CHINESE JOURNAL OF CHEMICAL PHYSICS VOLUME 28, NUMBER 4 AUGUST 27, 2015

ARTICLE

SP^3-Hybridization Feature of Ag_4 Superatom in Superatomic Molecules[†]

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(Dated: Received on May 21, 2015; Accepted on July 2015)

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_4X_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_4X_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 $1S^2|1P^6|1D^{10}|2S^21F^{14}|2P^61G^{18}|2D^{10}3S^21H^{22}|\cdots$, 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, $\cdots$.

Jellium model is powerful in dealing with clusters of spherical symmetry, while when the clusters are nonspherical, 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_8 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_{10}, 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-

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[†] Dedicated to Professor Qing-shi Zhu on the occasion of his 70th birthday.

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DOI:10.1063/1674-0068/28/cjcp1505105

sality of superatoms in forming superatomic molecules. Based on the jellium model, the electronic sequence of Ag_4 is $1S^2 1P^2$, where the effective valence electrons are from $5s^1$ rather than the filled $4d^{10}$ shell. The open shell Ag_4 superatom in molecular state obtains closed shell by SP^3 hybridization with four ligands. Firstly, we will illustrate the similarities of Ag_4 superatom with sp^3 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 Ag_4X_4 as shown in Fig.1. The first one is with T_d symmetry. The four Ag atoms form a tetrahedron of superatomic features and the four ligand atoms locate above each surface of Ag_4 superatom. With this structure, Ag_4 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 vertexal of one parallelogram is the midpoint of another. All the T_d 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 Ag_4 superatom and sp^3 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 Ag_4Au_4 and Ag_4Cl_4.

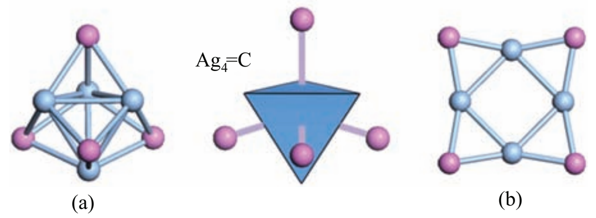


FIG. 1 The schematic of molecules Ag_4X_4 with (a) T_d and (b) planar symmetries. Ag: stone blue, ligand: pink.

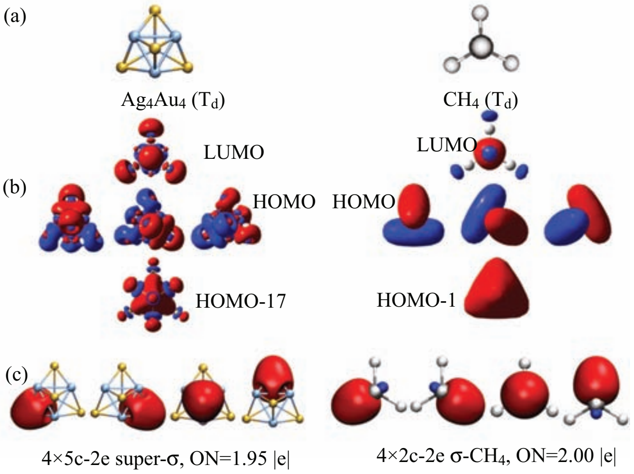


FIG. 2 (a) The structures of superatomic molecule Ag_4Au_4 (left) and corresponding simple molecule CH_4 (right). Comparison of (b) their orbital shapes and (c) their AdNDP chemical bonding patterns.

For Ag_4Au_4, there is one effective valence electron in the outermost layer of Au atom, so it can mimic some behaviors of the simple molecule CH_4. The canonical Kohn Shan MOs of Ag_4Au_4 (left) and CH_4 (right) are shown in Fig.2. As we have already known, the main MOs of CH_4 are four sp^3 bonding MOs (HOMO, HOMO-1) and one anti-bond MO (LUMO). In the left, the corresponding MOs of Ag_4Au_4 are demonstrated, with four super SP^3 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 Ag_4Au_4 is not consecutive. The similarity of MOs pictures demonstrates that Ag_4Au_4 can be an analogue of CH_4.

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

DOI:10.1063/1674-0068/28/cjcp1505105

[35−38]. The method partitions the electronic density as low centers as possible per electron pair, like as *n*-center two electron (*n*c-2e) bonds, including core electrons, lone pairs (LPs), 2c-2e bonds and so on. Through AdNDP analysis, Ag_4Au_4 is found with four 5c-2e super σ-bonds between the superatom Ag_4 and any vertexal Au atoms. The occupancy number (ON) is 1.95 |e|, so Ag_4 can form a filled shell. For the simple molecule CH_4, 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 Ag_4Au_4, AdNDP finds forty lone pairs (d_{xy,yz,xz,x^2-y^2,z^2}), 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 CH_4 and not shown.

Similarly, Ag_4Cl_4 can mimic the features of simple molecule CCl_4. For comparison their MOs are drawn in the same direction and the same position is shown in Fig.3. Because of sp^3 bonding of C atom, CCl_4 has four bonding MOs (HOMO-3, HOMO-4) and one antibond MO (LUMO). The MOs of CCl_4 also need to be picked out due to the valence electrons $3s^23p^5$ of Cl atom. As for SP^3 bonding of Ag_4Cl_4, four super SP^3 hybridization bonding MOs (HOMO-11, HOMO-12) and one super anti-bonding MO (LUMO) are presented. In Ag_4Cl_4, AdNDP finds four 5c-2e super σ-bonds, with ON=2.00 |e|, making the Ag_4 as an eight electron shell. It is found with twenty 4d LPs (ON=1.98−2.00 |e|) and twelve LPs (s and $p_{x,y}$ with ON=1.99 and 1.90 |e|) which have arisen from the contribution of 4d and $3s^23p^5$ orbital electrons of Ag and Cl atoms, respectively. For CCl_4, there are four σ type C−Cl (ON= 2.00 |e|) and twelve LPs (s and $p_{x,y}$ with ON=1.99 and 1.94 |e|). As one can see, their similarities are apparent.

From the analyses of MOs shapes and AdNDP bonding patterns, we deduce that the Ag_4 superatom can mimic the features of the C atom in the formation of sp^3 hybridization.

In addition, the chemical bonding of ring molecules Ag_4Au_4 and Ag_4Cl_4 are analyzed in the frame of traditional valence bond theory. Figure 4 plots the AdNDP chemical bonding of planar Ag_4Au_4. It has forty d type LPs (ON=1.95−2.00 |e|) and four 3c-2e σ Ag−Au bonds (ON=1.95 |e|), where the 3c-2e σ bonds are delocalized in one vertexal Ag atom and the nearest neighbor two Au atoms. Figure 5 gives the bonding patterns of planar Ag_4Cl_4. There are eight 2c-2e σ Ag−Cl bonds (ON=1.98 |e|), twenty 4d type LPs (ON=1.96−2.00 |e|) and eight LPs (s and p_x with ON=1.97 and 1.98 |e|), which are produced by the 4d and $3s^23p^5$ valance electrons of Ag and Cl atoms, respectively. The eight σ bonds are typical Louis bonds.

C. Stability analysis

To determine the stabilities of superatomic molecules, the energies of superatomic and planar Ag_4X_4 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 Ag_4H_4), while the planar configurations are more stable for the ligands with seven effective valence electrons, for instance the F, Cl and Br.

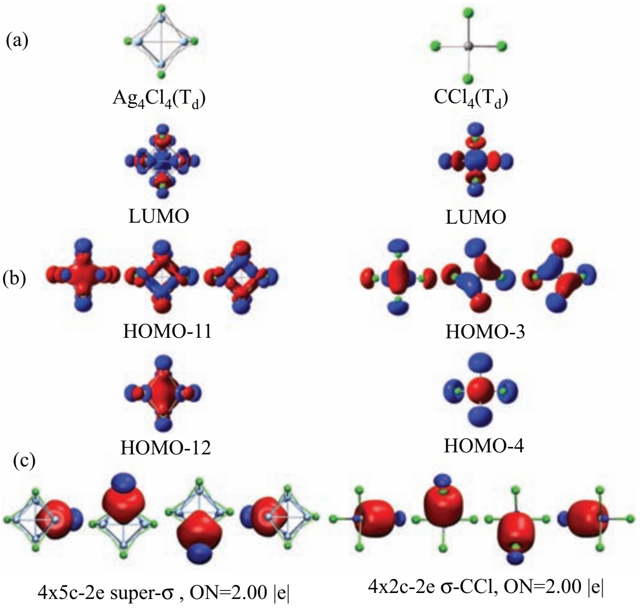


FIG. 3 Comparison of the (a) geometries, (b) MO diagrams, and (c) AdNDP chemical bonding patterns of superatomic molecule Ag_4Cl_4 (left) and corresponding simple molecule CCl_4 (right).

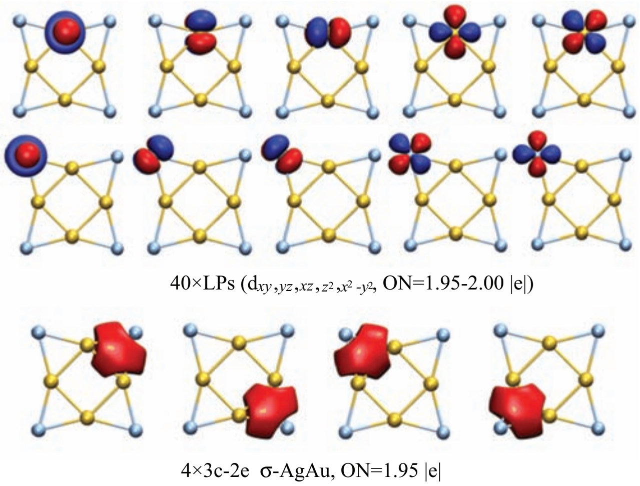
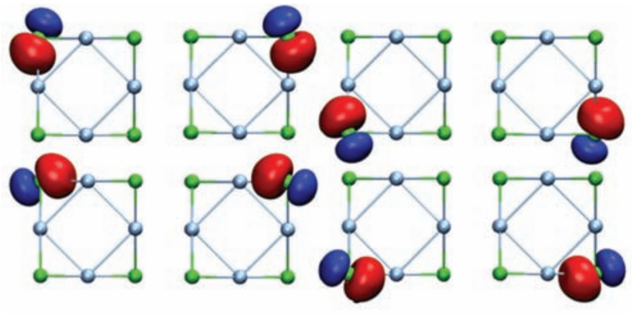


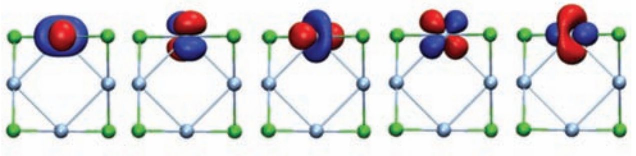
FIG. 4 AdNDP localized natural bonding patterns of planar molecule Ag_4Au_4.

In Table I, we also calculate the binding energies, which are defined as E_b=E(Ag_4X_3)+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_3), E(Ag_4X_4) and E(X) represent the energies of molecules Ag_4X_3, Ag_4X_4 and atom

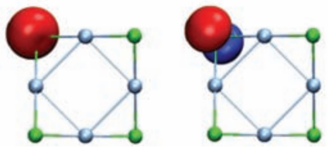
DOI:10.1063/1674-0068/28/cjcp1505105



8×σ-AgCl, ON=1.98 |e|



20×LPs (4d$_{xy,yz,xz,z^2,x^2-y^2}$, ON=1.96-2.00 |e|)



8×LPs (s, p$_x$), ON=1.97, 1.98 |e|

FIG. 5 AdNDP localized natural bonding patterns of planar molecule Ag$_4$Cl$_4$.

TABLE I Relative energies E_r of Ag$_4$X$_4$, where the energies of their own T$_\mathrm{d}$ motifs are chosen as references with 0.00 eV, and binding energies E_b of Ag$_4$X$_4$.

X	$E_\mathrm{r}$$^\mathrm{a}$/eV	E_b/eV
Li		2.36
Na	1.28	1.92
K	1.17	1.85
Cu	1.18	2.71
Ag	1.00	2.47
Au	0.82	3.25
H	−2.42	1.93
F	−1.10	3.93
Cl	−0.86	3.79
Br	−0.67	3.69

[a] Planar Ag$_4$Li$_4$ is instable with an image frequency.

X, respectively. The positive binding energies show that Ag$_4$ superatom can bind stably with all the mentioned ligands, though some planar structures will be more stable. Hence, the superatomic molecules Ag$_4$X$_4$ exist stably in nature.

D. Aromaticity

It is now known that the stabilities of clusters are enhanced by their closed electronic shells, geometric shells, and the existence of large H-L gaps [39]. Obviously, the tetrahedral superatom Ag$_4$ has a closed geometric shell and also a full electron shell by bonding with four ligands. Besides, for cage molecules, aromaticity is an important property, which can be measured by nucleus independent chemical shifts (NICS) values [40]. In the case of T$_\mathrm{d}$ motifs, we calculate two types of NICS values, one at the center of the whole molecules and another at the center of the small tetrahedrons composed by each face of Ag$_4$ and the above capped ligand atom. The NICS values are −48.21, −16.96, and −9.86, −10.90 ppm for the representative superatomic molecules Ag$_4$Au$_4$ and Ag$_4$Cl$_4$. They all have large negative values, which mean that the electrons are delocalized and the superatomic molecules are aromatic. Moreover, the H-L gaps of Ag$_4$Au$_4$ and Ag$_4$Cl$_4$ are 2.68 and 3.11 eV, respectively. The large gaps suggest that these superatomic molecules should be very inert and stable.

For comparison, the aromaticity of planar molecules is also calculated at the similar positions, the center of the whole molecules and of the triangles, where the latter are consisted of any vertexal atoms and the nearest neighbor two atoms. For planar Ag$_4$Au$_4$ molecule, the NICS values of the large ring and the small ring are 8.84 and −9.66 ppm, which predict the existence of delocalized bonds at the triangles. The results are in good agreement with 3c-2e σ Ag-Au bonds. Similarly, the corresponding NICS values of planar Ag$_4$Cl$_4$ are −4.50 and −21.80 ppm. Also, the gap calculations show large values for ring molecules Ag$_4$Au$_4$ (2.09 eV) and Ag$_4$Cl$_4$ (3.56 eV). Remarkably, the planar structure of Ag$_4$Cl$_4$ is more stable than its superatomic molecule structure.

IV. CONCLUSION

In this work, a number of superatomic molecules Ag$_4$X$_4$ (X=H, Li, Na, K, Cu, Ag, Au and F, Cl, Br) are studied to demonstrate that the superatom Ag$_4$ can mimic the features of sp^3 hybridization C atom. Their similarities are quite obvious after comparing the MOs shapes and bonding patterns of representative superatomic molecules Ag$_4$X$_4$ (X=Au, Cl) and corresponding simple molecules CX$_4$ (X=H, Cl). The calculations of energies further demonstrate that the superatomic molecules Ag$_4$X$_4$ are all stable, where Ag$_4$ can be bound with all the involved ligand elements. Besides, the large H-L gaps and highly aromaticity indicate that the superatomic molecules should be very stable.

The existence of stable superatomic molecules implies that we can use supeatoms 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 clus-

DOI:10.1063/1674-0068/28/cjcp1505105

ters assembled materials has been presented by Castleman group [41], which can be used to guide our further works.

V. ACKNOWLEDGMENTS

This work is supported by the National Key Basic Research Program (No.2011CB921404), the National Natural Science Foundation of China (No.21273008, No.21421063, No.91021004, and No.21233007), the Chinese Academy of Sciences (No.XDB01020300), and USTCSCC, SCCAS, Tianjin, and Shanghai Supercomputer Centers.

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