four Ag atoms form a tetrahedron of superatomic features and the four ligand atoms locate above each surface of Ag₄ superatom. With this structure, Ag₄ obtains closed shells by sharing electronic pairs with ligands, such as atoms H [24, 25], Li [26, 27], Na [28], K, Cu [29], Ag [30], Au [31, 32], F [24, 33], Cl [24, 33], and Br [24, 34]. The second one has a planar structure. The set of four Ag atoms (or four ligand atoms) composes of one (or another) parallelogram, where a vertex of one parallelogram is the midpoint of another. All the T₄ and planar structures are verified to be real local minima by frequency check.

B. Molecular orbitals and chemical bonding analysis

First of all, we will give a visual comparison between the Ag₄ superatom and sp³ hybridization C atom based on their MO shapes and chemical bonding. To facilitate discussion, the superatomic molecules are divided into two classes in accordance with the effective electrons of ligand elements. The representative superatomic molecules are Ag₄Au₄ and Ag₄Cl₄.

For Ag₄Au₄, there is one effective valence electron in the outermost layer of Au atom, so it can mimic some behaviors of the simple molecule CH₄. The canonical Kohn Sham MOs of Ag₄Au₄ (left) and CH₄ (right) are shown in Fig.2. As we have already known, the main MOs of CH₄ are four sp³ bonding MOs (HOMO, HOMO-1) and one anti-bond MO (LUMO). In the left, the corresponding MOs of Ag₄Au₄ are demonstrated, with four super SP³ hybridization bonding MOs (HOMO, HOMO-17) and one super anti-bond orbit (LUMO). Due to the effects of d orbital, the comparable MOs order of Ag₄Au₄ is not consecutive. The similarity of MOs pictures demonstrates that Ag₄Au₄ can be an analogue of CH₄.

Then, the bonding patterns are compared. They are analyzed by the adaptive natural density partitioning (AdNDP) method, which is developed by Zubarev and Boldyrev for chemical bonding analysis [21], and has been successfully applied to a set of typical aromatic organic molecules, golden clusters, and other molecules.
[35–38]. The method partitions the electronic density as low centers as possible per electron pair, like as n-center two electron (nv-2e) bonds, including core electrons, lone pairs (LPs), 2c-2e bonds and so on. Through AdNDP analysis, Ag₄Au₄ is found with four 5c-2e super σ-bonds between the superatom Ag₄ and any vertexal Au atoms. The occupancy number (ON) is 1.95 |e|, so Ag₁ can form a filled shell. For the simple molecule CH₄, it has four 2c-2e σ C–H bonds with ON=2.00 |e|, also giving an eight electron shell. Both of them are with the same bonding patterns. Moreover, for Ag₄Au₄, AdNDP finds forty lone pairs (dx,y,2s,xz,y2,xz,z2), which are produced by the d orbital electrons of Au and Ag atoms. These lone pairs do not correspond to any MOs of the simple molecule CH₄ and not shown.

Similarly, Ag₄Cl₄ can mimic the features of simple molecule CCl₄. For comparison their MOs are drawn in the same direction and the same position is shown in Fig.3. Because of sp³ bonding of C atom, CCl₄ has four bonding MOs (HOMO-3, HOMO-4) and one anti-bond MO (LUMO). The MOs of CCl₄ also need to be picked out due to the valence electrons 3s²3p⁵ of Cl atom. As for SP³ bonding of Ag₄Cl₄, four super SP³ hybridization bonding MOs (HOMO-11, HOMO-12) and one super anti-bonding MO (LUMO) are presented. In CCl₄, sp³ hybridization of Ag atom, Ag₄Cl₄ and (c) AdNDP chemical bonding patterns of superatomic molecule Ag₄Cl₄ (left) and corresponding simple molecule CCl₄ (right).

C. Stability analysis

To determine the stabilities of superatomic molecules, the energies of superatomic and planar Ag₁X₄ are calculated. Table I lists their relative energies. In comparison, the favourable motifs of energies are the superatomic molecules for the ligands with one valence electron in the outermost layer (except for Ag₄H₄), while the planar configurations are more stable for the ligands with seven effective valence electrons, for instance the F, Cl and Br.

In Table I, we also calculate the binding energies, which are defined as $E_b=E(Ag_4X_4)+E(X)−E(Ag_4X_4)$, where X represents the H, Li, Na, K, Cu, Ag, Au and F, Cl, Br atoms. $E(Ag_4X_4), E(Ag_4X_4)$ and $E(X)$ represent the energies of molecules Ag₁X₄, Ag₄X₄ and atom.
The existence of stable superatomic molecules implies that we can use superatoms as building blocks to compose molecules, even to build up the materials with tailored properties. However, there is still a long way to go, not only it is difficult to find suitable stable building blocks, but also the superatom does not act like a real atom, where the relative orientation of superatoms are very important to design, especially, and there are no ready-made models. Fortunately, a protocol of chus-
ners assembled materials has been presented by Castle-
man group [41], which can be used to guide our further works.

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