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Communications: Chain and double-ring polymeric structures: Observation of $Al_nH_{3n+1}^-$ (n=4–8) and $Al_4H_{14}^-$

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A pulsed arc discharge source was used to prepare gas-phase, aluminum hydride cluster anions, $Al_nH_m^-$, exhibiting enhanced hydrogen content. The maximum number of hydrogen atoms in $Al_nH_m^-$ species was $m=3n+1$ for $n=5-8$, i.e., $Al_nH_{3n+1}^-$, and $m=3n+2$ for $n=4$, i.e., $Al_4H_{14}^-$, as observed in their mass spectra. These are the most hydrogen-rich aluminum hydrides to be observed thus far, transcending the 3:1 hydrogen-to-aluminum ratio in alane. Even more striking, ion intensities for $Al_nH_m^-$ species with $m=3n+1$ and $m=3n+2$ hydrogen atoms were significantly higher than those of nearby $Al_nH_m^-$ mass peaks for which $m<3n+1$, i.e., the ion intensities for $Al_nH_{3n+1}^-$ and for $Al_4H_{14}^-$ deviated from the roughly bell-shaped ion intensity patterns seen for most $Al_nH_m^-$ species, in which m ranges from 1 to $3n$. Calculations based on density functional theory showed that $Al_nH_{3n+1}^-$ clusters have chain and/or double-ring polymeric structures. © *2010 American Institute of Physics*. [doi:10.1063/1.3458912]

Complex aluminum hydrides may have uses both as propellants and as hydrogen storage materials[1,2] since both applications prize substances which are light-weight and hydrogen-rich. Until recently, however, aluminum hydride chemistry was largely limited to alane, AlH_3, and the alanates, e.g., $LiAlH_4$. Solid alane has eight known phases, and these are usually described as hydrogen-bridged polymeric networks.[3–6] Also, molecular alane and dialane (Al_2H_6) have been studied in both cryogenic matrices[7,8] and the gas phase[9] as well as on surfaces.[10] Alanates are alkali metal salts with AlH_4^-, an anion whose aluminum atom is tetrahedrally coordinated and in which the octet rule is satisfied.[11]

Over the past several years, efforts to investigate other compositions of aluminum hydrides have moved into the gas phase, where many different compositions can be prepared, identified via mass spectrometry, and separately characterized. As a result, both beam experiments and computational studies have been conducted. Theoretical studies include work on Al_nH_{3n} neutral clusters, where they were found to have cyclic structures, as well as work on small $Al_nH_{3n}^-$ anionic clusters, where their electron binding energies were computed.[12–21] Experimental studies have focused on photoelectron spectroscopy of aluminum hydride cluster anions, $Al_nH_m^-$, generated in both laser vaporization and pulsed arc discharge sources.[22–28]

In the present paper, we report on the formation of homologous series of $Al_nH_m^-$ cluster anions, generated in a pulsed arc discharge source, identified by mass spectrometry, and structurally characterized by calculations based on density functional theory (DFT). Among these species, the maximum number of hydrogen atoms bonded to their aluminum moieties is $m=3n+1$ for $n=5-8$, i.e., $Al_nH_{3n+1}^-$, and $m=3n+2$ for $n=4$, i.e., $Al_4H_{14}^-$. Typically, aluminum hydride cluster anions have hydrogen-to-aluminum ratios (m:n) that are not larger than that of alane, i.e., 3:1. However, under some source conditions, strong ion intensities of hydrogen-rich aluminum hydride cluster anions with $m>3n$ were reproducibly observed. Our calculations showed that $Al_nH_{3n+1}^-$ (n=4–8) clusters have both chain and cyclic double-ring polymeric structures, which are nearly degenerate energetically. These structural motifs afford them a mechanism for propagation and self-assembly.

In a pulsed arc discharge source, electrical discharges are periodically struck between an anode and a grounded cathode of conducting sample material, while helium gas from a pulsed valve flows through the discharge region.[22,25] In the present experiments, the cathode was aluminum metal, and hydrogen gas was injected into the source's condensation (exit) channel via a second pulsed valve. Upon initiation of the discharge, a plasma containing aluminum and hydrogen atoms (the latter formed by the dissociation of H_2) expanded down the condensation channel, where the mixture cooled, clustered, and reacted. (Typical operating conditions included discharge voltages of 100–200 V and pulsed valve backing pressures of 200 psi for both helium and hydrogen.) Extending the condensation channel tended to enhance the formation of hydrogen-rich aluminum hydride anions. After expanding into vacuum, the resulting anions were extracted into a time-of-flight mass spectrometer and mass analyzed.

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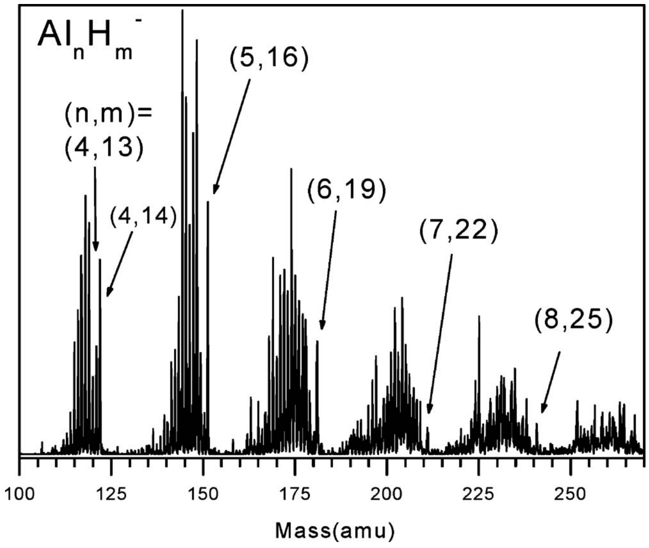

FIG. 1. Mass spectrum of $Al_nH_m^-$ cluster anions showing up to $m=3n+1$ for $n=5-8$ and up to $m=3n+2$ for $n=4$.

A typical mass spectrum showing $Al_nH_m^-$ species that were produced in these experiments is presented in Fig. 1. Figures 2(a)–2(d) provide magnified, separate versions of these mass spectra for $n=4-7$, respectively. Several observations can be made from these mass spectra. The maximum number of hydrogen atoms in $Al_nH_m^-$ species was observed to be $m=3n+1$ for $n=5-8$, i.e., $Al_nH_{3n+1}^-$, and $m=3n+2$ for $n=4$, i.e., $Al_4H_{14}^-$. These are the most hydrogen-rich aluminum hydrides to be observed thus far, transcending the 3:1 hydrogen-to-aluminum ratio of alane. Even more striking, ion intensities for $Al_nH_m^-$ species with $m=3n+1$ and $m=3n+2$ hydrogen atoms were significantly stronger than the ion intensities of nearby $Al_nH_m^-$ species for which $m<3n+1$. Typically, for a given n, the ion intensities of $Al_nH_m^-$ species in the mass spectra grow with increasing m until reaching a maximum after which they decrease; this pattern suggests governance by kinetics. Under many source conditions, this series terminates at $m=3n$. In these studies, however, the ion intensities for $Al_nH_{3n+1}^-$ and for $Al_4H_{14}^-$ deviated from the usual roughly bell-shaped ion intensity patterns, instead exhibiting relatively intense ion signals which may suggest enhanced stabilities. In regard to species with the stoichiometry, $Al_nH_{3n+2}^-$, this was observed only for $n=4$. Interestingly, the ion intensity of $Al_4H_{14}^-$ was even stronger than that of $Al_4H_{13}^-$.

We took care to exclude the possibility that the existence of contaminants may cause the unexpected pattern in the mass spectrum. Based on the stoichiometries seen in the mass spectra, we speculated that polymer chain structures would provide an explanation for the $m=3n+1$ species. In order to explore our hypothesis and provide further insights into the electronic structure, we carried out DFT calculations on $Al_nH_{3n+1}^-$ anionic clusters. We employed Becke's three parameter hybrid functional with Lee, Yang, and Parr correlation functional form[29,30] and an all electron 6−311++G(3df,3pd) basis set for Al and H atoms. All calculations were carried out using GAUSSIAN 03 code.[31] In the geometry optimization procedure, the convergence criterion for energy was set to 10^{-9} hartree, while the gradient was converged to 10^{-4} hartree/Å.

The lowest energy structures of $Al_nH_{3n+1}^-$ ($n=4-7$) obtained from our calculations are shown in Fig. 3. Our calcu-

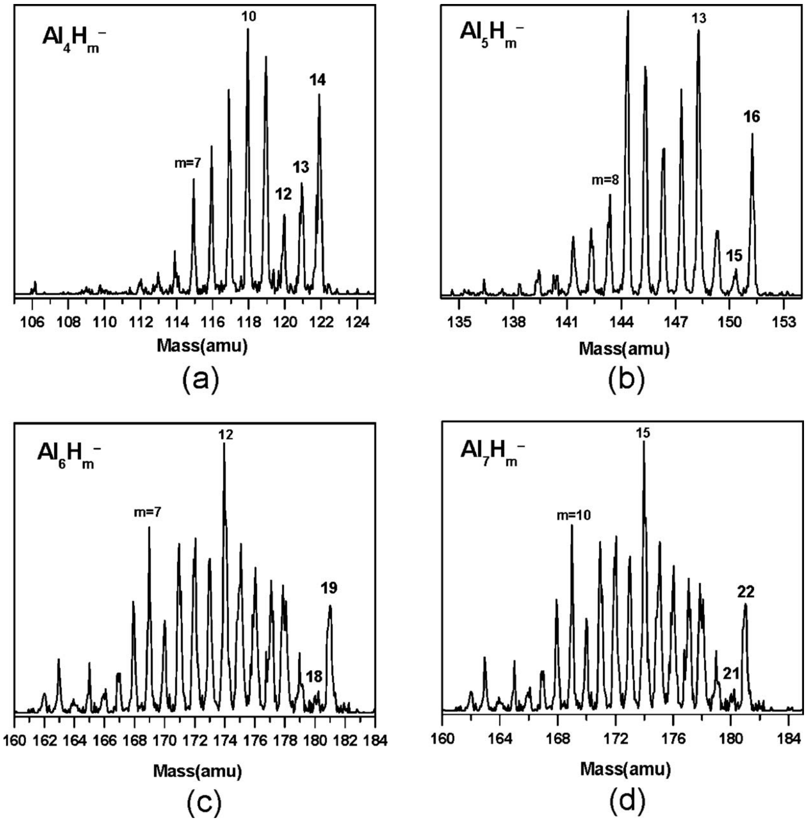

FIG. 2. Mass spectrum of the (a) $Al_4H_m^-$, (b) $Al_5H_m^-$, (c) $Al_6H_m^-$, and (d) $Al_7H_m^-$ series.

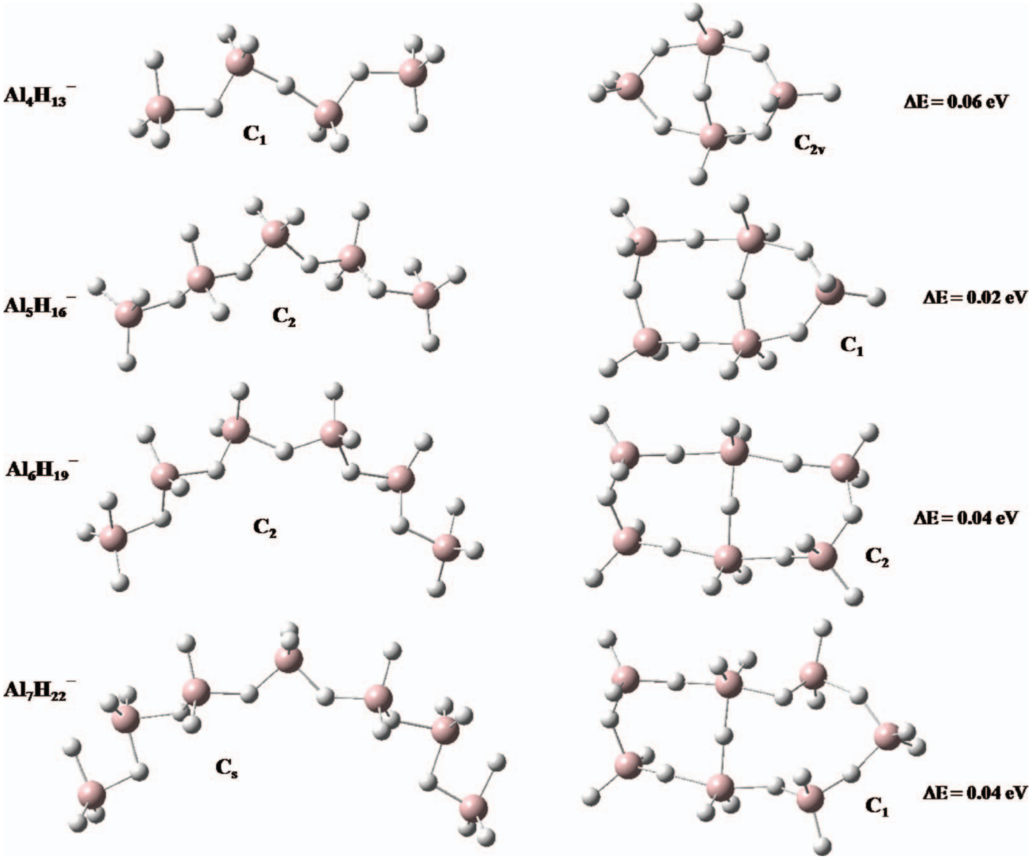

FIG. 3. Calculated structures and the corresponding point groups of $Al_nH_{3n+1}^-$ (n=4–7) clusters using DFT method. Chain structures (left) and double-ring (right) structures are found to be comparably stable. The relative energies are calculated with respect to the chain structures.

lations found polymerlike chain structures to be the most stable isomers for these anionic species. As expected, in these polymeric structures each Al atom has tetrahedral coordination. These results confirm our speculation regarding the possibility of open structures for these hydrogen-rich clusters. In addition, however, cyclic (ringlike) structures were also found to be very close in energy ($\Delta E \sim 0.07$ eV) to the ground state open structures (Fig. 3). In these cyclic structures, the additional hydrogen atom bridges two nonadjacent aluminum atoms, dividing the cyclic structure into two rings (double-ring), and those two aluminum atoms exhibit a fivefold coordination. Although Al atoms are usually tetrahedrally coordinated, it is noteworthy here that in an earlier study[12] on neutral Al_nH_{3n} clusters, dibridged linear structures containing fivefold coordinated Al atoms were also reported to be energetically very close to the ground state cyclic structures. Lastly, structures with higher symmetry (e.g., planar-Al framework) were found not to be energetically favorable.

In both chain and double-ring polymeric isomers, the average Al–H_{bridge} bond length remained approximately constant at 1.74 Å even as the size of the cluster increased from $Al_4H_{13}^-$ to $Al_7H_{22}^-$. This distance is slightly larger than the Al–H_{bridge} bond length (1.70 Å) observed for neutral Al_nH_{3n} clusters. The thermodynamic stability of these hydrogen-rich species was studied by calculating the relative stability of $Al_nH_{3n+1}^-$ against fragmentation into $Al_{n-1}H_{3n-2}^-$ and AlH_3 units as follows: $E_n = -[E(Al_nH_{3n+1}^-) - E(Al_{n-1}H_{3n-2}^-) - E(AlH_3)]$, where n=5–7. The fragmentation energies, thus calculated are E_5=1.06 eV, E_6=1.04 eV, and E_7=0.98 eV. Thus, we see that energy gain in sequential addition of AlH_3 units is more or less independent of the size of the cluster, n. This trend once again clearly supports our conclusion regarding the polymerlike nature of the $Al_nH_{3n+1}^-$ cluster, where addition of a monomer (AlH_3) does not result in substantial energy gain.

One of the observed $Al_4H_m^-$ species presents an unresolved issue. While the situation for $Al_4H_{12}^-$ and $Al_4H_{13}^-$ is similar to that of the other $Al_nH_{3n}^-$ and $Al_nH_{3n+1}^-$ clusters described above, the observation of $Al_4H_{14}^-$ (the only $m=3n+2$ species to be observed) defied our computational efforts to define it. Moreover, the ion intensity of $Al_4H_{14}^-$ is typically double that of $Al_4H_{13}^-$. According to our calculations, neither chain nor the cyclic $Al_4H_{13}^-$ isomers can accommodate another hydrogen atom. Other trial explanations have also failed in one or more critical ways. This enigmatic species remains a subject of our computational studies.

This report extends our knowledge of aluminum hydride cluster chemistry. Our experiments found that a maximum of $3n+1$ hydrogen atoms can attach to aluminum cluster anions for n=5–8, while $3n+2$ can do so for n=4. Our computational calculations revealed that $Al_nH_{3n+1}^-$ clusters can have chain and/or cyclic double-ring polymeric structures. In view of the fivefold coordination of aluminum atoms in the double-ring structures and the existence of $Al_4H_{14}^-$, it can be anticipated that still other stoichiometries and structures might be possible among aluminum hydride cluster anions. These may provide pathways for synthesizing novel hydrogen-containing materials.

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[1] L. Schlapbach and A. Zűttel, Nature (London) **414**, 353 (2001).
[2] M. Felderhoff, M. C. Weidenthaler, R. Von Helmot, and U. Eberle, Phys. Chem. Chem. Phys. **9**, 2643 (2007).
[3] F. M. Brower, N. E. Matzek, P. F. Reigler, H. W. Rinn, C. B. Roberts, D. L. Schmidt, J. A. Snover, and K. Terada, J. Am. Chem. Soc. **98**, 2450 (1976).
[4] P. B. Kempa, V. Thome, and M. Herrmann, Part. Part. Syst. Charact. **26**, 132 (2009).
[5] Y. A. Yartys, R. V. Denys, J. P. Maehien, C. Frommen, M. Fichtner, B. M. Bulychev, and H. Emerich, Inorg. Chem. **46**, 1051 (2007).
[6] J. P. Maehlen, V. A. Yartys, R. V. Denys, M. Fichtner, Ch. Frommen, B. M. Bulychev, P. Pattison, H. Emerich, Y. E. Filinchuk, and D. Chernyshov, J. Alloys Compd. **446–447**, 280 (2007).
[7] L. Andrews and X. Wang, Science **299**, 2049 (2003).
[8] F. A. Kurth, R. A. Eberlein, H. Schnöckel, A. J. Downs, and C. R. Pulham, J. Chem. Soc., Chem. Commun. **1993**, 1302.
[9] P. Breisacher and B. J. Siegal, J. Am. Chem. Soc. **86**, 5053 (1964).
[10] S. Chaudhuri, S. Rangan, J.-F. Veyan, J. T. Muckerman, and Y. J. Chabal, J. Am. Chem. Soc. **130**, 10576 (2008).
[11] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 2nd ed. (Interscience, New York, 1966).
[12] H. Kawamura, V. Kumar, Q. Sun, and Y. Kawazoe, Phys. Rev. A **67**, 063205 (2003).
[13] B. K. Rao, P. Jena, S. Burkart, G. Ganteför, and G. Seifert, Phys. Rev. Lett. **86**, 692 (2001).
[14] S. X. Tian, J. Phys. Chem. A **109**, 4428 (2005).
[15] J. Liu, Y. Han, and Q. Ge, Chem.-Eur. J. **15**, 1685 (2009).
[16] D. J. Goebbert, H. Hernandez, J. S. Francisco, and P. G. Wenthold, J. Am. Chem. Soc. **127**, 11684 (2005).
[17] B. J. Duke, C. Liang, and H. F. Schaefer III, J. Am. Chem. Soc. **113**, 2884 (1991).
[18] M. Shen, C. Liang, and H. F. Schaefer III, Chem. Phys. **171**, 325 (1993).
[19] R. A. Chiles and C. E. Dykstra, Chem. Phys. Lett. **92**, 471 (1982).
[20] J. Moc, K. Bober, and K. Mierzwicki, Chem. Phys. **327**, 247 (2006).
[21] J. I. Martínez and J. A. Alonso, J. Chem. Phys. **129**, 074306 (2008).
[22] S. Burkart, N. Blessing, B. Klipp, J. Müller, G. Ganteför, and G. Seifert, Chem. Phys. Lett. **301**, 546 (1999).
[23] L.-F. Cui, X. Li, and L.-S. Wang, J. Chem. Phys. **124**, 054308 (2006).
[24] X. Li, A. Grubisic, S. T. Stokes, J. Cordes, G. Ganteför, K. H. Bowen, B. Kiran, M. Willis, P. Jena, R. Burgert, and H. Schnöckel, Science **315**, 356 (2007).
[25] A. Grubisic, X. Li, S. T. Stokes, J. Cordes, G. Ganteför, K. H. Bowen, B. Kiran, P. Jena, R. Burgert, and H. Schnöckel, J. Am. Chem. Soc. **129**, 5969 (2007).
[26] B. Kiran, P. Jena, X. Li, A. Grubisic, S. T. Stokes, G. Ganteför, K. H. Bowen, R. Burgert, and H. Schnöckel, Phys. Rev. Lett. **98**, 256802 (2007).
[27] H. R. Siekmann, C. Lueder, J. Faehrmann, H. O. Lutz, and K. H. Meiwes-Broer, Z. Phys. D: At., Mol. Clusters **20**, 417 (1991).
[28] A. Grubisic, X. Li, S. T. Stokes, K. Vetter, G. Ganteför, K. H. Bowen, P. Jena, B. Kiran, R. Burgert, and H. Schnöckel, J. Chem. Phys. **131**, 121103 (2009).
[29] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
[30] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[31] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.