

Photoelectron spectroscopic study of carbon aluminum hydride cluster anions

Xinxing Zhang, Haopeng Wang, Gerd Ganteför, Bryan W. Eichhorn, Boggavarapu Kiran, and Kit H. Bowen

Citation: *The Journal of Chemical Physics* **145**, 154305 (2016); doi: 10.1063/1.4964934

View online: <http://dx.doi.org/10.1063/1.4964934>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/145/15?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Low oxidation state aluminum-containing cluster anions: \$Cp^*Al_nH^-\$, \$n = 1-3\$](#)

J. Chem. Phys. **145**, 074305 (2016); 10.1063/1.4959847

[Photoelectron spectroscopy of boron aluminum hydride cluster anions](#)

J. Chem. Phys. **140**, 164317 (2014); 10.1063/1.4871884

[Photoelectron spectroscopic study of iron-pyrene cluster anions](#)

J. Chem. Phys. **135**, 204301 (2011); 10.1063/1.3661984

[Structural evolution and stabilities of neutral and anionic clusters of lead sulfide: Joint anion photoelectron and computational studies](#)

J. Chem. Phys. **135**, 134311 (2011); 10.1063/1.3635406

[Photoelectron spectroscopy of cold aluminum cluster anions: Comparison with density functional theory results](#)

J. Chem. Phys. **132**, 104303 (2010); 10.1063/1.3352445



NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP | Applied Physics
Reviews

Photoelectron spectroscopic study of carbon aluminum hydride cluster anions

Xinxing Zhang,¹ Haopeng Wang,¹ Gerd Ganteför,² Bryan W. Eichhorn,³
 Boggavarapu Kiran,^{4,a)} and Kit H. Bowen^{1,a)}

¹Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, USA

²Facultat für Physik, Universität Konstanz, 78457 Konstanz, Germany

³Department of Chemistry, University of Maryland at College Park, College Park, Maryland 20742, USA

⁴Department of Chemistry, McNeese State University, Lake Charles, Louisiana 70609, USA

(Received 16 August 2016; accepted 4 October 2016; published online 20 October 2016)

Numerous previously unknown carbon aluminum hydride cluster anions were generated in the gas phase, identified by time-of-flight mass spectrometry and characterized by anion photoelectron spectroscopy, revealing their electronic structure. Density functional theory calculations on the $\text{CAI}_{5-9}\text{H}^-$ and $\text{CAI}_{5-7}\text{H}_2^-$ found that several of them possess unusually high carbon atom coordination numbers. These cluster compositions have potential as the basis for new energetic materials. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4964934>]

INTRODUCTION

Elements such as hydrogen, boron, aluminum, nitrogen, and carbon are among the most attractive building blocks of propellants because upon combustion they form stable oxides, e.g., H_2O , B_2O_3 , Al_2O_3 , NO_2 , and CO_2 , with correspondingly high energy releases. Compounds derived from combinations of these elements should in principle be good fuels, although not all of them are. Hydrocarbons, of course, are very often good fuels. Solid AlH_3 , on the other hand, has a mixed record. Due to poor thermal stability and material purity issues, AlH_3 has not been widely used as a propellant,^{1,2} even though on a small scale, it performs better than hydrocarbons and elemental aluminum.¹⁻⁴ More complex aluminum hydrides, however, may offer better prospects. Gas phase studies discovered and characterized hundreds of previously unknown aluminum hydride cluster anions, Al_yH_z^- ,⁵⁻¹¹ and with them their corresponding neutral aluminum hydride cluster compositions. Recent studies of the reactions between these aluminum hydride cluster anions and oxygen found that their products were overwhelmingly aluminum oxides.¹² Intuitively, boranes^{13,14} should be good propellants due to their relatively light weight and high energy release upon oxidation, e.g., $\Delta H_{298}^0 = -482.9$ kcal/mol for the reaction, B_2H_6 (g) + 3O_2 (g) \rightarrow B_2O_3 (s) + $3\text{H}_2\text{O}$ (g).¹⁵ Unfortunately, this highly exothermic reaction cannot be achieved due to kinetic traps, which effectively block the reaction from proceeding to full oxidation. These traps were identified to be hydrogen, boron, and oxygen containing molecules, collectively known as HOB compounds.¹⁶⁻²¹

In addition to compounds made from combinations of two of these elements, we have also explored three element combinations in the gas phase, e.g., boron-aluminum-hydride cluster anions, $\text{B}_x\text{Al}_y\text{H}_z^-$.²² In the present work, we report studies of numerous carbon aluminum hydride cluster anions, $\text{C}_x\text{Al}_y\text{H}_z^-$, which we identified by mass spectrometry, characterized by

anion photoelectron spectroscopy, and in some cases further explored through density functional theory calculations. Gas phase studies of such clusters are limited to Bernstein's work on neutral and cationic $\text{C}_x\text{Al}_y\text{H}_z$ clusters, which he augmented with density functional theory calculations.²³ In the solution phase, on the other hand, there have been several reports of carbaalanes being synthesized.²⁴⁻²⁹

EXPERIMENTAL AND COMPUTATIONAL METHODS

Anion photoelectron spectroscopy is conducted by crossing a mass-selected, negative ion beam with a fixed-energy photon beam and analyzing the energies of the resultant photodetached electrons. This technique is governed by the well-known energy-conserving relationship, $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$, EBE, and EKE are the photon energy, electron binding energy (photodetachment transition energy), and the electron kinetic energy, respectively. Our photoelectron instrument, which has been described elsewhere,³⁰ consists of an ion source, a linear time-of-flight mass spectrometer, a mass gate, a momentum decelerator, a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser operated at various harmonics for photodetachment, and a magnetic bottle electron energy analyzer having a resolution of 35 meV at $\text{EKE} = 1$ eV. All photoelectron spectra were calibrated against the well-known photoelectron spectrum of Cu^- .³¹

In this work, carbon aluminum hydride cluster anions were generated by a pulsed arc cluster ionization source (PACIS), which has been described in detail elsewhere.³² This PACIS source has proven to be a valuable tool for generating metal and metal hydride cluster anions.³³⁻⁴¹ Briefly, a ~ 30 μs long, 150 V electrical pulse applied across the anode and sample cathode of the discharge chamber vaporizes aluminum and carbon atoms and forms plasma. The cathode had been prepared by mixing and pressing aluminum and carbon powder into a well on top of an ultra-pure aluminum rod. About 200 psi of ultra-high purity hydrogen gas was then injected into

^{a)}Electronic addresses: kbowen@jhu.edu and kiran@mcneese.edu

the arc region, where it was subsequently dissociated into hydrogen atoms. The plasma mix was then directed down in a 20 cm flow tube, where its components interacted and cooled, forming cluster anions. The resulting cluster anions were then mass-selected prior to photoelectron spectroscopic studies.

Electronic and geometrical structure calculations were performed in the cases of selected clusters, $\text{CAI}_{5-9}\text{H}^{-/0}$ and $\text{CAI}_{5-7}\text{H}_2^{-/0}$. Structural calculations were performed with an unbiased systematic search based on the genetic algorithm (GA).⁴² In this method, initial structures were generated through a random population (parents) and subsequently allowed to cross-breed (children). Each successful “generation” becomes parents in the next set so on. This process continued until the lowest and highest energies of five structures remain constant in at least five generations. In our method, all levels of each structure were fully optimized without any constraints, using the BP functional and def2-SV(P) basis set,⁴³ all employing TURBOMOLE.⁴⁴ Lowest energy isomer was further optimized using density functional theory (DFT) at the B3LYP/6-311+g(d,p) level of theory.^{45–48} Vertical transitions from the ground state of the anions to higher states of the neutral clusters were calculated with the generalized Koopman’s theorem.⁴⁹ All of the calculations were carried out using the Gaussian 09 program.⁵⁰ For the geometry optimization, the convergence criterion for energy was set to 10^{-9} Hartree, while the gradient was converged to 10^{-4} Hartree/Å. Vibrational frequency calculations were carried out to verify the stability of these clusters; all of them were found to have positive frequencies. The vertical detachment energies (VDEs) and the adiabatic detachment energies (ADEs) were calculated for the lowest energy isomers and compared with the measured values to verify the reliability of the predicted structures. The VDE is the energy difference between the ground state anion and its neutral counterpart at the geometry of the anion. The ADE is calculated to be the energy difference between the lowest energy anion and its corresponding neutral with the neutral relaxed into its nearest local minimum. If both the anion and neutral are in their lowest energy states, the ADE of the anion equals the electron affinity (EA) of the neutral.

EXPERIMENTAL RESULTS

Figure 1 presents a typical mass spectrum containing both aluminum hydride cluster anions and carbon aluminum cluster hydrides, these having been generated in the PACIS source. We observed $\text{C}_x\text{Al}_y\text{H}_z^-$ clusters, where $x = 0-3$, $y = 1-9$, and $z = 1-4$. While changing the ratio between carbon and aluminum powders in the sample cathode gave us different sets of cluster stoichiometries, we present only the mass spectrum in Figure 1 as an example. Cluster groups with different x values are marked by identifying symbols in Figure 1. Due to the mass coincidences, i.e., $m(\text{C}_2\text{Al}_y\text{H}_{z+3}) = m(\text{Al}_{y+1}\text{H}_z)$, care was taken when comparing the spectra of $\text{C}_2\text{Al}_y\text{H}_{z+3}^-$ and $\text{Al}_{y+1}\text{H}_z^-$ in order to confirm the purity of their photoelectron spectra. Unlike the study on neutral carbon aluminum hydride clusters²³ which used conventional laser vaporization cluster source and hydrocarbons or H_2 in the expansion gas, our PACIS source generated much larger cluster anions, this possibly being due to its high current and power output.

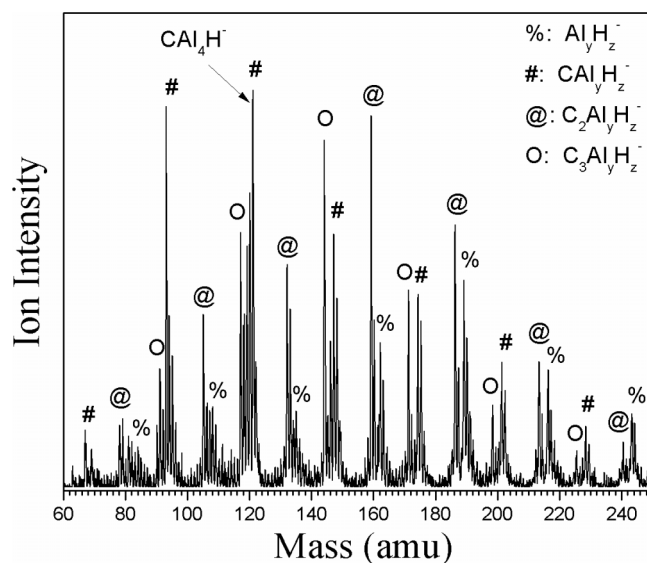


FIG. 1. A typical mass spectrum of the aluminum hydride cluster anions (Al_yH_z^-) and carbon aluminum hydride cluster anions ($\text{C}_x\text{Al}_y\text{H}_z^-$).

Figure 2 presents all of the photoelectron spectra measured with 355 nm (3.49 eV) photons. In each block of spectra in Figure 2, we fix x and z , allowing y , the number of aluminum atoms, to vary. The EBE value of the intensity maximum in the lowest electron binding energy band in each spectrum corresponds to the vertical detachment energy (VDE) of that mass-selected cluster anion. The electron affinity (EA) value in each case was estimated by extrapolating the lower EBE side of the lowest EBE band to zero. That EBE value was taken to be the EA value of that cluster anion’s neutral counterpart. Bands to the high EBE side of the lowest EBE band are due to transitions from the cluster anion’s ground state to higher electronic states of its corresponding neutral cluster. Due to the fact that aluminum has an odd number of electrons, the total number of electrons in the clusters in each block has an odd-even variation. This gives rise to an odd-even variation in their EA values, owing to the fact that the electron binding energy of a closed-shell system should be higher than that of an open-shell system. All of the experimental EA and VDE values are tabulated in Table I.

THEORETICAL RESULTS AND DISCUSSION

The calculated global minimum structures of the cluster anions, $\text{CAI}_{5-9}\text{H}^-$ and $\text{CAI}_{5-7}\text{H}_2^-$, are shown in Figure 3. We present the structures of these species because they possess unusually high carbon atom coordination numbers. Both CAI_5H^- and CAI_5H_2^- have unique planar tetra-coordinated carbon (PTC) structures, where the carbon atom is surrounded by four aluminum atoms in a planar manner. While carbon is well known to be tetra-coordinated in a tetrahedron center, the PTC structure has also been observed in $\text{Na}(\text{Al}_4\text{C})^-$ and CAI_5^- cluster anions^{51,52} as well as in the $[(\text{Al}_4\text{C})(\text{C}_5\text{H}_5)\text{M}]^q$ -complex.⁵³ For CAI_6H^- , however, the six aluminum atoms form a distorted triangular prism with the carbon atom at its center, this resulting in a coordination number of six. The hydrogen atom bridges one of the Al–Al edges. A similar

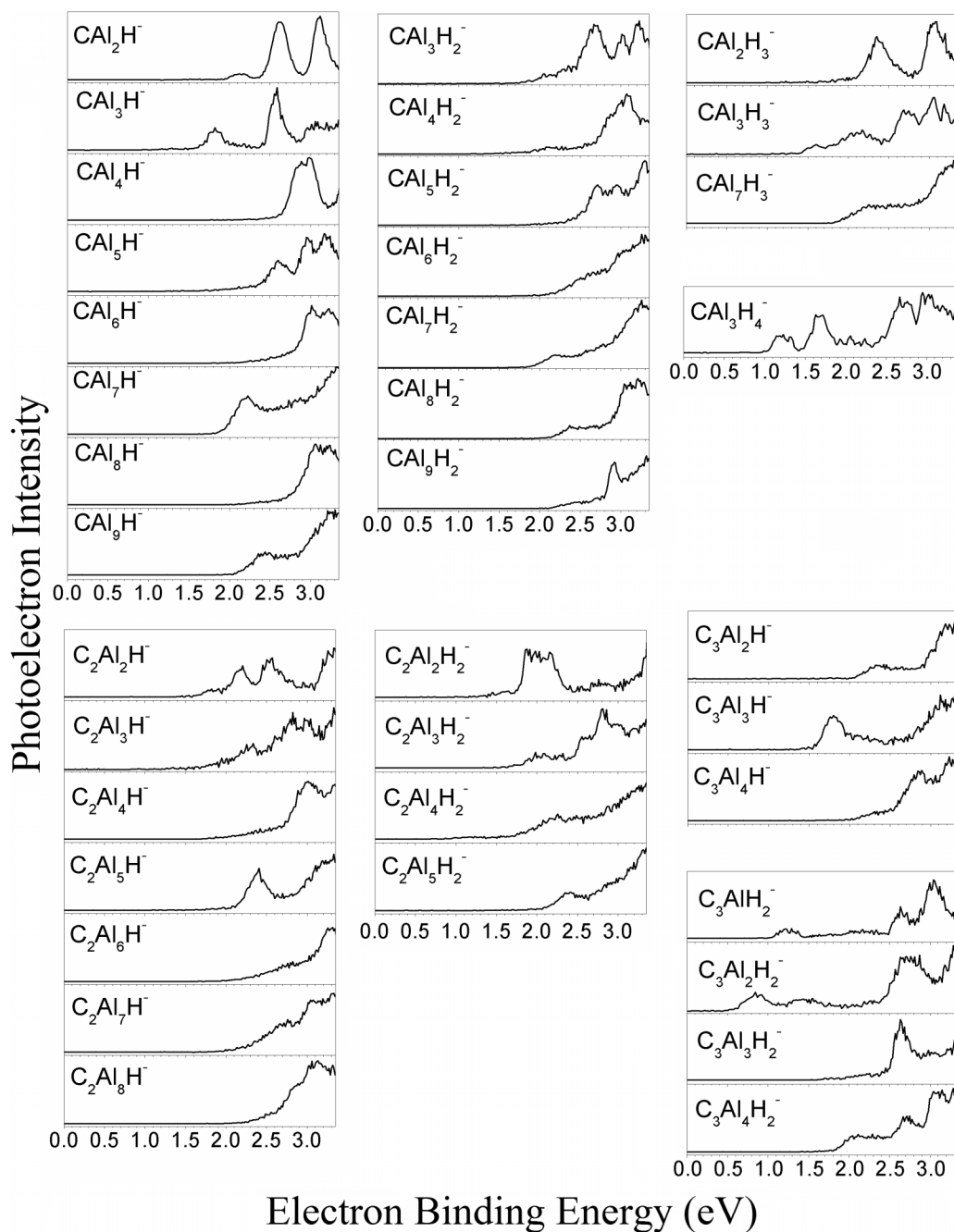


FIG. 2. The photoelectron spectra of $C_xAl_yH_z^-$ measured with 355 nm laser, where $x=0-3, y=1-9, z=1-4$.

hexa-coordinated structure was observed in the CAI_6^- cluster anion.⁵⁴ For CAI_7H^- , the carbon atom stays inside the cage of seven aluminum atoms, and its coordination number increases to seven! Again, the hydrogen atom bridges one of the Al–Al edges. The structure of CAI_7H^- is also very similar to that of the CAI_7^- cluster anion.⁵⁴ In CAI_8H^- , the coordination number of carbon does not increase further. Instead, the carbon atom dwells in the center of an octahedron made from six aluminum atoms. The remaining two aluminum atoms occupy two face sites of the octahedron, and the hydrogen atom is radially bonded to one of these two aluminum atoms. This structure, however, is very different from that of CAI_8^- .⁵⁴ In CAI_9H^- , the carbon atom no longer stays in a cage. It is bound to the hydrogen atom and coordinated by three other

aluminum atoms, giving it a coordination number of four. For $CAI_6H_2^-$, the carbon atom has a coordination number of five. In $CAI_7H_2^-$, it decreases to four, where the carbon atom is “squeezed” out of the aluminum cage, just as in CAI_9H^- .

To summarize, in both $CAI_{5-9}H^-$ and $CAI_{5-7}H_2^-$ series, we observe clear structural evolutions. The coordination number of the carbon atom first increases and then decreases in each series. As the cluster stoichiometries become more complex, the carbon atom initially tends to be surrounded by multiple aluminum atoms, before moving to the edge of an aluminum cluster as the number of aluminum atom increases. In the $CAI_5H_{1,2}^-$ cluster anions, carbon has very unique PTC structures, and surprisingly, in the cases of $CAI_{6-8}H^-$ cluster anions, the coordination number of the carbon atom

TABLE I. Experimental electron affinity and vertical detachment energy values for all carbon aluminum hydride cluster anions ($C_xAl_yH_z^-$) in this study. All values are in eV.

	x = 1		x = 2		x = 3		
	EA	VDE	EA	VDE	EA	VDE	
z = 1	y = 1						
	y = 2	1.9	2.13	1.9	2.21	2.1	2.34
	y = 3	1.6	1.82	1.9	2.29	1.6	1.80
	y = 4	2.6	2.88	2.6	3.01	2.1	2.36
	y = 5	2.3	2.57	2.1	2.41		
	y = 6	2.7	3.01	2.3	2.80		
	y = 7	1.8	2.15	2.2	2.70		
	y = 8	2.6	3.05	2.5	3.09		
	y = 9	2.1	2.44				
z = 2	y = 1				1.0	1.23	
	y = 2			1.6	1.88	0.6	0.85
	y = 3	2.4	2.68	1.8	2.07	2.4	2.64
	y = 4	1.8	2.11	1.7	2.24	1.8	2.11
	y = 5	2.5	2.72	2.1	2.41		
	y = 6	2.2	2.60				
	y = 7	1.9	2.24				
	y = 8	2.1	2.37				
	y = 9	2.2	2.47				
z = 3	y = 2	2.1	2.35				
	y = 3	1.4	1.60				
	y = 7	1.8	2.28				
z = 4	y = 3	1.0	1.19				

increases to six and even to seven. In $CAI_5H_{1,2}^-$ and $CAI_{6-7}H^-$, the hydrogen atom(s) only slightly distorts the structures of CAI_{5-7}^- ,^{52,54} whereas in CAI_8H^- and $CAI_{6,7}H_2^-$, they have very different structures than CAI_{6-8}^- .⁵⁴

To validate the above calculated structures, we also computed the ADE and VDE values of these clusters,

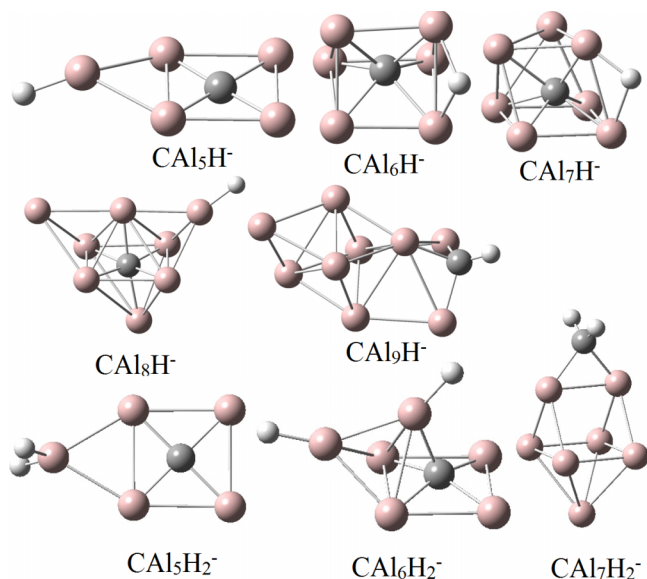


FIG. 3. The calculated global minimum structures of $CAI_{5-9}H^-$ and $CAI_{5-7}H_2^-$.

TABLE II. Experimental and theoretical electron affinity and vertical detachment energy values for $CAI_{5-9}H^-$ and $CAI_{5-7}H_2^-$. The calculated vertical transitions from the ground state of the anions to the higher electronic states of the neutral clusters are also presented. All values are in eV.

	Expt.	Theo.	Calculated higher vertical transitions
	EA/VDE	EA/VDE	
CAI_5H^-	2.3/2.57	2.05/2.43	2.81, 3.13, 3.89, 4.40
CAI_6H^-	2.7/3.01	2.69/2.99	3.31, 3.43, 3.51, 3.63, 3.91
CAI_7H^-	1.8/2.15	1.83/1.96	3.20, 3.48, 3.83, 3.86
CAI_8H^-	2.6/3.05	2.51/2.92	3.14, 3.38, 3.73, 4.11
CAI_9H^-	2.1/2.44	2.16/2.34	2.93, 3.02, 3.23, 3.35, 3.53, 4.07
$CAI_5H_2^-$	2.5/2.72	2.63/2.81	3.16, 3.63, 4.31
$CAI_6H_2^-$	2.2/2.60	2.29/2.45	2.82, 2.96, 3.30, 3.41, 3.48, 3.53
$CAI_7H_2^-$	1.9/2.24	2.10/2.31	2.95, 3.03, 3.39, 3.86

compared them with those extracted from experiments and tabulated them in Table II. Good consistency between experiment and theory was observed for all of these clusters. Calculated VDE values and vertical transitions to higher electronic states of the neutral clusters were also tabulated in Table II and plotted as stick spectra over-laying the experimental photoelectron spectra in Figure 4. Again, good agreement was observed.

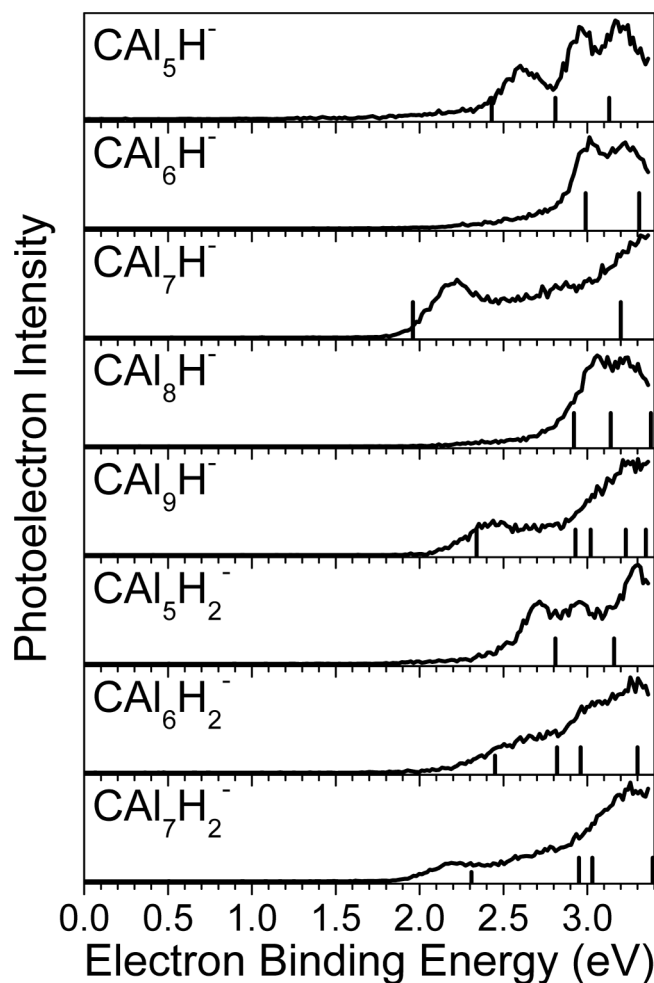


FIG. 4. Photoelectron spectra and calculated vertical transitions (displayed as stick spectra) of $CAI_{5-9}H^-$ and $CAI_{5-7}H_2^-$.

In the solution phase, there have been several reports of carbaalanes being synthesized,^{24–29} they all having cage structures and fulfilling the Wade-Mingos rules.^{55–57} In those clusters, the vacant covalent sites of the carbon and aluminum atoms on the cage surface are either occupied by hydrogen atoms or other organic groups, which stabilize the whole cage. In the current study, on the other hand, the clusters are also prone to form cages, however, due to the fact that there are not enough hydrogen atoms (partially in order to avoid mass coincidences in the mass spectrum), the clusters tend to form small, packed cages other than polyhedral skeletons. Being small and packed helps to obtain as much covalent bonding as possible within themselves. Hence, we cannot apply the Wade-Mingos rules to the clusters in this study; they are essentially different from those reported carbaalanes.

CONCLUSION

Searching for cluster stoichiometries with potential for expanding available propellant compositions, we generated about numerous carbon aluminum hydride cluster anions in the gas phase, identified them with a time-of-flight mass spectrometry, and characterized them with anion photoelectron spectroscopy. DFT calculations were conducted to search for geometries and calculate electronic structure information for $CA_{15.9}H^-$ and $CA_{15.7}H_2^-$. Among these two series of clusters, the observed structural evolution showed that the coordination number of carbon first increases and then decreases as the number of aluminum atoms increases. Unusually high coordination numbers of carbon were found for CA_6H^- , CA_7H^- , CA_8H^- , and $CA_6H_2^-$. In $CA_5H_{1,2}^-$, special planar tetra-coordinated carbon (PTC) structures were observed. Calculated electronic structure-related values for these cluster systems agree well with those obtained from our spectra. Like their cousins, i.e., aluminum hydride clusters^{5–11} and boron-aluminum-hydride clusters,²² these carbon aluminum hydride clusters may provide insight into new classes of energetic materials.

ACKNOWLEDGMENTS

This material is based upon work supported by the Air Force Office of Scientific Research (AFOSR), under Grant No. FA9550-15-1-0259. B.K. acknowledges the support from the McNeese Endowed Professorship grant.

¹J. Graetz and J. J. Reilly, *J. Phys. Chem. B* **109**, 22181 (2005).

²G. Young, N. Piekielek, S. Chowdhury, and M. R. Zachariah, *Combust. Sci. and Technol.* **182**, 1341 (2010).

³T. Bazyn, R. Eyer, H. Krier, and N. Glumac, *J. Propul. Power* **20**, 427 (2004).

⁴V. Weiser, N. Eisenreich, A. Koleczko, and E. Roth, *Propellants, Explos., Pyrotech.* **32**, 213 (2007).

⁵B. Kiran, P. Jena, X. Li, A. Grubisic, S. T. Stokes, G. F. Gantefoer, K. H. Bowen, R. Burgert, and H. Schnoekel, *Phys. Rev. Lett.* **98**, 256802 (2007).

⁶A. Grubisic, X. Li, G. F. Gantefoer, K. H. Bowen, B. Kiran, P. Jena, R. Burgert, and H. Schnoekel, *J. Am. Chem. Soc.* **129**, 5969 (2007).

⁷A. Grubisic, X. Li, S. T. Stokes, K. Vetter, G. F. Gantefoer, K. H. Bowen, P. Jena, B. Kiran, R. Burgert, and H. Schnoekel, *J. Chem. Phys.* **131**, 121103 (2009).

⁸X. Li, A. Grubisic, K. H. Bowen, A. K. Kandalam, B. Kiran, G. F. Gantefoer, and P. Jena, *J. Chem. Phys.* **132**, 241103 (2010).

⁹X. Zhang, H. Wang, E. Collins, A. Lim, G. Gantefoer, B. Kiran, H. Schnoekel, B. Eichhorn, and K. H. Bowen, *J. Chem. Phys.* **138**, 124303 (2013).

¹⁰J. D. Graham, A. M. Buytendyk, X. Zhang, E. L. Collins, K. Boggavarapu, G. Gantefoer, B. W. Eichhorn, G. L. Gutsev, S. Behera, P. Jena, and K. H. Bowen, *J. Phys. Chem. A* **118**, 8158 (2014).

¹¹X. Li, A. Grubisic, S. T. Stokes, J. Cordes, G. F. Gantefoer, K. H. Bowen, B. Kiran, M. Willis, P. Jena, R. Burgert, and H. Schnoekel, *Science* **315**, 356 (2007).

¹²X. Zhang, H. Wang, G. Gantefoer, B. Eichhorn, and K. Bowen, *Int. J. Mass Spectrom.* **404**, 24 (2016).

¹³W. N. Lipscomb, in *Boron Hydrides* (W. A. Benjamin, Inc., New York, 1963).

¹⁴N. Greenwood, A. E. *Chemistry of the Elements*, 2nd ed. (Elsevier Science, Amsterdam, The Netherlands, 1997).

¹⁵F. D. Rossini, "Selected values of chemical thermodynamic properties," Natl. Bur. Stand. Circ. 300 (1952).

¹⁶J. F. Ditter and I. Shapiro, *J. Am. Chem. Soc.* **81**, 1022 (1959).

¹⁷W. H. Bauer and S. Wiberley, *Borax to Boranes* (Advances in Chemistry American Chemical Society, Washington, DC, 1961).

¹⁸H. C. Baden, S. E. Wiberley, and W. H. Bauer, *J. Phys. Chem.* **59**, 287 (1955).

¹⁹A. T. Whatley and R. N. Pease, *J. Am. Chem. Soc.* **76**, 1997 (1954).

²⁰W. Roth and W. H. Bauer, *J. Phys. Chem.* **60**, 639 (1956).

²¹W. Roth and W. H. Bauer, *Fifth Symposium on Combustion* (Reinhold, New York, 1955), p. 710.

²²H. Wang, X. Zhang, Y. Ko, G. F. Gantefoer, K. H. Bowen, X. Li, K. Boggavarapu, and A. Kandalam, *J. Chem. Phys.* **140**, 164317 (2014).

²³F. Dong, S. Heimbuch, Y. Xie, J. J. Rocca, and E. R. Bernstein, *Phys. Chem. Chem. Phys.* **12**, 2569 (2010).

²⁴W. Uhl and F. Breher, *Angew. Chem., Int. Ed.* **38**, 1477 (1999).

²⁵W. Uhl, F. Breher, A. Mbonimana, J. Gauss, D. Haase, A. Lützen, and W. Saak, *Eur. J. Inorg. Chem.* **2001**, 3059.

²⁶A. Stasch, M. Ferbinteanu, J. Prust, W. Zheng, F. Cimpoesu, H. W. Roesky, J. Magull, H. Schmidt, and M. Noltemeyer, *J. Am. Chem. Soc.* **124**, 5441 (2002).

²⁷A. Stasch, S. S. Kumar, V. Jancik, H. W. Roesky, J. Magull, and M. Noltemeyer, *Eur. J. Inorg. Chem.* **2004**, 4056–4060.

²⁸A. Stasch, H. W. Roesky, D. Vidovic, J. Magull, H. Schmidt, and M. Noltemeyer, *Inorg. Chem.* **43**, 3625 (2004).

²⁹B. Creton, S. Kahlal, M. T. Garland, Z. Lin, J. Halet, and J.-Y. Saillard, *J. Cluster Sci.* **18**, 271 (2007).

³⁰M. Gerhards, O. C. Thomas, J. M. Nilles, W. J. Zheng, and K. H. Bowen, *J. Chem. Phys.* **116**, 10247 (2002).

³¹J. Ho, K. M. Ervin, and W. C. Lineberger, *J. Chem. Phys.* **93**, 6987 (1990).

³²X. Zhang, Y. Wang, H. Wang, A. Lim, G. Gantefoer, K. H. Bowen, J. U. Reveles, and S. N. Khanna, *J. Am. Chem. Soc.* **135**, 4856–4861 (2013).

³³A. S. Ivanov, X. Zhang, H. Wang, A. I. Boldyrev, G. Gantefoer, K. H. Bowen, and I. Černušák, *J. Phys. Chem. A* **119**, 11293 (2015).

³⁴J. Joseph, K. Pradhan, P. Jena, H. Wang, X. Zhang, Y. J. Ko, and K. H. Bowen, *J. Chem. Phys.* **136**, 194305 (2012).

³⁵X. Zhang, B. Visser, M. Tschurl, E. Collins, Y. Wang, Q. Wang, Y. Li, Q. Sun, P. Jena, G. Gantefoer, U. Boesl, U. Heiz, and K. H. Bowen, *J. Chem. Phys.* **139**, 111101 (2013).

³⁶A. Buytendyk, J. Graham, H. Wang, X. Zhang, E. Collins, Y. J. Ko, G. Gantefoer, B. Eichhorn, A. Regmi, K. Boggavarapu, and K. H. Bowen, *Int. J. Mass Spectrom.* **365–366**, 140 (2014).

³⁷H. Wang, X. Zhang, J. Ko, A. Grubisic, X. Li, G. Gantefoer, H. Schnoekel, B. Eichhorn, M. Lee, P. Jena, A. Kandalam, B. Kiran, and K. H. Bowen, *J. Chem. Phys.* **140**, 054301 (2014).

³⁸H. Wang, Y. Ko, X. Zhang, G. Gantefoer, H. Schnoekel, B. W. Eichhorn, P. Jena, B. Kiran, A. K. Kandalam, and K. H. Bowen, *J. Chem. Phys.* **140**, 124309 (2014).

³⁹X. Zhang, G. Gantefoer, K. H. Bowen, and A. Alexandrova, *J. Chem. Phys.* **140**, 164316 (2014).

⁴⁰X. Zhang, G. Liu, G. Gantefoer, K. H. Bowen, and A. N. Alexandrova, *J. Phys. Chem. Lett.* **5**, 1596 (2014).

⁴¹X. Zhang, P. Robinson, G. Gantefoer, A. Alexandrova, and K. H. Bowen, *J. Chem. Phys.* **143**, 094307 (2015).

⁴²D. M. Deaven and K. M. Ho, *Phys. Rev. Lett.* **75**, 288 (1995).

⁴³F. Weigenda and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).

⁴⁴TURBOMOLE V6.2, 2010, a Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007, available from <http://www.turbomole.com>.

- ⁴⁵A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- ⁴⁶A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ⁴⁷C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- ⁴⁸R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980).
- ⁴⁹J. C. Phillips, *Phys. Rev.* **123**, 420 (1961).
- ⁵⁰M. J. Risch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson *et al.*, GAUSSIAN 09, Revision A.1, Gaussian, Inc., Wallingford, CT, 2009.
- ⁵¹X. Li, H. Zhang, L. Wang, G. D. Geske, and A. I. Boldyrev, *Angew. Chem., Int. Ed.* **39**, 3630 (2000).
- ⁵²A. I. Boldyrev, J. Simons, X. Li, and L. S. Wang, *J. Chem. Phys.* **111**, 4993 (1999).
- ⁵³L. Yang, Y. Ding, and C. Sun, *J. Am. Chem. Soc.* **129**, 658 (2007).
- ⁵⁴C. Ashman, S. N. Khanna, and M. R. Pederson, *Chem. Phys. Lett.* **324**, 137 (2000).
- ⁵⁵D. M. P. Mingos, *Nat. Phys. Sci.* **236**, 99 (1972).
- ⁵⁶K. Wade, *Adv. Inorg. Chem. Radiochem.* **18**, 1 (1976).
- ⁵⁷R. E. Williams, *Chem. Rev.* **92**, 177 (1992).