

# On the origin of planarity in $Al_5^-$ and $Al_5$ clusters: The importance of a four-center peripheral bond

Grant D. Geske and Alexander I. Boldyrev<sup>a)</sup>

*Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300*

Xi Li and Lai-Sheng Wang<sup>b)</sup>

*Department of Physics, Washington State University, 2710 University Drive, Richland, Washington 99352*

*and W. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National*

*Laboratory, MS K8-88, P. O. Box 999, Richland, Washington 99352*

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*Ab initio* calculations were combined with anion photoelectron spectroscopy to unravel the structural origin of  $Al_5$  and  $Al_5^-$ . Well-resolved photoelectron spectra of  $Al_5^-$  were obtained and compared to theoretical calculations performed at various levels of theory. It was shown that the best agreement between the experimental and theoretical data is for a planar  $C_{2v}$  structure. Analyses of the electronic structure and molecular orbitals revealed that the planarity in  $Al_5$  and  $Al_5^-$  are due to the presence of a four-center peripheral bond that is common in a whole family of planar pentaatomic species recently uncovered. © 2000 American Institute of Physics.

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Aluminum clusters have been extensively studied both experimentally<sup>1-14</sup> and theoretically.<sup>15-28</sup> A number of theoretical investigations concluded that Al clusters up to five atoms are planar and there is a transition from planar to three-dimensional structures beyond  $Al_5$ . However, the origin of the planarity in  $Al_5$  and  $Al_5^-$  have not been understood and explored. It is also true that the planar structure of  $Al_5$  and  $Al_5^-$  has not yet been verified experimentally. Recently, we have investigated a series of five-atom molecules ( $CAI_4^-$ ,  $CAI_3Si^-/CAI_3Ge^-$ ,  $CAI_2Si_2/CAI_2Ge_2$ ) that contain a tetracoordinate planar carbon (TCPC) in a nearly square geometry.<sup>29-33</sup> We found that the highest occupied molecular orbital (HOMO) in these TCPC molecules is a four-center bonding orbital between the four peripheral ligand atoms. We further found that the occupation of this four-center orbital is crucial for the planarity of these species. This led to our proposal of a 17/18-electron rule for pentaatomic planar molecules with a first-row central atom and four ligand atoms from the second or third row. For example, the 17-electron  $CAI_4^-$  is a TCPC molecule because of the single occupation of the four-center bonding orbital, whereas the 16-electron  $CAI_4$  is tetrahedral.<sup>31</sup> Extension of this concept to planar Si or Ge species in  $SiAl_4/SiAl_4^-$  or  $GeAl_4/GeAl_4^-$  revealed two important effects.<sup>34</sup> First, the Si or Ge atom is too large to fit in the square of  $Al_4$  so that the molecules distort to a planar  $C_{2v}$  structure. Second, the four-center bonding orbital is no longer the HOMO, so that even the neutral  $SiAl_4$  or  $GeAl_4$  can still maintain a nearly planar global minimum structure, in contrast to the tetrahedral structure of  $CAI_4$ . The purpose of this communication is to show that the planarity of  $Al_5/Al_5^-$  derives from the same

origin as that in  $SiAl_4$  or  $GeAl_4$  and, further, to confirm the planar structure of  $Al_5/Al_5^-$ , in a combined experimental and theoretical effort.

Experimental electronic structure information on  $Al_5$  is obtained using anion photoelectron spectroscopy (PES). The experiment was performed with a magnetic-bottle time-of-flight PES apparatus equipped with a laser vaporization cluster source.<sup>35</sup> Briefly,  $Al_5^-$  anions were produced by laser vaporization of an Al target with a helium carrier gas. Clusters formed from the laser vaporization source were entrained in the carrier gas and underwent a supersonic expansion. The anions in the beam were extracted and subjected to a time-of-flight mass analysis. The  $Al_5^-$  anions were selected and decelerated before photodetachment by a laser beam. For the current experiment two detachment photon energies were used: 355 nm (3.496 eV) and 193 nm (6.424 eV). 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.

The photoelectron spectra of  $Al_5^-$  are shown in Fig. 1 at the two detachment-photon energies. The data shown in Fig. 1 represent the best-resolved spectra for  $Al_5^-$  yet reported. The 355 nm spectrum [Fig. 1(a)] revealed three well-resolved bands, at 2.285 eV (X), 2.640 eV (A), and 2.935 eV (B). The 193 nm spectrum [Fig. 1(b)] shows at least two additional features at 4.04 eV (C) and 4.48 eV (D). Signal-to-noise ratio at the highest binding energy side in the 193 nm spectrum became rather poor. We also noted that the intensity of the A-band was significantly enhanced in the 193 nm spectrum compared to that of the 355 nm spectrum. The obtained vertical detachment energies (VDEs) for the five observed features are summarized in Table I and are compared to *ab initio* calculations (see below). The adiabatic detachment energy (ADE) or the electron affinity of  $Al_5$  was measured to be  $2.23 \pm 0.05$  eV.

<sup>a)</sup>Electronic mail: boldyrev@cc.usu.edu

<sup>b)</sup>Electronic mail: ls.wang@pnl.gov

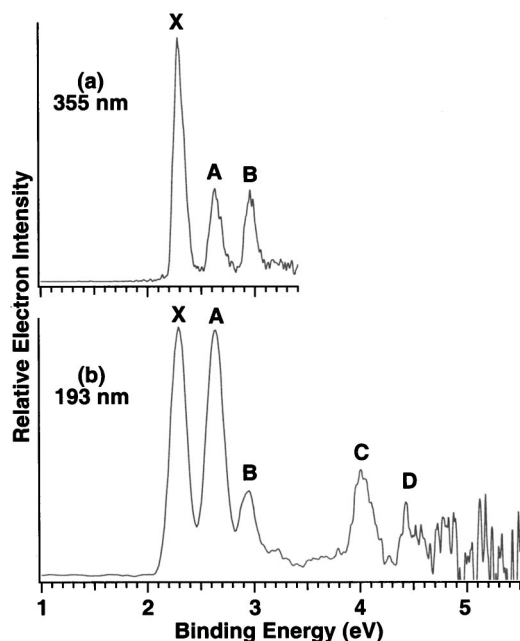


FIG. 1. Photoelectron spectra of  $\text{Al}_5^-$  at (a) 355 nm (3.496 eV) and (b) 193 nm (6.424 eV).

In the theoretical study, we first optimized the planar structure of  $\text{Al}_5^-$  as reported in the literature [ $C_{2v}$ -I, Fig. 2(a)] employing analytical gradients with polarized split-valence basis sets (6-311+ $G^*$ ) with a hybrid method, which includes a mixture of Hartree–Fock exchange with density functional exchange–correlation (B3LYP). This structure was found indeed to be a minimum for  $\text{Al}_5^-$ , consistent with the literature.<sup>17,22</sup> Then, we refined the geometries using the second-order Møller–Plesset perturbation theory (MP2/6-311+ $G^*$ ) level of theory. Surprisingly the planar structure for  $\text{Al}_5^-$  was found to be a second-order saddle point. Geometry optimization at the MP2 level following the mode with the higher imaginary frequency led to the  $C_{2v}$ -II structure [Fig. 2(c)]. However, the  $C_{2v}$ -II structure is not a minimum, but a first-order saddle point. Further geometry optimization following the out-of-plane imaginary

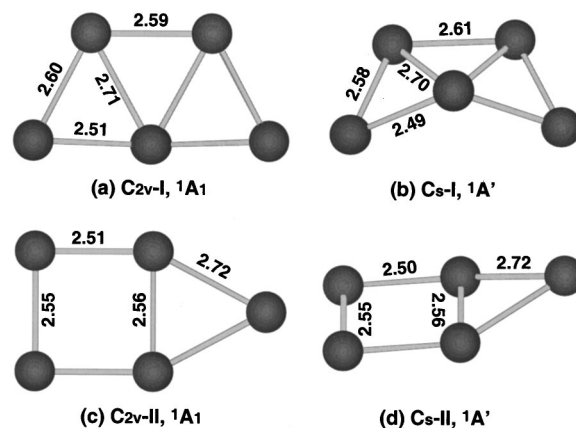


FIG. 2. Optimized structures for  $\text{Al}_5^-$  at the MP2/6-311+ $G^*$  level of theory. Bond lengths shown are in Å.

frequency mode led to the  $C_s$ -II [Fig. 2(d)] structure, which is a minimum at the MP2/6-311+ $G^*$  level of theory. The planar  $C_{2v}$ -II structure was found to be just 0.033 kcal/mol higher in energy. Therefore, when the zero-point energy (ZPE) corrections were taken into account ( $\Delta\text{ZPE}=0.049$  kcal/mol) the vibrationally averaged structure is essentially planar. Then we optimized the geometry of  $\text{Al}_5^-$  at the MP2 level from the  $C_{2v}$ -I structure following the second imaginary mode—an out-of-plane deformation. This led to the butterfly structure [ $C_s$ -I, Fig. 2(b)], which was also found to be a first-order saddle point. Further geometry refinement along the  $C_s$ -I imaginary frequency again led to the  $C_s$ -II structure, which was found to be more stable by 4.16 kcal/mol (4.00 kcal/mol with ZPE correction) for  $\text{Al}_5^-$  at MP2/6-311+ $G^*$ . In light of the MP2 results, we decided to optimize the geometry of the  $C_{2v}$ -II structures of  $\text{Al}_5^-$  using the B3LYP/6-311+ $G^*$  method and found that at the B3LYP level of theory the  $C_{2v}$ -II structure is a first-order saddle point corresponding to a transition state on the  $C_{2v}$ -I  $\rightarrow C_{2v}$ -II  $\rightarrow C_{2v}$ -I' (which is a permutational isomer of the  $C_{2v}$ -I structure) intramolecular rearrangement for  $\text{Al}_5^-$ . The barrier was found to be just 0.86 kcal/mol (0.81 kcal/mol with ZPE correction) for  $\text{Al}_5^-$  at B3LYP/6-311+ $G^*$ . One can

TABLE I. Experimental and theoretical vertical (VDE) and adiabatic (ADE) electron detachment energies in eV from the first five detachment channels of  $\text{Al}_5^-$ .

	VDE (exp)	ADE (exp)	$C_{2v}$ -I MO	VDE <sup>a</sup> (theo)	$C_s$ -I MO	VDE <sup>a</sup> (theo)	$C_{2v}$ -II MO	VDE <sup>a</sup> (theo)	$C_s$ -II MO	VDE <sup>a</sup> (theo)
X	2.285 $\pm 0.010$	2.23 $\pm 0.05$	$3b_2$	2.20 (0.86)	$3a''$	2.22 (0.86)	$5a_1$	2.26 (0.86)	$6a'$	2.28 (0.86)
A	2.640 $\pm 0.015$		$4a_1$	2.60 (0.86)	$5a'$	2.54 (0.86)	$1b_1$	2.66 (0.85)	$5a'$	2.63 (0.86)
B	2.935 $\pm 0.020$		$1b_1$	2.82 (0.86)	$4a'$	2.78 (0.86)	$4a_1$	2.80 (0.86)	$4a'$	2.79 (0.86)
C	4.04 $\pm 0.04$		$2b_2$	4.07 (0.82)	$2a''$	3.94 (0.82)	$2b_2$	3.73 (0.84)	$2a''$	3.72 (0.84)
D	4.48 $\pm 0.08$		$3a_1$	4.42 <sup>b</sup> (0.79) <sup>b</sup>	$3a'$	4.42 <sup>b</sup> (0.75)	$3a_1$	4.92 <sup>b</sup> (0.75)	$3a'$	4.91 <sup>b</sup> (0.74)

<sup>a</sup>At the UOVGF/6-311+ $G(2df)$  level of theory using CCSD(T)/6-311+ $G^*$  geometry. Pole strength is given in parentheses.

<sup>b</sup>VDE beyond 4.4 eV shows relatively low pole strength, suggesting that the one-electron detachment picture will break down at high excitation energies (Ref. 18).

see that the potential energy surface of  $\text{Al}_5^-$  is very flat. Moreover we found that the excited triplet state for  $\text{Al}_5^-$  is just 5 kcal/mol (at B3LYP/6-311+G\*) higher in energy than the singlet  $C_{2v}$ -I structure.

Geometry of neutral  $\text{Al}_5$  was also first optimized at the B3LYP/6-311+G\* level of theory. We found that the  $C_{2v}$ -I( $^2B_2$ ) structure is a minimum in agreement with the literature, but the  $C_{2v}$ -II( $^2A_1$ ) structure is a second-order saddle point. Then we optimized the geometry of the  $C_{2v}$ -II( $^2A_1$ ) structure of  $\text{Al}_5$  allowing the out-of-plane deformation along the second imaginary frequency. The optimized  $C_s$ -II( $^2A'$ ) structure was found to be a first order saddle point corresponding to a transition state on the  $C_{2v}$ -I- $C_s$ -II- $C_{2v}$ -I' intramolecular rearrangement for  $\text{Al}_5$ . The barrier was found to be just 2.72 kcal/mol (2.42 kcal/mol with ZPE correction) for  $\text{Al}_5$  at B3LYP/6-311+G\*. Unfortunately, at the MP2 and coupled-cluster single, double, and triple approximate excitations [CCSD(T)] levels of theory the wave functions were found to have a high spin-contamination and therefore we will not discuss these results.

As one can see, our results for  $\text{Al}_5^-$  at the B3LYP and MP2 levels of theory are inconclusive. The  $C_{2v}$ -II (after vibrational averaging) structure is a minimum with the  $C_{2v}$ -I (also after vibrational averaging) structure being a transition state at the MP2/6-311+G\* level of theory; but at the B3LYP/6-311+G\* level of theory the reverse is true. Geometry optimization and frequency calculations at CCSD(T) levels are beyond our computational facilities currently, but we performed single-point CCSD(T)/6-311+G(2df) calculations using the MP2/6-311+G\* geometries. These calculations gave the following order of energetics for  $\text{Al}_5^-$ :  $C_s$ -I (0.0 kcal/mol),  $C_{2v}$ -I (0.052 kcal/mol),  $C_s$ -II (0.049 kcal/mol), and  $C_{2v}$ -II (0.076 kcal/mol). It seems that the planar  $C_{2v}$ -I structure (after ZPE correction) is indeed the global minimum, as reported in the literature. However, because the potential energy surface is so flat along the  $C_{2v}$ -I  $\rightarrow$   $C_{2v}$ -II  $\rightarrow$   $C_{2v}$ -I' intramolecular rearrangement, it is difficult to make a final conclusion about the true global minimum based on the current calculations. We therefore used additional information from the *ab initio* photoelectron spectrum calculated using the outer valence Green function (OVGF) method<sup>36</sup> incorporated in GAUSSIAN 98<sup>37</sup> and compared them with the experimental results.

The theoretical VDEs are compared to the experimental data in Table I. First, we found that the calculated VDEs are almost the same for  $C_{2v}$ -I and  $C_s$ -I, as well as for  $C_{2v}$ -II and  $C_s$ -II, showing that deviations from planarity do not affect appreciably the calculated photoelectron spectra because after ZPE corrections in fact both structures are planar anyway. So in reality and in the following discussion, we only need to refer to the two planar structures. Second, *ab initio* photoelectron spectrum for the  $C_{2v}$ -I structure is in excellent agreement with the experimental spectrum for all five detachment channels observed. On the other hand, even though the VDEs for the first three detachment channels from the  $C_{2v}$ -II structure are in good agreement with the experiment, the fourth and fifth VDEs deviate considerably from the experiment. The excellent agreement between theoretical results for the  $C_{2v}$ -I structure and the experimental data lets us

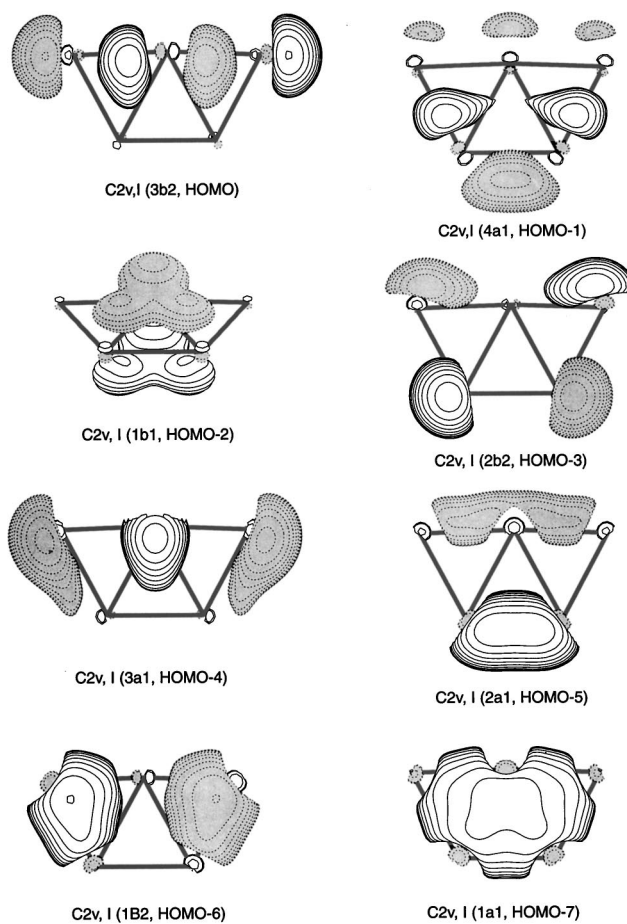


FIG. 3. Valence molecular orbital pictures (Ref. 40) for the  $C_{2v}$ -I  $\text{Al}_5^-$  [see Fig. 2(a)].

favor the original planar structure of  $\text{Al}_5$  and  $\text{Al}_5^-$ . However, the origin of the planarity still remains to be explained. This is addressed in the following.

Figure 3 shows the eight valence MOs for  $\text{Al}_5^-$ .  $\text{Al}_5^-$  is isoelectronic with  $\text{SiAl}_4$ , which we have recently found to have a similar  $C_{2v}$  planar structure.<sup>34</sup> Not surprisingly the canonical MO ordering of  $\text{Al}_5^-$  is the same as in  $\text{SiAl}_4$ . The key orbital is HOMO-1 (Fig. 3), which represents the peripheral four-center bond. This orbital is the HOMO in TCPC molecules,<sup>29-33</sup> thus leading to the 17/18-electron rule, i.e., only 17- or 18-electron systems can have this four-center MO occupied and are thus planar. However, the four-center MO drops in energy in  $\text{SiAl}_4$  and  $\text{Al}_5^-$  to HOMO-1, which is filled even though there are only 16 valence electrons. The distorted structure (from a perfect square) is due to the fact that Al or Si is much larger than C and can no longer fit into the center of a square  $\text{Al}_4$ . The stabilization of the four-center bonding MO in  $\text{Al}_5^-$  and  $\text{SiAl}_4$  is in turn due to the less electronegativity of Al and Si relative to that of C. Both  $\text{Al}_5^-$  and  $\text{SiAl}_4$  are valent-isoelectronic to  $\text{CAI}_4$ , which has a tetrahedral structure with a  $^1A_1$  ( $1a_1^2 1t_2^2 2a_1^2 2t_2^6$ ) electronic configuration. The first four MOs ( $1a_1^2 1t_2^6$ ) are C-Al  $\sigma$ -bonds and the other MOs ( $2a_1^2 2t_2^6$ ) are four lone-pairs from the Al 3s. Therefore, in the ionic limit, the structure of  $\text{CAI}_4$  can be viewed as ( $\text{C}^{4-} + 4 \text{Al}^+$ ). A natural population

analysis (NPA) of the effective charges gave rise to  $Q(C) = -3.03|e|$  and  $Q(Al) = +0.76|e|$  (at QCISD/6-311+G\*). We tested the tetrahedral ( $T_d$ ,  $^1A_1$ ) structure for  $Al_5^-$  and found it to be a minimum at the B3LYP/6-311+G\* level of theory and a second-order saddle point at the MP2/6-311+G\* level of theory. However, the  $T_d(^1A_1)$  structure is substantially higher in energy [by 42.4 kcal/mol at CCSD(T)/6-311+G(2df)//MP2/6-311+G\*] than the  $C_{2v}$ -I structure. An analysis of the NPA effective charges for the  $T_d$   $Al_5^-$  found:  $Q(Al_{\text{central}}) = -2.32|e|$  and  $Q(Al_{\text{ligand}}) = +0.33|e|$ ; and the central Al is too negative for it to be stable. In the global minimum  $C_{2v}$ -I structure of  $Al_5^-$ , the NPA calculated charges were  $Q(Al_{\text{central}}) = -0.60|e|$ ,  $Q(Al_{\text{peripheral-central}}) = -0.17|e|$ , and  $Q(Al_{\text{peripheral-terminal}}) = -0.03|e|$ . Clearly the effective charge on the central Al is substantially reduced in the  $C_{2v}$ -I structure. Hence one electron pair on the central Al in the  $T_d$  structure is transferred to the peripheral bond (HOMO-1) in the  $C_{2v}$ -I structure, making it more stable than the  $T_d$  structure. Thus the origin of the planarity of  $Al_5^-$  is due to the lowering of the four-center MO and its occupation in the planar  $C_{2v}$ -I structure, similar to what we found recently in  $SiAl_4$  and  $GeAl_4$ .<sup>34</sup> The central Al atom in the  $C_{2v}$ -I  $Al_5$  and  $Al_5^-$  is tetracoordinated, and thus belongs to a whole family of tetracoordinate planar atoms including C, B, N, O, Si, and Ge.<sup>29-33,38,39</sup>

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