Beyond Classical Stoichiometry: Experiment and Theory

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Most known molecules and compounds follow fixed stoichiometry and can be rationalized on the basis of classical valence theories. However, nonstoichiometric species, particularly in the gas phase, are common. These species cannot be easily understood by classical valence considerations because they do not have the full octet of valence electrons—they are valence unsaturated molecules with dangling bonds. We consider nonstoichiometric molecules consisting of only four or five atoms and show the great variety of molecules and bonding that can be derived from this class of seemingly simple species. We demonstrate that gas-phase photodetachment photoelectron spectroscopy using a laser vaporization source and ab initio quantum calculations provide an ideal approach to characterize and understand the structure and bonding of nonstoichiometric molecular and cluster species. Specifically, we review our recent progress in the design and characterization of the first pentaatomic tetracordinate planar carbon molecules, $\text{CAl}_4^-$, $\text{CAl}_3\text{Si}^-$, $\text{CAl}_3\text{Ge}^-$, and a salt complex, $\text{Na}^{+}[\text{CaI}_2^2-]$ containing a planar carbon building block. We also review our recent discovery of an all-metal aromatic species, $\text{Al}_2^{2-}$, in a series of bimetallic clusters, $\text{M}^{+}[\text{Al}_2^{2-}]$ ($\text{M} = \text{Cu, Li, Na}$), as well as the $\text{Ga}_2^{2-}$ and $\text{In}_2^{2-}$ analogues. We also show the existence of aromaticity in a series of isoelectronic singly charged anions, $\text{MAI}_1^-$ ($\text{M} = \text{Si, Ge, Sn, Pb}$), and how aromaticity helps stabilize the heterocyclic structure over a pyramidal isomer. We show how, by pursuing and understanding the concept of nonstoichiometry, one can extend the classical valence theory and discover new structures and new types of bonding.

1. Introduction

Stoichiometry plays a central role in contemporary chemistry. It is based on earlier discoveries of the concept of conservation of matter and the concept of definitive proportions in chemical combination and chemical compounds. The name “stoichiometry” was introduced in chemistry by Richter1 and was originated from the Greek words “στοιχείον” which means “element,” and “μετρέων”, which means “measuring”.2 However, at the dawn of modern chemistry there were considerable confusion and controversy regarding chemical equivalence and combining proportions. It took an eight-year debate between two prominent chemists, Berthollet and Proust, at the turn of the nineteenth century, to firmly establish stoichiometry (definitive proportions) in chemistry. Berthollet believed that the composition of a compound was indefinite with respect to the various elements and may vary over a wide range. To support his view, Berthollet used examples of solutions, alloys, glasses, metal oxides, and basic salts, which all seemed to have variable compositions. The numerous incorrect analyses reported at that time led him to believe that the change in composition was continuous rather than intermittent. Proust in his numerous papers in the Journal de Physique between 1802 and 1808 overturned Berthollet’s position with sound experimental analyses and evidence. The victory of Proust was fortunate for chemistry, because the concept of stoichiometry was crucial for the subsequent development of the theory of chemical atoms by Dalton.3

However, despite the firm root of stoichiometry in chemistry, nonstoichiometric substances and molecules, which do not follow the “octet rule”, do exist. In particular, with the development of modern gas-phase techniques and matrix isolation, more and more nonstoichiometric molecules are being observed. In fact, nonstoichiometric molecules are becoming the rules rather than exceptions from such gas-phase techniques as laser vaporization or sputtering. In Figure 1 we show a time-of-flight mass spectrum of gaseous species from laser vaporization of a mixed graphite/aluminum target. Despite the fact that bulk aluminum carbide has a definitive stoichiometry of $\text{Al}_4\text{C}_3$, one can see that in the gas phase almost any combination of Al and C is possible. We emphasize that we only consider chemically bound species in this article. Weakly bound van der
Later, Marsden and co-workers\textsuperscript{15} are suboxides of alkali metals.\textsuperscript{6} Rubidium and cesium form different subject matter. The Al\textsubscript{n}Waals species, which are also prevalent in the gas phase, are a.

Nonstoichiometric molecules represent a challenge and new opportunity in chemistry. The vast majority of known main-group chemical compounds obey the “octet rule”, which dictates the stoichiometric compositions of stable species. For example, the octet rule requires that atoms of the first and second rows are most stable when they are surrounded by eight valence electrons. On the basis of this rule one can predict the stoichiometry of hydrides to be \( \text{CH}_4 \), \( \text{NH}_3 \), \( \text{H}_2 \text{O} \), and \( \text{HF} \). While hyperstoichiometric hydrides such as \( \text{NH}_4 \), \( \text{NH}_3^- \), \( \text{H}_2 \text{O}^- \), and \( \text{H}_2\text{O}^- \) are known,\textsuperscript{4,5} they are not thermodynamically stable species. However, many nonstoichiometric molecules and clusters involving heavier main group elements are stable species toward spontaneous decay. In the cases of \( \text{Al}_n\text{C}_n^- \), one might expect that only the \( \text{Al}_2\text{C}_2 \) molecule would be stable in the gas phase, because it is a stoichiometric molecule as in the bulk and the valences of both Al and C are satisfied [(\( \text{Al}^{1+}\text{C}^{2-} \)). Yet, as seen in Figure 1, even though the \( \text{Al}_2\text{C}_2 \) species exists, there are many other stable and nonstoichiometric gaseous \( \text{Al} \)–\( \text{C} \) species.

![Figure 1](image)

**Figure 1.** Time-of-flight mass spectrum of \( \text{Al}_2\text{C}_2^- \) clusters from laser vaporization of a composite Al/C target.

Waal's species, which are also prevalent in the gas phase, are a different subject matter. The \( \text{Al}_n\text{C}_n^- \) species shown in Figure 1 certainly represent examples of chemically bound species, yet with a variety of composition.

Nonstoichiometric molecules have also been studied computationally predicted and characterized hyperberillium \( \text{Be}_2\text{O} \) and \( \text{BeOB} \),\textsuperscript{23} and hypermagnesium \( \text{Mg}_2\text{O} \), \( \text{Mg}_2\text{O}_2 \),\textsuperscript{24,25} and \( \text{Mg}_2\text{C} \) species.\textsuperscript{26} Castlemoan and co-workers\textsuperscript{27} experimentally observed an unusually high-intensity mass spectral peak for the \( \text{Mg}_2\text{O}^- \) cation in agreement with the theoretical prediction of the exceptional stability of neutral \( \text{Mg}_2\text{O} \) and the \( \text{Mg}_2\text{O}^- \) cation.\textsuperscript{24,25} Andrews experimentally observed vibrational spectra of \( \text{Be}_2\text{O} \) in a matrix isolation experiment.\textsuperscript{28,29}

Bolydrev, Schleyer, and others also predicted computationally that hyperaluminum \( \text{Al}_2\text{O} \) and \( \text{Al}_2\text{O}_3 \), and \( \text{Al}_2\text{N}^- \) species\textsuperscript{31} should be stable molecules in the gas phase. \( \text{Al}_2\text{N} \) and \( \text{Al}_2\text{N}^- \) have been experimentally observed and characterized by Wang, Jena, and co-workers.\textsuperscript{32} Wang and co-workers have also characterized a series of \( \text{Al}_2\text{O} \) species using anion photoelectron spectroscopy.\textsuperscript{33,34} The structures of these hyperaluminum molecules have been subsequently investigated theoretically by Rohlfing.\textsuperscript{35} Ghanty and Davidson\textsuperscript{35} and very recently by Ortiz and co-workers.\textsuperscript{36} A series of hyperaluminum carbon species, \( \text{Al}_2\text{C}_2^- \) and \( \text{Al}_2\text{C}_n^- \) have also been studied in a joint experimental and theoretical effort by Wang, Bolydrev, and co-workers.\textsuperscript{37–41} Nonstoichiometric \( \text{Al}_n\text{S}_x \) species were observed by Kaya and co-workers\textsuperscript{42,43} and the reactivities of these species were studied by Parent.\textsuperscript{44,45} Anderson and co-workers experimentally observed and characterized a series of hyper-boron \( \text{B}_x\text{O} \) species.\textsuperscript{46} Recently, Bowen and co-workers have investigated \( \text{Al}^-\text{C} \) and \( \text{Al}^-\text{Li} \) mixed clusters using anion photoelectron spectroscopy.\textsuperscript{47,48} Jena and co-workers have performed theoretical calculations on the same systems.\textsuperscript{49,50}

Hypersilicon clusters have been studied more extensively.\textsuperscript{51–94} Margrave et al.,\textsuperscript{51} Graham et al.,\textsuperscript{52–56} Saykally et al.,\textsuperscript{57} and Rohlfing et al.\textsuperscript{58} studied \( \text{Si}_n\text{C}_n \) species spectroscopically. Ab initio calculations of the \( \text{Si}_n\text{C}_n \) species were performed by Schaefer et al.\textsuperscript{59,60} Sabin et al.\textsuperscript{61,62} Rittby.\textsuperscript{56,63} Rohlfing et al.,\textsuperscript{58} and Bolydrev et al.\textsuperscript{59} Schwarz and co-workers performed mass spectroscopic studies of \( \text{Si}_x \) and \( \text{Si}_x \) species.\textsuperscript{64} Brough and Morse studied \( \text{Si}_n\text{O} \) spectroscopically.\textsuperscript{65} Ab initio calculations of \( \text{Si}_n \) were performed by Bolydrev and Simons.\textsuperscript{66} \( \text{Si}_x \) were calculated by Schaefer et al.,\textsuperscript{70} as well as by Bolydrev, Simons, and others.\textsuperscript{66,71} Wang, Nicholas, and co-workers\textsuperscript{72–76} have characterized a series of \( \text{Si}_x \) and \( \text{Ge}_x \) species using anion photoelectron spectroscopy and ab initio calculations.

Weltner et al.\textsuperscript{77} studied \( \text{Si}_x \) using ESR while Gingerich and co-workers obtained thermodynamic data for \( \text{Si}_x \) and \( \text{Si}_x \).\textsuperscript{78,79} There have also been a few studies of nonstoichiometric \( \text{III} – \text{V} \) semiconductor clusters. Smalley and co-workers pioneered the experimental study of \( \text{Ga}_n\text{As}_n \) clusters.\textsuperscript{80–83} Weltner et al. studied small \( \text{Ga}_n\text{As}_n \) clusters using matrix ESR spectroscopy.\textsuperscript{84} Mandich and co-workers studied \( \text{In}_x\text{P}_n \) clusters.\textsuperscript{85} Neumark et al. have studied nonstoichiometric \( \text{In}_x\text{P}_n \), \( \text{Ga}_x\text{P}_n \), and \( \text{B}_x\text{N}_n \) clusters using anion photoelectron spectroscopy.\textsuperscript{86–88} Smalley et al.\textsuperscript{82,83} and Balasubramanian and Feng\textsuperscript{89–94} have performed quantum chemical studies of a number of small \( \text{III} – \text{V} \) semiconductor clusters.

Relatively fewer investigations have been done on gaseous nonstoichiometric transition metal species. Knickelbein\textsuperscript{95,96} measured the ionization potentials of \( \text{Sc}_x\text{O} \) (\( n = 5–36 \)) and \( \text{Y}_x\text{O} \) (\( n = 2–31 \)). Yang, Hackett, Salahub, and co-workers performed combined spectroscopic and theoretical studies of \( \text{Nb}_x\text{O}_y \) and \( \text{Nb}_x\text{C}_y \). Wang and co-workers have studied extensively non-
stoichiometric transition metal oxide species\textsuperscript{99–106} and carbide clusters\textsuperscript{107–112} using anion photoelectron spectroscopy. Andrews and co-workers\textsuperscript{113–116} identified a number of nonstoichiometric oxides of transition metals and f-block metals using matrix isolation. Schaefer and co-workers,\textsuperscript{117} Bauschlicher,\textsuperscript{113,116} and Gutsev, Rao, and Jena\textsuperscript{118,119} performed ab initio calculations on transition metal oxide species. Recently, Leopold and co-workers reported an anion photoelectron spectroscopy investigation of a series of nonstoichiometric transition metal oxide species, V$_2$O, Nb$_2$O, and Ta$_2$O.$^{120}$ Aluminum–cobalt clusters have been studied by Knickelbein and Menezes.$^{121}$ In a series of articles\textsuperscript{122–124} Jellinek and Krissinel calculated nonstoichiometric Al–Ni clusters. Kaya and co-workers studied a number of aluminum–transition metal clusters.$^{125}$ Hackett and co-workers\textsuperscript{126} also studied Y$_3$C$_2$ and Y$_3$C$_2^+$ by combining the PFI-ZEKE experiments with DFT calculations.

The discovery of the metallo-carboheterenedenes (met-cars) by Castleman and co-workers\textsuperscript{127,128} represents a new interesting class of nonstoichiometric molecular clusters, which contain a carbon-to-metal ratio of 1.5 (M$_2$C$_2$). Many experimental\textsuperscript{129–140} and theoretical\textsuperscript{141–152} works have focused on the met-cars. Although the structures of these clusters are still not definitively determined, the C$_2$ dimers are now known to be an important building block of the met-cars.$^{153}$ Boldyrev and Simons studied small magnesium carbide clusters.$^{154}$ They found that the C$_2^2$ moiety exhibits both 1- and 2-fold coordination to the Mg$_2$ and theoretical\textsuperscript{141} Al–Ni clusters. Kaya and co-workers studied a number of aluminum–transition metal clusters.$^{125}$ Hackett and co-workers\textsuperscript{126} also studied Y$_3$C$_2$ and Y$_3$C$_2^+$ by combining the PFI-ZEKE experiments with DFT calculations.

Recently, using a combined experimental and theoretical approach, we have investigated and characterized a number of nonstoichiometric molecules with the number of valence electrons from 8 (CH$_4$) up to 32 (CF$_4$) and their expected ground-state molecular structures. The structure and stability of CH$_4$ and CF$_4$ can be easily predicted by the classical valence theory. Both CH$_4$ and CF$_4$ are stoichiometric molecules with mono- valent ligands (H or F) coordinated to the central atom C through σ-bonding and they both obey the octet rule. Their tetrahedral structure can be rationalized and understood on the basis of their closed-shell electron configurations: 1a$_1^2$1t$_2^6$ for CH$_4$ and 1a$_1^2$1t$_2^6$2a$_2^6$2t$_2^6$1e$_4^3$t$_1^6$1t$_1^6$ for CF$_4$. Those pentaatomic molecules, with valence electrons from 9 to 31, are nonstoichiometric with probably one exception, CAL$_4$, which can be considered as a stoichiometric molecule if the Al ligands are considered to be monovalent. In the following, we analyze the structure and bonding of these nonstoichiometric molecules along the direction of increasing valence electrons.

### 2.1. Pentaatomic Species with 9 and 10 Valence Electrons

The first type of MX$_4$ pentaatomic nonstoichiometric molecules we consider has 9 valence electrons. Under the $T_d$ structure the electronic configuration is 1a$_1^1$1t$_2^6$2a$_2^1$. The highest occupied molecular orbital (HOMO), 2a$_1$, is antibonding with respect to the central atom–ligand interactions, but it is bonding with respect to ligand–ligand interactions, as shown in Figure 2b for a representative 9 electron species, OL$_4^+$. Therefore, the structure and stability of the 9 electron species are determined by both the central atom–ligand interactions and the ligand–ligand interactions. This is a completely new type of bonding, which cannot be present in the stoichiometric MX$_4$ species. Actually, the 2a$_1$ orbital exhibits a similarity with the Rydberg bond in the NH$_4$ and NH$_4^-$ species.$^{4,5}$ Because of the a$_1$ symmetry of the HOMO, one would expect that the 9-valence-electron species should be stable at the $T_d$ symmetry, if the distances between the ligands are close enough to allow overlaps between ligand atomic orbitals. A good criterion for that is the ligand–ligand distances in MX$_4$ lie between the $X-X$ bond lengths in $X_2$ and $X_2^+$, because of the ionic bonding between the $X$ and $X$. Recently, Schleyer and co-workers\textsuperscript{166} predicted that OL$_4^+$ has a global minimum at the $T_d$ symmetry, as shown in Figure 2a. To these data, the Li$_4$ distance is in the structure 2.878 Å, which indeed lies between the bond lengths in Li$_2$ (2.704 Å) and Li$_2^+$ (3.085 Å) at the same level of theory. Similarly, we found, using the same level of theory (B3LYP/6-311+G*$^{*}*$, that ONa$_4^+$ has a global minimum at the $T_d$ symmetry, because the Na$_4$...Na distance (3.477 Å) lies between those in Na$_2^+$ (3.052 Å) and Na$_2^+$ (3.603 Å). However, when the ligand–ligand distance is too long, the tetrahedral structure will be distorted. We performed calculations for the SLi$_4^+$ cation encountered in nonstoichiometric molecules compared to stoichiometric molecules is the presence of strong ligand–ligand interactions that can lead to new types of chemical bonds. As an example, let us consider a set of main-group pentaatomic molecules, MX$_4$, containing a main-group atom M and four identical ligands X. The global minimum structures and their upper occupied molecular orbitals (MOs) of a selected set of MX$_4$ type molecules are presented in Figure 2 (details of the theoretical methods are described in section 3.2. below). If the M–X and X–X distances in a MX$_4$ molecule are close enough for optimal orbital overlaps between the pairs of atoms in the global minimum structure, the atom M will be located at the center and the geometry of MX$_4$ can be predicted by considering the Jahn–Teller effect. This simple model works well for many nonstoichiometric MX$_4$ molecules with 9–18 valence electrons, as discussed below.

In Table 1, we present electronic configurations of pentaatomic molecular systems with the number of valence electrons from 8 (CH$_4$) up to 32 (CF$_4$) and their expected ground-state molecular structures. The structure and stability of CH$_4$ and CF$_4$ can be easily predicted by the classical valence theory. Both CH$_4$ and CF$_4$ are stoichiometric molecules with mono- valent ligands (H or F) coordinated to the central atom C through σ-bonding and they both obey the octet rule. Their tetrahedral structure can be rationalized and understood on the basis of their closed-shell electron configurations: 1a$_1^2$1t$_2^6$ for CH$_4$ and 1a$_1^2$1t$_2^6$2a$_2^6$2t$_2^6$1e$_4^3$t$_1^6$1t$_1^6$ for CF$_4$. Those pentaatomic molecules, with valence electrons from 9 to 31, are nonstoichiometric with probably one exception, CAL$_4$, which can be considered as a stoichiometric molecule if the Al ligands are considered to be monovalent. In the following, we analyze the structure and bonding of these nonstoichiometric molecules along the direction of increasing valence electrons.

### 2. Pentatomic Nonstoichiometric Molecules and Ligand–Ligand Bonding

As mentioned in the Introduction, conventional valence models,\textsuperscript{164,165} such as the octet rule or the valence-shell electron-pair repulsion (VSEPR) model based on the octet rule, are not applicable to nonstoichiometric molecules, because atoms in such species do not have a full octet. One new feature
Figure 2. Structures and the highest occupied molecular orbitals (HOMO) of selected pentaatomic nonstoichiometric molecules.
TABLE 1: Electron Configurations and Expected Symmetries Based on the Jahn–Teller Effect for Nonstoichiometric MX₄ Species Containing between 8 and 32 Valence Electrons

<table>
<thead>
<tr>
<th>representative molecule</th>
<th>no. of valence electrons</th>
<th>electronic configuration at ( T_d ) structure</th>
<th>expected minimum structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄, CN₄</td>
<td>8</td>
<td>( 1a_1^2t_1^4 )</td>
<td>( T_d )</td>
</tr>
<tr>
<td>OLi₄⁺, ONa⁺</td>
<td>9</td>
<td>( 1a_1^2t_2^2a_1^1 )</td>
<td>( T_d )</td>
</tr>
<tr>
<td>OLi₄, ONa₄</td>
<td>10</td>
<td>( 1a_1^2t_1^2a_2^1 )</td>
<td>( T_d )</td>
</tr>
<tr>
<td>CMg₄</td>
<td>11</td>
<td>( 1a_1^2t_2^2a_2^1 )</td>
<td>( D_{2d} )</td>
</tr>
<tr>
<td>CMg₄</td>
<td>12</td>
<td>( 1a_1^2t_2^2a_2^1 )</td>
<td>( D_{2d} )</td>
</tr>
<tr>
<td>OMe₄</td>
<td>13</td>
<td>( 1a_1^2t_2^2a_2^1 )</td>
<td>( D_{2d} )</td>
</tr>
<tr>
<td>OMg₄</td>
<td>14</td>
<td>( 1a_1^2t_1^2a_2^1 )</td>
<td>( D_{2d} )</td>
</tr>
<tr>
<td>CAl₄</td>
<td>15</td>
<td>( 1a_1^2t_2^2a_2^1 )</td>
<td>( D_{2d} )</td>
</tr>
<tr>
<td>CAl₄⁺</td>
<td>16</td>
<td>( 1a_1^2t_2^2a_2^1 )</td>
<td>( T_d )</td>
</tr>
<tr>
<td>OLi₄⁻</td>
<td>17</td>
<td>( 1a_1^2t_2^2a_2^1 )</td>
<td>( D_{4h} )</td>
</tr>
<tr>
<td>OLi₄⁺, CAl₄²⁻</td>
<td>18</td>
<td>( 1a_1^2t_2^2a_2^1 )</td>
<td>( D_{4h} )</td>
</tr>
<tr>
<td>CSi₄</td>
<td>19</td>
<td>( 1a_1^2t_2^2a_2^1 )</td>
<td>( D_{4h} )</td>
</tr>
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<td>( D_{4h} )</td>
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<td>( D_{4h} )</td>
</tr>
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<td>C₂Si₄⁺</td>
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</tr>
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<tr>
<td>CO₄⁺</td>
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<tr>
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<tr>
<td>CF₄⁺</td>
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<tr>
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</tr>
<tr>
<td>CF₄⁺</td>
<td>32</td>
<td>( 1a_1^2t_2^2a_2^1 )</td>
<td>( D_{4h} )</td>
</tr>
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at B3LYP/6-311+G* and found that at the \( T_d \) symmetry the Li...Li distance is 3.764 Å, which is well above the upper limit of 3.085 Å for Li⁺. Consequently, the \( T_d \) structure is a third-order saddle point at this level of theory. The search for the global minimum leads to a \( C_{3v} \) (\( \bar{A}1 \)) structure as shown in Figure 2e, in which the distances between the three Li atoms not along the 3-fold axis are shortened to 2.991 Å in order to better accommodate the ligand–ligand bonding interactions. The HOMO for this structure is shown in Figure 2d and it reflects the clearly the desire for ligand–ligand bonding.

The pentaatomic hyperstoichiometric molecules OLi₄ and ONa₄ with 10 valence electrons have been predicted to have a tetrahedral structure by Schleyer and co-workers.⁹ and ONa₄ has been observed experimentally by Wu.¹⁰ The ligand–ligand distances are in the right range for both molecules: 2.840 Å for Li–Li in OLi₄ and 3.496 Å for Na–Na in ONa₄. Both species have the 2a₁-HOMO doubly occupied, as shown in Figure 2f for Na₂O₄, and the anticipated global minimum tetrahedral structure (Figure 2e). The HOMO is a totally symmetric pure ligand peripheral bond, which is responsible for the stability and structure of these species. For the SLi₄ molecule, the Li–Li distance is again too long (3.620 Å), similar to that in SLi₄⁺, and thus the \( T_d \) structure is no longer stable and becomes a third-order saddle point. Two structures, a \( C_{3v} \) (Figure 2g) and \( C_{2v} \), (Figure 2i) with close energies, are found two structures for OMg₄ with very close energies. One structure has a butterfly-type \( D_{2d} \) (\( \bar{A}1 \)) symmetry (Figure 2m). The HOMO of this isomer is a filled nonbonding degenerate 2e orbital (Figure 2n,o), but its HOMO–MO is a ligand–ligand bonding orbital (Figure 2p). Therefore, the stability of the \( D_{2d} \) OMg₄ isomer comes from the 2a₁-HOMO (\( 1 \)) orbital, which is analogous to the peripheral bonding MO in Na₂O (Figure 2f). The calculated Mg–Mg bond length (2.921 Å) between adjacent ligands is again close to the Mg–Mg bond (2.861 Å) in the linear HMG–MgH molecule at the same level of theory. The second isomer of OMg₄ is more stable by 1.4 kcal/mol and has \( C_{3v} \) (\( \bar{A}1 \)) symmetry, as shown in Figure 2q. However, the accuracy of our ab initio calculations is not sufficient to conclude which of these structures is the global minimum. It should also be pointed out that OMg₄ is not a very stable molecule with a dissociation energy of only 7.9 kcal/mol to OMg₃ + Mg.

The 16-valence-electron species CAl₄ is expected to have a tetrahedral structure (Figure 2r) on the basis of its closed-shell electron configuration, \( 1a_1^2t_2^2a_2^1t_2^2 \). The first four (1a₁ and 1t₂) orbitals are the C–Al orbitals, which is expected to undergo Jahn–Teller distortions toward a \( D_{2d} \) (\( \bar{A}1 \)) geometry. Indeed, this structure was found to be a global minimum in our ab initio calculations at the B3LYP/6-311+G* and MP2/6-311+G* levels of theory. But it became a second-order saddle point at the CCSD(T)/6-311+G* level of theory. Distortion along the \( a_2α \) mode of imaginary frequency leads to a \( C_{3v} \) (\( \bar{B}1 \)) pyramidal structure with the carbon atom lying just 0.0056 Å above the Al₃ plane and with an inversion barrier of only 0.002 kcal/mol. Distortion along the \( b_2β \) mode of imaginary frequency leads to a butterfly type \( D_{2d} \) (\( \bar{A}1 \)) structure, which turns out to be the global minimum at the CCSD(T)/6-311+G* level of theory. However, the deviation from planarity in the butterfly structure is also rather small with the energy difference between \( D_{2d} \) (\( \bar{B}1 \)) and \( D_{4h} \) (\( \bar{B}1 \)) being 0.14 kcal/mol. Therefore, when zero-point vibrational motion is considered, the vibrationally averaged structure is actually planar.
confirmed pentaatomic tetracoordinate planar carbon molecule,\textsuperscript{38} which will be discussed in detail in the next section 4.

The 18-valence-electron OAl\textsubscript{4} molecule has the 1\textsubscript{a}1\textsubscript{g}2\textsubscript{t}1\textsubscript{e}, 2\textsubscript{a}2\textsubscript{t}2\textsubscript{e}1\textsubscript{e} electronic configuration and it is expected to be distorted toward a square-planar D\textsubscript{4h} (1\textsubscript{A}1g) structure with a singlet state or stay as a triplet state (1\textsubscript{A}2g) under the tetrahedral symmetry. Boldyrev and Schleyer\textsuperscript{30} showed that the square-planar singlet state is the global minimum (Figure 2w) and the tetrahedral triplet state is an excited isomer 24.4 kcal/mol higher in energy. The 1\textsubscript{b}2\textsubscript{g}HOMO (originated from the 1\textsubscript{e}MO at the tetrahedral symmetry) (Figure 2x) is a four-center ligand--ligand bonding MO with no contribution from the central atom. This is another new type of chemical bonding not known before.

With the increase of the number of valence electrons in the MX\textsubscript{4} molecules we see that between CH\textsubscript{4} and CF\textsubscript{4} there is a large class of stable and chemically bound nonstoichiometric species with several new types of chemical bonding related to the ligand--ligand interactions. In the 9 and 10 valence MX\textsubscript{4} species, the 2\textsubscript{a}1\textsubscript{g}HOMO represents a unique chemical bond between all four ligands (Figure 2b,f). Yet it is antibonding with respect to the central atom--ligand interactions. The 12-valence-electron systems exhibit a two-electron four-center bond, which is bonding within each pair of ligands, but antibonding between the two pairs (Figure 2i). The 18-valence-electron systems reveal an even more interesting two-electron four-center ligand--ligand bond in the plane of the molecule (Figure 2x). All these new types of chemical bonds are not present in the stoichiometric molecules.

A similar analysis can be done for other MX\textsubscript{4} and more generally MX\textsubscript{y} species, where we expect even more interesting chemical bonding may be found.

Another important finding from the ab initio studies of the nonstoichiometric molecules is a large number of low-lying isomers, as a result of low-lying vacant MOs. Depending on the electronegativity and structural restrictions, in some cases, the global minimum and low-lying isomers may switch their stability even upon isoelectronic substitutions. Therefore, in theoretical searches for a global minimum it is necessary to consider a large number of potential candidates, whereas in experimental studies presence of low-lying isomers is possible.

Since nonstoichiometric species outlined above do not follow the classical valence rules, new chemical bonds are found. Our goal is to be able to understand systematically the chemical bonding in one series of species and identify common threads among otherwise seemingly uncharted territories. Understanding the presence of the new bonding possibilities and uncovering common features among a series of nonstoichiometric species can help us design and identify novel chemical structures. Because of the novelty of these species it is especially important to rely on combined efforts of theory and experiment in this endeavor. In the next section we will describe our experimental and theoretical techniques and our united theory/experiment approach to probe new nonstoichiometric molecules.

3. Experimental and Theoretical Methods

3.1. Experimental Method. The experimental apparatus used to synthesize and characterize nonstoichiometric species in our laboratory involves a laser vaporization cluster source and a magnetic-bottle photoelectron spectrometer. Details of the experimental setup have been published elsewhere.\textsuperscript{172,173} Briefly, mixed targets containing the appropriate atoms required to synthesize the nonstoichiometric species are vaporized by an intense pulsed laser beam. The laser-induced plasmas are cooled by a high pressure helium carrier gas, initiating nucleation and formation of small molecular and cluster species. These species, entrained in the helium carrier gas, undergo a supersonic expansion to form a collimated molecular beam. Negatively
charged species are extracted from the beam and subjected to a time-of-flight mass analysis. Typically, complicated mass spectra with a variety of compositions are obtained, such as that shown in Figure 1, which was produced by laser vaporization of a graphite-aluminum two-component target. The single natural isotope of aluminum makes it an ideal component to synthesize mixed clusters characteristic of the nonstoichiometric species, in which we are generally interested. A given anion of interest is mass-selected and decelerated before being detached by a laser beam. A variety of detachment laser photon energies are available (532, 355, 266, and 193 nm). High photon energy spectra are particularly important because they reveal more electronic transitions, which are essential to facilitate comparisons with theoretical predictions. Low photon energies in general yield better resolved spectra for the ground-state transitions, allowing more accurate determination of adiabatic electron affinities of the neutral species and vibrational resolution in some cases. The resolution of the apparatus is about 25 meV for 1 eV electrons.

3.2. Theoretical Methods. Theoretical characterization of new nonstoichiometric anionic species consists of two steps. First, we need to determine the electronic state and the geometry of the most stable structure of the anionic species. This includes geometry optimizations and frequency calculations that are first performed by employing analytical gradients with polarized split-valence basis sets (6-311+G*)174–176 using the hybrid method, a mixture of Hartree–Fock exchange with density functional exchange-correlation (B3LYP).177–179 Then, the geometries are refined using the second-order Møller–Plesset perturbation theory (MP2)180 for large systems and with the infinite-order coupled-cluster method at the all singles and doubles (CCSD) level with the noniterative inclusion of triple excitations CCSD(T)181–183 and the same basis sets for relatively small systems.

The second step is to calculate ab initio PES spectra, which will be compared with the experimental data. In the past, assignment of molecular photoelectron spectra often was based on molecular orbital calculations and Koopmans’ theorem.184 Unfortunately, ab initio Hartree–Fock (HF) orbital energies produce large errors in ionization energies, completely misordering the final states in many cases. Therefore, HF orbitals cannot be used for interpreting PES of new species. Quasiparticle approximations in electron propagator theory (EPT) are convenient generalization of the Koopmans picture. In quasiparticle approximations, electrons assigned to canonical MOs are subjected to a correlated, energy-dependent potential. Earlier development of EPT was made by Lindberg and Ohrn,185 Pickup and Goscinski,186 and Simons and Smith,187 who originally called their theory the Equations of Motion (EOM) method. The most popular approximation of EPT, known as the outer valence Green Function method (OVGF) was developed by Cederbaum and co-workers188,189 and incorporated in Gaussian-98 by Ortiz and Zakrzewski.190–193 More recently, the partial third-order electron propagator theory (P3) was developed by Ortiz194,195 and incorporated in Gaussian-94 by Ortiz and Zakrzewski.193,195 Both OVGF and P3 are so-called direct methods, in which the ionization processes are considered as one-electron detachment processes. Corrections for electron correlation and relaxation are added directly to the one-electron MO energy. These methods allow one to perform calculations much faster and avoid spin-contamination when the initial state is a closed shell. Most importantly, these methods allow us to calculate one-electron vertical detachment energies (VDEs) from all occupied valence MOs, including transitions into final states that may have the same symmetry. The latter is a significant advantage compared to conventional methods to calculate VDEs at the MPn and CCSD(T) level of theories, which use energy differences between a given anion and the various states of its corresponding neutral. These are known as indirect methods, in which only transitions to the lowest state for a given symmetry can be calculated.

On the basis of our previous experience, we expect that both the OVGF and P3 methods can provide accuracies for VDEs within 0.1 eV for detachments from MOs near the HOMO and about 0.3 eV for detachments from deeper MOs for the nonstoichiometric molecules considered here. For recent reviews in the development of the electron propagator theory and its applications, see refs 196–198.

3.3. Combined Experimental and Theoretical Approach to Elucidate the Structure and Bonding of Nonstoichiometric Species. We emphasize that a photoelectron spectrum represents the electronic fingerprint of a given cluster. The correct identification of the global minimum of a given anion should allow accurate predictions of its vertical electron detachment energies using OVGF or P3. This predicted spectrum can then be compared with the experimental PES spectrum. Close agreement between the theory and experiment lends support for the predicted cluster structures, from which detailed analyses of chemical bonding and molecular orbitals ensue. For relatively small systems, such as the pentaatomic nonstoichiometric species focused in this article, complete and exhaustive searches for the global minima are feasible. Satisfying agreement has always obtained when the predicted spectra of the global minimum anions are compared to the experimental PES data. This is particularly effective when the anions are closed shell because in these cases all the one-electron detachment channels can be predicted using OVGF or P3. When the anions are open-shell with a single unpaired electron, both singlet and triplet final states can be observed in PES spectra. But the OVGF and P3 methods in general do not allow singlet excited states to be predicted. Fortunately, appropriate substitutions have in general allowed us to tune the electronic structure of a given anion to a closed-shell configuration. The application of the electron propagator methods has been invaluable for our combined experimental and theoretical approach to characterize nonstoichiometric species.

4. Pentaatomic Tetracoordinate Planar Carbon Molecules

As discussed in Section 2, nonstoichiometric molecules open new opportunities in designing previously unknown structures. Our first success in going beyond classical stoichiometry in designing new structures is to solve a long standing challenge in chemistry: how to make molecules containing tetracoordinate planar carbon. That the tetracoordinated tetravalent carbon atom prefers a tetrahedral arrangement of its four ligands was first recognized independently by J. H. van’t Hoff and J. A. LeBel in 1874. However, since the pioneering theoretical formulation of hypothetical tetracoordinate-planar-carbon (TPC) molecules by Hoffmann and co-workers thirty years ago,199 there have been substantial research efforts to design new molecules that may contain a tetracoordinate planar carbon.200–212 Schleyer and co-workers200–202 have computationally tested and predicted a wide variety of candidate molecules for TPC, many of which were reviewed recently.202 Keese and co-workers203,204 performed calculations on promising candidates and synthesized many such molecules. Radom and co-workers205,206 studied computationally a class of polycyclic hydrocarbons, called alkaplanes, in which
TPC can be achieved again by steric constraints. A divanadium complex, characterized structurally by Cotton and Miller, 207 is probably the first compound with a TPC. A variety of organometallic compounds, mostly containing group 4 and 5 elements, have since been reported by Erker, Gleiter, and co-workers to possess TPC.208–210

4.1. Experimental and Theoretical Characterization of the First Pentaatomic Tetracoordinate Planar Carbon Molecules: CAl4−, CAl3Si−, and CAl3Ge−. In our efforts to design new TPC molecules, we concentrate on small pentaatomic species, the smallest molecules to contain a TPC, which can be achieved again by steric constraints. A divanadium dianion was studied both experimentally and theoretically and was established to be the first pentaatomic species containing a planar carbon.38

The CAl4− anion, being electronically open-shell, is expected to be able to accept one more electron into its four-center ligand bond (Figure 2x). The CAl4− anion was studied both experimentally and theoretically and was established to be the first pentaatomic species containing a planar carbon.38

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The TPC dianion, 


corresponds to the four-center, $1b_2$ peripheral ligand–ligand bond (Figure 2x). The CAl4− anion was studied both experimentally and theoretically and was established to be the first pentaatomic species containing a planar carbon.38

Figure 3. Photoelectron spectra of CAl3Si−, CAl3Ge−, and NaCAl4− at 266 nm (4.661 eV). Vertical bars represent theoretical vertical detachment energies from the global minimum planar structure in each case. Data from refs 158 and 161.

Figure 4. Global minimum structure and the four-center highest occupied molecular orbitals for (a) CAl3Si−, (b) CAl3Ge−, and (c) NaCAl4−. Data from refs 158 and 161.
Figure 5. Photoelectron spectra of (a) SiAl\textsubscript{4}\textsuperscript{+}, (b) GeAl\textsubscript{4}\textsuperscript{+}, and (c) Al\textsubscript{5}\textsuperscript{−} at 355 nm (3.496 eV) and their respective global minimum structures. Selected bond lengths are in Å. Data from refs 159 and 160.

4.2. Other Pentaatomic Planar Species: SiAl\textsubscript{4}\textsuperscript{−}, GeAl\textsubscript{4}\textsuperscript{−}, and Al\textsubscript{5}\textsuperscript{−} Clusters. Pentaatomic planar carbon structures have also been theoretically predicted for mixed types of ligands: CAl\textsubscript{4}Si\textsubscript{2},\textsuperscript{211} C\textsubscript{2}Ga\textsubscript{3}Si\textsubscript{2}, and C\textsubscript{2}Al\textsubscript{3}Ge\textsubscript{2}.\textsuperscript{212} However, these species are more challenging to investigate experimentally because of the existence of cis and trans isomers and the fact that their anions are open shell systems. The 18-electron rule for planarity of the pentaatomic molecules have also been tested for molecules with central B, N, and O species. All of them have been found to have similar tetracoordinate square-planar structures.

We have further extended our searches for TPC molecules to include Si and Ge. The chemistry of Si and Ge is dominated by their tendency to form tetracoordinate tetrahedral structures, just as the tetracoordinate tetrahedral carbon. Our finding of TPC suggests that the heavier group IV elements may also be made to replace the central carbon in TPC. It is, however, not clear if the planar structure would be preserved when the first row central atom is substituted by a second or third row atom because of their increased atomic sizes. These molecules would be isoelectronic with the species containing a first row central atom, but the central cavity might be too small to accommodate the second or third row atom in the square-planar structure and their electronegativities are also too close. To address this question, we investigated SiAl\textsubscript{4}\textsuperscript{−} and GeAl\textsubscript{4}\textsuperscript{−} and their corresponding neutrals both experimentally and theoretically.\textsuperscript{159}

Figure 5 shows the PES spectra of SiAl\textsubscript{4}\textsuperscript{−} and GeAl\textsubscript{4}\textsuperscript{−} and their ground-state structures. Indeed, we found that the cavity of the Al\textsubscript{4} square is too small to fit the heavier Si or Ge atom. Although the planar structures are preserved, the Al\textsubscript{4} square is distorted to a trapezoid. Figure 6 shows the top few MOs of the C\textsubscript{2v} SiAl\textsubscript{4}\textsuperscript{−}. These MOs are similar to those found in the square-planar CAl\textsubscript{4} and the four-center peripheral bond can still be clearly identified. More interestingly, we note that the four-center MO is now stabilized and becomes HOMO–2 in SiAl\textsubscript{4}\textsuperscript{−}. This suggests that the SiAl\textsubscript{4} neutral resulting from removing the HOMO (which is dominated by contributions from the central atom) electron in SiAl\textsubscript{4}\textsuperscript{−} should still be planar because the four-center MO critical for planarity is still fully occupied. This is indeed the case. In fact, we found that the ground-state structure of the neutral SiAl\textsubscript{4} is very similar to the SiAl\textsubscript{4}\textsuperscript{−} anion with very small geometry changes.\textsuperscript{159} This is completely different from the CAl\textsubscript{4}\textsuperscript{−} case, where upon electron detachment the neutral ground state of CAl\textsubscript{4} becomes tetrahedral because the single occupation of the four-center bond is removed. This again proves the importance of the four-center peripheral bond in stabilizing the planar structure in the pentaatomic species.

The above analysis indicates that the 16-electron Al\textsubscript{5}\textsuperscript{−} cluster, which is isoelectronic with SiAl\textsubscript{4}, should also possess a similar planar structure. In fact, the Al\textsubscript{5} cluster had been known to be a C\textsubscript{2v} planar species, but its origin has never been explained. To confirm that the planarity of Al\textsubscript{5} and Al\textsubscript{5}\textsuperscript{−} is related to the concept derived from the TPC work, we carried out a combined experimental and theoretical investigation.\textsuperscript{160} The Al\textsubscript{5}\textsuperscript{−} anion is a closed-shell system and should give a rather simple PES spectrum because only doublet neutral states can be accessed by removing an electron from each of its filled MOs. The PES spectrum of Al\textsubscript{5}\textsuperscript{−} measured at 355 nm is shown in Figure 6c and compared to those of SiAl\textsubscript{4}\textsuperscript{−} and GeAl\textsubscript{4}\textsuperscript{−}. It is indeed relatively simple with three well-resolved peaks at this photon energy. The optimized structure of Al\textsubscript{5}\textsuperscript{−} anion with very small geometry changes.\textsuperscript{159} This is also compared to those of SiAl\textsubscript{4}\textsuperscript{−} and GeAl\textsubscript{4}\textsuperscript{−}. They are almost identical with very small bond length differences among the three species. The top four occupied MOs of Al\textsubscript{5}\textsuperscript{−} are also compared to those of SiAl\textsubscript{4}\textsuperscript{−}, as shown in Figure 6. The extra electron in the HOMO of SiAl\textsubscript{4}\textsuperscript{−} is absent in Al\textsubscript{5}\textsuperscript{−}, whose occupied MOs are nearly identical to the corresponding MOs of SiAl\textsubscript{4}\textsuperscript{−}. This similarity between the structure and MOs of Al\textsubscript{5}\textsuperscript{−} and SiAl\textsubscript{4}\textsuperscript{−} unequivocally confirmed that the origin of the planarity of Al\textsubscript{5}\textsuperscript{−} can be traced to the four center bond (HOMO–1), despite the fact that we found, unlike that of SiAl\textsubscript{4}\textsuperscript{−}, the potential energy
surfaces of Al$^-$ and Al$^+$ are rather flat relative to intramolecular rearrangements and their structures are rather fluxional.\textsuperscript{160}

From the above analyses on CaAl$_4$, CaAl$_4^-$, CaAl$_5^-$, CSiAl$_4^-$, CSiAl$_3^-$, SiAl$_3^-$, and SiAl$_4^-$, we see that the detailed understanding of the pentaatomic nonstoichiometric species can be used to predict structures and bonding in metal clusters, such as Al$_5^-$ and Al$_5^+$, and the simple electron counting rules that we developed on the basis of the occupation of the MOs have some predictive power.

5. Aromaticity in All-Metal Systems\textsuperscript{162,163}

Alloy clusters consisting of two or more types of atoms constitute a vast number of gaseous nonstoichiometric molecules. Whereas known bulk alloy materials may have definitive compositions, Berthollet may have well been right as far as gaseous alloy clusters are concerned, because in the gas phase almost any combination of atoms is possible. We have been interested in using aluminum as a base metal to explore nonstoichiometric alloy clusters and have obtained preliminary experimental and theoretical results for a number of systems. There are two advantages of using aluminum as the base metal to investigate alloy clusters. First, Al has a single natural isotope, greatly simplifying the alloy cluster mass analyses. Second, the electronic structures of Al and its clusters are relatively simple and well understood, simplifying the theoretical treatments of the alloy clusters to some extent and affording more accurate theoretical calculations. Our first detailed experimental and theoretical characterization of aluminum alloy clusters was along the line of our planar carbon work described in section 4 above. Our subject was the CuAl$_4^-$ cluster, which led to our discovery of aromaticity in all-metal systems,\textsuperscript{162} which will be discussed in this section.

5.1. All-Metal Aromatic Molecules: MAl$_4^-$ (M = Cu, Li, Na).\textsuperscript{162} As shown in section 4.2, the pentaatomic MAl$_4^-$ species changes from a square-planar TPC to a trapezoidal structure when M is changed from C to Si or Ge because of the increased atomic size (Figure 5). More interestingly, we found that the four-center MO essential for the planar structure has dropped in energy from HOMO in CaAl$_4^-$ to HOMO$-2$ in SiAl$_4^-$ (Figure 5). Consequently, even the 16-electron Al$_4^-$ or the 15-electron Al$_5^-$ also assume a similar trapezoidal planar structure as SiAl$_4^-$ (Figure 5). Since the four-center MO is still HOMO$-1$ in Al$_5^-$, it would be natural to infer that the 14-valence-electron CuAl$_4^-$ might also have a similar planar structure as that of SiAl$_4^-$ or Al$_5^-$ because the four-center MO would still be doubly occupied. Extensive theoretical searches led to two low-lying isomers for CuAl$_4^-$, a $C_4$ square-pyramidal structure (Figure 7a) and a side-capped $C_2$ planar structure (Figure 7b) with the former being the global minimum. Even though a trapezoidal structure similar to SiAl$_4^-$ was found to be a minimum, it was much higher in energy. Figure 8a shows the PES spectrum of CuAl$_4^-$ (Figure 8a).

This was a surprising result because we expected that the trapezoidal structure to be the most stable on the basis of the MO analyses of SiAl$_4^-$ and Al$_5^-$ (Figure 8a). Close examination of the two low-lying isomers of CuAl$_4^-$ revealed more surprises. They both appear to contain an Al$_4^-$ square with very minor geometrical modifications in the two isomers. Detailed analyses of the electronic structure further revealed that the Al$_4^-$ square can be viewed as an Al$_4^-$ dianion and the two isomers of CuAl$_4^-$ should be viewed as an Al$_4^-$ dianion coordinated by a Cu$^+$ cation. To gain more insight into the structural and bonding properties of the CuAl$_4^-$ system, we further performed a detailed theoretical investigation of the isolated Al$_5^-$ species. Even though this dianion was not expected to be stable as a gaseous species toward autodetachment of an electron, we anticipated that metastable local minima could be located due to the long range Coulomb barrier existing in gaseous multiply charged anions.\textsuperscript{215}

Indeed, we found a perfect square-planar structure for the

![Figure 7. Structures of Al$_5^-$ and the two low-lying structures of CuAl$_4^-$, LiAl$_4^-$, and NaAl$_4^-$](image)

![Figure 8. Photoelectron spectra of (a) CuAl$_4^-$, (b) LiAl$_4^-$, and (c) NaAl$_4^-$ at 266 nm (4.661 eV). Vertical bars represent theoretical vertical detachment energies from the global minimum pyramidal structure in each case. Data from ref 162.](image)
isolated $\text{Al}_4^{2-}$ (Figure 7c). Most interestingly, the isolated square-planar $\text{Al}_4^{2-}$ seems to undergo very little structural change in forming the $\text{CuAl}_4^{-}$ molecule. To understand the planarity and structural integrity of the $\text{Al}_4^{2-}$ unit, we analyzed its valence MOs, as shown in Figure 9. Clearly the HOMO, which is doubly occupied, is a delocalized $\pi$-orbital. The HOMO$-1$ and HOMO$-2$ are $\sigma$-bonding orbitals, where the HOMO$-2$ is reminiscent of the four-center bond in the TPC species. The rest of the occupied MOs are essentially $\text{Al}_3s$ lone pairs. The observation of the delocalized $\pi$-HOMO is interesting. Moreover, we found that a similar delocalized $\pi$-orbital is also present in $\text{CuAl}_4^{-}$ in both its pyramidal and planar isomers. In fact, the valence MOs of $\text{CuAl}_4^{-}$ are essentially identical to that of the bare $\text{Al}_4^{2-}$ dianion. We suspected that this $\pi$-orbital holds the key to understanding the structure and bonding of the $\text{CuAl}_4^{-}$ species and why $\text{Al}_4^{2-}$ seems to exhibit such structural tenacity in both isomers.

Upon careful examination of its structure and bonding, we recognized that $\text{Al}_4^{2-}$ exhibits characteristics of aromaticity. First of all, it possesses two completely delocalized $\pi$-electrons, satisfying the $(4n + 2)$ electron-counting rule for aromatic compounds. Second, $\text{Al}_4^{2-}$ has a perfect square structure, due to the delocalization of the $\pi$-electrons, which is exactly what one would expect for an aromatic system.

To confirm the aromaticity in $\text{Al}_4^{2-}$, we reasoned that the alkali metal cations might be better to stabilize it than $\text{Cu}^+$ and they would have much less perturbation. We used a similar strategy previously to stabilize the common inorganic dianion, $\text{SO}_4^{2-}$, in the gas phase by making $\text{NaSO}_4^-$ or $\text{KSO}_4^-$ complexes. We thus carried out theoretical investigations of $\text{LiAl}_4^-$ and $\text{NaAl}_4^-$ and, as expected, found two isomers similar to those of $\text{CuAl}_4^-$, again with the pyramidal structure as the global minimum for both alkali systems, as shown in Figure 7. More importantly, the $\text{Al}_4^{2-}$ unit in both isomers of $\text{LiAl}_4^-$ and $\text{NaAl}_4^-$ are indeed nearly identical to the bare $\text{Al}_4^{2-}$ dianion, more so than in the $\text{CuAl}_4^-$ system. We further obtained the PES spectra of $\text{LiAl}_4^-$ (Figure 8b) and $\text{NaAl}_4^-$ (Figure 8c), which are indeed very similar to that of $\text{CuAl}_4^-$. Again the calculated vertical detachment energies for the global minimum pyramidal structures of both alkali systems were found to be in excellent agreement with the experimental spectra. We thus confirmed the unique electronic structure of $\text{Al}_4^{2-}$ and the conjecture that aromaticity is responsible for its structural stability in the various isomers of the $\text{MAI}_4^-$ systems.

Aromaticity usually refers to cyclic, planar, or conjugated molecules that possess $(4n + 2)$ $\pi$-electrons and have specific chemical and structural stability. Aromaticity has been extended to include inorganic, organometallic compounds, and three-dimensional structures, though they are in general still organic systems. Analogy can be made about our newly discovered aromatic $\text{Al}_4^{2-}$ cluster with the prototypical aromatic system, benzene, in which aromaticity is responsible for its perfect hexagonal structure with all equal C–C bonds, rather than the classical alternating single and double bonds. Furthermore, like benzene in $\text{M(C}_6\text{H}_6)^2^-$ type sandwich complexes, the $\text{Al}_4^{2-}$ dianion also preserves its structural integrity in forming the
MAI₄⁻ complexes. Finally, we found that the vibrational frequencies for the isolated Al₂₂⁻ dianion are also very similar to those in both the pyramidal and planar structures of the three MAI₄⁻ species. We also investigated theoretically the structures of neutral M₂Al₄ species and found again that the most stable structures contain the intact Al₂₂⁻ dianion. This opens the possibility that bulk compounds or solids with the aromatic Al₂₂⁻ building blocks might be feasible.

5.2. Aromaticity in Heterocyclic MAl₃⁻ Clusters (M = Si, Ge, Sn, Pb). The concept of nonstoichiometry gives us great flexibilities to design new molecules and new structures. To further confirm and extend the idea of aromaticity in Al₂₂⁻, we asked if an isoelectronic, singly charged hetero-cluster MAl₃⁻ would also exhibit aromaticity, where M is a group IV atom. For these species, either a heterocyclic or trigonal pyramidal structure can be conceived. If aromaticity exists in these species, the heterocyclic structure should have an advantage. In fact, we previously investigated CAl₃⁻ and found that it actually has a C₃ᵥ structure without any Al−Al bonding. Thus, substitution of one Al by Si, Ge, Sn, or Pb in Al₂₂⁻ would give us an opportunity to study how the stability and property of the delocalized π-MO, which should exist in the cyclic structure, would change when the electronegativity and covalency change from Si to Pb.

Figure 10 shows the PES spectra of MAI₃⁻ (M = Si, Ge, Sn, Pb). The spectra are similar with systematic changes when M is heavier, suggesting that these species should all have similar structures. A low binding energy tail, due to a minor isomer, was observable in the spectra of SiAl₃⁻. It was observable in the spectra of GeAl₃⁻ and almost completely gone in the spectra of PbAl₃⁻, which shows four relatively sharp and well-resolved peaks. Our extensive theoretical searches found that the global minimum for MAI₃⁻ is indeed a heterocyclic structure, each with a low-lying pyramidal isomer, as shown in Figure 11. The calculated VDEs of the four lowest lying vertical one-electron detachment processes for the cyclic isomers were shown as vertical bars in Figure 10. Good agreement was obtained for all four anions between the calculated VDEs of the cyclic structures and the experimental spectra. The only serious deviation was seen for the B peak of PbAl₃⁻, which was probably caused by a strong spin−orbit effect, not taken into account in our calculation. On the other hand, the calculated VDEs for the low-lying pyramidal isomers do not agree with the main experimental PES features. The first VDEs for all the four pyramidal isomers are lower than that for the global minimum cyclic structure, suggesting that the lower binding energy tail in the PES spectra might be due to this isomer. More interestingly, along the SiAl₃⁻−GeAl₃⁻−SnAl₃⁻−PbAl₃⁻ series the presence of the second isomer in the experimental PES spectra is decreasing, suggesting that the isomer is less and less populated in the experiment. This observation is in complete agreement with the results of our ab initio calculations, where along the SiAl₃⁻−GeAl₃⁻−SnAl₃⁻−PbAl₃⁻ series the relative energies of the second isomer is steadily increasing, being 14.7, 18.4, 29.2, and 33.4 kcal/mol for this series, respectively. The excellent overall agreement between the calculated spectra for the cyclic structures and the experimental data, as well as the presence of the low-lying isomers in the experiment and the relative stability of the two isomers from the calculations, lend considerable credence for the cyclic global minimum structure for the MAI₃⁻ species and its low-lying pyramidal isomers. The origin of the planarity and cyclization of MAI₃⁻ is revealed from detailed analyses of their occupied MOs, which are shown in Figure 12 for SiAl₃⁻ in detail. The
MOs for the other species are similar and only their delocalized \( \pi \) orbitals are shown. The similarity of the MOs of the MAI3\(^-\) species and those for Al4\(^2-\) (Figure 9) is obvious. Thus, the stability of the cyclic structure relative to the pyramidal structure for the MAI3\(^-\) species is attributed to the presence of the delocalized \( \pi \) bond, i.e., aromaticity. We note that the \( \pi \) orbital tends to be more localized in SiAl3\(^-\) and becomes more delocalized in PbAl3\(^-\). This trend coincides with the trend of stability for the cyclic isomers relative to the pyramidal ones. In the lighter CAI\(^-\) species we found that the pyramidal structure was the only minimum.\(^{37}\) The instability of the CAI\(^-\) planar cyclic isomer is a result of the complete localization of the two \( \pi \) electrons on the C atom, because it is much more electronegative than Al. This observation again indicates the importance of the delocalized \( \pi \) orbital or aromaticity in the hetero-systems.

5.3. Aromatic Ga4\(^2-\) and In4\(^2-\) in Gas-Phase Clusters and Organometallic—Ga4 Molecules and Possible Aromatic Clusters as Building Blocks of Solid Materials. We further investigated the aromaticity in the isoelectronic systems of Al4\(^2-\):

\[ \text{GaAl} \] and InAl\(^-\). We obtained PES spectra of NaGaAl\(^-\) and NaInAl\(^-\) and found that they are nearly identical to that of NaAl3\(^-\). Our theoretical investigations confirmed that indeed these isoelectronic series have identical structure and bonding properties.\(^{219}\)

While all-metal aromatic systems (M4\(^2-\)) have been proved to be present in the gas-phase clusters, the question is: can such building blocks be made in bulk materials? The answer is yes. Recently, Twamley and Power synthesized a remarkable organogallium molecule, K2[Ga4(C6H3-2,6-Trip2)] (Trip = C6H2-2,4,6-iPr3), whose X-ray structure shows clearly a square-planar Ga4\(^2-\) unit, stabilized by two K\(^+\) cations and coordinated and protected by the two bulky organic ligands.\(^{220}\) We have carried out model calculations and showed that the structure and bonding of the Ga4\(^2-\) unit in this organometallic molecules are in fact similar to those in our gaseous clusters. It possesses the same two \( \pi \)-electrons and is indeed aromatic, explaining its four equal Ga–Ga bonds and near square structure. Therefore, the K2[Ga4(C6H3-2,6-Trip2)] species can be considered as the first crystal structure containing the all-metal (Ga4\(^2-\)) building block. Solid alloy materials may also be synthesized to contain the aromatic M4\(^2-\) units if they can be completely separated in bulk crystals, because close contacts between two M4\(^2-\) units may lead to fusion.\(^{221}\) The fact that the Ga4\(^2-\) unit can exist in the organometallic molecules is due to its complete isolation and protection by the two bulky ligands.\(^{220}\)
obtained theoretical insight\textsuperscript{22} that a well-known Na–Hg alloy (Na\textsubscript{3}Hg\textsubscript{2}),\textsuperscript{223} containing Hg\textsubscript{4} squares as building blocks,\textsuperscript{224} in fact consist of aromatic Hg\textsuperscript{6} units, which are isosteric and isoelectronic to Al\textsubscript{2}\textsuperscript{2–}. We should point out that the two \(\sigma\)-bonding orbitals (Figure 9) in the M\textsubscript{4}\textsuperscript{2–} species are also important and render them \(\sigma\)-aromaticity,\textsuperscript{218,219,222} in addition to \(\pi\)-aromaticity. A recent calculation showed that a significant diamagnetic ring current originates in the \(\sigma\) system.\textsuperscript{224} Robinson and co-workers\textsuperscript{17} studied organometallic compounds containing aromatic Ga\textsubscript{2}\textsuperscript{2–} unit.

We believe that aromaticity may be a rather common phenomenon in solid-state chemistry or inorganic solid materials, not just in organic chemistry. We reiterate that the expansion of aromaticity in the new territory was made possible due to our understanding and pursuance of the structure and bonding in new nonstoichiometric species and going beyond classical stoichiometry and classical valence models.

6. Conclusions and Perspectives

Although the majority of known molecules and compounds are stoichiometric according to the classical valence theory and the idea of stoichiometry has helped put chemistry on the right track at the dawn of modern chemistry, now at the beginning of the 21st century and two hundred years after the great debate between Berthollet and Proust, it is time again to recognize the importance of nonstoichiometry. Whereas nonstoichiometric molecules, such as NO\textsubscript{2}, are well-known in chemistry, the number of nonstoichiometric species we can create in the gas phase with the laser vaporization or sputtering techniques is in fact infinite. Yet there is no theoretical model that allows us to readily predict and rationalize their structures and other molecular properties. While it is true that computational chemistry has been developed to the point that it can treat nearly every small molecular system to a satisfactory level of accuracy and indeed has been applied to numerous novel and nonstoichiometric molecules, the sheer number of possible nonstoichiometric species demands development of simple and qualitative models that possess predictive powers and allow classes of new species to be understood and rationalized. New research paradigms combining state-of-the-art experimental data and ab initio theories are needed and new concepts and ideas need to be synthesized from seemingly unrelated facts and observations. A few first steps in the new direction are described in this article and our initial efforts have already yielded a few surprises. But much more is waiting to be done.

While the nonstoichiometric species emphasized here are for gaseous clusters, the ideas and concepts may have ultimate relevance to bulk solid materials. Stoichiometry, or the lack thereof, has profound effects on the properties and structures of any composite materials and it is even more important in the emerging field of nanomaterials and nanotechnology. As a matter of fact, the very nature of any materials interface entails nonstoichiometry.

One way to extend the knowledge from the gas-phase species to solid materials is to design new building blocks based on extra stability of certain nonstoichiometric species. While cluster science has made major strides in this area by searching for “magic” clusters, it remains a trial-and-error affair. A systematic and interactive approach between theory and experiment, through understanding of the structure and bonding in these species and the nature of their extra stability, is crucial for making further progress. We have shown that planar tetra-coordinate carbon species, such as [CAL\textsubscript{2}\textsuperscript{2–}], might be viable in solid materials. The finding of all-metal aromatic systems, [Al\textsubscript{2}\textsuperscript{3–}], [Ga\textsubscript{2}\textsuperscript{3–}], [In\textsubscript{2}\textsuperscript{3–}], or [Tl\textsubscript{2}\textsuperscript{3–}], has already been suggested to be connected to a newly synthesized organometallic compound and Na–Hg amalgams.

The relevance of nonstoichiometry to nanomaterials and nanotechnology is conspicuous. After all, nanoparticles are small and contain only a few tens to a few thousands atoms. At these small sizes, one expects that impurity atoms will play more critical roles in determining the properties and structure of a nanoparticle. Thus understanding how impurity atoms will modify properties of nanoparticles will be important for tuning their chemical, electronic, and magnetic properties. Additionally, concepts in nonstoichiometric species may help direct the atomic assembling of desirable nanomaterials and interparticle interactions.

Certainly, many important bulk materials, such as the high temperature superconductors or many alloy materials, are intrinsically nonstoichiometric materials. Defect sites in bulk materials and materials’ interfaces, such as the important Si/\textsubscript{SiO\textsubscript{2}} interface or catalytic particle/substrate interfaces, are nonstoichiometric in nature. Many amorphous and glassy materials are nonstoichiometric too. Nonstoichiometric materials are intrinsically challenging to characterize experimentally and theoretically, but they may lie at the core of our current search for novel materials with tailored properties. Under thermodynamic equilibrium, one ultimately obtains the most thermodynamically stable products, which are usually stoichiometric. However, under nonequilibrium conditions, a great variety of compositions may be possible, and these are in fact the very strategies with which many novel materials have been synthesized, as well as the majority of the gas-phase molecules emphasized in this article.

Nonstoichiometry is only relative to stoichiometry and represents another level of complexity. While stoichiometric molecules and materials have been well understood since the time of Berthollet and Proust two centuries ago, nonstoichiometric species and materials may become a major theme and present a great new frontier in chemistry and materials science in the coming century. The chemical intuition of Berthollet, who was advocating the idea of indefinite chemical compositions at the dawn of chemistry two centuries ago, might have been way ahead of his time, but he may have been right after all.

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References and Notes

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