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FEATURE ARTICLE

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 tetracoordinate planar carbon molecules, CAl_4^-, CAl_3Si^-, CAl_3Ge^-, and a salt complex, $Na^+[CAl_4^{2-}]$ containing a planar carbon building block. We also review our recent discovery of an all-metal aromatic species, Al_4^{2-}, in a series of bimetallic clusters, $M^+[Al_4^{2-}]$ (M = Cu, Li, Na), as well as the Ga_4^{2-} and In_4^{2-} analogues. We also show the existence of aromaticity in a series of isoelectronic singly charged anions, MAl_3^- (M = 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 Richter[1] and was originated from the Greek words “*στοιχειον*”, which means “element,” and “*μϵτρϵιν*”, 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 provided him with examples in the cases of oxides and salts. Furthermore, the fact that some metals formed several oxides 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 overthrew 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 Al_4C_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

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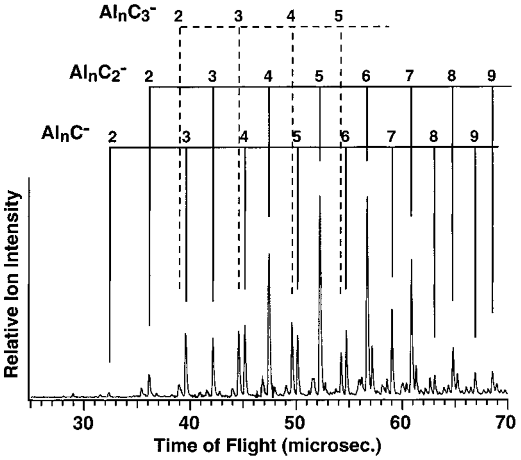


Figure 1. Time-of-flight mass spectrum of $Al_nC_x^-$ clusters from laser vaporization of a composite Al/C target.

Waals species, which are also prevalent in the gas phase, are a different subject matter. The $Al_xC_y^-$ species shown in Figure 1 certainly represent examples of chemically bound species, yet with a variety of composition.

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 CH_4, NH_3, H_2O, and HF. While hyperstoichiometric hydrides such as NH_4, NH_4^-, H_3O, and H_3O^- are known,[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 Al_xC_y, one might expect that only the Al_4C_3 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 $[(Al^{3+})_4(C^{4-})_3]$. Yet, as seen in Figure 1, even though the $Al_4C_3^-$ species exists, there are many other stable and nonstoichiometric gaseous Al−C species. We cannot predict and rationalize their structures and relative stabilities easily from any known valence models. There is clearly a need to go beyond the classical valence models and advance new chemical concepts capable of treating and rationalizing these new nonstoichiometric species.

Nearly two hundred years after the great debate between Berthollet and Proust, nonstoichiometric species have attracted the attention of many research groups over the last two decades owing to the developments of sophisticated gas-phase experimental techniques and theoretical methods. A large amount of experimental and theoretical data has been accumulated with a substantial body of literature.[6−156]

Probably the best known nonstoichiometric binary compounds are suboxides of alkali metals.[6] Rubidium and cesium form highly colored crystals containing fused octahedral metal clusters with oxygen atoms in the center of the metal octahedra. These include bi-octahedral Rb_9O_2 and tri-octahedral $Cs_{11}O_3$.[6] In 1978, Wu, Kudo, and Ihle[7,8] experimentally observed Li_3O as a stable molecule in the gas phase, which formally violates the octet rule. Schleyer and co-workers subsequently performed theoretical calculations on Li_3O and many other hyperalkali species.[9−14] Later, Marsden and co-workers[15−18] studied similar hyperalkali metal species with 7 to 12 alkali metal atoms. Kudo and Wu verified by mass spectrometry the existence of many theoretically predicted hyperalkali metal molecules,[19−22] including a remarkable hyperlithium molecule, CLi_6,[22] although structural and spectroscopic information on these species is not readily available experimentally.

Boldyrev, Simons, and Schleyer computationally predicted and characterized hyperberillium Be_2O and BeOB,[23] and hypermagnesium Mg_2O, Mg_3O, Mg_4O,[24,25] and Mg_3C species.[26] Castleman and co-workers[27] experimentally observed an unusually high-intensity mass spectral peak for the Mg_2O^+ cation in agreement with the theoretical prediction of the exceptional stability of neutral Mg_2O and the Mg_2O^+ cation.[24,25] Andrews experimentally observed vibrational spectra of Be_2O in a matrix isolation experiment.[28,29]

Boldyrev, Schleyer, and others also predicted computationally that hyperaluminum Al_3O and Al_4O,[30] and Al_4N^- species[31] should be stable molecules in the gas phase. Al_4N and Al_4N^- have been experimentally observed and characterized by Wang, Jena, and co-workers.[32] Wang and co-workers have also characterized a series of Al_xO_y species using anion photoelectron spectroscopy.[33,34] The structures of these hyperaluminum molecules have been subsequently investigated theoretically by Rohlfing,[33] Ghanty and Davidson[35] and very recently by Ortiz and co-workers.[36] A series of hyperaluminum carbon species, $Al_xC_y^-$ and Al_xC_y, have also been studied in a joint experimental and theoretical effort by Wang, Boldyrev, and co-workers.[37−41] Nonstoichiometric Al_xS_y species were observed by Kaya and co-workers[42,43] and the reactivities of these species were studied by Parent.[44,45] Anderson and co-workers experimentally observed and characterized a series of hyper-boron B_nO^+ species.[46] Recently, Bowen and co-workers have investigated Al−Cu and Al−Li mixed clusters using anion photoelectron spectroscopy,[47,48] and Jena and co-workers have performed theoretical calculations on the same systems.[49,50]

Hypersilicon clusters have been studied more extensively.[51−94] Margrave et al.,[51] Graham et al.,[52−56] Saykally et al.,[57] and Rohlfing et al.[58] studied Si_xC_y species spectroscopically. Ab initio calculations of the Si_xC_y species were performed by Schaefer et al.,[59,60] Sabin et al.,[61,62] Rittby,[56,63−65] Rohlfing et al.,[58] and Boldyrev et al.[66] Schwarz and co-workers performed mass spectroscopic studies of Si_xO and Si_xN species.[67,68] Brough and Morse studied Si_2N spectroscopically.[69] Ab initio calculations of Si_xN were performed by Boldyrev and Simons.[68] Si_xO were calculated by Schaefer et al.,[70] as well as by Boldyrev, Simons, and others.[66,71] Wang, Nicholas, and co-workers[72−76] have characterized a series of Si_xO_y and Ge_xO_y species using anion photoelectron spectroscopy and ab initio calculations. Weltner et al.[77] studied Si_xO using ESR while Gingerich and co-workers obtained thermodynamic data for Si_xC and Si_xN.[78,79] There have also been a few studies of nonstoichiometric III−V semiconductor clusters. Smalley and co-workers pioneered the experimental study of Ga_xAs_y clusters.[80−83] Weltner et al. studied small Ga_xAs_y clusters using matrix ESR spectroscopy.[84] Mandich and co-workers studied In_xP_y clusters.[85] Neumark et al. have studied nonstoichiometric In_xP_y, Ga_xP_y, and B_xN_y clusters using anion photoelectron spectroscopy.[86−88] Smalley et al.[82,83] and Balasubramanian and Feng[89−94] have performed quantum chemical studies of a number of small III−V semiconductor clusters.

Relatively fewer investigations have been done on gaseous nonstoichiometric transition metal species. Knickelbein[95,96] measured the ionization potentials of Sc_nO ($n = 5−36$) and Y_nO ($n = 2−31$). Yang, Hackett, Salahub, and co-workers performed combined spectroscopic and theoretical studies of Nb_3O[97] and Nb_3C_2.[98] Wang and co-workers have studied extensively nonstoichiometric transition metal oxide species[99−106] and carbide clusters[107−112] using anion photoelectron spectroscopy. Andrews and co-workers[113−116] identified a number of nonstoichiometric oxides of transition metals and f-block metals using matrix isolation. Schaefer and co-workers,[117] Bauschlicher,[113,116] and Gutsev, Rao, and Jena[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_3O, Nb_3O, and Ta_3O.[120] Aluminum−cobalt clusters have been studied by Knickelbein and Menezes.[121] In a series of articles[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[126] also studied Y_3C_2 and $Y_3C_2^+$ by combining the PFI-ZEKE experiments with DFT calculations.

The discovery of the metallocarbohedrenes (met-cars) by Castleman and co-workers[127,128] represents a new interesting class of nonstoichiometric molecular clusters, which contain a carbon-to-metal ratio of 1.5 (M_8C_{12}). Many experimental[129−140] and theoretical[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+} sites in the two $(MgC_2)_2$ and $(MgC_2)_4$ clusters, reminiscent of what is seen in the transition metal met-car compounds. The researches on met-cars have been extensively reviewed.[155,156]

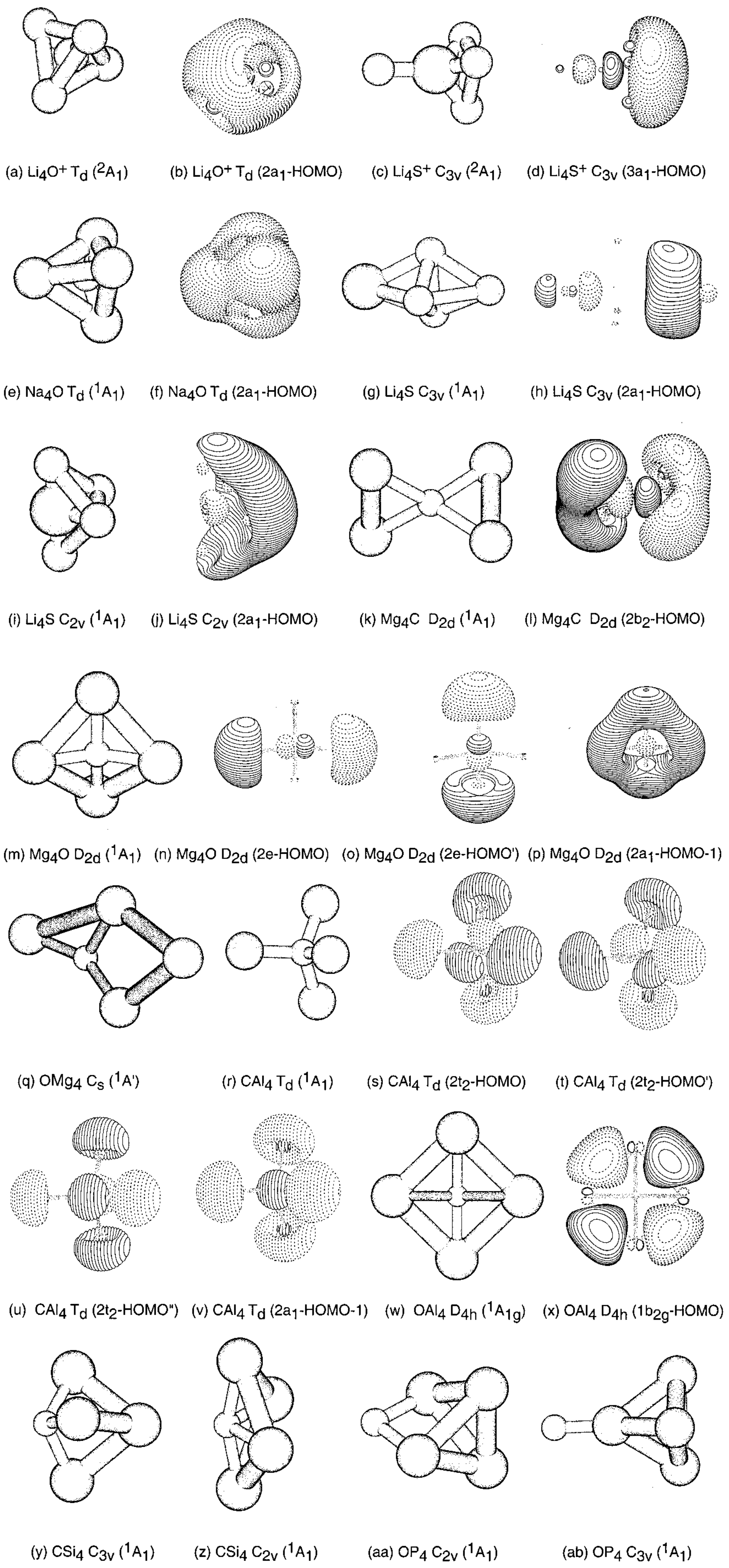
Recently, using a combined experimental and theoretical approach, we have investigated and characterized a number of novel gaseous nonstoichiometric species.[37−41,157−163] The purpose of this Feature Article is to systematize the ideas of nonstoichiometry and to review recent progress and development in our laboratories, which led to observations of the first 5-atom planar carbon molecules,[38,158,161] Napoleon hat type 4-atom species,[157] and more recently, all-metal aromaticity.[162,163] In the next section we provide one simple model that provides a framework to help understand bonding in a series of pentaatomic nonstoichiometric molecules. We selected this class of molecules because they have been studied reasonably well and are easier to comprehend. Our experimental and theoretical approaches will be described in section 3, followed by a presentation in section 4 on our recent experimental and theoretical characterizations of a number of pentaatomic tetracoordinate planar carbon molecules. In section 4 we also extend the ideas of the pentaatomic planar carbon species to elucidate the structure and bonding of a number of non-carbon-containing pentaatomic species. In section 5, we discuss our recent discovery of aromaticity in all-metal cluster systems, which is a direct consequence of the prior work on the pentaatomic planar species. We also demonstrate that the ideas and concepts developed for the gas-phase species may provide significant insight into the structure and bonding of condensed-phase materials. The article concludes with some perspectives of the field of nonstoichiometric chemistry in section 6.

2. Pentaatomic Nonstoichiometric Molecules and Ligand−Ligand Bonding

As mentioned in the Introduction, conventional valence models,[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 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 monovalent 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 $1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^4 3t_2^6 1t_1^6$ for CF_4. Those pentaatomic molecules between, 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 $1a_1^2 1t_2^6 2a_1^1$. 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, OLi_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 that 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 M and X. Recently, Schleyer and co-workers[166] predicted that OLi_4^+ has a global minimum at the T_d symmetry, as shown in Figure 2a. According to these data, the Li...Li distance in that structure is 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...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



(a) Li_4O^+ T_d ($^2A_1$) (b) Li_4O^+ T_d ($2a_1$-HOMO) (c) Li_4S^+ C_{3v} ($^2A_1$) (d) Li_4S^+ C_{3v} ($3a_1$-HOMO)

(e) Na_4O T_d ($^1A_1$) (f) Na_4O T_d ($2a_1$-HOMO) (g) Li_4S C_{3v} ($^1A_1$) (h) Li_4S C_{3v} ($2a_1$-HOMO)

(i) Li_4S C_{2v} ($^1A_1$) (j) Li_4S C_{2v} ($2a_1$-HOMO) (k) Mg_4C D_{2d} ($^1A_1$) (l) Mg_4C D_{2d} ($2b_2$-HOMO)

(m) Mg_4O D_{2d} ($^1A_1$) (n) Mg_4O D_{2d} (2e-HOMO) (o) Mg_4O D_{2d} (2e-HOMO') (p) Mg_4O D_{2d} ($2a_1$-HOMO-1)

(q) OMg_4 C_s ($^1A'$) (r) CAl_4 T_d ($^1A_1$) (s) CAl_4 T_d ($2t_2$-HOMO) (t) CAl_4 T_d ($2t_2$-HOMO')

(u) CAl_4 T_d ($2t_2$-HOMO") (v) CAl_4 T_d ($2a_1$-HOMO-1) (w) OAl_4 D_{4h} ($^1A_{1g}$) (x) OAl_4 D_{4h} ($1b_{2g}$-HOMO)

(y) CSi_4 C_{3v} ($^1A_1$) (z) CSi_4 C_{2v} ($^1A_1$) (aa) OP_4 C_{2v} ($^1A_1$) (ab) OP_4 C_{3v} ($^1A_1$)

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 MX_4 Species Containing between 8 and 32 Valence Electrons

representative molecule	no. of valence electrons	electronic configuration at T_d structure	expected minimum structure
CH_4, CNa_4	8	$1a_1^{2}1t_2^{6}$	T_d
OLi_4^+, ONa_4^+	9	$1a_1^{2}1t_2^{6}2a_1^{1}$	T_d
OLi_4, ONa_4	10	$1a_1^{2}1t_2^{6}2a_1^{2}$	T_d
	11	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{1}$	
CMg_4	12	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{2}$	D_{2d}
	13	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{3}$	
OMg_4	14	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{4}$	D_{2d}
	15	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{5}$	
CAl_4	16	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}$	T_d
CAl_4^-	17	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{1}$	D_{4h}
OAl_4, CAl_4^{2-}	18	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{2}$	D_{4h}
	19	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{3}$	
CSi_4	20	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{4}$	
CSi_4^-	21	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{4}3t_2^{1}$	
	22	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{4}3t_2^{2}$	
	23	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{4}3t_2^{3}$	
	24	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{4}3t_2^{4}$	
	25	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{4}3t_2^{5}$	
OP_4	26	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{4}3t_2^{6}$	
	27	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{4}3t_2^{6}1t_1^{1}$	
CO_4	28	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{4}3t_2^{6}1t_1^{2}$	D_{2d}
	29	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{4}3t_2^{6}1t_1^{3}$	
	30	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{4}3t_2^{6}1t_1^{4}$	
CF_4^+	31	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{4}3t_2^{6}1t_1^{5}$	
CF_4	32	$1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{4}3t_2^{6}1t_1^{6}$	T_d

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 3.085 Å for Li_2^+. 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} ($^2A_1$) structure as shown in Figure 2c, 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 that structure is shown in Figure 2d and it reflects clearly the desire for ligand−ligand bonding.

The pentaatomic hyperstoichiometric molecules OLi_4 and ONa_4 with 10 valence electrons have been predicted to have a tetrahedral structure by Schleyer and co-workers[9,11] and OLi_4 has been observed experimentally by Wu.[19] The ligand−ligand distances are in the right range for both molecules: 2.840 Å for Li−Li in OLi_4 and 3.496 Å for Na−Na in ONa_4. Both species have the $2a_1$-HOMO doubly occupied, as shown in Figure 2f for Na_4O, 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 SLi_4 molecule, the Li−Li distance is again too long (3.620 Å), similar to that in SLi_4^+, 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 as minima with the C_{3v} one being more stable in our calculations by 3.1 kcal/mol [CCSD(T)/6-311+G(2df)//MP2(full)/6-311+G*]. In both structures ligand−ligand distances are shortened, allowing more effective ligand−ligand bonding, as evidenced in their HOMOs (Figure 2h,j).

2.2. Pentaatomic Species with 12, 14, and 16 Valence Electrons. In the nonstoichiometric CMg_4 molecule with 12 valence electrons (Table 1), two electrons occupy the triply degenerate HOMO ($2t_2$) under the T_d structure. The T_d-CMg_4 is thus expected to be subjected to Jahn−Teller distortions, giving rise to a lower symmetry CMg_4. Indeed, our ab initio calculations (B3LYP/6-311+G*) yielded a D_{2d} ($^1A_1$) structure (Figure 2k). The $2b_2$-HOMO (Figure 2l) is bonding between each pair of ligand atoms, but antibonding between the two pairs. This is again a new type of chemical bond. It is a two-electron four-center bond, but split between two pairs of ligands. The calculated Mg−Mg bond length (2.908 Å) within each pair of ligands is very similar to the Mg−Mg bond (2.861 Å) in the linear HMg−MgH molecule at the same level of theory, again showing the importance of the ligand−ligand bonding.

An example of pentaatomic nonstoichiometric molecules with 14 valence electrons is OMg_4. Under T_d symmetry, its HOMO ($2t_2$, Table 1) is filled with four electrons and it would be Jahn−Teller unstable similar to the 12-electron system, CMg_4. We found two structures for OMg_4 with very close energies. One structure has a butterfly-type D_{2d} ($^1A_1$) symmetry (Figure 2m). The HOMO of this isomer is a filled nonbonding degenerate 2e orbital (Figure 2n,o), but its HOMO−1 is a ligand−ligand bonding orbital (Figure 2p). Therefore, the stability of the D_{2d} OMg_4 isomer comes from the $2a_1$-(HOMO−1) orbital, which is analogous to the peripheral bonding MO in Na_4O (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 OMg_4 is more stable by 1.4 kcal/mol and has C_s ($^1A'$) 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 OMg_4 is not a very stable molecule with a dissociation energy of only 7.9 kcal/mol to OMg_3 + Mg.

The 16-valence-electron species CAl_4 is expected to have a tetrahedral structure (Figure 2r) on the basis of its closed-shell electron configuration, $1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}$. The first four ($1a_1^2$ and $1t_2^6$) orbitals are the C−Al σ-bonds. The next four ($2a_1^2$ and $2t_2^6$) orbitals are bonding and antibonding linear combinations of the Al 3s orbitals (Figure 2s−v). When all bonding, nonbonding and antibonding MOs are occupied, the net bonding effect from these MOs is zero and they are essentially Al 3s lone pairs. The above orbital occupancy clearly describes a situation with four σ-bonds and no net bonding or antibonding interactions among the ligands. This result suggests that each Al in CAl_4 can be viewed as monovalent with a 3s lone-pair and therefore it is not really a nonstoichiometric molecule in a strict sense.

2.3. Pentaatomic Species with 17 and 18 Valence Electrons. Addition of an electron to the 1e-LUMO of T_d CAl_4, consisting of Al 3p orbitals lying perpendicular to the Al−C bond axes, leads to a $1a_1^{2}1t_2^{6}2a_1^{2}2t_2^{6}1e^{1}$ electron configuration with a ^2E state for CAl_4^-, which is expected to undergo Jahn−Teller distortions toward a D_{4h} ($^2B_{2g}$) 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.[38] Distortion along the a_{2u} mode of imaginary frequency leads to a C_{4v} ($^2B_1$) pyramidal structure with the carbon atom lying just 0.0056 Å above the Al_4 plane and with an inversion barrier of only 0.002 kcal/mol. Distortion along the b_{2u} mode of imaginary frequency leads to a butterfly type D_{2d} ($^2B_1$) 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} ($^2B_1$) and D_{4h} ($^2B_{2g}$) being 0.14 kcal/mol. Therefore, when zero-point vibrational motion is considered, the vibrationally averaged structure is actually planar. This was the first experimentally confirmed pentaatomic tetracoordinate planar carbon molecule,[38] which will be discussed in detail in the next section 4.

The 18-valence-electron OAl_4 molecule has the $1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^2$ electronic configuration and it is expected to be distorted toward a square-planar D_{4h} ($^1A_{1g}$) structure with a singlet state or stay as a triplet state ($^3A_1$) under the tetrahedral symmetry. Boldyrev and Schleyer[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 $1b_{2g}$-HOMO (originated from the 1e-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. The $1b_{2g}$-HOMO in OAl_4 is responsible for the planarity of this molecule and is important to understand the first discovered pentaatomic tetracoordinate planar carbon molecules, as will be discussed in more detail in the next section.

2.4. Pentaatomic Species with 19−27 Valence Electrons. With the increase of the number of valence electrons in the MX_4 species, two trends are clearly seen. First, the central atom−ligand (M−X) and ligand−ligand distances are getting shorter: R(Na−O) = 2.14 Å and R(Na−Na) = 3.50 Å in Na_4O compared to R(Al−O) = 1.965 Å and R(Al−Al) = 2.778 Å in Al_4O. Second, the difference in electronegativity of M and X is getting smaller. Both these effects create problems for placing atom M at the center of the MX_4 cluster. The center atom M should have a full octet of valence electrons first (if the central atom is more electronegative than the ligand), before molecular orbitals involving ligand−ligand interactions will start to be filled. This is the case in all the molecules considered above. However, for molecules such as CSi_4 (20 valence electrons), a central C in a T_d structure would have to assume a formal charge of −4. Such a high formal negative charge for the central C in CSi_4 is certainly unfavorable. As a result, CSi_4 adopts a global minimum geometry with the carbon atom coordinated to the face of the Si_4 cluster according to ab initio calculations by Kishi et al.[167] (Figure 2y). However, there is a low-lying isomer (Figure 2z) with the carbon atom being at the center. The same is true for the 26-valence-electron OP_4 molecule, which has a structure with the oxygen atom coordinated to the edge of the P_4 tetrahedron according to ab initio calculations by Jarrett-Sprague, Hillier and Gould (Figure 2aa).[168] Like in many nonstoichiometric species, OP_4 has a low-lying isomer (Figure 2ab) with the oxygen atom coordinated to the vertex of the P_4 tetrahedron. Clearly, for MX_4 molecules with the number of electrons between 19 and 27, the Jahn−Teller distortion model is not a useful tool anymore. New valence models capable of predicting the global minimum structure are needed.

2.5. Pentaatomic Species with 28−31 Valence Electrons. When the number of valence electrons reaches 28, the Jahn−Teller distortion model can be useful again. In recent ab initio calculations, Averyanov, Khait, and Puzanov[169] predicted that the CO_4 molecule has the carbon atom at the center with two O_2 groups coordinated to it. The electronic structure of the CO_4 molecule can be considered as the carbon atom formally being +4 and the O_2 groups formally being −2, even though the true charges are certainly smaller. The electronic configuration at the T_d symmetry for the CO_4 molecule is $1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^4 3t_2^6 1t_1^2$. On the basis of this electronic configuration and the direction of the Jahn−Teller distortion we can predict a D_{2d} geometry, which indeed was found to be the global minimum. In the CO_4 molecule, all ligand−ligand bonding and all but two ligand−ligand antibonding MOs are occupied. Therefore, the net bonding effect is such that we have four M−X bonds and two X−X bonds. When two more electrons are added in the CO_2F_2 molecule (30 valence electrons), the global minimum structure is C_{2v} with four M−X bonds and only one X−X (O−O) bond.[170,171] Finally, in the CF_4 molecule (32 valence electrons), the electronic configuration is $1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^4 3t_2^6 1t_1^6$ and its global minimum structure is T_d symmetry with only four M−X bonds and no X−X bonding, because all X−X bonding and antibonding MOs are occupied.

2.6. New Bonding in Nonstoichiometric Molecules. From the above short overview of the MX_4 molecules we see that between CH_4 and CF_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_4 species, the $2a_1$−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 2l). 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_n and more generally M_kX_n 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.[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 Moller−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 Linderberg and Ohrn,[185] Pickup and Goscinki,[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-workers[188,189] and incorporated in Gaussian-98 by Ortiz and Zakrzewski.[190−193] More recently, the partial third-order electron propagator theory (P3) was developed by Ortiz[194,195] 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 been 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-workers[200−202] have computationally tested and predicted a wide variety of candidate molecules for TPC, many of which were reviewed recently.[202] Keese and co-workers[203,204] performed calculations on promising candidates and synthesized many such molecules. Radom and co-workers[205,206] studied computationally a class of polycyclic hydrocarbons, called alkaplanes, in which

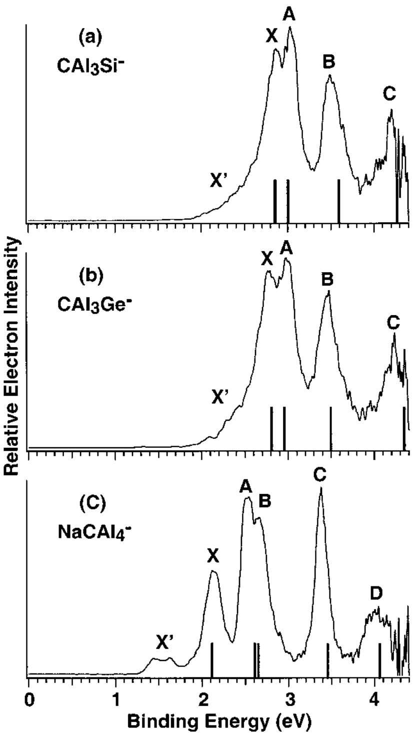


Figure 3. Photoelectron spectra of CAl_3Si^-, CAl_3Ge^-, and $NaCAl_4^-$ at 266 nm (4.661 eV). Vertical bars represent theoretical vertical detachment energies from the global minimum planar structure in each case. Data from refs 158 and 161.

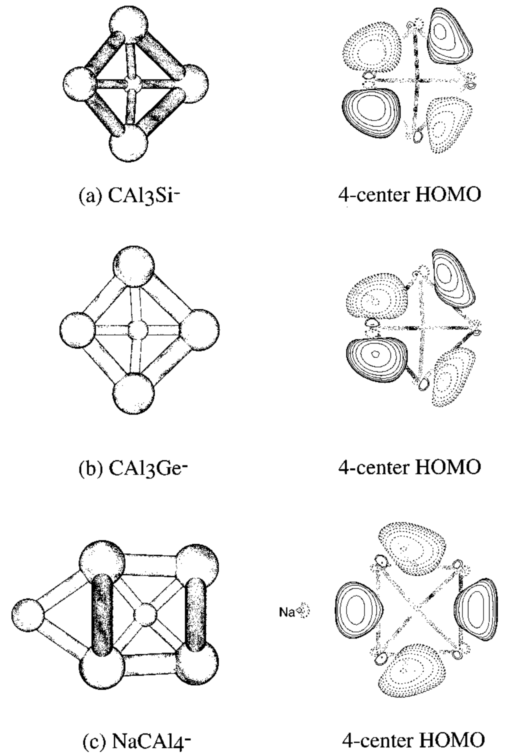


Figure 4. Global minimum structure and the four-center highest occupied molecular orbitals for (a) CAl_3Si^-, (b) CAl_3Ge^-, and (c) $NaCAl_4^-$. Data from refs 158 and 161.

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: CAl_4^-, CAl_4^{2-}, CAl_3Si^-, and CAl_3Ge^-. In our efforts to design new TPC molecules, we concentrate on small pentaatomic species, the smallest molecules to contain a TPC, in which the bonding of the central carbon atom to its four ligands can be easily traced. Furthermore, planarity in these species would not be enforced by their molecular architecture as part of a large molecule, but rather by their intrinsic and unique electronic structure. On the basis of a simple MO picture as presented in Table 1, we found a general rule for achieving planarity in pentaatomic species composed of a first-row central atom and four second- or third-row ligand atoms: such species should possess 17- or 18-valence electrons.[38,158,211,212] According to the canonical order of MOs in T_d MX_4 species as presented in Table 1, the electronic configurations are expected to be $1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^1$ and $1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^2$ for 17- and 18-valence-electron species, respectively. Both configurations are not stable toward Jahn−Teller distortion (see Figure 2w for the 18-electron case). The 16-valence-electron species, such as CAl_4, may be stable at the T_d structure (Figure 2r) if the central atom is electronegative (like C) due to the $1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^0$ closed-shell electronic configuration. Here, the first four ($1a_1^2$ and $1t_2^6$) orbitals are the C−Al σ-bonds and the remaining ($2a_1^2$ and $2t_2^6$) four orbitals are lone-pair orbitals localized on the Al atoms. The central C atom has a full octet in the T_d structure and therefore one (17 e) or two (18 e) electrons will occupy the 1e orbital, leading to Jahn−Teller distortions to a lower symmetry D_{4h} structure (Figure 2w). The HOMO of the D_{4h} species now corresponds to the four-center, $1b_{2g}$ peripheral ligand−ligand bond (Figure 2x). The CAl_4^- anion was studied both experimentally and theoretically and was established to be the first pentaatomic species containing a planar carbon.[38]

The CAl_4^- anion, being electronically open-shell, is expected to be able to accept one more electron into its four-center ligand−ligand bonding $1b_{2g}$-HOMO, forming a closed-shell, 18-valence-electron dianion, CAl_4^{2-}. However, this doubly charged anion is not expected to be stable toward electron autodetachment in its isolated state due to strong Coulomb repulsion between the two extra electrons, analogous to the sulfate dianion (SO_4^{2-}), which is well-known to be unstable in the gas phase.[213,214] We employed two strategies to circumvent this problem. The first one is to use isoelectronic substitution. Si is next to Al in the periodic table and has one more valence electron than Al. If we substitute one Al in CAl_4^{2-} by Si (or Ge), we obtain a 18-electron system in a singly charged form, CAl_3Si^- (or CAl_3Ge^-), which is the preferred charge state for both experimental and computational convenience.[158] A second strategy is to stabilize the CAl_4^{2-} dianion by a counterion (M^+), resulting in an overall singly charged species, $M^+[CAl_4^{2-}]$.[161] The latter strategy has been used previously to stabilize the SO_4^{2-} species in our laboratory.[214] Figure 3 shows our experimental PES spectra for the three 18-electron TPC species, CAl_3Si^-, CAl_3Ge^-, and $Na^+[CAl_4^{2-}]$, compared with the theoretical predictions of the vertical transitions. The ground-state structures and the four-center bonding HOMO are shown in Figure 4. We provided the first experimental realization of a salt-stabilized TPC dianion, $Na^+[CAl_4^{2-}]$.[161] We also investigated theoretically the neutral $(Na^+)_2[CAl_4^{2-}]$ species and confirmed that the TPC dianion, CAl_4^{2-}, can indeed maintain its structural integrity in the presence of the two countercations. These findings represent the first step toward the realization of bulk materials based on crystal structural units containing a new building block, the TPC dianion $[CAl_4^{2-}]$.

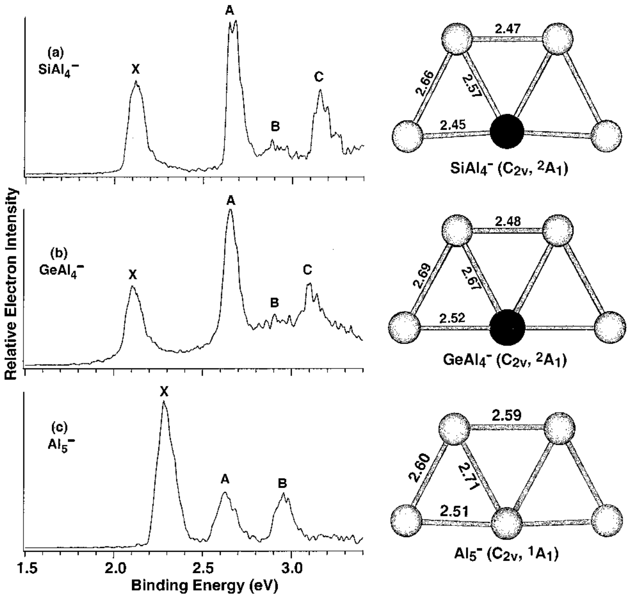


Figure 5. Photoelectron spectra of (a) $SiAl_4^-$, (b) $GeAl_4^-$, and (c) Al_5^- at 355 nm (3.496 eV) and their respective global minimum structures. Selected bond lengths are in Å. Data from refs 159 and 160.

4.2. Other Pentaatomic Planar Species: $SiAl_4^-$, $GeAl_4^-$, and Al_5^- Clusters.

Pentaatomic planar carbon structures have also been theoretically predicted for mixed types of ligands: CAl_2Si_2,[211] CGa_2Si_2, and CAl_2Ge_2.[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 $SiAl_4^-$ and $GeAl_4^-$ and their corresponding neutrals both experimentally and theoretically.[159]

Figure 5 shows the PES spectra of $SiAl_4^-$ and $GeAl_4^-$ and their ground-state structures. Indeed, we found that the cavity of the Al_4 square is too small to fit the heavier Si or Ge atom. Although the planar structures are preserved, the Al_4 square is distorted to a trapezoid. Figure 6 shows the top few MOs of the C_{2v} $SiAl_4^-$. These MOs are similar to those found in the square-planar CAl_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 $SiAl_4^-$. This suggests that the $SiAl_4$ neutral resulting from removing the HOMO (which is dominated by contributions from the central atom) electron in $SiAl_4^-$ 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 $SiAl_4$ is very similar to the $SiAl_4^-$ anion with very small geometry changes.[159] This is completely different from the CAl_4^- case, where upon electron detachment the neutral ground state of CAl_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.

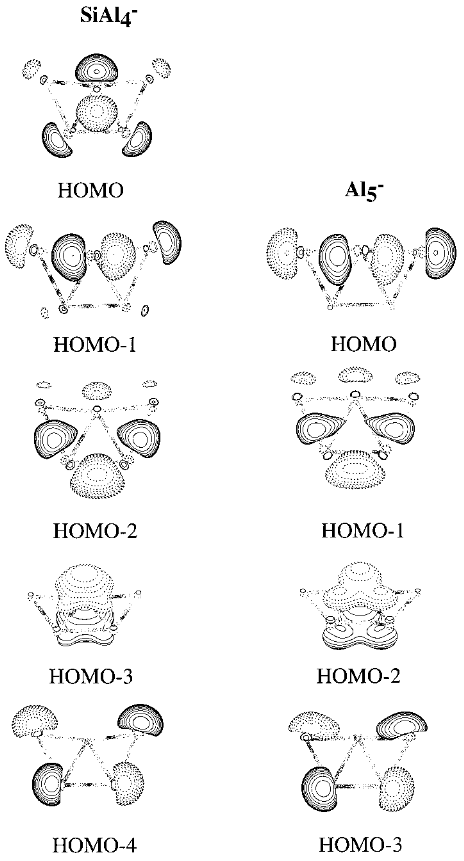


Figure 6. Comparison of the top few occupied molecular orbitals of $SiAl_4^-$ and Al_5^-. Data from refs 159 and 160.

The above analysis indicates that the 16-electron Al_5^- cluster, which is isoelectronic with $SiAl_4$, should also possess a similar planar structure. In fact, the Al_5 cluster had been known to be a C_{2v} planar species, but its origin has never been explained. To confirm that the planarity of Al_5 and Al_5^- is related to the concept derived from the TPC work, we carried out a combined experimental and theoretical investigation.[160] The Al_5^- 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_5^- measured at 355 nm is shown in Figure 5c and compared to those of $SiAl_4^-$ and $GeAl_4^-$. It is indeed relatively simple with three well-resolved peaks at this photon energy. The optimized structure of Al_5^- is also compared to those of $SiAl_4^-$ and $GeAl_4^-$. They are almost identical with very small bond length differences among the three species. The top four occupied MOs of Al_5^- are also compared to those of $SiAl_4^-$, as shown in Figure 6. The extra electron in the HOMO of $SiAl_4^-$ is absent in Al_5^-, whose occupied MOs are nearly identical to the corresponding MOs of $SiAl_4^-$. This similarity between the structure and MOs of Al_5^- and $SiAl_4^-$ unequivocally confirmed that the origin of the planarity of Al_5^- can be traced to the four center bond (HOMO−1), despite the fact that we found, unlike that of $SiAl_4^-$, the potential energy surfaces of Al_5^- and Al_5 are rather flat relative to intramolecular rearrangements and their structures are rather fluxional.[160]

From the above analyses on CAl_4, CAl_4^-, CAl_4^{2-}, $CSiAl_3^-$, $CSiAl_3$, $SiAl_4^-$, 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[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,[162] which will be discussed in this section.

5.1. All-Metal Aromatic Molecules: MAl_4^- (M = Cu, Li, Na).[162] As shown in section 4.2, the pentaatomic MAl_4^- species changes from a square-planar TPC to a trapezoid 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 CAl_4^- to HOMO−2 in $SiAl_4^-$. Consequently, even the 16-electron Al_5^- 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_{4v} square-pyramidal structure (Figure 7a) and a side-capped C_{2v} 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 $CuAl_4^-$. Vertical detachment energies were also calculated for the two low-lying isomers and only those from the global minimum square pyramidal structure were found to agree with the experimental data (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^-. Close examination of the two low-lying isomers of $CuAl_4^-$ revealed more surprises. They both appeared 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 a Al_4^{2-} dianion and the two isomers of $CuAl_4^-$ should be viewed as an Al_4^{2-} 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_4^{2-} 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.[215] Indeed, we found a perfect square-planar structure for the

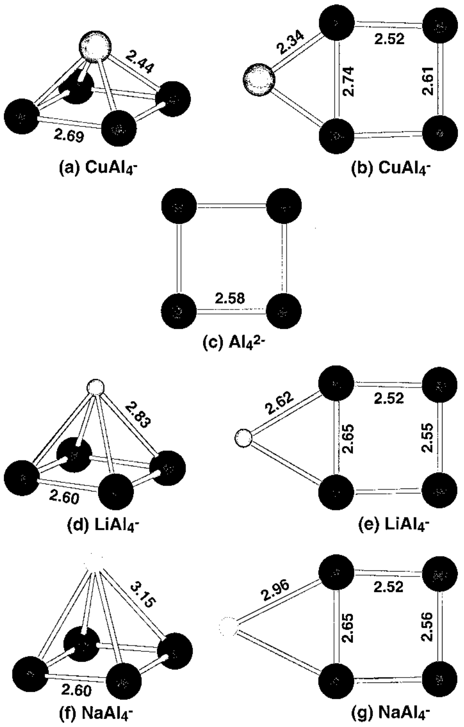


Figure 7. Structures of Al_4^{2-} and the two low-lying structures of $CuAl_4^-$, $LiAl_4^-$, and $NaAl_4^-$. Selected bond lengths are in Å. Data from ref 162.

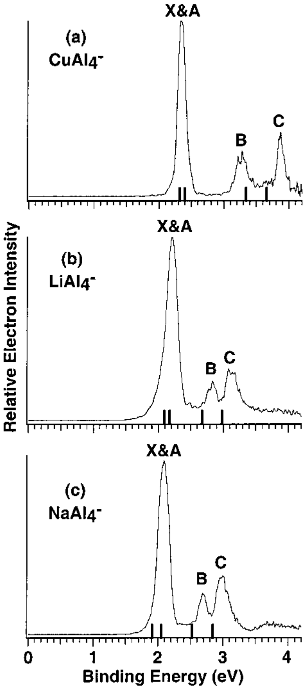
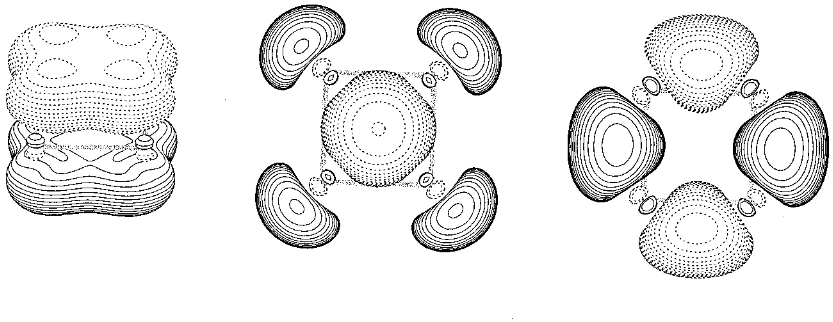
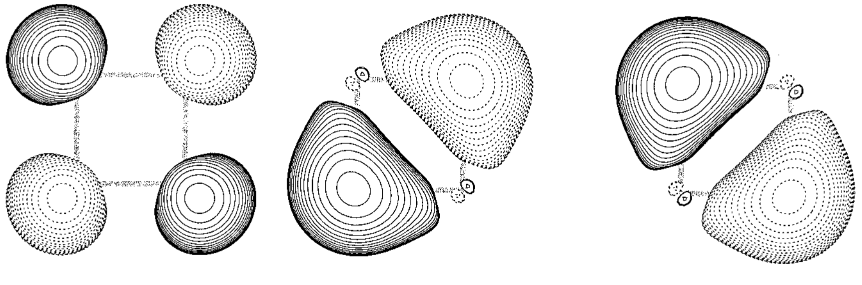


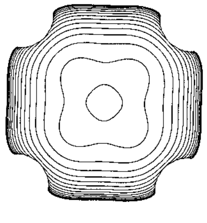
Figure 8. Photoelectron spectra of (a) $CuAl_4^-$, (b) $LiAl_4^-$, and (c) $NaAl_4^-$ at 266 nm (4.661 eV). Vertical bars represent theoretical vertical detachment energies from the global minimum pyramidal structure in each case. Data from ref 162.



HOMO ($1a_{2u}$) HOMO-1 ($2a_{1g}$) HOMO-2 ($1b_{2g}$)



HOMO-3 ($1b_{1g}$) HOMO-4 ($1e_u$) HOMO-4 ($1e_u$)



HOMO-5 ($1a_{1g}$)

Figure 9. Occupied valence molecular orbitals of Al_4^{2-}. Data from ref 162.

isolated Al_4^{2-} (Figure 7c). Most interestingly, the isolated square-planar Al_4^{2-} seems to undergo very little structural change in forming the $CuAl_4^-$ molecule. To understand the planarity and structural integrity of the Al_4^{2-} unit, we analyzed its valence MOs, as shown in Figure 9. Clearly the HOMO, which is doubly occupied, is a delocalized π-orbital. The HOMO−1 and HOMO−2 are σ-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 Al 3s lone pairs. The observation of the delocalized π-HOMO is interesting. Moreover, we found that a similar delocalized π orbital is also present in $CuAl_4^-$ in both its pyramidal and planar isomers. In fact, the valence MOs of $CuAl_4^-$ are essentially identical to that of the bare Al_4^{2-}. We suspected that this π-orbital holds the key to understanding the structure and bonding of the $CuAl_4^-$ species and why Al_4^{2-} seems to exhibit such structural tenacity in both isomers.

Upon careful examination of its structure and bonding, we recognized that Al_4^{2-} exhibits characteristics of aromaticity.[162] First of all, it possesses two completely delocalized π-electrons, satisfying the $(4n + 2)$ electron-counting rule for aromatic compounds. Second, Al_4^{2-} has a perfect square structure, due to the delocalization of the π-electrons, which is exactly what one would expect for an aromatic system.

To confirm the aromaticity in Al_4^{2-}, we reasoned that the alkali metal cations might be better to stabilize it than Cu^+ and they would have much less perturbation. We used a similar strategy previously to stabilize the common inorganic dianion, SO_4^{2-}, in the gas phase by making $NaSO_4^-$ or KSO_4^- complexes.[214] We thus carried out theoretical investigations of $LiAl_4^-$ and $NaAl_4^-$ and, as expected, found two isomers similar to those of $CuAl_4^-$, again with the pyramidal structure as the global minimum for both alkali systems, as shown in Figure 7. More importantly, the Al_4^{2-} unit in both isomers of $LiAl_4^-$ and $NaAl_4^-$ are indeed nearly identical to the bare Al_4^{2-} dianion, more so than in the $CuAl_4^-$ system. We further obtained the PES spectra of $LiAl_4^-$ (Figure 8b) and $NaAl_4^-$ (Figure 8c), which are indeed very similar to that of $CuAl_4^-$. 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 Al_4^{2-} and the conjecture that aromaticity is responsible for its structural stability in the various isomers of the MAl_4^- systems.[162]

Aromaticity usually refers to cyclic, planar, or conjugated molecules that possess $(4n + 2)$ π-electrons and have specific chemical and structural stability. Aromaticity has been extended to include inorganic,[216] organometallic compounds,[217] and three-dimensional structures,[218] though they are in general still organic systems. Analogy can be made about our newly discovered aromatic 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 $M(C_6H_6)_2$-type sandwich complexes, the Al_4^{2-} dianion also preserves its structural integrity in forming the

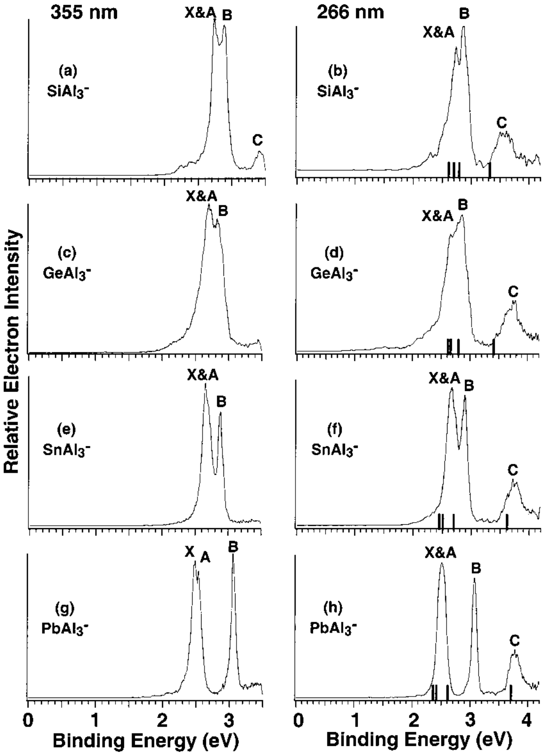


Figure 10. Photoelectron spectra of $SiAl_3^-$, $GeAl_3^-$, $SnAl_3^-$, and $PbAl_3^-$ at 355 and 266 nm. Vertical bars represent theoretical vertical detachment energies from the global minimum cyclic structure in each case. Data from ref 163.

MAl_4^- complexes. Finally, we found that the vibrational frequencies for the isolated Al_4^{2-} dianion are also very similar to those in both the pyramidal and planar structures of the three MAl_4^- species. We also investigated theoretically the structures of neutral M_2Al_4 species and found again that the most stable structures contain the intact Al_4^{2-} dianion. This opens the possibility that bulk compounds or solids with the aromatic Al_4^{2-} building blocks might be feasible.

5.2. Aromaticity in Heterocyclic MAl_3^- Clusters (M = Si, Ge, Sn, Pb).[163] 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 Al_4^{2-}, we asked if an isoelectronic, singly charged hetero-cluster MAl_3^- 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 CAl_3^- and found that it actually has a C_{3v} structure without any Al−Al bonding.[37] Thus, substitution of one Al by Si, Ge, Sn, or Pb in Al_4^{2-} 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 MAl_3^- (M = Si, Ge, Sn, Pb).[163] 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 observed in the spectra of $SiAl_3^-$. It was observable in the spectra of $GeAl_3^-$ and almost completely gone in the spectra of $PbAl_3^-$, which shows four relatively sharp and well-resolved peaks. Our extensive theoretical searches found that the global minimum for MAl_3^- 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 $PbAl_3^-$, 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 $SiAl_3^- \rightarrow GeAl_3^- \rightarrow SnAl_3^- \rightarrow PbAl_3^-$ 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 $SiAl_3^- \rightarrow GeAl_3^- \rightarrow SnAl_3^- \rightarrow PbAl_3^-$ 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 structures for the MAl_3^- species and its low-lying pyramidal isomers. The origin of the planarity and cyclization of MAl_3^- is revealed from detailed analyses of their occupied MOs, which are shown in Figure 12 for $SiAl_3^-$ in detail. The

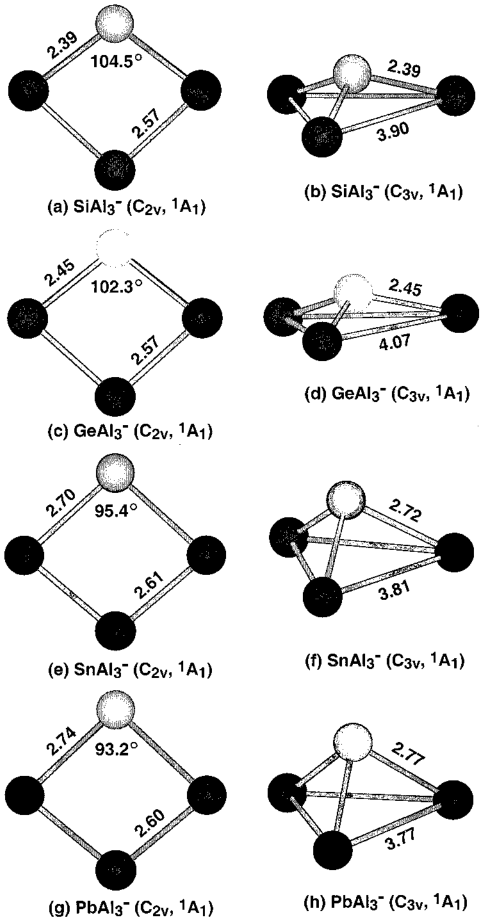
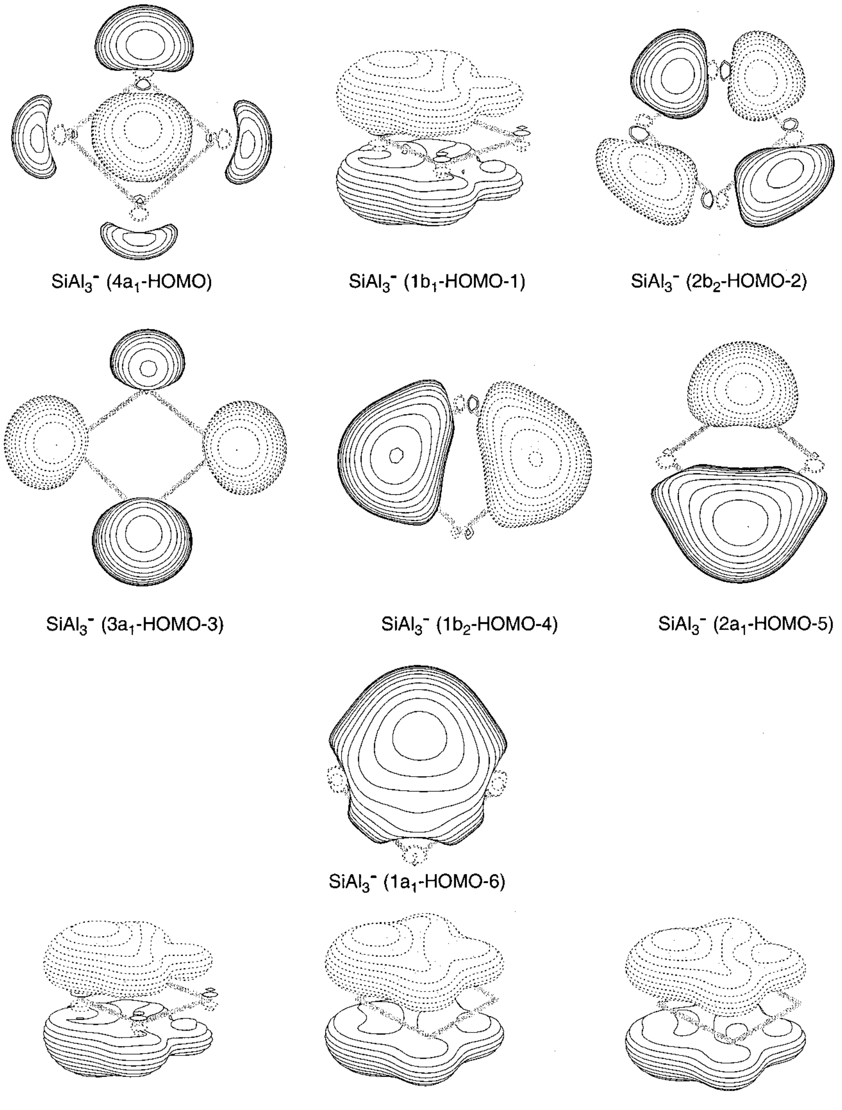


Figure 11. Two low-lying structures of $SiAl_3^-$, $GeAl_3^-$, $SnAl_3^-$, and $PbAl_3^-$. Selected bond lengths are in Å. Data from ref 163.



$SiAl_3^-$ ($4a_1$-HOMO) $SiAl_3^-$ ($1b_1$-HOMO-1) $SiAl_3^-$ ($2b_2$-HOMO-2)

$SiAl_3^-$ ($3a_1$-HOMO-3) $SiAl_3^-$ ($1b_2$-HOMO-4) $SiAl_3^-$ ($2a_1$-HOMO-5)

$SiAl_3^-$ ($1a_1$-HOMO-6)

$GeAl_3^-$ ($1b_1$-HOMO-1) $SnAl_3^-$ ($1b_1$-HOMO) $PbAl_3^-$ ($1b_1$-HOMO)

Figure 12. Top occupied molecular orbitals of $SiAl_3^-$ and the π orbitals of $GeAl_3^-$, $SnAl_3^-$, and $PbAl_3^-$, all for the cyclic ground-state structures. Data from ref 163.

MOs for the other species are similar and only their delocalized π orbitals are shown. The similarity between the MOs of the MAl_3^- species and those for Al_4^{2-} (Figure 9) is obvious. Thus, the stability of the cyclic structure relative to the pyramidal structure for the MAl_3^- species is attributed to the presence of the delocalized π bond, i.e., aromaticity. We note that the π orbital tends to be more localized in $SiAl_3^-$ and becomes more delocalized in $PbAl_3^-$. This trend coincides with the trend of stability for the cyclic isomers relative to the pyramidal ones. In the lighter CAl_3^- species we found that the pyramidal structure was the only minimum.[37] The instability of the CAl_3^- planar cyclic isomer is a result of the complete localization of the two π electrons on the C atom, because it is much more electronegative than Al. This observation again indicates the importance of the delocalized π orbital or aromaticity in the hetero-systems.

5.3. Aromatic Ga_4^{2-} and In_4^{2-} in Gas-Phase Clusters and Organometallic−Ga_4 Molecules and Possible Aromatic Clusters as Building Blocks of Solid Materials. We further investigated the aromaticity in the isoelectronic systems of Al_4^{2-}: Ga_4^{2-} and In_4^{2-}. We obtained PES spectra of $NaGa_4^-$ and $NaIn_4^-$ and found that they are nearly identical to that of $NaAl_4^-$. Our theoretical investigations confirmed that indeed these isoelectronic series have identical structure and bonding properties.[219]

While all-metal aromatic systems (M_4^{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, $K_2[Ga_4(C_6H_3\text{-}2,6\text{-}Trip_2)_2]$ (Trip = C_6H_2-2,4,6-$^iPr_3$), whose X-ray structure shows clearly a square-planar Ga_4^{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 $-Ga_4^{2-}$ unit in this organometallic molecules are in fact similar to those in our gaseous clusters. It possesses the same two π-electrons and is indeed aromatic, explaining its four equal Ga−Ga bonds and near square structure. Therefore, the $K_2[Ga_4(C_6H_3\text{-}2,6\text{-}Trip_2)_2]$ species can be considered as the first crystal structure containing the all-metal (Ga_4^{2-}) building block. Solid alloy materials may also be synthesized to contain the aromatic M_4^{2-} building blocks if they can be completely separated in bulk crystals, because close contacts between two M_4^{2-} units may lead to fusion.[221] The fact that the Ga_4^{2-} unit can exist in the organometallic molecules is due to its complete isolation and protection by the two bulky ligands.[220] We have obtained theoretical insight[222] that a well-known Na−Hg alloy (Na_3Hg_2),[223] containing Hg_4 squares as building blocks,[224] in fact consist of aromatic Hg_4^{6-} units, which are isosteric and isoelectronic to Al_4^{2-}. We should point out that the two σ-bonding orbitals (Figure 9) in the M_4^{2-} species are also important and render them σ-aromaticity,[218,219,222] in addition to the π-aromaticity. A recent calculation showed that a significant diamagnetic ring current originates in the σ system.[224] Robinson and co-workers[217] studied organometallic compounds containing aromatic Ga_3^{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_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 tetracoordinate carbon species, such as $[CAl_4^{2-}]$, might be viable in solid materials. The finding of all-metal aromatic systems, $[Al_4^{2-}]$, $[Ga_4^{2-}]$, $[In_4^{2-}]$, or $[Tl_4^{2-}]$, 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/SiO_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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