

# Photoelectron spectroscopy of pentaatomic tetracoordinate planar carbon molecules: $\text{CAI}_3\text{Si}^-$ and $\text{CAI}_3\text{Ge}^-$

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## Abstract

We report a temperature-dependent photoelectron spectroscopy study of  $\text{CAI}_3\text{Si}^-$  and  $\text{CAI}_3\text{Ge}^-$ , the first pentaatomic planar-carbon molecules characterized in both their anionic and neutral states. Significantly improved spectra were obtained under cold experimental conditions, allowing us to determine the electron affinities of  $\text{CAI}_3\text{Si}$  (2.77 eV) and  $\text{CAI}_3\text{Ge}$  (2.70 eV) for the first time. Three photon energies were used and the 193-nm spectra revealed two additional detachment features, allowing a total of six detachment channels to be observed for each anion. The measured vertical detachment energies and electron affinities were compared with the previous theoretical predictions, and excellent agreement was observed. © 2002 Elsevier Science B.V. All rights reserved.

The idea of tetrahedral carbon was first proposed in 1874 by van't Hoff and LeBel and it has become the cornerstone of stereochemistry. However, since the pioneering theoretical work on tetracoordinate planar carbon (TPC) molecules by Hoffmann et al. [1], there have been considerable research efforts at designing molecules that may contain a TPC [2–14]. Recently, we have characterized a series of pentaatomic species containing a TPC using photoelectron spectroscopy (PES) and ab initio calculations [15–17]. The pentaatomic species are the smallest molecules possible to

contain a TPC and afforded us opportunities to completely examine their chemical structures and chemical bonding. Of particular interest are the two isoelectronic TPC molecules,  $\text{CAI}_3\text{Si}^-$  and  $\text{CAI}_3\text{Ge}^-$  (Fig. 1), which are electronically closed-shell with 18-valence electrons [16]. Upon detachment of an electron from their highest occupied molecular orbitals (HOMO), the resulting neutral species were also found to be planar, analogous to the 17-valence electron  $\text{CAI}_4^-$  [15]. However, the previous PES spectra for  $\text{CAI}_3\text{Si}^-$  and  $\text{CAI}_3\text{Ge}^-$  were taken only at 266 nm with a considerable low-energy tail near the detachment threshold in each case [16]. Although it was successfully interpreted as due to a combination of hot band transitions and contribution from another isomer, the

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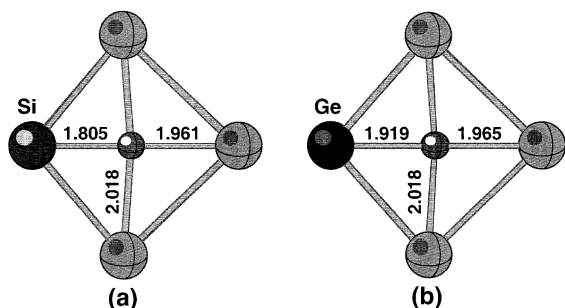


Fig. 1. Structures of the two pentaatomic planar molecules, (a)  $\text{CAI}_3\text{Si}^-$  ( $C_{2v}, {}^1A_1$ ) and (b)  $\text{CAI}_3\text{Ge}^-$  ( $C_{2v}, {}^1A_1$ ). Selected bond lengths are in Å. Data are from [16].

low-energy tail cast some doubt about the planarity of the neutral species because the tail could be an indication of a large geometry change between the ground states of the anions and the neutrals.

In this Letter, we report a PES study of  $\text{CAI}_3\text{Si}^-$  and  $\text{CAI}_3\text{Ge}^-$  at well-controlled experimental conditions and various photon energies. We show that the low-energy tail can be eliminated with colder anions, resulting in much sharper PES spectra. The improved data allowed us to obtain the adiabatic detachment energies (ADE) of the two anions, or the electron affinities (EA) of the corresponding neutrals. Furthermore, the 193 nm spectra revealed two additional detachment channels, as predicted theoretically. The current experimental data all agree well with the previous theoretical calculations, firmly establishing the first pentaatomic TPC molecules as both anions and neutral molecules.

The experiments were performed with a magnetic-bottle time-of-flight PES apparatus equipped with a laser vaporization cluster source [18]. The  $\text{CAI}_3\text{Si}^-$  and  $\text{CAI}_3\text{Ge}^-$  anions were produced by laser vaporization of a graphite/Al/Si and graphite/Al/Ge target, respectively, with a pure helium carrier gas. Clusters formed from the source were entrained in the He carrier gas and underwent a supersonic expansion. The anion species in the beam were analyzed using a time-of-flight mass spectrometer and the anions of interest 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 and 193 nm from an ArF

excimer laser were used for photodetachment. The electron kinetic energy resolution of the apparatus was better than 30 meV for 1 eV electrons. As we showed previously, the vibrational temperatures of cluster anions from the laser vaporization source span a wide range, depending on the residence time of the clusters in the nozzle [19–23]. Clusters that leave the nozzle late (long residence time) are usually much colder. We used a large waiting room nozzle in the current experiment in order to increase the residence time and produce colder anions [19,20].

The spectra of  $\text{CAI}_3\text{Si}^-$  and  $\text{CAI}_3\text{Ge}^-$  under the cold experimental conditions were shown in Figs. 2 and 3, respectively, at the three photon energies. Fig. 4 shows the temperature-dependent spectra for the two TPC molecules at 266 nm. The spectra under the ‘hot’ conditions were similar to the data previously obtained [16]. Clearly, the low-energy tail was significantly reduced in both spectra under

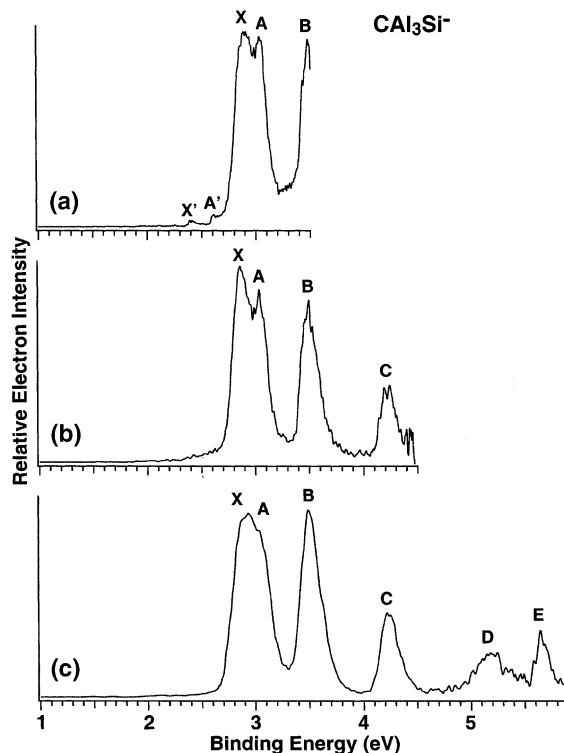


Fig. 2. Photoelectron spectra of  $\text{CAI}_3\text{Si}^-$  at (a) 355 nm (3.496 eV), (b) 266 nm (4.661 eV), and (c) 193 nm (6.424 eV).

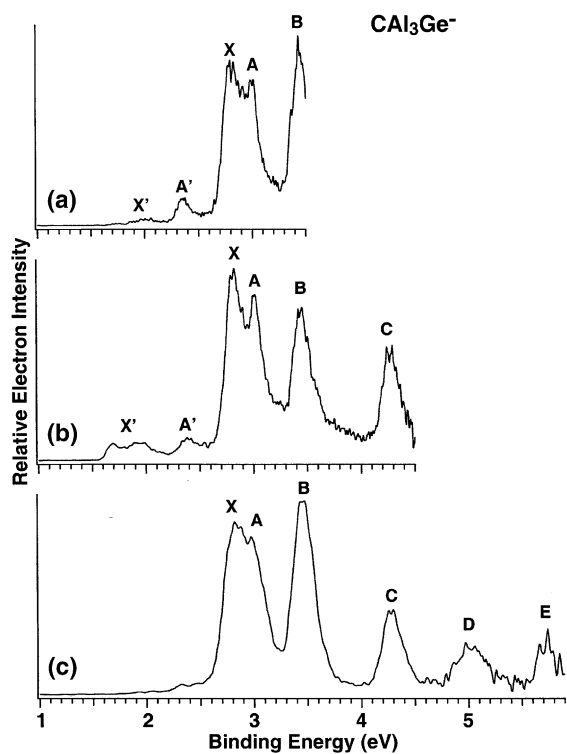


Fig. 3. Photoelectron spectra of  $\text{CAI}_3\text{Ge}^-$  at (a) 355 nm, (b) 266 nm, and (c) 193 nm.

the ‘cold’ conditions, but not completely eliminated. Surprisingly, the tail part of the  $\text{CAI}_3\text{Ge}^-$  spectra was resolved into well-separated features ( $X'$  and  $A'$  in Fig. 3) under the cold conditions. These weak features were likely due to impurities because the mass spectra from the mixed targets were quite complicated [16] and there could be very weakly populated impurity anions with different compositions and the same mass in the anion beam. The impurity problem was much less severe in the case of  $\text{CAI}_3\text{Si}^-$ , but the weak tail part was still resolved into two well-separated features in the 355 nm spectra ( $X'$  and  $A'$  in Fig. 2a). The main features ( $X$ ,  $A$ ,  $B$ ,  $C$ ) in the 266 nm spectra, though better resolved, are consistent with the data previously reported. At 193 nm, two extra features ( $D$  and  $E$ ) were observed at higher binding energies for both species. At 355 nm, the  $X$  and  $A$  bands were surprisingly not much better resolved than those in the 266 nm spectra probably due to the complicated Franck–Condon profiles of each band. As predicted previously [16], the two species have  $C_{2v}$  symmetry and each possesses three totally symmetric modes, which could all be active in the photodetachment. There were hints of vibrational structures in the  $X$  band at 355 nm for  $\text{CAI}_3\text{Ge}^-$  (Fig. 3a) and the  $C$  band in the 266 nm (Figs. 2b

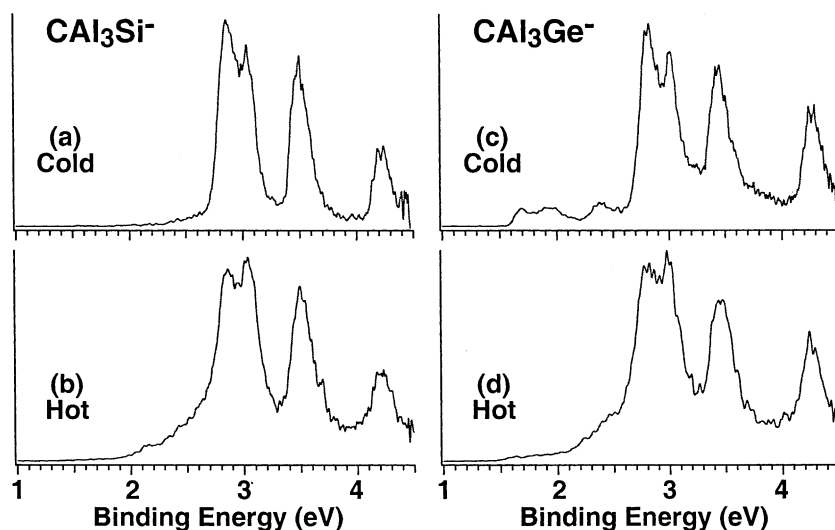


Fig. 4. The 266-nm photoelectron spectra of  $\text{CAI}_3\text{Si}^-$  and  $\text{CAI}_3\text{Ge}^-$  at two experimental conditions.

and 3b). All the vertical detachment energies (VDEs) obtained currently are given in Table 1, compared with the previous theoretical calculations. Within the experimental uncertainties, the VDEs of the first four features (*X*, *A*, *B*, *C*) agree well with those previously reported. The long low-energy tails in the previous PES spectra prevented us from determining the EAs for the two neutral TPC molecules (the ADEs of the *X* band in each case). Due to the lack of clearly resolved vibrational structures, we determined the ADE in each case by drawing a straight line along the leading edge of the *X* band and then adding the instrumental resolution to the intersection with the binding energy axis. The EAs so obtained are given in Table 2 and compared with previous theoretical predictions.

The structures of the two pentaatomic TPC molecules are shown in Fig. 1 with nearly identical geometries, except for the difference in the C–Si and C–Ge bondlengths. It was thus expected that the PES spectra would be also very similar, which was born out in our experiment. A  $C_s$  isomer was also predicted for each anion more than 20 kcal/

Table 1  
Observed vertical detachment energies (VDE) for  $CAI_3Si^-$  and  $CAI_3Ge^-$  compared to previous theoretical calculations [16]

	VDE (exp.) <sup>a</sup>	Detachment channel	VDE (theo.) <sup>b</sup>
$CAI_3Si^-$			
$X^2B_2$	2.87 (4)	$3b_2$	2.85 (0.87)
$A^2B_2$	3.03 (3)	$2b_2$	3.00 (0.87)
$B^2A_1$	3.49 (3)	$5a_1$	3.61 (0.86)
$C^2A_1$	4.21 (3)	$4a_1$	4.31 (0.84)
$D^2B_1$	5.18 (5)	$1b_1$	5.14 (0.86)
$E^2A_1$	5.65 (5)	$3a_1$	6.09 (0.80)
$CAI_3Ge^-$			
$X^2B_2$	2.80 (4)	$3b_2$	2.81 (0.87)
$A^2B_2$	3.00 (4)	$2b_2$	2.95 (0.87)
$B^2A_1$	3.45 (3)	$5a_1$	3.51 (0.86)
$C^2A_1$	4.26 (4)	$4a_1$	4.37 (0.84)
$D^2B_1$	4.97 (6)	$1b_1$	4.92 (0.86)
$E^2A_1$	5.74 (6)	$3a_1$	6.14 (0.79)

All energies are in eV.

<sup>a</sup> Current measurements. Numbers in parentheses indicate uncertainties in the last digit.

<sup>b</sup> From [16]. The numbers in parentheses indicate the pole strength, which is a measure of the feasibility of the single-particle approximation. See [16].

Table 2  
Adiabatic electron affinities (EA) of  $CAI_3Si$  and  $CAI_3Ge$  in eV

	EA (exp.) <sup>a</sup>	EA (theo.) <sup>b</sup>
$CAI_3Si$	$2.77 \pm 0.06$	2.67
$CAI_3Ge$	$2.70 \pm 0.06$	2.66

<sup>a</sup> Current measurements.

<sup>b</sup> From [16].

mol higher in energy [16]. This isomer had lower VDEs (2.27 eV for the first detachment channel of the  $C_sCAI_3Si^-$ ) and was apparently populated in the hot spectra. This isomer and the hot band transitions were indeed almost entirely responsible for the low-energy tail in the hot spectra of  $CAI_3Si^-$ , although the impurity features seemed also to make a contribution to the tail in the hot spectra of  $CAI_3Ge^-$ . Clearly, the  $C_s$  isomer almost completely disappeared under the cold conditions.

The valence electron configuration of  $CAI_3Si^-$  and  $CAI_3Ge^-$  are identical:  $\dots 3a_1^2 1b_1^2 4a_1^2 5a_1^2 2b_2^2 3b_2^2$ . The  $3b_2$  HOMO is an interesting four-center  $\sigma$ -orbital. Removal of an electron from the  $3b_2$  HOMO results in the  $^2B_2$  ground state of neutral  $CAI_3Si$  and  $CAI_3Ge$ , which both were predicted to be planar. The main geometry changes between the anions and the neutrals were shown to be along the C–Si or C–Ge bond. The relatively sharp *X* band and the small difference between the ADE and VDE of the *X* band are consistent with the small geometry changes between the anion and neutral ground states, confirming the theoretical predictions. The predicted EAs of the two neutral TPC molecules are in excellent agreement with the experimental data (Table 2). The overall agreement between the experimental and theoretical VDEs are excellent, as shown in Table 1. The *D* and *E* channels were newly observed and the experimental VDEs of these two channels are also in excellent agreement with the theoretical predictions. The theoretical VDEs for the *E* channel appeared to be slightly higher, probably due to the limitation of the theoretical method at such high excitation energies, as indicated by the relatively smaller pole strength.

In summary, we report a temperature-dependent PES study of two pentaatomic TPC molecules,  $CAI_3Si^-$  and  $CAI_3Ge^-$ , at various photon

energies. We showed that the anion temperatures had a significant effect on the PES data, confirming that the low-energy tails observed previously were indeed due to hot band transitions and contributions from another isomer, which were largely eliminated under cold experimental conditions. Six detachment features from the top six occupied molecular orbitals of the anions were observed. The measured EAs and the VDEs were all in excellent agreement with the previous theoretical predictions, allowing a more thorough characterization of the first pentaatomic tetracoordinate planar carbon molecules in both their anionic and neutral states.

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### References

- [1] R. Hoffmann, R.W. Alder, C.F. Wilcox Jr., *J. Am. Chem. Soc.* 92 (1970) 4992.
- [2] J.B. Collins, J.D. Dill, E.D. Jemmis, Y. Apeloig, P.v.R. Schleyer, R. Seeger, J.A. Pople, *J. Am. Chem. Soc.* 98 (1976) 5419.
- [3] A. Streitwieser, S.M. Bachrach, A. Dorigo, P.v.R. Schleyer, in: A.-M. Sapse, P.v.R. Schleyer (Eds.), *Lithium Chemistry: A Theoretical and Experimental Overview*, Wiley, New York, 1995, p. 1.
- [4] K. Sorger, P.v.R. Schleyer, *J. Mol. Struct.* 338 (1995) 317.
- [5] D. Stahl, F. Maquin, T. Gaumann, H. Schwarz, P.-A. Carrupt, P. Vogel, *J. Am. Chem. Soc.* 107 (1985) 5049.
- [6] R. Keese, *Nachr. Chem. Tech. Lab.* 30 (1982) 844.
- [7] W. Luef, R. Keese, *Adv. Strain Org. Chem.* 3 (1993) 229.
- [8] M.P. McGrath, L. Radom, *J. Am. Chem. Soc.* 114 (1992) 8531.
- [9] D.R. Rasmussen, L. Radom, *Angew. Chem. Int. Ed.* 38 (1999) 2876.
- [10] G. Erker, J. Wicher, K. Engel, F. Resenfeldt, W. Dietrich, C. Kruger, *J. Am. Chem. Soc.* 102 (1980) 6344.
- [11] D. Rottger, G. Erker, *Angew. Chem. Int. Ed.* 36 (1997) 812.
- [12] D. Rottger, G. Erker, R. Frohlich, M. Grehl, S. Silverio, I. Hyla-Kryspin, R. Gleiter, *J. Am. Chem. Soc.* 117 (1995) 10503.
- [13] P.v.R. Schleyer, A.I. Boldyrev, *J. Chem. Soc. Chem. Commun.* 1536 (1991).
- [14] A.I. Boldyrev, J. Simons, *J. Am. Chem. Soc.* 120 (1998) 7967.
- [15] X. Li, L.S. Wang, A.I. Boldyrev, J. Simons, *J. Am. Chem. Soc.* 121 (1999) 6033.
- [16] L.S. Wang, A.I. Boldyrev, X. Li, J. Simons, *J. Am. Chem. Soc.* 122 (2000) 7681.
- [17] X. Li, H.F. Zhang, L.S. Wang, G.D. Geske, A.I. Boldyrev, *Angew. Chem. Int. Ed.* 39 (2000) 3630.
- [18] A.I. Boldyrev, L.S. Wang, *J. Phys. Chem. A.* 105 (2001) 10759.
- [19] L.S. Wang, H.S. Cheng, J. Fan, *J. Chem. Phys.* 102 (1995) 9480.
- [20] L.S. Wang, H. Wu, in: M.A. Duncan (Ed.), *Advances in Metal and Semiconductor Clusters. IV. Cluster Materials*, JAI Press, Greenwich, 1998, p. 299.
- [21] X. Li, H. Wu, X.B. Wang, L.S. Wang, *Phys. Rev. Lett.* 81 (1998) 1909.
- [22] J. Akola, M. Manninen, H. Hakkinen, U. Landman, X. Li, L.S. Wang, *Phys. Rev. B* 60 (1999) R11297.
- [23] L.S. Wang, X. Li, in: *Proceedings of the International Symposium on Clusters and Nanostructure Interfaces*, October 25–28, 1999, Richmond, VA, in: P. Jena, S.N. Khanna, B.K. Rao (Eds.), *Temperature Effects in Anion Photoelectron Spectroscopy of Metal Clusters*, World Scientific, NJ, USA, 2000, p. 293.