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"Napoleon Hat" Structure of Tetraatomic Molecules. A Combined Photoelectron Spectroscopy and Ab Initio Study of $CAlSi_2^-$ and Its Neutral

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We report a combined experimental and theoretical investigation of nonstoichiometric species, $CAlSi_2^-$ and its neutral. Photoelectron spectra of $CAlSi_2^-$ were measured at two photon energies; three major detachment features were observed with a broad ground-state transition. Ab initio calculations were performed on the $CAlSi_2^-$ anion, which was found to have two low-lying isomers, a cis-C_s and a trans-C_{2v} species, both with a "Napoleon Hat" type of structure. Electron detachment energies from the anions and spectroscopic properties for both the anions and neutrals were calculated. The cis isomer was found to be the ground state by comparing the theoretical results with the experimental measurements. Evidence of the trans isomer was inferred by comparing the theoretical detachment transitions to the experimental spectra. The neutral ground state, resulting from detaching an electron from the cis isomer, was found to undergo a significant geometry change from the "Napoleon Hat" structure to an "Eiffel Tower" structure, consistent with the broad photodetachment transition of the ground state, whereas the trans isomer maintained the "Napoleon Hat" structure in both its anion and neutral states. The novel "Napoleon Hat" structure was due to a new three-center bond, which involves the three peripheral ligands, and was a general structural feature of a 16-valence-electron tetraatomic species consisting of elements from the first and second series of the periodic table.

Introduction

The structure of stoichiometric tetraatomic molecules that obey the octet rule are well established in chemistry.[1−3] The AH_3 molecules have a planar triangular structure if the central atom (A) is a IIIA atom (B−Tl). This structure can be rationalized based on the valence-shell electron-pair repulsion (VSEPR) model;[4−6] they have a triangular pyramidal structure (which is a distorted tetrahedral structure with one ligand atom substituted by a lone pair of the central atom) if the central atom is a VA atom (N−Bi); or they have T-shaped structures (distorted trigonal bipyramidal structures with two equatorial ligand atoms substituted by lone pairs of the central atom) if the central atom is a halogen atom (Cl−At). The latter have been studied, yet only theoretically.[7,8] When one, or two, or all hydrogen atoms are substituted by halogen atoms or other monovalent ligands, the structures of these tetraatomic molecules remain the same. The VSEPR theory can be used to describe and predict the structure of the AX_3 molecules because the only bonding interactions are between the central atom and its attached atoms or "ligands". However, in nonstoichiometric molecules, which do not obey the octet rule, such as Al_3O or $CAlSi_2^-$ and $CAlSi_2$ studied here, the classical valence theory and the VSEPR theory are not applicable anymore. Therefore, one may expect that new types of chemical bonds and novel molecular structures may be discovered for such molecules.

Nonstoichiometric molecules and clusters have recently attracted the substantial attention of both experimentalists and theoreticians.[9−97] Such species can be viewed as exotic molecules. However, experimentally they are challenging to study owing to the difficulty of their formation. We have found that the laser vaporization cluster source technique is a versatile experimental technique that can produce nonstoichiometric species consisting of almost any elements. Combining a laser vaporization source and negative ion photoelectron spectroscopy (PES), we have investigated a number of nonstoichiometric species.[60−62,71−73,77,82,85−95,97] The negative ion technique offers convenient size selectivity, and PES is quite suitable to provide electronic and vibrational information about the neutral species. We have found that combining PES and ab initio calculations is a particularly powerful approach to investigate the structure and bonding of nonstoichiometric species. Using this approach, we have investigated a series of hyperaluminum species,[91−95] among which we have discovered the first gaseous pentaatomic planar carbon molecule, CAl^{4-}.[92] We have found that it is rather rewarding to focus on the few-atom systems, because they are less computationally demanding and allow us to perform exhaustive geometry searches. Therefore, although PES is not a structural determination technique, our strategy, to concentrate on the smaller systems, allows us to obtain definitive and detailed electronic and structural information about interesting nonstoichiometric molecules.

In this work, we present a combined PES and ab initio study of two tetraatomic molecules, $CAlSi_2^-$ and $CAlSi_2$. We found that these species possess a new type of chemical bond, a three-center peripheral bond that gives them a "Napoleon Hat" type of structure, which is predicted by ab initio calculations and confirmed by excellent agreement between the theoretical detachment transitions and the experimental results.

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Methods

Experimental Method. The experiments were performed with a magnetic-bottle time-of-flight PES apparatus equipped with a laser vaporization cluster source. Details of the experiment have been described previously.[97−100] Briefly, the $CAlSi_2^-$ anions were produced by laser vaporization of a graphite/Al/Si mixed target with a pure helium carrier gas. The clusters formed from the laser vaporization source were entrained in the He carrier gas and underwent a supersonic expansion. The anion species in the beam were extracted perpendicularly into a time-of-flight mass spectrometer. Various mixed clusters composed of $C_xAl_ySi_z^-$ were formed from the source. The $CAlSi_2^-$ anions were selected and decelerated before photodetachment by a laser beam. For the current experiment, the third and fourth harmonic outputs (355 and 266 nm) from a Nd:YAG laser were used for photodetachment. The energy scales were calibrated with the known spectra of Cu^-, and the electron kinetic energy resolution of the apparatus was better than 30 meV for 1 eV electrons.

Computational Methods. We initially optimized the geometries of $CAlSi_2^-$ and $CAlSi_2$ employing analytical gradients with polarized split-valence basis sets (6-311+G*)[101−103] using the hybrid method, which includes a mixture of Hartree−Fock exchange with density functional exchange-correlation (B3LYP).[104−106] Then, the geometries were refined using the CCSD(T) method[107−109] and the same basis sets. Finally, the energies of the lowest-energy structures were refined using the CCSD(T) level of theory and the more extended 6-311+G(2df) basis sets. All core electrons were kept frozen in treating the electron correlation at the CCSD(T) levels of theory. Vertical electron detachment energies from the lowest-energy singlet structure of $AlCSi_2^-$ were calculated using the outer valence Green function (OVGF) method[110−114] incorporated in Gaussian-98. The 6-311+G(2df) basis sets were used in all OVGF calculations, and all calculations were performed using the Gaussian-98 program.[115]

Results

Experimental Results. The PES spectra of $CAlSi_2^-$ are shown in Figure 1 at the two photon energies. The 355-nm spectrum exhibits two detachment bands (X and A). The ground state band (X) with a vertical binding energy (VDE) of 2.54 eV has a broad low-energy tail. The A band with a VDE of 3.04 eV is relatively narrow with discernible fine features, probably due to vibrational structures. The 266-nm spectrum revealed one additional broad band (B) at a VDE of about 3.6 eV. There appeared to be weak signals beyond 4 eV, but the poor statistics due to significant photoelectron noises in these energy ranges prevents us from definitively identifying any further detachment features. The broad tail of the X band was surprising and made it very difficult for us to determine the adiabatic electron binding energy. We tried to obtain PES spectra at different source conditions but could not eliminate the tail. It should be pointed out that the $CAlSi_2^-$ anions were not particularly abundant, and we only had a limited ability to tune the source conditions. Thus, the anions could still be quite hot, even under the coldest source conditions that we could manage. The large tail could have several origins: (1) large geometry changes between the ground states of the anion and the neutral, (2) thermal effects due to hot band transitions from vibrationally excited anions, and (3) the presence of isomers with lower electron binding energies. The A band still shows fine features, even at 266 nm. We can tentatively identify a vibrational spacing of about 400 cm^{-1}. The congested nature of the A band indicates that there is probably more than one vibrational mode active.

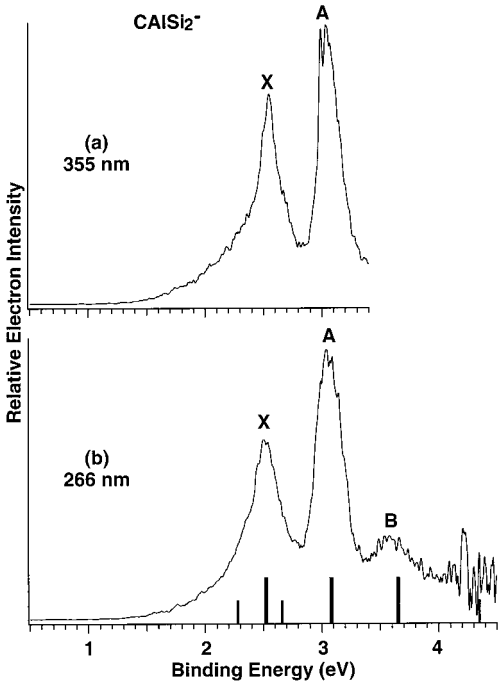

Figure 1. Photoelectron spectra of $CAlSi_2^-$ at (a) 355 nm (3.496 eV) and (b) 266 nm (4.661 eV). The observed detachment channels are labeled X, A, and B. Vertical lines indicate results of ab initio calculations: thick and tall lines, theoretical vertical detachment energies from the anion ground state; thin and short lines, theoretical vertical detachment energies from a low-lying isomer of the anion.

The B band is also quite broad, probably due to detachment of a bonding or antibonding electron, that is, a significant geometry change between the anion and the neutral state corresponds to the B band.

The experimental data will be discussed and interpreted based on our theoretical results. As we will show, the three main features (X, A, and B) correspond to detachment from the lowest-energy isomer of $CAlSi_2^-$. Excellent agreement between the calculated VDEs and the experimental measurements are obtained, as indicated by the thick bars in Figure 1b. The Franck−Condon profiles of the X, A, and B bands are consistent with the nature of the MOs, from which electrons are removed. We, indeed, found large geometry changes between the ground states of the anion and the neutral. We also found a low-lying isomer, which seemed to be present in the experiment. The thin bars in Figure 1b correspond to calculated VDEs from this isomer, clearly consistent with the experiment and suggesting that, indeed, this isomer is present.

Theoretical Results. *$CAlSi_2^-$*. In the search for the global minimum, we found two T-shaped, cis and trans structures (Figure 2) as the most stable species. Although these structures look somewhat similar to the T-shaped structures of ClF_3, BrF_3, and $BrClF_2$, they are different. The cis and trans structures of $AlCSi_2^-$ have ligand−ligand bonding interactions, as shown in Figure 3, whereas in $BrClF_2$, all ligand−ligand interactions are repulsive. Consequently, the T-shaped structures of $CAlSi_2^-$ are due to the peripheral bond between the axial and the two equatorial ligands, whereas the T-shaped structure in $BrClF_2$ is due to repulsion between the two lone pairs of the central atom and between the lone pairs and the ligands, as well as between the ligands. To distinguish these two types of structures we propose to call the structures of $CAlSi_2^-$ as "Napoleon Hat" structures, to underline the ligand−ligand bonding, noting the analogy between the hat of the famous French general Napoleon and the molecular structure (Figure 2). At the B3LYP/6-311+G*

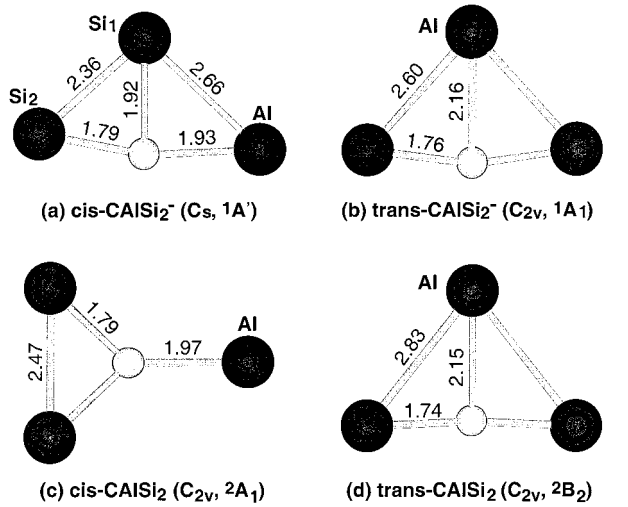

Figure 2. Ab initio structures of (a) *cis*-$CAlSi_2^-$, (b) *trans*-$CAlSi_2^-$, (c) *cis*-$CAlSi_2$, and (d) *trans*-$CAlSi_2$ optimized at the CCSD(T)/6-311+G* level of theory.

TABLE 1: Observed Vertical Electron Binding Energies (VDE, eV) from the Photoelectron Spectra of $CAlSi_2^-$

	VDE (eV)	vib. freq. (cm^{-1})
X	2.54 (0.04)	
A	3.04 (0.04)	400 (60)
B	3.6 (0.1)	

level of theory, the global minimum of $CAlSi_2^-$ was found to have a singlet C_s ($^1A'$, $1a'^2 2a'^2 3a'^2 4a'^2 1a''^2 5a'^2 6a'^2 7a'^2$) cis structure (characterized in Table 2). The C_{2v} ($^1A_1$, $1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 1b_1^2 5a_1^2 3b_2^2$) trans-structure was found to be a local minimum only 2.76 kcal/mol higher in energy [at the CCSD(T)/6-311+G(2df) level of theory]. Optimized geometries and harmonic frequencies are almost the same at B3LYP/6-311+G* and at our highest CCSD(T)/6-311+G* level of theory. We also optimized geometry of the "Y"-type structure, which was found to be the first-order saddle point.

$CAlSi_2$. Upon electron detachment from the HOMO, the corresponding neutral $CAlSi_2$ trans structure is still similar (as well as the structure of HOMO, Figure 3) to that of the corresponding anion, maintaining the "Napoleon Hat" features despite a substantial increase in the ∠Al−C−Si valence angle from 82.7° to 92.7°. In the neutral $CAlSi_2$ cis structure, changes are more drastic upon electron detachment, and the resulting structure has a Y-shape with significant Si−Si bonding interactions and no Al−Si interactions. We propose to call the Y-shape structure of $CAlSi_2$ an "Eiffel Tower" structure, to underline the ligand−ligand (Si−Si) bonding, noting the analogy between the famous Paris landmark and the molecular structure (Figure 2c). We emphasize that these names are used to distinguish the novel structures and bonding found in the current work from the T- and Y-shaped structures in previously known stoichiometric molecules (also see Discussion Section). We will also continue to use *cis*-$CAlSi_2$, even though there is no cis or trans isomer for the "Eiffel Tower" structure, to keep the connection of the origin of the "Eiffel Tower" neutral structure with the original *cis*-$CAlSi_2^-$ anion. The structure of the HOMO of the neutral "Eiffel Tower" structure is now quite different from that of the "Napoleon Hat" anion (Figure 4). At the B3LYP/6-311+G* level of theory, the global minimum of $CAlSi_2$ was found to be the C_{2v} ($^2A_1$, $1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 1b_1^2 3b_2^2 5a_1^1$) "Eiffel Tower" structure (Table 3). The C_{2v} ($^2B_2$, $1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 1b_1^2 5a_1^2 3b_2^1$) "Napoleon Hat" structure was found to be a first-order saddle point 2.69 kcal/mol higher in energy [at the CCSD(T)/6-311+G(2df) level of theory]. Geometry optimization along the imaginary mode (out-of-plane) led to a slightly nonplanar C_s ($^2A''$) structure that is just 0.0067 kcal/mol lower in energy then the C_{2v} ($^2B_2$) structure. When ZPE

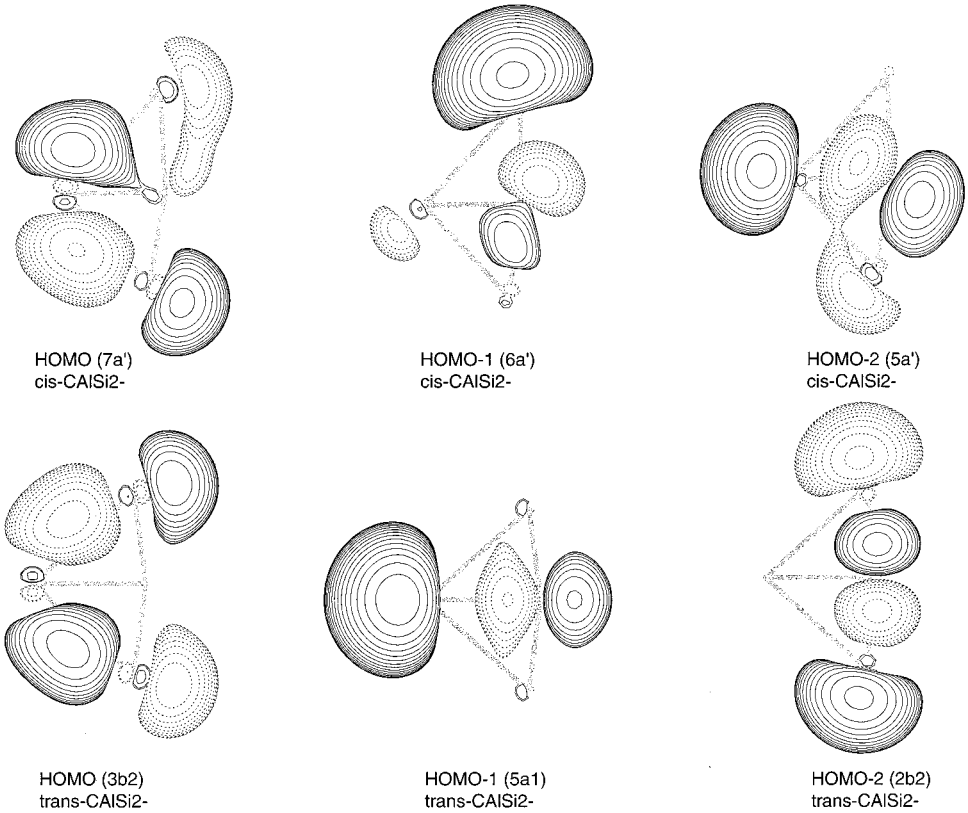

Figure 3. Molecular orbital picture[118] showing the HOMO, HOMO-1, and HOMO-2 of *cis*-$CAlSi_2^-$ and *trans*-$CAlSi_2^-$.

TABLE 2: Calculated Molecular Properties of $CAlSi_2^-$

trans-$CAlSi_2^-$, C_{2v}, $^1A_1$	B3LYP/6-311+G*	CCSD(T)/6-311+G*	*cis*-$CAlSi_2^-$, C_s, $^1A'$	B3LYP/6-311+G*	CCSD(T)/6-311+G*
R(C−Al), Å	2.177	2.160	R(C−Al), Å	1.927	1.931
R(C−Si), Å	1.746	1.756	R(C−Si_1), Å	1.906	1.915
R(Al−Si), Å	2.636	2.604	R(C−Si_2), Å	1.781	1.788
∠AlCSi	83.69°	82.68	∠$AlCSi_1$	90.54°	87.66
∠SiCSi	167.38°	165.36	∠Si_1CSi_2	79.73°	78.99
E_{tot}, au	−859.568298	−858.020269	E_{tot}, au	−859.570738	−858.022874
ΔE_{tot}, kcal/mol	1.53	1.63	ΔE_{tot}, kcal/mol	0.00	0.00
$\omega_1(a_1)$, cm^{-1}	556	560	$\omega_1(a')$, cm^{-1}	993	997
$\omega_2(a_1)$, cm^{-1}	433	443	$\omega_2(a')$, cm^{-1}	640	648
$\omega_3(a_1)$, cm^{-1}	247	260	$\omega_3(a')$, cm^{-1}	453	455
$\omega_4(b_1)$, cm^{-1}	175	155	$\omega_4(a')$, cm^{-1}	348	361
$\omega_5(b_2)$, cm^{-1}	1125	1123	$\omega_5(a')$, cm^{-1}	190	217
$\omega_6(b_2)$, cm^{-1}	258	279	$\omega_6(a'')$, cm^{-1}	172	161

TABLE 3: Calculated Molecular Properties of $CAlSi_2$

trans-$CAlSi_2^-$, C_{2v}, $^2B_2$	B3LYP/6-311+G*	CCSD(T)/6-311+G*,[a]	*cis*-$CAlSi_2^-$, C_{2v}, $^2A_1$	B3LYP/6-311+G*	CCSD(T)/6-311+G*
R(C−Al), Å	2.186	2.152	R(C−Al), Å	1.973	1.974
R(C−Si), Å	1.732	1.736	R(C−Si_1), Å	1.790	1.793
R(Al−Si), Å	2.891	2.828	R(Si−Si), Å	2.483	2.472
∠AlCSi	94.38°	92.68°	∠AlCSi	136.10°	136.42°
E_{tot}, au	−859.492415	−857.952043	E_{tot}, au	−859.497177	−857.956672
ΔE_{tot}, kcal/mol	2.99	2.90	ΔE_{tot}, kcal/mol	0.00	0.00
$\omega_1(a_1)$, cm^{-1}	543	546	$\omega_1(a_1)$, cm^{-1}	978	1000
$\omega_2(a_1)$, cm^{-1}	362	402	$\omega_2(a_1)$, cm^{-1}	423	434
$\omega_3(a_1)$, cm^{-1}	164	170	$\omega_3(a_1)$, cm^{-1}	261	270
$\omega_4(b_1)$, cm^{-1}	138	56i	$\omega_4(b_1)$, cm^{-1}	165	173
$\omega_5(b_2)$, cm^{-1}	1106	1114	$\omega_5(b_2)$, cm^{-1}	721	739
$\omega_6(b_2)$, cm^{-1}	95	138	$\omega_6(b_2)$, cm^{-1}	79	116

[a] This structure is a first-order saddle point at the CCSD(T)/6-311+G* level of theory. Geometry optimization along the imaginary mode leads to the slightly nonplanar (C_s, $^2A''$) structure (E_{tot} = −857.952053 au, R(C−Al) = 2.152 Å, R(C−Si) = 1.737 Å, R(Al−Si) = 2.831 Å, ∠SiCAl = 92.83°), which is just 0.0067 kcal/mol lower in energy than the (C_{2v}, $^2B_2$) structure, and, after the ZPE corrections, the vibrationally averaged structure is actually planar.

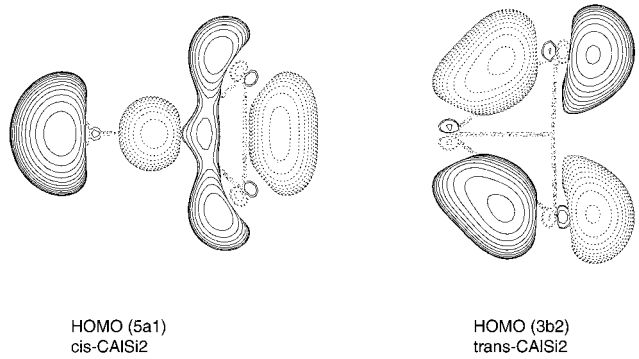

Figure 4. Molecular orbital picture[118] showing the HOMO *cis*-$CAlSi_2$ and *trans*-$CAlSi_2$.

corrections are taken into account, the vibrationally averaged structure is essentially planar. Optimized geometries of the C_s ($^2A''$) and C_{2v} ($^2B_2$) structures are almost the same at the CCSD(T)/6-311+G* level of theory.

Both the anion and neutral species are found to be very stable. We calculated D_e = 96.0 kcal/mol for *cis*-$CAlSi_2^-$ (C_s, $^1A'$) → CSi_2 (C_{2v}, $^1A_1$) + Al^- (^3P) and D_e = 52.6 kcal/mol for *cis*-$CAlSi_2$ (C_{2v}, $^2A_1$) → CSi_2 (C_{2v}, $^1A_1$) + Al (^2P) (all at the CCSD(T)/6-311+G(2df)//CCSD(T)/6-311+G* levels of theory). The substantial stability of the cis anion is due to the bonding between the central atom and ligands as well as to the bonding interactions among the ligand Al and Si atoms.

The calculated vertical and adiabatic electron detachment energies for the *cis*-$CAlSi_2^-$ ground state were VDE = 2.51 eV [OVGF/6-311+G(2df)] and ADE = 2.16 eV [CCSD(T)/6-311+G(2df)]; for the *trans*-$CAlSi_2^-$ isomer, VDE = 2.28 eV [OVGF/6-311+G(2df)] and ADE = 2.16 eV [CCSD(T)/6-311+G(2df)]. The large difference between the VDE and ADE of the cis isomer is due to the large geometry changes between the ground states of the anion and the neutral species.

Interpretation of the Experimental Spectra. In Table 4, we present the results of our calculations of the four major low-lying vertical one-electron detachment processes from the cis-C_s ($^1A'$) and the trans-C_{2v} ($^1A_1$) isomers of $CAlSi_2^-$, together with the experimental data. Calculated VDEs are also shown by vertical bars in Figure 1 (the tall and thick bars for the cis structure and the short and thin bars for the trans structure).

Band X. The band X (Figure 1), peaking at 2.54 ± 0.04 eV, agrees well with the calculated VDE of 2.51 eV [OVGF/6-311+G(2df)] from the 7a′-HOMO of the global minimum *cis*-$CAlSi_2^-$ structure. The X band is very broad with a long low-energy tail, consistent with the large geometry changes between the ground states of the anion and the neutral species found in our calculations. It is also likely that the trans isomer, which has a VDE of 2.28 eV, was present and contributed to the broad tail. The existence of the trans isomer is also evident by comparing its second and third detachment channels with the experimental data, as shown in Figure 1. The contribution of the second detachment channel (VDE = 2.68 eV) of the trans isomer was shown more clearly in the 355-nm spectrum. The contribution of the third detachment channel (VDE = 4.37 eV) is also consistent with the weak signals above 4 eV in Figure 1b, despite the poor statistics in this spectral range. Because of the long tail of the X band and contributions from the trans isomer, it is difficult to determine the 0−0 transition. According to our ab initio calculations, the adiabatic electron detachment energy is 2.16 eV [CCSD(T)/6-311+G(2df)]. It is seen that the tail of the X band extends further to the left of the theoretical

TABLE 4: Comparison of Calculated and Experimental Electron Detachment Processes of $CAlSi_2^-$

	experiment VDE (eV)	*cis*-$CAlSi_2^-$ electron detachment from MO	theory VDE[a] (eV)	*trans*-$CAlSi_2^-$ electron detachment from MO	theory VDE[a] (eV)
X	2.54 (0.04)	7a′	2.51 (0.88)	$3b_2$	2.28 (0.88)
A	3.04 (0.04)	6a′	3.08 (0.87)	$5a_1$	2.68 (0.87)
B	3.6 (0.1)	5a′	3.66 (0.87)	$2b_2$	4.37 (0.86)
		1a″	4.83 (0.87)	$1b_1$	4.60 (0.86)

[a] At the OVGF/6-311+G(2df)//CCSD(T)/6-311+G* level of theory. Pole strength is given in parentheses.

ADE, possibly due to hot band transitions from vibrationally excited anions.

Band A. The second vertical electron detachment takes place from the 6a′ (HOMO-1) of the *cis*-$CAlSi_2^-$ with a theoretical VDE of 3.08 eV [OVGF/6-311+G(2df)] (Table 4). This value agrees well with the second detachment feature (A), which was observed at 3.04 ± 0.04 eV (Figure 1). The 6a′ MO is primarily a lone pair of the aluminum atom (Figure 3), and electron detachment from this MO should not lead to a large geometry change. Indeed, the A band is relatively narrow. The A band also contains discernible vibrational features, with a spacing of about 400 cm^{-1}, which should be due to the C−Al stretching, since the 6a′ MO has a slight C−Al antibonding character (Figure 3). The 400 cm^{-1} vibrational spacing is consistent with the C−Al stretching frequency of the anion ($\omega_3 = 455$ cm^{-1}, Table 2). Unfortunately, we were not able to calculate the geometry relaxation and frequencies for the first excited state of $CAlSi_2$. Based on the nonbonding nature of the 6a′ MO, we can infer that the geometry and vibrational frequencies of the first excited state of *cis*-$CAlSi_2$ should not be too different from the cis anion.

Band B. The third vertical electron detachment should occur from the 5a′ (HOMO-2) with a theoretical VDE of 3.66 eV [OVGF/6-311+G(2df)] (Table 4). This value also agrees well with the third detachment feature (B), which was observed at a VDE of about 3.6 ± 0.1 eV. The 5a′ MO has strong antibonding characters between C and Si(2) and between the two Si. Removal of a 5a′ electron is expected to lead to significant geometry changes in the neutral $CAlSi_2$, again consistent with the broad nature of the B band.

As given in Table 4, the pole strengths in all the calculated detachment channels are larger than 0.8. Therefore, the OVGF method is expected to be valid, and all the electron detachments can be considered as primarily one-electron processes.

Discussion

The overall agreement between the experimental PES spectra and the theoretical calculations is quite satisfying. The excellent agreement between the calculated VDEs of the *cis*-$CAlSi_2^-$ and the main PES features (X, A, and B) confirmed that the ground state of $CAlSi_2^-$ is the cis isomer. Our data also indicated the presence of the trans isomer. Because the cis and trans isomers have very close energies, one would not have been able to firmly conclude which one should be the ground state without comparison with the PES results.

From our experimental data and the ab initio calculations we conclude that tetraatomic 16-valence-electron molecules composed of a central atom of the first row atoms and three ligand atoms of the second row atoms should all have the "Napoleon Hat" structure. To better understand when the "Napoleon Hat" structure should be favored, let us examine the occupancy pattern of the valence MOs in the high-symmetry D_{3h} structures. The canonical order of the occupied valence MOs of the D_{3h} BF_3, which has 24 valence electrons, is $1a_1'^2 1e'^4 2a_1'^2 2e'^4 1a_2''^2 3e'^4 1e''^4 1a_2'^2$. The first three orbitals ($1a_1'^2$ and $1e'^4$) are the B−F σ-bonds, and the remaining 9 orbitals are lone pairs localized on F and lying perpendicular and parallel to the B−F bond axes. The above orbital occupancy describes a situation with three σ bonds and no net bonding or antibonding interactions among the ligands. If we assume that this order of MOs remains valid for other triangular molecules with 16 valence electrons, such species would have a $1a_1'^2 1e'^4 2a_1'^2 2e'^4 1a_2''^2 3e'^2$ electronic configuration. Even though the first three orbitals ($1a_1'^2 1e'^4$) again describe three σ bonds, this configuration would be subjected to first-order Jahn−Teller distortions in the singlet state, leading to a planar C_{2v}-type structure, in line with our findings of the "Napoleon Hat" structure. The C_{2v}-distortion (C_s in *cis*-$CAlSi_2^-$) occurs due to bonding interactions between the ligands, as seen clearly in Figure 3.

When only 14 valence electrons are present, as in NAl_3,[95] the D_{3h} triangular geometry with a $1a_1'^2 1e'^4 2a_1'^2 2e'^4 1a_2''^2$ valence electronic configuration is not Jahn−Teller-active. As expected, it is found to be a stable minimum with three σ-bonds and three lone pairs. Therefore, the presence of 16 valence electrons is crucial to achieve the "Napoleon Hat" structure because the aufbau orbital occupancy causes unbalanced bonding and antibonding ligand−ligand interactions in the triangular case.

How common is the "Napoleon Hat" structure for tetraatomic 16-valence-electron molecules? We should mention that such a structure was found previously to be the global minimum for two other 16-valence electron nonstoichiometric molecules: OAl_3^-,[82,84] and CSi_3.[56,57] We extended the study of such species and performed preliminary B3LYP/6-311+G* calculations for a series of 16-electron nonstoichiometric molecules, $OSiAl_2$, $NSiAl_2^-$, BSi_3^-, CSi_3, NSi_3^+, OAl_3^-, and FAl_3; results are summarized in Tables 5 and 6. We found that, indeed, all these species have minima of the "Napoleon Hat" structures. Moreover, for $OSiAl_2$ and $NSiAl_2^-$, the trans isomers are lower in energy than the cis isomers, in contrast to the results for $CAlSi_2^-$. Therefore, we believe that the "Napoleon Hat" structure should be a common structural feature for 16-valence-electron, tetraatomic molecules.

Our previous discussion resolved the situations of 14- and 16-valence-electron tetraatomic species: whereas the former forms a stable D_{3h} structure, the latter prefers the "Napoleon Hat". However, the 15-valence-electron case remains to be addressed.

As we have seen above, for the 15-valence-electron *cis*-$CAlSi_2$ isomer, the "Napoleon Hat" structure is not stable. The key feature of the 16-electron "Napoleon Hat" structure is the three-center peripheral bond (HOMO), which is fully occupied. This HOMO becomes singly occupied in the 15-electron case, and consequently the molecule is rearranged into a C_{2v} ($^2A_1$) "Eiffel Tower" structure upon geometry optimization. Although the *trans*-$CAlSi_2$ isomer maintains the "Napoleon Hat" structure, it is somewhat higher in energy than the cis isomer. Among other 15-valence-electron tetraatomic molecules, OAl_3[28] and NAl_3^-,[95] have been studied previously. In fact, both species were found to have the "Napoleon Hat" structures, with the "Eiffel

TABLE 5: Calculated Molecular Properties of $OSiAl_2$ and $NSiAl_2^-$ [a]

	trans-$OSiAl_2$, C_{2v}, $^1A_1$	*trans*-$NSiAl_2^-$, C_{2v}, $^1A_1$		*cis*-$OSiAl_2$, C_s, $^1A'$	*cis*-$NSiAl_2^-$, C_s, $^1A'$
R(A−Si), Å	1.801	1.792	R(A−Si), Å	1.705	1.692
R(A−Al), Å	1.896	1.861	R(A−Al_1), Å	2.137	2.041
R(Si−Al), Å	2.674	2.612	R(A−Al_2), Å	1.835	1.826
∠<SiAAl	92.59°	91.26°	∠SiAAl	83.74°	85.83°
∠AlAAl	174.82°	177.48°	∠AlCAl	95.52°	95.22°
E_{tot}, au	−849.685018	−829.243777	E_{tot}, au	−849.679518	−829.240377
ΔE_{tot}, kcal/mol	0.00	0.00	ΔE_{tot}, kcal/mol	3.45	2.13
$\omega_1(a_1)$, cm^{-1}	605	699	$\omega_1(a')$, cm^{-1}	775	983
$\omega_2(a_1)$, cm^{-1}	356	413	$\omega_2(a')$, cm^{-1}	443	490
$\omega_3(a_1)$, cm^{-1}	189	209	$\omega_3(a')$, cm^{-1}	311	422
$\omega_4(b_1)$, cm^{-1}	185	182	$\omega_4(a')$, cm^{-1}	267	295
$\omega_5(b_2)$, cm^{-1}	605	800	$\omega_5(a')$, cm^{-1}	152	183
$\omega_6(b_2)$, cm^{-1}	243	266	$\omega_6(a'')$, cm^{-1}	169	180

[a] At the B3LYP/6-311+G* level of theory.

TABLE 6: Calculated Molecular Properties of BSi_3^-, CSi_3, NSi_3^+, OAl_3^-, and FAl_3[a]

	BSi_3^-, C_{2v}, $^1A_1$	CSi_3, C_{2v}, $^1A_1$	NSi_3^+, C_{2v}, $^1A_1$	OAl_3^-, C_{2v}, $^1A_1$	FAl_3, C_{2v}, $^1A_1$
R(A−X_1), Å	2.088	1.792	1.900	2.011	2.344
R(A−$X_{2,3}$), Å	1.890	1.861	1.714	1.830	2.019
R(X_1−$X_{2,3}$), Å	2.424	2.612	2.513	2.769	2.858
∠$X_1AX_{2,3}$	74.88°	91.26°	87.97°	92.15°	81.49°
E_{tot}, au	−893.370186	−829.243777	−923.015021	−802.703823	−827.231988
$\omega_1(a_1)$, cm^{-1}	589	699	607	432	303
$\omega_2(a_1)$, cm^{-1}	430	413	503	345	218
$\omega_3(a_1)$, cm^{-1}	301	209	276	200	127
$\omega_4(b_1)$, cm^{-1}	135	182	221	171	110
$\omega_5(b_2)$, cm^{-1}	977	800	1003	668	269
$\omega_6(b_2)$, cm^{-1}	342	266	295	237	188

[a] At the B3LYP/6-311+G* level of theory.

Tower" structure being a first-order saddle point. We believe that the fact that the "Eiffel Tower" structure is more stable for the *cis*-$CAlSi_2$ isomer relative to the Napoleon Hat structure is simply due to the single occupancy of the HOMO—the single electron prefers to be localized between the two more electronegative Si atoms rather than forming a three-center peripheral bond involving Al. Therefore, if all the ligands are of the same type, the 15-electron tetraatomic species still prefers the "Napoleon Hat".

We would like to stress that the three-center peripheral bond, which is present in both cis-$CAlSi_2^-$ and trans-$CAlSi_2^-$ and is responsible for the "Napoleon Hat" structure, is a new type of chemical bond, which does not exist in stoichiometric molecules discussed in the Introduction. While three-center bonds, such as the bridging B−H−B bond in B_2H_6, are well-known in chemistry, the three-center bond we are discussing here is different. The HOMO in the "Napoleon Hat" structure is bonding with respect to ligand−ligand interactions without the participation of the central atom. Another new feature of this three-center bond is that the wave function changes signs when it passes through the equatorial ligand (Figure 3).

Examining the HOMO of both the *cis*- and *trans*-$CAlSi_2^-$ isomers, one can see that the two axial ligands have some additional electron density located outside of the bonding ligand−ligand area. An additional atom, such as Al^+, can be coordinated to the "Napoleon Hat" structure to form a four-center peripheral bond, which is exactly what we have previously found in a series of tetracoordinated pentaatomic planar molecules, such as *cis*-CSi_2Al_2,[116] *trans*-CSi_2Al_2,[116] *cis*-CSi_2Ga_2,[117] *trans*-CSi_2Ga_2,[117] *cis*-CGe_2Al_2,[117] *trans*-CGe_2Al_2,[117] Al_4O,[28] Al_4^{N-},[95] and Al_4C^-.[94] The novel molecular structure and new types of chemical bonds discovered hitherto suggest that there are abundant possibilities of finding other new types of structures and chemical bonds in nonstoichiometric molecules and clusters.

Conclusions

We report a combined experimental and theoretical investigation of the structures and bonding in $CAlSi_2^-$ and its corresponding neutral. Photoelectron spectra of the anions were measured, and the electron detachment energies from several MOs of the anions were obtained. The vertical electron detachment energy of $CAlSi_2^-$ was determined to be 2.54 eV. Detachment transitions to the first and second electronic excited states of the neutral species were also observed. Geometry optimizations of the anions were carried out, and two low-lying isomers, a *cis*- and *trans*-$CAlSi_2^-$, both with a "Napoleon Hat" type of structure, were discovered. The cis isomer was predicted to be the ground state of the anions and was confirmed by the excellent agreement between the experimental and theoretical VDEs. Significant geometry changes between the ground states of the cis anion and its corresponding neutral were observed, consistent with the experimental observation of a broad photodetachment band. The ground-state neutral was found to have a C_{2v} "Eiffel Tower" structure, whereas the trans isomer maintains its "Napoleon Hat" structure in both its anion and neutral ground states. Evidence of the existence of the trans isomer was also obtained by comparing the calculated VDEs with the experimental photoelectron spectra. We found that a new three-center bond involving the three ligands is responsible for the "Napoleon Hat" structure for the 16-electron tetraatomic species.

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